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Rémi F. André

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Sorbonne Université

Ecole doctorale 397, Physique et Chimie des Matériaux

*Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP)*

**Tailored routes to metal-containing nanoparticles  
for hydrogenation reactions in solution:  
surface design for H<sub>2</sub> activation**

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Thèse de doctorat de Chimie de Sorbonne Université

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## Abstract

In this thesis work, the use of metal-containing nanoparticles such as carbides, oxides and phosphides is explored for colloidal catalysis. In an attempt to build a Frustrated Lewis Pair (FLP)-like catalytic system for H<sub>2</sub> activation, the synergy with a molecular Lewis base is assessed. In the bibliographic introduction, the stakes and the challenges of H<sub>2</sub> activation in solvent are presented, with an emphasis on the use of non-purely metallic catalysts for the hydrogenation of model compounds. In the first part, early transition metal carbides and hydrides are synthesized *via* solid-state metathesis. The influence of process parameters is explored to tune the phase speciation in the products. The most promising carbon-supported catalysts, Mo<sub>2</sub>C/C and W<sub>2</sub>C/C, are studied for gas phase and liquid phase hydrogenations of olefins. In the second part, cerium and indium oxides are obtained *via* hydrothermal pathways. The relevance of oxygen defects in CeO<sub>2-x</sub> is established for H<sub>2</sub> gas phase activation and semi-hydrogenation of phenylacetylene in solvent. The last part is dedicated to the non-aqueous syntheses of molybdenum and tungsten oxides, and nickel carbide and phosphides. The syntheses mechanisms are studied by means of NMR for the organic species and XAS and XRD for the nature of the inorganic species. The catalytic activity of the unsupported nanoparticles is finally evaluated for the hydrogenation of nitrobenzene and phenylacetylene in various solvents.

Dans ces travaux de thèse, nous avons exploré différentes classes de nanoparticules métalliques telles que des carbures, des oxydes et des phosphures, pour des applications en catalyse colloïdale. Afin de construire un système catalytique de type « Paire de Lewis Frustrée », la synergie avec des bases de Lewis moléculaires a été étudiée. En introduction, les enjeux et les défis de l'activation de H<sub>2</sub> en solvant sont présentés, avec un focus sur les catalyseurs non purement métalliques pour l'hydrogénation de composés modèles. Dans la première partie, des carbures et des hydrides de métaux de début de transition ont été synthétisés par métathèse solide-solide. Nous avons exploré l'influence de différents paramètres de procédé sur la spéciation de phase des produits. Les catalyseurs supportés les plus prometteurs, Mo<sub>2</sub>C/C et W<sub>2</sub>C/C, ont été étudiées pour l'hydrogénation d'oléfines en phase gaz et en solvant. Dans la deuxième partie, des oxydes de cerium et d'indium ont été produits par voie hydrothermale. L'importance de défauts d'oxygène dans CeO<sub>2-x</sub> pour l'activation de H<sub>2</sub> en phase gaz et pour la semi-hydrogénation du phénylacétylène a été établie. La dernière partie est dédiée à la synthèse solvothermale d'oxydes de molybdène et de tungstène, ainsi qu'à celle de carbure et de phosphures de nickel. Les mécanismes de synthèse ont été étudiés par RMN pour la partie organique et par XAS et DRX pour la partie inorganique. L'activité catalytique des nanoparticules non supportées a finalement été évaluée pour l'hydrogénation du nitrobenzène et du phénylacétylène dans plusieurs solvants.



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## List of abbreviations

acac	Acetylacetonate
ac-b	Acetylene black
ATR	Attenuated Total Reflectance
BF	Bright Field
CUS	Coordinatively Unsaturated Site
DCM	Dichloromethane
DFT	Density Functional Theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
d.o.	Degree of Oxidation
DOS	Density Of States
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EDX	Energy Dispersive X-Ray Spectroscopy
EELS	Electron Energy-Loss Spectroscopy
EXAFS	Extended X-Ray Fine Structure Spectroscopy
FAL	Furfuryl alcohol
FF	Furfural
FLP	Frustrated Lewis Pair
FTIR	Fourier Transform IR
GC-FID	Gas Chromatography – Flame Ionization Detector
GIC	Graphite Intercalation Compound
HAADF	High Angle Annular Dark Field
HCD	Heterolytic Cleavage of Hydrogen
5-HMF	5-hydroxymethylfurfural
HRTEM	High Resolution Transmission Electron Microscopy
HDC	Hydrodecarboxylation
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
INS	Inelastic Neutron Scattering
IR	InfraRed spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
MAS	Magic Angle Spinning
MCR-ALS	Multivariate Curve Resolution – Alternating Least Squares
2-MF	2-methylfuran
MOF	Metal-Organic Framework
MSSM	Modified Solid-State Metathesis

NAP-XPS	Near-Ambient Pressure XPS
NP	Nanoparticle
NMR	Nuclear Magnetic Resonance
OAc	Oleic acid
OAl	Oleyl alcohol
OAm	Oleylamine
ODE	1-octadecene
PXRD	Powder X-Ray Diffraction
r.t.	Room temperature
SAED	Selection Area Electron Diffraction
SAXS	Small Angle X-Ray Scattering
SEM	Scanning Electron Microscopy
SHS	Self-propagating High temperature Synthesis
SPO	Secondary Phosphine Oxide
SSM	Solid-State Metathesis
ss-NMR	Solid-state NMR
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
TM	Transition Metal
TMC	Transition Metal Carbide
tmp	Tetramethylpiperidine
TOP	Trioctylphosphine
TPD	Temperature-Programmed Desorption
UHV	Ultra-High Vacuum
XANES	X-Ray Absorption Near Edge Spectroscopy
XAS	X-Ray Absorption Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

## Résumé en Français

Les réactions d'hydrogénation en catalyse colloïdale impliquent en général l'utilisation de métaux réduits tels que le nickel ou les platinoïdes (Re, Ru, Os, Rh, Ir, Pd, Pt). Bien que très efficaces, ces catalyseurs peuvent présenter différents inconvénients tels que l'utilisation d'éléments rares et coûteux, leur faible stabilité à l'air (caractère pyrophorique), une faible chimiosélectivité ou encore une résistance modérée à l'empoisonnement. Afin de contourner ces limites, nous nous sommes intéressés dans cette thèse à l'utilisation de nanoparticules de composés métalliques (carbures, oxydes, phosphures) pour l'hydrogénation en solvant de différentes molécules modèles telles que le phénylacétylène, le styrène ou le nitrobenzène.

L'activité catalytique des composés étudiés étant attendue comme plus faible que celle des métaux réduits, nous avons tenté de l'améliorer *via* l'ajout d'un co-catalyseur moléculaire. La stratégie poursuivie est inspirée du développement de la catalyse par les paires de Lewis frustrées (Frustrated Lewis Pairs, FLP), *i.e.* la rupture hétérolytique de liaisons chimiques par deux partenaires, un acide et une base de Lewis, tous deux encombrés stériquement (Figure 1A). Le concept, initialement développé en chimie moléculaire, a récemment été adapté en catalyse hétérogène où les deux sites actifs sont en surface d'un matériau, de type oxyde par exemple ( $\text{CeO}_2$ ,  $\text{In}_2\text{O}_3$ ).<sup>1</sup> Nous tentons ici de réaliser une FLP colloïdale où l'un des deux partenaires est une nanoparticule inorganique (acide de Lewis) et l'autre un composé moléculaire (base de Lewis) (Figure 1B). Le choix du partenaire inorganique pour la catalyse a été réalisé suivant trois grands axes :

- des matériaux déjà connus pour leur activité catalytique en solvant, par exemple  $\text{Mo}_2\text{C}$  ou  $\text{W}_2\text{C}$  pour l'hydrogénation du furfural, et  $\text{Ni}_2\text{P}/\text{Ni}_{12}\text{P}_5$  pour celle d'alcènes et de nitroarènes
- des matériaux dont le centre métallique est connu pour être un acide de Lewis, comme des oxydes de tungstène ( $\text{W}_{18}\text{O}_{49}$ ) ou de molybdène ( $\text{MoO}_x$ )
- des matériaux dont l'activité catalytique tout solide de type FLP a déjà été démontrée, en phase gaz à haute température ( $> 200\text{ °C}$ ) pour  $\text{In}_2\text{O}_3$ , et en solvant pour  $\text{CeO}_{2-x}$

Dans tous les cas, l'activation de  $\text{H}_2$  a été explorée en solvant à la fois en absence et en présence de co-catalyseurs de type bases de Lewis moléculaires, telles que la triphénylphosphine.



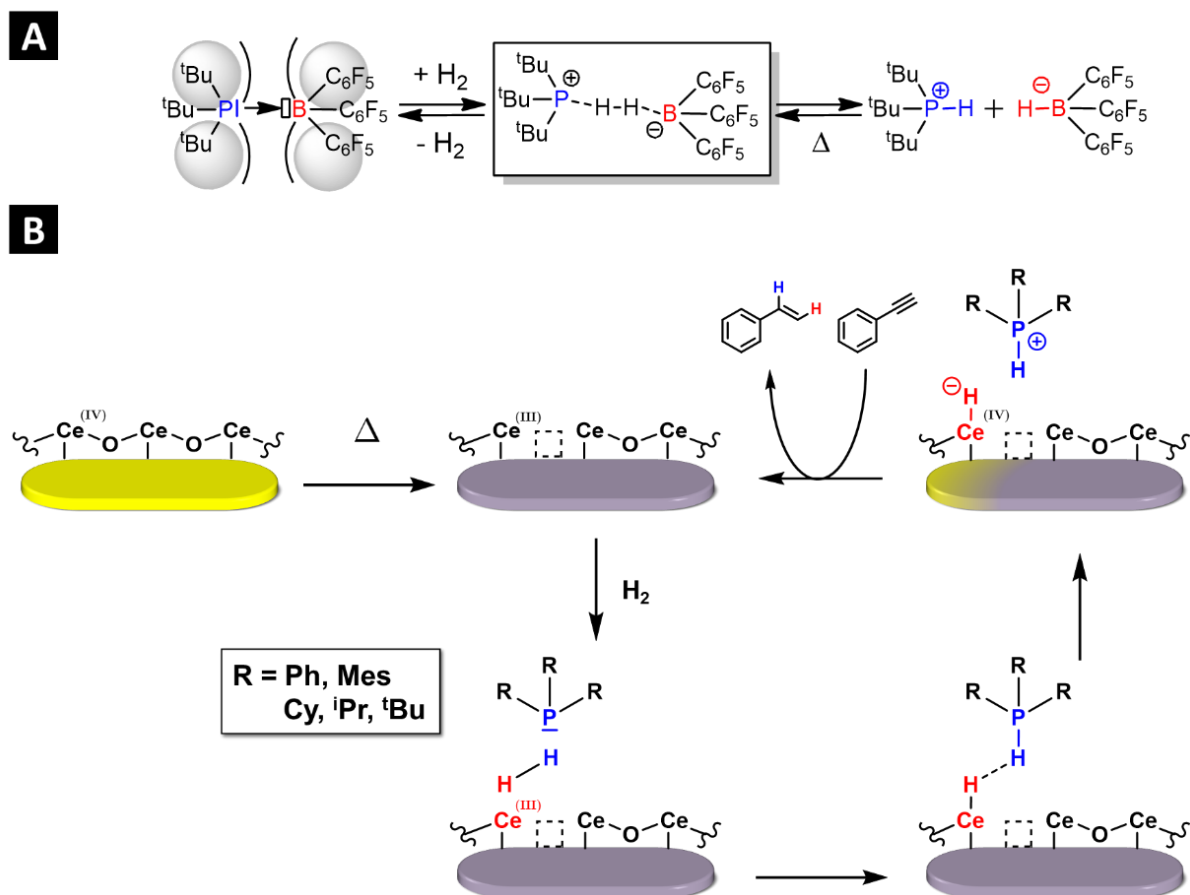


Figure 1. (A) Rupture hétérolytique d'une liaison H-H par FLP moléculaire.<sup>1</sup> (B) Illustration d'une catalyse hypothétique de type FLP entre un site acide de Lewis situé sur une nanoparticule de  $\text{CeO}_{2-x}$  et une base de Lewis encombrée, pour l'hydrogénation du phénylacétylène.

Dans la première partie de cette thèse, nous avons ciblé la synthèse de nanoparticules de carbures métalliques des groupes IV (Zr, Hf), V (Nb, Ta) et VI (Mo, W) pour l'hydrogénation d'oléfines. Les matériaux ont été obtenus par métathèse solide-solide entre un chlorure métallique ( $\text{MCl}_x$ ) et du potassium, soit inséré dans du graphite ( $\text{KC}_8$ ), soit dispersé dans de l'acétylène black ( $\text{KC}_4$ ) (Chapitre II).<sup>2,3</sup> Les deux poudres sont mélangées sous atmosphère inerte et réagissent spontanément pour former des nanoparticules de  $\text{M}(0)$  et  $\text{MC}/\text{M}_2\text{C}$  supportées sur carbone, et de la sylvite ( $\text{KCl}$ ) comme coproduit (Figure 2). La poudre est alors lavée pour retirer le chlorure de potassium. Cette voie de synthèse sans solvant présente des avantages à la fois sur le plan de la nature des objets produits pour la catalyse (pas de ligands de surface, nanoparticules à haute surface spécifique et finement dispersées) et sur le plan de la synthèse elle-même si l'on se réfère aux critères de la chimie verte (pas de solvant, pas de chauffage extérieur, déchets non toxiques). Nous avons pu estimer la température de réaction lors de la combustion par des considérations thermodynamiques. L'énergie libérée est calculée *via* la formule de

Hess à partir des enthalpies de formation des réactifs et des produits, et la capacité calorifique du milieu est fixée principalement par la sylvite et le graphite. Une température théorique, dite adiabatique, peut ainsi être déduite : la réaction la plus exothermique avec  $\text{WCl}_6$  est limitée par l'évaporation de  $\text{KCl}$  à  $1500\text{ }^\circ\text{C}$  et la moins exothermique avec  $\text{ZrCl}_4$  se produit à environ  $1000\text{ }^\circ\text{C}$ .

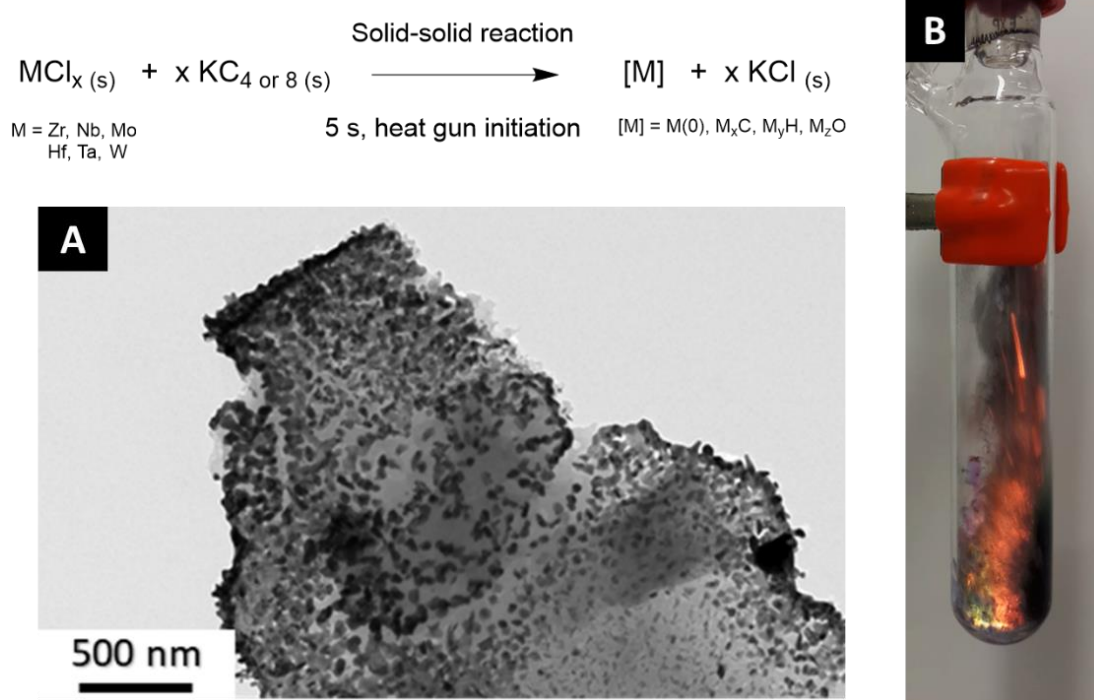


Figure 2. (A) Image MET d'un échantillon de  $\text{Mo}_2\text{C}$  supporté sur graphite par métathèse solide-solide entre  $5 \text{ KC}_8$  et  $\text{MoCl}_5$ . (B) Photo de la réaction lors de la combustion.

La spéciation de phase en fonction de divers paramètres de réaction (support carbone, granulométrie des précurseurs, phase gaz, échelle) a été étudiée par DRX : le point le plus remarquable est l'augmentation de la proportion de carbures vis-à-vis du métal lorsque la température de réaction augmente. De plus, nous avons découvert par sérendipité l'obtention possible d'hydrures métalliques pour les métaux du groupe IV ( $\text{ZrH}_2$  et  $\text{HfH}_{1.7}$ ) et V ( $\text{NbH}_{0.8}$  et  $\text{Ta}_2\text{H}$ ) pour les réactions conduites dans le vide. Des études complémentaires sur la morphologie des nanoparticules par HRTEM et sur la composition du matériau avant neutralisation nous ont permis de proposer un mécanisme en plusieurs étapes (Figure 3). Des nanoparticules métalliques sont d'abord formées et carburées *in situ* du fait des hautes températures puis les surfaces métalliques non carburées réagissent au contact des solvants de lavage (eau et éthanol) pour former des hydrures. Enfin, nous avons montré par XPS que la surface du matériau est oxydée au contact de l'air.

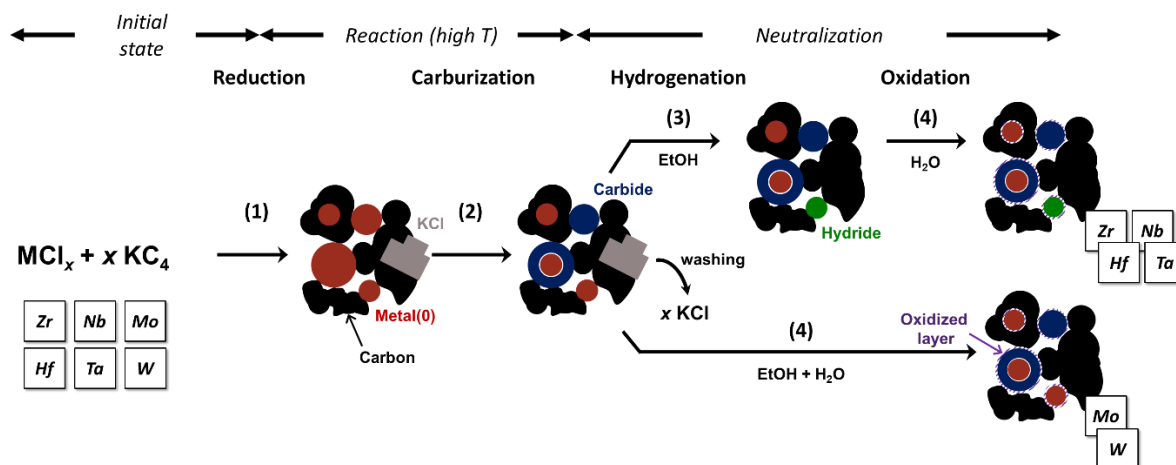


Figure 3. Proposition de mécanisme pour la formation de nanoparticules métalliques, de carbures et d'hydrures. Haut : éléments susceptibles de former des hydrures. Bas : éléments ne formant pas d'hydrures.

Parmi les matériaux synthétisés dans le Chapitre II, les carbures de molybdène et de tungstène  $Mo_2C/C$  et  $W_2C/C$  sont les catalyseurs les plus prometteurs vis-à-vis de l'activation de  $H_2$  si l'on considère les travaux de Boudart sur l'hydrogénation en phase gaz ou la littérature sur le furfural (Chapitre III).<sup>4</sup> Des résultats préliminaires ont démontré que  $Mo_2C/graphite$  est actif pour l'hydrogénation du butadiène en butène en phase gaz à partir de 120 °C. Lors de la première rampe de chauffe, il est apparu que l'activité était anormalement élevée aux alentours de 100 °C, supposément à cause d'une élévation locale de la température due à la réduction d'une couche d'oxyde. Les carbures  $W_2C/acetylene\ black$  et  $Mo_2C/graphite$  ont également été étudiés respectivement pour l'hydrogénation en solvant du styrène et du phénylacétylène. Dans le premier cas, le produit majoritaire de la réaction consiste en un dimère, le (E)-1,3-diphényl-1-butène, présumément obtenu par catalyse acide avec des traces de  $H^+$  sur le graphite, mais la formation d'éthylbenzène n'a pas été détectée. Dans le deuxième cas, la réaction menée à 100 °C sous 7, 15 et 30 bar de  $H_2$  n'a mené qu'à la formation de traces de styrène.

Dans la deuxième partie de cette thèse, nous avons produit par voie hydrothermale des nanoparticules d'oxyde de cérium ( $CeO_{2-x}$ ) (Chapitre IV) et d'indium ( $In_2O_3$ ) (Chapitre V) pour l'activation de  $H_2$ . Dans le Chapitre IV, nous avons voulu reproduire dans un premier temps le matériau utilisé par Qu *et al.* pour l'hydrogénation en solvant d'alcènes et d'alcynes comme point de départ de notre étude.<sup>5</sup> Les auteurs reportent une synthèse en deux étapes d'un oxyde de cérium riche en défauts, assurant donc une proportion importante de  $Ce^{(III)}$  en surface. Une fois les conditions de synthèse optimisées, nous avons été en mesure de reproduire un

matériau semblable à celui reporté par Qu *et al.* (Figure 4). Il est toutefois apparu que l'attribution des phases en DRX proposée par les auteurs de l'étude n'est pas cohérente : après une semaine à l'air à température ambiante, le matériau initial,  $\text{Ce}(\text{OH})_3$ , a jauni et le diffractogramme a évolué vers une phase non reportée dans les bases de données et non mentionnée dans la littérature. Nous avons caractérisé le matériau par différentes techniques (DRX, XAS, XPS et IR) et ainsi démontré l'oxydation de  $\text{Ce}^{(\text{III})}$  en  $\text{Ce}^{(\text{IV})}$  malgré l'absence de formation de  $\text{CeO}_2$ . Cette évolution du matériau diverge des travaux reportés de la littérature.

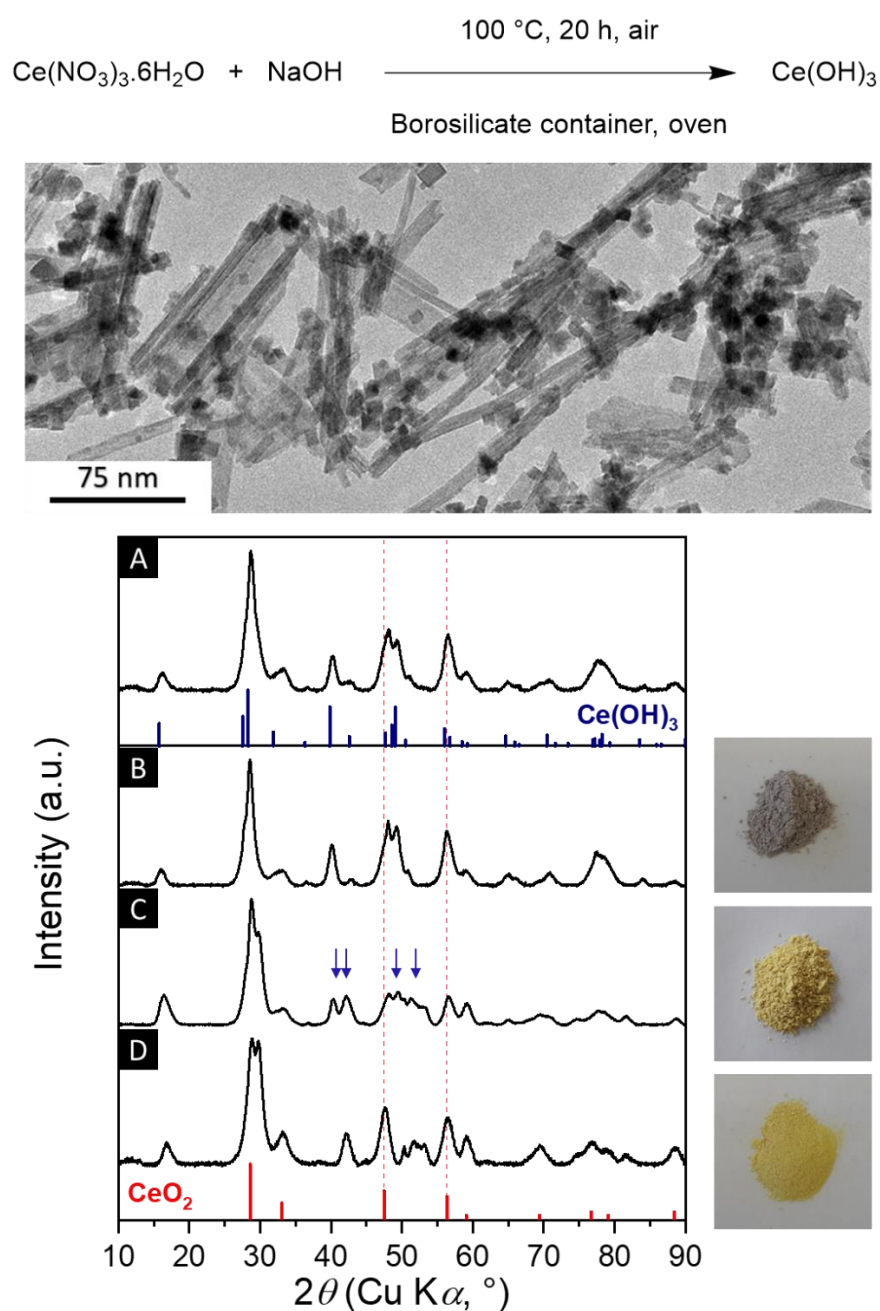


Figure 4. Synthèse de trihydroxyde de cérium et d'oxyde de cérium par voie hydrothermale (avec cliché MET). Diffractogrammes RX de (A)  $\text{Ce}(\text{OH})_3$  deux heures après synthèse, (B)

Ce(OH)<sub>3</sub> stocké sous Ar pendant quatre jours, (C) Ce(OH)<sub>3</sub> stocké à l'air pendant un jour, (D) Ce(OH)<sub>3</sub> stocké à l'air pendant quatre jours. Les flèches bleus soulignent la présence simultanée de deux phases : Ce(OH)<sub>3</sub> et Ce(OH)<sub>3</sub> « vieilli ».

Dans un second temps, nous avons soumis les matériaux préalablement synthétisés, CeO<sub>2</sub> et Ce(OH)<sub>3</sub> vieilli, à une étape de calcination sous Ar à 200 °C afin d'augmenter le nombre de défauts d'oxygène en surface du matériau et ainsi générer des sites réactifs Ce<sup>(III)</sup>. Pour les nanobâtonnets de CeO<sub>2</sub>, une étude XPS sur la région Ce 3d a démontré une augmentation du ratio de Ce<sup>(III)</sup> de surface de 30 % à 50 %. Nous avons enfin pu montrer par XPS que l'addition de H<sub>2</sub>, même à très basse pression (0.14 mbar), sur CeO<sub>2-x</sub> est responsable d'une oxydation des sites Ce<sup>(III)</sup> de surface (le ratio de Ce<sup>(III)</sup> en surface passe de 75 % à 50 %), interprétée comme la formation d'hydrure de surface sur les lacunes d'oxygène (Figure 5).<sup>6</sup> Les différents catalyseurs à base d'oxyde de cérium, éventuellement calcinés sous Ar, ont enfin été étudiés pour la semi-hydrogénation du phénylacétylène en styrène à 100 °C sous 7 bar de H<sub>2</sub> dans le toluène. Des rendements de l'ordre de 5-15 % ont été obtenus mais la large barre d'erreur ne permet pas de conclure quant à l'impact de l'addition de PPh<sub>3</sub>.

Dans le chapitre V, deux catalyseurs à base d'indium ont été synthétisés par voie hydrothermale à 100 °C depuis des précurseurs de sels de nitrates d'indium. Suivant les travaux d'Ozin *et al.*, le dopage à 1 % de la phase cubique In<sub>2</sub>O<sub>3</sub> par des atomes de bismuth a été réalisée.<sup>7</sup> Le catalyseur c-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub> a été étudié pour l'hydrogénation du phénylacétylène sous 7 bar de H<sub>2</sub> à 100 °C, 150 °C et 200 °C. Une faible activité catalytique a été détectée (rendement inférieur à 10 %) pour les températures supérieures à 100 °C ainsi que la formation d'acétophénone. L'ajout de triphénylphosphine n'a pas eu d'effet déterminant sur le produit de la catalyse. Le deuxième catalyseur, In<sub>2</sub>O<sub>3</sub> rhomboédrique, n'a pas encore été étudié en catalyse.

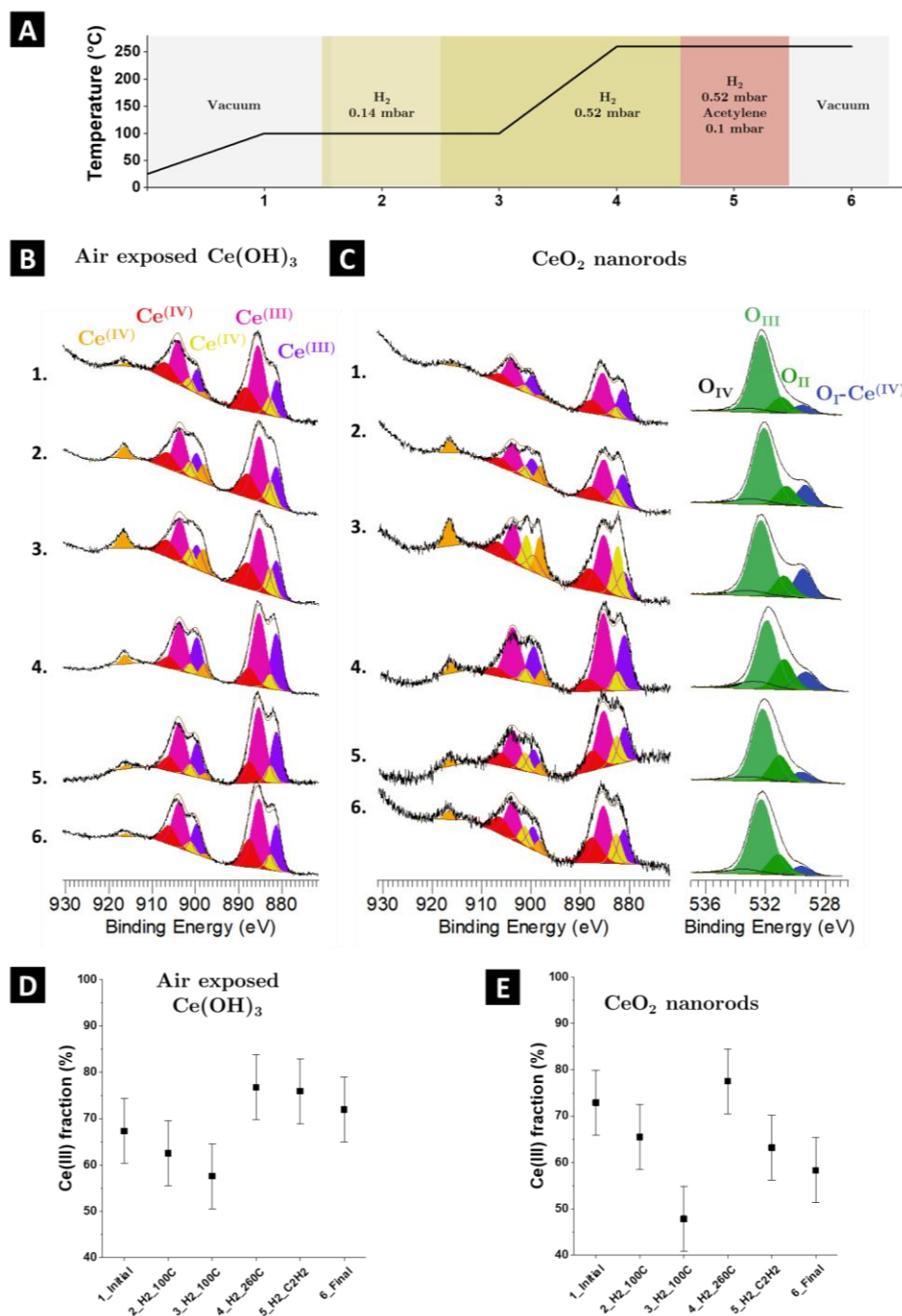


Figure 5. (A) Traitement température + gaz appliquée aux catalyseurs dans l'enceinte de l'appareil de NAP-XPS. (B,C) NAP-XPS de la région Ce 3d et O 1s pour les catalyseurs d'oxyde de cérium et (D,E) évolution du ratio Ce<sup>(III)</sup>/Ce<sup>(IV)</sup> en surface des catalyseurs.

La dernière partie de cette thèse est dédiée aux synthèses conduites dans des solvants à haute température d'ébullition tels que l'oleylamine (OAm), l'alcool oléique (OAl) ou l'acide oléique (OAc). Dans le chapitre VI, la synthèse de nanofils d'oxyde de tungstène, W<sub>18</sub>O<sub>49</sub>, a été adaptée du travail de Leite *et al.*<sup>8</sup> et celle d'oxydes de molybdène du travail de Tatsuma *et al.*<sup>9</sup> Pour la première, la réaction a

été reproduite avec succès après purification du précurseur,  $WCl_6$ , qui contenait des traces de  $W(0)$ . Pour les secondes, la décomposition thermique de  $MoO_2(acac)_2$  dans l'oleylamine a conduit à une poudre dont l'analyse par diffraction RX n'est pas informative sur la composition chimique du matériau (Figure 6). L'analyse par microscopie électronique en transmission révèle la présence de nanoparticules de diamètre inférieur à 5 nm. Une synthèse similaire a été réalisée dans l'acide oléique. Aucune poudre n'a pu être isolée du fait de l'excellente stabilité colloïdale de la suspension. Les différents oxydes de molybdène synthétisés ont été étudiés en spectroscopie d'absorption X (XAS) afin de déterminer d'une part le degré d'oxydation (d.o.) et l'environnement chimique du molybdène, et d'autre part afin d'étudier le mécanisme de formation des nanoparticules. La synthèse dans l'oleylamine conduit à un d.o. compris entre +IV et +VI mais le produit ne semble pas être un mélange de  $MoO_2$  et  $MoO_3$ , ce qui indiquerait la présence d'oxydes intermédiaires. La réaction dans l'acide oléique conduit à un matériau dont le spectre XAS est très proche de celui de  $MoO_2$ . Les nanofils d'oxyde de tungstène déficitaires en oxygène,  $W_{18}O_{49}$ , et les nanoparticules d'oxydes de molybdène produites dans l'oleylamine ont été utilisées pour l'hydrogénation en phase liquide du nitrobenzène et du phénylacétylène en conditions relativement dures (150 °C, 30 bar  $H_2$ ). Aucune conversion n'a été obtenue pour le nitrobenzène et un rendement en styrène de 13 % et 26 % a été respectivement obtenu pour  $MoO_x$  et  $W_{18}O_{49}$ .

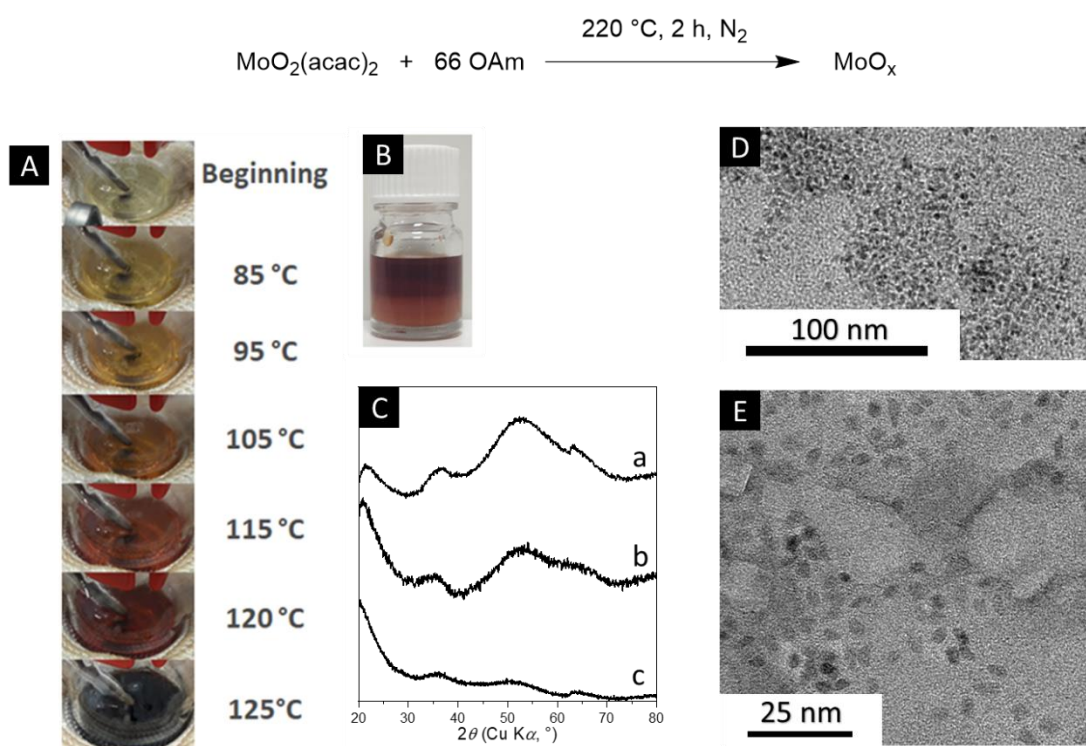


Figure 6. Synthèse de  $MoO_x$  par décomposition thermique de  $MoO_2(acac)_2$  dans l'oleylamine. (A) Evolution de la couleur de la suspension et (B) état final. (C) Diffractogramme RX des

produits de synthèse (a : DAM comme solvant, b,c : OAm). (D-E) Images MET des nanoparticules synthétisées dans l'oleylamine.

Dans le chapitre VII, la synthèse des nanoparticules de carbures et phosphures de nickel est adaptée du travail de Tracy *et al.*<sup>10</sup> Elle consiste en une décomposition thermique de  $\text{Ni}(\text{acac})_2$  à 250 °C pendant 2 h dans un mélange oleylamine/1-octadecène pour former des nanoparticules de carbure de nickel. Dans une deuxième étape et sans isolation préalable des nanoparticules, l'ajout d'un agent phosphurant, la trioctylphosphine (TOP), permet la phosphuration des nanoparticules à 300 °C en 30 min. La quantité de TOP ajoutée ainsi que la température d'injection mènent à différentes phases :  $\text{Ni}_2\text{P}$  ou  $\text{Ni}_{12}\text{P}_5$ . Une famille de nanoparticules de compositions différentes ( $\text{Ni}_3\text{C}$ ,  $\text{Ni}_2\text{P}$  et  $\text{Ni}_{12}\text{P}_5$ ) mais de tailles similaires a ainsi été obtenue pour comparaison de leurs activités catalytiques. L'étude comparative a été initiée avec le carbure de nickel ( $\text{Ni}_3\text{C}$ ) pour l'hydrogénation du nitrobenzène en aniline et du phénylacétylène en éthylbenzène dans différents solvants (Figure 7). Une hydrogénation quantitative a pu être obtenue à respectivement 60 °C et 100 °C dans l'éthanol, ce qui constitue la première mention de  $\text{Ni}_3\text{C}$  comme catalyseur « colloïdal » pour l'activation de  $\text{H}_2$ .

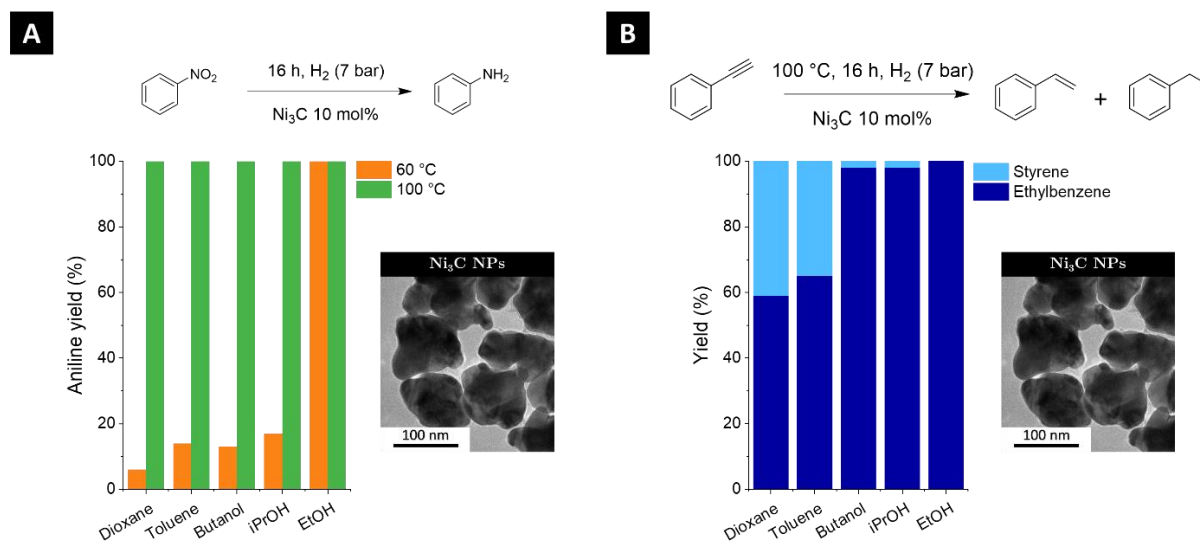


Figure 7. Hydrogénation (A) du nitrobenzène et (B) du phénylacétylène en présence de nanoparticules de  $\text{Ni}_3\text{C}$  dans différents solvants. Conversions déterminées par RMN.

En conclusion, nous avons synthétisé des nanoparticules appartenant à différentes familles (carbures, oxydes et phosphures) et selon différentes voies de synthèse (métathèse solide, hydrothermale, solvothermale) avec d'éventuels traitements post-synthèse (calcination). Les matériaux obtenus présentent donc une



diversité de phase mais également d'états de surface. Lors des tests catalytiques pour l'hydrogénation du phénylacétylène,  $\text{CeO}_2$  est apparu comme actif à 100 °C sous 7 bar de  $\text{H}_2$  bien qu'il soit encore difficile de trancher quant à l'effet de l'addition d'une phosphine. Le nitrobenzène et le phénylacétylène ont également pu être hydrogénés en présence de  $\text{Ni}_3\text{C}$  dans des conditions douces, respectivement 60 °C et 100 °C sous 7 bar de  $\text{H}_2$ . Différentes perspectives sont envisagées : d'une part l'utilisation de conditions plus dures pour l'hydrogénation avec  $\text{Mo}_2\text{C}/\text{C}$ ,  $\text{W}_2\text{C}/\text{C}$ ,  $\text{CeO}_2$  et  $\text{In}_2\text{O}_3$  afin de pouvoir détecter une potentielle amélioration de la réactivité en présence de phosphine, d'autre part l'étude comparative du carbure  $\text{Ni}_3\text{C}$  et des phosphures  $\text{Ni}_2\text{P}$  et  $\text{Ni}_{12}\text{P}_5$  pour l'activation de  $\text{H}_2$ , éventuellement avec ajout d'une phosphine. Enfin, l'étude plus rationalisée du mécanisme de formation d'oxydes de Mo par décomposition thermique de  $\text{MoO}_2(\text{acac})_2$  dans l'oleylamine ou l'acide oléique.

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## General introduction

Environmental issues have become of paramount importance for chemists during these past decades. They obviously include the limitation of the release of carbon dioxide and other greenhouse gases in the atmosphere. The global challenge of climate change should however not totally overshadow other critical points, such as materials scarcity (Figure 1) or anthropogenic pollution with metals in environment, due for instance to the mining activity or the waste disposal. These last points have a particular resonance for the inorganic chemistry community: a large number of catalytic processes in industrial chemistry indeed rely on the use of metal-containing catalysts. As catalysis is considered as one of the twelve principles of Green Chemistry, its use will undoubtedly increase in future. Its applications cover industrially relevant fields as vast as ammonia production *via* the Haber-Bosch process, polymerization reactions with the Ziegler-Natta process, fuels synthesis *via* the Fischer-Tropsch process or petroleum refinery through cracking on zeolites. More recently, environmental standards in auto industry have lowered the limit concentrations of  $\text{NO}_x$ , CO and hydrocarbons in exhaust emissions, increasing the use of platinum and rhodium in catalytic converters which now represents respectively 50 % and 80 % of their global productions.

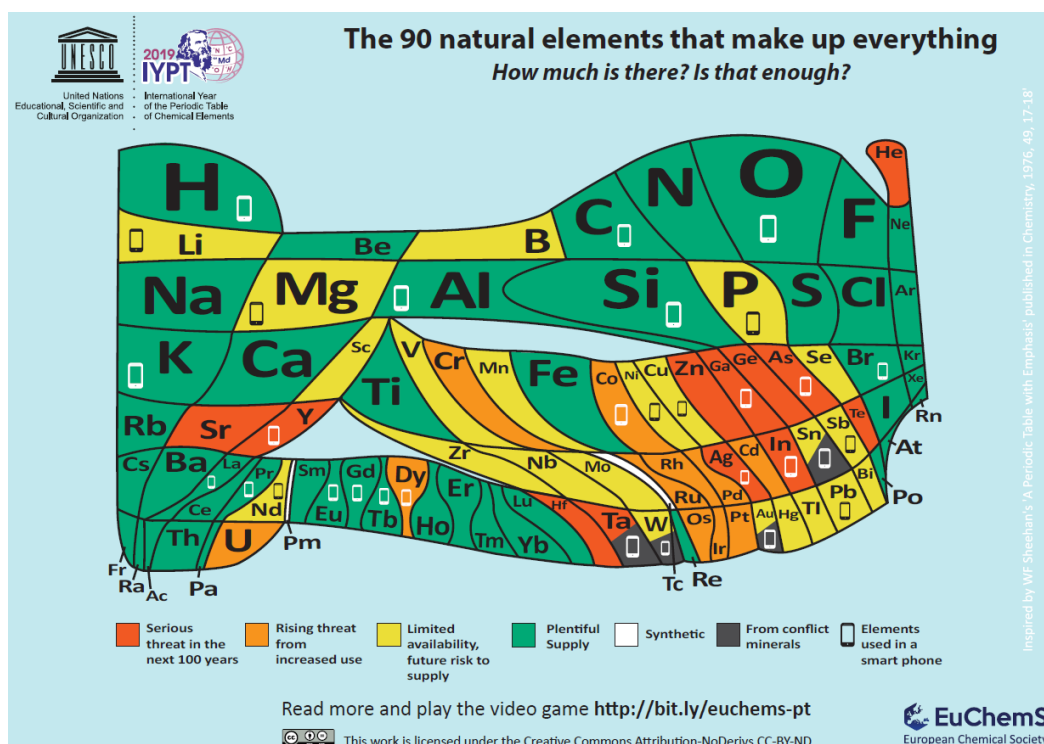


Figure 1. The periodic table of the element scarcity. The areas of the cases relate to the abundance of the atoms of each element on a logarithmic scale.

One particular example of industrial relevant catalyzed reaction is the hydrogenation: from petroleum refinery to biomass transformation and from fat hydrogenation to fine chemical syntheses,  $H_2$  activation is crucial for several fields of the chemical industry. These hydrogenation reactions are generally catalyzed by either nickel, the undeniable star of the catalytic reduction, or platinoid elements (Ru, Os, Rh, Ir, Pd, Pt). Despite their high efficiency, the scarcity of these last ones makes them very demanded and expensive, with prices exceeding that of gold. Furthermore, their extraction may be subject of international tensions in the future considering 91 % of the known stocks worldwide are currently held by a single country, South Africa. There is currently a demand for more adaptable and sustainable catalysts. Adaptable first because the nature of the raw feedstocks in chemical industry will be more and more diverse, complex and non-stable in composition with the growing importance of the biomass and wastes in raw supplies. Sustainable then because the demand for the rarest of the chemical elements will be higher and higher with the increase and diversification of their uses: larger demand for chemicals and therefore for catalysts, stricter environmental standards requiring depollution modules and concurrence with new technologies (electronics, batteries, alternative energies). I believe catalysts choice will be less and less guided by the optimal performance but rather by a delicate balance between the performance and the environmental impact and cost of the catalyst production.

“Research and Development” departments in industry have the necessary striking force to screen and optimize the catalysts for all the relevant reactions. Nonetheless, the design of new concepts and the development of rational tools to study catalytic mechanisms still belong to the domain of academic research to my opinion. This is the reason why I believe our role, as academic researchers, is to lead this exploration for new active compounds and catalytic systems, with a particular focus on the materials which are still only accessible in laboratories. The boom of the “nano” research these past decades has permitted the synthesis of a large variety of metal-containing nanoparticles such as borides, carbides, nitrides and phosphides, not yet fully explored as to their catalytic potential. Besides, our understanding of the reaction mechanism at the surface of the catalyst and the progresses in materials science allow us to better design the surfaces of the materials, in particular as to the exposed facets, the defects or the presence of doping elements.

The strategy of the present work is to synthesize a variety of nanoparticles of various compositions (carbides, oxides, phosphides) to test their catalytic activity toward hydrogenation in solvent. We then envision a boost of their activity through the addition of a molecular co-catalyst which will help the heterolytic cleavage of the  $H_2$  molecule. The concept is inspired from the recent development of the Frustrated Lewis Pair (FLP) chemistry, and adapted to inorganic surfaces: the  $H_2$  molecule is located between a Lewis acid center and a Lewis basic center which are too sterically

hindered to form a Lewis adduct. The H–H bond is thus weakened and more easily cleaved in a hydride and a proton. A more in-depth description and analysis of the associated stakes will be done in first chapter. Our main objective in this thesis is not to build an efficient catalytic system that would be able to compete with the ones currently used in industry, but rather determine whether such a catalytic concept in colloidal chemistry is possible and determine what would be the critical parameters.

In **chapter I**, we first briefly reviewed the key concepts behind H<sub>2</sub> activation on metal-containing nanoparticles and we aggregated the main results obtained these past years in colloidal hydrogenation with non-purely metallic catalysts. The experimental part of this PhD thesis is then divided in six chapters grouped in three parts. Each part corresponds to one type of materials synthesis: solid-state syntheses for Part 1 (Chapter II and III), hydrothermal syntheses for Part 2 (Chapter IV and V) and solvothermal syntheses in high-boiling point solvents for Part 3 (Chapter VI and VII). We considered this division of the work as the most meaningful both for the materials syntheses and the catalytic aspect. The concepts used for rationalizing the catalyst syntheses indeed differ depending on the reaction medium. Besides, the state of the materials surface, crucial for catalysis, is highly dependent on the chosen pathway: few ligands are expected for solvent-free syntheses whereas surface hydroxyls and organic ligands are present for respectively hydrothermal and solvothermal reactions. We developed in **chapter II** a solvent-free synthesis of nanocarbides and nanohydrides of early transition metals by solid-state metathesis between metal chlorides and potassium graphite. Molybdenum and tungsten carbides previously synthesized were studied for hydrogenation of alkenes in gas and liquid phases in **chapter III**. We explored in **chapter IV** the syntheses of cerium hydroxide and oxide in aqueous solution. An unreported cerium hydroxide phase was obtained and characterized in depth. Different thermal treatments in view of the catalytic applications were studied. Reduced cerium oxide (CeO<sub>2</sub>) was then explored for H<sub>2</sub> activation in the gas phase, and for semi-hydrogenation of phenylacetylene in solvent. We pursued in **chapter V** with the syntheses of indium oxide and bismuth-doped indium oxide in aqueous solution. Catalytic tests were also performed for semi-hydrogenation of phenylacetylene in solvent. The **chapter VI** deals with the syntheses of metal oxides (MoO<sub>x</sub> and W<sub>18</sub>O<sub>49</sub>) in high-boiling point solvents (oleylamine, oleic acid and oleyl alcohol). In the case of the molybdenum oxide synthesis, an *in situ* X-Ray Absorption Spectroscopy (XAS) study was conducted to better understand the nature of the objects. Preliminary catalytic tests for hydrogenation of phenylacetylene and nitrobenzene were performed in solvent. We finally studied in **chapter VII** the syntheses of nickel carbide and phosphides nanoparticles in high-boiling point solvents (oleylamine, 1-octadecene, octyl ether and trioctylphosphine). The catalytic activity of Ni<sub>3</sub>C was characterized for nitrobenzene and phenylacetylene hydrogenation in different solvents.

We adopted an exploratory approach to develop materials for hydrogenation reactions. Preliminary catalytic trials were therefore performed during the catalyst synthesis development and guided some of our synthetic choices. Most of the experimental work focused on the catalyst syntheses, this choice can be explained by three factors. First, the three-phase heterogeneous catalysis was a new competence in the laboratory and the experimental setup had to be installed in the course of the PhD, thereby postponing the first catalysis experiments. Then, we found by serendipity intriguing results during the catalysts development (unexpected phases for solid-state metathesis in Chapter II and unreported cerium-containing phase in Chapter IV) and we chose to study them more in-depth. Finally, as the experimental time was limited due to the exceptional situation in 2020 and 2021, we chose to favor the topics more susceptible to be ended in the course of the PhD, *i.e.* the materials syntheses. The choice of study of some metals or systems rather than others was also led by the opportunity to access synchrotron facilities, which allowed us to perform experiments not initially planned, though of high interest. This in particular justifies the Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) study of cerium oxide (Chapter IV) and the *in situ* XAS study of the solvothermal synthesis of molybdenum oxides (Chapter VI).

## Chapter I

# Literature review on metal-containing catalysts for hydrogenation in solvent

This chapter is built as a tutorial to understand what are the key concepts in colloidal hydrogenation reactions. It is structured as follows: we first briefly discuss the context of hydrogenation reactions with a focus on the limitations of purely metallic materials, the range of relevant substrates and the classical setups used in academic works. In the second part, we present the different reported mechanisms for H<sub>2</sub> activation on inorganic surfaces (heterolytic *versus* homolytic dissociation) as well as the characterization techniques (TPD, IR, INS, NMR, XPS) used to evidence the H<sub>2</sub> splitting. Third, we report a number of representative works on the use of metal-containing nanoparticles for liquid-phase hydrogenations. We finally explain our work philosophy as to the development of a colloidal catalysis based on the Frustrated Lewis Pair (FLP) chemistry.

### I.1. Context of colloidal hydrogenation reactions

In the context of hydrogenation reactions, heterogeneous catalysis is often understood as a reaction where the substrate is in the gas phase while the catalyst is in the solid phase. For reactions performed in a solvent (or, more precisely, in a dispersion) with dispersed particles of catalyst, one can encounter the terms “liquid phase heterogeneous catalysis”, “three-phase hydrogenation catalysis” or “colloidal catalysis”. In these situations, the substrate is soluble in the solvent and the catalyst is a solid, highly dispersed or in suspension.<sup>1</sup>

#### I.1.1 From conventional catalysts to catalysts with new compositions

Typical catalysts for hydrogenation reactions are finely divided late transition metals such as Ru, Os (Group VIII), Rh, Ir (Group IX) or Ni, Pd, Pt (Group X).<sup>1,2</sup> These catalysts can be used as stand-alone particles, *i.e.* non supported colloids, or, more often, supported on a polymer or an inorganic nanostructured material (activated charcoal, graphite, zeolite, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>). The support acts both as a catalyst modifier by exacerbating the activity or controlling the selectivity and as an aid to recover it after reaction. These metal catalysts are particularly efficient which renders challenging the selective or partial hydrogenation often required in fine chemistry.<sup>1</sup> For instance, Pd has to be deactivated by supporting it on CaCO<sub>3</sub> or BaSO<sub>4</sub> and treating it with Pb(OAc)<sub>2</sub> or PbO (Lindlar<sup>®</sup> catalyst) to avoid the total hydrogenation of



alkynes in alkanes.<sup>3</sup> Besides, the high surface area and reactivity of finely divided Ni and Pd catalysts, commonly used in industry and academic works, make them pyrophoric and therefore difficult to handle on large scales. The scarcity of the rarest of these metals, the platinoids (Ru, Os, Rh, Ir, Pd, Pt), coupled with a growing demand, makes them more and more expensive and objects of international tensions. For instance, South Africa alone concentrates 91 % of their known stocks.<sup>4</sup> More abundant metals, generally early transition or first row metals (Mn, Fe, Co, Ni, Cu), should therefore be envisioned as lower-cost alternatives, in a strategy of diversification of catalysts.<sup>5</sup>

The limited resistance of the previously mentioned reduced metals to poisonous elements from the reaction crude (oxygen, nitrogen, carbon, sulfur) or from poisoning molecules (carbon monoxide, phosphines, amines) leads to deactivation issues.<sup>6</sup> In contrast, the catalytic activity of early transition metal carbides for instance is generally more tolerant to the insertion of nitrogen or sulfur atoms.<sup>7</sup> The corresponding nitrides and sulfides are indeed also active, to the contrary of those of noble metals. This deactivation issue of the metallic catalysts is expected to be more and more pregnant with the increasing use of biomass and the increase of concentrations of impurities (N and S) in the fossil-based feedstocks (petroleum is extracted from deeper stocks than before).<sup>8</sup>

The catalytically active surfaces of purely metallic nanoparticles may be modified during the catalysis, either by a surface oxidation or by an *in situ* light element incorporation leading to carbide, phosphide or sulfide surface species. For instance, Sautet *et al.* reported a study on the surface carbidization of nickel catalysts when exposed to a slight pressure of hydrocarbon molecules.<sup>9</sup> The dissolution of small amounts of carbon in the subsurface region of the catalyst drastically modifies its electronic structure. This effect has an impact on the adsorption energy of substrates and thus on the chemoselectivity. In those cases, the active catalytic sites are no longer reduced metal atoms and should be better described by metal-containing materials, comforting the interest in nanoparticles fully composed of these species.

All the aforementioned points justify the current research for new phases in hydrogenation reactions and for rationalization of the known active phases. Most of the works so far focused on relatively hard conditions of reaction relevant for oil refinery or biomass hydroprocessing. However, as will be developed later, a growing number of works report their use in more sensitive chemistries such as those of fine chemicals or sugars.

### I.1.2 Substrate molecules

Hydrogenation reactions consist in the addition of hydrogen atoms in a molecule. This incorporation of H may result in the reduction of an insaturation ( $C=C$ ,  $C\equiv C$ ,

C=O, C=N, C≡N, NO<sub>2</sub>) or in a C–X bond cleavage (X = C, N, O, S). In this last case, the term hydrogenolysis may be found.<sup>10</sup> The scope of hydrogenation reactions in solvent covers a wide range of substrates with different stakes and challenges.

**Petroleum refinery.** During the petroleum refinery, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are required to remove all traces of sulfur and nitrogen from the raw feedstocks.<sup>8</sup> Typical impurities consist in thiols, thiophenes (dibenzothiophene) and sulfides for sulfur and amines (carbazole), pyridines, quinolines and porphyrins for nitrogen. Their removal by HDS and/or HDN produces respectively hydrogen sulfide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>). These hydroprocessing reactions are usually run at high temperatures and elevated H<sub>2</sub> pressures. The purification of the oil is needed first to avoid any poisoning of the catalysts used in the downstream refinery steps and then to limit the final release of pollutant gases such as SO<sub>x</sub> or NO<sub>x</sub> during combustion. Hydrodeoxygenation (HDO) processes are used for C–O bond cleavage, but in a lesser extent in petroleum refinery. They are nonetheless the subject of a growing interest these past decades due to the development of biorefinery, as detailed just below. Typical industrial catalysts are similar for HDS, HDN and HDO reactions and consist in cobalt or nickel promoted molybdenum or tungsten disulfides supported on metal oxides (γ-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, zeolites).<sup>8,11</sup> We do not intend to exhaustively report the works on hydroprocessing as this vast field has already been the topic of numerous reviews and books. We can nonetheless stress the variety of the current research with the use of transition metal nitrides, carbides or phosphides.<sup>12,13</sup>

**Biomass valorization.** In volume, most of the bio-sourced molecules originate from carbohydrate monomers or polymers (sugars, cellulose, hemi-cellulose), phenolic polymers (lignin) and fatty esters (vegetal oils) (Figure 1).<sup>14</sup> The transformation of these chemicals has two main possible outcomes: as energy carriers or fuels (energy-driven refinery) or as higher-added value chemicals for further transformation (material-driven refinery). In the first case, a decrease of the oxygen content is targeted in order to improve the calorific value of the compound. In the second case, hydrogenation reactions must be performed in order to obtain similar molecules than the ones currently obtained from petroleum refinery. The molecules originating from biomass are indeed more oxidized than the ones from fossil resources. For both energy- and material-driven refineries, the acid-mediated dehydration reaction and the hydrodeoxygenation process (HDO) are essential. Two carbonyl compounds derived from carbohydrates should be considered in particular as to hydrogenation: the furfural (FAL) and the 5-hydroxymethylfurfural (HMF). These two furanic aldehydes are obtained from acid-catalyzed dehydration of xylose and hexose, themselves obtained from cellulose and hemicellulose.<sup>15,16</sup> The reductive upgrading of FAL and HMF leads to more than 30 industrially-relevant molecules, including methylfuran and dimethylfuran which are good substitutes to ethanol as liquid biofuel.<sup>17</sup> Lignin is a complex polymer composed of methoxylated phenols (coumaryl, coniferyl and sinapyl

alcohols). Handling and interpreting by  $^1\text{H}$  NMR the chemical transformations of lignin in the context of academic research is quite challenging due to its complexity. Model molecules are thus studied instead of lignin. In order to represent the chemical diversity of the lignocellulosic polymers, these model molecules include phenol ( $\text{Ph-OH}$ ), anisole ( $\text{Ph-OCH}_3$ ), guaiacol ( $\text{HO-Ph-OCH}_3$ ) and benzyloxybenzene ( $\text{Ph-O-CH}_2\text{-Ph}$ ). Finally, the hydrodecarboxylation (HDC) of natural fatty acids allows the production of renewable liquid fuels. Considering the complexity of actual raw feedstocks, only a selection of fatty acids were chosen as model substrates in academia, they include stearic ( $\text{C}_{18}$ ), palmitic ( $\text{C}_{16}$ ) and lauric ( $\text{C}_{12}$ ) acids for the saturated compounds and oleic and linoleic acids for the unsaturated ones.

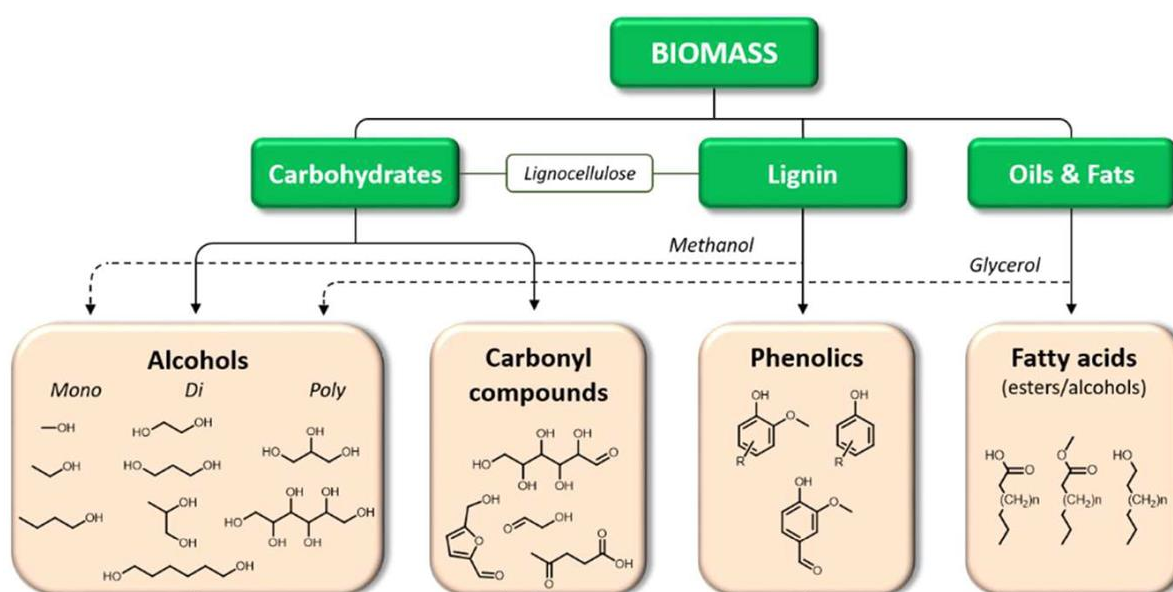


Figure 1. Overview of various bio-based platform molecules. Adapted from reference [14].

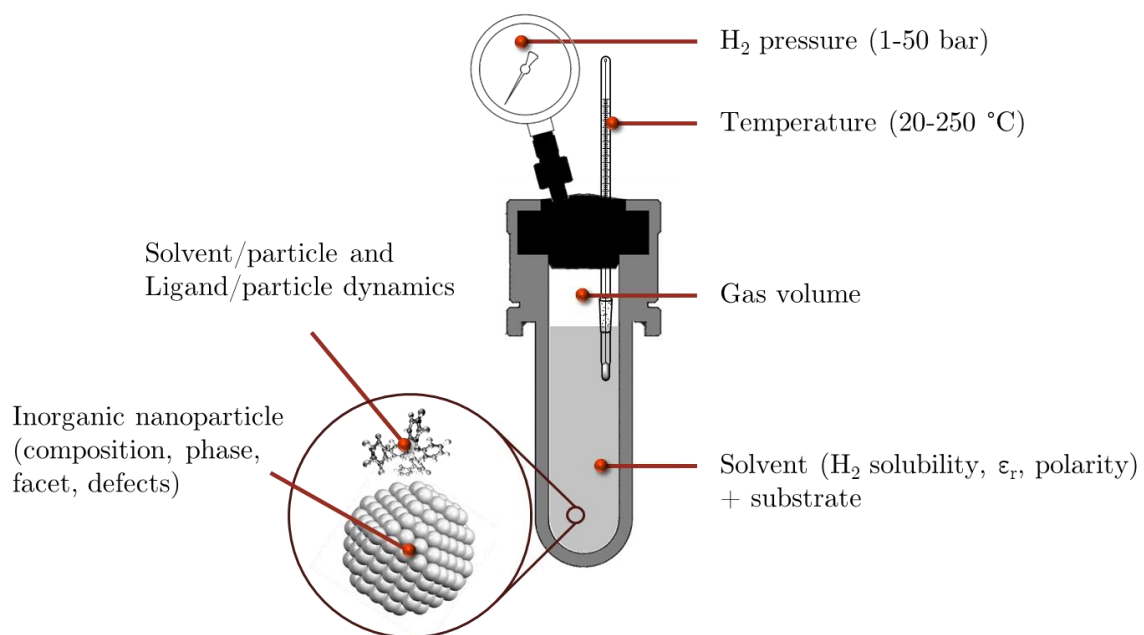
**Fine chemicals.** Hydrogenation reactions of unsaturated compounds in fine chemistry (drugs, dyes, agrochemicals, fragrances...) are very common steps for which chemoselectivity is crucial considering the high density of functions in the substrates molecules. For instance, the partial hydrogenation of alkynes and nitriles is known for being challenging as the olefinic bond is generally more easily reduced than the  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{N}$  ones. Usual substrates include alkenes and alkynes, aromatic rings, nitriles, imines, carbonyl moieties (aldehydes, ketones, esters, carboxylic acids), phenols, epoxides and nitro compounds.<sup>2</sup> Furthermore, removal of several protection groups such as activated ethers occurs through a hydrogenolysis step. Most of the academic works reporting the use of new catalysts generally optimize the reaction conditions on phenyl-derivative model substrates (styrene, phenylacetylene, benzonitrile, benzaldehyde, nitrobenzene...), easier to reduce than alkyl-connected groups. They then explore the

“strength” of the catalyst by screening a number of activated or deactivated moieties. The chemoselectivity may finally be illustrated on industrial-relevant molecule transformation such as citral selective hydrogenation in citronellal (C=C reduction) or geraniol (C=O reduction).<sup>18</sup>

**Phenylacetylene semi-hydrogenation.** The selective semi-hydrogenation of phenylacetylene in styrene is a specific case which is an important industrial process for the alkyne removal from styrene feed stocks.<sup>19</sup> Phenylacetylene indeed deactivates the styrene polymerization catalyst, thereby lowering the quality of the produced polystyrene: it must be considered as a poisonous impurity in the styrene monomer. The main challenge for this particular compound is therefore the selectivity of the reaction as the catalyst should be active only on traces (phenylacetylene) and not on the main compound of the mix (styrene). This is achieved by a fine tuning of the adsorption energies of the two molecules on the catalyst.

### I.1.3 Experimental setups for hydrogenation

In academic works, liquid phase hydrogenation reactions are usually performed in batch with an autoclave. The autoclave is charged with the liquid phase in equilibrium with a gas phase of pure H<sub>2</sub> at a given pressure (Scheme 1). Autoclaves in glass generally accommodate pressures up to *ca.* 10 bar whereas steel autoclaves are needed for higher pressures (up to 100 bar). Reactivity obtained at pressures as low as 1 atm makes possible the use of regular glassware equipped with a rubber balloon instead of pressurized setups. This point renders the work accessible to a much broader audience. Indicating the volume of the gas phase is necessary to determine the number of moles of H<sub>2</sub> and therefore the molar ratio H<sub>2</sub>:substrate. Due to the small size of H<sub>2</sub> molecules and the limited intermolecular interactions, the model of ideal gas may be applied and the number of moles of H<sub>2</sub> is directly proportional to the pressure on a fairly large range of pressure. The molar concentration under 1 bar at 20 °C is of 41.0 mmol.L<sup>-1</sup> and that at 100 bar is overestimated by only 6 % (3.8 mol.L<sup>-1</sup> instead of 4.1 mol.L<sup>-1</sup>).<sup>20</sup>



Scheme 1. Classical setup for hydrogenation reaction in solvent with critical points.

## I.2. Theoretical and experimental tools to study H<sub>2</sub> dissociation

### I.2.1 Microscopic description

**Elemental steps.** Hydrogenation reactions are usually decomposed in several elemental steps describing (1) the physical/molecular adsorption of H<sub>2</sub> at the surface of the catalyst, (2) its chemical adsorption, *i.e.* the bond cleavage, (3) the adsorption of the substrate, (4) the hydrogen transfer and (5) the product desorption. The H<sub>2</sub> activation refers to steps (1-2). The chemisorption differs from the physisorption by a substantial modification of the bonds in the adsorbate molecule, the H–H bond here. All the states of this mechanism are characterized by a Gibbs free energy  $G$ , usually referred to as the free energy, and the different steps present an activation barrier  $E_{\text{act}}$ . A negative change in free energy,  $\Delta G$ , denotes a favorable evolution *i.e.* the reaction is thermodynamically favored. A low energy barrier denotes an easy reaction *i.e.* the reaction is kinetically favored. Their values are commonly expressed in eV or in kJ/mol (1 eV  $\equiv$  96 kJ/mol) and are usually obtained *via* theoretical calculations by Density Functional Theory (DFT), or *via* kinetic experiments.

When modelling the reaction, a “zero energy” has to be set because free energy is not absolute. Two conventional choices exist: the zero energy may either refer to the energy of a clean surface and H<sub>2</sub> in the gas phase, or to the physisorbed state H<sub>2</sub><sup>\*</sup>. The difference is small considering the low energy engaged in the physisorption of H<sub>2</sub>, typically of the order of magnitude of 0.1 eV.<sup>21</sup> The degree of activation of H<sub>2</sub> is given by the length of the H–H bond: a weakening of the H–H bond is associated with its elongation. For instance, upon H<sub>2</sub> activation on WC first at the top of a W site, the H–H bond length evolved from 75 pm, its standard value in H<sub>2</sub> (gas), to 96 pm.<sup>22</sup> In some cases, as  $\beta$ -Mo<sub>2</sub>C(001), stable molecular H<sub>2</sub> adsorption without the dissociation in two hydrogen atoms is not possible on any site and the H<sub>2</sub> dissociation is barrier-less: the molecule dissociates spontaneously without any activation barrier.<sup>23</sup> The larger the adsorption energy, the more favorable the H<sub>2</sub> dissociation, leading to higher coverage adsorption. In an ideal case, the surface–H bond should be strong enough to favor the H<sub>2</sub> cleavage and weak enough to allow the H transfer to the substrate a in second time. Indeed, the higher in energy the surface–H state, the lower the activation barrier of the hydrogen transfer step and the more thermodynamically favorable the reaction: this is the Sabatier principle. The H<sub>2</sub> activation (steps 1-2) is slowed down if the substrate molecules are adsorbed too strongly or if the product desorbs too slowly as these molecules impend the access to the surface to H<sub>2</sub>. Ideally, the rate of H<sub>2</sub> activation should exceed that of product desorption, itself exceeding that of reactant adsorption.<sup>11</sup> A rapid product desorption also limits the risk of over-hydrogenation, as for phenylacetylene total hydrogenation in ethylbenzene.<sup>19</sup>

**Molecular hydrogen dissociation.** Two limit mechanisms, homolytic and heterolytic, are proposed for molecular hydrogen dissociation on surfaces. Both mechanisms are reported for metal oxides, and will be illustrated below on these materials, but the transposition is possible at least to metal nitrides<sup>24</sup> and sulfides.<sup>11</sup>

- (1) the homolytic (radical) mechanism produces two hydrogen atoms  $\text{H}\cdot$
- (2) the heterolytic (polar) mechanism produces a proton  $\text{H}^+$  and a hydride  $\text{H}^-$

In the homolytic mechanism, the two  $\text{H}\cdot$  combine with oxygen atoms to form two hydroxyl groups  $\text{O-H}$  and the charge neutrality of the material is respected by the reduction of one or two metal sites (the reduced metal centers are either isolated or delocalized in the conduction band) (Figure 2A, a)).<sup>25,26</sup> This dissociation mechanism is therefore thought to be possible only for reducible metal compounds such as  $\text{TiO}_2$  or  $\text{CeO}_2$  (both  $\text{M}^{3+}$  and  $\text{M}^{4+}$  states are stable). In the heterolytic mechanism, the  $\text{H-H}$  bond is broken along a  $\text{M-O}$  bond and yields to an  $\text{O-H}$  bond and a  $\text{M-H}$  bond (Figure 2A, b)). This latter species is regarded as a surface hydride  $\text{H}^-$  considering the difference in electronegativity ( $\chi(\text{M}) < \chi(\text{H})$ ). The degree of oxidation of the metal  $\text{M}$  has not formally changed as the  $\text{M-O}$  was cleaved too and this mechanism is possible for both non-reducible metal oxides such as  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  and reducible ones such as  $\text{ZnO}$ ,  $\text{Ga}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$ .<sup>26</sup> The heterolytic dissociation of  $\text{H}_2$  may lead to the homolytic product *via* a subsequent transfer of the hydrogen atom from the metal to an oxygen: this transfer was demonstrated for  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$  but also for metal-supported  $\text{MgO}$ .<sup>21,25,27-29</sup> The two pathways, homolytic and heterolytic, with subsequent  $\text{H}$  migration are illustrated on Figure 2 for a  $\text{Co}_3\text{O}_4(110)$  facet (Figure 2B). Finally, on defective surfaces with reduced metal centers, the  $\text{H}_2$  molecule may dissociate in two hydride species associated with the oxidation of the metal, as proven for  $\text{ZrO}_2$  and  $\text{CeO}_2$  (Figure 2A, c)).<sup>26,30</sup>

The presence of a  $\text{M-H}$  stretching vibration band in infrared spectroscopy or inelastic neutron scattering suggests a heterolytic dissociation of  $\text{H}_2$  (*vide infra*). The absence of experimental evidence of a  $\text{M-H}$  species is nonetheless not sufficient to exclude the radical mechanism considering a possible rearrangement. The polarity of the  $\text{M-O}$ , or  $\text{M-S}$  bond in the case of metal sulfides, induces a charge separation in the  $\text{H}_2$  molecule in the transition state and thus favors its heterolytic splitting in ( $\text{H}^+$ ,  $\text{H}^-$ ) rather than its homolytic splitting (Figure 3A). The  $\text{H}_2$  activation mechanism is therefore highly dependent on the nature of the  $\text{M-X}$  bond. The reader may refer to different DFT studies conducted on  $\text{H}_2$  dissociation on  $\text{Co}_3\text{O}_4$ ,<sup>21</sup>  $\text{TiO}_2$ ,<sup>27,28</sup>  $\text{ZrO}_2$ ,<sup>31</sup>  $\text{MgO}$ ,<sup>29,32,33</sup>  $\text{CeO}_2$ ,<sup>25,34</sup>  $\text{Ce}_2\text{O}_3$ ,<sup>35</sup>  $\text{MoS}_2$ ,<sup>36</sup>  $\text{Ni}_2\text{P}$ ,<sup>37</sup>  $\text{Mo}_2\text{C}$ ,<sup>23,38</sup> and  $\text{WC}$ .<sup>22</sup>

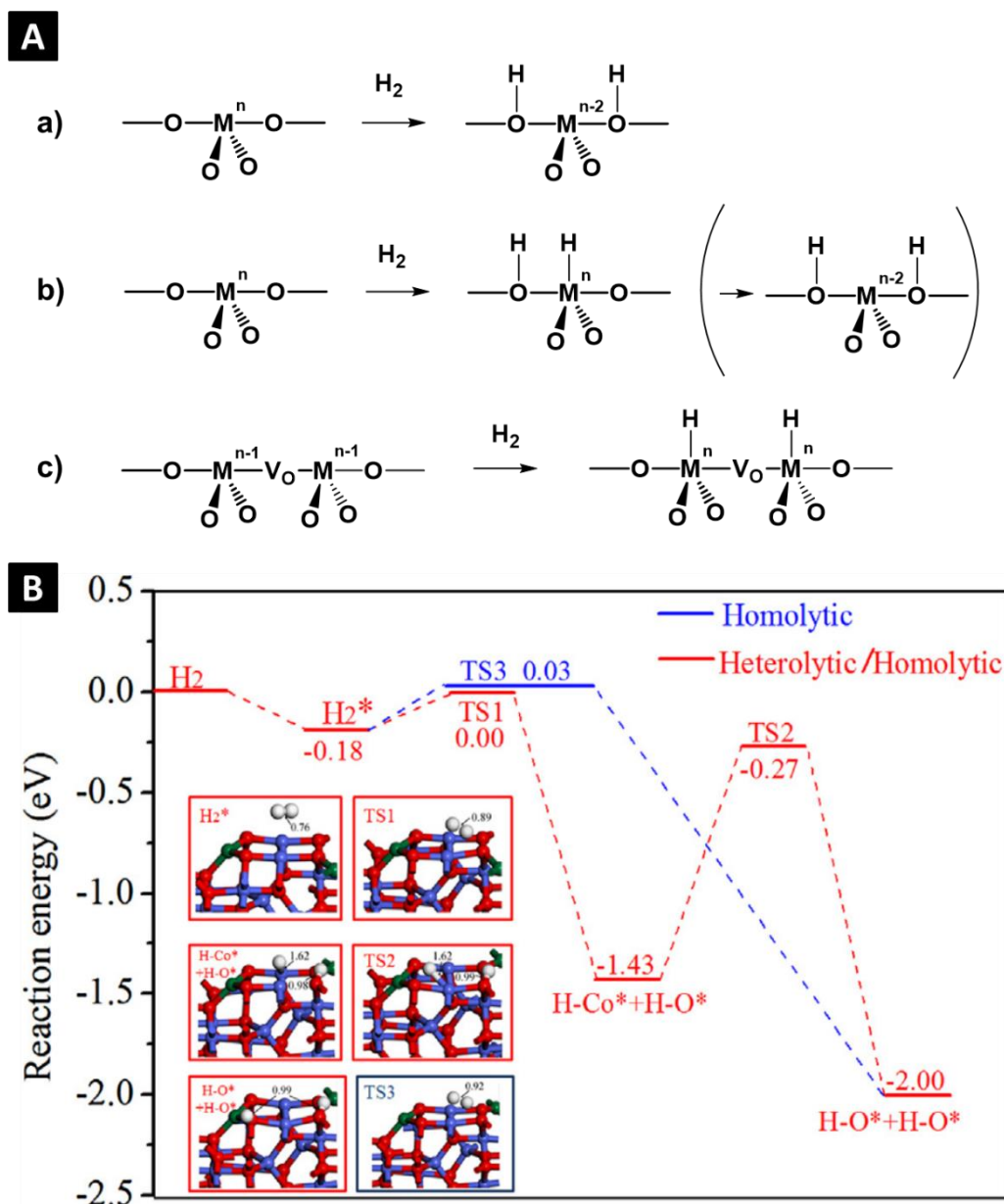


Figure 2. (A) a) Homolytic and b) Heterolytic activation of H<sub>2</sub> on metal oxide surfaces. c) H<sub>2</sub> activation on reduced metal oxide. (B) Energy profiles for homolytic and heterolytic H<sub>2</sub> dissociation pathways with the corresponding optimized geometries for the related states on perfect Co<sub>3</sub>O<sub>4</sub>(110) surface. The unique step of the homolytic pathway (blue curve) is exothermic ( $\Delta_{\text{ads}}G = -1.82$  eV) with an energy activation of  $E_{\text{act}} = 0.21$  eV. In the case of the heterolytic pathway (red curve), the first step is exothermic ( $\Delta_{\text{ads}}G = -1.25$  eV) with an energy activation of  $E_{\text{act}} = 0.18$  eV. After the heterolytic dissociation, the H atom linked to the Co atom migrates to a contiguous O atom to produce the homolytic product. This step is exothermic ( $\Delta G = -0.57$  eV) but with a high activation energy of  $E_{\text{act}} = 1.16$  eV, making it kinetically unfavorable. Reproduced from reference [21].



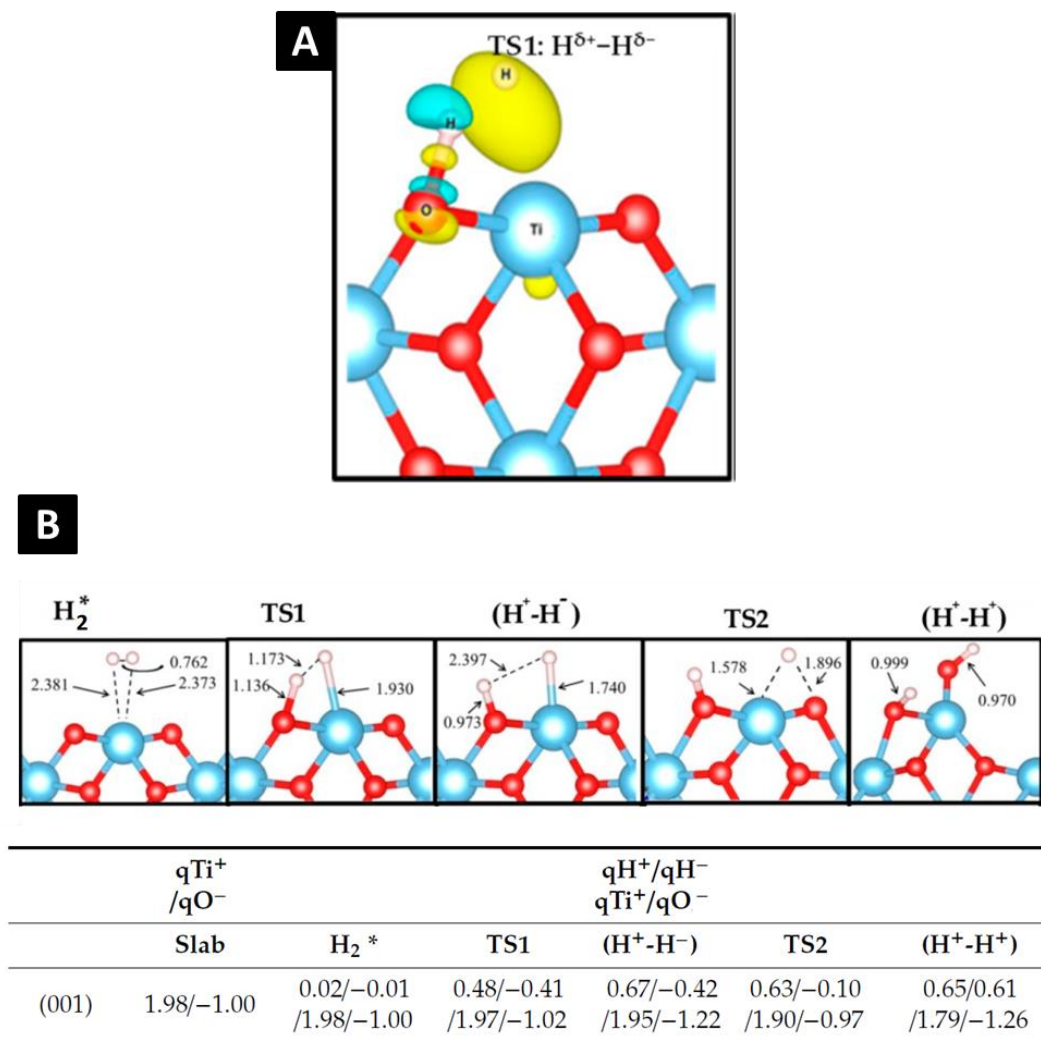


Figure 3. (A) Charge density difference of transition state illustrating the formation of the  $\text{H}^{\delta+}-\text{H}^{\delta-}$  tight ion pair on the  $\text{TiO}_2(001)$  surface. Yellow and green iso-surfaces show an electronic density gain and depletion, respectively. (B) Bader charges ( $|e|$ ) of H, Ti and O in the  $\text{H}_2$  dissociation process and in subsequent transfer from Ti to O process. Adapted from reference [27].

**Catalytic site.** Catalytically active sites are of different nature on surface. They generally correspond to metal atoms which are not fully coordinated (typically 6 neighbors for many transition metals) and display dangling bonds, hence the term of coordinatively unsaturated site (CUS) (Figure 4A). These sites exist owing to the presence of singularities on the surface such as edges, corners, steps and kinks or vacancies on terraces (Figure 4B). The CUS term is often found in literature for  $\text{H}_2$  activation by  $\text{MoS}_2$  due to the importance of sulfur vacancies in the corresponding catalysts but the concept is valid for all materials.<sup>38,39</sup>



Different positions exist for the hydrogen location before and after H–H bond cleavage. The H atoms do not necessarily stay at the top of an atom (site **t**) but may also occupy a bridge position between two atoms (site **b**) or even a hollow site between three atoms or more (site **h**) (Figure 4C).<sup>23</sup> Sites **t** are not always on metal atoms, the H may also be at the top of a carbon atom for instance, as in the case of WC(0001) or Mo<sub>2</sub>C(101).<sup>22,38</sup> The low coordination of CUS renders the heterolytic cleavage easier as the M–H bond stabilizes the metal atom.<sup>27</sup> Post-dissociation migration of the hydrogen atoms may also occur before they react with a substrate molecule (Figure 4D).

**Orbital description & electron Density of States (DOS).** So far, the description of the mechanisms we presented relied on concepts inherited from homogeneous catalysis with discrete species, precise degrees of oxidation and charges. But the complexity and versatility of heterogeneous catalysis precisely relies on the complex interaction between the substrate, a molecule, and a material surface whose electron description should integrate its band structure according to Nørskov *et al.*<sup>41</sup> One of the challenges is therefore to develop concepts and descriptors of the properties monitoring the activity and selectivity of the catalysts. Achieving this point would permit the rationalization of the already known catalytic materials and the development of new ones. The *d*-band model has proved its efficiency to understand the substrate adsorption and/or activation on a metal-containing surface. It relies on the interactions between the orbitals of the substrate and the *s* and *d* states of the surface (Figure 5). The strength of the M–H bond, and thus the adsorption of the substrate, is characterized by the filling of the antibonding orbitals between the adsorbate state and the metal *d* states (stressed in orange). The surface may be considered as a reservoir of electron at the Fermi level  $E_{\text{Fermi}}$  and these electrons are susceptible to fill the antibonding orbitals of the surface–substrate complex. The Fermi level also corresponds to the *d* band center. As the antibonding states are always higher in energy than the *d* states, the higher in energy the *d* states are (relative to the Fermi level), the emptier the antibonding states and the stronger the M–H bond. Variations in the width of the *d* band of the material are compensated by a shift in energy of the *d* band. There is therefore a great interest in the determination and engineering of the electron density of states (DOS) of the catalyst.

Different strategies may be considered such as the insertion of light elements in the metal lattice or the doping with other metal atoms.<sup>37</sup> Electron-enriched metal sites tend to have a lower Fermi level and therefore render the H desorption more favorable. On the contrary, electron-deficient metal sites lead to higher Fermi level and therefore render the H<sub>2</sub> adsorption more favorable. The doping of metallic phases with light elements generally decreases the electron density on the metal atoms considering the difference in electronegativities between the transition metals and the *p*-block elements, thereby favoring the H<sub>2</sub> dissociation.

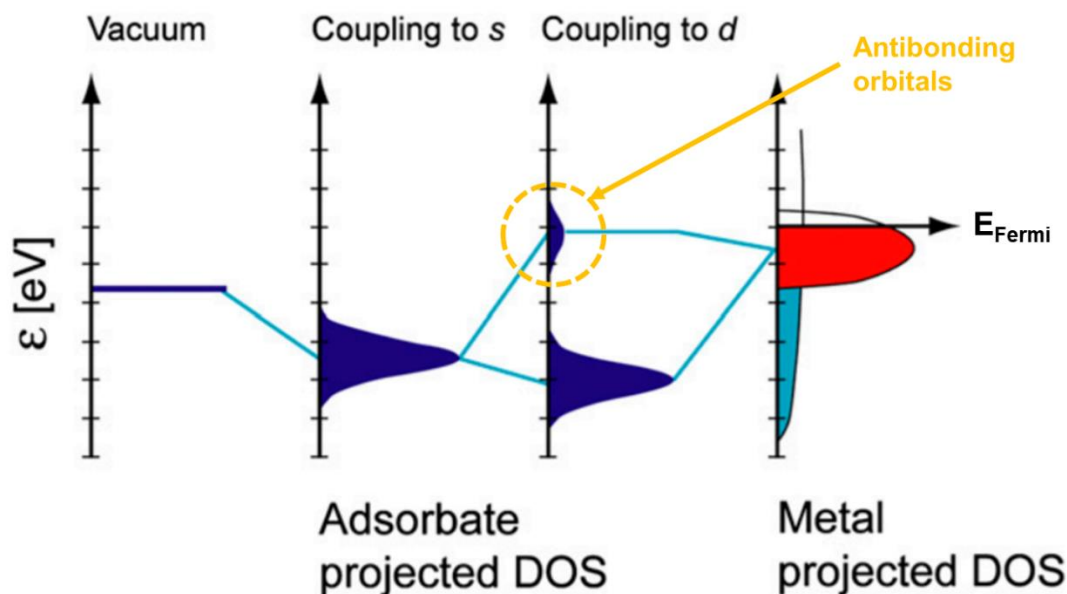


Figure 5. Bond formation at a transition-metal surface. Schematic illustration of the formation of a chemical bond between an adsorbate valence level (left) and the  $s$  and  $d$  states of a transition-metal surface (right). Adapted from reference [41].

Finally, the description of the material surface with orbitals and band structures is a reminder that the homolytic/heterolytic models proposed are simplifications, especially concerning the charges born by the different atoms. The Bader analysis thus indicates the electronic density estimated around a particular atom by DFT calculations and they do not correspond to integer values. A certain degree of delocalization of the charges is expected for covalent and metallic materials, and eventually for ionic ones such as metal oxides. For instance, for the heterolytic cleavage of  $\text{H}_2$  on  $\text{TiO}_2(001)$ , the system is described as an ion pair ( $\text{H}^+-\text{H}^-$ ) or ( $\text{H}^+-\text{H}^+$ ) whereas the charges never exceed 0.7 on the H atom (Figure 3B).<sup>27</sup> Moreover, the charge conservation is not respected if only the four atoms directly involved are considered (O, Ti, 2 H): this is the sign of a delocalization of the charges to nearby atoms or to the whole nanoparticles.

**Parameters.** For a given chemical composition of a catalyst, the free energies of the transition states and of the intermediate species, and thereby the H–H splitting, depend on different characteristics. Both the crystal facet engineering and the defect engineering matter for designing the most active catalyst, and DFT calculations prior to the synthesis help the determination of the best catalyst:

- (1) **the crystal phase.**
- (2) **the crystal facet exposed.** Depending on the exposed facet, the accessible surface atoms may vary. For instance,  $\beta\text{-Mo}_2\text{C}$  (001) and (100) facets are

terminated only by Mo atoms whereas (101) and (201) facets present a mix of C and Mo atoms.<sup>23</sup>

- (3) **the presence of vacancies and defects.**
- (4) **the presence of metal dopants (Fe, Co, Ni...).** These atoms may modify the electronic structure and thereby the H<sub>2</sub> activation even without being directly involved and forming M–H bond.<sup>37,42</sup>
- (5) **the surface coverage** with adsorbates (H atoms or substrate). Several H<sub>2</sub> molecule may dissociate at the surface of the catalyst at the same time, the saturation is reached when the stepwise adsorption energy of the n+1 molecule of H<sub>2</sub> equals 0:  $\Delta_{\text{ads}}G(n + 1) = G(2n + 2 \text{ H}^*/\text{slab}) - (G(2n \text{ H}^*/\text{slab}) + G(\text{H}_2)) = 0$ . The activity of the catalyst generally decreases with the H<sub>2</sub> coverage but the nature of the adsorption may also vary: molecular *vs* dissociative for instance.<sup>37,38</sup>

## I.2.2 Experimental techniques for H<sub>2</sub> activation characterization

The vast majority of the techniques presented here in order to characterize the activation of H<sub>2</sub> on the material surface are performed under vacuum or in the gas phase. This limitation clearly makes the *operando* study of heterogeneous catalysts in solution challenging if not impossible today.

### I.2.2.1. Thermal technique

**H<sub>2</sub>-Temperature Programmed Desorption (H<sub>2</sub>-TPD).** This technique allows the determination of the energy of adsorption of H<sub>2</sub> at the surface of the catalyst and the eventual formation of subsurface hydrides.<sup>43</sup> This technique is performed in the gas phase after a treatment of the material under high vacuum. The material surface is first saturated with H<sub>2</sub> molecules at room temperature, the temperature is then gradually increased and the amount of desorbed H<sub>2</sub> is recorded. Two main points are informative in the measurement:

- Area under the TPD profile. In most of the systems, this area is proportional to the amount of adsorbed H<sub>2</sub> molecules, from which can be determined the surface coverage  $\theta(\text{H}_2)$ .
- Peak maximum position ( $T_{\text{max}}$ ). The temperature at which there is a maximum of H<sub>2</sub> desorption, noted  $T_{\text{max}}$ , is related to the activation energy for desorption: the higher  $T_{\text{max}}$ , the larger the activation energy. H<sub>2</sub> adsorption is generally spontaneous, with virtually no activation energy, consequently, the activation energy of desorption equals the energy of adsorption.

The vast majority of real systems do not present a single peak but rather complex features. Each peak corresponds to one specific adsorption site characterized by a density of sites (area) and an adsorption energy ( $T_{\text{max}}$ ). These adsorption sites may even consist in the formation of subsurface hydride species for materials such as Pd or Ni. To the best of our knowledge, there is no common experimental method which would provide the same data for H<sub>2</sub> adsorption energy in solvent.

### I.2.2.2. Vibrational spectroscopies

Structures of surface isolated hydrides in heterogeneous catalysis are less understood than hydrides in molecular complexes, mostly due to the difficulty in revealing structures on/in solids and because of the large number of potential active sites and geometries.<sup>26,44</sup> Vibrational spectroscopy experiments can nonetheless evidence the existence of metal–H bond or X–H bond where X is a light element. The position in energy of the band is also informative on the bond strength.

**Infrared spectroscopy (IR).** Copéret *et al.* recently reviewed the splitting of H<sub>2</sub> on a large number of bulk metal oxides and summarized the typical IR and Raman

bands  $\nu_{M-H}$  expected or observed, with the associated binding types (top, bridge, terminal).<sup>26</sup> DFT calculations may also be used as qualitative guide to identify the M–H frequencies obtained experimentally.<sup>27,34</sup> Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is an infrared technique which does not necessitate any treatment of the sample prior to measurements, it can therefore be used for operando studies. For instance, Ozin *et al.* recorded the DRIFTS spectra of the hydroxyl and hydride fingerprint regions in the case of indium oxide catalyst put in presence of H<sub>2</sub> (1 bar, room temperature) (Figure 6A,C-D).<sup>45</sup> They thus evidenced the formation of In–H<sup>–</sup> and protonated hydroxyl species In–OH<sub>2</sub><sup>+</sup> on different metal sites or with different geometries ( $\phi_1$  to  $\phi_6$  for hydride,  $\nu_1$  to  $\nu_4$  for hydroxyl).

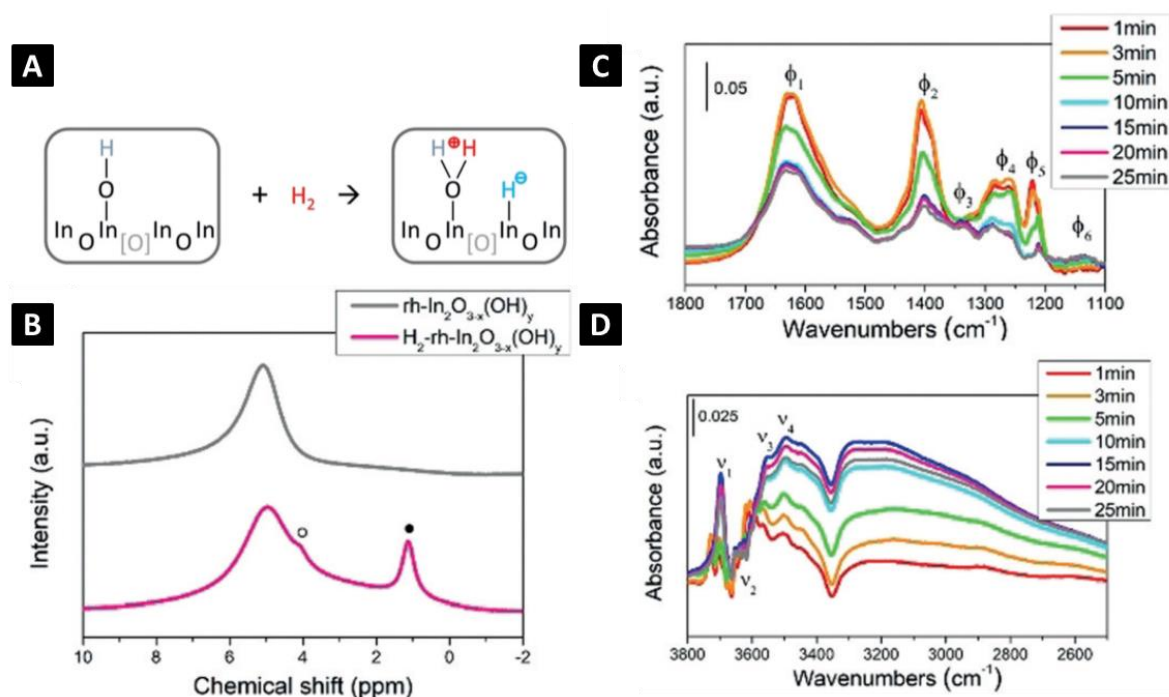


Figure 6. (A) Illustration of the heterolysis reaction pathway for the dissociation of H<sub>2</sub> on rh-In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub>, (B) Solid-state <sup>1</sup>H MAS NMR spectra of rh-In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> where filled dot (1.14 ppm) can be assigned to In–H<sup>–</sup> and circle (4.05 ppm) to In–OH<sub>2</sub><sup>+</sup>. Grey and pink spectra correspond to respectively before and after exposure to H<sub>2</sub> (1 bar) at room temperature. (C–D) Operando DRIFTS study of rh-In<sub>2</sub>O<sub>3-x</sub>(OH)<sub>y</sub> under H<sub>2</sub> atmosphere at room temperature (C: hydride region, D: hydroxyl region). Adapted from reference [45].

**Inelastic Neutron Scattering (INS).** Neutron scattering is very well suited for studying hydrogen environment as the incoherent neutron cross section of H is higher than any other atoms, meaning neutron scattering signal is dominated by that of hydrogen. Wu *et al.* recently reviewed the use of INS for hydrides characterization in heterogeneous catalysis, in particular for metal oxides and sulfides.<sup>44</sup> Contrarily to IR or Raman spectroscopies, all modes of vibration or rotation can be detected with INS. This technique is nonetheless less used considering the difficulty to access a neutron

source. Among different works, we can mention the direct observation of cerium hydride Ce–H species on cerium dioxide by Ramirez-Cuesta *et al.* and that of Mo–H species on molybdenum nitride by Thompson *et al.*<sup>24,46</sup> This was the first time the H<sub>2</sub> heterolytic dissociation on CeO<sub>2</sub> was formally proved as other vibrational techniques failed to detect the hydride species.

### I.2.2.3. Direct probing of the hydrogen

**<sup>1</sup>H Magic Angle Spinning Nuclear Magnetic Resonance (<sup>1</sup>H MAS NMR).** Upon activation of H<sub>2</sub> at the surface of a material, the solid state <sup>1</sup>H MAS NMR spectrum may display new peaks corresponding to surface species (M–OH<sup>+</sup>, M–OH<sub>2</sub><sup>+</sup>, M–H<sup>–</sup>). Hosono *et al.* reported a work on the NMR characterization of hydride species in metal oxides and demonstrated the attribution is not straightforward.<sup>47</sup> The electronic density around the H nuclei is indeed different from what is expected from the formal oxidation states: the density near the hydrogen atom in M–OH<sup>+</sup> for instance exceeds that of hydrogen in M–H<sup>–</sup>. This NMR characterization was used to characterize the H<sub>2</sub> splitting on indium oxide by Ozin *et al.* (Figure 6A–B).<sup>45</sup> Two peaks grew after the addition of H<sub>2</sub> (1 bar) on the catalyst: one was attributed to a hydride species In–H<sup>–</sup> and another to a protonated hydroxyl group In–OH<sub>2</sub><sup>+</sup>. Such a technique may therefore comfort a heterolytic dissociation mechanism over a homolytic one.

### I.2.2.4. Indirect probing *via* the metal center

A large number of characterization techniques for atom environments and oxidation degree over inorganic solid surfaces rely on the interaction between the studied atom and X–rays or high energy electrons. They therefore cannot be used for direct study of hydrogen atoms considering the low atomic number of the element and therefore its limited interaction with the X–rays and with the electrons. To circumvent this issue, the presence of adsorbed hydrogen may be indirectly detected on the metal center.

**X–ray Photoelectron Spectroscopy (XPS).** XPS is a powerful technique allowing the determination of the chemical composition and electronic configuration of atoms at the extreme surface of a material.<sup>48</sup> The degree of oxidation and the evolution of the close chemical environments of all the atoms can therefore be monitored with time. This technique was extensively used for the study of gas phase heterogeneous catalysts. Its main limitation is the need for Ultra-High Vacuum (UHV) as an X–ray beam is required and its interaction with gas molecules of atmosphere would extinguish it. With powerful beams, typically those available in synchrotron facilities, a low pressure of gas, up to *ca.* 5 mbar, can be introduced while measuring the surface state of the sample. This mode is termed Near Ambient Pressure XPS (NAP-XPS). For instance, Freund *et al.* used NAP-XPS to demonstrate H<sub>2</sub> could be split at the Ce<sup>(III)</sup> sites on reduced cerium oxide catalyst to form surface hydride species.<sup>30</sup> Such a mechanism implies the oxidation of the Ce<sup>(III)</sup> atoms in Ce<sup>(IV)</sup> ones. This effect was indeed observed



on the Ce 3d region which a Ce<sup>(III)</sup> fraction decreasing upon exposure to H<sub>2</sub> (Figure 7). The technique can *a priori* be applied to any system which may present a modification of the degree of oxidation of the metal center, and is therefore well suited to prove the heterolytic dissociation of H<sub>2</sub> or its splitting on oxygen vacancy sites.

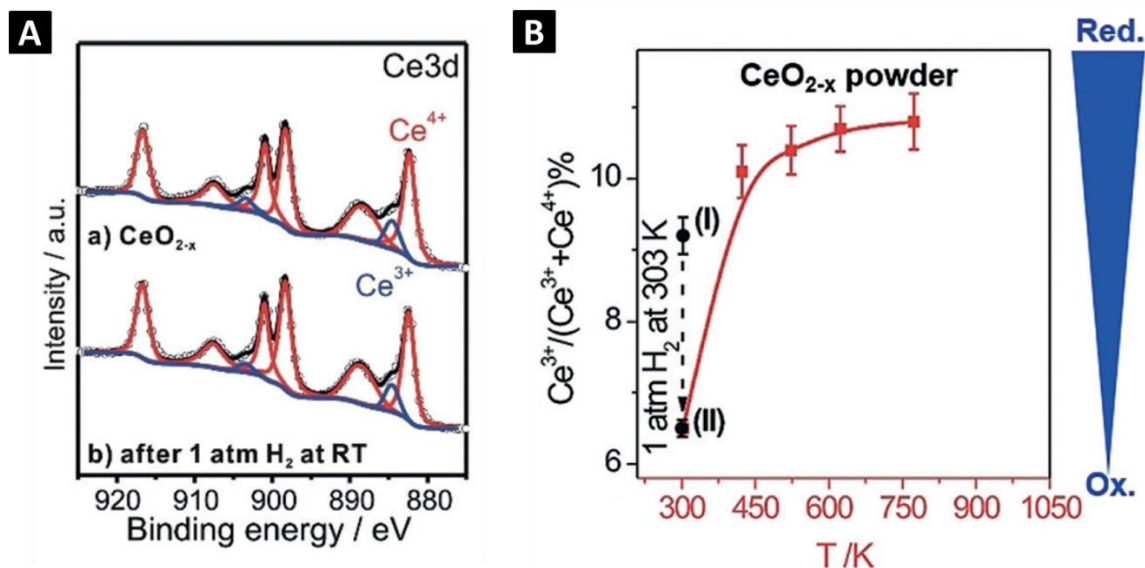


Figure 7. (A) Ce 3d XP spectra of CeO<sub>2-x</sub> powder before (a) and after (b) exposure to 1 atm H<sub>2</sub> at r.t. (B) Ce<sup>3+</sup> concentration in CeO<sub>2-x</sub> (I) before and (II) after H<sub>2</sub> treatment (1 atm, 1 h, r.t.) and subsequent heating, determined from Ce 3d region XPS. Adapted from reference [30].

#### I.2.2.5. Chemical reactivity

**H<sub>2</sub>/D<sub>2</sub> scrambling.** The catalytic activity of a material toward H<sub>2</sub> activation may be evidenced by the formation of HD, detected by mass spectrometry, when exposed to a H<sub>2</sub>/D<sub>2</sub> mix. These experiments are usually performed in flux in the gas phase.<sup>49</sup> Studying the production and the release of HD as a function of temperature can thus be informative on the formation of transient surface hydride species and on the strength of the interaction between the surface and H/D (interaction strength and surface coverage). When looking at the H<sub>2</sub>/D<sub>2</sub> exchange rate on metal oxides, no direct connection could be drawn between the efficiency of the exchange and the nature of the activation mechanism (heterolytic *versus* homolytic).<sup>26</sup>

### I.2.3 Reactions in solvent: where is the difference?

#### I.2.3.1. Solubility of H<sub>2</sub> in solvents

Molecular hydrogen concentration in the liquid phase depends on mainly three factors: the pressure of H<sub>2</sub> in the gas phase, the temperature and the nature of the solvent. Figure 8 displays the evolution of the molar H<sub>2</sub> concentration as a function of temperature and H<sub>2</sub> pressure for several common solvents. First, it appears the range of concentration in H<sub>2</sub> is close for all the solvents, between 2 and 6 mmol/L under

1 atm of H<sub>2</sub> at 25 °C, and that there is no clear trend concerning the polarity of the solvent. While there may be a more favorable solubilization of H<sub>2</sub> in non-polar solvents (*n*-alkanes, toluene), this effect is counterbalanced by physical characteristics of the liquids such as their density or molar mass. Then, H<sub>2</sub> concentration increases for all solvents with temperature, on average of 50 % between 25 °C and 100 °C. Finally, in agreement with Henry's law, the concentration in H<sub>2</sub> is proportional to the partial pressure in H<sub>2</sub> in the gas phase. All these results indicate that H<sub>2</sub> may be dissolved in non-negligible quantities in all common solvents and that increasing the H<sub>2</sub> pressure is a more efficient way to solubilize H<sub>2</sub> than increasing the temperature. This analysis however does not prejudge of the best conditions for the catalysis itself: the temperature has also a critical importance to kinetically favor the solubilization of H<sub>2</sub> and to overcome the activation barriers of its activation. The solubility of H<sub>2</sub> evolves linearly with the pressure in the gas phase so the progressive consumption of H<sub>2</sub> diminishes its concentration in the liquid phase, thereby lowering the reaction rate. Although this correction is usually small when high H<sub>2</sub> pressures are used, it may be significant for atmospheric pressures or close.

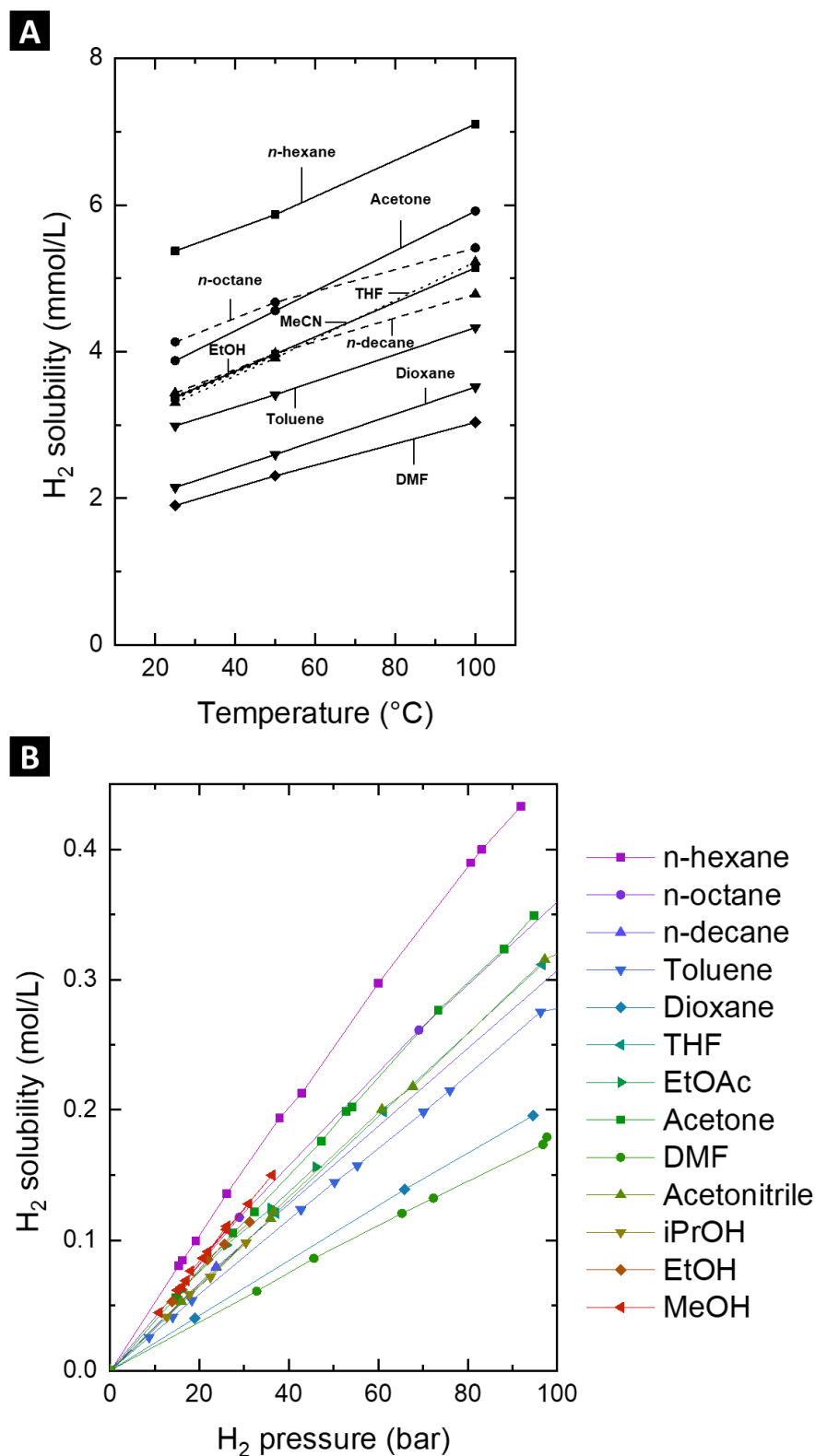


Figure 8.  $H_2$  solubility in various solvents (A) under 1 atm of  $H_2$  at different temperatures and (B) at 25  $^{\circ}C$  under different pressures. The polarities of the solvents according to the Miller chart are the following: *n*-hexane (0.009), *n*-octane, *n*-decane, toluene (0.099), dioxane (0.164), THF (0.207), ethyl acetate (0.228), acetone (0.355), DMF (0.386), acetonitrile (0.46), isopropanol (0.617), ethanol (0.654), methanol (0.762). Data extracted from references <sup>[50,51]</sup>.

### I.2.3.2. Reaction medium: impact on adsorption and solvation energies

The presence of a liquid phase in heterogeneous catalysis may alter the free energies of the different states, and thereby the reaction mechanism, because of the interactions between the solvent molecules and the reagents/products/reaction intermediates. These modifications are generally related to the polarity of the solvent and its capacity to stabilize ions and ion pairs, rationalized through its dielectric constant  $\epsilon_r$ . Modeling liquid-phase reactions is nonetheless more challenging than gas-phase reactions which are closer to the *in vacuo* conditions of DFT regular calculations.<sup>40,52,53</sup> Nonetheless, barring an increase in calculation cost, different methods were developed to take into account the solvent: (1) implicit-solvent models, (2) explicit-solvent models and (3) microsolvation models (Figure 9). In case (1), also termed Continuum Solvation Models (CSM), the solvent molecules are not individually modelled but instead considered as a continuum, and correction terms in free energy calculations for solutes are added. This is a mean-field approach based on the dielectric constant of the liquid, it therefore finds limitations in the modelling of directional interactions such as hydrogen bonding and asymmetrically charged solvents. In case (2), all solvent molecules are modelled and their interactions with the catalyst and solutes are taken into consideration. Although straightforward, this approach is highly costly as to calculation time. Moreover, static calculations at 0 K cannot be representative of the dynamic character of the solvent. Molecular dynamic simulations can overcome this limitation but at the cost of a further increase in calculation time. Case (3) corresponds to a mix of cases (1) and (2), one may find the terms of (hybrid-)cluster-continuum models. The principle consists in modelling short-range directional interactions through the addition of a few explicit solvent molecules and the long-range electrostatic interactions by using continuum models. Calculation times are therefore kept reasonable.

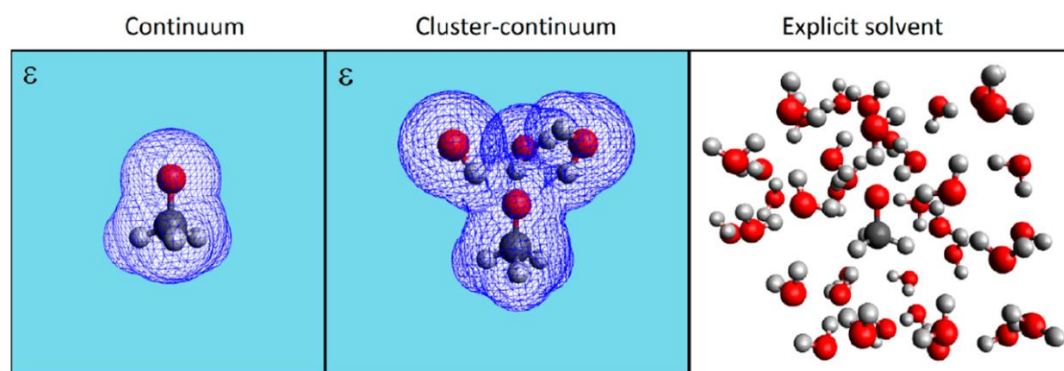


Figure 9. Different approaches to treat solvation of a methoxide ion in water: Continuum, Cluster-Continuum, and Explicit-Solvent. The light-blue background represents a dielectric continuum that approximates the solvent with a relative permeability of  $\epsilon$ . The blue mesh represents the solute–solvent interface. Color code for atoms: dark gray, C; red, O; white, H.

Reproduced from reference [54].

### I.3. Metal-containing catalysts for colloidal hydrogenation

This section does not intend to exhaustively list the use of non-purely metallic active phases for H<sub>2</sub> activation in solvent but rather indicate what are the currently most studied materials. If a material led to numerous works, we only mention the pioneering studies. We chose to mention the main reviews and some works realized under mild conditions.<sup>1,5,55-58</sup>

Metal-containing compounds are expected to possess a different reactivity from the parent metals through mainly two effects:<sup>59</sup>

- (a) Ligand effect: the introduction of light elements in the metal lattices increases the lattice parameters, thereby decreasing the extent of the M–M interaction and narrowing the *d*-electron band. The modification of the *d*-orbitals is amplified by the charge transfer from the light element to the metal and the hybridization of the *d*-orbitals of the metal and the *sp*-orbitals of the light element. The electron deprived metal sites are therefore less susceptible to fill the antibonding orbitals of M–H, which favors the H<sub>2</sub> activation.<sup>58</sup>
- (b) Ensemble effect: the presence of a second element in the material modifies the geometric arrangement of the metal atoms at the surface and therefore may create different adsorption sites. Furthermore, the presence of light element vacancies increases the number of coordinatively unsaturated sites (CUS), expected to be more catalytically active.

The type of bonding in materials may be defined among ionic, metallic and covalent. The ionic character is characterized by a high difference in electronegativity between the different elements composing the material and the metallic character by a low average electronegativity. Depending on the percentage of importance of each component, the material is placed on the Van Arkel-Ketelaar triangle (Figure 10). The Pauling electronegativities of boron ( $\chi(\text{B}) = 2.04$ ) and phosphorus ( $\chi(\text{P}) = 2.19$ ) are closer to those of transition metals than the other light elements ( $\chi(\text{C}) = 2.55$ ,  $\chi(\text{N}) = 3.04$ ,  $\chi(\text{O}) = 3.44$  and  $\chi(\text{S}) = 2.58$ ), a more pronounced covalent or metallic character is therefore expected, associated with a better electron delocalization. On the contrary oxides present a more marked ionic character. Nitrides and carbides present an intermediate nature. Finally, silicides ( $\chi(\text{Si}) = 1.90$ ) are generally considered as intermetallic compounds with a predominant metallic character for the bonding. As previously developed, the mechanism at stake for H<sub>2</sub> dissociation at the surface of the particle has two extreme descriptions: the homolytic dissociation and the heterolytic one. This distinction may be put in relation with the nature of the bonding in the material: heterolytic dissociation would be more often observed for ionic bonding, *i.e.*

for oxides, sulfides and eventually nitrides and homolytic for covalent and metallic compounds, *i.e.* phosphides, carbides, silicides, borides and eventually nitrides.

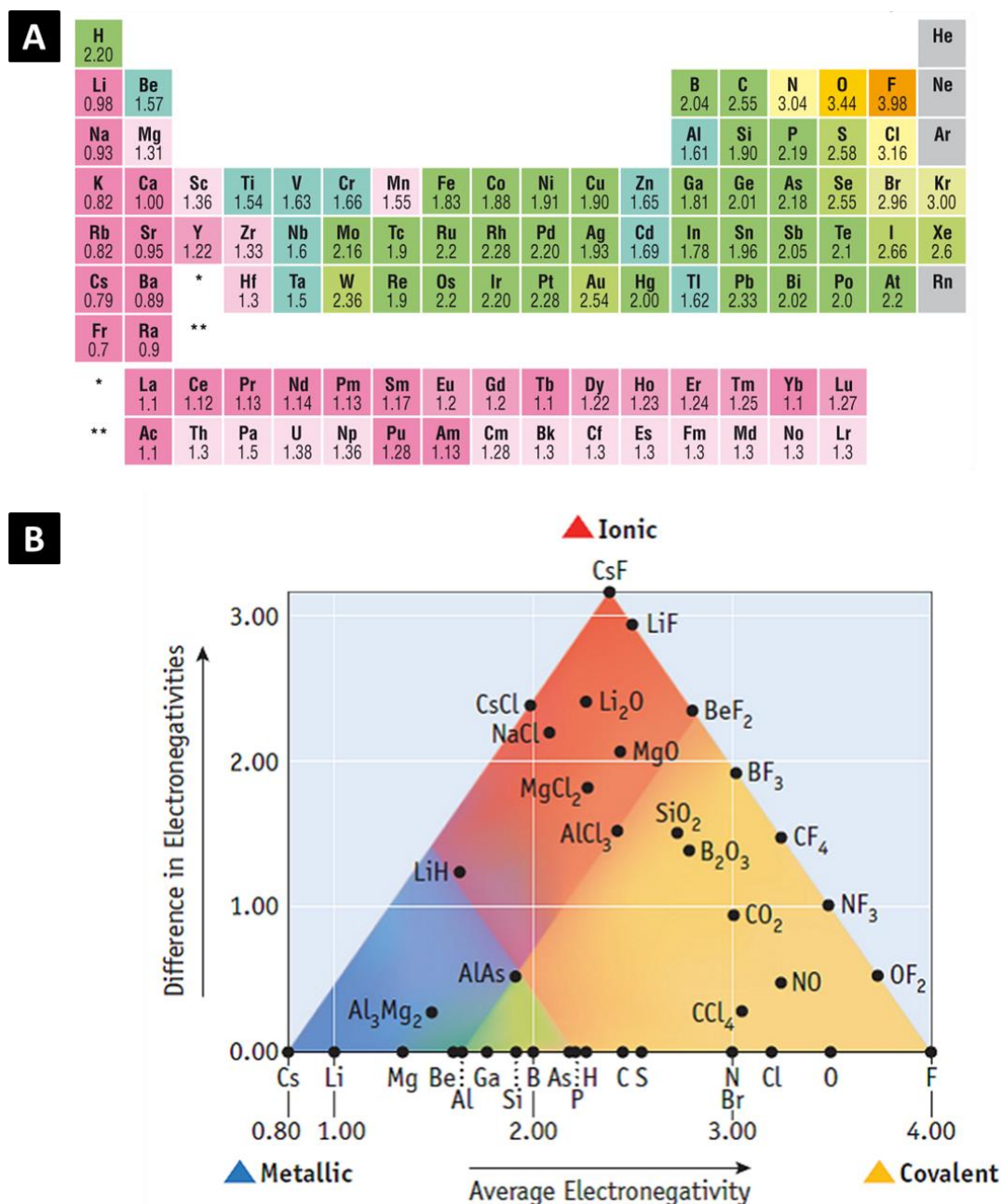


Figure 10. (A) Pauling electronegativities of elements. (B) Van Arkel-Ketelaar triangle.

### 1.3.1 Metal borides

Boron alloys of nickel and cobalt have been extensively reported for hydrogenation reactions, including HDO, HDS and HDN processes.<sup>56,58,60,61</sup> Works mentioning metal borides generally do not refer to a specific crystallographic phase but

rather to amorphous nanoscale materials. If such, they are denoted M–B where M is the metal. A high number of the reactions were performed with substrates in the gas phase but we can nonetheless stress the use of Ni–B and Co–B alloys for hydrogenation of sulfolene, sugars (glucose, fructose, maltose), aldehydes and ketones (furfural, crotonaldehyde, benzaldehyde, cinnamaldehyde), nitro compounds and nitriles in solvent, all summarized by the reviews of Tao *et al.* and Sanchez *et al.*<sup>58,61</sup> For instance, the hydrogenation of nitrobenzene was reported with amorphous nickel boride, Ni–B, under mild conditions (90 °C, 10 bar H<sub>2</sub>, EtOH),<sup>62</sup> and that of citral with Co<sub>2</sub>B/Ni<sub>7</sub>B<sub>3</sub> (150 °C, 15 bar H<sub>2</sub>, hexane). Different chemoselectivities were obtained in the last case: Co<sub>2</sub>B preferentially hydrogenates C=O bonds while Ni<sub>7</sub>B<sub>3</sub> is selective for C=C bonds.<sup>18</sup>

Ref.	Material	Substrate	Solvent	P(H <sub>2</sub> )	T, t
<b>Borides</b>					
18	Co <sub>2</sub> B	Citral (C=O)	Hexane	15 bar	150 °C, 4 h
18	Ni <sub>7</sub> B <sub>3</sub>	Citral (C=C)	Hexane	15 bar	80-150 °C, 4 h
63	Ni–B	Nitrobenzene	MeOH	4 bar	65-100 °C, 2 h
62	Ni–B	Nitrobenzene	EtOH	10 bar	90 °C, <i>n.a.</i>
<b>Silicides</b>					
64,65	NiSi <sub>x</sub>	Phenylacetylene	EtOH	4 bar	50 °C, 5 h
66	Ni <sub>2</sub> Si	Nitroarenes/Nitriles Aldehydes/Ketones Alkenes/Alkynes	H <sub>2</sub> O/MeOH	10- 50 bar	40-130 °C, 20 h
67	M <sub>2</sub> Si (Fe, Co, Ni)	Cinnamaldehyde	EtOH	10 bar	90 °C, 4 h
<b>Phosphides</b>					
68	Fe <sub>2</sub> P@C	Nitroarenes	H <sub>2</sub> O/THF	50 bar	120 °C, 12 h
69	Co <sub>2</sub> P/CN <sub>x</sub>	Nitroarenes	H <sub>2</sub> O/THF	50 bar	60 °C, 6 h
70	Co <sub>2</sub> P	Nitriles	iPrOH/NH <sub>3</sub>	1-40 bar	130-150 °C, 20 h
71	Co <sub>2</sub> P	Furfural	H <sub>2</sub> O	40 bar	130 °C, 2 h
72	Co <sub>2</sub> P	Aldehydes/Ketones	H <sub>2</sub> O/NH <sub>3</sub>	1-10 bar	100 °C, 6-48 h
49	Ni <sub>2</sub> P	Alkynes	Dioxane	6 bar	85 °C, 10 h
73	Ni <sub>2</sub> P	Nitroarenes	EtOH	10 bar	80 °C, 10 h
74,75	Ni <sub>2</sub> P/MO <sub>x</sub>	Maltose/Glucose	H <sub>2</sub> O	1-20 bar	r.t.-100 °C, 24 h
76	Ni <sub>2</sub> P, Ni <sub>5</sub> P <sub>4</sub>	Alkynes	Toluene	10- 20 bar	30-70 °C, flux

Table 1. Examples of hydrogenation reactions in solvent catalyzed by metal borides, silicides and phosphides.

### 1.3.2 Metal silicides

The use of metal silicides compounds in catalysis was recently reviewed by Liang *et al.*<sup>57</sup> Their use in HDS reaction is considered in particular due to the high stability of the materials toward H<sub>2</sub>S poisoning, even higher than that of carbides, nitrides and phosphides. Fewer works reported HDO reactions: Ni<sub>2</sub>Si was used for lignin and diphenylether hydrogenation. As to fine chemistry, different metal silicides M<sub>2</sub>Si@C (M = Fe, Co, Ni) were reported for the selective hydrogenation of cinnamaldehyde with a selectivity echoing that reported for the metal borides: Co<sub>2</sub>Si@C preferentially hydrogenates polar C=O bonds, to the contrary of Ni<sub>2</sub>Si@C, more active on C=C bonds.<sup>67</sup> Cobalt silicides (CoSi and CoSi<sub>2</sub>), obtained by pyrolysis of CoCl<sub>2</sub> and Si, were proved to hydrogenate phthalic anhydride in the liquid phase (180-220 °C, 40 bar H<sub>2</sub>, 4-hydroxybutanoic lactone).<sup>77</sup> The semi-hydrogenation of phenylacetylene in styrene was achieved with various Ni-Si compounds (NiSi<sub>2</sub>, NiSi, Ni<sub>2</sub>Si) under mild conditions (50-80 °C, 4-10 bar of H<sub>2</sub>, EtOH).<sup>64,65</sup> Finally, Beller *et al.* reported the use of nickel silicide catalysts for the hydrogenation of a large scope of substrates including nitroarenes, aldehydes, ketones, nitriles, quinolines, alkenes and alkynes (40-130 °C, 10-50 bar H<sub>2</sub>, H<sub>2</sub>O/MeOH mixture).<sup>66</sup> The catalyst was produced by pyrolysis of [Ni(OAc)<sub>2</sub>] and 1,10-phenanthroline on metal oxides.

### 1.3.3 Metal phosphides

The introduction of phosphorus atoms into metals, also termed “phosphorus-alloying (P-alloying)” was found to significantly improved the catalytic activity of the parent metal for H<sub>2</sub> activation. Two roles were identified for the phosphorus: first, the stabilization of the metallic character of the catalyst in air, which is not the case for the purely metallic compounds, and then, the ligand effect previously described. DFT calculations indeed reveal the insertion of P increases the *d*-electron density near the Fermi level of the material.<sup>73</sup> The use of different binary and ternary metal phosphides (Ni-P, Co-P, Fe-P, Mo-P, W-P, Ni-Mo-P) for high temperature HDO of vegetal oils, phenol, anisole and guaiacol and for hydrotreating reactions has been reviewed by Sanchez *et al.*<sup>58</sup>

**Iron phosphide.** Wan *et al.* reported the use of a carbon supported iron phosphide Fe<sub>2</sub>P@C for hydrogenation of nitroarenes in anilines (120 °C, 50 bar, H<sub>2</sub>O/THF mixture).<sup>68</sup> The catalyst was synthesized by pyrolysis of phosphorus-containing Fe-MOF (Metal Organic Framework) at 900 °C. This is to the best of our knowledge the only occurrence of iron phosphide catalyst for hydrogenation reaction if we exclude the hydrotreatment ones.

**Cobalt phosphide.** The first mention of the use of cobalt phosphide for colloidal hydrogenation is the work by Queen *et al.* on the hydrogenation of nitroarenes in anilines (60 °C, 50 bar H<sub>2</sub>, H<sub>2</sub>O/THF mixture).<sup>69</sup> The catalyst was synthesized by



pyrolysis of MOF nanocubes with red phosphorus to produce a  $\text{Co}_2\text{P}/\text{CN}_x$  composite. The authors performed a hot extraction experiment which confirmed the catalysis is heterogeneous and does not occur through molecular species which would have leached from the nanoparticles. Jitsukawa *et al.* reported the use of cobalt phosphide  $\text{Co}_2\text{P}$  for the hydrogenation of aliphatic and aromatic nitriles in primary amines (130 °C, 1 bar  $\text{H}_2$ , *i*PrOH) (Figure 11A).<sup>70</sup> The nanoparticles were synthesized *via* a solvothermal route with  $\text{CoCl}_2$  in hexadecylamine, 1-octadecene and triphenylphosphite. Cobalt phosphide  $\text{CoP}$  also displayed a catalytic activity although lower than  $\text{Co}_2\text{P}$  (Figure 11C). Other phosphides such as  $\text{Ni}_2\text{P}$ ,  $\text{Fe}_2\text{P}$  and  $\text{Cu}_3\text{P}$  did not lead to any hydrogenation under similar conditions. DFT calculations indicated the free energy for the adsorption of  $\text{H}_2$  on  $\text{Co}_2\text{P}$  is  $\Delta_{\text{ads}}G = -1.13$  eV, which is even larger than on metallic Co. Once adsorbed on a *t* site (phosphorus atom), the H–H bond length increased from 0.79 Å to 2.02 Å, indicating a kinetically favored  $\text{H}_2$  dissociation, in agreement with the experimental results. The good catalytic activity of  $\text{Co}_2\text{P}$  was attributed by spectroscopic studies to its metallic nature and to the increase in *d*-electron density near the Fermi level due to the phosphidization of Co. The use of ammonia as part of the solvent mixture was not discussed in the article even though it may be considered as a hydrogen donor. A similar catalyst was used for furanic aldehydes hydrogenation (130 °C, 40 bar  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ).<sup>71</sup> Finally, Mitsudome *et al.* recently reported the use of  $\text{Co}_2\text{P}$  nanorods, synthesized *via* a solvothermal pathway, for the reductive amination of carbonyl compounds (100 °C, 1-10 bar  $\text{H}_2$ ,  $\text{H}_2\text{O}/\text{NH}_3$ ).<sup>72</sup>

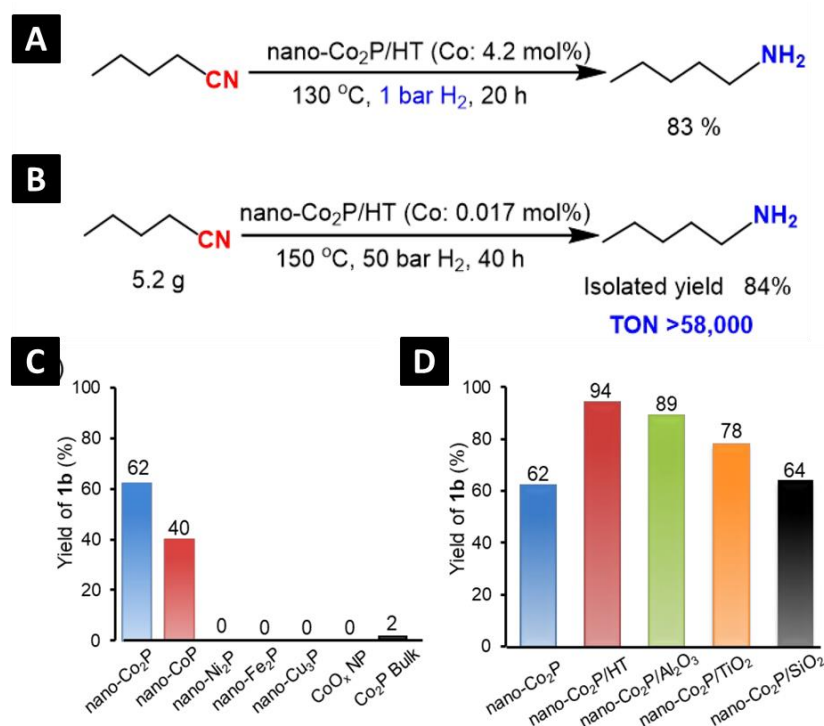


Figure 11. (A) Hydrogenation of pentanenitrile **1a** under ambient pressure of  $\text{H}_2$  and (B) gram scale experiment. (C) Catalytic performance of various metal phosphides and Co oxide

nanoparticles in hydrogenation of **1a**. (D) Catalytic performance of nano-Co<sub>2</sub>P and nano-Co<sub>2</sub>P on different supports. Reaction condition: catalyst (metal: 4.2 mol%), **1a** (0.5 mmol), iPrOH (3 mL), NH<sub>3</sub> aq. (1.2 mL), 130 °C, 40 bar H<sub>2</sub>, 1 h. Adapted from reference [70].

**Nickel phosphide.** Among the first works on colloidal hydrogenation with metal phosphides, Zhang *et al.* reported the possible use of silica supported nickel phosphides (Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub>) for the selective reduction of cinnamaldehyde in hydrocinnamaldehyde (120 °C, 30 bar H<sub>2</sub>, cyclohexane).<sup>78</sup> The selectivity for the C=C reduction rather than the C=O reduction was high (90 %). The others metal phosphides which were investigated (Fe<sub>2</sub>P, CoP, Co<sub>2</sub>P, MoP, WP) led to much lower yields (< 4 % *versus* 50-80 % for Ni-P). A few years later, Corma *et al.* demonstrated the catalytic activity of Ni<sub>2</sub>P nanoparticles for the hydrogenation of phenylacetylene and styrene (85 °C, 6 bar H<sub>2</sub>, dioxane).<sup>49</sup> The catalyst was found to be chemoselective for the formation of alkene and not alkane, to the contrary of Ni(0) catalysts. Pérez-Ramírez also reported the activity of Ni<sub>2</sub>P and Ni<sub>5</sub>P<sub>4</sub> in continuous-flow three-phase semi-hydrogenation of terminal alkyne (30-70 °C, 10-20 bar H<sub>2</sub>, toluene).<sup>76</sup> The catalysts displayed an induction time of 2 h, attributed to the reduction of the oxide layer covering the surface, but then reached stable performance on stream for more than 24 h. They in particular studied the evolution of the reaction rates as a function of pressure and temperature. The use of Ni<sub>2</sub>P as hydrogenating catalyst was then extended to nitroarenes in mild conditions (80 °C, 10 bar H<sub>2</sub>, EtOH) by Zou *et al.*<sup>73</sup> The authors stressed the difficulty in releasing the H atoms once these are adsorbed at the surface of Ni<sub>2</sub>P due to its strong affinity. To circumvent this issue, they suggest to tune the *d*-band of Ni by anchoring the nanoparticles on phosphorus-doped carbon (PC). DFT calculations confirmed the electron donation of carbon toward Ni. Consequently, the desorption energy of H decreased from -1.12 eV to -0.56 eV in Ni<sub>2</sub>P/PC and the Ni-H bond length increased from 1.65 Å to 1.9 Å, making the properly said hydrogenation step more thermodynamically and kinetically favorable. Finally, Mitsudome *et al.* reported the possible use of metal oxide supported Ni<sub>2</sub>P nanoparticles for the hydrogenation of sugars (glucose, maltose) in polyols under mild conditions (r.t.-100 °C, 1-20 bar, H<sub>2</sub>O).<sup>74,75</sup>

### I.3.4 Metal carbides and nitrides

Metal carbides and nitrides are generally studied and commented together concerning their catalytic applications. They indeed display similar crystalline phases with close electronic configurations.<sup>7,12,56,79</sup> One has to pay attention to the possibility of incorporating other atoms to form ternary phases. For instance, Mo<sub>2</sub>C, W<sub>2</sub>C and WC are known to incorporate O, N and S atoms, at least on the extreme surface of the catalyst, during respectively HDO, HDN and HDS reactions.<sup>7</sup> This issue is nonetheless not necessarily critical as catalyst deactivation is generally limited. Tungsten

monocarbide (WC) was investigated for hydrogenation reactions by Levy and Boudart in 1973.<sup>80</sup> They elucidated the electronic structure of the material and highlighted its similarity with platinum. They thus reported the gas phase reduction of butadiene in butene. Unfortunately, WC activity is observed only at relatively high temperatures (150 °C to 400 °C) and WC as a stand-alone catalyst is rarely mentioned. Interesting results were nonetheless obtained when WC was doped with Ni or Co in particular for hydrodeoxygenation reactions. Group VI metal carbides ( $\alpha$ -MoC,  $\beta$ -Mo<sub>2</sub>C, WC and W<sub>2</sub>C) are efficient catalysts for biomass derived molecules hydrogenation but mainly in the gas phase.<sup>81</sup> Dongil recently reviewed the use of metal nitrides in heterogeneous catalysis.<sup>59</sup> The nitridation of metals of end of transition (Fe, Co, Ni, Cu) being more difficult than early transition metals, most of the works on hydrogenation reactions with metal nitrides focus on molybdenum and tungsten nitrides.<sup>12</sup>

Ref.	Material	Substrate	Solvent	P(H <sub>2</sub> )	T, t
<b>Carbides</b>					
82	$\alpha$ -MoC, $\beta$ -Mo <sub>2</sub> C	Furfural	Alcohol	10-20 bar	150 °C, 6 h
83	WC	Nitroarenes, Phenylacetylene	EtOH	10 bar	100 °C, flux
<b>Nitrides</b>					
84	$\beta$ -Mo <sub>2</sub> N	Nitroarenes	EtOH	11 bar	150 °C, flux
82	$\gamma$ -Mo <sub>2</sub> N	Furfural	Alcohol	10-20 bar	150 °C, 6 h
24	$\gamma$ -Mo <sub>2</sub> N-H <sub>x</sub>	Crotonaldehyde	EtOH	<i>n.a.</i>	70 °C, 1 h
85	CoN <sub>x</sub> /CN	Phenols	Dodecane	20 bar	200 °C, 2 h
86	CoN <sub>x</sub> /CN	Nitroarenes	H <sub>2</sub> O	5 bar	110 °C, 1 h
87	CoN <sub>x</sub>	Nitroarenes	Scope	1-3.5 bar	40-110 °C, 12 h
88	Ni <sub>3</sub> N	Benzonitrile Nitrobenzene	EtOH	25 bar	50-150 °C, flux
89	Ni <sub>3</sub> N	Alkyne	EtOH	20 bar	100 °C, 5 h

Table 2. Examples of hydrogenation reactions in solvent catalyzed by metal carbides and nitrides.

**Early transition metals.** In the 1970s, Horányi *et al.* reported a series of works mentioning the catalytic activity of WC for the liquid-phase hydrogenation of organic compounds.<sup>90-92</sup> Even though the reaction temperature was only of 40-90 °C, the conditions were relatively harsh as the medium was a solution of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The authors reported the reduction of nitroarenes and quinones but not of C=C nor C≡C bonds. To the best of our knowledge, the reactions were not reproduced. Later, nanostructured WC was reported for nitroarenes hydrogenation to aromatic amines

under mild conditions in continuous flow (100 °C, 10 bar H<sub>2</sub>, EtOH).<sup>83</sup> The reaction was chemoselective as no reduction of C=C, C=O or C≡N bonds occurred. Ma *et al.* recently disclosed the furfural hydrogenation in furfuryl alcohol (FAL) and in 2-methylfuran (2-MF) by  $\alpha$ -MoC and  $\beta$ -Mo<sub>2</sub>C (150 °C, 10-20 bar H<sub>2</sub>, alcohol).<sup>82</sup> Depending on the molecular size of the alcohol, the product selectivity was different: 95 % of 2-MF were obtained with 2-butanol *versus* 95 % of FAL with MeOH (Figure 12A). The reaction required a pressure of H<sub>2</sub> to proceed but the alleged mechanism relies on a hydrogen transfer *via* the solvent (Figure 12B).

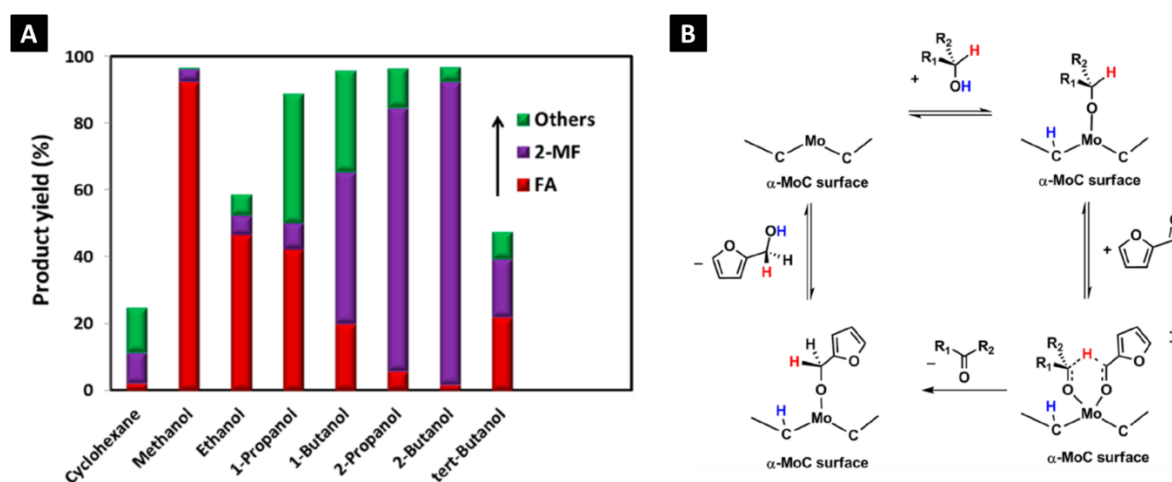


Figure 12. (A) Solvent effects on product yields of furfural hydrogenation on  $\alpha$ -MoC catalysts (150 °C, 20 bar H<sub>2</sub>, 1 mL furfural, 50 mL solvent, 150 mg  $\alpha$ -MoC, 6 h; FA for furfuryl alcohol, 2-MF for 2-methyl furan). (B) Plausible Pathway for Transfer Hydrogenation of Furfural by an Alcohol on  $\alpha$ -MoC Surfaces. Reproduced from reference [82].

Keane *et al.* reported the first use of molybdenum nitride,  $\beta$ -Mo<sub>2</sub>N for liquid phase hydrogenation of nitroarenes in flux (150 °C, 11 bar H<sub>2</sub>, EtOH).<sup>84</sup> The nitridation of metallic Mo is thought to be responsible for the good catalytic activity of Mo<sub>2</sub>N. Indeed, the interstitial nitrogen atoms led to a higher  $d$ -electron density at the Fermi level and therefore an increased capacity for H<sub>2</sub> adsorption. The H<sub>2</sub> adsorption and dissociation on Group VI metal nitrides is not yet perfectly understood but several authors suggest a heterolytic dissociation on nitrogen deficient sites. H<sub>2</sub> chemisorption experiments led to the hypothesis of the formation of a stable hydride phase in the nitride sub-surface. This hypothesis was also formed by Thompson *et al.* who studied the H<sub>2</sub> uptake by  $\gamma$ -Mo<sub>2</sub>N and the use of the formed compound,  $\gamma$ -Mo<sub>2</sub>N-H<sub>x</sub>, for the hydrogenation of crotonaldehyde.<sup>24</sup> Finally, Ma *et al.* reported the possible use of both phases,  $\beta$ -Mo<sub>2</sub>N and  $\gamma$ -Mo<sub>2</sub>N, for furfural hydrogenation in 2-methylfuran and furfuryl alcohol (150 °C, 20 bar H<sub>2</sub>, iPrOH).<sup>82</sup>

**Late transition metals.** We could not find any mention of a carbide of Fe, Co, Ni or Cu as a catalyst for H<sub>2</sub> activation in solvent, though the catalytic activity of some of these materials for Fischer-Tropsch process has been studied. Cobalt nitrides, CoN<sub>x</sub>, were reported by Zhang *et al.* for hydrodeoxygenation of lignin-derived phenols (200 °C, 20 bar H<sub>2</sub>, dodecane).<sup>85</sup> The catalyst was obtained by pyrolysis of Co(NO<sub>3</sub>)<sub>2</sub> and cellulose. The authors also reported a cobalt nitride catalyst obtained by calcination of cobalt phthalocyanine for the hydrogenation of large scope of nitroarenes under very mild conditions (40-110 °C, 1-3.5 bar H<sub>2</sub>), quantitative conversions were reached at 110 °C for many solvents (H<sub>2</sub>O, THF, CH<sub>3</sub>CN, EtOH, iPrOH, toluene, EtOAc).<sup>87</sup> A similar catalyst obtained by pyrolysis of Ce(NO<sub>3</sub>)<sub>2</sub> and histidine over silica was used for nitroarenes hydrogenation (110 °C, 5 bar H<sub>2</sub>, H<sub>2</sub>O).<sup>86</sup> The most common nickel nitride phase, Ni<sub>3</sub>N, was also reported by Giordano *et al.* for its hydrogenation activity toward nitrobenzene and benzonitrile (50 °C, 25 bar H<sub>2</sub>, EtOH).<sup>88</sup> This material is however metastable: a treatment at 250 °C in a H<sub>2</sub>/Ar (3:1) flux leads to the release of nitrogen as N<sub>2</sub> and NH<sub>3</sub> and Ni<sub>3</sub>N totally decomposes at temperatures beyond 400 °C.<sup>93</sup> Bai *et al.* also reported the use of Ni<sub>3</sub>N anchored on an N-doped carbon for the semi-hydrogenation of alkynes in alkenes (100 °C, 20 bar H<sub>2</sub>, EtOH).<sup>89</sup>

### 1.3.5 Metal oxides

**Cerium oxide.** While the use of ceria CeO<sub>2</sub> for nitroarenes hydrogenation was already mentioned with hydrazine as H source, the use of CeO<sub>2</sub> for H<sub>2</sub> activation in the liquid phase was first reported by Pérez-Ramírez *et al.* for a continuous flow alkyne hydrogenation by metal oxide supported CeO<sub>2</sub>.<sup>94</sup> The catalyst was obtained by wet impregnation of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> with an acidified solution of cerium ammonium nitrate. XPS measurements indicated a Ce<sup>(III)</sup> percentage of 28 % at the surface of the catalyst. Alkyne conversions superior to 80 % were obtained only for H<sub>2</sub> pressures superior to 50 bar and for temperatures beyond 140 °C in toluene. However, the selectivity towards the alkenes was excellent for both aliphatic and aryl alkynes. Later, highly defective cerium oxide nanoparticles were reported by Qu *et al.* for their hydrogenation catalytic activity of alkenes and alkynes under milder conditions (6 bar, 100 °C, toluene) following a heterolytic dissociation mechanism (Figure 13).<sup>95</sup> The surface defects on cerium oxide are typically associated with surface Lewis acidic sites, composed of two adjacent Ce<sup>(III)</sup> atoms (Ce<sub>I</sub> and Ce<sub>II</sub> on Figure 13a), and basic sites, composed of surface lattice oxygens (O<sub>IIc</sub>). The developed catalyst, termed PN-CeO<sub>2</sub> and presenting a Ce<sup>(III)</sup> surface fraction of 30 %, was in capacity to hydrogenate styrene but the activity was quenched in presence of Lewis acids or bases (pyrrole, pyridine) likely due to their adsorption on the Ce<sub>I</sub>, Ce<sub>II</sub> and O<sub>IIc</sub> sites (Figure 13d). DFT calculations on ideal and reduced CeO<sub>2</sub>(110) surfaces revealed the activation barrier for the heterolytic splitting of H<sub>2</sub> is lower for a defective structure (0.17 eV) than for an ideal one (0.65 eV) (Figure 13e).

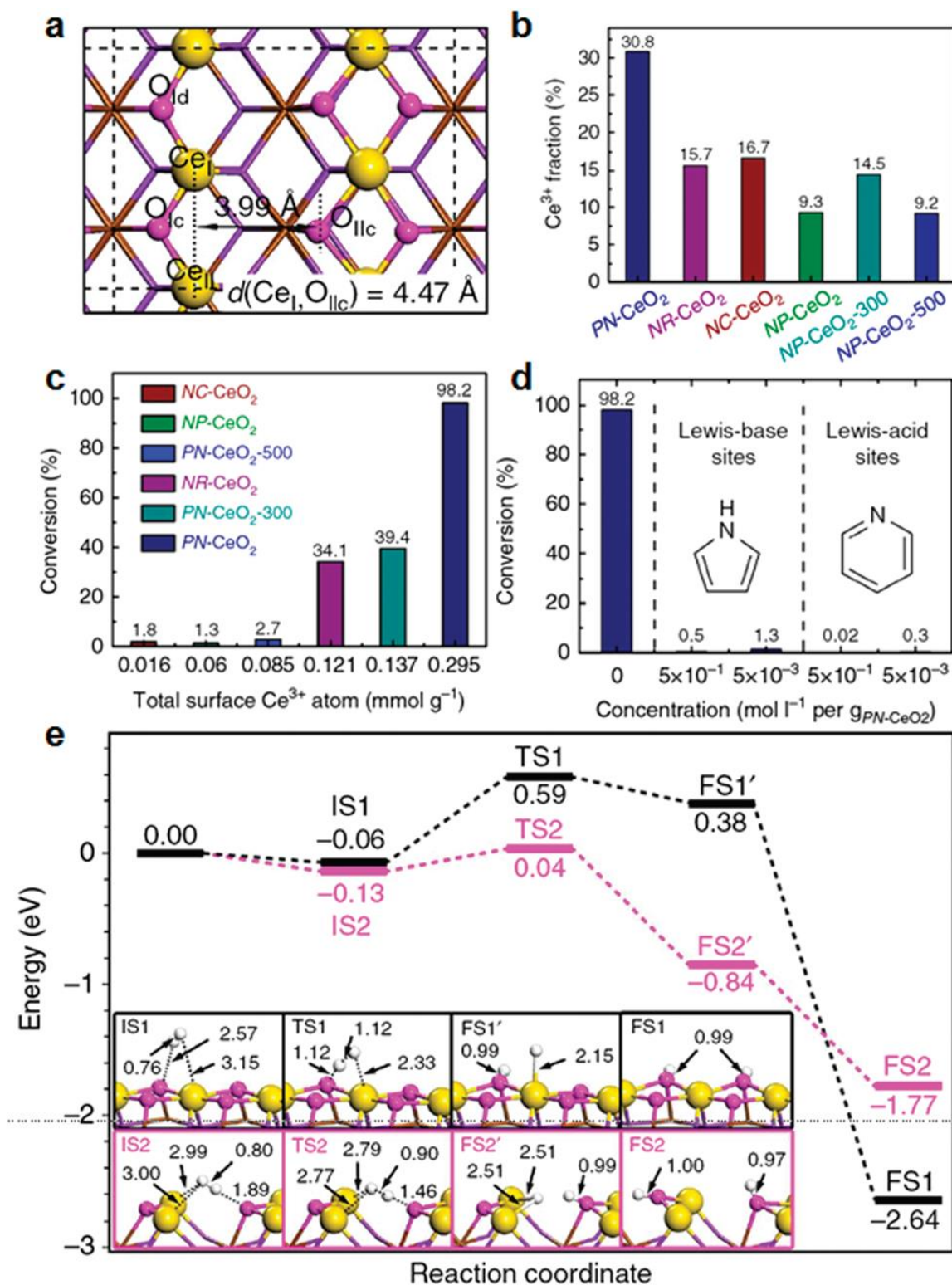


Figure 13. Surface regulations on CeO<sub>2</sub> for the construction of surface FLP-like catalytic sites and their performance for hydrogenation. (a) DFT calculations on the possibility by the surface regulations for the formation of independent surface Lewis acidic sites and Lewis basic sites on CeO<sub>2</sub>(110) and the construction of surface FLP sites. (b) Surface fractions of Ce<sup>3+</sup> for various CeO<sub>2</sub>. (c) Catalytic hydrogenation activity versus the surface fractions of Ce<sup>3+</sup>. Reaction conditions: styrene (1.0 mmol), toluene (0.5 ml) and catalysts (20.0 mg) at 100 °C, 10 bar H<sub>2</sub>, 14 h. (d) Influences of a molecular Lewis-base or Lewis-acid on the

catalytic activity of CeO<sub>2</sub> for the hydrogenation of styrene. (e) Energy profiles for H<sub>2</sub> dissociation on ideal CeO<sub>2</sub>(110) in the black curve and CeO<sub>2</sub>(110) with two oxygen vacancies in the red curve. The optimized structures of the initial states (IS), transition states (TS) and final states (FS) are labelled with bond distances (in Å). Reproduced from reference [95].

Ref.	Material	Substrate	Solvent	P(H <sub>2</sub> )	T, t
<b>Oxides</b>					
96	WO <sub>2.72</sub>	Alkenes	Cyclohexane	30 bar	100 °C, 3 h
96	WO <sub>2.72</sub>	Nitroarenes	EtOH	30 bar	120 °C, 5 h
94	CeO <sub>2</sub> /MO <sub>x</sub>	Alkynes	Toluene	50 bar	140 °C, flux
95	CeO <sub>2-x</sub>	Alkenes/Alkynes	Toluene	6-30 bar	100 °C, 14 h
97	γ-Fe <sub>2</sub> O <sub>3</sub>	Nitroarenes	H <sub>2</sub> O/THF	50 bar	120 °C, 12 h
98	α-Fe <sub>2</sub> O <sub>3</sub> , FeO, γ-Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>	Nitroarenes	H <sub>2</sub> O/THF	30 bar	150 °C, 10 h
99,100	Co <sub>3</sub> O <sub>4</sub>	N-heteroarene, Nitriles, Aldehydes/Ketones	Toluene EtOH iPrOH	20-40 bar	100-130 °C, 20 h
<b>Sulfides</b>					
101	FeS <sub>2</sub>	Nitroarenes	iPrOH	5 bar	60 °C, 7 h
102	NiS, Ni <sub>7</sub> S <sub>6</sub> , Ni <sub>4</sub> S <sub>3</sub>	Nitrobenzene	EtOH	40 bar	150 °C, 24 h
103	FeS <sub>2</sub> , NiS <sub>2</sub> , CoS <sub>2</sub>	Nitroarenes	MeOH	30 bar	110 °C, 12 h
104	MoS <sub>2</sub>	Nitrobenzene	Toluene	30 bar	100 °C, 6 h
105	MoS <sub>2</sub>	Nitroarenes	EtOH	20 bar	120 °C, 5 h
106	WS <sub>2</sub>	Nitroarenes	H <sub>2</sub> O/THF	20-50 bar	120 °C, 12 h

Table 3. Examples of hydrogenation reactions in solvent catalyzed by metal oxides and sulfides.

**Tungsten oxide.** In the case of tungsten trioxide WO<sub>3</sub>, DFT calculations show the adsorption of H<sub>2</sub> is unfavorable on WO<sub>3</sub>(001) ( $\Delta_{\text{ads}}G = 0.436$  eV) and that the activation energy of the H<sub>2</sub> cleavage is high ( $E_{\text{act}} = 1.643$  eV), in agreement with the low increase in H–H bond length (from 0.749 Å to 0.759 Å).<sup>96</sup> On the contrary, oxygen-deficient tungsten oxide WO<sub>2.72</sub>(001) leads to a favorable adsorption ( $\Delta_{\text{ads}}G = -0.346$  eV) and a lower energy barrier for H<sub>2</sub> cleavage ( $E_{\text{act}} = 0.902$  eV), in agreement with the larger weakening of the H–H bond (from 0.749 Å to 1.392 Å). These results clearly indicate that the presence of oxygen vacancies increases the hydrogenation catalytic activity of WO<sub>3</sub>. The calculations are validated by experimental data: WO<sub>2.72</sub> hydrogenates alkenes and nitroarenes under moderate conditions in ethanol or

cyclohexane (30 bar  $H_2$ ,  $< 150\text{ }^\circ\text{C}$ ). Interestingly, the catalyst presents a better hydrogenation selectivity than Ni(0) when several groups are present on the substrate molecule: for instance,  $WO_{2.72}$  does not hydrogenate C=C in aromatic rings where Ni(0) does. We can nonetheless remind the propension of tungsten oxide to be *in situ* reduced by  $H_2$  to form bronze phases  $H_xWO_3$ .

**Late transition metals.** Beller *et al.* reported the use of iron oxide  $\gamma\text{-Fe}_2\text{O}_3$  for the chemoselective hydrogenation of nitroarenes (120  $^\circ\text{C}$ , 50 bar of  $H_2$ ,  $H_2O/THF$  mixture).<sup>97</sup> The catalyst was produced by pyrolysis of  $[\text{Fe}(\text{OAc})_2]$  and 1,10-phenanthroline on metal oxides. Based on X-ray photoelectron spectra of the N 1s region, the authors suggest the formation of  $\text{FeN}_x$  centers in addition of the iron oxide. These results were extended to different iron oxides,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , FeO and  $\text{Fe}_3\text{O}_4$ , by Zou *et al.* in similar conditions (150  $^\circ\text{C}$ , 30 bar  $H_2$ ,  $H_2O/THF$  mixture).<sup>98</sup> The catalysts were prepared from  $\text{FeCl}_3$  and ethylene glycol followed by a calcination step and displayed a microflower morphology. The normalized catalytic activity of all the iron oxides were in the same range. While  $\alpha\text{-Fe}_2\text{O}_3$ , FeO and  $\text{Fe}_3\text{O}_4$  displayed similar activities for the first and the second run of the reaction, that of  $\gamma\text{-Fe}_2\text{O}_3$  increased in the second run of the reaction. This effect was attributed to the partial reduction of the material according to XPS. Interestingly, phenylacetylene was quantitatively hydrogenated in styrene by  $\text{Fe}_3\text{O}_4$  at 120  $^\circ\text{C}$ . Following a similar catalyst synthesis, Beller *et al.* also disclosed the catalytic activity of  $\text{Co}_3\text{O}_4$  for the hydrogenation of quinolines and N-heteroarenes (120  $^\circ\text{C}$ , 20-40 bar  $H_2$ , toluene), and of nitriles, ketones and aldehydes (100-130  $^\circ\text{C}$ , 20-40 bar  $H_2$ , EtOH or iPrOH).<sup>99,100</sup> The catalyst was produced by calcination of  $[\text{Co}(\text{OAc})_2]$  with 1,10-phenanthroline over  $\alpha\text{-Al}_2\text{O}_3$ . As for iron oxide,  $\text{CoN}_x$  centers were detected by XPS.

### I.3.6 Metal sulfides

As for metal oxides, both heterolytic and homolytic mechanisms are detected for  $H_2$  activation on metal sulfides with a high importance given to structural defects. The topic has been reviewed in 2002 by Breysse *et al.*<sup>11</sup> The authors covered the most conventional catalysts,  $\text{MoS}_2$  and  $\text{WS}_2$ , eventually doped with Ni or Co, but also noble metal sulfides such as  $\text{RuS}_2$ . Although the study concerns hydroprocessing and gas phase  $H_2$  activation, most of the concepts may be applied to liquid phase hydrogenation. The presence of sulfhydryl S-H was evidenced by different spectroscopic techniques (IR, INS, MAS NMR) but the existence of M-H bonds is less convincing. The main point concerning  $\text{MoS}_2/\text{WS}_2$  is the importance of the sulfur vacancies: the optimal Sulfur/Metal ratio for  $H_2$  activation was determined to be 1.95 and not 2. On near stoichiometric sulfides, the predominant mechanism for  $H_2$  activation is the homolytic dissociation on two sulfur atoms. The heterolytic dissociation mechanism involves sulfur atoms and coordinatively unsaturated metal sites (CUS) and are therefore not favored on stoichiometric materials. At high temperatures, one of the main limitations



of sulfur-defective MoS<sub>2</sub>/WS<sub>2</sub> is the progressive substitution of sulfur atoms by oxygen atoms, provided by water traces for instance, which deactivate the surface. The activity is maintained by addition of H<sub>2</sub>S or CS<sub>2</sub> in the reaction feed.

**Early transition metals.** Molybdenum and tungsten disulfides have been extensively studied for hydroprocessing or electrocatalysis but more rarely for hydrogenation reaction in the liquid phase in soft conditions. Two recent works report the use of sulfur deficient molybdenum disulfide (MoS<sub>2-x</sub>) for the hydrogenation of nitroarenes. In the first one, by Xie *et al.*, MoS<sub>2-x</sub> microflowers efficiently hydrogenated nitrobenzene in aniline (100 °C, 30 bar H<sub>2</sub>, toluene).<sup>104</sup> Commercial MoS<sub>2</sub> displayed a lower, though non-negligible, activity under similar conditions. The authors attributed the enhanced activity of the sulfur deficient MoS<sub>2</sub> to the higher number of coordinatively unsaturated Mo sites and proposed a heterolytic splitting of H<sub>2</sub>, resulting in the formation of Mo–H and S–H. In the second work, a one-pot nitro-reduction and reductive amination yielding a secondary amine was studied.<sup>105</sup> A nitroarene Ar<sub>1</sub>-NO<sub>2</sub> and a benzaldehyde derivatives Ar<sub>2</sub>-CHO react to form Ar<sub>1</sub>-NH-CH<sub>2</sub>-Ar<sub>2</sub> (120 °C, 20 bar H<sub>2</sub>, EtOH). The authors also showed nitrobenzene was quantitatively hydrogenated in aniline in absence of aldehyde. The catalyst was exposed to different pretreatments and the authors correlated a high activity with a high number of sulfur and molybdenum vacancies. DFT calculations in this study revealed the adsorption free energy of H<sub>2</sub>,  $\Delta_{\text{ads}}G$ , gradually decreased from -0.5 eV to -1.3 eV when sulfur vacancies were added to the model. In the meantime, the adsorption energy of the substrates also decreased, making the whole reaction thermodynamically more favorable. Schaak *et al.* reported the use of defect-rich WS<sub>2</sub> nanostructures for the hydrogenation of a broad scope of nitroarenes (120 °C, 20-50 bar H<sub>2</sub>, H<sub>2</sub>O/THF mixture).<sup>106</sup> As for metal oxides and MoS<sub>2</sub>, the defects play an important role both for the activity of the material and for the good selectivity towards nitro group hydrogenation. Considering the higher proportion of defects in nanostructures than in bulk, the authors recommended the use of MoS<sub>2</sub> and WS<sub>2</sub> nanosheets and indeed, the same reaction with bulk WS<sub>2</sub> did not lead to any conversion. These two materials (MoS<sub>2</sub> and WS<sub>2</sub>) are in particular known for the near-zero free energy of adsorption of H<sub>2</sub> on edge and defect sites ( $\Delta_{\text{ads}}G \approx 0$  eV), *i.e.* the adsorption step is not thermodynamically limiting. DFT calculations showed the rate-determining step with WS<sub>2</sub> was the transfer of the hydrogen to the adsorbed substrate ( $E_{\text{act}} = 0.97$  eV).

**Late transition metals.** A few examples of late transition metal sulfides were reported, mainly with Fe and Ni. Recent work by Guo *et al.* reported the catalytic activity of iron disulfide (FeS<sub>2</sub>) nanoparticles, or pyrite, for nitroarenes hydrogenation (60 °C, 5 bar H<sub>2</sub>, iPrOH).<sup>101</sup> The catalyst was synthesized by solvothermal route from FeCl<sub>2</sub> and elemental sulfur. A negative adsorption enthalpy for H<sub>2</sub> was obtained by DFT calculations for the three possible configurations: both H on a Fe site ( $\Delta_{\text{ads}}G = -0.91$  eV), both H on a S site ( $\Delta_{\text{ads}}G = -0.29$  eV) or one H on S and one on Fe ( $\Delta_{\text{ads}}G$

= -1.11 eV). H<sub>2</sub>-TPD experiment indicated an adsorption energy of -0.97 eV, coherent with the DFT calculations. Schaak *et al.* extended these results to bulk off-the-shelf FeS<sub>2</sub> though under stronger conditions (120 °C, 50 bar H<sub>2</sub>, H<sub>2</sub>O/THF mixture).<sup>107</sup> The authors in particular stressed the selectivity towards other insaturations (C=C, C=O, C≡C, C≡N) and the simplicity of this readily available catalyst. Finally, flowerlike nickel sulfides (NiS, Ni<sub>3</sub>S<sub>4</sub>, Ni<sub>7</sub>S<sub>6</sub>) microparticles were reported for chloronitrobenzene hydrogenation (150 °C, 40 bar H<sub>2</sub>, EtOH).<sup>102</sup> Their syntheses were performed with NiCl<sub>2</sub> in a water/ethanolamine mixture with thiourea as the sulfur source.

## I.4. Toward the “NanoFLP” system

### I.4.1 Frustrated Lewis Pair catalysis

At the beginning of the 2000s, the activation of H<sub>2</sub> and other small molecules in solvent was studied by Stephan, Erker *et al.* by the mean of Frustrated Lewis Pairs (FLP).<sup>108</sup> The principle of this homogeneous catalysis is to put in presence two molecules acting as a Lewis base (LB) and a Lewis acid (LA) whose reactive centers are both sterically hindered (Figure 14A). They typically consist in a tertiary phosphine (P<sup>t</sup>Bu<sub>3</sub>, PCy<sub>3</sub>, PMes<sub>3</sub>) or an amine (lutidine, tetramethylpiperidine) and a tertiary borane (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) or an alumane (Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). The Lewis pair would be stabilized by forming a Lewis adduct LB–LA but the formation of such a molecular complex is hampered by the bulky groups present on the two species. A “reactive pocket” is nonetheless formed with a Lewis acidic and basic sides and this catalytic site may heterolytically cleave chemical bonds such as H–H or C–O (Figure 14B). In the case of H<sub>2</sub>, the activated proton and hydride subsequently react to hydrogenate different substrates such as an imine in the seminal work of Stephan *et al.* (Figure 14C).<sup>109</sup>

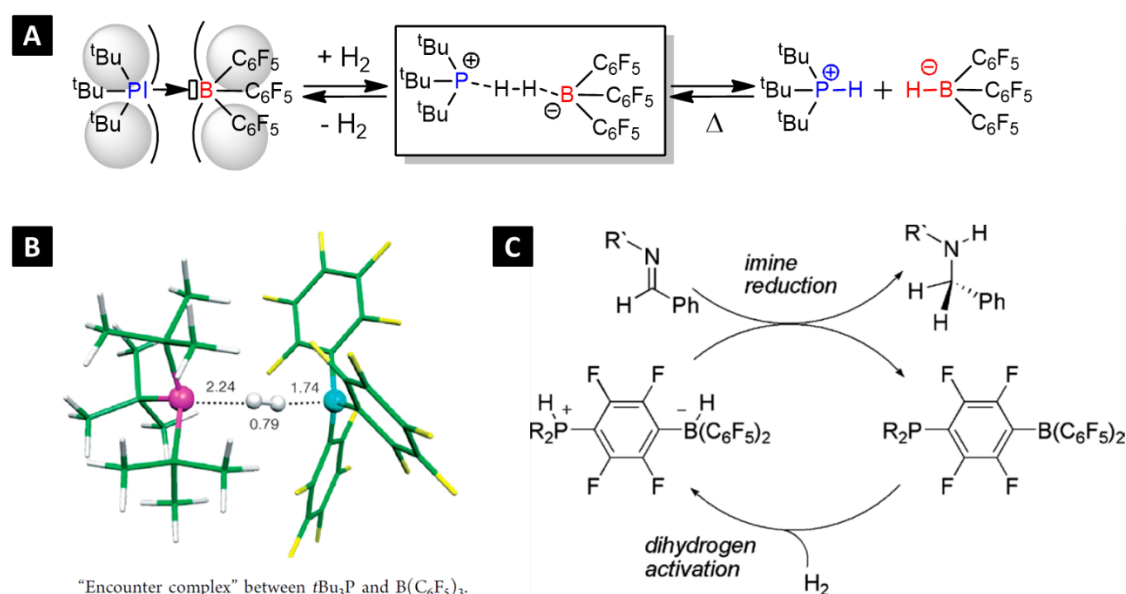


Figure 14. (A) Activation of H<sub>2</sub> *via* a Frustrated Lewis Pair. (B) Geometry of the encounter complex of P<sup>t</sup>Bu<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> activating H<sub>2</sub>. (C) Hydrogenation of an imine after H<sub>2</sub> activation by FLP. Reproduced from references [108,109].

The FLP concept has been very fruitful these past two decades in homogeneous catalysis and has then reached the field of heterogeneous catalysis (Figure 15),<sup>110</sup> although the formal attribution of these new catalytic systems to an FLP may be subject to discussion.<sup>111</sup> Different configurations were reported: (a-b) semi-solid systems

where either the base or the acid is a molecular species and (c-d) all-solid systems for which the basic and acid sites are both situated at the surface of the solid catalyst, the “frustration” originating from the rigidity of the atomic positions. For this last category, we can in particular mention the use of defective cerium oxides by Qu *et al.*<sup>95,112,113</sup> (already mentioned in a previous section, Figure 13) and that of defective indium oxides by Ozin *et al.*<sup>111,114–116</sup> This last case was briefly mentioned earlier in the characterization section (Figure 6A). The authors suggest the presence of oxygen vacancy sites is related to that of unsaturated surface In sites presenting a Lewis acid character. The H<sub>2</sub> molecule is then cleaved to form a hydridic In–H<sup>–</sup> and a protonic In–OH<sub>2</sub><sup>+</sup> species. It was found a high concentration of oxygen defects increased the catalytic activity of the material.

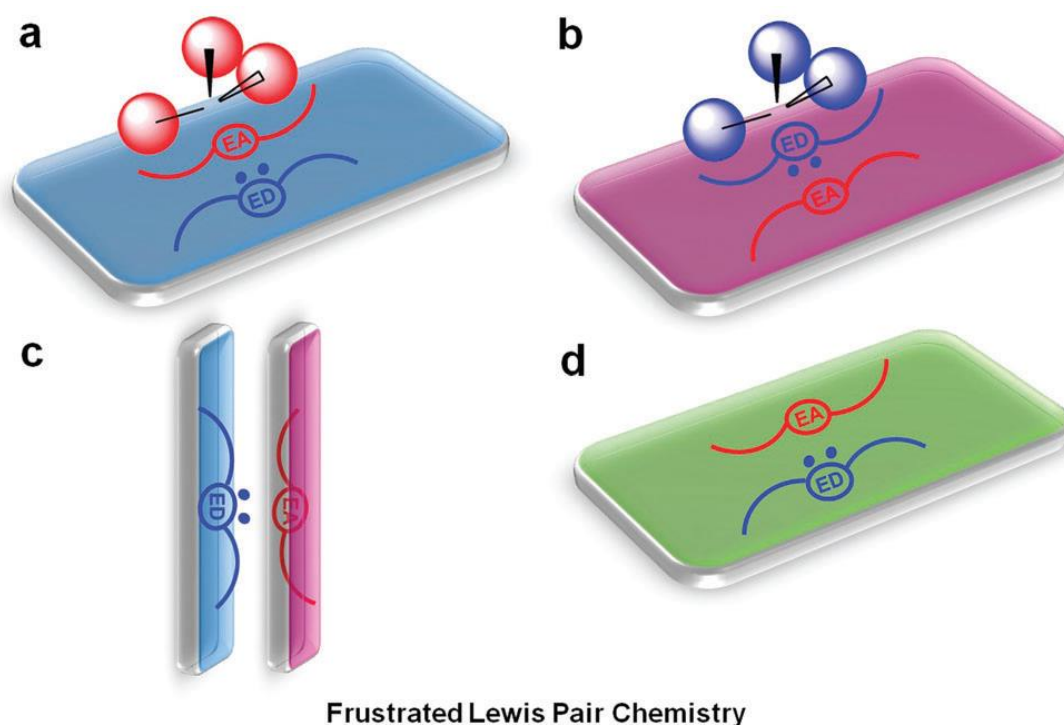


Figure 15. Schematic chemistry of semi-solid and solid FLPs: (a) semi-solid FLP catalyst with the combination of a molecular Lewis acid and a solid Lewis base; (b) semi-solid FLP catalyst with the combination of a molecular Lewis base and a solid Lewis acid; (c) all solid FLP catalyst based on a solid Lewis acid and a solid Lewis base; and (d) all solid FLP catalyst within one solid. Reproduced from [110].

## I.4.2 Boosting the surface reactivity of nanoparticles with ligands

In a certain number of cases, the heterolytic cleavage of dihydrogen (H<sub>2</sub>) on metallic or metal-containing nanoparticles in solvent is promoted *via* a metal-ligand cooperative mechanism: a Lewis basic site of the ligand binds the proton and the coordinated metal atom acts as a Lewis acid and takes the hydride.<sup>117</sup> This mechanism naturally echoes the concept of semi-solid FLP with the combination of a Lewis base and a metal surface (Figure 15b). Few examples only were mentioned in literature but we will exemplify it with the case of gold surfaces.

Following the seminal work of Guo *et al.* on the hydrogenation of N-benzylidenemethylamine with Au powder (50 °C, 20 bar H<sub>2</sub>, toluene),<sup>118</sup> Rossi *et al.* reported the formation of active sites on Au nanoparticles *via* the addition of different N-containing bases (Figure 16A).<sup>119</sup> The Au-piperazine system was found to be the most efficient and selective for the semi-hydrogenation of phenylacetylene in styrene with a Au:PhCCH:base molar ratio of 1:100:100. The complete reaction was achieved in 5 hours under mild conditions (80 °C, 6 bar H<sub>2</sub>, EtOH), whereas no reactivity was observed without base. As described in Figure 16B, Rossi *et al.* proposed a mechanism inspired by the FLP chemistry: the H<sub>2</sub> molecules are heterolytically dissociated between the Au surface and the piperazine. The activation barrier for this step was estimated by DFT to be 0.32 eV, much lower than the activation on clean Au(111) surface (1.45 eV). The two following steps, *i.e.* the transfer of the hydride and of the proton on the alkyne, have activation barriers of respectively 0.74 eV and 0.13 eV. The authors of the study then reported the possible use of an Au@N-doped carbon/TiO<sub>2</sub> catalyst for the hydrogenation of biomass molecules (5-HMF and furfural) following a similar pathway.<sup>120</sup>

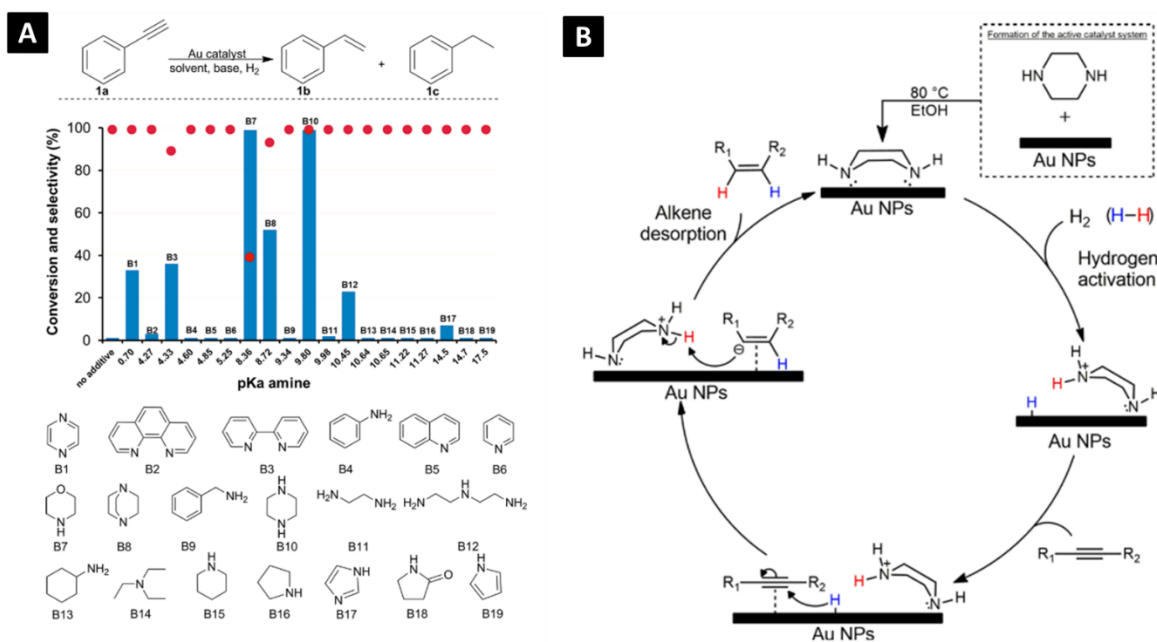


Figure 16. (A) Screening of nitrogen-containing bases for phenylacetylene hydrogenation with Au/SiO<sub>2</sub> catalyst. Reaction conditions: 1 mmol of 1a, 0.01 mmol of Au (50 mg of Au/SiO<sub>2</sub>), 1 mmol of amine, 2 mL of ethanol, 100 °C, 6 bar of H<sub>2</sub>, 24 h. (B) Proposed mechanism for gold-catalyzed catalytic hydrogenation of alkynes into cis-alkenes via a frustrated Lewis pair approach. Reproduced from [119].

Van Leeuwen *et al.* developed a similar system with the use of a Secondary Phosphine Oxide (SPO) ligand placed on the surface of gold nanoparticles (Figure 17).<sup>121</sup> These ligands act both as a stabilizer for the nanoparticle suspension and as a co-catalyst: the authors indeed demonstrated the mechanism goes through an HCD. The oxygen atom of the SPO acts as Lewis base and captures the proton H<sup>+</sup> while a surface hydride species H<sup>-</sup> is formed on the gold surface. A selective hydrogenation of a large number of aldehydes was thus achieved under relatively mild conditions (40–60 °C, 40 bar H<sub>2</sub>, THF/hexane mixture). A screening over different SPOs was performed and revealed that the degree of polarization of P=O is crucial for the HCD mechanism to occur. A strong polarity of the bond is required, typically obtained with aryl groups on the phosphorus center rather than alkyl ones.

The field of heterolytic cleavage of hydrogen on metal nanoparticles in cooperation with a ligand is still in its infancy, hence the relatively low number of published works and the inhomogeneity of the works. The interest for these catalytic systems is nonetheless growing rapidly and led to a few reviews.<sup>110,117,122</sup>

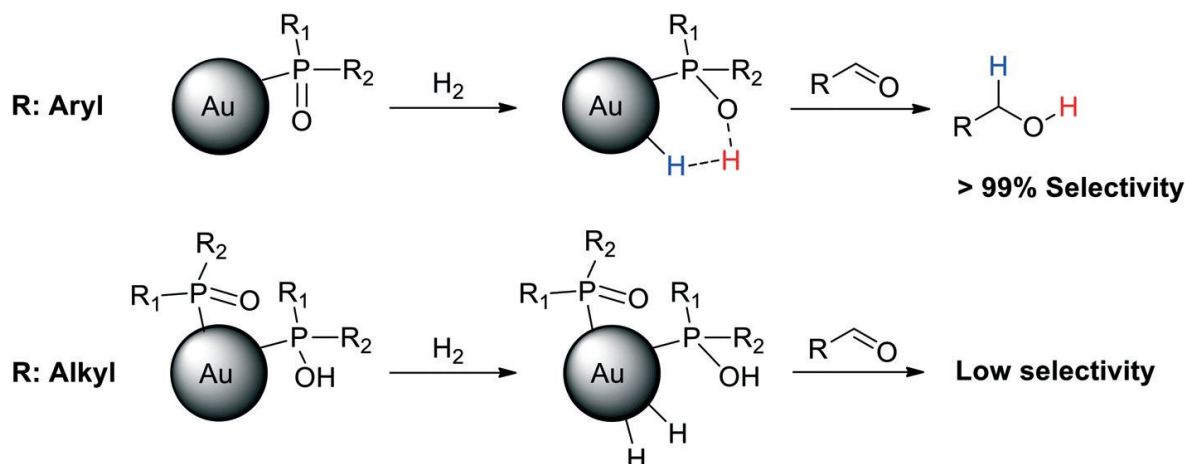


Figure 17. Au NPs ligated by aryl SPOs exhibit a strong polarity of the P=O bond, which favours the HCD and thus the selective hydrogenation of aldehydes. Au NPs ligated by alkyl SPOs show a low polarity of the P=O bond, which hinders the heterolytic H<sub>2</sub> activation.

These Au NPs display low selectivity in aldehyde hydrogenation. Reproduced from reference [121].

### I.4.3 Philosophy of work

Most of the ligand-assisted colloidal catalysis developed so far for the heterolytic cleavage of hydrogen imply the use of noble metals such as Au or Ru.<sup>117</sup> There is however to the best of our knowledge very few works mentioning the use of non-noble metal containing nanoparticles such as metal carbides, metal oxides or nickel derivatives compounds. The goal of this PhD thesis is therefore to explore the possible use of these materials for an FLP-like activation of H<sub>2</sub> in solvent *via* the implication of a molecular base. We chose to use tertiary phosphines (PPh<sub>3</sub>, PCy<sub>3</sub>) as Lewis bases in a first time and to vary the inorganic nanoparticle following three main strategies:

- Materials already known for their catalytic activity in solvent for H<sub>2</sub> activation, for instance Mo<sub>2</sub>C or W<sub>2</sub>C for furfural hydrogenation, or Ni<sub>2</sub>P/Ni<sub>12</sub>P<sub>5</sub> for nitroarenes and olefins reduction
- Materials whose metallic center is known for being a Lewis acid, such as tungsten oxides (W<sub>18</sub>O<sub>49</sub>) or molybdenum oxides (MoO<sub>x</sub>)
- Materials already known for an all solid FLP catalytic activity, in gas phase at high temperature for In<sub>2</sub>O<sub>3</sub>, or in solvent for CeO<sub>2-x</sub>

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# Part 1

## Solvent-free syntheses



## Chapter II

# Solid-state metathesis of carbide and hydride nanoparticles

*Note: the results discussed in this chapter are reported under another form in the following article: “Early Transition Metal Nano-carbides and Nano-hydrides from Solid-State Metathesis initiated at Room Temperature”, by R. F. André, F. D’Accriscio, A. P. Freitas, G. Crochet, C. Ulhaq, M. Bahri, O. Ersen, C. Sanchez and S. Carencio, **Green Chemistry**, just accepted (2021).*

### II.1. Refractory compounds syntheses by solid-state metathesis

Transition metal carbides (TMC) are interstitial alloys formed by the incorporation of carbon atoms into the close-packed lattices of transition metals (TM). Due to their catalytic activity similar to Pt-group metals, molybdenum carbide ( $\text{Mo}_2\text{C}$ ) and tungsten carbides ( $\text{WC}$  and  $\text{W}_2\text{C}$ ) are studied as a substitute to rare and expensive metals, in particular for electrochemical<sup>1</sup> and hydrogenation reactions.<sup>2,3</sup> Most of the TMC syntheses require an extended reaction time (up to one week) at elevated temperatures ( $> 800\text{ }^\circ\text{C}$ ) between the metal precursor and a carbon source such as graphite, a polymer or light hydrocarbons.<sup>4</sup> To limit the oxidation of the material, the reaction is usually conducted under a reductive or an inert atmosphere. The high temperatures and the long reaction times are critical for these syntheses to overcome the solid-state diffusion barrier of carbon into metal. They represent a costly step in terms of energy.

Energy-saving alternative pathways were established during the past decades for the production of ceramics and refractive materials, and are now used by manufacturers.<sup>5-7</sup> For instance, Self-propagation High-temperature Syntheses (SHS) were extensively studied by Merzhanov *et al.* in the 1980s.<sup>7</sup> In an SHS, the reaction liberates enough heat so that the solid-state reaction is self-sustained at high temperature, without need for external heating. Highly exothermic reactions are needed to enter in this regime. Although the reaction is initiated at low temperatures, the reaction temperature can go above  $1300\text{ }^\circ\text{C}$  within a second, leading to highly crystalline products, and rapidly decreases to room temperature. SHS were initially used on compressed powder mixtures, yielding bulk TMC among other compounds, and were then extended to TMC nanoparticles (NPs).<sup>8,9</sup>

Transition metal halide salts have been used as the metallic source due to their simplicity and in order to obtain highly exothermic reactions. When these particular reagents are used, SHS reactions are called Solid-State Metathesis (SSM) reactions. They permit the formation of refractive compounds containing a light element, such as carbides, nitrides, silicides or phosphides. SSM reactions were studied by Kaner, Parkin *et al.*<sup>6,10</sup> When using a metal chloride, a reducing agent is needed to reduce the metallic center. It is usually a derivative of an alkaline or earth-alkaline metal in combination with the light element to be inserted. The heat released by the reaction of the two solid partners allows an exchange of atoms between the two compounds to yield the targeted phase, hence its name “metathesis”.<sup>11</sup> Various works report the use of  $\text{MgB}_2$  for borides,<sup>12</sup>  $\text{CaC}_2$ ,  $\text{SrC}_2$ ,  $\text{Al}_4\text{C}_3$  for carbides,<sup>8,9</sup>  $\text{Li}_3\text{N}$ ,  $\text{NaN}_3$  for nitrides,<sup>13-15</sup>  $\text{Mg}_2\text{Si}$ ,  $\text{CaSi}_2$  for silicides,<sup>16</sup>  $\text{Na}_3\text{P}$  for phosphides,<sup>17</sup>  $\text{Na}_2\text{S}$  for sulfides,<sup>18</sup> *etc.* The metal chloride ( $\text{MCl}_x$ ) and the reducing agent are introduced in stoichiometric conditions as regard to the electron transfer, *i.e.*  $x$  electrons provided by  $x$  alkaline metal atoms or  $x/2$  earth-alkaline metal atoms for one  $\text{MCl}_x$ . In some cases, the excess of light element (B, C, N, Si, S or P) is recovered under its elemental form as a byproduct of the reaction, *e.g.* graphitic carbon or  $\text{N}_2$ . The reaction is driven by the high lattice energy of the coproduced chloride salt ( $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ ).<sup>8,9,15,18,19</sup> When the precursor is a TM oxide, the reaction is called a Modified Solid-State Metathesis (MSSM) and is driven by the formation of the alkaline oxide, such as  $\text{Li}_2\text{O}$ ,  $\text{CaO}$  or  $\text{SrO}$ .<sup>14,20</sup> In both cases, SSM and MSSM, the reaction enthalpy is largely negative (500-2000 kJ/mol per atom of metal), hence the high exothermicity and reaction temperatures. The reaction is either initiated by mixing or grinding of the reagents for the more reactive mixtures, or by gradually heating the powder mixture up to the point the partners suddenly react: this temperature is called the ignition temperature  $T_{\text{ig}}$ .

Our group recently developed an expeditious way to access finely divided NPs dispersed on a carbon support *via* an SSM reaction initiated under ambient conditions between a metal chloride ( $\text{MCl}_x$ ) and metallic potassium dispersed in carbon,  $\text{KC}_8$  or  $\text{KC}_4$ .<sup>19</sup> Potassium-graphite ( $\text{KC}_8$ ) is an intercalation compound of potassium atoms in graphite, it was first reported in the 1920s<sup>21</sup> and was then widely used as a reagent or a catalyst considering its excellent properties as a reducing agent.<sup>22,23</sup> Potassium in acetylene black ( $\text{KC}_4$ ) is not an intercalation compound but is obtained by impregnation of liquid potassium into 50 nm large particles of acetylene black. The potassium-containing compound ( $\text{KC}_8$  or  $\text{KC}_4$ ) reduces the metal chloride to form  $\text{KCl}$  along with metal(0) or carbide NPs. The  $\text{KC}_4/\text{KC}_8$  process presents many advantages in terms of green chemistry: no solvent, no high or prolonged heating, non-toxic reagents and innocuous wastes. Moreover, it is versatile and can be applied to numerous early transition metals (Ti, V, Mo, W in the initial work,<sup>19</sup> Zr, Nb, Mo, Hf, Ta, W in the present one).

The influence of the different process parameters was not studied so far and is the object of the present work, which also provides a rationalization of the results in the framework of SSM reactions. The present study also investigates the formation of carbides with additional elements: Zr, Hf, Nb and Ta. While exploring different reaction conditions, a synthetic path to metal hydride nanoparticles was found by serendipity. We exploit here the specificities of  $\text{KC}_4$  and  $\text{KC}_8$  to tune the phase speciation of the reaction product. We first discuss the nature of the products of the reaction performed with metals of the Group IV (Zr, Hf), Group V (Nb, Ta) and Group VI (Mo, W). The products were analyzed by a combination of spectroscopies and microscopies. We put these results in light of thermodynamic considerations based on the enthalpies of reaction. We demonstrate that the reaction is not under thermodynamic control. Then, we explore the influence of different process parameters (nature of carbon support, precursor granularity, gas phase, scale...) on the metal speciation by Powder X-ray Diffraction (PXRD). Finally, we propose a mechanism for the NPs synthesis and subsequent modifications.

## II.2. Solid-state metathesis and chemical trends with $\text{KC}_8$ and $\text{KC}_4$

### II.2.1 Combustion reaction

**Synthesis II.1. Preparation of  $\text{KC}_8$  or  $\text{KC}_4$ .** In a Schlenk tube and in glovebox, 1 g of metallic potassium cut in pieces (25.57 mmol, 1 equiv.) and 2.46 g of dry graphite (204.56 mmol, 8 equiv.) (or 1.23 g of dry acetylene black 50 % compressed (102.28 mmol, 4 equiv.)) were mixed. The tube was put under static vacuum and heated with a heat gun under vigorous stirring for at least 1 h in order to obtain a homogeneous powder. Metallic potassium melts and was incorporated into the carbon phase to form a bronze powder for  $\text{KC}_8$  or a black powder for  $\text{KC}_4$ . The obtained powder (100 % yield) was then stored under inert atmosphere.

[*Caution*] Potassium and final compounds are pyrophoric: the reaction must be conducted in the absence of dioxygen and water. The  $\text{KC}_8$  and  $\text{KC}_4$  reagents should be used within the month in order to provide reproducible results.

**Synthesis II.2. Solid-state metathesis with  $\text{KC}_8$  or  $\text{KC}_4$ .** In a Schlenk tube and in glovebox, 100 mg of  $\text{KC}_4$  (1.15 mmol, 1 equiv.) were mixed with metal chloride  $\text{MCl}_x$  (1.15/x mmol, 1/x equiv.) by gentle hand-shaking (caution: the mixture may explode at room temperature) and the Schlenk tube was taken out of the glovebox. The gas phase was eventually removed or changed for  $\text{N}_2$ . The reaction was initiated by gentle heating with a heat gun. Once the reaction was over, the Schlenk tube was let to cool down to room temperature and filled with  $\text{N}_2$  (caution: the mixture is still

pyrophoric). The solid was neutralized by careful addition of ethanol (10 mL) and subsequent addition of water (20 mL). Moderate heating and bubbling occurred during a few minutes. The mixture was shaken and eventually sonicated before being centrifuged (9,000 rpm, 10 min, 20 °C). The supernatant was removed and the black solid was let to dry at air.

In Synthesis II.2., the reaction is a solid-state combustion where the reducing agent is potassium (K), either dispersed in acetylene black at 0.25 equivalent (corresponding composition:  $KC_4$ ) or inserted in graphite ( $KC_8$ ). The oxidant is a metal chloride of general formula  $MCl_x$  ( $M = Zr, Nb, Mo, Hf, Ta, W$ ). In Eq. 1,  $MCl_x$  and the reducing agent are introduced in stoichiometric proportions, *i.e.* one equivalent of K per electron to provide to the chloride for its full reduction. The oxidation number of the metal M is reduced to (0) to form NPs supported on carbon, with KCl salt and carbon as the main coproducts. Here, [M] denotes a species containing a metal(0), a metal carbide, a metal hydride or a metal oxide.



The solid reagents were mixed by handshaking in a Schlenk tube under argon. Alternatively, the gas phase was changed for  $N_2$ , or removed to perform the reaction under static vacuum, before shaking the Schlenk. Mixtures with metal chlorides of Group V and VI spontaneously ignited within seconds or minutes under vacuum while an initial activation with gentle heating (below 75 °C) was required for Group IV metals. Snapshots of the reactions performed with  $ZrCl_4$  and  $KC_4$  under Ar displayed an initiation point in the powder followed by a progression of the reaction front in the powder, at the speed of *ca.* 5 cm/s (Figure 1), confirming the classification of the reaction as a Self-propagation High-temperature combustion Synthesis (SHS). Similar behaviors were observed with the other metals. In all cases but more particularly for reactions with  $KC_4$  under vacuum, a black particulate solid was spread over the walls of the reaction tube, due to the explosivity of the reaction. Iridescences were also observed on the glass vessel: they can be explained by the formation of a thin layer of a compound (probably metallic potassium or KCl) which has been previously sublimed by the heat released by the reaction. The traces of unreacted pyrophoric  $KC_4$  or  $KC_8$  were finally neutralized with ethanol, and the powder was washed with water to remove KCl and traces of unreacted metal chloride. During the washing step, the supernatants sometimes displayed characteristic colors of metal complexes (blue for W, brown for Mo, grey for Zr, Nb, Hf and Ta), indicating that not all the reagents were consumed.

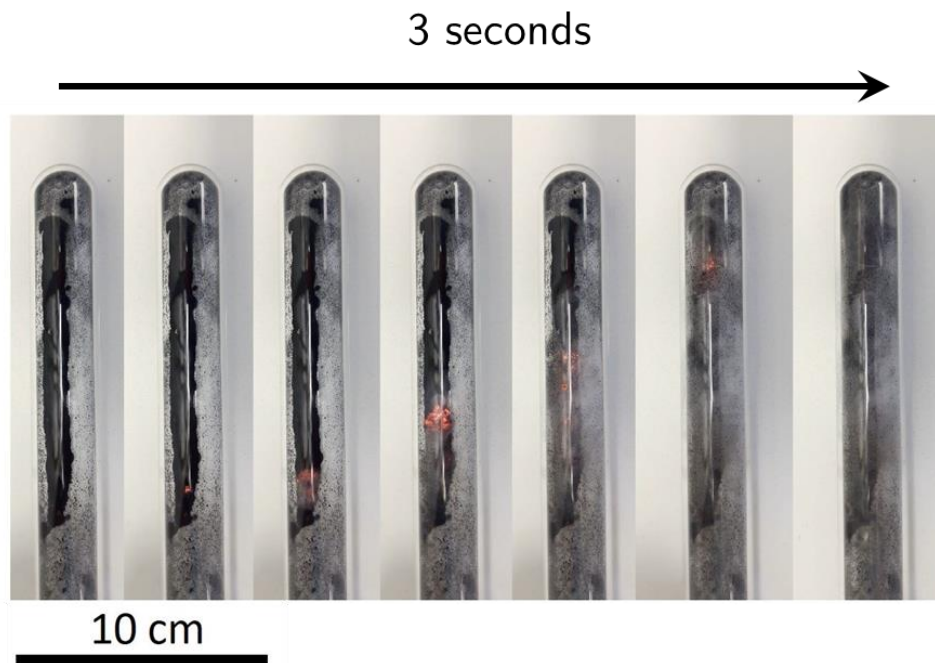


Figure 1. A sequence of photographs showing the ignition and reaction stage of a SSM reaction (Synthesis II.2.) between  $\text{ZrCl}_4 + 4 \text{KC}_4$  under Ar, covering a time span of about 3 seconds. The reaction was initiated through external heating by using a heat gun.

## II.2.2 Structural and morphological characterization

Figure 2 displays the Powder X-Ray Diffraction (PXRD) patterns of the crystalline inorganic products of the reactions between the metal chlorides and  $\text{KC}_4$  under argon (Synthesis II.2.). All the metal chloride precursors used in this study, to the exception of  $\text{MoCl}_3$ , are either soluble or hydrolyzed in water, the traces of unreacted precursor are therefore not detected by PXRD in the final product. Despite of the washing step, traces of sylvite ( $\text{KCl}$ ) appear on all the diffractograms and the its diffraction peak at  $28.3^\circ$  was used as a common calibration peak for the angle position  $2\theta$  of the detector. For the interpretation of diffractograms, although PXRD is not a quantitative method, we assumed the phases leading to the strongest diffraction peaks are the major crystalline ones. We worked under the assumptions that the phases identified in PXRD are representative of the sample, that there is only a limited amount of amorphous material and that the oxidation layer of the objects exposed to air is small enough to be neglected in a first approach.

**Group IV metals.** Metallic zirconium and hafnium can form a variety of phases but only  $\alpha$ -Zr and  $\alpha$ -Hf are detected here (Figure 2A-B, peaks at respectively  $36.4^\circ$  and  $37.0^\circ$  indicated by red dashed lines). These phases are the low-temperature metallic phases: the phase transition towards the high-temperature ones  $\alpha \rightarrow \beta$  occurs at respectively  $862^\circ\text{C}$  and  $1780^\circ\text{C}$  for  $\text{Zr}(0)$  and  $\text{Hf}(0)$ .<sup>24</sup> The other major species



detected for these two reactions are the metal hydrides (peaks at respectively  $32.4^\circ$  and  $33.0^\circ$ , indicated by green dashed lines), attributed to  $\text{ZrH}_2$  and  $\text{HfH}_{1.74}$ , which are the closest reported hydride phases in the JCPDS (Joint Committee on Powder Diffraction Standards) database. The exact stoichiometries are here undetermined as transition metal hydrides are insertion compounds with hydrogen atoms in the interstitial positions: the number of hydrogen atoms per metal atom can range from 0.8 to 2 for Zr and Hf with little impact on the PXRD spectra. On diffractogram A, peaks at  $33.0^\circ$  and  $38.3^\circ$  (indicated by blue dashed lines) are attributed to  $\text{ZrC}$ . Early transition metal carbides are known to be nonstoichiometric due to carbon vacancies: zirconium and hafnium carbides are solid solutions with a continuum of stoichiometries from  $\text{MC}_{0.5}$  to  $\text{MC}_{1.0}$  with small variations of the cell parameters (respectively 0.17 % and 0.5 % of variation between the two extremes).<sup>4</sup> The peaks are broadened here due to the small size of the crystallites: the precise stoichiometry of the carbide cannot be stated.<sup>25</sup> All the powders were washed with ethanol and water and then exposed to air, surface oxidation is therefore expected. Accordingly, the diffractograms display a peak at respectively  $30.2^\circ$  and  $30.4^\circ$  (indicated by violet dashed lines) attributed to  $\text{ZrO}_2$  and  $\text{HfO}_2$  respectively (Figure 2A-B). Although the Scherrer formula could not be applied using these peaks, their broadness indicates a small crystallite size or an amorphous phase.

**Group V metals.** On diffractograms C and D of Figure 2, peaks at respectively  $34.4^\circ$  and  $34.9^\circ$  (indicated by blue dashed lines) are attributed to  $\text{Nb}_6\text{C}_5$  and  $\text{TaC}$ . By reaction of metal with graphite, different phases of niobium and tantalum carbides can be obtained below  $1500^\circ\text{C}$ :  $\text{M}(0)$ ,  $\beta\text{-M}_2\text{C}$ ,  $\text{M}_6\text{C}_5$ ,  $\zeta\text{-M}_4\text{C}_3$  and  $\delta\text{-MC}$ .<sup>26</sup> Diffraction patterns of  $\text{Nb}_6\text{C}_5$ ,  $\zeta\text{-Nb}_4\text{C}_3$  and  $\delta\text{-NbC}$  are close and our experimental diffraction patterns could match each of them. We arbitrarily chose to indicate  $\text{Nb}_6\text{C}_5$  and  $\text{TaC}$ .  $\text{TaO}$  is isostructural with  $\text{TaC}$  and presents the same lattice parameters: its presence cannot be excluded at this point. Metal hydrides  $\text{NbH}_{0.8}$  and  $\text{TaH}_{0.5}$  are also detected at respectively  $36.1^\circ$  and  $37.6^\circ$  (indicated by green dashed lines).  $\text{NbH}_{0.8}$  pattern is a better match than  $\text{NbH}$  and other H-richer niobium hydrides. We hypothesize the pronounced triangular shape of the peaks obtained with  $\text{TaCl}_5$  is due to the superposition of broad and thin diffraction peaks, resulting from the polydispersity in size of the crystallites.

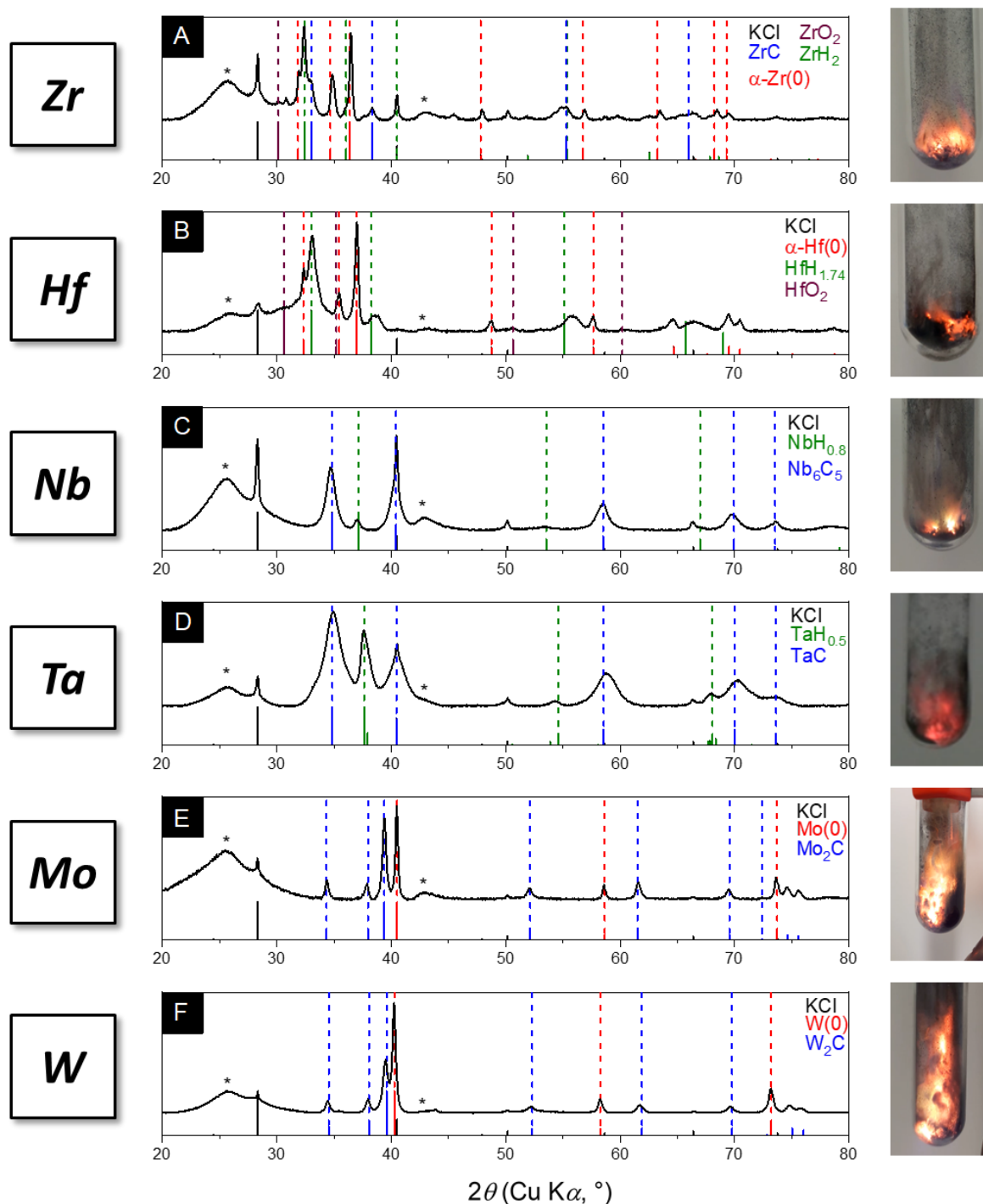


Figure 2. (Left) PXRD patterns of washed powders obtained by the reaction of  $KC_4$  and metal chlorides under Ar according to Synthesis II.2.: (A)  $ZrCl_4$ , (B)  $HfCl_4$ , (C)  $NbCl_5$ , (D)  $TaCl_5$ , (E)  $MoCl_5$ , (F)  $WCl_6$ . Asterisks indicate the acetylene black peaks. (Right) Snapshots of the explosion observed in the corresponding reaction.

**Group VI metals.** On diffractograms E and F, peaks at respectively  $40.5^\circ$  and  $40.3^\circ$  (indicated by red dashed lines) are attributed to Mo(0) and W(0). KCl salt generates a diffraction peak at  $40.5^\circ$  which is almost underneath the first diffraction

peak of metallic molybdenum and tungsten, hence the shoulder which appears at the right of the peak of W(0) at  $40.3^\circ$ . Metal carbides  $M_2C$  (indicated by blue dashed lines) are also present for both metals. Tungsten and molybdenum carbides contain small amounts of carbon vacancies and the phase stoichiometries are more precise than for Group IV and V metal carbides. Starting from  $MoCl_5$ , a single phase of hexagonal  $\beta$ - $Mo_2C$  is obtained, which corresponds to the most common molybdenum carbide and the most thermally stable, the other one being  $\alpha$ - $MoC$ . In spite of the excess of carbon, the major phase obtained with tungsten is  $\beta$ - $W_2C$  and not  $WC$ .<sup>27</sup>

**Overview.** All the reactions described above result in metallic, metal carbide and/or metal hydride phases. The reactions with the six chloride salts were also conducted under static vacuum: they displayed fairly similar behaviors and results than the reactions conducted under argon. Phase speciation for metals in the same column present strong similarities:

(1) metal chlorides of the Group IV (Zr and Hf) form a mixture of mainly the metal(0) and the metal hydride  $MH_y$ , but also of the metal carbide  $MC$  for Zr and of traces of the metal oxide  $MO_2$ ,

(2) metal chlorides of the Group V (Nb and Ta) form the metal hydride  $MH_y$ , or the metal carbide  $MC$  in varying proportions under vacuum and in Ar,

(3) metal chlorides of the Group VI (Mo and W) form mainly the metal(0) and the carbide  $M_2C$ .

**Morphology description.** Scanning Electron Microscopy (SEM) images revealed a homogeneous aspect of the samples at a length-scale larger than the micron. All samples were studied by Transmission Electron Microscopy (TEM), after washing, for morphology description and most of the sample correspond to either 5-25 nm large nanoparticles supported on carbon or nanostructured zones with structuration length of the same order of magnitude (Figure 3). These nanostructured zones look like the sintering of several particles. No objects larger than the initial size of the carbon support particles were observed. The different objects are systematically obtained from a batch to another: the diversity therefore does not originate from variability between experiments but rather from an inhomogeneity of the reaction medium. In a few samples of syntheses from  $MoCl_5$  and  $WCl_6$ , metal-containing particles present a core-shell morphology (core and shell of typically 10 nm) whose origin and composition are discussed later in this study.

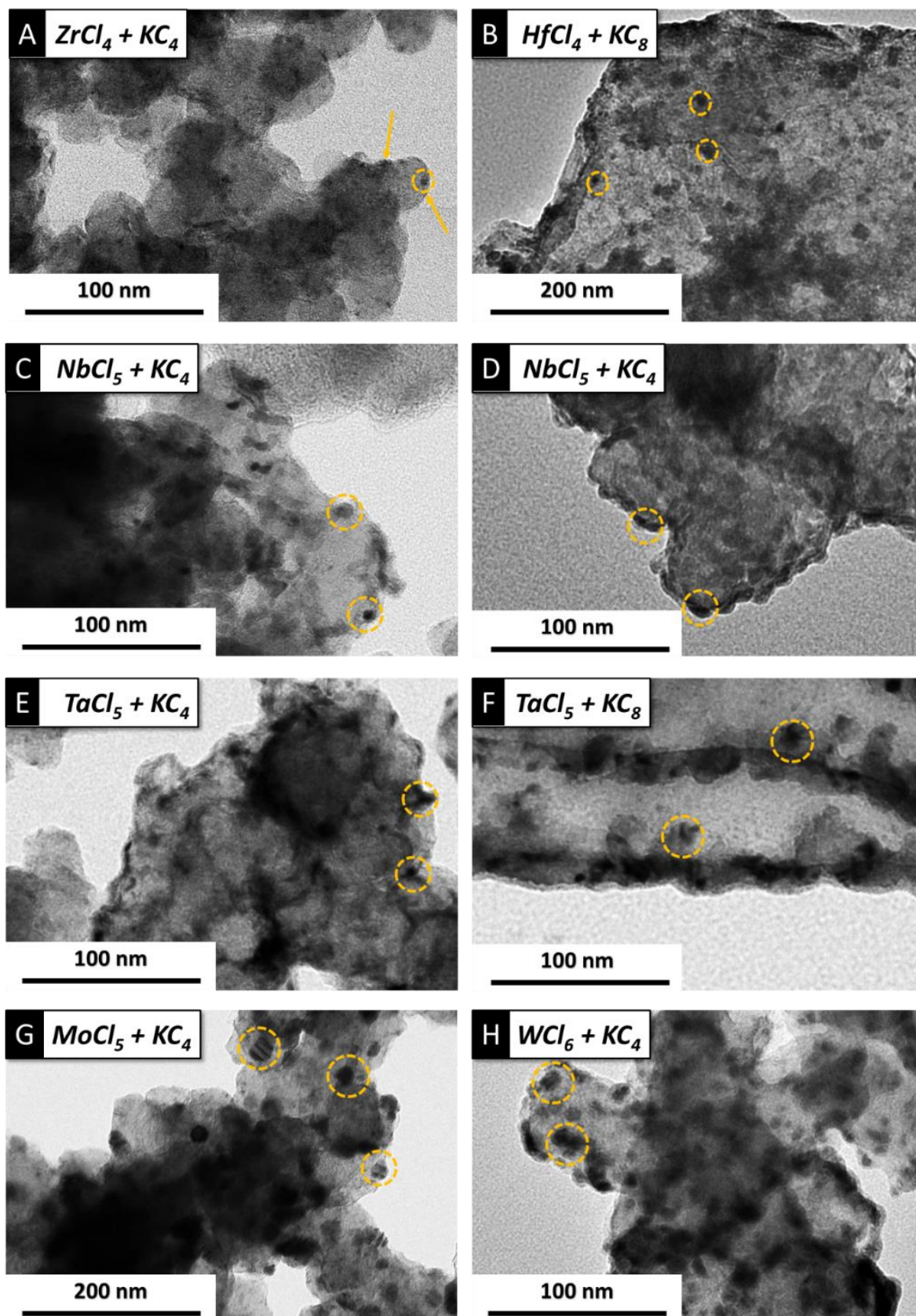


Figure 3. TEM images of different particles supported on carbon supports from reaction between  $KC_4/KC_8$  and metal chlorides (Synthesis II.2.).  $KC_4$  corresponds to an acetylene black support and  $KC_8$  to a graphite one.

**Surface oxidation state.** X-ray Photoelectron Spectroscopy (XPS) performed on NPs synthesized under Ar from  $\text{MoCl}_5$  and  $\text{KC}_4$ , and subsequently washed with water and exposed to air, unsurprisingly confirms the presence of surface oxidation with a species at 232.7 eV ( $3d_{5/2}$  peak) in the Mo 3d region (Figure 4A). Details on the experimental conditions are given in Appendix I ES.1.9. The presence of reduced molybdenum was noted with a peak at 228.4 eV ( $3d_{5/2}$  peak). It can be attributed both to Mo(0) and  $\text{Mo}_2\text{C}$  species. Considering the penetration depth of the XPS technique (1-2 nm for Mo), only the extreme surface of the nanoparticles was probed here.<sup>28</sup> Because XPS is a surface-sensitive method, the molybdenum sample was also analyzed with X-ray Absorption Near-Edge Spectroscopy (XANES) at the Mo K-edge (experimental conditions given in Appendix I ES.9.) in order to determine the average oxidation state of the atoms in the nanoparticles. On Figure 4B, the spectrum of the sample is compared with three reference samples: metallic Mo(0),  $\text{MoO}_2$  and  $\text{MoO}_3$ . None of these compounds has a spectroscopic signature close to that of the sample. However, the edge position of the Mo nanocarbide is located at 20 007.5 eV, closer to the Mo(0) metallic edge (20 003.9 eV) than to these of the oxides  $\text{MoO}_2$  and  $\text{MoO}_3$  (20 016.5 eV and 20 020.5 eV, respectively). The spectrum of the sample is even closer to the spectrum of molybdenum carbide from literature.<sup>29,30</sup> In particular, features (a), (b) and (c) on Figure 4B (respectively, a shoulder *ca.* 20 011 eV, an inflexion point *ca.* 20 033 eV and a maximum *ca.* 20 039 eV) are similar to the ones observed for the samples MoC-G and  $\text{Mo}_2\text{C}$ -G from reference [30]. Overall,  $\text{Mo}_2\text{C}$  describes the best the average environment of Mo atoms in the sample, in agreement with PXRD observations. XANES thus confirms that the main product is reduced molybdenum, although this was not clear from XPS measurements. This discrepancy is explained by the fact XPS can only probe the extreme surface containing oxidized species. The limited depth of oxidation of the nanoparticles is supported by the fact we observed distinct diffraction fringes of  $\text{Mo}_2\text{C}$  phase on nanoparticles as small as 5 nm in diameter. Samples of other metals were also analyzed by XPS: the metal is mostly observed at an elevated oxidation degree (+4 for Zr and Hf, +5 for Nb and Ta, +6 for W).

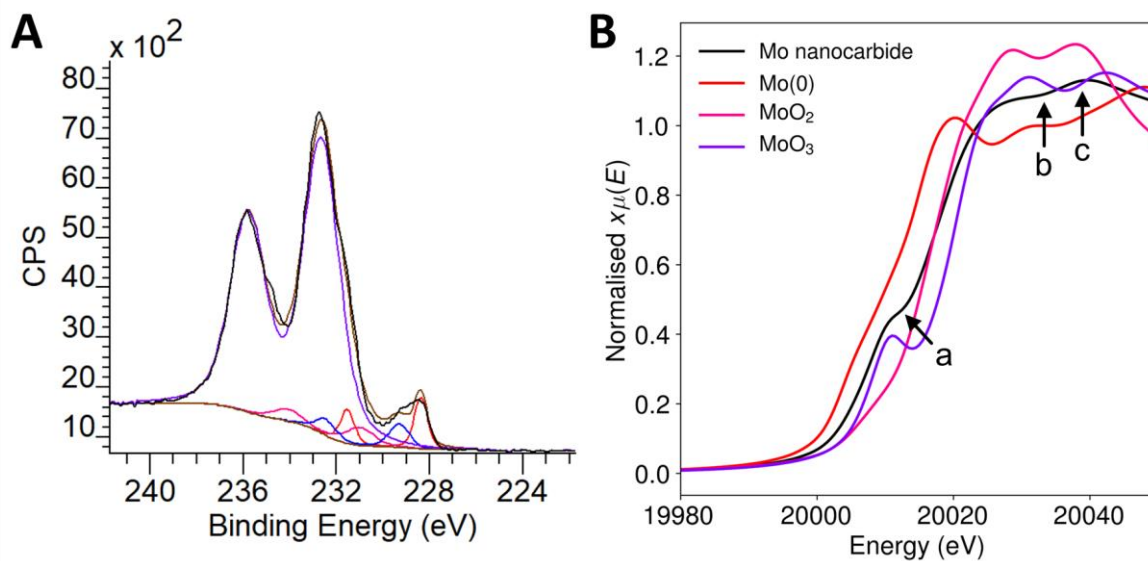


Figure 4. Redox state of sample Mo nanocarbide from XPS and Mo K-edge XANES measurements. (A) XPS of the Mo 3d region, black: measured signal, red: contributions attributed to Mo(0), blue: Mo(+II), magenta: Mo(+IV), purple: Mo(+VI), brown: sum of all 4 contributions. (B) Mo K-edge XANES measurements, black: sample Mo nanocarbide pellet, red: Mo(0) sheet, magenta: MoO<sub>2</sub> pellet, purple: MoO<sub>3</sub> pellet. Features (a), (b) and (c) are features characteristic of the signal of molybdenum carbide.

### II.2.3 Determination of reaction temperature by thermodynamic considerations

**Ignition and combustion temperatures.** Reactions with ZrCl<sub>4</sub> and HfCl<sub>4</sub> are less explosive than the ones with NbCl<sub>5</sub>, TaCl<sub>5</sub> and MoCl<sub>5</sub>, themselves less explosive than the one with WCl<sub>6</sub> (Figure 2, snapshots). The combustion temperature, *i.e.* the highest temperature reached during the explosion, is expected to be one of the key parameters for the phase speciation of the metal. Considering the brevity of the reaction, *ca.* one second, and its high exothermicity, a large amount of energy is liberated in a short period of time and a small space, leading to high temperatures. As a first approach of the released energy by the SSM reaction, we can compare the differences of standard electrochemical potentials ( $\Delta E^\circ = E^\circ(\text{MCl}_x) - E^\circ(\text{K})$ ) between K and MCl<sub>x</sub> for the different metal chlorides. Standard potentials are not reported for all the chloride salts, we therefore compare the  $\Delta E^\circ$  with metal oxides of similar degrees of oxidation (ZrO<sub>2</sub>, HfO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>) (Table 1, column 1). A larger difference in standard potentials corresponds to an easier and more exothermic reduction of the corresponding metal chloride and thus to a more violent reaction. Metal oxides from the same column have similar redox potentials and  $\Delta E^\circ$  increases from Group IV to Group VI (1.4 V for Group IV, 2.2 V for Group V and above 2.8 V

for Group VI). This trend is consistent with the increase in exothermicity observed on Figure 2.

N°	1	2	3	4	5
Metal salt	$\Delta E^\circ$ potassium-oxides	Released energy (kJ/mol)	Adiabatic temperature $T_{ad}$	Chloride salt $T_m$	Carbide Gibbs energy of formation at 1500 °C (kJ/mol)
ZrCl <sub>4</sub>	1.38 V	642	990 °C	331 °C (subl.)	-181 (ZrC)
HfCl <sub>4</sub>	1.42 V	633	970 °C	432 °C	*
NbCl <sub>5</sub>	2.29 V	1231	1490 °C	205 °C	-133 (NbC)
TaCl <sub>5</sub>	2.18 V	1170	1420 °C	216 °C	-140 (TaC)
MoCl <sub>3</sub>	*	824	1500 °C	410 °C	-63 (Mo <sub>2</sub> C)
MoCl <sub>5</sub>	2.89 V **	1502	1500 °C	194 °C	-63 (Mo <sub>2</sub> C)
WCl <sub>6</sub>	2.84 V	1841	1500 °C	275 °C	-38 (W <sub>2</sub> C) and -33 (WC)

\*No data available. \*\*For Mo(V): we used the average  $E^\circ$  of MoO<sub>2</sub> (0.15 V) and MoO<sub>3</sub> (0.07 V)

Table 1. Thermodynamic considerations for the reactions conducted on the different metal chlorides with stoichiometric proportions of KC<sub>4</sub>. (1) Difference in standard potential  $E^\circ$  between potassium (-2.93 V) and the corresponding oxide. The redox half-equations are given in water with M(0) as the reducing agent.<sup>31</sup> (2) Absolute value of molar reaction enthalpy of the reaction of formation of the metal.<sup>32</sup> (3) Adiabatic temperature  $T_{ad}$  determined with Eq. 2 and considering the eventual melting and evaporation of KCl. (4) Melting temperature of the corresponding chloride salt (for ZrCl<sub>4</sub>, sublimation temperature). (5) Standard Gibbs energy of formation, per atom carbon, of the most common carbide phases from elemental reagents (M(0) and graphite).

A more rigorous approach for the exothermicity of the reactions is the calculation of the reaction enthalpy. To calculate it, we define the ignition temperature  $T_{ig}$  as the temperature at which the reaction is triggered in the powder mixture. The heat released by the reaction at  $T_{ig}$ , noted  $|\Delta_{\text{reaction}} H_{T_{ig}}^0|$ , corresponds to the absolute value of the enthalpy of reaction, *i.e.* the difference in enthalpy of formation between the reagents and the products. It can be calculated using Hess's law, the useful data for the calculations of released energy by the reaction are given in Appendix II, TC.2. and the results in Table 1, column 2. The high exothermicity

of the reaction is due to the large negative enthalpy of formation of the coproduced salt KCl. To simplify the thermodynamic calculations, we made the assumption that M(0), KCl and graphitic carbon are the only products and we did not take into account the formation of carbides from M(0) and graphite, which is also exothermic but in a much smaller extent. We assumed the conversion is total. The change in the enthalpy of formation of the different chloride salts between room temperature and the ignition temperature  $T_{\text{ig}}$  (always inferior to 75 °C) can be neglected as it is below 1 % between room temperature and 75 °C (*cf.* Ellingham approximation). Reactions with chlorides of metals of Group IV liberate less heat than reactions with metals of Group V and Group VI, the more exothermic reaction being the one with  $\text{WCl}_6$ . The estimated energies released during the explosion are consistent with the visual observations of the reaction and with the evolution of  $\Delta E^\circ$ .

**Adiabatic temperature.** We define the adiabatic temperature  $T_{\text{ad}}$  as the theoretical maximum temperature reached by the mixture if we consider the system as thermally isolated.  $T_{\text{ad}}$  is a theoretical temperature, to be distinguished from the actual temperature during the reaction, termed combustion temperature and noted  $T_{\text{comb}}$ . It seems reasonable to consider the system as pseudo-adiabatic considering the brevity of the reaction. All the energy released by the reaction is then dissipated in the heating of the powder and eventual endothermic state changes (melting and evaporation of KCl). As the enthalpy is a state function,  $T_{\text{ad}}$  may be defined independently on how the system actually reaches its final state (Figure 5).<sup>7</sup> We note  $C_p$  the heat capacity of the products (KCl salt, graphite and metal(0)): it is a function of the temperature and of the physical state of the compounds. The models we chose for their values are given in Appendix II, TC.2..  $T_{\text{ad}}$  is determined by Eq. 2: if  $T_{\text{ad}}$  is beyond the melting point  $T_{\text{fus}}$  (770 °C) or the boiling point  $T_{\text{vap}}$  (1500 °C) of KCl, we also have to take into account the enthalpy of fusion  $\Delta H_{\text{fus}}^0(\text{KCl})$  and the enthalpy of evaporation  $\Delta H_{\text{vap}}^0(\text{KCl})$  of the salt.<sup>6</sup> All the other compounds (metals, carbides and graphite) have melting or degradation temperatures far beyond the boiling point of potassium chloride and their physical state do not change on the temperature range relevant here.

$$|\Delta_{\text{reaction}} H_{T_{\text{ig}}}^0| = \int_{T_{\text{ig}}}^{T_{\text{fus}}} C_p(T) dT + x \Delta H_{\text{fus}}^0(\text{KCl}) + \int_{T_{\text{fus}}}^{T_{\text{ad}}} C_p(T) dT \quad (2)$$

This method does not pretend to give an exact value of the combustion temperature  $T_{\text{comb}}$ , however it gives an upper limit: the adiabatic temperature  $T_{\text{ad}}$ . The actual combustion temperatures are certainly lower due to a not total conversion and to the heat transfers towards the Schlenk tube walls and to the gas phase if there is one. A similar study about the sulfuration of  $\text{MoCl}_5$  with  $\text{Na}_2\text{S}$  to form  $\text{Mo}_2\text{S}$  gave an adiabatic temperature of 1450 °C (boiling point of NaCl) and optical pyrometry measurements indicated an actual temperature close to 1100 °C.<sup>6</sup>



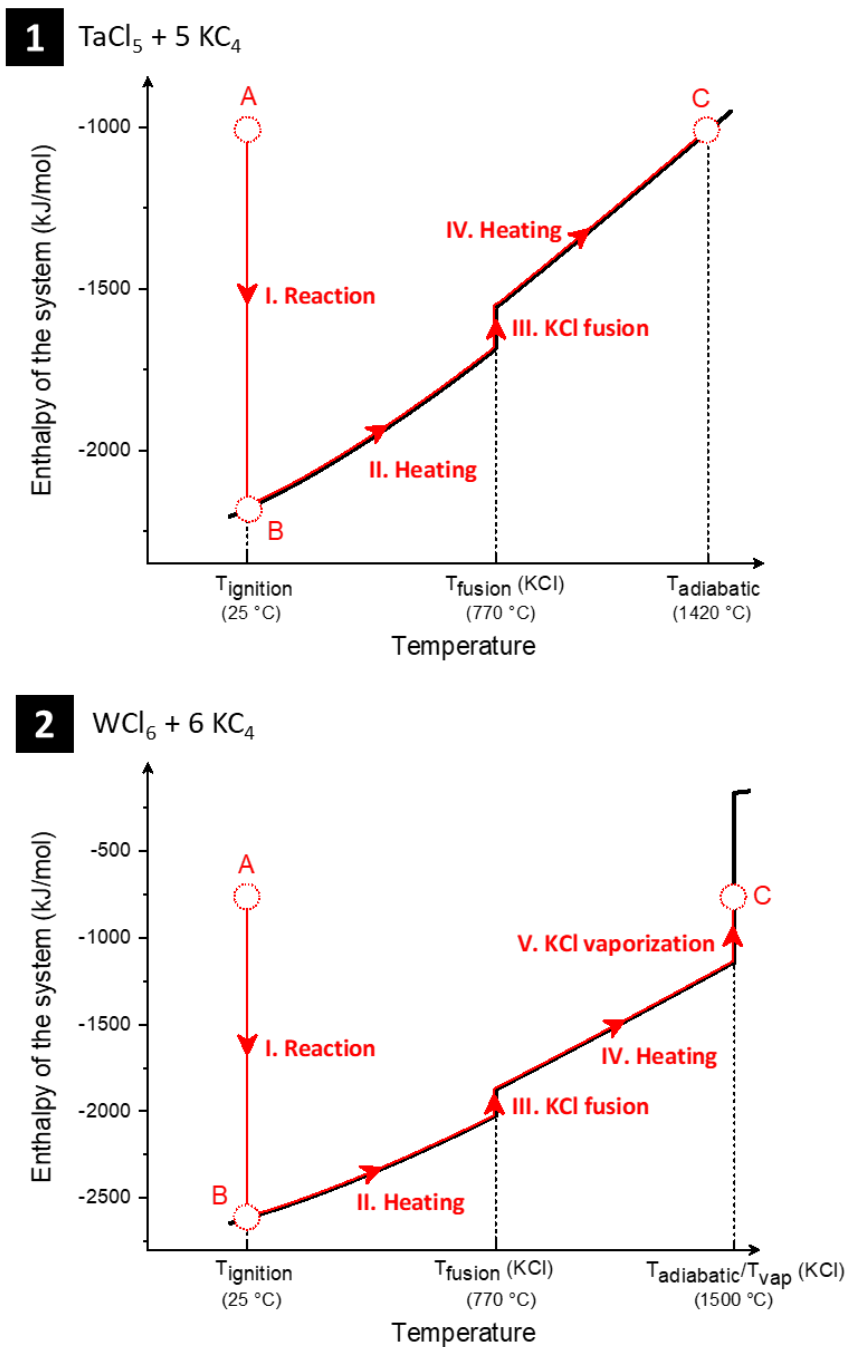
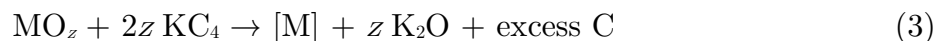


Figure 5. Illustrations of a hypothetical thermodynamic pathway of the reaction (1)  $\text{TaCl}_5 + 5 \text{KC}_4 \rightarrow \text{Ta}(0) + 5 \text{KCl} + 20 \text{C}$  and (2)  $\text{WCl}_6 + 6 \text{KC}_4 \rightarrow \text{W}(0) + 6 \text{KCl} + 24 \text{C}$ . (A) Initial state before reaction starts, (B) hypothetical state just after reaction but before temperature elevation, (C) final state of the system at the adiabatic temperature  $T_{\text{ad}}$ . A and C have equal total enthalpies.

The reaction was conducted here on small quantities ( $\approx 0.2$  mmol of chloride salt) and the released energy was eventually absorbed by the Schlenk tube, whose temperature elevation did not exceed 50 °C. All the reactions presented here have  $T_{\text{ad}}$  close or above 1000 °C (Table 1, column 3) except metals from Group IV whose

adiabatic temperatures are approximately 400 °C lower than those of the other metals. The combustion temperatures are high enough to exceed the metal chloride melting points (Table 1, column 4): as soon as the reaction initiated, the metal chloride melts and triggers the reaction in its vicinity. This melting propagates the reaction zone and maintains a high temperature until all the reagents are consumed (Figure 1).

**Modified Solid-State Metathesis (MSSM).** A similar reaction was attempted on carbon dispersed potassium ( $\text{KC}_4$ ) and molybdenum oxide ( $\text{MoO}_3$ ) precursor instead of molybdenum chloride ( $\text{MoCl}_5$ ). This Modified Solid-State Metathesis (MSSM, “modified” as the precursor is an oxide and not a chloride) presents the advantages of a cheap and stable precursor. The reaction failed to produce carbides or any other products even if the mixture was heated above 100 °C. If we consider Eq. 3, the reaction enthalpy for  $\text{MoO}_3$  is -160 kJ/mol. By comparing this value with the enthalpies of reaction with metal chlorides, comprised between -623 kJ/mol and -1841 kJ/mol, we can conclude the low exothermicity of the reaction with  $\text{MoO}_3$  impends the self-propagation *via* high temperatures.



Calculations made for the other metal oxides led to less exothermic reactions than with  $\text{MoCl}_5$ , or even endothermic ones (all the results are given in Appendix II, TC.2.). The difference between MSSM and SSM in our case is the important difference in standard enthalpy of formation of the coproduced salt (-394 kJ/mol for  $\text{K}_2\text{O}$  vs. -818 kJ/mol for 2  $\text{KCl}$ ). Sylvite ( $\text{KCl}$ ) is a thermodynamic well, which leads to a strongly exothermic reaction, contrarily to  $\text{K}_2\text{O}$ . MSSM for carbide synthesis was nonetheless successfully reported in other studies when the reducing agent was  $\text{CaC}_2$  or  $\text{SrC}_2$ : this is made possible by the large enthalpy of formation of  $\text{CaO}$  and  $\text{SrO}$  (-635.7 kJ/mol and -592 kJ/mol respectively).<sup>20</sup> The experimental validation of the reactivity of  $\text{KC}_4$ ,  $\text{KC}_8$ ,  $\text{CaC}_2$  and  $\text{SrC}_2$  with metal chlorides and of only  $\text{CaC}_2$  and  $\text{SrC}_2$  with metal oxides confirms the pertinence of our model for calculating enthalpies of reaction.

**Thermodynamic control versus process control.** All the Gibbs energies of formation of the carbide phases from the metal(0) and elemental carbon ( $\Delta G_f^0(\text{carbides})$ ) are negative (Table 1, column 5) and the system presents large excess of graphitic carbon, at least 20 atoms of C per metal atom. If the system had reached a thermodynamic equilibrium, there should be no metal(0) left to the benefice of carbide. On the contrary, metal(0) and hydride phases, deriving from metal(0), were detected. These phases were even obtained in higher proportions for Group IV metals than for Group VI ones whereas the Gibbs energy of formation of the carbide is higher for  $\text{Mo}_2\text{C}$  and  $\text{W}_2\text{C}$  than for  $\text{ZrC}$  and  $\text{HfC}$ . This consideration

comforts our hypothesis that the reaction is under kinetic control and not thermodynamic one. In this system, the reaction products speciation is in great part determined by the combustion temperature and the quality of the reagents contact, these two points being themselves related to different process parameters.

### II.3. Study of the process parameters impact

The reaction between the chloride salts and potassium is not under thermodynamic control as previously shown. We therefore studied the influence of different process parameters on the metal phase speciation. PXRD is not a quantitative method so the pie-charts displaying the phase speciation of the crystalline part in this section must be regarded as trends rather than absolute ratios. Methods for exactly quantifying the proportion of each phase are beyond the scope of this study as only the evolution of the proportions is relevant here. For readability reasons, comparisons of diffractograms are displayed only on a small angle range showing relevant peaks. The reactions were all performed twice and the results are rather reproducible although the reactions are delicate to conduct. The commented trends are stable and consistent through the different studied metals.

**Carbon source.** The nature of the carbon support, acetylene black *vs.* graphite, was identified as having an importance on the proportion of carbide *vs.* metal(0) for Group VI metals. In the case of  $\text{MoCl}_5$ , there is more carbide when the reaction is performed with potassium graphite ( $\text{KC}_8$ ) than with potassium acetylene black ( $\text{KC}_4$ ) (Figure 6A). Similar results are obtained with  $\text{WCl}_6$  (data not shown). The difference in enthalpy of formation of  $\text{KC}_4$  and  $\text{KC}_8$  is of 2.5 kJ/mol so the relative change in reaction enthalpy is below 2 %: the heat released by the reaction is virtually the same for  $\text{KC}_4$  and  $\text{KC}_8$ . The quantity of carbon is however doubled, increasing the heat capacity of the medium and thereby limiting the combustion temperature. The decrease in the adiabatic temperature from  $\text{KC}_4$  to  $\text{KC}_8$  is between 200 °C and 400 °C (Appendix II, TC.2.). If we consider the carbide phase as the phase favored by high temperatures, this explanation based on the reaction enthalpy goes against the observed trend as the proportion of carbide should increase with adiabatic temperature and should therefore be higher with  $\text{KC}_4$ , which is not the case. The origin of the difference between  $\text{KC}_4$  and  $\text{KC}_8$  reactions could not be definitely identified but several hypotheses are proposed. The graphitic carbon may be more easily decomposed than acetylene black and thus diffuses more quickly in metal NPs. The contact between the two precursors powders may be more intimate for graphite than for acetylene black due for instance to the grain size and self-cohesion of the powder. Finally, as  $\text{KC}_8$  is more compact than  $\text{KC}_4$ , the explosion disperses less the mixture of powders (as observed with a naked eye) and the heat dissipation may be lower for  $\text{KC}_8$  leading to higher temperatures locally, hence a better carbon insertion.

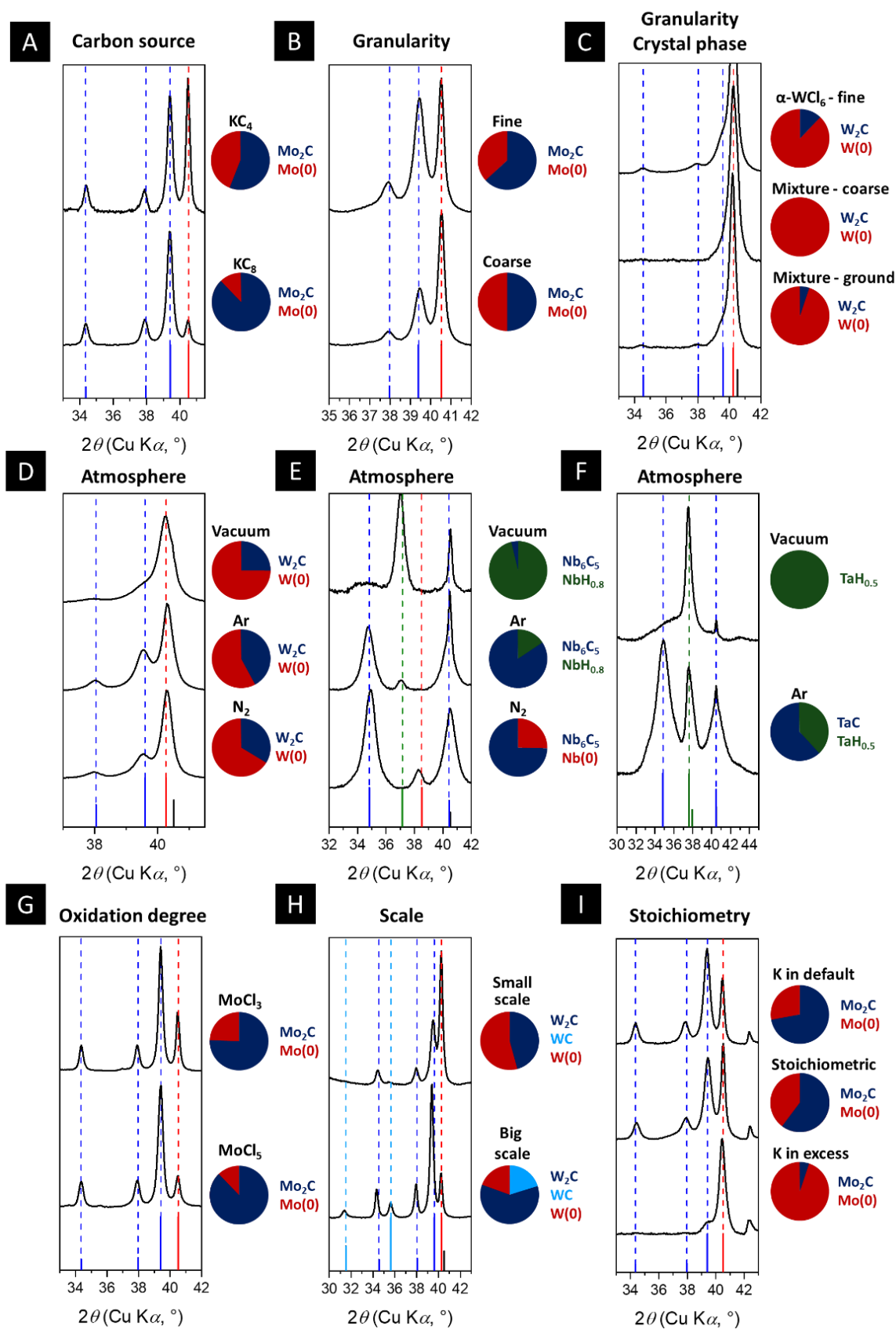


Figure 6. Details of diffractograms of powders obtained by reaction with metal chlorides under different conditions. (A)  $\text{MoCl}_5$  under Ar with  $\text{KC}_4/\text{KC}_8$ , (B)  $\text{MoCl}_5$  fine/coarse under vacuum with  $\text{KC}_8$  (C)  $\text{WCl}_6$  fine/coarse/ground under vacuum with  $\text{KC}_4$ , (D)  $\text{WCl}_6$  under

vacuum/Ar/N<sub>2</sub> with KC<sub>4</sub> (E) NbCl<sub>5</sub> under vacuum/Ar/N<sub>2</sub> with KC<sub>4</sub>, (F) TaCl<sub>5</sub> under vacuum/Ar with KC<sub>4</sub>, (G) MoCl<sub>3</sub>/MoCl<sub>5</sub> under Ar with KC<sub>8</sub>, (H), WCl<sub>6</sub> under Ar with KC<sub>4</sub> at small/big scale and (I) MoCl<sub>5</sub> under Ar with KC<sub>8</sub> in default/in stoichiometric proportion/in excess. Pie charts are guides for the eyes of the repartition in the different phases.

**Precursor grain size.** Particle size of MoCl<sub>5</sub> and WCl<sub>6</sub> was found to influence the phase speciation of the products, in favor of the metal for an increasing grain size (Figure 6B-C). To generate bigger crystal grains, two precursors, MoCl<sub>5</sub> and WCl<sub>6</sub>, were recrystallized under vacuum at 210 °C and the products were collected and used as is without grinding (more details in Appendix I, ES.1.). Due to the air degradation of the precursors, no quantitative measurements of the grain size of the recrystallized powders of MoCl<sub>5</sub> and WCl<sub>6</sub> were performed but the commercial powder has granularity below 1 mm whereas that of recrystallized precursors is above. An increase in the precursor grain size leads to a lower contact area between the reagents which may result in a lower conversion if not all the precursor has reacted. The loss in heat released by the reaction may lead to a lower combustion temperature and therefore explain the lower conversion to carbide.

**Precursor crystal phase.** As the reaction occurs between two solids, we investigated whether the crystal phase of the precursor has an impact on the products. Tungsten hexachloride (WCl<sub>6</sub>) displays two crystal phases: the  $\alpha$ -rhombohedral phase (corresponding to the commercial product) and the  $\beta$ -hexagonal phase.<sup>33</sup> The recrystallization of  $\alpha$ -WCl<sub>6</sub> at 210 °C under vacuum led to a mixture of  $\alpha$ -WCl<sub>6</sub> and  $\beta$ -WCl<sub>6</sub> (the phase transition at atmospheric pressure is tabulated at 177 °C). Although no absolute quantification of the two phases was performed by PXRD, we can estimate the major phase of the recrystallized compound is  $\beta$ -WCl<sub>6</sub> (data shown in Appendix I, ES.1.), assuming they lead to a similar signal. To limit the influence of the granularity, the recrystallized mixture of  $\alpha$ -WCl<sub>6</sub> and  $\beta$ -WCl<sub>6</sub> was ground to obtain a finer powder, however not as fine as the commercial  $\alpha$ -WCl<sub>6</sub> as extensive grinding triggers a reaction on WCl<sub>6</sub> (beige-red coloration of the powder instead of deep purple). The peaks of tungsten carbide W<sub>2</sub>C (34.5°, 38.0° and 39.6°) were not visible for coarse precursor grains but they reappeared on the diffractogram of the reaction with “ground” WCl<sub>6</sub> (Figure 6C). This indicates the difference in metal speciation between commercial  $\alpha$ -WCl<sub>6</sub> and the mixture of  $\alpha$ -WCl<sub>6</sub> and  $\beta$ -WCl<sub>6</sub> from the recrystallization is probably due to precursor granularity and not to crystal phase. This result is supported by a difference of enthalpies of formation between  $\alpha$ -WCl<sub>6</sub> and  $\beta$ -WCl<sub>6</sub> of only 21 kJ/mol at room temperature, accounting for a negligible change in the enthalpy of reaction of 1 %.

**Inert gas (Ar/N<sub>2</sub>) versus vacuum.** The metal speciation radically changes whether the reaction is performed under vacuum or in Ar or N<sub>2</sub>-filled Schlenk tubes. In the case of MoCl<sub>5</sub> and WCl<sub>6</sub>, the absence of gas phase leads to a higher proportion of metal(0) *vs.* metal carbide M<sub>2</sub>C whereas the ratio M(0)/M<sub>2</sub>C seems less affected by the nature of the gas (Ar or N<sub>2</sub>) (Figure 6D). For Group V metals (Nb and Ta), the only product detected was a hydride (NbH<sub>0.8</sub> and TaH<sub>0.5</sub>) when there is no gas phase (Figure 6E-F). The presence of hydrides may be surprising considering there is theoretically no stoichiometric source of hydrogen but we hypothesized the hydride NPs originate from the metallic NPs, this point will be discussed in detail later. The differences in the diffractograms between the experiments with the two gases are smaller than between gas and vacuum. Therefore, the impact of this parameter on the reaction does not originate from a chemical phenomenon linked to the nature of the gas molecules but rather from a physical phenomenon. We did not consider the heat dissipation by the gas phase as a credible explanation. Indeed, Ar has a molar heat capacity of 12.5 J/mol/K which corresponds to a heat capacity of 12.5 mJ/K for the entire volume (25 mL) of the Schlenk tube. The energy needed to elevate the temperature of the gas of 1000 °C is 12.5 J whereas the minimum energy released by the reaction of 0.29 mmol of HfCl<sub>4</sub> (the less exothermic reaction) is 152 J. If the entire gas volume of the Schlenk was immediately heated to the combustion temperature, it would account for only 8 % of the total released energy. We do not believe such a decrease of energy is enough to strongly modify the phase speciation. Another possible explanation is the self-cohesion of the powder mixture: as mentioned earlier, a black particulate solid is spread over the Schlenk tube during the explosion and this is particularly true for reactions under vacuum. This spreading may lead to a higher heat dissipation or a lower conversion and therefore to lower combustion temperatures. Finally, the melting and boiling points of KCl decrease under vacuum which may also limit the combustion temperature. Even though we cannot decide the mechanism at stake here, this process parameter (gas phase) is clearly critical.

We noticed that the reactions more often self-ignited (*i.e.* without heat gun activation) under vacuum, or sometimes during the gas evacuation, than similar reactions under inert gas. Conducting the reaction under vacuum leads to a lower ignition temperature (high reactivity) but also to a lower combustion temperature (low proportion of carbides *vs.* metal(0) and hydrides compared to reactions under Ar or N<sub>2</sub>).

**Oxidation number.** The reaction performed with a molybdenum chloride of lower degree of oxidation (MoCl<sub>3</sub> *vs.* MoCl<sub>5</sub>) led to the same metallic and carbide phases (Figure 6G). We also detect traces of unreacted MoCl<sub>3</sub> which did not hydrolyze or degrade, even in water, to the contrary of MoCl<sub>5</sub>. Experiments showed a comparable phase speciation of the molybdenum. The heat released by the reaction of KC<sub>8</sub> with MoCl<sub>3</sub> (817 kJ/mol) is only 55 % of the heat released by the reaction with

$\text{MoCl}_5$  (1489 kJ/mol) but the total heat capacity of the mixture with  $\text{MoCl}_3$  is 70 % that of the one with  $\text{MoCl}_5$ , we can therefore expect similar combustion temperatures. We conclude the impact of the initial oxidation number is limited if close combustion temperatures are reached.

**Scale.** The reactions of this study were conducted on the scale of 100 mg of  $\text{KC}_4$  or 155 mg of  $\text{KC}_8$ . The scale up of the reaction has an important impact on the phase speciation, at least for Mo and W. Figure 6H shows the diffractograms obtained for the reaction conducted on  $\text{WCl}_6$  and  $\text{KC}_4$  under Ar with 100 mg and 500 mg of  $\text{KC}_4$ . The proportion of metallic particles is lowered when the scale is increased, to the benefit of carbide. Furthermore, another carbide, WC, was detected in addition of  $\text{W}_2\text{C}$ . We hypothesized the increase in mass of the reaction medium diminishes losses of heat by dissipation. Higher combustion temperatures may be attained, leading to a more complete carburization of the metallic NPs and more carbon-rich carbide phases. Indeed, WC is usually obtained at higher temperatures than  $\text{W}_2\text{C}$ .<sup>34</sup>

**Stoichiometry.** We finally explored the potential impact of a default or an excess of the reducing agent ( $\text{KC}_8$ ) *vs.* the metal source in the case of  $\text{MoCl}_5$ . The same crystal phases were obtained, whatever the K: $\text{MoCl}_5$  stoichiometry (0.5, 1 or 2). A higher proportion of carbide was observed when the potassium was introduced in default or in stoichiometric amount. The presence of the same crystallographic phases indicates the reaction of reduction of the metal salt by  $\text{KC}_8$  does not go through stable species with intermediary oxidation states but directly to the metallic or the metal carbide nanoparticles. As the heat released by the reaction is limited by the reagent in default, whereas the heat capacity is imposed by the whole mixture, the combustion temperature would normally be maximal for a K: $\text{MCl}_x$  ratio of 1. Thermodynamic calculations give an adiabatic temperature of respectively 1100 °C, 1250 °C and 830 °C for the K: $\text{MoCl}_5$  ratio of 0.5, 1 and 2. The reaction with the lowest adiabatic temperature, *i.e.* corresponding to the potassium introduced in excess, was indeed the one producing the smallest amount of carbide *vs.* the metal(0).



## II.4. Mechanism proposal

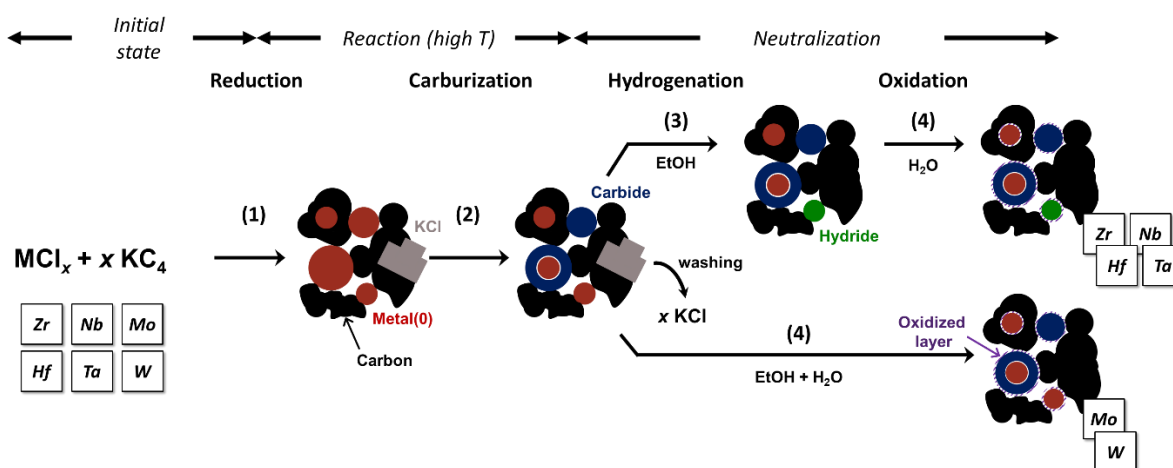
**Reaction initiation.** The initiation of the reaction, *i.e.* the self-ignition of the mixture, depends mainly on two parameters: the nature of the chloride salt and the gas phase. The more reactive compound is  $\text{WCl}_6$  followed by  $\text{MoCl}_5$ ,  $\text{NbCl}_5$ ,  $\text{TaCl}_5$  and then  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ ,  $\text{MoCl}_3$ . Under vacuum, only  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$  and  $\text{MoCl}_3$  needed heat gun activation, the other precursors self-ignited within a few minutes or during gas evacuation. Under Ar, the required heating increased from  $\text{WCl}_6$  to  $\text{MoCl}_3$ . Roughly, metal chlorides with high melting point require a stronger heating, with an exception for  $\text{WCl}_6$  which is the most reactive but has a higher melting point (275 °C) than  $\text{MoCl}_5$  (194 °C),  $\text{TaCl}_5$  (216 °C) and  $\text{NbCl}_5$  (205 °C) (Table 1, column 4). MacKenzie *et al.* attributed the self-ignition temperature to the lowest temperature at which one of the two reagents undergoes a physical state change.<sup>8</sup> Tungsten hexachloride  $\text{WCl}_6$  undergoes a crystallographic phase transition  $\alpha \rightarrow \beta$  at a lower temperature (177 °C) than the melting point of the second more reactive precursor,  $\text{MoCl}_5$ . The trend mentioned by MacKenzie is therefore in agreement with our observations. Interestingly in our case, even though the trend is respected (including  $\text{WCl}_6$  if we take into account the solid phase transition), there is no need to attain the actual physical state change temperature to trigger the reaction. We could not explain such a high reactivity with  $\text{KC}_4$ - $\text{KC}_8$ . Applying vacuum decreases the melting points of all the chloride salts: we hypothesize this effect is significant enough to explain the higher reactivity observed under vacuum than in Ar.

**Reduction step.** In this study, metallic phases are reported for all the metals (Figure 2). For a series of reactions, the crude was analyzed by PXRD in capillary under argon after reaction but before neutralization with ethanol or water (Figure 8). Potassium chloride (KCl) is systematically detected in high proportions, the reduction of the metal chlorides in metallic or carbide phases is therefore allowed by the oxidation of  $\text{KC}_4$  or  $\text{KC}_8$  in  $\text{K}^+$ . If alternative pathways exist, they were not detected. The presence of metallic phases comforts the hypothesis made by the community according to which the solid-state carbide metathesis reactions go along a sequential reduction-recombination pathway and that the metallic state is an intermediate of the reaction (Eq. 3).<sup>25</sup> The carbon element is not directly transferred from  $\text{KC}_4$  or  $\text{KC}_8$  to the metal chloride. Most of the nanoparticles formed during this step are supported on the carbon (Scheme 1, step (1)).



**Carburization step.** To the exception of Hf, carbide phases were reported for all metals but in varying proportions depending on the group of the metal and on the process parameters. The reactions with Group VI metals tend to produce more

carbides than Group IV and Group V metals and the carbide phase was usually obtained in higher proportions when process parameters favored high temperatures (fine granularity of the precursors, presence of a gas phase or large scale). We also detected traces of WC in addition of  $W_2C$  on reactions led on large scales between  $WCl_6$  and  $KC_4$  (Figure 6H). Under thermodynamic control, tungsten monocarbide (WC) is synthesized at higher temperatures than ditungsten carbide ( $W_2C$ ). We suggest all the carbide phases are obtained by carburization of the preformed metallic NPs. This carburization corresponds to the diffusion of carbon atoms from the graphite or the acetylene black to the metallic NPs (Scheme 1, step (2)).



Scheme 1. Proposed reaction mechanism. Top: elements that form metal hydrides, bottom: elements that do not form metal hydrides.

On several samples with  $WCl_6$ , core-shell structures were observed with TEM (Figure 7A-B). According to the contrast, the core is more electron-rich than the shell. Diffraction fringes appear on STEM micrograph for the core (Figure 7B) and the corresponding distance ( $2.2 \text{ \AA}$ ) could correspond to W ( $2.24 \text{ \AA}$  theoretically). Energy Dispersive X-ray Spectroscopy (EDS) performed on the different zones reveals that they all contain high amounts of carbon, which was expected considering the presence of graphite in the whole sample, and negligible amounts of oxygen (Figure 7C-F). Although EDS is not quantitative for light elements, the hypothesis of a tungsten oxide ( $WO_3$ ) shell can be excluded. The shell and the core could not be discriminated by EDS: both contain significant amounts of tungsten. No diffraction fringes could be observed in the shell, preventing a direct phase identification: we cannot be decided based on these micrographs whether the shell contains a carbide phase or inclusion of tungsten atoms into a carbon shell. However, as the number of tungsten atom per volume unit slightly decreases when  $W(0)$  is transformed in  $W_2C$ , a core-shell structure  $W@W_2C$  would be consistent with the observed contrast (dark for core, light for shell).

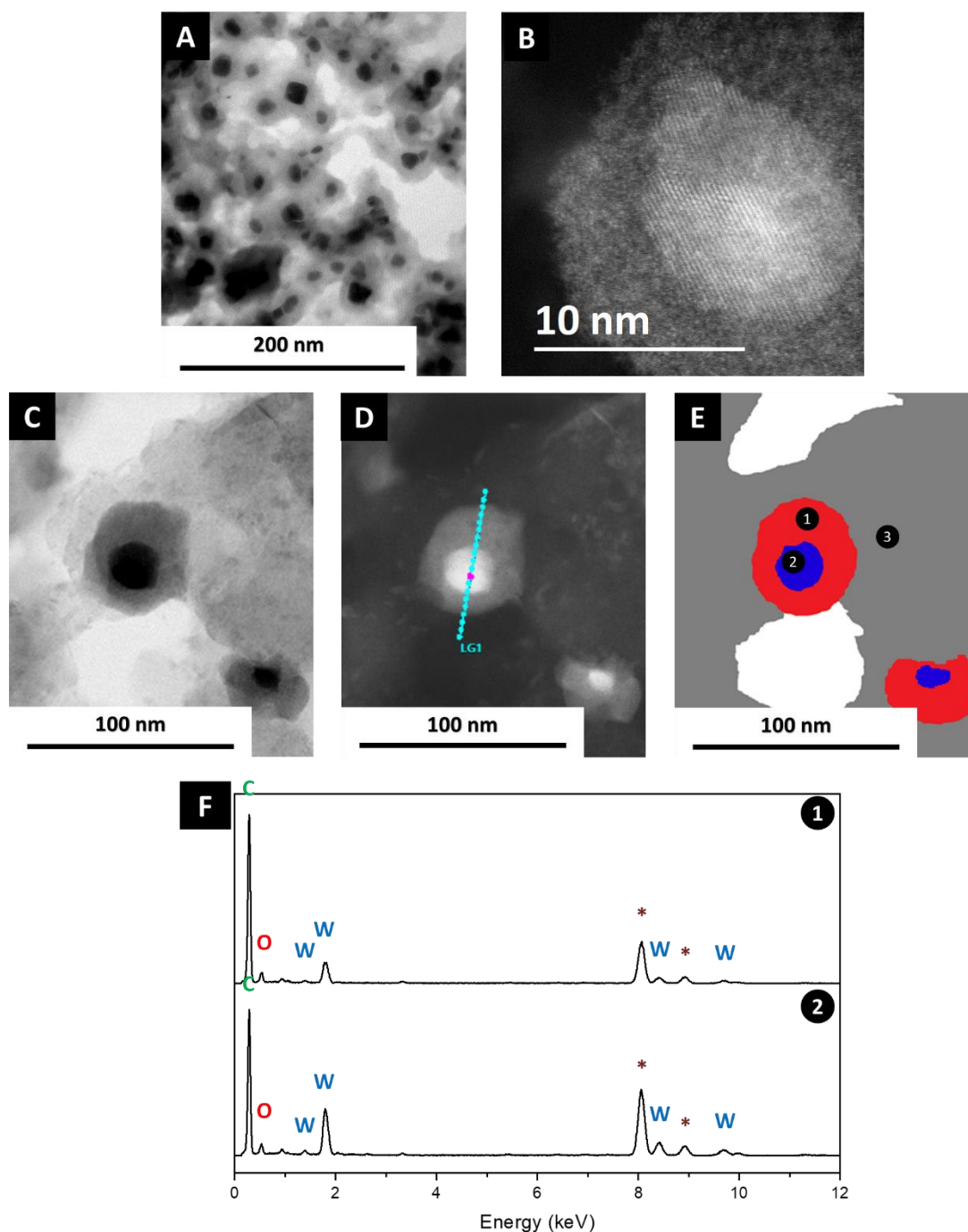


Figure 7. Core-shell particles *via* the reaction of  $\text{WCl}_6$  with  $\text{KC}_8$  under vacuum. (A, C) Bright-Field and (B, D) High Angle Annular Dark-Field Scanning Transmission Electron Microscopy of tungsten-containing NPs supported on graphite. (E) Scheme of the sample with suggested phases (blue = metallic tungsten, red =  $\text{W}_2\text{C}$  or carbon with tungsten atoms and grey = graphite). (F) EDS spectra of the zones (1) and (2) (the asterisks correspond to Cu, from the EDS anode).

Hehemann *et al.* studied the mechanism of carburization of tungsten metal particles by acetylene black into tungsten carbides WC and  $\text{W}_2\text{C}$ .<sup>35</sup> The commonly

accepted pathway is a two-stage process starting with the formation of ditungsten carbide ( $W_2C$ ) followed by carburization in WC:  $W(0) \rightarrow W_2C \rightarrow WC$ . Carbon diffuses more rapidly in  $W_2C$  than in WC, the carbon initially in contact with the metallic particle reacts to form a thin outer shell of WC. From this WC shell, metallic tungsten is converted to  $W_2C$ . As long as the metallic core has not completely reacted, the WC outer shell does not significantly grow and stays thin. If the complete carburization of  $W(0)$  is not attained, the major phase is thus  $W_2C$ . In our study, according to PXRD, the final product is a mixture of the “intermediate”  $W_2C$  and of  $W(0)$  which leads us to hypothesize that  $W(0)$  nanoparticles are not fully carburized. The only partial transformation of the metallic NPs is due to both the brevity of the reaction ( $< 1$  s) and the too low temperatures. All the other studies on similar SSM reactions comports tungsten carbides report the WC phase with no formation of the  $W(0)$  phase. However, higher ignition points are reported ( $> 200$  °C) and the powder mixture is heated after reaction (at least 1 h at 500 °C).<sup>8,9</sup> We hypothesize a similar mechanism is operating for other metals, core-shell Mo@Mo<sub>2</sub>C structures were for instance observed by reaction of a carburizing agent (1-chlorobutane) on metallic NPs.<sup>36</sup>

**Hydrogenation reaction.** One of the major products for reactions with  $ZrCl_4$ ,  $HfCl_4$ ,  $NbCl_5$  and  $TaCl_5$  is the metal hydride (Figure 2). Due to their electronegativity, early transition metals (Groups IV and V) easily form hydrides. No common metal hydride phases are reported in literature for Mo and W under standard pressures, *i.e.* below 1 GPa.<sup>37,38</sup> However, one key point of the reduction of metal chlorides with  $KC_4$  or  $KC_8$  is the theoretical absence of oxygen and hydrogen atoms in the mixture before the neutralization step with EtOH. To elucidate the origin of the metal hydrides ( $MH_y$ ), we conducted a series of PXRD in capillary under argon on powders from reactions with  $ZrCl_4$ ,  $NbCl_5$  and  $TaCl_5$ , before exposure to ethanol or air (Figure 8A-C). For the three metal chlorides, a metallic phase ( $Zr(0)$ ,  $Nb(0)$  and  $Ta(0)$ ) and a hydride phase ( $ZrH_2$ ,  $NbH_{0.8}$  and  $TaH_{0.5}$ ) were present, the same phases as the ones present after neutralization. Not all the peaks could be attributed for diffractograms in capillary but as these peaks are not present anymore after the washing step, they certainly correspond to air- or water-sensitive compounds. Because there is theoretically no H atom in the reaction before the neutralization, the hydrogens probably come from impurities in the graphite or acetylene black.

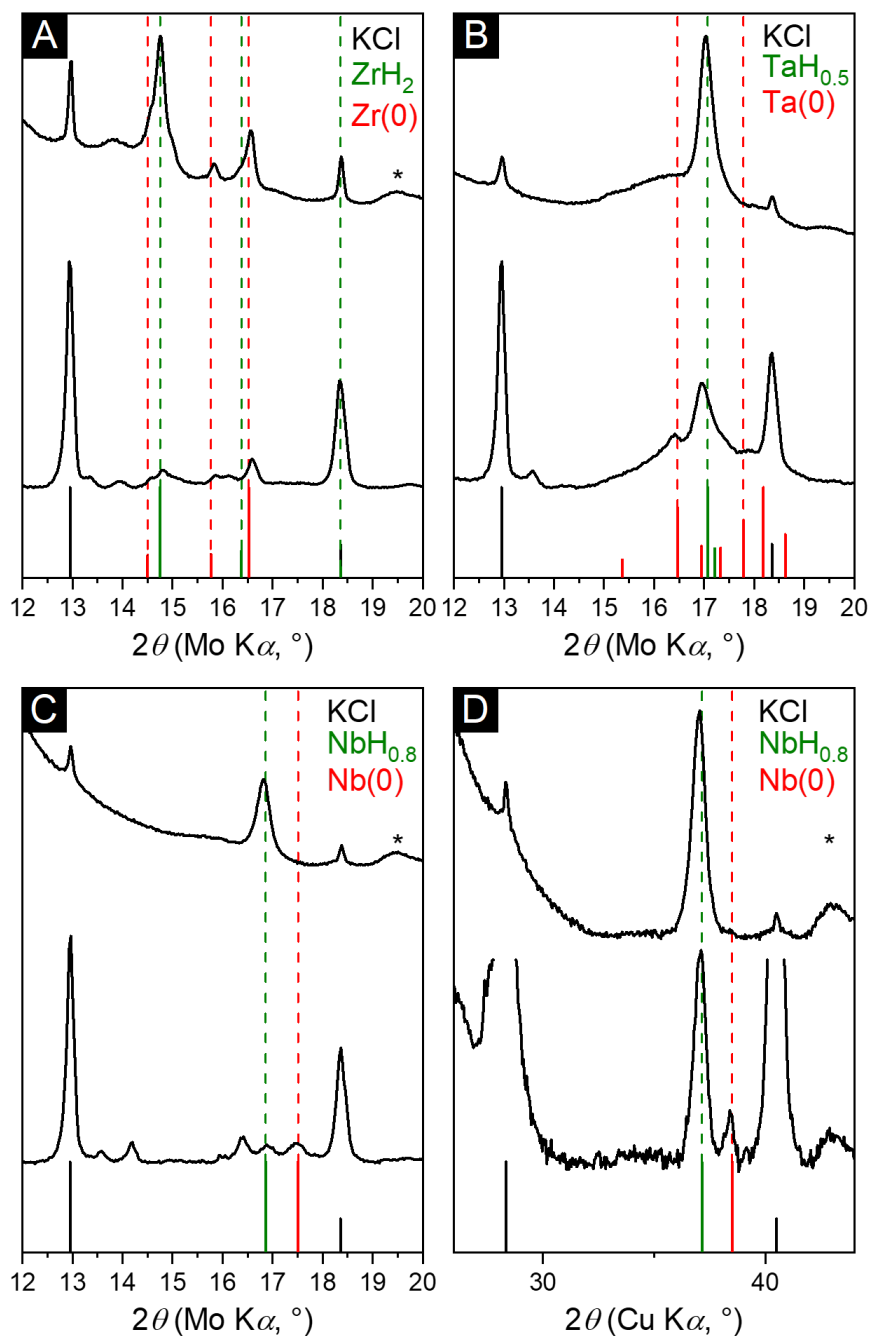
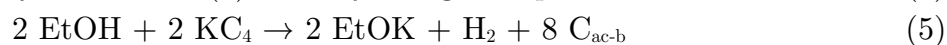


Figure 8: PXRD pattern of the products of the reaction with a stoichiometric mixture  $\text{MCl}_x + x \text{KC}_4$  performed under vacuum. (A)  $\text{ZrCl}_4$ , after neutralization (top) and before neutralization (under Ar in capillary) (bottom). (B)  $\text{TaCl}_5$ , after neutralization (top) and before neutralization (under Ar in capillary) (bottom). (C)  $\text{NbCl}_5$ , after neutralization (top) and before neutralization (under Ar in capillary) (bottom). (D)  $\text{NbCl}_5$  after neutralization with EtOH and water (top) and before neutralization after exposure to air (bottom).

Prolonged bubbling was observed during the addition of ethanol on the crude mixture (neutralization step). It may originate either from the neutralization of potassium, producing thereby  $\text{H}_2$  gas (Eq. 5), or from the surface oxidation of the metallic nanoparticles. NPs of metals such as  $\text{Zr(0)}$ ,  $\text{Hf(0)}$ ,  $\text{Nb(0)}$  or  $\text{Ta(0)}$  are indeed

particularly reactive with protic solvents. PXRD of the samples after neutralization display a decrease of the M(0) peak and an increase of the MH<sub>y</sub> peak (Figure 8A-C). Hydride formation can therefore be explained by hydrogenation of the metallic NPs formed upon reaction and which have not been carburized (Scheme 1, step (3)).<sup>1</sup> Two mechanisms are possible: either ethanol directly reacts with the metallic surface to provide H atoms and form organic species (Eq. 4) or ethanol reacts with leftover KC<sub>4</sub> or KC<sub>8</sub> to produce *in situ* H<sub>2</sub> (Eq. 5)<sup>39</sup> which diffuses in the metal (Eq. 6). This last hypothesis (Eq. 5 + 6) is less probable as significant amounts of KC<sub>4</sub> or KC<sub>8</sub> are needed to form the hydrides. For instance, ZrCl<sub>4</sub> reacts with 4 equiv. of KC<sub>4</sub> to form Zr(0) and 2 others equiv. of KC<sub>4</sub> would be needed to form ZrH<sub>2</sub>.



The exothermicity of the hydrogenation reaction is coherent with the moderate temperature elevation of the Schlenk when the solvent is added.<sup>37</sup> Contrarily to the usual hydride syntheses, there is no need for prolonged period of reaction at high temperatures probably because of the small size of the nanoparticles: diffusion of hydrogen atoms in the metal is fast. Figure 8C-D display diffractograms of the reaction of NbCl<sub>5</sub> with 5 KC<sub>4</sub>: the reaction crude under inert atmosphere (Figure 8C, bottom), after exposure to air (Figure 8D, bottom) and after washing (Figure 8D, top). A simple exposure to traces of water from atmosphere is enough to start producing hydrides, although metallic phase is still present, whereas there is exclusively metal hydride after the washing step.

The distribution of the phases within each NP is still unclear as it could contain metal hydride, metal(0) and metal carbide. In particular, we could not determine if metal(0) detected after the neutralization (Figure 2A,B for Zr, Hf and Figure 6E, N<sub>2</sub> for Nb) was not hydrogenated because it was inaccessible due to an oxide, a hydride or a carbide shell or because it was imbedded in the carbon support. In the case of the reaction of NbCl<sub>5</sub> with KC<sub>4</sub> under Ar, Nb(0) was detected but not the hydride (Figure 6E). This may be due to the formation of a carbide shell around the nanoparticles, preventing the solvent and/or H<sub>2</sub> to access the metallic part and consequently react with it. This description of the hydrogenation step comforts our choice of discussing together the metallic and hydride phases when we commented the impact of exothermicity on the possible formation of the carbide phase.

Most of the research on metal hydride materials is focused on Group I (Li, Na, K), Group II (Be, Mg, Ca), Group X (Ni, Pd, Pt) and Group XIII (B, Al) metals and

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<sup>1</sup> The reader has to be careful with the KCl residual peaks which may be at the same positions as other peaks, typically one of ZrH<sub>2</sub>: we suggest to look at the main peak at 14.8° for this phase.

essentially for hydrogen storage applications, *i.e.* in dry environments with microparticles. There are therefore few descriptions of transition metal hydride surfaces in solvent such as H<sub>2</sub>O or EtOH. The metal hydride nanoparticles synthesized here were stable over several weeks based on their XRD patterns, however, surface oxidation may occur, acting as a passivation barrier.

**Oxidation reaction.** In PXRD, crystalline metal oxides were detected both for ZrCl<sub>4</sub> and HfCl<sub>4</sub> (Figure 2) but not for all the other metals. The diffraction peaks are extremely broad, indicating a thin oxide layer at the surface of the NPs. All the XPS results indicate the presence of an oxidized layer but limited to the extreme surface of the NPs (Scheme 1, step (4)). This oxidation is limited by the soft conditions at which it occurs: the neutralization step is done at ambient temperature, under a protection of N<sub>2</sub> and with EtOH. For metals of Group V and VI, as no crystalline oxide phase was detected, we attribute the oxidized species detected by XPS to a surface oxycarbide or to hydroxylated surface metal atoms. XRD allows the detection of crystalline phases and is not suitable to characterize the presence of amorphous ones: amorphous oxides are likely to be present along with crystalline hydrides.

## II.5. Reagent choice and potential products

**Scale up.** If a scale up is envisioned, the natural combustion temperature of the system may differ from the desired one. When temperatures lower than the adiabatic ones are targeted, a common technique consists in diluting the initial mixture with an inert salt, such as NaCl or KCl, which will act as a heat absorber, due to the salt melting enthalpy. On the contrary, when higher temperatures are targeted, one can surround the reactive powder by another SHS-active mixture, which will liberate heat too when the reaction will be triggered. This last technique is termed “chemical oven” and limits the cooling by heat transfer. Together, these two strategies, inert salt addition and “chemical oven”, allow the monitoring of the combustion temperature and therefore the phase speciation. They are more suited to scales larger than the ones used in the present work.<sup>5</sup> At first view, the explosivity of the reaction may be in conflict with the twelfth principle of Green Chemistry calling for safer chemistry procedures. Three aspects must be discussed: the high temperatures reached by the medium, the pyrophoricity of the reagents and the explosivity due to gas dilatation. The first point is inherent to many chemistries and in particular that of refractory compound synthesis: we believe industries are already in capacity to deal with it as large scale applications, *i.e.* more than 10 000 tons per year, are already reported using SHS principle.<sup>5</sup> For the second point, one great advantage of the synthesis is that  $KC_4$  and  $KC_8$  may be formed in situ from metallic potassium and then mixed with the metal chloride, thereby limiting the need to transport highly reactive compounds. Finally, considering the risk of thermal dilatation of the gases in the closed vessel, we suggest to run the reaction in vacuum if the phase speciation is compatible with such conditions or to connect the vessel to a Schlenk line (or a container of inert gas), which will act as a “pressure buffer”. With such precautions, no particular risk is expected while running the experiment.

**Reagent choices.** This study is the continuation of works from the 1990s using  $Al_4C_3$ ,  $CaC_2$  or  $SrC_2$  carbides as reducing agents, but with potassium derived compounds ( $KC_4$  and  $KC_8$ ).<sup>8,19,25</sup> While the three first ones are carbides *stricto sensu* (equivalent terms, methide and acetylide, may also be found),  $KC_4$  is an impregnation compound without particular known crystallographic structure and  $KC_8$  is a Graphite Intercalation Compound (GIC). Although there are a few occurrences of potassium carbide  $K_2C_2$  in the literature, this compound appears to be much less studied and common than  $KC_8$ . On the contrary, GICs include  $LiC_6$ ,  $CaC_6$ ,  $SrC_6$  and others. Carbides and GICs have undoubtedly different structures and properties but for the study of solid-state metathesis, we considered the comparison was relevant as they have comparable elemental compositions and both present a reductive character.  $KC_8$  and  $KC_4$  were chosen as they are easily prepared on a gram scale in one step



from potassium and graphite at 100 °C under Ar, which is not the case of CaC<sub>6</sub> (metallic calcium melts at 842 °C *vs.* 63 °C for metallic potassium).

We could not determine why the use of KC<sub>4</sub> or KC<sub>8</sub> allows the ignition to be done at ambient, or close, conditions but this is an obvious energy-saving advantage. The ignition temperatures of the reactions reported in our present work are between room temperature and 75 °C, while the similar reactions using calcium carbide CaC<sub>2</sub> as the reducing agent was initiated at 200 °C at the lowest and necessitates a heating at 500 °C for at least one hour to fully crystallize the products.<sup>9</sup> To the best of our knowledge, all the other carbide syntheses *via* the SSM route have ignition temperatures of 200 °C at least. Ignition at room temperatures are reported but for other families of materials, such as nitrides or sulfides.<sup>5</sup> We hypothesize the combination of the low ignition temperatures (< 75 °C) and the absence of heating after reaction explain the unexpected production of hydrides (ZrH<sub>2</sub>, HfH<sub>1.7</sub>, NbH<sub>0.8</sub> and TaH<sub>0.5</sub>) *via* metallic particles, never reported for SSM. These hydride phases do not *strico sensu* result from the SSM as they are the products of the hydrogenation of small metallic particles. However, they are among the smallest metal hydride NPs reported as these phases are usually synthesized by metal microparticles hydrogenation with H<sub>2</sub>.

We mentioned earlier the use of metal oxides as precursors, instead of metal chlorides. Although the substitution of the metal chloride by a similar metal oxide would have been of high interest, in particular in terms of green chemistry (simpler reagents, not air or water sensitive, no use of Cl), we demonstrated the MSSM was not possible when the reducing agent is potassium for thermodynamic reasons (formation of K<sub>2</sub>O). On the contrary, MSSM with CaC<sub>2</sub> and metal oxides was successfully reported by Nartowski *et al.* in the case of V<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>.<sup>20</sup> The authors nonetheless indicated the mixtures ignited at much higher temperatures than with metal chlorides (480-650 °C for MSSM *vs.* 200-350 °C for SSM) and that there was no thermal flash at the ignition. They noticed instead a darkening of the powder over 20 seconds. This may be interpreted as a lower exothermicity. Moreover, a longer annealing step was needed for MSSM (12 h at 1000 °C instead of 1 h at 500 °C for SSM). All these observations are coherent with our thermodynamic calculations. Indeed, among the metals studied both in this article and by Nartowski *et al.* (Nb, Ta, Mo, W), the theoretical enthalpies of reaction are between -144 kJ/mol and +282 kJ/mol for MSSM with KC<sub>8</sub> (no reaction), between -974 kJ/mol and -409 kJ/mol for MSSM with CaC<sub>2</sub> (moderate reaction), between -1305 kJ/mol and -707 kJ/mol for SSM with CaC<sub>2</sub> (explosive reaction) and between -1826 kJ/mol and -817 kJ/mol for SSM with KC<sub>8</sub> (explosive reaction) (ES).

**Transition and f-block metals.** Similar works on SSM of metal carbide nanoparticles report attempts to use metal chlorides of late transition (beyond

column VI) but all failed to produce carbides. This systematic result was named the “chromium enigma”. One advanced explanation is the poor stability of the corresponding metal carbides with high temperature in comparison with early transition metals: the carbides are formed but immediately melt or degrade. We present in

Table 2 the melting temperatures of the majority of the stable carbide phases of transition metals in relation with the adiabatic temperature for a hypothetical reaction between  $\text{KC}_8$  and the corresponding metal chloride. First, it appears the melting temperatures of the carbides of all the metals studied in this work, and from a previous study in our group,<sup>19</sup> (Ti, Zr, Hf, V, Nb, Ta, Mo, W) are above the boiling point of KCl and thereby above the adiabatic temperature, to the noticeable exception of MoC (1220 °C), which was indeed not obtained in our study. Then, for scandium and yttrium carbides, the melting temperature (respectively 1864 °C and 1645 °C) are well above the adiabatic temperatures (520 °C and 460 °C) but there are doubts about the possibility to ignite the reaction considering the low enthalpies of reaction for SSM between  $\text{ScCl}_3$  or  $\text{YCl}_3$  and  $\text{KC}_8$  (-272 kJ/mol and -235 kJ/mol). These enthalpies of reaction are comparable with the ones obtained for MSSM reactions with  $\text{KC}_8$  and which were unsuccessful. Lanthanide and actinide elements, to the exception of Pm, form at least one stable carbide, the most common ones being  $\text{M}_2\text{C}_3$  and  $\text{MC}_2$ .<sup>40</sup>  $\text{M}_2\text{C}_3$  carbides are generally stable up to *ca.* 1500 °C while  $\text{MC}_2$  decomposes at *ca.* 2200 °C. The limiting point here seems to be the same as for Sc and Y: the low enthalpy of reaction. The example of  $\text{LaCl}_3$ , expected to be representative of all lanthanides, leads to a reaction enthalpy of only -147 kJ/mol.

Concerning Cr and Mn, the situation is in the middle: the degradation temperatures are around the boiling point of KCl (1500 °C) and therefore technically accessible although the adiabatic temperature is systematically below. Nartowski *et al.* reported the synthesis of  $\text{Cr}_3\text{C}_2$  when using  $\text{CaC}_2$ .<sup>25</sup> Iron presents several carbide phases between  $\text{Fe}_2\text{C}$  and  $\text{Fe}_4\text{C}$ , all metastable. The only relevant one here is the cementite  $\text{Fe}_3\text{C}$  whose degradation is particularly slow, literature indicating a limit degradation temperature of 1252 °C.<sup>41</sup> Cobalt presents two main metastable carbide phases,  $\text{CoC}_2$  and  $\text{CoC}_3$ , for which the literature defines a degradation temperature of respectively 469 °C and 491 °C.<sup>42</sup> Nickel presents only one metastable carbide phase,  $\text{Ni}_3\text{C}$ . The compound does not melt but is decomposed into Ni(0) and C. As the phase is metastable, there is no defined degradation temperature but the usual range of degradation temperatures is 300-500 °C.<sup>43</sup> Nickel and cobalt carbides would be undoubtedly degraded if formed during the SSM but the case of iron carbide is borderline. There is up to now no mention of a common carbide phase for Ru, Rh, Pd, Re, Os, Ir and Pt. Metals of column XI (Cu, Ag, Au) form explosive acetylide  $\text{M}_2\text{C}_2$  and those of column XII (Zn, Cd, Hg) form not well characterized carbides, these compounds are therefore beyond the scope of this work.

Metal	Carbide	Melting temperature	Adiabatic temperature	Metal	Carbide	Melting temperature	Adiabatic temperature
Sc	ScC	2270 °C	520 °C (ScCl <sub>3</sub> )	Cr	Cr <sub>3</sub> C <sub>2</sub>	1811 °C	930 °C (CrCl <sub>3</sub> )
	Sc <sub>4</sub> C <sub>3</sub>	1864 °C			Cr <sub>7</sub> C <sub>3</sub>	1766 °C	
Y	YC <sub>2</sub>	2415 °C	460 °C (YCl <sub>3</sub> )	Mo	Cr <sub>23</sub> C <sub>6</sub>	1576 °C	1250 °C (MoCl <sub>5</sub> )
	Y <sub>2</sub> C <sub>3</sub>	1645 °C			MoC	1220 °C	
La	LaC <sub>2</sub>	2360 °C	320 °C (LaCl <sub>3</sub> )	W	Mo <sub>2</sub> C	2605 °C	1280 °C (WCl <sub>6</sub> )
	La <sub>2</sub> C <sub>3</sub>	1415 °C			WC	2785 °C	
Ti	TiC	3067 °C	770 °C (TiCl <sub>3</sub> )		W <sub>2</sub> C	2785 °C	
Zr	ZrC	3445 °C	770 °C (ZrCl <sub>4</sub> )	Mn	Mn <sub>7</sub> C <sub>3</sub>	1333 °C	770 °C (MnCl <sub>2</sub> )
Hf	HfC	3928 °C	770 °C (HfCl <sub>4</sub> )		Mn <sub>5</sub> C <sub>2</sub>	1171 °C	
V	VC	2656 °C	900 °C (VCl <sub>3</sub> )	Fe	Mn <sub>3</sub> C	1052 °C	1140 °C (FeCl <sub>3</sub> )
	V <sub>8</sub> C <sub>7</sub>	2650 °C			Mn <sub>23</sub> C <sub>6</sub>	1034 °C	
	V <sub>2</sub> C	2191 °C					
Nb	NbC	3608 °C	1040 °C (NbCl <sub>5</sub> )	Co	Co <sub>2</sub> C	469 °C (d)	1040 °C (CoCl <sub>2</sub> )
	Nb <sub>2</sub> C	2504 °C			Co <sub>3</sub> C	491 °C (d)	
Ta	TaC	3965 °C	1000 °C (TaCl <sub>5</sub> )	Ni	Ni <sub>3</sub> C	300-500 °C (d)	1050 °C (NiCl <sub>2</sub> )
	Ta <sub>2</sub> C	3330 °C					

Table 2. Melting temperatures of all common carbide phases of transition metals and adiabatic temperature for a hypothetical SSM reaction between KC<sub>8</sub> and the different chloride salts. Fe, Co and Ni developing only metastable carbide phases, the decomposition temperatures are indicated instead of the melting temperatures. Data are taken from references <sup>24,44,45</sup>.

## II.6. Conclusion

We demonstrated the possible use of  $KC_4$  and  $KC_8$  to produce a variety of carbon-supported nanoparticles (metal(0), carbide, hydride) derived from early transition metals (Zr, Hf, Nb, Ta, Mo and W). We showed the possibility to partially modify the combustion temperature and therefore the phase speciation of the reaction by playing on several process parameters. This is particularly interesting as the usual parameters used in chemistry such as the concentration, the reaction temperature and the reaction time are not relevant for solid-state metathesis reactions. Furthermore, this study of the process parameters resulted in a proposed mechanism in four steps: reduction, carburization, hydrogenation and surface oxidation. Using thermodynamic considerations, we demonstrated that the simplest reagents were used and we delineated the scope of this process in terms of reachable compounds. In comparison to the state of the art, our process presents significant gains in energy while preserving the scalability, the versatility, the atom economy and the absence of toxic wastes.

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## Chapter III

### Catalysis with carbon-supported metal carbides

The synthesis of finely dispersed molybdenum and tungsten carbides nanoparticles supported on carbon was achieved in chapter II (Synthesis II.2.). These two materials,  $\text{Mo}_2\text{C}$  and  $\text{W}_2\text{C}$ , have already been studied in the context of hydrogenation reactions both in the gas phase and in solvent.<sup>1-3</sup> Following our “NanoFLP” target, *i.e.* the boosting of the catalytic activity of metal-containing compounds through the addition of sterically hindered molecular bases, we tested different metal carbides for hydrogenation of styrene and phenylacetylene in solvent. In a second time, the addition of co-catalysts is envisioned.

#### III.1. Hydrogenation of butadiene

*Note: the work described in this section was performed thanks to a collaboration with Dr. Laurent Delannoy from the Laboratoire de Réactivité de Surface at Sorbonne Université. He performed the gas phase catalytic tests.*

In the first section, we attempted a known hydrogenation reaction in the gas phase with  $\text{Mo}_2\text{C}$ /graphite in order to assess the possible access by the molecules to the active phase. Indeed, the XPS analysis performed in chapter II proved the presence of an oxidized shell at the surface of  $\text{Mo}_2\text{C}/\text{C}$  and the TEM pictures of the catalysts suggest the nanoparticles are imbedded in a carbon shell. This preliminary study was conducted on butadiene as molybdenum carbide was reported to selectively hydrogenate butadiene in butene at 35 °C in a mixture  $\text{H}_2/\text{C}_4\text{H}_6/\text{N}_2$  (9.1/4.5/86.4).<sup>4</sup> We expect here a hydrogenation of butadiene in  $\text{C}_4$  hydrocarbons (1-butene, cis-butene, trans-butene and butane).

Experimentally, the  $\text{Mo}_2\text{C}$ /graphite catalyst (Synthesis II.2. with  $\text{KC}_8$  and  $\text{MoCl}_3$ ), mixed with carborundum SiC (20 mg of catalyst/180 mg of SiC), was disposed between two silica wool plugs in a Quartz U-shaped tube reactor (Figure 1). The catalytic loading [Mo] in the  $\text{Mo}_2\text{C}$ /graphite-SiC is expected to be 2.5 wt.% based on the mass of the precursors. The system was purged with  $\text{N}_2$  during 3 h before switching to the reactive mixture at 1 bar (3,000 ppm of butadiene in  $\text{H}_2:\text{He}$  (20:80)). The oven, initially at 20 °C, was heated to 300 °C with a heating ramp of 2 °C/min. Every 30 °C, the reactive mixture was sampled and the catalytic activity was determined by Gas Chromatography-Flame Ionization Detector (GC-FID).

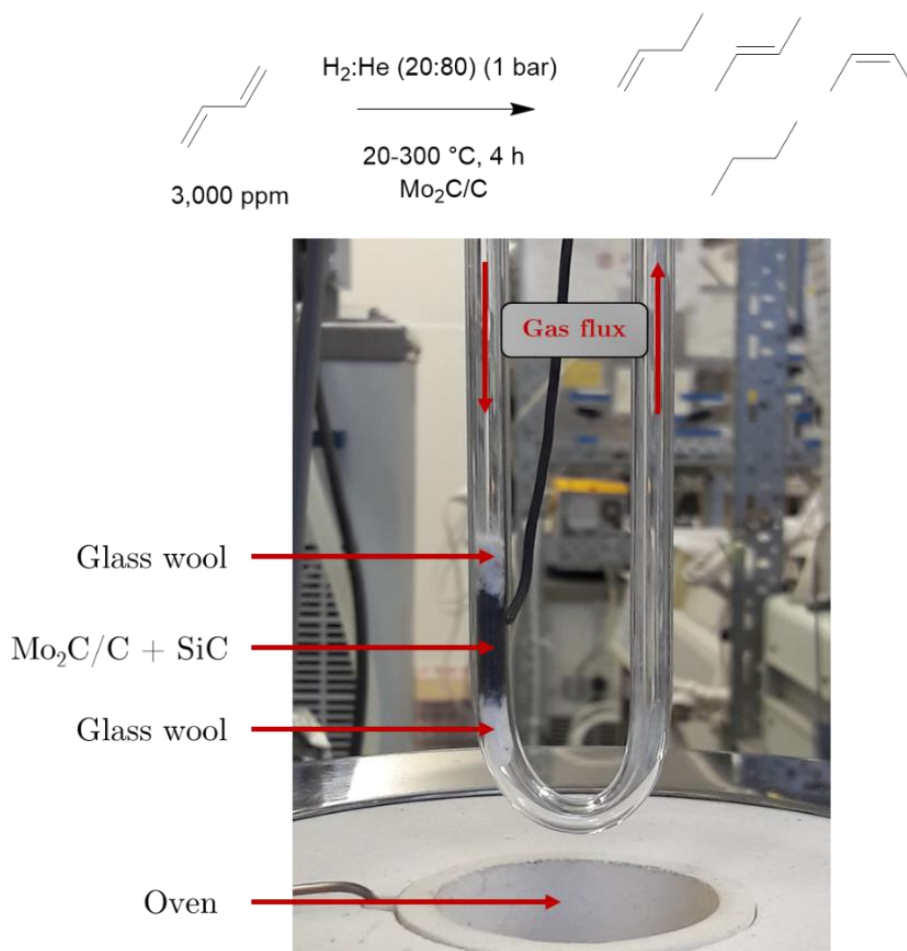


Figure 1. Gas-phase hydrogenation of butadiene with  $\text{Mo}_2\text{C}/\text{graphite}$  in a flux of  $\text{H}_2:\text{He}$  (20:80).

No conversion of butadiene was observed at temperatures below  $120 \text{ }^\circ\text{C}$  (Figure 2A). During the first heating ramp, total conversion of butadiene was observed at  $120 \text{ }^\circ\text{C}$ , with a non-negligible formation of butane (10 %), which is the fully hydrogenated product. This attests of the catalytic activity of  $\text{Mo}_2\text{C}$ . A total conversion for such moderate temperatures seemed nonetheless abnormally high, especially considering the diminution at  $150 \text{ }^\circ\text{C}$  to only 23 %. We suspected a modification of the surface occurred. We therefore stopped the heating ramp at  $150 \text{ }^\circ\text{C}$  and went back to  $120 \text{ }^\circ\text{C}$  until stabilization of the conversion, at *ca.* 4 % after one hour. We then pursued the heating ramp up to  $300 \text{ }^\circ\text{C}$  (Figure 2B). The conversion of the butadiene gradually increased up to 30 % at  $210 \text{ }^\circ\text{C}$  and then decreased to 15 % at  $300 \text{ }^\circ\text{C}$ . With increasing temperature, the selectivity towards the mono-hydrogenated product “trans-2-butene” decreased to the benefit of “cis-2-butene”. The proportion of butane, which started to be formed at  $210 \text{ }^\circ\text{C}$ , increased with temperature although staying a minor species.

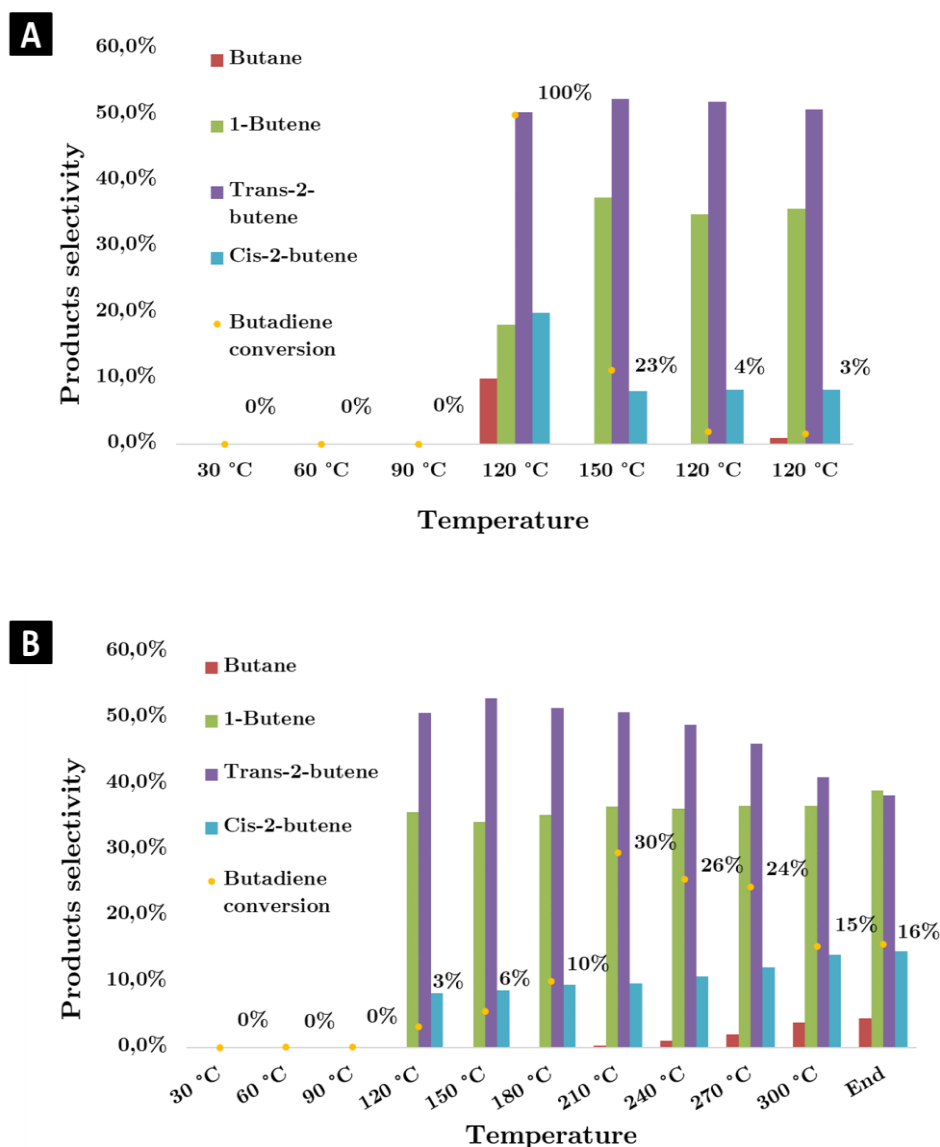


Figure 2. Hydrogenation of butadiene by Mo<sub>2</sub>C/C: selectivity and conversion as a function of temperature. (A) First heating ramp and (B) second heating ramp.

We hypothesized the particularly high catalytic activity observed at 120 °C during the first heating ramp was due to a local intense heating. Although the oven was only at 120 °C, the oxidized surface of the nanoparticles, characterized by XPS in the previous chapter, was probably reduced *in situ* by H<sub>2</sub>. This reduction is exothermic, resulting in higher temperature for the catalytic sites, hence the high conversion of butadiene in butene and butane. This high activity was not observed during the second heating ramp because all the oxide shell was reduced. Much modest conversions were then measured at 120 °C (3 % butadiene conversion, no butane formation).

Although this study was not further pushed, the preliminary results indicate first that the synthesized material is actually active for hydrogenation reactions in gas phase under relatively mild conditions (0.2 bar  $H_2$ ,  $< 200$  °C). Then, they suggest that an activation step at temperatures beyond 120 °C under  $H_2$  is required to access the  $Mo_2C$  material beneath the oxidized shell.

## III.2. Liquid phase catalysis

The Mo<sub>2</sub>C/graphite synthesized in Synthesis II.2. with MoCl<sub>3</sub> and KC<sub>8</sub> was shown to display a catalytic activity in butadiene hydrogenation in the gas phase. We therefore attempted the hydrogenation in solvent of simple olefins, styrene and phenylacetylene. Conversion and yield were determined by <sup>1</sup>H NMR without isolation of the product. Catalytic data should therefore be interpreted with a consequent error bar: this is not problematic as the focus of the study was put on the possibility or not to perform the reaction and not on a fine optimization of the reaction conditions.

### III.2.1 Styrene dimerization

The carbon supported catalysts W<sub>2</sub>C/ac-b and Mo<sub>2</sub>C/graphite developed in Chapter II (Synthesis II.2.) were studied for hydrogenation of styrene.<sup>1</sup> Their metal loadings are expected to be respectively 39 wt.% and 25 wt.% according to the mass of the precursors. First attempts were made in toluene at 100 °C under 7 bar of H<sub>2</sub> following Catalysis III.1.

**Catalysis III.1. Hydrogenation of styrene.** Under Ar, 50 mg of catalyst powder from Synthesis II.2. (0.05 equiv. of [W] for W<sub>2</sub>C/ac-b or 0.07 equiv. of [Mo] for Mo<sub>2</sub>C/graphite) were introduced in a 25 mL autoclave. To the autoclave were added 230 µL of styrene (2 mmol, 1 equiv.) and 1 mL of solvent. The autoclave was closed and the atmosphere was changed for H<sub>2</sub> (7 bar) after 2 cycles vacuum/H<sub>2</sub> (1 bar). The autoclave was then introduced in a preheated oil bath at 100 °C for 16 h. After reaction, the autoclave was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

A blank reaction confirmed the absence of reactivity of acetylene black as no conversion of styrene was detected after 16 h at 100 °C in toluene (Table 1, entry 1). While attempting at reducing the styrene under different conditions, no ethylbenzene was formed for none of the preliminary tests but instead a collection of products, including one major species with a 40 % selectivity (Figure 3). This species was attributed to the linear dimer (E)-1,3-diphenyl-1-butene, recognizable in <sup>1</sup>H NMR with its specific pattern at *ca.* 6.6 ppm. The <sup>1</sup>H NMR spectrum of the product was previously attributed and the pattern corresponds to the ethylenic protons.<sup>5,6</sup> Mo<sub>2</sub>C/graphite was also studied for this reaction led to the same product as for W<sub>2</sub>C/ac-b with a low conversion yield (Table 1, entry 2). In presence of W<sub>2</sub>C/ac-b, conversion and selectivity seem unaffected by the nature of the gas phase as similar values are obtained under an oxidative atmosphere (air), an inert one (Ar) or a reductive one (H<sub>2</sub>, 7 bar) (Table 1, entries 3-5). However, the catalytic activity is

<sup>1</sup> These catalytic trials were performed before the gas phase experiment, hence the absence of reductive pre-treatment.

highly affected by the nature of the solvent: styrene dimerizes in toluene, is oxidized in DMSO and does not react in 1-butanol (Table 1, entries 3, 6-7). All the results displayed were obtained with the same batch of  $W_2C/ac-b$ . When we attempted to reproduce the results with different batches of  $W_2C/ac-b$ , the same products were obtained but with very variable yields, with sometimes only traces of dimer and merely no conversion of styrene.

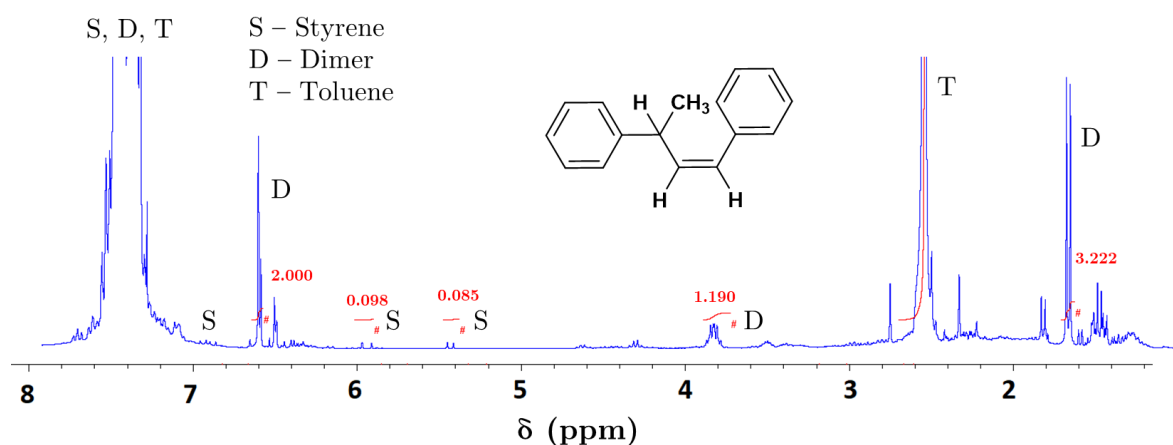
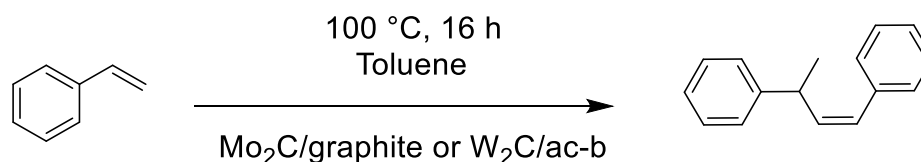


Figure 3. Typical  $^1H$  NMR spectrum of Catalysis III.1. with  $W_2C/ac-b$ , in toluene under  $H_2$ .



	Catalyst	Solvent	Gas	Styrene conversion (%)	Styrene dimer selectivity (%)
1	ac-b	Toluene	Air	0	-
2	$Mo_2C/graphite$	Toluene	Air	12	52
3	$W_2C/ac-b$	Toluene	Air	98	37
4	$W_2C/ac-b$	Toluene	Ar	98	44
5	$W_2C/ac-b$	Toluene	$H_2$ (7 bar)	97	45
6 <sup>a</sup>	$W_2C/ac-b$	DMSO	Air	29	0
7	$W_2C/ac-b$	1-butanol	Air	0	-

Table 1. Solvent and gas effect on styrene dimerization by molybdenum and tungsten carbides. Reaction conditions: 230  $\mu$ L of styrene (2 mmol), 50 mg of catalyst, 1 mL of solvent, 100 °C, 16 h in autoclave (25 mL). Conversion and yield determined by NMR.

<sup>a</sup>Styrene oxide and benzaldehyde were obtained.

No catalytic activity was obtained when a base such as butylamine or a tertiary phosphine ( $\text{PCy}_3$  or  $\text{P}^t\text{Bu}_3$ ) was added (Table 2) to the reaction medium. These two molecules are both a Brønsted and a Lewis base so we could not determine whether the loss of catalytic activity is due to an abstraction of all the potential surface acidic protons by the base or to a saturation of the catalyst surface with the ligands, impeding the approach of the substrate.

	Catalyst	Organic base	Styrene conversion (%)	Selectivity (%)		
				Benzaldehyde	Styrene oxide	Styrene dimer
1	$\text{W}_2\text{C}/\text{ac-b}$	-	98	0	0	37
2 <sup>a</sup>	$\text{W}_2\text{C}/\text{ac-b}$	Butylamine	0	-	-	-
3 <sup>b</sup>	$\text{W}_2\text{C}/\text{ac-b}$	$\text{PCy}_3$	0	-	-	-
4 <sup>b</sup>	$\text{W}_2\text{C}/\text{ac-b}$	$\text{P}^t\text{Bu}_3$	0	-	-	-

Table 2. Study of the addition of an organic base on styrene dimerization by tungsten carbide supported on acetylene black, following Catalysis III.2. Reaction conditions: 230  $\mu\text{L}$  of styrene (2 mmol), 50 mg of catalyst, 1 mL of toluene, 100 °C, air, 16 h. Conversion and yield determined by NMR. <sup>a</sup>2 drops of butylamine. <sup>b</sup>Addition of 50 mg of phosphine ( $\text{PCy}_3$  or  $\text{P}^t\text{Bu}_3$ ).

We interpreted the results as following: the styrene dimerization was catalyzed by residual Brønsted sites on the carbon-supported nanoparticles. Such residual protons were probably generated during the washing step of the catalysts, explaining why the catalytic results were very poorly repeatable. The addition of Brønsted bases such as 1-butanol, amines or phosphines neutralized the catalytic sites, thereby leading to no catalysis even with a batch known for being active otherwise. Supplementary experiments with strong acids such as trifluoroacetic (TFA) or trichloroacetic acids were run in similar conditions and indeed led to the (E)-1,3-diphenyl-1-butene dimer, in addition with other unidentified products.

A literature survey was conducted and comforted our hypothesis. Head-to-tail dimerization of vinylarene molecules, such as styrene, was reported with a variety of catalytic systems. Initially, styrene dimerization was obtained with strong Brønsted acids such as sulfuric acid or phosphoric acid but the selectivity towards the linear dimer was too low. The first developed homogeneous catalysts with good selectivities were transition metal complexes with Pd,<sup>5-12</sup> Ni,<sup>13,14</sup> or Co.<sup>15</sup> It appeared the activity drastically increased in presence of triflate salts  $\text{In}(\text{OTf})_3$ ,<sup>7,8</sup>  $\text{Cu}(\text{OTf})_2$ ,<sup>8</sup>  $\text{Ag}(\text{OTf})$ ,<sup>11</sup> or acids such as  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ <sup>6,9,10</sup> or TFA.<sup>5</sup> Transition metal-free routes were developed



with the exclusive use of acids such as  $\text{InBr}_3$ ,<sup>16</sup>  $\text{TfOH}$ ,<sup>17,18</sup>  $\text{AcClO}_4$ ,<sup>18,19</sup> or  $\text{HClO}_4$ .<sup>17</sup> As to heterogeneous catalysts, there is, to the best of our knowledge, only mention of zeolites.<sup>20–22</sup> Grigor'eva *et al.* extensively studied this reaction in the past decades and reported the possible dimerization of vinylarenes, in particular of styrene and  $\alpha$ -methylstyrene. They reported linear and cyclic dimers and trimers while realizing the reaction between 80 °C and 120 °C in chlorobenzene or neat.

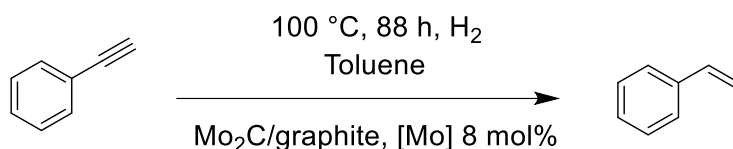
Considering the very poor reproducibility of the catalytic results (large series of unsuccessful reactions were performed, although not shown here), the dimerization of the styrene and the absence of hydrogenation activity under these conditions, we did not push further in this direction.

### III.2.2 Phenylacetylene semi-hydrogenation

The hydrogenation of styrene with metal carbide NPs in the previous section proved to be unsuccessful and one main problem arose: the competitive dimerization/polymerization of the alkene. We therefore attempted here the hydrogenation of a close alkyne, the phenylacetylene. The same catalyst as the one used for gas phase hydrogenation was used: molybdenum carbide supported on graphite,  $\text{Mo}_2\text{C}/\text{graphite}$  (metal loading of 25 wt.%). The reactions were conducted at higher  $\text{H}_2$  pressures in a steel autoclave following Catalysis III.2.

**Catalysis III.2. Semi-hydrogenation of phenylacetylene.** In air, 60 mg of catalyst powder  $\text{Mo}_2\text{C}/\text{graphite}$  (Synthesis II.2. with  $\text{MoCl}_3$  and  $\text{KC}_8$ ,  $[\text{Mo}]$  25 wt.%, 0.08 equiv.  $[\text{Mo}]$ ) were introduced in a 25 mL steel autoclave (Teflon reaction cuve). To the autoclave was added 220  $\mu\text{L}$  of phenylacetylene (2 mmol, 1 equiv.) and 1 mL of toluene. The autoclave was closed and the atmosphere was changed for  $\text{H}_2$  (7, 15 or 30 bar) after 2 cycles vacuum/ $\text{H}_2$  (1 bar). The autoclave was then introduced in a preheated oil bath at 100 °C for 88 h. The pressure increased to *ca.* 40 bar. After reaction, the autoclave was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

The semi-hydrogenation of phenylacetylene in styrene occurred in the conditions of Catalysis III.2. but with very low yields, below 2 % even when  $\text{H}_2$  pressure was set to 30 bar. There is nonetheless no degradation of the phenylacetylene in byproducts. Such low conversions impend us from concluding  $\text{Mo}_2\text{C}/\text{graphite}$  is an active catalyst for  $\text{H}_2$  activation under these conditions.



	Catalyst	H <sub>2</sub> pressure	Styrene yield (%)
1	Mo <sub>2</sub> C/graphite	7 bar	Traces
2	Mo <sub>2</sub> C/graphite	15 bar	1.2 %
3	Mo <sub>2</sub> C/graphite	30 bar	1.5 %

Table 3. Semi-hydrogenation of phenylacetylene with Mo<sub>2</sub>C/graphite. Reaction conditions: 220  $\mu$ L of phenylacetylene (2 mmol), 60 mg of Mo<sub>2</sub>C/graphite (0.16 mmol [Mo] estimated, 8 mol%), 1 mL of toluene, H<sub>2</sub> ( $x$  bar,  $x$  mmol), 100 °C during 88 h in autoclave (25 mL). Conversion and yield determined by NMR.

### III.2.3 Conclusion on hydrogenation reactions in solvent

The hydrogenation reactions of olefins with Mo<sub>2</sub>C and W<sub>2</sub>C nanoparticles supported on graphite or acetylene black were unsuccessful with no reduction at all of styrene in ethylbenzene at 100 °C under 7 bar of H<sub>2</sub> and only traces of styrene formation from phenylacetylene at 100 °C under 30 bar of H<sub>2</sub>.

We nonetheless demonstrated in the first part that the Mo<sub>2</sub>C/graphite catalyst is active for butadiene hydrogenation for temperatures above 120 °C with an optimum at *ca.* 200 °C, and that a reduction of the oxidized shell is needed. We therefore suggest the study of phenylacetylene and styrene hydrogenations at elevated temperatures, *i.e.* 150-200 °C, before concluding as to the inefficiency of the developed materials for these reactions. Furthermore, the hydrogenation of aromatic aldehydes such as benzaldehyde or furfural could be attempted as  $\beta$ -Mo<sub>2</sub>C is known to be an active catalyst of furfural hydrogenation under 20 bar H<sub>2</sub> at 150 °C in isopropanol.<sup>2</sup>

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## Part 2

### Hydrothermal syntheses



## Chapter IV

# Syntheses of defective cerium oxide nanoparticles for H<sub>2</sub> activation

Cerium oxides have been extensively studied in the context of catalysis due to the versatility of the degree of oxidation of cerium.<sup>1</sup> Cerium is indeed stable both as Ce<sup>(III)</sup> and Ce<sup>(IV)</sup> which makes it unique among the rare earth metals. The oxidation Ce<sup>(III)</sup> → Ce<sup>(IV)</sup> in cerium oxides occurs under ambient conditions with atmospheric dioxygen.<sup>2</sup> The most common cerium oxide is CeO<sub>2</sub> but this raw formula actually covers a large variety of composition as oxygen vacancies are intrinsically present in cerium oxide and are charge-compensated by the presence of Ce<sup>(III)</sup>. A rigorous description would therefore be Ce<sup>(IV)<sub>1-x</sub>Ce<sup>(III)</sup><sub>x</sub>O<sup>(-II)</sup><sub>2-0.5x</sub>. The percentage  $x$  of Ce<sup>(III)</sup> may vary from 0 % up to 40 % for nanoparticles prepared *via* usual synthetic pathways.<sup>1</sup> The amount of Ce<sup>(III)</sup> may be increased *a posteriori* by treatments such as calcination in inert atmosphere,<sup>3</sup> or reaction with reducing agents like ascorbic acid.<sup>4</sup> The color of the material depends on the oxidation state of the surface cerium atoms: the violet and the yellow colors are respectively associated to Ce<sup>(III)</sup> and Ce<sup>(IV)</sup>.<sup>2</sup> Reduced cerium oxides are typically violet or grey while oxidized ones are yellow or off white.</sup>

The hydrothermal synthesis of cerium oxide nanoparticles below 50 nm has been the object of multiple works.<sup>1,2,5,6</sup> These syntheses use a variety of precursors (CeCl<sub>3</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>) and precipitating agents (NaOH, KOH, NH<sub>4</sub>OH), and with different reaction conditions including the temperature (typically 100-250 °C), the nature of the reaction vessel (Teflon autoclave, Borosilicate vessel, Nalgene vessel), the treatment of the initial suspension and the washing step, among others.<sup>2</sup> In most cases, the synthesis parameters allow the control to some extent of the shape, the size and the defect density of the nanocrystals. Unfortunately, discrepancies and conflicting results emerged, stressing the high sensitivity of these syntheses to the reaction conditions. The easiness and the dynamic character of the reduction/oxidation processes in CeO<sub>2</sub> render delicate the study and characterization of the degree of oxidation by techniques such as X-ray Photoelectron Spectroscopy (XPS).<sup>7</sup>

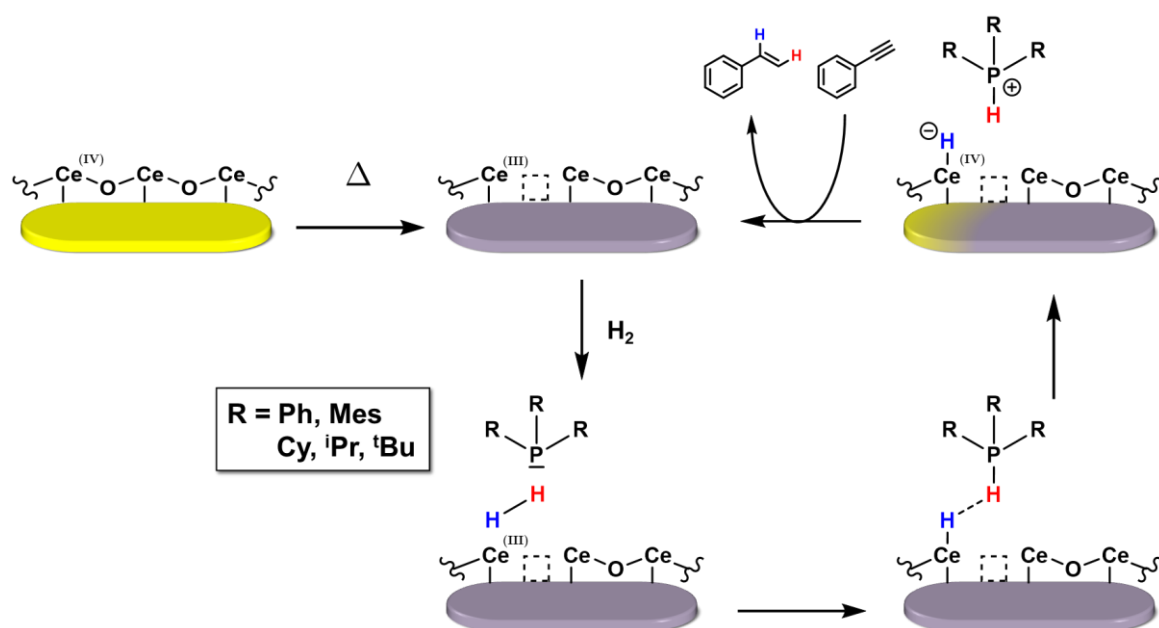
As developed in Chapter I, Qu *et al.* recently reported the use of cerium oxide nanoparticles for hydrogenation of alkenes and alkynes in toluene under soft conditions.<sup>8</sup> This study is among the most disruptive of this past decade as to activation of H<sub>2</sub> with metal oxides in the liquid phase. The authors demonstrated the catalytic activity essentially relies on the presence of defects in the CeO<sub>2</sub> structure. The active sites are situated at the vicinity of an oxygen vacancy (V<sub>o</sub>) with two Ce<sup>(III)</sup> at the surface of the nanoparticles. To create such sites, a high density of Ce<sup>(III)</sup> is required,



typically more than 30 % on the surface. The surface oxygen vacancies on cerium oxide were reported to favor H<sub>2</sub> activation by heterolytic cleavage and to stabilize the so-formed hydride Ce–H.<sup>9</sup> This last species could not be characterized by infrared spectroscopy but was recently evidenced by Freund *et al.* by XPS in the case of a highly defective cerium oxide.<sup>10</sup>

Guo *et al.*<sup>12</sup> and Rossi *et al.*<sup>13–15</sup> reported hydrogenation reactions of alkenes and alkynes with gold nanoparticles whose catalytic activity is exacerbated by the presence of imines or amines. They both suggest the mechanism at stake is a Frustrated Lewis Pair (FLP)-like one and that one H<sup>+</sup> is captured by the imine/amine while the H<sup>–</sup> counterpart stays on the gold surface. The hydride and the proton then successively react with the substrate molecule. No such mechanism was however reported so far for metal oxide materials, or any other compound displaying an ionic character.

As Qu *et al.* managed an all solid FLP-like splitting of H<sub>2</sub> at the surface of cerium oxide and Freund *et al.* proved the stability of Ce–H hydride species, we wondered whether the H<sub>2</sub> activation could be performed between a cerium atom in CeO<sub>2</sub> and a phosphine ligand according to an FLP-like mechanism. We imagined a heterolytic cleavage of H<sub>2</sub> with H<sup>+</sup> captured by the phosphine and H<sup>–</sup> on the surface of the nanoparticle as a surface hydride (Scheme 1). This theoretical mechanism relies on the ability of cerium to easily switch from Ce<sup>(III)</sup> to Ce<sup>(IV)</sup> and vice versa. As cerium oxide is known for its catalytic activity for hydrogenation of acetylene in gas phase<sup>16</sup> and of phenylacetylene in solvent, though with moderate activity,<sup>8</sup> we chose this last molecule (PhCCH) as model substrate.



Scheme 1. Hypothetical H<sub>2</sub> activation at the surface of a defective cerium oxide nanoparticle for hydrogenation of phenylacetylene according to an FLP-like mechanism.

Different objectives were thus pursued in this chapter:

- (1) The reproduction of the material reported by Qu *et al.* as a starting point
- (2) The optimization of the ratio of surface Ce<sup>(III)</sup> in CeO<sub>2</sub> for H<sub>2</sub> activation by different reductive post-synthesis treatments
- (3) The study of the impact of the addition of phosphine ligands on the catalytic activity for hydrogenation of phenylacetylene

We first attempted at reproducing the material obtained by Qu *et al.* *via* a two-step protocol (Section IV.1.). When a reproducible synthesis of the targeted material was finally achieved, with similar XRD pattern than the reported one, it appeared there were discrepancies in the analysis of the XRD data between our work and that of Qu *et al.* As the intermediate material at the end of the first step was not reported or discussed in literature, we performed an in-depth characterization (Section IV.2.). The cerium oxide samples from Sections IV.1. and IV.2. were then subjected to thermal treatments to increase the surface Ce<sup>(III)</sup> ratio (Section IV.3). The catalysts were finally studied for the activation of H<sub>2</sub> in the gas phase (Section IV.4.1.) and for the hydrogenation of phenylacetylene in solvent (Section IV.4.2.).

## IV.1. Tailored hydrothermal synthesis of defective cerium oxide catalyst

### IV.1.1 Cerium oxide nanorods

Cerium oxide nanoparticles were synthesized by hydrothermal treatment of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with a 6 M NaOH solution at 100 °C, followed by extensive washing with water.<sup>6</sup>

**Synthesis IV.1. Cerium oxide nanorods.** In a 250 mL Borosilicate vessel, 3.91 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (9 mmol, 1 equiv.) were dissolved in 30 mL of distilled water to yield a colorless limpid solution. Meanwhile, 43 g of NaOH pellets (1.075 mol, 6 M) were dissolved in 150 mL of water and the resulting solution was slowly added to the cerium nitrate solution. A yellow-brown precipitate appeared at the first drops, followed by a yellow gel and a grey gel and finally a violet suspension. The turbid violet solution was stirred 30 min and distributed in 4 Nalgene vessels of 50 mL, which were then put in a preheated oil bath at 100 °C for 20 h. After reaction, the solution was let to cool down naturally to r.t. A grey-violet powder sedimented at the bottom of the vessel, the supernatant was colorless. The whole suspensions were brought together and centrifugated (9,000 rpm, 10 min, 20 °C). The grey powder was washed 6 times with 30 mL of  $\text{H}_2\text{O}$  and once with 30 mL of EtOH: along the washings, the powder gradually turned beige. The obtained beige powder (1.45 g, 94 % yield) was then dried under  $\text{N}_2$  and stored under air.

According to XRD, the material obtained with Synthesis IV.1. is isostructural with cerium oxide  $\text{CeO}_2$  [PDF card N°00-034-0394], with a crystallite size *ca.* 12 nm, calculated with the Scherrer formula applied to the peaks at 29°, 33°, 47° and 69° (Figure 1A). TEM images reveal the product consists in polycrystalline nanorods and nanocubes (Figure 1B-C) with typical sizes ranging from 100 nm to 200 nm for nanorods length and 12 nm for their diameter, and of 10-20 nm for nanocubes diameter. Selection Area Electron Diffraction (SAED) comforts the XRD attribution to  $\text{CeO}_2$  (Figure 1D). As cerium oxide is known for its large tolerance to oxygen vacancies, the XRD attribution does not give information on the actual average oxidation degree of the cerium. This material will be referred to as  $\text{CeO}_2$  nanorods.

After reaction, the sediment in the reaction vessel was grey-violet and the powder gradually turned beige during the several washings with water. The grey-violet color before the washing step indicated the material was partially reduced, at least in surface, and the color change that surface cerium atoms were oxidized by contact with atmospheric  $\text{O}_2$ . Their oxidation may occur without structural modifications, *i.e.* the  $\text{CeO}_2$  phase was probably already formed before the washing but with a consequent number of oxygen defects to accommodate the surface  $\text{Ce}^{\text{(III)}}$  atoms. When the powder was dried in oven at 60 °C in air after the washing steps, as frequently done in

literature, it turned deep yellow. The drying step is therefore not innocent and not limited to the simple removal of water molecules.

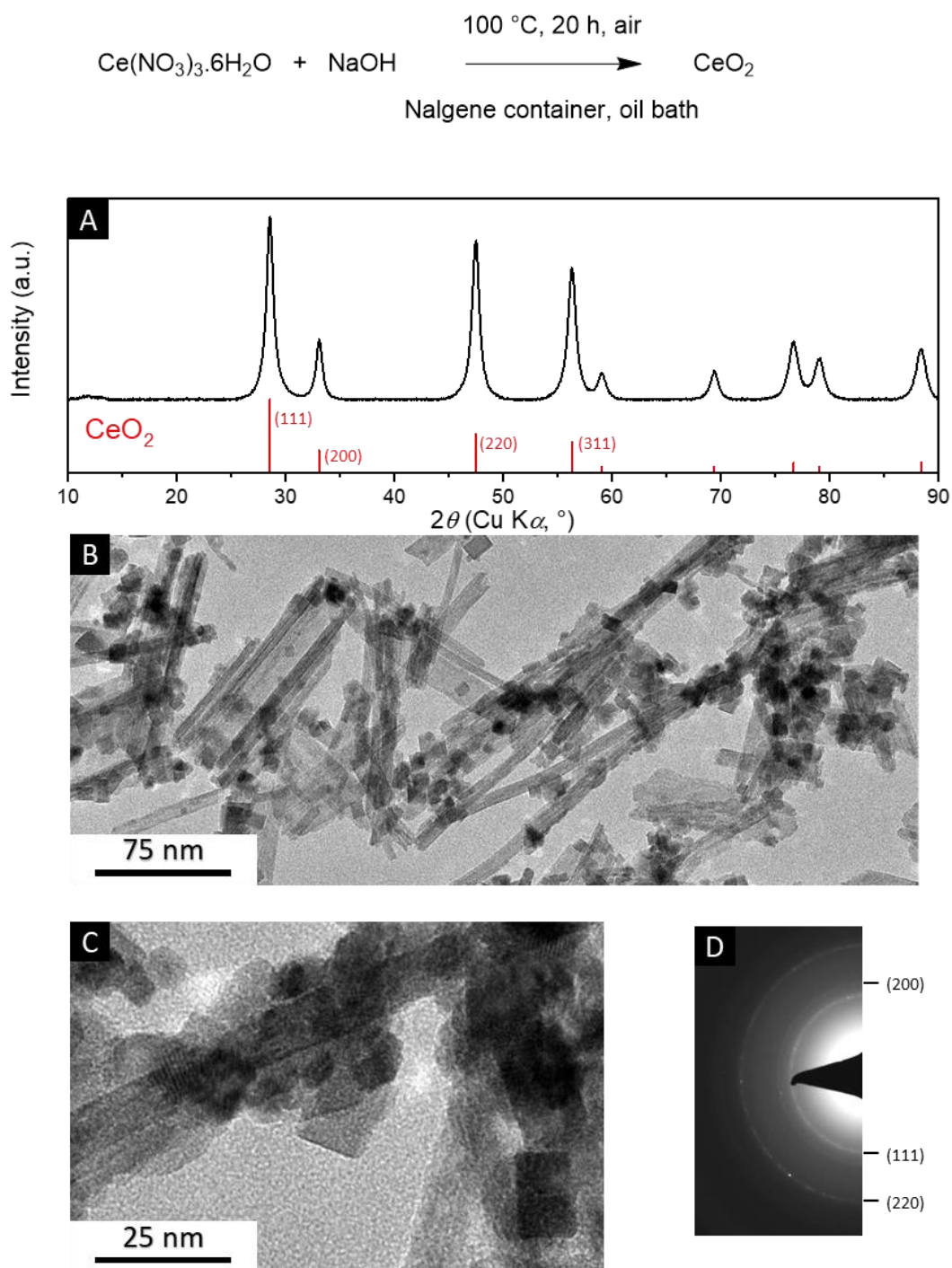


Figure 1. Synthesis of  $\text{CeO}_2$  nanoparticles according to Synthesis IV.1. (A) XRD pattern with lattice planes attribution, (B-C) TEM images and (D) electron diffraction pattern.

The turbid violet solution obtained after stirring but before reaction at 100 °C was isolated to be studied. Initially violet, it turned ochre after two washings with water and one with ethanol and then yellow in less than 24 h when stored in air. XRD indicates the material is cerium oxide  $\text{CeO}_2$  with 5 nm crystallite size (Figure 2a) and TEM images reveal sheet-like particles. Cerium nitrate is known to form cerium trihydroxide  $\text{Ce}(\text{OH})_3$  in the presence of basic solutions, then  $\text{Ce}(\text{OH})_3$  decomposes in  $\text{CeO}_2$  when exposed to air, with broad features in XRD.<sup>2,5</sup> We hypothesize such an evolution occurred in our case, explaining the presence of  $\text{CeO}_2$  but with different morphology than the particles obtained after hydrothermal treatment at 100 °C.

Alternatively, the heating step was conducted at 75 °C in a 50 mL Nalgene vessel or at 100 °C in a 25 mL Teflon autoclave. Both gave the same results than the heating at 100 °C in the Nalgene vessel, on the basis of XRD (Figure 2b-d). However, the reaction conducted at a higher temperature of 180 °C in the Teflon autoclave produced quasi exclusively nanocubes with larger size according to XRD and TEM, around 25 nm (Figure 2e). Finally, the reaction was once conducted in a regular glass reaction tube and the glass leached due to the high pH: this was obvious as micron sized rolled up objects were observed in TEM and a cancrinite phase ( $\text{Al}_3\text{Na}_4\text{O}_{14.35}\text{Si}_3$ ) was the major species in XRD.

We concluded cerium oxide nanorods could be obtained when the reaction temperature is *ca.* 100 °C. Higher temperatures (180 °C) leads to the same crystallographic phase but a different morphology, large nanocubes, which presents a lower surface/volume ratio, detrimental to catalysis. The use of a Teflon autoclave or a Nalgene vessel does not seem to lead to significantly different materials but the use of regular glass should be prohibited for this reaction due to leaching issues. We retained the conditions “100 °C in Nalgene vessel” for the production of cerium oxide for catalysis.

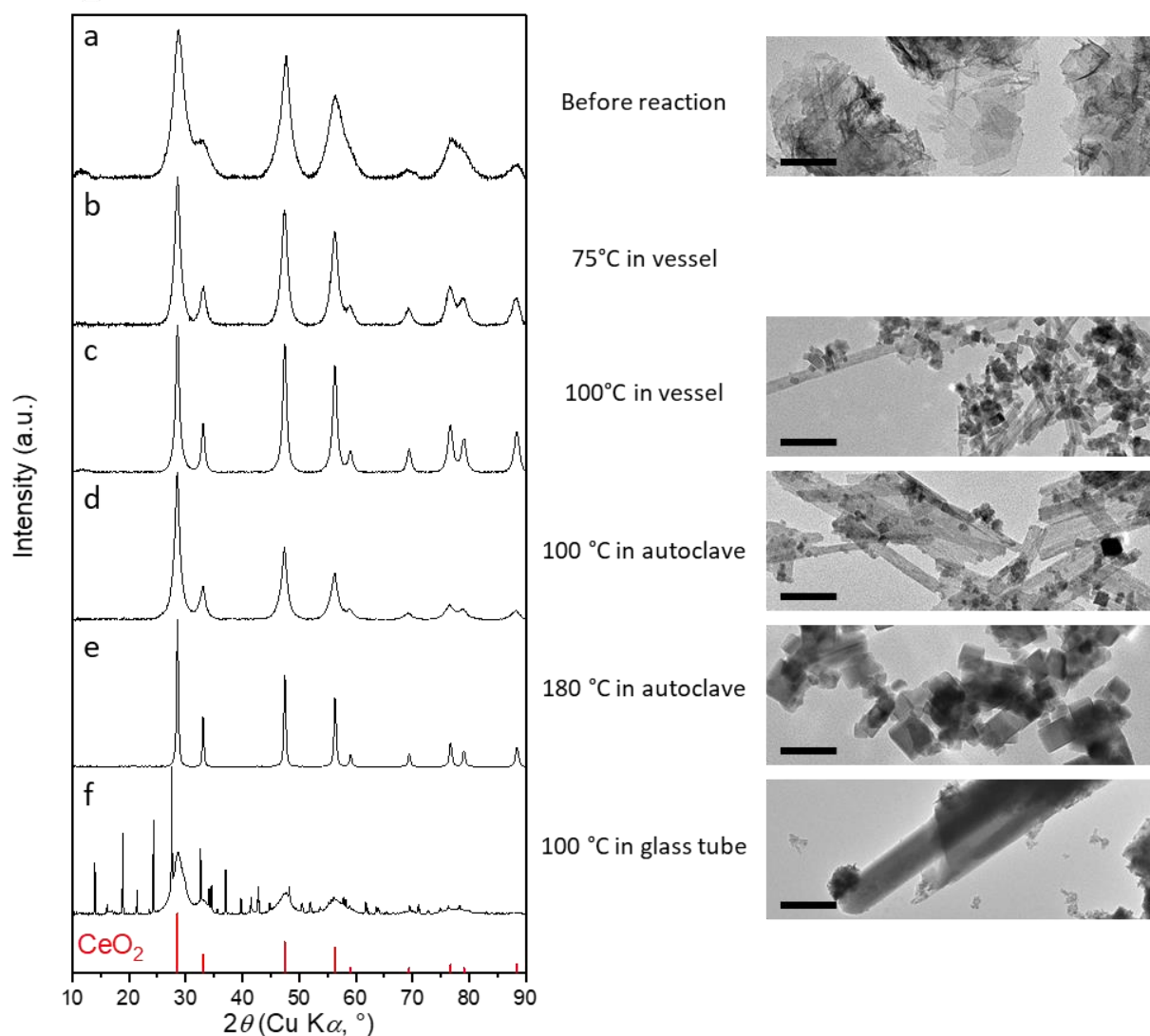


Figure 2. Synthesis of  $\text{CeO}_2$  under different conditions with structural and morphological characterizations by XRD (left) and TEM (right). (a) Washed grey gel obtained after 30 min of stirring. Powder obtained after 20 h in a Nalgene vessel (b) at 75 °C or (c) 100 °C. Powder obtained after 20 h in a Teflon autoclave (d) at 100 °C or (e) 180 °C. (f) Powder obtained after 20 h in a glass reaction tube at 100 °C. Scale bars on TEM images represent 50 nm except for (f) where it represents 500 nm. The calculated Scherrer sizes on XRD are respectively 5 nm, 8 nm, 12 nm, 9 nm and 25 nm for (a-e).

#### IV.1.2 Toward $\text{Ce}^{(\text{III})}$ rich cerium oxide and cerium hydroxide

We then attempted to reproduce the materials synthesized by Qu *et al.*, which displayed excellent properties as to hydrogenation of alkenes and alkynes in toluene.<sup>3,8</sup> Their protocol consists in two steps: first the synthesis of a “non-porous  $\text{CeO}_2$  nanorods precursor” (NP- $\text{CeO}_2$  precursor) by hydrothermal treatment of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with  $\text{NaOH}$  at 100 °C for 20 h in a Pyrex bottle in an oven, then its dehydration in  $\text{CeO}_2$  by hydrothermal treatment at 160 °C during 12 h. The NP- $\text{CeO}_2$  precursor was

identified by Guo *et al.* as a mixture of  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$ , this point will be discussed later.<sup>3</sup> The diffraction pattern is particularly recognizable due to the peaks at *ca.*  $52^\circ$ , forming a thin peak and a quasi-plateau (Figure 3).

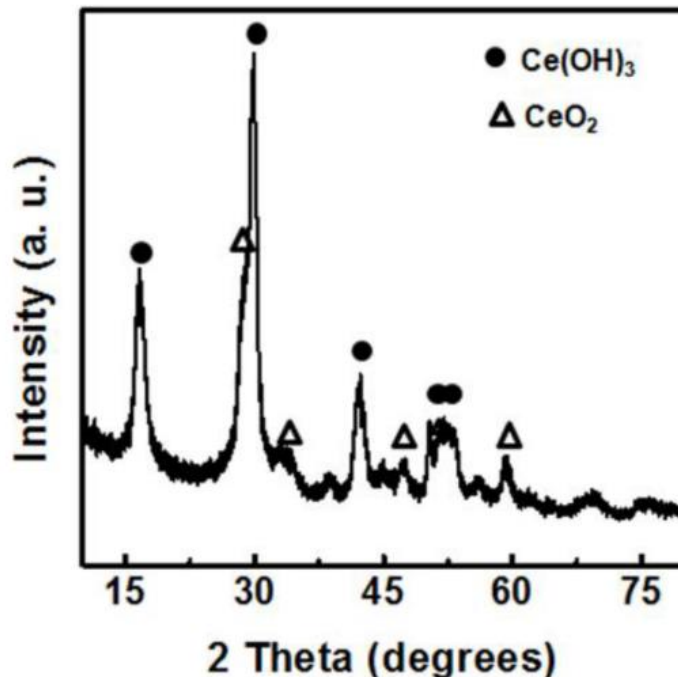


Figure 3. XRD pattern of the targeted material with phase attribution, from reference [8].

In order to favor the formation of  $\text{Ce}(\text{OH})_3$  phase instead of  $\text{CeO}_2$ , obtained in Synthesis IV.1, we explored the influence of different parameters such as (1) the nature of the reaction vessel (Nalgene/Borosilicate), (2) the nature of the precipitating agent ( $\text{NaOH}/\text{KOH}$ ), (3) the concentration of the base and (4) the reaction temperature ( $75^\circ\text{C}/100^\circ\text{C}$ ).

The reaction was first conducted with  $[\text{NaOH}] = 6\text{ M}$  or with  $[\text{KOH}] = 4.3\text{ M}$  in either a Borosilicate vessel or a Nalgene vessel. This last one is supposedly less air-tight than the Borosilicate one. Reactions in Nalgene vessels led to XRD-pure  $\text{CeO}_2$  and the peaks were thinner than in Borosilicate vessels (Figure 4a-b *vs* c-d). For reactions conducted in Borosilicate vessels, a lower proportion of  $\text{CeO}_2$  was obtained with  $\text{KOH}$  than with  $\text{NaOH}$  (Figure 4c-d), in favor of the phase with the characteristic pattern at *ca.*  $52^\circ$ . We therefore used  $\text{KOH}$  and Borosilicate vessels for the following experiments. The reaction was then conducted with a  $\text{KOH}$  concentration of  $4.3\text{ mol/L}$  and of  $0.43\text{ mol/L}$ , both corresponding to  $\text{pH}$  above 13, and either at  $75^\circ\text{C}$  or  $100^\circ\text{C}$  (Figure 4e-h). The proportion of  $\text{CeO}_2$  was higher for low  $\text{KOH}$  concentrations both at  $75^\circ\text{C}$  and  $100^\circ\text{C}$ . The proportion of  $\text{CeO}_2$  was also higher when the reaction temperature was set to  $100^\circ\text{C}$  both at low and high  $\text{KOH}$  concentrations. As a consequence, we

kept the KOH concentration at 4.3 mol/L and the reaction temperature at 100 °C for the following experiments. We can nonetheless notice the robustness of the reaction as similar diffractograms were obtained even when varying the nature and the concentration of the precipitating agent and the reaction temperature.

As previously mentioned, we noticed the powder gradually turned yellow during the several washings with water. To determine whether these washings significantly increase the proportion of CeO<sub>2</sub> of the material, we performed XRD measurements on the samples both before and after washing (data not shown). We did not observe any growth of the CeO<sub>2</sub> phase due to the washing. However, before the washing step, a potassium carbonate phase was detected, probably originating from the reaction of atmospheric CO<sub>2</sub> with the highly basic wet powder.

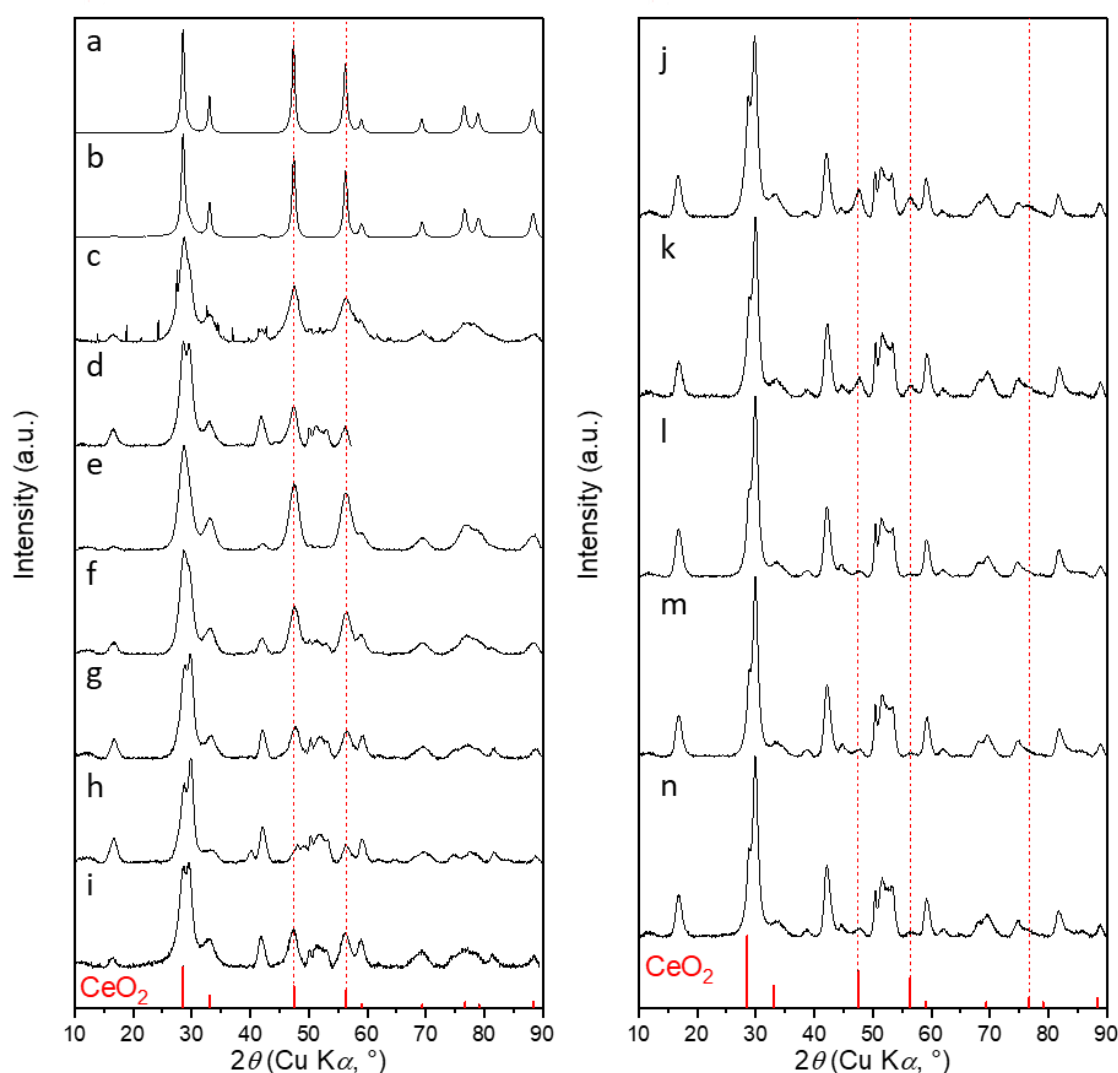


Figure 4. XRD measurements of cerium oxide/hydroxides powders for reactions performed at 100 °C, (a) with [NaOH] = 6 M in a 50 mL Nalgene vessel, (b) with [KOH] = 4.3 M in a Nalgene vessel (50 mL), (c) with [NaOH] = 6 M in a Borosilicate vessel (66 mL) and (d) with



[KOH] = 4.3 M in a Borosilicate vessel. Reactions performed in a Borosilicate vessel (e) with [KOH] = 0.43 M at 75 °C, (f) with [KOH] = 0.43 M at 100 °C, (g) with [KOH] = 4.3 M at 75 °C, (h) with [KOH] = 4.3 M at 100 °C (i) with [KOH] = 4.3 M at 100 °C in cryodegassed water. Reactions performed in Borosilicate vessel (66 mL) at 100 °C with [KOH] = 4.3 M, (j) 12 mL Borosilicate vessel filled, in air, (k) 36 mL Borosilicate vessel filled, in air, (l) 12 mL Borosilicate vessel filled, in N<sub>2</sub>, (m) 36 mL Borosilicate vessel filled, in N<sub>2</sub> and (n) 66 mL Borosilicate vessel fully filled with the solution. As a guide to the eye, the red dotted lines stress the peak positions of CeO<sub>2</sub> not superimposed with the other phases.

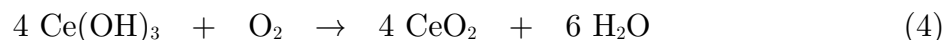
Wang *et al.* reported that a solution of Ce(NO<sub>3</sub>)<sub>3</sub> and NaOH under stirring turns yellow in 20 min if exposed to air while it stays grey-violet if maintained in a sealed vessel.<sup>2</sup> We therefore hypothesized the oxidation of all the Ce<sup>(III)</sup> from the cerium nitrate precursor occurs with the dissolved O<sub>2</sub> in water and from the oxygen present in the gas phase in equilibrium inside the closed vessel. The solubility of O<sub>2</sub> in pure water is  $s(\text{O}_2) = 0.28$  mmol/L at 20 °C and decreases if salinity increases. Considering the reaction is conducted in air in a reaction volume  $V_{\text{reaction}}$  in a closed vessel  $V_{\text{vessel}}$ , and with  $V_{\text{mol}} = 24$  L/mol the molar volume of a gas, the maximal available amount of dioxygen  $n(\text{O}_2)$  is given by Eq. (1), (2) and (3).

$$n(\text{O}_2) = n_{\text{dissolved}} + n_{\text{gas}} \quad (1)$$

$$n_{\text{dissolved}} = s(\text{O}_2) \cdot V_{\text{reaction}} \quad (2)$$

$$n_{\text{gas}} = 0.2 (V_{\text{vessel}} - V_{\text{reaction}})/V_{\text{mol}} \quad (3)$$

For instance, with  $V_{\text{reaction}} = 36$  mL and  $V_{\text{vessel}} = 66$  mL, we obtain  $n_{\text{dissolved}} = 0.010$  mmol and  $n_{\text{gas}} = 0.25$  mmol. For this reaction volume, 1.8 mmol of Ce(NO<sub>3</sub>)<sub>3</sub> were introduced. If we consider Eq. (4) for the oxidation of Ce<sup>(III)</sup> in Ce<sup>(IV)</sup>, 0.25 equiv. of O<sub>2</sub> are required per cerium atom, *i.e.* 0.45 mmol in the example case.



We first note the amount of initially dissolved O<sub>2</sub> would only oxidize 2 % of the cerium atoms. We can therefore neglect its contribution in a first approach, meaning the deoxygenation of water is probably not crucial to limit the formation of Ce<sup>(IV)</sup>. For comparison, we ran the reaction in water deoxygenated by N<sub>2</sub> bubbling during 4 h and in water degassed by 3 freeze-pump-thaw cycles. As more CeO<sub>2</sub> was obtained with cryodegassed water, we decided to only use deoxygenated water by N<sub>2</sub> bubbling (Figure 4h-i). Then, we note that if the entirety of the O<sub>2</sub> available in the gas phase is consumed for cerium oxidation, which seems unlikely, it would result in the oxidation of 55 % of the material (Table 1, entry 2).

	Liquid volume / Gas volume	Gas phase	n(O <sub>2</sub> )	n(Ce <sup>(III)</sup> )	Maximal theoretical Ce <sup>(IV)</sup> percentage
1	12 mL/44 mL	Air	0.45 mmol	0.6 mmol	100 %
2	36 mL/30 mL	Air	0.25 mmol	1.8 mmol	55 %
3	12 mL/44 mL	N <sub>2</sub>	0 mmol	0.6 mmol	0 %
4	36 mL/30 mL	N <sub>2</sub>	0 mmol	1.8 mmol	0 %
5	66 mL/0 mL	<i>n.a.</i>	0 mmol	3.3 mmol	0 %

Table 1. Theoretical oxidation ratio of the cerium atoms for a reaction conducted in a 66 mL air-tight Borosilicate vessel in the case of a reaction solution with [Ce] = 0.05 mol/L.

To investigate whether this explanation of the origin of the cerium oxidation is valid, we ran 5 experiments all originating from the same Ce(NO<sub>3</sub>)<sub>3</sub> + KOH solution batch. Three levels of filling of the Borosilicate vessel were chosen: 12 mL, 36 mL and 66 mL (*i.e.* the totality of the container) and for the non-entirely filled conditions, the gas phase was either air or N<sub>2</sub>. In all cases, the CeO<sub>2</sub> was present but was the minor phase (Figure 4j-n): when the gas phase was air (j-k), the proportion of CeO<sub>2</sub> was higher, and the higher the gas volume, the more intense the CeO<sub>2</sub> peaks. For reactions conducted with N<sub>2</sub> in the gas phase or with no gas phase (l-n), there is no significant difference between the diffractograms. We validated the fact a part of the oxidation of Ce<sup>(III)</sup> in Ce<sup>(IV)</sup> originates from the O<sub>2</sub> initially present in the gas phase in equilibrium with the solution, at least for reactions conducted in Borosilicate vessels. Not all the atmospheric O<sub>2</sub> is consumed as the CeO<sub>2</sub> stays at the state of traces. The residual presence of CeO<sub>2</sub>, even with theoretically no O<sub>2</sub> available, may be explained by either O<sub>2</sub> traces or by alternative oxidation pathways. Besides, CeO<sub>2-x</sub> is known to accommodate defects up to  $x = 0.5$ , which would correspond to Ce<sub>2</sub>O<sub>3</sub>, *i.e.* only Ce<sup>(III)</sup>. This analysis comforts a work from Qu *et al.* in 2016: conducting a similar synthesis of cerium oxide under different O<sub>2</sub> partial pressures (from 1 bar to 0 bar), they showed the percentage of Ce<sup>(III)</sup> in the final CeO<sub>2</sub> increases from 19.7 % to 25.4 %.<sup>17</sup>

In conclusion, we demonstrated we could produce both regular CeO<sub>2</sub> and the NP-CeO<sub>2</sub> precursor targeted for our catalysis study. For this latter material, an optimization allowed us to establish a reproducible protocol which led to almost no CeO<sub>2</sub> and quasi exclusively the targeted material.

## IV.2. Structural study of cerium hydroxide $\text{Ce}(\text{OH})_3$ aging

### IV.2.1 Structural characterization

By limiting the presence of  $\text{O}_2$  in the reaction medium and playing on several parameters, we successfully limited the proportion of  $\text{CeO}_2$  in the sample. For the rest of this section, the synthesis conditions for cerium trihydroxide are the following (Synthesis IV.2.).

**Synthesis IV.2. Cerium trihydroxide  $\text{Ce}(\text{OH})_3$ .** In a 66 mL Borosilicate vessel and under a flux of  $\text{N}_2$ , 780 mg of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (1.8 mmol, 1 equiv.) were dissolved in 6 mL of deoxygenated water by  $\text{N}_2$ -bubbling during 4 h to yield a colorless limpid solution. Meanwhile, 8.64 g of KOH (154 mmol, 4.3 M) were dissolved in 30 mL of deoxygenated water and the resulting solution was slowly added to the cerium nitrate solution. A yellow-brown precipitate appeared at the first drops, followed by a yellow gel and a grey gel and finally a violet suspension. The vessel was closed under  $\text{N}_2$  and let to react during 30 min at r.t. and was then put in a preheated oven at 100 °C for 20 h. After reaction, the solution was let to cool down naturally to r.t. A grey powder sedimented at the bottom of the vessel, the supernatant was colorless. The solution was centrifugated under air. The powder was washed 6 times with 30 mL of  $\text{H}_2\text{O}$  and once with 30 mL of EtOH without excessive shaking nor use of sonication during redispersion.<sup>1</sup> The obtained grey powder (326 mg, 95 % yield) was then dried under  $\text{N}_2$  and stored under argon.

**X-ray diffraction.** The obtained material from Synthesis IV.2. evolved over time if stored in air. From initially grey, the powder gradually turned yellow in a few days whereas it stayed grey if stored in Ar. In the fresh sample (synthesis less than 2 hours ago), cerium trihydroxide  $\text{Ce}(\text{OH})_3$  [PDF card N°00-055-0556] peaks account for most of the signal (Figure 5A). The diffraction pattern does not evolve significantly when the material is stored in Ar, even after one week (Figure 5B), but is modified if stored in air (Figure 5C-D). XRD measurements on the sample after several months in air do not display any further modification (data not shown). We will refer to fresh and aged  $\text{Ce}(\text{OH})_3$  for respectively the material stored in Ar immediately after synthesis and the one exposed to air for at least one week. All diffractograms presented in the previous section correspond to aged samples.

The presence of  $\text{CeO}_2$  cannot be excluded *a priori* on the fresh sample as all its diffraction peaks are beneath those of  $\text{Ce}(\text{OH})_3$ . However, in aged samples, peaks at 47° and 56° are revealed (stressed by red dotted lines). On one particular batch, no

<sup>1</sup> One batch was washed thoroughly with non-deoxygenated water with vigorous agitation in air and then dried under a flux of  $\text{N}_2$ . An XRD was recorded and nearly no  $\text{CeO}_2$  was detected (data not shown), the precautions concerning the washing step are therefore probably excessive but we chose to keep them.

signal at all is observed at  $47^\circ$  and  $56^\circ$  (Figure 6B): we concluded first that these two “non-observed” peaks correspond to  $\text{CeO}_2$  traces and not to a new phase and then that there is no production of  $\text{CeO}_2$  during aging. This aging phenomenon was observed on all our batches with the same final pattern, in particular the recognizable plateau between  $50^\circ$  and  $55^\circ$ . XRD measurement performed after 1 day in air displays both the  $\text{Ce}(\text{OH})_3$  phase and its “aged form” (Figure 5C): there are two distinct phases (stressed by blue arrows). In the final product, the phase which is not  $\text{CeO}_2$  looks like a shifted pattern of  $\text{Ce}(\text{OH})_3$  (Figure 6A-B). The shift occurring toward the high angles, it would correspond to a contraction of the crystal structure.

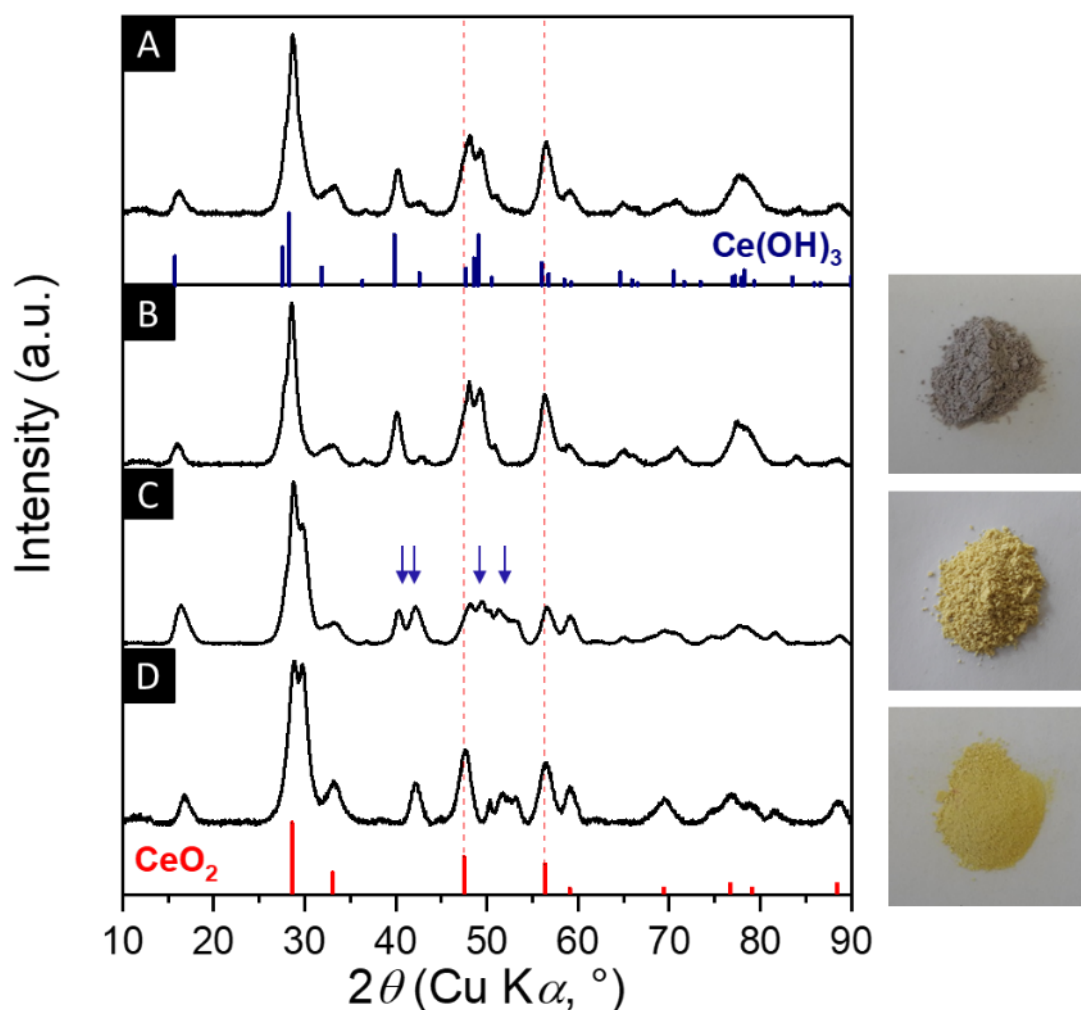


Figure 5. Left: XRD patterns of the aging of cerium trihydroxide from Synthesis IV.2. (A) Fresh sample, (B) after 4 days in Ar, (C) after 1 day in air, (D) after 4 days in air. Blue arrows stress the simultaneous presence of two crystallographic phases. Right: pictures of the corresponding samples. As a guide to the eye, the red dotted lines stress the peak positions of  $\text{CeO}_2$  not superimposed with the “aged  $\text{Ce}(\text{OH})_3$  phase”.

Three points should be stressed at this stage:

- (1) The XRD of our material termed “aged  $\text{Ce}(\text{OH})_3$ ” matches perfectly with the “non porous precursor with a mixed phase  $\text{Ce}(\text{OH})_3/\text{CeO}_2$ ” reported by Qu *et al.* (Figure 3) but there seems to be a discrepancy between the attribution they suggest (mix of  $\text{CeO}_2$  and  $\text{Ce}(\text{OH})_3$ ) and the diffractogram. There is no mention of aging or evolution of the precursor in their article.
- (2) Intriguingly, no phase could match the diffractogram of aged  $\text{Ce}(\text{OH})_3$  in the JCPDS database. The current section will therefore be devoted to its analysis.
- (3) To the best of our knowledge, there is no mention in the literature of an evolution of  $\text{Ce}(\text{OH})_3$  in a crystalline material different from  $\text{CeO}_2$ .<sup>5</sup> This point will be further discussed later.

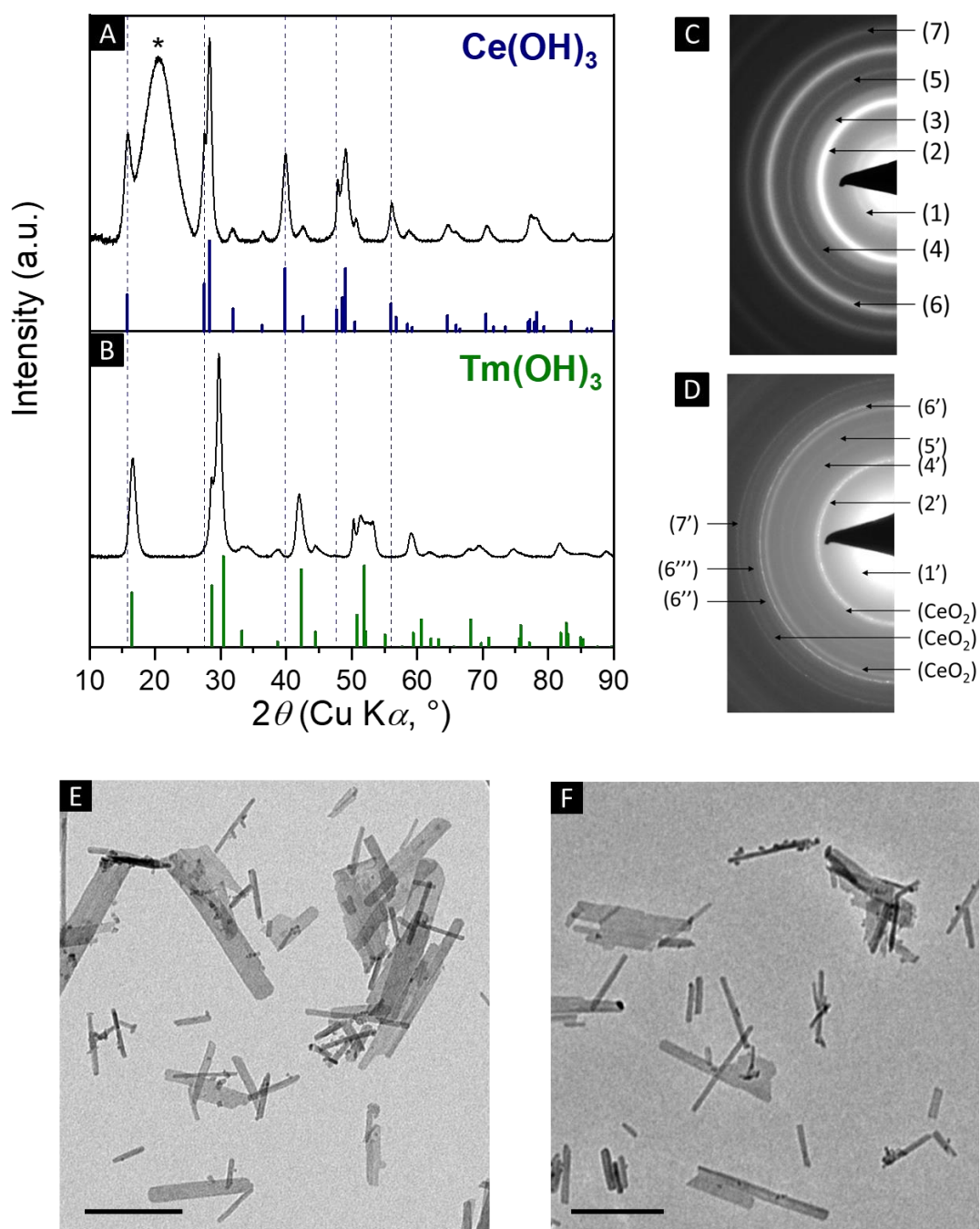


Figure 6. Aging phenomenon of  $\text{Ce(OH)}_3$ . XRD patterns of (A) the fresh  $\text{Ce(OH)}_3$  (the asterisk denotes the big hump due to the presence of a protection dome) and (B) the aged  $\text{Ce(OH)}_3$  (the comparison with  $\text{Tm(OH)}_3$  is discussed in section IV.3.2.). As a guide to the eye, blue dotted lines were plotted for a few peaks of  $\text{Ce(OH)}_3$ . (C-D) Corresponding electron diffraction patterns. TEM images of the sample (E) before aging and (F) after one week aging (scale bars represent 100 nm on both images).

**Electron microscopy.** Cerium trihydroxide from Synthesis IV.2. crystallized in polydisperse nanorods very similar to the ones obtained with  $\text{CeO}_2$  in Synthesis IV.1: the average length was 100 nm for a mean width of 10 nm (Figure 6E). We noticed the

presence of large plates which look like the sintering of several rods. Very few cubes were also produced. Upon aging in air, we did not observe any modification of the morphology of the nanoparticles (Figure 6F). When zooming on the aged sample, we nonetheless observed a beam damage of the material: black zones appeared and moved along the nanorods until stabilization after a few minutes (Figure 7A,B). This damage may be due to the reduction of the sample with electrons or, more probably, to the heat produced by the beam. The global morphology was preserved but numerous defects appeared, with characteristic size below 5 nm (Figure 7C). Such a behavior was not observed on the fresh  $\text{Ce}(\text{OH})_3$  nor on  $\text{CeO}_2$ .

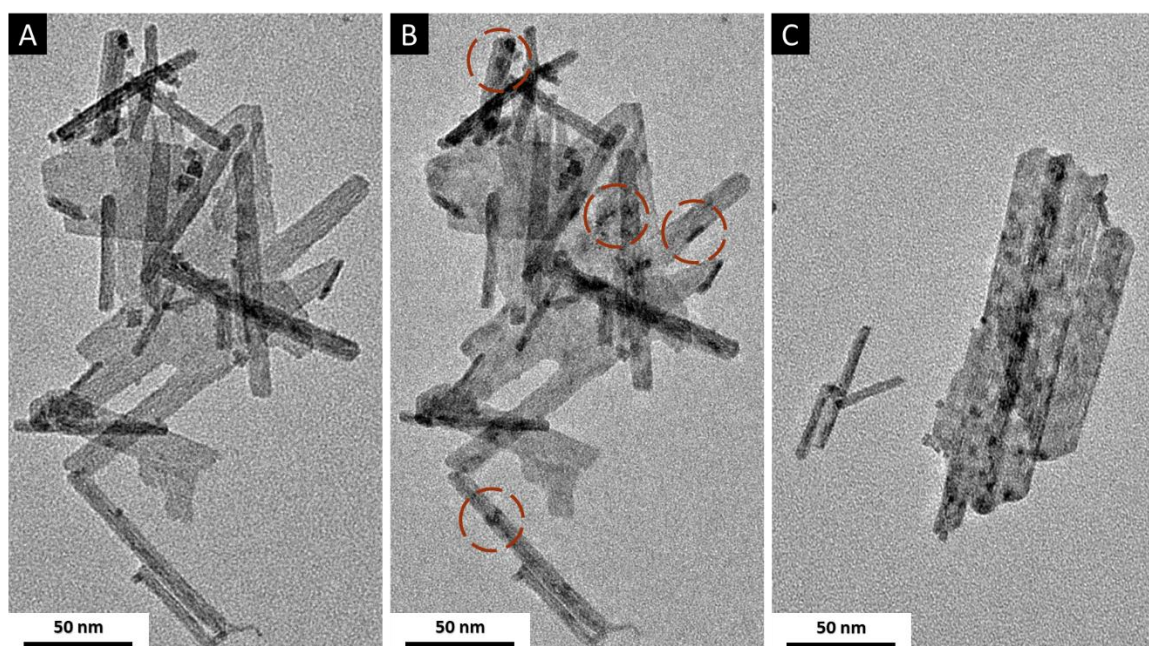


Figure 7. (A-C) TEM images of the electron beam damages to aged  $\text{Ce}(\text{OH})_3$  (A and B were taken a few second apart, red circles stress the beam damages).

**Electron diffraction.** As a second structural method to characterize distances, we performed SAED on fresh  $\text{Ce}(\text{OH})_3$  and aged  $\text{Ce}(\text{OH})_3$  (Figure 6C-D). We used the shifts between the diffraction distances measured on a  $\text{CeO}_2$  sample from a previous synthesis and the theoretical distances to estimate the error bar. For  $\text{CeO}_2$ , the measured distances were 3.22 Å, 2.78 Å, 1.98 Å and 1.69 Å and the theoretical ones are 3.12 Å, 2.71 Å, 1.91 Å and 1.63 Å for respectively the (111), (200), (220) and (311) planes (peaks at 29°, 33°, 47° and 56°, *cf.* Figure 1 for (hkl) attribution). The error bar for SAED is therefore *ca.* 0.1 Å. To facilitate the cross-interpretation of the data from XRD and electron diffraction, we reported together the distances obtained by electron diffraction and the distances estimated using XRD peaks (Table 2). For fresh  $\text{Ce}(\text{OH})_3$ , all diffraction rings could reasonably be attributed to a diffraction peak in XRD (Table

2, left and Figure 6A,C): we noted that all the measured distances by electron diffraction are slightly larger than the expected ones, as for the aforementioned  $\text{CeO}_2$  sample. However, we could not detect any ring that would correspond to the XRD peak at  $42.6^\circ$ , probably due to its low intensity. The selection rules for diffraction are different for X-rays and electrons and this may explain why intense peaks in XRD such as the one at  $39.8^\circ$  have a much lower relative intensity in electron diffraction (ring (5)). The sample of aged  $\text{Ce}(\text{OH})_3$  contained traces of  $\text{CeO}_2$ : we attributed three rings at  $3.12 \text{ \AA}$ ,  $1.97 \text{ \AA}$  and  $1.70 \text{ \AA}$ , slightly larger than the other ones, to this last phase (Table 2, right and Figure 6B,D). All the other rings could reasonably be attributed to XRD diffraction peaks and we suggest the rings 1, 2, 4, 5, 6 and 7 in fresh  $\text{Ce}(\text{OH})_3$  became respectively the rings 1', 2', 4', 5', {6', 6'', 6'''} and 7' in aged  $\text{Ce}(\text{OH})_3$ .

Fresh $\text{Ce}(\text{OH})_3$					Aged $\text{Ce}(\text{OH})_3$				
	Electron diffraction	X – ray diffraction		(hkl)		Electron diffraction	X – ray diffraction		
		$2\theta$	Distance				$2\theta$	Distance	
1	$5.65 \text{ \AA}$	$15.7^\circ$	$5.62 \text{ \AA}$	(100)	1'	$5.51 \text{ \AA}$	$16.6^\circ$	$5.36 \text{ \AA}$	
2	$3.21 \text{ \AA}$ (I)	$27.4 - 28.3^\circ$	$3.24 \text{ \AA} - 3.15 \text{ \AA}$	(110) – (101)	2'	$3.22 \text{ \AA}$ (I)	$28.6 - 29.7^\circ$	$3.12 \text{ \AA}$	
3	$2.82 \text{ \AA}$	$31.8^\circ$	$2.81 \text{ \AA}$	(200)					
4	$2.52 \text{ \AA}$	$36.4^\circ$	$2.47 \text{ \AA}$	(111)	4'	$2.45 \text{ \AA}$	$38.7^\circ$	$2.33 \text{ \AA}$	
5	$2.31 \text{ \AA}$	$39.8^\circ$	$2.26 \text{ \AA}$	(201)	5'	$2.20 \text{ \AA}$	$42.0^\circ$	$2.15 \text{ \AA}$	
	-	$42.6^\circ$	$2.12 \text{ \AA}$	(210)		-	$44.0^\circ$	$2.05 \text{ \AA}$	
6	$1.94 \text{ \AA}$ (I)	$47.7 - 50.6^\circ$	$1.90 \text{ \AA} - 1.80 \text{ \AA}$	(002) – (300) – (211)	6'	$1.88 \text{ \AA}$ (I)	$50.3^\circ$	$1.81 \text{ \AA}$	
					6''	$1.84 \text{ \AA}$	$51.3^\circ$	$1.78 \text{ \AA}$	
					6'''	$1.79 \text{ \AA}$	$53.3^\circ$	$1.72 \text{ \AA}$	
7	$1.68 \text{ \AA}$	$55.9 - 56.7^\circ$	$1.64 \text{ \AA} - 1.62 \text{ \AA}$	(112) – (220)	7'	$1.62 \text{ \AA}$	$59.1^\circ$	$1.56 \text{ \AA}$	

Table 2. Diffraction distances obtained by electron diffraction (I denotes the strongest rings) and the estimated corresponding peak in PXRD (angle and distance) for a fresh  $\text{Ce}(\text{OH})_3$  sample and an aged one.

**Infrared spectroscopy.** Attenuated Total Reflectance-Fourier Transform InfraRed (ATR-FTIR) analysis was performed on fresh and aged  $\text{Ce}(\text{OH})_3$  (Figure 8A). In fresh  $\text{Ce}(\text{OH})_3$ , an O–H stretching band of the hydroxide is detected at  $3606 \text{ cm}^{-1}$  (Figure 8B). This band splits in two at  $3597 \text{ cm}^{-1}$  and  $3586 \text{ cm}^{-1}$  and loses intensity upon aging. The splitting may be the mark of a loss of symmetry in the crystal structure or of the presence of different sites. Another Ce–OH stretching band, specific of the hydroxide, is present at  $650 \text{ cm}^{-1}$  (Figure 8C).<sup>18</sup> The band is shifted and splits in two



at  $741\text{ cm}^{-1}$  and  $713\text{ cm}^{-1}$  upon aging. As no IR spectrum could be found in literature for  $\text{Ce}(\text{OH})_3$ , this attribution was done on the basis of that of  $\text{La}(\text{OH})_3$  IR spectrum, expected to be very similar: bands at  $3610\text{ cm}^{-1}$ ,  $645\text{ cm}^{-1}$  and  $510\text{ cm}^{-1}$  were respectively attributed to O–H, La–OH and La–O vibrations.<sup>19</sup> The broad band at  $3350\text{ cm}^{-1}$  and the thin one at  $1640\text{ cm}^{-1}$  are attributed to respectively O–H stretching and O–H scissor bending of adsorbed water molecules. We suggest the bands between  $1600\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$  are attributed to C=O stretching and those at  $1097\text{ cm}^{-1}$  and  $1047\text{ cm}^{-1}$ , on fresh  $\text{Ce}(\text{OH})_3$ , to C–O stretching of surface carbonate  $\text{CO}_3^{2-}$  species as carbon dioxide from atmosphere is known for being easily adsorbed on metal oxides and hydroxides.<sup>20,21</sup> We could not attribute the intense and broad band at  $1000\text{ cm}^{-1}$  observed in both samples and whose origin is still under investigation. We excluded the nitrate ions at the surface of ceria as more intense peaks would have also been observed at *ca.*  $1200\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ .<sup>22</sup> The presence of sharp peaks in the characteristic hydroxide region confirms that bulk hydroxyl groups are still present in aged  $\text{Ce}(\text{OH})_3$  and not only surface hydroxyls.

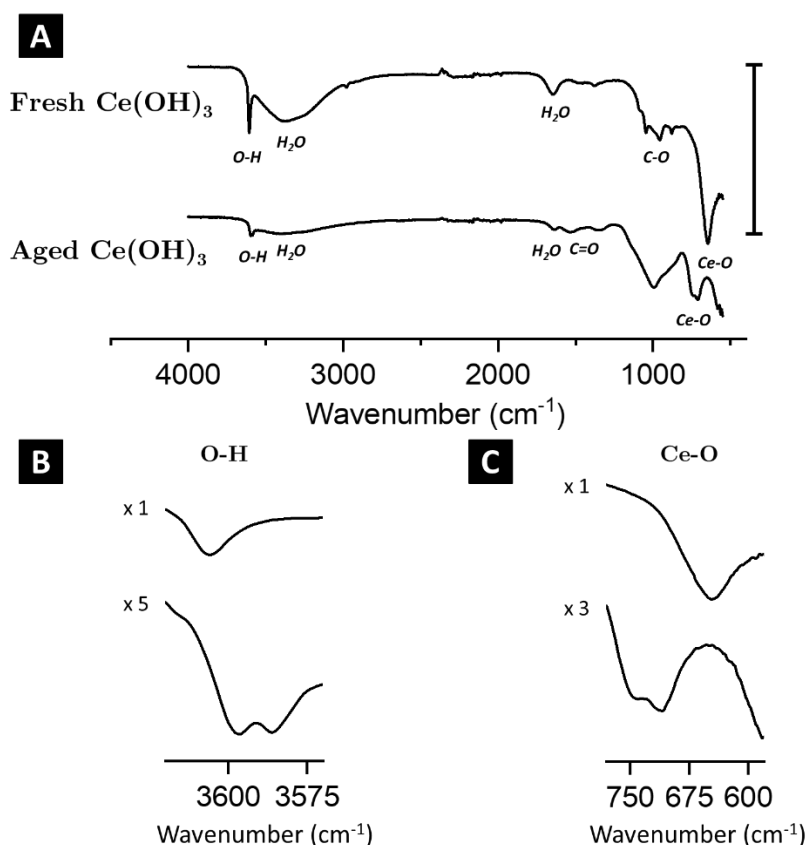


Figure 8. (A) ATR-FTIR spectra of fresh and aged  $\text{Ce}(\text{OH})_3$ . Zooms on the (B) O–H and (C) Ce–O regions (top: fresh  $\text{Ce}(\text{OH})_3$ , bottom: aged  $\text{Ce}(\text{OH})_3$ ). The vertical bar denotes a 50 % absorption.

**X-Ray Photoelectron Spectroscopy.** The oxidation state of surface cerium and oxygen atoms in fresh  $\text{Ce}(\text{OH})_3$ , aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  nanorods were studied by means of XPS and results are displayed on Figure 9.  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was used as a  $\text{Ce}^{\text{(III)}}$  reference as this salt is stable under air and commercial  $\text{CeO}_2$  was used as a cerium dioxide reference. The peak fitting procedure is developed in the experimental section and was based on already published works.<sup>10,23-27</sup> The Ce 3d high-resolution X-ray photoelectron spectra are typically composed of five doublets, two characteristic of  $\text{Ce}^{\text{(III)}}$  (in pink and violet) and three of  $\text{Ce}^{\text{(IV)}}$  species (in yellow, orange and red). The multiple peaks arise from the different occupancies of the Ce 4f level in the final state. For  $\text{Ce}^{\text{(IV)}}$ , the peaks V''' and U''' (orange component) result from the  $\text{Ce } 3d^9 \text{ O } 2p^6 \text{ Ce } 4f^0$  final state, the peaks U, V, U'' and V'' (red and yellow components) from a mixture of the  $\text{Ce } 3d^9 \text{ O } 2p^5 \text{ Ce } 4f^1$  and  $\text{Ce } 3d^9 \text{ O } 2p^4 \text{ Ce } 4f^2$  final states. For  $\text{Ce}^{\text{(III)}}$ , the four peaks  $U_0$ ,  $V_0$ ,  $U'$  and  $V'$  (pink and violet components) result from a mixture of the  $\text{Ce } 3d^9 \text{ O } 2p^6 \text{ Ce } 4f^1$  and  $\text{Ce } 3d^9 \text{ O } 2p^5 \text{ Ce } 4f^2$  final states. We chose a linear background even though the Shirley algorithm is usually chosen for heavy atoms because the Shirley background is not well defined on zones with multiple peaks with no absolute maxima, which is our case. The spin-orbit coupling values for the five doublets were estimated on the reference spectra and were in agreement with literature: 18.35 eV for  $\text{Ce}^{\text{(III)}}$  components and 18.5 eV for  $\text{Ce}^{\text{(IV)}}$  ones. The peak positions were constrained on a range of approximately 0.8 eV around the expected position. The integration of the peak areas allows an estimation of the  $\text{Ce}^{\text{(III)}}$  and  $\text{Ce}^{\text{(IV)}}$  fractions, the error bar for this procedure being estimated at *ca.* 10 %.<sup>10</sup>

According to our fit, cerium nitrate salt  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is composed of 91 %  $\text{Ce}^{\text{(III)}}$  which is compatible with a fully reduced state if we consider an error bar of *ca.* 10 %. Fresh  $\text{Ce}(\text{OH})_3$  is composed of 77 % of  $\text{Ce}^{\text{(III)}}$ , whereas aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  nanorods display a lower  $\text{Ce}^{\text{(III)}}$  fraction (respectively 28 % and 26 %), similar to commercial  $\text{CeO}_2$  (29 %). The surface  $\text{Ce}^{\text{(IV)}}$  species in the fresh  $\text{Ce}(\text{OH})_3$  are either inherent of the synthesis or correspond to a slow surface oxidation during the washing steps of the material or during the sample preparation for XPS. The difference with aged  $\text{Ce}(\text{OH})_3$  is however large enough to conclude that aging in air is the dominant process leading to  $\text{Ce}^{\text{(IV)}}$ .

As largely developed in the literature, cerium dioxide presents both  $\text{Ce}^{\text{(III)}}$  and  $\text{Ce}^{\text{(IV)}}$  atoms at the surface, with a  $\text{Ce}^{\text{(III)}}$  fraction typically up to 30 %. This  $\text{Ce}^{\text{(III)}}$  is however mostly present at the surface: by changing the incident angle of the beam in XPS, Freund *et al.* proved the cerium oxide they studied comported 17 % of  $\text{Ce}^{\text{(III)}}$  within the topmost 1.7 nm but only 6 % within the topmost 3.5 nm.<sup>10</sup>

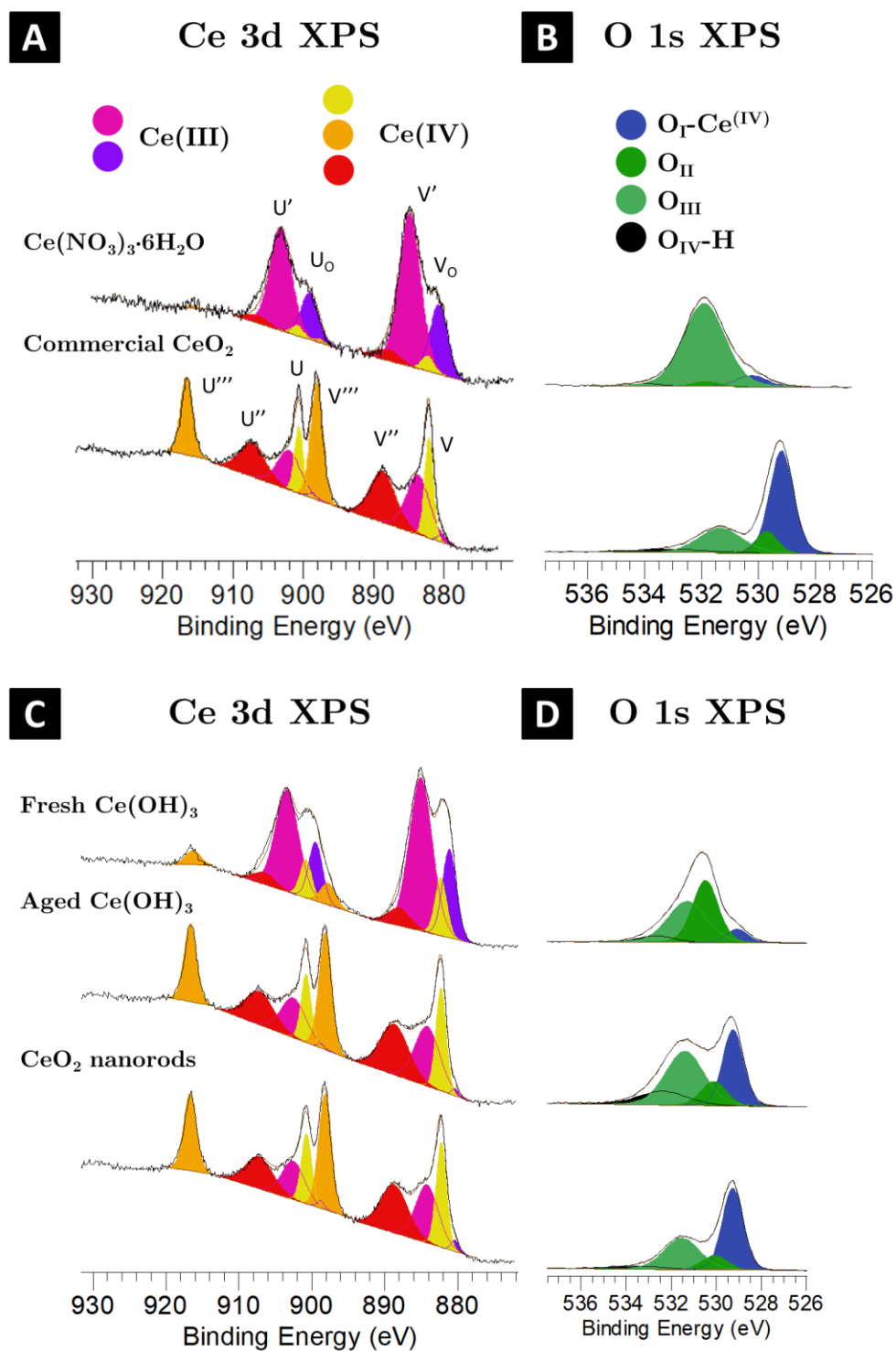


Figure 9. XPS spectra: (A) Ce 3d region and (B) O 1s region of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and commercial cerium oxide with deconvolution of  $\text{Ce}^{\text{(III)}}$  and  $\text{Ce}^{\text{(IV)}}$  peaks and of different oxygen peaks. (C) Ce 3d region and (D) O 1s region of fresh  $\text{Ce}(\text{OH})_3$ , aged  $\text{Ce}(\text{OH})_3$  (Synthesis IV.2.) and  $\text{CeO}_2$  nanorods (Synthesis IV.1.)

XPS spectra of O 1s core level are displayed in Figure 9B and D for all samples. The oxygen signal for cerium nitrate essentially originates from water molecules and nitrate ions. The oxygen spectra of the other samples can be deconvoluted in four components: a blue component denoted O<sub>I</sub> at a binding energy of *ca.* 529.2 eV, attributed to lattice oxygens linked to Ce<sup>(IV)</sup> atoms, two green components, denoted O<sub>II</sub> and O<sub>III</sub>, at *ca.* 530.1 eV and 531.4 eV and a broad black component O<sub>IV</sub>, merely not visible in these spectra, at *ca.* 532.5 eV, generally ascribed to surface hydroxyl OH or adsorbed water H<sub>2</sub>O. The deconvolution with only three components (O<sub>I</sub>, O<sub>II</sub> and O<sub>IV</sub>) which may be found in different works gave here a fit of low quality.<sup>10</sup> There is consensus in literature on the attribution of O<sub>I</sub> to lattice oxygens linked to oxidized cerium atoms. There is however no consensus on the attribution of O<sub>II</sub> and O<sub>III</sub>. Among the different possibilities, they are either associated to oxygens linked to Ce<sup>(III)</sup> atoms or to “adsorbed” oxygens, *i.e.* surface hydroxyls or carbonates.<sup>28</sup> The energy split of 2.2 eV between O<sub>I</sub> and O<sub>III</sub> is in line with literature: Palmqvist *et al.* reported an energy split of 1.9 eV between the contributions of what they reported as O-Ce<sup>(III)</sup> and O-Ce<sup>(IV)</sup> while Pfau *et al.* reported 2.4 eV.<sup>29,30</sup> During the reduction of CeO<sub>2</sub> films, Reichling *et al.* modelled the O 1s with four peaks just as us and attributed the two ones of medium energies (O<sub>II</sub> and O<sub>III</sub>) to oxygens linked to Ce<sup>(III)</sup>.<sup>26</sup> In this context, the presence of Ce<sup>(III)</sup> was explained by surface defects consisting in oxygen vacancies. Considering the difficulty in ascribing accurately chemical species to components O<sub>II</sub> and O<sub>III</sub>, our analysis below only relies on the area evolution of the O<sub>I</sub> component associated to O-Ce<sup>(IV)</sup> and is qualitative.

Similar spectra are obtained for commercial CeO<sub>2</sub> and CeO<sub>2</sub> nanorods from Synthesis IV.1. with a relatively important and sharp O<sub>I</sub> peak, in agreement with the Ce 3d spectra (high ratio of Ce<sup>(IV)</sup>). Aged Ce(OH)<sub>3</sub> also displays a non negligible O<sub>I</sub> peak but a much higher contribution of O<sub>III</sub>, probably accounting for a more defective structure. As to fresh Ce(OH)<sub>3</sub>, the main contribution is clearly O<sub>III</sub> and the O<sub>I</sub> peak is small, thereby denoting the limited number of Ce<sup>(IV)</sup> atoms.

**X-ray Absorption Spectroscopy (XAS).** XAS spectroscopy at the Ce L<sub>III</sub>-edge was used to characterize the oxidation degree of the cerium atoms in the core of the material and not only on surface. The experiments were performed by Benedikt Lassalle-Kaiser, beamline scientist on the LUCIA beamline at the SOLEIL synchrotron. Details on the protocols are given in Appendix I (ES.9). Figure 10 displays the XAS spectra of pellets of commercial Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, commercial CeO<sub>2</sub>, CeO<sub>2</sub> from Synthesis IV.1. and aged Ce(OH)<sub>3</sub> from Synthesis IV.2. The positions of the edges indicate aged Ce(OH)<sub>3</sub> (5725.8 eV) possesses an average oxidation degree for Ce identical to that of commercial CeO<sub>2</sub> (5725 eV) and CeO<sub>2</sub> from Synthesis IV.1. (5725.4 eV), *i.e.* mostly Ce<sup>(IV)</sup>. Cerium nitrate, an air-stable Ce<sup>(III)</sup> salt, has an edge-shift situated at lower energy (5723.3 eV), in coherence with a more reduced state.

Although the XRD patterns of  $\text{CeO}_2$  from Synthesis IV.1. and aged  $\text{Ce}(\text{OH})_3$  are different (Figure 1 and Figure 6B), their XAS spectra are very similar.

Schuman *et al.* reported a complete Ce L<sub>III</sub>-edge investigation of cerium oxides.<sup>31</sup> They decomposed the signal in four peaks (Figure 10, inset): two main ones, A and B, at high energies assigned to a mixture of final configurations  $4f^05d^1$  and  $4f^15d^1$ , a low energy shoulder C originating from the splitting of the 5d orbitals in the cubic crystal field of  $\text{O}^{2-}$  and a pre-edge peak D resulting from a forbidden  $2p_{3/2} \rightarrow 4f$  transition. They assigned the signal at 5723 eV to  $\text{Ce}^{(\text{III})}$  atoms and that at 5725 eV to  $\text{Ce}^{(\text{IV})}$  atoms. The doublet feature at 5741.5 eV in commercial  $\text{CeO}_2$  sample spectrum could not be explained and was not present in the spectra displayed by Schuman *et al.* Otherwise, our spectra are coherent with their data. We interpreted the similarity between  $\text{CeO}_2$  and aged  $\text{Ce}(\text{OH})_3$  spectra as similar environment and oxidation degree for Ce in these materials and concluded the aging of  $\text{Ce}(\text{OH})_3$  in air leads to its total oxidation.

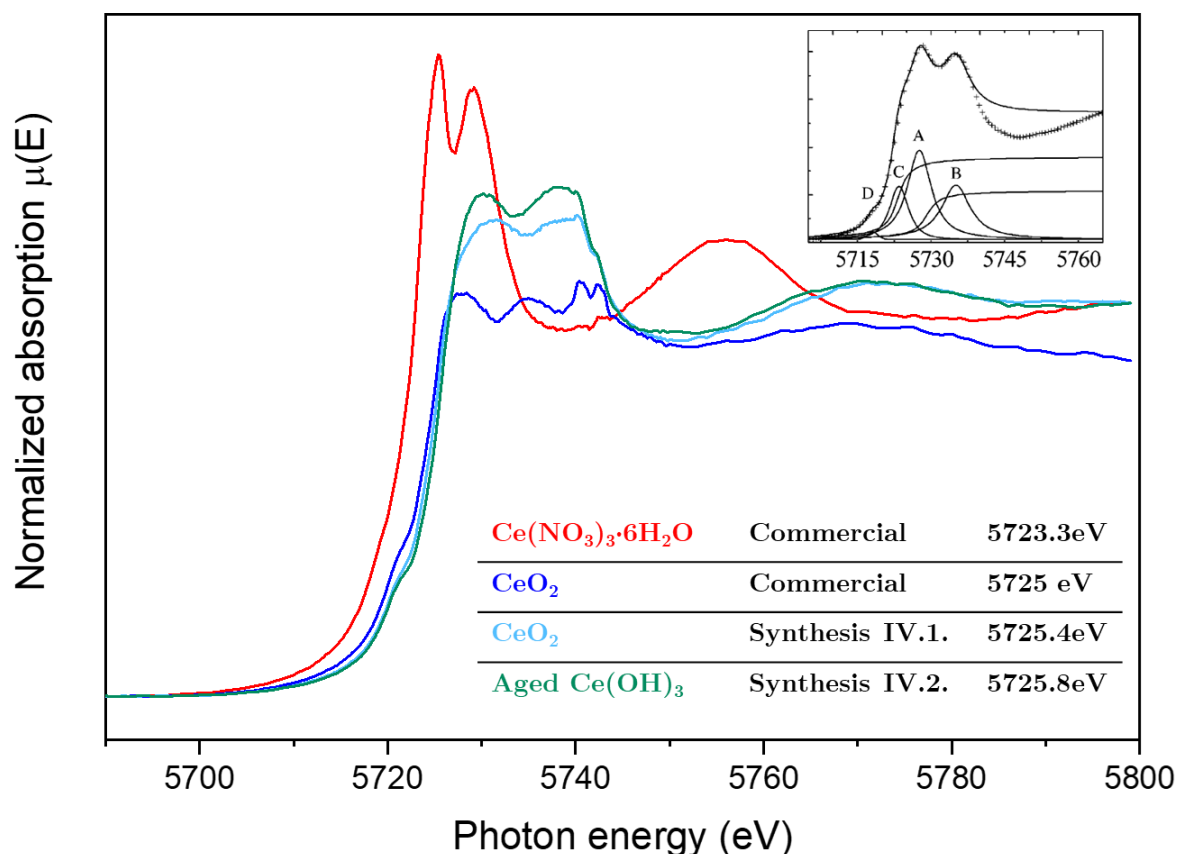


Figure 10. Ce L<sub>III</sub>-edge XAS spectra at 5725 eV of commercial  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , commercial  $\text{CeO}_2$ ,  $\text{CeO}_2$  from Synthesis IV.1. and aged  $\text{Ce}(\text{OH})_3$  from Synthesis IV.2., measured as pellets in graphite. Edge values are indicated for each. Inset is a reproduction of a typical spectrum of  $\text{CeO}_2$  from reference [31].

## IV.2.2 Structural comparison with lanthanide hydroxides

The XRD patterns obtained with fresh and aged  $\text{Ce}(\text{OH})_3$  were compared with the ones of other lanthanide hydroxides  $\text{Ln}(\text{OH})_3$ , studied by Milligan *et al.* in the 1970s.<sup>32-35</sup> Lanthanide hydroxides are generally synthesized under similar conditions than the ones described in Synthesis IV.2. of  $\text{Ce}(\text{OH})_3$ , *i.e.* by addition of a base ( $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$  or  $\text{KOH}$ ) in an aqueous solution of  $\text{Ln}(\text{NO}_3)_3$ . When heated, these hydroxides usually form the metal oxyhydroxide  $\text{LnOOH}$  at *ca.* 300-350 °C and then the metal sesquioxide  $\text{Ln}_2\text{O}_3$  at *ca.* 450-500 °C.<sup>36</sup> Cerium is an exception as there is no mention of a metal oxyhydroxide  $\text{CeOOH}$  and as the most stable oxide is  $\text{CeO}_2$  and not  $\text{Ce}_2\text{O}_3$ . The exception of cerium may be explained by the high stability of  $\text{Ce}^{(\text{IV})}$  in comparison with other  $\text{Ln}^{(\text{IV})}$  and the capacity of  $\text{CeO}_2$  to accommodate a large number of oxygen deficiencies. To the exception of cubic  $\text{Lu}(\text{OH})_3$ , all  $\text{Ln}(\text{OH})_3$  crystallize in a hexagonal structure ( $\text{P6}_3/\text{m}$ , space group N°176) where the lanthanide cation  $\text{Ln}^{(\text{III})}$  is at the center of a triaugmented trigonal prism whose 9 vertexes are occupied by oxygen atoms. The triaugmented trigonal prism is one of the two typical  $\text{AX}_9$  VSEPR structures: it consists in a trigonal prism composed of two equilateral triangles and three equatorial faces onto which were attached rectangular base pyramids (Figure 11A). There are therefore 6 equivalent positions  $\text{P}_\text{A}$  corresponding to the vertexes of the initial trigonal prism (apical position) and 3 equivalent ones  $\text{P}_\text{B}$  corresponding to the tops of the three pyramids (equatorial position). In this crystallographic structure, the  $c$ -axis of the  $6_3$ -screw rotation is the generatrix of the trigonal prism and the mirror  $m$  is the plane containing the central cation and the three positions  $\text{P}_\text{B}$ .

$\text{CeO}_2$  adopts a different structure, the fluorite face-centered one, in which the cerium cations are linked to 8 oxygens  $\text{O}^{2-}$  forming the corners of a cube. The oxygens are in tetrahedral environment. All Ce–O bonds are equivalent.

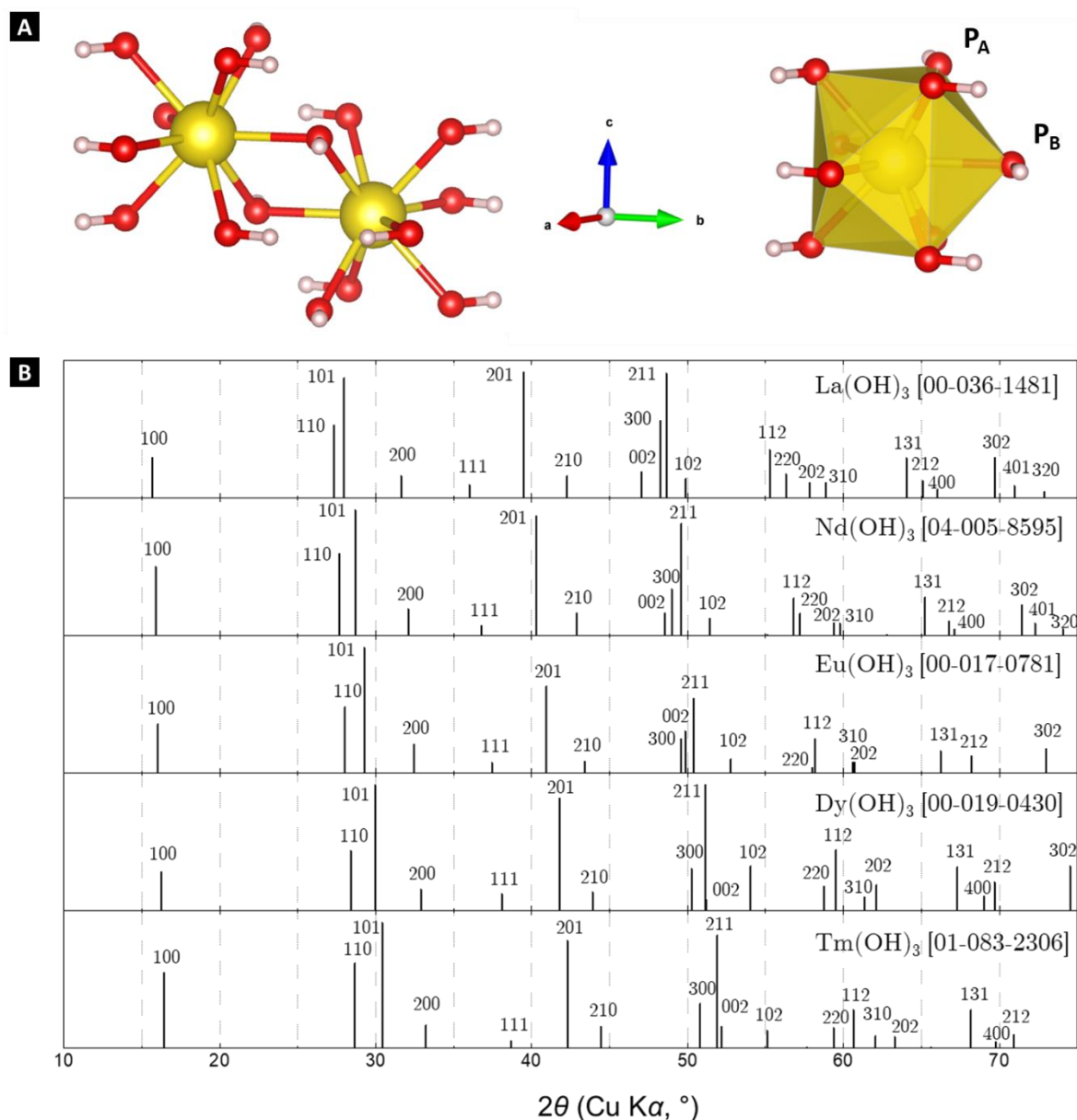


Figure 11. (A) Local environment of Ln atoms in lanthanide trihydroxides (yellow = Ln, red = O, white = H). Yellow polyhedron delineates the triaugmented trigonal prism. Positions P<sub>A</sub> and P<sub>B</sub> are respectively the apical and the equatorial positions. Pictures created with VESTA.<sup>37</sup> (B) XRD patterns of Ln(OH)<sub>3</sub> with hkl attributions, from top to bottom: La(OH)<sub>3</sub>, Nd(OH)<sub>3</sub>, Eu(OH)<sub>3</sub>, Dy(OH)<sub>3</sub> and Tm(OH)<sub>3</sub>.

We reported in Table 3 the distances M–O<sub>apical</sub> and M–O<sub>equatorial</sub> as well as their ratio for all the lanthanide trihydroxides. We notice a decrease of both M–O<sub>apical</sub> and M–O<sub>equatorial</sub> from respectively 2.588 Å and 2.551 Å for La to 2.371 Å and 2.430 Å for Yb. The distance ratio  $d(\text{M-O}_{\text{apical}})/d(\text{M-O}_{\text{equatorial}})$  also decreased from 1.014 to 0.976. Through the lanthanide series, there are therefore both a contraction of the distances (of 8.4% for M–O<sub>apical</sub> and 4.8% for M–O<sub>equatorial</sub>) and a deformation of the structure (distance ratio from 1.014 to 0.976). As to XRD, this structural evolution results in a

shift of the peaks toward the high angles (contraction of the crystal lattice) but not of the same amount for all peaks. Consequently, the global aspect of the diffractogram changes from La to Yb with peaks which swap their respective positions (Figure 11B). This is notably the case for  $\{(002), (300), (211)\}$  diffraction peaks *ca.*  $50^\circ$  and  $\{(112), (220), (202), (310)\}$  diffraction peaks *ca.*  $62^\circ$ . This evolution is related to the “lanthanide contraction” *i.e.* the ionic radius of  $\text{Ln}^{3+}$  which decreases from 121.6 ppm for  $\text{La}^{3+}$  to 104.2 ppm for  $\text{Yb}^{3+}$  when in the coordination IX (Table 3).

Structure	M–O bond length (Å)		Distance ratio	Ionic radius of $\text{Ln}^{3+}$ (pm)
	O in $P_A$ (apical)	O in $P_B$ (equatorial)		
$\text{La}(\text{OH})_3$	2.588	2.551	1.014	121.6
$\text{Ce}(\text{OH})_3$	2.567	2.529	1.015	119.6
$\text{Pr}(\text{OH})_3$	2.538	2.516	1.009	117.9
$\text{Nd}(\text{OH})_3$	2.522	2.492	1.012	116.3
$\text{Sm}(\text{OH})_3$	2.487	2.478	1.004	113.2
$\text{Eu}(\text{OH})_3$	2.473	2.466	1.003	112
$\text{Gd}(\text{OH})_3$	2.462	2.465	0.999	110.7
$\text{Tb}(\text{OH})_3$	2.444	2.458	0.994	109.5
$\text{Dy}(\text{OH})_3$	2.429	2.452	0.991	108.3
$\text{Ho}(\text{OH})_3$	2.416	2.444	0.989	107.2
$\text{Er}(\text{OH})_3$	2.403	2.439	0.985	106.2
$\text{Tm}(\text{OH})_3$	2.396	2.429	0.986	105.2
$\text{Yb}(\text{OH})_3$	2.371	2.430	0.976	104.2

Table 3. Crystallographic characteristics of some lanthanide trihydroxides: M–O distances for oxygen in apical and equatorial positions and their ratio  $d(\text{M}-\text{O}_{\text{apical}})/d(\text{M}-\text{O}_{\text{equatorial}})$ . Data are reproduced from references.<sup>32–35</sup> Ionic radii are those given by Shannon for coordination IX.<sup>38</sup>

The final state of  $\text{Ce}(\text{OH})_3$  exposed to air matches relatively well with hexagonal  $\text{Ln}(\text{OH})_3$  for metals of the end of the lanthanide series such as  $\text{Tm}(\text{OH})_3$  (Figure 6B). Our intermediate conclusion is therefore that  $\text{Ce}(\text{OH})_3$  evolves in a structurally close structure with an ionic radius of the lanthanide of *ca.* 105.2 pm, to be compared to 119.6 pm for  $\text{Ce}^{\text{III}}$ . A natural reasoning would be that the central ion is  $\text{Ce}^{\text{IV}}$ , resulting from the oxidation of  $\text{Ce}^{\text{III}}$  in air, in agreement with the XPS and XAS data and with literature.<sup>11</sup> No ionic radius is reported for  $\text{Ce}^{\text{IV}}$  in coordination IX but values for coordination VIII and X are respectively 97 and 107 pm which would be coherent with the expected value of 105.2 pm.<sup>38</sup>



### IV.2.3 Phase proposal

If the Ce<sup>(III)</sup> atoms of fresh Ce(OH)<sub>3</sub> did actually oxidize in Ce<sup>(IV)</sup> upon aging while conserving a similar crystallographic structure (P6<sub>3</sub>/m, coordination IX), the charge neutrality would not be respected in “Ce<sup>(IV)</sup>(OH)<sub>3</sub><sup>+</sup>”. Indeed, cerium presents this particularity that the only crystalline reported hydroxide is not at the same degree of oxidation that the cerium atoms in the most common oxide, CeO<sub>2</sub>. In order to respect the charge neutrality of the material, rearrangements have to operate, they can consist in:

- (1) Defects of Ce<sup>(IV)</sup> atoms,
- (2) Abstraction of H<sup>+</sup> from the hydroxide,
- (3) Additional interstitial anions such as O<sup>2-</sup> or HO<sup>-</sup>

In case (1), Ce<sub>0.75</sub>(OH)<sub>3</sub>, a lower occupancy state of the Ce positions would result in different peak intensities but not in different peak positions compared to a hypothetical hexagonal “Ce(OH)<sub>3</sub><sup>+</sup>” phase. Case (2) would correspond to a cerium oxyhydroxide CeO(OH)<sub>2</sub>. Due to the small ionic radii difference between HO<sup>-</sup> and O<sup>2-</sup> (respectively 134 pm and 138 pm) and to the low contribution of H in the XRD diffraction, moderate variations are expected from a hypothetical “Ce(OH)<sub>3</sub><sup>+</sup>” phase. Finally, case (3) would formally correspond to Ce(OH)<sub>4</sub> or CeO<sub>0.5</sub>(OH)<sub>3</sub> with potentially larger structural modifications. Considering the phase modification occurs even in presence of negligible water quantities, which would be the source of HO<sup>-</sup>, we favor the hypotheses (2) and (3) which only necessitate O<sub>2</sub>.

Three distinct relevant materials “oxide/hydroxide of cerium” are reported in the scientific community:

- (1) Cerium(III) trihydroxide, Ce(OH)<sub>3</sub>, [N° CAS 15785-09-8], an air sensitive grey solid.
- (2) Cerium(IV) dioxide (also termed ceric oxide or ceria), CeO<sub>2</sub>, [N° CAS 1306-38-3], a light yellow solid.
- (3) Cerium(IV) tetrahydroxide (also termed hydrous cerium oxide), Ce(OH)<sub>4</sub>, [N° CAS 12014-56-1], a bright yellow solid.

The name of this last material (3) presents ambiguities as researchers and manufacturers mention it either as a hydroxide Ce(OH)<sub>4</sub> or as a hydrous cerium oxide CeO<sub>2</sub> · 2H<sub>2</sub>O, of same elemental composition. A work led by Balasubramanian *et al.* showed that this material has a local structure comparable with CeO<sub>2</sub> (similar XRD patterns and EXAFS oscillations at the Ce L<sub>III</sub>-edge) but is disordered at long ranges, typically distances > 4 Å.<sup>39</sup> This disorder results in an XRD pattern close to CeO<sub>2</sub> but with broader peaks. As there is no sharp OH signal in Raman spectroscopy, typical of true hydroxides,<sup>40</sup> the authors suggested the term cerium tetrahydroxide Ce(OH)<sub>4</sub> is not adequate, and proposed “disordered hydrous cerium oxide” whose formula would

be  $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ . Hydrous metal oxides correspond to poorly crystalline or amorphous materials containing hydration water molecules and whose elemental composition is not precisely known: they are generally formed by sol-gel chemistry and may be calcined to form crystalline metal oxides. There is no entry in the JCPDS X-ray diffraction database for  $\text{Ce}(\text{OH})_4$  and most of the literature works mentioning this phase do not report any XRD measurements or structural characterization: either the authors indicate the material was used as received or it originated from the oxidation of  $\text{Ce}(\text{OH})_3$  in air.<sup>2,5,11,41</sup> The only occurrences of X-ray diffractograms of  $\text{Ce}(\text{OH})_4$  correspond to broad  $\text{CeO}_2$  and the material we bought from Strem Chemicals displayed this feature too (XRD in Figure 12C).<sup>39,42-44</sup> As no crystalline structure exists for  $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  other than that of  $\text{CeO}_2$ , we will prefer the writing  $\text{CeO}_2 \cdot x\text{H}_2\text{O}$  (with  $x$  close to 2) rather than  $\text{Ce}(\text{OH})_4$ .<sup>45,46</sup> Furthermore, the elemental composition cannot be formally established and the writing  $\text{CeO}_2 \cdot x\text{H}_2\text{O}$  gives flexibility as to the hydration water molecule number, contrarily to  $\text{Ce}(\text{OH})_4$ .

The material we synthesized is clearly different from what is termed cerium tetrahydroxide  $\text{Ce}(\text{OH})_4$ , in the literature, based on the XRD pattern. The modifications of the XRD and of the IR spectra between fresh and aged  $\text{Ce}(\text{OH})_3$  attest of atoms movements in the crystal structure. We could not decide whether the material we termed “aged  $\text{Ce}(\text{OH})_3$ ” is a non-reported cerium oxide/hydroxide phase or a metastable state along the transformation of  $\text{Ce}(\text{OH})_3$  in  $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ . To elucidate its crystallographic structure, a Rietveld refinement on the diffractograms of the fresh and aged samples is ongoing.

We already stressed that, to the best of our knowledge, all articles mentioning the synthesis and the aging of  $\text{Ce}(\text{OH})_3$  report a  $\text{CeO}_2$  or  $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$  final phase with a fluorite-like structure. For instance, Golberg *et al.* synthesized  $\text{Ce}(\text{OH})_3$  nanotubes by hydrothermal treatment of  $\text{CeCl}_3$  with a 12 M NaOH solution in an autoclave between 100 °C and 150 °C.<sup>5</sup> The obtained tubes, of several hundreds of nanometers in length were exposed to air for several days under ambient conditions and, to the contrary of our results, the  $\text{Ce}(\text{OH})_3$  phase directly evolved toward a cubic phase  $\text{CeO}_2$  with broad peaks. The authors attributed the broadness of the peaks to a certain level of disorder associated with the presence of water molecules and called their material “ $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ ”, in agreement with Balasubramanian’s work. The material, initially purple, gradually turned yellow. The spontaneous oxidation of  $\text{Ce}(\text{OH})_3$  in  $\text{CeO}_2$  in air led to broken and irregular particles. So far, we could not find explanation on why the  $\text{Ce}(\text{OH})_3$  phase we produced evolved in a different way than in Golberg’s work but this result is reproducible and is similar to Qu’s work.

## IV.3. Post-synthesis treatments

### IV.3.1 Hydrothermal dehydration

As the targeted non porous CeO<sub>2</sub> precursor was successfully synthesized, we applied the second step described by Qu *et al.* as a hydrothermal treatment of the powder in an autoclave at 160 °C.<sup>3</sup>

**Thermal treatment IV.1. Hydrothermal dehydration.** In a 25 mL Teflon autoclave, 80 mg of 7-days aged Ce(OH)<sub>3</sub> powder obtained from Synthesis IV.2. were dispersed by sonication in 17 mL of deoxygenated water to yield a yellow suspension. The autoclave was closed under air and let to react in a preheated oven at 160 °C for 20 h. After reaction, the solution was let to cool down naturally to r.t. The solution was centrifugated under air (9,000 rpm, 10 min, 20 °C) and the powder was washed once with 30 mL of EtOH. The obtained powder was then dried on the bench under air.

The material obtained from Synthesis IV.2. followed by Thermal treatment IV.1. is an off-white powder and is isostructural with cerium dioxide CeO<sub>2</sub> according to XRD (Figure 12A), with a crystallite size close to 10 nm, in agreement with Qu's work.

### IV.3.2 Dry calcination in inert and reductive atmosphere

Considering the off-white color of the CeO<sub>2</sub> catalyst after Thermal treatment IV.1., the surface Ce<sup>(III)</sup> ratio is certainly low. We therefore also attempted at creating surface defects in the cerium oxide *via* another thermal treatment under stronger conditions. We applied a “dry” treatment, *i.e.* a calcination at high temperature (Thermal treatment IV.2.), to the different cerium-containing materials we synthesized (CeO<sub>2</sub> nanorods, fresh Ce(OH)<sub>3</sub> and aged Ce(OH)<sub>3</sub>) and to commercial Ce(OH)<sub>4</sub>. Fresh Ce(OH)<sub>3</sub> is understand as Ce(OH)<sub>3</sub> from Synthesis IV.2. which has not been exposed to air and was stored in Ar while aged Ce(OH)<sub>3</sub> is understand as Ce(OH)<sub>3</sub> from Synthesis IV.2. which has been exposed at least 7 days to air and which does not present any signal of Ce(OH)<sub>3</sub> in XRD.

**Thermal treatment IV.2. Dry calcination under Ar or pure H<sub>2</sub>.** In an Ar-filled glovebox, 100 mg of powder (CeO<sub>2</sub> from Synthesis IV.1. or fresh or 7-days aged Ce(OH)<sub>3</sub> powder from Synthesis IV.2.) were introduced in a 25 mL glass autoclave. The Ar atmosphere was eventually changed for pure H<sub>2</sub> (7 bar) after two cycles vacuum/H<sub>2</sub>. The autoclave was introduced in an oil bath which was then heated to 60 °C, 100 °C or 200 °C for 2 h. A pressure of 8 bar was attained at 200 °C. After reaction, the solution was let to cool down naturally to r.t. and the autoclave pressure was released in the glovebox.

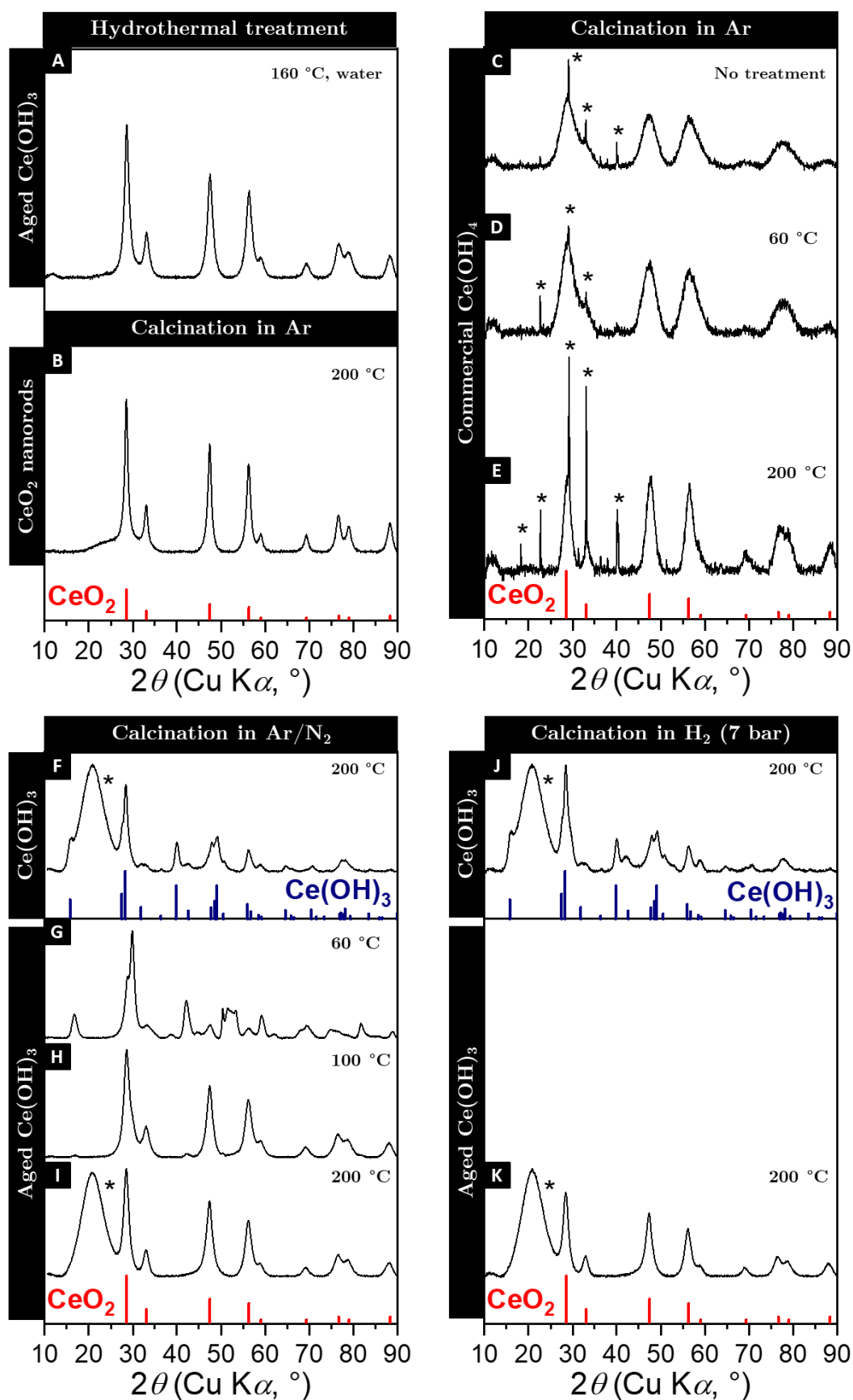


Figure 12. XRD patterns cerium oxide samples after treatments. (A) Cerium oxide from hydrothermal treatment IV.1. applied to aged  $\text{Ce}(\text{OH})_3$ . (B) Calcinated  $\text{CeO}_2$  in Ar at 200  $^\circ\text{C}$

(Thermal treatment IV.2.). (C) commercial  $\text{Ce}(\text{OH})_4$  as received and after calcination under Ar (D) at 60 °C and (E) at 200 °C (asterisks denote impurities). (F) fresh  $\text{Ce}(\text{OH})_3$  after calcination at 200 °C and (G-I) aged  $\text{Ce}(\text{OH})_3$  after calcination at 60 °C, 100 °C and 200 °C under Ar (Thermal treatment IV.2.). (J) fresh  $\text{Ce}(\text{OH})_3$  and (K) aged  $\text{Ce}(\text{OH})_3$  after calcination at 200 °C under  $\text{H}_2$  (asterisks indicate the signal due to the protective plastic dome).

**Cerium oxide.** The cerium dioxide powder from Synthesis IV.1, *i.e.* the  $\text{CeO}_2$  nanorods, initially beige-yellow, was let to react in an autoclave during 2 h at 200 °C in inert (Ar) or reductive atmosphere ( $\text{H}_2$ , 7 bar) according to Thermal treatment IV.2. The observations, X-ray diffractograms and IR spectra were similar whatever was the gas phase during the calcination (Ar or  $\text{H}_2$ ). The  $\text{CeO}_2$  powder first turned grey at *ca.* 150 °C and then violet after a few minutes at 200 °C. As long as the powder was kept under argon after the calcination, there was no change of color over weeks. It however instantaneously turned back to yellow when exposed to air, because of the reoxidation of surface cerium atoms. An XRD measurement of the powder right after its exposure to air was performed and no phase change was observed: the sample was composed of cubic  $\text{CeO}_2$  with similar peak widths (Figure 12B). It is noteworthy that a treatment at only 100 °C for 2 h does not affect the color of the powder: the formation of oxygen vacancies and the reduction of  $\text{Ce}^{(\text{IV})}$  in  $\text{Ce}^{(\text{III})}$  is then expected to occur mainly above 100 °C. The same treatment applied to commercial cerium oxide  $\text{CeO}_2$ , initially light grey, did not lead to any visual change.

**Commercial  $\text{Ce}(\text{OH})_4$ .**  $\text{Ce}(\text{OH})_4$  from a commercial provider was calcinated under Ar at 60 °C and 200 °C to establish a comparison point with aged  $\text{Ce}(\text{OH})_3$ . According to XRD, the initial state corresponds to a broad  $\text{CeO}_2$  pattern, in line with aforementioned literature,<sup>39</sup> with the presence of an unidentified species (Figure 12C-E). When calcinated at 60 °C, the  $\text{CeO}_2$  was not modified whereas a calcination at 200 °C led to thinner peaks, associated to a larger crystallite size. We hypothesized the calcination at 200 °C dehydrated the material and consequently increased its crystallinity. We assumed the difference in intensity of the different impurity peaks in spectra C-E is not related to their growth during calcination but rather to the inhomogeneity of the commercial powder.

**Fresh and aged  $\text{Ce}(\text{OH})_3$ .** The same Thermal treatment IV.2. was applied to fresh and 7-days aged  $\text{Ce}(\text{OH})_3$  from Synthesis IV.2. The experiments were run under inert gas (Ar for fresh  $\text{Ce}(\text{OH})_3$  and  $\text{N}_2$  for aged  $\text{Ce}(\text{OH})_3$ ) and under 7 bar of  $\text{H}_2$  with similar observations for both gases (Figure 12F-K). Fresh  $\text{Ce}(\text{OH})_3$ , initially grey, turned lilac whereas aged  $\text{Ce}(\text{OH})_3$ , initially yellow, turned off white. The four calcinated samples at 200 °C were analyzed by XRD with a sample holder equipped with an air-tight plastic dome. XRD measurements reveal that fresh  $\text{Ce}(\text{OH})_3$  was not

structurally modified (Figure 12F,J) whereas aged  $\text{Ce}(\text{OH})_3$  was transformed in cerium oxide (Figure 12I,K). The  $\text{CeO}_2$  phase has small crystallite size *ca.* 10 nm in all cases according to Scherrer analysis. The formation of  $\text{CeO}_2$  is not total at 100 °C, even though well advanced (Figure 12H). At a lower temperature of 60 °C, there is merely no transformation of the aged  $\text{Ce}(\text{OH})_3$  in  $\text{CeO}_2$  (Figure 12G). This difference of evolution between fresh and aged  $\text{Ce}(\text{OH})_3$  is coherent with the aforementioned beam damage we observed: the heat produced by the electron beam was enough to trigger the  $\text{CeO}_2$  formation. We concluded a calcination step of aged  $\text{Ce}(\text{OH})_3$  produces a highly defective cerium oxide, suitable for catalysis.

Considering that most of the  $\text{CeO}_2$  synthesis protocols in literature include a drying final step in an oven at 60 °C overnight, the material may be transformed before the diffractograms are recorded, explaining the lack of characterization of aged  $\text{Ce}(\text{OH})_3$  in literature. Although  $\text{Ce}(\text{OH})_3$  is known to form  $\text{CeO}_2$  by calcination in air, no data could be found in the literature regarding the dehydration of  $\text{Ce}(\text{OH})_3$  under an inert or reductive atmosphere at only 200 °C. The formation of  $\text{CeO}_2$  from  $\text{Ce}(\text{OH})_3$  in an ammonia atmosphere was nonetheless reported by Golberg *et al.* at 450 °C.<sup>5</sup>

**Infrared spectroscopy.** We previously showed that two sharp peaks at *ca.* 3600  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$  are characteristic of a hydroxide material, respectively of the O–H and Ce–OH stretching vibrations. If a dehydration occurs, a modification of the peaks is expected. We therefore studied by ATR-FTIR the calcinated samples at 200 °C in Ar of fresh  $\text{Ce}(\text{OH})_3$ , aged  $\text{Ce}(\text{OH})_3$  (both from Synthesis IV.2.) and  $\text{CeO}_2$  (Synthesis IV.1.) (Figure 13). For fresh  $\text{Ce}(\text{OH})_3$ , the two hydroxide peaks in FTIR were not modified in position nor intensity after the calcination step, indicating the hydroxide is still present, in agreement with XRD. We noticed a decrease in intensity of the peaks linked to adsorbed water (broad bands at 3400  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$ ), which was expected due to the high temperatures. On the contrary, for aged  $\text{Ce}(\text{OH})_3$ , the peaks at 3590  $\text{cm}^{-1}$  and 730  $\text{cm}^{-1}$  were not present any more after the calcination and a new peak appeared at 550  $\text{cm}^{-1}$ , identical to the FTIR spectra of pristine and calcined  $\text{CeO}_2$  nanorods. The unidentified band at 1000  $\text{cm}^{-1}$  was preserved by the calcination for both fresh and aged  $\text{Ce}(\text{OH})_3$ . No particular modification of the spectrum of calcined  $\text{CeO}_2$  was detected. FTIR measurements comfort the formation of  $\text{CeO}_2$  from aged  $\text{Ce}(\text{OH})_3$  and the disappearance of any hydroxide phase.

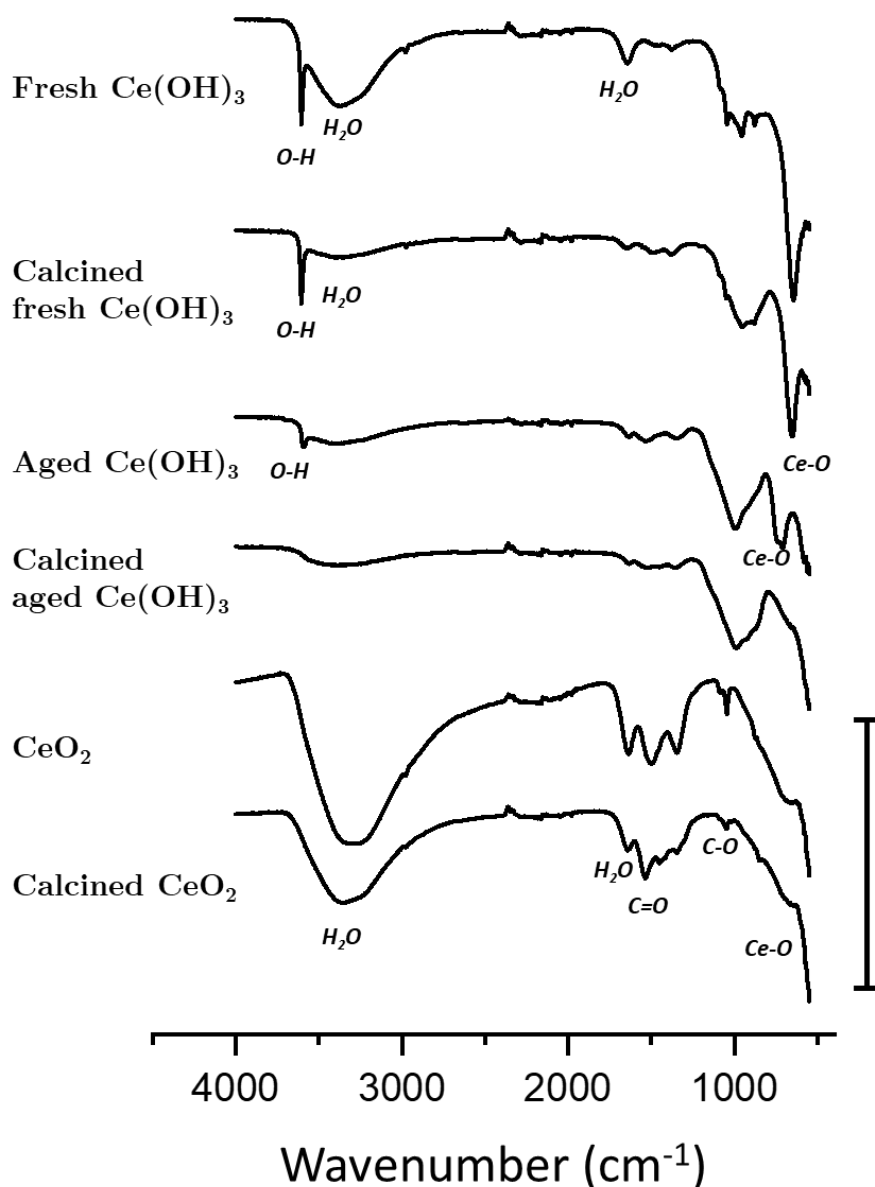


Figure 13. ATR-FTIR spectra of fresh  $\text{Ce}(\text{OH})_3$ , calcined fresh  $\text{Ce}(\text{OH})_3$ , aged  $\text{Ce}(\text{OH})_3$ , calcined aged  $\text{Ce}(\text{OH})_3$ ,  $\text{CeO}_2$  nanorods and calcined  $\text{CeO}_2$  nanorods (the vertical bar indicates 50 % absorption).

### IV.3.3 NAP-XPS: *in situ* measurements of thermal annealing

Considering the difference in the products and the striking color changes occurring during the dry thermal treatments, we chose to study the evolution of the oxidation state of Ce and O at the surface of the cerium oxide nanorods and of the cerium hydroxide  $\text{Ce}(\text{OH})_3$  by Near-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS). The experiments were performed on the TEMPO B beamline at the SOLEIL synchrotron. The protocol is described in the Appendix I ES.8. There is technically no gas pressure in the experiments commented in Section

IV.3.3. but we retained the term of NAP-XPS experiments for two reasons: first, the samples were subjected to thermal treatments (calcination at 500 °C) that generate a background pressure of gas, usually delicate to achieve in laboratory instruments, and then the samples at the end of the experiments described in Figure 14 were directly used for actual NAP-XPS experiments which will be the object of section IV.4.1. The setup allows the *in situ* study of the calcination step *in vacuo* and then the impact of the exposition of the reduced material to a few mbar of H<sub>2</sub>. The sample preparation for NAP-XPS requires a deposition of the powder by drop casting from a suspension in ethanol on a gold-coated silicon wafer, to the contrary of the lab XPS measurements where the powders are pressed as pellets: we therefore indicated the fresh Ce(OH)<sub>3</sub> from Synthesis IV.2. as “air-exposed”. The powder was already yellow by the time it was introduced in the inert measurement chamber of the NAP-XPS. The two samples, air exposed Ce(OH)<sub>3</sub> from Synthesis IV.2. and CeO<sub>2</sub> nanorods from Synthesis IV.1., were disposed on the same sample holder and were subjected to the same conditions: the thermal treatment consisted in heating ramps of 10 °C/min and 1 h plateaus during which the XPS measurements were performed. The fitting of the Ce 3d region on noisy data is delicate as there is superimposition of 5 doublets with close positions and close splitting values for four of them (violet and yellow components on one side and pink and red ones on the other) (Figure 14). The peak positions were therefore slightly more constrained than for lab-measurements previously discussed.

In normal configuration (electron beam perpendicular to the probed surface), the probed depth for a laboratory instrument operating at 1486.6 eV is estimated to be 3.5 nm in the Ce 3d region.<sup>10</sup> The initial state of Ce(OH)<sub>3</sub> comports a Ce<sup>(III)</sup> fraction of 33 %, in line with the oxidation of the extreme surface during the sample preparation in air (Figure 14A). The initial state is therefore very similar to that of cerium oxide nanorods regarding the cerium oxidation state (Ce<sup>(III)</sup> fraction of 34 %). An important increase in the Ce<sup>(III)</sup> fraction occurred upon temperature increase, from 33 % at r.t. to 67 % at 500 °C for Ce(OH)<sub>3</sub> and from 34 % to 73 % for CeO<sub>2</sub>. This evolution is in perfect agreement with the color changes: from grey to lilac in the case of Ce(OH)<sub>3</sub> and from yellow to grey-violet in the case of CeO<sub>2</sub>. We can note the reduction of cerium atoms occurs in the full range from room temperature to 400 °C and then seems to get stabilized. Calcination at 200 °C can be performed in the laboratory and would correspond to a Ce<sup>(III)</sup> fraction of *ca.* 55 % which is satisfactory for us (Figure 14C). Finally, the oxidation state was not deeply modified upon cooling to 100 °C (final state), indicating the stability of the so-formed highly oxygen-defective cerium oxide.

The increase in Ce<sup>(III)</sup> concentration with calcination is in agreement with Freund’s work on cerium oxide microparticles although the extent of the modification of the oxidation state of cerium is higher in our case: from 34 % to 73 % for cerium oxide nanorods *versus* 6 % to 9.2 % for microparticles, for a similar treatment (30 min at 500 °C under vacuum).<sup>10</sup> We attribute this difference to the characteristic size of the



particles: as oxygen vacancies are more easily formed near surface, high surface/volume ratio favors the formation of defective materials.

A similar behavior was observed for the O 1s spectra (Figure 14B). In comparison with the previously displayed spectra, a proper fit required the introduction of a fourth large component attributed to water or hydroxyl group (black component).<sup>10</sup> The initial states of both air exposed  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  nanorods display particularly broad features in comparison to the measurements performed with a lab-instrument. The differences may be caused by the difference in X-Ray beam energy (1100 eV for synchrotron, 1486.6 eV for laboratory), the nature of the samples (deposition *versus* powder) or the drop casting method. Besides,  $\text{CeO}_2$  is known for presenting electron charge issues at temperatures below 100 °C. In the case of fresh  $\text{Ce}(\text{OH})_3$ , the  $\text{O}_I\text{-Ce}^{(\text{IV})}$  peak got sharpened upon calcination at 100 °C, probably due to a  $\text{CeO}_2$  formation, in line with our previous calcination experiments (Figure 12I). Then, the contribution of  $\text{O}_I$  gradually decreased in favor of those of  $\text{O}_{\text{II}}$  and  $\text{O}_{\text{III}}$ , accounting for the defects and the reduction of  $\text{Ce}^{(\text{IV})}$  in  $\text{Ce}^{(\text{III})}$  as observed with the Ce 3d spectra. The final state contains a more important contribution of surface hydroxyl/water, it may be due to the cooling of the material from 500 °C down to 100 °C: as the temperature goes down, hydroxyls may form on surface from the adsorption of background water molecules. The observations are in agreement with those for  $\text{CeO}_2$  nanorods calcination which contain merely no  $\text{Ce}^{(\text{IV})}$  in the end.

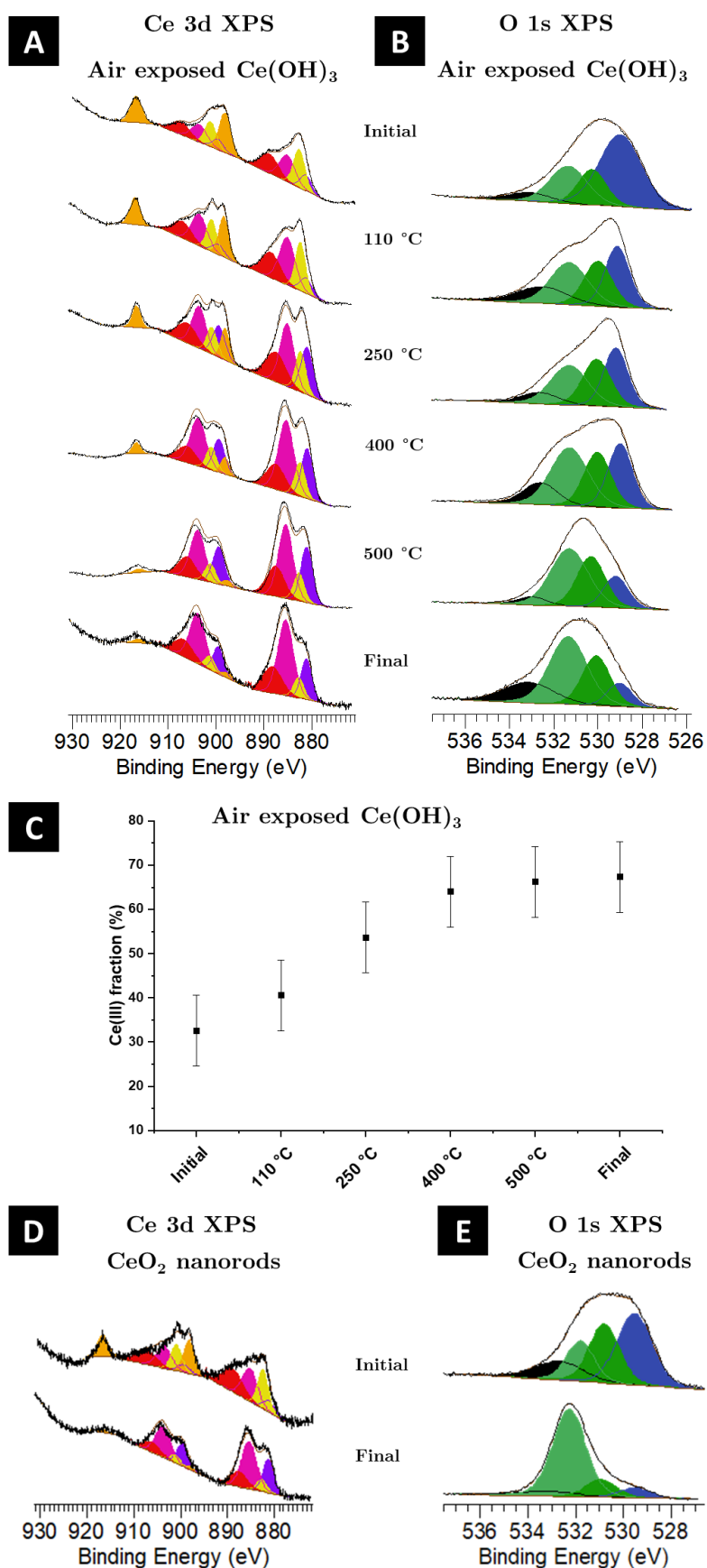


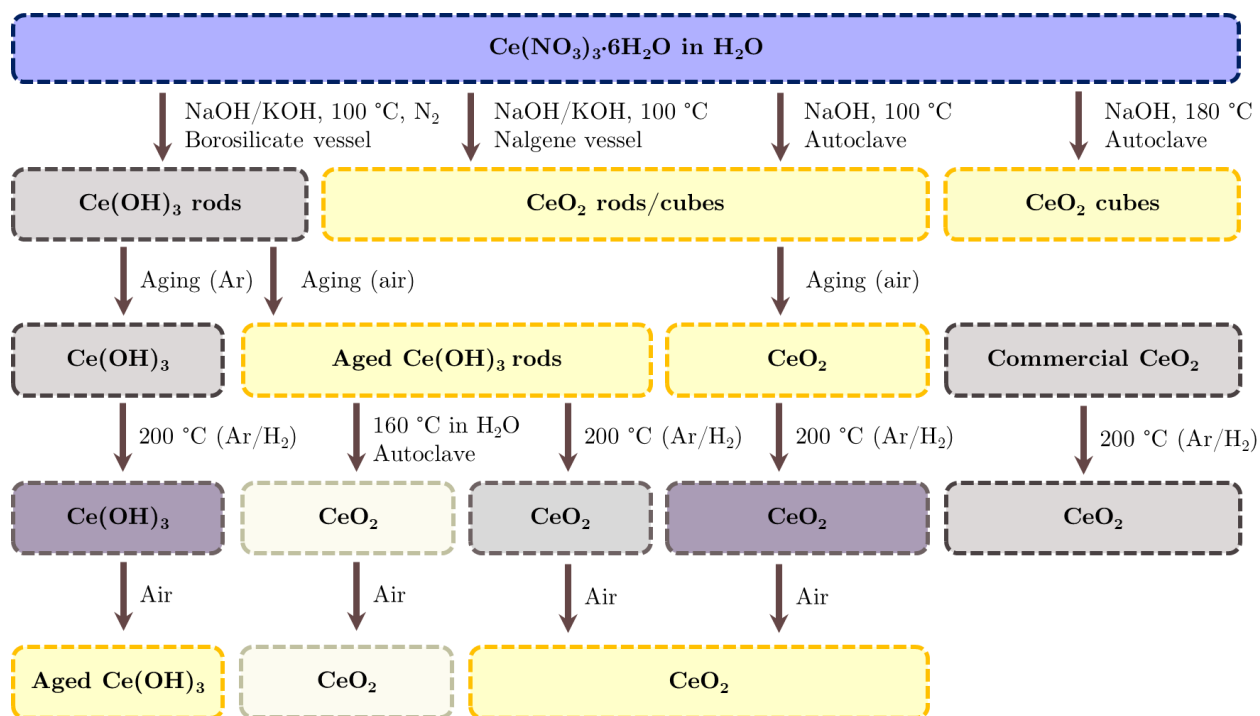
Figure 14. (A) NAP-XPS Ce 3d spectra of air exposed  $\text{Ce}(\text{OH})_3$  along calcination in vacuum and of (D)  $\text{CeO}_2$  nanorods before and after calcination at 500 °C in vacuum. Color code is

identical to Figure 9Figure 8: violet and pink for Ce<sup>(III)</sup>, yellow, orange and red for Ce<sup>(IV)</sup>. (B) NAP-XPS O 1s spectra of air exposed Ce(OH)<sub>3</sub> along calcination in vacuum. (C) Evolution of the Ce<sup>(III)</sup> fraction as a function of the temperature for the air exposed Ce(OH)<sub>3</sub> sample determined with Ce 3d (black) and O 1s (red).

#### IV.3.4 Summary of the syntheses and treatments of cerium-containing phases

We synthesized cerium oxide CeO<sub>2</sub> and cerium hydroxide Ce(OH)<sub>3</sub> by hydrothermal treatment of Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O precursor with an alkali solution of NaOH and KOH and demonstrated the crucial importance of the nature of the reaction vessel, and to a lower extent of the gas phase, to obtain Ce(OH)<sub>3</sub> (Scheme 2). The hydroxide phase evolved in ambient conditions to a new one with an unknown XRD pattern. We fully characterized this unexpected material by means of XRD, TEM, SAED, FTIR, XPS and XAS and suggested it results from the oxidation of some Ce<sup>(III)</sup> sites in Ce<sup>(IV)</sup> while preserving the global crystallographic structure. This is in contradiction with literature works reporting the evolution in crystalline CeO<sub>2</sub> under ambient conditions. Work is currently ongoing for a better crystallographic description of the unknown phase by means of Rietveld refinement on XRD data.

In order to obtain catalytic materials, different thermal treatments were applied to the materials to increase the Ce<sup>(III)</sup> fraction at the surface of the material: Ce<sup>(III)</sup> fraction up to 55 % could be obtained in conditions reproducible in the laboratory, *i.e.* a 2 h calcination at 200 °C in absence of air under Ar or H<sub>2</sub>.



Scheme 2. Recapitulative scheme of the different hydrothermal reaction conditions and treatments. The colors of the cases correspond to those of the powders. Materials indicated are those identified by XRD and the morphology, determined by TEM, is preserved along the post-synthesis treatments.

## IV.4. Hydrogenation reactions by reduced cerium oxide

### IV.4.1 NAP-XPS of hydrogen activation by reduced cerium oxide in the gas phase

As developed in introduction, we believe the presence of oxygen vacancies at the surface of the cerium oxide is essential to its use as a Lewis acid for an FLP-like catalysis. We therefore investigated the presence of these oxygen vacancies and the ability of Ce<sup>(III)</sup> atoms to react with H<sub>2</sub> by NAP-XPS. Freund *et al.* showed the addition of H<sub>2</sub> on a reduced cerium oxide increases the surface Ce<sup>(IV)</sup> ratio through the formation of Ce–H hydride species.<sup>10</sup> This hydride, and consequently the H<sub>2</sub> activation, may thus be indirectly probed by a growth of the Ce<sup>(IV)</sup> components in Ce 3d XPS spectra and of the O<sub>I</sub>–Ce<sup>(IV)</sup> component in O 1s XPS spectra. As no phenylacetylene could be introduced in the NAP-XPS chamber, we chose to inject acetylene as a model substrate at the end of the H<sub>2</sub> activation experiment to detect a potential hydrogenation reaction. We chose a final temperature of 250 °C and an H<sub>2</sub>:acetylene ratio of *ca.* 5 to be as close as possible to the conditions of semi-hydrogenation with cerium oxide developed by Pérez-Jamírez *et al.*<sup>16</sup> The two cerium oxide catalysts were disposed on the same sample holder and were therefore subjected to the same conditions: one catalyst originated from air exposed Ce(OH)<sub>3</sub> dehydration (Synthesis IV.2.) and the other was the CeO<sub>2</sub> nanorods from Synthesis IV.1.

The catalysts contained high concentration of oxygen defects after the calcination step at 500 °C in the NAP-XPS chamber (*cf.* section IV.3.3., 30 min at 500 °C under ultra high vacuum). As cerium oxide charges under the X-ray beam at low temperatures, we measured the initial state at 100 °C, then added a low pressure of H<sub>2</sub> (0.14 mbar then 0.52 mbar), then increased the temperature up to 250 °C, then introduced the acetylene (0.1 mbar of acetylene) and finally measured the final state when all gases were removed (Figure 15A).

Both the samples displayed initial Ce<sup>(III)</sup> ratio *ca.* 70 % (Figure 15, state 1). Upon exposure to 0.14 mbar of H<sub>2</sub> at 100 °C, we observed the growth of the Ce<sup>(IV)</sup> orange component at 917 eV (state 2) on the Ce 3d XPS spectra indicating the cerium atoms got oxidized in Ce<sup>(IV)</sup>. Increasing the H<sub>2</sub> pressure further decreased the Ce<sup>(III)</sup> concentration down to respectively 58 % and 48 % (state 3). However, heating to 250 °C induced the reduction of the cerium atoms to the initial levels, or close (state 4). In the O 1s spectra, the main feature is the growth of the O<sub>I</sub> blue component from state 1 to state 3. As this component is associated to oxygen in oxidized environment, *i.e.* linked to Ce<sup>(IV)</sup> atoms, we concluded the surface Ce<sup>(III)</sup> atoms in reduced cerium oxide get oxidized by H<sub>2</sub> even at low pressures. This oxidation is however reversible upon heating as shown by state 4. The addition of acetylene did not significantly modify the spectra envelope of neither the Ce 3d nor O 1s regions.

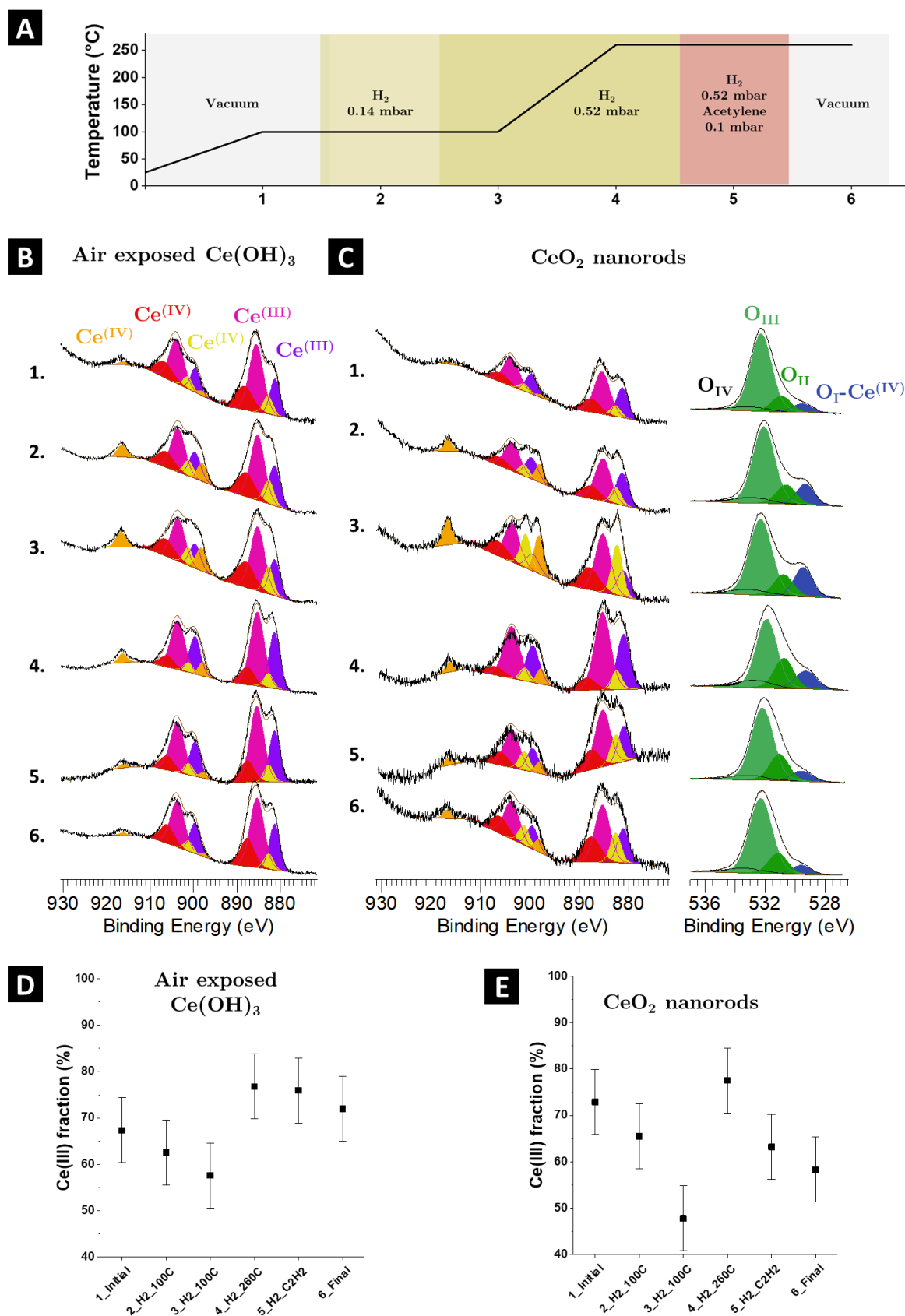
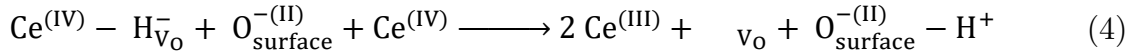
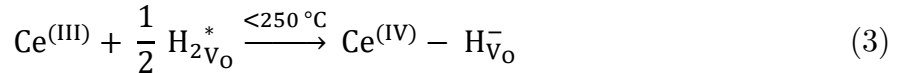
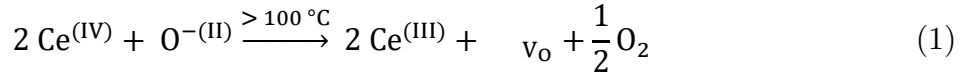


Figure 15. (A) *In situ* treatment of the samples in the NAP-XPS device: (1) vacuum/100 °C, (2) H<sub>2</sub> 0.14 mbar/100 °C, (3) H<sub>2</sub> 0.52 mbar/100 °C, (4) H<sub>2</sub> 0.52 mbar/260 °C, (5) H<sub>2</sub> 0.52 mbar + acetylene 0.1 mbar/260 °C and (6) vacuum/260 °C. NAP-XPS Ce 3d and O 1s

spectra of (A) air exposed Ce(OH)<sub>3</sub> and of (B) CeO<sub>2</sub> nanorods. Color code is identical to Figure 9: pink and violet for Ce<sup>(III)</sup>, yellow, orange and red for Ce<sup>(IV)</sup>. Evolution of the Ce<sup>(III)</sup> fraction based on Ce 3d spectra for (D) the air exposed Ce(OH)<sub>3</sub> sample and (E) the CeO<sub>2</sub> nanorods sample.

We showed the reduction of cerium dioxide under vacuum led to the formation of surface Ce<sup>(III)</sup> atoms, presumably due to defect formation (according to Eq. (1)). Furthermore, these oxygen vacancies may adsorb H<sub>2</sub> (according to Eq. (2)) and then activate it by forming Ce–H hydride species (according to Eq. (3)). The H linked to the cerium atom is thought to be situated in an oxygen vacancy and to be negatively charged considering the increase in the oxidation state of the cerium, hence the hydride terminology.<sup>10</sup> Upon heating, typically above 200 °C, the hydride species recombine as H<sub>2</sub> and desorb from the cerium oxide (according to reverse Eq. (3) and (2)).



Our observations therefore agree with the hydrogen adsorption-induced oxidation of reduced cerium oxide reported by Freund *et al.*<sup>10</sup> but, like for the calcination step previously studied, the extent of the phenomenon is much higher in our case, presumably due to the high surface/volume ratio of the objects. DFT studies for oxygen defective CeO<sub>2</sub>(111) indicated the recombination of two Ce<sup>(IV)</sup>–H<sup>–</sup> species in H<sub>2</sub> is more kinetically favored than the formation of the homolytic dissociation product according to Eq. (4), *i.e.* the migration of the proton from the metal site to a surface oxygen site accompanied with a reduction of two Ce<sup>(IV)</sup> in Ce<sup>(III)</sup>.<sup>10</sup> This indicates the Ce<sup>(IV)</sup>–H<sup>–</sup> species are relatively stable at moderate temperatures, and potentially active for hydrogenation reactions, and that there is a limited formation of hydroxyls. Although the samples used in this experiment were calcinated at 500 °C prior to H<sub>2</sub> exposure, which is not reproducible in laboratory, we hypothesized the calcination at 200 °C already formed a significant number of surface Ce<sup>(III)</sup> atoms (surface fraction of 55 % at 250 °C *vs.* 32 % and 68 % for respectively the initial and final state at 500 °C, *cf.* Figure 9), and thus of active sites for H<sub>2</sub> activation. We therefore chose to heat the pre-catalyst samples used for liquid catalysis at 200 °C during 2 h in presence of H<sub>2</sub>.

## IV.4.2 Liquid phase hydrogenation of styrene and phenylacetylene

Inspired by the recent literature on acetylene hydrogenation by  $\text{CeO}_2$  in the gas phase<sup>16,47</sup> and the results obtained in the liquid phase for alkene and alkyne hydrogenation,<sup>8</sup> we chose styrene and phenylacetylene ( $\text{PhCCH}$ ) as model substrates. The set of reaction conditions was chosen close to that of Qu's work, *i.e.* the reaction was conducted in toluene at 100 °C under 7 bar  $\text{H}_2$  during 16 h, in autoclave, with 40 mg of material for 2 mmol of substrate.<sup>8</sup>

**Catalysis IV.1. Olefin hydrogenation in toluene.** In air, 40 mg of pre-catalyst powder (0.24 mmol, 0.12 equiv. of  $[\text{Ce}]$ ) were introduced in a 25 mL glass autoclave. The atmosphere was changed for  $\text{H}_2$  (7 bar) after 2 cycles vacuum/ $\text{H}_2$ . The autoclave was introduced in a preheated oil bath at 200 °C for 2 h. The pre-catalyst powder, initially yellow, turned grey. After reaction, the autoclave was let to cool down naturally to r.t. and introduced in an Ar-filled glovebox where it was reopened. To the autoclave were added 2 mmol of alkene or alkyne (210  $\mu\text{L}$  of styrene or 220  $\mu\text{L}$  of phenylacetylene, 1 equiv.), anhydrous toluene (1 mL) and eventually a phosphine (0.1 mmol, 0.05 equiv.). The autoclave was closed and the atmosphere was changed for  $\text{H}_2$  (7 bar) after 2 cycles vacuum/ $\text{H}_2$ . The autoclave was then introduced in a preheated oil bath at 100 °C for 16 h. The powder was suspended in solution with stirring. After reaction, it was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

**Styrene hydrogenation.** No hydrogenation of styrene occurs with  $\text{CeO}_2$  nanorods from Synthesis IV.1. whatever was the pre-treatment: raw (no pre-treatment), reduced during 2 h at 100 °C or at 200 °C. Instead, a small fraction of styrene polymerized, as attested by a broad signal at *ca.* 6.60 ppm in  $^1\text{H}$  NMR. The same results were observed when 5 mol% of tricyclohexylphosphine ( $\text{PCy}_3$ ) were added.

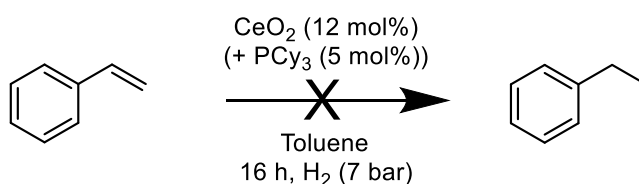
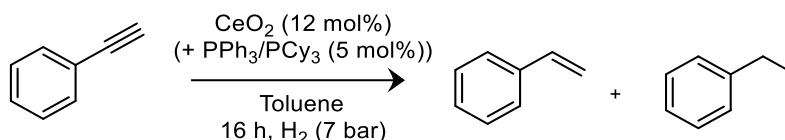


Figure 16. Hydrogenation of styrene with cerium oxide.



**Phenylacetylene semi-hydrogenation.** First studies on phenylacetylene with a pre-catalyst batch initially containing a mix of aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$ , led to a 12 % conversion yield of phenylacetylene without phosphine, and to higher yields (35 % and 75 %) in presence of  $\text{PPh}_3$  or  $\text{PCy}_3$  (5 mol%), with even a small proportion of ethylbenzene (Table 4, entries 1-3). The good catalytic activity of this batch supports the results displayed by Qu *et al.* Unfortunately, these interesting results could not be reproduced on another batch, although we explored more than ten different batches of pre-catalyst leading to XRD-pure aged  $\text{Ce}(\text{OH})_3$ , mix of aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  or XRD-pure  $\text{CeO}_2$ , as well as different post-synthesis treatments (no calcination, calcination at 200 °C, hydrothermal treatment at 160 °C in autoclave). The difficulties in obtaining as high catalytic activities as those obtained with the first batch underline the sensitivity of the catalyst synthesis, as already stressed by Qu *et al.* in their articles.<sup>3,17</sup> When following the hydrothermal treatment at 160 °C during 16 h in autoclave proposed by Qu *et al.*, no reactivity at all was observed (Table 4, entries 4-5). When using raw materials without calcination, no reactivity was observed at 100 °C (Table 4, entries 6 and 8) although a consequent one was obtained at 200 °C (Table 4, entries 7 and 9): respectively 40 % and 77 % conversion of phenylacetylene for aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  nanorods. Finally, if the first batch was excluded, no significant difference in phenylacetylene hydrogenation was detected between reduced pure aged  $\text{Ce}(\text{OH})_3$  and reduced mix of aged  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$ , both of them displaying a conversion *ca.* 1-2 % (Table 4, entries 10 and 12 and Figure 17, entries 1 and 3). Reduced  $\text{CeO}_2$  nanorods from Synthesis IV.1 led to slightly higher styrene yields, *ca.* 8 % (Table 4, entry 14 and Figure 17, entry 5).



Entry	Catalyst	Phosphine (5 mol%)	Temp.	Styrene yield	Ethylbenzene yield
Highly active batch <sup>a</sup>					
1	Mix aged Ce(OH) <sub>3</sub> /CeO <sub>2</sub>	-	100 °C	12 %	0 %
2		PPh <sub>3</sub>		30 %	5 %
3		PCy <sub>3</sub>		65 %	10 %
Hydrothermal treatment <sup>b</sup>					
4	Aged Ce(OH) <sub>3</sub>	-	100 °C	0 %	0 %
5		PPh <sub>3</sub>		1 %	0 %
Non calcinated catalysts <sup>c</sup>					
6	Aged Ce(OH) <sub>3</sub>	-	100 °C	0 %	0 %
7		-	200 °C	40 %	0 %
8	CeO <sub>2</sub>	-	100 °C	0 %	0 %
9		-	200 °C	61 %	16 %
Calcinated catalysts <sup>d</sup>					
10	Aged Ce(OH) <sub>3</sub>	-	100 °C	1 %	0 %
11		PPh <sub>3</sub>		5 %	0 %
12	Mix aged Ce(OH) <sub>3</sub> /CeO <sub>2</sub>	-		1 %	0 %
13		PPh <sub>3</sub>		4 %	0 %
14	CeO <sub>2</sub>	-		8 %	0 %
15		PPh <sub>3</sub>		7 %	0 %

Table 4. Hydrogenation of phenylacetylene with different cerium oxide samples according to Catalysis IV.1. For entries 1-3 and 10-15, the samples were reduced by calcination at 200 °C during 2 h under H<sub>2</sub> (7 bar). Yields were determined by NMR. <sup>a</sup>Data corresponding to a single batch of catalyst. <sup>b</sup>Hydrothermal treatment at 160 °C for 16 h in water autoclave, two experiments per condition with identical results. <sup>c</sup>No calcination performed before catalysis. Unidentified products with aromatic protons at 200 °C. <sup>d</sup>Average results, correspond to data on Figure 3.

Although we could not obtain a consequent hydrogenation of phenylacetylene in similar conditions than the targeted ones,<sup>8</sup> our results are in line with Pérez-Ramírez *et al.* on alkyne hydrogenation with CeO<sub>2</sub>/TiO<sub>2</sub>: at 100 °C in toluene, they report a reasonable conversion (above 50 %) of 1-hexyne in 1-hexene when H<sub>2</sub> pressure was higher than 50 bar, and only residual conversion below 10 bar of H<sub>2</sub>.<sup>47</sup> Moreover, our results clearly indicate the hydrogenation catalytic activity of a cerium oxide stand-

alone catalyst exists at 100 °C, even though with moderate efficiency, at the condition of reducing it at high temperature, hence the importance of oxygen vacancies.

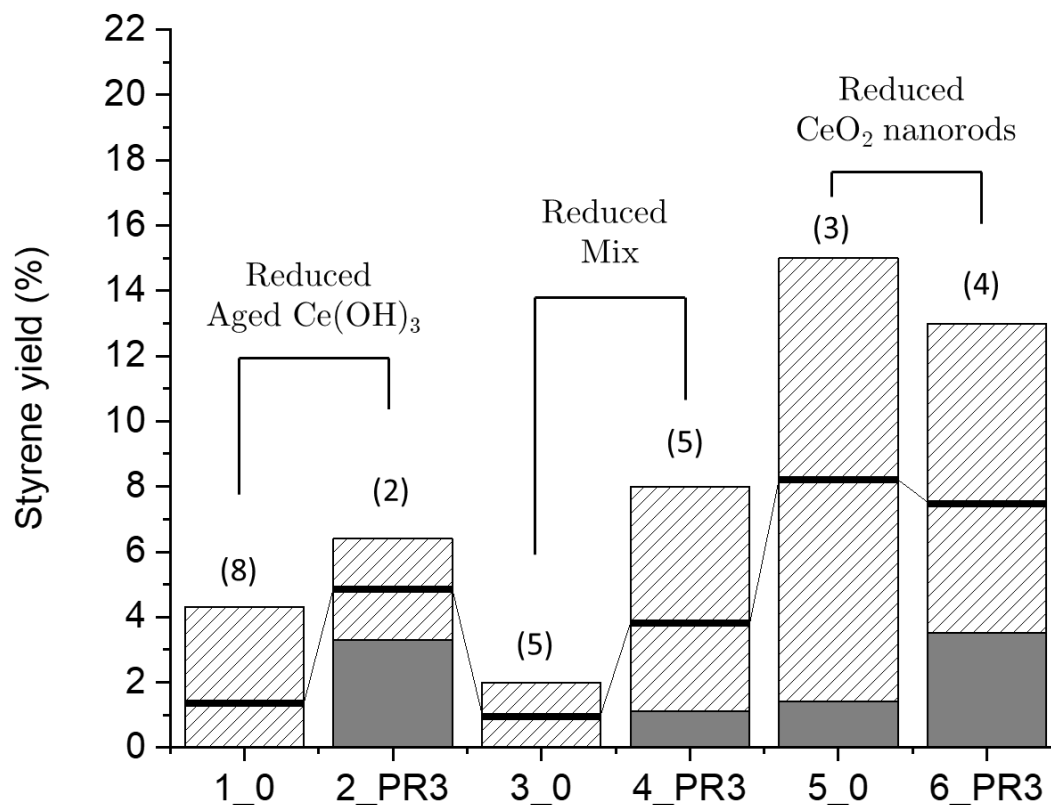


Figure 17. Styrene yield obtained during phenylacetylene semi-hydrogenation by reduced cerium oxide samples, from (1-2) aged  $\text{Ce}(\text{OH})_3$ , (3-4) an aged mix of  $\text{Ce}(\text{OH})_3$  and  $\text{CeO}_2$  and (5-6)  $\text{CeO}_2$  nanorods. Triphenylphosphine ( $\text{PPh}_3$ ) at 5 mol% was added in experiments 2, 4 and 6. The dashed sectors indicate the ranges of obtained yields, the black line denoting the average. The figures in brackets indicate the number of experiments per bar. Conversion yields were determined by NMR.

**Phosphine addition.** An increase in phenylacetylene hydrogenation rate was observed upon addition of  $\text{PPh}_3$  or  $\text{PCy}_3$  when aged  $\text{Ce}(\text{OH})_3$  or a mix aged  $\text{Ce}(\text{OH})_3/\text{CeO}_2$  was used (*ca.* 5 % conversion in presence of phosphine *vs.* 1 % without) (Figure 17, entries 1-4). No meaningful difference is observed between the styrene yield for reduced  $\text{CeO}_2$  nanorods with and without addition of a phosphine (Figure 17, entries 5-6). Although the results with aged  $\text{Ce}(\text{OH})_3$  seem encouraging, the very large variability in the obtained yields and the poor reproducibility of the results impend us from formally asserting there is an impact of the phosphine.

### IV.4.3 Conclusion on the catalytic activity of cerium oxide

In summary, we proved with NAP-XPS the capacity of defective cerium oxide obtained by calcination at 500 °C to activate H<sub>2</sub> in the gas phase *via* the Ce<sup>(III)</sup> atoms. We then used the catalyst for the liquid phase semi-hydrogenation of phenylacetylene under mild conditions (100 °C, 7 bar H<sub>2</sub>, toluene). Limited conversion yields were obtained and the results obtained by Qu *et al.* could not be fully reproduced. We stressed the large variability of the catalytic activity depending on the cerium oxide pre-catalyst batch and treatment.

As the conversion yields are too low for assessing the impact of the phosphine on the hydrogenation, we suggest as perspective to use stronger conditions (150 °C or higher H<sub>2</sub> pressures). Indeed, when the reaction was conducted at 200 °C, high conversions were attained as well as conversion to ethylbenzene. In this regime, we will certainly be able to study the impact of the addition of PPh<sub>3</sub> or PCy<sub>3</sub>. We suggest to use reduced cerium oxide from Synthesis IV.1. as the synthesis of this material is more straightforward and common in literature, and already displays higher catalytic activities. Even though the proposed conditions would be limiting for practical applications, we estimate the interest resides in the possibility of boosting the reactivity of a metal oxide with a phosphine, a concept still relatively unexplored.

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## Chapter V

# Indium oxide catalysts for phenylacetylene hydrogenation

Indium oxide  $\text{In}_2\text{O}_3$  recently raised interest as a stand-alone catalyst for gas phase hydrogenation of  $\text{CO}_2$  and acetylene.<sup>1,2</sup> In 2014, Ozin *et al.* reported the possibility to use hydroxylated indium oxide nanoparticles  $\text{In}_2\text{O}_{3-x}(\text{OH})_y$  as a photocatalyst for  $\text{CO}_2$  reduction in CO and  $\text{H}_2\text{O}$  according to the Reverse Water Gas Shift (RWGS) reaction.<sup>3,4</sup> The  $\text{H}_2$  molecule was thought to be heterolytically cleaved on two close sites, [In] and [In-O], the indium site playing the role of a Lewis acid and the oxygen one that of a Lewis base. The authors thus revisited the  $\text{H}_2$  activation on transition metal oxides surfaces with a mechanism related to Frustrated Lewis Pair (FLP) catalysis.<sup>5</sup> They also proved the substitution of 1 % of the indium atoms by bismuth ones increased the photocatalytic activity due to a better light absorption and to the stronger Lewis acidity of  $\text{Bi}^{\text{(III)}}$ .<sup>6,7</sup> They finally achieved the hydrogenation of  $\text{CO}_2$  in methanol at 270 °C with rhombohedral  $\text{In}_2\text{O}_3$ .<sup>2</sup> As to acetylene, Pérez-Ramírez *et al.* reported its selective hydrogenation in ethylene (> 85 % selectivity) in the presence of cubic  $\text{In}_2\text{O}_3$ .<sup>1</sup> The reaction was conducted in flux at atmospheric pressure with a  $\text{H}_2:\text{C}_2\text{H}_2$  feed ratio of 30. A sharp increase in activity occurred between 250 °C (< 5 % conversion) and 350 °C (> 95 % conversion). There is however, to the best of our knowledge, no published work reporting the use of indium oxide as a stand-alone catalyst for hydrogenation reaction in solvent.

One of the targets of this thesis is the construction of an FLP-like catalytic system at the surface of NPs between a molecular base and a metal cation. In Chapter IV, we focused on the use of ceria with cerium atoms as the Lewis acidic centers. In this Chapter, we suggest to test in solvent the catalytic activity of  $\text{In}_2\text{O}_3$  which already proved its ability to activate  $\text{H}_2$  in the gas phase following a solid FLP mechanism. We envision a boost in catalytic activity by addition of a Lewis base such as a phosphine. The objective of Chapter V is not to obtain a performant catalyst but rather to investigate whether a system “metal oxide (Lewis base)/phosphine (Lewis base)” is in capacity to activate  $\text{H}_2$  in solvent. We targeted the hydrogenation of phenylacetylene as a model substrate with catalysts similar to the ones used by Ozin, Pérez-Ramírez and coworkers. We are potentially interested in both the cubic and rhombohedral indium oxide phases as they both displayed a catalytic activity in  $\text{CO}_2$  hydrogenation. We chose to target both the pristine and a bismuth doped phases, even though no photocatalytic activity was investigated here, because  $\text{Bi}^{\text{(III)}}$  atom sites are stronger Lewis acids than  $\text{In}^{\text{(III)}}$  ones in  $\text{Bi}_x\text{In}_{2-x}\text{O}_3$  phases.<sup>7</sup>

## V.1. Syntheses of indium oxide catalysts

There are two main stable phases for In<sup>(III)</sup> oxide: the cubic one (bixbyite type), c-In<sub>2</sub>O<sub>3</sub>, and the rhombohedral one (corundum type), rh-In<sub>2</sub>O<sub>3</sub>. To maximize the surface/volume ratio, essential for colloidal catalysis, we focused on the synthesis of In<sub>2</sub>O<sub>3</sub> nanoparticles smaller than 100 nm. c-In<sub>2</sub>O<sub>3</sub> NPs can be obtained from an aqueous solution of InCl<sub>3</sub> or In(NO<sub>3</sub>)<sub>3</sub> heated at 100-200 °C.<sup>8</sup> Fu *et al.* in particular studied the case of In(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O in a binary mixture DMF/H<sub>2</sub>O at 150 °C: the product phase was determined by the amount of water. They obtained 4-8 nm large c-In<sub>2</sub>O<sub>3</sub> NPs in absence of water and 20 nm large InOOH NPs in presence of 8.8 % of water.<sup>8</sup> Ozin *et al.* reported similar syntheses. No comparable hydrothermal synthesis directly leading to rh-In<sub>2</sub>O<sub>3</sub> could be found: a dry calcination of indium oxyhydroxide InOOH is the usual pathway.<sup>9</sup> To keep a high specific area hardly achievable with purely solid state syntheses, we propose the calcination of InOOH NPs obtained *via* the hydrothermal treatment in rh-In<sub>2</sub>O<sub>3</sub> NPs, in line with Ozin's work.<sup>2</sup>

### V.1.1 Bismuth doped cubic indium oxide

We reproduced in Synthesis V.1. the synthesis in one step of bismuth doped cubic indium oxide c-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub> reported by Ozin *et al.*<sup>7</sup> and Fu *et al.*<sup>8</sup>

**Synthesis V.1. Cubic Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub>.** In a borosilicate vessel in air, 1.2 g of In(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O (3.1 mmol, 1 equiv.) and 11 mg of Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O (0.031 mmol, 0.01 equiv.) were dissolved in 68 mL of anhydrous DMF (0.87 mol, 285 equiv.). Once the salts were dissolved after 30 min stirring (slightly turbid solution), the solution was transferred in three Teflon autoclaves of 25 mL. The autoclaves were sealed and put in an oven at 150 °C for 24 h. After reaction, the solution was let to cool down naturally to r.t. A grey-brown powder sedimented at the bottom of the autoclave. The whole solutions were brought together and centrifugated (9,000 rpm, 10 min, 20 °C). The powder was washed once with 30 mL of H<sub>2</sub>O and once with 30 mL of EtOH, without change of aspect. The obtained grey-brown powder (471 mg, 110 % yield) was then dried under flux of N<sub>2</sub> and stored under air. The excess of mass may be either attributed to residual solvents or to nitrate ions which would not have been washed away.

The material obtained in Synthesis V.1. is isostructural with cubic In<sub>2</sub>O<sub>3</sub> [PDF card N°04-004-3575] according to XRD with a crystallite size *ca.* 8 nm, calculated with the Scherrer formula applied to the peaks at 22°, 31° and 36° (Figure 1A). TEM images reveal the material consists in crystalline and relatively monodisperse 6 nm large nanoparticles, partially aggregated when dispersed in EtOH (Figure 1B-C). Selected area electron diffraction comforts the XRD attribution to c-In<sub>2</sub>O<sub>3</sub> (Figure 1D). If compared to c-In<sub>2</sub>O<sub>3</sub> which is a white powder, the brown color obtained here supports the insertion of bismuth atom. Indeed, Ozin *et al.* reported a darkening of

the powder color with an increasing Bi content: they attributed it to a change in the bandgap energy (1.212 eV for pristine  $\text{In}_2\text{O}_3$  versus 0.818 eV in  $\text{Bi}_{0.02}\text{In}_2\text{O}_3$ ).<sup>7</sup> The absence of any peak but those of *c*- $\text{In}_2\text{O}_3$  in XRD, the presence of only one type of particle in TEM and the difference of powder color led us to consider the bismuth atoms were inserted in the indium oxide structure with little distortion, as previously reported. The material will be later referred to as *c*- $\text{Bi}_{0.02}\text{In}_2\text{O}_3$ .

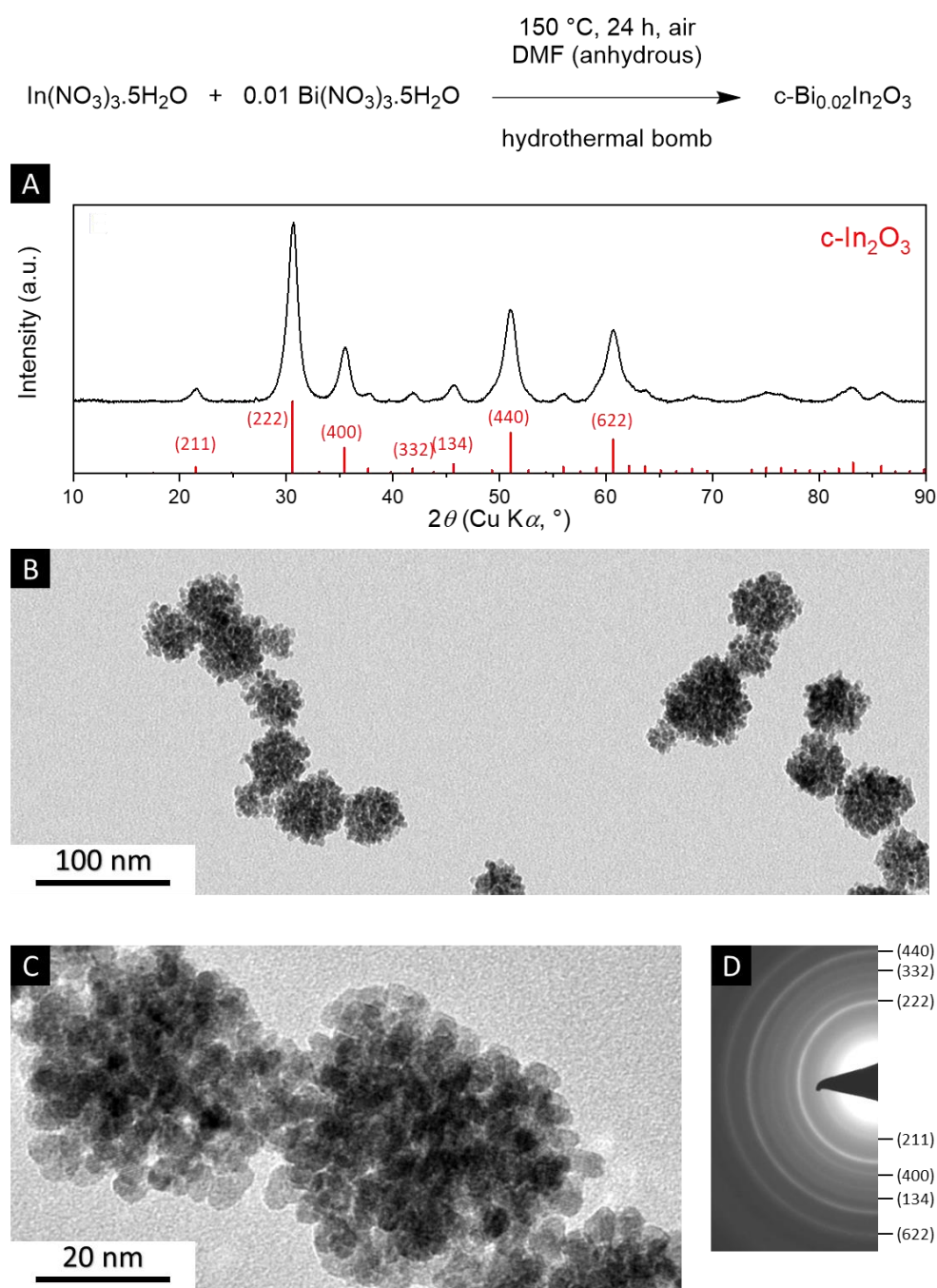


Figure 1. Synthesis and characterization of *c*- $\text{Bi}_{0.02}\text{In}_2\text{O}_3$  from Synthesis V.1. with (A) powder XRD with (hkl) attributions, (B-C) TEM images and (D) selected area electron diffraction pattern.

### V.1.2 Pristine and bismuth doped rhombohedral indium oxide

The rhombohedral rh-In<sub>2</sub>O<sub>3</sub> phase, without bismuth doping, was obtained by formation of InOOH in DMF,<sup>8</sup> followed by a calcination step (Synthesis V.2.).<sup>2</sup>

**Synthesis V.2. Rhombohedral In<sub>2</sub>O<sub>3</sub>.** In a borosilicate vessel, 240 mg of In(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O (0.614 mmol, 1 equiv.) were dissolved in 0.64 mL of water (35.5 mmol, 58 equiv.) and 13.6 mL of anhydrous DMF (0.175 mol, 285 equiv.) were added. After 30 min stirring, once the solution was limpid, the solution was transferred in a Teflon autoclave of 25 mL. The autoclave was sealed and put in a preheated oven at 150 °C for 24 h. After reaction, the solution was let to cool down naturally to r.t. on the bench. A white powder sedimented at the bottom of the autoclave. The whole solution was centrifugated (9,000 rpm, 10 min, 20 °C) and the powder was washed once with 10 mL of H<sub>2</sub>O, once with 10 mL of EtOH and then dried under flux of N<sub>2</sub> without change of aspect. The white powder was placed in a ceramic crucible which was transferred to a muffle furnace. The material was heated during 3 h at 350 °C (heating ramp of 10 °C/min) under air before being cooled down to r.t. The powder turned yellow (70 mg, 78 % yield) and was finally stored under air.

The intermediate product (before calcination at 350 °C) consists in XRD-pure indium oxyhydroxide InOOH [PDF card N°04-009-3421] with a crystallite size *ca.* 10 nm, calculated with the Scherrer formula applied to the peaks at 26° and 49° (Figure 2A). TEM images reveal the product consisted in crystalline 10 nm large nanoparticles (Figure 2B), and electron diffraction comforts the XRD attribution to InOOH (Figure 2C). The final product consists in XRD-pure rhombohedral In<sub>2</sub>O<sub>3</sub> [PDF card N°00-022-0336] with a crystallite size *ca.* 10 nm, calculated with the Scherrer formula applied to the peaks at 22.5°, 46° and 50.5° (Figure 2D). The morphology is not affected by the calcination step according to TEM images (Figure 2E). The material will later be referred to as rh-In<sub>2</sub>O<sub>3</sub>.

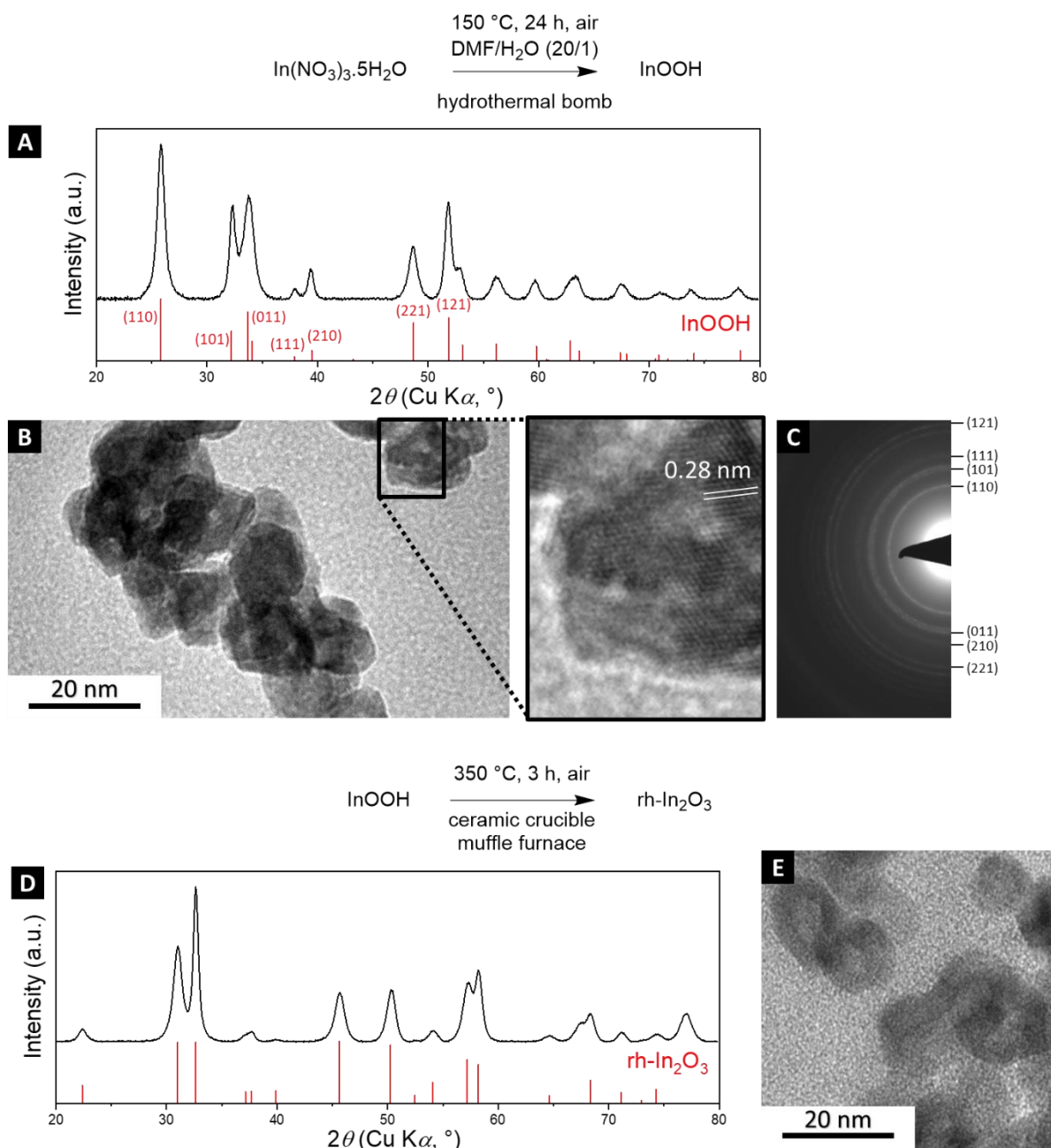


Figure 2. Synthesis and characterization of InOOH and rh-In<sub>2</sub>O<sub>3</sub> from Synthesis V.2. (A) powder XRD, (B) TEM images and (C) electron diffraction of the intermediate material. (D) powder XRD and (E) TEM image of the final material.

In order to introduce acidic Bi<sup>(III)</sup> atoms in rh-In<sub>2</sub>O<sub>3</sub>, the synthesis of a bismuth doped rhombohedral indium oxide rh-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub> phase was attempted *via* a bismuth doped indium oxyhydroxide Bi<sub>0.01</sub>InOOH phase. The protocol was similar to the one used for non-doped rh-In<sub>2</sub>O<sub>3</sub> (Synthesis V.2.) with the substitution of 1 % of the indium nitrate precursor by the bismuth nitrate one (Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O). The material after the hydrothermal step was a grey powder (372 mg, 82 %). According to XRD, it was composed of InOOH as the major species and of Bi(0) [PDF card N°00-005-0519] as a minor species (Figure 3A): the Bi<sub>0.01</sub>InOOH was not formed. After the calcination step, the powder turned ochre, a part of the InOOH was converted into rh-In<sub>2</sub>O<sub>3</sub> and the Bi(0) phase disappeared in favor of the tetragonal bismuth oxide β-Bi<sub>2</sub>O<sub>3</sub> [PDF card N°04-007-1443] (Figure 3B). As the synthesis of a bismuth doped rhombohedral indium oxide rh-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub> phase failed following this route, no further work was conducted in this direction.

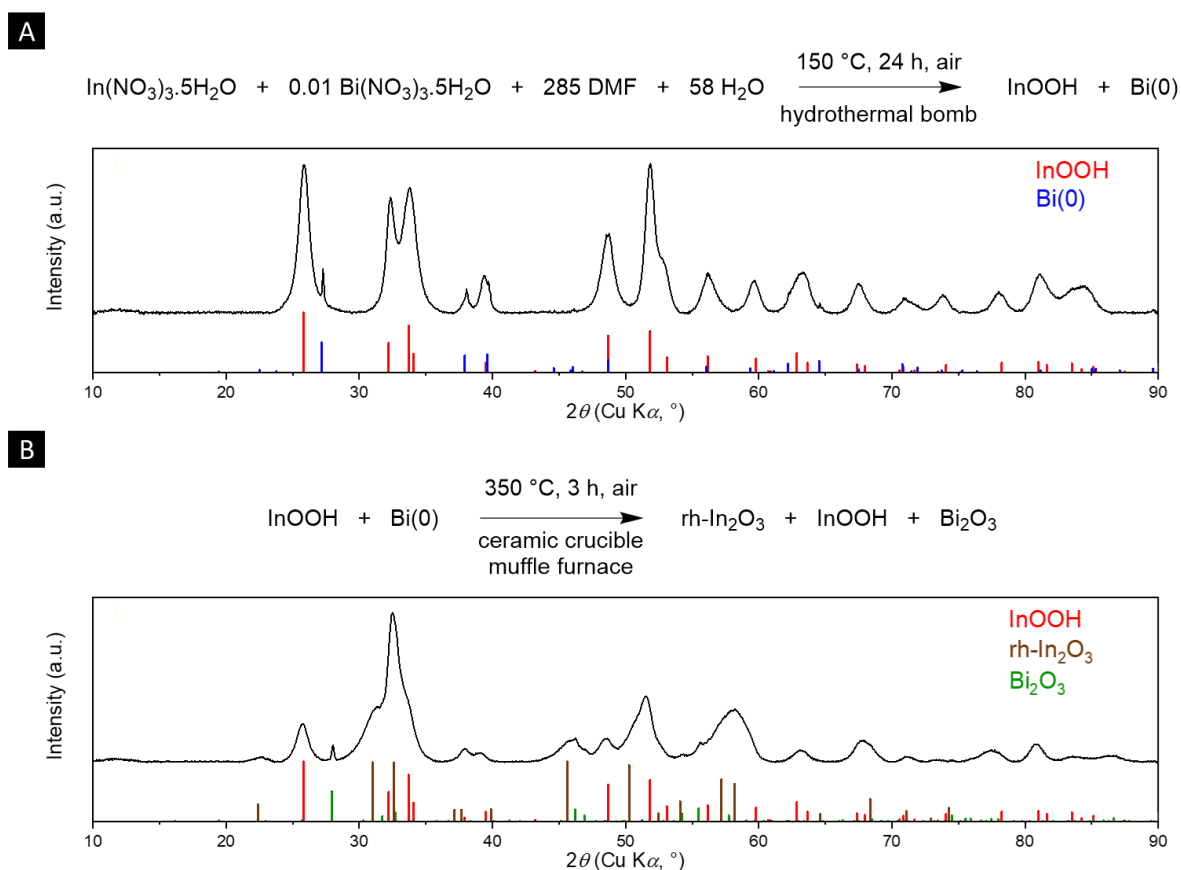


Figure 3. Attempt at the synthesis of rh-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub>. Powder XRD (A) of the intermediate product and (B) of the final product.

## V.2. Hydrogenation reactions

To test the catalytic activity of indium oxide catalysts for hydrogenation reactions, a protocol similar to that used for ceria catalysts was followed (Catalysis IV.1.): the reaction was conducted overnight in toluene with an  $H_2$  pressure of 7 bar (Table 1). The catalyst loading was of 5.3 mol% based on the number of In atoms. The crude reaction was directly analyzed using  $^1H$  NMR (Figure 4). At 100 °C, no reproducible conversion of phenylacetylene in styrene was recorded both in absence and presence of  $PPh_3$  (entries 1-6). Instead, low amounts of acetophenone were detected at 2.63 ppm and 7.99 ppm, the oxidation reaction being presumably catalyzed by the metal oxide. Increasing the reaction temperature to 150 °C led to a higher oxidation yield in acetophenone (6 % vs 2 % on average at 100 °C) and to the hydrogenation of  $PhCCH$  in styrene with a modest yield between 2 % and 10 % (entries 7-9). Though low, this conversion attested the catalytic activity of  $c-Bi_{0.02}In_2O_3$  as no hydrogenation occurred without catalyst. At 200 °C, 25 % of the initial phenylacetylene were recovered at the end of the reaction while the combined yields of styrene and acetophenone accounted for only 12 to 20 % (entries 10-11). Ill-defined signals appeared in the aromatic region in  $^1H$  NMR, we therefore hypothesized side reactions occurred either on phenylacetylene or on the formed styrene, for instance oligomerization reactions. The possible effect of the addition of a phosphine at 150 °C or 200 °C is in the error bar of the conversion yield and we cannot conclude at this stage on the possible synergy between the NPs and the molecular base on  $H_2$  activation.

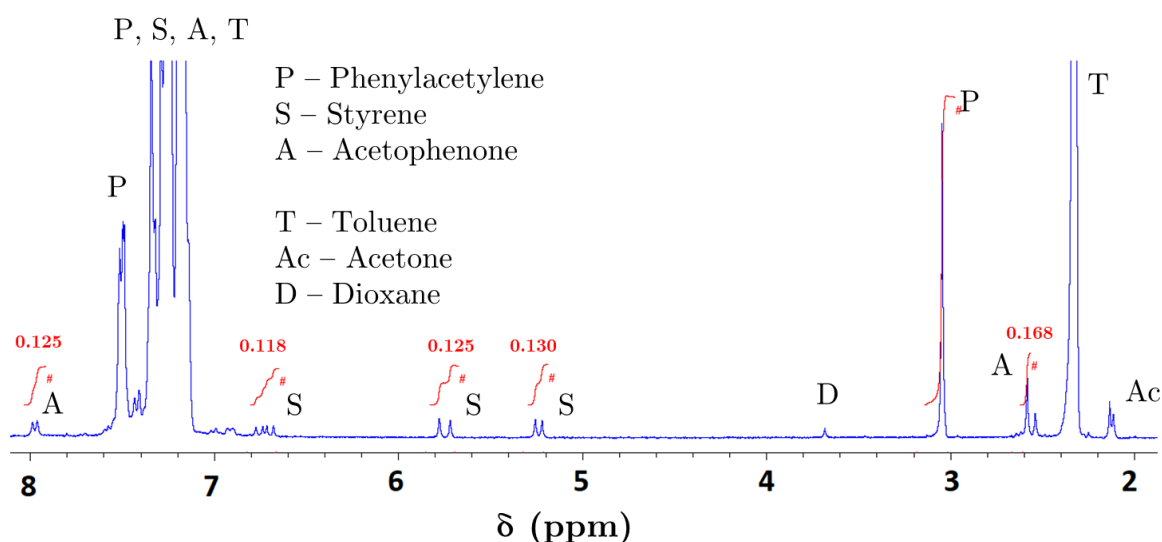


Figure 4.  $^1H$  NMR spectrum of crude reaction phenylacetylene in toluene at 150 °C in presence of  $Bi_{0.02}In_2O_3$ . Traces of acetone and dioxane do not originate from the synthesis.





	Catalyst (5.3 mol%)	Phosphine (10 mol%)	Temp.	PhCCH conversion	Styrene yield	Acetophenone yield
1	c-Bi <sub>0.02</sub> In <sub>2</sub> O <sub>3</sub>	-	100 °C	< 10 %	0 %	3 %
2				< 10 %	0 %	2 %
3				< 10 %	0 %	2 %
4		PPh <sub>3</sub>		< 10 %	2 %	1 %
5				< 10 %	0 %	2 %
6				< 10 %	0 %	1 %
7		-	150 °C	10 %	2 %	6 %
8				17 %	10 %	6 %
9				PPh <sub>3</sub>	10 %	3 %
10		-	200 °C	75 %	4 %	8 %
11				PPh <sub>3</sub>	75 %	8 %

Table 1. Hydrogenation of phenylacetylene with indium oxide catalysts. Reaction conditions: 220  $\mu$ L of phenylacetylene (2 mmol), 30 mg of catalyst (0.106 mmol, [In] 5.3 mol%), 1 mL of toluene (9.4 mmol), H<sub>2</sub> (7 bar, 7 mmol), 16 h in autoclave (25 mL). Conversion and yield determined by NMR.

### V.3. Conclusion

In conclusion, two types of indium oxide nanoparticles were synthesized following protocols from literature (c-Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub>, rh-In<sub>2</sub>O<sub>3</sub>) and the bismuth doped one was tested for phenylacetylene hydrogenation in toluene. At 100 °C, no hydrogenation was observed but a low conversion in acetophenone, an oxidation product, occurred. At higher temperatures, 150 °C and 200 °C, styrene was detected as a minor species, in addition to acetophenone. There did not seem to be a strong influence of the presence of PPh<sub>3</sub>. The low activity of the catalyst at these temperatures could have been expected as high hydrogenation rates of acetylene and CO<sub>2</sub> in gas phase were obtained only for temperatures between 230 °C and 300 °C.<sup>1,2</sup>

We suggest complementary experiments could be performed to study the hydrogenation activity of rh-In<sub>2</sub>O<sub>3</sub> as Ozin *et al.* reported a higher activity for this polymorph than for c-In<sub>2</sub>O<sub>3</sub>,<sup>2,10</sup> or to use a model substrate having a chemistry closer to that of CO<sub>2</sub> such as benzaldehyde. Furthermore, we showed in Chapter I that the H<sub>2</sub> pressure has a crucial importance on the gas solubility and therefore on the reaction yields, we estimate catalytic trials at moderate temperatures, *i.e.* 150 °C, but higher H<sub>2</sub> pressures, typically 30 bar, would be worthwhile to conclude on the impact of the phosphine.

## V.4. Bibliography

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## Part 3

### Solvothermal syntheses



## Chapter VI

# Non-aqueous syntheses of molybdenum and tungsten oxides for hydrogenation reactions

In this chapter, we target the use of early transition metal oxides as hydrogenation catalysts in colloidal solutions. There are rare occurrences in literature of the use of these compounds for H<sub>2</sub> activation in solvent. As developed in Chapter I, numerous works on the use of metal oxides for H<sub>2</sub> activation stressed the role of the oxygen defects to create active sites.<sup>3-5</sup> Seebauer *et al.* studied in 2014 the relation between the Fermi level position of a series of metal oxides and their catalytic activity for reactions implying their Lewis acidity.<sup>2</sup> They concluded WO<sub>3</sub> and MoO<sub>3</sub> were the more susceptible to present a strong Lewis acidity on the metallic center. We therefore chose MoO<sub>3-x</sub> and WO<sub>3-x</sub> as potential FLP-like catalysts. A work by Wang *et al.* reported in 2015 the reduction of linear and cyclic olefins as well as of nitroarenes by oxygen deficient tungsten oxide WO<sub>2.72</sub>.<sup>1</sup> They proved the catalytic activity of the material was linked to the presence of defects, the reaction rate was indeed directly proportional to the surface oxygen vacancies density. A DFT study supported this conclusion: the H<sub>2</sub> splitting was found to be more favorable on WO<sub>2.72</sub> than on WO<sub>3</sub> on both the thermodynamical and kinetical aspects. To the best of our knowledge, there is no mention of molybdenum oxide as a stand-alone hydrogenation catalyst in solvent.

To minimize the surface hydroxyl group density which would occupy the oxygen vacancy sites and potentially protonate the molecular co-catalyst, we performed the syntheses in non-aqueous conditions. Furthermore, this synthetic pathway also leads to organophilic surface ligands that will improve the colloidal stability of the metal oxides during catalysis.

Different goals were pursued in this chapter:

- (1) Synthesizing molybdenum and tungsten oxides following non aqueous pathways and characterizing their surface state (surface ligands, active sites) for catalytic applications
- (2) Reproducing the results obtained by Wang *et al.* on the use of W<sub>18</sub>O<sub>49</sub> for hydrogenation reactions and extending them to the use of MoO<sub>x</sub> particles
- (3) Studying the impact of the addition of a cocatalyst, such as a tertiary phosphine, as mentioned for cerium oxide and indium oxide catalysts in Chapters IV and VI

We developed in the first section (VI.1.) the study of the non-aqueous syntheses of tungsten oxide ( $W_{18}O_{49}$ ) and molybdenum oxide ( $MoO_x$ ,  $2 < x < 3$ ) nanoparticles. For this last material, a more in-depth study of the synthesis was required than for  $W_{18}O_{49}$  due to the difficulty to characterize it by XRD. The materials were then tested in section VI.2. for hydrogenation reactions of nitrobenzene and phenylacetylene. This last section only reports preliminary data.

## VI.1. Non-aqueous metal oxide syntheses in high boiling point solvents

In a solvothermal nanoparticle synthesis, the solvent molecule may have different roles beyond the sole one of reaction medium: it may be the reducing agent if the degree of oxidation of the metal center diminishes,<sup>6</sup> it may provide light elements by decomposition for non-purely metallic particles syntheses (oxide<sup>7,8</sup> carbide,<sup>9</sup> phosphide<sup>10</sup>) and it may ensure the stability of the colloidal suspension by playing the role of ligand. This versatility allows simple reactions to be run with only one metal precursor, typically a metal chloride, alkoxide, acetate or acetylacetonate complex, and one liquid reagent, typically oleylamine or benzyl alcohol.<sup>11,12</sup> But this versatility also complicates the understanding of the reaction mechanisms as the organic and inorganic processes are intertwined. Correlating the two aspects requires the use of multiple characterization techniques: NMR (Nuclear Magnetic Resonance), GC-MS (Gas Chromatography – Mass Spectrometry) and FTIR (Fourier Transform Infrared) to monitor the molecular species transformations and XRD (X-Ray Diffraction), XAS (X-Ray Absorption), XPS (X-Ray Photoelectron Spectroscopy), SAXS (Small Angle X-Ray Scattering) and electron microscopy for the inorganic counterpart (crystal phase, local environment of the atoms, degree of oxidation, morphology).<sup>6,12-15</sup>

Our approach focuses here on the understanding of the mechanism leading to the NPs formation. Indeed, we target a fine understanding of the surface state: what are the surface ligands, what is the environment of the surface metal atoms. These points are crucial for the catalytic reactions envisioned and will be addressed through a use of a combination of organic (NMR) and inorganic (XRD, XAS, electron microscopy) characterization techniques. To simplify the system and therefore its rationalization, we used solvents which are classical reaction media for non-aqueous NPs syntheses and basic precursors ( $WCl_6$  and  $MoO_2(acac)_2$ ). We present here a study of the syntheses of tungsten and molybdenum oxides in high boiling point solvents (oleylamine, oleic acid and oleyl alcohol) and in mixtures thereof.

### VI.1.1 Tungsten oxide $W_{18}O_{49}$ nanowires

We first reproduced the synthesis reported by Leite *et al.* for the synthesis of tungsten oxide nanowires ( $W_{18}O_{49}$ ) in a mixture oleyl alcohol/oleylamine (8/0.5) (v/v) (Synthesis VI.1.).<sup>16</sup>

**Synthesis VI.1. Tungsten oxide nanowires.** In a 25 mL three-necked round-bottom flask, 8 mL of oleyl alcohol (OAl) (25.2 mmol, 66 equiv.) and 0.5 mL of oleylamine (OAm) (1.51 mmol, 4 equiv.) were degassed under vacuum at r.t. during 20 min and the flask was purged with  $N_2$  three times. Under  $N_2$ , 150 mg of  $WCl_6$  (0.38 mmol, 1 equiv.) were added to the solution. The resulting yellow solution was heated up to 220 °C under stirring. It turned violet-blue at approximately 80 °C and white fumes appeared at 120 °C. The solution became dark blue at 170 °C and was let to react 2 h 30 at 220 °C. After cooling to r.t. under  $N_2$ , acetone (10 mL) was added to the crude solution and a dark blue solid was isolated by centrifugation (9,000 rpm, 10 min, 20 °C). The blue supernatant was removed and the particles were redispersed in toluene (2 mL), precipitated by adding acetone (4 mL) and centrifugated. This operation was repeated another time. The obtained blue-violet powder (78 mg, 91 % yield) was then dried under  $N_2$  and stored under inert atmosphere.

The XRD of the obtained powder, displayed on Figure 1A, is attributed to an oxygen-deficient tungsten oxide  $W_{18}O_{49}$  [PDF card N°00-064-0773]. No calculations of the Scherrer size of the crystallites can be performed considering the large width of the peaks: the characteristic size is below 5 nm for the peaks (200), (202) and (240) at respectively 28.2°, 37.0° and 56.7°. The diffraction peaks corresponding to the lattice planes (020) and (040) at 23.5° and 48.1° are thinner than the (200), (202) and (240) ones, indicating the objects are anisotropic with the **b** axis as the preferential direction (Figure 1E). Transmission Electron Microscopy reveals the objects are nanowires, 100-500 nm long and 1-2 nm wide (Figure 1B-C). The highly anisotropic morphology is coherent with the XRD peaks of different width depending on the crystallographic direction: the nanowires have grown along the **b** direction. The electron diffraction pattern is in line with the XRD with two intense rings corresponding to the (020) and (040) diffraction planes (Figure 1D).

Depending on the batch, the powder color varied from royal blue to petrol blue. As comparison, tungsten trioxide ( $WO_3$ ) is yellow-green. The blue color in oxygen-deficient tungsten oxides is due to a cation-to-cation charge transfer between  $W^{(VI)}$  and a reduced tungsten atom,  $W^{(V)}$  or  $W^{(IV)}$ .<sup>17</sup> These two lower oxidation states are allowed by the loss of oxygen atoms in  $W_{20}O_{58}$  ( $WO_{2.9}$ ) and  $W_{18}O_{49}$  ( $WO_{2.72}$ ) but are absent of  $WO_3$ .



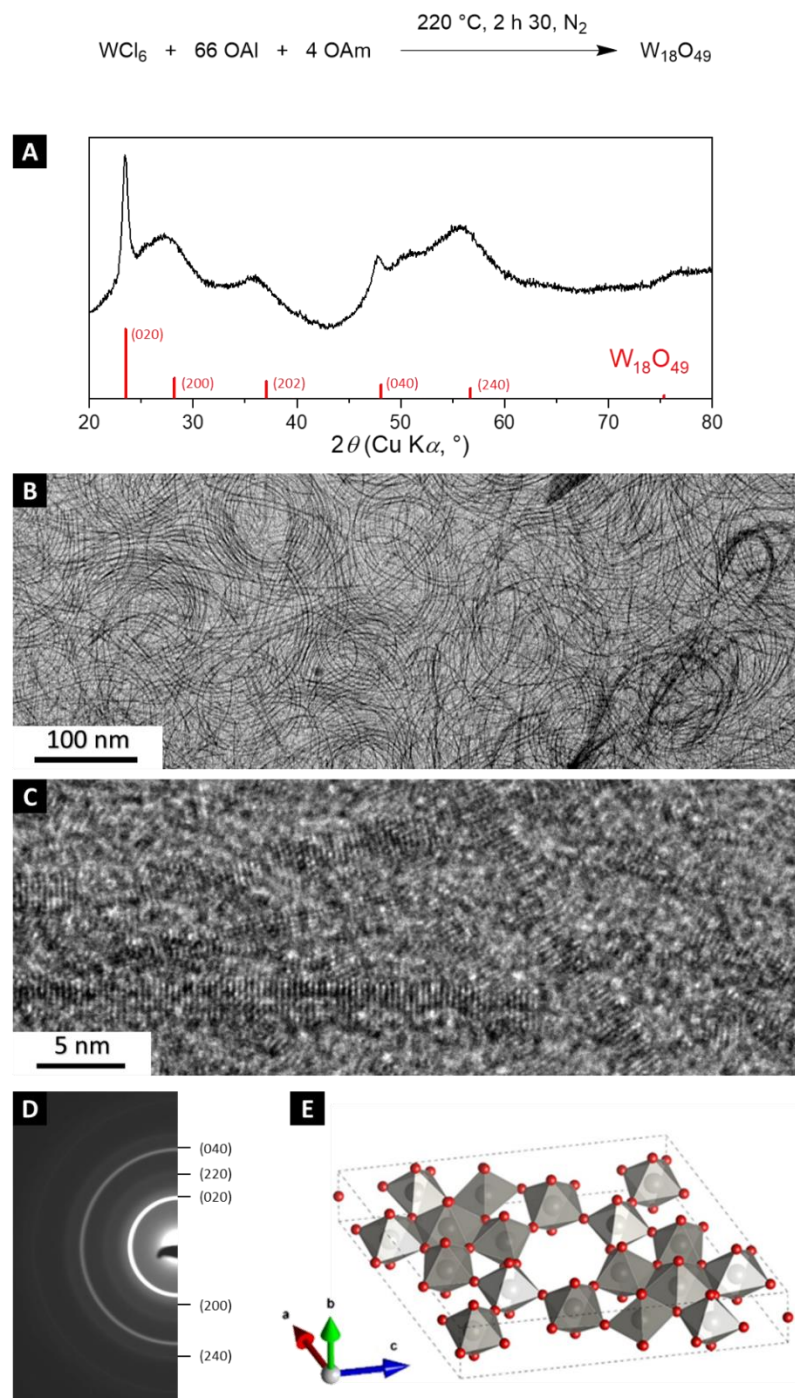


Figure 1. Synthesis and characterization of  $\text{W}_{18}\text{O}_{49}$  nanowires with (A) powder XRD with (hkl) attributions, (B-C) TEM images and (D) electron diffraction pattern. (E) Crystal structure of  $\text{W}_{18}\text{O}_{49}$  (red: oxygen, grey; tungsten). Picture created with Vesta software.<sup>18</sup>

On the first attempts at synthesizing  $\text{W}_{18}\text{O}_{49}$  nanowires,  $\text{W}(0)$  was systematically detected in XRD (peaks at  $40^\circ$ ,  $58^\circ$  and  $73^\circ$ , Figure 2). These peaks, corresponding to an minor species, were only detected because the XRD signal of the main product ( $\text{W}_{18}\text{O}_{49}$ ) was particularly broad. We first hypothesized the metallic tungsten may originate from a reduction by oleylamine as this last molecule is known for being a

reducing agent when nanoparticles are formed from  $M(\text{acac})_2$ .<sup>11</sup> We therefore explored sets of conditions in order to limit this reduction reaction, playing on the OAl/OAm/OAc ratio and on the reaction temperature (Table 1). For OAl/OAm ratios of 8/3, 8/1 and 8/0.5 at 220 °C, the W(0) peaks were always present (Figure 2, entries 1-3). The absence of oleylamine or its substitution by oleic acid also led to a material identified as  $W_{18}O_{49}$  by XRD but the syntheses were much more explosive and had to be stopped before their ends (Figure 2, entries 4-5). Moreover, TEM images revealed ill-formed agglomerated particles rather than well dispersed nanowires. We concluded the presence of oleylamine was essential to the formation of the tungsten oxide nanowires, probably as a ligand molecule. When reaction temperature was set to 260 °C, hexagonal tungsten trioxide ( $WO_3$ ) 100 nm large cube-like nanoparticles were obtained in addition of the  $W_{18}O_{49}$  nanowires (Figure 2, entry 6).

	Oleyl alcohol (OAl)	Oleylamine (OAm)	Oleic acid (OAc)	Temperature	XRD phase attribution	Morphology
1	8 mL	3 mL	-	220 °C	$W_{18}O_{49} + W(0)$	Nanowires
2	8 mL	1 mL	-	220 °C	$W_{18}O_{49} + W(0)$	Nanowires
3	8 mL	0.5 mL	-	220 °C	$W_{18}O_{49} + W(0)$	Nanowires
4	8 mL	-	-	220 °C	$W_{18}O_{49} + W(0)$	Ill-shaped
5	8 mL	-	0.5 mL	220 °C	$W_{18}O_{49} + W(0)$	Ill-shaped
6	8 mL	1 mL	-	260 °C	$WO_3$	Cubes
7	8 mL	0.5 mL	-	240 °C	$W_{18}O_{49} + W(0)$	Nanowires
8 <sup>a</sup>	8 mL	0.5 mL	-	240 °C	$W_{18}O_{49} + W(0)$	Nanowires
9 <sup>b</sup>	8 mL	0.5 mL	-	220 °C	$W_{18}O_{49}$	Nanowires

Table 1. Sets of conditions for  $W_{18}O_{49}$  nanowires syntheses from Synthesis VI.3. <sup>a</sup> $WCl_6$  from Strem Chemicals. <sup>b</sup> $WCl_6$  from Sigma Aldrich, purified by sublimation.

Finally, considering as unlikely that tungsten was reduced to its metallic state from  $W^{(VI)}$ , we investigated whether the W(0) was already present in the metal hexachloride precursor ( $WCl_6$ ). PXRD of the commercial  $WCl_6$  powder from Sigma-Aldrich was recorded and revealed traces of W(0) in addition of  $\alpha$ - $WCl_6$  at 73.3° (Figure 3). We therefore used  $WCl_6$  from two different providers (Sigma Aldrich and Strem Chemicals) but the same W(0) residual signal was observed in both cases (Figure 2, entries 7-8). These traces were certainly a leftover of the chlorination of W(0) by  $Cl_2$  for the  $WCl_6$  production. The commercial precursor was purified by sublimation (experimental procedure for sublimation described in Appendix I ES.1.) and no W(0) signal was recorded anymore on the final diffractograms of the  $W_{18}O_{49}$  nanowires

(Figure 2, entries 9). For the rest of the work and the catalysis section, we only used purified  $WCl_6$ . This  $W(0)$  signal was also present, although not commented, in the work of Leite<sup>16</sup> but not in the one of Niederberger.<sup>7</sup>

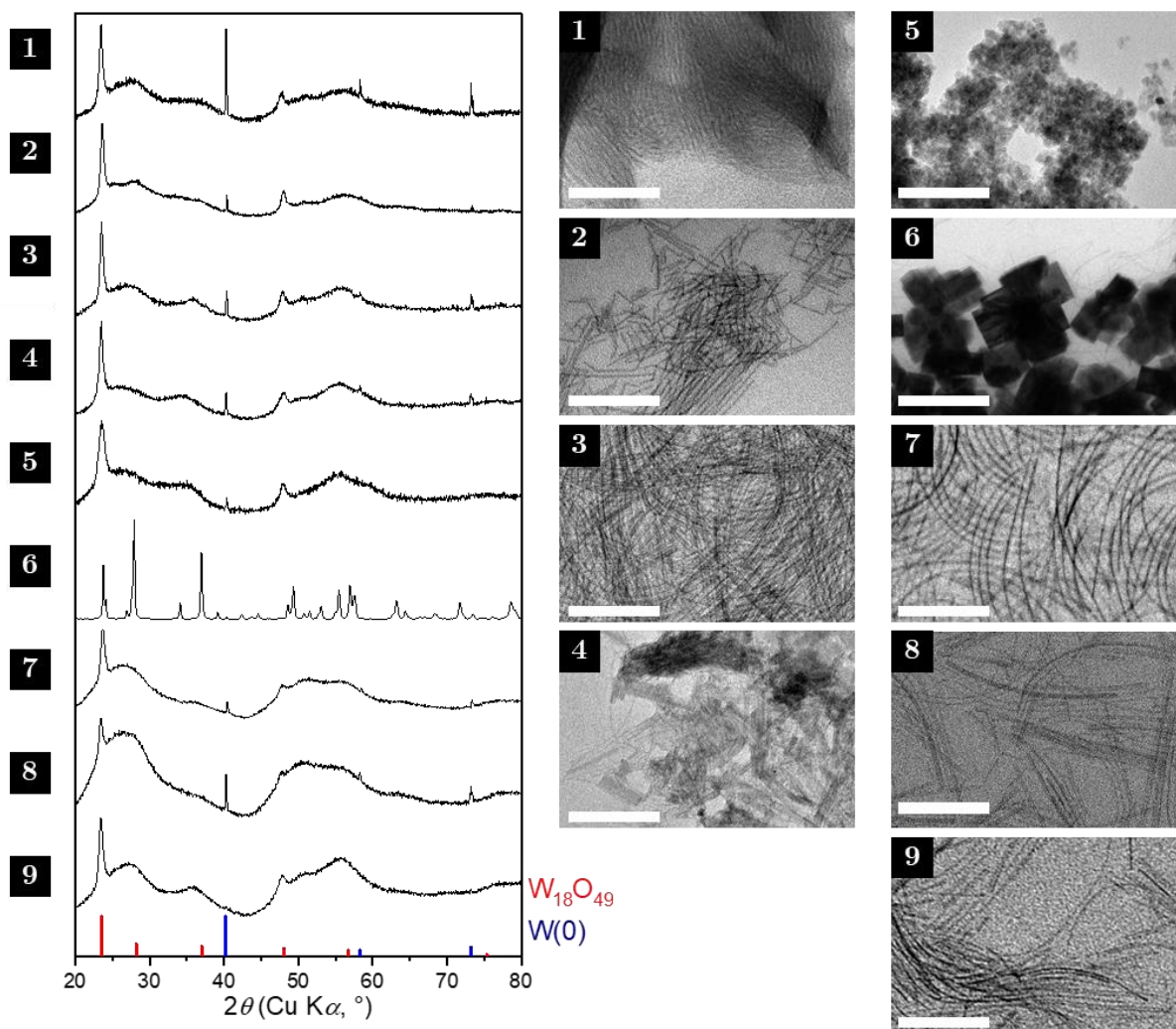


Figure 2. Powder X-ray diffractograms and TEM images of tungsten oxides for different sets of experimental conditions (numbers refer to Table 1). Dispersion solvent was THF for (1) and hexane for (2-9). The scale bar represents 50 nm, except for (6) where it represents 200 nm.

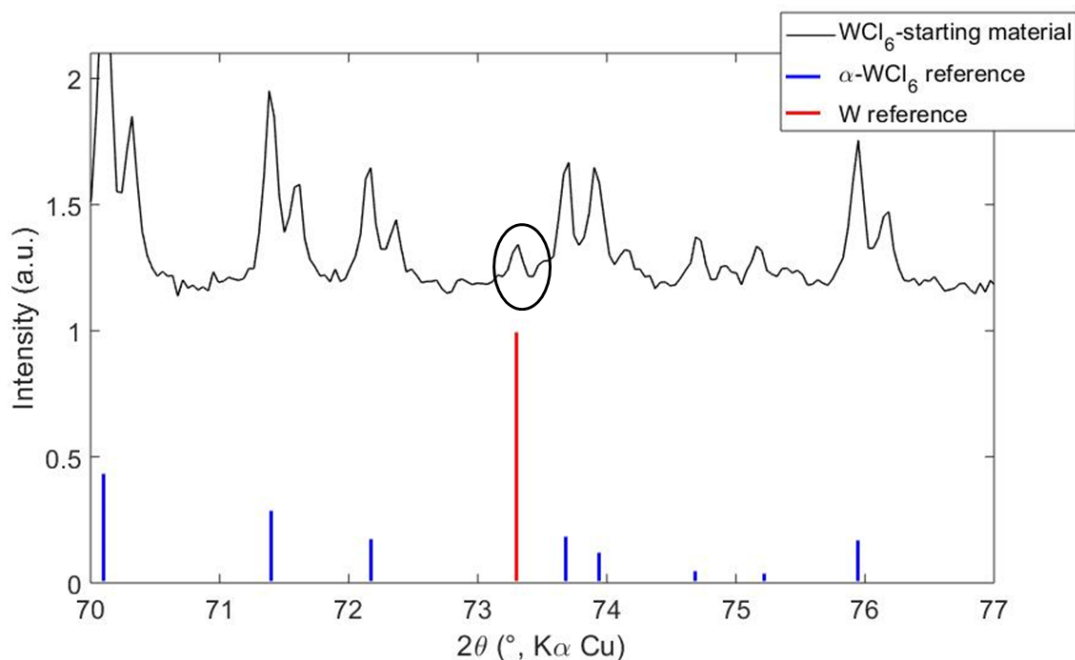


Figure 3. Zoom on the XRD pattern of the  $\text{WCl}_6$  precursor from Sigma-Aldrich. All diffraction peaks are doublet as the X-ray beam from the copper anode is not perfectly monochromatic but comports two contributions,  $\text{K}\alpha_1$  and  $\text{K}\alpha_2$ .

### VI.1.2 Molybdenum oxide nanoparticles

We then attempted a synthesis of  $\text{MoO}_x$  ( $2 < x < 3$ ) nanoparticles by thermal decomposition of  $\text{MoO}_2(\text{acac})_2$  in pure oleylamine (OAm) (Synthesis VI.2.) or oleic acid (OAc) (Synthesis VI.3.). This synthetic pathway is at the intersection of a work by Tatsuma *et al.* synthesizing oxygen deficient molybdenum oxides in fatty acids from  $\text{MoO}_2(\text{acac})_2$ ,<sup>19</sup> and of Niederberger *et al.* using  $\text{MoO}_2\text{Cl}_2$  as precursor in a mixture benzyl alcohol/acetophenone to synthesize  $\text{MoO}_2$  nanoparticles.<sup>13</sup> In this last work, the authors described a complete study of the synthesis mechanism with *in situ* XAS measurements.

**Synthesis VI.2. Molybdenum oxide nanoparticles in OAm.** In a round-bottom flask, 10 mL of oleylamine (OAm) (30.4 mmol, 66 equiv.) were degassed under vacuum at r.t. during 20 min and the flask was purged with N<sub>2</sub> three times. Under N<sub>2</sub>, 150 mg of MoO<sub>2</sub>(acac)<sub>2</sub> (0.46 mmol, 1 equiv.) were added to the solution. The resulting pale-yellow solution was heated up to 220 °C under agitation and turned gradually from pale yellow to dark brown between 85 °C and 125 °C. Condensation of a colorless liquid was observed at 115 °C. The solution was let to react 2 h at 220 °C. After cooling to r.t. under N<sub>2</sub>, methanol (10 mL) was added to the crude solution and a brown solid was isolated by centrifugation (9,000 rpm, 10 min, 20 °C). The supernatant was removed and the particles were redispersed in toluene (5 mL), precipitated by adding methanol (10 mL) and centrifugated. This operation was repeated another time. The obtained brown powder (63 mg) was then dried under a flux of N<sub>2</sub> and stored in air.

[*Caution*] OAm and OAc are degraded upon heating if exposed to air, emitting acrid smokes and irritating white fumes. Their respective smoke points are situated *ca.* 150 °C and 120 °C respectively.

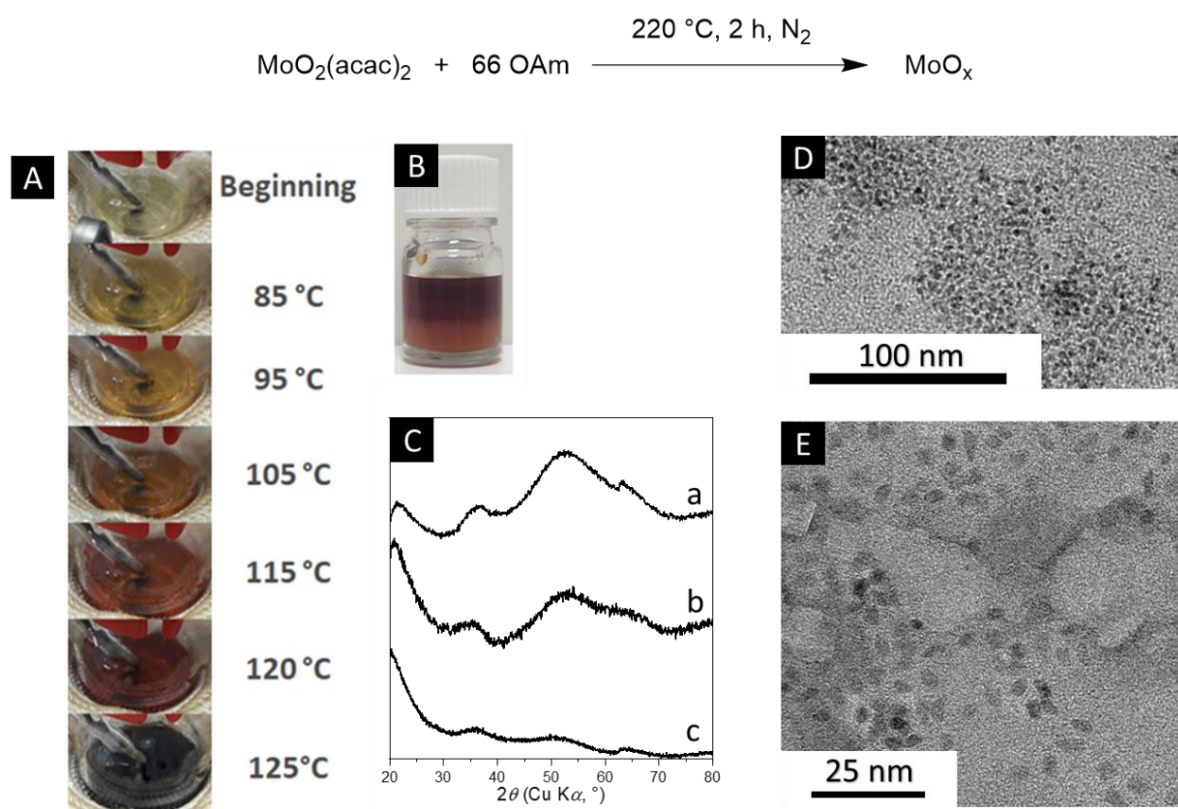


Figure 4. Molybdenum oxide synthesis from MoO<sub>2</sub>(acac)<sub>2</sub> in OAm according to Synthesis VI.2. (A) Color evolution and (B) final state of the solution. (C) XRD of the powders when solvent was decylamine (DAm) (a) ( $T_{\text{reaction}} = 217 \text{ }^\circ\text{C}$ ) and OAm (b-c). (D-E) TEM images of nanoparticles synthesized in OAm.

**Synthesis VI.3. Molybdenum oxide nanoparticles in OAc.** In a round-bottom flask, 10 mL of oleic acid (OAc) (32 mmol, 69 equiv.) were degassed under vacuum at r.t. during 20 min and the flask was purged with N<sub>2</sub> three times. Under N<sub>2</sub>, 150 mg of MoO<sub>2</sub>(acac)<sub>2</sub> (0.46 mmol, 1 equiv.) were added to the solution. The resulting yellow suspension (solid not dissolved) was heated up to 220 °C under agitation. At approximately 50 °C, the solid dissolved and the solution turned dark blue within a few minutes *via* green and turquoise. The solution turned gradually from blue to dark brown between 100 °C and 140 °C. The solution was let to react 2 h at 220 °C and then let to cool down to r.t. under N<sub>2</sub>. The nanoparticles could not be isolated by addition of a counter-solvent (acetone, EtOH, MeOH). They were stored as a stable suspension in OAc under N<sub>2</sub>. The solution turned green-grey after a few hours if exposed to air.

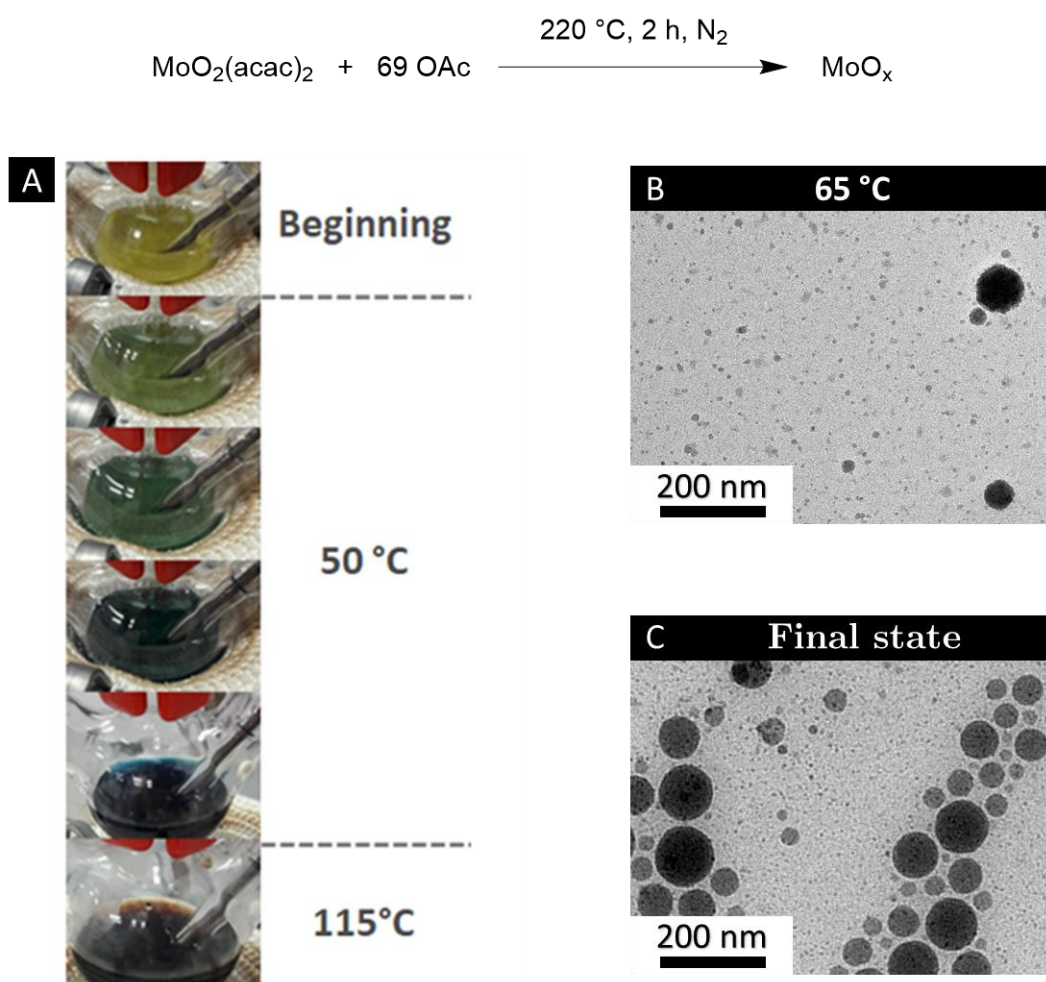


Figure 5. Molybdenum oxide synthesis from MoO<sub>2</sub>(acac)<sub>2</sub> in OAm according to Synthesis VI.3. (A) Color evolution of the solution. TEM images of (B) an aliquot collected at 65 °C and (C) of the final state.

**Non aqueous synthesis in OAm.** Synthesis VI.2. reports the synthesis with oleylamine as solvent. The precursor was first dissolved at room temperature and formed a pale-yellow solution, suggesting the formation of a complex between oleylamine and  $\text{MoO}_2(\text{acac})_2$ . Upon heating, the solution gradually turned brown (Figure 4A). This color was attributed to plasmonic transitions in  $\text{MoO}_x$  nanoparticles.<sup>19</sup> The absorbed frequencies depend on the size of the particles and on the density of charge carriers, *i.e.* oxygen defects here.<sup>20</sup> A kinetic study by UV-visible spectroscopy would therefore be of interest to determine whether the apparent colour change from yellow to brown was only due to the nanoparticles concentration or if the characteristic energies of the plasmonic transitions themselves were modified during the reaction. Just after synthesis, the colloidal suspension was stable but a light brown material sedimented along the following hours/days (Figure 4B). The XRD of the collected powder is not informative on the chemical composition of the material because of the broadness of the measured diffractograms (Figure 4C). However, the pattern was reproducible from batch to batch, even when substituting the OAm solvent by the similar one decylamine (DAm) (all other parameters kept identical, including solvent volume). TEM of the material dispersed in THF reveals the presence of elongated nanoparticles (Figure 4D-E). Their typical size is close to 2 nm, in line with the broad diffractogram features. Based on close works of reduction of  $\text{MoO}_2(\text{acac})_2$  in fatty acids,<sup>19</sup> we can suggest the obtained material was an amorphous molybdenum oxide and will be referred to as  $\text{MoO}_x$ -OAm in the following.

**Non aqueous synthesis in OAc.** In Synthesis VI.3 in oleic acid and contrarily to Synthesis VI.2., the precursor  $\text{MoO}_2(\text{acac})_2$  did not dissolve as a pale-yellow solution but rather stayed suspended as yellow aggregates (Figure 5A). Upon heating to 50 °C, the yellow solid disappeared to form a deep blue solution. Aliquots were collected at different times of the reaction to perform UV-vis measurements but the color of the solution changed to dark green in a few seconds once removed from the  $\text{N}_2$  protected round bottom flask. This color change was probably due to the oxidation of molybdenum species when exposed to air. We observed the transition from the yellow ill-dissolved  $\text{MoO}_2(\text{acac})_2$  precursor to the blue solution also occurred at room temperature on longer timescales, typically a few days.

We could not determine whether the blue color displayed between 50 °C and 100 °C correspond to plasmonic transitions in the molybdenum oxide nanoparticles already formed or from the color of a molybdenum dioxo complex. One could imagine a neutral complex  $[\text{MoO}_2(\text{OAc})_2]$  between a  $[\text{MoO}_2]^{2+}$  moiety and oleate ions. The complex geometry would be either a tetrahedron, a distorted octahedron with the carboxylate ligands coordinating the metal in a  $\kappa^2(\text{O},\text{O}$ -bidentate) mode,<sup>21</sup> or even a polynuclear species. We could not find any mention in the literature of a  $[\text{MoO}_2]$ -oleate complex but oleate complexes of a large range a metals ( $\text{Zn}^{22}$ ,  $\text{Cd}^{22}$ ,  $\text{Fe}^{23,24}$ ,  $\text{Mn}^{25}$ ) leading to NPs by thermal decomposition are reported. These oleate complexes generally have

ill-defined stoichiometries with dynamic structures, making them difficult to describe.<sup>24</sup> Resolving the structure of this hypothetical molybdenum complex was beyond the scope of this work.

When the temperature was increased above 120 °C, the suspension turned brown, just as with pure OAm (Figure 5A). We interpreted this last evolution as the formation of molybdenum oxide nanoparticles and the quasi-total consumption of the blue coloured complex if it existed. No XRD study was performed on MoO<sub>x</sub>-OAc as the powder could not be isolated by addition of a counter-solvent. The suspensions were stable for at least 6 months under ambient conditions in air. TEM of the final solution reveals the presence of spherical nanoparticles (Figure 5C). The particles are polydisperse with diameters ranging from 10 to 200 nm. TEM of an aliquot collected at 65 °C already displays the presence of spherical nanoparticles: they seem smaller (up to 60 nm in diameter) than at the end of the reaction but the large polydispersity in size renders size measurement by TEM delicate. We envision a kinetic study of the morphology by collecting aliquots at different moments of the reaction course. Electron microscopy is by essence a technique which is not representative of the whole sample, we therefore used other techniques sensitive to the average signal, such as XAS mentioned later.

**Non aqueous synthesis in OAm/OAc mixture.** Finally, the reaction was run in a mixture of both solvents OAm/OAc (90:10) (v:v). The color evolution of the reaction medium was similar to the one with pure OAm and the XAS spectrum of the liquid crude at the end of the reaction was very close to that of pelletized MoO<sub>x</sub>-OAm from Synthesis VI.2. (*cf.* below Figure 8). The suspension was as stable as the reaction in pure OAc. These observations suggest the dominant synthesis mechanism was the one associated with OAm as solvent but that the OAc molecules helped at the nanoparticles suspension stability and prevented the sedimentation. We conclude oleate ions are excellent ligands for these metal oxides in organic solvents. Considering the hydrophobic moieties of OAc and OAm are the same, we interpret the sedimentation with OAm as the absence of tight bond between the nanoparticle and the amine ligand. Although the stability of the suspension is limited, the loose coordination of the OAm molecules compared to the oleate ions at the nanoparticle surface favors the approach of substrate molecules in the context of catalysis.

**NMR study.** <sup>1</sup>H solution NMR was performed on reaction crudes to enlighten the molecular reactions at stake during the nanoparticle syntheses. The <sup>1</sup>H NMR spectrum of MoO<sub>2</sub>(acac)<sub>2</sub> in CDCl<sub>3</sub> was first recorded under ambient conditions (Figure 6C). Signals measured at 5.80 ppm (H<sup>8</sup>), 2.16 ppm (H<sup>7,9</sup>) and 2.14 ppm (H<sup>7,9</sup>), all singlets, correspond to respectively the ethylenic and the methyl protons of the bound acac<sup>-</sup> ligands in MoO<sub>2</sub>(acac)<sub>2</sub>.<sup>26</sup> Free acetylacetonone (acacH) was also detected as an equilibrium between the dione, at 3.60 ppm (H<sup>1</sup>, CH<sub>2</sub> singlet) and 2.24 ppm (H<sup>2</sup>,



two CH<sub>3</sub> singlet), and the enol tautomer, at 15.46 ppm (H<sup>6</sup>, OH singlet), 5.50 ppm (H<sup>4</sup>, CH singlet) and 2.05 ppm (H<sup>3,5</sup>, two CH<sub>3</sub> singlet). Although the two methyl groups of the enol tautomer are chemically different, their chemical shifts are close enough to appear as a singlet. Free acetylacetone was detected in a solution of MoO<sub>2</sub>(acac)<sub>2</sub> in CDCl<sub>3</sub> even when using dried aprotic solvents and freshly sublimed MoO<sub>2</sub>(acac)<sub>2</sub>.<sup>26</sup>

We prepared a highly concentrated suspension of MoO<sub>2</sub>(acac)<sub>2</sub> in oleic acid to be in capacity to detect organic products of the nanoparticle synthesis. The solution **A** (5 OAc molecules per MoO<sub>2</sub>(acac)<sub>2</sub>) was heated to 50 °C and produced a blue solution. The NMR spectrum of this solution **A** displays signals of MoO<sub>2</sub>(acac)<sub>2</sub>, acetylacetone and oleic acid but no other product (data not shown). We cannot consider the presence of acacH in the <sup>1</sup>H NMR spectrum at 50 °C as a proof of the protonation of acac<sup>-</sup> by oleic acid as free acetylacetone signals were already present in the NMR spectrum of MoO<sub>2</sub>(acac)<sub>2</sub>. The concentrated solution **A** was then heated in a close reaction tube at 200 °C during two hours: it turned brown, as observed in Synthesis VI.3. After reaction, no MoO<sub>2</sub>(acac)<sub>2</sub> was detected anymore by <sup>1</sup>H NMR and the signal of acetylacetone was more intense (Figure 6A). An integration of the peaks gave a final ratio 5:1 for OAc:acacH, to be compared with the ratio 5:2.2 for OAc:acac<sup>-</sup> at 50 °C: not all the acetylacetonate ligands produced free acetylacetone. We do not have hypothesis on the molecular reactions at stake. At the end of the reaction, two intense peaks appeared at 2.09 ppm and 2.17 ppm (stressed by black arrows on Figure 6A) and modest ones at 1.83 ppm and *ca.* 2.5-2.6 ppm. The peak at 2.17 ppm could correspond to acetone but the other ones were not identified. Similar results were obtained with the crude of the regular reaction Synthesis VI.3. conducted in round bottom flask with diluted conditions (69 OAc molecules per MoO<sub>2</sub>(acac)<sub>2</sub>). The new features were less obvious considering the lower initial concentration of MoO<sub>2</sub>(acac)<sub>2</sub> and the evaporation of volatile compounds (T<sub>boiling</sub>(acacH) = 140 °C). We concluded the molybdenum precursor MoO<sub>2</sub>(acac)<sub>2</sub> was entirely consumed to produce inorganic molybdenum species, presumably molybdenum oxides, and that there was a limited transformation of the solvent OAc (Figure 6A-B).

Xia *et al.* recently published a mechanistic study of the formation of Pt nanoparticles from Pt(acac)<sub>2</sub> while using oleic acid as solvent.<sup>27</sup> The authors reported the formation of Pt<sup>(II)</sup>-oleate complex at 80 °C which were then decomposed in nanoparticles at 120 °C. The reduction of the metal center was associated to the decarbonylation/decarboxylation of OAc in CO/CO<sub>2</sub> and an alkyl chain. Hyeon *et al.* proposed a similar mechanism for the decomposition of Fe<sup>(III)</sup>-oleate in Fe<sub>3</sub>O<sub>4</sub> nanoparticles: they suggested the decomposition of metal carboxylates produced thermal free radicals R·, RCOO· and RC·O.<sup>28</sup> Similar mechanisms could be considered here for the decomposition in MoO<sub>x</sub> (Scheme 1).

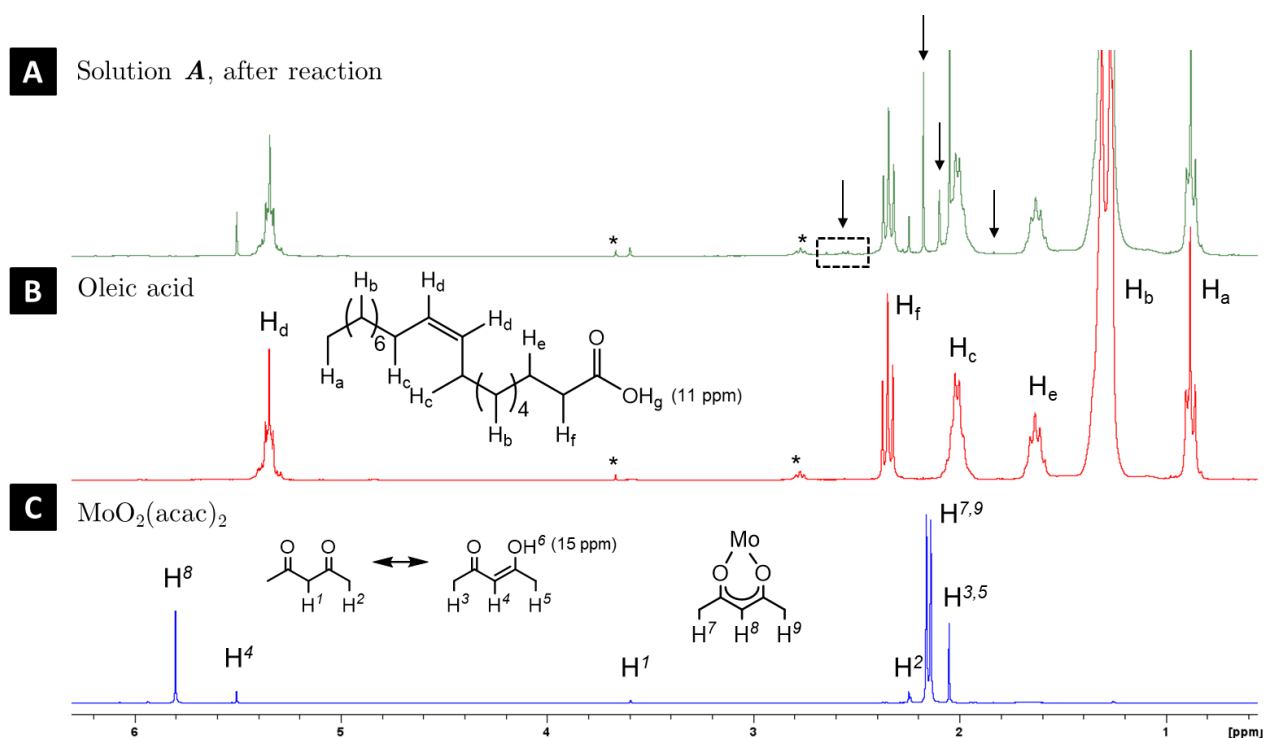
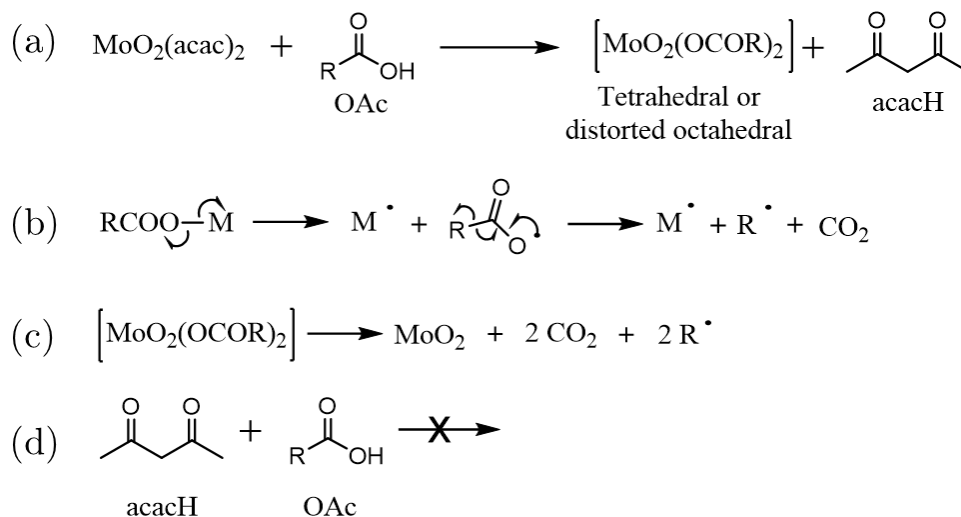


Figure 6.  $^1\text{H}$  NMR spectra of (A) solution **A** after reaction, (B) oleic acid and (C)  $\text{MoO}_2(\text{acac})_2$  in  $\text{CDCl}_3$ . Asterisks indicate impurities in OAc and the black arrows the main new features corresponding to neither OAc nor acetylacetonate.



Scheme 1. Proposed reaction mechanism with OAc. (a) Ligand exchange with OAc, (b) reductive decarboxylation, (c) decarboxylation of the intermediate complex, (d) no reaction between oleic acid and acetylacetonate. R designates the oleyl group.

The same NMR experiments were conducted with OAm as solvent, both in a concentrated solution **A'** (5 OAm molecules per  $\text{MoO}_2(\text{acac})_2$ ) in a close reaction tube at 200 °C and in a diluted one **B'** in round-bottom flask (Synthesis VI.2.) (Figure 7).

For both reactions **A'** and **B'**, no acetylacetonone nor  $\text{MoO}_2(\text{acac})_2$  were detected at the end but new peaks were observed. At the end of reaction **A'**, we noticed the absence of the signal  $\text{H}_f$  at 2.67 ppm of the  $-\text{CH}_2-$  moiety linked to the amino group, denoting the oleylamine solvent has entirely reacted to form new species (Figure 7A). A precedent study on  $\text{Ni}(\text{acac})_2$  reduction by oleylamine reported the condensation of oleylamine on acetylacetonone to form a keto-ene-amine (Scheme 1).<sup>6</sup> The presence of this last molecule was confirmed in our work by a singlet at 10.9 ppm (secondary amine hydrogen atom), one at 4.94 ppm (ethylenic proton of the keto-ene function) and a triplet at 3.30 ppm (proton in  $\alpha$  of the NH group) (Figure 7A, stressed by blue arrows). As for reactions in OAc, the new features observed in  $^1\text{H}$  NMR were less intense for the regular reaction in diluted conditions but were still present (Figure 7B). The oleylamine peaks did not significantly decreased in intensity in **B'** indicating the oleylamine reactivity in the concentrated conditions was linked to a stoichiometric reaction with the precursor and not to a catalytic one with the final nanoparticles.

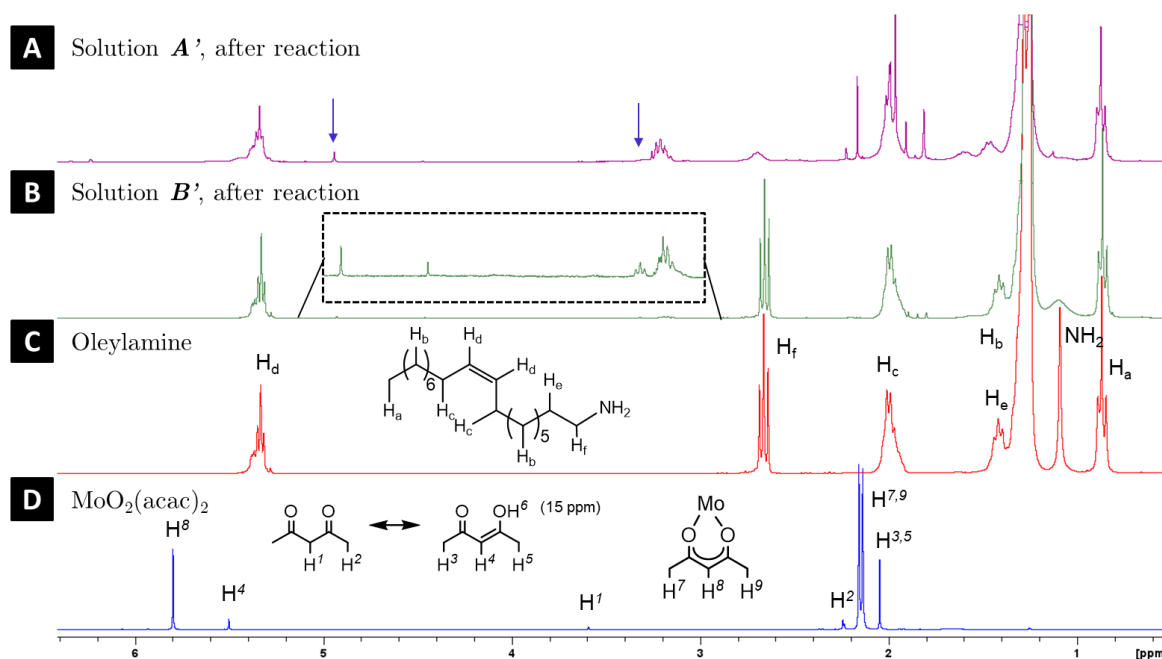
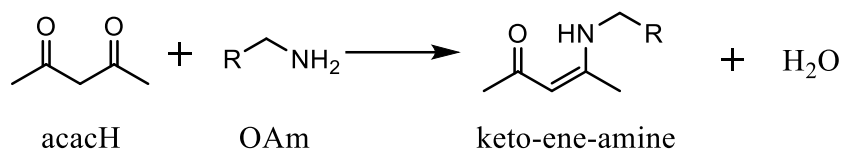


Figure 7.  $^1\text{H}$  NMR spectra of (A) solution **A'** after reaction, (B) solution **B'** after reaction (Synthesis VI.1.), (C) oleylamine and (D)  $\text{MoO}_2(\text{acac})_2$  in  $\text{CDCl}_3$ . Blue arrows indicate the position of the keto-ene-amine peaks.

The molecular mechanisms at stake in the OAc/OAm syntheses are still under investigation but these NMR spectra clearly demonstrate different pathways were followed in OAc and in OAm. This presumably led to different final oxidation degrees for Mo, surface state and nanoparticle ligands. The difference between the two solvents

is still to be rationalized as only a small number of works in literature focused on the reaction mechanisms with pure OAc.<sup>27</sup>



Scheme 2. Condensation reaction between acetylacetone and oleylamine to form a keto-ene-amine. R designates the oleyl group.

**X-ray absorption spectroscopy.** Characterization of the inorganic part was impossible or poorly informative by XRD, we therefore studied the samples by XAS at the Mo K-edge at 20 000 eV to get insight into the molybdenum oxidation states and local environments. The experiments were performed on the ROCK beamline at the SOLEIL synchrotron and details on the protocols are given in Appendix ES.8. Figure 8 displays the XAS spectra of pellets of the precursor  $\text{MoO}_2(\text{acac})_2$ , of two references,  $\text{MoO}_2$  and  $\alpha\text{-MoO}_3$ , and of  $\text{MoO}_x\text{-OAm}$  nanoparticles (fresh and 8 months old). In both  $\text{MoO}_2$  and  $\alpha\text{-MoO}_3$ , the molybdenum atoms are in a distorted octahedral environment. The positions of the edges indicate the synthesized  $\text{MoO}_x\text{-OAm}$  particles (20 018 eV) possess an average oxidation degree for Mo comprised between +IV ( $\text{MoO}_2$ : 20 016 eV) and +VI ( $\text{MoO}_3$ : 20 020 eV,  $\text{MoO}_2(\text{acac})_2$ : 20 019.5 eV), in line with a chemical composition  $\text{MoO}_x$  with  $2 < x < 3$ . Although the  $\text{MoO}_x\text{-OAm}$  pattern looks closer to  $\text{MoO}_2$  than to  $\alpha\text{-MoO}_3$  (double peaks **a** and extremum **b**), the presence of a shoulder **c** in the pre-edge region and the shift of the extremum **d** towards lower energies impend its attribution to  $\text{MoO}_2$ . A linear fit of  $\text{MoO}_2$  and  $\alpha\text{-MoO}_3$  gave poor results: the  $\text{MoO}_x\text{-OAm}$  material is therefore probably a mixture of different molybdenum oxides of intermediate compositions. Upon aging in air,  $\text{MoO}_x\text{-OAm}$  evolved and its XAS spectrum presents an edge shift at higher energy, *ca.* 20 019 eV, corresponding to a higher oxidation state. The intensification of the pre-edge **c**, the disappearance of **a** in favor of a maximum **e** are similar to features displayed by  $\text{Mo}_4\text{O}_{11}$  or *h*- $\text{MoO}_3$ .<sup>29</sup> Besides, the absence of the maximum **f** in old  $\text{MoO}_x\text{-OAm}$  comforts our hypothesis old  $\text{MoO}_x\text{-OAm}$  is not  $\alpha\text{-MoO}_3$ . We also measured in a liquid cell a reference of molybdate  $\text{MoO}_4^{2-}$  in an aqueous solution, the supernatant of the crude of the  $\text{MoO}_x\text{-OAm}_{(\text{liq})}$  synthesis and the  $\text{MoO}_x\text{-OAc}$  solution. The spectrum of the  $\text{MoO}_x\text{-OAm}_{(\text{liq})}$  supernatant presents strong similarities with that of  $\text{MoO}_4^{2-}$ , in particular the important pre-edge at 20 010 eV, the inflexion point *ca.* 20 025 eV and the very flat oscillations in the EXAFS region. The pre-edges are attributed to a forbidden transition  $1s \rightarrow 4d$ , generally relaxed in tetrahedral environment, and to a lesser extent in distorted octahedral geometries. The flat oscillations in the EXAFS region suggest a high disorder, *i.e.*

molecular species or a poorly crystalline object. We concluded not all the molybdenum atoms were consumed for the nanoparticles synthesis in Synthesis VI.2. with OAm and that molecular species, probably with tetrahedral geometry, are still present in the liquid crude. As the edge shift in the supernatant  $\text{MoO}_x\text{-OAm}_{(\text{liq})}$  (20 020.4 eV) is close to the  $\alpha\text{-MoO}_3$  one (20 020 eV), the molybdenum atoms should be at a high oxidation degree, *i.e.* +V or +VI. The absence in the supernatant  $\text{MoO}_x\text{-OAm}_{(\text{liq})}$  of the characteristic features observed in the pelletized sample  $\text{MoO}_x\text{-OAm}$  indicates most of the particles have precipitated out of solution after synthesis.

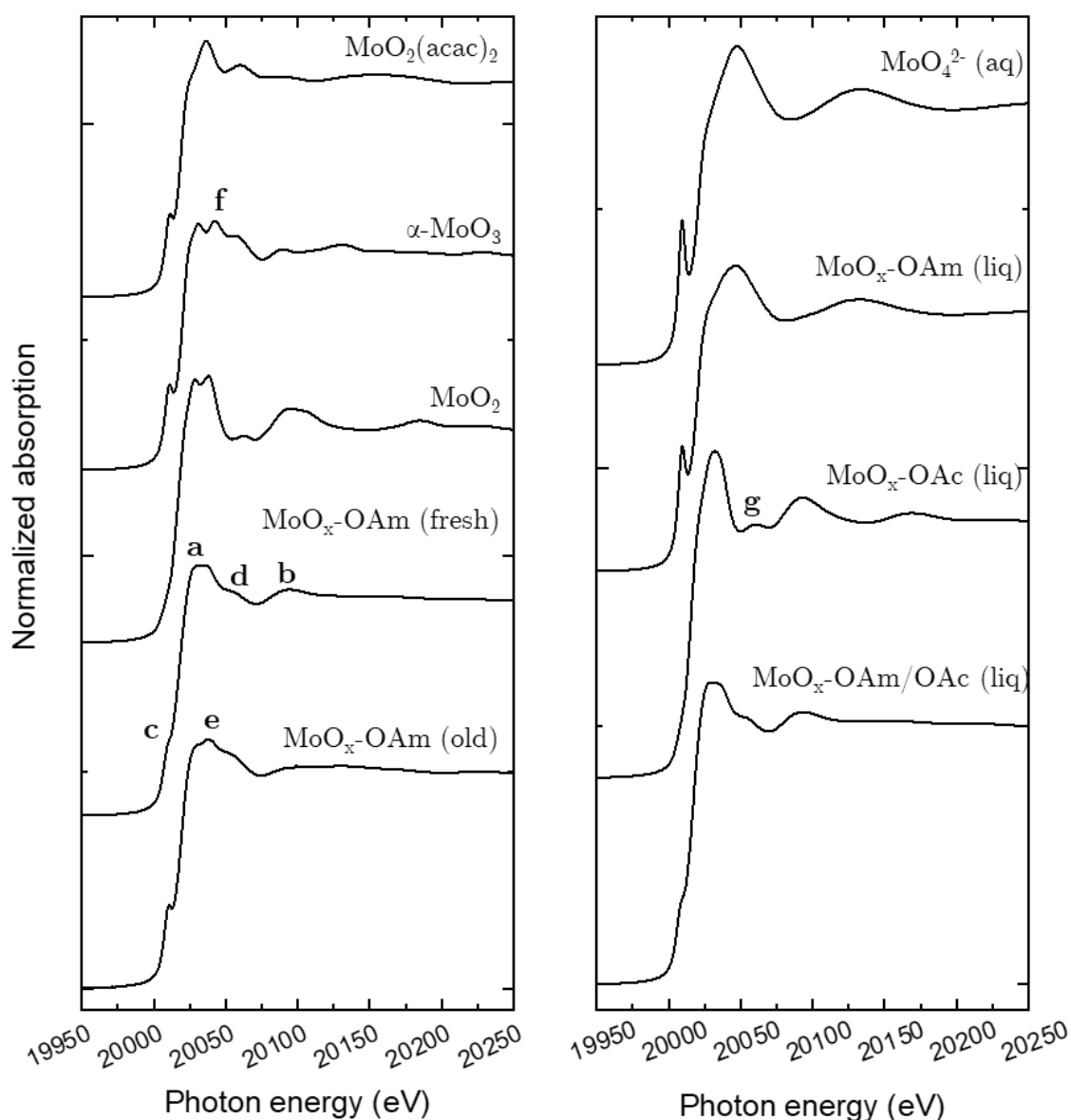


Figure 8. Mo K-edge XAS spectra at 20 000 eV of references  $\text{MoO}_2$ ,  $\alpha\text{-MoO}_3$ ,  $\text{MoO}_2(\text{acac})_2$  and of sample  $\text{MoO}_x\text{-OAm}$  (fresh and 8 months old), measured as pellets in graphite, and of reference  $\text{MoO}_4^{2-}(\text{aq})$  and of samples  $\text{MoO}_x\text{-OAm}$  (crude supernatant),  $\text{MoO}_x\text{-OAc}$  and  $\text{MoO}_x\text{-OAm-OAc}$ , measured in a liquid cell.

The XAS spectrum of  $\text{MoO}_x\text{-OAc}$  corresponds to a species in a reduced environment (edge at 20 015.3 eV) with no pre-edge at all. The XAS fingerprint is close to that of  $\text{MoO}_2$  but with broader features. The maximum  $\mathbf{g}$  is at the same energy that for  $\text{MoO}_2$ , contrarily to the maximum in  $\text{MoO}_x\text{-OAm}$ . We therefore concluded small molybdenum dioxide nanoparticles were formed in Synthesis VI.3., and stayed suspended in solution thanks to the oleic acid capping agent. Moreover, considering the absence of pre-edge, we suggest that limited amount of molecular species are still present in the solution at the end of the reaction, at least none presenting a tetrahedral or strongly distorted octahedral environment.

XAS study clearly demonstrated that the chemical natures of the final objects were different whether OAc or OAm was used as solvent. With oleylamine, intermediate oxides  $\text{MoO}_x$  ( $2 < x < 3$ ) were synthesized whereas poorly crystalline or small  $\text{MoO}_2$  particles were obtained with OAc. The XAS spectrum of the supernatant of the Synthesis VI.2. in OAm strengthened the hypothesis of the formation of a molecular complex between  $[\text{MoO}_2]^{2+}$  and the solvent molecule, OAm in this case. In both Syntheses VI.2. and VI.3., the oxidation state of Mo decreased from +VI in the precursor ( $\text{MoO}_2(\text{acac})_2$ ) to +IV/+V in the product: a modification of the solvent or ligand molecules should therefore be expected as redox reactions were implied.

**XAS *in situ* study.** The reaction progress of Syntheses VI.2. and VI.3. was monitored by *in situ* XAS. The reaction cell used on the beamline was not perfectly air-tight and the solvents burnt and decomposed when heated at temperatures higher than their fume points (respectively 150 °C and 120 °C for OAm and OAc), we therefore limited the reaction temperatures to 140 °C for synthesis in OAm and 120 °C for reaction in OAc (Figure 9A-C). We also added a plateau at 60 °C of 30 min before the ramp toward the highest temperatures. All the XAS spectra were normalized in order to obtain an edge jump of 1. However, studying the actual edge jump value (plotted in red in Figure 9) is an efficient way to determine the evolution of Mo atom concentration in the X-ray beam path. The edge jump thus reflects the dissolution/consumption of the precursor and the stability of the objects in the suspension. The initial precursor concentration was adjusted to target an edge jump of 1 for a total dissolution. A first experiment was conducted without preliminary mixing of the precursor  $\text{MoO}_2(\text{acac})_2$  in OAm (Figure 9A), a second one with preliminary mixing (Figure 9B) and a third one in OAc with preliminary mixing (Figure 9C). XAS spectra at different moments of the reaction are displayed on the right panels of Figure 9. The limited stirring capacity of the device could not permit a total suspension of the precursor grains from beginning. The stirring was intermittent because it was coupled with the heating power, hence the initial edge jumps lower than 1.

In the non-homogenized reaction in OAm, the Mo concentration in solution increased with temperature until a maximum right after the beginning of the plateau

at 140 °C (Figure 9A,D). As the edge jump was close to 1 at the maximum, we estimated all the Mo atoms were put in solution from  $\text{MoO}_2(\text{acac})_2$ . XAS spectrum D1 corresponding to the initial state presents strong similarities with the  $\text{MoO}_4^{2-}$  solution (Figure 8) which strengthens the hypothesis of the complex formation at the early stage of the reaction. The XAS signature evolved between room temperature and 60 °C (spectrum D2) and became close to that of the supernatant of the crude at the end of the reaction (Figure 8,  $\text{MoO}_x\text{-OAm}_{(\text{liq})}$ ). The important pre-edge in D2 suggests a tetrahedral or a distorted octahedral environment while the flat oscillations indicate the Mo atoms are still in molecular species. We concluded there was a modification of the complex upon heating to 60 °C, for instance ligand exchange, rearrangement or dimerization. Upon heating to 140 °C, the spectrum evolved with a decrease of the pre-edge and sharper oscillations (spectrum D3). After 2 h at 140 °C, the tendency was confirmed with a final pattern D4 close to that measured for pelletized  $\text{MoO}_x\text{-OAm}$  (Figure 8,  $\text{MoO}_x\text{-OAm}$  (fresh)). As the XAS signature changed during the plateau at 140 °C, we deduced the thermal decomposition reaction was not immediate at 140 °C. The edge jump diminution from 0.95 to 0.65 during the first hour of the plateau was attributed to the sedimentation of formed particles. The slow increase of the molybdenum concentration after 2 h of reaction might be explained by the gradual degradation of the solvent. Indeed, at this temperature, OAm burns when in contact with  $\text{O}_2$ : the solvent volume diminishes and the Mo concentration increases.

The reaction initially homogenized displayed similar evolution, confirming the repeatability of the observations (Figure 9B,E). The initial edge jump was of 0.5, indicating the XAS spectrum of the initial state was representative of the greatest part of the Mo atoms in the medium. The absence of the  $\text{MoO}_2(\text{acac})_2$  signature at the initial stage confirmed the decomposition of  $\text{MoO}_2(\text{acac})_2$  in another compound, presumably a complex with OAm molecules. We can stress once again the difference between room temperature and 60 °C, much clearer in this case due to the higher signal/noise ratio. From the plateau at 60 °C, *i.e.* when the whole amount of precursor was mixed with the solvent, to the end of reaction, identical spectra and edge jumps were recorded than the reaction with no preliminary mixing.

Contrarily to the reactions in OAm, the initial state of the reaction in OAc has a XAS signature corresponding to  $\text{MoO}_2(\text{acac})_2$  (Figure 8 and Figure 9-F1, similarity stressed by an arrow), denoting the absence of new complex formation at room temperature at short timescales. Although the initial state was homogenized, the edge jump was low, *ca.* 0.2, because the metal precursor sedimented in spite of the stirring. Upon reaction course, the edge jump constantly increased from 0 to nearly 1 with a characteristic reaction time *ca.* 2 h, denoting the absence of sedimentation. The intermediate state (F2) during the plateau at 60 °C could not be clearly identified but was different from the molecular species observed with OAm. As there are similarities between F2 and spectra D3/E3, we suggest a mix between molecular species and

molybdenum oxide particles. The presence of nanoparticles at this temperature would be coherent with the TEM observations of the aliquot collected at 65 °C. The XAS signature of the final state F4 was close to the *ex situ* measurements of the reaction performed at 220 °C (Figure 8, MoO<sub>x</sub>-OAc<sub>(liq)</sub>), but with a non negligible shoulder in the pre-edge region. This pre-edge may be the sign of an incomplete consumption of a molecular precursor MoO<sub>2</sub>-oleate at 120 °C.

We have qualitatively commented the evolution of the XAS spectra, with all the limitations of such an approach, but a quantitative study using the MCR-ALS approach (Multivariate Curve Resolution-Alternating Least Square) is ongoing. This approach is a statistical technique relying on a high number of spectra (typically hundreds or thousands) acquired during the reaction. It allows the extraction of the different XAS components constituting of the system: molecular species, intermediate states, inorganic materials. We will thus first interpret chemically the extracted spectra, and then determine the proportions of the different chemical components at all times of the reaction.<sup>13,15</sup>

In summary, we synthesized molybdenum oxide nanoparticles by thermal decomposition of MoO<sub>2</sub>(acac)<sub>2</sub> in oleylamine, MoO<sub>x</sub>-OAm, or in oleic acid, MoO<sub>x</sub>-OAc. The NMR and XAS studies performed on both reaction conditions indicated different reaction pathways were followed, resulting in different objects. As aforementioned, the mechanism of the decomposition of M(acac)<sub>2</sub>/M(acac)<sub>3</sub> precursor in oleylamine solvent to form M(0) nanoparticles has already been extensively studied,<sup>11</sup> to the contrary of reactions in oleic acid. The particularity of the syntheses reported here is that the product was not a purely metallic particle but a molybdenum oxide, among a large variety of intermediate oxides between MoO<sub>2</sub> and MoO<sub>3</sub>. We therefore suggest as a perspective to exploit these different possible outcomes as a way to probe the difference in the synthesis mechanisms with OAm and OAc. We could also compare the results with a M(0) synthesis, for instance from Ni(acac)<sub>2</sub> or Pd(acac)<sub>2</sub>. This comparative study on both the solvent and the metal would be of interest in a field where the mechanisms at stake with OAc are not fully understood yet.



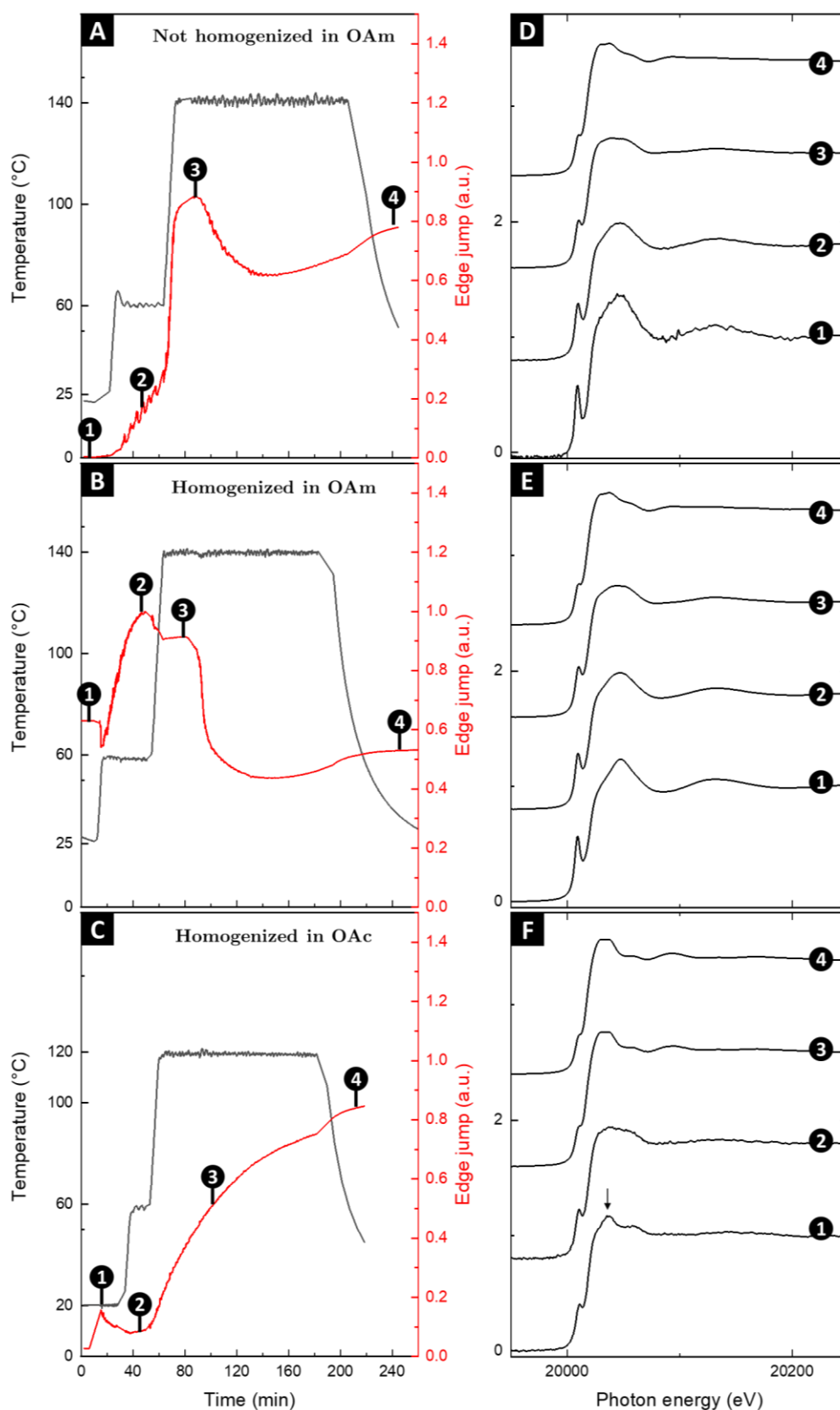


Figure 9. Temperature and edge jump of the *in situ* experiments (A) in OAm, with the precursor initially at the bottom of the liquid reaction cell, (B) in OAm and (C) in OAc, with the precursor initially dispersed. (D-F) Corresponding Mo K-edge X – ray absorption spectra for indicated times (arrow on F1 stresses the similarity with  $\text{MoO}_2(\text{acac})_2$  spectrum).

### VI.1.3 Conclusion on metal oxides syntheses

We could successfully reproduce a synthesis of XRD-pure  $W_{18}O_{49}$  nanowires from  $WCl_6$  in oleyl alcohol and oleylamine. The nanowire morphology is favorable for catalytic applications considering the high number of exposed tungsten atoms. The presence of oxygen vacancies associated to  $W^{(IV)}$  and  $W^{(V)}$  cations is also expected to help at the activation of  $H_2$  as hydride species, made possible by the oxidation of the [W] sites. As to molybdenum oxides, the obtained crystal phase was not well determined but XAS measurements revealed an intermediate degree of oxidation for Mo, between +IV and +VI. This intermediate oxidation degree is probably associated to oxygen vacancies and therefore to active sites for  $H_2$  activation. A powder could be isolated when synthesis was run in oleylamine, making possible the use of the catalyst for the next section. This was not the case for the synthesis in oleic acid which was therefore excluded for catalytic trials. Work is still ongoing to better understand the nature of the ligands at the surface of the nanoparticles, originating from thermal decomposition of  $MoO_2(acac)_2$ : so far, we only could identify OAm leftover and a condensation product with acetylacetone for thermal decomposition of  $MoO_2(acac)_2$  in OAm.

Although there are still elements to be enlightened on the synthesis mechanism, the reaction is reproducible and the obtained materials present the expected characteristics: high surface/volume ratios, good suspension stability in organic solvents and presence of oxygen defects and of metallic centers with versatile oxidation degrees. We therefore used the  $W_{18}O_{49}$  and  $MoO_x$ -OAm materials for preliminary catalytic experiments.

## VI.2. Hydrogenation reactions

As aforementioned, oxygen deficient tungsten oxide  $\text{WO}_{2.72}$ , obtained from  $\text{WCl}_6$  and ethanol, was recently reported for its catalytic activity for nitroarenes and alkynes hydrogenation (30 bar  $\text{H}_2$ , 150 °C, 15 h).<sup>1</sup> The tungsten oxide synthesized in this PhD thesis has a similar chemical composition but the synthetic pathway was different as we used a mixture of oleylamine and oleyl alcohol. Hydrogenation of phenylacetylene and nitrobenzene were attempted with  $\text{W}_{18}\text{O}_{49}$  and  $\text{MoO}_x\text{-OAm}$  following Catalysis VI.1. Considering the expected low catalytic activity of the materials compared to conventional catalysts, we first used relatively hard conditions, *i.e.* an  $\text{H}_2$  pressure of 30 bar and a reaction temperature of 150 °C. We chose toluene and EtOH as solvents for reactions with  $\text{W}_{18}\text{O}_{49}$  to match with the conditions reported by Wang *et al.*,<sup>1</sup> and THF for reactions with  $\text{MoO}_x\text{-OAm}$  in order to have stable suspensions. Results are given in Table 2.

**Catalysis VI.1. Hydrogenation with metal oxides.** In air, 0.2 mmol of catalyst powder (25.6 mg of  $\text{MoO}_x\text{-OAm}$  or 45.5 mg of  $\text{W}_{18}\text{O}_{49}$ , 0.1 equiv. of [M]) were introduced in a 25 mL steel autoclave (Teflon reaction cuve). To the autoclave was added 2 mmol of substrate (220  $\mu\text{L}$  of phenylacetylene or 210  $\mu\text{L}$  of nitrobenzene, 1 equiv.) and 1 mL of solvent. The autoclave was closed and the atmosphere was changed for  $\text{H}_2$  (30 bar) after 2 cycles vacuum/ $\text{H}_2$  (1 bar). The autoclave was then introduced in a preheated oil bath at 150 °C for 16 h. The pressure increased to *ca.* 40 bar. After reaction, the autoclave was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

Phenylacetylene was hydrogenated in styrene with yields of respectively 22 % and 13 % and partially over-hydrogenated in ethylbenzene (entries 1-2 and Figure 10). These preliminary data proved the two synthesized metal oxides were active catalysts for alkyne/alkene hydrogenation though not chemoselective as total hydrogenation in ethylbenzene occurred at moderate styrene yields. On the contrary, nitrobenzene was not hydrogenated in aniline by any of the two catalysts (entries 3-4). The catalytic activity toward  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  hydrogenation and not toward  $\text{NO}_2$  reduction is sufficiently unusual to be noticed.

In summary, we proved the possible use of Group VI metal oxides (Mo, W) synthesized *via* a non-aqueous pathway for hydrogenation reactions in solvent. The organic ligands did not completely impend the catalytic reactions to occur. However, the experimental conditions used in this preliminary study (30 bar  $\text{H}_2$ , 150 °C, 16 h, [M] 10 mol%) were already strong for liquid phase catalysis with limited conversion yields in hydrogenation of phenylacetylene. We therefore suggest to directly evaluate the impact of the addition of a co-catalyst, such as a phosphine or an amine, on the reaction yield and selectivity.

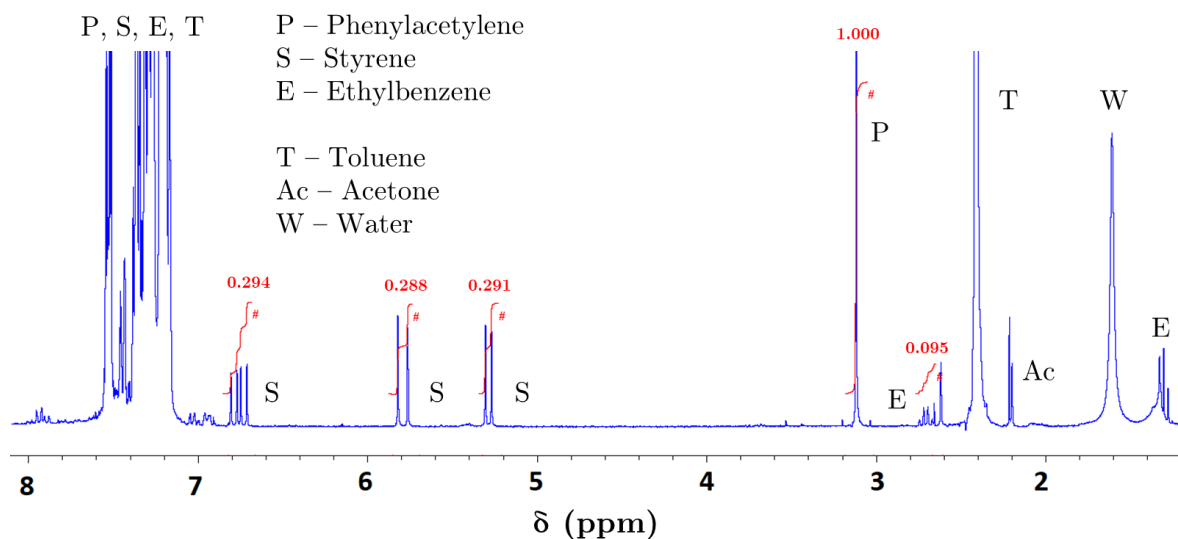
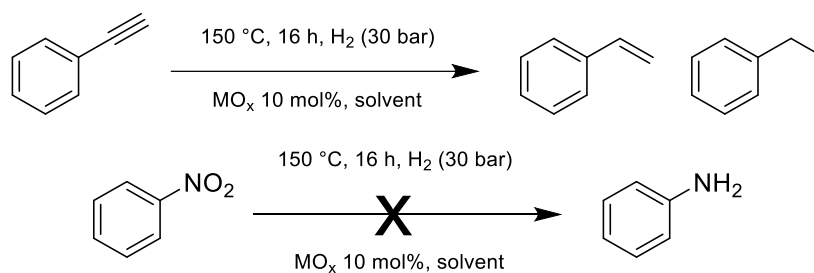


Figure 10.  $^1\text{H}$  NMR spectrum of crude reaction of hydrogenation of phenylacetylene in toluene at  $150\text{ }^\circ\text{C}$  in presence of  $\text{W}_{18}\text{O}_{49}$ . Traces of acetone do not originate from the synthesis.



	Catalyst (mol%)	Substrate	Solvent	Temp.	Substrate conversion	Products
1	$\text{W}_{18}\text{O}_{49}$	Phenylacetylene	Toluene	$150\text{ }^\circ\text{C}$	26 %	Styrene: 22 % Ethylbenzene: 4 %
2	$\text{MoO}_x\text{-OAm}$	Phenylacetylene	THF	$150\text{ }^\circ\text{C}$	13 %	Styrene: 13 % Ethylbenzene: < 1 %
3	$\text{W}_{18}\text{O}_{49}$	Nitrobenzene	EtOH	$150\text{ }^\circ\text{C}$	0 %	-
4	$\text{MoO}_x\text{-OAm}$	Nitrobenzene	THF	$150\text{ }^\circ\text{C}$	0 %	-

Table 2. Hydrogenation of styrene phenylacetylene ( $\text{PhCCH}$ ) and nitrobenzene ( $\text{PhNO}_2$ ) with metal oxide catalysts. Reaction conditions:  $220\text{ }\mu\text{L}$  of  $\text{PhCCH}/210\text{ }\mu\text{L}$  of  $\text{PhNO}_2$  (2 mmol), 25.6 mg of  $\text{MoO}_x/45.5\text{ mg}$  of  $\text{W}_{18}\text{O}_{49}$  (0.2 mmol,  $[\text{M}]$  10 mol%), 1 mL of solvent,  $\text{H}_2$  (30 bar, 30 mmol), 16 h in autoclave (25 mL) at  $150\text{ }^\circ\text{C}$ . Conversion and yield determined by NMR.

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## Chapter VII

# Nickel-containing nanoparticles for hydrogenation in solvent

*Note: this chapter partially consists in the work of Léna Meyniel, intern for 6 months under my supervision. Her work covers a part of the synthesis section (literature review, syntheses, characterizations and data interpretation).*

Nickel is a widely used catalyst for hydrogenation reactions in liquid phase with for instance the well-known Raney<sup>®</sup> nickel, a finely divided nickel mixed with aluminum, patented by Murray Raney in 1926.<sup>1</sup> Different nickel-based catalysts have since been developed for the hydrogenation of unsaturated compounds in the context of fine chemistry.<sup>2</sup> As already mentioned, different limitations exist for this metal: low resistance to poisonous elements (N, P, S), pyrophoricity, poor chemoselectivity. As a consequence, in the past years a series of work targeted the use of nickel compounds for colloidal hydrogenation: borides,<sup>3,4</sup> nitrides,<sup>5</sup> silicides,<sup>6</sup> phosphides,<sup>4,7</sup> and sulfides.<sup>8</sup> The insertion of light elements such as carbon or phosphorus in the metal lattice modifies the *d*-band electronic structure of the material, although the extent and the sense of the modification are challenging to predict.<sup>9-11</sup> Such a modification may give a noble metal-like catalytic behavior and favors the H<sub>2</sub> activation, as was shown on WC for instance.<sup>12</sup> Nickel carbide was reported as an active catalyst for vegetal oil hydrotreatment at 400 °C and under 30 bar of H<sub>2</sub>, and similar conversions were obtained with nickel sulfides and phosphides.<sup>13</sup> However, to the best of our knowledge, there is no mention of Ni<sub>3</sub>C catalyst in colloidal hydrogenation of olefin or nitro compounds. Furthermore, although phosphine assisted heterolytic splitting of H<sub>2</sub> at the surface of noble metal was reported by Rossi *et al.*<sup>14</sup>, the influence of phosphine additives have rarely been explored for catalyst nanoparticles that are not purely metallic.

In the context of this thesis, nickel carbides and phosphides were thought to be interesting catalysts as they display an intermediate metallic/covalent character, although at different degree: the electronegativity of phosphorus ( $\chi(\text{P}) = 2.19$ ) indeed differs from that of the carbon ( $\chi(\text{C}) = 2.55$ ). So far in our study, the covalent character was only present in the carbides studied in chapter II/III and the corresponding catalysts had a limited activity. In this chapter, we considered the use of nickel carbide (Ni<sub>3</sub>C) and nickel phosphides (Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub>) nanoparticles for colloidal hydrogenation of model substrates such as phenylacetylene or nitrobenzene.



Three main goals are pursued:

- (1) Investigating whether  $\text{Ni}_3\text{C}$  displays a catalytic activity for hydrogenation, and eventually comparing the catalytic activity of  $\text{Ni}_3\text{C}$  with  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$  nanoparticles of similar size and surface state
- (2) Studying the catalytic activity of a catalyst ( $\text{Ni}_3\text{C}$ ,  $\text{Ni}_{12}\text{P}_5$  or  $\text{Ni}_2\text{P}$ ) over a variety of substrates (alkyne, nitroarene, furanic aldehyde) under similar conditions in order to establish a bridge between the works from fine chemistry and hydroprocessing communities
- (3) Investigating the influence of an additional phosphine ligand on the conversion and selectivity

Nickel-containing nanoparticles are synthesized in organic solvents with temperatures in the 200-300 °C range. Their surface is therefore expected to be covered with organic ligands (amines, phosphines) to the contrary of most of the materials presented so far. Different experimental issues or concerns are commented, in particular on the influence of the reaction temperature on the product phase. In the first section, we report the synthesis of  $\text{Ni}_3\text{C}$  nanoparticles, which are subsequently phosphidized in either  $\text{Ni}_2\text{P}$  or  $\text{Ni}_{12}\text{P}_5$ . The catalysts are characterized by XRD, TEM and XAS. In the second section, the reactivity of  $\text{Ni}_3\text{C}$  is studied for the hydrogenation of nitrobenzene ( $\text{PhNO}_2$ ) and phenylacetylene ( $\text{PhCCH}$ ).

## VII.1. Nickel carbide and phosphide syntheses

### VII.1.1 One-step nickel phosphide synthesis

A direct solvothermal synthesis of  $\text{Ni}_2\text{P}$  nanoparticles was first attempted following the work of Robinson *et al.*<sup>15</sup> The Synthesis VII.1. was conducted in an oleylamine (OAm)/dioctyl ether ( $\text{Oct}_2\text{O}$ )/trioctylphosphine (TOP) (2/1/1) (v/v/v) mixture. Nickel nanoparticles were first formed by thermal decomposition of  $\text{Ni}(\text{acac})_2$  and the trioctylphosphine introduced in excess, 5.6 equiv. per atom of Ni, constituted the phosphorus source.

**Synthesis VII.1. One-step synthesis of  $\text{NiP}_x$  nanoparticles.** In a 50 mL three-necked round-bottom flask, 10 mL of oleylamine (8.1 g, 30.4 mmol, 13.3 equiv.) and 5 mL of dioctyl ether (4 g, 16.6 mmol, 7.3 equiv.) were degassed under vacuum at r.t. during 20 min and the flask was purged with  $\text{N}_2$  three times. Under  $\text{N}_2$ ,  $\text{Ni}(\text{acac})_2$  (586 mg, 2.28 mmol, 1 equiv.) and TOP (5 mL, 11.2 mmol, 4.9 equiv.) were added to the solution. The resulting blue gelatinous solution was heated to 230 °C: it became limpid at 55 °C, emerald green at 80 °C and a black suspension at 140 °C. Explosions occurred *ca.* 215 °C and the temperature increase slowed down in this temperature range. The solution was let to react for 1 h 30 at 230 °C and target temperature was then set to 300 °C for 3 h (the actual reaction temperatures were between 270 °C and

300 °C). After cooling to r.t. under N<sub>2</sub>, ethanol (20 mL) was added to the crude solution and a black solid was isolated by centrifugation (9,000 rpm, 10 min, 20 °C). The yellowish biphasic supernatant was removed and the solid was redispersed in hexane (10 mL) and washed with ethanol (20 mL) and centrifugated. This operation was repeated another time. The obtained black powder (190 mg, 112 % yield) was then dried under N<sub>2</sub> and stored in air.

The yields obtained in Syntheses VII.1. to VII.6. with high boiling point solvents are excellent and sometimes higher than 100 %. This is due to the presence of a non-negligible organic shell around the nanoparticles. We nonetheless considered they are indicative of quantitative reactions.

We first performed Synthesis VII.1. and stopped it at the end of the first plateau at 230 °C. The obtained powder consisted in a mixture of Ni<sub>12</sub>P<sub>5</sub> [PDF card N°00-022-1190] and Ni<sub>2</sub>P [PDF card N°04-003-1863] nanoparticles (equivalent to respectively NiP<sub>0.42</sub> and NiP<sub>0.5</sub>) (Figure 1Aa). The temperature setpoint of the heating device for the second plateau was always 300 °C but different maximal reaction temperatures were obtained for each batch, as low as 270 °C. An important reflux was observed at 260 °C, even though the measured temperature kept increasing. The reaction crude was a ternary mix of OAm, Oct<sub>2</sub>O and TOP with boiling points of respectively 364 °C, 292 °C and 287 °C. Considering the evaporation temperatures were all above 270 °C, the mixture certainly presents a eutectic. The composition of the liquid fraction thus differed from that of the gas fraction which evaporated. As the vapors condensed along the air refrigerant, the total composition did not diverge with time. However, evaporation is an endothermic process and consumed part of the power delivered by the heating mantle. For some of our syntheses, 100 % of the nominal power of the heating mantle was delivered before the targeted temperature of 300 °C was reached. A combination of different experimental conditions either related to the delivered power (aging of the heating mantle) or to the heat losses (quality of the thermal insulation, contact between the heating mantle and the round-bottom flask) may explain the different temperatures obtained for the second plateau although the solvents mix was always the same. This point is not mentioned in the different works reporting the colloidal syntheses of nickel phosphides and carbides but we noticed the control of temperature is not performed the same way depending on the groups.<sup>15-17</sup> Indeed, where Brock *et al.* directly put the thermocouple in contact with the heating mantle near the round-bottom flask, Carencio *et al.* placed it in a glass finger in the solution.<sup>18,19</sup> Besides, some groups indicate a reaction temperature of 350 °C, well above the boiling points of the major part of the solvent: we believe they actually indicate the set point of the heating mantles. All these points prove the literature protocols for this NiP<sub>x</sub> syntheses are not homogeneous and that a careful attention should be brought to the temperature control.

Even though not intentionally, we therefore performed a series of reactions with different temperatures for the second plateau. Considering the instability of the heating device mentioned earlier, the temperatures are indicative and may have fluctuated during the plateau. The phase speciation of the product between the different nickel phosphides was analyzed by XRD (Figure 1Ab-f for some of the relevant data). When the temperature of the plateau was increased from 270 °C to 290 °C, the proportion of  $\text{Ni}_{12}\text{P}_5$  decreased in favor of  $\text{Ni}_2\text{P}$ , as can be observed with the diminution of the intensity of the peaks at 38° and 49°. For temperatures in the 280 °C-295 °C range, the product was nearly XRD-pure  $\text{Ni}_2\text{P}$ , plus three unattributed very broad peaks at 29°, 42° and 49°. The  $\text{Ni}_{12}\text{P}_5$  phase was excluded due to the important peak at 29°, not referenced for this phase. Beyond 295 °C, a more phosphorus-rich nickel phosphide phase,  $\text{Ni}_5\text{P}_4$  (equivalent to  $\text{NiP}_{0.8}$ ) [PDF card N°04-014-7901] appeared, with in particular peaks at 46° and 56°. TEM images of the NPs produced at 270 °C and 300 °C revealed similar morphologies were obtained: monodisperse 8 nm large spherical nanoparticles (Figure 1B-G). Electron diffraction fringes appeared at high magnifications and SAED patterns confirmed the presence of the  $\text{Ni}_2\text{P}$  phase: the NPs are crystalline. We can stress the critical role of the washing steps as particles were severely aggregated for one batch (Figure 1B) and presented a thick organic shell (Figure 1C), probably composed of TOP ligands. The main result is that increasing the reaction temperature leads to more phosphorus-rich phases but that obtaining XRD-pure samples with this protocol is challenging. As this conclusion is shared by the authors of the initial work and as we are more interested in the catalytic applications in the synthesis development, we did not push further in this direction.<sup>15</sup>

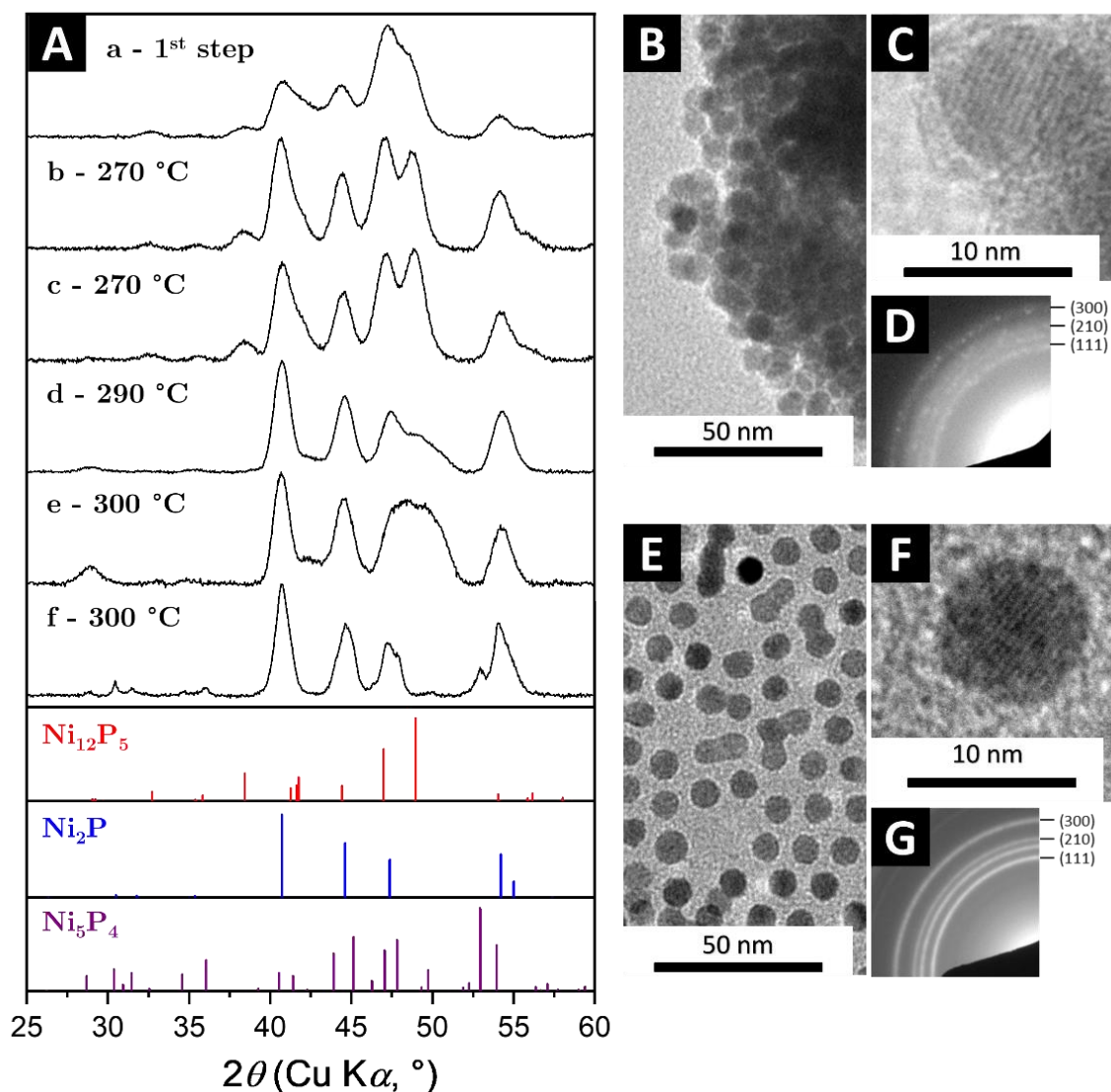


Figure 1. (A) PXRD patterns of powders obtained by Synthesis VII.1. after (a) the first plateau at 230 °C and (b-e) after the second plateau at respectively 270 °C, 270 °C, 290 °C, 300 °C and 300 °C. Transmission Electron Microscopy images and corresponding selected area electron diffraction (reference:  $\text{Ni}_2\text{P}$ ) of (B-D) sample b (270 °C) and (E-G) sample f (300 °C).

### VII.1.2 Synthesis of nickel carbide Ni<sub>3</sub>C and subsequent phosphidization

The direct synthesis of XRD-pure nickel phosphides Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P proved to be unsuccessful following Synthesis VII.1. We therefore chose to reproduce the two-step procedure for Ni<sub>12</sub>P<sub>5</sub> NPs synthesis *via* Ni<sub>3</sub>C reported by Tracy *et al.*<sup>17</sup> In this synthetic pathway, the nickel phosphide nanoparticles are obtained by phosphidization of nickel carbide nanoparticles in a one-pot synthesis. The authors reported the Ni<sub>12</sub>P<sub>5</sub> phase and we adapted the protocol to form Ni<sub>2</sub>P nanoparticles as well. The nickel carbide and phosphide nanoparticles have similar dimensions which will permit the comparison of their catalytic activities in section VII.2.

Colloidal syntheses of transition metal carbides (Fe<sub>3</sub>C, Co<sub>2</sub>C, Co<sub>3</sub>C, Ni<sub>3</sub>C) require the use of a carbon source and a high enough temperature to decompose it.<sup>20</sup> One common and easily available carbon source is 1-octadecene (ODE), introduced in large excess in the reaction medium. It is most of the time used in combination with long-chain alkylamines, such as oleylamine (OAm) or hexadecylamine (HDA), or fatty acids, such as oleic acid (OAc). The use of ODE as carburizing agent in colloidal syntheses is justified by its low cost, its high boiling point (315 °C), convenient for NPs synthesis, and its relatively moderate decomposition temperature. It is important to note that no absolute decomposition temperature may be given for ODE, or any other carbon source, as the carburization process is thermodynamically possible at temperatures as low as 200 °C but is kinetically too slow to be observed.<sup>21</sup> The first stage of the Ni(0) carburization is challenging to observe with XRD and one can incorrectly assume pure metallic nickel was obtained.<sup>21</sup> If solvents are compared as to their carburization capacity, both the reaction temperature and reaction time should be indicated. For instance, Kobayashi *et al.* studied the thermolysis of Ni(acac)<sub>2</sub> in pure OAm at different temperatures: for a reaction time of 30 min, they obtained pure cubic Ni(0) until a reaction temperature of 260 °C (Figure 2A) and observed Ni<sub>3</sub>C at 280 °C and higher temperatures.<sup>22</sup> When the reaction was conducted at 240 °C, a longer reaction time (180 min *versus* 30 min) was enough to form Ni<sub>3</sub>C (Figure 2B). The phase indicated as hcp-Ni(0) in Figure 2 was proven in an ulterior work of Schaak *et al.* to be a misattribution of the Ni<sub>3</sub>C phase.<sup>21</sup> The surface state of the Ni(0) NPs may also infer on the carburization process. For instance, Tracy *et al.* reported the C uptake in an OAm/ODE (50/50) mixture at 230 °C in 30 min but the addition of minute amount of TOP ligands prevented the carburization of the Ni(0) NPs under similar conditions.<sup>17</sup> The authors hypothesized the TOP ligands are tightly bound at the surface of the nanoparticles and impend the approach of the ODE, responsible for the C uptake. The exact decomposition mechanism of ODE is rarely mentioned in the different works. As higher temperatures are required for carburization with OAm than with ODE, both

comporting a C=C bond, we suggest the higher reactivity of ODE is linked to the terminal position of the double bond.

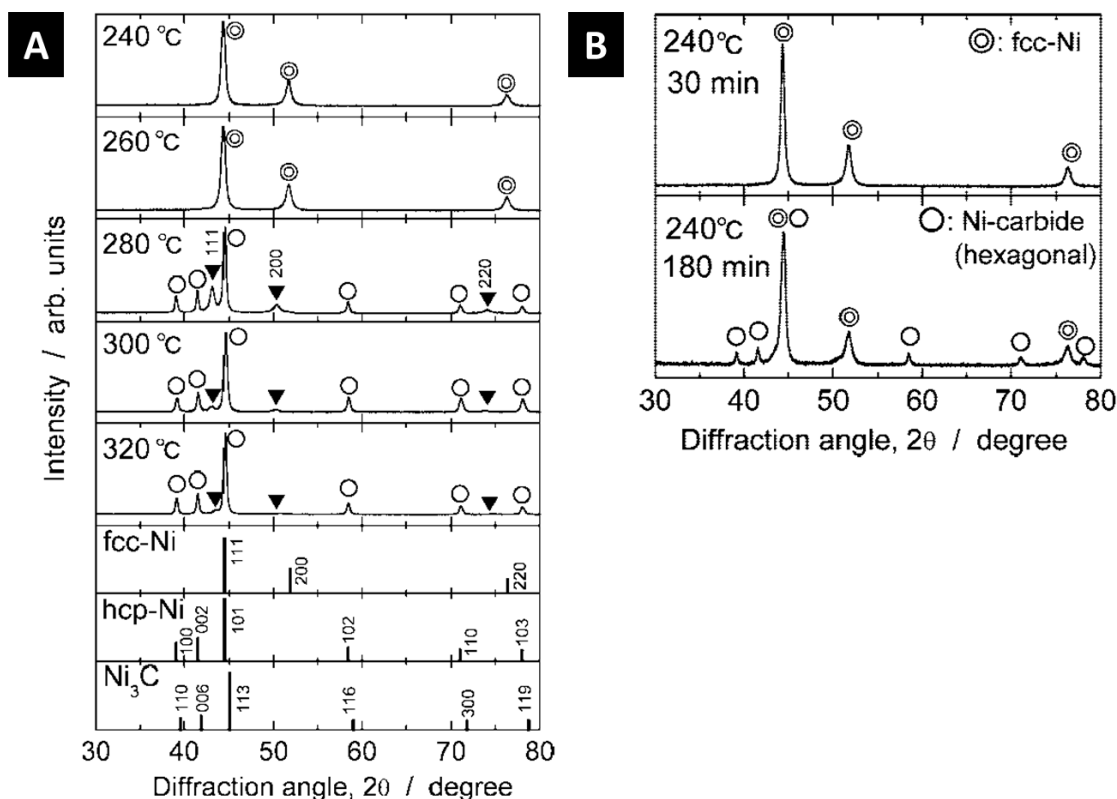


Figure 2. PXRD patterns of reaction product of thermolysis of Ni(acac)<sub>2</sub> in pure OAm. (A) Reaction time of 30 min for all reactions. (B) 240 °C for both reactions. The figures are reproduced from reference [22].

**Nickel carbide Ni<sub>3</sub>C.** We first reproduced in Synthesis VII.2. the first step of the protocol used by Tracy *et al.* for Ni<sub>3</sub>C synthesis in an OAm/ODE (50/50) mixture.<sup>17</sup> We did not add TOP in order to avoid any surface contamination by phosphorus or formation of nickel phosphide phases.

**Synthesis VII.2. Nickel carbide nanoparticles.** In a 100 mL three-necked round-bottom flask, 15 mL of oleylamine (12.2 g, 45.6 mmol, 8.9 equiv.) and 15 mL of 1-octadecene (11.8 g, 46.9 mmol, 9.15 equiv.) were degassed under vacuum at 60 °C during 20 min and the flask was purged with N<sub>2</sub> three times. Under N<sub>2</sub>, Ni(acac)<sub>2</sub> (1.32 g, 5.14 mmol, 1 equiv.) was added to the solution. The resulting blue gelatinous solution was heated up to 250 °C under agitation. The solution was homogeneous and turned emerald green at 80 °C and darkened progressively with the heating ramp. A black suspension was obtained at 205 °C and explosions occurred at 236 °C. The increase in temperature stopped for a few minutes and then reached 250 °C. The

solution was let to react 2 h at 250 °C. After cooling to r.t. under N<sub>2</sub>, ethanol (30 mL) was added to the crude solution and a solid was isolated by centrifugation (9,000 rpm, 10 min, 20 °C). The yellow biphasic supernatant was removed and the particles were redispersed in hexane (15 mL) before adding ethanol to precipitate them (15 mL). This operation was repeated another time. The obtained black powder (348 mg, 108 % yield) was then dried under N<sub>2</sub> and stored under air.

When performed several times at 230 °C during 30 min, the Synthesis VII.2. did not systematically provide XRD-pure Ni<sub>3</sub>C [PDF card N°04-007-3753] as Ni(0) [PDF card N°03-065-2865] traces were also observed (Figure 3A). To avoid this metallic leftover, the reaction temperature was increased to 250 °C and the reaction time to 2 h: this strategy was successful as pure Ni<sub>3</sub>C was then systematically obtained (Figure 3A). TEM images of the NPs formed in Synthesis VII.2. are displayed in Figure 3B-C: they have irregular shapes and are polydisperse in size with diameters ranging from 50 nm to 100 nm. This contrast in shape with the NPs formed in Synthesis VII.1. is explained by the absence of TOP which plays the role of ligand. Selected area electron diffraction performed on the sample confirmed the Ni<sub>3</sub>C phase attribution by XRD (Figure 3D).

The observed temperature plateau at 236 °C and the explosions in the liquid were systematically observed for all batches. We suggest this temperature corresponds to a maximum rate of decomposition of 1-octadecene and of the carburization of the nanoparticles. The heat provided by the heating mantle was partially used for these chemical endothermic processes and the medium temperature stopped increasing as long as the carburization reaction was not complete. To examine this point and in order to catch reaction intermediates, Synthesis VII.2. was run and stopped during the heating ramp, right before (230 °C) or after (250 °C) the critical temperature of 236 °C. The reactions were treated as for the regular reactions and the obtained powders characterized by XRD (Figure 3A). When stopped at 230 °C, the reaction led to a mixture of Ni<sub>3</sub>C (major phase) and Ni(0) (minor phase) and the two phases were associated to crystallites of similar size *ca.* 10 nm according to Scherrer analysis. When heated to 250 °C, merely all the product was Ni<sub>3</sub>C and the Scherrer size of the crystallites increased to 22 nm. At this stage, we cannot decide whether the actual size of the crystallites increased during the heating ramp or if the size was preserved and the crystallinity, *i.e.* the quality of the crystalline order of the atoms, increased. As only traces of Ni(0) were still present for the reaction interrupted when the temperature reached 250 °C, increasing the reaction time to 2 h was probably not necessary.

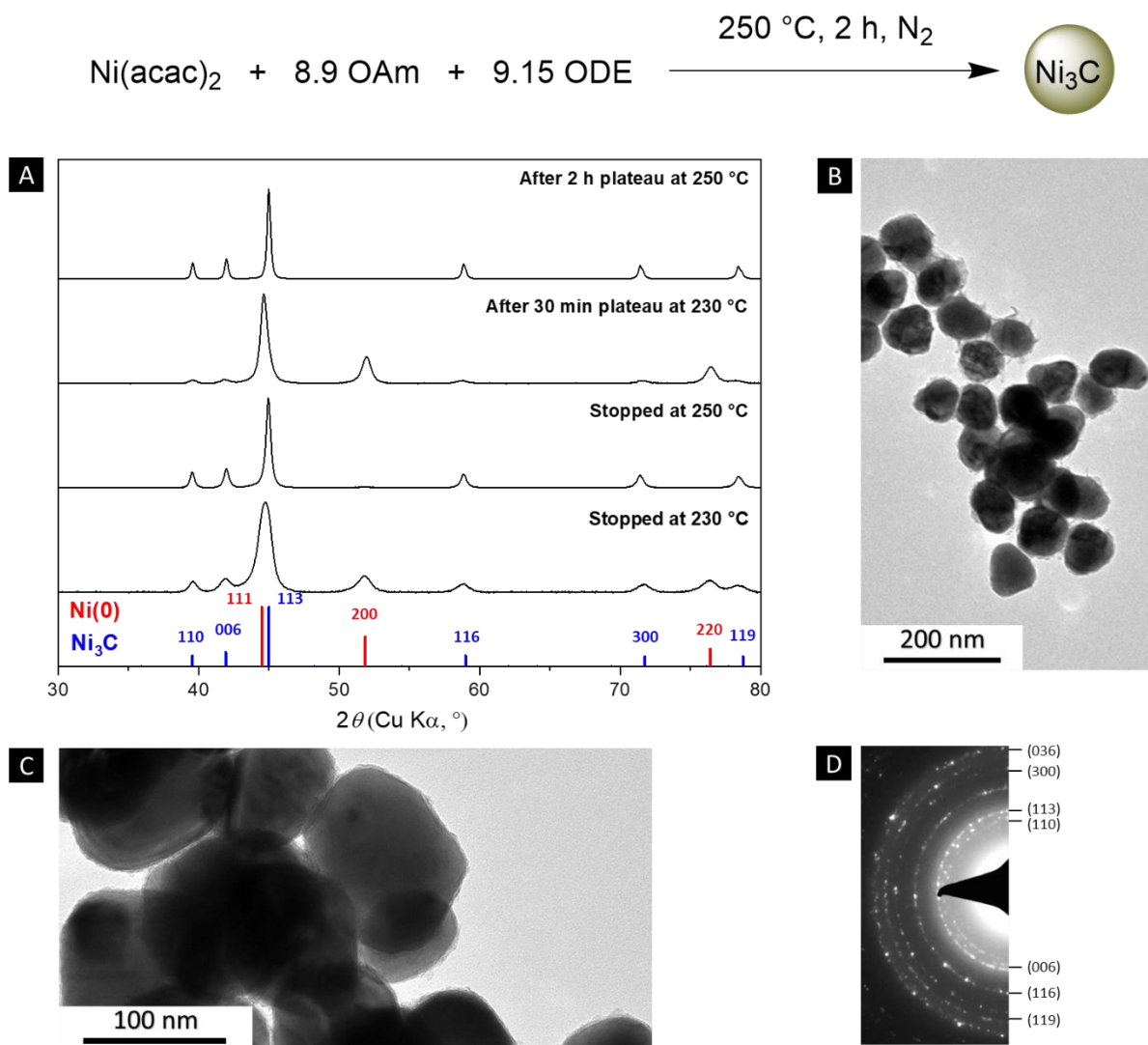


Figure 3. Structural and morphology characterizations of nickel carbide  $\text{Ni}_3\text{C}$  nanoparticles from Synthesis VII.2. (A) XRD of the powders with (hkl) attribution, (B-C) TEM images and (D) selected area electronic diffraction pattern.

**Nickel carbide phosphidization.** A synthesis of  $\text{Ni}_{12}\text{P}_5$  nanoparticles was developed according to the protocol developed by Tracy *et al.*<sup>17</sup> The protocol was similar to Synthesis VII.2. followed by an injection of trioctylphosphine (TOP) as phosphidizing agent. The amount of TOP and the temperature of the injection were varied in Syntheses VII.3., VII.4. and VII.5. in order to obtain different nickel phosphide phases.

**Synthesis VII.3.** Identical to Synthesis VII.2. until after the plateau of 2 h at 250 °C. The solution was then cooled down to r.t. 0.9 mL of TOP (2.02 mmol, 0.4 equiv.) were added by briefly opening one neck. The temperature was increased to 300 °C and the solution was let to react for 30 min at this temperature. After cooling to r.t.,



the crude was treated with an identical process than Synthesis VII.2. to yield a black powder (337 mg) which was dried under  $N_2$  and stored under air.

In Synthesis VII.3., the TOP was injected after the reaction crude was cooled down to r.t. This low-temperature injection is safer than a hot-injection. The experiment was performed twice, one with 30 min of reaction at a targeted reaction temperature of 300 °C and one with 2 h of reaction at 350 °C, with similar results. The PXRD of the recovered powders are displayed on Figure 4 and are very similar to  $Ni_3C$ . A broad extra peak appeared at 47.7° and could not be attributed.

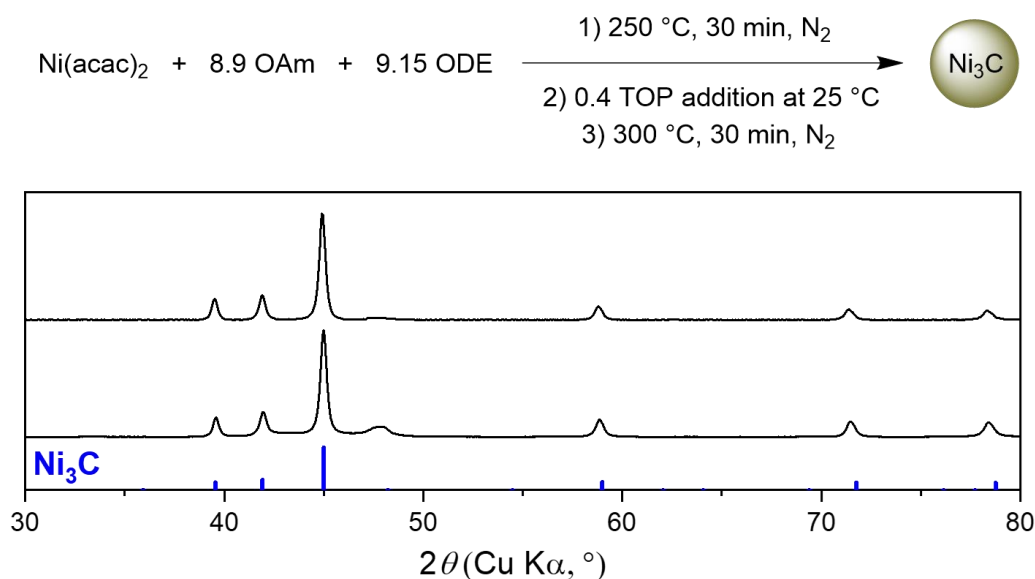


Figure 4. Attempt at phosphidization of nickel carbide nanoparticles according to Synthesis VII.3.: XRD of the powders (top: 30 min at 300 °C, bottom: 2 h at 350 °C).

**Synthesis VII.4. Two-step nickel phosphide  $Ni_{12}P_5$ .** Identical to Synthesis VII.2. until after the plateau of 2 h at 250 °C. The solution was then heated toward 300 °C. When 285 °C were reached, 0.9 mL of TOP (2.02 mmol, 0.4 equiv.) were injected with a syringe by briefly opening one neck. The temperature slightly decreased and then reached 300 °C. The solution was let to react for 30 min at this temperature. After cooling to r.t., the crude was treated with an identical process than Synthesis VII.2. to yield a black powder (375 mg, 102 % yield) which was then dried under a flux of  $N_2$  and stored under air.

Synthesis VII.4. led to  $Ni_{12}P_5$  XRD-pure NPs and was successfully reproduced several times in our lab with similar results, denoting the robustness of the protocol (Figure 5A). The crystalline NPs are 100 nm large irregular spheres with a core-shell morphology (Figure 5B-C). In TEM, the core of the particles is lighter than the shell: the contrast is interpreted as a higher electron density in the shell. We suggest the

dark shell is the phosphide phase which was obtained upon decomposition of the TOP ligands at the surface of the nickel carbide NPs. The phosphorus atoms diffuse at the surface while the nickel atoms are pulled toward the exterior of the nanoparticles. This Ni atom migration results in a modification of the core of the nanoparticle. The phenomenon is often referred to as “nanoscale Kirkendall effect” in literature.<sup>16,23</sup> The chemical nature of the core was not investigated, it may consist in a void or in amorphous carbon originating from the carbide phase, hence the lower electron density. The solubility of carbon in nickel is good and it would be surprising that the phosphide formation would be responsible for the whole exsolution of carbon from the nickel phase. One possibility is the synthesized NPs are isostructural with  $\text{Ni}_{12}\text{P}_5$  but consist in a ternary mixture of nickel, carbon and phosphorus. To the best of our knowledge, the characterization of mixed Ni–P–C systems, “nickel phosphocarbide”, has not been reported in literature.

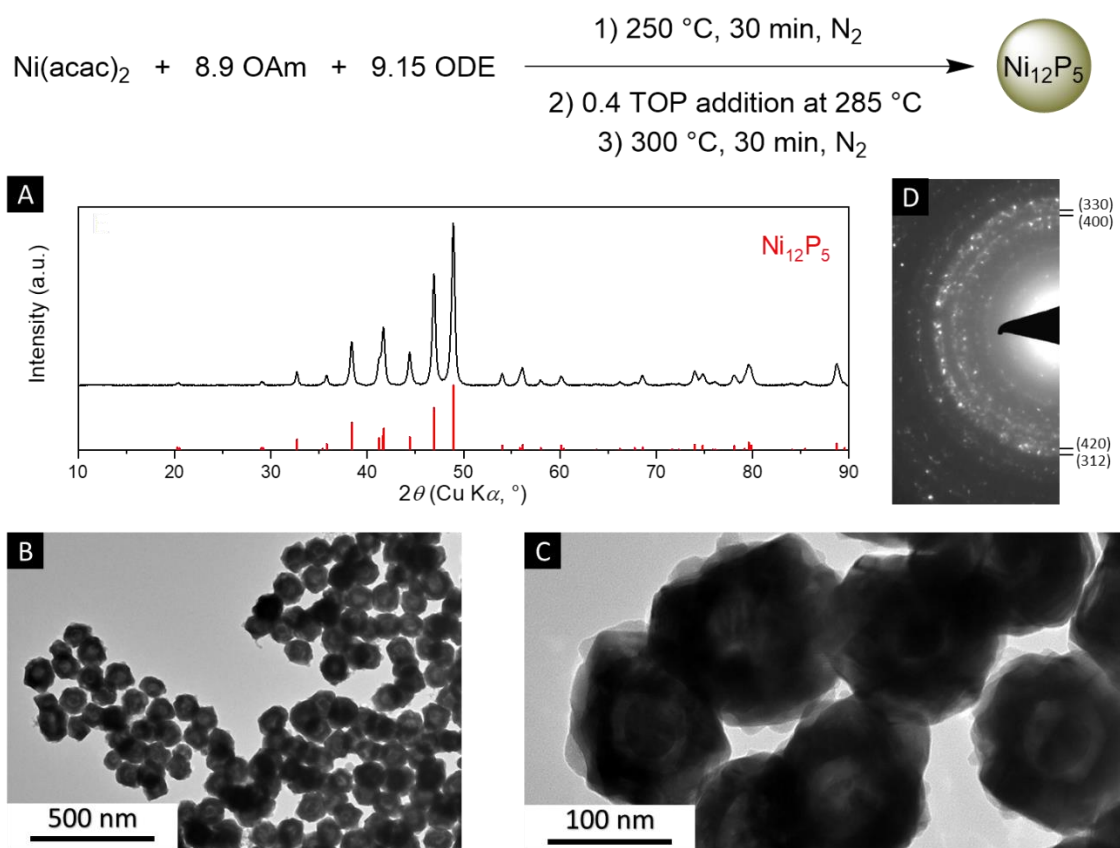


Figure 5. Synthesis of nickel phosphide  $\text{Ni}_{12}\text{P}_5$  nanoparticles according to Synthesis VII.4. with structural and morphology characterizations. (A) XRD of the powder, (B-C) TEM images and (D) electronic diffraction pattern.

**Synthesis VII.5. Two-step nickel phosphide  $\text{Ni}_2\text{P}$ .** Identical to Synthesis VII.2. until after the plateau of 2 h at 250 °C. 1.8 mL of TOP (4.04 mmol, 0.8 equiv.) were added by briefly opening one neck. The solution was then heated to 300 °C. Explosions occurred *ca.* 290 °C. The temperature slightly decreased and then reached 300 °C. The solution was let to react for 30 min at this temperature. After cooling to r.t., the crude was treated with an identical process than Synthesis VII.2. to yield a black powder (370 mg, 98 % yield), was dried under  $\text{N}_2$  and stored under air.

The quantity of TOP was doubled in Synthesis VII.5. compared to Synthesis VII.4. in order to obtain a more phosphorus-rich phosphide phase. Synthesis VII.5. was performed once and led to  $\text{Ni}_2\text{P}$  XRD-pure NPs (Figure 6A). The increase in TOP proportion was therefore a successful strategy. As for  $\text{Ni}_{12}\text{P}_5$  NPs in Synthesis VII.4., the irregular spheres have a core-shell morphology with a light core and a dark shell. A similar synthesis mechanism is therefore expected. So far, we could not explain why changing the injection temperature and the TOP:Ni ratio has such a dramatic impact on the final phase, especially considering its high purity (no traces of  $\text{Ni}_{12}\text{P}_5$ ). We believe performing several times the experiment to check its reproducibility is essential before commenting the difference between Synthesis VII.4. and VII.5.

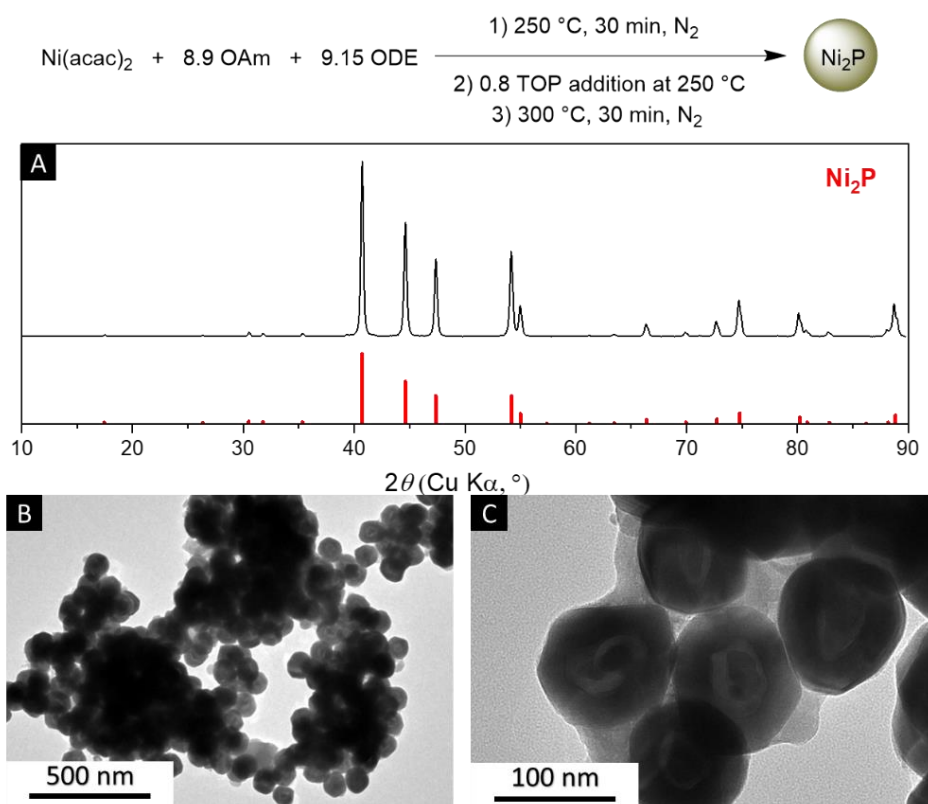


Figure 6. Synthesis of nickel carbide  $\text{Ni}_2\text{P}$  nanoparticles according to Synthesis VII.5. with structural and morphology characterizations. (A) XRD of the powder, (B-C) TEM images.

**X-ray absorption spectroscopy.** To further explore the structural features of the crystalline samples, characterization of the nickel-containing nanoparticles was performed by XAS at the Ni K-edge at 8333 eV. The experiments were performed on the ROCK beamline at the SOLEIL synchrotron and details on the protocols are given in Appendix I ES.9.

Figure 7 displays the XAS spectra and the Fourier transforms spectra in the R-space of Ni<sub>2</sub>P, Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>3</sub>C phases reported in literature.<sup>24-27</sup> For Ni<sub>2</sub>P, two main peaks are observed at 1.78 Å and 2.24 Å, corresponding to respectively the first shell Ni–P and Ni–Ni distances.<sup>25</sup> For Ni<sub>12</sub>P<sub>5</sub>, the position and the low intensity of the white line support the metallic character of the material and indicate the Ni atoms have a low oxidation state.<sup>26</sup> Two coordination shells at 1.80 Å and 2.15 Å were observed in the EXAFS spectrum, corresponding to respectively the Ni–P and Ni–Ni distances. If compared with pure Ni(0) reference, the Ni–Ni bond peak intensity is largely decreased which is interpreted as a lower number of direct Ni–Ni bonds, in accordance with the theoretical crystal structure. For Ni<sub>3</sub>C, the EXAFS region differs totally with these of the Ni(0) reference.<sup>27</sup> The characteristic distances observed with the Fourier transform of the spectra revealed the first Ni and C shells for Ni<sub>3</sub>C (at respectively 1.41 Å and 2.38 Å) and the first Ni shell for Ni(0) (2.19 Å). All the values are in line with the crystallographic data with literature: we can note in particular an increase of Ni–Ni distance upon carburization.

Figure 8 displays the XAS spectra of the Ni(0) foil (used as a reference) and of pellets of Ni<sub>3</sub>C, Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P from respectively Syntheses VII.2., VII.4. and VII.5. We can first note the XAS spectra and the Fourier transforms spectra are similar to the ones reported in literature for the corresponding phases (see Table 1 for distances), indicating that most of the material is actually composed of the phase attributed by XRD. Nonetheless, considering the close positions of the Ni–P and Ni–Ni distances in the EXAFS spectra, we cannot exclude at this stage the presence of traces of carbide (Ni<sub>3</sub>C) or that of a phosphocarbide phase in the phosphidized samples. On Figure 8B are plotted zooms of the edge regions for all samples. Considering the flatness of the curves, determining an inflexion point is challenging and the edge position can be hardly defined. This is a consequence of the metallic character of the materials with complex electronic structures around the Fermi level.<sup>28</sup> Even though ill-defined, the positions of the edges are close to that of Ni(0), indicating the materials are mostly reduced.

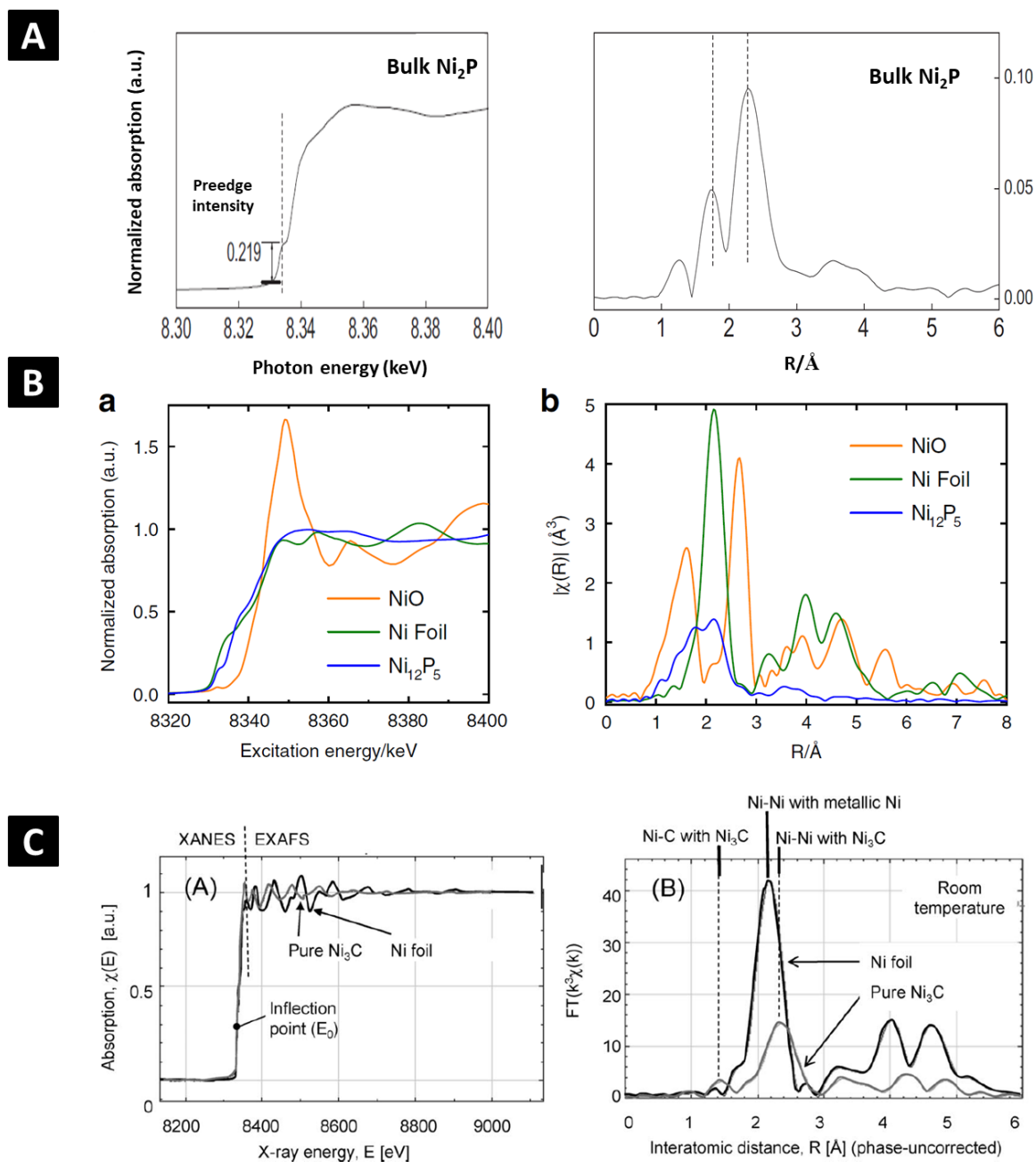


Figure 7. X-ray absorption spectra (left) and  $k^3$ -weighted Fourier transform spectra in the  $R$ -space (right) of (A)  $\text{Ni}_2\text{P}$ , (B)  $\text{Ni}_{12}\text{P}_5$  and (C)  $\text{Ni}_3\text{C}$ . Adapted from respectively references [25], [26] and [27].

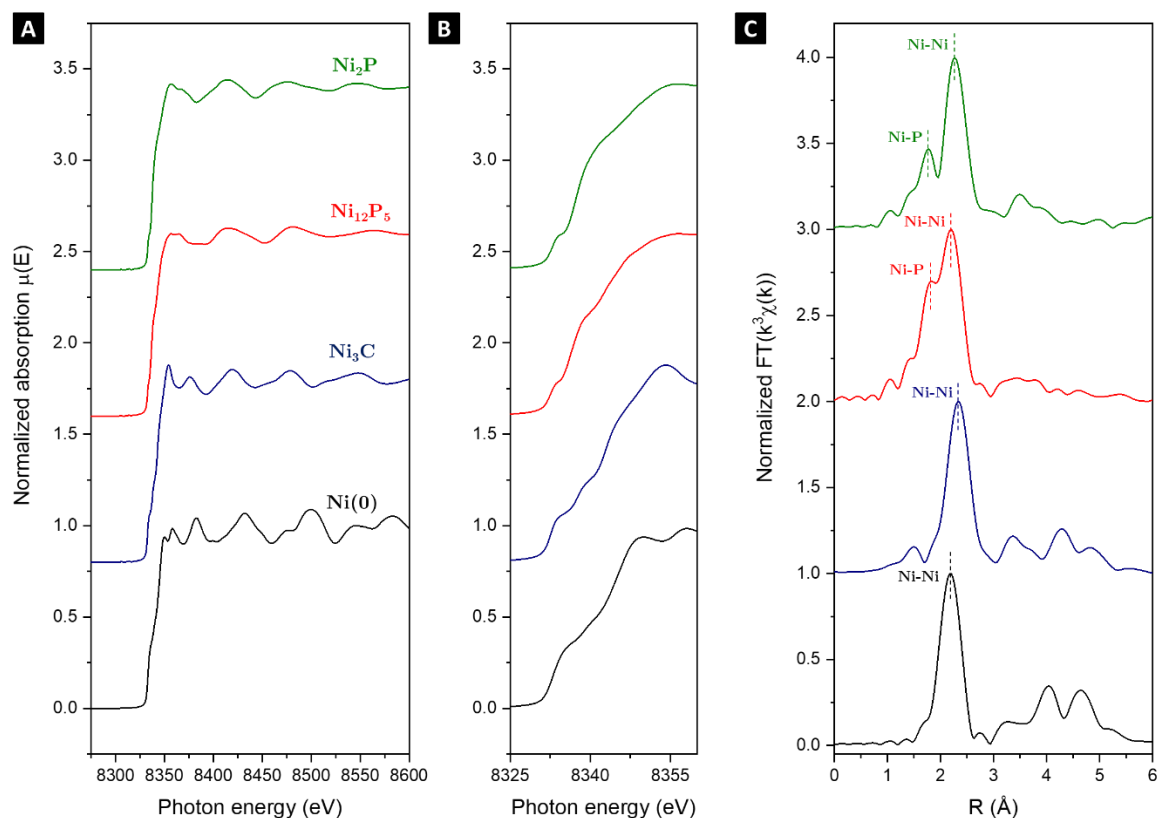


Figure 8. (A) Ni K-edge XANES spectra with (B) zoom on the edge region. (C)  $k^3$ -weighted Fourier transforms in the R-space of a reference Ni(0) foil, Ni<sub>3</sub>C nanoparticles (Synthesis VII.2.) and the subsequent phosphidized samples of Ni<sub>12</sub>P<sub>5</sub> (Synthesis VII.4.) and Ni<sub>2</sub>P (Synthesis VII.5.), measured as pellets in graphite.

	Ni–Ni / Å	Ni–C / Å	Ni–P / Å
Ni(0) foil	2.20 (2.19)	-	-
Ni <sub>2</sub> P	2.27 (2.24)	-	1.77 (1.78)
Ni <sub>12</sub> P <sub>5</sub>	2.21 (2.15)	-	1.83 (1.80)
Ni <sub>3</sub> C	2.35 (2.38)	1.50 (1.41)	-

Table 1. Characteristic distances (peak positions) extracted from EXAFS spectra in Figure 8C, data in brackets correspond to the ones from literature (Figure 7).

**Materials stability.** The stability of the catalysts from Syntheses VII.2. ( $\text{Ni}_3\text{C}$ ), VII.4. ( $\text{Ni}_{12}\text{P}_5$ ) and VII.5. ( $\text{Ni}_2\text{P}$ ) under oxidizing conditions was studied. The materials were subjected to dry calcination treatment in air at 200 °C according to Thermal treatment VII.1.

**Thermal treatment VII.1. Dry calcination in air.** The isolated powders from Syntheses VII.2. ( $\text{Ni}_3\text{C}$ ), VII.4. ( $\text{Ni}_{12}\text{P}_5$ ) and VII.5. ( $\text{Ni}_2\text{P}$ ) were placed in open glass cups and introduced in a muffle furnace. A heating ramp to 200 °C (10 °C/min) was launched and the powders were let at this temperature for 2 h. The furnace was then let to naturally cool down to room temperature. The powders did not undergo any change concerning their visual aspect.

After Thermal treatment VII.1., the  $\text{Ni}_3\text{C}$  sample and the two nickel phosphides originating from the two-step protocols were characterized by XRD and XAS (Figure 9). The spectra and diffractograms before calcination (solid lines) and after calcination (dotted lines) are perfectly identical. This denotes the structural stability of the NPs toward oxidation in spite of the high surface/volume ratio. The stability of the materials in bulk as probed with XAS and XRD is nonetheless not enough to conclude on the stability of their surfaces which are the relevant part of the objects for catalysis. XPS studies of the samples before and after Thermal treatment VII.1. are envisioned to elucidate this question.

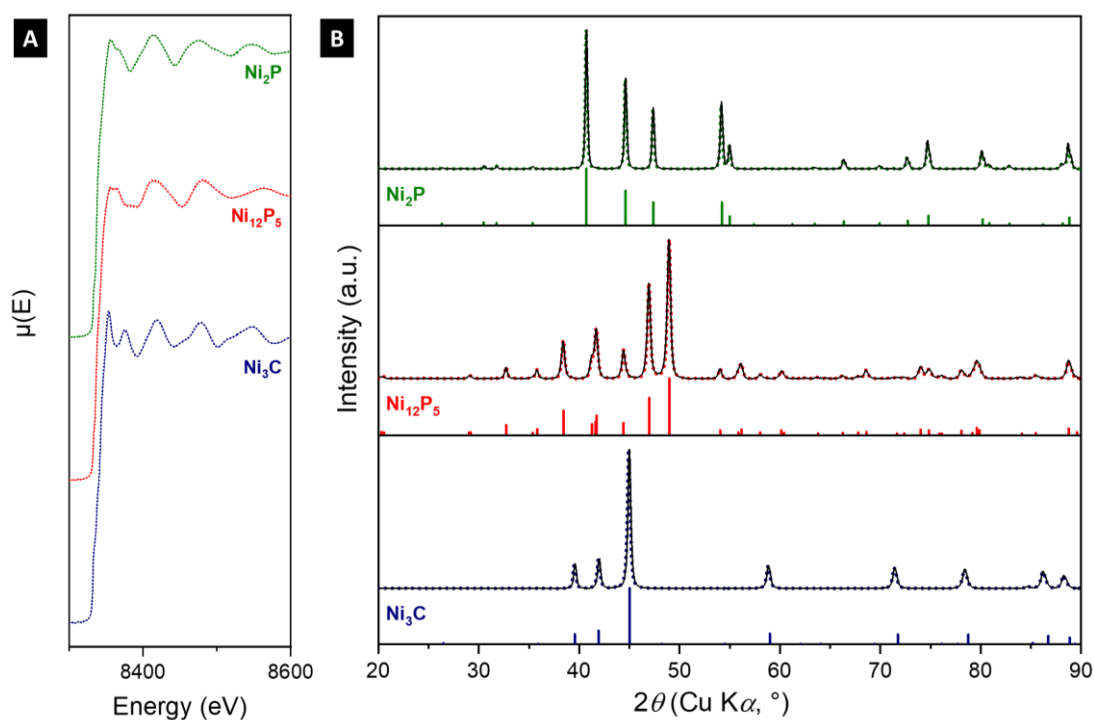


Figure 9. (A) Ni K-edge XANES spectra and (B) XRD spectra of materials from Syntheses VII.2. ( $\text{Ni}_3\text{C}$ ), VII.4. ( $\text{Ni}_{12}\text{P}_5$ ) and VII.5. ( $\text{Ni}_2\text{P}$ ), before (solid lines) and after (dotted lines) Thermal treatment VII.1.

### VII.1.3 Carbide-free nickel(0) nanoparticle synthesis

As just developed in the above section, Ni(0) nanoparticles may be easily carburized in Ni<sub>3</sub>C in presence of a carburizing agent such as 1-octadecene (ODE). Even in the absence of ODE, works report the synthesis of Ni<sub>3</sub>C from Ni(acac)<sub>2</sub> in oleylamine at temperatures as low as 240 °C, provided the reaction time is long enough.<sup>22</sup> The temperature triggering the carbide formation from the metal being just above the usual synthesis temperature of the Ni(0) nanoparticles (*ca.* 210 °C), there is a risk the carbide phase got formed, even in small quantities, during an overshoot of the heating ramp or due to an ill-calibrated thermocouple. We propose here a synthesis of Ni(0) performed in decylamine rather than in oleylamine. With this new procedure, the temperature cannot exceed the boiling point of decylamine (DAm) at 217 °C, much lower than that of oleylamine at 364 °C. Previous works already proved the reducing character of oleylamine, required for Ni(0) formation, was not linked to the C=C double bond but rather to the amino group, there is therefore no problem in using DAm for the thermal decomposition of Ni(acac)<sub>2</sub> in Ni(0).<sup>29</sup> The synthesis was conducted with and without TOP as ligand for nanoparticle size control (Synthesis VII.6.).

**Synthesis VII.6. Carbide-free Ni(0) nanoparticles in DAm.** In a 25 mL three-necked round-bottom flask, 9 mL of decylamine (7.1 g, 45 mmol, 37.2 equiv.) were degassed under vacuum at r.t. during 20 min and the flask was purged with N<sub>2</sub> three times. Under N<sub>2</sub>, Ni(acac)<sub>2</sub> (310 mg, 1.21 mmol, 1 equiv.) and eventually TOP (0.43 mL, 0.96 mmol, 0.8 equiv.) were added to the solution. The solution was heated to 217 °C with a heating mantle. The resulting solution became emerald green then turquoise and finally a black suspension *ca.* 190 °C. The solution was let to react 2 h at reflux and was then cooled to r.t. under N<sub>2</sub>. A black solid was aggregated on the stirring bar and the supernatant was yellowish. The black solid was washed three times with 10 mL. The obtained black powder (69 mg, 97 % yield) was then dried under N<sub>2</sub> and stored in air.

XRD patterns of the particles formed in Synthesis VII.6. are displayed in Figure 10A: Ni(0) NPs are obtained both with and without TOP with respective Scherrer sizes of 8 nm and 25 nm. TEM images of the samples reveal the NPs are spherical in presence of TOP and irregular in absence of TOP (Figure 10B-C) with dimensions coherent with the Scherrer analysis. The TOP acts as a ligand in the synthesis and regulates the growth of the NPs, leading to smaller and more spherical objects. The NPs obtained with Synthesis VII.6. are similar to the ones obtained following a similar synthesis in OAm.<sup>18</sup> The use of DAm solvent instead of OAm in order to obtain a reproducible reaction temperature of 217 °C is therefore validated.



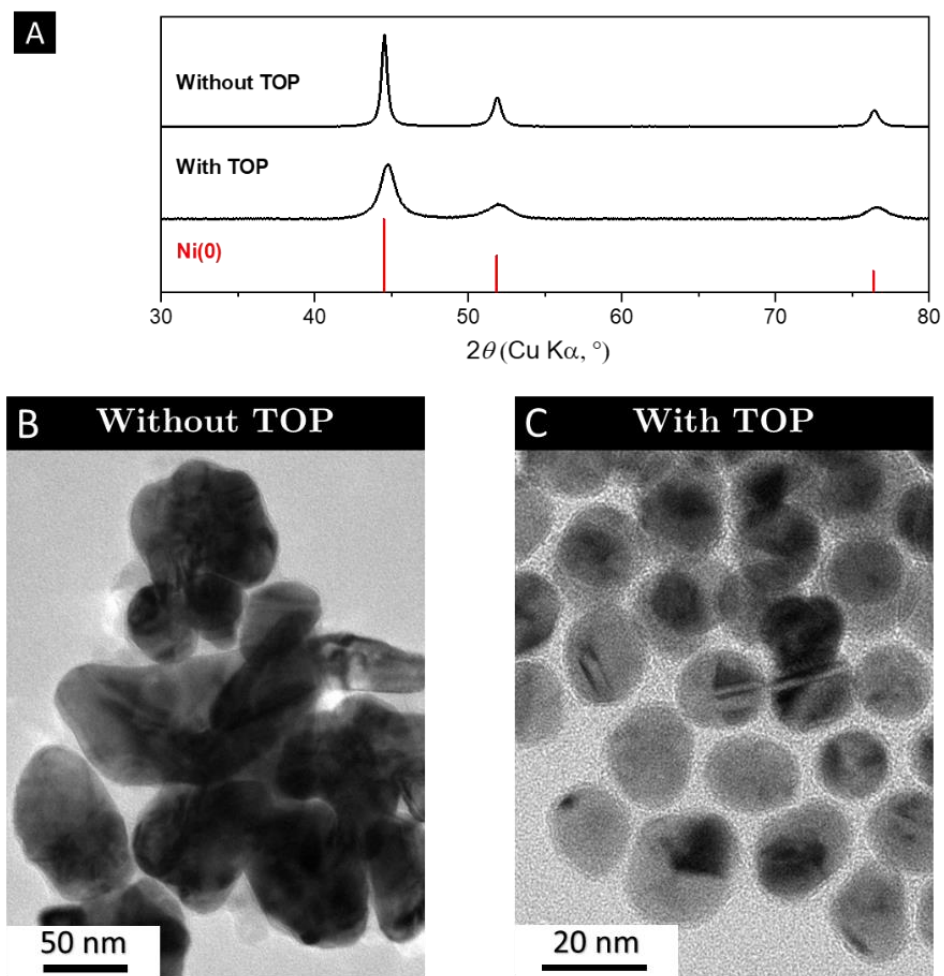


Figure 10. (A) XRD spectra of Ni(0) nanoparticles obtained from Synthesis VII.6. without (top) and with TOP (bottom). Corresponding TEM images of the samples (B) without and (C) with TOP.

## VII.2. Hydrogenation reactions

The use of different nickel-containing nanoparticles for hydrogenation reactions in the liquid phase was reviewed in Chapter I. Hydrogenation reactions of nitrobenzene (PhNO<sub>2</sub>) and phenylacetylene (PhCCH) under soft conditions were reported with respectively Ni<sub>2</sub>P or Ni<sub>12</sub>P<sub>5</sub> (100 °C, 10 bar H<sub>2</sub>, EtOH)<sup>30</sup> and Ni<sub>2</sub>P (85 °C, 6 bar H<sub>2</sub>, dioxane)<sup>7</sup>. There is however no mention of the use of nickel carbide (Ni<sub>3</sub>C) for hydrogenation reaction in solvents. We explored whether this phase, easier to obtain than nickel phosphide as nanoparticles and more resistant to poisoning than Ni(0), is also active for the reduction of the model compounds PhNO<sub>2</sub> and PhCCH.

A series of experiments was also performed to study the hydrogenation of furfural in furfuryl alcohol by Ni<sub>2</sub>P nanoparticles from Synthesis VII.1. and by Ni<sub>3</sub>C nanoparticles from Synthesis VII.2. under mild conditions (90 °C, 7 bar, iPrOH). The catalysis were successful with a conversion in furfuryl alcohol of *ca.* 50 % for Ni<sub>2</sub>P and *ca.* 4 % for Ni<sub>3</sub>C. We nonetheless chose not to display the results as these experiments were purely exploratory, the protocols for the catalysis not yet fully operational at that time and because the Ni<sub>2</sub>P synthesis was not reproducible.

### VII.2.1 Nitrobenzene hydrogenation

**Catalysis VII.1. Nitrobenzene hydrogenation.** In air, 12.5 mg of Ni<sub>3</sub>C from Synthesis VII.2. (0.2 mmol, 0.1 equiv. of [Ni]), 1 mL of solvent and 210 µL of nitrobenzene (2 mmol, 1 equiv.) were introduced in a 25 mL glass autoclave. The nanoparticles were suspended by sonication during *ca.* 1 min. The autoclave was closed and the atmosphere was changed for H<sub>2</sub> (7 bar) after 2 cycles vacuum/H<sub>2</sub>. The autoclave was then introduced in a preheated oil bath at 60 °C or 100 °C for 16 h. The pressure initially increased to *ca.* 8 bar and then decreased to *ca.* 5 bar (the characteristic time of decrease depended on the solvent). After reaction, the autoclave was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

Hydrogenation of nitrobenzene in aniline was attempted at 100 °C in a variety of solvents (EtOH, iPrOH, 1-butanol, dioxane, toluene) with nickel carbide Ni<sub>3</sub>C (10 mol%) as catalyst (Catalysis VII.1.). Black suspensions were recovered for all solvents, indicating the colloidal stability of the Ni<sub>3</sub>C NPs was good during catalysis. After 2 h, the pressure had dropped by 2.5 bar, 1.5 bar, 1 bar, 0.5 bar and 0.5 bar for respectively EtOH, iPrOH, toluene, dioxane and 1-butanol. The pressure after 2 h being close to the final one for EtOH (5 bar) we suggest the reaction was over much before the end of the 16 h duration. Complete conversions were obtained for all solvents with a 100 % selectivity to aniline at 100 °C (Figure 11A). Upon decrease of reaction temperature, the conversion dropped below 20 % for all solvents expect EtOH for which a complete conversion was still obtained. We concluded the H<sub>2</sub>

activation for nitro group hydrogenation on Ni<sub>3</sub>C NPs was more favorable in protic and polar solvents than in apolar ones and that there is still a margin of progression as to the temperature and H<sub>2</sub> pressure for the reaction run in EtOH.

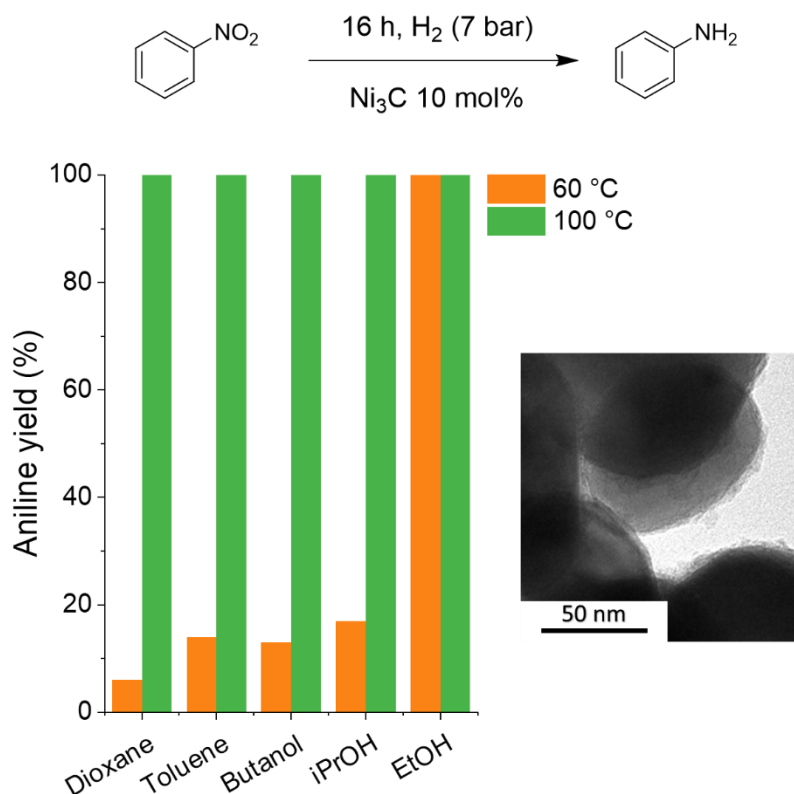


Figure 11. Hydrogenation of nitrobenzene with Ni<sub>3</sub>C according to Catalysis VII.1. Yields determined by NMR.

The protocol for Catalysis VII.1. was chosen after optimization. In the original one, a simple stirring but no sonication was performed to disperse the NPs. It appeared *a posteriori* the sonication step was essential to well disperse the NPs and obtain optimal and well reproducible results. The results obtained without sonication with Ni<sub>3</sub>C from Synthesis VII.2. and Ni<sub>12</sub>P<sub>5</sub> from Synthesis VII.4. are displayed in Figure 12. We believe they should be treated as a proof of concept and not directly compared with those obtained with Catalysis VII.1. It appears Ni<sub>12</sub>P<sub>5</sub> NPs indeed have a catalytic activity for PhNO<sub>2</sub> hydrogenation, and apparently lower than Ni<sub>3</sub>C NPs. The reactions with Ni<sub>12</sub>P<sub>5</sub> and Ni<sub>2</sub>P NPs following Catalysis VII.1. are currently under investigation to be compared with those with Ni<sub>3</sub>C.

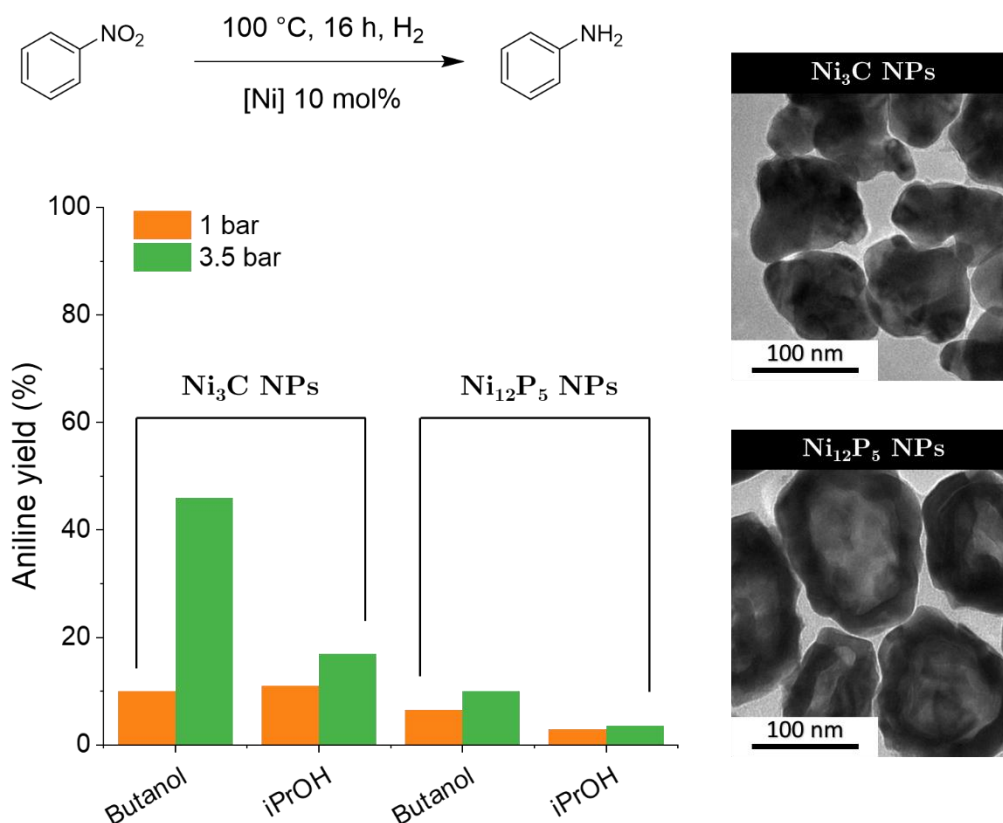


Figure 12. Hydrogenation of nitrobenzene with Ni<sub>3</sub>C and Ni<sub>12</sub>P<sub>5</sub> according to modified Catalysis VII.1. (no sonication, 330  $\mu\text{L}$  PhNO<sub>2</sub>, 1.67 mL of solvent, with lower H<sub>2</sub> pressures). Yields determined by NMR.

## VII.2.2 Phenylacetylene hydrogenation

**Catalysis VII.2. Phenylacetylene hydrogenation.** In air, 12.5 mg of Ni<sub>3</sub>C from Synthesis VII.2. (0.2 mmol, 0.1 equiv. of [Ni]), 1 mL of solvent and 220  $\mu\text{L}$  of phenylacetylene (2 mmol, 1 equiv.) were introduced in a 25 mL glass autoclave. The nanoparticles were suspended by sonication during *ca.* 1 min. The autoclave was closed and the atmosphere was changed for H<sub>2</sub> (7 bar) after 2 cycles vacuum/H<sub>2</sub>. The autoclave was then introduced in a preheated oil bath at 100  $^\circ\text{C}$  for 16 h. The pressure initially increased to *ca.* 8 bar and then decreased to *ca.* 5 bar (the characteristic time of decrease depended on the solvent). After reaction, the autoclave was let to cool down naturally to r.t. before opening. An aliquot of the liquid phase was studied by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

Hydrogenation of phenylacetylene in styrene and ethylbenzene was attempted at 100  $^\circ\text{C}$  in a variety of solvents (EtOH, iPrOH, 1-butanol, dioxane, toluene) with nickel carbide Ni<sub>3</sub>C (10 mol%) as catalyst (Catalysis VII.2.). All the phenylacetylene was hydrogenated in the different studied solvents and a more important overhydrogenation was observed for the protic and polar solvents (alcohols) (Figure 13A).

Reactions at lower temperatures and with  $\text{Ni}_{12}\text{P}_5$  and  $\text{Ni}_2\text{P}$  NPs following are currently under investigation to be compared with those with  $\text{Ni}_3\text{C}$ .

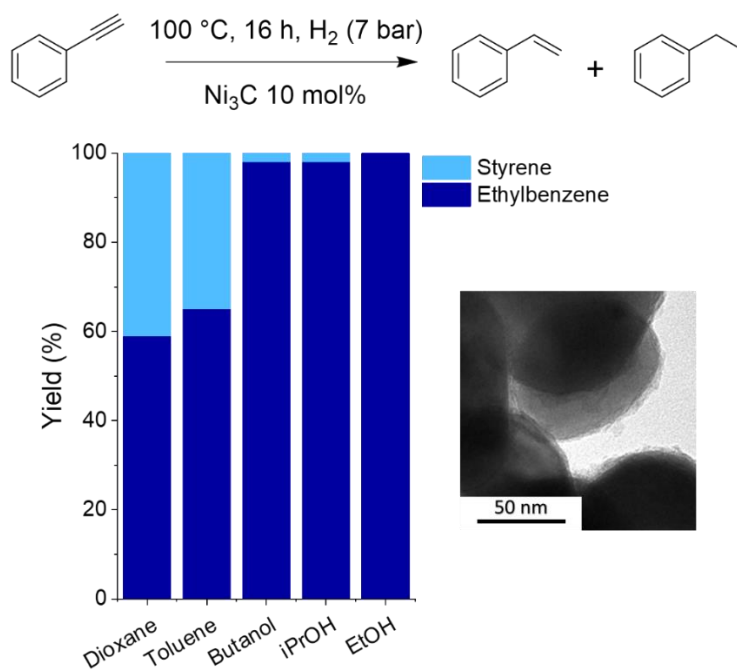


Figure 13. Hydrogenation of phenylacetylene with  $\text{Ni}_3\text{C}$  according to Catalysis VII.2. Yields determined by NMR.

### VII.3. Conclusion

We attempted the solvothermal synthesis of  $< 10$  nm large NPs of nickel phosphide ( $\text{Ni}_2\text{P}$ ,  $\text{Ni}_{12}\text{P}_5$ ) but the materials were not XRD-pure which would have complicated the catalytic results interpretations. We nonetheless provided a few clues on the influence of temperature on phase speciation and stressed the critical importance of the heating setup on the reaction temperature. By following and adapting a previously published two-step protocol, we successfully synthesized a family of comparable 100 nm large nickel-containing NPs ( $\text{Ni}_3\text{C}$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$ ). The phosphide NPs were obtained by hot-injection of TOP in a  $\text{Ni}_3\text{C}$  NPs suspension and displayed a core-shell morphology. For these optimized syntheses, the catalysts appeared XRD-pure and the XAS signatures were coherent with the ones reported in literature. The absence of modification of the XAS spectra upon oxidizing conditions denoted the core stability of the NPs.

Nickel carbide proved to be an efficient catalyst for nitrobenzene reduction in aniline and for phenylacetylene hydrogenation in ethylbenzene, with a total conversion in EtOH at respectively 60 °C and 100 °C. An important influence of the solvent was observed with the highest activities obtained in alcohols (1-butanol, 2-propanol, ethanol) compared to dioxane and toluene. The same solvent trend was followed for both nitro and alkyne hydrogenation. Preliminary data on furfural hydrogenation indicated  $\text{Ni}_3\text{C}$  has a catalytic activity for C=O hydrogenation under soft conditions (90 °C, 7 bar  $\text{H}_2$ ). Catalytic hydrogenation of furfural in furfuryl alcohol with  $< 10$  nm large  $\text{Ni}_{12}\text{P}_5$ - $\text{Ni}_2\text{P}$  NPs was obtained with a higher conversion than with  $\text{Ni}_3\text{C}$ .

Different perspectives based on these results are envisioned:

- (1) The use of softer conditions and shorter reaction times for nitrobenzene and phenylacetylene hydrogenation with  $\text{Ni}_3\text{C}$  as complete conversions were obtained in both cases, and the extension to other substrates such as benzaldehyde or benzonitrile.
- (2) Reproducible syntheses of comparable  $\text{Ni}_{12}\text{P}_5$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}(0)$  NPs have been established. We suggest using all these NPs for similar reactions (with the  $\text{Ni}(0)$  NPs as a benchmark catalyst) to compare the catalytic activities (conversions and chemoselectivities)
- (3) Studying the impact of the addition of a phosphine on the hydrogenation reactions

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## General conclusion and Perspectives

The objective of this PhD work was to develop the syntheses of metal-containing nanoparticles for H<sub>2</sub> activation in solvent. To do so, we targeted three main categories of syntheses: solvent-free, in water and in organic solvent. As the H<sub>2</sub> splitting on non-purely metallic catalyst surfaces is largely guided by the presence of defects and singularities leading to coordinatively unsaturated sites (CUS), we favored the syntheses susceptible to create such active sites. We therefore devoted a particular attention to the mechanisms of nanoparticles formation.

### *From nanoparticles syntheses...*

**Part 1 – Solid-state metathesis.** The solid-state metathesis of several early transition metal nanocarbides and nanohydrides was deeply investigated in this PhD work, essentially through XRD and TEM. Using the results obtained with the different metals (Zr, Nb, Mo, Hf, Ta and W), we could propose a mechanism for their formation: reduction, carburization, hydrogenation and finally oxidation. A rational understanding of the reactivity was established with thermodynamic considerations: the temperature of combustion was indeed estimated with the enthalpy of reaction and the heat capacity of the reactive mixture. We evidenced the influence of several parameters on the phase speciation in the product, such as the nature of the carbon support, the presence of a gas phase or the scale of the reaction. The thermodynamic considerations previously mentioned seemed to exclude the extension of this SSM reaction to late transition metals and rare-earth metals, as well as the substitution of the metal chloride precursors by metal oxides. The nanoparticles of the initially targeted phases (Mo<sub>2</sub>C, W<sub>2</sub>C) could be easily obtained in gram scale quantities. Besides, they are already disposed on a conductive carbon support, very well suited for electrocatalysis and colloidal catalysis.

**Part 2 – Hydrothermal syntheses.** Cerium hydroxide and oxide nanorods were synthesized following a hydrothermal route: a solution of Ce(NO<sub>3</sub>)<sub>3</sub> was mixed with a solution of NaOH or KOH, the precipitating agent, and then heated at 100 °C. We demonstrated the crucial importance of the reaction container (Teflon autoclave, Nalgene vessel or Borosilicate vessel) on the obtained phase: either a cerium oxide, CeO<sub>2</sub>, for the Teflon autoclave and the Nalgene vessel or a cerium trihydroxide, Ce(OH)<sub>3</sub>, for the Borosilicate vessel. During the development of a catalytically active cerium oxide phase, we reported an unusual evolution of the Ce(OH)<sub>3</sub> phase in an unknown crystalline compound. By comparison with other lanthanide hydroxides, we suggested this compound may correspond to a cerium(IV) hydroxide or oxyhydroxide

rather than a cerium oxide. In addition of the crystallographic characterization (XRD, SAED), different techniques were used to establish the degree of oxidation of cerium (XPS, XAS), the presence of hydroxyl groups (IR) and of multiple defects upon heating (TEM). There is an ongoing study to elucidate the crystal structure of the aged  $\text{Ce}(\text{OH})_3$ . The synthesis of indium oxide nanoparticles was then successfully achieved according to literature protocols, and yields to similar results than the published ones.

**Part 3 – Solvothermal syntheses.** The synthesis of tungsten oxide nanowires was achieved from  $\text{WCl}_6$  in an oleyl alcohol/oleylamine mixture. As this structure presents tungsten atoms at various degrees of oxidation and oxygen defects, we estimated the materials would be of interest for  $\text{H}_2$  activation. We also conducted the synthesis of molybdenum oxides nanoparticles in oleylamine and oleic acid. The characterization of the nanoparticles was quite challenging considering the amorphous structure in the first case and the failure to isolate the nanoparticles in the second case. We therefore used XAS to determine what were the oxidation degrees of the metallic center (Mo) in each case. To our surprise, the two materials were different: an intermediate metal oxide  $\text{MoO}_x$  ( $2 < x < 3$ ) for the synthesis in OAm and a phase close to  $\text{MoO}_2$  for the synthesis in OAc. The study by  $^1\text{H}$  NMR of the crudes of reaction revealed the organic byproducts were substantially different. The study of the mechanism of formation of these metal oxides would be of interest in order to compare OAm and OAc as solvents for nanoparticles syntheses. Up to now, most of the mechanistic studies with OAm focused on reduced metals (Pd, Ni, Cu) and the study of  $\text{MoO}_x$  nanoparticles would enlarge the scope. *In situ* XAS data on the formation of molybdenum oxides in OAm and OAc are currently under investigation using the MCR-ALS approach. Finally, the syntheses of two nickel phosphide ( $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$ ) and one nickel carbide ( $\text{Ni}_3\text{C}$ ) nanoparticles were achieved in an oleylamine/1-octadecene/trioctylphosphine mixture. The one-pot two-step procedure (carburization followed by phosphidization) was first developed by Tracy *et al.* to obtain the  $\text{Ni}_{12}\text{P}_5$  phase but we adapted it to form  $\text{Ni}_2\text{P}$  nanoparticles (higher amount of injected TOP and lower temperature of injection).

### *...to colloidal catalysis...*

**Hydrogenation with metal carbides.** Hydrogenation of styrene and phenylacetylene was attempted with  $\text{Mo}_2\text{C}$  and  $\text{W}_2\text{C}$  nanoparticles supported on carbon. No catalytic activity for hydrogenation of styrene was obtained for  $\text{W}_2\text{C}$ . Preliminary data indicated the  $\text{Mo}_2\text{C}$  sample possessed a catalytic activity in gas phase hydrogenation of butadiene but a very poor one at  $100\text{ }^\circ\text{C}$  for phenylacetylene reduction in solvent. As the reduction of an oxidized shell around the nanoparticles at temperatures higher than  $120\text{ }^\circ\text{C}$  seemed necessary, we suggest for the future the use of temperatures in the range  $150\text{-}200\text{ }^\circ\text{C}$  for the hydrogenation reaction. In addition of

their use in hydrogenation catalysis, Mo<sub>2</sub>C/C samples are currently under study, through collaborations, for Reverse Water Gas Shift reaction (RWGS) and electrocatalysis, respectively at the LSFC by the group of Helena Kaper and at the FHI by the group of Beatriz Roldan. Besides, the quite unique formation of nanoparticles of supported metal hydrides would be the occasion to investigate their catalytic activity, for the Haber Bosch process for instance as the catalysis by isolated tantalum hydride species was previously reported.

**Hydrogenation with metal oxides.** Hydrogenation of phenylacetylene was studied in presence of CeO<sub>2</sub> and Bi<sub>0.02</sub>In<sub>2</sub>O<sub>3</sub>. The results presented in this PhD work confirmed and extended first the H<sub>2</sub> adsorption on reduced CeO<sub>2</sub> already presented by different published works on close materials and then the alkyne hydrogenation in solvent. The preliminary data for phenylacetylene and nitrobenzene hydrogenations with W<sub>18</sub>O<sub>49</sub> and MoO<sub>x</sub> nanoparticles showed very poor yields even at elevated temperature (150 °C) and under high H<sub>2</sub> pressures (30 bar). We could eventually suggest the study of the addition of a phosphine or amine to boost the reactivity but we think it would be more pertinent to focus on the cerium and indium oxide catalysts.

**Colloidal hydrogenation with nickel-containing nanoparticles.** The catalytic activity for colloidal hydrogenation with nickel carbide (Ni<sub>3</sub>C) nanoparticles was reported for the first time in this PhD work. Although Ni–C catalysts have already been mentioned in gas phase hydrogenation or for hydrotreatment, there was no published work on its use for nitro compounds or olefins reduction in solvent. Experiments are planned to first reach the mildest conditions as possible (temperature, pressure, metal loading) and then extend the scope of the studied substrates (nitrile, ketone, aldehyde). We envision then the comparative study of the catalytic activity of the phosphide phases (Ni<sub>2</sub>P, Ni<sub>12</sub>P<sub>5</sub>) and the carbide one.

Multiple categories of materials were synthesized in this work, we therefore concentrated our effort on the ones leading to the most interesting results with our current setup, *i.e.* the cerium containing phases and the nickel containing phases. Up to recently, the laboratory was equipped with a gas system allowing pressures up to only 7 bar, but has now been upgraded to 100 bar. Different catalysts (metal oxides, early transition metal carbides), for which lower activities are expected according to preliminary results, will therefore be the object of a postdoctoral work in the laboratory with higher H<sub>2</sub> pressures.

### *...to reach a “Nano” Frustrated Lewis Pair*

**H<sub>2</sub> activation.** The most promising results as to the construction of a NanoFLP system, *i.e.* a colloidal activation of H<sub>2</sub> in solvent between a molecular base and an inorganic nanoparticle, were obtained with the cerium oxide nanoparticles. We indeed demonstrated the stability of surface hydride species on reduced cerium oxide. Now we

developed reproducible syntheses for defective CeO<sub>2</sub> and nickel-containing nanoparticles, we suggest as a perspective to study the influence of the presence of phosphines (PCy<sub>3</sub>, P<sup>t</sup>Bu<sub>3</sub>, PPh<sub>3</sub>) or amines (tmp, lutidine) on the hydrogenation reactions, eventually after increasing the reaction temperature to have higher yields.

**CO<sub>2</sub> activation.** The CO<sub>2</sub> molecule is known for its affinity with metal oxide surfaces. A perspective we envision is the activation of the C=O bond of carbon dioxide, on the different metal oxides we synthesized, with the eventual addition of a molecular base. Activation of CO<sub>2</sub> *via* an FLP mechanism is indeed currently under investigation in the laboratory by Cyprien Poucin (PhD 2019-2022) and Anthony Ropp (PhD 2021-2024).

To conclude, it is time to look back at the initial question of this PhD: “Can we develop tailored syntheses of new metal-containing catalysts for colloidal hydrogenation, resistant to poisoning and without rare elements?” Our contribution to the answer can be decomposed in several points:

- We first developed a synthetic method of early transition carbides nanoparticles, easily performed in laboratory, with common precursors and on the scale of several grams. The metals present in these materials (Ti, V, Zr, Nb, Mo, W) are abundant enough not to present tensions as to their supply for catalytic applications. Some of the corresponding materials (Mo<sub>2</sub>C, WC) are currently the object of intense research by the heterogeneous catalysis community.
- Cerium oxide is already used on large scales for catalytic applications and we exposed an unreported evolution of a hydroxide precursor for the CeO<sub>2</sub> nanoparticles synthesis. We also confirmed there is a potential for selective hydrogenation reactions in solvent in addition of that of acetylene in gas phase. Although cerium is a rare-earth element, its natural abundance, 66 ppm in the Earth crust, is between those of Cu (60 ppm) and Ni (84 ppm): its supply is therefore not problematic.
- We paved the way for a simple solvothermal synthesis of small and defective molybdenum oxide nanoparticles.
- We demonstrated the catalytic activity of Ni<sub>3</sub>C for hydrogenation of nitro compounds and olefins, unheard of so far. Nickel carbide is expected to be more tolerant to deactivation by light element insertion than Ni(0) and the synthesis of XRD-phase pure nanoparticles *via* solvothermal pathway is more straightforward than those of the nickel phosphide counterparts.

# Appendix I

## Experimental section

### ES.1. Chemicals

Unless otherwise stated, all chemicals were used as received and without purification.  $\text{NbCl}_5$  (99.9 %),  $\text{WCl}_6$  (99.9 %), K (99.5 %), phenylacetylene (98 %), styrene (99 %), toluene (99.8 %), tetrahydrofuran (99 %), hexane (98 %), 1-butanol (97 %), butylamine (99.5 %),  $\text{PPh}_3$  (98 %), NaOH (98 %), KOH (98 %), oleylamine (OAm) (98 %), oleic acid (85 %), oleyl alcohol (85 %), 1-octadecene (ODE) (90 %), octyl ether (99 %), furfural (99 %), dioxane (99.5 %), DMF (99.8 %), DMSO (95 %), acetone (97 %),  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (98 %),  $\text{MoO}_3$  (99 %) and  $\text{CeO}_2$  (99.9 %) were purchased from Sigma-Aldrich. Ethanol (96 %), methanol (95 %) and isopropanol (95 %) were purchased from VWR.  $\text{ZrCl}_4$  (99.5 %),  $\text{MoCl}_3$  (99.5 %),  $\text{PCy}_3$  (97 %), TOP (97 %),  $\text{MoO}_2(\text{acac})_2$  (95 %),  $\text{Ni}(\text{acac})_2$  (95 %) and  $\text{Ce}(\text{OH})_4$  were purchased from Strem Chemicals.  $\text{HfCl}_4$  (99.9 %),  $\text{MoCl}_5$  (99.6 %),  $\text{TaCl}_5$  (99.8 %), carbon black acetylene (99.9 %, 50 % compressed), natural graphite powder (99.9 %, Ultra F purity),  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.5 %) and  $\text{In}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9 %), were purchased from Alfa Aesar.

Commercial  $\text{WCl}_6$  from Sigma Aldrich and Strem Chemicals was contaminated with traces of metallic W(0). It was purified by recrystallization in a Schlenk tube under static vacuum at 210 °C during 2 h. The solid at the bottom of the Schlenk gradually sublimates (red gas phase) and recrystallizes as big violet crystals on the glass walls in the cold part of the Schlenk

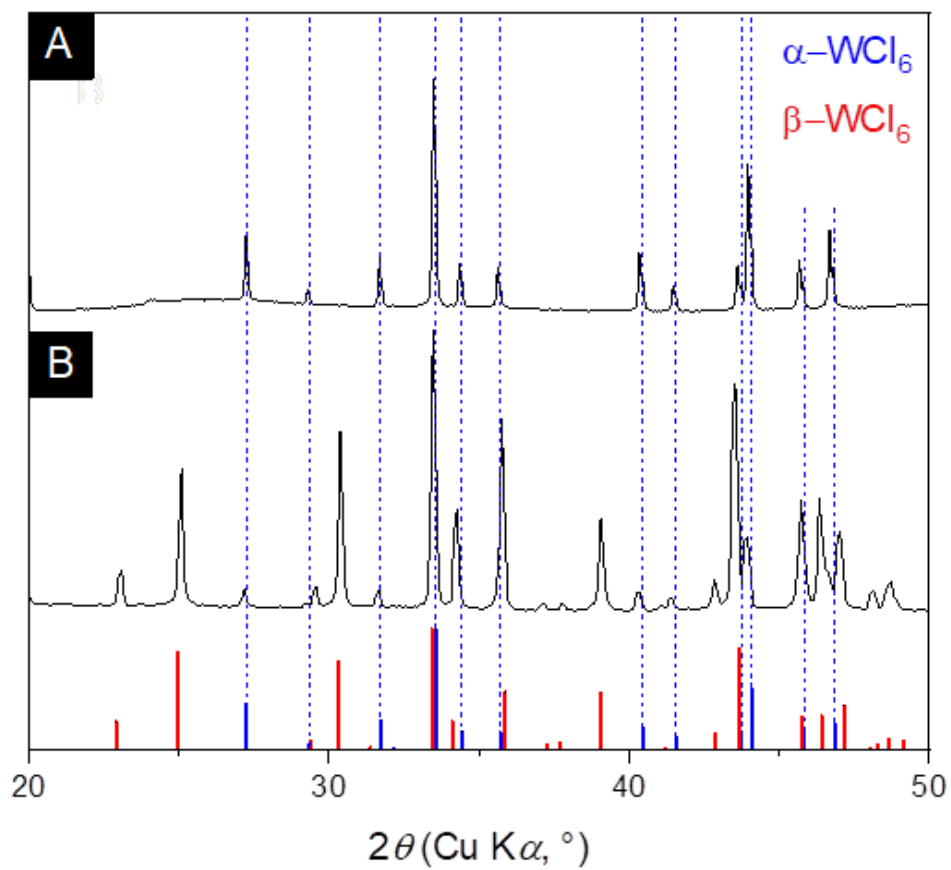


Figure 1: PXRD pattern of (A) commercial  $\text{WCl}_6$  and (B) recrystallized sample (210 °C under vacuum).

## ES.2. Nanoparticle syntheses and catalysis

The different synthetic protocols and catalysis protocols were given along the PhD thesis. The hydrothermal syntheses in Chapters IV and V were performed in borosilicate vessels, Nalgene vessels or hydrothermal bombs as shown in Figure 2.

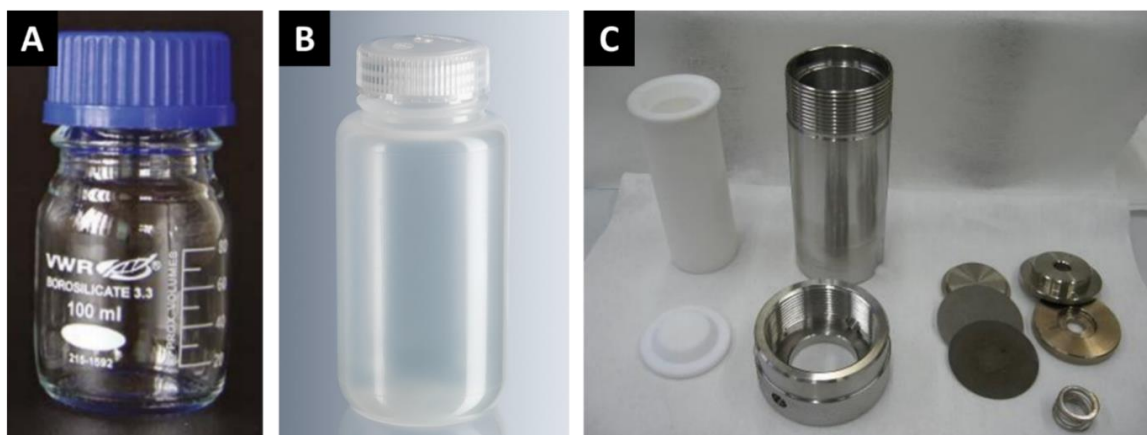


Figure 2. Typical glassware used for hydrothermal syntheses of  $\text{CeO}_2$  and  $\text{In}_2\text{O}_3$  catalysts. (A) Borosilicate vessel (reproduced from [www.vwr.com](http://www.vwr.com)), (B) Nalgene vessel, (C) Teflon autoclave/hydrothermal bomb.

The solvothermal syntheses in Chapters VI and VII were performed in regular glassware under  $\text{N}_2$  with the use of a Schlenk ramp. The round-bottom flask was disposed in a heating mantle and the temperature was regulated with the aid of a thermocouple inserted in a glass finger directly in contact with the solution (Figure 3). After reactions, the glassware was thoroughly washed with aqua regia to remove any trace of metals.



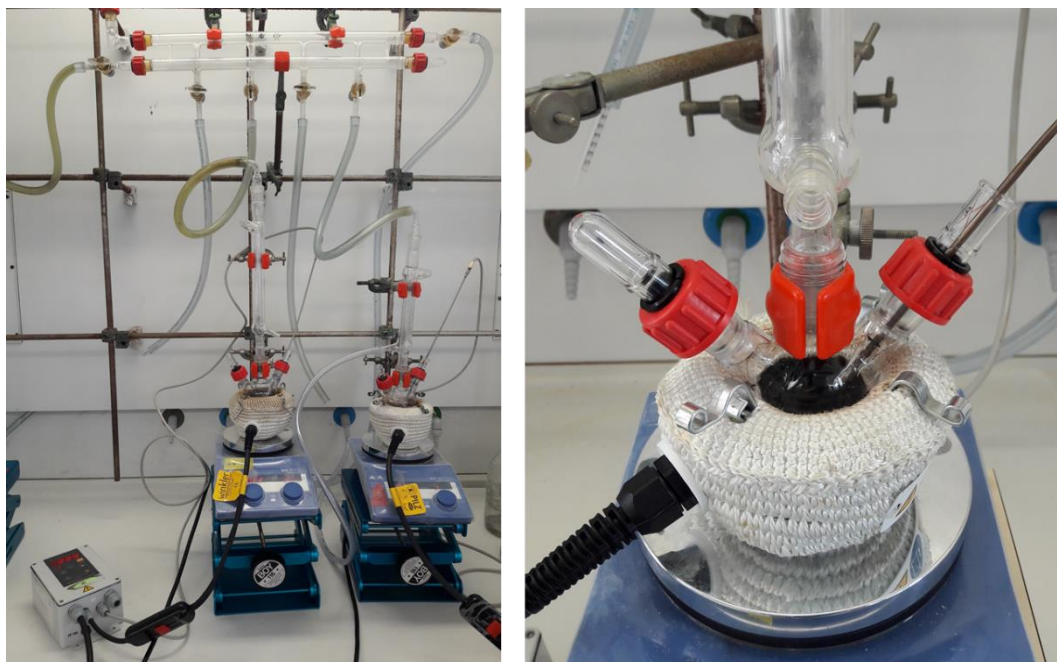


Figure 3. Typical setup used for solvothermal syntheses of  $\text{MoO}_x$ ,  $\text{W}_{18}\text{O}_{49}$  and nickel containing NPs.

Liquid phase catalysis under a pressure of  $\text{H}_2$  were performed in a Büchi autoclave composed of a head and a container, in glass for pressures below 7 bar and in Teflon + steel for pressures below 100 bar (Figure 4). The autoclaves were then directly disposed in an oil bath for heating.



Figure 4. Typical Büchi autoclave used for catalytic experiments under pressure. Left: Teflon cuve. Right: glass cuve. Photo reproduced from the Büchi website ([www.buchiglas.fr](http://www.buchiglas.fr))

### ES.3. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were measured with a Spectrum 400 PerkinElmer spectrometer. The solids were pressed on the crystal in Attenuated Total Reflectance (ATR) mode and the transmittance was recorded on the 4000-550  $\text{cm}^{-1}$  range with steps of 0.5  $\text{cm}^{-1}$ .

### ES.4. Nuclear Magnetic Resonance (NMR)

NMR experiments were performed on a Bruker AV<sup>III</sup> 300 MHz. For catalysis and synthesis crudes analysis, an aliquot of the solution was collected and directly mixed with  $\text{CDCl}_3$ . Spectra were acquired after locking to  $\text{CDCl}_3$  signal and shimming. Typical  $^1\text{H}$  NMR spectra are acquired in 5 min and treated with TopSpin software with calibration on the signal of  $\text{CHCl}_3$  (7.26 ppm) if possible, otherwise on toluene methyl (2.36 ppm).

### ES.5. Powder X-Ray Diffraction (XRD)

X-ray diffraction patterns of dry powders were measured on a Bruker D8 diffractometer using  $\text{Cu K}\alpha$  radiation at 1.5406 Å. Measurements in capillary were performed on a Bruker D8 diffractometer using  $\text{Mo K}\alpha$  radiation at 0.7093 Å. Typical diffractograms were collected with steps of 0.05 ° and a scanning speed of 3 s/point. Backgrounds of the patterns are subtracted and heights of the samples are corrected (KCl was used as an internal reference for solid-state metathesis reactions) using the DiffracEVA software. Debye-Sherrer analysis were conducted using DiffracEva software. Most of the PDF/JCPDS cards used in this work were listed in the body of the text.

Phase	PDF N°	Phase	PDF N°
$\alpha$ -Zr(0)	[04-008-1477]	ZrH <sub>2</sub>	[00-017-0314]
ZrC	[00-035-0784]	ZrO <sub>2</sub>	[04-007-0952]
$\alpha$ -Hf(0)	[00-038-1478]	HfH <sub>1.74</sub>	[00-005-0641]
		HfO <sub>2</sub>	[00-053-0560]
Nb(0)	[00-034-0370]	NbH <sub>0.8</sub>	[01-081-6188]
Nb <sub>6</sub> C <sub>5</sub>	[04-007-6990]		
Ta(0)	[00-004-0788]	Ta <sub>2</sub> H	[00-032-1281]
TaC	[00-035-0801]	TaO	
Mo(0)	[04-014-7435]	Mo <sub>2</sub> C	[04-001-2996]
W(0)	[00-004-0806]	WC	[00-051-0939]
W <sub>2</sub> C	[04-014-5679]		
KCl	[00-041-1476]		

Phase	PDF N°	Phase	PDF N°
CeO <sub>2</sub>	[00-034-0394]	Ce(OH) <sub>3</sub>	[00-055-0556]
La(OH) <sub>3</sub>	[00-036-1481]	Nd(OH) <sub>3</sub>	[04-005-8595]
Eu(OH) <sub>3</sub>	[00-017-0781]	Dy(OH) <sub>3</sub>	[00-019-0430]
Tm(OH) <sub>3</sub>	[01-083-2306]		
c-In <sub>2</sub> O <sub>3</sub>	[04-004-3575]	rh-In <sub>2</sub> O <sub>3</sub>	[00-022-0336]
InOOH	[04-009-3421]		
Bi(0)	[00-005-0519]	β-Bi <sub>2</sub> O <sub>3</sub>	[04-007-1443]
W <sub>18</sub> O <sub>49</sub>	[00-064-0773]		
Ni(0)	[03-065-2865]	Ni <sub>3</sub> C	[04-007-3753]
Ni <sub>2</sub> P	[04-003-1863]	Ni <sub>12</sub> P <sub>5</sub>	[00-022-1190]
Ni <sub>5</sub> P <sub>4</sub>	[04-014-7901]		

## ES.6. Transmission Electron Microscopy (TEM)

For TEM analysis, a drop of a diluted solution of nanoparticles dispersed in ethanol (for hydrothermal syntheses) or hexanes (for solid-state and solvothermal syntheses) was allowed to dry on an amorphous carbon coated copper grid. TEM images were collected with a TWIN 120 (TECNAI SPIRIT) operating at 120 kV. STEM bright field (BF) and high angle annular dark field (HAADF) images were acquired using a probe corrector Cs JEOL 2100F microscope operating at 200 kV.

## ES.7. Energy Dispersive X-Ray Spectroscopy (EDXS)

EDXS measurements were performed on a SEM Hitachi S-3400N operating at 10 keV. The samples were pressed on a carbon tape installed on a SEM sample holder. Measurements were performed in 3 zones to insure a better representativity of the analysis.

## ES.8. X-Ray Photoelectron spectroscopy (XPS)

XPS spectra were acquired on an Omicron Argus X-ray photoelectron spectrometer, using a monochromated Al K $\alpha$  ( $h\nu = 1486.6$  eV) radiation source having a 300 W electron beam power. The samples were analyzed under ultra-high-vacuum conditions ( $10^{-8}$  Pa). After recording a broad range spectrum (pass energy of 100 eV), high-resolution spectra were recorded for the C 1s, O 1s, Ce 3d core XPS levels (pass energy of 20 eV). The binding energies were calibrated with respect to the C 1s peak at 284.8eV (adventitious carbon). Fitting of X-ray photoemission spectra has been performed using the CasaXPS software package.

All NAP-XPS spectra were collected on the TEMPO B beamline at SOLEIL synchrotron (electron energy of 2.7 GeV and average ring current of 450 mA). The samples were dispersed in ethanol by sonication during 10 min and then drop-casted on a gold coated silicon wafer. They were then disposed on a unique sample holder and introduced in the NAP-XPS setup (pressure of  $10^{-9}$  mbar). The measurements were performed on different spots to minimize the impact of the beam damage. The incident photon energy was of 1100 eV for all experiments. Pass energy of 50 eV was used. Binding energies were calibrated using the Au  $4f_{7/2}$  peak at 84 eV.

Ceria is known for charging at low temperatures: the spectra measured below 150 °C were calibrated on the satellite peak of Ce 3d at 916.6 eV. Spectra in the Ce 3d region were background-corrected by subtraction of three linear function defined in the ranges 919-913 eV, 913-894 eV and 894-878 eV and fitted with a linear combination of intensity envelopes from Ce<sup>(IV)</sup> and Ce<sup>(III)</sup> species. All peaks were fitted using the Gaussian-Lorentzian line shape GL(30) as an approximation of the Voigt curve. Constraints were imposed on signal intensity ratios (peak area ratio of 3:2 for  $3d_{5/2}:3d_{3/2}$ ), separation between spin-orbit split peaks (18.35 eV for Ce<sup>(III)</sup> doublets and 18.5 eV for Ce<sup>(IV)</sup> doublets, determined on the reference compounds) and peak width (similar values of Full Width Half Maximum (FWHM) for both peaks of any spin-orbit split doublet). As the signals are broad and the data quite noisy for experiments performed on the Synchrotron beamline, more strict peak positions and peak widths were imposed than for laboratory instrument, as summarized in Table ES.1. and ES.2.

Species		Binding energy (eV)	Doublet splitting (eV)	FWHM (eV)	Color
Laboratory instrument (1486.6 eV)					
Ce <sup>3+</sup>	Ce $3d_{5/2}$ U <sub>0</sub> /V <sub>0</sub>	881.3-878	18.35	1-3.5	Violet
	Ce $3d_{5/2}$ U'/V'	885.6-883.3	18.35	1-5	Pink
Ce <sup>4+</sup>	Ce $3d_{5/2}$ U/V	882.8-881.9	18.5	1-2	Yellow
	Ce $3d_{5/2}$ U''/V''	888.9-887.6	18.5	1-5	Red
	Ce $3d_{5/2}$ U'''/V'''	898.4-897.7	18.5	1-3.5	Orange
Synchrotron beamline (1100 eV)					
Ce <sup>3+</sup>	Ce $3d_{5/2}$ U <sub>0</sub> /V <sub>0</sub>	881.3-881.05	18.35	2.6-3.1	Violet
	Ce $3d_{5/2}$ U'/V'	885.6-885.2	18.35	3-3.8	Pink
Ce <sup>4+</sup>	Ce $3d_{5/2}$ U/V	882.8-882.35	18.5	2.5-2.9	Yellow
	Ce $3d_{5/2}$ U''/V''	888.9-887.6	18.5	3-5	Red
	Ce $3d_{5/2}$ U'''/V'''	898.4-897.7	18.5	2-2.8	Orange

Table ES.1. Fitting parameters used in CasaXPS for Ce 3d region.

Species	Binding energy (eV)	FWHM (eV)	Color
Laboratory instrument (1486.6 eV)			
O <sub>I</sub>	529.6-529	0.8-1.3	Blue
O <sub>II</sub>	531.3-529	1-2	Dark green
O <sub>III</sub>	531.6-531.3	0.2-1.5	Light green
O <sub>IV</sub>	536-532	0.28-7	Black
Synchrotron beamline (1100 eV)			
O <sub>I</sub>	529.6-529	0.8-2.5	Blue
O <sub>II</sub>	531.3-529	1-2	Dark green
O <sub>III</sub>	533-531.3	0.2-1.5	Light green
O <sub>IV</sub>	536-532	0.28-7	Black

Table ES.2. Fitting parameters used in CasaXPS for O 1s region.

### ES.9. X-Ray Absorption Spectroscopy (XAS)

All XAS data were collected on different beamlines at SOLEIL (electron energy of 2.7 GeV and average ring current of 450 mA). Spectrum processing was carried out using the Athena/Demeter software following literature procedures.<sup>1</sup> Normalization was performed using a linear fit of the pre-edge and post-edge regions and the edge height was normalized to unity with the post-edge values asymptotically approaching zero. The absorption threshold was determined by the first zero (not corresponding to a pre-edge peak) of the first derivative. For solid samples, a 6 mg portion of the powder was diluted in *ca.* 55 mg of graphite and compressed to form a 10 mm diameter pellet.

Mo K-edge and Ni K-edge XAS data were collected on the ROCK beamline. The incoming photons were selected with a Si (220) double-crystal monochromator. Ion chambers filled with a mixture of nitrogen and helium were installed in front of and behind the sample, which simultaneously detected the incident and transmitted X-ray intensities. Fourier transforms of the Ni-EXAFS spectra were carried out in a K-range from 3.0 to 13.9 Å<sup>-1</sup>.

Ce L<sub>III</sub>-edge XAS data were collected on the LUCIA beamline. The measurements were carried out under vacuum (10<sup>-2</sup> mbar) in fluorescence mode with an outgoing photon angle of 2°. The incoming photons were selected with a Si (111) double-crystal monochromator.

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<sup>1</sup> Ravel, B. & Newville, M. ATHENA: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **12**, 537–541 (2005)

## Appendix II

### Thermodynamic calculations

#### TC.1. Heat capacity models

Heat capacity of solid KCl as a function of reduced temperature  $t$  ( $t=T(K)/1000$ ) in J/mol/K<sup>1</sup>:

$$C_p(\text{KCl}) = 35.41 + 70.03 t - 91.38 t^2 + 52.52 t^3 + 0.1534 t^{-2}$$

KCl melts at 770 °C (1043 K) with a standard fusion enthalpy of 25.5 kJ/mol.

Liquid KCl heat capacity is estimated constant at 73.6 J/mol/K.

KCl boils at 1500 °C (1773 K) with a standard evaporation enthalpy of 162.4 kJ/mol.

Heat capacity of solid CaCl<sub>2</sub> as a function of reduced temperature  $t$  in J/mol/K:

$$C_p(\text{CaCl}_2) = 87.30 - 35.08 t + 44.13 t^2 - 9.85 t^3 - 0.6742 t^{-2}$$

CaCl<sub>2</sub> melts at 772 °C (1045 K) with a standard fusion enthalpy of 28.5 kJ/mol.

Liquid CaCl<sub>2</sub> heat capacity is estimated constant at 102.5 J/mol/K.

CaCl<sub>2</sub> boils at 1935 °C (2208 K).

Heat capacity of graphite as a function of reduced temperature  $t$  in J/mol/ K<sup>2</sup>:

$$C_p(\text{graphite}) = 27.02 + 0.0457 t - 4.528 t^{-1} - 2.179 t^{-2} + 0.7991 t^{-3} - 0.07207 t^{-4}$$

Heat capacity of metal (very close values for all the metals studied here, based on Tantalum) as a function of reduced temperature  $t$  in J/mol/K:

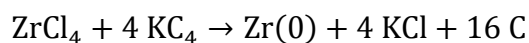
$$C_p(\text{metal}) = 20.69 + 17.29 t - 15.68 t^2 + 5.608 t^3 + 0.06158 t^{-2}$$

Pyrex glass has a heat capacity of 0.75 J/g/K which corresponds to a heat capacity of 7.5 J/K for the 10 g of the glass walls of the Schlenk tube near the powder. The auto-initiated reaction with WCl<sub>6</sub> released 300 J which would correspond to a final elevation of 45 °C of the part of the vessel in contact with the reaction. This order of magnitude is coherent with the feeling of heat with hand.

## TC.2. Enthalpies of formation and of reaction

Unless otherwise stated, all the thermodynamical data are from the Thermodynamical tables of the NIST-JANAF.<sup>1</sup> The released energy by the reaction corresponds to the absolute value of the enthalpy of reaction, determined via Hess's law.

For instance, for the reaction with  $\text{ZrCl}_4$ :



$$\Delta_{\text{reaction}}H^\circ = \Delta_f H^\circ(\text{Zr}) + 4 \Delta_f H^\circ(\text{KCl}) + 16 \Delta_f H^\circ(\text{C}) - (\Delta_f H^\circ(\text{ZrCl}_4) + 4 \Delta_f H^\circ(\text{KC}_4))$$

By definition, the enthalpy of formation of  $\text{Zr}(0)$  and graphite is zero.

$$\Delta_{\text{reaction}}H^\circ (\text{kJ/mol}) = 4 (-436.7) - (-980.5 + 4 (-30.9)) = -642.7$$

Compounds	Enthalpy of formation (kJ/mol)	Compounds	Enthalpy of formation (kJ/mol)
<b>Chlorides</b>		<b>Oxides</b>	
ScCl <sub>3</sub>	-944.8		
YCl <sub>3</sub>	-982.4		
LaCl <sub>3</sub>	-1070.7		
TiCl <sub>3</sub>	-721.7		
ZrCl <sub>4</sub>	-980.5	ZrO <sub>2</sub>	-1097.5
HfCl <sub>4</sub>	-990	HfO <sub>2</sub>	<i>no data</i>
VCl <sub>3</sub>	-580.7		
NbCl <sub>5</sub>	-797.5	Nb <sub>2</sub> O <sub>5</sub>	-1899.5
TaCl <sub>5</sub>	-859	Ta <sub>2</sub> O <sub>5</sub>	-2046
CrCl <sub>2</sub>	-395.4		
CrCl <sub>3</sub>	-556.5		
MoCl <sub>3</sub>	-393	MoO <sub>2</sub>	-587.9
MoCl <sub>5</sub>	-527.2	MoO <sub>3</sub>	-745.2
WCl <sub>4</sub>	-443.1		
WCl <sub>6</sub>	-593.7	WO <sub>3</sub>	-842.9
MnCl <sub>2</sub>	-481.2		
FeCl <sub>2</sub>	-341.7		
FeCl <sub>3</sub>	-399.2		
CoCl <sub>2</sub>	-312.5		
NiCl <sub>2</sub>	-304		
<b>Alkaline derivatives</b>			
KC <sub>4</sub>	-30.9	KCl	-436.7
KC <sub>8</sub>	-33.4	K <sub>2</sub> O	-363.2
CaC <sub>2</sub>	-62.8	CaCl <sub>2</sub>	-795.8
		CaO	-635.7
SrC <sub>2</sub>	-60	SrCl <sub>2</sub>	-828.8
		SrO	-592

Table TC.1. List of enthalpies of formation of the different relevant compounds.



Starting material	Enthalpy of reaction per atom of transition metal (kJ/mol)			
	Reduction by $KC_4$	Reduction by $KC_8$	Reduction by $CaC_2$	Reduction by $SrC_2$
<b>Chlorides</b>				
$TiCl_3$	-496	-488	-378	-432
$ZrCl_4$	-642	-632	-485	-557
$HfCl_4$	-633	-623	-476	-548
$VCl_3$	-637	-629	-519	-573
$NbCl_5$	-1231	-1219	-1035	-1125
$TaCl_5$	-1170	-1157	-974	-1063
$CrCl_2$	-416	-411	-338	-373
$CrCl_3$	-661	-653	-543	-597
$MoCl_3$	-824	-817	-707	-760
$MoCl_5$	-1502	-1489	-1305	-1395
$WCl_4$	-1180	-1170	-1023	-1095
$WCl_6$	-1841	-1826	-1605	-1713
$ScCl_3$		-272		
$YCl_3$		-235		
$LaCl_3$		-147		
$MnCl_2$		-330		
$FeCl_2$		-470		
$FeCl_3$		-818		
$CoCl_2$		-499		
$NiCl_2$		-507		
<b>Oxides</b>				
$ZrO_2$	495	505	-48	34
$HfO_2$	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
$Nb_2O_5$	197	197	-482	-380
$Ta_2O_5$	270	282	-409	-307
$MoO_2$	-15	-5	-558	-476
$MoO_3$	-160	-144	-974	-851
$WO_3$	-61	-46	-876	-753

Table TC.2. List of enthalpies of reaction for SSM and MSSM reactions.

Starting material	Adiabatic temperature $T_{ad}$		
	Reduction by $KC_4$	Reduction by $KC_8$	Reduction by $CaC_2$
$TiCl_3$	1000 °C	770 °C	1520 °C
$ZrCl_4$	990 °C	770 °C	1500 °C
$HfCl_4$	970 °C	770 °C	1470 °C
$VCl_3$	1270 °C	900 °C	> 1935 °C
$NbCl_5$	1490 °C	1040 °C	> 1935 °C
$TaCl_5$	1420 °C	1000 °C	> 1935 °C
$CrCl_2$	1210 °C	860 °C	1900 °C
$CrCl_3$	1310 °C	930 °C	> 1935 °C
$MoCl_3$	1500 °C	1130 °C	> 1935 °C
$MoCl_5$	1500 °C	1250 °C	> 1935 °C
$WCl_4$	1500 °C	1230 °C	> 1935 °C
$WCl_6$	1500 °C	1280 °C	> 1935 °C
$ScCl_3$		520 °C	
$YCl_3$		460 °C	
$LaCl_3$		320 °C	
$MnCl_2$		770 °C	
$FeCl_2$		980 °C	
$FeCl_3$		1140 °C	
$CoCl_2$		1040 °C	
$NiCl_2$		1050 °C	

Table TC.3. Adiabatic temperatures for SSM reactions with  $KC_4$  and  $KC_8$ . The determination of the adiabatic temperature is done graphically:  $T_{ad}$  is the temperature of the system when its enthalpy corresponds to the enthalpy of the reagents before reaction.  $KCl$  melts at 770 °C and boils at 1500 °C.  $CaCl_2$  melts at 772 °C and boils at 1935 °C.

## References

1. Chase, M. W. *NIST-JANAF Thermochemical Tables, 4th Edition*. (1998).
2. Butland, A. T. D. & Maddison, R. J. The specific heat of graphite: An evaluation of measurements. *J. Nucl. Mater.* **49**, 45–56 (1973).



## Appendix III

### Written and oral contributions

#### Articles

[1] F. D'Accriscio, E. Schrader, C. Sassoie, M. Selmane, R. F. André, S. Lamaison, D. Wakerley, M. Fontecave, V. Mougél, G. Le Corre, H. Grützmacher, C. Sanchez, S. Carenco. A single molecular stoichiometric P-source for phase-selective synthesis of crystalline and amorphous iron phosphide nanocatalysts. *ChemNanoMat* **6**, 1208-1219 (2020).

[2] A. P. Freitas, R. F. André, C. Poucin, T.K.-C. Le, J. Imbao, B. Lassalle-Kaiser, S. Carenco. Guidelines for Molybdenum oxidation state and geometry from X-ray absorption spectroscopy at the Mo L<sub>2,3</sub>-edges. *The Journal of Physical Chemical C*, **in press** (2021).

[3] R. F. André, F. D'Accriscio, A. P. Freitas, G. Crochet, C. Ulhaq, M. Bahri, O. Ersen, C. Sanchez, S. Carenco. Early transition metal nano-carbides and nano-hydrides from solid-state metathesis initiated at room temperature. *Green Chemistry*, **in press** (2021).

#### Orals

##### International

[4] “Early transition metal nano-carbides and nano-hydrides from solid-state metathesis initiated at room temperature” by R. F. André, F. D'Accriscio, A. P. Freitas, G. Crochet, S. Carenco, at 5<sup>th</sup> EuChemS Conference on Green and Sustainable Chemistry (5<sup>th</sup> EuGSC), **2021**.

##### National

[5] “Insights into solid-state synthesis of finely dispersed early transition metal carbides and hydrides nanoparticles supported on carbon” by R. F. André, F. D'Accriscio, G. Crochet, S. Carenco, at GECat, **2021**.

##### Local

[6] “Solid-solid synthesis of early transition metal carbide nanoparticles” by R. F. André, S. Carenco, at Journée annuelle de l'Institut des Matériaux de Paris Centre (IMPC), **2019**.

## Posters

### National

[7] “Hydrogenation of model compounds with nickel carbide and phosphide in mild conditions” by R. F. André, L. Meyniel, S. Carencó, at SCF2021-Catalysis, **2021**.

### Local

[8] “Energy efficient solid-state metathesis reactions for nanocarbides synthesis” by R. F. André, F. D’Accriscio, A. P. Freitas, G. Crochet, S. Carencó, at Journées de l’Ecole Doctorale 397 “Physique et Chimie des Matériaux”, **2020**.

### Workshops

[9] “Non-hydrolytic syntheses of Lewis acidic metal oxide nanoparticles” by R. F. André, S. Carencó, at SchoolCat Summer School, **2019**.

[10] “Energy efficient solid-state metathesis reactions for nanocarbides synthesis” by R. F. André, F. D’Accriscio, A. P. Freitas, G. Crochet, S. Carencó, at Green Chemistry Online Postgraduate Summer School, **2020**.



# Abstract

In this thesis work, the use of metal-containing nanoparticles such as carbides, oxides and phosphides is explored for colloidal catalysis. In an attempt to build a Frustrated Lewis Pair (FLP)-like catalytic system for H<sub>2</sub> activation, the synergy with a molecular Lewis base is assessed. In the bibliographic introduction, the stakes and the challenges of H<sub>2</sub> activation in solvent are presented, with an emphasis on the use of non-purely metallic catalysts for the hydrogenation of model compounds. In the first part, early transition metal carbides and hydrides are synthesized *via* solid-state metathesis. The influence of process parameters is explored to tune the phase speciation in the products. The most promising carbon-supported catalysts, Mo<sub>2</sub>C/C and W<sub>2</sub>C/C, are studied for gas phase and liquid phase hydrogenations of olefins. In the second part, cerium and indium oxides are obtained *via* hydrothermal pathways. The relevance of oxygen defects in CeO<sub>2-x</sub> is established for H<sub>2</sub> gas phase activation and semi-hydrogenation of phenylacetylene in solvent. The last part is dedicated to the non-aqueous syntheses of molybdenum and tungsten oxides, and nickel carbide and phosphides. The syntheses mechanisms are studied by means of NMR for the organic species and XAS and XRD for the nature of the inorganic species. The catalytic activity of the unsupported nanoparticles is finally evaluated for the hydrogenation of nitrobenzene and phenylacetylene in various solvents.

Dans ces travaux de thèse, nous avons exploré différentes classes de nanoparticules métalliques telles que des carbures, des oxydes et des phosphures, pour des applications en catalyse colloïdale. Afin de construire un système catalytique de type « Paire de Lewis Frustrée », la synergie avec des bases de Lewis moléculaires a été étudiée. En introduction, les enjeux et les défis de l'activation de H<sub>2</sub> en solvant sont présentés, avec un focus sur les catalyseurs non purement métalliques pour l'hydrogénation de composés modèles. Dans la première partie, des carbures et des hydrides de métaux de début de transition ont été synthétisés par métathèse solide-solide. Nous avons exploré l'influence de différents paramètres de procédé sur la spéciation de phase des produits. Les catalyseurs supportés les plus prometteurs, Mo<sub>2</sub>C/C et W<sub>2</sub>C/C, ont été étudiées pour l'hydrogénation d'oléfines en phase gaz et en solvant. Dans la deuxième partie, des oxydes de cerium et d'indium ont été produits par voie hydrothermale. L'importance de défauts d'oxygène dans CeO<sub>2-x</sub> pour l'activation de H<sub>2</sub> en phase gaz et pour la semi-hydrogénation du phénylacétylène a été établie. La dernière partie est dédiée à la synthèse solvothermale d'oxydes de molybdène et de tungstène, ainsi qu'à celle de carbure et de phosphures de nickel. Les mécanismes de synthèse ont été étudiés par RMN pour la partie organique et par XAS et DRX pour la partie inorganique. L'activité catalytique des nanoparticules non supportées a finalement été évaluée pour l'hydrogénation du nitrobenzène et du phénylacétylène dans plusieurs solvants.