



Hybrids of Polyoxometalates supported on mesoporous silica and magnetic core-shell nanoparticles for anchored homogeneous catalysis

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THÈSE DE L'UNIVERSITÉ PIERRE ET MARIE CURIE

École doctorale de Chimie Moléculaire de Paris Centre - École doctorale 406

Présentée par

Ourania MAKRYGENNI

Pour obtenir le grade de

DOCTEUR de l'UNIVERSITÉ PIERRE ET MARIE CURIE

**Hybrids of Polyoxometalates supported on mesoporous
silica and magnetic core-shell nanoparticles for anchored
homogeneous catalysis**

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Introduction

Introduction

It is widely acknowledged that there is a growing need for more environmentally acceptable processes and catalysts in the chemical industry. This trend has become known as “Green Chemistry” or “Sustainable Technology”¹⁻³. Green Chemistry represents an attractive pathway because it targets the improvement of chemical activities whilst avoiding the undesirable side effects of toxic and hazardous chemicals. In addition, the rising demand for a sustainable environment from society is placing tremendous pressure on chemists to transform highly energy consumptive chemical processes to energy neutral ones.

In particular, in the field of oxidation reactions, there is a constant search for catalytic processes working under mild conditions and using O₂, i.e. a “green” reagent that could substitute the conventional oxidants (CrO₃, MnO₄, HNO₃, etc.) used at a laboratory or in industrial scale, leading to stoichiometric amounts of non-valuable by-products.

Even though heterogeneous catalysis is favored for many applications, a lot of catalytic processes employed for the manufacture of bulk, as well as fine chemicals are homogeneous in nature. However, homogeneous catalysts suffer from several drawbacks related to the handling of sensitive metal-ligand complexes, deactivation or poisoning of the catalyst during reaction. Furthermore, in most cases, they are not easily recovered and thus, are difficult to be recycled. Economic and / or environmental consequences may result. On one hand, the catalysts components (metals and ligands) can be particularly expensive in such a way that it is not possible to be satisfied with a single use. On the other hand, their difficult separation can lead to contamination of the products, causing problems for certain applications, in particular in the case of pharmaceutical industry, food chemistry and also for the environment. Therefore, the majority of industrial-scale catalysts are desirably heterogeneous so that they can be easily separated and tailored in accordance to continuous and large-scale operations. Yet, in contrast to their homogeneous counterparts, they are much more difficult to develop practically, due to their complexity, which precludes their analysis at a molecular level and development through structure–reactivity relationships. In addition, the scope of traditional heterogeneous catalysts is rather limited to the participation of available active sites on the surface of the support.

To extend the possible applications of heterogeneous catalysis, several attempts have been made to combine a homogeneous catalyst with high selectivity with a solid support

Introduction

bringing a better industrial handling, a potential use in cleaner technology and leading eventually to some synergism. Such approach is known as “heterogenization of homogeneous catalytic systems” or “anchored homogeneous catalysis”^{4,5}. These third generation catalysts are known not only to preserve the activity and selectivity of their homogeneous catalysts constituents but also to allow facile recovery and reuse of the catalyst akin to the use of supports. However, during applications, problems associated with leaching of the active homogeneous catalytic species have been reported. As a result, chemists seek to develop tighter links between the support and the homogeneous catalyst precursor.

The goal of the present PhD work is the elaboration of new materials based on silica oxides (mesoporous silica SBA-15, magnetic core-shell nanoparticles) combined with nucleophilic (vacant) polyoxometalates for applications in the field of anchored homogeneous catalysis for mild oxidations reactions.

Polyoxometalates (POMs) are a class of discrete anionic metal oxides in groups 5 and 6, which are built via the condensation of metal oxide polyhedra (MO_x , $\text{M} = \text{W}^{\text{VI}}$, Mo^{VI} , V^{V} , Nb^{V} , Ta^{V} , etc., and $x = 4-7$) with each other in a corner-, edge-, or rarely in a face-sharing manner⁶⁻⁸. Metal atoms (also called addenda atoms) involved are atoms that can change their coordination with oxygen from 4 to 6 due to the condensation of the MO_x polyhedra in solution upon acidification. Although oxygen is the main ligand that coordinates with the addenda atoms, other atoms/groups such as sulfur, bromine, nitrosyl, and alkoxy have been substituted in some previously reported POMs clusters.

When the POMs frameworks exclusively contain the addenda metals (from groups 5 and/or 6) and oxygen, the clusters are called isopolymetalates, such as the Lindqvist type anion $[\text{M}_6\text{O}_{19}]^{2-}$. When the POMs include additional elements, they are known as heteropoly complexes, which can be formed via the condensation of MO_x polyhedra around a central heteroatom when the solution is acidified. Many different elements can act as heteroatoms in heteropoly complexes with various coordination numbers: 4-coordinate (tetrahedral) in Keggin and Wells-Dawson structures (e.g., PO_4^{3-} , SiO_4^{4-} , and AsO_4^{3-}); 6-coordinate (octahedral) in Anderson-Evans structures (e.g., $\text{Al}(\text{OH})_6^{3-}$ and TeO_6^{6-}); and 12-coordinate (Silverton) in $[(\text{UO}_2)_2\text{Mo}_{12}\text{O}_{30}]^{8-}$.

One property of POMs, among others, is that they are transition metal (TM) oxoanion nanosized clusters stable against hydrolysis (assuming that pH is controlled during the

process) and toward strong oxidation conditions. However, lacunary (or vacant) complexes may be obtained through basic degradation of complete species by formal removal of one or several oxo metal fragments. The chemistry of such lacunary species has been widely studied during the 60^{ies} to 80^{ies} decades, in particular in the case of Keggin or Dawson type heteropolyanions.

These vacant species are also capable to act as versatile multidentate inorganic ligands with strong chelate effects, due to the presence of nucleophilic oxygen atoms that delimitate the lacuna. Since they are p-donor (*via* the oxo ligands) and p-acceptor ligands (*via* the d⁰ metal centers) simultaneously, they are able to accommodate cations in a wide range of oxidation states. Moreover, the charge of POMs can easily be tuned by varying the central heteroatom inside of the oxometalate core. This influences their redox and/or acidic properties and, consequently, allows a modulation of the stabilization of transition metal (TM) cations. In parallel, these lacunary species may be also functionalized by organic functions, since they are able to react with one or several organic derivatives from the P block (organosilanes, organophosphonates, organoarsonates, organostannates, etc.). This led to a new class of compounds that were defined as hybrid derivatives of POMs.

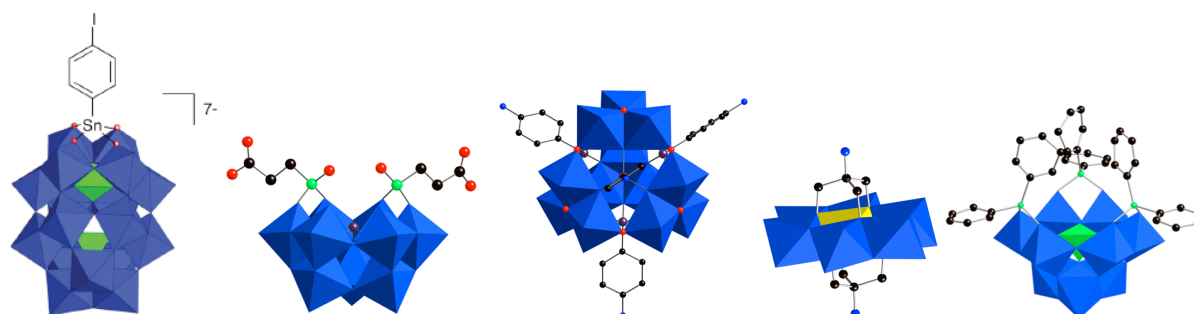


Figure 1: polyhedral structures of some hybrid derivatives of POMs (from left to right: organostannyle, organophosphonyle, trisalkoxo, organosilyle and organoarsonyle derivatives).

These remarkable properties have a close relationship with their structures and compositions. The well-defined atomic connectivity of POMs provides the compositional diversity required by a rigorous assessment of the consequences of composition on catalytic reactivity. Keggin-type POMs are the most well-studied structures in catalysis due to their unique stability. With tempting prospects in the industry, these robust catalysts have been studied for decades.

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In more detail, POMs, especially their TM derivatives, have been thoroughly considered as intrinsic oxidation catalysts either in homogeneous or heterogeneous conditions. In the latter case, POMs are generally immobilized directly on oxide supports in order to circumvent their very low surface area in the solid state. In most of these examples, POMs are not strongly chemically bonded to the support.

Following on from the abovementioned, an important parameter taken into account during the work carried out for this PhD dealing with liquid/solid heterogeneous catalysis was the nature of the bond between the support and the POMs. Thus, it was deemed necessary to form a covalent bond in order to minimize the leaching of the active catalytic molecules, i.e. the polyoxometalates.

In this respect, POMs and supports with complementary organic functions were prepared. Secondly, a coupling reaction was implemented. For this purpose, bis-organophosphonate $\{RP=O\}$ derivatives of trivacant POMs were used, in which the introduced R function can easily be post-functionalized. It is noteworthy that this covalent approach has been barely applied to the POMs chemistry.

Two different pathways were followed for the accomplishment of the main goal of the PhD. These pathways were chosen depending upon the support used for the grafting of POMs.

The first part of the manuscript is based on the use of mesoporous silica, and especially SBA-15, as a support for the anchored homogeneous catalytic system. The corresponding part is divided into two chapters, as different methodologies were followed in each of them and explored.

The first chapter consists of the functionalization of the SBA-15 with primary amine groups and the covalent grafting of Keggin-type POMs bearing carboxylic acid functions. The corresponding amide bond was successfully obtained using a coupling reagent. Various physical techniques for the characterization of the obtained hybrid materials are displayed. Once the existence of the covalent linkage was verified, the anchored homogeneous catalyst was tested for the epoxidation of alkenes such as cyclooctene or cyclohexene. In addition, computational calculations were performed on the functionalized POMs in order to study the influence of the carboxylic acid functions in the catalytic performance. Finally, studies at the

synchrotron SOLEIL were carried out after the introduction of lanthanum in the hybrid materials for their full characterization.

In the second chapter, diverse coupling methods were tried out and presented. In the first place, SBA-15 was tentatively functionalized with epoxy groups for their reaction with POMs bearing carboxylic acid functions. Another method detailed was based on the covalent linkage of the functionalized POM and support through an intermediate. More specifically, SBA-15 and POMs were functionalized with amine groups and were coupled through the use of a cross-linker (*p*-phenylene diisothiocyanate) bearing the necessary functions. In all cases, the resulting materials were characterized by various techniques. In correspondence to the previous sub-chapter, the catalytic performance of the hybrid materials was tested for the epoxidation of cyclooctene.

The second part addresses the synthesis and characterization of hybrid nanocatalysts based on magnetic core-shell nanoparticles grafted with POMs. To begin with, the synthesis of the maghemite core, their encapsulation into a silica shell and their functionalization was demonstrated. The effect of the alteration on the size of the maghemite core and the core-shell was studied and the materials were characterized by numerous physical techniques. The grafting of POMs onto core-shell nanoparticles was accomplished by the same means as described in the first chapter for the mesoporous materials. In conclusion, the hybrid nanocatalysts were also tested under mild conditions for the epoxidation of cyclooctene. Particular emphasis was given to the ease of separation and recyclability of the synthesized nanomaterials.

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Part 1

Covalent immobilization of hybrids of Polyoxometalates onto mesoporous materials

I Introduction

During the past decades, continuous attention was given to POMs-based catalytic materials because of their numerous advantages in catalysis¹. In the first place, POMs exhibit very strong Bronsted type acidity (in their heteropolyacid form), making them suitable for various acidic reactions²⁻⁴. Furthermore, some POMs possess basic properties and can be used in base-catalytic reactions^{5,6}. In addition, it is well known that POMs have fast and reversible multi-electron redox behaviors under mild conditions, and they are able to react with H₂O₂ to form peroxo species. This characteristic makes them generally efficient candidate catalysts for the oxidation of alkanes, aromatics, olefins, alcohol, etc^{2,7-10}. Equally important, the chemical properties of POMs, their acid-base strength, redox potential and solubility in aqueous or organic media, can be facilely and finely altered in a wide range on purpose through smoothly varying their composition and structure. Moreover, compared with common organometallic complexes, POMs are thermally and oxidatively stable toward oxygen donors.

Various POMs (including transition metal derivatives of POMs) have been used extensively as efficient homogeneous catalysts in different reactions, owing to the above unique properties. Nevertheless, POMs are usually soluble in many polar solvents, causing difficulties in the recovery, separation, and recycling of the catalysts. This potentially affects their use in systems that require environmentally friendly efficient transformations and sustainable development. As a result, it is necessary to develop easily recoverable and recyclable POMs-based catalysts for practical application in industry. To achieve this, heterogeneous catalysts are preferred because of the advantages of facile catalyst/product separation. Though this may be true, POMs-based catalysts also suffer from some disadvantages, such as leaching of the active sites and low activity^{2,9}. Likewise, POMs-based catalysts, most of the times, exhibit inferior catalytic performance than their homogeneous counterparts, mainly due to diffusion limitations of the active sites.

In order to overcome the above drawbacks, many approaches have been proposed to improve the stability and catalytic performance. Generally, POMs-based heterogeneous catalysts can be prepared mainly by two strategies: the “immobilization” and the “solidification” of the catalytically active POMs⁴. The former involves supporting the POMs active species on various supports (porous materials, polymers, clays...), while the latter involves preparing insoluble POMs salts. Due to the low specific surface obtained by the

preparation of insoluble POMs salts, in the next paragraphs the different strategies used for the immobilization of POMs, according to the literature, will be developed.

I.1 POMs-based metal organic frameworks (MOFs)

Metal–organic framework (MOF) materials are a class of crystalline porous coordination polymers with open frameworks, which are able to act as unique candidate carriers for the encapsulation of various active centers, due to their high surface areas, permanent porosity, and adjustable hydrophilic–hydrophobic channel properties¹¹.

In 2005, Ferey et al. incorporated the lacunary heteropolytungstate $K_7PW_{11}O_{39}$ within the cages of MOF MIL-101, with a rigid zeotype crystal structure, large pores and surface area, as well as good stability.¹² Later, Balula and coworkers prepared a series of heterogeneous catalysts by supporting various POMs on MIL-101(Cr), and used them in different oxidation reactions, including in the epoxidation of olefins, the oxidations of styrene and cyclooctane, and the oxidative desulfurization¹³. Moreover, phosphotungstic acid $H_3PW_{12}O_{40}$ is often encapsulated into MIL-101(Cr) or Zr-based UiO-67¹⁴ as a recyclable solid acid catalyst for various organic reactions, such as in the alcoholysis of styrene oxide to β -alkoxyalcohol¹⁵. It was also shown that the POMs are easily *in situ* modified or extracted without degradation from the materials¹⁶.

Moreover, other series of POMs-based MOF crystalline materials possessing the features of both POMs and MOFs have also attracted significant attention in recent years. The Versailles group has indeed reported the formation of reduced polyoxomolybdates-based MOFs by hydrothermal syntheses^{17,18}, and their use as efficient electrocatalysts. In 2009, Liu and Su et al. obtained a series of crystalline compounds through a one-step hydrothermal reaction of the precursors, where the catalytically active Keggin anions, $PW_{12}O_{40}^{3-}$, were alternately arrayed as non-coordinating guests in the cuboctahedral cages of the HKUST-1 host matrix, named NENU-*n* series¹⁹.

In 2011, Hill et al. succeeded to introduce $[CuPW_{11}O_{39}]^{5-}$ into the pores of HKUST-1, resulting in a new crystalline catalyst. The synthesized catalyst showed a good catalytic performance for aerobic decontamination. The results were better than the POM or the MOF moieties alone²⁰.

I.2 Polymer-supported POMs catalysts

Polymeric materials, especially organic polymers, have been widely studied due to their tunable abundant structure, functionality, and easy ability to process²¹. Polymers are suitable as supports for heterogeneous catalysts, because of their advantage of easy production and low weight. Moreover, the organic framework of polymers enables them to have good compatibility with organic substrates. Therefore, in the last decade the fabrication of POMs/polymer hybrid materials or polymer-supported POMs catalysts has attracted great interest²².

Leng and Wang worked extensively in the field of POMs-based hybrids for various catalytic reactions, such as esterifications²³, H₂O₂-mediated epoxidation of alkenes^{24,25}, oxidation of alcohols^{26,27} and hydroxylation of benzene²⁸. The catalysts were synthesized by anion exchange of different organic groups functionalized poly or ionic copolymers with Keggin heteropolyacids. In 2012, the group synthesized a heteropolyanion-based cross-linked ionic copolymer by the anion-exchange of a newly task-specific designed amino-containing ionic copolymer with a Keggin heteropolyacid²⁴. The obtained hybrid catalyst was tested for a liquid-solid heterogeneous epoxidation of alkenes with aqueous H₂O₂. The results were promising as the supported system exhibited a 98.5% conversion for the cyclooctene with 100% selectivity. These values are higher compared to the POM alone, showing the efficiency of the hybrid material.

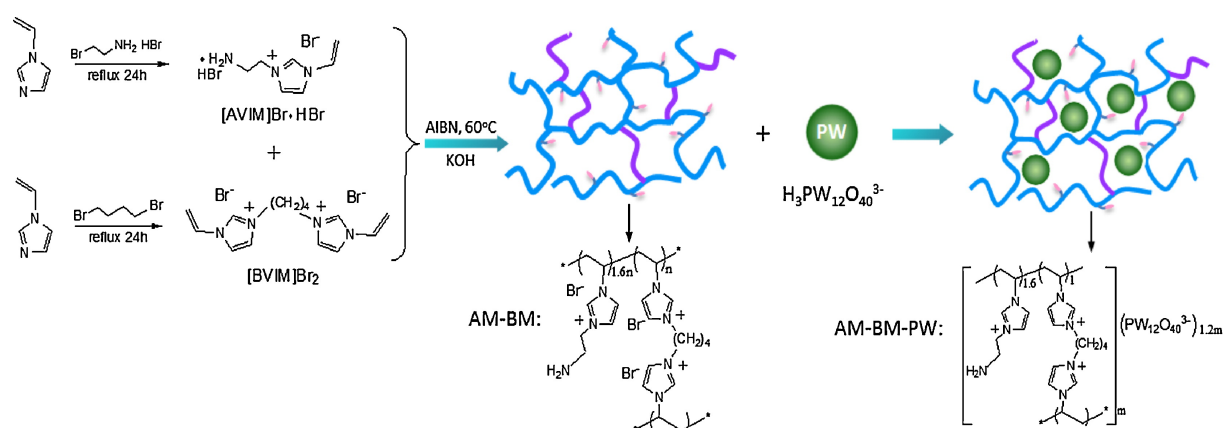


Figure I-1: Synthesis of the ionic hybrid AB-BM-POM²⁴.

In general, surface properties, the microenvironment and porosity can influence dramatically the interactions between the catalyst and the surface, the substrate accessibility and the mass transfer efficiency²⁹. Due to these factors, many mesoporous polymers were synthesized and used as supports for heterogeneous catalysts. In addition, many approaches have been proposed in order to study the porous effects of polymeric supports for POMs-based catalyzed reactions.

Ryoo et al. in 2011 synthesized an ordered mesoporous polymeric material (MPM)³⁰. The obtained MPM materials were further functionalized with ammonium groups and a the Ishi-Venturello polyperoxotungstate anion, $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$, was immobilized through its introduction as a counter ion to the ammonium group. The hybrid material showed good catalytic performance in the liquid-phase epoxidation of olefins, using an aqueous solution of H_2O_2 as the oxidant, as well as easy filtration and reuse of the catalyst without a significant loss of activity.

Finally, Xiao et al. carried out a synthesis of a hybrid catalyst where the POM is covalently grafted on the surface of a polymer. The covalent immobilization was achieved through the surface reaction of two azido-organically modified POM clusters with the functionalized group on the channel surface of the macroporous resin via click chemistry. The synthesized catalyst showed high activity and selectivity for the tetrahydrothiophene oxidation. The advantage of this approach was the multiple reuses of the catalyst and the fact that no catalytic activity was observed³¹.

I.3 Mesoporous transition metal oxide supported POMs catalysts

With the development of materials science and synthetic technology, various mesoporous transition metal oxide materials, such as ZrO_2 , ZnO_2 , Cr_2O_3 , Fe_2O_3 have been synthesized and applied as catalyst supports. Their tunable chemical composition, pore structure, inert framework to resist the corrosion of the guest species, and the capability to provide strong host–guest interactions for higher catalytic performance make them ideal for supports. As a result, much effort has been made towards the immobilization of POMs active sites on mesoporous transition metal oxides to synthesize anchored homogeneous catalysts.

Armatas and coworkers used the 12-phosphomolybdic acid (PMA) combined with nanocrystalline ZrO_2 or with mesoporous nanocomposite frameworks of chromium(III) oxide

to prepare new hybrid catalysts. In the first case, the synthesis was carried out through a surfactant-assisted sol-gel copolymerization route and different PMA loadings were tried out for the prepared materials. By different characterization techniques they proved that the PMA preserved intact their Keggin structure into the mesoporous frameworks. These materials were used in the oxidation of alkenes using hydrogen peroxide as oxidant and they exhibited exceptional stability³². In the second case, the same Keggin-type POM was used with chromium(III) oxide for the synthesis of well-ordered mesoporous frameworks. Hexagonal mesoporous SBA-15 was used as hard template. As before, the hybrid materials were used in oxidation reactions and specifically in the oxidation of 1-phenylethanol with H_2O_2 as an oxidant³³. In 2014, ordered mesoporous composite catalysts consisting of nanocrystalline tetragonal ZrO_2 and heteropolytungstic clusters, i.e. 12-phosphotungstic (PTA) and 12-silicotungstic (STA) acids, were prepared via a surfactant-assisted co-polymerization route. They demonstrated that the inclusion of PTA and STA clusters in the mesoporous framework has a beneficial effect on the catalytic activity of these materials. Although zirconium oxide and heteropoly acids alone show little catalytic activity, the ZrO_2 -PTA and ZrO_2 -STA heterostructures exhibit surprisingly high activity in hydrogen peroxide mediated oxidation of 1,1-diphenyl-2-methylpropene under mild conditions³⁴.

Furthermore, Guo and coworkers also prepared a series of mesoporous $H_3PW_{12}O_{40}/ZrO_2$ -Si(Et/Ph)Si and $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si hybrid catalysts by a one-pot template-assisted sol-gel condensation-hydrothermal treatment route³⁵⁻³⁷. The former catalyst was utilized as environmentally friendly solid acid catalysts in the transesterification of low-cost Eruca Sativa Gars oil with methanol to produce fatty acid methyl esters under atmosphere refluxing. The prepared catalyst exhibited higher catalytic activity compared with alkyl-free $H_3PW_{12}O_{40}$ - ZrO_2 ³⁵. In 2013, they used the synthesized catalysts for the esterification of levulinic acid with various alcohols under mild conditions due to their pore morphologies, textural properties and acidity³⁶.

I.4 Zeolites-supported POMs catalysts

Zeolites can be used as supports for the synthesis of new hybrid catalysts. Different types of heterogeneization of POMs can be achieved with zeolites used as supports. POMs, and in most cases HPAs, are sometimes impregnated onto the surface of zeolites or are encapsulated in the pores.

Wang and coworkers prepared by an impregnation method a $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on dealuminated ultra-stable Y zeolite (DUSY), and then its physico-chemical properties were characterized. The DUSY-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst exhibited high catalytic activity in the liquid phase acetalization of ethylacetoacetate with ethylene glycol for synthesizing fructose. However, continuous leaching of the HPAs into the reaction medium led to a poor catalytic stability³⁸.

Mukai et al also used a Y-type zeolite for the encapsulation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as a catalyst for the esterification of acetic acid with ethanol³⁹. The authors investigated the influence of the Si/Al ratio of the zeolite on the amount of encapsulation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ molecules. They concluded that $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ could be formed within the supercages of the support when the number of aluminum atoms per unit cell is roughly in the range of 4–20. When the number exceeds this range, the support was likely to be destroyed during catalyst synthesis, since the durability in acidic solutions is low for supports with high aluminum contents. Moreover, it was difficult to encapsulate $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ using supports with extremely low aluminum contents.

The same group, two years later, investigated the influence of other parameters on the amount of HPA encaging and the stability of the resulting encaged catalyst, such as the temperature and the solvent⁴⁰. It was found that by adjusting the reaction temperature, the stability of the resulting encaged catalyst could be enhanced to higher levels. Moreover, it was found that by adding *t*-butyl alcohol to the solution used for the catalyst synthesis, an active and stable encaged catalyst could be prepared, even at low synthesis temperatures.

A new type of nanohybrid material $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ /nanoclinoptilolite was fabricated by Jarrahi et al, and performed as an efficient and reusable catalyst in the mild and one-pot condensation of different acetophenones. These types of zeolites contained open tetrahedral cages, generating a system of channels, the sizes of which are determined by the content of silicon. These cages are formed with a network of eight-membered and ten-membered rings⁴¹.

1.5 Mesoporous silica-based materials

Mesoporous silica materials have various excellent textural parameters, such as large surface area and pore volume, and narrow pore size distribution, as well as special quantum size effects^{42,43}. Furthermore, the synthesis and modification of mesoporous silica can be

facilely tuned in a continuous wide arrangement. Therefore, mesoporous silica materials, especially the high ordered mesoporous silicas⁴³, have been widely used as common supports to immobilize POMs for heterogeneous catalysis reactions.

Different strategies to prepare POMs-loaded mesoporous silica catalytic materials exist, such as impregnation, sol–gel techniques, ion exchange, and covalent grafting.

The immobilization of POMs onto the surface of mesoporous silica can be divided in three categories. The first one deals with nonvacant heteropolyacids that are bound to silica supports through the protonation of hydroxyl groups of the surface and by the interaction of the resulting $\equiv\text{SiOH}_2^+$ species with external oxygen atoms of the POMs. The second category concerns the POMs anchoring inside the channels of mesoporous materials that have been functionalized with positive alkylammonium or imidazolium groups. Finally, the third category deals with the POMs that are covalently grafted on the surface.

1.5.1 Immobilization of Heteropolyacids (HPA) onto mesoporous silica by electrostatic interactions

There is a variety of examples of HPAs immobilized onto mesoporous supports and it is difficult to be exhaustive in this domain. In this paragraph, several representative examples are given for the purpose of illustration. Most examples referred to applications using the POMs as acid catalysts.

Kaur and Kozhevnikova prepared silica-supported HPA catalysts by impregnating Aerosil 300 silica with an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ^{44,45}. Their catalytic activity was tested in Friedel–Crafts acylation and in Fries rearrangement of aryl esters, respectively. During the reaction, even in non-polar solvents, such as dodecane, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ leached from the silica support. However, the catalyst could be separated by filtration and, after a simple work-up, such as washing with dichloroethane, reused, although with reduced activity.

Yadav and co-workers synthesized $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on hexagonal mesoporous silica⁴⁶. This catalyst was found to be very active and also stable without any deactivation in an environmentally benign route for acetoveratrone synthesis.

Blasco et al. used the same HPA ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) and then supported it on three different carriers: a commercial silica, a high surface area amorphous aluminosilicate (MSA) and an all

silica-mesoporous MCM-41. Their catalytic properties were determined for the alkylation of 2-butene with isobutene⁴⁷. The high surface area of the MCM-41 and MSA supports showed higher acid dispersions compared with SiO₂, but H₃PW₁₂O₄₀/SiO₂ showed the maximum activity, selectivity to trimethylpentane and stability. They showed that the activity of HPA depends directly on its interaction with the functional group on the support. Thus, in the H₃PW₁₂O₄₀/MSA samples, in which there is a stronger interaction between the HPA and the surface sites of the aluminosilicate lower catalytic activity was predicted. In the H₃PW₁₂O₄₀/MCM-41 samples, partial blockage of the monodimensional pores of MCM-41 decreased the accessibility of the reactants to the Bronsted acid sites of the HPA located inside the pores. The solution to this pore blockage could be the use of a MCM-41 sample with a larger pore diameter.

Y. Chen compared the structural and catalytic properties of MCM-41 and SBA-15 as supports for H₃PW₁₂O₄₀⁴⁸. The results revealed that the mesoporous materials retained the typical hexagonal mesopores for the support of H₃PW₁₂O₄₀. It was found that HPA exhibited higher dispersion within MCM-41 than those within SBA-15 and other mesoporous molecular sieves. Moreover, the as-prepared materials were found to be the efficient catalysts for the green synthesis of benzoic acid. In particular, HPA/MCM-41 exhibited the best catalytic properties due to its suitable textural and structural characteristics.

Recently, Popa et al. prepared a series of HPAs–mesoporous silica composites from NiHPMo₁₂O₄₀ by supporting them on SBA-15 mesoporous silica in different concentrations of the active phase⁴⁹. By impregnating Ni²⁺ salt on mesoporous silica, the thermal stability of the Keggin structure increased in comparison with its parent bulk HPA. Indeed, the total acidity of the weak and strong acidic sites of NiHPMo₁₂O₄₀/SBA-15 composites was obviously increased in comparison with the bulk Ni salt.

1.5.2 Non-covalent immobilization of POMs onto mesoporous materials functionalized with alkylammonium/imidazolium groups

Anchoring procedures inside the channels of mesoporous materials or at the surface of oxide nanoparticles that have been functionalized with positive alkylammonium or imidazolium groups have been used more recently. These electrostatic interactions, even if they strengthen the POM–support link, do not however completely avoid the leaching of the

Part 1: Covalent immobilization of hybrids of Polyoxometalates onto mesoporous materials

supported active phase, in particular in the case of catalytic processes taking place in conventional polar solvents or *a fortiori* in ionic liquids. Several examples are given below.

Kera and co-workers were among the first to prepare catalysts by depositing HPA on silica gel by using their ion-exchange properties when modified by agents having an amino group. The amounts of HPA adsorbed and/or deposited tended, in fact, to increase in proportion to the degree of the modification⁵⁰.

One decade later, Amini et al. immobilized $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_{15}\text{P}_5\text{W}_{30}\text{O}_{110}$ on the inner surface of mesoporous MCM-41, fume silica and silica-gel by means of chemical bonding to aminosilane groups⁵¹. Among the functionalized silica materials, MCM-41 showed the largest amine to silica and the least heteropolyacid to silica ratios. The materials were characterized by different characterization methods such as IR spectroscopy, BET surface area analysis and low-angle XRD.

Yamanaka et al. synthesized catalysts comprising HPA and organografted mesoporous silica⁵². The materials were used towards the ester hydrolysis in water with exceptionally high catalytic activity. They showed that the nanostructure based on mesoporous silica allows the aqueous reaction mixture to easily reach the active sites, despite their being surrounded by hydrophobic moieties.

The group of Richards et al. developed a hybrid catalyst of tetrairon(III)-substituted polytungstates immobilized on 3-aminopropyltriethoxysilane-modified SBA-15⁵³. The synthesized material showed an excellent catalytic performance for solvent-free aerobic oxidation of long-chain n-alkanes using air as the oxidant under ambient conditions through a classical free-radical chain autoxidation mechanism. Moreover, the anchored catalyst could be recycled multiple times without loss of catalytic activity.

Nomiya and co-workers presented a novel method for grafting transition metal-substituted polyoxometalates (TMSP) onto a modified silica surface⁵⁴. Keggin-type vanadium(V)-substituted polyoxomolybdate, $[\text{PMo}_{11}\text{V}^{\text{V}}\text{O}_{40}]^{4-}$ (PMoV), was electrostatically anchored to a modified silica surface having cationic ammonium moiety. This PMoV-grafted silica material exhibited activities that were higher than those of homogeneous PMoV reactions for oxidation of various alcohols with 1 atm of dioxygen in the presence of isobutyraldehyde (IBA).

Fraissard et al. developed a procedure for preparing acid onium salts of Keggin heteropolyacids via ion exchange on amorphous silica functionalized with pyridinium and alkylimidazolium cations ($\text{SiO}_2\text{-Q}$)⁵⁵. The interaction between HPA and the surface-grafted cations afforded acid salts of HPA with intact Keggin structure.

I.5.3 Covalent grafting of POMs onto mesoporous materials

A few examples have been described in which POMs can be covalently bound to an oxide support. This covalent linking can be achieved following two different approaches.

In the first one, transition-metal substituted POMs are attached onto the surface via coordination of the transition-metal centers of the POMs with nitrogen atoms of alkylamine-substituted porous materials. This approach has been used with $[\text{M}(\text{H}_2\text{O})\text{-PW}_{11}\text{O}_{39}]^{5-}$ ($\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$) for example. The work of Stein was one of the first demonstrating a covalent linkage between POMs and mesoporous silica⁵⁶. Transition-metal-substituted polyoxometalates (TMSP) of the type $[\text{M}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{5-}$ ($\text{M} = \text{Co}, \text{Zn}$) and $[\text{SiW}_9\text{O}_{37}\{\text{Co}^{\text{II}}(\text{H}_2\text{O})\}_3]^{10-}$ have been chemically anchored to modified macroporous (400 nm pores), mesoporous (2.8 nm pores), and amorphous silica surfaces. The open coordination site available to these TMSP clusters allowed them to be chemically anchored to the surfaces of the functionalized supports. The catalytic activities of the supported TMSP clusters were tested by the epoxidation of cyclohexene to cyclohexene oxide in the presence of isobutyraldehyde. A few supplementary examples have been more recently described^{57,58}.

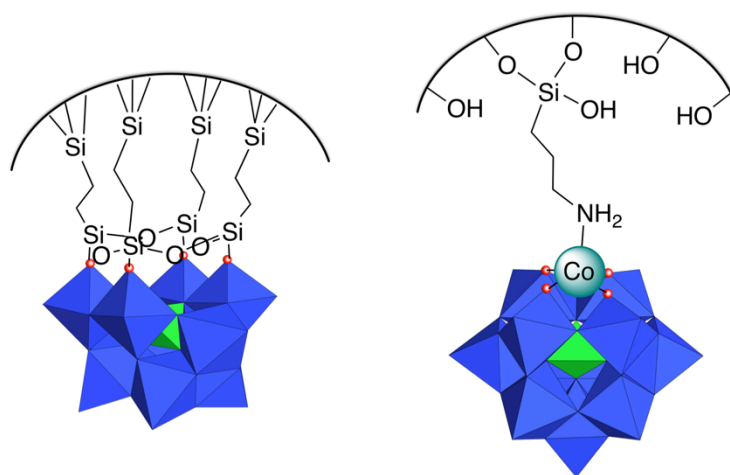


Figure I-2: Schematic representation of the covalent linking of POMs by grafting organosilanes onto the silica or by direct coordination of TMSPs with organically modified supports^{56,59}.

However, lots of questions remain on the strength of the link between the transition cations and the surface during the catalytic process, while these cations play also the role of active centers.

The second approach deals with the direct grafting of Keggin type mono or divacant POMs on the surface of ordered porous silica architectures via organosilane moieties. In this case, POMs have been incorporated either by their copolymerization with silicon precursors either by a postsynthesis route.

Concerning the second approach, Stein prepared a three-dimensionally ordered macroporous (3DOM) silica materials functionalized with highly dispersed polyoxometalate clusters direct synthesis⁵⁹. Lacunary γ -decaturtungstosilicate clusters were incorporated into the wall structures of macroporous silica by reaction of the clusters in acidic solution with tetraethoxysilane, with or without addition of the polyfunctional linking group 1,2-bis(triethoxysilyl)ethane, followed by condensation around polystyrene colloidal crystals. Removal of the polystyrene template by extraction with a tetrahydrofuran/acetone solution produced the porous hybrid materials. The materials were demonstrated to exhibit catalytic activity for the epoxidation of cyclooctene with an anhydrous H_2O_2 / t -BuOH solution at room temperature.

Yang et al synthesized Novel polyoxometalate (POM)-grafting mesoporous hybrid silicas, $\text{XW}_{11}/\text{MHS}$ ($\text{X} = \text{P}, \text{Si}$) and $\text{TBAPW}_{11}\text{Si}_2/\text{MHS}$ by co-condensation and post-synthesis routes based on the employment of Keggin-type monovacant XW_{11} or a Si-substituted compound $\text{TBAPW}_{11}\text{Si}_2$ as POMs precursors in the presence of block copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123) under acidic conditions^{60,61}. These materials, especially the co-condensed samples, exhibited stable and reversible photochromic properties under UV irradiation although no special organic component was supplied additionally as an electron donor.

However in both cases the authors have pointed out some breaking of POMs/surface links, due to the relative weakness of the $\{\text{Si}-\text{O}-\text{W}\}$ bonds, even after a moderate heating of the materials (45°C). Furthermore, due to the binding strategy implemented, no more nucleophilic oxygen atoms are available for metal substitution.

Part 1: Covalent immobilization of hybrids of Polyoxometalates onto mesoporous materials

Considering these two disadvantages inherent to such approaches, the work presented in the following chapter was oriented towards the use of trivacant Keggin-type polyanions bearing two alkylphosphonate/arsenate groups covalently grafted onto the surface of functionalized mesoporous silica. This approach has some advantages over the others mentioned above, such as the existence of strong links between the POMs and the support and the existence of free coordination sites in the final materials.

Chapter 1

Covalent grafting of hybrids of Polyoxometalates onto amino functionalized SBA-15 by the formation of amide bonds

I Synthesis and functionalization of mesoporous SBA-15

I.1 Synthesis of SBA-15

The synthetic protocol of well-ordered hexagonal mesoporous silica structures SBA-15 followed the procedure described by D. Zhao in 1998. In this synthesis, the tunable large uniform pore sizes are obtained owing to the use of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO), Pluronic123[®]. This amphiphilic block copolymer, in particular, is a good candidate because of its mesostructural ordering properties and amphiphilic character.

Various investigations of the synthesis of mesoporous silica materials have concluded to two possible mechanisms:

(a) The first implicates the self-assembly of the surfactant at high concentration into a crystalline phase and subsequent polymerization of the silica framework around the preformed micellar aggregates.

(b) In the second mechanism, the cooperative self-assembly of the surfactant and inorganic species is directed by the aqueous inorganic silica precursor to obtain liquid crystalline phase with hexagonal, cubic or lamellar shape. In this case, the concentration of surfactant remains at low values.

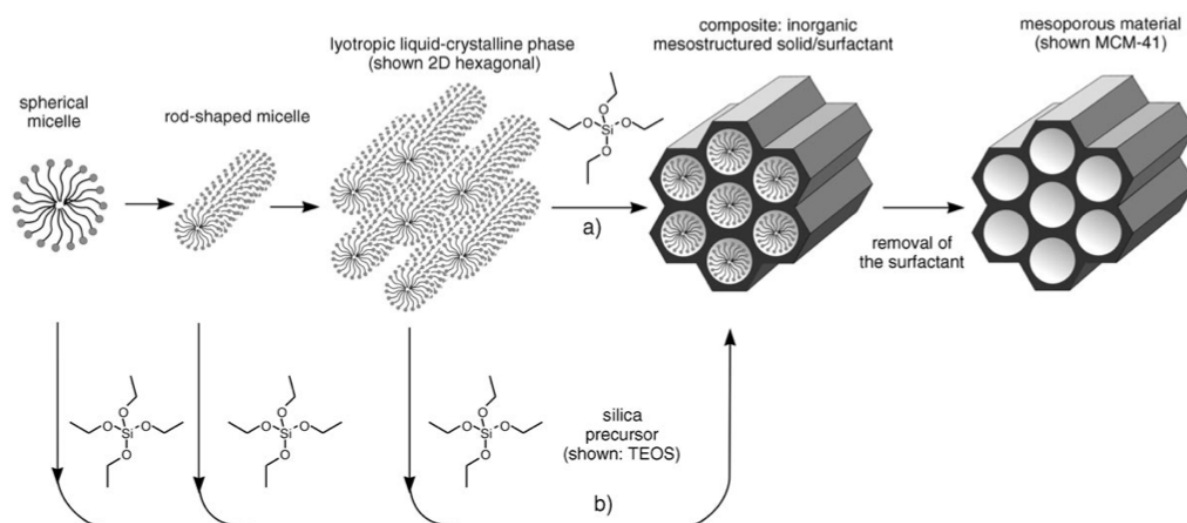


Figure I-1: Pathways for the synthesis of mesoporous silica materials: a) true liquid-crystal template mechanism, b) cooperative liquid-crystal template mechanism⁷⁸.

A very important condition for the mesophase formation is the existence of an attractive interaction between the template and silica precursor. This interaction can guarantee the subsequent inclusion of the structure-directing agent (SDA) in the final material without the occurrence of phase separation. Huo et al. described these interactions and divided them into four categories⁶².

(a) Under basic conditions, where the silica species are present as anions and cationic quaternary ammonium surfactants are used as the SDA, the synthetic pathway is termed (S^+I^-).

(b) Under acidic conditions, i.e. below the isoelectronic point of silica (pH=2), the inorganic species are positively charged. In this case, an anionic SDA (S^-) is used to direct the self-assembly of cationic inorganic silica species (I^+) through the S^-I^+ pathway.

(c) Sometimes, X^- (usually halides), a mediator ion, may be added to direct the mesophase formation via the $S^+X^-I^+$.

(d) Finally, when negatively charged surfactants (S^-) are used, it is also possible to work under basic condition whereby a mediator ion M^+ (usually alkali ions) can be added to ensure interaction between equally negatively charged species via $S^-M^+I^-$.

The interactions described in the above pathways are predominantly electrostatic in nature. In addition, there is also the possibility to have attractive interactions mediated by hydrogen bonds, for example, when neutral (S^0 , as long-chained amine) or nonionic surfactants (N^0 , polyethylene oxide) and uncharged silica species (S^0I^0 or N^0I^0) or ions pairs (S^0) (XI^0) pathways are present.

The nature, concentration and temperature, can lead to different liquid crystal phases being formed by surfactants in lyotropic systems. The phases include micellar, cubic micellar, lamellar or reversed-phase micellar phases.

During this work, the surfactant was dissolved in acidic medium (pH<2) under low heating, leading to rod like micelles. Then, after the full dissolution, TEOS was added. The hydrolysis of TEOS and the condensation of Si-OH functions led to the formation of a hybrid solid.

Subsequently, the latter product underwent a hydrothermal treatment, which improves the mesoscopic regularity. The last step was a calcination treatment whose goal is the removal of the template affording mesoporosity.

I.2 Functionalization of SBA-15

There is a real need to modify or functionalize SBA-15 materials in order to overcome its limitations such as its low acidity strength and enhance or optimize its catalytic activity by supporting⁶³ or immobilizing⁶⁴ on other elements or catalysts⁶⁵. SBA-15 is one of the best contenders to be modified and functionalized since it has controllable pore size, pore volume and high surface area⁶⁶.

Modification and functionalization of SBA-15 can be categorized into the following types:

- Functionalization of SBA-15 with organic groups, such as sulfonic, aminopropyl, imidazole or triazole units^{65,67},
- Enzyme immobilization onto SBA-15 i.e., cytochrome-c^{64,68},
- Metal deposition, such as Pd-Zn, Co,^{69,70}
- Metal incorporation within the framework of different types of SBA-15 i.e., Al, Ce, La, Ti, Mg.⁶³

Various methods of modification and functionalization have been employed which include direct synthesis, post synthesis impregnation and grafting or acid catalyzed sol-gel method.^{65,71,72}. From here onwards, only direct synthesis and post-grafting will be further developed.

I.2.1 Direct synthesis

Two research groups first reported the co-condensation method in 1996.^{73,74} Direct synthesis of modified SBA-15 engages the copolymerization of the silica source, for example TEOS, with organotrialkoxysilane in the presence of a templating agent. Apart from silane groups, this method was explored and developed by co-condensing silica source with different groups of metal i.e. transition, alkaline earth, rare earth metals^{59–61}.

From different studies, Zhao et al.⁷⁵ reported that this approach enables a higher and more homogeneous surface coverage of organosilane functionalities and structure than post-grafting. However, the ability of calcination is not possible and hence it is more difficult to eliminate any remaining of organic reagents.

I.2.2 Post-grafting

Grafting is another method commonly used in performing surface modification by covalently linking organosilane species of type $(R'O)_3SiR$ with surface silanol groups (free and germinal silanol). By post-grafting, functionalization with a variety of organic groups can be achieved in this way by changing the organic residue R (Figure I-2).

It has been reported that the post-grafting method has its downside aspects^{76,77}. This method includes a number of disadvantages such as (1) the reduction of pore size and pore volume caused by the attachment of functional moieties on the surface; (2) its time consuming nature as two steps are necessary to accomplish the modification process; (3) density limitation of reactive silanol groups; (4) difficulties in controlling the loading and position of the organosilane.

However, the strong advantage of this modification lies in the fact that under the synthetic conditions used, the mesostructure of the starting silica phase is usually retained. In addition, the intermediate step of calcination allows the elimination of any other organic reagents.

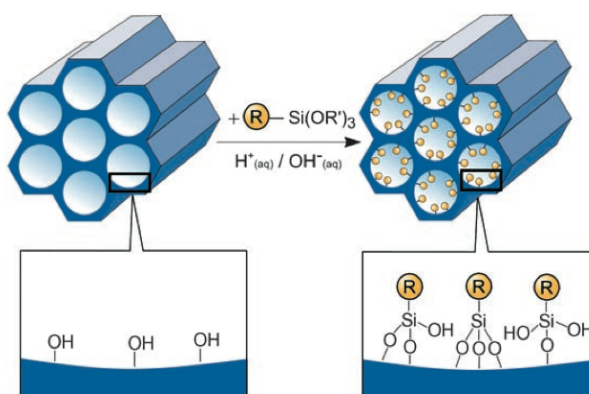


Figure I-2: Grafting of mesoporous silica with terminal organosilanes of type $(R'O)_3SiR$, where R = organic functional group⁷⁸.

During this PhD work, the procedure of post-grafting was used for the functionalization of SBA-15 with aminopropyl functions. Such treatment has been described thoroughly due to the commercial availability of 3-aminopropyltriethoxysilane^{78–80}. Grafting protocols vary in the solvent used, the expected loadings and the post-synthesis treatments. Here, the solvent used was toluene. The whole reaction was carried out in a nitrogen atmosphere. The SBA-15 used should already be dried before the functionalization procedure. In the experimental procedure, the targeted loading of aminopropyl groups was 4 mmol/g. A few minutes of ultrasonication were necessary for the full dispersion of the reagents in the mixture, and then refluxing was followed.

I.3 Characterization techniques

I.3.1 Thermogravimetric analysis (TGA)

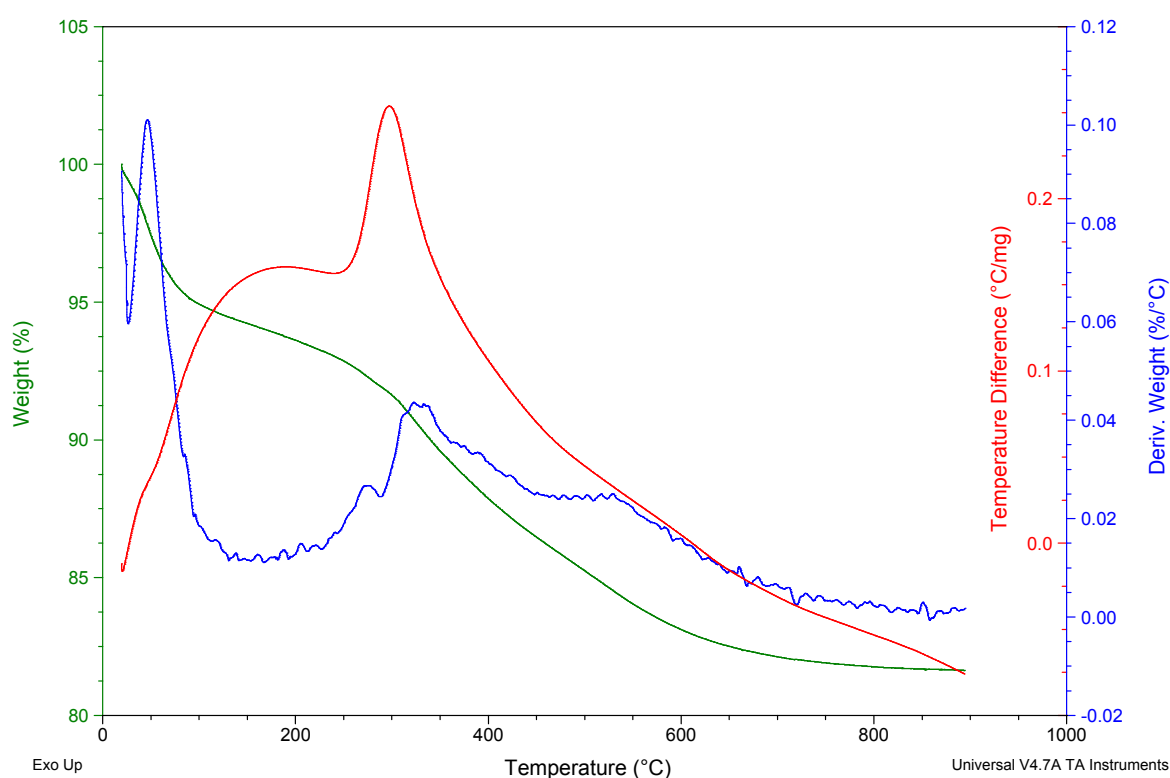


Figure I-3: Thermogram of amino-functionalized SBA-15 under air from RT up to 900°C.

Thermogravimetric analysis was performed on the amino-functionalized SBA-15 for a precise calculation of the quantity of functions grafted on the surface. The thermogram of SBA-NH₂ was executed under air, varying from room temperature up to 900°C. As seen from the graph (Figure I-3), two weight losses can be observed. The first one (4.5%), below 100°C,

corresponds to the loss of water adsorbed on the silica surface. The second one (18%), in the range of 100-900°C, can be attributed to the decomposition of aminopropyl functions. Thus, from this analysis, it can be demonstrated that amino-functionalized SBA-15 has a loading of 2.4 mmol of NH_2 per g (ca. 60% incorporation yield).

I.3.2 X-Ray Diffraction (XRD) studies

The XRD patterns of SBA-15 before and after functionalization with amino-propyl functions were recorded at 2θ from 0.5 to 5°. As seen in the figure below, the resulting diffractogram exhibits three peaks. The first one, more intense than the other two, is assigned to the (100), the second one to the (110) and the last one to the (200) reflections of the expected $P6m$ structure, thus confirming the hexagonal structuration of the mesoporosity of SBA-15. As clearly seen by the diffractogram, post functionalization is a mild method that does not alter the structuration of SBA-15.

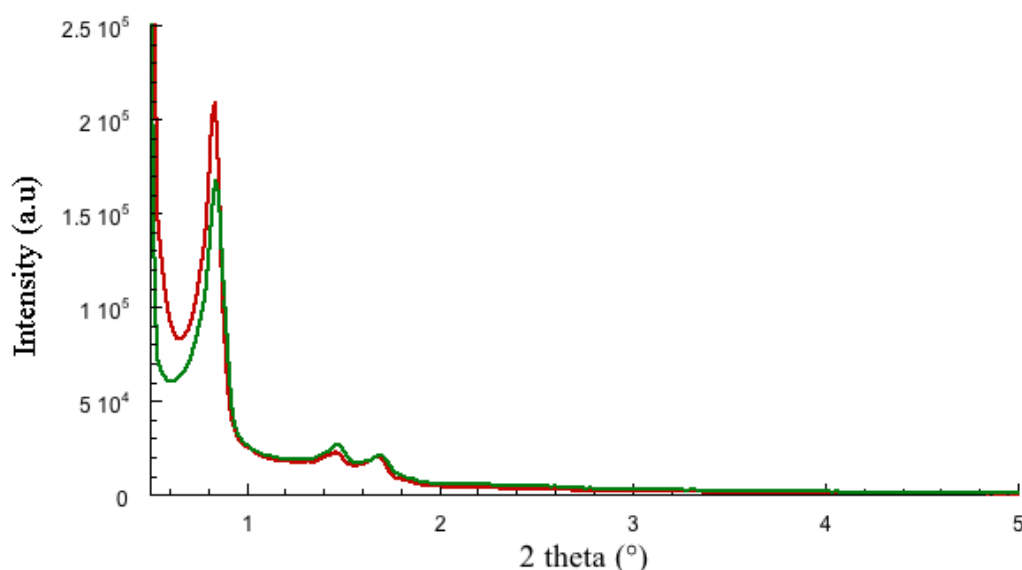


Figure I-4: Comparison of XRD patterns for SBA-15 (green line) and amino-functionalized SBA-15 (red line).

I.3.3 Determination of the surface by BET method

As demonstrated by the nitrogen adsorption-desorption studies in Figure I-5, the pure and modified SBA-15 materials show type IV isotherms according to the IUPAC classification with H1 hysteresis loop that is representative of mesopores with size interval

compatible with SBA-15. The volume adsorbed for all isotherms shows a sharp increase suggesting the capillary condensation of nitrogen within the uniform mesoporous structure.

The physicochemical properties of pure and modified SBA-15 are summarized in Table I-1. A decrease in the surface area and the BJH average pore diameter are observed after the functionalization, indicating the presence of the pendent functional groups on the mesoporous channel surface partially blocking the adsorption of nitrogen molecules. The condensation point shifts slightly towards lower relative pressures after modification, which is also an implication of the reduction in pore size derived from the organic modification.

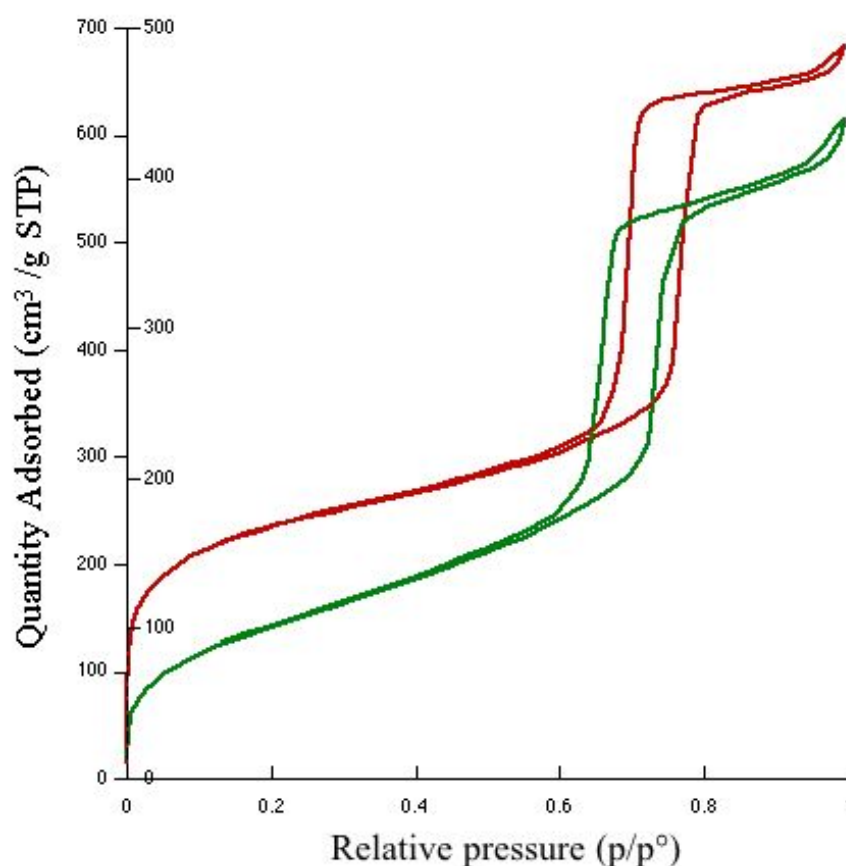


Figure I-5: Nitrogen adsorption-desorption isotherms of SBA-15 (red line) and amino-functionalized SBA-15 (green line).

The pore sizes were calculated from the isotherms desorption branches using the Barret-Joyner-Hallenda (BJH) formula. This method is used for the determination of pore-size distribution for materials with pores larger than 4 nm, hence suitable for SBA-15.

	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA-15	804	0.97	6.7
SBA-NH ₂	376	0.69	5.8

Table I-1: Textural data of pure and amino-functionalized SBA-15.

I.3.4 High-Resolution Transmission Electron Microscopy (HR-TEM)

Transmission electron microscopy confirmed the structure of SBA-NH₂. The micrographs obtained by HR-TEM displayed organized tubular networks (Figure I-6).

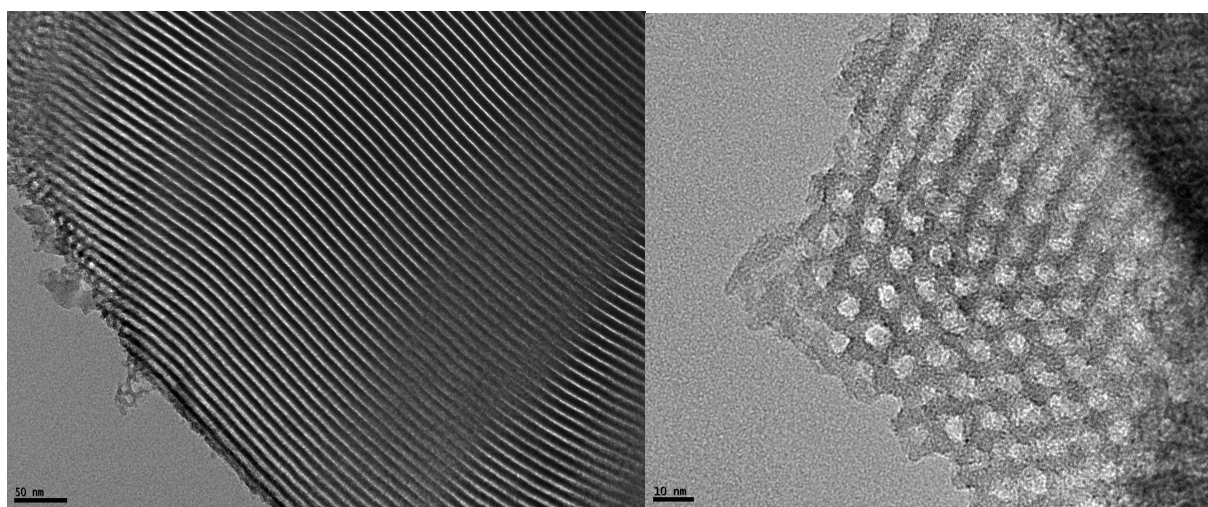


Figure I-6: HR-TEM micrograph of amino-functionalized SBA-15 after microtome cutting.

II Covalent grafting of POMs onto amino-functionalized SBA-15

II.1 Strategy for the covalent grafting

As cited before, the first attempt to get a covalent linking of POMs with functionalized silica support was achieved using silyl derivatives. By co-polymerization of TEOS alone or of a mixture of TEOS and 1,2-bis(triethoxysilyl)ethane with silyl derivatives of lacunary POMs in the presence of the SDA, mesoporous materials with Si-O-W covalent bonds toward α -[SiW₁₁O₃₉{O-(SiOH)₂}]⁴⁻ or γ -[SiW₁₀O₃₆{RSi- μ -O}₄]⁴⁻ moieties were formed⁶⁰. This strategy afforded regular mesoporous hybrid silica supports with POMs covalently grafted on the surface. One example of these systems showed limited catalytic activity for the epoxidation of cyclooctene, explained by the decreased accessibility of the catalytic site. Another main drawback of these hybrid materials was the cleavage of the link between the surface and the POMs. The {Si-O-W} bonds are relatively weak upon heating, even at 45°C. In addition, all the nucleophilic oxygen atoms of the vacant POMs used were unavailable for metal substitution, due to the binding strategy used. The latter argument is really important, as generally these are the atoms where the catalysis takes place.

These disadvantages enhance the need of testing other strategies of post functionalization. The functionalization of trivacant polyoxoanionic POMs with organophosphonic acids RPO(OH)₂ was already carried out over the past years in the E-POM group. During this work, trivacant Keggin-type polyanions bearing two alkylphosphonate/arsonate groups with carboxylic terminal functions were used.⁸¹ Such trivacant POMs can be functionalized with different R groups bearing useful pending terminations, (including carboxylic acid functions). The bis-organophosphonate/arsonate derivatives selected were A, α -[X^VW₉O₃₄{RP/AsO}₂]⁵⁻ and B, α -[X^{III}W₉O₃₃{RP/AsO}₂]⁵⁻ derivating from A, α -[X^VW₉O₃₄]⁹⁻ (X=P, As) or B, α -[X^{III}W₉O₃₃]⁹⁻ (X=As, Bi). Since only two phosphonate/arsonate groups are grafted to the lacuna of the trivacant anions, from the six oxygen atoms available only four are involved in the POM anchoring. This particularity can be used as an advantage, owing to the fact that the free oxygen atoms in the lacuna of the grafted POMs can serve as ligands toward lanthanides or d transition metal cations.⁸²

Functionalized lacunar hybrids of POMs used in the grafting step can be easily obtained in a large scale, (potentially up to 100 g), in a one-pot synthesis. The synthesis can be implemented even when the R group is a reactive pending function. Such procedure is carried out in refluxing acetonitrile or DMF and in the presence of aqueous concentrated HCl. The resulting hybrid complexes are stable towards heating, hydrolysis and acidic or moderately basic conditions due to the robustness of {P-O-W} bonds compared to {Si-O-W} bonds.

As indicated before, until now organosilyl derivatives of POMs were anchored onto a surface by using co-condensation methods. However, the organophosphonyl-derivatives retained in this study cannot follow the same procedure. Despite the existence of commercially available reactants such as $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$, it is indeed difficult to proceed to a controlled specific grafting of the phosphonyl groups on the trivacant POMs without saturating the POMs vacancy with silyl functions.

The drawbacks mentioned above enhanced the need for another strategy, which consists of the simultaneous preparation of functionalized POMs and silica supports with complementary organic functions. Thus, hybrid of POMs and SBA-15 were modified independently by the introduction of carboxylic acid groups and primary amine functions respectively, whose reaction leads to connection through strong amide bonds.

II.2 POMs functionalization and characterization techniques

For the purpose of this work, the previously synthesized bis-carboxylate derivative $\text{B},\alpha\text{-}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})\text{-(CH}_2\text{CH}_2\text{CO}_2\text{H)}\}_2]^{5-}$ was used. This compound was synthesized in acidic medium with tetrabutylammonium cations serving as transfer agents (Figure II-1). The reaction was already carried out for A-type phosphotungstates with formula $\text{A},\alpha\text{-}[\text{PW}_9\text{O}_{34}\{\text{RPO}\}_2]^{5-}$. Herein, the organo-phosphonate derivative with B-type with $\text{X} = \text{As}$ ($\text{B},\alpha\text{-}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}]^{9-}$) was selected as it has some advantages over the A-type. The B-type precursors offer higher stability than the A-type, which facilitates the formation of {P(O)R} derivatives with a reactive R function. In the case of the $\text{A},\alpha\text{-}[\text{PW}_9\text{O}_{34}]^{9-}$ anion, an inconvenient to consider is the undesired parallel formation of $(^n\text{Bu}_4\text{N})_3[\text{PW}_{12}\text{O}_{40}]$, decreasing the yield of the reaction with a conversion of 40%. This parallel formation of the other product is only due to the anion used, as for example in the case of $[\text{SiW}_9\text{O}_{34}]^{10-}$ no lateral products exist. In comparison, the synthesis of

$(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (or POM-COOH) was achieved with a 90% yield.

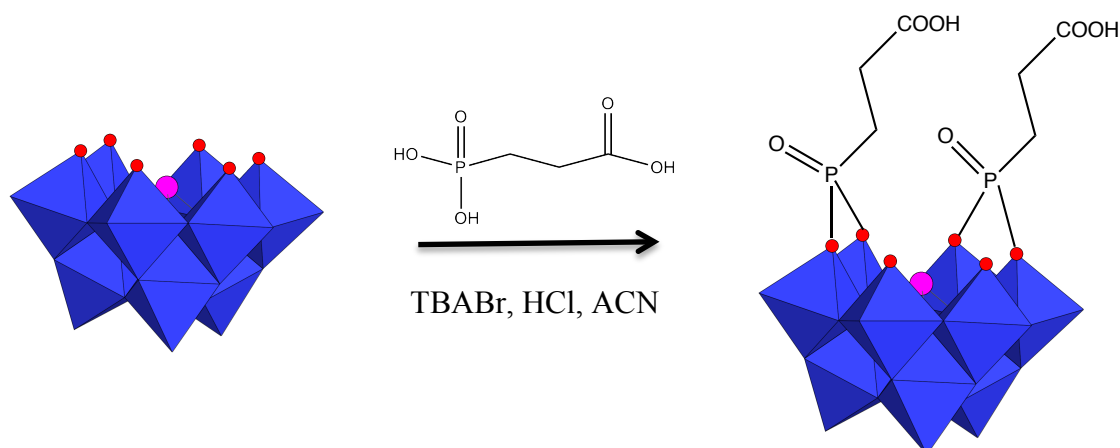


Figure II-1: Synthetic route for $(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$. Oxygen atoms are represented in red, arsenic in pink and $\{\text{WO}_6\}$ octahedra in blue.

This complex is characterized by the presence of four nucleophilic oxygen atoms groups. Among these four, two are provided by the $\{\text{RP}=\text{O}\}$ groups and two are unsaturated atoms in the lacuna of the $\{\text{XW}_9\}$ anion. A metallic cation can be bound to these four oxygen atoms,^{82,83} in particular lanthane La^{3+} ions. The properties of these ligands will be explored later in a following section.

The synthesized POM-COOH can be characterized by different spectroscopic methods. Specifically, Infra-Rouge Spectroscopy, ^{31}P and ^{13}C NMR allowed the characterization of the synthesized POMs and their comparison once they are grafted on supports. In addition, NMR will be an indispensable tool for the characterization of the complex containing lanthane ions.

The ^{31}P NMR spectrum displays a single peak at +29.0 ppm in CD_3CN corresponding to the two equivalent phosphorous atoms coming from the $\{\text{RPO}\}$ groups. In the ^1H spectrum, four signals attributed to three tetrabutylammonium cations are revealed. In addition, two multiplets appointed to the two different $-\text{CH}_2$ groups associated to propionic acid chains are observed in the range of [2.18-2.30] and [2.70-2.90] ppm respectively, partially covered by those of tetrabutylammonium cations. The presence of $-\text{COOH}$ functions cannot be verified by the ^1H NMR but by $\{^1\text{H}\}^{13}\text{C}$ NMR. Alongside the four signals of the tetrabutylammonium

ions (13.5, 19.2, 23 and 57.5 ppm) and the signals from the $-\text{CH}_2\text{CH}_2\text{COOH}$ chains (28.0 and 23.4 ppm), a doublet exists at 174.3 ppm ($^3J_{\text{P-C}} = 23$ Hz) associated with the $-\text{COOH}$ groups.

The IR spectrum of POM-COOH exhibits several characteristic bands of terminal $\text{W}=\text{O}_\text{t}$ and bridging $\text{W}-\text{O}_\text{b}-\text{W}$ bonds, as known for the tungstates, in the range of $[700-1000\text{ cm}^{-1}]$. Moreover, two bands at 1025 and 1005 cm^{-1} appointed to $\nu(\text{As}-\text{O}_\text{c})$ and to $\nu_{\text{asym}}(\text{P}=\text{O})$ of the $\{\text{RP}=\text{O}\}$ groups respectively can be observed. Finally, the evidence of the existence of carboxylic functions is proved by the presence of a $\nu_{\text{C}=\text{O}}$ band at 1725 cm^{-1} and of several smaller bands in the range $[3000-3600\text{ cm}^{-1}]$, with the strongest at 3440 cm^{-1} fitting for pure ν_{OH} .

Finally, POM-COOH was characterized by ^{183}W NMR spectroscopy. The characterization of the $\{^{31}\text{P}\}^{183}\text{W}$ NMR spectrum was described previously by Villanneau et al⁸². In the following table, the values of the different peaks are presented.

δ (ppm)	
Table II-1: Chemical shift of POM-COOH.	-215.7 (s, 1W)
	-117.5 (d, $^2J_{\text{P-W}} = 11.8$ Hz, 2W)
	-117.6 (d, $^2J_{\text{P-W}} = 10.1$ Hz, 2W)
	-112.5 (s, 2W)
	-111.7 (s, 2W)
$\{^{31}\text{P}\}^{183}\text{W}$ NMR spectrum of	

II.3 Covalent grafting of polyoxometalates onto SBA-15 and characterization of the resulting material

The formation of peptide bonds starting from POMs with carboxylic acids functions has been adapted from previous methods already described in the E-POM group for organic/inorganic Wells-Dawson-type POM hybrids^{84,85}. The procedure required the use of an activating agent (isobutylchloroformiate, $^i\text{BuOC}(\text{O})\text{Cl}$) in the presence of a base (triethylamine, NEt_3) in a POM-COOH/ NEt_3 / $^i\text{BuOC}(\text{O})\text{Cl}$ molar ratio of 1/6/6.

In the following figure, the series of reactions between the POM anion, triethylamine and isobutylchloroformate are presented. The POM anion is presented as RCO_2H and the amino functionalized SBA-15 as RNH_2 , for a simpler representation.

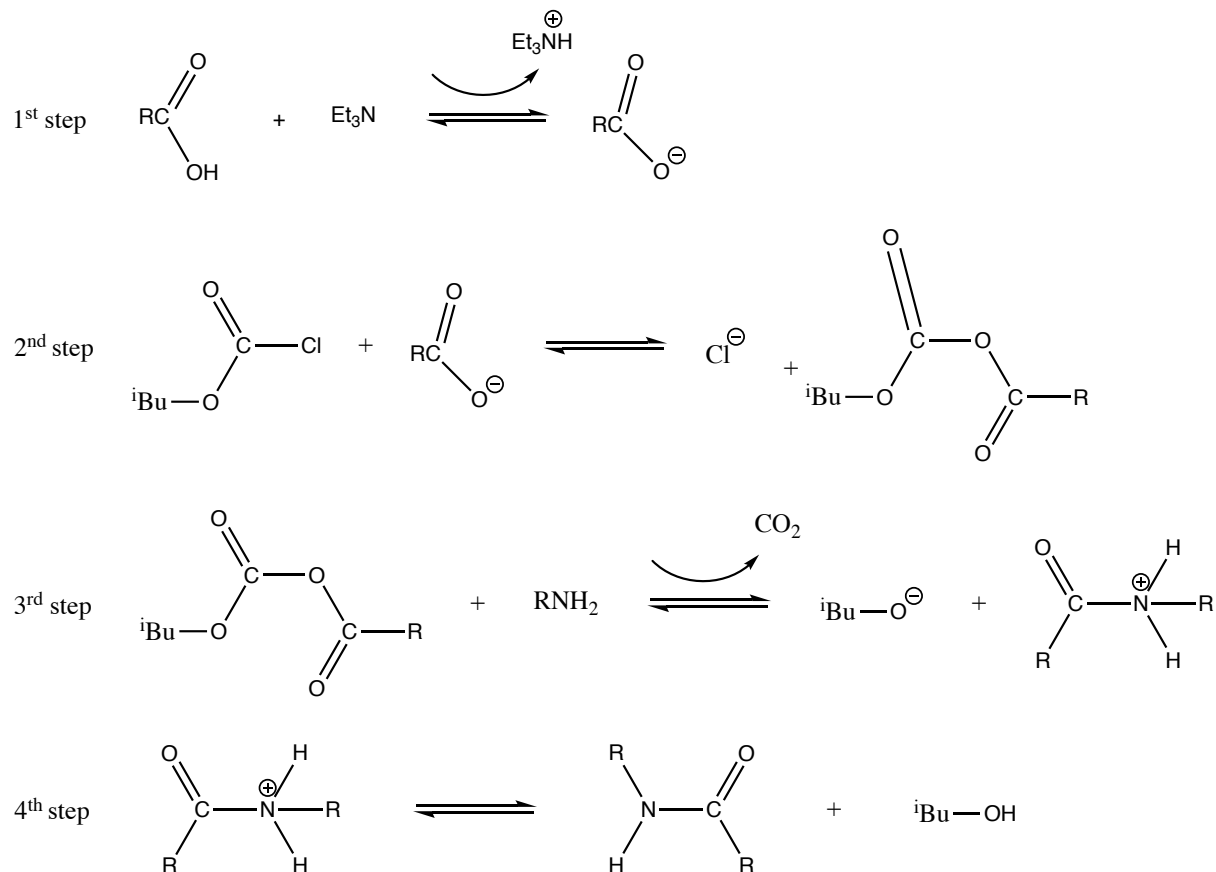


Figure II-2: Accepted mechanism for the covalent attachment of POM-COOH through amide bonds.

II.3.1 Infra-Red Spectroscopy

IR spectra of amino-functionalized SBA-15 were recorded before and after grafting of POMs. This technique used to evidence the presence of POMs is not ideal, as shown in the following figure. Indeed, in the range of $800\text{--}1200\text{ cm}^{-1}$, intense bands attributed to the $\nu_{\text{Si-O}}$ vibrators are highly pronounced and mask the characteristic bands of POMs. Nonetheless, the enhancement of a shoulder peak at 950 cm^{-1} , assigned to the $\nu_{\text{W=O}}$ of POM-COOH, could be observed.

The success of the covalent grafting of POMs onto the SBA-15 can be demonstrated by IR spectroscopy (Figure II-3). Two new bands related to the presence of amide function can be identified. The first one at 1685 cm^{-1} and the second one at 1530 cm^{-1} are corresponding to $\nu_{\text{C=O}}$ and δ_{NH} bands, respectively. A peak at 1636 cm^{-1} correlated to δ_{OH} is present in both spectra recorded before and after grafting of POMs onto the support.

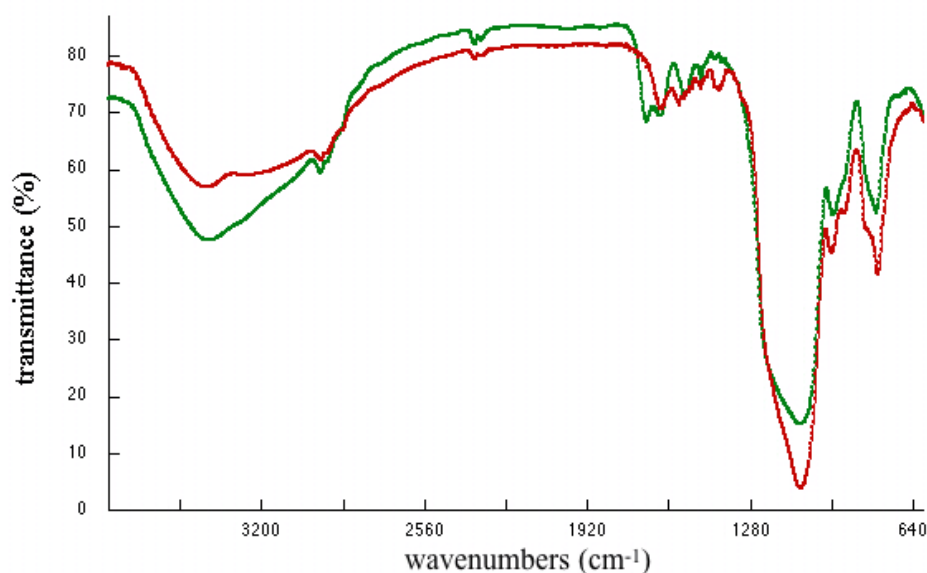


Figure II-3: IR spectra of amino-functionalized SBA-15 (red line) and POMs anchored onto amino-functionalized SBA-15 (green line).

II.3.2 CP-MAS NMR Spectroscopy

The presence of amide bonds in the final materials has been investigated also by ^{13}C CP MAS NMR spectroscopy. Figure II-4 shows the spectrum of the NH_2 -functionalized SBA-15 silica after reaction with POM-COOH. In the range 50 to 100 ppm, this spectrum displays predominantly the signals of the aliphatic carbon atoms from the aminopropyl groups of the surface and tetrabutylammonium cations. More interestingly, the two signals observed at 176 ppm and 182 ppm respectively were assigned to carbon atoms of two different carbonyl functions. In more detail, these signals were respectively attributed to the C atom of amide functions formed during the coupling reaction (176 ppm) and to the C atoms of residual carboxylic functions (182 ppm). These values are also in accordance with that expected for these functional groups in the literature. The obtained results confirmed that the covalent linking of POM-COOH onto the NH_2 -functionalized support was performed successfully, and hence it was proposed that most of grafted POMs entities are linked through

only one amide function, probably because the distance between the carboxylic functions does not match with the distribution of the NH_2 groups at the surface.

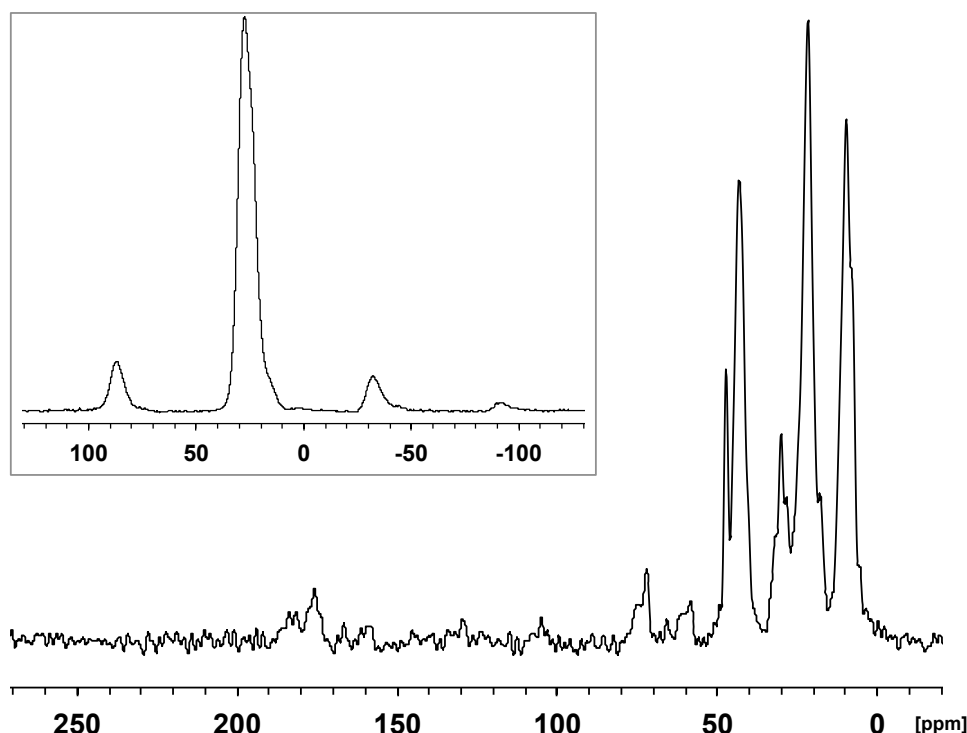


Figure II-4: ^{13}C CP MAS NMR spectrum (Inset: ^{31}P CP MAS NMR spectrum) of POMs anchored onto SBA-15 support.

II.3.3 High-Resolution Transmission Electron Microscopy (HR-TEM)

The hybrid material was characterized also by HR-TEM, with microtome cutting. The first information that can be extracted by the observation of the amino-functionalized SBA-15 after the grafting of POMs is the absence of change in the intrinsic structure of the mesoporous support. This result is very important, as the structure remained intact even in the presence of triethylamine used for the grafting procedure, as already confirmed by XRD (Figure II-5).

Subsequently, POMs had to be detected on the surface of SBA-15. However, by classical HR-TEM this could not be possible, even at high magnification, proving at the same time that POMs were not found in the surface of the material. Hence, microtome cutting proved to be a useful tool, by identifying and locating precisely the POMs inside the pores of the material. As seen by the following Figure II-5, the POM-COOH seems to be regularly distributed at the periphery of the channels. The average size of each black dot is considered

to be 0.9 nm, corresponding to the size of one isolated POM. Thus, by the covalent grafting of the POMs, the formation of aggregates is avoided.

The covalent grafting of POMs onto the pore walls of SBA-15 through the formation of amide functions is a favorable procedure to get dispersed isolated anions. This conclusion could not have been achieved without the use of microtome cutting combined with the image contrast provided by heavy W atoms originating from the polyoxometalates.

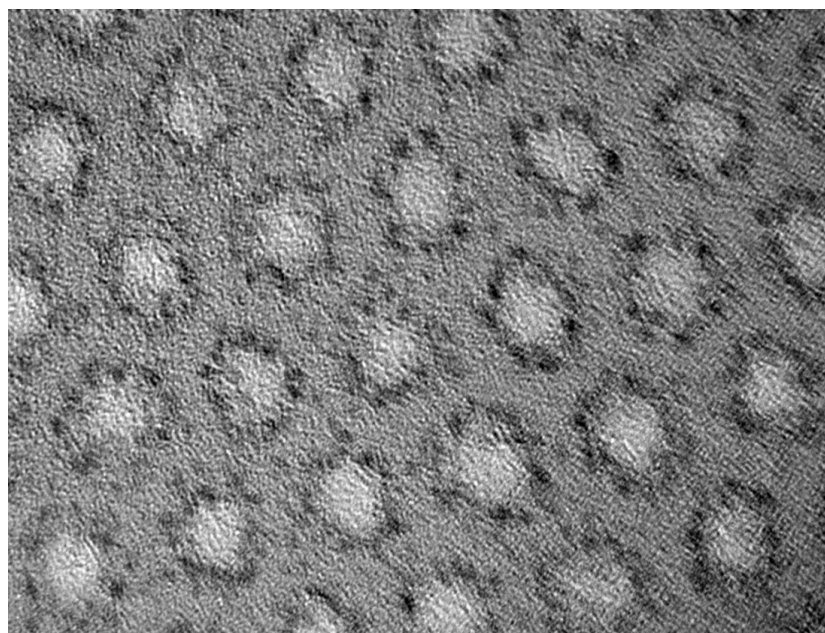


Figure II-5: HR-TEM micrograph of POMs-decorated amino functionalized SBA-15.

For the purpose of comparison, another sample with non-covalently bound POM-COOH supported on SBA-NH₂ was prepared. The method used was the wet impregnation of SBA-NH₂ with a solution of POM-COOH in acetonitrile. By HR-TEM microscopy, it was confirmed that aggregates were formed. Additionally, the distribution of POMs was highly irregular in the different grains of SBA-NH₂.

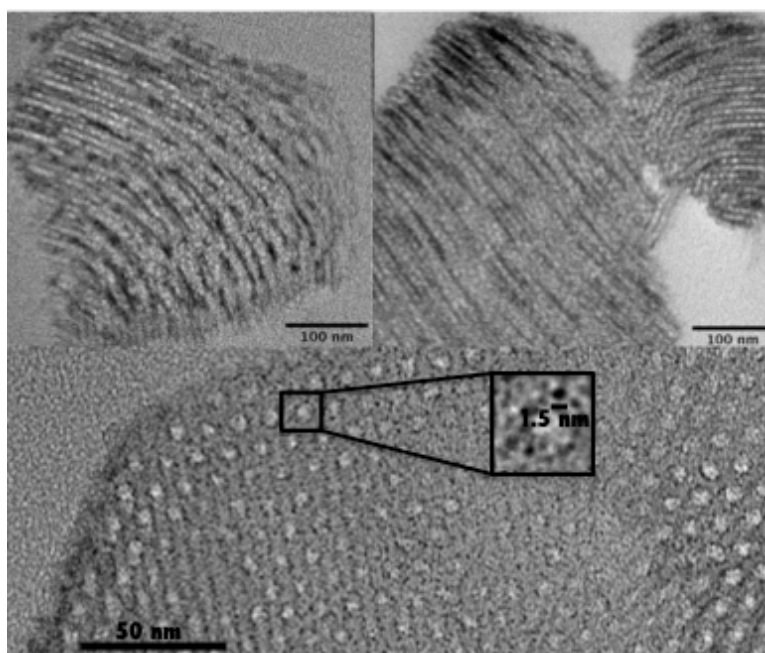


Figure II-6: HR-TEM micrographs of SBA-NH₂ supports covered by TBA₃NaH(POM-COOH) after wet impregnation.

II.3.4 Determination of the surface by BET method

The values of the pore diameters decrease continuously over the steps, which are compatible with the inclusion of the major part of the amine groups, then the POMs within the porosity. After the functionalization step of the support by amine groups and the formation of amide bonds, variations in textural parameters can reach nearly 60-75%, hence showing the importance of starting from silicic supports with particularly large specific surfaces.

Support	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
SBA-15	804	0.97	6.7
SBA-NH ₂	376	0.69	5.8
SBA-NH ₂ /POMs-COOH	185	0.33	4.7

Table II-2: Textural data of SBA-15 support before and after POMs grafting.

III Catalytic studies of anchored homogeneous catalyst

Hybrid derivatives of heteropolytungstates that do not contain any additional transition-metal ions,⁷ including organo-phosphonyl derivatives of POMs,^{86,87} have been extensively tested as catalyst precursors in alkenes epoxidation reactions with H₂O₂ as oxidant^{1,7,9,88}. Among these examples, only the group of Bonchio used organophosphonyl derivatives of trivacant POMs.⁸⁶ However, the experimental conditions required a relatively high reaction temperature with microwave assistance. As a result, the need for a less energy-consuming approach is crucial.

The initial step of this work dealt with the study of the catalytic performance of the homogeneous catalyst prior to anchorage. Different heteropolytungstates, previously synthesized in the group, were studied. The model reaction is the epoxidation of cyclooctene or cyclohexene with aqueous H₂O₂ at room temperature. In some cases, the temperature was raised to 50°C in order to compare to the tests performed under heterogeneous conditions. The molar ratio of catalyst/ alkene/ H₂O₂ used was equal to 1/ 250/ 250. In the absence of the catalyst, no reaction occurred and the quantity of H₂O₂ remained stable, with no consumption in the absence of cyclooctene/cyclohexene.

III.1 Epoxidation of cyclooctene or cyclohexene in the presence of soluble POMs

The catalytic activity of POM-COOH was compared to that of TBA₃H[AsW₉O₃₃{tBuPO}₂], i.e. another functionalized POM synthesized before in the team with the same B, α -[AsW₉O₃₃]⁹⁻ platform bearing *tert*-butyl groups instead of carboxylic acid ones. The epoxidation of cyclooctene into cyclooctene oxide was performed in acetonitrile and at room temperature. It is important to note that the epoxide was the only product formed, meaning that the selectivity is 100%. In the following table, the results of cyclooctene conversion are presented as a function of time. The results were obtained in the presence of a standard compound (decane) and the mass balance was verified.

Catalyst	T (°C)	3 h	6 h	24 h
POM-COOH	20	59.5	88.5	96
TBA ₃ H[AsW ₉ O ₃₃ {tBuPO} ₂]	20	0	2.4	7.5
TBA ₃ H[AsW ₉ O ₃₃ {tBuPO} ₂]	50	20.6	97	100

Table III-1: Epoxidation conversion of cyclooctene in the presence of two functionalized soluble POMs.

The comparison of POM-COOH with TBA₃H[AsW₉O₃₃{tBuPO}₂] proved to be interesting for the complete understanding of the contribution of POM into the catalytic mechanism. As mentioned before, both POMs are based on the same B, α -{AsW₉O₃₃}⁹⁻ subunit but differ by their pendant arms. TBA₃H[AsW₉O₃₃{tBuPO}₂] is functionalized with two {tBuPO} phosphonate groups instead of carboxypropyl functions for POM-COOH. As seen from the Table III-1, at room temperature, the behavior of these two complexes is totally different, as the conversion for the TBA₃H[AsW₉O₃₃{tBuPO}₂] does not increase sufficiently even after 24 h (7.5%). However, when the temperature is augmented up to 50°C, the results obtained with TBA₃H[AsW₉O₃₃{tBuPO}₂] are similar with the ones of POM-COOH at room temperature. Regarding this outcome, a conclusion can be given on the role of carboxylic functions. Their notable importance can be understood as their absence led to a sharp decline

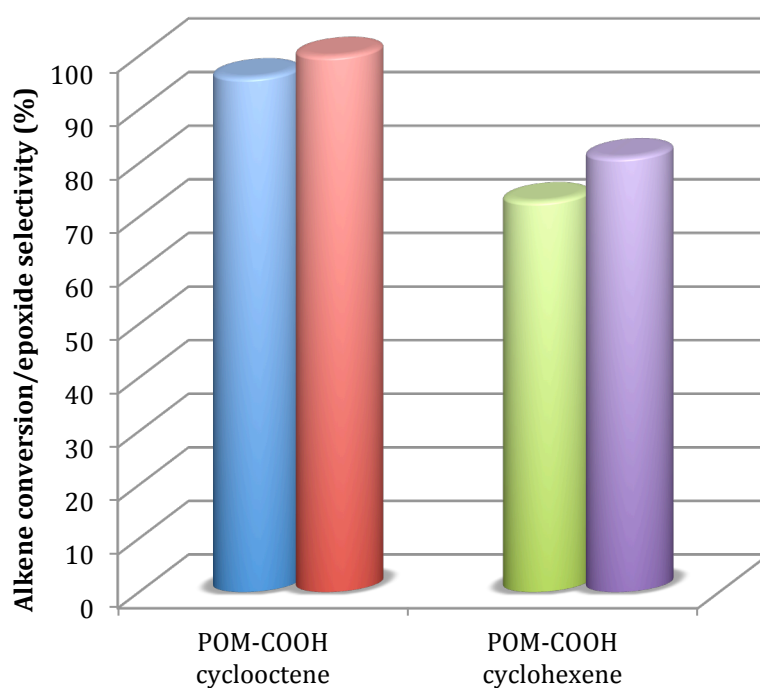


Figure III-1: Diagram for alkene conversion (left bar) and epoxide selectivity (right bar) for (left to right) cyclooctene and cyclohexene with POM-COOH in homogeneous conditions.

in the conversion of cyclooctene. This hypothesis can be confirmed by cases already discussed in the literature for the role of acids and of carboxylic acids in the epoxidation of alkenes^{86,89}.

The epoxidation of cyclohexene with aqueous H₂O₂ was also studied. The quantities were adjusted from those used for cyclooctene, respecting the molar ratios of H₂O₂/catalyst/alkene. The same experimental conditions were applied; therefore the reaction was performed in acetonitrile and at room temperature. The conversion with POM-COOH as a catalyst was found to be 73% after 24 h with a final selectivity in the epoxide around 81%. The results can be easily compared with other POMs-based catalysts, such as the example of Ishii-Venturello catalyst (ⁿ-Bu₄N)₃[PO₄{WO(O₂)₂}₄] with a 84% conversion of cyclohexene in 6 h⁹⁰. Nonetheless, the epoxide selectivity differs in these two cases, with the latter complex attaining a percentage of 98%.

III.2 Theoretical study of the catalytic reactivity of (ⁿ-Bu₄N)₃NaH[AsW₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂] (POM-COOH)

Having in mind these results, it was interesting to understand the particular reactivity of POM-COOH compared to the ^t-Bu derivative TBA₃NaH[AsW₉O₃₃{^t-BuPO}₂], which does not contain any acidic functions. Indeed, as mentioned previously, whatever the conditions used (homogeneous or in its heterogenized form, see next paragraph), POM-COOH systematically showed better catalytic performances for the epoxidation of alkenes in the presence of H₂O₂.

Several explanations may be proposed which are linked to the presence of the carboxylic functions. The presence of several acidic protons in the vicinity of {W=O} reactive centers is obviously one possible explanation. However, the formation of peracid functions from the function -CH₂CH₂COOH which is linked to the POM may also be considered as a mechanism that can hardly be ruled out at the outset.

In order to check the relevance of such mechanistic path, Pr. Hélène Gérard, from the Laboratoire de Chimie Théorique (LCT) of the UPMC, has realized a DFT study (using Gaussian 09, B3PW91 functional, with 6-31G** / SDD (W et As) basis set and the SMD continuum solvation model for acetonitrile). The goal was to analyze the energetic and structural factors associated to the competition between this peracid and the peroxotungsten

(VI) functions. The study was carried out on a model system of the anionic part of the POM, namely $\{\text{NaH}[\text{AsW}_9\text{O}_{33}(\text{P}(\text{O})\text{Me})(\text{P}(\text{O})\text{R})]\}^{3-}$ ($\text{R} = \text{Me}$ or $\text{CH}_2\text{CH}_2\text{COOH}$). This simple model, involving a single carboxylic acid function, was validated by verifying that this dissymmetry does not lead to energetic difference between the two WO positions of the lacuna. In particular, no H-bond scheme leading to especially stable conformations could be located.

Since the proton of this model was not experimentally located, the determination of the position of the H^+ counterion in the case $\text{R} = \text{Me}$ was carried out by optimizing the geometry of different regioisomers associated to the different possible protonation positions. As expected, when the proton is localized on one of the two nucleophilic O atoms that delimit the lacuna (Figure III.2) the isomers are much more stable than the other ones (-17.2 $\text{kcal}\cdot\text{mol}^{-1}$). This is in accordance with the experimental results obtained by the group of Mizuno in the case of other lacunary POMs such as $[\text{g}-\{\text{SiW}_{10}\text{O}_{32}(\text{H}_2\text{O})_2\}_2(\text{m}-\text{O})_2]^{4-}$ ⁹¹. It is also confirmed that the W atoms from the POM-COOH lacuna are involved for the formation of peroxotungsten (IV).

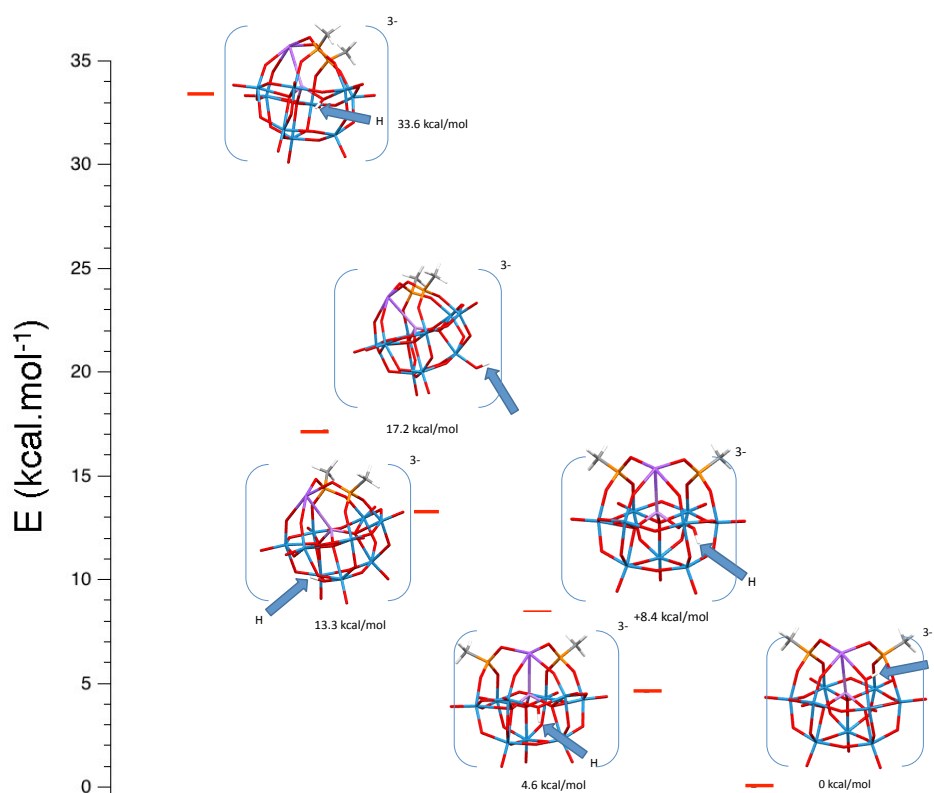


Figure III-2: Energy of the different regioisomers of $\{\text{NaH}[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2]\}^{3-}$ anion as a function of the position of the H^+ counterion (indicated by blue arrows).

The next step dealt with the $R = \text{CH}_2\text{CH}_2\text{COOH}$ model in order to optimize the structures of the two possible peroxo isomers. These isomers were obtained by formal substitution of $-\text{OOH}$ with $-\text{OH}$ groups in $\{\text{W}-\text{OH}\}$ and $\{\text{CO}_2\text{H}\}$ functions respectively. This led to the peroxotungstic $\{\text{Na}[\text{AsW}_9\text{O}_{32}(\text{OOH})\{\text{P}(\text{O})\text{CH}_3\}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}]\}^{3-}$ and $\{\text{NaH}[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_3\}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OOH}\}]\}^{3-}$ peracid derivatives (respectively noted $\{\text{W}-\text{OOH}\}$ and $\{\text{peracid}\}$ Figure III-3). The energy difference between both isomers was found equal to $1.4 \text{ kcal}\cdot\text{mol}^{-1}$. The most stable $\{\text{W}-\text{OOH}\}$ was found to be 0.4 kcal/mol above the model POM and H_2O_2 taken as separated species.

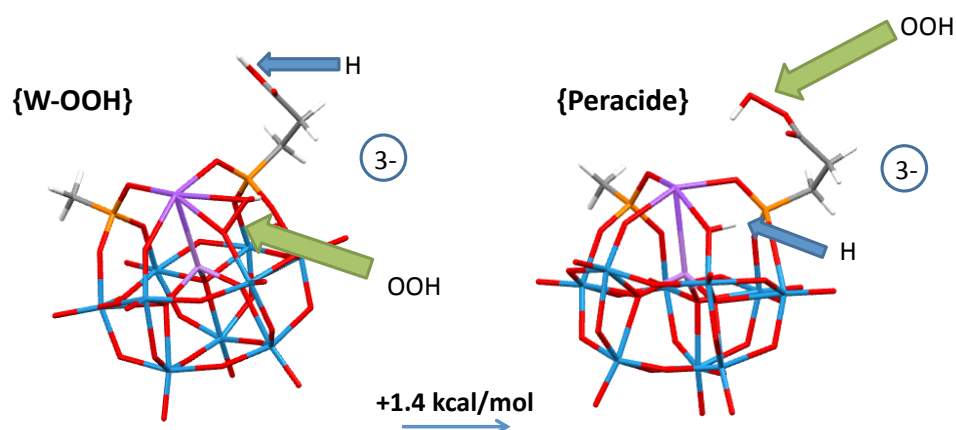


Figure III-3: Optimized structures of the two possible peroxo isomers.

Similar results were obtained after the coordination of a water molecule or a model alkene (ethylene) ligand on the central Na atom, but also in absence of Na^+ counterion coordinated to the lacuna. In other words, both isomers are close in energy, so that both remain energetically viable species.

In conclusion, both the peracid and peroxotungstic paths involve thermodynamically viable chemical intermediates. Transition states for epoxide formation were located for models of both function ($\text{Me}-\text{C}(\text{O})\text{OOH}$ and $\text{W}(\text{O})(\text{OH})_3(\text{OOH})$) and exhibit similar activation barriers (16.2 and 16.6 kcal/mol respectively). The complete elucidation of the mechanism will thus require the localization of the different transition states on the complete system in order to obtain more detailed kinetic information. As a conclusion, for the time being, the present study allowed to pave the way to several attractive hypotheses, starting from competitive chemical processes on the carboxylic and $\{\text{W}=\text{O}\}$ sites to synergetic effects between both groups, in terms of protons exchange up to now.

III.3 Epoxidation of cyclooctene or cyclohexene in the presence of the covalently anchored catalyst POM-COOH/ SBA-NH₂

The POM-COOH/ SBA-NH₂ catalyst was used towards cyclooctene and cyclohexene epoxidation in analogous conditions as for its homogeneous counterpart.

Previously in the group, two other anchored POMs-based catalysts, *i.e.* POM-COOH/MCF-NH₂ and POM-NH₂/SBA-COOH were synthesized⁹². In the POM-COOH/MCF-NH₂ material, the same POM, *i.e.* POM-COOH was grafted on the surface of an amino-functionalized mesocellular foam (MCF) silica characterized by a 3D pore network. In POM-NH₂/SBA-COOH, POM-COOH was replaced by $[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)\}_2]^{5-}$ (POM-NH₂) and grafted onto SBA-15 bearing carboxypropyl, instead of aminopropyl functions. Among these two systems and the one synthesized during this work, the most efficient was the POM-COOH/SBA-NH₂.

With a cyclooctene conversion of 76% after 24 h, the catalytic performances of POM-COOH/SBA-NH₂ turned out to be rather high. However, an important difference between the heterogeneous and homogeneous catalysts was observed at early stages with a delay in the second case (3.2% vs. 59.5% after 3 h and 11.7% vs. 88.5% after 6 h). Various explanations can be proposed. Some of them include lower diffusion rates of the substrate or different accessibility to the active sites in heterogeneous conditions. The other two systems, POM-NH₂/SBA-COOH and POM-COOH/MCF-NH₂, led to lower cyclooctene conversions, *i.e.* 19% and 41%, respectively (Table III-2).

Catalyst	T (°C)	3 h	6 h	24 h
POM-NH ₂ /SBA-COOH	20	1	3.5	19
POM-COOH/MCF-NH ₂	20	1	9	41
POM-COOH/SBA-NH ₂	20	29	53	87

Table III-2: Epoxidation of cyclooctene with covalently anchored catalysts.

X-ray fluorescence (XRF) and chemical elemental analysis determined the POMs contents of the three materials at once. The obtained results are given in Table III-3. It is worth noting that both techniques gave similar trends for the W/Si ratio, with the higher content in POMs being observed in the case of the -NH₂ functionalized supports. The POMs

contents (given in mmol per g of materials, based on the chemical elemental analysis results) are in the range of 3.5×10^{-2} to 1×10^{-1} mmol g⁻¹ of functionalized support. This corresponds to the following POMs loadings: (1) 9.2 wt % based on the anions $[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)\}_2]^{5-}$ (POM-NH₂) for POM-NH₂/SBA-COOH, (2) 22.0 and 28.9 wt % based on the anions $[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]^{5-}$ (POM-COOH), respectively, for POM-COOH/MCF-NH₂ and POM-COOH/SBA-NH₂.

	XRF (W/Si molar ratio)	Elemental analysis (W/Si molar ratio)	POMs loading (mmol/g)
POM-NH₂/SBA-COOH	0.087	0.120	0.1
POM-COOH/MCF-NH₂	0.020	0.028	0.035
POM-COOH/SBA-NH₂	0.047	0.084	0.085

Table III-3: W/Si molar ratio and POMs loading for covalently anchored catalysts.

A recyclability test was carried out in the case of POM-COOH/SBA-NH₂. The catalyst was filtered, rinsed, dried and tested again. After 24 h, the conversion of cyclooctene was equal to 81%, indicating a good stability of this catalyst.

The anchored polyoxometalate POM-COOH/SBA-NH₂ was also tested for the epoxidation of cyclohexene. Like cyclooctene, the catalytic activity stayed at low levels in the first hours of the reaction. However, with a percentage of 74.5%, the final conversion (*i.e.* after 24 h) was found to be slightly higher than the one obtained with the corresponding homogeneous catalyst. In addition, an interesting point was the significant increase in the selectivity once the POM-COOH was covalently grafted on the surface of the SBA-NH₂ (94% vs. 81%).

Upon further inspection of Table III-2, other interesting observations can be made. Firstly, a surprising difference between the catalytic activity of POM-COOH grafted on SBA-NH₂ and the same POM grafted on MCF-NH₂ is revealed. Indeed, even after 24 h of reaction with POM-COOH/MCF-NH₂ as a catalyst, the conversion of cyclooctene reaches 41%. This result gives further insight into the effect of the support on the epoxidation rate. The most significant difference between these two systems is related to the nature of porosity.

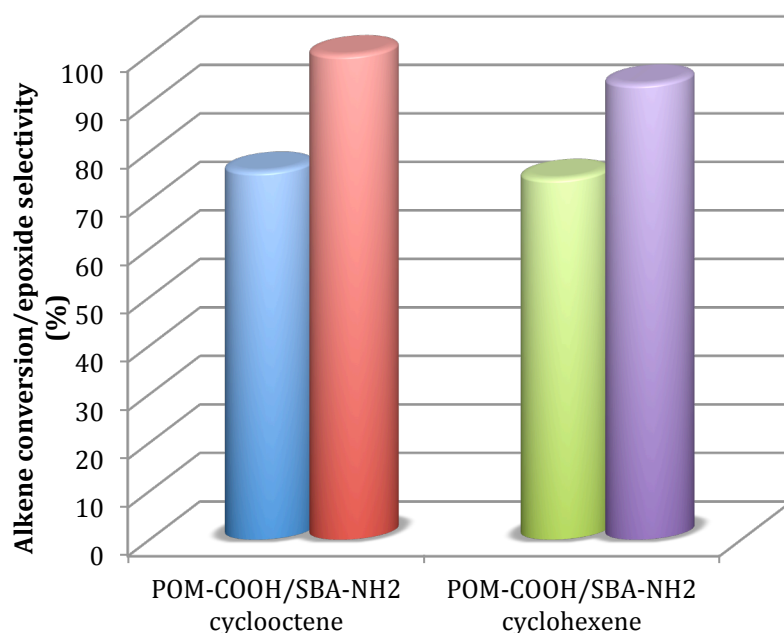


Figure III-4: Diagram for alkene conversion (left bar) and epoxide selectivity (right bar) for (left to right) cyclooctene and cyclohexene with POM-COOH/SBA-NH₂.

The mesocellular foam with a 3D pore network, which was expected to facilitate the diffusion of the reactants, apparently led to a more difficult accessibility of the active sites and as a consequence to a lower percentage towards the epoxidation of cyclooctene. Besides this explanation, the irregularities in the organization of the active sites inside the support compared to those inside POM-COOH/SBA-NH₂, as seen by the HR-TEM micrograph in Figure III-5, can also strengthen the theory of the reduced catalytic activity.

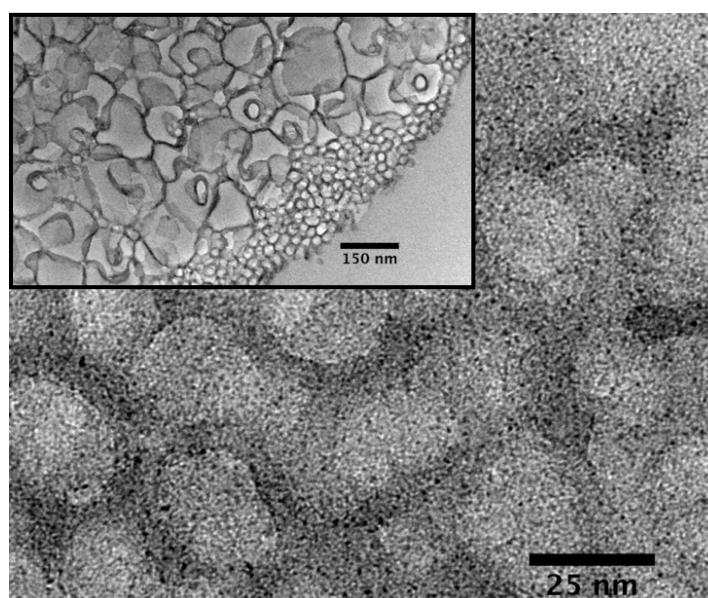


Figure III-5: HR TEM micrographs (microtome cuttings) of POM-COOH/MCF-NH₂ at different magnifications.

Secondly, POM-COOH/SBA-NH₂ and POM-NH₂/SBA-COOH supported catalysts behave very differently, the latter leading to very poor results (19% of conversion after 24 h). However, such difference between POM-NH₂ and POM-COOH was not so obvious in solution (cyclooctene conversion after 24 h equal to 97 and 96% respectively). Such an elevated gap of behavior between the homogeneous and heterogeneous catalysts could be attributed to the reduction of exposed surface. This theory can be proved from the existence of small aggregates combined with the irregular organization of POM-NH₂ on the surface of SBA-CO₂H (Figure III-6). Moreover, according to Table III-3, POM-NH₂/SBA-COOH showed the lowest POM loading of the three systems described, resulting in use of larger amounts of product. Thus, this action led to strong diffusion limitations.

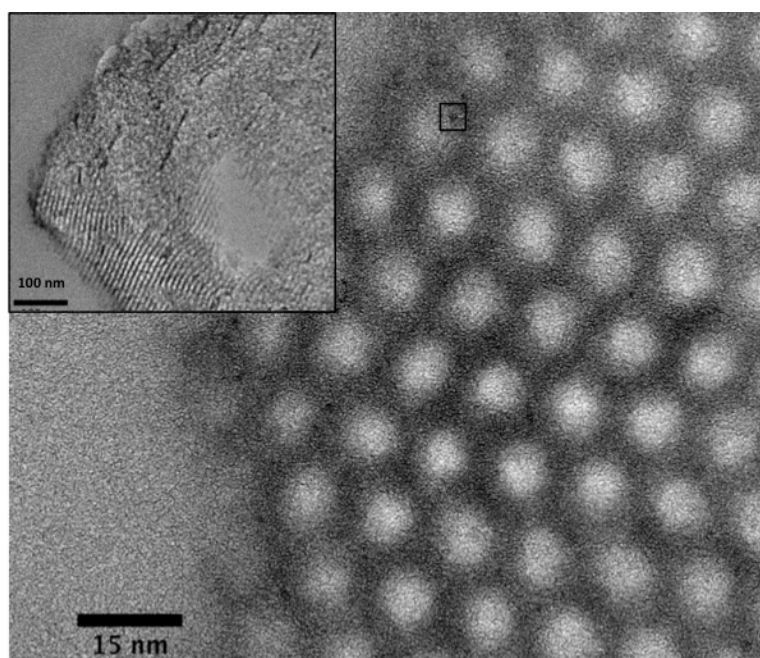


Figure III-6: HR TEM micrographs (microtome cutting) of POM-NH₂/SBA-CO₂H at different magnifications.

III.4 Further evidence for the true heterogeneous catalytic role of covalently anchored homogeneous POM-COOH/SBA-NH₂

Given that the activity of the supported POM-COOH anion covalently bound to SBA-NH₂ was very promising, it was crucial to determine the true nature of such catalysis. Indeed, an argument had to be given in order to prove that the POM in POM-COOH/SBA-NH₂ behaves as a supported catalyst and not as a homogeneous one deriving from partial lixiviation process. The experiment performed, named “hot filtration”

test. was suggested by R. A. Sheldon and co-workers⁹³. For this study, a new test using fresh POM-COOH/SBA-NH₂ was initiated and then treated as shown below:

- (i) The POM-COOH/SBA-NH₂ was removed from the catalytic medium after 5 h of reaction using filters with 0.2 μm pores.
- (ii) The activity of the resulting filtrate was verified after 24 h.

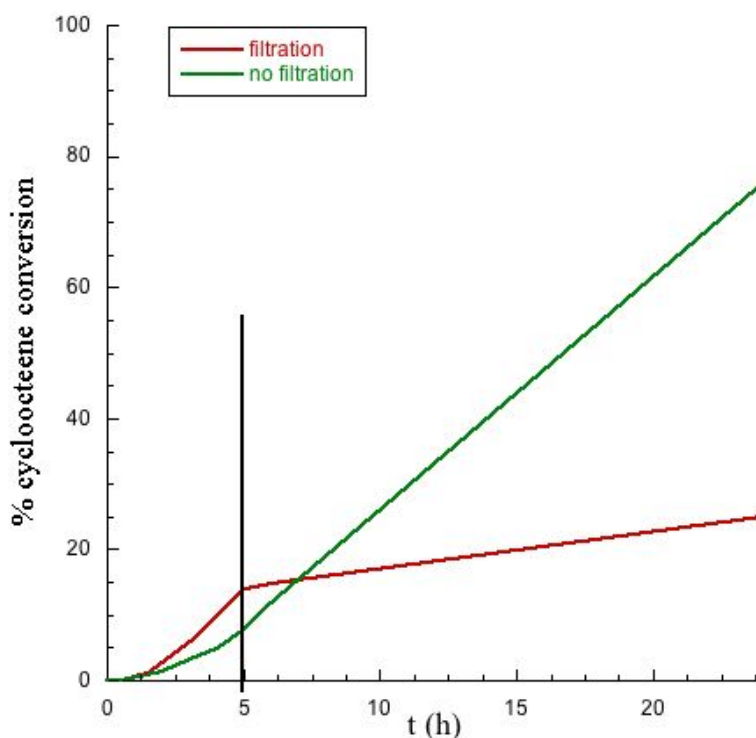


Figure III-7: Catalytic activity of POM-COOH/SBA-NH₂ for the epoxidation of cyclooctene with (green line) and without filtration (red line).

After these steps, the catalytic activity obtained in the new experiment was compared to that of the reference test (with no filtration). In further detail, when filtration occurred (5 h) cyclooctene conversion was almost 14% and, after 24 h, the latter reached 25%, whereas without filtration the final conversion rose to 76%. Such difference between the two tests is in favor of a true heterogeneous catalytic role of the POM in POM-COOH/SBA-NH₂. Otherwise, both experiments (with or without filtration) would have led to the same results. The slight increase after filtration can be explained by remaining silica grains, with a size smaller than 200 nm, in the solution. These grains are visible by HR-TEM microscopy. This appears to be a more probable explanation than the lixiviation of active sites in the catalytic medium.

From the information given above, the POM-COOH/SBA-NH₂ supported system can be considered as a truly anchored catalyst.

IV Incorporation of La^{3+} : characterization techniques and applications

Up until this point, the synthesis of hybrid POMs was described, obtained by strong interactions between the organic and inorganic units. As already shown, their covalent immobilization on surfaces, like mesoporous materials, can make them attractive candidates for reactivity studies.

The next proposed step is the design of bifunctional systems based on inorganic/organic POMs incorporating further heterometallic cations. Depending on the type of cation chosen, new catalytic, luminescent or magnetic properties can be targeted. However, a few examples of hybrid derivatives of POMs can be used as ligands for the complexation of transition-metal cations through oxygen atoms^{94,95}.

The coordination chemistry of vacant organophosphonate POMs derivatives with La^{3+} was already studied. The anion $\text{A-}\alpha\text{-}[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\text{R}\}_2]^{5-}$ with $\text{R}=\textit{t}\text{Bu}, \text{Ph}$ is able to form discrete monomeric complexes in which the cations are bound to the oxygen atoms of the $\{\text{PW}_9\text{O}_{34}\}$ units and/or the $\{\text{RP}=\text{O}\}$ groups^{26,82}. Other anions were also tested with examples including organoarsenyl derivatives of $\text{A-}\alpha\text{-}[\text{PW}_9\text{O}_{34}]^{9-}$ and organophosphonyl derivatives of $\text{A-}\alpha\text{-}[\text{PW}_9\text{O}_{34}]^{9-}$ and $\text{B-}\alpha\text{-}[\text{AsW}_9\text{O}_{33}]^{9-}$.

The reaction carried out for the synthesis of these hybrids consists of mixing the functionalized POMs with different equivalents of $\text{La}(\text{NO}_3)_3$ at room temperature in acetonitrile⁸³. Complexes of lanthanum ions with a 1:1 POM/ La^{3+} stoichiometry can be obtained starting from 1.5 equivalent of $\text{La}(\text{NO}_3)_3$. After recrystallization in *N,N*-dimethylformamide, the single crystals obtained were analyzed by X-ray diffraction analysis. Figure IV-1 shows the structures of $[\text{PW}_9\text{O}_{34}\{\text{P}(\text{O})\textit{t}\text{Bu}\}_2\{\text{La}(\text{dmf})_5(\text{H}_2\text{O})\}]^{2-}$ and $\{[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}\}_x$. As seen from the crystal structures and the proposed formula, the 2nd anion could not be isolated as a discrete complex in the solid state, but a polymeric assembly.

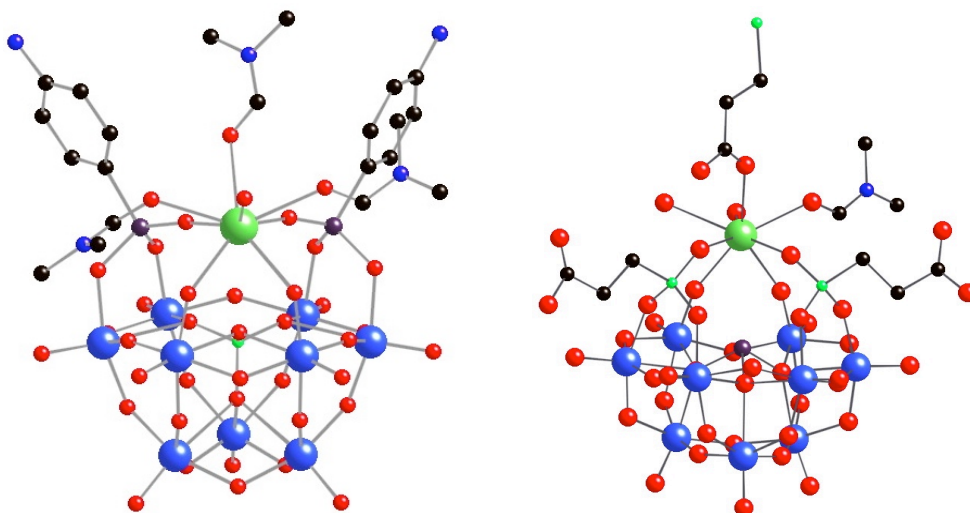


Figure IV-1: structure of anion $[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2\{\text{La}(\text{dmf})_3(\text{H}_2\text{O})_2\}]^{2-}$ (left) and details of the coordination of La^{3+} ions in polymeric $\{[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}\}_x$ (right).

In more detail, each lanthanum ion was coordinated by one carboxylic function of a second $\{[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}\}$ subunit, with zigzag chains formed (Figure IV-2). The second carboxylic acid function remained free in all cases.

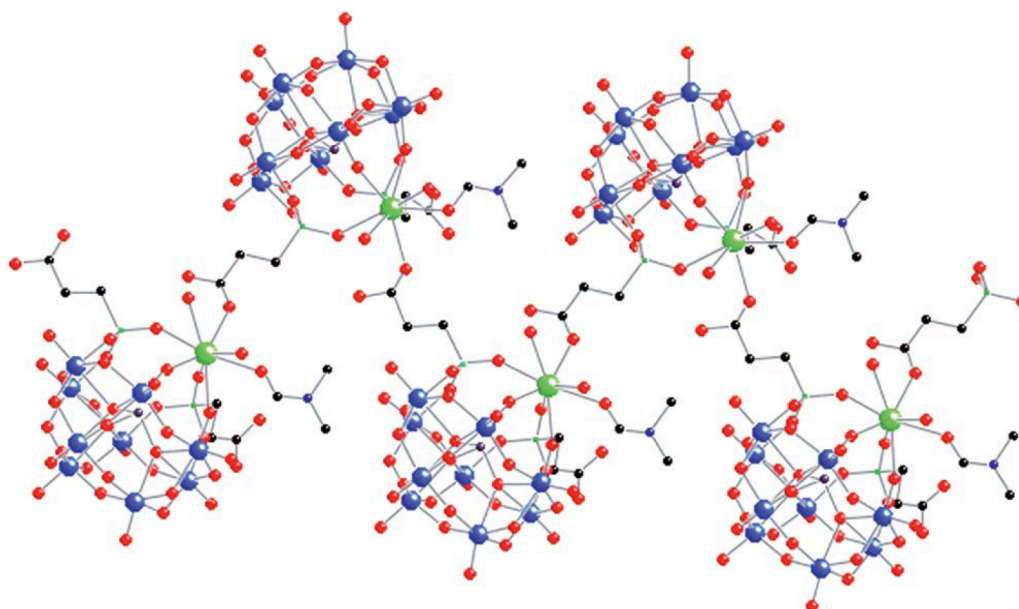


Figure IV-2: Structure of the polymeric compound $\{[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}\}_x$.

However, this organization is only observed for the solid state as in solution the polymer cannot be conserved.

This hypothesis was also confirmed by NMR spectroscopy (^{31}P and ^{13}C) proving the equivalence of all carboxylic chains in solution. Furthermore, The comparison of the spectroscopic data of the two complexes (without and with La^{3+}) is instructive since the chemical shifts of the carbon from the COOH group are very close. This indicates that there is no interaction between the carboxylate and the lanthanum in $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}$. In the following table, the values for the corresponding NMR peaks are presented.

	$^{13}\text{C}\{^1\text{H}\}$	$^{31}\text{P}\{^1\text{H}\}$
	δ (ppm)	
LaCPOM-COOH	175.2 (d, 2 C, -COOH)	19.07
POM-COOH	174.3 (d, 2 C, -COOH)	29.0

Table IV-1: Chemical shift of $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}$.

It is worth noting that the chemical shift associated to the $\{\text{P}=\text{O}\}$ groups in both complexes are extremely different, since the complexation of the La^{3+} involves the $\{\text{P}=\text{O}\}$ groups in $[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]^{2-}$. Thus, the results presented are of great interest for the characterization of the supported La^{3+} complexes, as the molecular complexes mentioned above will be used as models.

Subsequently, La^{3+} ions will be incorporated into POMs-supported materials. A first sample was prepared by wet impregnation of POM-COOH/SBA-NH₂ with a $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ solution. The amount of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ added was calculated in order to have a final ratio $\text{La}/\text{POMs-COOH} = 1$ in the material ($\text{LaCPOM-COOH/SBA-NH}_2$). The ^{31}P CP-MAS NMR spectrum of the $\text{LaCPOM-COOH/SBA-NH}_2$ sample was recorded and compared to that of the initial POM-COOH/SBA-NH₂ (Figure IV-3). In accordance with the data obtained in the homogeneous solution, the chemical shift of the $\text{LaCPOM-COOH/SBA-NH}_2$ sample decreased from 28 ppm (for POM-COOH/SBA-NH₂) to 22 ppm for the La^{3+} incorporated sample. This significant shift is a first clue for a selective La^{3+} uptake by the POMs in the final materials. However, in order to obtain a final proof of this assessment, a XAS study had

to be performed at the La L_{III} edge of the different compounds and materials described in the following paragraphs.

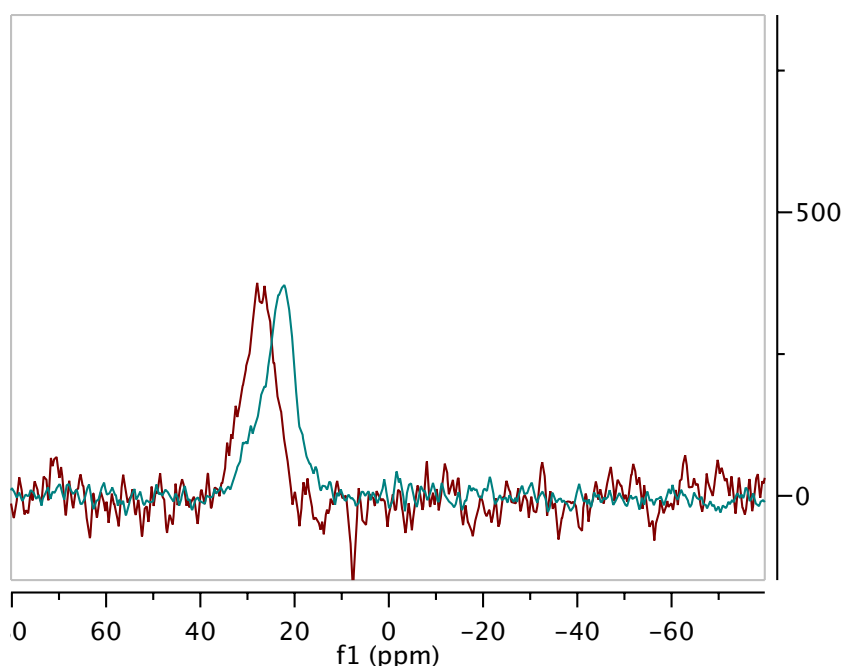


Figure IV-3: ^{31}P CP-MAS NMR spectra of $^-\text{LaCPOM-COOH/SBA-NH}_2$ (in green) and of POM-COOH/SBA-NH_2 (in red).

IV.1 Characterization by Extended X-ray Absorption Fine Spectroscopy

In order to better characterize the synthesized materials and especially localize the La^{3+} ions in the pores of SBA-15, a XAS study at the L_{III} edge of La at low temperature (70 K) was performed at Synchrotron SOLEIL in Saclay. EXAFS spectroscopy, in particular, is a powerful tool for the characterization of non-crystallized materials, being in solution, gas, or in the solid state. Indeed, it provides local structural information around a specific element (in the present study La^{III} ions), *i.e.* number and nature of neighboring atoms, but it can also provide the distances from these neighboring atoms. In addition, XANES spectra of the materials may be recorded in parallel, providing information on the oxidation state of the targeted elements. However in this study, XANES is not useful since there is no ambiguity on the oxidation state of La.

IV.1.1 EXAFS characterization of model compounds

EXAFS spectra at the L_{III} edge were first recorded at solid state from molecular models previously synthesized in the E-POM group. Two compounds were obtained from the

reaction of POM-COOH or POM-NH₂ with La(NO₃)₃·xH₂O and they were characterized by single-crystal X-ray diffraction. The structures of the anions [PW₉O₃₄{As(O)C₆H₄-*p*-NH₂}₂{La(dmf)₃(H₂O)₂}]²⁻ (LaCPOM-NH₂) and {[AsW₉O₃₃{P(O)CH₂CH₂CO₂H}₂{La(dmf)(H₂O)₂}]²⁻}_x (LaCPOM-COOH) were presented in the Figure IV-1.

For illustration purposes, the normalized absorption spectrum of a solid sample of LaCPOM-COOH is presented in Figure IV-4. The spectrum displayed two distinct absorption edges, corresponding respectively at the L_{III} (5490 eV) and L_{II} (5896 eV) edges. Due to the close proximity of the L_{II} edge, the absorption spectrum was cut at 5883 eV for all spectra. The E⁰ value was fixed at 5489.5 eV and the normalization was effectuated using a spline with k weight = 3 in the range of 5588-5883 eV for all spectra. The forward Fourier Transforms (FFT) were obtained using a Kaiser-Bessel window (dk = 2) in the k space in the range of 3.6-8.8 Å⁻¹.

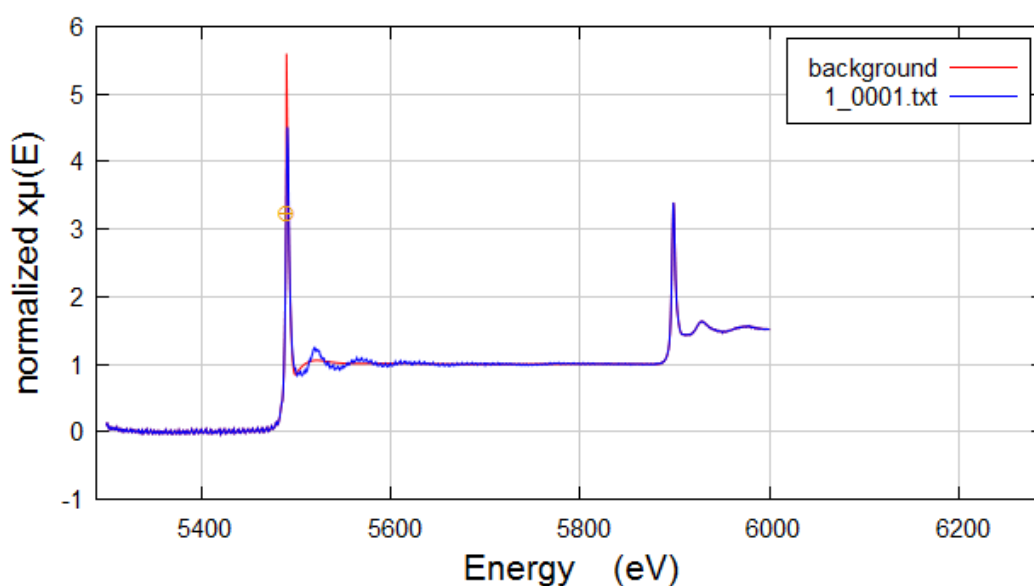


Figure IV-4: normalized absorption spectrum of LaCPOM-COOH.

The EXAFS signal (extracted from the absorption spectrum) and the corresponding FT of both compounds are displayed in Figure IV-5.

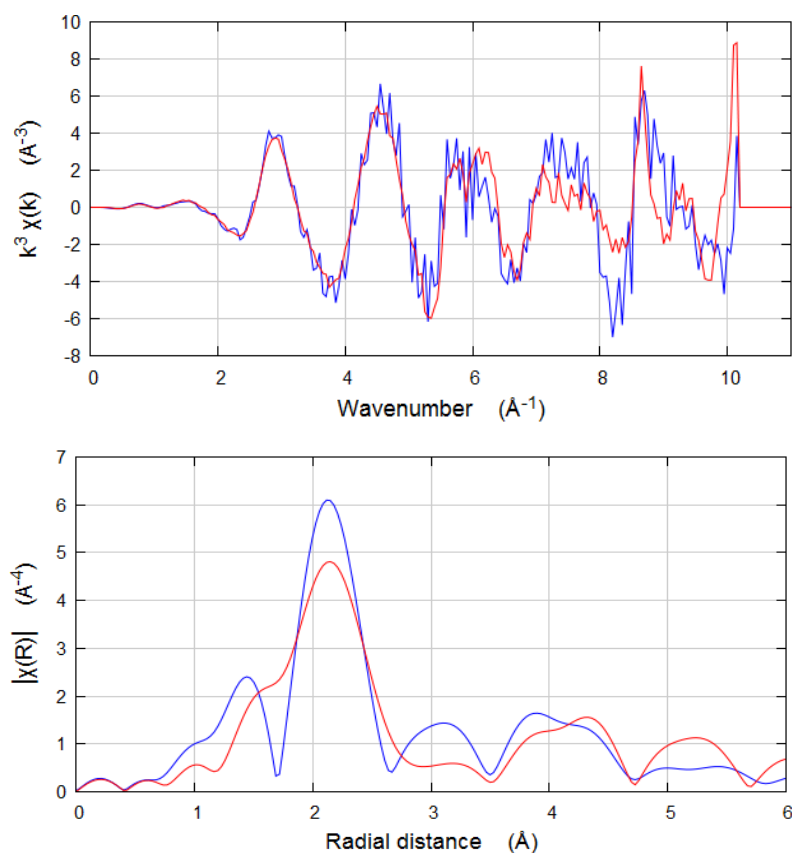


Figure IV-5: EXAFS signals (up) and FT (down) for compounds LaCPOM-COOH (in blue) and LaCPOM-NH₂ (in red).

Even if there are some differences in the structure of both complexes (distances and nature of atoms in the second shell of neighbors), the EXAFS spectra are relatively close. Consequently, the spectra of all samples used in this study will be compared to the spectrum of the complex LaCPOM-COOH as a unique model compound.

The EXAFS signal of LaCPOM-COOH was then modeled by using FEFF calculations and the structural parameters (phases and amplitudes) were extracted from the X-ray data of the compound LaCPOM-COOH.

Figure IV-6 shows the modulus and the real part of the FT for the experimental and calculated spectra of LaCPOM-COOH.

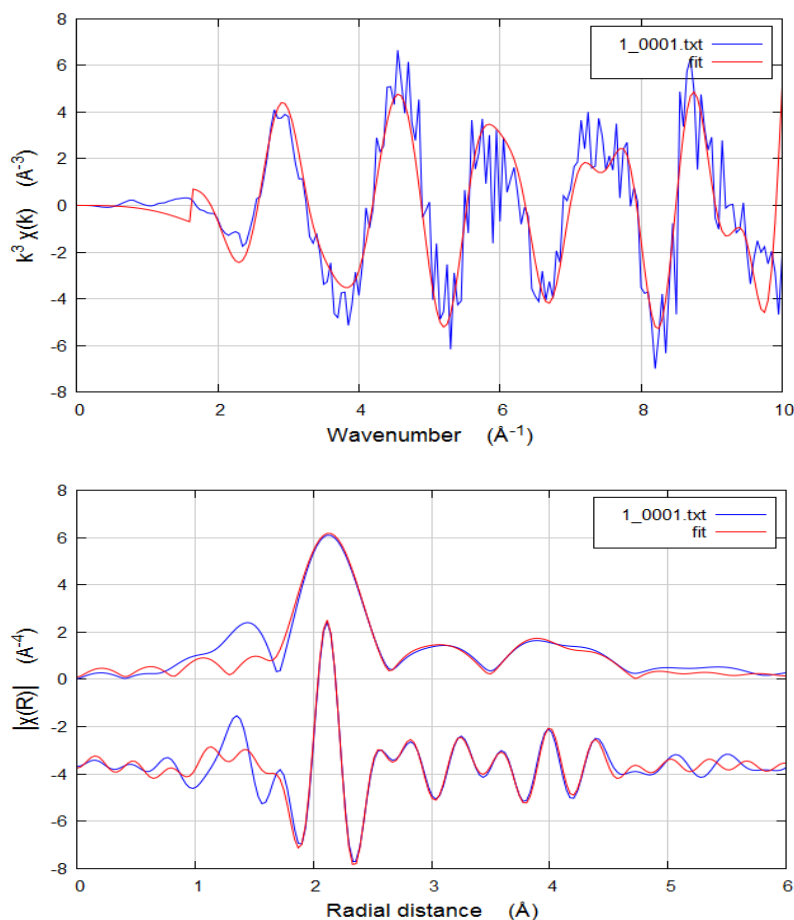


Figure IV-6: EXAFS spectrum (up), modulus and real part of the FT (bottom) for the experimental (in blue) and calculated (in red) spectra of LaCPOM-COOH.

The calculated structural parameters of LaCPOM-COOH are gathered in Table IV-2. These results were obtained by taking into account the 8 different FEFF paths with the higher rank, from 89 calculated paths. These 8 paths then defined 3 individual neighboring shells, the 2nd and 3rd including several multiple scattering paths.

A single value of DE° (adjustment to the E° used in the normalization step) was fitted for all paths, while DR (adjustment of the interatomic distance) and $|\sigma^2|$ (mean square variation in path length) were respectively determined for all paths or shells.

Shell	Path	Nb of neighbors (N.S0 ²)	DE° (eV)	R (Å)	σ ²
1 st shell	La-O	8		2.622 ± 0.033	0.0061
2 nd shell	La-As	1		3.618 ± 0.039	
	La-O-P *	2		3.969 ± 0.4.16	
	La-P	2		4.027 ± 0.376	
	La-C	2		3.970 ± 0.447	0.0058
	La-O-C *	2		3.350 ± 0.130	
3 rd shell	La-W	2	9.907 ± 0.830	4.178 ± 0.096	0.0086
	La-O-W *	4		3.893 ± 0.101	0.0009

Table IV-2: Calculated FEFF structural parameters of LaCPOM-COOH; * paths with multiple scattering.

These parameters are in close agreement with the X-ray structure obtained for this compound. For the purpose of comparison the value for the average La-O distance obtained was 2.554 Å from X-ray data, compared to 2.622 Å in the present study. Even at long distance the FEFF calculations appear satisfying, since the experimental La-W distance is of 4.215 Å (X-ray data) while the FEFF calculation of the spectrum gave 4.178 Å. However, due to a relatively low signal over noise ratio at high R values, one might wonder about the relevance of the use of the third shell for the characterization of the following samples.

IV.1.2 EXAFS characterization of the LaCPOM-COOH/SBA-NH₂ materials

Firstly, three different samples were prepared by wet impregnation of POM-COOH/SBA-NH₂ with different volumes of a La(NO₃)₃·xH₂O solution. The amount of La(NO₃)₃·xH₂O added was calculated in order to have a final ratio La/POMs-COOH x = 0.75, 1 and 2. These three samples were thus labeled LaCPOM-COOH/SBA-NH₂(x:1).

A control sample was also prepared by wet impregnation of SBA-NH₂ supports with a solution of La(NO₃)₃·xH₂O and labeled LaCSBA-NH₂. The amount of La(NO₃)₃·xH₂O added here was the same as in LaCPOM-COOH/SBA-NH₂(1:1). Furthermore, the mass of POM-COOH/SBA-NH₂ and SBA-NH₂ supports used was chosen so that the number of -NH₂ functions was identical in both samples.

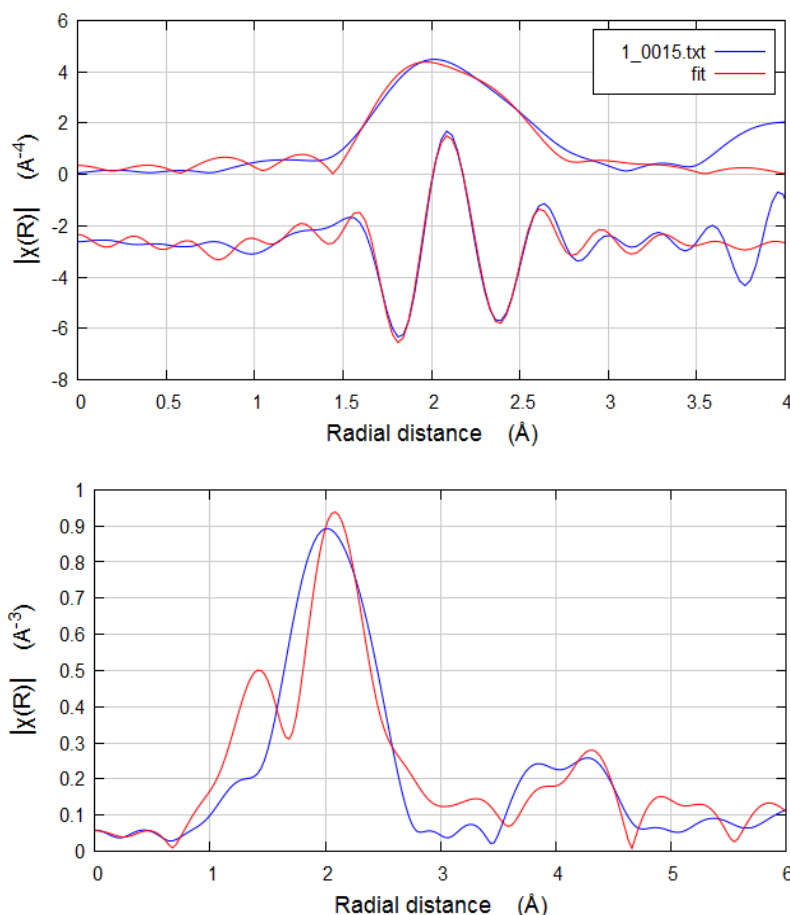


Figure IV-7: (Top) Calculated (red) and experimental (blue) FT of the first shell of LaCSBA-NH₂ EXAFS spectrum (calculation in the range 1.5 - 4 Å). (Bottom) Comparison of the FT of the experimental LaCSBA-NH₂(blue) and LaCPOMs-COOH/SBA-NH₂(1:1) (red) EXAFS spectra.

The figure IV-7 (top) compares the FT of LaCSBA-NH₂ EXAFS spectrum with that of LaCPOM-COOH. As expected, the FT were significantly different for the first and second shells. Indeed, unlike the model compound, the La-O shell in LaCSBA-NH₂ had to be calculated by using two sets of distances (3 oxygen atoms at 2.487 Å and 4 oxygen atoms at 2.668 Å). Furthermore, there is no peak in the FT corresponding to a second shell in the range 2.7 and 3.5 Å, which is consistent with the absence of As and P atoms from the POM-COOH in the environment of the La^{III} ions in LaCSBA-NH₂. However, the presence of peaks in the

range 3.5-4.5 Å is necessarily explained by the presence of noise since there is no heavy atom expected at this distance of the La^{3+} . Consequently, the modeling of the third shell in the other samples is not relevant in the frame of this study since there is an uncertainty on the real nature of the peaks at this distance (noise or W atoms).

In addition, the FT of the experimental $\text{La}\text{CPOM-SBA-NH}_2$ and $\text{LaCPOM-COOH/SBA-NH}_2(1:1)$ EXAFS spectra were compared (Figure IV-7, bottom). This comparison is instructive since the peaks corresponding to the first shells are not superimposable, in term of mean distance and width. The La-O distances distribution in $\text{LaCPOMs-COOH/SBA-NH}_2(1:1)$ is thus narrow and can be modeled with a single set of 8 O atoms located at $2.658 (\pm 0.053)$ Å ($|\sigma^2| = 0.0102$), close to what was calculated for the model compound. The calculated distances obtained for La-As and La-P are respectively $3.538 (\pm 0.167)$ Å and $3.939 (\pm 0.094)$ Å, and are also in accordance with the structural data of the molecular model LaCPOM-COOH . This data was modeled by taking into account the same 8 FEFF paths used for LaCPOM-COOH .

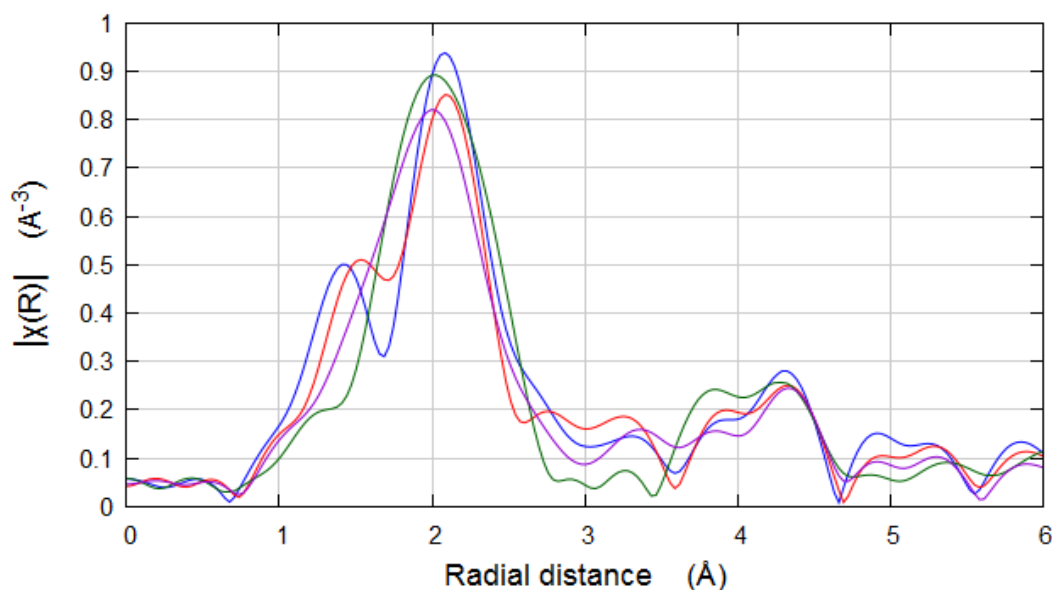


Figure IV-8: Comparison of the FT of the different $\text{LaCPOMs-COOH/SBA-NH}_2(x:1)$ samples with $x = 0.75$ (red), 1 (blue), 2 (violet) EXAFS spectra, and of SBA-NH_2 (green).

Finally, the La-O distributions for the different $\text{LaCPOMs-COOH/SBA-NH}_2 (x:1)$ samples were also compared in Figure IV-8. These La-O distances were found dependent on the x ratio. Indeed for $x = 0.75$ and 1, the top of the peak attributed to the La-O shells was both at the R position corresponding to the distance observed in LaCPOM-COOH . On the

contrary, the peak observed for $x = 2$ is significantly displaced towards the lower value of R and was found close to what was observed with $\text{La}\text{CSBA-NH}_2$.

In conclusion, it seems certain that for $x < 1$, the La^{3+} ions introduced in the materials are for the most part coordinated by the POMs that are linked to the mesoporous supports. Indeed, even if the W atoms originate from POM-COOH are hardly observable in the vicinity of La^{3+} ions (due to a high signal-over-noise ratio in the experimental conditions used), the second shell of neighbors can be fairly modeled by taking into account the presence of As and P atoms from POM-COOH. Furthermore, the La-O distances and distribution are in accordance with those observed in the molecular model compound $\text{La}\text{CPOM-COOH}$. Finally, for $x > 1$, the extra La^{3+} ions introduced in the materials have a local environment identical to La^{3+} ions found in $\text{La}\text{CSBA-NH}_2$, as expected. It is noteworthy that this environment can be distinguished from that of POMs-coordinated La^{3+} ions by using EXAFS.

V Conclusion

During this chapter, the synthesis and characterization techniques of three POMs-containing mesoporous silica supports were presented. The catalytic activity of these materials in the epoxidation of cyclooctene and cyclohexene in the presence of hydrogen peroxide was also demonstrated. These POMs-anchored materials (POM-COOH/SBA-NH₂, POM-COOH/MCF-NH₂ and POM-NH₂/SBA-COOH) were obtained through amide coupling reactions between POMs hybrids and functionalized silica supports bearing each complementary pending groups.

Two different POMs, with either carboxylic acid (TBA₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂]) or aniline functions (TBA₄H[PW₉O₃₄{As(O)(C₆H₄NH₂)}₂]) were used. Both POMs were shown to be efficient catalysts for cyclooctene epoxidation with aqueous H₂O₂ at room temperature in homogeneous conditions (acetonitrile). The bis-carboxylic acid derivative TBA₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂] showed also interesting properties for the epoxidation of cyclohexene at room temperature, either in homogeneous conditions or after covalent immobilization on the SBA-NH₂ support, with an increased selectivity into epoxycyclohexane in the latter case. Further studies by computational methods supported these results in catalysis compared to other POMs.

POMs-anchored materials showed various catalytic performances in the epoxidation of cyclooctene, with conversions in the range 19-97% after 24 h. The POMs organization throughout the materials appeared to be a determining parameter. The structuration of the POMs at the pore (SBA-15) or cell (MCF) level of the materials that could be observed by HR-TEM (after microtome cutting) showed a decrease of the POMs nanostructuration from POM-COOH/SBA-NH₂ to POM-NH₂/SBA-COOH materials with some aggregates in the latter case. This behavior had the same impact on the catalytic activity of the anchored homogenous catalysts, *i.e.* the best activity for the material with the most ordered POMs.

Moreover, recyclability experiments and a filtration test were performed in the case of the POM- COOH /SBA-NH₂ (before completion of the cyclooctene epoxidation reaction). The results clearly indicated that this material could be considered as a truly anchored catalyst thus precluding the hypothesis of significant leaching of the active species.

Finally, bifunctional systems based on inorganic/organic POMs incorporating further heterometallic cations were designed. The coordination chemistry of vacant organophosphonate POMs derivatives with La^{3+} was already studied. POMs-supported systems with La^{3+} incorporated were synthesized and characterized by EXAFS spectroscopy. This technique provided local structural information around a specific element (in the present study La^{III} ions), *i.e.* number and nature of neighboring atoms, but it also provided the distances from these neighboring atoms. This technique, in addition with preliminary results obtained by ^{31}P CP-MAS NMR spectroscopy, gave solid arguments for a selective uptake of the incorporated La^{3+} ions by the POMs grafted onto the SBA- NH_2 supports. This is a clear demonstration that the POMs acted as efficient ligands for La^{3+} even in the solid state due to their strong chelate effect.

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Chapter 2

New strategies for the covalent grafting of hybrids of Polyoxometalates onto functionalized SBA-15

I Synthesis and functionalization of mesoporous SBA-15 with 3-glycidypropyl-trimethoxysilane

The work of this chapter is devoted on the functionalization of the SBA-15 by GLYMO in order to obtain epoxy groups. These functional groups, being highly reactive, should be easily post-functionalized with nucleophilic pending groups of hybrids of POMs.

In the previous chapter, SBA-15 and POMs were simultaneously functionalized with complementary groups for the formation of amide bonds. The idea behind the present method was to simplify the procedure of grafting used in the previous chapter, as no coupling agent is needed in this case. In addition, a better control of the quantity of POMs grafted on the surface could be achieved, which is not evident by the use of isobutyl chloroformate. Another advantage of this method is the variation of the POMs used for the covalent grafting. Up to now, mostly POM-COOH was used for the covalent grafting onto supports. Here, there is the possibility to use various POMs presenting nucleophilic functions (hydroxyl, amines). Finally, in the case of coupling between -COOH and -NH_2 functions, a parasitic acidic-basic reaction can be generated leading to -CO_2^- and -NH_3^+ functions. Thus, the use of a direct linking of acid-free POMs avoids the risk of an ionic interaction that can be provoked.

Different groups have already used 3-glycidypropyl-trimethoxysilane (GLYMO) for the functionalization of silica surfaces. One of the first papers dealing with the modification of the surface of mesoporous silica (MCM-41) by GLYMO was published in 2005 by Kao et al¹. Herein, the modified MCM-41 was introduced into PEO-based polymer electrolytes and then the conductivity of these composite electrolytes was studied. They concluded that the GLYMO group on the surface of MCM-41 played an active role in affecting the conductivity of the composites since its hydrophilic property provides better specific surface interactions with the electrolyte components. The hydroxyl end group of the PEO chain could interact with GLYMO, thus providing tethering of the PEO chains to the inorganic network. Other studies were carried out for the enhancement of conductivity in polymer electrolytes using epoxy-functionalized mesoporous silica surfaces². Similar as before, the study revealed that surface tailoring of silica with epoxy group increased the electrochemical performances of the resulting polymer electrolytes

Another use of epoxy-functionalized mesoporous materials is for drug delivery. Hence, mesoporous silica nanoparticles were functionalized with GLYMO in order to get nanocarriers for controlled drug release. The groups of Peng et al. and Hong et al were interested in this kind of application^{3,4}.

Other applications include the synthesis of materials in the coatings industry. In particular, TiO₂ nanocrystals were incorporated into silica sol modified with GLYMO for the preparation of high refractive index hybrid coatings⁵.

Finally, different groups made use of epoxy-functionalized mesoporous silica materials for catalytic applications. The epoxy function group allows the grafting of different types of catalysts (enzymes, Ti) either directly through the epoxy ring or by its post-functionalization. The first example was in 2000, when Smet et al. grafted a titanium (IV) silsesquioxane complex onto MCM-41 for the epoxidation of alkenes with interesting catalytic results with the advantage of no leaching⁶. They also studied and characterized by IR spectroscopy the different amounts of GLYMO introduced on the surface. In 2007, Jarzebski et al. modified siliceous mesostructured cellular foams (MCF) with four organosilanes, including GLYMO, for the covalent immobilization of invertase and glycoamylase enzymes⁷. The final activity of MCF-based preparations depended, however, not only on a type and density of functional groups used in the enzyme bonding but also on the organosilane compound used in the surface modification. The protein binding via oxirane ring proved not to be effective for the grafting of invertase unlike in the case of glycoamylase where it was highly successful. Recently, SBA-15 was modified with GLYMO and then, 2-aminothiazole or aminopropyl-triazole ligands were bound⁸. Afterwards, silver nanoparticles were deposited on these ligand-functionalized SBA-15 materials. The synthesized materials were used for the reduction of methylene blue.

I.1 Functionalization of SBA-15 with 3-glycidypropyl-trimethoxysilane (GLYMO)

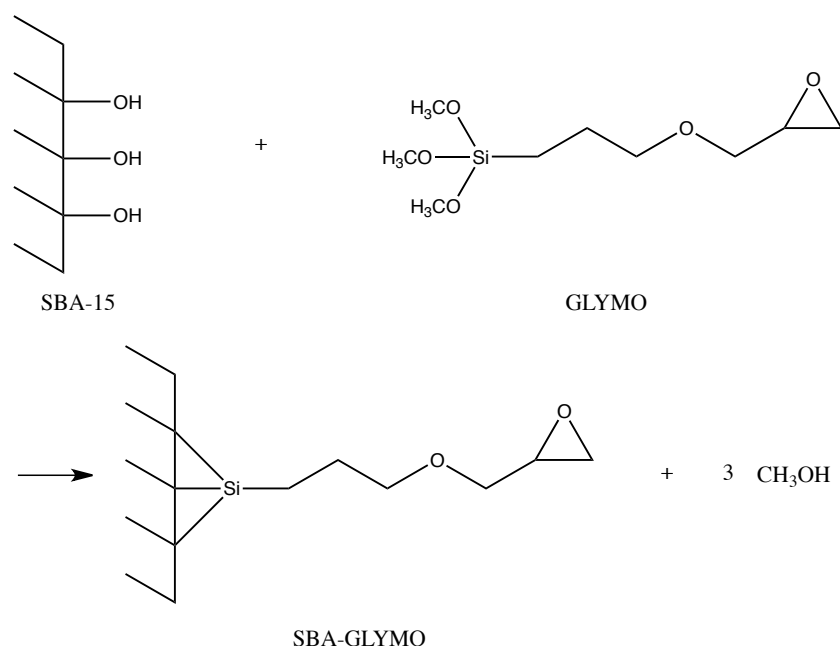


Figure I-1: Reaction scheme between GLYMO and silanol groups of SBA-15 surface.

Among the different methods of functionalization of SBA-15 exposed in the previous chapter, this method belongs to the category of post-grafting. Herein, the desired functions are the epoxy groups, brought by 3-glycidypropyl-trimethoxysilane. The reaction was carried out in a nitrogen-controlled atmosphere with toluene as solvent. Like previously, prior to the functionalization step, the SBA-15 silica was dried by heating up to 350°C. The targeted loading of epoxy rings was either 2 or 4 mmol/g to maximize the incorporation of 3-glycidypropyl-trimethoxysilyl groups. Their dispersion inside the pores of silica was favored through the ultrasonication of the suspension of SBA-15 and GLYMO for some minutes at room temperature before refluxing. Once the reaction was completed, the synthesized material was purified by washing it with same quantities of toluene, ethanol and acetone.

I.2 Characterization techniques

I.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on the epoxy-functionalized SBA-15 for a precise calculation of the quantity of functions grafted on the surface, as described in the previous chapter.

The thermogram of SBA-GLYMO was executed under air from room temperature up to 900°C. As seen from the graph I-2, four weight losses can be observed for the material prepared with a nominal loading of 2 mmol.g⁻¹. The first one (4%), under 100°C, corresponds to the loss of water adsorbed on the silica surface. The third and the fourth weight losses (10%) in the range of 100-900°C, can be attributed to the thermal decomposition of epoxy functions. Thus, from this analysis, it can be demonstrated that functionalized SBA-15 with epoxy rings has a loading of 0.84 mmol of GLYMO per g (ca. 42% incorporation yield).

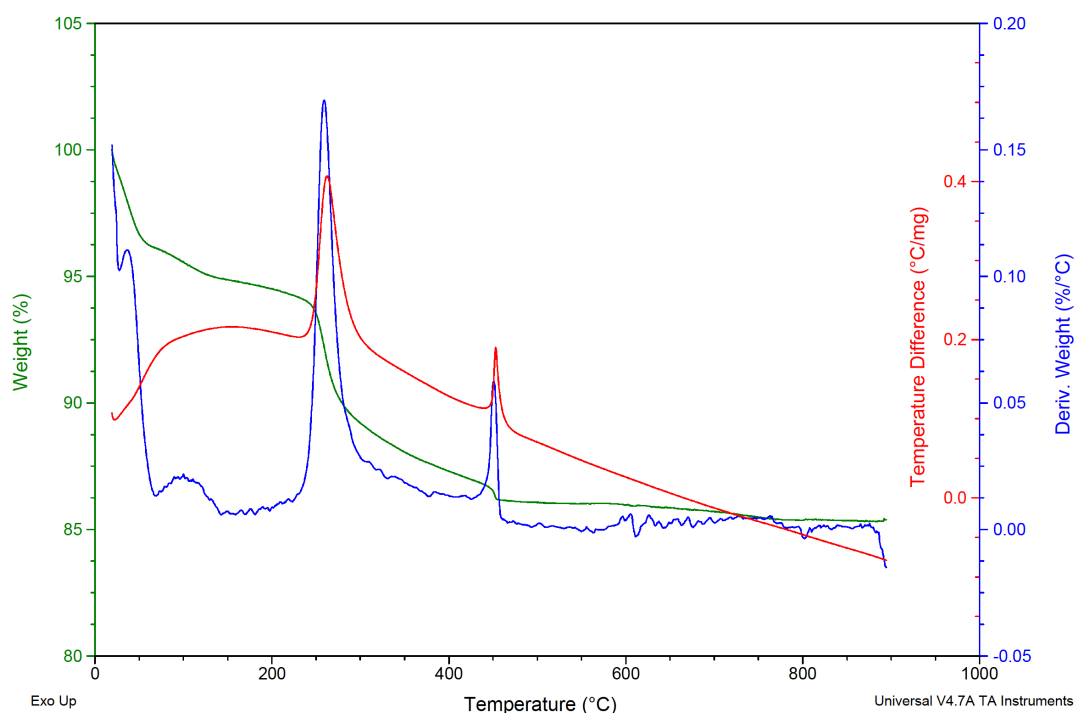


Figure I-2: Thermogram of SBA-15 functionalized with GLYMO from RT up to 900°C, under air (quantity of GLYMO introduced 2 mmol/g).

In a second attempt, the quantity of GLYMO introduced was increased twofold. As in the former figure I-2, here three main weight losses can be noticed. The loss of water adsorbed on the silica surface corresponds to 2.5%. The decomposition of epoxy functions counts for 13.5% and it happens in the range of 100-900°C. As a result, from this analysis, it can be demonstrated that the functionalized SBA-15 has a loading of 1.2 mmol of GLYMO per g (ca. 30% incorporation yield). From this thermogram, it is clear that even if the initial quantity of reagent is increased, the yield does not act the same, indicating signs of saturation.

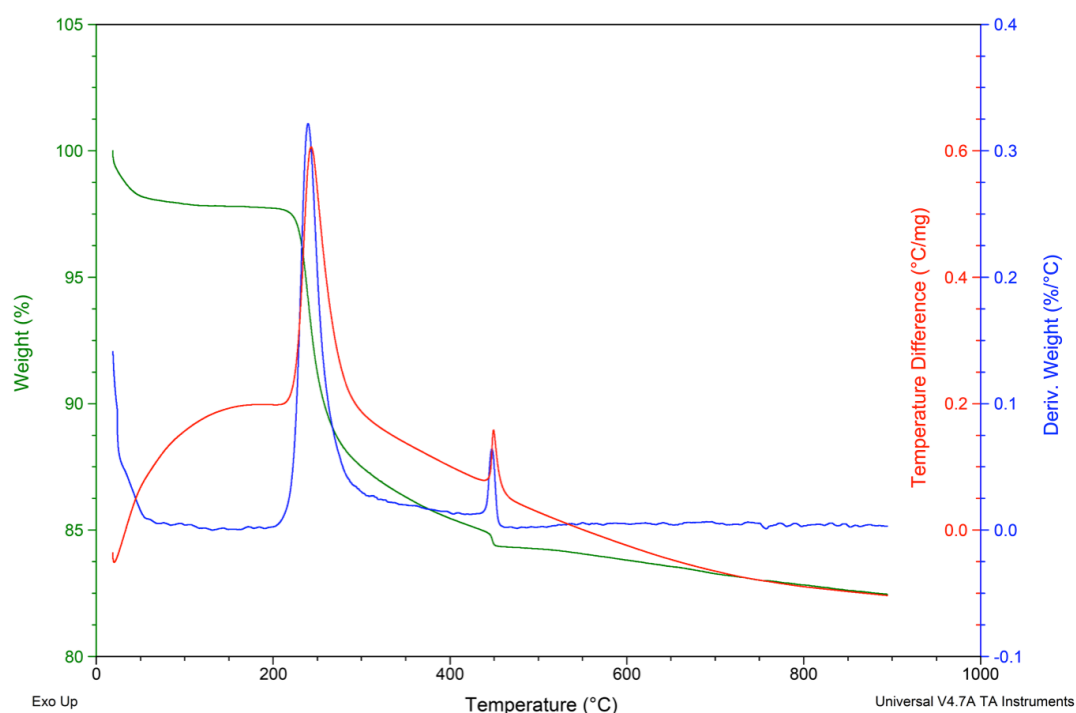


Figure I-3: Thermogram of SBA-15 functionalized with GLYMO from RT up to 900°C, under air (quantity of GLYMO introduced 4 mmol/g).

I.2.2 Infra-Red spectroscopy

Figure I-4 shows the FTIR (ATR) studies for the dry powder sample of epoxy-modified SBA-15. However, the GLYMO functionalization on silica surface could not be confirmed with this technique, as the characteristic bands were not present in the spectrum. According to literature, strong bands at 2927 cm^{-1} and 2856 cm^{-1} corresponding respectively to asymmetric and symmetric stretching of $-\text{CH}_2$ group appear for the materials functionalized with GLYMO². In the present spectrum, the ν_{SiO} vibration (1067 cm^{-1}) and the δ_{OSiO} (around 490 cm^{-1}) are dominating and thus overlap any other bands in the same area, such as the ν_{OC} of the epoxy ring.

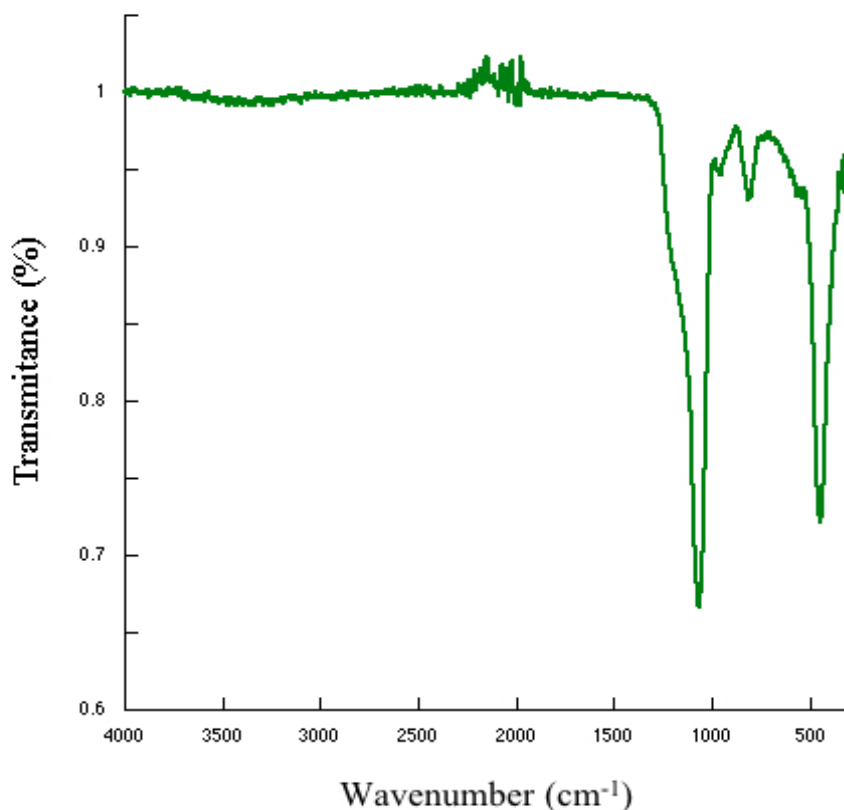


Figure I-4: FTIR spectrum of SBA-15 functionalized with GLYMO.

I.2.3 Determination of the surface by N₂ sorption measurements

As demonstrated by the nitrogen adsorption-desorption studies in Figure I-5, the volume adsorbed for both isotherms shows a sharp increase suggesting the capillary condensation of nitrogen within the uniform mesoporous structure. Hence, pure and modified SBA-15 synthesized materials show type IV isotherms according to the IUPAC classification with H1 hysteresis loop that is representative of mesopores with size interval compatible with SBA-15. From the Figure I-5 a decrease in the volume of mesopores and micropores can be seen.

The physicochemical properties determined from the isotherms of pure and epoxy-modified SBA-15 are presented in Table I-1. A decrease in the surface area and the BJH average pore diameter are observed after the functionalization, indicating the presence of pendent functional groups on the mesoporous channel surface partially blocking the adsorption of nitrogen molecules. The condensation point shifts slightly toward lower relative pressures after modification, which is also an indication of the reduction in pore size derived from the presence of the organic modification.

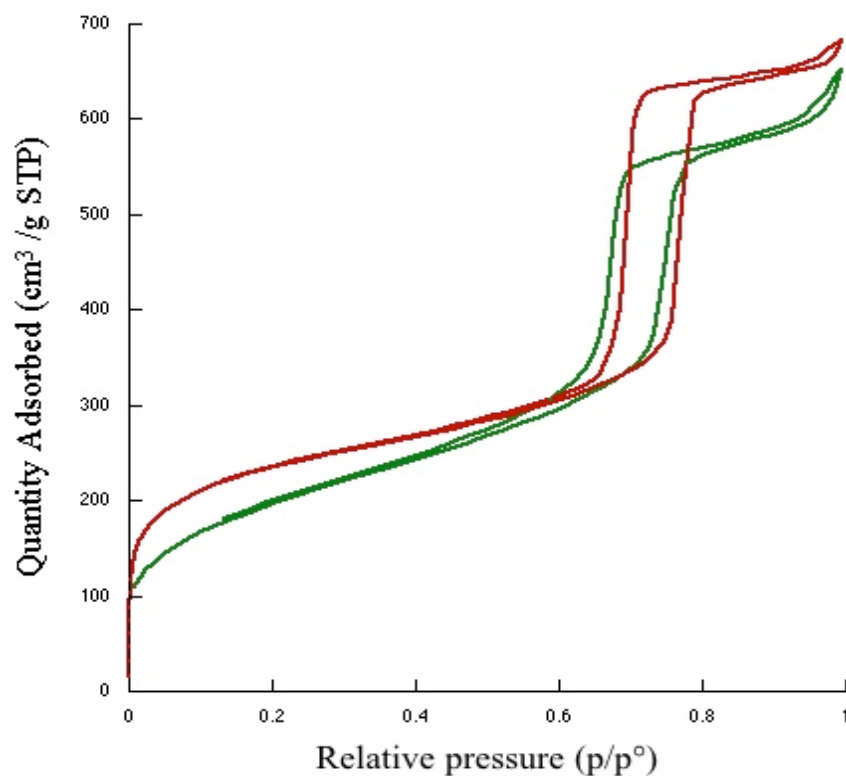


Figure I-5: Nitrogen adsorption-desorption isotherms of SBA-15 (red line) and SBA-15 functionalized with GLYMO (green line).

The pore sizes were calculated from the isotherms desorption branches using the Barret-Joyner-Hallenda (BJH) formula. The pore volume values were given for a single point adsorption at $p/p^0 = 0.974$.

	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA-15	804	1.02	6.7
SBA-GLYMO	705	0.94	5.9

Table I-1: Textural data of pure and SBA-15 functionalized with GLYMO.

II Covalent grafting of POMs onto epoxy-functionalized SBA-15

II.1 Strategy for the covalent grafting

During Chapter 1, trivacant Keggin-type polyanions bearing two alkylphosphonate groups with carboxylic terminal functions were used. In this work, two more trivacant Keggin-type polyanions were synthesized and used. The first one bears two alkylphosphonate groups with alcohol terminal functions and the second one two aniline terminal functions. The bis-organo derivatives selected are $B,\alpha-[As^{III}W_9O_{33}\{P(O)(CH_2CH_2OH)\}_2]^{5-}$ and $A,\alpha-[PW_9O_{34}\{As(O)C_6H_4-NH_2\}_2]^{5-}$ respectively.

Required functionalized lacunar POMs hybrids were easily obtained in a one-pot synthesis. The synthesis was carried out in refluxing acetonitrile or DMF and in the presence of aqueous concentrated HCl. The resulting organic-soluble hybrid complexes are stable towards heating, hydrolysis and acidic or moderately basic conditions due to the robustness of {P-O-W} bonds.

As already explained and discussed, hybrids of POMs and SBA-15 were modified independently by the introduction of alcohol or aniline groups and epoxy functions respectively, whose reaction leads to connection through strong covalent bonds. This was achieved by the opening of the oxirane ring of the linker molecule using nucleophile functions of hybrid POMs.

II.2 POMs functionalization and characterization techniques

The bis-aniline derivative $A,\alpha-[PW_9O_{34}\{As(O)C_6H_4-NH_2\}_2]^{5-}$ was synthesized in acidic medium with tetrabutylammonium cations serving as transfer agents. The yield of the reaction affording $(^nBu_4N)_3NaH[PW_9O_{34}\{As(O)C_6H_4-NH_2\}_2]$ (or POM-NH₂) was 60%.

For the characterization of POM-NH₂, various spectroscopic methods were used. ¹H NMR was performed on the functionalized POM and the characteristics peaks were identified. In the range of 6 ppm, the protons derived from the -NH₂ functions were observed

(singlet at 6.02 ppm in D₆-dmsO) and the aromatic protons were found as two doublets at 6.72 and 7.39 ppm (see figure III-4).

The IR spectrum of POM-NH₂ exhibits several characteristic bands of terminal W=O_t and bridging W-O_b-W bonds, as known for the tungstates, in the range of [700-1000 cm⁻¹]. The evidence of the existence of amine functions was verified by the presence of ν_{NH} bands at 3231 and 3361 cm⁻¹.

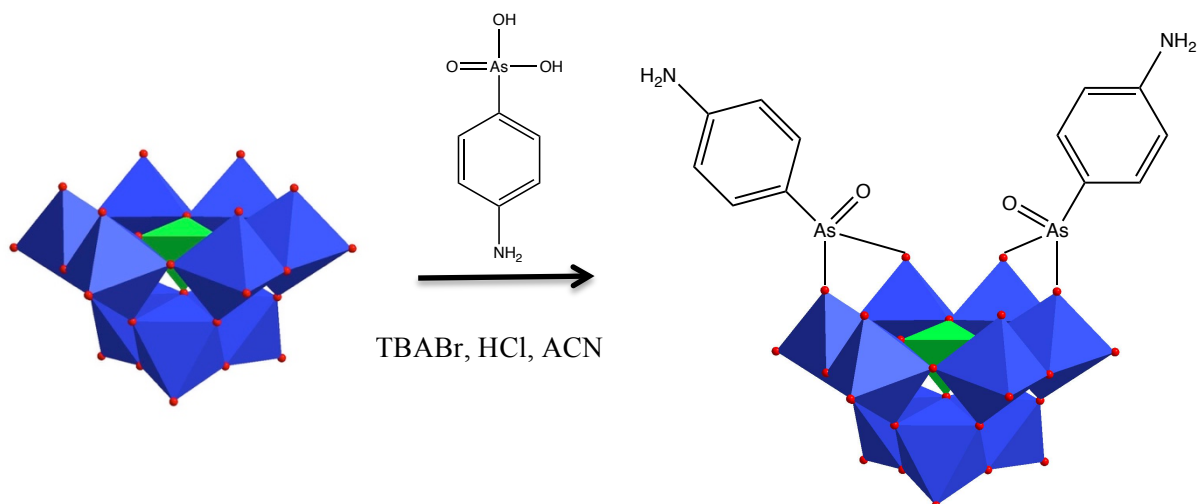


Figure II-1: Synthetic route for (nBu₄N)₃NaH[PW₉O₃₄{As(O)C₆H₄-NH₂}₂]. Oxygen atoms are represented in red, phosphorus in green and {WO₆} octahedra in blue.

Following the same philosophy, the organo-phosphonate derivative with alcohol terminal groups B,α-[As^{III}W₉O₃₃{P(O)(CH₂CH₂OH)}₂]⁵⁻ was synthesized in acidic medium with tetrabutylammonium cations serving as transfer agents (Figure II-1). The synthesis of (nBu₄N)₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂OH)}₂] (or POM-OH) was achieved with a 70% yield.

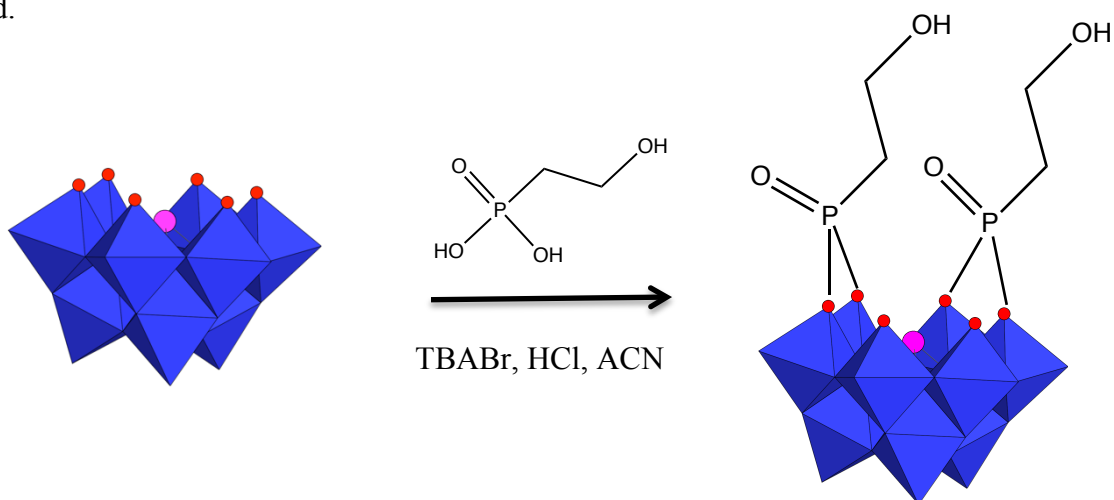


Figure II-2: Synthetic route for (nBu₄N)₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂OH)}₂]⁵⁻. Oxygen atoms are represented in red, arsenic in pink and {WO₆} octahedra in blue.

The synthesized POM-OH was characterized mainly by NMR. The ^{31}P NMR spectrum displayed a single peak at +26.6 ppm in CD_3CN corresponding to the two equivalent phosphorous atoms coming from the {RPO} groups.

II.3 Covalent grafting of polyoxometalates onto SBA-15 and characterization of the resulting materials

The formation of covalent bonds involving POMs with aniline or alcohol terminal groups and SBA-15 functionalized with 3-glycidyloxypropyl-trimethoxysilyl groups does not need a prior activation step.

In the following figures, the mechanisms of reactions between POMs anions and the epoxy-functionalized SBA-15 are presented.

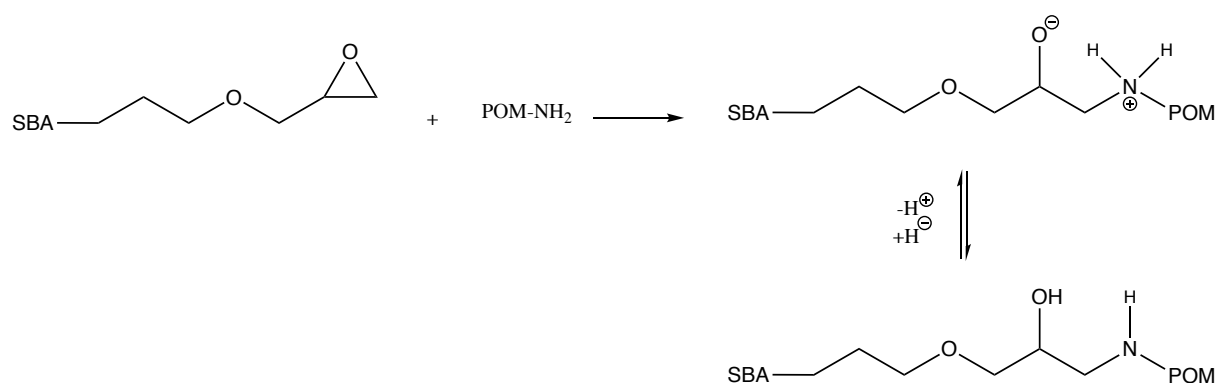


Figure II-3: Synthetic route for the covalent attachment between POM-NH₂ and epoxy-functionalized SBA-15.

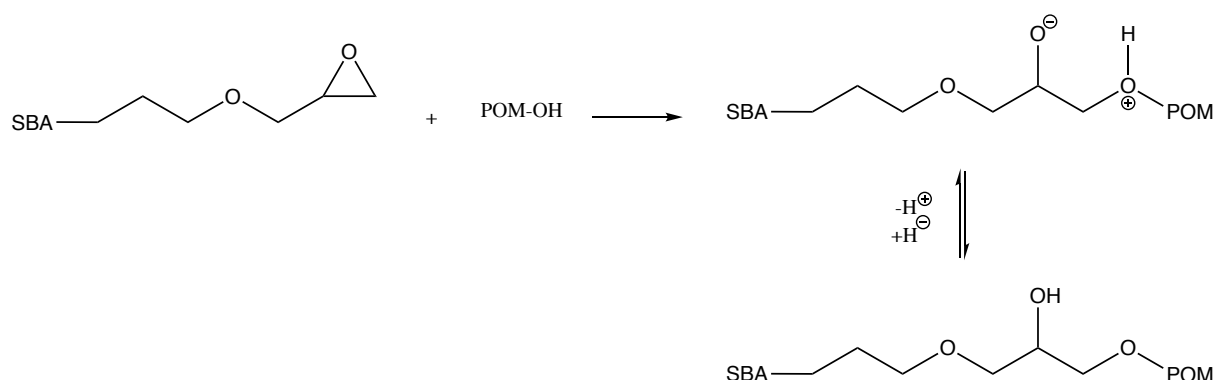


Figure II-4: Synthetic route for the covalent attachment between POM-OH and epoxy-functionalized SBA-15.

The synthesis of the POMs-supported systems was carried out in room temperature overnight, regardless the POM used for the grafting. Afterwards, the product was filtered and washed by Soxhlet with acetonitrile as the solvent.

Different ratios were used for the grafting in order to optimize the synthetic procedure. In the beginning, the ratio used for the grafting was the same as for the system of POM-COOH onto SBA-NH₂, i.e. POM-NH₂ or POM-OH /GLYMO equal to 1/6. Following this procedure, there is one POM for six epoxy functions. For the second try, the quantity of POMs was increased twofold resulting to a ratio POM-NH₂ or POM-OH /GLYMO equal to 1/3.

II.3.1 High-Resolution Transmission Electron Microscopy (HR-TEM)

The hybrid material SBA-GLYMO/POM-NH₂ was characterized also by HR-TEM, with microtome cutting. In the previous chapter, the evidence of POMs, once they were grafted on the surface, was performed by HR-TEM and it proved to be a powerful tool.

The first information that can be extracted by the observation of the materials resulting from the grafting of POMs is the absence of change in the intrinsic structure of the mesoporous support (Figure II-5).

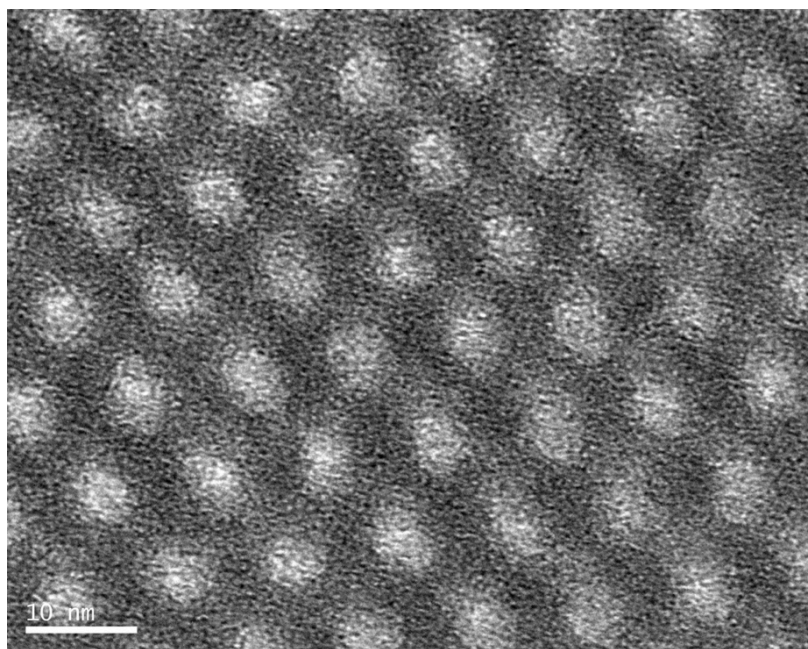


Figure II-5: HR-TEM micrograph of epoxy-functionalized SBA-15/ POMs-NH₂ after microtome cutting.

Subsequently, POMs, if present, should be detected on the surface of SBA-15, as it was mentioned for the case of POM-COOH/SBA-NH₂. However, as indicated in figure II-5, POMs are not visible in the periphery of the channels.

II.3.2 Fluorescence X-Ray Spectroscopy (XRF)

The poor grafting of POMs was equally validated by X-ray fluorescence spectroscopy (XRF, see Table II-1).

	% W by XRF	POMs loading (%)
POM-NH ₂ /SBA-GLYMO	3.04	6
POM-OH/SBA-GLYMO	1.94	3.87
POM-NH ₂ /SBA-COOH	5.83	11.63

Table II-1: Percentage of W determined by XRF and corresponding calculated values of POM loadings starting from SBA-GLYMO or SBA-COOH.

The POM-NH₂/SBA-COOH system is also presented for a better comparison. As seen from the values exposed in the table, the POMs are grafted in lower amounts when using SBA-GLYMO. As explained and presented in the previous chapter, the POM-NH₂/SBA-COOH system was the one with the poorest grafting of POMs among others and, as a result, it had a reduced catalytic activity. Herein, it is clear that the POMs loading for epoxy-functionalized SBA-15 is even inferior to the latter, regardless to the POM used.

II.3.3 Determination of textural parameters

As presented in Figure II-6, epoxy-functionalized SBA-15 and POMs-supported on the functionalized SBA-15 were characterized by non-reversible type IV N₂ adsorption-desorption isotherms. Compared to the corresponding isotherms for the bare (Figure I-5) and epoxy-functionalized SBA-15 supports the POMs-loaded sample showed decreased total N₂ uptake.

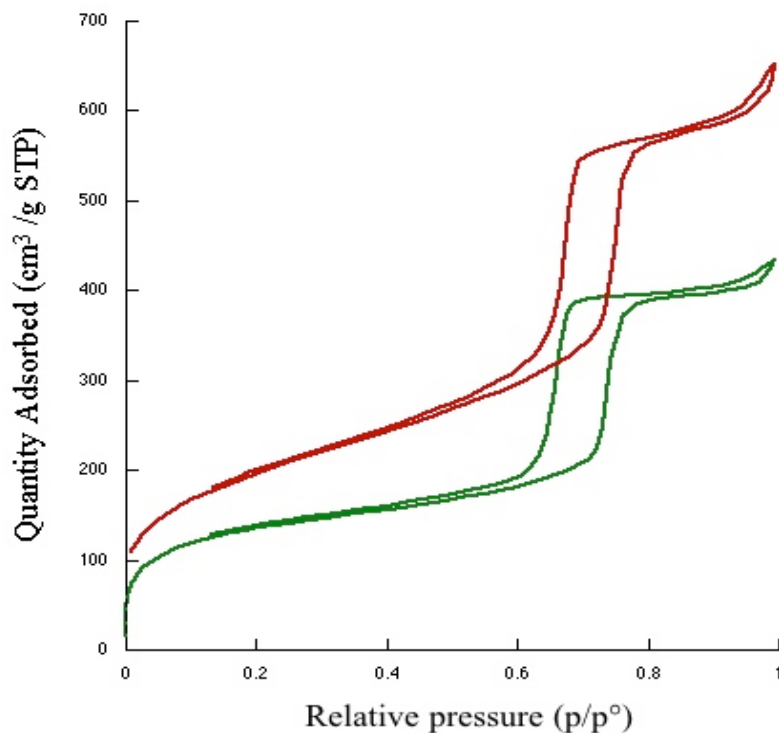


Figure II-6: Nitrogen adsorption-desorption isotherms of SBA-15 functionalized with GLYMO (red line) and epoxy-functionalized SBA-15 decorated with POMs (green line).

Support	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA-15	804	1.02	6.7
SBA-GLYMO	705	0.94	5.9
SBA-GLYMO/POM-NH ₂	411	0.65	5.4

Table II-2: Textural data of SBA-15 support before and after POMs grafting.

The values of most of the textural parameters decrease continuously over the steps, a fact compatible with the inclusion of epoxy groups, then the POMs within the porosity. After the functionalization step of the support by epoxy groups, variations in textural parameters can reach nearly 10-20%, hence showing the limited grafting of GLYMO into the pores. As a result, the POMs grafting does not have a high impact on textural values of SBA-15, confirming the results obtained by HR-TEM and XRF measurements.

III Other strategies of covalent grafting of POMs onto amino-functionalized SBA-15

III.1 Strategy for the covalent grafting

As discussed in the previous chapter, the immobilization of POMs with functionalized SBA-15 was carried out through covalent linking. Both moieties were simultaneously functionalized with complementary organic functions. Thus, their reaction resulted in connection through strong amide bonds.

In the first part of this work, as described before, the grafting procedure onto the SBA-NH₂ required the use of a coupling agent (isobutylchloroformiate). Other coupling agents have been also used for establishing amide bonds at the surface of an SBA-NH₂. The most commonly used agent for coupling with amine groups, forming stable amide bonds, is N-Hydroxysuccinimide (NHS)⁹. However, the NHS ester's immobilization efficiency depends on several parameters, for example pH value, concentration and ionic strength.

Another strategy that can be explored is the anchoring of functionalized POMs through the use of a cross-linker. Thus, the cross-linker reacts with the anchoring layer of SBA-15 bearing reactive moieties such as amine functions and the useful function of the hybrid of POM. In this case, cross-linkers can be found in the final materials since they are responsible for the covalent bond between both partners. The most commonly used cross-linkers carries two similar groups (such as dialdehydes),^{10,11} which are able to form a specific covalent bond with the surface at one end and another covalent bond with the desired molecule at the other end. Another cross-linker used to immobilize molecules on amino-functionalized surfaces is the 1,4-phenylene diisothiocyanate (PDITC). This strategy is mostly used in biological applications and the grafting of proteins on surfaces for the generation of biochips.

One of the first examples is based on the activation of glass slides by PDITC. Smith et al. activated the surfaces for the grafting of oligonucleotides and their subsequently use for the analysis of genetic polymorphisms¹². Several years later, Niemeyer et al. prepared functionalized amino-silica surfaces for the same goal, the fabrication of DNA microarrays. Different cross linkers were used for the immobilization of DNA using pre-fabricated

polyamidoamine starburst dendrimers. PDITC was one of the three options presented in this work¹³.

Boujday et al. studied extensively the use of PDITC as a cross linker between enzymes and silanized surfaces. Firstly, different linkers were tested, differing by their reactive functional group but also by the geometry of the bifunctional groups positioned meta- or para- to the aromatic cycle¹⁴. The enzyme adsorption was monitored *in situ*. Later, they studied the protein binding to self-assembled monolayers and the influence of the addition of a rigid cross-linker as the PDITC in this system¹⁵.

Finally, Jiang et al functionalized magnetic nanoparticles with APTES and PDITC for the further investigation of specific interaction between biomolecules and chloroperoxidases¹⁶. This was the first time that a different support than silica, glass or gold surfaces was functionalized with PDITC.

As explored, PDITC is a cross linker widely used in the domain of biology. Thus, its use for the grafting of POMs onto amino-functionalized SBA-15 had to be explored. Up to know, no known examples exist in the literature combining the use of this specific cross linker and hybrid of POMs.

III.2 POMs functionalization and characterization

The strategy used in this part was to post-functionalize the POM-NH₂ with the PDITC prior to the grafting step onto the SBA (as described in Figure III-1). Indeed aniline functions are less nucleophilic than the propylamine grafted on the SBA. Furthermore, the characterization of the post-functionalized POM is easy to perform with the characterization techniques for molecular compounds.

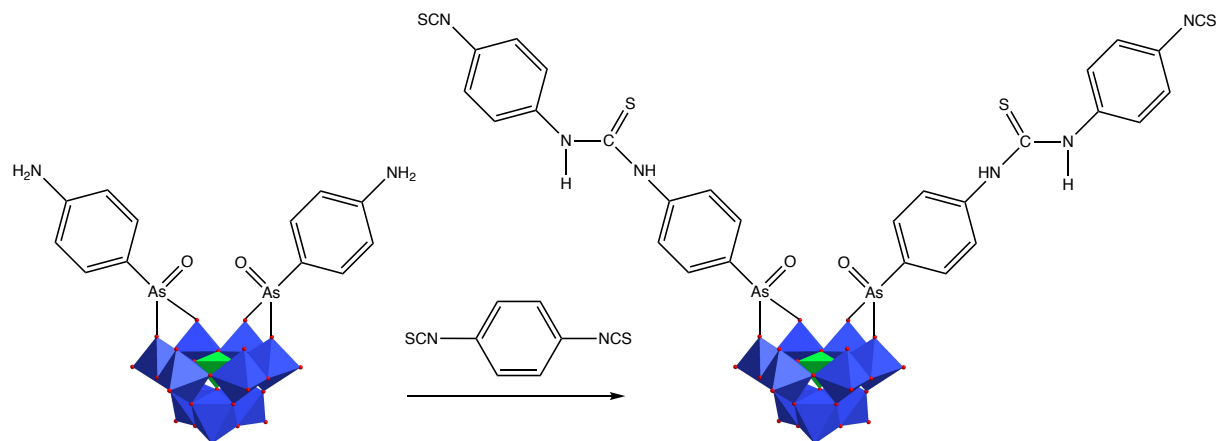


Figure III-1: Synthetic route for functionalization of $(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-NH}_2\}_2]$ by PDITC.

The experimental protocol was chosen in order to avoid the formation of POMs dimers by direct reaction of two equivalents of POMs with the two SCN terminations of the cross linker at once. The reaction was thus carried out in (moderately) dilute solution and with a large excess of PDITC in acetonitrile. It is noteworthy that the formation of thiourea functions is relatively slow at room temperature when reacting with aniline functions, as expected. The crude product which contained in majority the desired $(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-NH-C(S)-NH-C}_6\text{H}_4\text{NCS}\}_2]$ (for short POM-PDITC) was obtained by slow evaporation (one week) of the solvent. However a large amount of unreacted PDITC was obtained together with the microcrystalline powder as shown by IR spectroscopy (Figure III-2). Careful washings with benzene allowed to obtain samples with less remaining PDITC. However, the reagent was still observed by ^1H NMR even after the washing step.

To summarize, POM-PDITC was characterized by IR (Figure III-2), ^1H (Figures III-3 and III-4) and ^{31}P NMR spectroscopies. Comparison of the IR spectra of POM-NH₂ and POM-PDITC in the range 1100 – 700 cm⁻¹ showed that the polyoxotungstate core was conserved during the post-functionalization reaction.

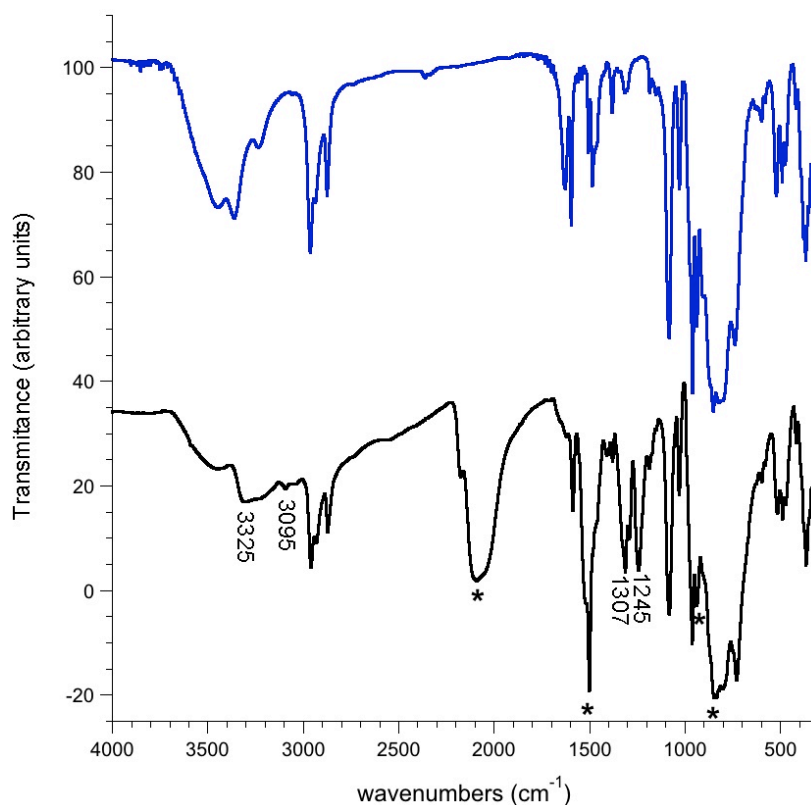


Figure III-2: IR spectra of POM-NH₂ (blue) and POM-PDITC after washing (black) * = peaks attributed to unreacted PDITC.

The spectrum of POM-PDITC clearly displays bands attributed to unreacted PDITC (marked by * on Figure III-2), especially the highly intense $\nu(\text{N}=\text{C}=\text{S})$ band at 2100 cm^{-1} . However, the $\nu_{\text{as}}(\text{NH})$ and $\nu_{\text{s}}(\text{NH})$ corresponding to the aniline function in POM-NH₂ have been replaced by a single and large band with a maximum at 3325 cm^{-1} , indicating the formation of thiourea functions. The presence of two bands in the range $1350\text{--}1200\text{ cm}^{-1}$ (corresponding to the equivalent of “amide I” ($\nu(\text{C}=\text{S})$ herein) and “amide III” bands) and of one narrow band at 1595 cm^{-1} (equivalent of “amide II”) is in accordance with the presence of thiourea functions. These three bands did not appear in the spectrum of PDITC. An enhancement of the $\nu(\text{CH}_{\text{ar}})$ at 3095 cm^{-1} is also observed but it is also due to the presence of PDITC.

The ^1H NMR spectrum of POM-PDITC in $\text{dms}\text{-}d_6$, before washing, is shown in Figure III-3. The anion is characterized by the presence of a singlet at 10.10 ppm (4H , $\text{NH}=\text{C}=\text{S}$) and two multiplets at 7.58 and 7.40 ppm (8H , CH_{ar}), and by the disappearance of the peak at 6.02 ppm , attributed to $-\text{NH}_2$ functions in the spectrum of POM-NH₂. Furthermore, the integration of the $^n\text{Bu}_4\text{N}^+$ signals is in accordance with the presence of three tetrabutylammonium counterions. However, as for the IR spectrum, the presence of unreacted

PDITC is revealed by the presence of a singlet at 7.50 ppm, even after washing with benzene (Figure III-4).

It is worth noting that this spectrum is strongly dependent on the solvent. Indeed, when the spectrum is performed in CD_3CN the profile of the bands is significantly different, since the CH_{ar} atoms are characterized by four separated doublets in the range 7.25 - 8.00 ppm, and by the modification of the chemical shift of the NH-C=S protons at 8.77 ppm.

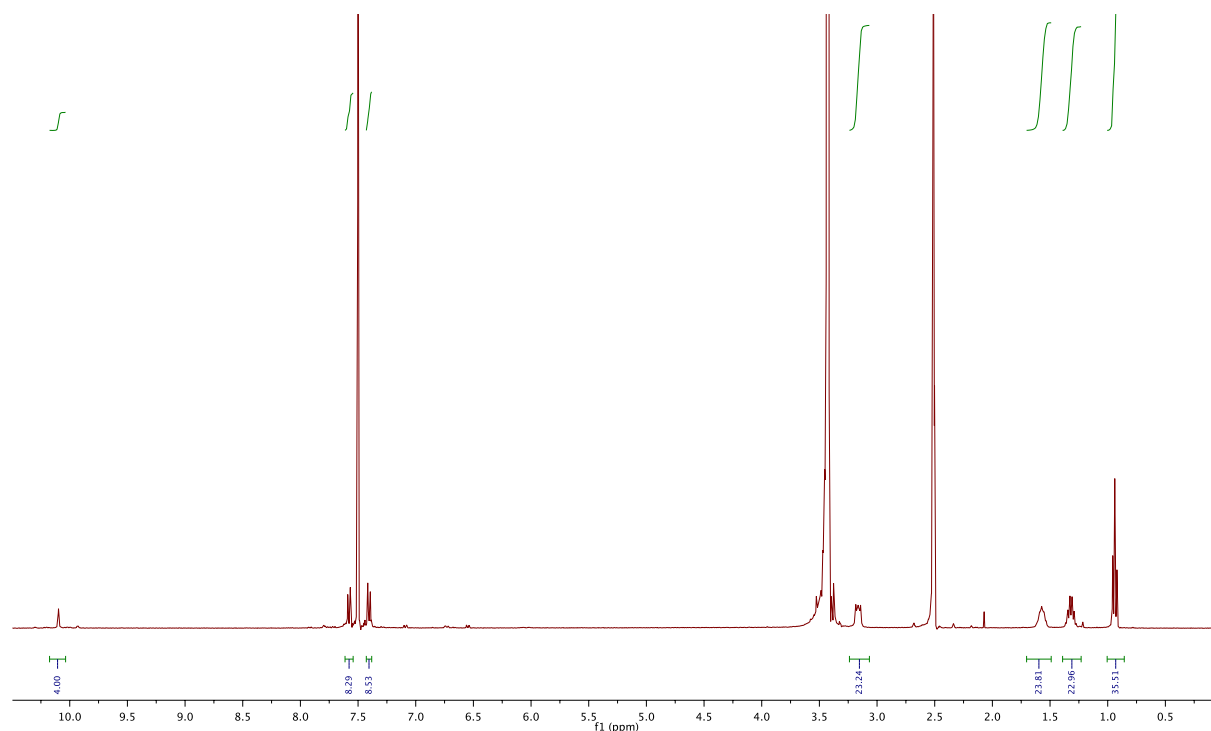


Figure III-3: ^1H NMR spectrum of POM-PDITC before washing with benzene dmsO-D_6 .

Finally, POM-PDITC has been also studied by ^{31}P NMR spectroscopy. The complex is characterized by a single peak at -12.23 ppm in dmsO-D_6 , close to that of POM-NH_2 (-12.37 ppm). Nevertheless, the spectrum of POM-PDITC after washing displays an additional signal at -15.05 ppm attributed to $[\text{PW}_{12}\text{O}_{40}]^{3-}$ as a contaminant.

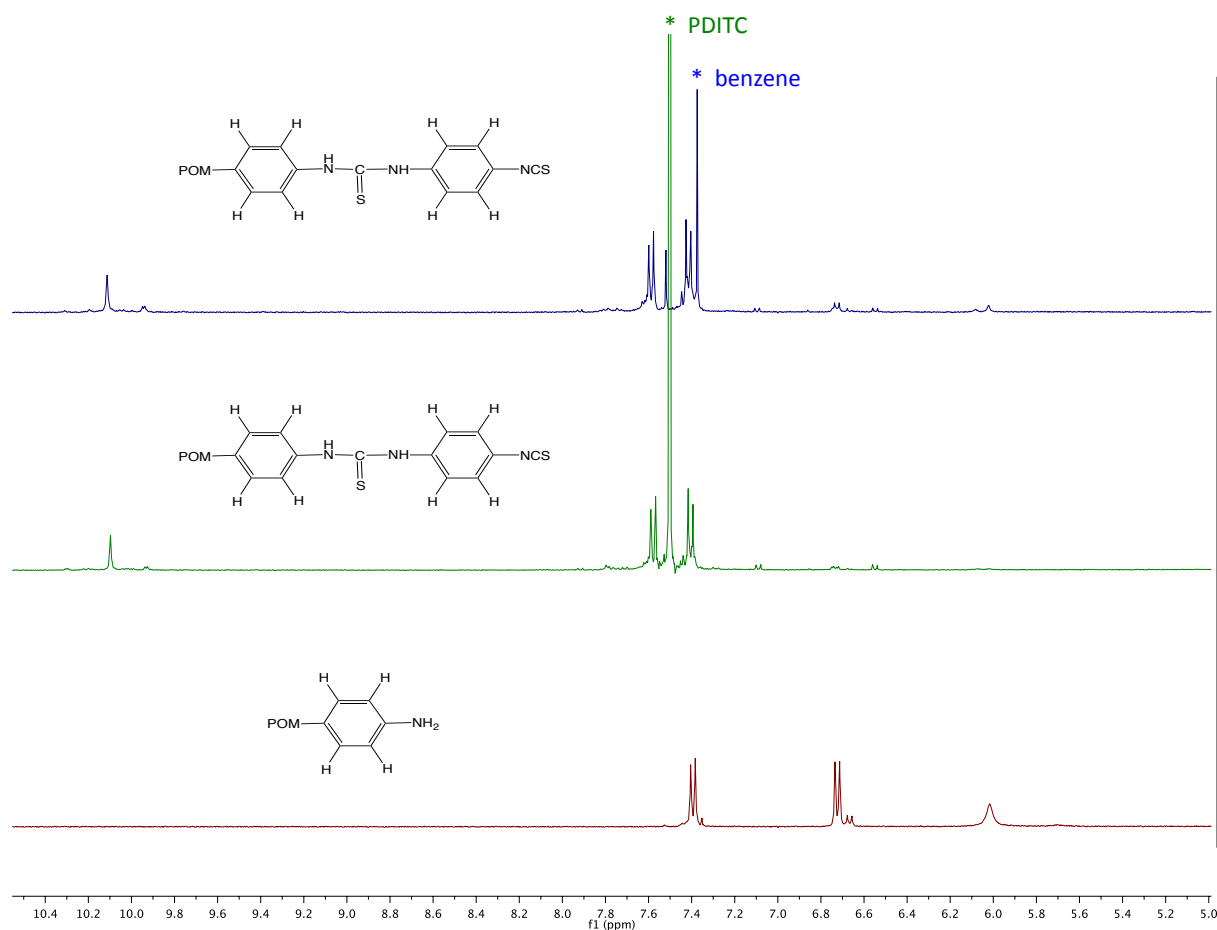


Figure III-4: Comparison of the ^1H NMR spectra (from bottom to top) of POM-NH₂, POM-PDITC before and after washing with benzene dmsO-D₆.

III.3 Covalent grafting of polyoxometalates onto SBA-15 and characterization of the resulting material

Similar to the case of epoxy-functionalized SBA-15, the grafting was carried out without the use of a coupling agent. On the contrary, the grafting was performed by using PDITC as the cross-linker. Once, the linking of PDITC with POMs-NH₂ was performed then it was grafted onto amino-functionalized SBA-15. The synthesis was carried out at room temperature and it was left under stirring for one week. The ratio POM-PDITC/-NH₂ functions, used for the grafting, was equal to 1/6. For the full characterization of the final synthesized material, different techniques were carried out.

III.3.1 High-Resolution Transmission Electron Microscopy (HR-TEM)

The hybrid material was characterized by HR-TEM. Similarly to previous examples, the intrinsic structure of the amino-functionalized SBA-15 is not affected by the grafting of POMs/PDITC.

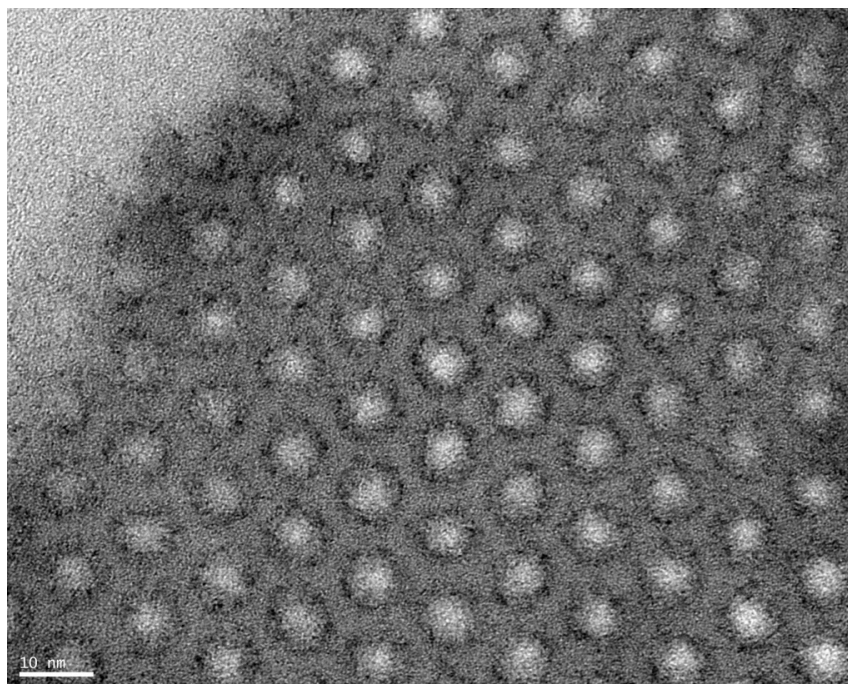


Figure III-5: HR-TEM micrograph of amino-functionalized SBA-15 decorated with POMs/PDITC.

In addition, in Figure III-5, POMs are clearly identified inside the channels of amino-functionalized SBA-15. The black dots measure the size of an isolated POM, indicating that POMs are not aggregated.

The examination of the elemental composition of the sample was achieved by X-Ray Energy-Dispersive Spectroscopy (XEDS).

The ratio S/W was found elevated compared to the theoretical one (1.3 vs. 0.5 respectively). This rise can be explained by the presence of unreacted PDITC in excess. After washing of the samples, this ratio decreases reaching to the value of 0.8. However, even after the washing step, it is noticed that unreacted PDITC still exists.

III.3.2 X-Ray Fluorescence Spectroscopy (XRF)

X-Ray Fluorescence was performed on the hybrid material for the determination of the POMs contents. The results provide complementary information for the analysis by EDX.

The Table III-1 presents the POMs loading calculated by the values obtained for each element. As is clearly visible, the POMs loading calculated for the percentage of S follows a twofold increase compared to the calculations generated from the other elements. The results are in accordance with the values obtained by XEDS.

XRF	SBA-NH ₂ /PDITC/POM-NH ₂	POMs loading (wt%)
% W	9.65	19
% As	0.835	18.2
% S	1.895	48.16

Table III-1: Percentage of W, As, S and POMs loading for POMs grafted materials calculated from each element.

III.3.3 X-Ray photoelectron Spectroscopy (XPS)

XPS spectrum was recorded on a solid sample of POM-PDITC immobilized onto amino-functionalized SBA-15. Full survey and high-resolution W_{4f} and N_{1s} spectra are displayed on Figure III-6.

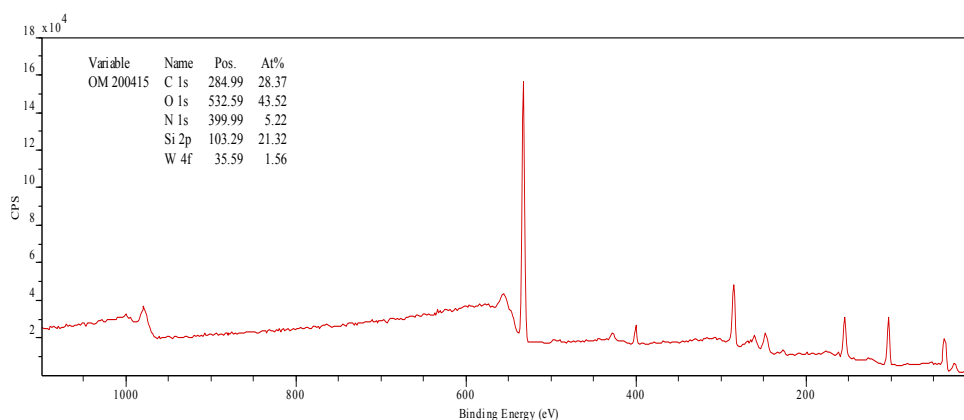


Figure III-6: Full XPS survey spectrum of POM-PDITC.

The W_{4f} peak was composed of a well-resolved spin-orbit doublet (35.6 and 37.7 eV for W_{4f}_{7/2} and W_{4f}_{5/2} respectively), typical of W^{VI} atoms on Keggin-type POMs^{17,18}. The N_{1s}

peak was composed by two unequivalent components. The less intense peak (402 eV) was assigned to ammonium ions (in the present case tetrabutylammonium), while the peak at lower energy (399.9 eV) may be associated to the propylamine functions covering the amino-functionalized SBA-15. High-resolution C_{1s} , O_{1s} and Si_{2p} spectra were also recorded but they did not give any supplementary significant informations.

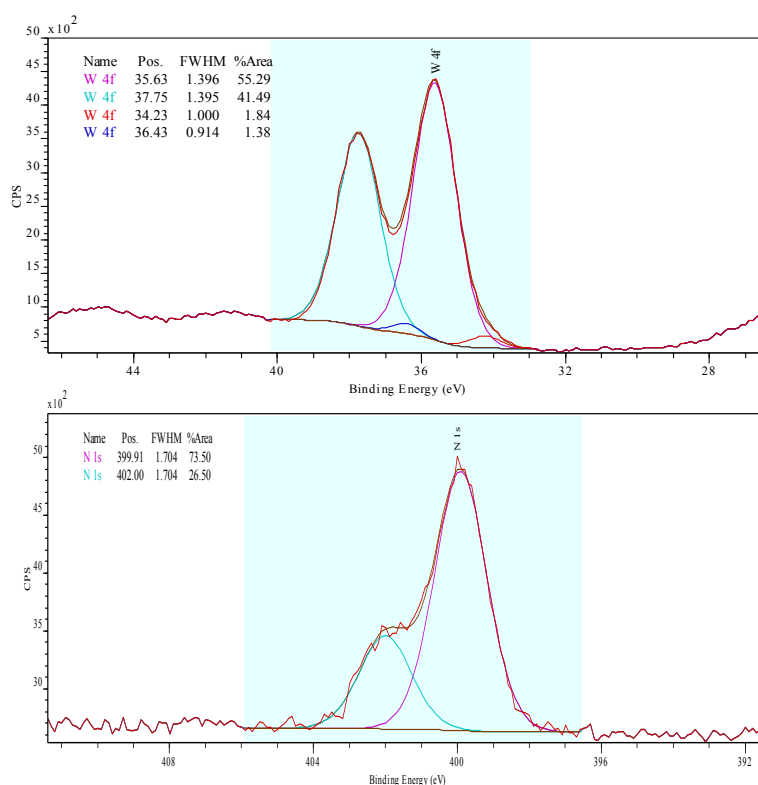


Figure III-7: High Resolution W_{4f} (top) and N_{1s} (bottom) spectra of POM-PDITC immobilized onto amino-functionalized SBA-15.

III.3.4 ^{13}C and ^{31}P CP-MAS NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of POM-PDITC was recorded on a sample that contained residual unreacted PDITC. It displays four peaks under 60 ppm attributed to the four carbon atoms of the tetrabutylammonium ions. Then, a massif composed by three major peaks is also observed in the range 120-150 ppm. This region is where the aromatic carbons are found. The carbon corresponding to the isothiocyanate function (from unreacted PDITC) is generally located at around 140 ppm. Lastly, the peak at 179 ppm may be tentatively assigned to the carbon atom from the $\{NH-C(=S)-NH\}$ thiourea function.

The ^{13}C CP-MAS NMR spectrum of POMs-supported on amino-functionalized SBA-15 was recorded. This spectrum displays the peaks attributed to the propylamine functions under 50 ppm, as already observed in the previous part. The massif attributed to the aromatic carbons is still present but ill-defined. Finally, a peak at 180 ppm is observed, which corresponds to the carbon atom of the thiourea function. The intensity of this peak seems particularly important compared to the pure POM-PDITC, and it is tempting to correlate this apparent increasing intensity to an increase of the number of thiourea functions in the supported materials. This may provide a direct evidence of the covalent grafting of POM-PDITC, provided that the supplementary thiourea functions result from the reaction of the amine groups with the -NCS group brought by the POM-PDITC and not with unreacted PDITC. This result particularly stresses the need of improving the washing steps after the synthesis of POM-PDITC.

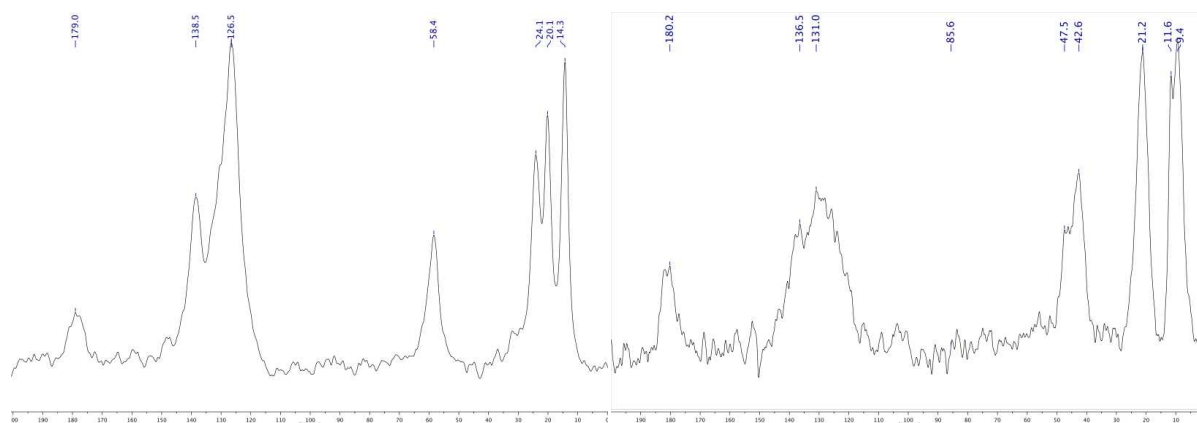


Figure III-8: ^{13}C CP-MAS NMR spectra of POM-PDITC (left) and of POM-PDITC immobilized onto amino functionalized SBA-15 (right).

Finally, the POM-PDITC grafted onto SBA-15 has been also studied by ^{31}P NMR spectroscopy (Figure III-9). The complex is characterized by a single peak at -12.8 ppm in accordance with the chemical shift observed in solution. No other phosphotungstate species were thus detected by this technique in the final hybrid material.

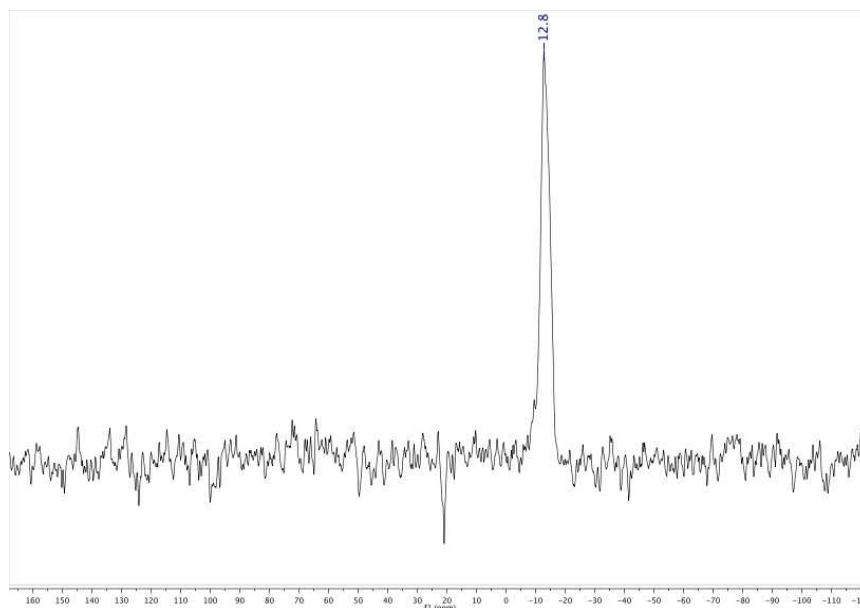


Figure III-9: ^{31}P CP-MAS NMR spectra of POM-PDITC immobilized onto SBA-15 NH_2 .

III.3.5 Determination of the surface by BET method

The pore properties of the materials were analysed by measurement of their nitrogen-adsorption-desorption isotherms and their Brunauer-Emmet-Teller (BET) surface areas; the results are shown in Figure III-10 and Table III-2.

Support	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SBA- NH_2	595	0.69	5.8
SBA- NH_2 /PDITC/POM- NH_2	438	0.68	4.6

Table III-2: Textural data of amino-functionalized SBA-15 before and after grafting of POMs/PDITC.

As shown in Figure III-10, the BET isotherms of the SBA-15 based materials exhibited the characteristic type IV adsorption-desorption patterns, which indicated that the as-prepared mesoporous silica was comprised of uniform mesoporous channels. When the SBA- NH_2 is grafted with POM- NH_2 /PDITC all the values of textural data are decreased significantly, showing that effectively the grafting was successful. The final BET specific surface area obtained was $438 \text{ m}^2/\text{g}$, a value significantly higher than the one obtained after the grafting of POM-COOH using isobutylchloroformiate. This is without any doubt due to a lower POMs content in the present case.

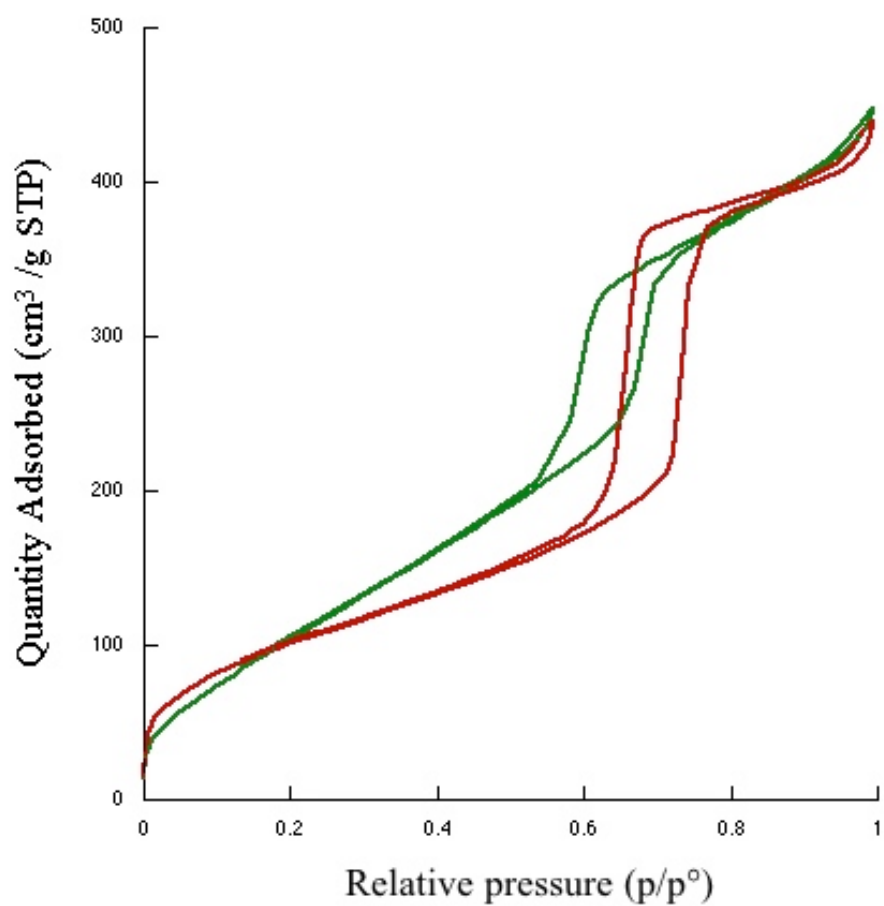


Figure III-10: Nitrogen adsorption-desorption isotherms of amino-functionalized SBA-15 (red line) and amino-functionalized SBA-15 decorated with POMs-NH₂/PDITC (green line).

IV Catalytic studies of anchored homogeneous catalyst

The catalytic studies follow the same approach as developed in the chapter 1. The first step was based on the study of the catalytic performance of the homogenous catalyst before the grafting. The model reaction is the epoxidation of cyclooctene with aqueous H_2O_2 at room temperature. In certain scenarios, the temperature was increased to 50°C , for the purpose of comparison with the tests performed under heterogeneous conditions. The molar ratio of catalyst/ alkene/ H_2O_2 used was equal to 1/ 250/ 250. In the absence of the catalyst, no reaction occurred and the quantity of H_2O_2 remained stable, with no consumption in the absence of cyclooctene.

IV.1 Epoxidation of cyclooctene in the presence of soluble POMs

The catalytic activity of POM-NH_2 was compared to that of POM-NH_2 functionalized with PDITC. The epoxidation of cyclooctene into cyclooctene oxide was performed in acetonitrile and at room temperature. The expected selectivity, as in the previous cases, is 100% with only product the epoxide. In the following graph, the results of cyclooctene conversion are presented. As indicated, the behavior of these two complexes was clearly

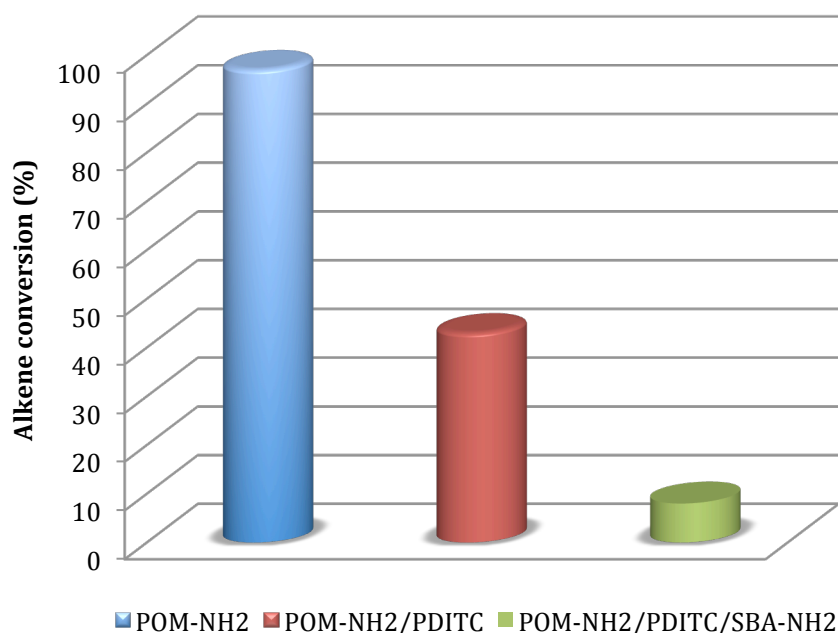


Figure IV-1: Diagram for cyclooctene conversion with POM-NH_2 , $\text{POM-NH}_2/\text{PDITC}$ and $\text{POM-NH}_2/\text{PDITC/SBA-NH}_2$.

different. The POM-NH₂ after 24 h has a conversion of 97% vs 43% once the PDITC is grafted on the amine-functions of the POM. Such a low result could be due to the steric hindrance generated by the PDITC functions. However, the absence of very basic functions (at the difference of POM-NH₂) that could help the deprotonation of hydroperoxide ligands after their coordination to the tungsten (+VI) cations may also be a reason for the catalytic decrease.

IV.2 Epoxidation of cyclooctene in the presence of the covalently anchored catalyst POM-NH₂/PDITC/SBA-NH₂

The POM/PDITC/SBA-NH₂ catalyst was used towards cyclooctene epoxidation in analogous conditions as for its homogenous counterpart.

Once the POM-NH₂/PDITC is grafted on the surface of amino-functionalized SBA-15 the cyclooctene conversion decreases significantly. It is noteworthy that an increase of the temperature up to 50 °C led a catalytic efficiency similar to that of POM-NH₂/PDITC in RT (53%).

There results can be compared to the previously reported system POM-NH₂/SBA-COOH. This supported catalyst had the same behavior as the POM-NH₂/PDITC/SBA-NH₂. In other words, at ambient temperature the conversion was equal to 19% but when the temperature was increased, there was an important rise of the cyclooctene conversion (87%).

Such decrease in both systems, after the grafting of functionalized POMs onto the surface of SBA silica, can be due to a reduction of the exposed surface area of the active component of the catalyst. Thus, a diminution of contact between reactants and catalysts is probably observed.

	Room Temperature	50 °C
POM-NH ₂ /SBA-COOH	19%	87%
POM-NH ₂ /PDITC/SBA-NH ₂	8%	53%

Table IV-1: Comparison of supported systems with POM-NH₂ at RT and 50 °C.

V Conclusion

This chapter was devoted to the grafting of hybrids of POMs with functionalized SBA-15 without the use of coupling agent.

In the first section, two different POMs, with either two aniline functions ($(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-NH}_2\}_2]$ or with two alcohol terminal groups ($(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{34}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{OH}\}_2]$ were prepared. In parallel, SBA-15 was functionalized with epoxy-functions with the use of GLYMO as the reagent. The epoxy-functionalized SBA-15 was characterized by BET, TGA and IR spectroscopy. However, the loading of the functions was not as desired and by IR it was not evident to observe the vibrations corresponding to these functions.

Subsequently, POMs were tentatively grafted on the epoxy-functionalized SBA-15 and the resulting material was characterized by HR-TEM microscopy, XRF spectroscopy and BET. All these techniques resulted in the same conclusion; the POMs loading was not sufficient and the grafting was not successful. By HR-TEM the POMs could not be detected even with microtome cutting. Different parameters in the synthetic procedure were tried out without improvement on the grafting.

Afterwards, another system was tested. Here, ($(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-NH}_2\}_2]$ (or POM-NH₂) was functionalized with 1,4-phenylene diisothiocyanate (PDITC), prior to the grafting step onto SBA-15. The resulting molecular hybrid was characterized by IR spectroscopy, ¹H and ³¹P NMR in order to verify the successful functionalization. The excess of PDITC was eliminated by washing steps. Then, POM/PDITC was grafted onto the surface of amino-functionalized SBA-15. Various physicochemical techniques contributed to the full characterization of the supported catalyst. XPS, ¹³C and ³¹P CP-MAS NMR spectroscopies, XRF, HR-TEM microscopy and BET are the techniques presented. HR-TEM was an essential technique for the identification of POMs inside the pores of SBA-15.

Finally, the functionalized POMs (POM/PDITC) and the POMs-supported material (POM-NH₂/PDITC/SBA-NH₂) showed interesting catalytic activities for the epoxidation of cyclooctene. The epoxidation efficiency declined after each step of functionalization, as

shown in Figure IV-1. However, the performance of the supported catalyst increased when the catalytic reaction was performed at 50 °C compared to room temperature. This behavior is comparable to the system previously mentioned, containing POM-NH₂ supported onto SBA-COOH.

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Part 2

Immobilization of hybrids of Polyoxometalates on magnetic core-shell nanoparticles

I Introduction

Nanomaterials are materials with one or more dimensions in the nanometer scale range (≤ 100 nm) and as a result show novel properties in contrast to their bulk materials. In recent years, nanoparticles have been researches' center of attention as the transition from microparticles to nanoparticles was seen to lead provoking changes in the physical and chemical properties of a material. Two of the most important characteristics, among others, are: (i) the small size of the particles leads to an increased surface area to volume ratio, resulting in the entrance in the domain of quantum effects, (ii) the increasing surface area to volume ratio leads to an increase in the dominance of the surface atoms of the nanoparticle over those in its interior.

I.1 Definition of core-shell

Initially, researchers studied single nanoparticles because of their improved properties compared to the bulk materials. Later, they found that heterogeneous, composite or sandwich colloidal semiconductor particles have better efficiency than their corresponding single particles^{1,2}. Ten years later, during the early 1990s, scientists synthesized multilayer semiconductor nanoparticles with the goal to improve the properties of such semiconductor materials. Hence, the terminology “core-shell” was first used³⁻⁵. At the same time, the advancement of characterization techniques has also greatly helped to establish the structures and properties of these different core-shell nanostructures. The definition of the core-shell nanomaterials can be now extended to the class of nanomaterials having distinct boundary materials covering (either fully or partially) the inner component as long as they can be separately identified.

I.1.1 Shape of nanoparticles

Different shape of nanoparticles can be synthesized owing to advances in new synthetic techniques. Except from spherical shape nanoparticles, other forms can include cube^{6,7}, prism⁸, hexagon⁹, octahedron⁶, rod¹⁰⁻¹², wire^{13,14}, etc. Apart from the size, shape can also have an influence on the properties of nanoparticles. On the one hand, blocking temperature, magnetic saturation and permanent magnetization of magnetic nanocrystals depends on particle size. On the other hand, coercivity of the nanocrystals is totally dependent

on the shape resulting from surface anisotropy effects¹⁵. In addition, chemical and physical properties can be affected such as catalytic activity and selectivity^{16,17}, electrical¹⁸ and optical properties¹⁹.

I.2 Classification of core-shell nanoparticles

Core-shell nanoparticles can be classified, according to the classification proposed by Paria²⁰, depending on the type of the materials used for their synthesis. As a result, two main classes exist; organics and inorganics. In order to be more precise, four big categories of nanoparticles can be described: (i) inorganic/inorganic, (ii) inorganic/organic, (iii) organic/inorganic and (iv) organic/organic.

I.2.1 Inorganic/inorganic core-shell nanoparticles

This is the most important family among the categories of core-shell nanoparticles, as it is a type widely used for optoelectronics, catalysis, quantum dots, biological imaging and numerous other applications. They can be categorized further into two main sub-categories, namely (i) silica based core-shell NPs or (ii) NPs composed by any other inorganic material.

(i) Silica based inorganic/inorganic core-shell nanoparticles

The advantages of using silica coating on a particle are widely known and more important than other inorganic or organic coatings. Firstly, silica is an inert material, making it suitable for blocking the core surface. Secondly, it increases the suspension stability as it reduces the distance and the interactions between the NPs. The core can be a metal, metal oxides, binary inorganic composites or metal salts, creating more sub-categories.

Noble metals are a category of metal cores extensively studied, especially using Au^{21–24} or Ag^{25–27} coated with silica. One of the first gold-silica core-shell nanoparticles studies was carried out by Mulvaney *et al.*, characterizing the synthesized materials by various techniques²¹. Other studies focused on other metals as core component including Ni²⁸, Co^{29,30} and Fe³¹. Finally, binary metal composite systems of Fe-Ni were also investigated^{32,33}.

In most cases, nanoparticles with metal oxide core are composed of a maghemite or magnetite core^{34,35}. Their synthesis is based in majority on the sol-gel method. These core-

shell nanoparticles have been used for biological applications³⁶ but also for catalytic reactions³⁷.

Finally, metal salts have been studied by researchers. The core-shell nanoparticles were synthesized by hydrolysis (shell of nanoparticle) and precipitation (core of nanoparticle)³⁸⁻⁴⁰.

(ii) Inorganic/inorganic (non silica) core-shell nanoparticles

Other materials apart from silica, like metals and metal oxides, can compose the nanoparticle's shell. Gold was used multiple times as the core, as described above, but also as the shell material. Coating the core with gold can be beneficial for the physical properties, such as biocompatibility or enhancing the chemical stability by protecting the core^{41,42}. As before, other metals can be used for the formation of shells, such as Ni, Co, Pd⁴³ or Cu⁴⁴.

Semiconductor nanoparticles (or quantum dots) can be included in the same family. A quantum dot can be defined as a semiconductor where excitons are confined within all three spatial dimensions. The elements used for the composition of semiconductor nanoparticles can originate from groups IVA, IIIA-VA, IIB-VIA and IB-VIIA. Quantum dots can have an important role in biological labeling⁴⁵, bioimaging purposes⁴⁶, solar cells⁴⁷ or catalysis⁴⁸.

I.2.2 Inorganic/organic core-shell nanoparticles

A core of metal, metallic compound, oxide or silica and a polymer shell or any other organic material with high density constitutes the core-shell nanoparticles of this family. The organic coating can have multiple advantages. Herein are presented two advantages; firstly, the metal core has increased oxidation stability⁴⁹ and secondly, it exhibits enhanced biocompatibility^{50,51}. In addition, the polymer coating has applications in different fields like catalysis, paints, cosmetics and inks⁵².

The material properties of the core can divide this category into two different groups: (i) magnetic/organic and (ii) non-magnetic/organic core-shell nanoparticles.

(i) Magnetic/organic core-shell nanoparticles

This family of core-shell nanoparticles, and especially with polymer coating is used mainly for MRI⁵³ and more generally in the biological field for drug targeting, magnetic cell

separation, etc. An important parameter to control during their synthesis is the stability of the core when an external magnetic field is applied. Therefore, the magnetic nanoparticles can be coated with different organic materials, such as polymers⁵⁴ and polysaccharides⁵³.

(ii) Non-magnetic/organic core-shell nanoparticles

These types of nanoparticles can be composed of a core made of metal, metal oxide or metal salt particles and a shell of different organic materials. They can play an important role in biological applications, with a tailor full of functional groups for further functionalization. Similar with other categories of core-shell nanoparticles, noble metals such as Au or Ag attract considerable attention⁵⁵. Examples of metal oxide nanoparticles serving as the core were also studied. TiO₂ nanoparticles coated with polymers, such as polystyrene are used in the field of flexible electronics⁵⁶. Finally, metal salts coated with conductive polymers are extensively investigated for their use in light emitting devices⁵⁷ or chemical sensors.⁵⁸

I.2.3 Organic/inorganic core-shell nanoparticles

Structurally, this family is the reverse of the previous family described above. The core is made of a polymer, such as polystyrene, poly(ethylene oxide). Metals, metal oxides, metal chalcogenides or silica can be the material composing the shell of these core-shell nanoparticles. Their particularity is the existence of dual properties of both organic and inorganic materials. During the last years, these core-shell nanoparticles proved to be important, as they can be used in various fields as material science, catalysis, microelectronics and biotechnology⁵⁹.

Furthermore, organic/inorganic core-shell nanoparticles are interesting for the synthesis of hollow inorganic particles. The organic material serves as the sacrificial core. Different organic materials can be used as a template for the formation of inorganic hollow nanoparticles.

I.2.4 Organic/organic core-shell nanoparticles

The final category consists of organic materials composing both the core and the shell. A review of the different routes of synthesis already exists and was made by Ballauff and Lu⁶⁰. Their review includes an extensive number of applications providing examples in drug delivery⁶¹, biomaterials⁶² and catalysis^{63,64}. One of the examples used is based on the

modification of the physical properties of the overall material, such as its toughness or the glass transition temperature, an important characteristic of a polymer.

I.3 Magnetic/silica core-shell nanoparticles

I.3.1 Synthesis of iron oxide nanoparticles

During the last decades, significant research has been developed around the synthesis of iron oxide NPs and its optimization leading to shape-controlled, stable and monodispersed nanoparticles. The most common methods, including co-precipitation, thermal decomposition, microemulsion, hydrothermal and sonochemical synthesis, give access to high quality iron oxide NPs. In addition, these NPs can also be prepared by other methods including laser pyrolysis techniques, microorganism or bacterial synthesis, etc.

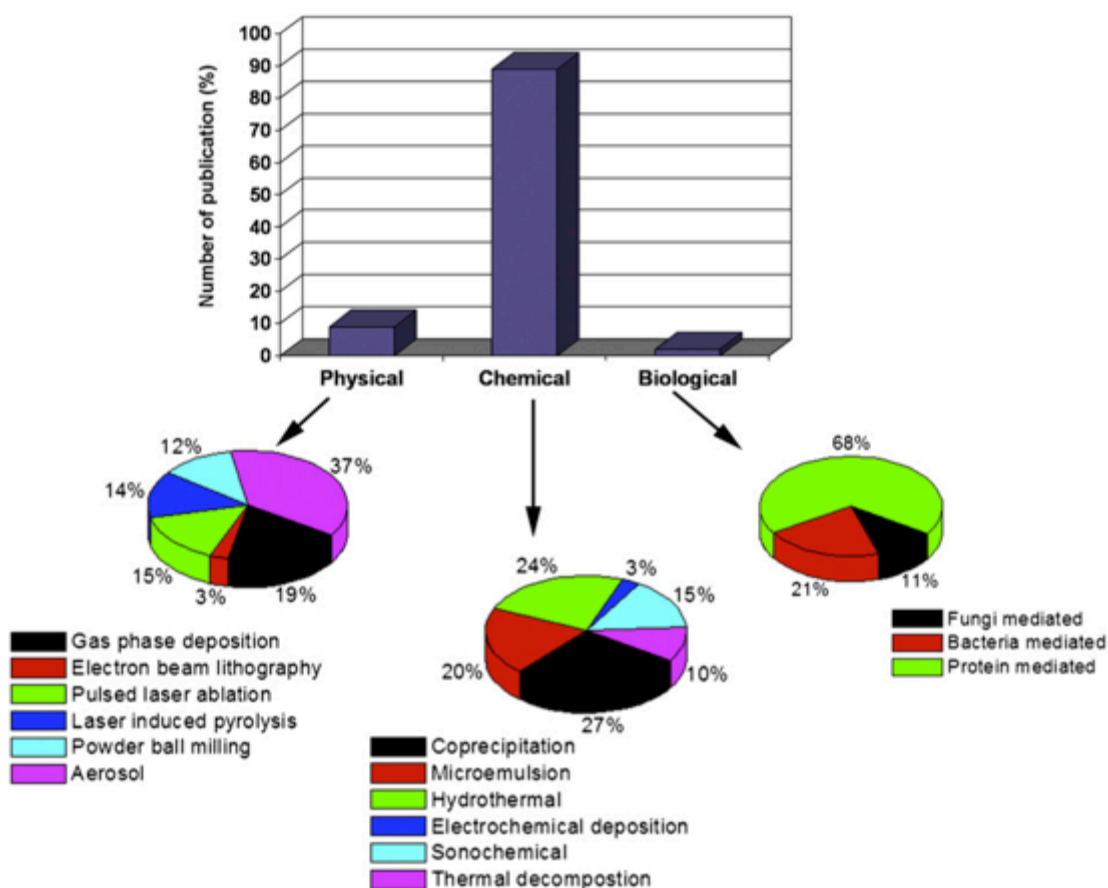


Figure I-1: Comparison of published works (up to date) on the synthesis of iron oxide NPs. Source: Institute of Scientific Information¹¹⁸.

As seen in Figure I-1, the chemical synthetic routes dominate among the others. In more details, one quarter of iron oxide nanoparticles are synthesized by co-precipitation, followed by hydrothermal and microemulsion. The different methods used are presented below.

Co-precipitation

The most conventional method for obtaining Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles is by co-precipitation, as first reported by Massart⁶⁵. This method consists of mixing ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions in a 1:2 molar ratio in highly basic or acidic solutions. The type of salt used, the reaction temperature, the pH value and other parameters influence the size and shape of the synthesized NPs.

Microemulsion

The microemulsion method consists of using water droplets as nanoreactors in a continuous phase (oil) in the presence of surfactant molecules. More specifically, iron precursors can be precipitated as iron oxide in the water phase located in the center of the micelles. Iron oxides do not precipitate in organic phase, as the iron precursors are unreactive in this phase^{66,67}. Surfactants are used as the precipitating agent but also as the capping agent⁶⁸. However, despite their use, the produced NPs are aggregated and most times need several stabilization treatments.

Hydrothermal synthesis

Hydrothermal synthesis, which has been reported as the oldest method for the synthesis of magnetite, consists of heating iron precursors in aqueous medium at high vapor pressure (generally in the range from 0.3 to 4 MPa). This technique offers a better crystallinity of the grains than other processes^{69,70}. Two pathways exist depending on whether the specific surfactants are used or not.

Sonochemical synthesis

In this process, a high-energy ultrasonication creates acoustic cavitations that can provide localized heat with a temperature of about 5000K. At high temperature, the formation and growth of nuclei and the implosive collapse of bubbles can take place. The advantage of

this method is the monodispersity of NPs combined with the variety of shapes. However, the main drawback is the scale of the synthesis as this is only aimed for small-scale production.

Thermal decomposition

Herein, an organic solution phase decomposition route is used and decomposition of $\text{Fe}(\text{cup})_3$ (cup = *N*-nitrosophenylhydroxylamine), $\text{Fe}(\text{acac})_3$ (acac = acetylacetonate), or $\text{Fe}(\text{CO})_5$ followed by oxidation leading to high quality monodispersed iron oxide NPs. Nonetheless a higher temperature is required followed by a complicated operation using toxic and expensive iron complexes. It is worth noting that the iron oxide NPs resulting from the thermal decomposition method, are usually dispersed in nonpolar solvents.

Each method has its advantages and its drawbacks. However, as seen by the Figure I-1, co-precipitation remains the principal method used for the synthesis. The numerous advantages overcome some of the drawbacks. This synthetic route offers a facile scale up strategy, with low cost and final dispersions with high concentration in NPs. The conditions used are mild and can be carried out in water without the need of surfactants. The only disadvantage, i.e. high polydispersity in size, can be neglected as the NPs can be sorted by adjustments in the synthetic protocol.

I.3.2 Synthesis and functionalization of core-shell magnetic NPs ($\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$) with PEG and amino groups

In terms of stability, magnetic NPs are very sensitive to oxidation and agglomeration due to their magnetic nature and also exhibit high chemical reactivities as well as strong magnetic dipole interactions. When oxidized, thin oxide layer generally form on the surface of the particles, which changes their properties dramatically. Natural agglomeration of these particles into larger clusters also restricts the use of such particles in various applications^{71,72}.

To overcome the aforementioned problems, several encapsulation procedures have been proposed, as mentioned in the previous above. Out of the various supports used for coatings and shells, silica delivers key advantages. Theoretically and experimentally, silica supports provide stability to MNPs by establishing equilibrium between the attractive and repulsive forces. The functionalization of silica shell by polyethylene glycol (PEG) chains also enhance the repulsive interactions between the NPs. Hence, silica coating allows the

generation of nanocatalysts that are inert, chemically and thermally stable under typical conditions where catalysts operate.

Thus, silica-based magnetically recoverable nanocatalysts have the following attractive features; (i) sufficient binding strength between the active species and magnetic support to enable recycling, (ii) good chemical inertness of the magnetic support, (iii) high saturation magnetization to facilitate magnetic separation, (iv) soft ferromagnetism for redispersion, (v) low cost, ready availability, mechanical robustness and straightforward synthesis, and (vi) a quasi-homogeneous dispersion can be achieved.

Sol-gel process

Almost all the silica-based core-shell silica NPs are synthesized using sol-gel chemistry, historically known as the Stöber method.⁷³ This wet chemical method entails the hydrolysis and subsequent condensation of silicon alkoxides or silicon halides in alcohol, water or a mixture thereof in the presence of a base catalyst, such as ammonia, to afford uniform colloidal microspheres.

The Si-OR bonds hydrolyze readily with water, even if only with moisture adsorbed on the surface, to form silanol Si-OH groups. These silanol groups can then condense with each other to form polymeric structures with very stable siloxane Si-O-Si bonds. This allows surface treatment, coupling and assembling of very dissimilar surfaces chemically, as between inorganic and organic materials.

Both particle size and distribution are important parameters in the synthesis and subsequent applications of nanoparticles. The increase in particle size, for example, leads to the decrease of the specific area. However, these important factors can be controlled by selectively choosing the reaction media and the physical parameters of the reaction as temperature, reactant concentration and pH of the media.

Influence of media's pH

The effect of pH on the particle size depends mainly on the reaction mechanism involved. This is especially true when H^+ or OH^- ions are directly involved in the reaction. In the case of the sol-gel process, the condensation step can be realized either in basic or acidic medium. When the pH of the reaction is acidic, the condensation reaction is slower than the

Part 2: Immobilization of hybrids of Polyoxometalates on magnetic core-shell nanoparticles

hydrolysis reaction, leading to the formation of microporous gel containing the nanoparticles. On the other hand, in basic conditions the mechanism is the inverse of the latter one leading to the formation of germs around of the NPs. A silica shell hence is formed by a nucleation step.

In addition, the catalyst's quantity, H^+ or OH^- ions, is a key parameter for the shell formation. Silica nanoparticles can be formed when the quantity is high enough during the synthesis. In addition, a low quantity of catalyst can cause problems in the homogeneity of the silica shell.

Quantity of organosilanes

By changing the quantity of organosilanes, an impact on the mean size of the silica shell can be observed, and hence, an impact on the size of the core-shell NP. However, this parameter can have the same result as the quantity of catalyst if there is no equilibrium. Insufficient quantity of precursor can affect the colloidal stability of the dispersion, by not reaching a total coverage of iron oxide NPs. During this process, a form of rosary is created with connecting iron oxide NPs and not distinct core-shell NPs.

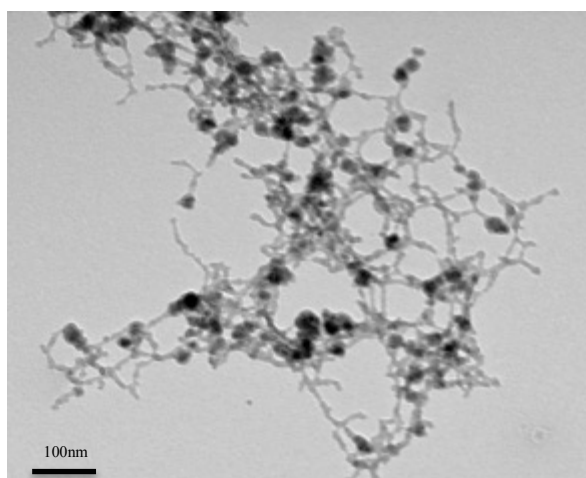


Figure I-2: TEM micrograph of core-shell MNPs synthesized with less quantity of organosilanes.

Solvent's influence

The nature of the synthesis medium can also have a significant effect on the quality of the synthesized core-shell NPs. In order to have a sufficient electrostatic repulsion, the medium has to be relatively polar. The sol-gel synthesis is carried out in a mixture of water/ethanol with every solvent contributing to the synthesis. Water can affect different parameters during the synthesis if the volume is not ideally adjusted. As a solvent with high

dielectric constant, it stabilizes the core-shell MNPs and facilitates with the individual coverage of each iron oxide NP separately. When the quantity is too low, aggregation is observed, leading to micrometric sized nanoparticles. Indeed, the quantity of water is proportional to the concentration of iron oxide NPs introduced; if one of them is increased, the other should follow this augmentation. However, it is important to mention that a high quantity of water increases the speed of hydrolysis of organosilanes, as mentioned before. A high speed can evoke the condensation of organosilanes in bulk, thus the formation of pure silica particles can be generated. The addition of ethanol can assist in solving this problem by decreasing the speed of the hydrolysis.

I.3.3 Functionalization of the silica shell

An important advantage of silica coating over iron oxide nanoparticles is the well-known surface chemistry and broad spectrum of functional groups for modifying the silica surface to give the desired properties. Surface functionalization allows control over the interactions between the NPs and various chemical systems, which is essential for the effective utilization of these materials in the field of catalysis.

The chemical attachment of organic groups to a silica surface can be carried out by three main methods; (i) incorporation of functional groups *via* sol-gel methodology (ii) chlorination of the silica surface followed by reaction of the Si-Cl with an appropriate functional molecule/reactant, and (iii) through reaction between organosilanes or organic molecules and silica surface functions⁷⁴. All three methods can be followed up by a post functionalization of existing organic groups at the surface.

Sol-gel techniques

This method consists of the incorporation of organofunctional groups into the solid matrix during the silica preparation. An organoalkoxysilane $(RO)_3SiR'$ is mixed with a silica precursor, typically tetraethylorthosilicate (TEOS). As with usual sol-gel techniques, the synthesis can be either acid or base catalyzed.

The most important impetus for this approach has occurred from the discovery of the MCMs^{75,76}, allowing the predictable formation of very regular mesoporous materials, which show a great deal of promise as highly selective catalysts. The materials were prepared using cationic surfactants as templates around which sol-gel process took place.

Deng et al. used this technique for the synthesis of magnetic yolk-shell mesoporous silica microspheres with supported Au nanoparticles⁷⁷.

Yang et al. employed N-heterocyclic carbene (1,3-bis((4-triethoxysilyl-2,6-diisopropylphenyl)-imidazol-3-ium-trifluoro-methane sulfonate)) over a framework of Si/Fe₃O₄. The NPs were prepared with a sol-gel process using CTAB surfactant as a template. After removing the CTAB, magnetic core-shell nanoporous organosilica microspheres with built-in NHC moieties were obtained⁷⁸.

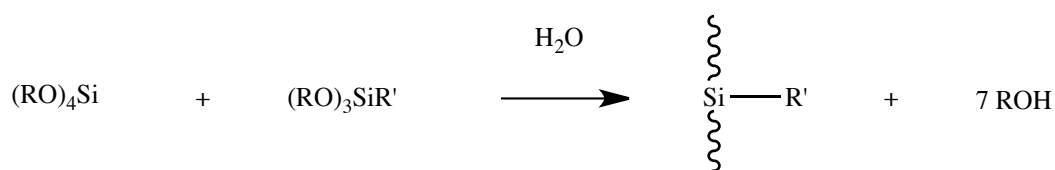


Figure I-3: Templated sol-gel synthesis of organo-functionalized silicas.

Surface chlorination and subsequent displacement

This is a much less frequently used method, although the advantage of forming a direct Si-C bond at the surface precludes the formation of bound oligomers and variable modes of attachment. Halasz and Sebastian developed a method in which the silica gel was first chlorinated using thionyl chloride⁷⁹. Thus, the Si-Cl material produced is reacted with a solution of a Grignard reagent or an organolithium species, leading to the displacement of the Cl and the formation of a Si-C surface bond (Figure II-3). The main drawback of this method is the limitation of possible functional groups introduced as a result of using organometallic reagents.

Karimi prepared sulfuric acid functionalized silica-coated magnetic nanoparticles (SSA-MNPs) by a simple one-step direct reaction of chlorosulfonic acid with silica-coated magnetite (Fe₃O₄) MNPs⁸⁰. The silica coated MNPs were prepared by modifying the surfaces of the magnetite nanoparticles with negatively charged citrate groups, and then coating with silica was achieved by reaction with tetraethylorthosilicate

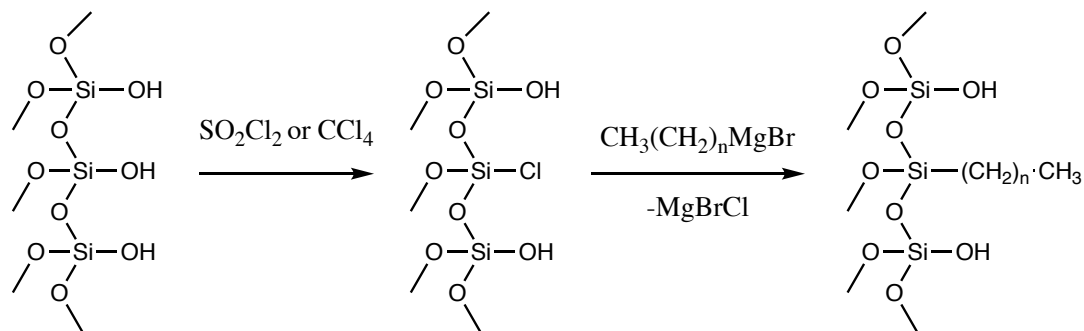


Figure I-4: Chlorination of silica surface and subsequent modification with Grignard reagent.

Grafting of functional organosilanes

This remains the most popular method, mostly due to its simplicity, in terms of experimental procedures. Herein, the surface hydroxyls are treated with organofunctionalized silanes, thus forming a Si-O-Si bond, which is more thermally and chemically robust than the Si-O-C bond. There are two ways of achieving this.

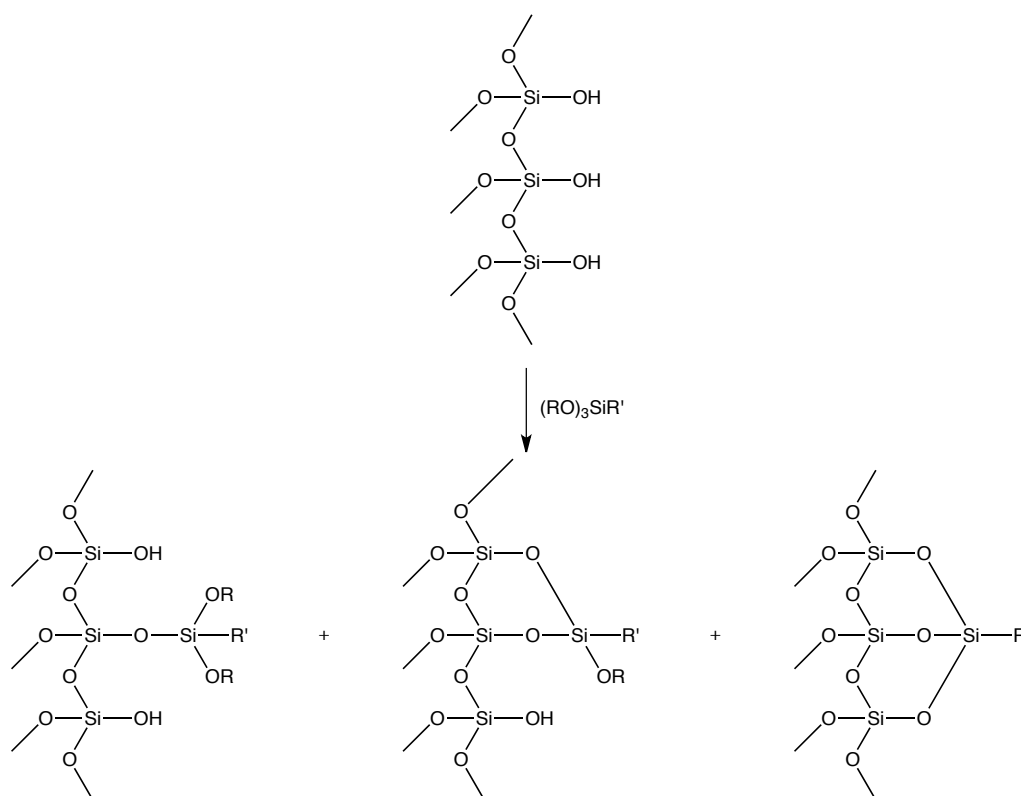


Figure I-5: Simplified grafting reaction at a silica surface.

The first involves the use of trialkoxysilanes that react with the silanol groups liberating the corresponding alcohol⁷⁴. Methoxy and ethoxy-silanes have been shown to be

the most effective due to their greater reactivity, despite the variety of trialkoxysilanes employed. However, the presence of three alkoxy groups means that the organosilanes can react *via* one, two or all three alkoxy groups (Figure I-5). This in turn leads to a possible degree of some degree of the organosilane's polymerization on the silica surface. The second method employs the use of chlorosilanes to react with the silanol functions, thus liberating HCl⁸¹.

Post modification

This is often a necessary step in the synthesis of chemically modified surfaces. One of the most common grafted functions is the primary amine, usually via 3-aminopropyl(trimethoxy)silane. This group behaves like a typical amine function and can thus be derivatized by formation of amides or imines, and by alkylation. Nucleophilic aromatic substitution of suitable activated rings is also possible (Figure I-6).

Newer methods for the functionalization of surface bound alkenes (from chlorination) include the Heck reaction. This methodology allows the attachment of a variety of aryl groups to the surface under solvent free conditions.

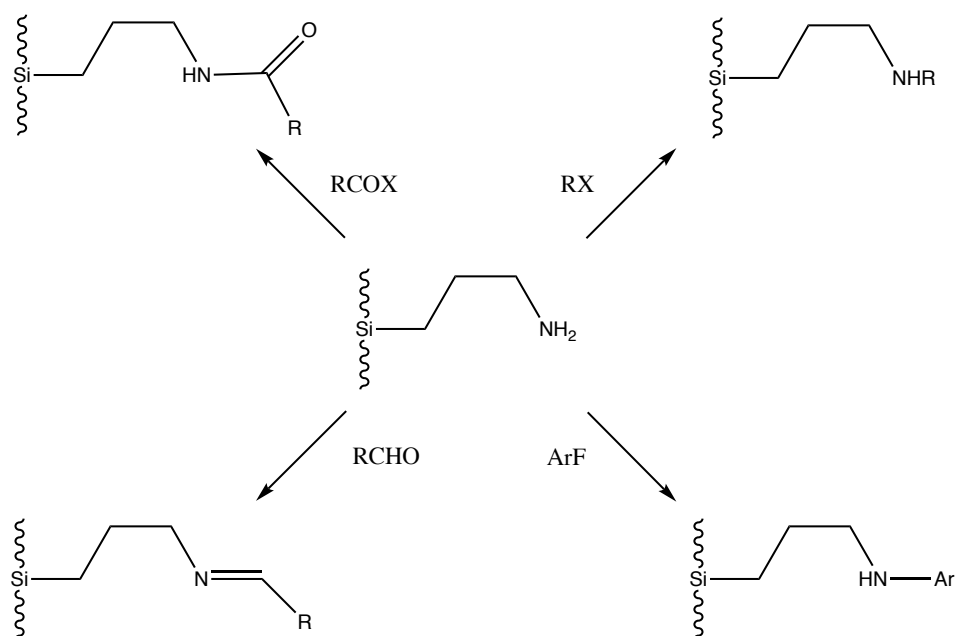


Figure I-6: Reactions of aminopropyl-functionalized silica.

Naeimi reported the preparation and application of $\text{Fe}_3\text{O}_4/\text{silica}$ sulfonic acid as an efficient and reusable catalyst for one-pot synthesis of 1-substituted 1H-tetrazoles from an amine, triethyl orthoformate and sodium azide⁸².

I.4 Applications of magnetic/silica core-shell nanoparticles

As previously mentioned, magnetic cores coated with silica are a family of core-shell nanoparticles with various applications due to their remarkable advantages. In more detail, magnetic core-shell nanoparticles are of great interest in catalysis and in biotechnology/biomedicine. They can be beneficial to assist in an effective separation of catalysts, nuclear waste, biochemical products and cells. However, during the continuation of the thesis, the catalytic applications will be extensively described.

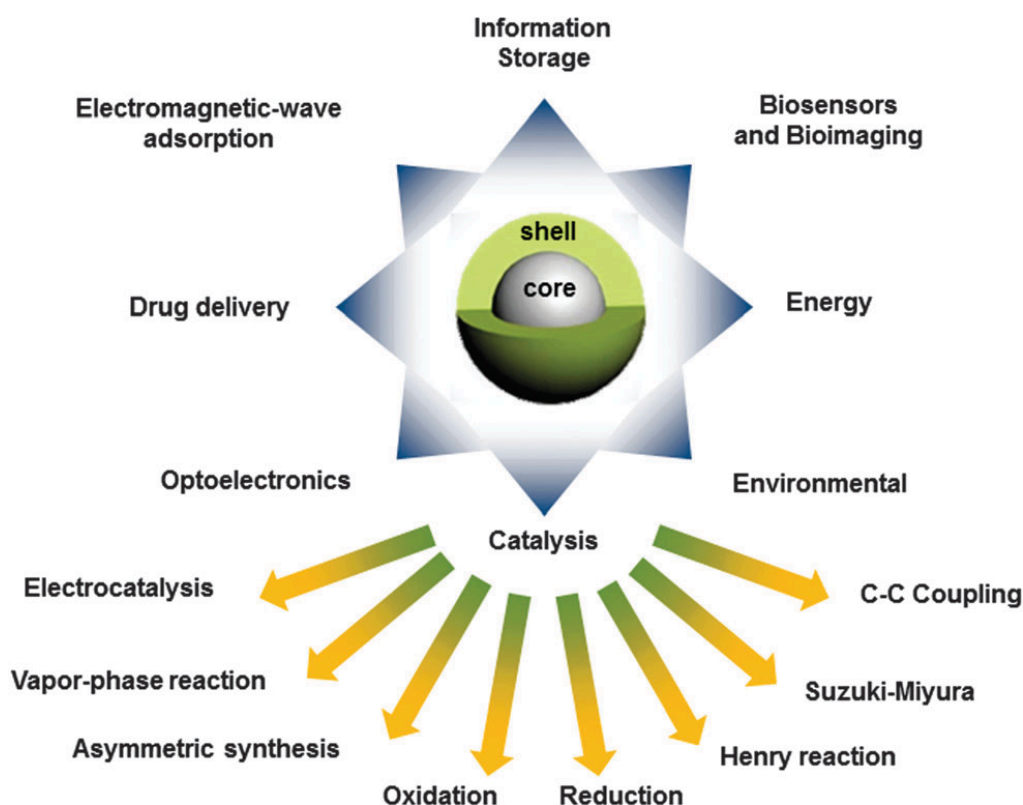


Figure I-7: Applications of core-shell NPs in various areas with emphasis in catalysis¹¹⁹.

I.4.1 Drug delivery

A very promising application of magnetic core-shell nanoparticles is in drug delivery as drug carriers. The procedure was proposed by Widder et al. in the 1970s by the so-called “magnetic drug delivery”⁸³. The concept includes injecting magnetic nanoparticles with drug

molecules attached and guiding them in a chosen site with the help of a localized magnetic field. The nanoparticles stay in place until the therapy is complete and afterwards are then removed. The advantage of this technique is that the magnetic carriers can carry a large dose of the desired drug with high local concentration, avoiding toxicity arising from high drug dose in other parts of the organism.

Hyeon and Moon presented a system composed of Fe_3O_4 cores coated with mesoporous silica and finally functionalized with PEG chains for biocompatibility. The core-shell NPs were doped with dye for simultaneous imaging and drug delivery. Finally, to examine the drug delivery they used the NPs as a carrier for doxorubicin, a drug used for the treatment of cancer⁸⁴. In the same concept, Zhang et al. used mesoporous silica to form the shell around magnetite cores. However, doxorubicin was grafted onto the surface of the magnetic nanoparticles instead of the silica surface. The advantages of this system are based on the protection of the drug molecules by the mesoporous silica shell and the slower release behavior compared to bare magnetite NPs⁸⁵. Another example using the same drug was described by Chen et al. where they immobilized it on the surface of the core-shell NP by an amide bond. The NPs were modified with acid functions for the grafting of the drug⁸⁶.

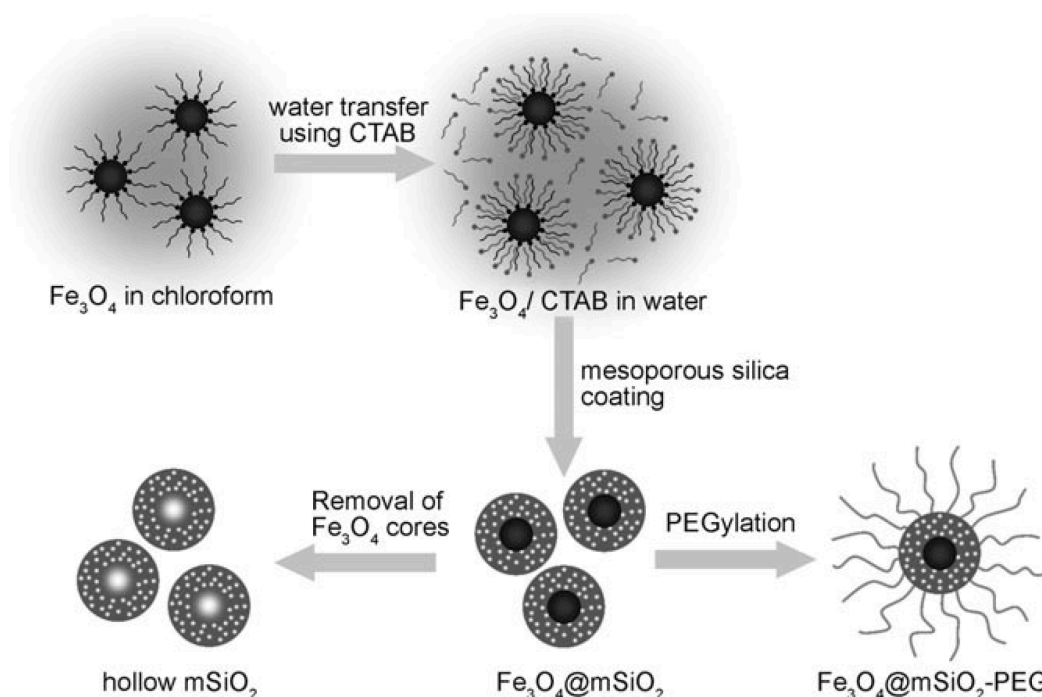


Figure I-8: Schematic representation of the synthetic procedure for magnetite/mesoporous silica core-shell NPs.

Finally, Siaugue et al. used core-shell NPs with PEG chains and amine functions serving for a covalent grafting of the active molecule. Herein, bleomycin was used, covalently anchored on the surface of the magnetic carrier in order to decrease its toxicity and thus induce a wider use in oncology⁸⁷.

I.4.2 Catalysis

After the creation of the branch of nanotechnology, important developments were created in the field of catalysis with the nanocatalysts. As a result, nanocatalysts were studied during the past decades with an emphasis in magnetic recoverable ones, in order to overcome problems related to their separation and regeneration.

Magnetic nanocatalysts have been used in a wide range of catalytic reactions, including oxidation, hydrogenation, C-C coupling, reduction, olefin metathesis and others.

(i) Carbon-carbon coupling reactions

Carbon-carbon bond formation is an important step in various preparative organic syntheses. In the following paragraphs, different examples will be cited.

Shylesh et al. synthesized an organic-inorganic hybrid heterogeneous catalyst by covalently grafting oxodiperoxo-molybdenum complexes onto magnetic NPs⁸⁸. The comparison of the catalytic activity of this system with other sileneous-Mo catalysts was carried out. The results showed a better performance of the magnetic NPs-catalyst for use in the Suzuki-Miyaura cross-coupling reaction. Beygzadesh et al. also used Pd supported nanocatalysts for further applications in Suzuki-cross coupling of aryl halides with arylboronic acids in aqueous media⁸⁹.

N-heterocyclic carbene nickel catalysts supported on magnetite/silica nanoparticles have been described by Yoon et al. The resulting catalyst was used in the C-S coupling of various aryl halides with thiols⁹⁰.

Similarly, Nador et al. demonstrated a versatile magnetically recoverable catalyst with copper NPs. Different coupling and cycloaddition reactions of terminal alkynes were tested for the evaluation of the catalyst. In more detail, the catalyst showed an increased efficiency for the Glaser alkyne dimerization reactions in THF⁹¹.

Recently, Sharma et al. studied a zirconium (IV) based nanocatalyst. The resulting hybrid material was tested for its efficiency in important organic transformations, as Friedel-Crafts and Pechmann condensation reactions⁹².

(ii) Olefin metathesis

The nanocatalysts enhanced the facility for the olefin metathesis reaction for the formation of C-C bonds. Byrnes et al. deposited a ruthenium (II) alkylidene catalyst onto the SMNPs giving rise to a 95% yield for the catalytic reaction⁹³.

(iii) Hydrogenation reactions

Hydrogenation is considered as one of the most widely used organic transformations in organic synthesis. Jacinto et al. were the first to report a magnetically recoverable Rh(0) nanoparticle-supported catalyst for the hydrogenation of cyclohexene. The system had outstanding results compared to commercial catalysts. For the same reaction, systems with Ru acting as the catalyst were also tested with a 99% conversion⁹⁴.

Latterly, Sharma et al. reported the synthesis of a highly efficient catalyst by covalent grafting of a copper (II) acetylacetonate complex onto silica-magnetite NPs functionalized with amine-moieties⁹⁵.

Li et al. fabricated a novel catalyst using a layer-by-layer assembly of polyelectrolyte-gold nanoparticle multilayer films SMNPs. The obtained hybrid material demonstrated high catalytic activity. The Au NPs were successfully immobilized in the polyelectrolyte layer without blocking the catalytic sites⁹⁶.

(iv) Oxidation

Oxidation reactions are of great importance to chemical industries because of their potential for generating a wide variety of important compounds used in the pharmaceutical and fine chemical industries.

Once again, Jacinto et al. prepared a Ru-supported nanocatalyst with effectiveness towards the oxidation of aryl and alkyl alcohols to aldehydes at 100°C. The oxidation proceeded smoothly with a high rate of conversion and selectivity, as no carboxylic acid was

formed. In addition, no leaching of the catalyst was observed. The same authors prepared a gold-based catalyst for oxidation reactions⁹⁷.

Sharma and Monga synthesized a valuable zinc-based SMNPs catalyst by a covalent pathway. 2-acetylpyridine was grafted with amine-functionalized silica-magnetite NPs, followed by a metallation with zinc acetate. The resulting material was efficient for oxidation of various aromatic amines to obtain azoxyarenes with high selectivity and an elevated turnover number (TON)⁹⁸.

Sun and co-workers composed an organic-inorganic hybrid heterogeneous catalyst with cobalt (II) or copper (II) acetylacetonate complexes. The later complexes were deposited onto the surface of SMNPs functionalized with 3-aminopropyltriethoxysilane (APTES). The catalytic performance was evaluated in the epoxidation of styrene using air as the oxygen source. Both systems showed excellent styrene conversion and good epoxide selectivity⁹⁹.

I.4.3 Catalysis with POMs

As shown before, MNPs-supported catalysts exhibit facile recycling controlled by simple magnetically driven separation. Therefore, several groups have attempted to prepare magnetically recoverable POMs catalysts for various reactions.

In 2011, Rafiee and Eevani synthesized a magnetically recoverable catalyst by immobilization of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on the surface of silica encapsulated Fe_2O_3 NPs. The catalyst showed an excellent distribution of acidic sites. The catalytic activity was evaluated for Mannich-type reactions of aldehydes, amines and ketones in water at room temperature. The obtained conversions were excellent with a recovery after catalysis in a yield of 95%¹⁰⁰.

A couple of years later, Zhang and coworkers prepared silica coated magnetic Fe_3O_4 and on their surface they immobilized heteropoly acids Keggin-type. The nanocatalyst was tested for the synthesis of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and fructose. Moreover, results of recycling were presented showing the advantages of this system compared to the homogeneous one¹⁰¹.

The same system was used as a photocatalyst in the UV light region. Fu et al. investigated the photocatalytic activity of the system by measuring the degradation of rhodamine B, resulting in excellent results with good stability¹⁰².

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Heteropoly acids supported on core-shell magnetic NPs were tested finally, in typical enamine-based asymmetric direct aldol reactions. The core-shell nanoparticles were functionalized with two types of functions, either amine-functions or imidazolium groups¹⁰³ (Figure I-9).

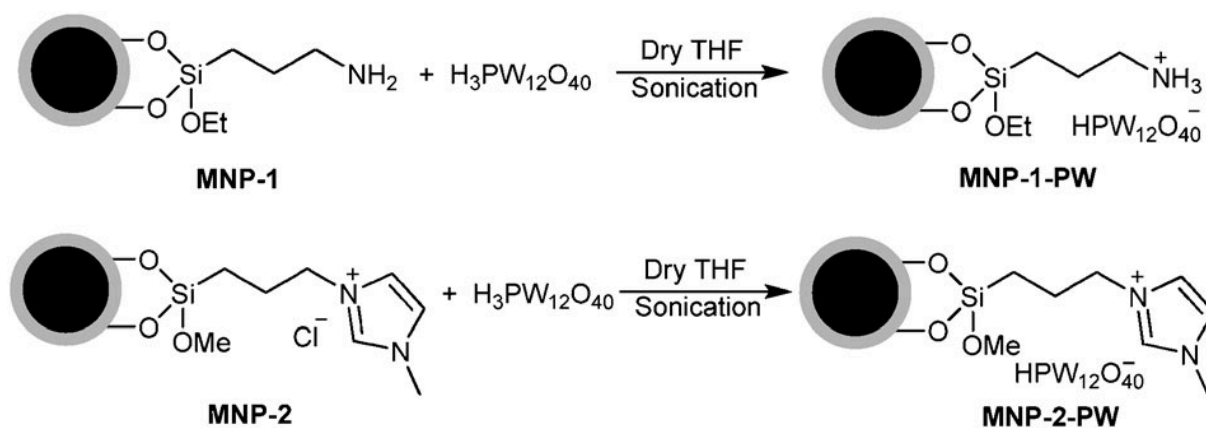


Figure I-9: Grafting of heteropoly acids at the surface of functionalized core-shell magnetic NPs.

II Synthesis and characterization of core-shell MNPs

The PHENIX laboratory has been working in the field of iron oxide nanoparticles for several years. Their objective is to use these NPs for biological applications and as result it is necessary to work in an environment favorable for this goal (aqueous media, pH 7.4). In other words, the dispersions of iron oxide nanoparticles are called ferrofluid. A ferrofluid solution is a colloidal suspension with an increased concentration of magnetic monodomain particles of typical size 100 nm.

In the following pages, two different sections will be parallel described containing information about two different synthetic routes for maghemite NPs. In the beginning, unsorted maghemite NPs were synthesized in order to be encapsulated in silica shell. However, the ulterior goal was to exploit the hyperthermia properties of the core-shell nanomaterials and in particular to perform hyperthermia assisted catalysis. The unsorted maghemite NPs do not show the ideal magnetic behavior under magnetic field because of their polydispersity in size, and especially their small diameter. As a result, importance was given in maghemite NPs with better magnetic response, achieved by synthesizing what will be called sorted maghemite NPs. These NPs have a decreased size polydispersity by increasing in the same time their mean diameter.

II.1 Synthesis of maghemite NPs and characterization

II.1.1 Synthesis of maghemite nanoparticles by co-precipitation

Unsorted nanoparticles

In the following figure I-1 a description of the different synthetic steps of maghemite nanoparticles ($\gamma\text{-Fe}_2\text{O}_3$) derived from the oxidation of a colloidal suspension of magnetite, obtained by co-precipitation at basic conditions, is presented¹⁰⁴. The synthesis was based on Massart's method.

The first step consists of an inorganic polycondensation reaction leading to a formation of the two precursors $\text{Fe}_2(\text{OH})_4$ and $\text{Fe}_3(\text{OH})_6$ after a basic addition (NH_4OH , NaOH , KOH etc.). Once the precursor concentration reaches a certain limit (critical limiting supersaturation), germs of magnetite start to appear (nucleation step) and grow according to

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the mechanism of ripening described by Ostwald¹⁰⁵. The process of nucleation is blocked when the concentration of the precursor reaches the lowest limit. Following this, the ripening gives birth to particles that possess their final characteristics following a final step of aging. The previously described method was presented by La Mer¹⁰⁶.

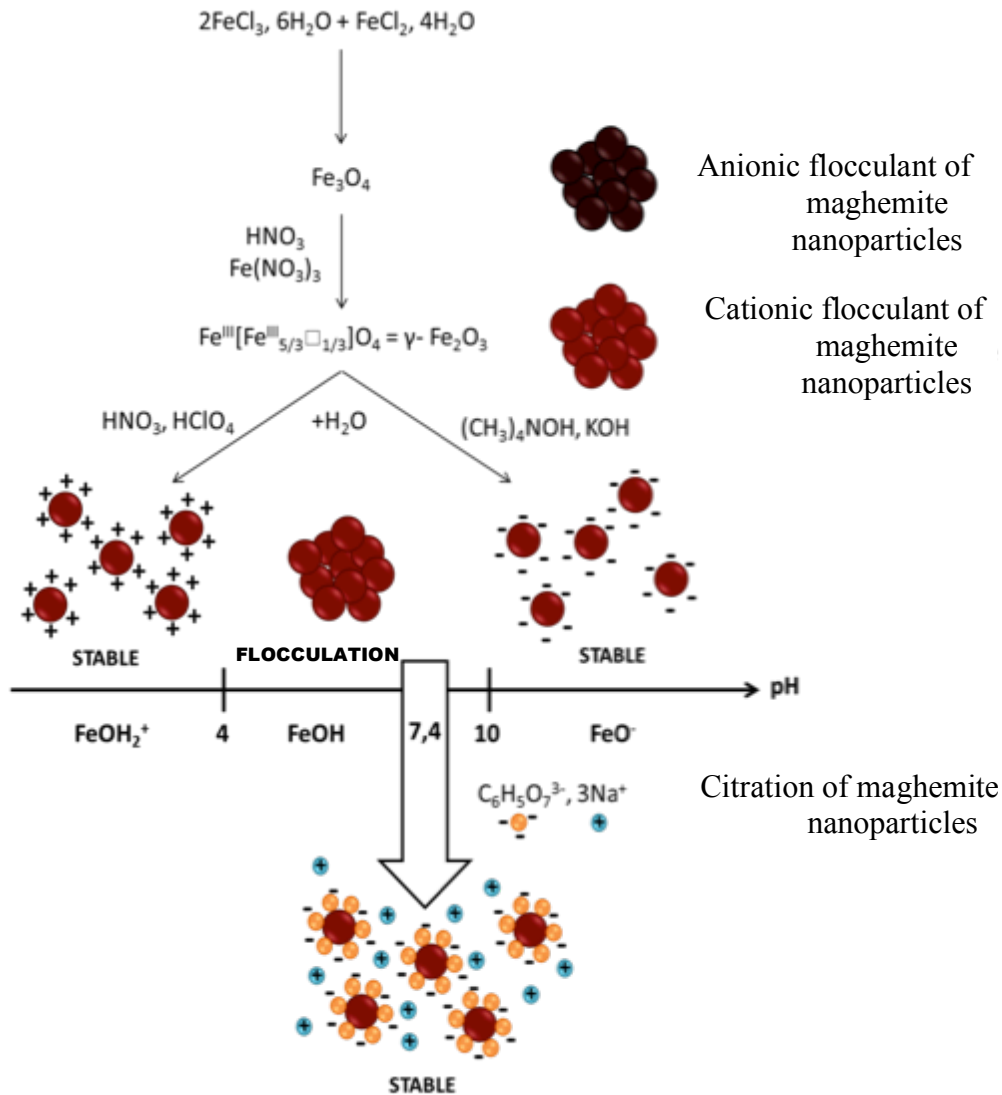


Figure II-1: Schematic representation of maghemite nanoparticles synthesis¹⁰⁴.

The size and shape of the iron oxide NPs depend on different parameters; the type of salt used (such as chlorides, sulfates, nitrates, perchlorates, etc.), the ferric and ferrous ions ratio, the reaction temperature, the pH value, the stirring rate, the dropping speed of basic solution are amongst some. The initial pH of the salt solution can affect the average size of the particles. For values of pH of 0.7 to 4.7, Gnanaprakash et al. observed an increase in the mean size from 6.4 to 9.9 nm. Furthermore, the reaction temperature can affect the formation of impurities during the step of magnetite synthesis by co-precipitation¹⁰⁷.

Once the magnetite nanoparticles are formed, they are consequently oxidized in acidic medium for the formation of cationic maghemite nanoparticles. This oxidation is realized in a mixed medium of $\text{HNO}_3/\text{Fe}(\text{NO}_3)_3$. The nanoparticles are then dispersed in acidic medium. If the nanoparticles are dispersed in a basic medium, the charge is negative. The suspension has electrostatic stability due to the strong repulsive force between charged particles. At the lower pH (acidic condition) and higher pH (alkaline condition), the particles create high surface charge that results in higher zeta potential values. These charges can originate from protonated groups Fe-OH , when the pH is acidic, and from deprotonated groups Fe-OH , when the conditions are alkaline. This condition provides enough electrostatic repulsion force between particles to prevent attraction and collision caused by Brownian motion.

The maghemite NPs were synthesized following the usual Massart's co-precipitation method, as mentioned before. At the end of the synthesis, when the medium is neutral, the point of zero charge exists and thus the nanoparticles have the tendency to aggregate. As a result, the maghemite NPs should be functionalized by different types of ligands for a better stability of the colloidal solution. Some examples include citric or folic acid¹⁰⁸, polymers like PVA¹⁰⁹, PEG¹⁰⁸ or acrylamide¹¹⁰. In this case the iron oxide NPs are functionalized by citrate ions containing carboxylic acid functions. The synthesis route is described in Annex 1. With this synthesis, unsorted maghemite nanoparticles may be easily obtained in high concentrations and large volume.

Sorted maghemite NPs

The sorted maghemite NPs synthesis was carried out by an inverse Massart's co-precipitation method. The difference between this protocol and the one of the unsorted maghemite NPs is based on the order of addition for each reagent. As far as is concerned, herein the iron (II) and iron (III) ions solutions were added dropwise in a solution of ammonia, giving polydisperse $\gamma\text{-Fe}_2\text{O}_3$ NPs. Size sorting step is included for the decrease of polydispersity by adding nitric acid. The ionic strength is increased due to nitric acid and hence leads to the flocculation of the larger and less stable nanoparticles. Then, the precipitated NPs were separated and functionalized by citrate ions, as done for the unsorted maghemite NPs.

Changes over the parameters of the synthesis can bring changes to the size of the synthesized maghemite NPs. During this chapter, two different batches of maghemite NPs were synthesized giving birth to NPs with different diameters (NPs12 nm and NPs9 nm).

II.1.2 Measurement of concentration

The concentration of the different dispersions was verified by flame emission spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Unsorted maghemite NPs

The final concentration of unsorted citrate maghemite NPs was found to be equal to 1 M by flame spectroscopy.

Sorted maghemite NPs

The final concentration of the 9 nm sorted maghemite NPs was found to be equal to 0.84 M and for the NPs12 nm the concentration is equal to 1.98 M.

II.1.3 Size measurement and distribution

The size and the aggregation are two important parameters for the use of MNPs in catalysis, as they affect the specific surface area and the access to the active sites of the catalyst. There are two techniques for the size measurement of the nanoparticles, which are complementary.

Dynamic light scattering (DLS) gives information about the hydrodynamic radius of the nanoparticle in solution. The theory behind DLS states that when a dispersed particle moves through a liquid medium, a thin electric dipole layer of the solvent adheres to its surface. This layer influences the movement of the particle in the medium. Thus, for this work, the hydrodynamic diameter is determined by the inorganic core along with any coating material (in particular the organic PEG chains attached to the surface of the particles) and the solvent layer that surrounds the particle as it moves under the influence of the Brownian motion.

On the other hand, when size is measured by transmission electron microscopy (TEM), the hydration layer is not observed; hence the given information is only about the

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inorganic core. The projected area diameter estimated by TEM is theoretically defined as the area of a sphere having the same area as the projected area of the nanoparticle resting in a stable position. As a result, the hydrodynamic diameter is always greater than the size estimated by TEM.

Ferrofluid samples are never monodispersed and a lognormal distribution P, D for the diameter of the spherical magnetic nanoparticles, is usually assumed:

$$P(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left(-\frac{\ln^2 D/D_0}{2\sigma^2}\right)$$

where σ is the standard deviation and $\ln D_0$ the mean value of $\ln D$. Henceforth, all the iron oxide NPs will be measured by this size distribution. The maximum of $P(D)$ corresponds to a diameter of :

$$D_{mp} = D_0 e^{-\sigma^2}$$

Unsorted maghemite NPs

The synthesized maghemite nanoparticles have a spherical shape and a size measured by TEM of 7 nm with a standard deviation $\sigma=0.3^{65}$. Figure II-2 shows the dispersion in size of the maghemite NPs. Observation by HR-TEM also validated that they are single-domain nanoparticles.

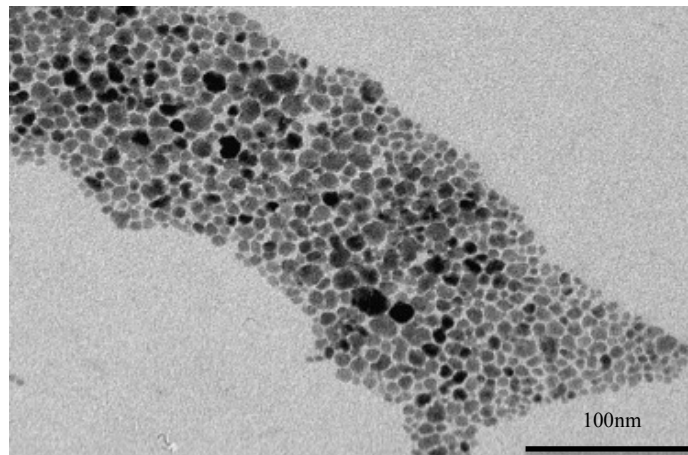


Figure II-2: TEM image of citrate maghemite NPs.

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In comparison, the hydrodynamic diameter measured by DLS is 15 nm. This result shows the hydrodynamic diameter is close to the one measured by TEM, indicating that the NPs show no aggregation.

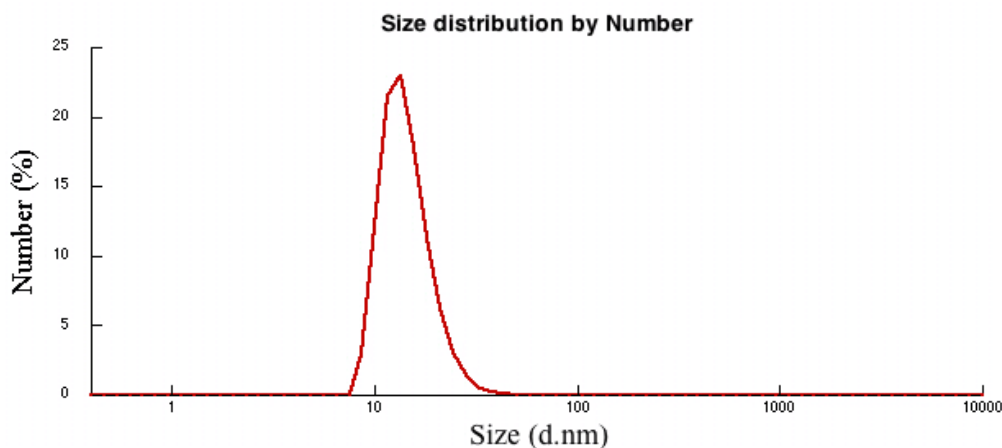


Figure II-3: DLS size distribution by number for maghemite NPs.

Sorted maghemite NPs

The NPs12 maghemite NPs have a size distribution of 11.7 nm with a narrow distribution. Figure II-4 demonstrates a TEM micrograph of the maghemite NPs.

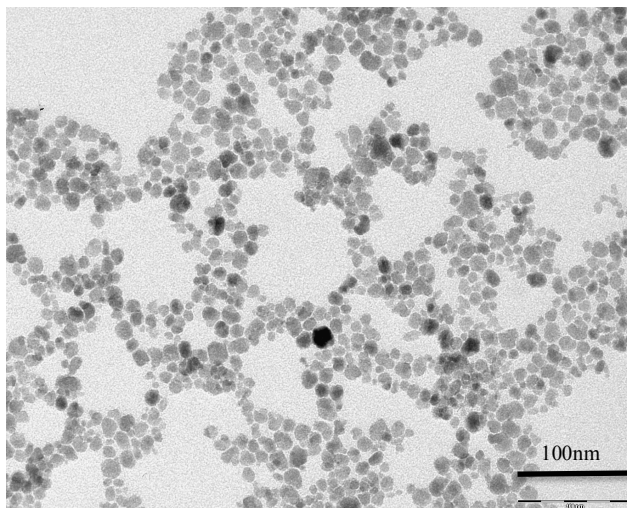


Figure II-4: TEM micrograph of NPs12 γ -Fe₂O₃ NPs.

The NPs9 synthesized maghemite nanoparticles have a spherical shape and their size, as measured by lognormal distribution, is 9 nm. The following Figure II-5 represents a

micrograph of the sorted maghemite NPs, giving information about the monodispersity of the synthesis.

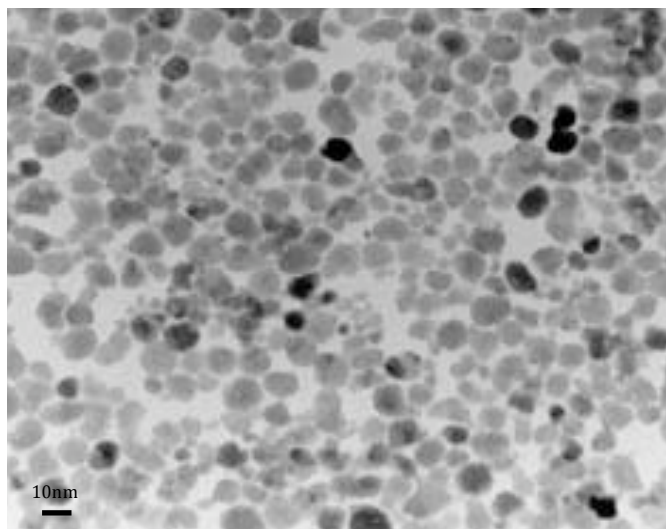


Figure II-5: TEM micrograph of sorted NPs9 γ -Fe₂O₃ nanoparticles.

The hydrodynamic diameter measured by DLS is 15 nm. The value obtained by DLS is similar to the one obtained by the size distribution by TEM, displaying that the ferrofluid is stable without signs of aggregation.

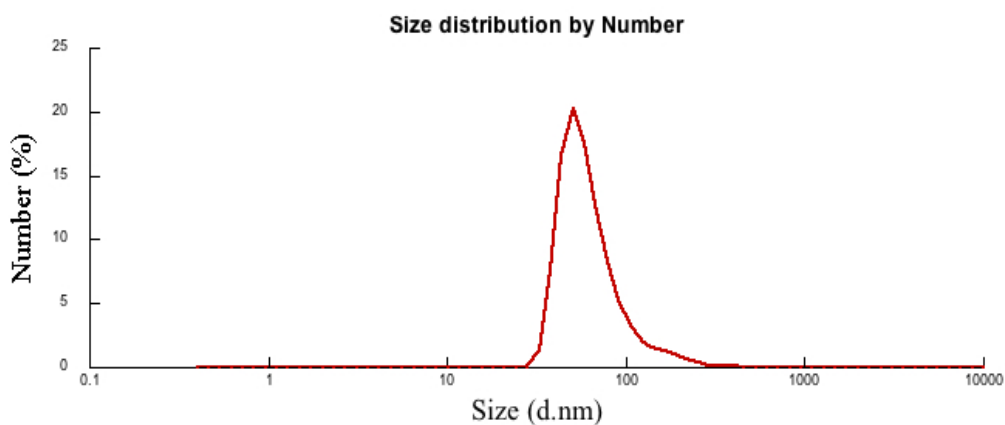


Figure II-6: Size distribution by number for sorted NPs9 maghemite NPs measured by DLS.

II.2 Synthesis of silica shell by sol-gel method and functionalization

A step of covering of the maghemite NPs with citrate ions was followed after their functionalization. This step was carried out by a method of sol-gel^{87,111}.

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The synthesis was carried out in a mixture of ethanol/water (2:1) by condensation of an alkoxy silane, the tetraethylorthosilicate (TEOS). An addition of ammoniac was necessary for the initiation of the condensation in a basic medium. The phase of the silica's shell formation lasted 2 h for the fully and homogeneous coverage of the maghemite NPs, before their functionalization.

In Figure II-7 the schematic representation of the formation of the unsorted maghemite NP/silica shell is described.

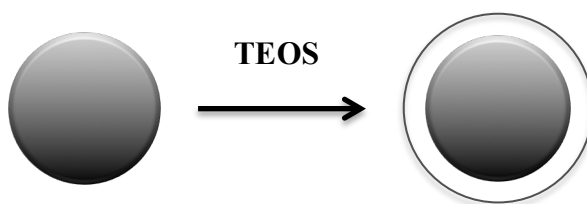


Figure II-7: Synthesis of core-shell NPs ($\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$) in an ethanol/water medium.

Next, the silica shell was functionalized by polyethyleneglycol (PEG) chains and amino groups. Herein, a simultaneous condensation of amino silane and PEG silane derivative compounds, 3-aminopropyltriethoxysilane (APTS) and 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEOS) respectively, with the addition of a small amount of TEOS was achieved. The PEG chains are responsible for the steric stability of the NPs. In addition, the amino groups are enhancing the colloidal stability by electrostatic interactions and they are a good candidate for posterior functionalization. Precisely, the amino groups are protonated in pH equal to 7 as the pKa of primary amines is around 10.

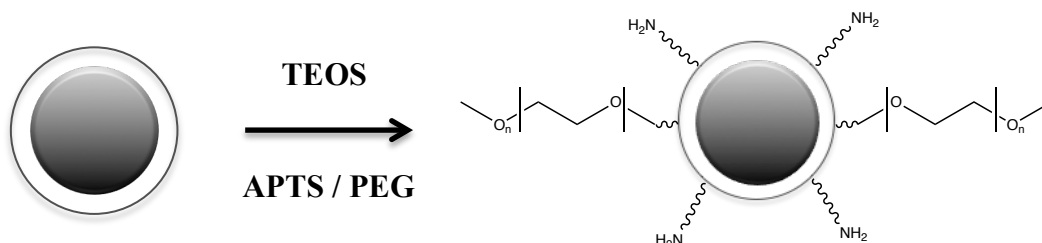


Figure II-8: Functionalization of core-shell NPs ($\gamma\text{-Fe}_2\text{O}_3/\text{SiO}_2$) by PEG chains and -NH_2 functions.

The order of addition of reagents during this step is of high importance. TEOS has to be added first as it has a crucial role during this synthetic step serving as the cross-linker of the silica. Its presence enhances the condensation of the other two organosilanes. APTS must

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be added last as its autocatalytic properties induce a high speed of condensation in comparison with PEOS.

Then, the mixture should be left under stirring for at least 12 h (overnight stirring). In the ethanolic medium the MNPs are colloidally stable. Subsequently, the MNPs were washed by two different ways:

(a) In the first protocol, diethylether was added to the reaction resulting in a precipitation of the NPs, coming from the decrease in the dielectric constant of the medium. The liquid phase was then eliminated and the NPs were washed twice with a mixture of ether/ethanol. The final step involved the core-shell NPs dispersion in acetonitrile, which serves as the solvent for the catalytic studies. Nonetheless, the MNPs were not fully dispersed and precipitation was observed even after several hours of ultrasonication.

(b) Consequently, another way of washing was tested. The MNPs, dispersed in ethanol/water, were transferred into falcon tubes and were centrifuged at 11.000 rpm for 20 min. The liquid phase was eliminated and the NPs were redispersed in absolute ethanol. The procedure was repeated twice and after each centrifugation step, the dispersion was left under ultrasonication for complete dispersion of the NPs. These NPs were finally dispersed in freshly distilled acetonitrile, followed by several minutes of sonication. In this medium, the colloidal suspension is stable for several months at room temperature.

During the different steps, the quantity of organosilanes changes depending on the addition of the different reagents. TEOS contributes with a percentage of 80% in the final quantity of organosilanes (60% after the first step and 20% at the second step of the synthesis); APTS and PEOS have 10% contribution each. The quantity of organosilanes is adjusted according to the total surface of magnetic NPs. Thus, the ratio of mmol Si/m² of these magnetic NPs can be fixed in order to obtain a successful coverage. Some equations that will help clarify the synthesis of the core-shell NPs are presented.

$$Nb\ mole\ Fe = C_{Fe}V$$

$$Nb\ mole\ Fe_2O_3 = \frac{C_{Fe}V}{2}$$

$$m_{Fe_2O_3} = M_{Fe_2O_3} \frac{C_{Fe}V}{2}$$

$$\text{Volume of } Fe_2O_3 = \frac{m_{Fe_2O_3}}{\text{Volumic mass } \rho}$$

$$\text{Nb magnetic NPs} = \frac{\text{Volume of } Fe_2O_3}{V_p}$$

where V_p is the volume of one particle.

$$\text{Total surface of magnetic NPs} = \pi d^2 \cdot \text{Nb magnetic NPs}$$

Core-shell NPs with unsorted cores

For the core-shell NPs with unsorted cores, during the second step, different protocols were also tried concerning the functionalization of the MNPs, having in mind the influence on the grafting of polyoxometalates at their surface and the catalytic properties of the synthesized materials. Each time, the amount of either PEOS or APTS were decreased twofold in order to study the effect on the grafting procedure and the catalysis. However, a decrease in the quantity of PEOS produced an unstable suspension of MNPs and their direct precipitation. This phenomenon was not observed once the quantity of PEOS was kept constant and the quantity of APTS was diminished.

In addition, except from acetonitrile, the MNPs were also dispersed in dimethylformamide (DMF) resulting in stable dispersions. The choice of solvents was done in correlation to the solubility of polyoxometalates, but also with the experimental protocols used for the grafting step of POMs.

The ratio mmol Si/m² should be 0.9 for the total coverage of iron oxide NPs. This coverage rate leads to a ratio of nSi/nFe for the 1st step of the synthesis equal to 6.7. The values are derived from the quantity of TEOS and iron oxide NPs introduced. For the 2nd step quantities of TEOS, APTS and PEOS are added and the ratio of this step is 4.4, thus the final ratio nSi/nFe of the synthesis is 11.1.

Core-shell NPs with sorted cores

The synthesis of the silica shell followed the same protocol concerning the steps to pursue but not the quantities introduced. As mentioned before, two iron oxide NPs were synthesized with different diameters.

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For the NPs12, two protocols were followed for the formation of the silica shell and the functionalization of the core-shell NPs. Referring to the previous arguments, the key parameter for the quantities introduced is the ratio mol Si/m^2 . For the first synthetic route (NPs12-A), a ratio of 0.44 mmol Si/m^2 was tried. This ratio led to $n\text{Si}/n\text{Fe}$ equal to 2.1 for the 1st step and 1.4 for the 2nd one. The final $n\text{Si}/n\text{Fe}$ was 3.5. The second synthetic route (NPs12-B) had a value of 0.87 mmol Si/m^2 . Herein, the value is the same as for the core-shell NPs with unsorted cores but leads to different ratio of $n\text{Si}/n\text{Fe}$. In further detail, after the 1st step for the formation of the silica shell, it was expected to obtain $n\text{Si}/n\text{Fe} = 4.2$ and after the 2nd step the quantities of organosilane introduced attended a value of 2.8 over the quantity of iron oxide NPs. The final ratio is equal to 7.

The different protocols' goal was to optimize the synthetic procedure for the formation of the silica shell. Precisely, as it can be seen for the NPs12-A the value of mmol Si/m^2 was divided by two compared to NPs12-B, for a decrease in the silica's shell thickness.

For the iron oxide NPs with size of diameter 9 nm, only one route was used, with the same value for the core-shell with unsorted cores as it concerns the quantity of Si over the surface of maghemite NPs. As a result, a 0.9 mmol Si/m^2 ratio led to $n\text{Si}/n\text{Fe}$ equal to 5.7 for the 1st step and 3.8 for the 2nd step. The final $n\text{Si}/n\text{Fe}$ is equivalent to 9.5.

As outlined before, the ratios $n\text{Si}/n\text{Fe}$ at the different steps of the synthesis are not the same as the maghemite NPs do not have the same size, even if the ratio mmol Si/m^2 is equal to some cases. The washing procedure was followed as previously described. The MNPs were finally dispersed in acetonitrile. In the following table, the different synthetic routes with the ratios used are presented for a clear image.

	NPs12-A	NPs12-B	NPs9	Unsorted NPs
$[\text{Si}]_f (\text{mmol/m}^2)$	0.44	0.87	0.9	0.88
1 st step $n\text{Si}/n\text{Fe}$	2.1	4.2	5.7	6.7
2 nd step $n\text{Si}/n\text{Fe}$	1.4	2.8	3.8	4.4
Final $n\text{Si}/n\text{Fe}$	3.5	7	9.5	11.1

Table II-1: Synthetic route's values for different maghemite NPs used.

II.2.1 Size measurement and distribution

Core-shell NPs with unsorted cores

The core-shell MNPs have universally a round shape. The average number of maghemite cores per particle is about 3, as counted at over 250 particles. The HR-TEM micrograph in Figure II-9 shows the spherical shape of the core-shell MNPs at the end of the synthesis. The mean diameter is around 47 nm. In this step of the synthetic route, the difference in size between the two techniques is significant. TEM does not take into account the size with the PEG chains, neither any solvation layer. In addition, it has to be mentioned that the size measurement by TEM is obtained at solid state, confirming the differences among these techniques mentioned before.

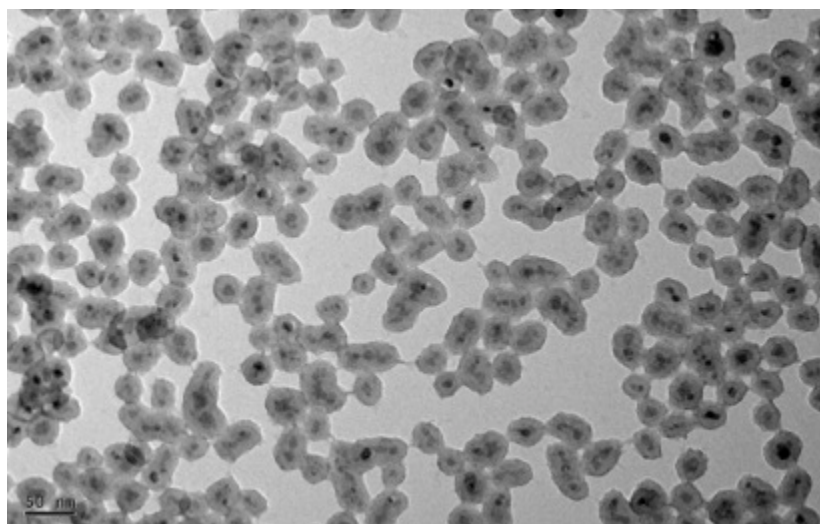


Figure II-9: HR-TEM micrographs of core-shell MNPs with unsorted cores.

The hydrodynamic diameter measured by DLS for the core-shell MNPs proved to have a slight difference for the solvents used for the final dispersion. In other words, for the MNPs dispersed in DMF the mean diameter by number is 50 nm.

When the core-shell MNPs are dispersed in acetonitrile, the mean hydrodynamic diameter is increased in comparison with the core-shell MNPs dispersed in DMF, reaching a size of 90 nm (Figure II-11).

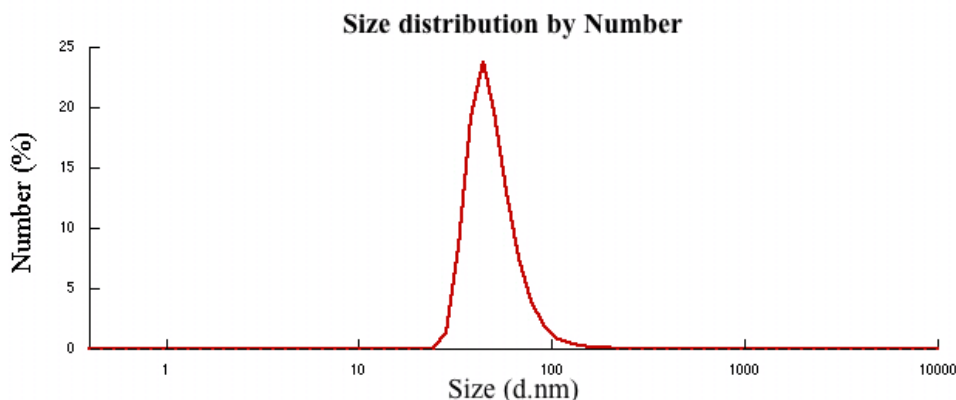


Figure II-10: Size distribution by number, measured by DLS, for core-shell MNPs with unsorted cores dispersed in DMF.

When the parameters of the synthesis are changed, i.e. when the PEG chains or the -NH_2 functions are decreased, there is no change in the average size measured by TEM. Thus, these modifications in the experimental protocols have thus no impact on the formation of the core-shell MNPs, as observed by TEM.

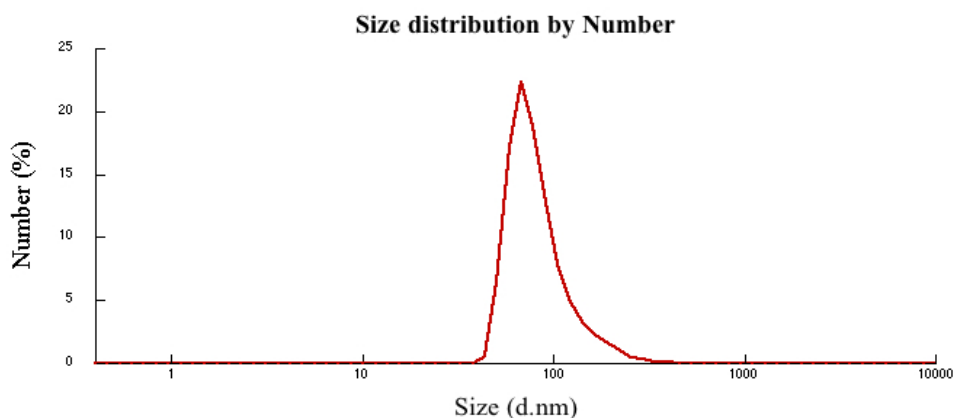


Figure II-11: Size distribution by number for core-shell MNPs dispersed in acetonitrile.

However, DLS is a more sensible technique concerning the changes in the organic functionalization having an influence in the mean hydrodynamic diameter of the core-shell MNPs in solution. The decrease in the quantity of PEG chains can cause alteration on the stability of the dispersion and in further detail the core-shell MNPs are precipitated after several minutes. This effect can also be seen by DLS as the number by intensity and by number is increased drastically compared to core-shell MNPs without modifications.

On the other hand the decrease in the quantity of -NH_2 functions does not alter the mean diameter, as seen by DLS, neither provokes precipitation of the suspension.

Core-shell NPs with sorted cores

The hydrodynamic diameter of the synthesized core-shell MNPs was measured by DLS. The mean diameter for core-shell MNPs with sorted cores of 12 nm diameter is around 40 nm (0.44 mmol Si/m^2) and 160 nm (0.87 mmol Si/m^2) depending on the synthetic protocol followed during the formation of silica shell. The important gap in the hydrodynamic size is due to poor dispersity of NPs12-B in acetonitrile, leading to aggregation.

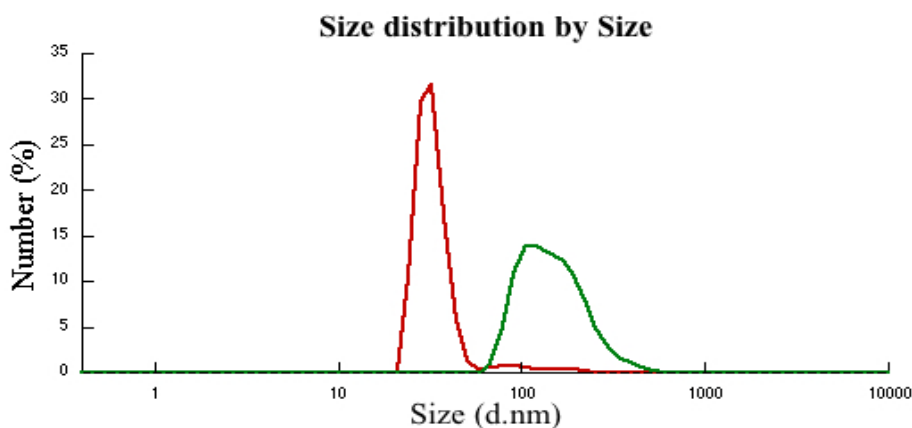


Figure II-12: Comparison of hydrodynamic diameter for core-shell MNPs with sorted cores of 12 nm synthesized by different protocols. Red line for NPs12-A and green for NPs12-B.

The spherical shape of the core-shell MNPs with sorted cores of 9 nm is figured in the TEM micrograph. The mean diameter is around 60nm.

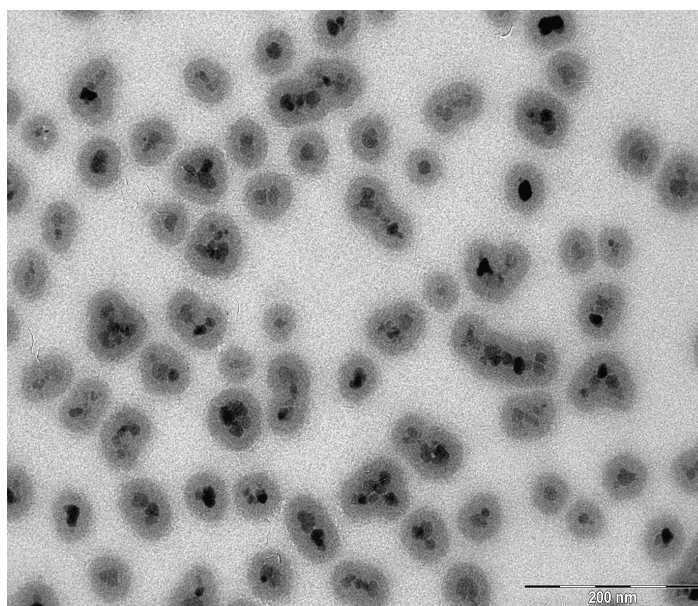


Figure II-13: TEM micrograph of core-shell MNPs with sorted cores of 9 nm.

In Figure IV-5 the hydrodynamic diameter of core-shell NPs with sorted core of 9 nm is presented. The average diameter is 80 nm. As discussed previously, the difference between the two techniques for the size measurement is not important at this stage of the synthesis.

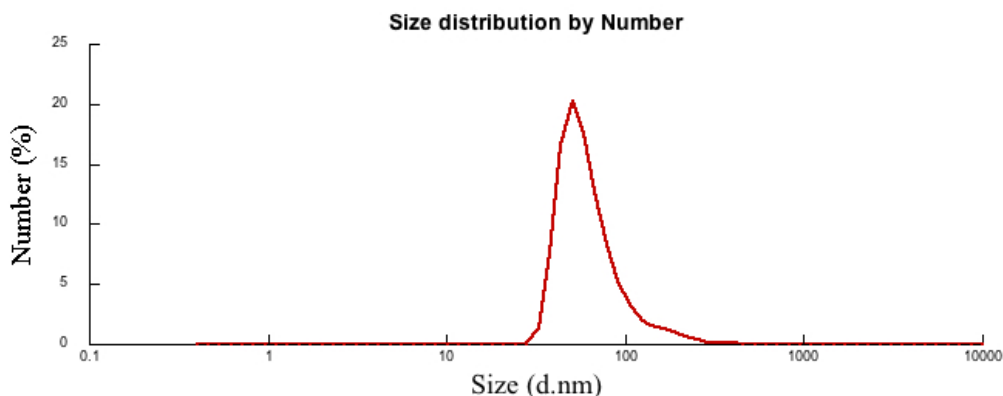


Figure II-14: DLS size distribution by number of core-shell MNPs with sorted cores of 9 nm.

In conclusion, it was demonstrated that the experimental conditions (and particularly the number of moles of Si/m^2) have an important influence on the size of the core-shell nanoparticles as seen from the NPs with core size of 12 nm (NPs12-A). Supplementary, the ratio can strongly influence the aggregation of the core-shell nanoparticles in the organic solvent.

The use of 9 nm maghemite NPs in the following studies was justified by the homogeneous dispersion of the core-shell NPs with synthesized with this type of core. This is indeed an important factor regarding the magnetic properties of the final materials and their further use in catalysis.

II.2.2 Measurement of concentration

The number of core-shell is calculated by dividing the number of magnetic NPs by the number of magnetic NPs found in each core-shell:

$$\text{Number of core shell} = \frac{\text{Nb magnetic NPs}}{\text{Nb of magnetic NPs per core shell}}$$

Core-shell NPs with unsorted cores

Once the maghemite NPs are encapsulated inside the silica shell, the concentration of Fe in the dispersions is in the range of 10^{-2} M, leading to a concentration $3.6 \cdot 10^{17}$ core-shell NPs per L.

Core-shell NPs with sorted cores

After the synthesis of silica shell and the functionalization of the core-shell MNPs, the concentration of Fe for the NPs12 is in the order of $2 \cdot 10^{-2}$ M, giving rise to concentrations of 10^{17} core-shell NPs per L of dispersion.

In regards to NPs9, the concentration of Fe is in the same range as all the other dispersions prepared ($4.5\text{--}7 \cdot 10^{-2}$ M) leading to a core-shell MNPs concentration per L at the range of 10^{18} .

II.2.3 Titration of amine functions

The quantity of -NH_2 functions on the surface is a really important criterion for the covalent grafting of POMs onto the surface of core-shell MNPs. The titration of the -NH_2 functions (introduced after the reaction with APTS) at the surface of the MNPs was performed according to a classical titration technique.

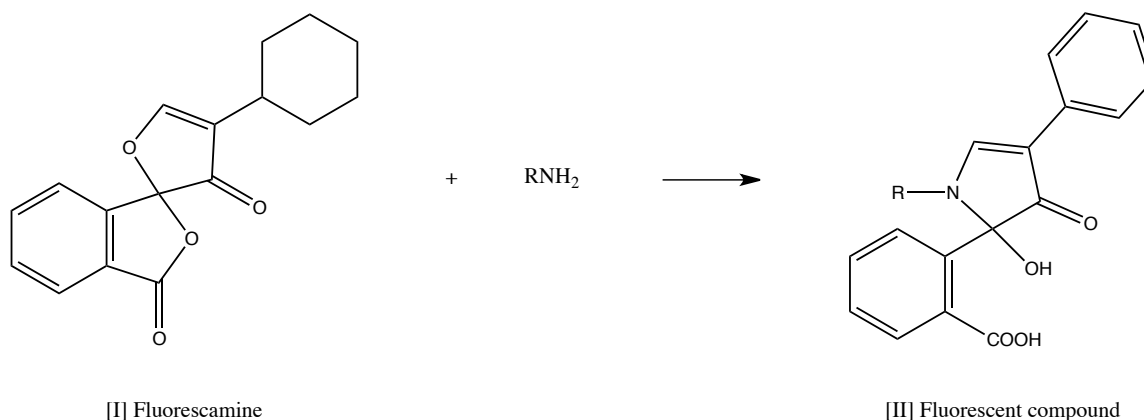


Figure II-15: Reaction of primary amines with fluorescamine.

The technique is based on the reaction of primary amino groups with fluorescamine to form highly fluorescent compounds. These compounds have an excitation maximum at 390nm and an emission maximum at 475 nm.

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For a better understanding of the calculations on the number of $-NH_2$ functions, the equations are essential and they are presented below.

$$Nb \text{ of } -NH_2 \text{ functions} = C_{NH_2} V$$

$$Nb \text{ of } -NH_2 \text{ functions per core shell} = \frac{C_{NH_2} V}{Nb \text{ of core shell NPs}}$$

$$Nb \text{ of } -NH_2 \text{ functions per nm}^2 = \frac{Nb \text{ of } -NH_2 \text{ functions per core shell}}{\text{surface of core shell}}$$

where surface of core-shell = πD^2 , with D the diameter of the core-shell.

Core-shell NPs with unsorted cores

In a typical sample, the $-NH_2$ concentration measured is $3.5 \cdot 10^{-3} \text{ mol L}^{-1}$, corresponding to *c.a.* 6500 $-NH_2$ functions per core-shell or 1 amine function/ nm^2 .

Core-shell NPs with sorted cores

In a typical sample of core-shell NPs with cores of 9 nm, the concentration of $-NH_2$ functions is $6 \cdot 10^{-3} \text{ mol L}^{-1}$, corresponding to *c.a.* 6000 functions per core-shell.

III Synthesis and characterization of POMs-decorated core-shell MNPs

III.1 Synthesis of POMs-decorated core-shell MNPs

III.1.1 Covalent grafting of POM-COOH with functionalized core-shell MNPs

The covalent grafting of hybrid of POMs onto the surface of core-shell MNPs was realized according to the strategy used in the previous chapter for the heterogenization of POMs onto the surface of mesoporous silica, by coupling complementary functions on the support and the POMs. In the present case, a reaction occurs between propylamine groups found at the surface of silica shell of the MNPs and carboxylic functions on the termination of the organic groups introduced in the POMs framework.

The POM used is the same as mentioned before for the grafting with amino-functionalized SBA-15 (Chapter 1) and it is the bis-phosphonyle derivative ($^n\text{Bu}_4\text{N}$)₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂] or TBA₃NaH(POM-COOH), containing two independent acid carboxylic functions.

As indicated before, silica coated maghemite NPs are generally prepared in aqueous media because of their use in biological applications. However, during this work, these NPs had to be stabilized in organic media since the coupling reaction between amine and carboxylic acid functions was carried out in dry organic solvents, as acetonitrile or DMF.

Once stable suspensions of core-shell MNPs were obtained in acetonitrile or DMF, POMs were then covalently immobilized at the surface of the MNPs. The formation of the amide bond was ensured using isobutyl chloroformate, in the presence of triethylamine for the deprotonation of carboxylic acid functions found on POMs. The protocol was adapted from the previous chapter, and POMs are in excess compared to the protocol used before. A second round of the grafting procedure was carried out in order to verify if the percentage of grafting could be increased.

III.1.2 Electrostatic deposition of POM-COOH onto functionalized core-shell MNPs

For a better understanding and characterization of the covalent bond between POMs and the core-shell MNPs, a synthesis with POMs electrostatically deposited on the surface of MNPs was performed. During this synthesis, isobutyl chloroformiate and triethylamine were not used and POMs were added in the colloidal dispersion of NPs and were left being stirred for some days before proceeding to washing by centrifugation. Finally, POMs were dispersed in acetonitrile or DMF.

III.2 Characterization techniques

III.2.1 High-Resolution Transmission Electron Microscopy (HR-TEM)

POM-COOH core-shell NPs with unsorted cores

After the grafting method, the presence of POMs onto the surface of the MNPs had to be verified. Firstly, the samples of POMs-decorated MNPs were observed by classical TEM in order to confirm that the synthetic route for the grafting did not alter the intrinsic structure of the MNPs, even by the presence of triethylamine. The shape of the MNPs remained spherical and no transformation in the silica shell was detected (Figure III-1).

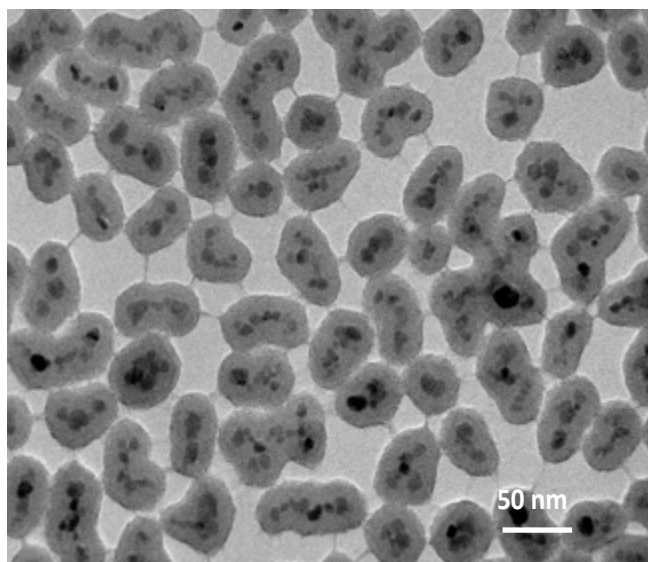


Figure III-1: TEM micrograph of POMs-decorated MNPs.

In a second time, POMs were localized in both MNPs suspensions (after covalent or electrostatic interactions) at different steps of their synthesis, by High Resolution Transmission Electron Microscopy (HR-TEM).

The main comparison that had to be made was before and after the washing procedure. The washing is a crucial step for the catalytic application. It can also be an indirect proof of covalent grafting or electrostatic deposition, by performing elemental analysis after each step. The washing was carried out by centrifugation at 10.000 rpm during 20 min in acetonitrile.

In Figure III-2, POMs-decorated MNPs are presented before the washing step. In this micrograph, POMs can be directly observed in the sample. Clearly, POMs are easily detectable by TEM because of the high electrons density of W atoms, as small isolated black dots. However, POMs are visible not only on the surface of the MNPs but all around and in between them. This result apparently indicates that, before the washing step, a quantity of POMs that has not reacted can be found in the sample solution, outside of the core-shell MNPs surface.

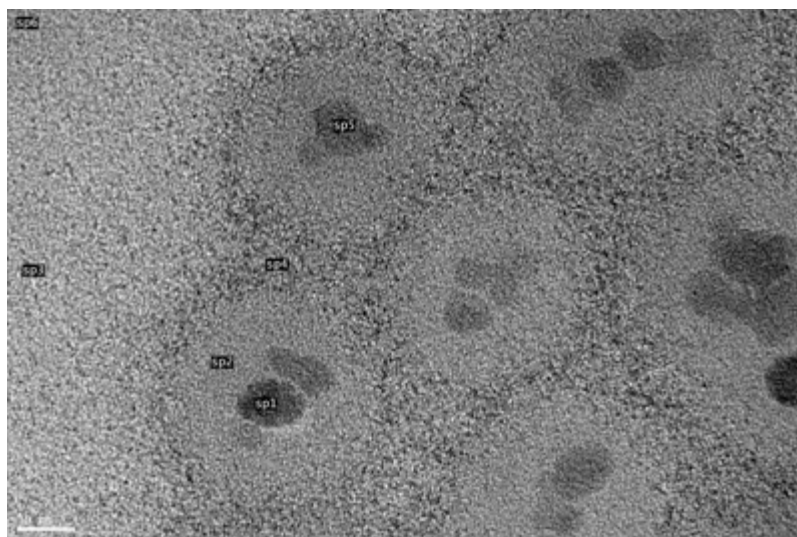


Figure III-2: HR-TEM micrograph of POMs-decorated MNPs before washing steps. Zones sp1 to sp6 are the zones where XEDS was performed.

The sample was also characterized by X-ray Energy Dispersive Spectroscopy (XEDS) for the examination of the elemental analysis of the samples in different areas of the sample. In Figure III-2, zones sp1, sp2, sp5 correspond to the surface of these MNPs whereas zones sp3, sp4 and sp6 are the ones outside of the grafting area. As seen from the XEDS spectra corresponding on the zones sp3 and sp4 an important quantity of W can be detected outside the surface of the MNPs (Figure III-3). Consequently, XEDS confirmed the presence of POMs, with the presence of W atoms, in the integrity of the sample, even far from the surface of the POMs-decorated MNPs.

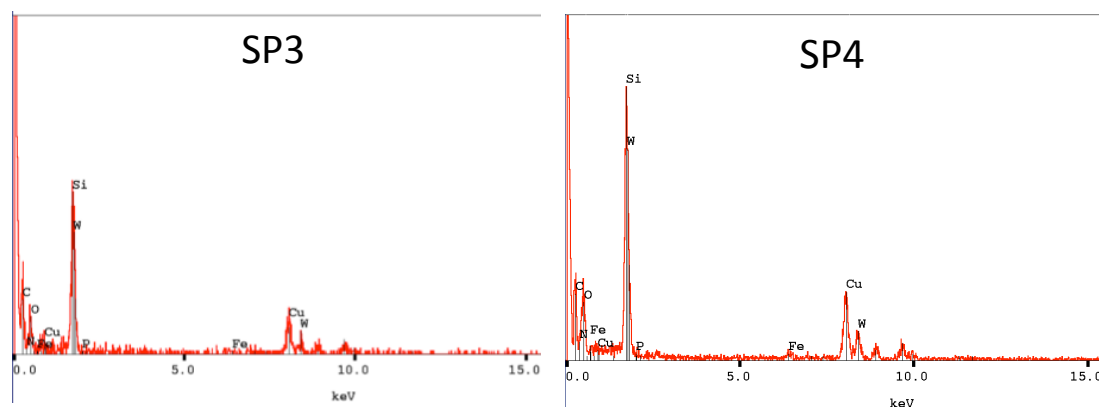


Figure III-3: XEDS spectra for zones sp3 and sp4 of a dispersion of POMs-decorated MNPs before washing.

In regards to these results, washing of the dispersion of MNPs appeared as an imperative step towards an optimized synthetic route. Washing was carried out by centrifugation of the sample for 20 min at 10.000 rpm and repeated three times. In Figure III-4, the vanishing of the ungrafted POMs from the dispersion of MNPs can be seen. After completing centrifugation twice, the black dots corresponding to POMs are to be found only on the silica shell. Thus, the ratio of Fe/W was found in the range of 1.60-2.84, for different experimental conditions followed (average value 2.2 ± 0.5).

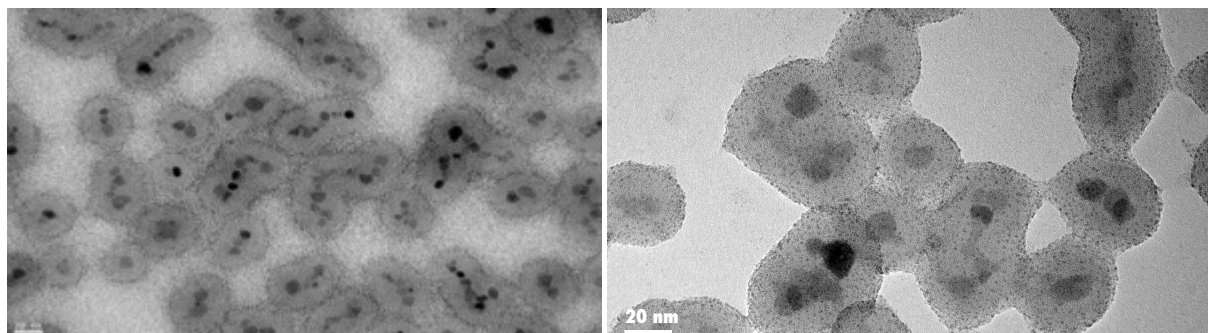


Figure III-4: HR-TEM micrographs of POMs-decorated core-shell MNPs with unsorted cores before and after washing by centrifugation.

In addition, after the centrifugation, POMs still exist on the surface of the MNPs, validating that the covalent binding strategy seems to be successful. Hence, they are strongly grafted on the surface of the MNPs to not be easily removed by leaching.

In parallel, to confirm this result, samples were studied in which POMs were electrostatically deposited onto MNPs, dispersed in DMF or CH_3CN . These samples were treated with the same washing procedure as the previous samples (centrifugation at 10.000 rpm for 20 minutes, repeated twice).

The resulting suspension of electrostatically deposited POMs-MNPs was then observed by HR-TEM. As seen from micrograph III-5, the distribution of the POMs onto the surface is less homogeneous compared to the covalent grafting strategy. However, it was found by XEDS that the W content of these samples was dependent upon change of the solvent. Indeed, the solvent that the MNPs are dispersed into, has an important role in an effective linkage of POMs. In DMF, a solvent more polar and dissociating than acetonitrile, the Fe/W ratio is higher than in acetonitrile after 3 several washing steps. The corresponding values are 5.17 for the dispersion in DMF and 1.83 for the MNPs dispersed in acetonitrile. In acetonitrile, the difference between the covalent and the ionic samples is not as obvious as expected. However, a slow decrease of the W contents after each additional washing step was detected. One explanation for such a relatively high content of POMs in the case of electrostatically grafted samples, could be due to the presence of PEG chains. Indeed, it has recently been shown that specific multipolar interactions between PEG chains and POMs are generated, and that these interactions can lead to the formation of POMs-PEG nanoassemblies stabilized by electrostatic repulsions between the negatively charged POMs in water¹¹².

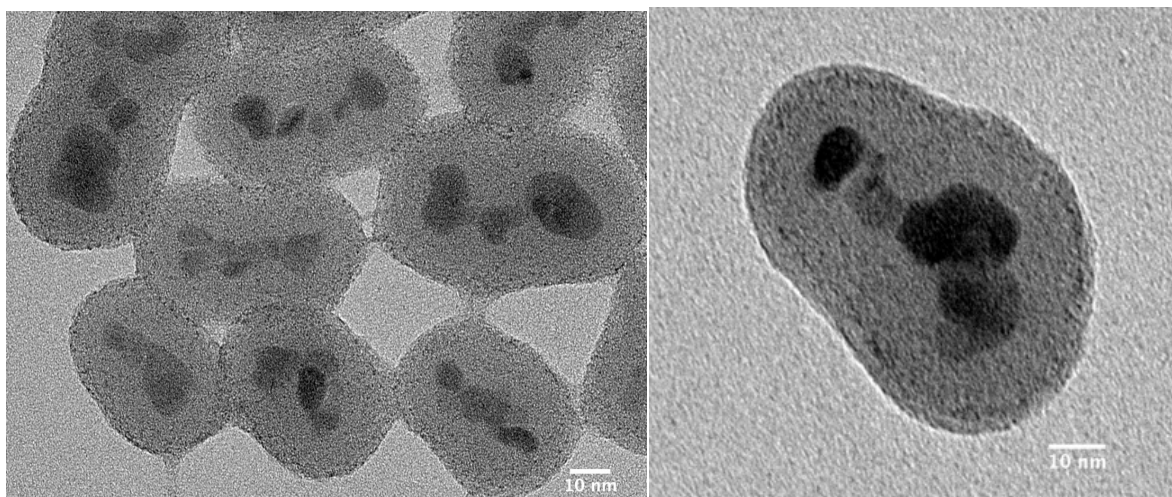


Figure III-5: HR-TEM micrographs of core-shell MNPs with electrostatically deposited POMs.

The concentrations of Fe and W were also measured by XEDS after each step of the washing process. Firstly, the initial dispersion of a typical sample was analyzed and the ratio Fe/W was found 0.5. Following this, the ratio was 1.15 and 1.71 with 3 or 6 washing steps respectively. Even with additional washings by centrifugation, the ratio was not significantly altered as expected for a covalent grafting.

For the samples containing core-shell MNPs with electrostatically deposited POMs, dispersed in acetonitrile, XEDS was performed at the same points of the synthetic procedure. A decrease in the concentration of W is detected after each washing step emphasizing the importance of the covalent grafting for the hybrid materials synthesized and their ulterior use in catalysis.

POM-COOH core-shell NPs with sorted cores

The HR-TEM micrographs were taken after the washing steps in order to eliminate the non-grafted POMs that are still in solution. Figures III-6 and III-7 show the magnification of a POMs-decorated core-shell MNP obtained with respectively the NPs12 and NPs9 sorted maghemite cores. In the following micrographs POMs, can easily be detected and are represented by black dots.

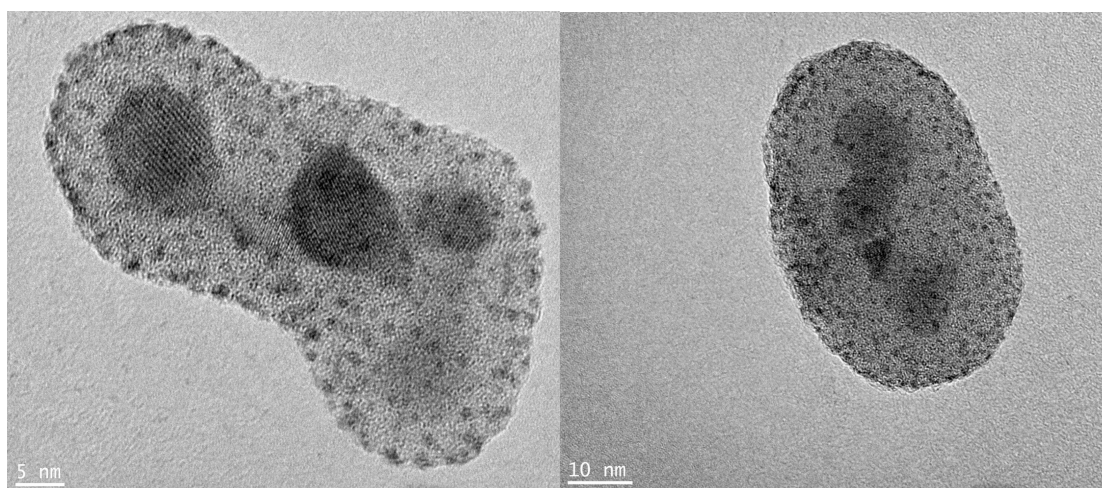


Figure III-6: HR-TEM micrographs of POMs-decorated core-shell MNPs with sorted cores of 12 nm. Left micrograph for NPs12-A and right micrograph for NPs12-B.

Different information can be extracted from the following HR-TEM micrograph. Firstly, the lattice fringes of the maghemite domain can be observed, regardless of the batch of maghemite used, confirming that each core corresponds to a single paragraph. In addition, in this magnification, POMs can easily be detected and represented by black dots. The size of these black dots, *i.e.* POMs, could be measured and it was found to be equal to 1.0 nm. This size conforms to the size of an isolated POM and not aggregates. Finally, the aggregation state of the core-shell NPs did not have any apparent effect on the grafting efficiency of POMs. Hence, the black dots are regularly distributed over the whole surface of the MNPs, leading to considerable coverage of the MNPs by POMs.

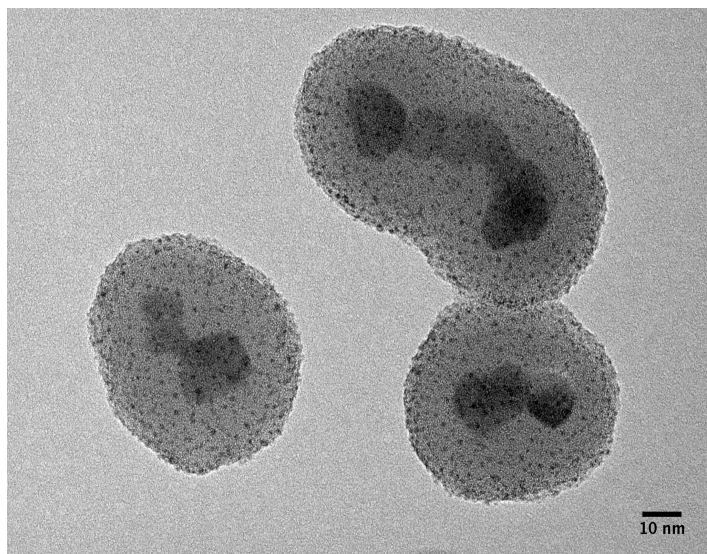


Figure III-7: HR-TEM micrograph of POMs-decorated core-shell MNPs with sorted cores of 9 nm.

III.2.2 Size measurement

POM-COOH core-shell NPs with unsorted cores

This outcome is in agreement with the results after the size measurement by TEM. The average diameter, in the case of POMs-decorated core-shell MNPs, is 47 ± 8 nm based on the count of an assembly of 120 MNPs (Figure III-8).

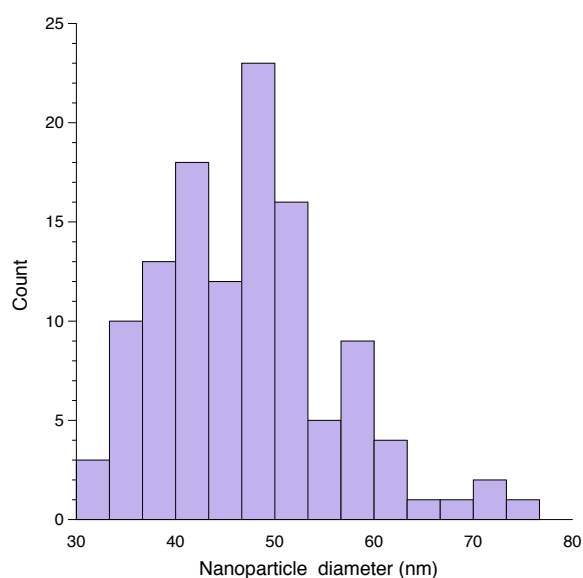


Figure III-8: Size histogram for POMs-decorated MNPs with unsorted cores, counted by TEM.

A better analysis of the result can be provided if the size of POM is taken into account. The approximate size of $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}]^{17}$ is 1.8 nm, measured using X-ray diffraction data.

In the following Figure III-9, the hydrodynamic size of POMs-decorated MNPs is demonstrated. The hydrodynamic size of the MNPs, measured by DLS, does not present a significant difference after the grafting of POMs. The average diameter before and after grafting is around 90 nm with a good polydispersity index.

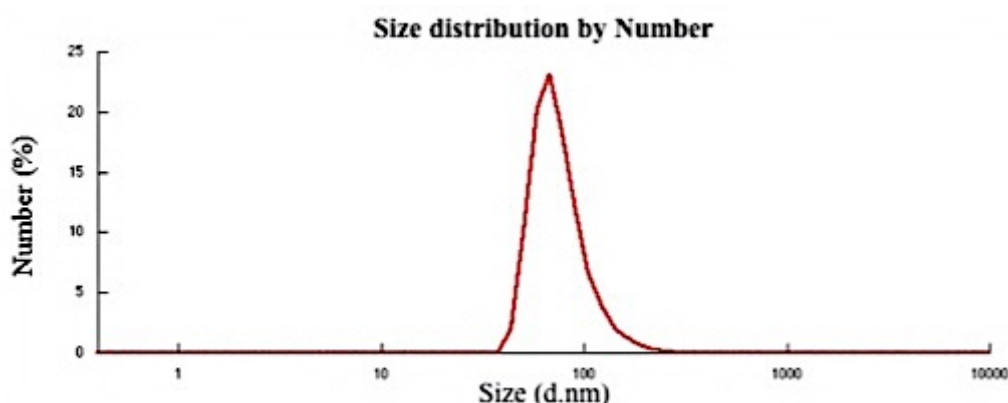


Figure III-9: DLS size distribution by number for POMs-decorated MNPs with unsorted cores dispersed in acetonitrile.

Finally, a comparison on the effect of the organic solvents used for the final dispersion on the size of the POMs-decorated core-shell NPs is made (figure III-10). The difference is not so significant, as the POMs-decorated MNPs in DMF have a size of 60 nm and the ones dispersed in acetonitrile are slightly larger, with a diameter of 90 nm. This difference is due to signs of slight aggregation when the hybrid materials are dispersed in acetonitrile.

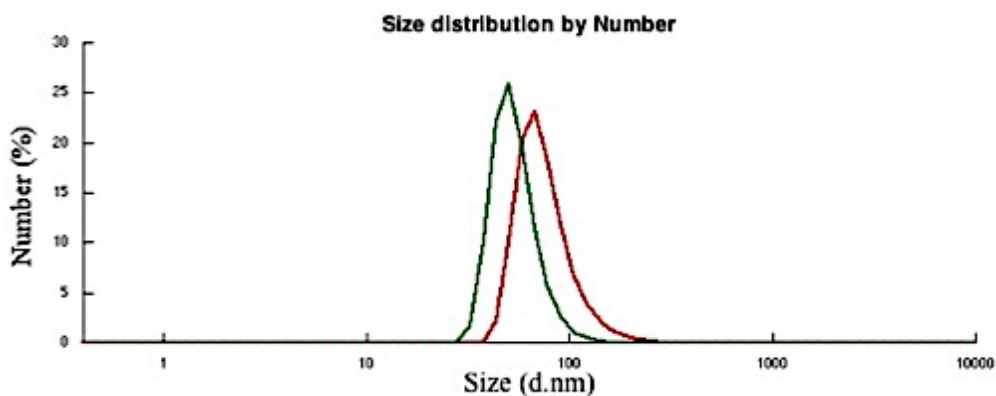


Figure III-10: Comparison of hydrodynamic size between POMs-decorated MNPs dispersed in DMF (green) and acetonitrile (red).

POM-COOH core-shell NPs with sorted cores

When it comes to size measured by TEM for the POMs-decorated MNPs with sorted cores of 9 nm, the average diameter is 56 ± 12 nm as shown on the size histogram, resulting from measuring 230 particles.

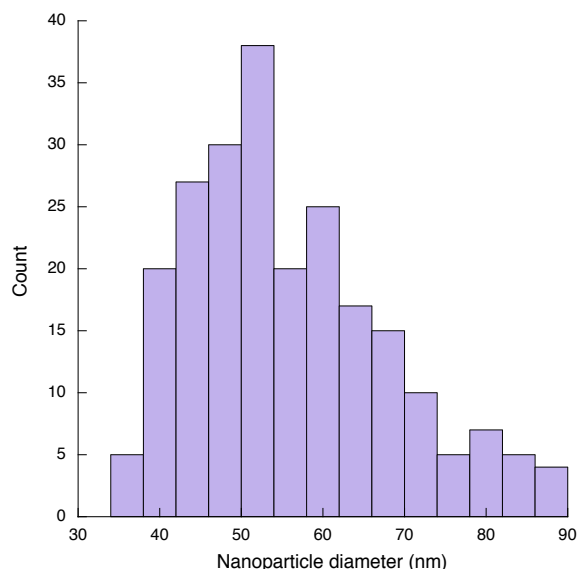


Figure III-11: Size histogram for POMs-decorated core-shell MNPs with sorted cores of 9 nm.

The POMs-decorated core-shell MNPs with sorted cores, of 12 nm however, present an interesting behavior concerning their hydrodynamic size. Before the POMs grafting, the two different protocols used for the synthesis gave core-shell NPs with a large difference in the size.

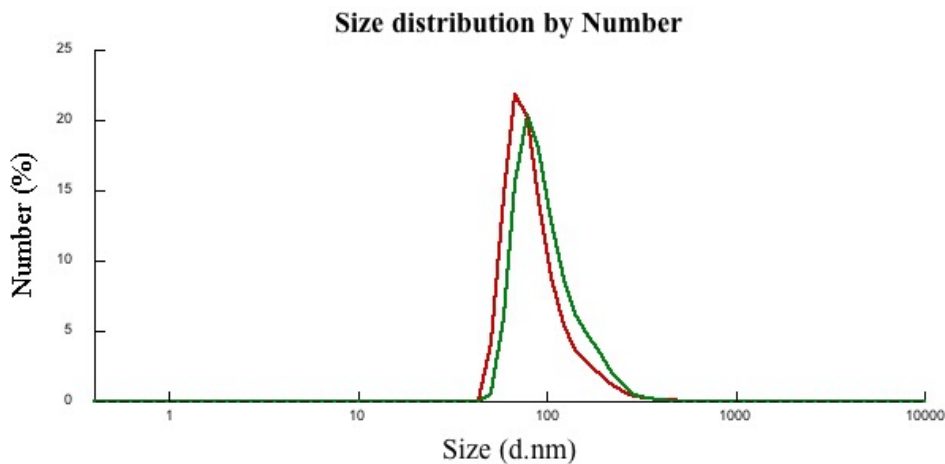


Figure III-12: POMs-decorated MNPs with sorted cores of 12 nm, synthesized by different protocols (red line MNPs NPs12-A and green line NPs12-B).

Nonetheless, this difference on the size shows to decrease significantly leading to magnetic NPs with similar size, indicating that when POMs are grafted on the surface the core-shell NPs are better dispersed in acetonitrile.

In Figure III-13, the hydrodynamic size of the core-shell MNPs with sorted cores (NPs9) is compared to the size of the POMs-decorated MNPs. As indicated, the difference before and after the grafting of POMs is not so significant, as after grafting the POMs-decorated MNPs have a mean diameter of 110 nm.

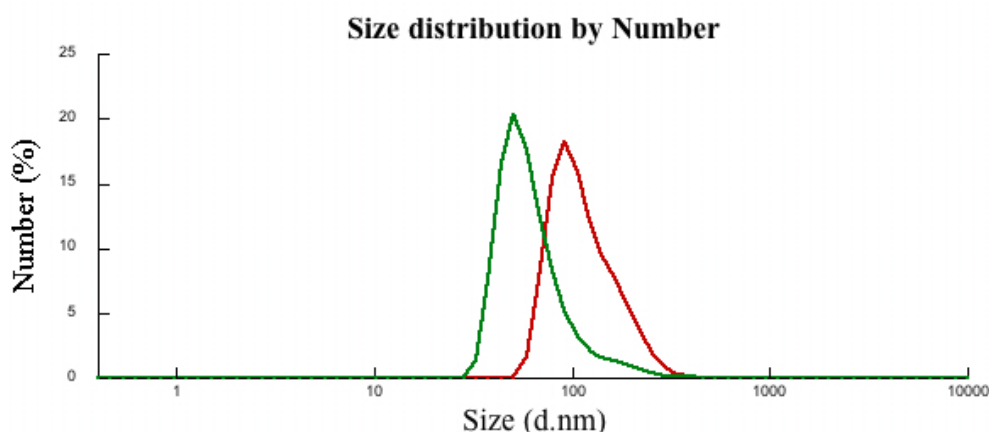


Figure III-13: Comparison of hydrodynamic size before (green line) and after (red line) grafting of POMs on the surface of core-shell MNPs.

However, both dispersions of core-shell NPs12-A and NPs12-B were not stable over time, unlike to core-shell NPs9 that showed no aggregation for several months. As a result, the studies that are to follow will be concentrated only at MNPs with core size of 9 nm.

III.2.3 Quantification of polyoxometalates on the surface of core-shell MNPs

After the size measurement by TEM, an important task had to be completed for a global characterization of the synthesized materials, *i.e.* the quantification of POMs grafted onto the surface of core-shell MNPs. The quantification was possible by performing XEDS and ICP on the samples under study.

POM-COOH decorated core-shell NPs with unsorted cores

By calculating the ratios of Si/Fe and Fe/W by XEDS, different conclusions can be drawn:

Part 2: Immobilization of hybrids of Polyoxometalates on magnetic core-shell nanoparticles

- In regards to the Si/Fe, by EXDS, the ratio was measured to be 7.9 (average value on 15 different samples). This value is lower than the initial ratio of 11.1, following the introduction of different reagents during the synthesis of core-shell MNPs ($n_{\text{TEOS}} + n_{\text{PEOS}} + n_{\text{APTES}}$)/ n_{Fe} . This result can be probably explained if grains of silica are formed but eliminated during the washing steps. By ICP the same ratio has a value of 9.9.
- The ratio Fe/W on the other hand by EXDS was found 2.2 after several washing steps. The initial ratio of Fe, originating from maghemite NPs, over W, originating from POM-COOH introduced, was equal to 0.5. These values can give an estimated grafting rate of POMs onto the surface of core-shell MNPs of 20%.

The results coming from the XEDS and ICP measurements can be used for the composition of POMs-decorated MNPs. Knowing the average diameter of the maghemite NPs (7 nm), the average number of cores in each core-shell MNPs (3 cores/ NP) and the ratio Fe/W, the coverage of MNPs by POMs can be calculated. The average number of POMs grafted on the surface is calculated at around 1250 POMs per MNP. For these calculations, the necessary equations are presented.

Knowing the ratio $C_{\text{Fe}}/C_{\text{W}}$ and the concentration of Fe, the concentration of W can be extrapolated. As a result:

$$\text{Nb of } W = C_{\text{W}}V \quad (1)$$

$$\text{Nb of POMs} = \frac{\text{Nb of } W}{9} \quad (2)$$

$$\text{Nb of POMs per core shell} = \frac{\text{Nb of POMs}}{\text{NB of core shell}} \quad (3)$$

In order to have an accurate image of the compactness of the surface, an approximate calculation of the maximum number of POMs that can be immobilized on the silica shell was performed. The MNPs are spherical with a mean diameter equal to 47 nm, giving rise to an available surface of 6940 nm². As mentioned before, the crystal structure of the polyoxometalate used for the grafting indicates a surface of 1.8 nm². Likewise, collision cross-section values, obtained by Travelling Wave Ion Mobility-Mass Spectroscopy (TW-IM-MS), for tetrabutylammonium salts of classical and hybrid POMs are generally in the range of 2.0-2.5 nm². Assembling all this information, a full coverage of the surface can be achieved

by grafting between 2800 to 3500 POMs per NP. Concluding, POMs cover up to 45% of the surface, leading to a pretty good coverage. Assuming that the majority of POMs are linked through only one amide function, as demonstrated previously on the mesoporous SBA-15 supports, 20% of the $-NH_2$ functions of the NPs are occupied.

POM-COOH core-shell NPs with sorted cores

As already discussed for the POMs-decorated core-shell MNPs with unsorted cores, the same procedure has to be realized for the quantification of POMs onto the surface of the core-shell MNPs with sorted cores (NPs9).

The calculations are based similarly in XEDS and ICP measurements for the ratios of Si/Fe and Fe/W.

- The Si/Fe, measured by XEDS, was found equal to 7.9 (average value). The initial theoretical ratio is 9.5 taking into account the different reagents containing Si. The explanation proposed related to organosilanes not reacted and eventually washed and eliminated at the end of the synthesis.
- For the Fe/W the results give rise to a ratio of 5.1.

The maximum number of POMs arranged onto the surface has to be calculated, as to obtain a rough idea of the POMs density. The mean diameter of these MNPs is equal to 56 nm with a maghemite core of 9 nm diameter. Hence, the available surface area for grafting is 10.000 nm^2 . Taking into account the size of the POMs, the maximum number that can be distributed on the silica shell is 5000 POMs per NP. By the ratio obtained, each NP is covered with a maximum of 1000 POMs, which can be converted to a 28% of grafting yield. Thus, 20-25% of the surface is covered by POMs, depending on the surface of the POMs for the calculation (2-2.5 nm), resulting in a satisfactory result.

III.2.4 X-ray Photoelectron Spectroscopy (XPS)

POM-COOH decorated core-shell NPs with unsorted cores

Photoelectron spectroscopy utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of the sample. For each and every element, there will be a characteristic

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binding energy associated with each atomic orbital. In other words, each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies, therefore, indicates the presence of a specific element in the sample under study. Furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique can also provide a quantitative analysis of the surface composition.

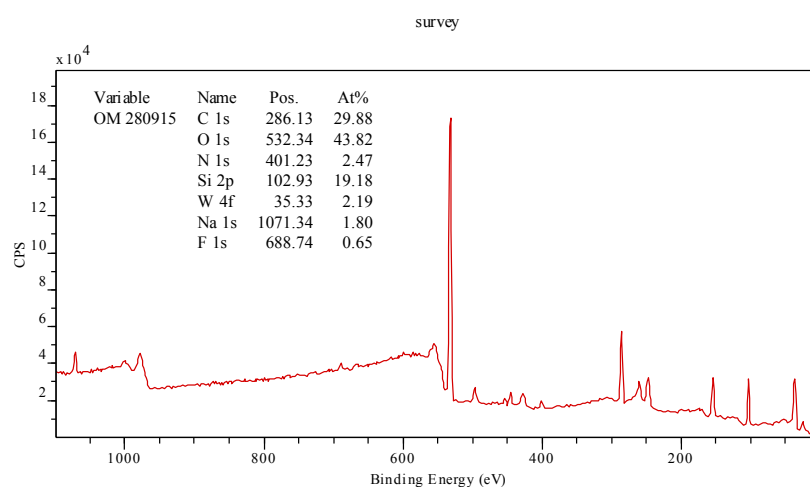


Figure III-14: Full XPS spectrum of POMs-decorated MNPs with unsorted cores.

The XPS spectrum of POMs-decorated MNPs was recorded on a solid sample, prepared by drying a suspension of the latter MNPs.

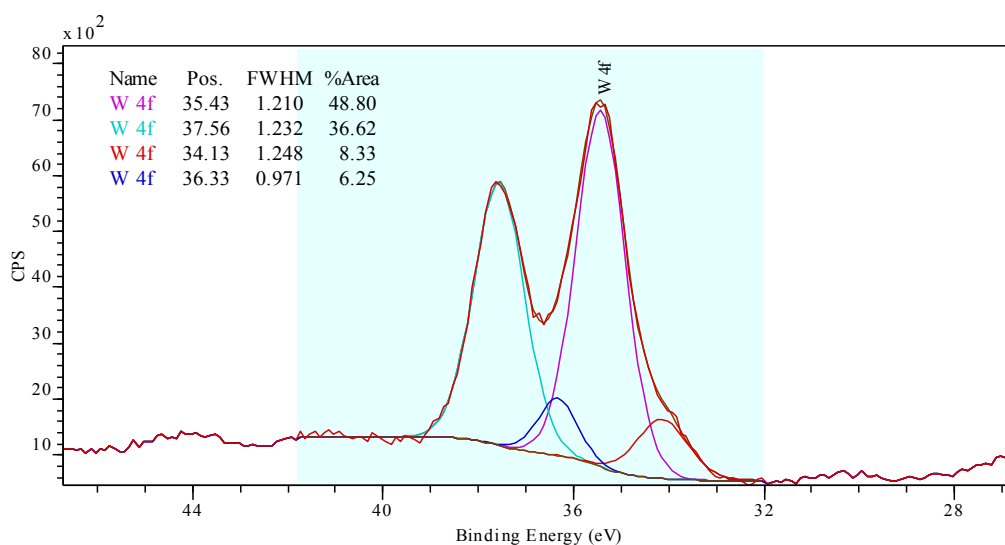


Figure III-15: High resolution W4f spectrum of dried POMs-decorated MNPs.

The high-resolution W4f, Si2p and N1s spectra are illustrated in Figures III-15, III-16 and III-17 respectively.

The W4f peak is composed of a well-resolved spin-orbit doublet (35.4 eV and 37.6 eV for W4f_{7/2} and W4f_{5/2} respectively), typical of W^{VI} atoms as described in literature for the Keggin-type POMs^{113,114}. In addition, the W4f peak displays additional contributions observed at 34.1 eV and 36.3 eV that can be attributed to a partial reduction of tungsten under X-ray irradiation, during the measurement.

The region that corresponds to Si2p of the sample gives rise to a peak at 102.9 eV characteristic of the Si-C bonds of APTS used for the functionalization of the surface. The presence of Si^{IV} sites originated from the SiO₂ of the silica shell should be expected at 104 eV. However, it is worth pointing out that in the present spectrum this peak cannot be distinguished. Equally important to note is the difficulty of identifying the peaks corresponding to Fe, due to the increased thickness of the silica shell covering the maghemite particles.

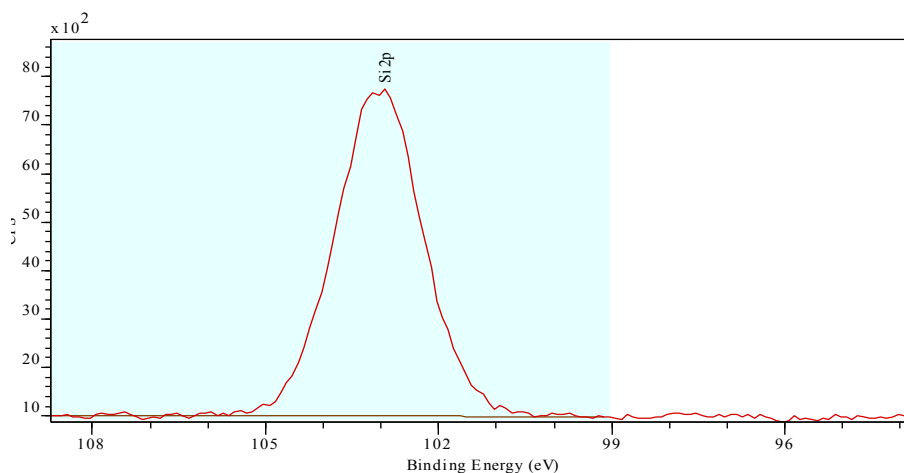


Figure III-16: Si2p XPS spectrum of POMs-decorated MNPs with unsorted cores.

In Figure III-17, two peaks can be detected in the region of N1s of the XPS spectrum, the first at 401.5 eV and the second at 399.6 eV. The first peak is attributed to ammonium ions. Two types of ammonium ions are expected in the POMs-decorated MNPs sample, tetrabutylammonium and triethylammonium ions. Owing to the use of triethylamine for the deprotonation of the carboxylic functions of POM-COOH during the grafting step, the presence of triethylammonium ions is expected. The latter peak of the XPS spectrum can be associated to the propylamine functions covering the MNPs.

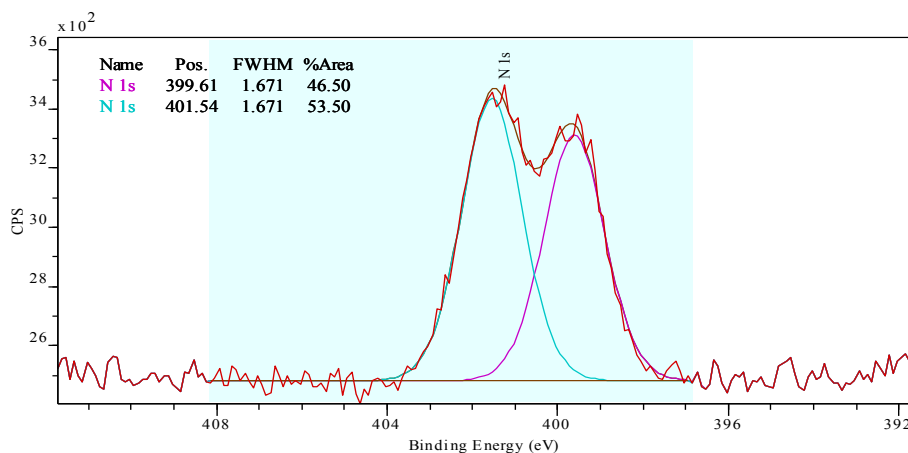


Figure III-17: High resolution N1s spectrum of dried POMs-decorated MNPs.

An important piece of information expected from this technique would have been the characterization of the covalent bond between the POMs and the functionalized MNPs, *i.e.* the observation of the peaks corresponding at N atoms at the amide bonds. However, the identification of these functions turned out unsuccessful as they are generally localized at energies around 400 eV, energy corresponding to simple amine groups that cover the surface.

III.2.5 Diffuse Reflectance Infra-Red Fourier Transform Spectroscopy (DRIFT)

POM-COOH decorated core-shell NPs with unsorted cores

The DRIFT spectrum of POMs-decorated core-shell MNPs with unsorted cores was recorded in a solid sample as mentioned for the XPS studies. As seen from the next Figure III-18, the spectrum was compared to those of POM-COOH and of core-shell MNPs before the grafting procedure.

Initially, the ATR spectrum of the hybrid synthesized material was recorded. However the result was not instructive as the sample is not concentrated enough in order to give results that could be useful. Hence, DRIFT was considered as an ideal solution.

The bands of maghemite NPs at low energy dominate both the spectra of the bare core-shell MNPs and POMs-decorated core-shell MNPs (peaks at 695 cm^{-1} , 635 cm^{-1} and 560 cm^{-1}). In addition, broad and intense peaks can differentiate the silica shell at 805 cm^{-1} , 950 cm^{-1} and at 1090 cm^{-1} .

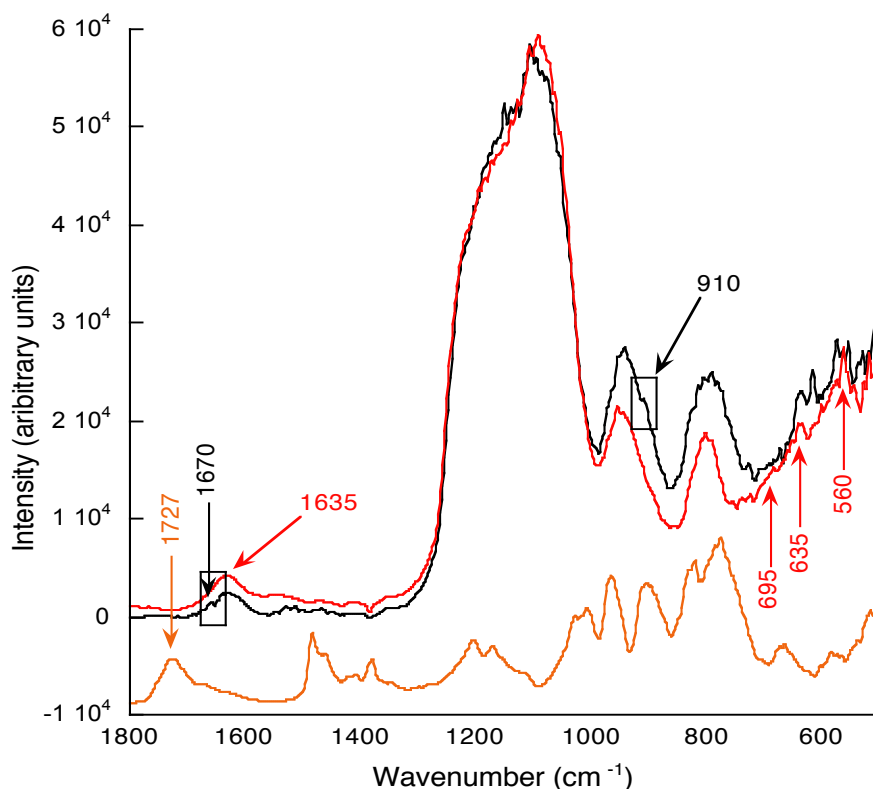


Figure III-18: Comparison of DRIFT spectrum of POMs-decorated core-shell MNPs (black) with those of core-shell MNPs (red) and of TBA₃NaH(POM-COOH) (orange).

Above all, the presence of POMs can be recognized by a more attentive comparison of the two spectra. The intensity and the width of the bands at 805 cm⁻¹ and 950 cm⁻¹ are increased in the case of POMs-decorated core-shell MNPs. Taking in consideration the DRIFT spectrum of TBA₃NaH(POM-COOH), the explanation can be derived by the superimposition with the most intense bands of the POMs (peaks at 965 cm⁻¹ and 780 cm⁻¹). Beyond the latter peaks, in all the spectra of POMs-decorated MNPs recorded, a shoulder at 910 cm⁻¹ can be noted. Thus, this band is certainly attributed to one of the $\nu(\text{W}=\text{O}_t)$ of the POMs, as it can be observed on the IR spectrum of TBA₃NaH(POM-COOH).

Likewise, a weak peak at 1670 cm⁻¹ was displayed at the DRIFT spectrum of POMs-decorated MNPs. This band should not be confronted with the $\delta(\text{OH})$ at 1635 cm⁻¹ of the residual water in the samples, as it should be ascribed to the $\nu(\text{C}=\text{O})$ of an amide (amide I band). Indeed, this result confirms the theory of the covalent linking of POMs at the surface of MNPs.

As described earlier in the chapter, another sample was prepared where POMs were electrostatically deposited on the surface of the MNPs. The DRIFT spectrum of POMs-electrostatically deposited core-shell MNPs was recorded for a complete understanding of the synthetic procedure (Figure III-19). In this case, the shoulder at 1670 cm^{-1} cannot be observed while a supplementary peak at 1720 cm^{-1} appeared. The latter band, being close to the $\nu(\text{CO})$ of carboxylic acid functions, indicates the existence of “free” POM-COOH.

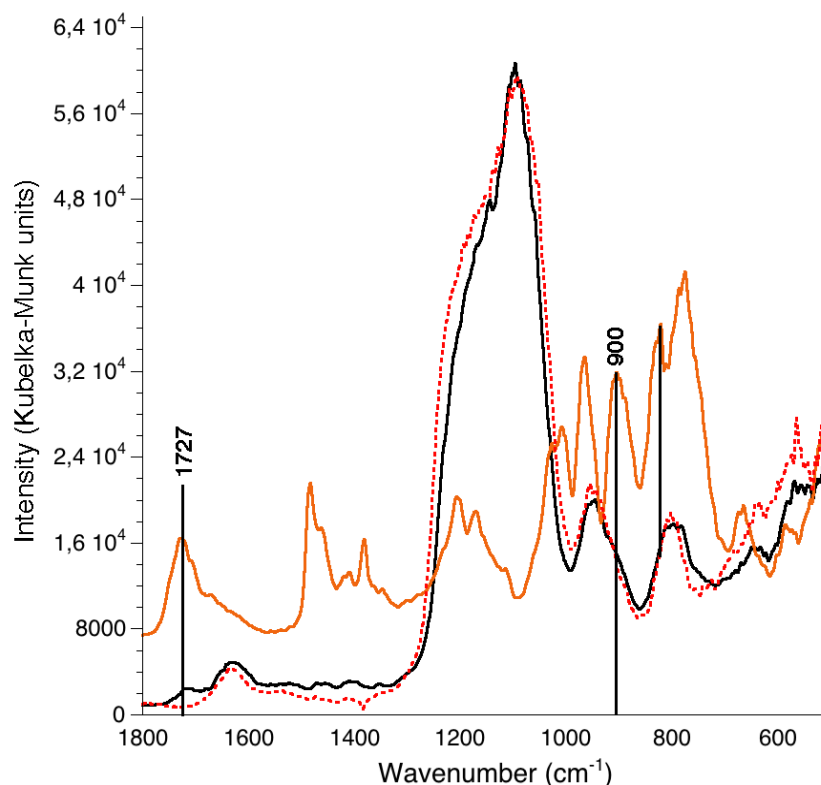


Figure III-19: DRIFT spectrum of TBA3NaH(POM-COOH) (orange), core-shell MNPs (red) and POMs electrostatically deposited on core-shell MNPs (black).

III.2.6 Measurement of magnetic properties

Magnetic materials are characterized by the presence of magnetic dipoles generated by the spinning of some of their electrons. Each of these polarized electrons can be aligned in a parallel or antiparallel fashion with respect to the neighboring ones in the crystal lattice. It is this type of interaction that gives rise to the macroscopic magnetic effect that is measured.

A material in a paramagnetic phase is characterized by randomly oriented (or uncoupled) magnetic dipoles, which can be aligned only in the presence of an external magnetic field and along its direction. This type of material has neither coercivity nor

remanence, which means that when the external magnetic field is switched off, the internal magnetic dipoles randomize again and no extra energy is required to demagnetize the material. Hence the initial zero net magnetic moment is spontaneously recovered. A nanoparticle with such magnetic behavior is superparamagnetic (SPM).

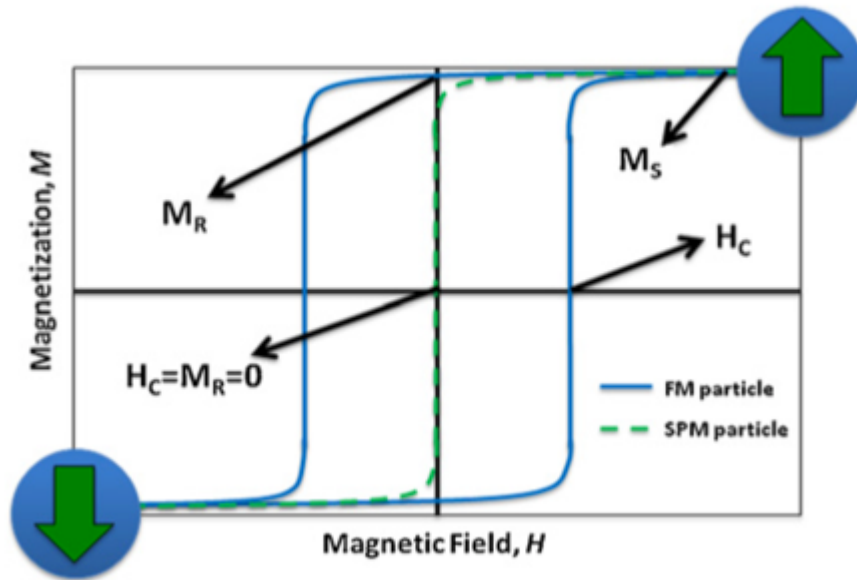


Figure III-20: Theoretical magnetization versus magnetic field curve for superparamagnetic (green) and ferromagnetic NPs (blue)¹²⁰.

Several parameters can describe the strength and the magnetization of the material. The first parameter is the saturation magnetization, M_S , which is the maximum value of magnetization that the material can reach under the effect of sufficiently high magnetic fields. Another parameter is the coercive field, H_C , the external field of opposite sign required to reduce the magnetization back to zero; this parameter also represents the minimum energy required for the reversal of the magnetization of the material. The third is the remanent magnetization, M_R , which indicates the residual magnetization at zero applied field. As already mentioned, for the maghemite NPs the last two parameters have a value of zero. In Figure III-20, these three parameters are presented for the ferromagnetic and superparamagnetic NPs.

POM-COOH decorated core-shell NPs with unsorted cores

The magnetic properties of the core-shell MNPs with unsorted cores and the POMs-decorated core-shell MNPs were investigated using a superconductive quantum interference device (SQUID).

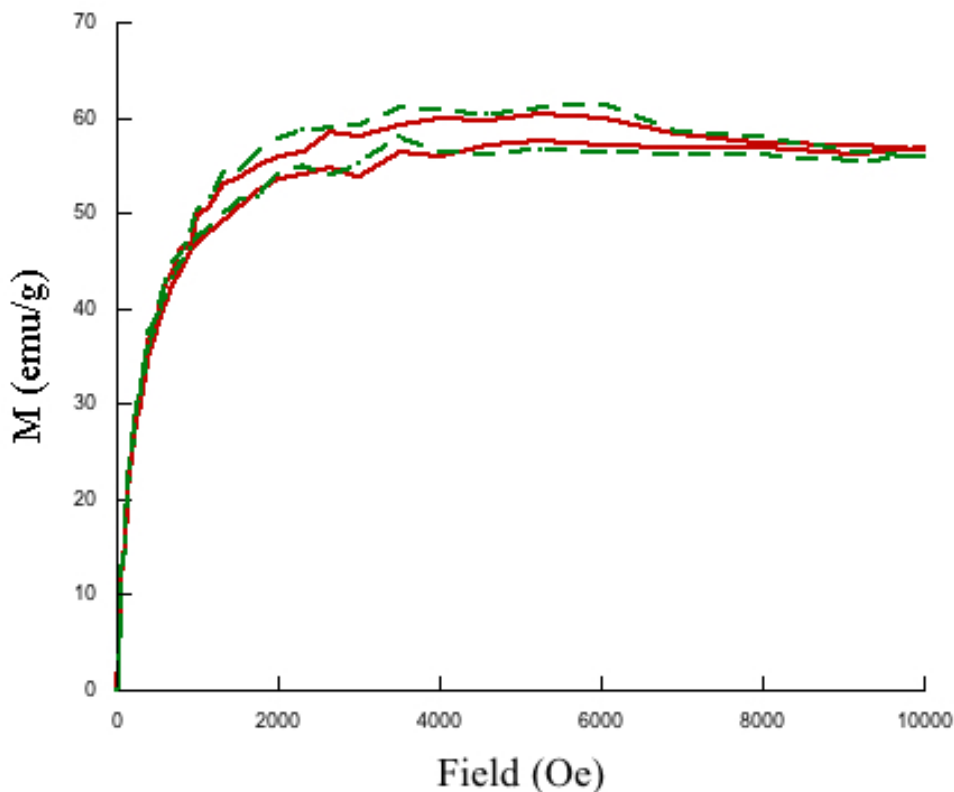


Figure III-21: Magnetic curves for core-shell MNPs with unsorted cores (red line) and for POMs-decorated core-shell MNPs (green line).

As expected, the grafting of the POMs does not influence the magnetization of the core-shell MNPs as the magnetic properties are solely due to the maghemite cores. In addition, the slight differences during the magnetic field rise and fall steps, can be attributed to the reorganization of magnetic NPs under the magnetic field, leading to the formation of dipolar chains under the magnetic field¹¹⁵.

POM-COOH decorated core-shell NPs with sorted cores

Magnetic measurements were also performed directly on suspensions of core-shell MNPs with sorted cores (NPS9) and POMs-decorated MNPs. Figure III-22 displays the magnetization curves for core-shell MNPs with unsorted and sorted cores, before and after the

grafting of POMs. The slight difference noticed between the saturation magnetization of core-shell MNPs with their equivalent with POMs can be due to an uncertainty during the estimation of the iron concentration in such diluted samples. However, improved results could be obtained through the analysis of dried samples in their solid state.

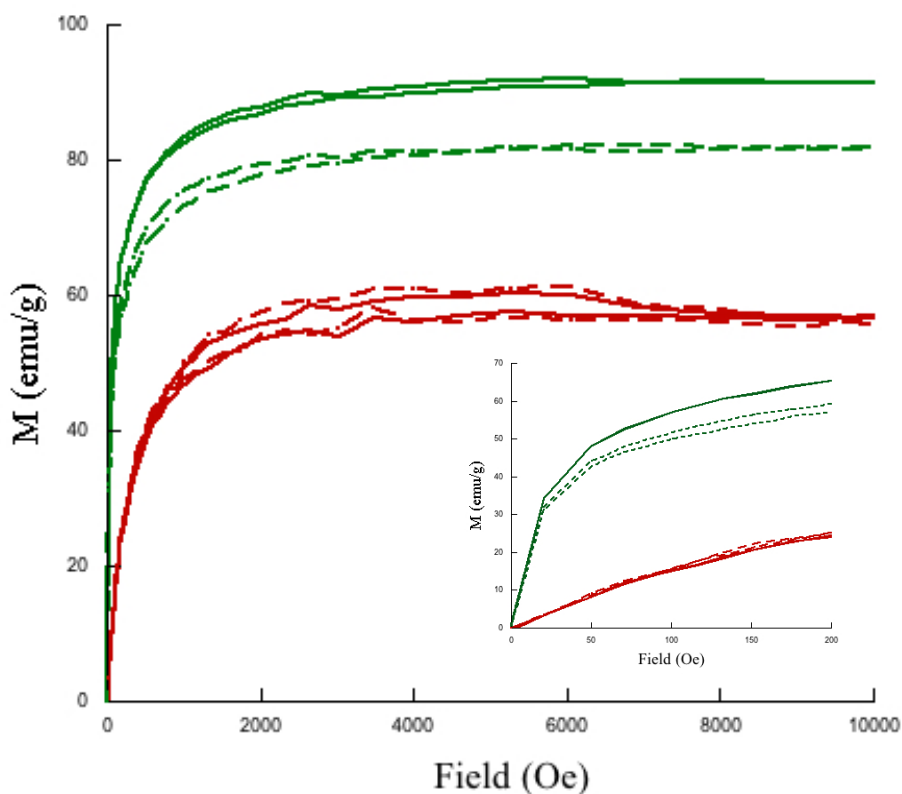


Figure III-22: Magnetic curves for core-shell MNPs with unsorted cores (red line - plain: non decorated, dash: POMs-decorated) and for POMs-decorated core-shell MNPs with sorted cores (green line - plain: non decorated, dash: POMs-decorated). Insert is a zoom in the region of 0 to 200 Oe.

Furthermore, due to the larger mean diameter of sorted maghemite cores compared to the unsorted ones, the saturation magnetization of the core-shell MNPs with sorted cores is higher (81 emu/g) than the core-shell MNPs with unsorted cores (61 emu/g). The slopes at small field indicate the larger magnetic susceptibility of the particles with sorted cores compared to the particles with unsorted cores, owing to the difference in diameter of the maghemite NPs. This result enhances the choice of using maghemite cores with increased size.

III.2.7 Hyperthermia measurements

Magnetic hyperthermia properties were determined on core-shell MNPs with sorted and unsorted cores, decorated or not with POMs. The temperature variation curves as a function of time for core-shell MNPs with sorted and unsorted cores, decorated with POMs, are presented in Figure III-23.

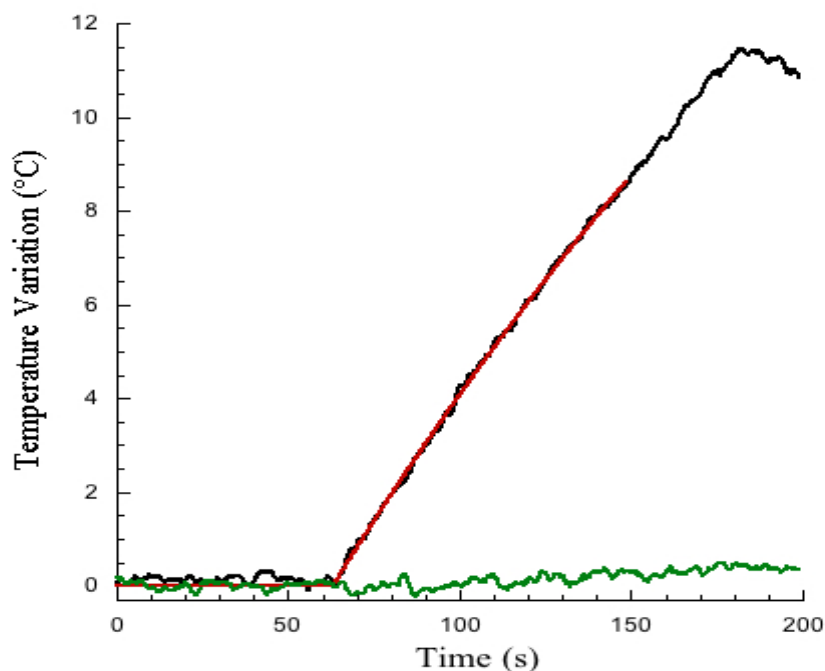


Figure III-23: Evolution of temperature variation over time under alternating magnetic field, for POMs-decorated core-shell MNPs with sorted (black line) and unsorted cores (green line).

As expected for core-shell MNPs with smaller, unsorted cores, no temperature variation was measured¹¹⁶. On the contrary, an important increase of the temperature, around 1°C per ten seconds, was observed for core-shell MNP with sorted cores once the alternating magnetic field was applied ($t = 60$ s).

The initial rise of the temperature, once the field is applied, was approximated by a linear increase as a function of time (red line in Figure III-23) and the slope dT/dt could thus be estimated. The specific loss power (SLP) was then calculated according to the following equation:

$$SLP = C_p \frac{m}{m_{MNP}} \frac{dT}{dt}$$

where C_p is the specific heat capacity of the solvent, m the mass of the sample and m_{MNP} the mass of magnetic nanoparticles in the sample. A value of $C_p = 2,227 \text{ J.g}^{-1}\text{K}^{-1}$ was used in acetonitrile.

The SLP calculated value of 52 W.g^{-1} for POMs-decorated core-shell MNPs with sorted cores is in good agreement with reported SLP values for sorted magnetic nanoparticles¹¹⁷.

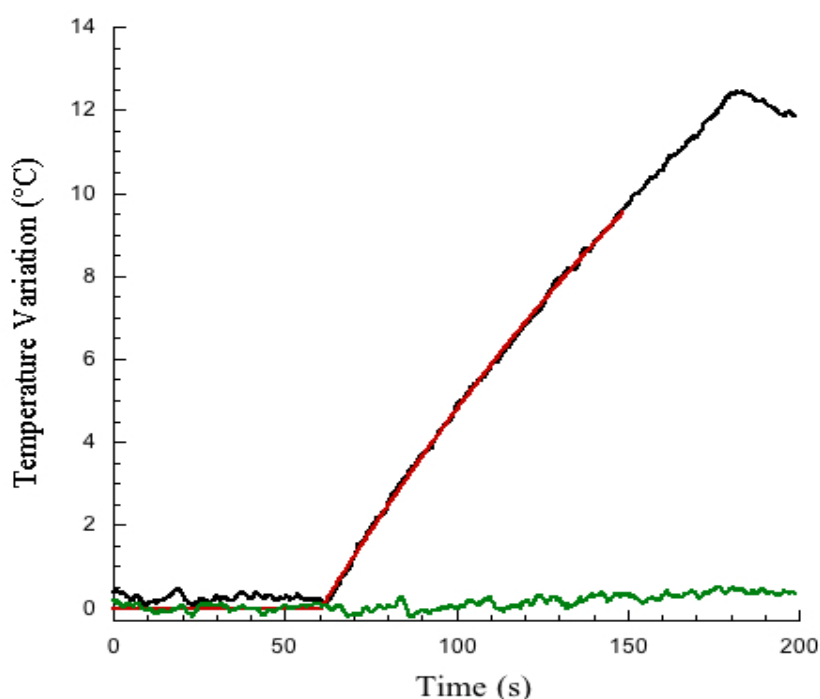


Figure III-24: Evolution of temperature variation over time under alternating magnetic field, for core-shell MNPs with sorted (black line) and unsorted cores (green line).

Similar results were obtained while studying core-shell MNPs with sorted and unsorted cores, but not decorated with POMs (Figure III-24). An SLP of 66 W.g^{-1} was calculated for core-shell MNPs with sorted cores. Comparison with the SLP of 52 W.g^{-1} for the same nanoparticles with POM grafted onto their surfaces evidences that magnetic hyperthermia properties are not affected by the surface decoration with catalysts.

IV Catalytic studies of POMs-decorated core-shell MNPs

IV.1 Comparison of mesoporous silica-based materials with magnetic NPs as supports for immobilization of POMs: Catalytic efficiency in “standard conditions”

Mesoporous silica materials, as seen in the previous chapters, have a variety of excellent textural parameters, such as larger surface area and pore volume, and narrow pore size distribution, as well as special quantum size effects. Furthermore, the synthesis and modification of mesoporous silica can be facilely tuned in a continuous wide arrangement.

However, mesoporous supports demand conventional separation methods from the reaction medium. As a result, core-shell MNPs offer a solution to this problem. They show superparamagnetism, which means that the particles are attracted to an external magnetic field but retain no residual magnetization after removal of the magnetic field. So, suspended core-shell MNPs can be easily removed from the solution using an external magnet without agglomeration after removing external magnet. The strategy of magnetic separation, taking advantage of the maghemite core, is typically more effective than filtration or centrifugation as it prevents loss of the catalyst. The magnetic separation is simple, economical and promising for industrial applications.

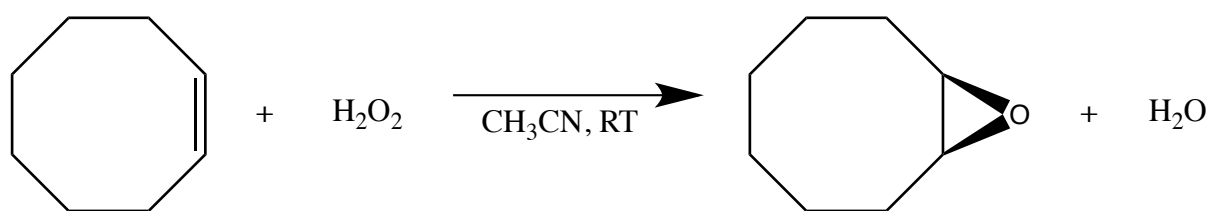


Figure IV-1: Epoxidation of cyclooctene by H₂O₂ in acetonitrile.

In the previous chapter, the catalytic capacities of POMs supported on SBA-15 were presented. For the POMs-decorated MNPs, the same model reaction was tested, with experimental conditions similar to what was described previously for the POMs supported SBA-15. In further detail, the epoxidation of cyclooctene was carried out with H₂O₂ (Figure IV-1). To start, the parameters used for this catalytic test were not altered in order to have a

base for comparison. The reaction was carried out in room temperature with the following catalyst/alkene/ H_2O_2 ratio 1:250:250.

Before all, the POM-COOH was tested in homogeneous conditions at room temperature in acetonitrile giving a TOF equal to 10 h^{-1} . The reaction cannot take place without the catalyst and the quantity of H_2O_2 introduced does not alter over time in the absence of cyclooctene.

Different “blank” tests were performed before verifying the catalytic effect of the supported system. Firstly, bare core-shell MNPs dispersed in acetonitrile were introduced in the reaction medium without the presence of POMs. As expected, no transformation of cyclooctene to the epoxide was noticed. From this test, information about the non-participation of the core-shell MNPs in the catalytic reaction can be deduced. Secondly, a small quantity of POM-COOH was added to the reaction medium. Upon the addition, the reaction started immediately. Thus, from this simple experiment few conclusions can be inferred; (i) the maghemite NPs, well protected by the silica shell, do not come in contact with H_2O_2 that can provoke its decomposition, and. (ii) the presence of core-shell NPs in the reaction medium does not inhibit the catalytic reaction.

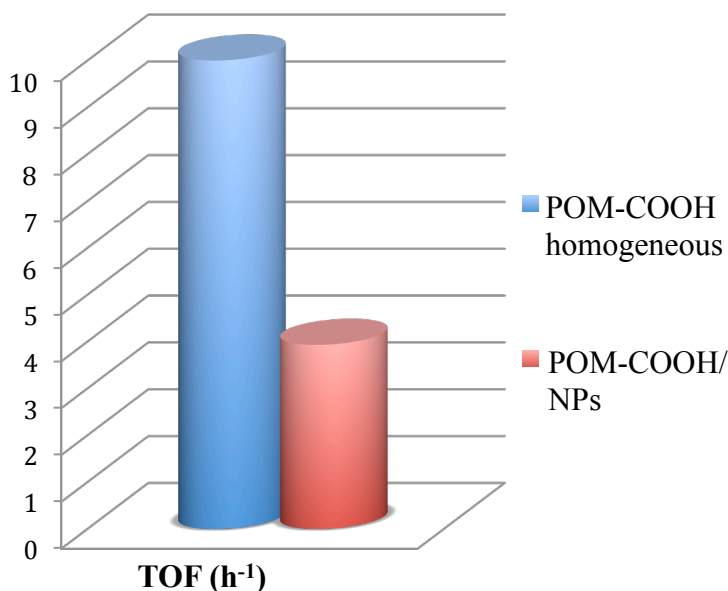


Figure IV-2: Catalytic activity of POM-COOH in homogeneous conditions vs. POMs-decorated MNPs dispersed in acetonitrile.

After these preliminary tests, the catalytic activity of the hybrid system core-shell MNPs with POM-COOH was evaluated. For the same conditions as for the homogeneous catalysis, the POMs-decorated core-shell MNPs with unsorted cores dispersed in acetonitrile were firstly tried out. The catalysis, carried out at room temperature (RT), gave a TOF equal to 4 h^{-1} (Figure IV-2). For the same sample but this time dispersed in DMF there was no catalytic activity. However, this result could not be reproduced and different essays of the catalytic reaction gave random results, with several times leading to not catalytic activity at all.

IV.2 Optimization of homogeneous supported catalysis with POMs-decorated core-shell MNPs

In a homogeneous catalytic reaction there are various variables, external or internal, that can be surveyed. Some of them include the temperature, the quantity of H_2O_2 , the ratio between the catalyst and the substrate for catalysis and finally the catalyst itself.

In the case of a suspended nanocatalyst, some other parameters may also have a role in the catalytic activity. The effect of PEG chains and $-\text{NH}_2$ functions was consequently studied. In the first place, the quantity of PEG chains was decreased twofold by keeping the quantity of $-\text{NH}_2$ constant and, following this, the opposite procedure was carried out. In both cases, the changes on the functionalization of the core-shell MNPs surface did not help with the catalytic activity of the system.

Subsequently, the quantity of H_2O_2 had to be studied for the highest conversion of cyclooctene. Different protocols were investigated in order to recover the catalytic activity of POMs.

In the beginning the quantity of H_2O_2 was multiplied by 2. The addition was executed either in one-step or by the progressive addition of the second equivalent of H_2O_2 . Likewise, doubling the ratio and gradually adding H_2O_2 did not induce the epoxidation of cyclooctene. Finally, increasing the initial quantity of H_2O_2 by 3 times activated the catalyst and the epoxide was formed with a conversion equal to 18.3%.

IV.2.1 Reactivity of POMs-decorated core-shell MNPs at 50°C as homogeneous supported catalyst

The TOF for a ratio of substrate/catalyst/H₂O₂ at 1:250:750 at RT showed a promising outcome up to now but not enough compared to polyoxometalate-based mesoporous materials. In view of the catalytic activity obtained, the last parameter that could be modified is the temperature of the catalytic reaction. The temperature was then increased to 50°C.

The catalytic activity of the POM-COOH was first evaluated in homogeneous conditions with a ratio of substrate/catalyst/H₂O₂ at 1:250:750. In these conditions, the POM-COOH displayed a TOF of about 300 h⁻¹. In addition, as what it has been completed at room temperature, the effect of the modifications on the surface of the core-shell MNPs was verified. For this, we compared the catalytic activity of standard core-shell MNPs with core-shell MNPs with half the quantity of PEG chains and with core-shell MNPs with less -NH₂ functions (Figure IV-3).

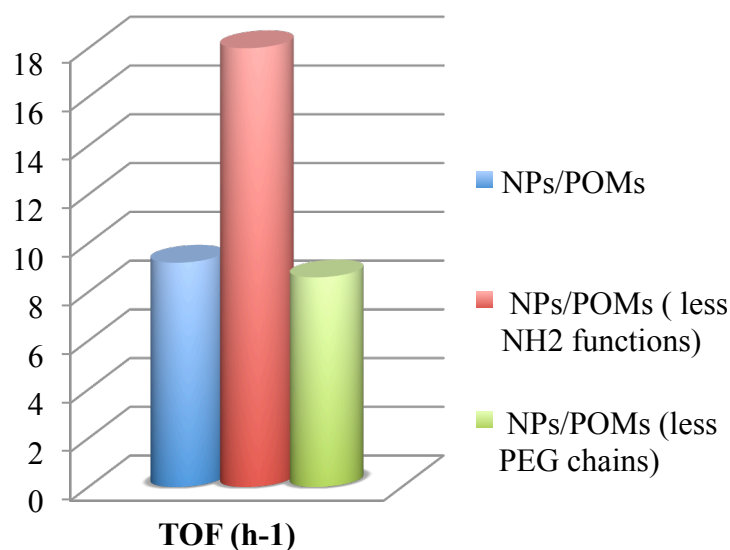


Figure IV-3: Catalytic activity of different systems of POMs-decorated MNPs at 50°C.

Despite a significantly lower catalytic activity than in homogeneous conditions, the significant result of the study is the obtainment of a fairly good cyclooctene conversion. As seen from Figure IV-3, the catalytic activity of POMs-decorated core-shell MNPs and POMs-decorated MNPs with less PEG chains is almost at the same level reaching a TOF of 9 h⁻¹. However, as the decrease of the quantity of PEG chains has an impact on the stability of the MNPs in the dispersion causing their precipitation, it was decided not to use this system

further in the following stages of the experiments. On the other hand, once the quantity of the amine functions is diminished by two, the TOF changes conversely. For both POMs-decorated core-shell MNPs and MNPs with less amine functions, the yield of conversion is almost 100% at 24 h of reaction, yet the turn over frequency of the latter is higher. This result is due to the quantity of POMs grafted on the surface of the MNPs being less important than in the standard core-shell MNPs system, according to the chemical analysis of both materials.

IV.3 Recycling of catalyst

In the beginning of the chapter, the advantages of catalysts immobilized on MNPs were presented, with the most important being the ease of separation from the reaction medium.

The feasibility of repeated use of POMs-decorated core-shell MNPs was examined. After each round of catalysis, the solution was centrifuged at 11.000 rpm for 10 minutes. Then, *via* magnetic concentration using a small permanent magnet externally, isolation of the nanocatalyst was easily accomplished. The procedure was repeated twice for fully washing of the catalytic system. The POMs-decorated MNPs were finally dispersed in the same quantity of acetonitrile as at the start. The catalyst was used at least 3 times without losing its reactivity.

Reagent	Yield of 1 st round	Yield of 2 nd round
POMs-NPs	19%	20%
POMs-NPs (less PEG chains)	8%	10%
POMs-NPs (less -NH ₂ functions)	2%	8%

Table IV-1: POMs-decorated MNPs recyclability at RT for the epoxidation of cyclooctene after 24h of reaction (ratio catalyst/ cyclooctene/ H₂O₂ = 1/250/750).

Table IV-1 and Table IV-2 display respectively the results from the investigation of recycling of POMs-decorated core-shell MNPs at RT for 2 consecutive rounds and at 50°C for 3 consecutive rounds of the same reaction. The results are given after 24h of reaction, and the same ratio cyclooctene/ H₂O₂ = 1/3 was used in all cases for the purpose of comparison.

Reagent	Yield of 1 st round	Yield of 2 nd round	Yield of 3 rd round
POMs-NPs	55%	90%	90%
POMs-NPs (less PEG chains)	75%	99%	99%
POMs-NPs (less -NH ₂ functions)	80%	99%	99%

Table IV-2: Recycling of POMs-decorated MNPs at 50°C for epoxidation of cyclooctene after 24h of reaction (ratio catalyst/ cyclooctene/ H₂O₂ = 1/250/750).

Regardless of the conditions used, the recycling of the catalyst at room temperature did not lead to any significant improvement of the cyclooctene conversion, which stayed very low. On the contrary, at 50°C, an important increase of the efficiency of the reaction from the first cycle of recycling was observed, occasionally until the reaction was complete. In order to precisely quantify this increase in the reaction speed, the nanocatalyst was characterized after the first round of catalysis by HR-TEM and XEDS.

The HR-TEM micrographs of the catalytic system after the first round of washing are displayed in Figure IV-4. At low magnification (Figure IV-4 left), it is clearly observed that no change in the shape and size of the core-shell MNPs has occurred after the catalytic test. Concerning the nanostructuration of the materials, the black dots that feature the POMs are still present (Figure IV-4 right) and no POMs aggregates were formed at the surface of the MNPs. However, if the distribution of POMs all over the particles is comparable to what is observed before the catalysis, the concentration of these black dots is apparently lower after the washing steps. This was confirmed by XEDS Fe/W ratio measurements. Indeed, the atomic percentage of W after the catalysis drops significantly with a Fe/W ratio to 3.7 (instead of 2.2 before catalysis). Thus, the catalytic reaction had an impact on the grafting of the POMs and part of these POMs was removed from the core-shell particles.

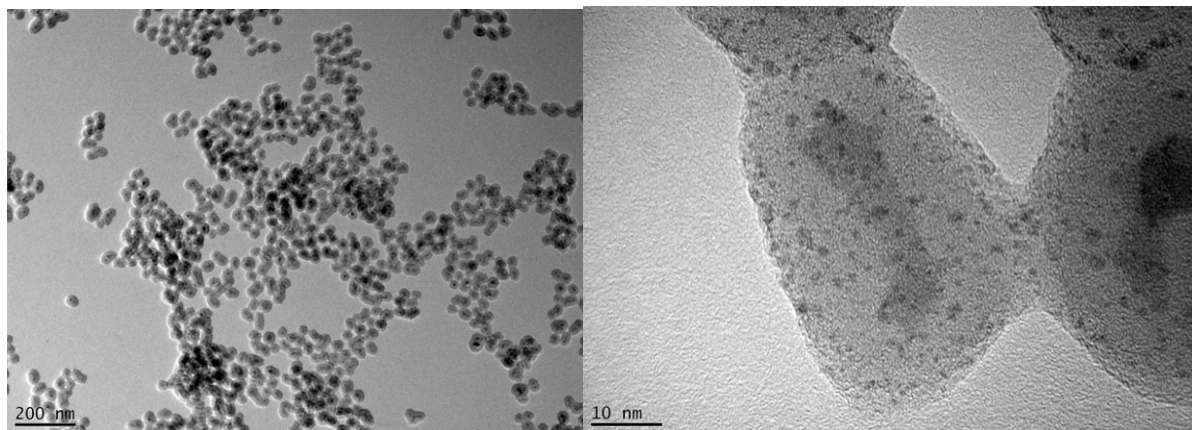


Figure IV-4: HR-TEM micrograph of POMs-decorated MNPs after catalytic test at different magnification.

However, as mentioned above, an increase of the catalytic activity after recycling the POMs-decorated MNPs was noticed at the same time. Then, taking into account the release of POMs during the first catalytic round, it was possible to evaluate a TOF after recycling, thanks to the XEDS measurements. The comparison between the POM-COOH in homogeneous conditions and the supported system before and after recycling at 50°C is presented in the following figure. The TOF number of POMs in homogeneous conditions is undoubtedly higher than in the case of the supported system. However, after the recycling step, a *ca.* 5-fold increase in the TOF is observed for the POMs-decorated MNPs (43 h⁻¹ compared to 9 h⁻¹ for the first round).

This increase is barely explained by the presence of remaining solubilized POMs in between the two rounds since the washing procedures used are without doubt sufficiently efficient. However, no certainty in the cause of this increase can be claimed at this time. An attractive assumption may lie in the stabilization of an activated POM/catalyst at the surface of the nanoparticle after the first round. In addition, if this theory stands, these active species may be “protected” by the stabilizing PEG shell around the nanoparticle. To substantiate this assumption, XPS spectroscopy could be an interesting tool since it would allow quantifying the W/As ratio in order to determine the composition, then consequently the structure of the POMs after catalysis.

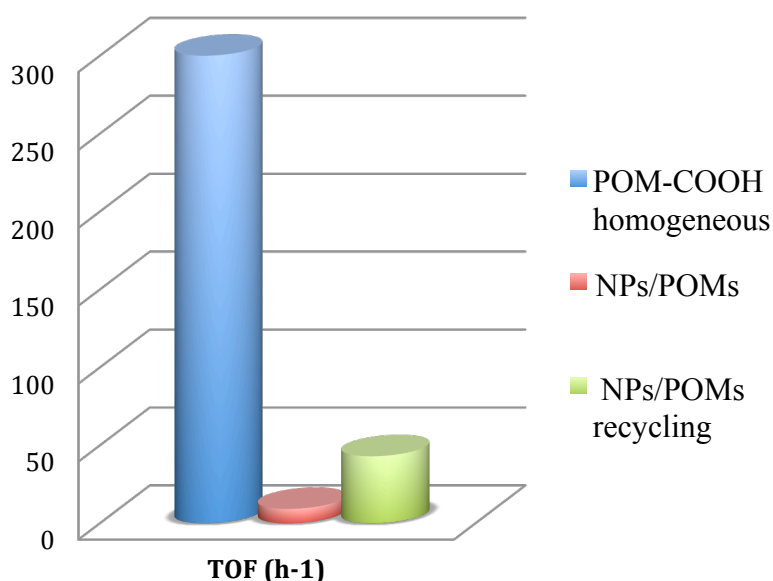


Figure IV-5: Recyclability of POMs-decorated MNPs and catalytic activity compared to homogeneous catalyst.

IV.4 Catalytic reactivity by hyperthermia

The goal of the various synthesis presented in the beginning of the chapter was the use of POMs-decorated MNPs as hyperthermia-assisted nanocatalysts. The capacity of heating under magnetic field was studied for core-shell MNPs with unsorted or sorted. As demonstrated, the core-shell MNPs with sorted cores showed excellent SLP values.

However, as it was the first time that assisted-hyperthermia catalysis was tried out, various parameters had to be adjusted. For example, the existing device of hyperthermia did not allow the stirring of the catalytic system. As a result, a special external stirring system, made of Teflon in order to not interfere with the magnetic field, had to be constructed. Another important parameter that led to difficulties and restraints in obtaining results was that the existing system could not work for more than 30 min, as the temperature increased rapidly affecting the electronic parts inside the device. Some tests of hyperthermia-assisted catalysis were carried out but 30 min were not enough to observe a catalytic activity.

All these problems made it difficult to perform catalytic tests in the conditions needed. On the contrary, there are several perspectives that can be considered. Firstly, a device with an electromagnetic coil and electronic parts resistant to an increased temperature should be

Part 2: Immobilization of hybrids of Polyoxometalates on magnetic core-shell nanoparticles

constructed. Secondly, as mentioned above, catalytic tests were performed with no results as even in a classical homogeneous supported catalytic system, no epoxidation is observed in the first 4 hours. Thus, it could be interesting to start the hyperthermia-assisted catalysis after these 4 hours and to compare the evolution to the latter system. However, due to lack of time, it was hardly possible to perform such experiment.

V Conclusion

In this part of the PhD work, the preparation of novel hybrid materials obtained by the covalent association of core-shell magnetic nanoparticles and hybrid polyoxometalates (POMs) was presented. For this purpose, the well-established procedure for the coupling of the bis-propanoic acid phosphonyle POM derivative $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (for short POM-COOH) with APTES-functionalized silica support was used. As a result, the preparation of POMs-decorated MNPs, in which the cores are constituted of crystalline maghemite domains, was succeeded. This strategy, as previously observed in the case of POMs-functionalized mesoporous materials, allowed an excellent nanostructuration of the POMs shell at the surface of the core-shell MNPs, as determined by High-resolution Transmission Electronic Microscopy. It was also revealed that the covalent anchorage of the POMs provided a strong link between the POMs and the MNPs, especially during the separation and rinsing steps of the preparation of the materials.

Furthermore, these hybrid nanomaterials were stabilized in organic media (acetonitrile and dimethylformamide), thus facilitating their processing and their potential use as catalysts for the transformation of organic compounds. Depending on the size of the core, two different types of magnetic core-shell NPs were synthesized. Firstly, the synthesis of magnetic core-shell NPs with unsorted cores was carried out. Following this, the magnetic cores were sorted by size before encapsulating them into the silica core, leading to what was called magnetic core-shell NPs with sorted cores. For the latter, two badges of sorted cores were tried out giving rise to core-shell magnetic NPs with different sizes. However, only one of them was kept for the following studies due to stability problems.

Subsequently, these core-shell MNPs were grafted with POMs and dispersed in organic media. The final materials were characterized by a variety of physical techniques, including spectroscopic methods (DRIFT, XPS, X-EDS), High-resolution Transmission Electronic Microscopy, DLS and magnetic measurements.

By DRIFT, the covalent grafting between the POMs and the core-shell magnetic NPs was established. For this reason, a sample, where POMs were electrostatically deposited on the surface of the core-shell MNPs, was synthesized. Comparing the DRIFT spectra of the

latter with the former, the covalent bonds could be proved. In addition, by X-EDS, it could be demonstrated that by washing the samples the ratio of W/Fe decreased significantly in the case of POMs electrostatically deposited on core-shell MNPs, enhancing the results obtained from DRIFT. This leaching is incompatible with a recycling process during the catalytic reaction.

In these nanomaterials, the presence of the maghemite core naturally allows their separation from colloidal solutions through the use of an external magnetic field. This provides an easier way for POMs/catalysts recovery than using conventional catalyst supports. As a result, the POMs-decorated core-shell MNPs were tested in the epoxidation of cyclooctene using hydrogen peroxide. Different tests were performed for a complete study of the catalytic activity. The materials demonstrated interesting catalytic results at 50°C. In addition, they could be recycled and reused several times conserving their catalytic activity and even increasing it.

Finally, these hybrid materials displayed very good hyperthermic behavior. This property is based on the principle that under an alternating magnetic field (AMF), a magnetic particle can generate heat by hysteresis loss. Such behavior is particularly relevant in the field of catalysis, by generating localized “hot points” at the surface of the MNPs, then at the exact place where the POMs are distributed.

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Conclusion

Conclusion

The goal of the present PhD work was the elaboration of new materials based on silica oxides (mesoporous silica SBA-15, magnetic core-shell nanoparticles) combined with nucleophilic (vacant) polyoxometalates for applications in the field of anchored homogeneous catalysis for mild oxidations reactions.

An important parameter taken into account during the work carried out for this PhD was the nature of the bond between the support and the POMs. It was deemed necessary to form a covalent bond in order to minimize the leaching of the active catalytic molecules, i.e. the polyoxometalates. It is worth noting that this covalent approach has been barely applied to the POMs chemistry.

Two different pathways were followed for the accomplishment of this objective. These pathways were chosen depending upon the support used for the grafting of POMs.

The first part of the manuscript was based on the use of mesoporous silica, and especially SBA-15, as a support for the anchored homogeneous catalytic system. Different strategies were presented for the covalent immobilization of POMs onto SBA-15.

In the first chapter, it was demonstrated that Keggin-type POMs bearing carboxylic acid functions were grafted onto the surface of amino-functionalized SBA-15 by the formation of amide bonds. The anchored homogeneous catalyst was shown to be efficient for the epoxidation of cyclooctene and cyclohexene with aqueous H_2O_2 . Finally, studies at the synchrotron SOLEIL were carried out after the introduction of lanthanum in the hybrid materials, providing local structure information.

In the second chapter, two more strategies were presented. The first one consisting of the synthesis of hybrids of POMs presenting nucleophilic functions (hydroxyl, amines) and their posterior grafting onto epoxy-functionalized SBA-15. However, the grafting proved to be unsuccessful. The second one dealt with the covalent linkage of the functionalized POM and support through an intermediate. SBA-15 and POMs were functionalized with amine groups and were coupled through the use of a cross-linker (*p*-phenylene diisothiocyanate) bearing the necessary functions. The system showed a good catalytic performance for the epoxidation of cyclooctene.

Conclusion

In the second part, the synthesis and characterization of hybrid nanocatalysts based on magnetic core-shell nanoparticles grafted with POMs was studied. Firstly, the synthesis of the maghemite core, their encapsulation into a silica shell and their functionalization was demonstrated. Then, the grafting of POMs onto amino-functionalized core-shell nanoparticles was accomplished by the same means as described in the first chapter for the mesoporous materials. In conclusion, the hybrid nanocatalysts were also tested under mild conditions for the epoxidation of cyclooctene. An important parameter to take into account was the ease of separation and recyclability of the synthesized nanomaterials.

Future research work is an indispensable part of this PhD. Concerning the first part of this thesis, more experiments can be carried out for a complete study. In more detail, all the materials containing La^{3+} anions, after their characterization, could be tested as catalysts. The existence of La^{3+} into the lacuna of POMs gives rise to new properties, allowing the further use of these systems for different types of catalysis. One example of their application could be the Lewis acid catalysis. In addition, the anchored homogeneous catalyst POM-COOH/SBA-NH₂ could be envisaged for use in more complex catalytic processes, as the cyclocarbonation. Specifically, this objective is already part of a PhD project starting in November through an ANR funding.

An important goal to fulfill, merely developed through the second part of the PhD thesis, is the optimization of the hyperthermia-assisted catalysis. As formerly mentioned, different parameters should be considered and adjusted (time of heating, construction of an adapted device). Nevertheless, the materials already synthesized are an important step towards the right direction.

Annexes

Annex A - Experimental Section

I Methods of characterization

I.1 Infrared Spectroscopy

Solids were characterized by attenuated total reflection infrared spectroscopy, using Tensor 27 FTIR equipped with a ZnSe crystal with resolution better than 1 cm^{-1} .

I.2 NMR Spectroscopy

The ^1H (300.13 MHz), ^{13}C (75.6 MHz), and $\{^1\text{H}\} \text{ } ^{31}\text{P}$ NMR (121.5 MHz) solution spectra were recorded in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probehead. ^{13}C CP MAS NMR spectra were recorded at 125.77 MHz on a Bruker AVANCE III 500 spectrometer (11.7 T) with a 4 mm Bruker probe and at a spinning frequency of 10 kHz (recycle delay = 5 s, contact time = 10ms). ^{31}P MAS NMR spectra were recorded at 283.31 MHz on a Bruker AVANCE III 700 spectrometer (16.4 T) equipped with 2.5 mm Bruker probe and at a spinning frequency of 30 kHz. Chemical shifts were referenced to tetramethylsilane (TMS) for ^{13}C and to 85% aqueous H_3PO_4 for ^{31}P .

I.3 Thermogravimetric Analysis

Thermogravimetric analyses (TGA) were performed under air with a TA-Instrument SDT Q600 between 20 and 900 °C (air flow: 100.0 mL min^{-1} , $10\text{ }^\circ\text{C min}^{-1}$).

I.4 BET measurements

N_2 sorption analyses of the pretreated materials (100 °C) were obtained at $-196\text{ }^\circ\text{C}$ using an ASAP-2020 Micromeritics apparatus.

I.5 Elemental analysis

Elemental analyses were performed by the Institut des Sciences Analytiques du CNRS (Villeurbanne, France).

I.6 X-Ray Diffraction

XRD measurements were carried out on a Bruker D8 Advance XRD diffractometer.

I.7 X-Ray Fluorescence

X-ray fluorescence analyses were conducted with an energy dispersive spectrometer (XEPOS with Turboquant powder software).

I.8 High-Resolution Transmission Electron Microscopy

HR-TEM analyses were realized on a microscope operating at 200 kV with a resolution of 0.18 nm (JEOL JEM 2011 UHR) equipped with an EDX system (PGT IMIX-PC). Samples of SBA-15 were dispersed in resin and cut with an ultramicrotome. The lamellas of 50 nm thickness were then deposited on Cu grid covered with an amorphous carbon film.

I.9 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra were performed on an Omicron (ESCA+) spectrometer, using an Al Ka X-ray source (1486.6 eV) equipped with a flood gun.

I.10 Dynamic Light Scattering

Dynamic Light Scattering measurements were performed on Malvern, Zetasizer Nano S.

I.11 Atomic Absorption

Atomic absorption (flame spectroscopy) measurements for iron analysis were performed with a Perkin-Elmer Analyst 100 spectrophotometer.

I.12 Hyperthermia measurements

Magnetic measurements were performed on a MPMS-XL7 Superconducting QUantum Interference Device. Magnetic hyperthermia properties of the nanoparticles were measured by recording the temperature of the solution of nanoparticles with a nonmetallic optical fiber thermometer (Fluoroptic, Luxtron) while excited by a magnetizing coil of a commercial radiofrequency ac magnetic field generator (MagneTherm, NanoTherics). A frequency of 535 Hz and a field of 21.4 mT were used in this experiment.

I.13 Quantification of amine functions

The first step of the protocol consists of preparing a solution of 5.60 mg fluorescamine dissolved in 100ml of pure ethanol. A calibration curve is made by measuring the fluorescence of solutions made with 20 μ L of APTES at known concentrations in ethanol (from 0 to 8 mM) in 5 mL of the

Annexes

fluorescamine solution. At the same time, 20 μL of the NPs sample are diluted in 5 mL of the fluorescamine solution too. Finally the prepared solutions are left for 2h in the dark prior to measurement. Fluorescamine reacts readily with primary amino groups to form highly fluorescent compounds that have an excitation maximum at 390 nm and an emission maximum at 475 nm.

Annex B - Synthesis and characterization

Synthesis of hybrid of POM ($(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (POM-COOH)

$\text{Na}_8\text{H}[\text{B},\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33}]\cdot 24\text{H}_2\text{O}$ (2.00 mmol, 5.75 g) was suspended into 50 mL of a solution of $(n\text{-Bu}_4\text{N})\text{Br}$ (8 mmol, 2.57 g) and 3-phosphonopropanoic acid (4.00 mmol, 0.62 g) in acetonitrile. Concentrated hydrochloric acid 37% (8 mmol, 0.66 mL) was added dropwise at room temperature. The resulting suspension was heated overnight at 83 °C, and then filtrated on a glass frit (no. 4). The solution was concentrated under vacuum to get a colorless oil. Ethanol and diethylether were successively added to the oil in order to remove the excess of phosphonopropanoic acid, and to recover the target compound as a white solid material. This compound can be recrystallized in hot DMF or acetonitrile (20 mL) (yield = 5.83 g, 89%).

Anal. Calculated for $\text{C}_{54}\text{H}_{120}\text{N}_3\text{Na}_1\text{As}_1\text{P}_2\text{W}_9\text{O}_{39}$: C, 19.96; H, 3.72; N, 1.29; As, 2.31; Na, 0.71; P, 1.91; W, 50.91. Found: C, 20.20; H, 3.80; N, 1.41; As 1.90; Na, 0.63; P, 1.60; W, 51.10

^1H NMR (300.13 MHz, CD_3COCD_3): δ (ppm) 2.18–2.30 (m, $\text{PCH}_2\text{CH}_2\text{COOH}$), 2.70–2.90 (m, $\text{PCH}_2\text{CH}_2\text{COOH}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3SOCD_3): δ (ppm) 23.4 (d, $^1J_{\text{P-C}} = 134$ Hz, 1C, $\text{PCH}_2\text{CH}_2\text{COOH}$); 28.0 (s, 1C, $\text{PCH}_2\text{CH}_2\text{COOH}$); and 174.3 (d, $^3J_{\text{P-C}} = 23$ Hz, 1 C, $\text{PCH}_2\text{CH}_2\text{COOH}$)

$\{^1\text{H}\}^{31}\text{P}$ NMR (121 MHz, $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$): δ (ppm) 29.0

^{183}W NMR (12.5 MHz, CD_3SOCD_3): δ (ppm) –215.7 (s, 1W); –117.5 (d, $^2J_{\text{P-W}} = 11.8$ Hz, 2W); –117.6 (d, $^2J_{\text{P-W}} = 10.1$ Hz, 2W); –112.5 (s, 2W); –111.7 (s, 2W)

IR (KBr, cm^{-1}): 3440(vs), 3200(m), 1725(m), 1662(m), 1202(m), 1178(m), 1025(m), 1005(m), 965(s), 905(s), 828(s), 778(vs), 663(w), 582(w), 514(m), 498(m).

Raman (solid, cm^{-1}): 1127 (w), 1054 (w), 996 (m), 974 (s), 941 (m), 903 (m), 747(m)

Synthesis of hybrid of POM ($(n\text{-Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{-p-NH}_2)\}_2]$ (POM-NH₂))

$\text{Na}_8\text{H}[\text{B},\alpha\text{-PW}_9\text{O}_{33}]\cdot 24\text{H}_2\text{O}$ (2.81 mmol, 8 g) was suspended into 50 ml of a solution of $(n\text{-Bu}_4\text{N})\text{Br}$ (11.24 mmol, 3.63 g) and aminophenyl arsenic acid (5.62 mmol, 1.228 g) in acetonitrile. Concentrated hydrochloric acid 37% (11.24 mmol, 1 ml) was added dropwise at room temperature. The resulting suspension was heated overnight at 83 °C, and then filtrated on a glass frit (no. 4). The solution was concentrated under vacuum to get a colorless oil. Ethanol and diethylether were successively added to the oil in order to remove the excess of phosphonopropanoic acid, and to recover the target compound as a white solid material. (yield = 6.4 g, 59%).

¹H NMR (300.13 MHz, CD₃CN): δ (ppm) 0.94 (m, 36H, CH₃), 1.33 (24H, CH₃CH₂CH₂), 1.58 (24H, CH₃CH₂CH₂), 3.17 (24H, CH₂N), 6.02 (4, NH₂), 6.72 (4H, aromatic in meta of NH₂), 7.39 (4H, aromatic in ortho of NH₂)

RMN ³¹P{¹H} (121.5 MHz): δ (ppm) – 10.71 in CD₃CN, - 12.37 in CD₃SOCD₃.

IR (KBr, cm⁻¹): 366(m), 519(m), 736(s), 818(vs), 850(vs), 938(s), 960(vs), 1027(m), 1081(s), 1596(m), 2874(m), 2962(m), 3232(s), 3361(m), 3446(m).

Synthesis of SBA-15

16 g of Pluronic P123 were weighted and dissolved in 480 ml of DI water. Afterwards, 80 ml HCl (37%) were added. The resulting solution was left under stirring and it was heated up to 40 °C until complete dissolution of Pluronic 123. After 4 h, 36 ml of TEOS were added to the solution, which was left under stirring and further heating for 24 h. Then, the solution was transferred in a FEP bottle and it was placed in the oven at 100 °C for 24 h. Once the hydrothermal treatment finished, it was left to reach room temperature and then the solution was filtered. The obtained white powder was washed with DI water (around 8 L) for the maximum elimination of the organic parts non-reacted. The washed solid was placed in the oven at 60 °C for an overnight drying. Finally, the dried solid is calcinated (24 °C min⁻¹) under air for 6 h at 550 °C.

Functionalization of SBA-15 with 3-aminopropyl groups

1.0 g SBA-15 silica, previously dried at 350 °C for 12 h, was dispersed in 50 mL of anhydrous toluene using an ultrasound bath for 5 min and magnetic stirring. The ultrasound bath serves for the complete dispersion of silica and as to avoid the formation of aggregates. Then, 3-(aminopropyl)triethoxysilane (APTES) (1 mL, 4 mmol) was added, and after 1 h, the resulting mixture heated up to 110 °C. Reflux was maintained for 20 h, after which the suspension was filtered. The recovered solid was washed

with toluene, acetonitrile, and ethanol (15 mL of each), and then air-dried. The resulting $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_{1.5}/8\text{SiO}_2$ solid was extracted with dichloromethane using a Soxhlet for 24 more hours.

Covalent binding of POM-COOH with SBA-NH₂

During this work several SBA-NH₂ were prepared and used, with various amounts of -NH₂ functions grafted at the surface of the native SBA-15. However, the protocols were adapted as a function of the amount of -NH₂, in order to have an initial POM-COOH/NH₂ ratio of 6. In a typical experiment, samples of $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (0.96 g, 0.316 mmol) and SBA-NH₂ silica (1.325 g, 1.6 mmol g⁻¹ of -NH₂ groups) were introduced in 100 mL Schlenk tubes and kept under vacuum overnight. The POM-COOH complex was dissolved under argon in 10 mL of freshly distilled acetonitrile. Triethylamine (260 μL , 1.9 mmol) was then added and the resulting mixture cooled in an ice bath at -30 °C. After 30 min, isobutylchloroformate (251 μL , 1.9 mmol) was introduced, and the resulting solution was stirred for 30 min (solution 1). In parallel, SBA-NH₂ was dispersed in distilled acetonitrile (5 mL) in the other Schlenk tube under argon. Solution 1 was then transferred to the dispersion of the support via cannula. The resulting suspension was stirred overnight at room temperature under argon, and then filtered. The recovered solid, i.e., POM-CO₂H/SBA-NH₂, was finally extracted using a Soxhlet over 2 days with acetonitrile as the solvent.

Synthesis of $\{(^n\text{Bu}_4\text{N})_2[\text{AsW}_9\text{O}_{33}\{\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}\}_2\{\text{La}(\text{dmf})(\text{H}_2\text{O})_2\}]\}_x$ (La $\subset$ POM-COOH)

$(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (1.00g, 0.31 mmol) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.20g, 0.46 mmol, 1.5 eqv) were dissolved in 10 ml of acetonitrile. The mixture was allowed to stand at room temperature for a few days, leading to the formation of a white precipitate. Since the IR spectrum of this solid shows that the expected compound $(^n\text{Bu}_4\text{N})_2(\mathbf{4})$ contains significant amounts of nitrates, it has been recrystallized in dmf at room temperature, leading to the formation of uncoloured crystals, suitable for an X-ray diffraction analysis ($m = 0.65$ g, yielding 65%).

Anal. Calcd for $\text{C}_{41}\text{H}_{93}\text{As}_1\text{La}_1\text{N}_3\text{O}_{42}\text{P}_2\text{W}_9$: C, 15.24; H, 2.90; N, 1.30. Found: C, 15.57; H, 3.00; N, 1.31.

³¹P{¹H} NMR (121.5 MHz, CD₃CN): δ (ppm) 19.07.

IR (KBr) ν_{max} (cm⁻¹): 674 (m), 747 (s), 784 (s), 823 (s), 887 (s), 968 (s), 1024 (s), 1111 (m), 1168 (s), 1253 (m), 1384 (m), 1437 (w), 1419 (w), 1484 (m), 1649 (s), 1718 (m), 2874 (m), 2935 (m), 2962 (s).

Synthesis of $(n\text{-Bu}_4\text{N})_2[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2\{\text{La}(\text{dmf})_3(\text{H}_2\text{O})_2\}]\cdot 3\text{dmf}$ (LaCPOM-NH₂)

$(n\text{-Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-}p\text{-NH}_2\}_2]$ (1.00g, 0.29 mmol) and $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.19g, 0.45 mmol, 1.5 eqv) were dissolved in 30 ml of acetonitrile. The solution was then refluxed overnight and allowed to stand at room temperature for a few days, during which a yellow microcrystalline precipitate formed. This precipitate was filtered then recrystallized in the minimum of dmf. After a few weeks, yellow single crystals of $(n\text{-Bu}_4\text{N})_2(\mathbf{3})\cdot 3\text{dmf}$ formed (0.41 g, 0.11 mmol, yielding 38.5 %), were collected and analysed by X-ray diffraction.

Anal. Calcd for $\text{C}_{62}\text{H}_{129}\text{As}_2\text{La}_1\text{N}_{10}\text{O}_{43}\text{P}_1\text{W}_9$: C, 20.25; H, 3.54; N, 3.81. Found: C, 20.07; H, 3.39; N, 3.51.

RMN $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz, CD_3CN): δ (ppm) -11.93.

IR (KBr) n_{max} (cm^{-1}): 3456 (s), 3363 (s), 3234 (w), 2962 (s), 2934 (m), 2874 (s), 1649 (vs), 1594 (s), 1504 (w), 1486 (w), 1385 (m), 1088 (s), 1031 (m), 962 (s), 940 (m), 914 (w), 850 (vs), 775 (s), 740 (s), 675 (sh), 522 (m).

Introduction of La^{3+} into POM-COOH/ SBA-NH₂ with ratio 0.75:1 [sample LaCPOM-COOH/SBA-NH₂ (0.75:1)]

It is considered that 0.1 mmol of POM-COOH is grafted onto the surface of 1g of POM-COOH/SBA-NH₂ (obtained from an initial SBA-NH₂ with 2.12 mmol g^{-1} of $-\text{NH}_2$ groups). 0.3g of POM-COOH/SBA-NH₂ (0.03 mmol de POM-COOH) were introduced in a small recipient with 0.010 g of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.02 mmol) and they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before evaporating the solvent.

Introduction of La^{3+} into POM-COOH/ SBA-NH₂ with ratio 1:1 [sample LaCPOM-COOH/SBA-NH₂ (1:1)]

0.3g of POM-COOH/SBA-NH₂ (corresponding to 0.03 mmol of POM-COOH) were introduced in a small recipient with 0.013 g of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.03 mmol) and they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before evaporating the solvent.

Introduction of La^{3+} into POM-COOH/SBA-NH₂ with ratio 2:1, [sample LaCPOM-COOH/SBA-NH₂ (2:1)]

0.3g of POM-COOH/SBA-NH₂ (corresponding to 0.03 mmol of POM-COOH) were introduced in a small recipient with 0.026 g of $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (0.06 mmol) and they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before evaporating the solvent.

Introduction of La^{3+} into SBA-NH₂ (sample LaCSBA-NH₂)

A control sample was also prepared by wet impregnation of a SBA-NH₂ support (2.12 mmol of -NH₂ groups per g of material) with a solution of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and labelled LaCSBA-NH₂. The amount of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ added here was the same as in LaCPOM-COOH/SBA-NH₂ (1:1). Furthermore, the mass of POM-COOH/SBA-NH₂ and SBA-NH₂ supports used was chosen so that the number of -NH₂ functions was identical in both samples. 0.2 g of SBA-NH₂ (corresponding to 0.42 mmol of -NH₂ functions) were then dispersed in 3 mL of CH₃CN and 0.013 g $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.03 mmol) were added. The solution was left under stirring for a few days before evaporating the solvent.

Synthesis of $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{OH})_2\}_2]$ (POM-OH)

Hydrolysis of phosphonic ester ($\text{OHCH}_2\text{CH}_2\text{PO}(\text{OMe})_2$):

In an inert atmosphere, phosphonic ester (1.3 mmol) is added in 2.5 ml of dry dichloromethane. Bromotrimethylsilane (0.53 ml, 3.9 mmol) is added dropwise at room temperature. The mixture is left overnight under stirring. Then, 10 ml of water are added. The two phases are mixed sufficiently and then they are separated. The aqueous phase is evaporated and the final product is obtained as a yellow solid.

$\text{Na}_8\text{H}[\text{B},\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33}] \cdot 24\text{H}_2\text{O}$ (2.00 mmol, 5.75 g) was suspended into 50 mL of a solution of $(n\text{-Bu}_4\text{N})\text{Br}$ (8 mmol, 2.57 g) and $\text{OHCH}_2\text{CH}_2\text{PO}(\text{OMe})_2$ (4.00 mmol, 0.56 g) in acetonitrile. Concentrated hydrochloric acid 37% (8 mmol, 0.66 mL) was added dropwise at room temperature. The resulting suspension was heated overnight at 83 °C, and then filtrated on a glass frit (no. 4). The solution was concentrated under vacuum to get a colorless oil. Ethanol and diethylether were successively added to the oil in order to remove the excess of any product not reacted, and to recover the target compound as a white solid material.

Functionalization of SBA-15 by GLYMO

Firstly, SBA-15 was treated overnight under heat in order to eliminate any remaining water. The reaction for the grafting of GLYMO must be carried out under oxygen-controlled atmosphere, so 1 g of SBA-15 was introduced in a two-neck flask under nitrogen. Then, 50 ml of dried toluene were added and the solution was mixed under ultrasonication until full dispersion of SBA-15. Afterwards, GLYMO (442 μL , 2 mmol) was added, and after 1 h, the resulting mixture heated up to 120 °C. Reflux was maintained for 20 h under agitation, after which the suspension was filtered. The recovered solid was washed with toluene, acetonitrile, and ethanol (15 mL of each), and then air-dried. The resulting solid was extracted with dichloromethane using a Soxhlet for 24 more hours.

Attempt for covalent binding of POM-COOH with SBA-GLYMO

Samples of $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$ (0.241 g, 0.07 mmol) and SBA-GLYMO silica (0.5 g, 0.84 mmol g^{-1} of epoxy groups) were introduced in a round flask and dispersed in 10 ml of acetonitrile. The mixture was left under overnight stirring at RT. Then, the final product was filtered and extracted with acetonitrile using a Soxhlet for 48 h.

Functionalization of POM-NH₂ with 1,4-phenylene diisothiocyanate (PDITC) $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})\text{C}_6\text{H}_4\text{-NH-C(S)-NH-C}_6\text{H}_4\text{NCS}\})_2]$

1 g (0.33 mmol) of $(n\text{-Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{-p-NH}_2)\}_2]$ was introduced in a round flask and dissolved in 50 ml of acetonitrile. Then, PDITC (0.51 g, 2.65 mmol) was added to the solution and the mixture was left under stirring at RT for 7 days. Afterwards, the solution is left for evaporation in air in order to obtain the desired product. The obtained crystals are washed with benzene, for the elimination of any PDITC that did not react.

RMN $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz): δ (ppm) – 11.23 in CD_3CN , - 12.23 in CD_3SOCD_3 .

^1H NMR (300.13 MHz, $\text{D}_6\text{-dmsO}$): δ (ppm) 0.94 (m, 36H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.33 (24H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.58 (24H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.17 (24H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 6.72 (8H, multiplet, aromatic in meta of NH thiourea), 7.41 (8H, multiplet, aromatic in ortho of thiourea), 10.11 (4H, s, -NH-C=S-).

IR (KBr, cm^{-1}): 369(m), 488(m), 510(m), 730(s), 806(sh), 850(vs), 938(sh), 963(s), 1027(m), 1083(s), 1245(s), 1307 (s), 1503 (s), 1595(m), 2874(m), 2936 (sh), 2962(s), 3039(w), 3095(w), 3325(m).

Covalent binding of POM-NH₂/PDITC with SBA-NH₂

Samples of POM-NH₂/PDITC (0.280 g, 0.083 mmol) and SBA-NH₂ silica (0.165 g, 2.12 mmol g^{-1} of -NH₂ groups) were introduced in a round flask and dispersed in 20 ml of acetonitrile. The mixture was left for stirring at RT for several days. Then, the final product was filtered and extracted with acetonitrile using a Soxhlet for 48 h.

Introduction of La^{3+} into POM-NH₂/ PDITC/ SBA-NH₂ (ratio 0.75:1)

It is considered that 0.06 mmol of POM-NH₂/PDITC are grafted onto the surface of 1g of SBA-NH₂ (obtained from an initial SBA-NH₂ with 2.12 mmol g^{-1} of -NH₂ group). 0.2g of POM-NH₂/ PDITC/ SBA-NH₂ (0.012 mmol of POM-NH₂/PDITC) were introduced in a small recipient with 0.004 g of

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.009 mmol) and they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before the evaporation of the solvent.

Introduction of La^{3+} into POM-NH₂/ PDITC/ SBA-NH₂ (ratio 1:1)

0.2g of POM-COOH/ SBA-NH₂ (0.012 mmol) were introduced in a small recipient with 0.052 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.012 mmol) and then they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before the evaporation of the solvent.

Introduction of La^{3+} into POM-NH₂/ PDITC/ SBA-NH₂ (ratio 2:1)

0.2g of POM-COOH/ SBA-NH₂ (0.012 mmol) were introduced in a small recipient with 0.104 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.024 mmol) and then they were dispersed in 3 ml of acetonitrile. The solution was left under stirring for a few days before evaporating the solvent.

Synthesis of unsorted maghemite nanoparticles

The unsorted maghemite nanoparticles were synthesized following the usual Massart's co-precipitation method. First, 1 L of a 22.5 % ammonia solution was quickly added to an acidic solution iron (II) and iron (III) ions (180 g of FeCl_2 , 100 mL of HCl 37%, 500 mL of deionized water, 715 mL of FeCl_3 27%, completed to 3 L with deionized water). After 30 min of stirring, the obtained Fe_3O_4 nanoparticles were washed with deionized water, and redispersed in nitric acid. Then, a solution of iron nitrate was added to the nanoparticles and the solution was boiled and agitated for 30 min, in order to oxidize the Fe_3O_4 nanoparticles into $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. The resulting nanoparticles were then washed with nitric acid once, with acetone 3 times, and with diethylether twice. Finally, they were redispersed in deionized water. In order to be stable at neutral pH, the nanoparticles were finally citrated with sodium citrate by heating the nanoparticles for 30 min. After being rinsed with acetone and diethylether, the resulting nanoparticles were dispersed in deionized water.

Synthesis of sorted maghemite nanoparticles with size of 11,7 nm

The synthesis followed the synthesis of unsorted maghemite nanoparticles, mentioned above. In order to obtain magnetic NPs with size of 11.7 nm, different steps of sorting procedure were performed.

Synthesis of sorted maghemite nanoparticles with size of 9 nm

The sorted maghemite nanoparticles were obtained by an inverse Massart's co-precipitation method. Indeed, the acidic equimolar iron (II) and iron (III) ions solution (124.25 g of FeCl_2 , 50 mL of HCl 37%, 250 mL of deionized water, 293.5 mL of FeCl_3 27%) was added dropwise over 4 h to 2 L of 5 % ammonia in water, under agitation. The washing and oxidation steps were then the same as above. After redispersion, the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were polydispersed in size. In order to decrease the polydispersity, 10 mL of nitric acid (52.5 %) were added to the solution. The addition of nitric acid increases the ionic strength leading to flocculation of the larger, thus less stable, nanoparticles. These precipitated nanoparticles were separated from the rest of the ferrofluid, rinsed with acetone and diethyl ether, and finally redispersed in deionized water. In order to ensure their stability and dispersion at neutral pH, the nanoparticles were finally citrated by heating with sodium citrate for 30 min. After being rinsed with acetone and diethylether, the resulting nanoparticles were dispersed in deionized water.

Synthesis of amino-functionalized core-shell MNPs with unsorted cores

In a bottle of 250 ml 400 μL of unsorted maghemite NPs were introduced ($c_{\text{Fe}} = 1 \text{ M}$, $n_{\text{Fe}} = 0.4 \text{ mmol}$). Afterwards, 25 ml of distilled water and 50 ml of absolute ethanol were inserted to the solution. The mixture was agitated for a couple of minutes before introducing 600 μL of tetraethoxyorthosilicate (TEOS, $n = 2.69 \text{ mmol}$) and 1.25 ml of a 30% ammonia solution ($n = 5.975 \text{ mmol}$). The resulting

dispersion was stirred for 2 additional hours. The functionalization of the silica shell by PEG chains and $-\text{NH}_2$ functions was carried out by the addition of 200 μl of TEOS ($n = 0.897 \text{ mmol}$), 230 μl of 3-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEOS, ($n = 0.424 \text{ mmol}$) and finally 100 μl of aminopropyltriethoxysilane (APTES, $n = 0.427 \text{ mmol}$). The mixture was stirred overnight. The washing procedure was carried out by 3 successive centrifugations of the solution at 10.000 rpm with absolute ethanol. Each washing step was followed by ultrasonication to completely disperse the NPs. These NPs were finally dispersed in 25 ml of freshly distilled acetonitrile, followed by several minutes of sonication.

Synthesis of amino-functionalized core-shell MNPs with 11.7 nm sorted cores (NPs12-A)

In a bottle of 250 ml, 375 μl of maghemite NPs with size of 11.7 nm were introduced ($c_{\text{Fe}} = 1.98 \text{ M}$, $n_{\text{Fe}} = 0.7425 \text{ mmol}$) with 25 ml of DI water and 50 ml of absolute ethanol. The mixture was agitated for a couple of minutes before introducing 350 μl of tetraethoxyorthosilicate (TEOS, $n = 1.569 \text{ mmol}$) and 0.75 ml of a 30% ammonia solution ($n = 3.585 \text{ mmol}$). The resulting dispersion was stirred for 2 additional hours. The functionalization of the silica shell by PEG chains and $-\text{NH}_2$ functions was carried out by the addition of 120 μl of TEOS ($n = 0.538 \text{ mmol}$), 135 μl of 3-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEOS, ($n = 0.249 \text{ mmol}$) and finally 60 μl of aminopropyltriethoxysilane (APTES, $n = 0.2564 \text{ mmol}$). The mixture was stirred overnight. The washing procedure was carried out by 3 successive centrifugations of the solution at 10.000 rpm with absolute ethanol. Each washing step was followed by ultrasonication to completely disperse the NPs. These NPs were finally dispersed in 25 ml of freshly distilled acetonitrile, followed by several minutes of sonication.

Synthesis of amino-functionalized core-shell MNPs with 11.7 nm sorted cores (NPs12-B)

The synthesis was carried out as previously reported for the NPs12-A, with different quantities introduced. In a bottle of 250 ml, 375 μl of maghemite NPs with size of 11,7 nm were introduced ($c_{\text{Fe}} = 1.98 \text{ M}$, $n_{\text{Fe}} = 0.7425 \text{ mmol}$) with 25 ml of DI water and 50 ml of absolute ethanol. The mixture was agitated for a couple of minutes before introducing 700 μl of tetraethoxyorthosilicate (TEOS, $n = 3.138 \text{ mmol}$) and 1.5 ml of a 30% ammonia solution ($n = 7.17 \text{ mmol}$). The resulting dispersion was stirred for 2 additional hours. The functionalization of the silica shell by PEG chains and $-\text{NH}_2$ functions was carried out by the addition of 240 μl of TEOS ($n = 1.076 \text{ mmol}$), 270 μl of 3-[methoxy(polyethyleneoxy)propyl]trimethoxysilane (PEOS, ($n = 0.498 \text{ mmol}$) and finally 120 μl of aminopropyltriethoxysilane (APTES, $n = 0.513 \text{ mmol}$). The mixture was stirred overnight. The washing procedure was carried out by 3 successive centrifugations of the solution at 10.000 rpm with absolute ethanol. Each washing step was followed by ultrasonication to completely disperse the NPs. These NPs were finally dispersed in 25 ml of freshly distilled acetonitrile, followed by several minutes of sonication.

Synthesis of amino-functionalized core-shell MNPs with 9 nm sorted cores (NPs9)

The synthesis was performed in two steps: the condensation of TEOS was followed by the functionalization of the silica shell by PEG chains and amino groups. For the 1st step, 1,20 mL of maghemite solution with sorted cores ($c_{\text{Fe}}=0.86$ M, $n_{\text{Fe}}=1.03$ mmol) with 25 ml of distilled water and 50 ml of absolute ethanol were added into a 100 mL flask. Then, 1.30 mL of TEOS ($n=5.87$ mmol) and 1.25 mL of 30% ammonia solution ($n=5.975$ mmol) were inserted to the mixture and the later was stirred for 2 hours. The second step consisted in the addition of 450 μL of TEOS ($n=2.02$ mmol), 495 μL of PEOS ($n=0.91$ mmol) and 225 μL of APTES ($n=0.96$ mmol). The mixture was agitated for 24 hours. The washing approach was the same as stated before for the unsorted NPs. Finally, the NPs were dispersed in 25 ml of freshly distilled acetonitrile.

Covalent grafting of POM-COOH with amino-functionalized core-shell MNPs

0.27 g (0.0875 mmol/1 eq) of POM-COOH were introduced in a 50 ml Schlenk tube and kept under vacuum for an overnight drying. Then, it was dissolved in 2 ml of freshly distilled acetonitrile under nitrogen. Then, 72.5 μL (0.525 mmol/6 eq) of triethylamine were added and the resulting mixture was cooled in an ice bath at -30 °C. After 30 min, isobutylchloroformiate (64.3 μL , 0.525 mmol/6 eq) was introduced and the solution was stirred for 30 min. In parallel, 25 ml of core-shell MNPs dispersed in distilled acetonitrile were introduced in another Schlenk tube under nitrogen and were transferred to the latter solution *via* a cannula. The resulting dispersion was stirred overnight at room temperature in an inert atmosphere. The NPs were finally washed with acetonitrile 3 times by centrifugation (10000 rpm for 20 minutes).

Electrostatic deposition of POM-COOH onto amino-functionalized core-shell MNPs

POM-COOH (0.27 g, 0.088 mmol) was introduced in a 50 ml round-bottom flask containing 25 ml of MNPs (with unsorted cores) dispersed in acetonitrile. The mixture was stirred for several days to have the highest initial tungsten amount possible. The NPs were finally washed with acetonitrile 3 times by centrifugation (10000 rpm for 20 minutes).

Annex C - X-Ray Absorption Spectroscopy

The X-ray Absorption Spectroscopy (XAS) is divided in two domains, using the synchrotron radiation, for the study of the fine structures observed in the vicinity of the absorption edge of a specific element:

- EXAFS (Extended X-ray Absorption Fine Structure), which studies the fine structures far from the energy edge, makes it possible to know the local radial distribution around a given absorbing atom: distance, Debye-Waller factor, nature and number of neighbouring atoms. This technique can be used in all types of materials (gas, liquid, amorphous or crystalline solid).

- XANES (X-ray Absorption Near Edge Structure) studies the fine structures at the energy edge and gives information about the electronic structure and symmetry of the absorbing centre. This technique was not used during this thesis.

The principle of the method is simple: a photon X of variable energy $E = h\nu$ excites an electron of the internal layers (in the case of the PhD it is an electron from the 1s at the L_{III} edge) of the absorber atom A. The absorption coefficient $m(E)$ is given by Fermi's golden rule:

$$m(E) \propto N(E) (\langle Y_{exc} | O_{dip} | Y_{fond} \rangle)^2 d(h\nu + E_{fond} - E_{exc})$$

where $N(E)$ is the density of vacant states; Y_{exc} and Y_{fond} the wave functions describing the excited and ground states with energies E_{exc} and E_{fond} , respectively, and O_{dip} the electric dipole transition operator.

If the energy of the photoelectron is lower than the ionization energy, "linked" excited states, corresponding to transitions of the electron to vacant levels, are obtained. Thus, fine absorption structures near the ionization edge (XANES) are acquired. Beyond the ionization edge (E_0), the photoelectron (with a mass m_e) leaves the absorbing atom and propagates in the continuum, with a kinetic energy E_{cin} and an associated wave with a vector wave k :

$$E_{cin} = h\nu - E_0$$

$$k = [8p^2 m_e / h^2] (h\nu - E_0)^{1/2}$$

The wave is retrodiffused by neighboring atoms. As a result, modulations of the absorption coefficient are observed with a decreasing amplitude in this zone of the spectrum. These modulations are due to the interferences between the outgoing wave and the backscattered waves. The importance of these structures depends on the nature and number N_j of neighboring atoms j and their distance R_j from the

absorbing atom. The photoelectron has a limited lifetime and a limited high energy path after the threshold. The technique, which has a local character, gives therefore information only on the closest neighbors; it is called the simple diffusion. This is less true at low kinetic energy, where the mean free path is larger and allows the establishment of a diffusion regime involving several neighbors. This phenomenon is called multiple diffusion.

The equation giving the expression of the signal EXAFS in a monoelectronic approximation involves a physical model with dipolar electrical transition, using simple planar waves diffusion and without relaxation of the electronic levels of the atoms. This equation is as follows:

$$c(k) = S_j N_j A_j(k, p) (1/R_j^2) \exp(-2R_j/l) \exp(-2k^2 s_j^2) \sin(2kR_j + f_{ij}(k))$$

where k is the wave vector associated with the photoelectron, N_j the number of neighbors at the distance R_j of the absorbing atom, s_j the Debye-Waller factor (it characterizes the standard deviation of distribution of the distances of the neighbors around the mean value R_j), $A_j(k, p)$ the backscattering amplitude of the neighboring atom j , $f_{ij}(k)$ is a phase factor which depends on the absorbing atom and the neighboring atom j , and l is the free path of the electron. The phase and amplitude parameters can be calculated ab initio or extracted from the experiment.

The main steps of the EXAFS signal analysis are:

- i. The obtainment of an experimental spectrum. It is also possible to add several EXAFS spectra for the same sample;
- ii. The extraction of the EXAFS signal by subtracting the continuous absorption bottom and the atomic absorption;
- iii. The Fourier transformation of the EXAFS signal;
- iv. The filtration of the various shells of neighboring atoms and the adjustment of the curve obtained by the theoretical expression by means of least squares programs.

I Preparation of the samples and EXAFS data processing and analysis

The samples were ground and homogeneously dispersed in cellulose pellets, and recovered with a kapton tape. The experiment was calibrated with a Vanadium metal foil. The EXAFS processing and analysis was performed by using the standard procedure "DEMETER" package (version 0.9.25). The EXAFS data processing was performed with the program « Athena » and the EXAFS Data Analysis using Feff was obtained with the program « Artemis ».

Annexes

The EXAFS signal was extracted from the data by subtracting a linear pre-edge background and normalized by the Lengeler-Eisenberger procedure. The E^0 value was fixed at 5489.5 eV and the normalization was effectuated using a spline with k weight = 3 in the range of 5588-5883 eV for all spectra. The pseudo-radial distribution function was given by the Fourier transform (FT) with a Kaiser-Bessel window with a smoothness parameter dk equal to 2. The k limits are equal to 3.6-8.8 Å⁻¹.

Publications

Efficiency of Polyoxometalate-Based Mesoporous Hybrids as Covalently Anchored Catalysts

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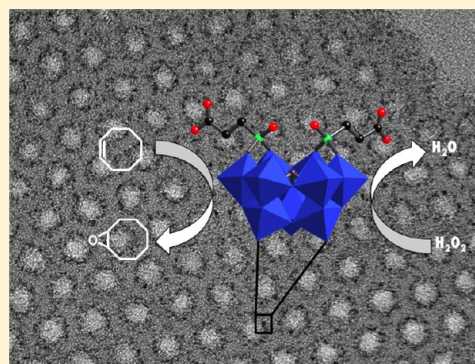
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Supporting Information

ABSTRACT: Polyoxometalate (POM) hybrids have been covalently immobilized through the formation of amide bonds on several types of mesoporous silica. This work allows the comparison of three POM-based mesoporous systems, obtained with three different silica supports in which either the organic functions of the support (amine vs carboxylic acid) and/or the structure of the support itself (SBA-15 vs mesocellular foams (MCF)) were varied. The resulting POM-based mesoporous systems have been studied in particular by high resolution transmission electronic microscopy (HR-TEM) in order to characterize the nanostructuration of the POMs inside the pores/cells of the different materials. We thus have shown that the best distribution and loading in POMs have been reached with SBA-15 functionalized with aminopropyl groups. In this case, the formation of amide bonds in the materials has led to the nonaggregation of the POMs inside the channels of the SBA-15. The catalytic activity of the anchored systems has been evaluated through the epoxidation of cyclooctene and cyclohexene with H₂O₂ in acetonitrile. The reactivity of the different grafted POMs hybrids has been compared to that in solution (homogeneous conditions). Parallels can be drawn between the distribution of the POMs and the activity of the supported systems. Furthermore, recycling tests together with catalyst filtration experiments during the reaction allowed us to preclude the hypothesis of a significant leaching of the supported catalyst.



1. INTRODUCTION

Regarding their unique properties in terms of thermal stability, resistance toward oxidative conditions, and/or hydrolysis (provided that pH conditions are controlled), polyoxometalates (POMs) have been thoroughly considered as intrinsic oxidation catalysts either in homogeneous or heterogeneous conditions.^{1–4} In the latter case, POMs are generally dispersed on oxide supports in order to circumvent their very low surface area in the solid state. In most examples, POMs are not strongly chemically bonded to the support. Studies generally involve either a simple physisorption or an electrostatic interaction with a positively charged support, acting like counterions.^{3,5–10} This strategy has also been recently applied to surface-modified graphene.¹¹ POMs may also be immobilized successfully into materials through various other strategies¹² such as their encapsulation into metal–organic frameworks (MOFs),^{13,14} their intercalation into layered double hydroxides,¹⁵ or their

one-pot embedding into a silica matrix via co-condensation sol–gel methods¹⁶ (including the covalent grafting of vacant POMs into the walls of hybrid supports).^{17,18}

We recently focused on the elaboration of new mesoporous materials functionalized with nucleophilic (vacant) POMs for applications in the field of anchored homogeneous catalysis.¹⁹ In this preliminary work, we demonstrated, for the first time, that functionalization of both the vacant polyoxometalate species and the mesoporous silica support by complementary organic functions provides an efficient strategy for their covalent linkage. The principle was illustrated using an organophosphonate derivative of trivacant POMs bearing carboxylic acid functionalities on one hand and an NH₂-functionalized mesoporous SBA-15 support on the other hand

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(Figure 1). It is noteworthy that, following this report, such a strategy has been applied to the grafting of organosilyl

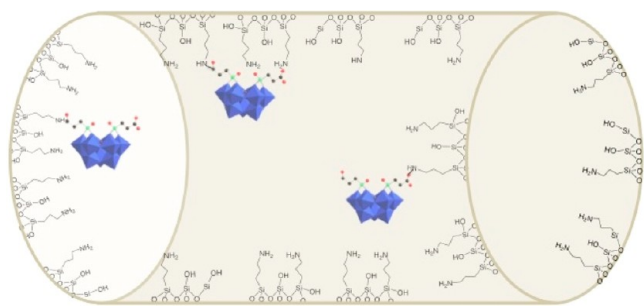


Figure 1. Covalent grafting of phosphonate derivatives of vacant POMs onto the walls of NH_2 -functionalized SBA-15 silica. Counterions associated with the POMs are not represented for sake of clarity.

derivatives of Dawson-type POMs onto macroporous polymer matrices, via azide alkyne Huisgen cycloaddition.²⁰

It is well-known that the efficiency of supported molecular catalysts is related not only to their accessibility but also to their dispersion and accessibility on the support. One of the keys for obtaining efficient materials are anchoring platforms with high specific surface and porosity, such as the SBA-15 silica used in our previous study.¹⁹ However, an increasing number of inorganic supports are now available in the literature for catalysis purposes, with morphology and/or composition and/or surface modification that can now be easily modulated.^{21,22} The effects of the modification of the support on the dispersion of the catalyst are thus questions we obviously need to address. Controlled immobilization of organometallic complexes in mesoporous silica has been reported.²³

In the present work, we propose an extended study of the grafting of hybrids POMs on various organically modified supports. Three mesoporous supports have been examined, in which either the organic functions displayed (aminopropyl vs carboxypropyl) or the type of material itself, SBA-15 vs MCF (siliceous MesoCellular Foam), was varied. We thus analyzed both effects on the dispersion of the POMs in the different materials, in particular by high resolution transmission electronic microscopy (HR-TEM). In addition, the dispersion has then been tentatively correlated with the catalytic efficiency of the supported POMs in the cyclooctene and cyclohexene epoxidation by H_2O_2 , used here as convenient model reactions.²⁴

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Solvents and other reagents were obtained from commercial sources and used as received, except for triethylamine and acetonitrile, which were distilled. The complexes $(^n\text{Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_6\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\}_2]$,¹⁹ $\text{TBA}_3\text{NaH}(\text{POM}-\text{CO}_2\text{H})$, and $(^n\text{Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)\}_2]$,^{25,26} $\text{TBA}_4\text{H}(\text{POM}-\text{NH}_2)$, were prepared as previously described.

Solids were characterized by attenuated total reflection infrared spectroscopy, using Tensor R27 FTIR equipped with a ZnSe crystal with resolution better than 1 cm^{-1} . Raman spectra were recorded on solid samples on a Kaiser Optica Systems HLSR spectrometer equipped with a near-IR laser diode working at 785 nm. The ^1H (300.13 MHz), ^{13}C (75.6 MHz), and $\{^1\text{H}\}$ ^{31}P NMR (121.5 MHz) solution spectra were recorded in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probehead. ^{13}C CP MAS NMR spectra were recorded at 125.77 MHz on a Bruker AVANCE III 500 spectrometer (11.7 T) with a 4 mm Bruker probe and at a spinning frequency of 10 kHz (recycle delay = 5 s, contact time = 10

ms). ^{31}P MAS NMR spectra were recorded at 283.31 MHz on a Bruker AVANCE III 700 spectrometer (16.4 T) equipped with 2.5 mm Bruker probe and at a spinning frequency of 30 kHz. Chemical shifts were referenced to tetramethylsilane (TMS) for ^{13}C and to 85% aqueous H_3PO_4 for ^{31}P . Thermogravimetric analyses (TGA) were performed under air with a TA-Instrument SDT Q600 between 20 and 900 °C (air flow: 100.0 mL min^{-1} , 10 °C min^{-1}). Elemental analyses were performed by the Institut des Sciences Analytiques du CNRS (Villeurbanne, France). N_2 sorption analyses of the pretreated materials (100 °C) were obtained at -196 °C using an ASAP-2020 Micromeritics apparatus. Small-angle XRD measurements were carried out on a Bruker D8 Advance XRD diffractometer. X-ray fluorescence analyses were conducted with an energy dispersive spectrometer (XEPOS with Turboquant powder software). HR-TEM analyses were realized on a microscope operating at 200 kV with a resolution of 0.18 nm (JEOL JEM 2011 UHR) equipped with an EDX system (PGT IMIX-PC). Samples were dispersed in resin and cut with an ultramicrotome. The lamellas of 50 nm thickness were then deposited on Cu grid covered with an amorphous carbon film.

2.2. Preparation of the Functionalized Supports. **2.2.1. SBA-15 Silica with 3-Aminopropyl Groups (SBA- NH_2).**¹⁹ SBA- NH_2 was obtained in a two-step procedure, after functionalization of a preformed SBA-15 with 3-aminopropyltriethoxysilane, as follows.

SBA-15 silica (1.0 g) previously dried at 350 °C for 12 h was dispersed in 50 mL of anhydrous toluene using an ultrasound bath for 5 min and magnetic stirring. Then, 3-(aminopropyl)triethoxysilane (APTES) (1 mL, 4 mmol) was added, and after 1 h, the resulting mixture heated up to 110 °C. Reflux was maintained for 24 h, after which the suspension was filtered. The recovered solid was washed with toluene, acetonitrile, and ethanol (15 mL of each), and then air-dried. The resulting $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiO}_{1.5}/8\text{SiO}_2$ solid was extracted with dichloromethane using a Soxhlet for 24 more hours.

2.2.2. SBA-15 Silica with Carboxypropyl Functions (SBA- CO_2H).²⁷ SBA- CO_2H support was prepared following a one-pot procedure synthesis: Pluronic 123 (4.0 g) was dissolved in 150 mL of an aqueous solution of HCl (pH ~ 1.5). The resulting clear solution was then added to a mixture of (4-butyronitrile)triethoxysilane (BNTES) (1.04 g, 4.5 mmol) and tetraethylorthosilicate (TEOS) (8.40 g, 40.4 mmol). The mixture was vigorously stirred for 3 h at room temperature until a transparent solution appeared. The solution was transferred to a hot bath at 60 °C, and NaF (76 mg, 1.8 mmol) was immediately added. In the present case, NaF was acting as catalyst for polycondensation process. A white precipitate was formed after a few minutes. After aging under regular stirring for 3 days at 60 °C, the resulting powder was filtered off, and the surfactant was selectively removed by Soxhlet extraction with ethanol for 24 h. After the material was suspended in 25 mL of a 50 wt % H_2SO_4 and stirred at 120 °C for 5 h. Subsequently, the solid was recovered by filtration, washed with water and acetone and dried at 120 °C under vacuum (0.1 mm Hg), $\text{HOOC}(\text{CH}_2)_3\text{SiO}_{1.5}/9\text{SiO}_2$ was obtained as a white powder.

2.2.3. MesoCellular Foam Silica with Aminopropyl Functions (MCF- NH_2). MCF- NH_2 was obtained in a two-step procedure, after functionalization of a preformed MCF²⁸ with 3-aminopropyltriethoxysilane, as follows.

First, Pluronic 123 (8.0 g) was added to 240 mL of distilled water and 40 mL of concentrated chlorhydric acid (37%). The mixture was heated at 40 °C until complete dissolution of Pluronic 123. Trimethylbenzene (9.2 mL, 8 g) was introduced dropwise as a swelling agent. After 2 h, TEOS (18 mL, 80 mmol) was also added dropwise, and the resulting suspension was further heated at 40 °C for 24 h. NH_4F (98 mg) was introduced 15 min before hydrothermal treatment. The latter was performed at 100 °C in a FEP bottle for an additional 24 h. The suspension was filtered, and the obtained solid was washed with water, dried at 60 °C, and finally calcined (24 °C min^{-1}) at 550 °C for 6 h.

Second, 1.0 g of freshly dried MCF silica (350 °C, 12 h) was added to 50 mL of anhydrous toluene. The resulting suspension was stirred at room temperature, and APTES (1.0 mL, 4 mmol) was introduced. After 2 h, the reaction mixture was heated until toluene reflux (110 °C) and maintained at this temperature for 24 h. Then, the suspension

Table 1. Textural Data of the Supports before and after POM Coupling

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	pore vol ($\text{cm}^3 \text{g}^{-1}$)	pore diameter or window for MCF (nm) desorption	pore diameter or cell for MCF (nm) adsorption
SBA-NH ₂	398	0.7	6.2	8.0
SBA-CO ₂ H	536	1.0	7.0	9.2
MCF-NH ₂	327	1.5	7.1	17.4
POM-CO ₂ H@SBA-NH ₂	185	0.33	4.7	7.0
POM-NH ₂ @SBA-CO ₂ H	477	1.0	6.2	9.2
POM-CO ₂ H@MCF-NH ₂	245	1.0	6.2	17.3

was filtered. The recovered solid was washed successively with 15 mL of toluene, 15 mL of acetone, and then 15 mL of ethanol, and air-dried for 24 h. Finally, the solid was extracted using a Soxhlet during 24 h with dichloromethane as the solvent.

2.3. Covalent Binding of TBA₃NaH(POM-CO₂H) with SBA-NH₂¹⁹ and MCF-NH₂. Samples of (ⁿBu₄N)₃NaH-[As^{III}W₉O₃₃{P(O)-(CH₂CH₂CO₂H)}₂] (0.66 g, 0.2 mmol) and SBA-NH₂ silica (0.60 g, 4 mmol g⁻¹ (nominal) of -NH₂ groups) (or MCF-NH₂, 0.60 g, 4 mmol g⁻¹ (nominal) of -NH₂ groups) were introduced in 100 mL Schlenk tubes and kept under vacuum overnight. The POM-CO₂H complex was dissolved under argon in 20 mL of freshly distilled acetonitrile. Triethylamine (164 μL , 0.12 g, 1.2 mmol) was then added and the resulting mixture cooled in an ice bath. After 30 min, isobutylchloroformate (156 μL , 0.16 g, 1.2 mmol) was introduced, and the resulting solution was stirred for 30 min (solution 1). In parallel, SBA-NH₂ or MCF-NH₂ silica was dispersed in distilled acetonitrile (5 mL) in the other Schlenk tube under argon. Solution 1 was then transferred to the dispersion of the support via cannula. The resulting suspension was stirred overnight at room temperature under argon, and then filtered. The recovered solid, i.e., POM-CO₂H@SBA-NH₂ or POM-CO₂H@MCF-NH₂, was finally extracted using a Soxhlet over 2 days with acetonitrile as the solvent. Chem Anal.: POM-CO₂H@SBA-NH₂: W(%) 19.12; Si(%) 23.08. POM-CO₂H@MCF-NH₂: W(%) 14.55; Si(%) 26.20.

2.4. Covalent Binding of TBA₄H(POM-NH₂) with SBA-CO₂H. Samples of (ⁿBu₄N)₄H[PW₉O₃₄{As(O)(C₆H₄NH₂)₂}₂] (0.26 g, 0.078 mmol) and SBA-CO₂H (0.5 g, 1.5 mmol g⁻¹ of -CO₂H groups) were each introduced in a 100 mL Schlenk tube and kept under vacuum overnight. The SBA-CO₂H support was then placed under argon with 10 mL of freshly distilled acetonitrile, and then *N*-hydroxysuccinimide (NHS; 1.8 mmol; 0.207 g) and 1-(3-(dimethylamino)propyl)-*N'*-ethylcarbodiimide hydrochloride (EDC; 0.9 mmol; 0.172 g) were successively introduced. The resulting suspension was stirred for 3 h at room temperature. In parallel, the TBA₄H(POM-NH₂) complex was placed under argon and dissolved in 10 mL of freshly distilled acetonitrile. This solution was then transferred to the dispersion of the support using a cannula. The resulting suspension was stirred overnight at room temperature under argon, and then filtered. The solid recovered, i.e., POM-NH₂@SBA-CO₂H, was extracted using a Soxhlet over 2 days with acetonitrile as the solvent. Chem Anal.: W(%) 5.83; Si(%) 31.05.

2.5. Preparation of the POM-CO₂H-Supported on SBA-NH₂ Sample by Incipient Wetness Impregnation. A sample of SBA-NH₂ (0.5 g) with a pore volume of 0.7 mL g⁻¹ was put in contact with 0.19 g of TBA₃NaH(POM-CO₂H) in 0.35 mL of CH₃CN. After complete absorption of the liquid phase by the SBA-NH₂ support, the sample was dried under vacuum. It is noteworthy that the amount of POMs introduced was equal to the amount of POMs found in the final POM-CO₂H@SBA-NH₂ material obtained after covalent grafting (W: 19.2%, corresponding to 28.9% of anions [As^{III}W₉O₃₃{P(O)-(CH₂CH₂CO₂H)}₂]⁵⁻ (POM-CO₂H)).

2.6. Catalytic Studies. In homogeneous conditions, experiments of cyclooctene (or cyclohexene) epoxidation were performed in a 50 mL round-bottom flask equipped with a condenser and magnetic stirrer at room temperature or at 50 °C. The catalysts, TBA₃NaH-(POM-CO₂H) or TBA₄H(POM-NH₂) (80 mg, 24 μmol /1 equiv), 20 mL of acetonitrile, 0.78 mL of cyclooctene or 0.60 mL of cyclohexene (6 mmol/250 equiv), 0.9 mL of decane (as an internal standard), and

0.6 mL of H₂O₂ (30%/6 mmol/250 equiv) were introduced successively in the flask. The resulting solutions were analyzed by gas chromatography on a Delsi Nermag DN 200 GC apparatus equipped with a flame ionization detector and a Macherey-Nagel Optima-5 capillary column (length 30 m, internal diameter 0.32 mm, thickness 1 μm).

In heterogeneous conditions, experiments of cyclooctene/cyclohexene epoxidation were performed in three 5 mL flasks (for analysis at 3, 6, and 24 h) under stirring at room temperature. The solid catalysts POM-CO₂H@SBA-NH₂ (40 mg), POM-NH₂@SBA-CO₂H (114 g), or POM-CO₂H@MCF-NH₂ (55 mg), corresponding to 1.2×10^{-3} mmol/1 equiv of POM-NH₂ or POM-CO₂H, 1 mL of acetonitrile, 39 μL of cyclooctene (250 equiv) or 30 μL of cyclohexene (250 equiv), 45 μL of decane, and 30 μL of H₂O₂ (30%, 250 equiv) were introduced successively in each flask. The supernatant of the resulting suspensions was analyzed by gas chromatography as described above. Blank reactions have been also performed with the different supports SBA-NH₂, SBA-CO₂H and MCF-NH₂, before the POMs-grafting steps. No catalytic activity was found for these materials in the absence of the POMs. For the recycling experiment, the catalyst has been filtered on a glass frit (por 4), rinsed with a few milliliters of CH₃CN, dried at air, and reused without any further treatments.

3. RESULTS AND DISCUSSION

In this work, three different POM-grafted materials were prepared in order to compare the nanostructuration of the active phase at the surface of the pores. These materials were obtained through the covalent binding of POM hybrids with three different functionalized mesoporous silica supports. In the continuity of our previous works, the strategy we used consisted of the coupling of complementary functions, one at the oxide-support and the second one on the termination of the organic groups introduced in the POM framework. In this respect, two different effects were studied: (1) the grafting reaction of POM hybrids on a given type of support (in the present case SBA-15 displaying anchoring aminopropyl or carboxypropyl functions); (2) the type of mesoporosity of the silica hosts, SBA-15 versus MCF, both functionalized with the same organic (aminopropyl) functions.

3.1. Characterization of SBA-NH₂, SBA-CO₂H, and MCF-NH₂ Materials.

3.1.1. Thermogravimetric Analyses. The thermogram of SBA-NH₂ (see Supporting Information Figure S1) performed under air from room temperature up to 900 °C shows two weight losses. The first one (3%), under 100 °C, can be attributed to the loss of water molecules weakly adsorbed on the silica surface. The second one (17%, 100–800 °C) can be assigned to the loss of aminopropyl functions. This analysis demonstrated that SBA-NH₂ is functionalized with 3 mmol of NH₂ g⁻¹ (ca. 75% incorporation yield).

Similarly, the thermogravimetric analysis of MCF-NH₂ exhibits two weight losses, respectively, of 2% and 15%. The second weight loss (100–800 °C) can still be attributed to aminopropyl functions. The MCF-NH₂ support was found to

be functionalized by 2.3 mmol of $\text{NH}_2 \text{ g}^{-1}$ (ca. 60% incorporation yield). In comparison, the TGA-DTA analysis of SBA- CO_2H shows that it was functionalized with 1.7 mmol of $-\text{CO}_2\text{H} \text{ g}^{-1}$ (ca. 100% incorporation yield).

3.1.2. Structural Study of SBA- NH_2 , SBA- CO_2H , and MCF- NH_2 Materials. The X-ray powder diffraction patterns at 2θ (0.5 – 3°) of the SBA- NH_2 and SBA- CO_2H materials (see Supporting Information, Figure S2a,b) exhibited three peaks, the first one being far more intense than the other two. These signals were, respectively, assigned to the (100), (110), and (200) reflections of the expected hexagonal $P6m$ structure. It is noteworthy that the intensities of the peaks related to the (110) and (200) reflections are smaller for SBA- CO_2H .

Transmission electron microscopy (TEM) confirmed the structure of SBA- NH_2 and SBA- CO_2H . The micrographs obtained by HR-TEM on both supports (see Supporting Information Figure S3) displayed the same organized tubular networks. Their textural data (see Table 1) were also comparable, although a larger specific surface was determined in the case of SBA- CO_2H . The micrographs of MCF- NH_2 confirmed the cellular foam structure of this support and the existence of cells with smaller apertures (windows) (Figure 2).

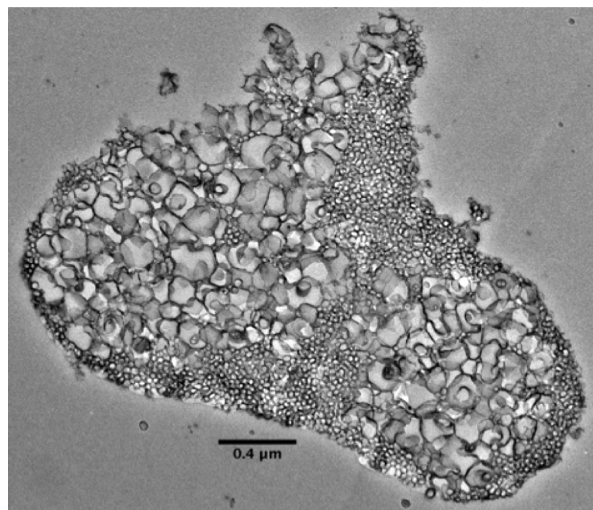


Figure 2. HR-TEM micrograph of MCF- NH_2 materials.

3.1.3. Nitrogen Physisorption. The nitrogen physisorption isotherms and the pore-size distribution of the two SBA supports are shown in Figure S4 (see Supporting Information). The adsorption/desorption isotherms are of type IV with a hysteresis loop. The pore sizes were calculated from the desorption branches of the isotherms using the Barret–Joyner–Hallenda (BJH) formula (Table 1). This method is used for the determination of the pore-size distribution of materials with pores larger than 4 nm, and it is appropriate for our silica supports (SBA- NH_2 and SBA- CO_2H). Values calculated from the adsorption branches were also determined in the case of MCF- NH_2 (Table 1).

3.2. Characterization Studies of the POM-Grafted Materials. Two different POMs, with organic functions complementary to those of the supports, were used: the previously reported $(n\text{-Bu}_4\text{N})_3\text{NaH}[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})-(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}]$ complex, $\text{TBA}_3\text{NaH}(\text{POM}-\text{CO}_2\text{H})$, which contains two carboxylic acid functions, and the bis-anilino derivative $\text{TBA}_4\text{H}(\text{POM}-\text{NH}_2)$, $(n\text{-Bu}_4\text{N})_4\text{H}[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)_2\}]$ (see Figure 3).²⁹

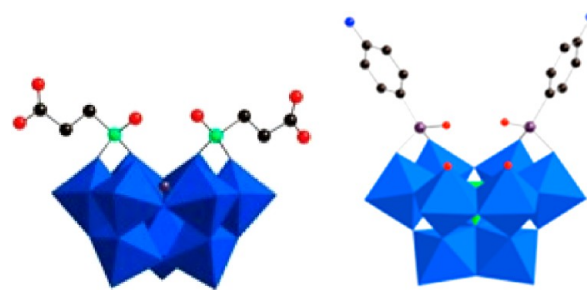


Figure 3. Structural representation of POM- CO_2H (left) and POM- NH_2 (right) anions. WO_6 and PO_4 polyhedra are shown in blue and green, respectively. The As, P, N, O, and C atoms are shown, respectively, in prune, green, blue, red, and black.

As previously reported,¹⁹ the $\text{TBA}_3\text{NaH}(\text{POM}-\text{CO}_2\text{H})$ complex was easily grafted onto the NH_2 -functionalized supports through the formation of amide bonds. For this purpose, isobutylchloroformate ($i\text{-BuOC}(\text{O})\text{Cl}$) was used as a coupling agent, in the presence of triethylamine. This procedure was repeated in the present work with SBA- NH_2 (POM- $\text{CO}_2\text{H}@$ SBA- NH_2), and adapted also to MCF- NH_2 (POM- $\text{CO}_2\text{H}@$ MCF- NH_2), which was not described until now. Both POM-functionalized amino supports were characterized by ^{13}C NMR (Supporting Information, Figure S5), ^{31}P CP-MAS NMR (Supporting Information, Figure S6), and Raman (Supporting Information, Figure S7) and IR spectroscopies, in order to confirm the integrity of the POMs after grafting and the formation of amide bonds (with ^{13}C CP-MAS NMR and IR). From this study, it was found that the spectra displayed similar patterns for both materials, in accordance with those previously reported.¹⁹ Additionally, the powder X-ray diffraction patterns of POM- $\text{CO}_2\text{H}@$ SBA- NH_2 (Supporting Information Figure S2c) displayed the diffraction peaks characteristic of the hexagonal structuration of the mesopores, indicating that the modified material kept the SBA-15 structure.

The second POM $\text{TBA}_4\text{H}(\text{POM}-\text{NH}_2)$ contains two aniline functions.²⁶ The coupling procedure between these anilines and the carboxylic functions of the SBA- CO_2H was adapted from previous work done by some of us dealing with gold surfaces functionalized with carboxylic acid moieties (see section 2.4).³⁰ X-ray fluorescence (XRF) and chemical elemental analysis determined POM contents of the three materials at once. The obtained results are given in Table 2. It is worth noting that

Table 2. W/Si Molar Ratio and POM Content for POM-Grafted Materials

	W/Si molar ratio		POMs content (mmol g^{-1})
	XRF	elem. anal.	
POM- $\text{CO}_2\text{H}@$ SBA- NH_2	0.087	0.120	0.1
POM- $\text{NH}_2@$ SBA- CO_2H	0.020	0.028	0.035
POM- $\text{CO}_2\text{H}@$ MCF NH_2	0.047	0.084	0.085

both techniques gave similar trends for the W/Si ratio, with the higher content in POMs being observed in the case of the $-\text{NH}_2$ functionalized supports. The POM contents (given in mmol per g of materials, based on the chemical elemental analysis results) are in the range 3.5×10^{-2} to 1×10^{-1} mmol g^{-1} of functionalized supports. This corresponds to the following POM loadings: (1) 9.2 wt % based on the anions $[\text{PW}_9\text{O}_{34}\{\text{As}(\text{O})(\text{C}_6\text{H}_4\text{NH}_2)_2\}]^{5-}$ (POM- NH_2) for POM-

$\text{NH}_2\text{@SBA-CO}_2\text{H}$, (2) 22.0 and 28.9 wt % based on the anions $[\text{As}^{\text{III}}\text{W}_9\text{O}_{33}\{\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2\}_2]^{5-}$ ($\text{POM-CO}_2\text{H}$), respectively, for $\text{POM-CO}_2\text{H@MCF-NH}_2$ and $\text{POM-CO}_2\text{H@SBA-NH}_2$.

$\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$ was also characterized by ^{31}P and ^{13}C CP-MAS NMR (see Supporting Information, Figure S8), and IR and Raman spectroscopies. Unfortunately, the significantly weaker content of POMs in $\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$ (W/Si molar ratio = 0.028 (0.02 by XRF), see Table 2) did not allow us to characterize the formation of amide bonds by all spectroscopies mentioned above.

Furthermore, textural data of this material were compared to those of $\text{POM-CO}_2\text{H@SBA-NH}_2$ and $\text{POM-CO}_2\text{H@MCF-NH}_2$. As expected, the greater the amount of POMs introduced ($\text{POM-CO}_2\text{H@SBA-NH}_2$), the greater the S_{BET} is decreased. We thus observed a significant diminution of the pore volume after grafting $\text{POM-CO}_2\text{H}$ anions onto SBA-NH_2 materials, consistently with our previous results. Such low values of S_{BET} are generally observed for other POMs/SBA-15 systems obtained by classical POMs deposition, at high POMs loading.³¹ On the other hand, the pore volume remained approximately constant in the case of $\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$. It is worth noting that pore volumes and diameter variations may be hardly compared in the three materials since MCF structure is obviously different due to the presence of windows and cells.

3.3. High Resolution Transmission Electron Microscopy (HR TEM) of the POM-Grafted Supports. All three POM-grafted supports ($\text{POM-CO}_2\text{H@SBA-NH}_2$, $\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$, and $\text{POM-CO}_2\text{H@MCF-NH}_2$) were characterized by high resolution TEM, after microtome cutting. The comparison between the supports before (see Figure 2 and Supporting Information Figure S3) and after POM grafting (Figures 4–6) was undoubtedly instructive. First of all, it can be observed at low magnification that the grafting of POMs did not alter the intrinsic structure of the supports, even in the presence of triethylamine.

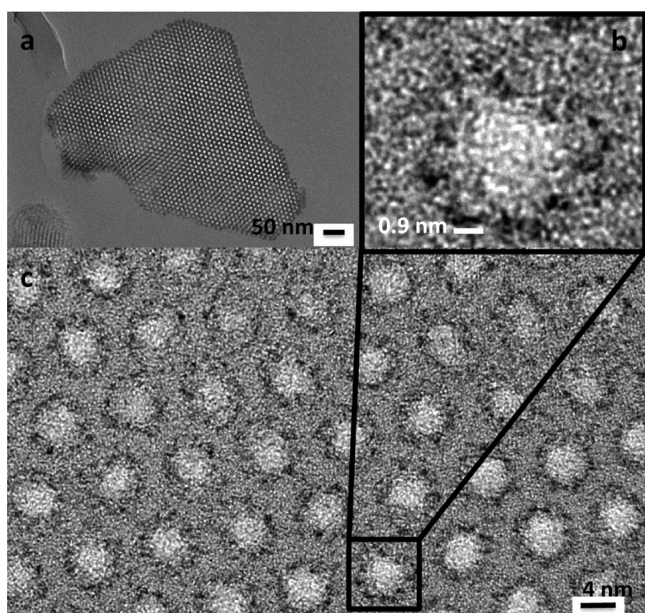


Figure 4. HR TEM micrographs (microtome cutting) of $\text{POM-CO}_2\text{H@SBA-NH}_2$ at different magnifications.

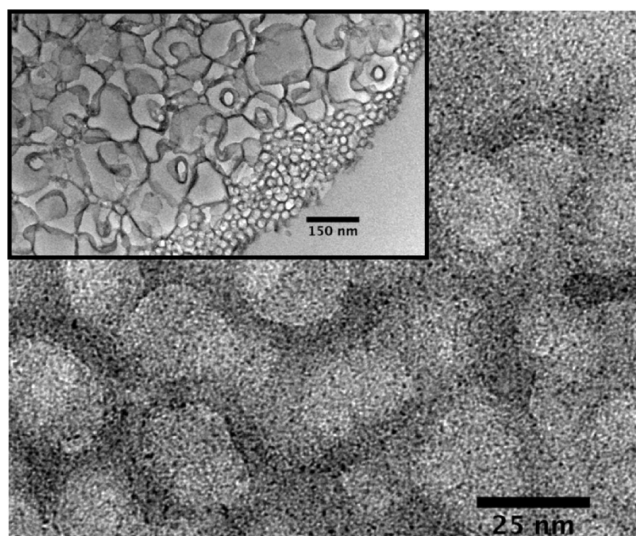


Figure 5. HR TEM micrographs (microtome cuttings) of $\text{POM-CO}_2\text{H@MCF-NH}_2$ at different magnifications.

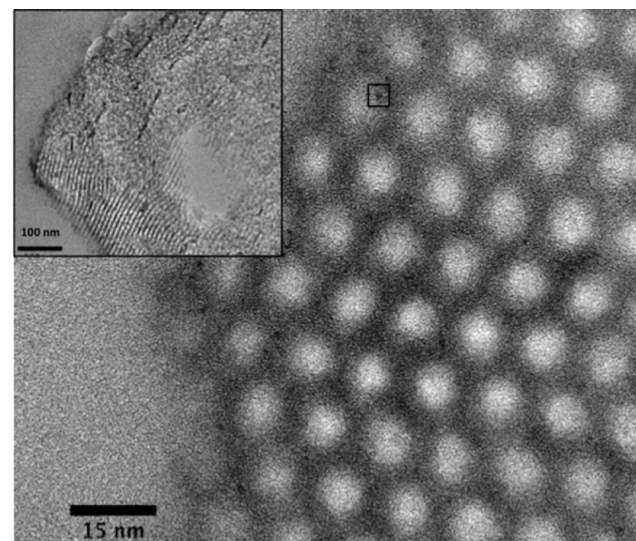


Figure 6. HR TEM micrographs (microtome cutting) of $\text{POM-NH}_2\text{@SBA-CO}_2\text{H}$ at different magnifications.

By classical HR-TEM, the presence of POMs at the surface of the silica grains was not observed, even at high magnification. In contrast, microtome cuttings turned out to be a powerful tool, since it was possible to clearly identify the presence and, above all, the exact location of the POMs inside the pores or cells of the materials. In the case of $\text{POM-CO}_2\text{H@SBA-NH}_2$ (Figure 4), we clearly observed the regular distribution of POMs at the periphery of the channels. POMs appeared thus arranged in a monolayer in the pores, covering almost the whole inner surface. The efficiency of the microtome cutting, combined with the image contrast provided by heavy W atoms in the silica matrix, led us to consider that POMs did not form aggregates in these materials (average size of “dark” dots about 0.9 nm, Figure 4b). The covalent grafting of POMs onto the walls through the formation of amide functions led then to isolated anions and, thus, facilitated in a very efficient way the nanostructure of the catalysts on the support.

Examination of the elemental composition of a single grain of material by X-ray energy-dispersive spectroscopy (XEDS, see

Supporting Information Figure S9 for more details) indicated that the ratio $W/Si = 0.16$ is on the same order of magnitude as that obtained by chemical analysis ($W/Si = 0.12$, Table 2). Moreover, XEDS also confirmed that the W atoms present in the solid were concentrated in the pores, with a measured W/Si ratio equal to 0.29 after deconvolution of the XEDS spectrum recorded on an area focused on one pore.

HR TEM micrographs of $POM-CO_2H@MCF-NH_2$ (Figure 5) also revealed the presence of POMs at the periphery of the cells. However, their distribution appeared less regular than in $POM-CO_2H@SBA-NH_2$ materials. This is obviously linked to the structure of the MCF silica, in which cells having walls with different intrinsic properties replaced cylindrical pores. Nevertheless, the size of the dots (attributed to the POMs) observed in all micrographs was mostly found to be around 1 nm. POMs still appeared as individual cluster anions, as observed in the case of $POM-CO_2H@SBA-NH_2$. As demonstrated in the previous materials, XEDS also confirmed that W atoms are mainly concentrated in the cells (Supporting Information, Figure S10).

HR-TEM micrographs of $POM-NH_2@SBA-CO_2H$ (Figure 6) showed far fewer “dark” dots attributed to POMs, as expected due to the weakest POMs contents. Furthermore, while the distribution of POMs in the $-NH_2$ functionalized supports appeared regularly in every pore of the silica, in particular for $POM-CO_2H@SBA-NH_2$, we observed that only a few channels are covered with POMs (insert in Figure 6). In addition, the size of the POMs containing dots was evaluated, and it was found to be larger than that in the previous materials (about 1.8 nm for the dot inside the black square in the top of Figure 6, and larger ones were observed on several other micrographs). This suggests that $POM-NH_2$ anions were not found in the form of isolated species but preferably of aggregates of a few clusters. This makes us question the covalent grafting of $POM-NH_2$ at the surface of the $SBA-CO_2H$ and, thus, the efficiency of the coupling procedure we used. XEDS was also performed on the materials, and we found that the W/Si ratio measured on a whole grain was identical (0.028) to the value found by chemical analysis. We also observed an increase of this value (up to 0.048) when the X-ray beam was concentrated on a single channel (Supporting Information, Figure S11). This increase led then to an unambiguous localization of the POMs in the SBA channels.

3.4. HR-TEM Study of Noncovalently Bound Anions $POM-CO_2H$ in Mesoporous SBA-15. For this study, in order to point out the added value of the covalent grafting procedure for the POM organization, we prepared a different $POM-CO_2H$ -supported $SBA-NH_2$ sample, obtained by incipient wetness impregnation of $SBA-NH_2$ with a solution (CH_3CN) of $TBA_3NaH(POM-CO_2H)$. In this experiment, the amount of POMs introduced was equal to that found in the final $POM-CO_2H@SBA-NH_2$ materials obtained after covalent grafting (approximately 40% in mass), with the volume of solvent corresponding to the pore volume of the $SBA-NH_2$ used ($0.7\text{ cm}^3\text{ g}^{-1}$). Several examples of HR-TEM micrographs obtained after microtome cutting are presented in Figure 7. First of all, we found by XEDS that the distribution of POMs was very irregular in the different grains of SBA-15. POMs were not present in all domains. Furthermore, in the case of POM-containing grains, POMs were generally not observed as isolated clusters (like in $POM-CO_2H@SBA-NH_2$ materials) but preferably as aggregates whose sizes were found in the 1.5–20 nm range. These micrographs also showed that some channels

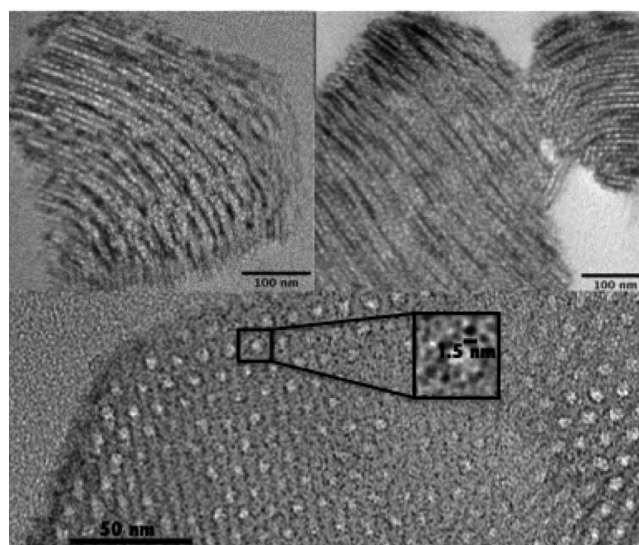


Figure 7. HR-TEM micrographs of $SBA-NH_2$ supports covered by $TBA_3NaH(POM-CO_2H)$ after wet impregnation.

were not “filled” at all by POMs (see Figure 7, top left and right), on the contrary to what was observed previously in $POM-NH_2@SBA-CO_2H$ samples. This seems to confirm that the nature of the interactions between $POM-NH_2$ anions and $SBA-COOH$ was probably not covalent.

3.5. Comparative Study of the Catalytic Performance of Homogeneous vs Anchored Homogeneous Catalysts: The Case Studies of Cyclooctene/Cyclohexene Epoxidation with H_2O_2 . **3.5.1. Epoxidation of Cyclooctene/Cyclohexene with H_2O_2 in Homogeneous Conditions.** Examples of the reactivity of heteropolytungstates that contain no additional transition-metal ions,^{3,32} including organophosphonyl derivatives of POMs^{33,34} in alkenes epoxidation processes can be found in the literature. Among all these studies, only one using organophosphonyl derivatives of trivalent POMs platforms was described so far, by the group of Bonchio.³³ Furthermore, the experimental conditions used in the present study may hardly be compared to those of Bonchio et al., who worked at very high temperature with microwave assistance.

Prior to the study of the catalytic performances of $TBA_3NaH(POM-CO_2H)$ and $TBA_4H(POM-NH_2)$ covalently supported onto mesoporous silica, we have checked the activity of the corresponding POMs under homogeneous conditions. The model reactions were, respectively, the epoxidation of cyclooctene and cyclohexene with aqueous H_2O_2 carried out at room temperature (excepted for some experiments specifically driven at 50 °C) in acetonitrile with the following catalyst/alkene/ H_2O_2 ratio equal to 1:250:250. As expected, no reaction occurred in the absence of the catalysts, and we also checked that no H_2O_2 consumption was detected in the absence of cyclooctene/cyclohexene.

Cyclooctene Epoxidation. With both complexes, the conversion of cyclooctene into epoxycyclooctane in acetonitrile and at room temperature was observed with very high yields (respectively, 96% and 97%, see Table 3, entries 1 and 2) after 24 h. It is also noteworthy that, in all experiments described in this section, we did not detect products other than epoxycyclooctane, so it can be considered that the epoxycyclooctane selectivity was 100%. Differences between the two POMs were however shown for short time reaction

Table 3. Epoxidation Conversion of Cyclooctene with Homogeneous and Anchored Catalysts^a

entry	catalyst	T (°C)	3 h	6 h	24 h
1	TBA ₃ NaH(POM-CO ₂ H)	20	59.5	88.5	96
2	TBA ₄ H(POM-NH ₂)	20	2.6	74	97
3	TBA ₃ NaH[AsW ₉ O ₃₃ { ^t BuPO} ₂]	20	0	2.4	7.5
4	TBA ₃ NaH[AsW ₉ O ₃₃ { ^t BuPO} ₂]	50	20.6	97	100
5	TBA ₄ H[PW ₉ O ₃₄ {PhPO} ₂]	20	0.7	13.6	98
6	POM-CO ₂ H@SBA-NH ₂	20	3.2	11.7	76
7	POM-CO ₂ H@SBA-NH ₂ (recycling)	20	10.2	23	81
8	POM-NH ₂ @SBA-CO ₂ H	20	1	3.5	19
9	POM-CO ₂ H@MCF-NH ₂	20	1	9	41
10	POM-NH ₂ @SBA-CO ₂ H	50	29	53	87

^aConditions: catalyst, 24 μmol (homogeneous conditions) or 1.2 μmol (heterogeneous conditions); acetonitrile, 20 mL (homogeneous conditions) or 1 mL (heterogeneous conditions). Ratio cyclooctene/catalyst = 250; cyclooctene/H₂O₂ (30%) = 1.

since a longer induction period seemed to be necessary for TBA₄H(POM-NH₂) catalyst (conversion 2.6% after 3 h).

For the sake of comparison, we also tested the catalytic performances of two other compounds, TBA₃NaH-[AsW₉O₃₃{^tBuPO}₂]₂ (Table 3, entries 3 and 4) and TBA₄H-[PW₉O₃₄{PhPO}₂]₂ (Table 3, entry 5) each related to (ⁿ-Bu₄N)₃NaH[AsW₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂]₂ (POM-CO₂H) and (ⁿ-Bu₄N)₄H[PW₉O₃₄{As(O)(C₆H₄NH₂)₂}₂]₂ (POM-NH₂), respectively. The TBA₄H[PW₉O₃₄{PhPO}₂]₂ complex contains the same A₉α-{PW₉O₃₄}⁹⁻ anionic platform as [PW₉O₃₄{As(O)(*p*-C₆H₄NH₂)₂}₂]⁵⁻ (POM-NH₂ anion), and two {As(O)Ph} groups instead of the {As(O)(*p*-C₆H₄NH₂)₂} ones. The catalytic behavior of this compound was analogous to that of TBA₄H(POM-NH₂), with a long induction time and a final conversion (after 24 h) close to 100% (Table 3, entry 5). We also compared the reactivity of TBA₃NaH(POM-CO₂H) with that of TBA₃NaH[AsW₉O₃₃{^tBuPO}₂]₂ based on a B₉α-{AsW₉O₃₃}⁹⁻ subunit on which two {^tBuPO} phosphonate groups have been grafted instead of the carboxypropyl functions in the POM-CO₂H anion. In the present case, we found that, at room temperature, the behavior of both complexes was clearly different since the conversion after 1 day was found to be very low (7.5%) with TBA₃NaH-[AsW₉O₃₃{^tBuPO}₂]₂ (Table 3, entry 3). It is noteworthy that an increase of the temperature up to 50 °C (Table 3, entry 4) led to a catalytic efficiency similar to that of TBA₃NaH(POM-CO₂H). Regarding these results, we concluded that, at room temperature, the carboxylic functions of POM-CO₂H anions could play a major role in the epoxidation process since the absence of these functions led to a dramatic decrease of the conversion of cyclooctene. These results could have been anticipated since the role of acids in general and of carboxylic acids in particular in epoxidation of alkenes (including cyclooctene) has been previously discussed in the literature, especially in POM chemistry.^{35–37}

Cyclohexene Epoxidation. The epoxidation reaction of cyclohexene with aqueous H₂O₂ was also studied, with the conditions being adapted from those used for cyclooctene. We first checked the activity of TBA₃NaH(POM-CO₂H) under homogeneous conditions in acetonitrile at room temperature. We thus found a good conversion of cyclohexene after 24 h (72.9%) and a final selectivity in the epoxide equal to 81.1%.³⁸ These results compare well with various other POM-based catalysts acting at room temperature (especially for the cyclohexene conversion rather than the selectivity).³² For comparison, in acetonitrile at 50 °C, the Ishii–Venturello

catalyst (ⁿ-Bu₄N)₃[PO₄{WO(O₂)₂}₄] produced cyclohexene epoxide with 98% selectivity at 84% conversion after 6 h.³⁹

3.5.2. Epoxidation of Cyclooctene and Cyclohexene with H₂O₂ by the Covalently Anchored Catalyst POM-CO₂H@SBA-NH₂. The catalytic activity of the three different anchored catalysts (POM-CO₂H@SBA-NH₂, POM-CO₂H@MCF-NH₂, and POM-NH₂@SBA-CO₂H, see descriptions in sections 3.2 and 3.3) toward cyclooctene epoxidation was also studied (Table 3, entries 6, 8, and 9) in the conditions used for their homogeneous counterparts (section 3.5.1). The most efficient precursor was POM-CO₂H@SBA-NH₂ (Table 3, entry 6), in which the POM-CO₂H anion was mostly grafted by only one carboxylic acid function, as established previously.¹⁹ For this supported catalyst, the rate of cyclooctene conversion was still relatively high, even if it is lower compared to that obtained in homogeneous conditions (76% vs 96% after 1 day, see Figure 8). These differences were emphasized at an early stage (3.2% vs 59.5% after 3 h and 11.7% vs 88.5% after 6 h), reflecting an

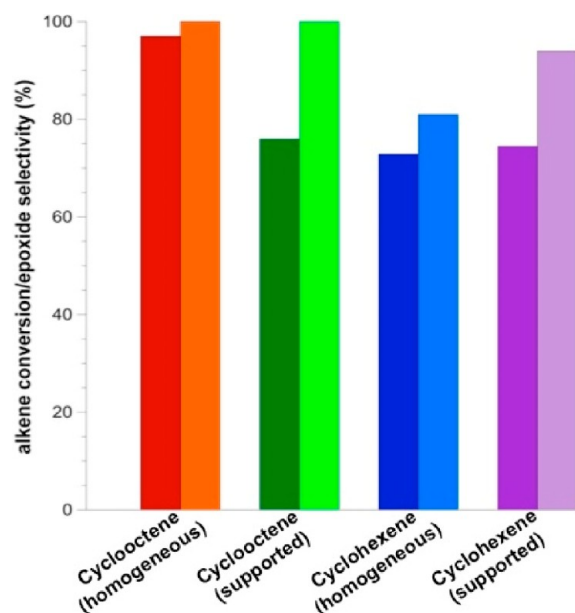


Figure 8. Column diagram for the alkene conversion (left bar) and epoxide selectivity (right bar) for (respectively, from left to right) cyclooctene with TBA₃NaH(POM-CO₂H) in homogeneous conditions and POM-CO₂H@SBA-NH₂ in heterogeneous conditions and for cyclohexene with TBA₃NaH(POM-CO₂H) in homogeneous conditions and POM-CO₂H@SBA-NH₂ in heterogeneous conditions.

important delay probably due to different phenomena (lower diffusion rates of the substrate or different accessibility to the active sites in heterogeneous conditions). A recyclability test was also performed with the POM-CO₂H@SBA-NH₂ catalyst recovered after 24 h through filtration. Interestingly, we observed a similar (if not higher) cyclooctene oxide rate (81%) after 1 day, indicating an excellent stability of the catalyst.

The catalytic activity of the supported POM-CO₂H anion covalently bound to SBA-NH₂ (POM-CO₂H@SBA-NH₂) was also studied in the case of cyclohexene. Similarly to cyclooctene, significant delays were observed in the cyclohexene conversion at the early stage of the reaction. However, in the present case the final conversion was found to be on the same order (if not higher) as that observed in homogeneous conditions (72.9% for the homogeneous catalyst, i.e., TBA₃NaH(POM-CO₂H), vs 74.5% for the supported one). Interestingly, the final selectivity into epoxycyclohexane was much higher after immobilization (94.0% vs 81.1%).

Regarding the important delay observed at the beginning of the reaction in both experiments using POM-CO₂H@SBA-NH₂ and despite the fact that the experimental conditions used here (acetonitrile during 1 day at room temperature) were much more gentle than the initial catalyst treatment before its use (Soxhlet for 2 days in refluxing acetonitrile), it was important to determine the true nature of the catalysis. In other words, did POM-CO₂H@SBA-NH₂ behave as a supported catalyst or a homogeneous one obtained through (partial) leaching processes? Indeed, it is now admitted that a simple conventional catalyst recycling experiment showing no significant loss of activity (Table 3, entry 7) is by no means a sufficient proof of heterogeneity in itself. According to the procedures defined by R. A. Sheldon and co-workers,⁴⁰ the strong immobilization of the catalyst was proven through another experiment where (i) the POM-CO₂H@SBA-NH₂ catalyst was removed (filtration after 5 h with 0.2 μ m porosity filters) before completion of the reaction (at room temperature) and (ii) the activity of the resulting filtrate was checked after 24 h. We then observed a dramatic lowering of the catalytic activity (see Figure 9) compared to the reference experiment (without filtration, see also Table 3, entry 6). Indeed while cyclooctene conversion was approximately 13.9% at the time of the filtration (at 5 h), the final conversion (at 24 h) within these experimental conditions hardly reached 25% versus 76% with the nonfiltered heterogeneous catalyst (Figure 9). We assume that the slight increase in the conversion after filtration (between 5 and 24 h) was probably due to the existence of remaining silica grains whose size was lower than 200 nm (size of the filter) in the solution, as observed by HR-TEM, instead of potential active species leached into solution. Nevertheless, regarding the results of the recyclability test and of the present experiment, one can be confident that the POM-CO₂H@SBA-NH₂ material can be considered as a truly anchored catalyst.

3.5.3. Epoxidation of Cyclooctene with H₂O₂. Comparison between Homogeneous and Covalently Anchored Catalysts. Concerning the catalytic activity of the other anchored catalysts, the scenario was surprisingly different with POM-CO₂H@MCF-NH₂ (Table 3, entry 9). After 1 day, only partial conversion of cyclooctene (41%) was observed, as the results of POM-CO₂H anion grafting onto a MCF-NH₂ instead of SBA-NH₂ support. With this experiment, we thus highlighted an effect of the support on the reaction rate. With the structure of

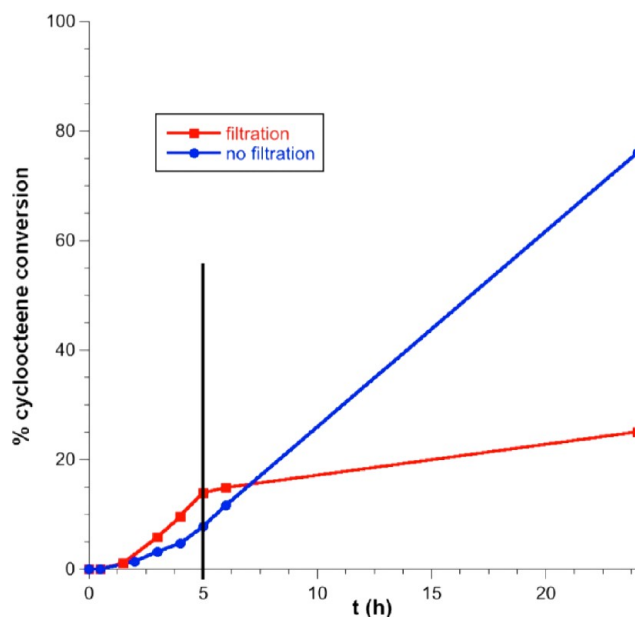


Figure 9. Catalytic activity of POM-CO₂H@SBA-NH₂ for the epoxidation of cyclooctene with aqueous H₂O₂ with (in red) or without (in blue) filtration. The black vertical line indicates the time for filtration.

the porosity being the main difference between SBA-NH₂ and MCF-NH₂ supports, it was tempting to hypothesize that variations of activity between POM-CO₂H@MCF-NH₂ and POM-CO₂H@SBA-NH₂ might be due to a poorer accessibility of the active sites in the particular case of MCF-NH₂. However, regarding the textural data, it is difficult to correlate *a priori* this decrease of the catalytic activity at the molecular level to the S_{BET} measured for both systems (lower for POM-CO₂H@SBA-NH₂ compared to for POM-CO₂H@MCF-NH₂, see Table 1). Another explanation could be related to the irregular organization of the active sites inside POM-CO₂H@MCF-NH₂ (see Figure 5) compared to those inside POM-CO₂H@SBA-NH₂ (see Figure 4) as shown by TEM micrographs. Existence of a tighter linkage (two carboxylic groups instead of one) between POM-CO₂H and MCF-NH₂ as the result of a surface geometry more adapted for multiple anchorage could also be invoked to explain the decrease of the reactivity of POM-CO₂H in POM-CO₂H@MCF-NH₂.

The existence of small aggregates as well as the irregular organization of POM-NH₂ in the third anchored catalyst, POM-NH₂@SBA-CO₂H, as shown in Figure 6, also had negative effects on cyclooctene conversion (Table 3, entry 8). Indeed, while in homogeneous conditions, we obtained a fair value after 1 day (97%), the conversion dramatically fell to 19% at ambient temperature in the case of POM-NH₂@SBA-CO₂H. Such a decrease is apparently due to a reduction of the exposed surface area of the active component of the catalyst and consequently a decrease of the contact between reactants and catalysts. POM-NH₂@SBA-CO₂H also culminated in the lowest POM loading of the three different anchored homogeneous catalysts so that significantly larger amounts of powder had to be used, leading to strong diffusion limitations. It is noteworthy that, for this specific solid material, a significant catalytic activity can be recovered at higher temperature (Table 3, entry 10).

The very encouraging results of the present study compare well with those obtained by Stein and co-workers.¹⁷ Indeed, in

their work, the incorporation of POM hybrids (derived from the γ -[SiW₁₀O₃₆]⁸⁻ platform) by covalent links into porous silica materials had led to moderate yields (up to 28%) in the epoxidation of cyclooctene (at room temperature, after 24 h). Such comparison consequently validates the use of bisphosphonate derivatives of trivacant POMs for the preparation of anchored homogeneous catalysts. Indeed, we observed the persistence of fairly good catalytic activity after immobilization of the latter (probably due to the presence of “lacunary” oxygen atoms after grafting), provided that the best POM organization on the chosen support may be found.

4. CONCLUSION

In this work, we have prepared and characterized three POM-containing mesoporous silica supports and studied their catalytic activity in the epoxidation of cyclooctene and cyclohexene in the presence of hydrogen peroxide. These POM-anchored materials (POM-CO₂H@SBA-NH₂, POM-CO₂H@MCF-NH₂, and POM-NH₂@SBA-CO₂H) were obtained through amide coupling reactions between POMs hybrids and functionalized silica supports bearing each complementary pending group.

Two different POMs, with either carboxylic acid (TBA₃NaH-[As^{III}W₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂]) or alkylamine functions (TBA₄H[PW₉O₃₄{As(O)(C₆H₄NH₂)}₂]), were used. Both POMs were shown to be efficient catalysts for cyclooctene epoxidation with aqueous H₂O₂ at room temperature in homogeneous conditions (acetonitrile). The bis-carboxylic acid derivative TBA₃NaH[As^{III}W₉O₃₃{P(O)(CH₂CH₂CO₂H)}₂] showed also interesting properties for the epoxidation of cyclohexene at room temperature, either in homogeneous conditions or after covalent immobilization on the SBA-NH₂ support, with an increased selectivity into epoxycyclohexane in the latter case.

POM-anchored materials showed various catalytic performances in the epoxidation of cyclooctene, with conversions in the range 19–97% after 24 h. These differences cannot be explained in terms of textural data since POM-CO₂H@SBA-NH₂, which presented the lowest S_{BET}, was also the best anchored catalyst. The POM organization throughout the materials appeared to be a determining parameter. The organization of the POMs at the pore (SBA-15) or cell (MCF) level of the materials that could be observed by HR-TEM (after microtome cutting) showed a decrease of the POM nanostructure from POM-CO₂H@SBA-NH₂ to POM-NH₂@SBA-CO₂H materials with some aggregates in the latter case. Trends emphasized for the catalytic activity of the anchored homogeneous catalysts were identical, i.e., the best activity for the material with the most ordered POMs.

Finally, recyclability experiments and a filtration test performed in the case of the POM-CO₂H@SBA-NH₂ (before completion of the cyclooctene epoxidation reaction) clearly indicated that this material can be considered as a truly anchored catalyst, thus precluding the hypothesis of significant leaching of the active species.

■ ASSOCIATED CONTENT

■ Supporting Information

Thermogravimetric analyses (TGA), weight losses, DTA curves and nitrogen adsorption/desorption isotherms of SBA-NH₂, SBA-COOH, and MCF-NH₂ materials. Powder X-ray diffraction patterns and TEM micrographs of SBA-NH₂, SBA-CO₂H, and POM-CO₂H@SBA-NH₂. ¹³C CP-MAS NMR

spectra of SBA-COOH, POM-NH₂@SBA-CO₂H, and POM-CO₂H@MCF-NH₂. ³¹P CP-MAS NMR spectra of POM-CO₂H@SBA-NH₂ and POM-CO₂H@MCF-NH₂. Raman spectra of POM-CO₂H@SBA-NH₂ and POM-CO₂H@MCF-NH₂ compared to that of TBA₃NaH(POM-CO₂H). Details (HR-TEM) of the zones of POM-CO₂H@SBA-NH₂, POM-CO₂H@MCF-NH₂, and POM-NH₂@SBA-CO₂H functionalized silica grains studied by XEDS and tables indicating the W/Si contents. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01216.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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[Hybrids of Polyoxometalates supported on mesoporous silica and magnetic core-shell nanoparticles for anchored homogeneous catalysis]

Abstract :

New materials based on silica oxides (mesoporous silica SBA-15, magnetic core-shell nanoparticles) combined with nucleophilic hybrids of (vacant) polyoxometalates were elaborated for applications in the field of anchored homogeneous catalysis for mild oxidations reactions. The main parameter taken into account was the formation of a covalent bond between the support and the POMs. Two different pathways were followed depending upon the support used for the covalently grafting of POMs. Firstly, Keggin-type POMs bearing carboxylic acid functions were grafted onto amino-functionalized SBA-15. Using the same support, other covalent immobilization methods were tried out, such as the use of a cross-linker. Secondly, hybrid nanocatalysts based on magnetic core-shell nanoparticles grafted with POMs were synthesized. All materials were characterized by a wide variety of physicochemical techniques. By HR-TEM, the POMs were localized inside the pores of SBA-15 and onto the surface of magnetic core-shell NPs, showing an excellent nanostructuration on the surface of both materials. Furthermore, the catalytic activity of the synthesized anchored homogeneous catalysts has been evaluated through the epoxidation of cyclooctene and cyclohexene with H_2O_2 in acetonitrile, resulting in fairly good conversions in some cases, compared to the homogeneous systems used in this study. Finally, particular attention was paid to the excellent catalytic behavior of POMs bearing carboxylic acid functions compared to other POMs of the same family. Thus, DFT calculations were performed in order to identify the cause of this enhanced reactivity.

Keywords: [Polyoxometalates, mesoporous materials, magnetic core-shell nanoparticles, anchored homogeneous catalysis, epoxidation]

Résumé :

De nouveaux matériaux à base de silice (silice mésoporeuse SBA-15 et nanoparticules cœur-coquille) associés à des hybrides de polyoxométallates lacunaires ont été élaborés pour des applications relevant de la catalyse homogène supportée, lors de réactions d'oxydation douce. Le critère principal a été la formation de liaisons covalentes entre les POMs et les deux types de supports utilisés. Des POMs à structure de Keggin portant des fonctions acide carboxylique ont été greffés sur des SBA-15 fonctionnalisées par des amines. Ce même support a été ensuite utilisé pour d'autres stratégies d'immobilisation covalente, comme l'utilisation d'un agent de réticulation. En parallèle, des nanocatalyseurs hybrides ont été synthétisés par l'association de nanoparticules cœur-coquille magnétiques et de POMs. Tous ces matériaux ont été caractérisés par une large gamme de techniques physicochimiques. L'utilisation de la microscopie électronique par transmission haute résolution a permis de localiser les POMs à l'intérieur des pores de la SBA-15 et à la surface des nanoparticules magnétiques, montrant ainsi une très bonne nanostructuration à leur surface. L'activité catalytique des catalyseurs homogènes supportés synthétisés a été évaluée au travers de l'époxydation du cyclooctène et du cyclohexène par H_2O_2 dans l'acétonitrile. De bonnes conversions ont ainsi été obtenues dans certains cas, en comparaison avec les systèmes homogènes testés lors de ce travail. Une attention particulière a été portée aux bonnes performances catalytiques du POM portant des fonctions acide carboxylique. Des calculs DFT ont ainsi été réalisés afin d'identifier la cause de cette réactivité particulière.

Mots clés : Polyoxométallates, matériaux mésoporeux, nanoparticules cœur-coquilles magnétiques, catalyse homogène supportée, époxydation]