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Leila Karam

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Sorbonne Université

Ecole doctorale de Physique et Chimie des matériaux

Laboratoire de réactivité de Surface

University of Balamand

Department of chemical engineering

New routes of preparation of active and stable mesoporous Ni-alumina based catalysts for methane dry reforming and CO₂ methanation

Par Leila KARAM

Dirigée par Mme Pascale MASSIANI et Mme Nissrine EL HASSAN

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Devant un jury composé de :

Mme Sophie Cassaignon	Professeure (SU-France)	Président
M. Axel Lofberg	Chercheur CNRS (Univ. Lille-France)	Rapporteur
M. Mohammad Ahmad	Professor (AUB-Lebanon)	Reviewer
M. Carlos Henriques	Associate Professor (IST-Portugal)	Examiner
M. Elie Chalhoub	Assistant Professor (UOB-Lebanon)	Invité
M. Julien Reboul	Chercheur CNRS (SU-France)	Invité
Mme Pascale Massiani	Chercheuse CNRS (SU-France)	Supervisor
Mme Nissrine El Hassan	Associate Professor (UOB-Lebanon)	Supervisor



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List of abbreviations

ALD	Atomic Layer Deposition
ATR	Auto Thermal reforming
BET	Brunauer-Emmet-Teller
BP	British Petroleum
CSDRM	Combined Steam Dry Reforming of Methane
CTAB	Cetyl Trimethyl Ammonium Bromide
DRM	Dry Reforming of Methane
EDF	Equilibrium Deposition Filtration
EDX	Energy Dispersive X-ray
EIA	Energy information administration
EISA	Evaporation Induced Self-Assembly
EOR	Enhanced oil recovery
EPA	Environmental Protection Agency
FTIR	Fourier transform infrared spectroscopy
FWHM	Full Width at Half Maximum
GHG	Green House Gas
HAADF	High Angular Annular Dark Field
ICDD	International Center for Diffraction Data
IPC	Intergovernmental Panel on Climate Change
IUPAC	International Union of Pure and Applied Chemistry
IWI	Incipient Wetness Impregnation
MAR	Microactivity-reference
MOF	Metal Organic Framework
OPEC	Organization of Petroleum Exporting Countries
POM	Partial Oxidation of Methane
RWGS	Reverse Water Gas shift
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
SRM	Steam Reforming of Methane
TCD	Thermal Conductivity Detector
TGA	Thermo-gravimetric analysis

TEM	Transmission Electron Microscopy
TOF	Turn Over Frequency
TPR	Temperature Programmed Reduction
WI	Wet Impregnation
WGS	Water Gas Shift
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

General introduction

Fossil fuels dependencies have been a serious addiction for most of the population since the middle of last century due to the need to ensure access to energy for quality of life and for economic development. Equally important, however, is the climate change problem encountered by the use of fossil fuels (non-renewable source) through the emissions of pollutants, CO₂ specifically, contributing to global warming. As an alternative energy source, hydrogen (H₂) and carbon monoxide (CO) mixture can be transformed following a specific reaction pathway to fuels, chemicals and electricity meeting everyone's need. There are several available processes to generate the required mixture of H₂ and CO from methane, like steam reforming, dry reforming, and partial oxidation reforming. In this work, the focus will be targeted toward dry reforming of methane since this reaction uses CH₄ and CO₂ as reactants, both of which are greenhouse gases. Even if CH₄ is a short-lived climate pollutant, its emission should not be underestimated. Indeed, CH₄ is not only obtained from gas production, but it is also emitted from livestock and rice paddies, ruminant animals, side products of industrial activities, landfills (biomass), and waste water treatment. CO₂ is mainly transferred to the atmosphere from combustion of fossil fuels. Thus, the conversion of both pollutants to energy will minimize fossil fuels dependency, and will contribute to reduce its disastrous climate consequences on the planet.

Dry reforming of methane process is an endothermic reaction that is still under research studies striving to find an active and stable catalyst. Although noble-metals can be active and stable, they are scarcely available and expensive which led to the development of transition metals, nickel specifically. The drawback of using Ni-based catalyst is the sintering of Ni and the formation of carbon under the harsh reaction condition. The recent approaches are targeted towards enhancing the performance of Ni supported on different oxides, mainly Al₂O₃, by 1) employing different methods of Ni deposition on the support, 2) altering the shape of the support and 3) adding a second promoter or metal. However, the preparation methods were not yet efficient enough to stabilize Ni against thermal agglomeration and carbon deposition.

In this thesis, catalysts that are highly active and stable in dry reforming of methane are synthesized inspired by different positive parameters seen in literature. Needless to say, the Al₂O₃ oxide was selected as support for Ni. The direct one-pot method that involves adding Ni within the synthesis of Al₂O₃ was adopted along with alteration in the shape of alumina to

ensure occlusion and confinement of nickel nanoparticles inside the pores or walls of structured oxide. MgO was also selected as basic dopant to prevent solid carbon accumulation.

This research work is a joint PhD between the “Laboratoire de réactivité de Surface” at Sorbonne University and the Department of chemical engineering at University of Balamand. It is also a part of a European ERANETMED project (SOL-CARE) that includes three European countries (Spain, Italy, Portugal) in addition to Lebanon.

The manuscript is divided into six main chapters. Chapter I provides a general overview on the non-renewable fossil fuels source of energy, their environmental issues, and the possible renewable alternative energy pathways involving C₁-based molecules (CO₂ and CH₄). A detailed explanation is presented on dry reforming of methane reaction, then the state of the art catalysts already used in the reaction are elaborated and analyzed to understand the challenges faced.

Chapter II is dedicated to the technical part involving the principle of all the used characterization techniques, the applied procedures on the tested materials (calcined, reduced, and spent), and the derived results from each equipment. The chapter also embraces an evaluation of the thermodynamic equilibrium of the reactions, and the experimental catalytic tests set-ups. Note however that this chapter will not introduce the conditions of preparation of the samples that will be described in the respective chapters where they will be developed.

Chapter III tackles the effectiveness of using MgO as basic dopant in mesoporous Ni-Al₂O₃ materials by one-pot synthesis. The chapter begins with a brief bibliographic recall on the existing Mg-based alumina materials. Then, the preparation methodology used in this thesis is described in details before presenting the obtained physicochemical properties, the reducibility and the catalytic performances. The focus will be on the effect of magnesium loading with a clear explanation on why its use should be optimized.

Chapter IV introduces a novel technique to occlude Ni nanoparticles inside Al₂O₃ pores following an innovative metal organic framework (MOF) route. Firstly, this chapter gives concise recalls on MOF materials, their types, and the reason behind choosing MIL-53(Al) as MOF sacrificial precursor in our study. Then, the preparation of mesoporous Ni-Al₂O₃ from MOF is described and the material obtained is compared structurally, physically and

catalytically to a second MOF-based sample prepared by impregnation and conventional Ni-Al₂O₃ material.

Chapter V applies the above-mentioned materials exhibiting good performances in dry reforming of methane to another reaction of interest in the energy domain, the CO₂ methanation that also consumes CO₂. A brief state of the art catalysts is given at the beginning of the chapter before explaining the preparation methods of the materials used and their physiochemical properties along with the catalytic tests results.

Chapter VI ends this report by treating some of the materials in a more realistic dry reforming gaseous conditions evolved from pyrolysis of biomass wastes as given by a Lebanese industry. The aim of this last part is to investigate the efficiency of our catalysts under harsh conditions of dry reforming that contains CH₄, CO₂, H₂ and CO in the reactants feed, making more difficult to obtain the expected H₂/CO products ratios.

I. Chapter I: Literature review



I.1. Sources of energy from fossil resources

Mixtures of hydrogen (H_2) and carbon monoxide (CO), known as syngas, are important in the energy domain since they can lead to the production of fuel. Such mixtures can be obtained from methane following different reforming reactions. In this chapter, the main resources of methane are presented along with the various pathways of converting it into H_2 and CO. Through the description, an interest is highlighted on the dry reforming of methane (DRM) reaction that will be in the core of this work and where CO_2 is used as a co-reactant. A state of the art is provided to summarize the advancements achieved in the existing catalysts for this reaction. The chapter ends with an outline of the objectives and methodology of the present thesis.

I.1.1. Main resources

a) Fossil fuels

Fossil fuels were discovered over 150 years ago. They are formed from organic matter deposited over the course of million years and fabricated by natural processes deep in the earth or under the sea bed by anaerobic decomposition of buried dead organisms. The fossil fuels such as oil, coal and natural gas extracted by human operations can be further transformed and refined into petroleum products [1–3]. In other words, fossil fuels exist in different forms (solid, liquid, gas) and they have a wide range of carbon content going from products with low carbon to hydrogen ratio like methane (volatile materials) to non-volatile pure carbon as anthracite coal. Oil, coal, and natural gas are known for being described as the energy of the world due to the versatile energy supplies they can offer [3,4] playing a crucial role in the 21st century world energy market with an average rate of production of about several million barrels per day. For instance, oil is the world's primary fuel source for transportation capable of being transformed not only into fuel oil, diesel oil, kerosene, gasoline, and liquefied petroleum gas (propane, butane), but also into other products like fertilizers, plastics and pharmaceutical compounds [2,5]. Coal is mainly used to produce electricity, steel, manufacture cement and synthesize liquid fuel as well as for heating [2,6]. Nowadays, the use of natural gas has been growing in a fast pace into the sector of electric power generation (heat, electricity) with an interesting reliance in other areas (industries, residential, commercial, pipeline and distribution) [2,7].

b) Methane (CH₄)

As natural gas transport is expensive and problematically hard due to the relatively low energy content in relative to its volume, the global market of oil is much bigger and a basic requirement for energy needs. Nevertheless, and in close relationship towards the tendency of using greener energy, the natural gas consumption has increased in the last decade for it is considered as the cleanest burning petroleum based fuel, and this tendency is planned to continue with a net worldwide increase of about 2.8% annually from 2001 to 2025 [8]. It is important to mention that CH₄ properties are utilized when speaking about natural gas because it accounts about 95% of its total volume. The other components with a total of 5%, contain traces of ethane, propane, butane, pentane, nitrogen, carbon dioxide and water vapor [8]. CH₄ gas is a prominent raw material with high abundance in remote areas distributed all around the world. According to BP statistical review and OPEC oil and gas data, Iran, Russia, Qatar and Turkmenistan have the highest natural gas reserves (Figure I-1) [9]. Methane has the ability to

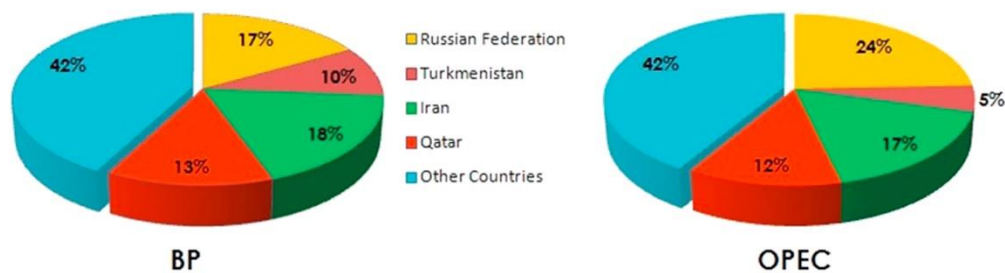


Figure I-1: Natural gas reserves distribution across the world [9]

produce more heat and light energy by mass (H/C ratio: 4/1) than other hydrocarbons and fossil fuels (oil (H/C<2/1), coal (H/C<1/1)) resulting in significantly less carbon dioxide and other pollutants that create smog and pollutes the environment. In other words, one should rely more on CH₄ and replace it for coal and oil to generate electricity and fuel transportation while contributing to environment protection.

I.1.2. Reserves, human consumption and potential depletion

There exists a dilemma about the persistence of this non-renewable source of energy (coal, oil and natural gas) and whether the existing reserves could withstand the intense consumption by the human being [1,10]. Estimations about fossil fuels reserves and availabilities differ and nobody can really have an accurate prediction on their exhaustion. Global energy consumption has increased by 2.2% (2.1 million barrels per day) in 2017 compared to an average of 1.7% for the previous 10 years (BP) [2]. The energy information

administration (EIA) has drawn a relation between the world fuel production and consumption as a function of time (Figure I-2) [11]. It is intelligible that there is an annual change in the world liquid fuels consumption with a positive (2014-2015) or negative (2017) relation between the amounts produced and consumed. EIA predicts that oil discoveries will decrease by 0.2 million b/d in 2019 making global demand outpaces production. In 2020, oil supply will increase by 0.1 million b/d.

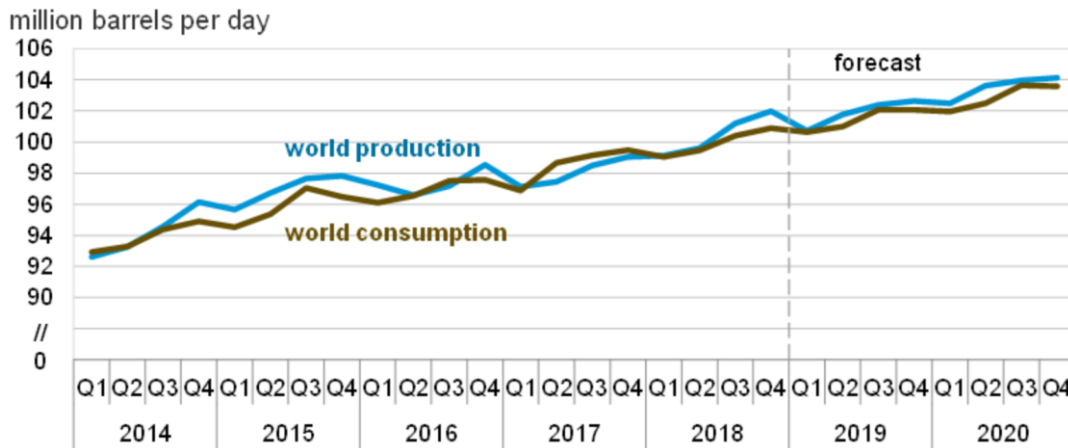


Figure I-2: World liquid fuels production and consumption balance, Source: Energy information administration [11]

On the other hand, scientists and oil companies have a consensus that oil production for the long term forecast has reached a peak (Figure I-3) and we will at a certain moment run out of oil supplies [10,12,13]. The size of oil reserves regularly discovered are getting smaller through years even if technologies (EOR: enhanced oil recovery) are highly advanced for finding new places to look for potential seams of oil. For instance, even if we take the most optimistic case scenario (4% depletion, green curve), in 2025 the world will be able to produce the same quantity of oil as in 1970.

Not to mention that the world population in 2025 will be 50% more than what we had in the 1970's [10]. This means that the new discoveries and technologies have only delayed the fall and it is a must that we reduce our

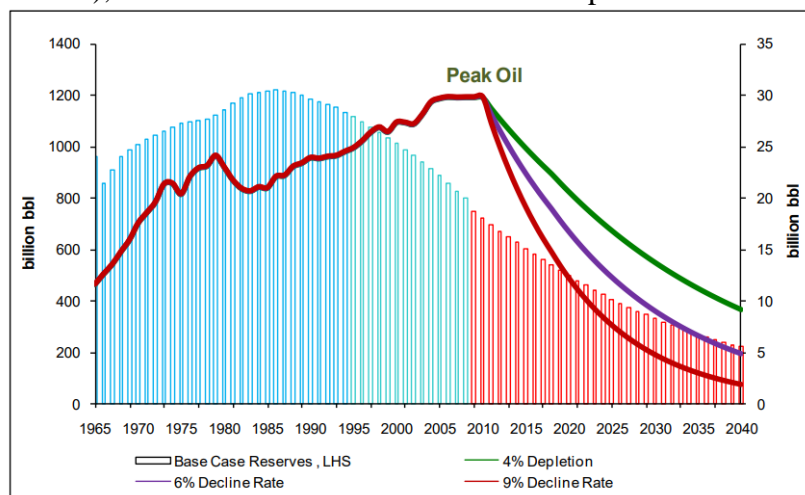


Figure I-3: Peak Oil Forecast, Source: BP statistical review of world energy 2009 [10]

dependence and adjust the falling oil supplies to avoid their depletion. In addition, shahriar Shafiee et al. calculated oil, coal and gas depletion following Klass and New model, and estimated that coal reserves will last until 2112 and it will be the single fossil fuel available after depletion of oil and gas in 2042 [1] if people continue to use them as source of energy. Concerning CH₄, no matter what is the amount of reserve available, it should not be allowed to escape into the atmosphere due to environmental reasons that will be mentioned in the following paragraph.

I.1.3. Environmental issue

I.1.3.1. CO₂ emissions

Another downstream of relying on this traditional method to produce energy, is the detrimental impact on the environment. Burning fossil fuels results in formation of carbon dioxide (CO₂) which is one of the primary greenhouse gases (GHG) responsible for global warming [7,14,15]. According to BP, the global emissions of CO₂ from energy had increased on a basis of 10-year average (2006-2016) by 1.3%. However, in 2017 only, CO₂ emitted faced a calamitous grown by 1.6% [2] which means that humans continue increasing dependencies on fossil fuels resources contributing to a calamitous effect on the environment.

The intergovernmental panel on climate change (IPCC) has summarized in the form of a graph (Figure I-4) the amount in Kg of CO₂ emitted per megawatt-hour (MWh) of energy produced from any type of fossil fuels [16]. We can see several points from this figure. For

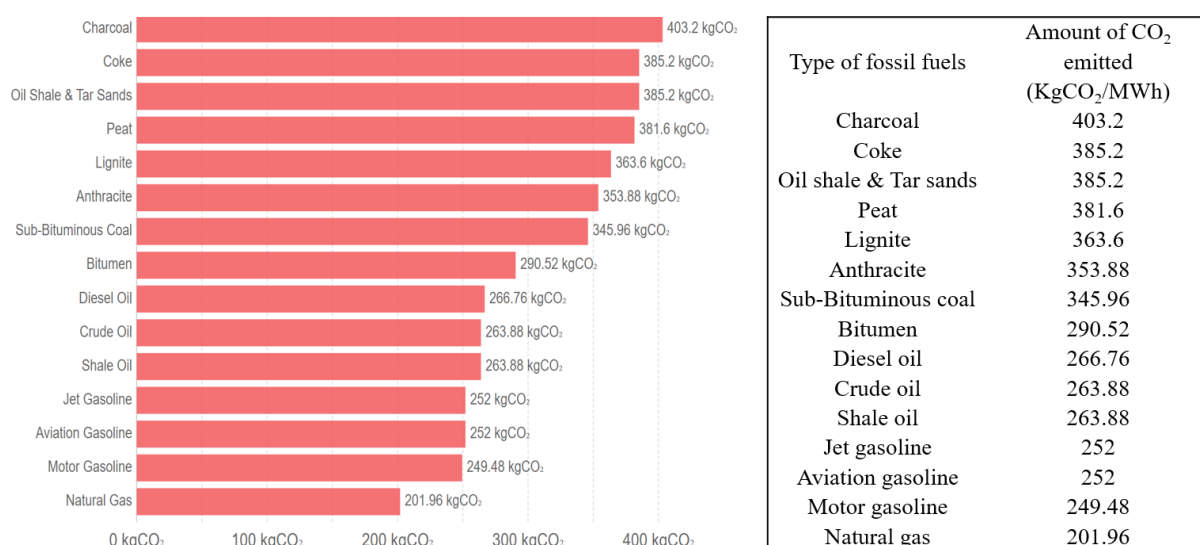


Figure I-4: Carbon dioxide (CO₂) emissions factor, measured in kilograms of CO₂ produced per megawatt-hour (MWh) of energy produced from a given fossil fuel source. Source: intergovernmental panel on climate change (IPCC) [16]

instance, the graph demonstrates that the combustion of coal is responsible for the highest percentage of CO₂ emissions (403.2 KgCO₂/MWh). The unconventional oil sources comes next such as oil shale and tar sands with 385.2 KgCO₂/MWh emissions. The conventional sources (diesel oil, crude oil, shale oil, and gasoline) also contribute to important CO₂ gas emissions. By comparison, natural gas

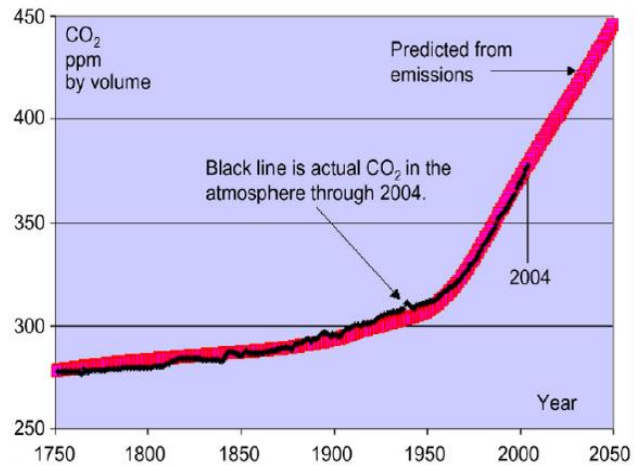


Figure I-5: Global carbon dioxide levels since the beginning of industrial revolution [17]

(CH₄) also results in an inevitable release of CO₂ but in much less quantity than other burning hydrocarbons (201.96 KgCO₂/MWh). This is why it is considered as the cleanest type of fossil fuels. Moreover, its burning results in very low amount of NO_x, particulates, and almost 0 SO₂ emissions [2,8]. Hence, CH₄ presents important advantages compared to the other hydrocarbon feedstock, even if its utilization also contributes to an average of 2% increase per year of CO₂ emissions which is planned to regularly continue as illustrated by predictions made until 2050 (Figure I-5) [17].

I.1.3.2. Diversity of deleterious impacts

An additional environmental issue related to using fossil fuels comes from the fact that people nowadays are facing difficulties in extracting oil and gas sources. They rely on fracking and the use of energy intensive methods prone to escape of more CO₂ gases and other air pollutants like sulfur dioxide from acid rain, nitrogen oxides (NO_x), mercury and carcinogenic chemicals [16,18,19].

This stark truth of CO₂ greenhouse emission in addition to the chronic gases are further boosted by scientific facts of sea levels rise, hotter temperatures, and the occurrence of storm weather patterns like tsunamis and hurricanes. They can also contribute to serious health complications in the human being such as lung malfunctioning, asthma, cancer and cardiovascular diseases. They can lead as well to the death of aquatic animals and pollution of ground water if any oil spill is triggered [20,21]. Not to mention that coal mines cause relocation and damage the vegetation, top-soil and contamination of rivers [22].

I.1.3.3. CH₄ and CO₂ as greenhouse gases

The negative consequences of burning fossil fuels and CH₄, and producing CO₂ is not the sole problem. It is significant to deem in mind that CH₄ (oxidized carbon) is also by itself a pollutant if released into the atmosphere as CO₂ gas (reduced carbon). CH₄ and CO₂ are considered as greenhouse gases because they both absorb and emit thermal infrared radiation at the range of our planet emitted wavelength, trapping the heat and making the planet warmer [7,17]. CH₄ is tougher than CO₂ as greenhouse gas with around 120 times more radiative force but it has a shorter lifetime effect with only 12.4 years average. In contrary, CO₂ is a complex molecule thermodynamically stable in the atmosphere with indefinite lifetime [23,24]. It is now well recognized that an effective way to control CH₄ and CO₂ emissions to air and reduce their negative effect in the atmosphere would be to use both as feedstock for energy production especially that there exist natural processes in which methane and CO₂ are emitted.

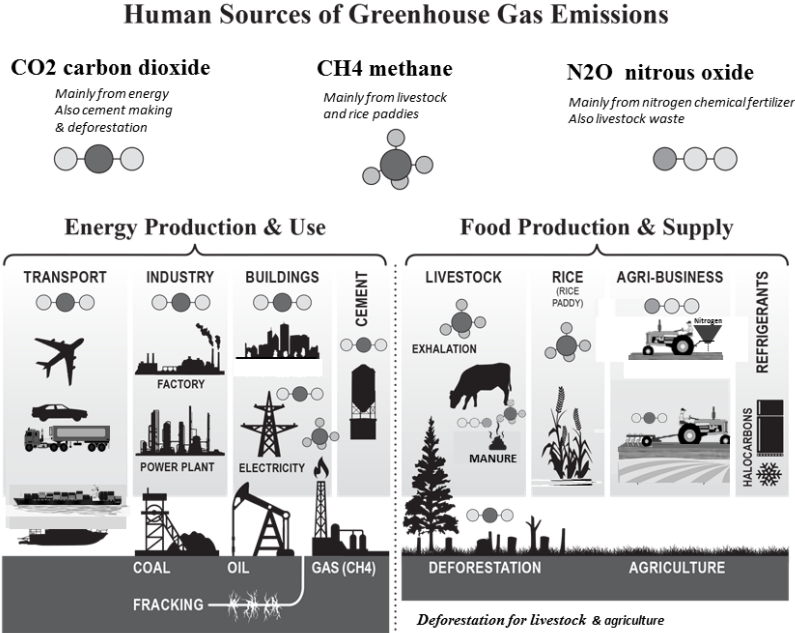


Figure I-6: Summary of human sources of greenhouse gas emissions [17]

Needless to say, Figure I-6 demonstrates that the concentrations of atmospheric greenhouse gases (CH₄ and CO₂) do not only come from burning of fossil fuels but they originate as well from different natural and human activities (biomass) sources [17,23]. Based on a balance between GHG sources and sinks (conversion of the species to different chemical compounds), the amount of GHG in addition to its residence time (RT) in the atmosphere are estimated to be 73% (RT: 150 years) for CO₂, 17% (RT: 12 years) for CH₄, and 8% (RT: 100 years) for other greenhouse gases (N₂O) [7,8,17,25,26]. In brief (Figure I-6), CH₄ is emitted

from livestock and rice paddies, and also from ruminant animals, side products of industrial activities, landfills, gas production, coal mining and waste water treatment. CO₂ is transferred to the atmosphere from production of cement, deforestation in addition to energy (combustion of fossil

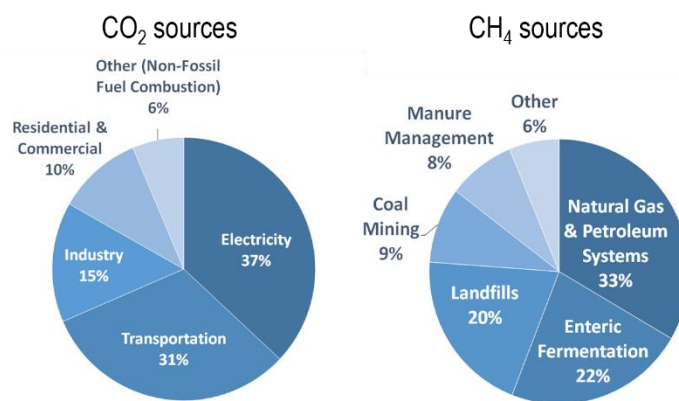


Figure I-7: Percentage of greenhouse gases sources [27]

fuels). According to the United States environmental protection agency (EPA), CO₂ sources come mainly from burning of fossil fuels (93%) while CH₄ sources are distributed between petroleum systems (33%), landfills (20%) and enteric fermentation (22%) (Figure I-7) [27]. Landfills and enteric fermentation are included in the biomass category that can be used as a source of energy limiting reliance on fossil fuels. This strategy is one of our interest and it will be tackled in more details in chapter VI of the thesis.

In order to mitigate the anthropogenic emissions (CH₄ and CO₂) a forward step has been taken by scientists considering few courses of action [17,28] such as improving the efficiency of combustion engine, minimizing utilization of fossil fuels, constructing energy-efficient building, frequent usage of recycled materials, shifting to low carbon energy sources, capture and sequestration of greenhouse gases, reducing deforestation, and fertile land management. Because these pathways are somehow daunting and require deeper investigations and studies to assure their efficiency and be pursued, chemists have been more concerned recently, as mentioned earlier, in utilizing CH₄ and CO₂ either together or separately as raw compounds for the production of useful fuels and chemicals. This is what will be elaborated in the next section.

I.3 Pathways for CH₄ and CO₂ conversions

There are several ways of converting CH₄ and CO₂ gases [17,28,29] through economic pathways. For example, CH₄ and CO₂ can be each used to produce chemicals such as food & beverages, solvent for pharma, fire extinguishers, solvents, and hydrocyanic acid. However, the market potential of fuel is 15 times higher than chemicals and speaking from the structural point of view, chemicals have higher molecular complexity than fuels which are made of simple

chains as in hydrocarbons [17]. Thus, the focus of researchers is mainly towards energy production.

Methane can be used **directly** for the production of heat and power generation by combustion (severe conditions needed to break the stable C-H bond) or it can be converted (**indirect** pathway) to produce a synthesis gas (called syngas) that is a mixture of hydrogen (H_2) and carbon monoxide (CO) [7,28–30]. CO_2 can be also converted (**indirect** pathway) to syngas. Making syngas is of strong interest because it is a crucial intermediate for the production of fuels needed for transportation and energy. The ratio of the syngas produced varies and depending on this value the targeted application is altered. Figure I-8 summarizes the main existing pathways for **syngas applications** [29,31]. An important route (in red) is the use of syngas as reactant in Fischer-Tropsch synthesis for the subsequent production of fuel (gasoline,

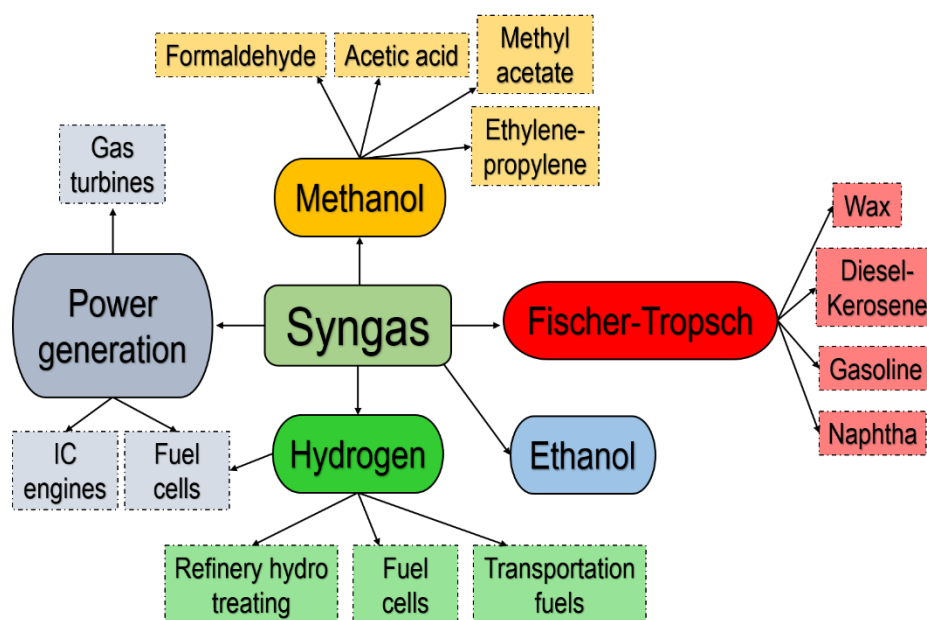


Figure I-8: Schematic with a brief summary about synthetic gas applications [29]

diesel, naphtha), another one (in grey) concerns power generation for fuel cells and gas turbines, a third one (in green) consists in using hydrogen as the source for transportation and refinery hydro treating and, finally, syngas can be converted to methanol to synthesize formaldehyde, acetic acid and ethylene propylene. In fact, in order to obtain the required syngas adapted to the targeted route, there are several reforming approaches in which methane reacts with variant oxidants (H_2O , CO_2 , O_2) to synthesize H_2 and CO with different ratios.

I.3.1. Different reforming processes for syngas production

Table I-1 illustrates the six existing methane reforming processes along with their chemical reactions, their enthalpy and their resultant H₂:CO ratio [7,29,30]. Reactions 1 and 2 are widely studied in literature and industrialized in some areas. These reactions in addition to reaction 3 rely on H₂O, O₂ or the combination of H₂O and O₂ to oxidize CH₄ resulting in an H₂:CO ratio between 2 and 3. In brief:

Table I-1: Chemical reactions of CH₄ reforming processes along with their corresponding enthalpy and H₂:CO ratios

Rxn	Reforming Processes	Chemical Reactions	ΔH_{298K} (kJ.mol ⁻¹)	H ₂ :CO ratio
1	Steam reforming (SRM)	$CH_4 + H_2O \rightarrow 3H_2 + CO$	+206	3:1
2	Partial oxidation (POM)	$CH_4 + 1/2O_2 \rightarrow 2H_2 + CO$	-38	2:1
3	Auto thermal reforming (ATR)	$CH_4 + x/2O_2 + (1-x)H_2O \rightarrow (3-x)H_2 + CO$	+206.2-241.8x	(2-3):1
4	Oxy-CO ₂ reforming	$3CH_4 + CO_2 + O_2 \rightarrow 6H_2 + 4CO$	+58	3:2
5	Dry reforming (DRM)	$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	+247	1:1
6	Bi-reforming (CSDRM)	$3CH_4 + CO_2 + 2H_2O \rightarrow 8H_2 + 4CO$	+220	2:1

- In **steam reforming (SRM)**, CH₄ is oxidized by a steam generating a syngas with a H₂:CO ratio of 3 suitable for H₂ production. This reaction is very endothermic and its process is divided into four steps. The first reformer operates at very high temperatures (800-900 °C) with pressure around *15-30 atm* demanding high energy investment to produce the steam itself. The second reformer works at a temperature of 1000 °C and uses a mixture of H₂O and O₂ in the feed. Then, H₂/CO ratio is adapted using successive reactions of water gas shift at 400 °C and 200 °C, respectively [7,32,33].
- **Partial oxidation (POM)** operates at lower temperature than SRM between 500 and 700 °C. The syngas produced has a ratio of 2 adequate for methanol synthesis and purification of CH₄ reactant is not always required. Despite these qualities, this reaction suffers from being highly exothermic. This problem can induce hot-spots in the reactor making the process more complicated and increase the risk of explosion. Pure oxygen supplies also come with a share of technical and economic problems inquiring industries to look for alternative solutions rather than cryogenic unit to separate oxygen from air [33–35].

- **Auto thermal reforming (ATR)** combines H₂O to the process of partial oxidation to solve the economic issue raised. The bright side of adding H₂O within the feed is the ability to impact and control the H₂/CO ratio in the gas product allowing a simpler adaptation to several downstream operations such as ammonia and methanol. However, safety concerns associated with the presence of oxygen have limited their use. In addition, this reaction is more energy demanding and part of the methane fed is invested to generate heat in order to reach the appropriate operating temperature and achieve an optimal conversion of methane to syngas avoiding soot formation [29].

Since the trend nowadays is toward curtailing CO₂ amount in the atmosphere which is also our main concern in this thesis, the focus becomes more towards the 3 next methane reforming reactions that consume such gas in addition to CH₄ (Rxn 4,5,6 in Table I-1):

- **Oxy-CO₂ reforming** resembles ATR in regards to the aim and outcome. The use of a sole O₂ carrier favors the thermodynamic production of H₂ and CO mixture. But, the economic barriers made it imperative to combine CO₂ in the process. Adding CO₂ within the feed leads to H₂/CO ratio of around 6/4 suitable for further use in ammonia and methanol synthesis processes. It has also the appeal of auto thermal operations especially that the latter consumes CO₂. However, safety concerns associated with the presence of oxygen have limited their use.
- **Dry reforming of methane (DRM)** uses only carbon dioxide as an oxidizing agent reacting with CH₄ to synthesize hydrogen and carbon monoxide. This reaction is recently attracting the attention of many scientists despite owing less favorable thermodynamics than the previous mentioned reactions. But, what makes this reaction more interesting is its ability to **greenly** consume the **natural gas** reducing the carbon impact by proportionally consuming **1 mole of carbon dioxide per one mole of methane** invested. The **product** is eventually a **syngas** with an **equimolar ratio of 1** used as a feedstock for the synthesis of large chain hydrocarbons by Fischer-Tropch approach. The energy invested in the reaction may be curtailed by the use of appropriate catalytic systems which would downstream open the opportunity to dry reforming to become an economical process competing SRM that is already industrially mature. What prevents DRM from being scaled up to industrial level, is the difficulty in finding a catalyst that could withstand the high temperature required (due to thermodynamic reasons that will be explained in chapter II) and resist deactivation by sintering and carbon deposition [7,33,36,37]. **This reaction, and more specifically the question of improvement of catalysts, is our core interest in this thesis.**

- **Combined steam and dry reforming of methane (CSDRM)** is a new emerging reforming reaction combining SRM and DRM. Compared to other CO₂ consuming reactions, this chemical reaction produces a “metgas” with an H₂:CO of 2 leading to formation of higher value products particularly methanol and its derivatives. This reaction has been rarely reported in literature due to its high endothermic feature and requirement of energy [7,29,38].

I.3.2. Dry reforming of methane regarding literature

The “web of science” research engine was used as a reliable basic source to estimate the amount of papers published on DRM, SRM, and POX through the years. Statistics were performed on two bases: topic and title search. Figure I-9 illustrates the number of publications for each of these 3 reactions (graphs A to C respectively) as a function of time (year). It is clear

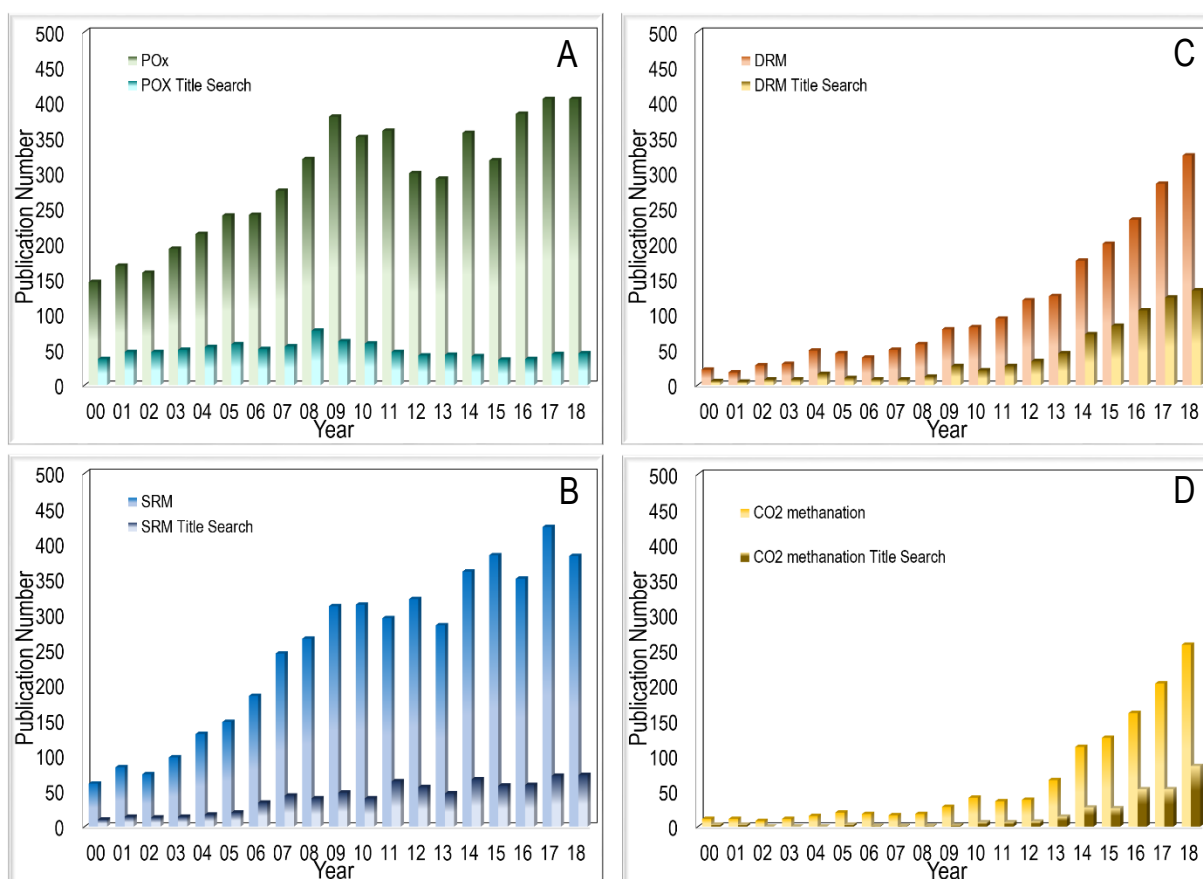


Figure I-9: Statistical histograms displaying the evolution of the publications number as a function of year for SRM, POX, DRM and CO₂ methanation reported studies. The search was evaluated between 2000 and 2018 using either the topic or title in the search engine

that the total number of publications for both SRM and POX (Figure I-9 A-B) is more numerous than DRM research papers as these reactions are more mature and already implemented in some industries. On the other hand, the number of publications available for

these two reactions does not follow any constant trend through time. A small increase is noticed for SRM and POX publications from 2003 till 2009 (200-350 papers) followed by a decrease from 2010 till 2013 (350-300 papers) and a stability in the 2014-2018 period (around 350 papers). In contrast, we can see from Figure I-9 C that the number of papers dealing with DRM reaction (CH_4 and CO_2 as reactants) exhibits a continuous increase in terms of research studies from 2000 till 2018 in response to the environmental CH_4 and CO_2 issues elaborated earlier. For example, 15 years earlier in 2004, only 50 publications were found related to DRM whereas in 2018, about 325 reports dealt with this reaction. This shows that there are so much work in this domain as will be seen in further paragraphs. The reason why we have such increment trend curve is the presence of deficient catalysts incapable of withstanding side reactions that lead to their deactivation despite the improvements made coining DRM in the research stage era. Note also that a similar trend is visible in Figure I-9 D for another reaction using CO_2 (methanation) to which we will also dedicate some interest as introduced in the next session.

I.3.3. Side reactions of catalytic dry reforming of methane

There are several side reactions that could be encountered during DRM. One should compromise his test conditions during operation of the main reaction to satisfy his needs by realizing high conversions and avoiding as much as possible the formation of side products or deactivation of the uploaded catalyst. A summary of the involved reactions are presented in Table I-2 [33,39]:

Table I-2: List of possible involved reactions in dry reforming of methane

Reactions	Equations	ΔH°_{298} (kJ/mol)	Temperature range ($^\circ\text{C}$)
Main reaction			
Dry reforming of methane (DRM)	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$	247	600-1000
Side reactions with no C(s) production			
Water gas shift (WGS)	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-42.1	200-500
Reverse water gas shift (RWGS)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	42.1	500-800
CO_2 methanation	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-165	100-500
Side reactions inducing C(s)			
CO_2 hydrogenation	$\text{CO}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{C}_{(s)}$	-90	100-500
CO dehydrogenation	$\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C}_{(s)}$	-131	100-500
CO disproportionation	$2\text{CO} \rightarrow \text{CO}_2 + \text{C}_{(s)}$	-172	100-600
CH_4 decomposition	$\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C}_{(s)}$	75	600-900

The main **DRM** process is a direct reaction between CH_4 and CO_2 and it is the most endothermic reaction in the series of equations because the CO_2 molecule is very stable. Hence, in order for it to act as an oxidant and interact with CH_4 a high energy is needed to activate it. **Water gas shift (WGS)** and **reverse water gas shift (RWGS)** are non-desirable side reactions that can thermodynamically occur in parallel to the main reaction. However, only the *RWGS* reaction is within the temperature range of *DRM* and thus it is more inclined to be triggered. This reaction consumes CO_2 and H_2 to produce CO and H_2O and thus reduces the ratio of H_2 : CO product to less than the required value (1, section I.3.1). The presence of H_2O in the product of the *RWGS* reaction is also a drawback. In fact, steam could oxidize the reduced active phase during the in-situ run, decreasing catalytic activity and deactivating the catalyst.

CO₂ methanation (Sabatier reaction), seen as possible undesirable reaction in Table I-2, is not in the thermodynamic range of *DRM*, however, it has also gained our attention in the present work because it is a particular technique that further curtails CO_2 emissions and produces CH_4 as an energy carrier. It has also been newly developed in literature since it is seen in Figure I-9 D that the number of research studies related to this application has been recently continuously increasing through time in a manner similar to that for *DRM*. Details about this reaction and a literature review will be explained in details in Chapter V.

The formation of carbon should be also taken into account because it is the most limiting feature deactivating *DRM* catalysts in most published studies. Table I-2 encloses the chemical reactions related to solid carbon deposition in methane reforming processes. In fact, there are four reactions that produce carbon as a product. **CO₂ hydrogenation** and **CO dehydrogenation** are exothermic reactions feasible at low temperatures and therefore they are exempted from being considered in *DRM* side reactions. On the other hand, **CO disproportionation** (Boudouard) and **CH₄ decomposition** reactions could strike simultaneously with the main reaction producing carbon that blocks the catalyst pore and covers the active sites [7,36,39]. In this PhD, stability experiments were operated mainly at 650 °C coining the probable formation of carbon deposits to *CH₄ decomposition* only. It is important to mention also that not all carbon deposits (C_α , C_β) are detrimental leading to catalyst deactivation (C_γ), but their continuous accumulation inside the reactor could increase pressure, plug the reactor, and cease the reaction [40].

I.4. State of the art catalysts for dry reforming of methane

Dry reforming of methane reaction needs a robust catalyst capable of withstanding the harsh operating conditions imposed by the reaction, i.e. the high temperature levels and the occurrence of possible side reactions mentioned above. Thus, researchers are trying to design a convenient catalyst using modern catalysis techniques combining several features like low cost, recyclability and environmentally benign ensuring 100% selectivity towards the desired products and good stability [41–44]. The catalytic activity, selectivity and stability per surface atom rely mainly on the type of metal adopted (active component), particle size, structure and location, reduction extent, accessibility of active metal sites, and choice of oxide support. Thus, the current section of this report tackles the type of catalysts employed in dry reforming covering the active phases, the promoters, and the supports examined in this reaction along with their corresponding catalytic activity and stability and the reason behind their deactivation if any. Note that in heterogeneous DRM catalysis, people use oxides as support for the metals and it has no direct catalytic role. In our case, we will focus on Al_2O_3 -based support because it is cheap, has a high attrition resistance and high thermal stability [45] that make it industrially enticing.

I.4.1. Type of metals and supports in dry reforming of methane

a) Noble and transition metals: The active metal elements are often divided into two categories: noble metals such as Pt, Ru, Pd, Ir and Rh, and transition metals like Ni, Fe, Cu and Co. A decent number of studies have concealed experimentally and theoretically the excellent activity and stability of precious noble metals in dry reforming of methane due to their high capability of hindering carbon deposition as well as tolerance towards corrosion and oxidation [37,46]. On the other side, these metals are not economically convenient for large-scale industrial service due to their high price and scarce availability [7,43]. Thus, the number of papers embracing noble metals as a primary active phase on Al_2O_3 support has diminished through years especially in the period of 2010-2019 inspecting around 6 papers of different noble metals (Pd, Pt, Ir, Rh) as main active phase with small to moderate amount (0.5-1 wt%) [47–53]. The presence of such small amount of noble metal is not enough to cast carbon formation and increasing further the amount of noble metals added enhance the activity and stability but increase a lot the price of the catalyst. As a consequence these samples were adjusted with alkaline or alkaline earth metals. The CO_2 activation is boosted to form O species

that reacts with $C_{(s)}$ to form CO enhancing basicity of the catalyst and resistance to deactivation [48,51–53]. Other non-alkaline oxygen carriers (PrO_2 , ZrO_2) were added to low amount noble metals to benefit from the transfer of oxygen to the reactants abating carbon filaments [47,50]. All the advances in drawing attention towards low-amount noble based-materials by altering them with promoters did not totally eliminate the presence of carbon, and higher loadings are still needed to avoid deactivation and ensure excellent activity and stability.

Due to the restrictions of noble metals (high cost and scarce availability), transition metals have invaded dry reforming of methane studies with nickel receiving much attention due to its vast availability, cheapness and agnate noble metals catalytic activity in DRM [54]. Nevertheless, using nickel promotes sintering and coke formation that are two major concerns in dry reforming decreasing catalytic stability [33,41,42]. Fewer attention has been given to Co- Al_2O_3 based catalysts since they are less performing in DRM [55–59]. They are sensitive to deactivation from oxidation by CO_2 perturbing its stability [55]. Thus, *the key in dry reforming studies is to design high carbon and sintering-resistance nickel-based catalysts*. In order to reach this goal, a design of highly active coke-resistant Ni- Al_2O_3 based catalysts can be achieved by utilizing promoters, alloying Ni with other metals, changing support characteristics and catalysts synthesis techniques.

b) Al_2O_3 as support for metal Ni: The supports are in direct physical contact with the supported active sites and affect their behavior and structure, not to mention that in some cases it could interfere in the chemical reactions. The used materials are expected to have a large surface area to efficiently disperse the metal nanoparticles, uniform size and shape morphology, strong mechanical strength, high thermal stability, high surface to volume ratio and a number of defect sites, corners, edges and kinks [43,44].

To date, there are many oxides that have been studied and investigated to support the active phase for methane dry reforming such as SiO_2 , Al_2O_3 , La_2O_3 , MgO , ZrO_2 , and CeO_2 [46,59]. Back in 2000 and 2002, studies showed that metal dispersion (Rh) increases in the order of $TiO_2 < La_2O_3 < CeO_2 < ZrO_2 < MgO < SiO_2 < MCM-41 < Al_2O_3$ [60,61]. Since *nickel is our main interest as active phase* we checked its performance over different supports in several literatures. Ruckenstein and Hu were the first to highlight the importance of the support nature for nickel. In their study, they proved that the activity and selectivity of the catalyst were highly dependent on the nature of the support following the order of $TiO_2 < SiO_2 < Al_2O_3$. They related such behavior to the metal-support interaction since it can activate and modify the

electronic and chemical properties of the active phase [62]. For instance, TiO_x molecules covered the active sites during reduction by migrating over the surface of Ni particles curtailing the surface free energy and decreasing the catalyst activity. Several other researchers asserted such assumption in their publications [37,46]. Zhang R.J. et al. [63] conducted similar studies to show the significant influence of the support types on the state of active phase (NiO species) and their dry reforming catalytic performance. This group related again the poor performances of SiO_2 , TiO_2 , and ZrO_2 based catalysts to the low reduction temperature commonly associated to weak interaction with the active Ni species. On the other side, Al_2O_3 based catalyst had very high stability for more than 100 h even at high gas hourly space velocity.

Despite the fact that both silica and alumina have received much attention compared to other supports type due to the high metal dispersion they provide [43], Al_2O_3 -based catalysts are still taking the most important space for DRM with almost 109 papers published between the years 2010- early 2019 compared to 55 papers for its silica counterpart (Data taken from Web of Science). In brief, these 2 supports differ chemically. Kinetics and mechanistic studies in literature stated that there is a dual function for DRM depending on the support nature. Thus, it is proved that on acidic or basic supports the CH_4 is activated on the metal and CO_2 on the carrier forming formates or oxy-carbonates. However, for inert materials like SiO_2 , CH_4 and CO_2 are activated on the metal only, following a mono functional pathway so when carbon forms by dehydrogenation of methane, the activation of CO_2 and reaction with carbon will become limited resulting in catalyst deactivation [46]. All this leads to inert SiO_2 weakly interacting with the metal, less stable and active compared to mildly acidic Al_2O_3 . This chemical difference was recently tackled by Xu Yan et al. [64] in a study where Ni/SiO_2 and $\text{Ni/Al}_2\text{O}_3$

were prepared by a same technique to elucidate the effect of the support properties on the catalytic performances. Results have indicated that Ni/SiO_2 depicts initially higher conversion, but poorer stability due to the reduction of Ni at lower temperature than that

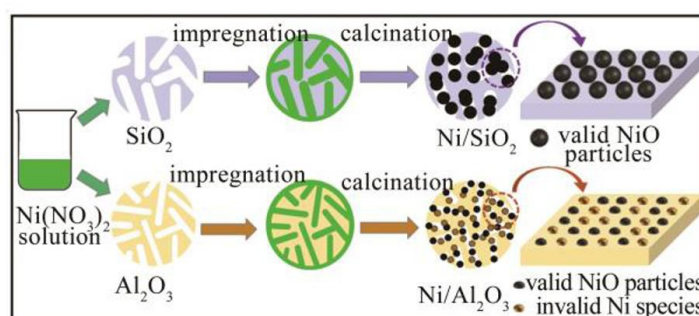


Figure I-10: Scheme representing effect of support on nickel particles [64]

of Al_2O_3 forming very large Ni particles of 31 nm and promoting the formation of coke precursors. $\text{Ni/Al}_2\text{O}_3$ kept stable for 50 h time on stream due to the formation of NiAl_xO_y species reducible at very high temperature stabilizing Ni nanoparticles (Figure I-10).

Another important chemical feature that can be addressed is the hydrophobicity and hydrophilicity in both supports. Al_2O_3 is more hydrophilic so its surface is more prone to be hydrated when in contact with H_2O and therefore less available for oxidizing metallic sites and more stable [46]. A study was done by our group on the effect of Ni-based silica and Ni-based alumina catalysts on their performance in reforming. Results indicated a re-oxidation of the Ni^0 active phase in silica-based materials while alumina-based samples preserved the metallic nickel state [65].

However, even if alumina appears to be a better support than silica, Ni-supported on Al_2O_3 still faces deficiencies due to the acidic feature of the support in addition to the common problem encountered on any support that is the high reaction temperature triggering agglomeration of Ni particle that in turn develops carbon. At the present moment, efforts are being made to adjust the Ni- Al_2O_3 stability and synthesize a material that could persist the high reaction temperatures with desirable small, active and stable metal nanoparticles.

I.4.2. Recent developments in stabilization of Ni- Al_2O_3 catalysts

The unstable status of Ni is related to its low Tammann temperature ($0.5T_{\text{melting point}}: 590^\circ\text{C}$) increasing the mobility of the bulk atoms and making the catalyst more susceptible to sintering [37,66]. Thus, deactivation of Ni- Al_2O_3 catalysts very often arises from nickel sintering or thermal agglomeration. Sintering induces a loss of active surface by structurally modifying the catalyst with crystalline growth of the active phase. This phenomenon is strongly favored in DRM by the elevated temperature applied (the reasons will be detailed in section II.2.1.1) and the atmosphere (H_2 , O_2) in contact with the catalyst. Carbon residues developed from CH_4 decomposition side reaction, as mentioned earlier, deactivate also the catalyst by either covering the active sites and/or by blocking the pores [67]. Many researchers attributed a correlation between nickel sintering and carbon formation suggesting that large nickel particles have higher carbon deposition rate during methane decomposition [68]. There are three types of carbon classified as **C α** , **C β** , and **C γ** . **C α** is known as the most reactive carbon species trivially eliminated by oxidation or reduction at low temperatures (300-450 $^\circ\text{C}$). This type of carbon does not deactivate the catalyst and can play an intermediate role in DRM reaction to *in-situ* form CO product. **C β** derives from carbon nanotubes can be removed also at temperatures not exceeding 600 $^\circ\text{C}$. This type of carbon does not lead to catalyst deactivation unless Ni particles become totally encapsulated within the nanotubes preventing access to the gaseous reactants. The formation of carbon nucleus detach and drive Ni nanoparticles away

from the Al_2O_3 support. If carbon nanotubes are formed in large amount they can contribute to reactor plugging and cease of reaction. $\text{C}\gamma$ is a graphitic crystalline carbon created from the interaction between $\text{C}\alpha$ and $\text{C}\beta$ or/and between carbons of the same type ($\text{C}\alpha$ - $\text{C}\alpha$ / $\text{C}\beta$ - $\text{C}\beta$) that gradually transform into $\text{C}\gamma$ with time on stream. $\text{C}\gamma$ is the most deleterious type of carbon demanding very high temperatures to be removed (600-850 °C) destroying catalyst stability [69,70].

Around 102 papers were published in the recent years (2010- early 2019) on the improvements made in synthesizing Ni-alumina catalyst that can resist sintering and carbon deposition. The table in the Appendix summarizes the advances done in literature during the past 10 years on Ni- Al_2O_3 preparation methods (17 publications). The table mainly comprises the type of Al_2O_3 used, the method of Ni insertion and its particle size with the test conditions applied, the CH_4/CO_2 conversions obtained, and the reasons of deactivation if any. Thus, the following paragraphs highlight on the main developments made concerning Ni- Al_2O_3 materials and their main results.

I.4.2.1. Alterations in Ni addition to Al_2O_3 support

I.4.2.1.1. Post-Ni addition to Al_2O_3

Taking a look into the Table, several researchers tested different methods of Ni deposition on *commercial* Al_2O_3 to enhance its performance. For instance, some used the wet impregnation (W.I.) method to add nickel. However, this technique usually results in a weak interaction between the Ni active phase and the Al_2O_3 support forming large nickel particles that triggered filamentous carbon during DRM reaction [71–74]. Incipient wetness impregnation (I.W.I) was developed to further improve the dispersion and is quite frequently used in many reforming application. It is based on adding a metal-containing solution with volume equivalent to the catalyst support volume [64,75]. The nickel particle size could be as small as 4 nm using this method [64], however Ni generally sinters during the high reaction temperature making it vulnerable to be encapsulated and detached from the Al_2O_3 matrix by carbon, decreasing drastically CH_4 conversion from 80 to 50% as seen in the table. Other techniques applied like the equilibrium deposition filtration technique (EDF) [72], and electrospinning [76], achieved nickel particle sizes of 12 and 6.5 nm respectively. Despite being innovative routes, they do not fit the industry requirements, like the W.I. and I.W.I. that are very simple to apply, and control of many parameters are needed and expensive. Not to mention

that for the case of electrospinning synthesized catalyst, a high amount of carbon was formed after 300 minutes of DRM reaction only [76].

I.4.2.1.2. Simultaneous Ni addition to Al₂O₃

In order to further minimize the particle size and enhance its distribution, few researchers have suggested the direct incorporation of Ni metal into the Al₂O₃ framework (Table in the Appendix) [77–79]. Newnham J. et al. compared the synthesis of Ni/Al₂O₃ using W.I. and I.W.I. to the one synthesized directly in a polyethylene bottle in presence of both Ni and Al precursor [80]. The latter catalyst showed a decrease of 10% in conversion in 10 h then it was stabilized for 200 h with only 2-3% conversion loss. However, the size of the Ni crystallite was sintered after test from 11 to 15 nm contributing eventually to the formation of a lot of carbon nanotubes. Zhan L. et al. [81] developed also a 2-step hydrothermal technique where Ni(OH)₂ nanoparticles were synthesized by a 1st-step hydrothermal then anchored into a 2nd-step hydrothermal in presence of alumina precursor to adjust the environment and form a thermally stable catalyst. The unique leaf-like Ni/Al₂O₃ obtained offers more active sites contributing to higher catalytic activity and stability as well as carbon resistance compared to one-step hydrothermal and conventional impregnation method.

In addition, the Table Appendix describes a new method to include Ni precursors within the synthesis of the support [77–79,82]. A comparison between impregnated Ni and one-pot (with Ni put in the synthesis mixture) Ni-Al₂O₃ shows that Ni can be trivially separated from the support when added after

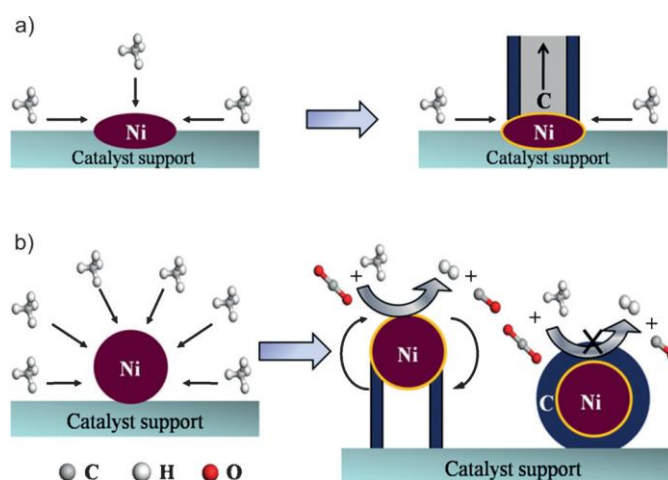


Figure I-11: Schematic representing the influence of Ni insertion in the catalyst on coke formation during DRM [82]

Al₂O₃ synthesis due to the weak interaction that forms destructive carbon in DRM (Figure I-11 b) encapsulating Ni particles by layers and increasing rate of catalyst deactivation. The “one-pot” route managed to form Ni particles in the range of 5-15 nm, with good stability but did not cast the development of carbon, for 28 % of carbon was formed on the spent catalyst compared to 64 % for its impregnated counterpart [77].

I.4.2.2. Alterations in Al₂O₃ nature

Trials were also made to increase the surface area of Al₂O₃ (Table in the Appendix) and further enhance the nickel dispersion and catalytic properties. Thus, the type of Al₂O₃ support was changed from being *commercial*, to *nanoflakes hollow hierarchical spheres* [83], *nanosheets/nanoplates* [84], *over coated oxide by ALD* [85], and *mesoporous oxide* [77]. The Ni deposited on *hollow hierarchical spheres* Al₂O₃ were in strong interaction with good dispersion, but the formation of coke during DRM was not eliminated [83]. A comparison was done between *nanosheets* and *nanoplates* alumina-based samples. The study showed that the *nanosheets* sample exhibited higher activity due to possessing a higher surface area (245 m².g⁻¹ compared to 48 m².g⁻¹ for the nanoplates) enhancing therefore Ni dispersion and metal-support interaction contributing to a better stability over 300 minutes time on stream [84]. Kim W. et al. [86] compared a unique *nanosheet* morphology to a random Al₂O₃ morphology prepared by *co-precipitation method*. The results demonstrated that the Al₂O₃ *nanosheet* catalyst exhibited better coke tolerance in DRM due to random-

connected large intersheet pore channels that facilitate transport of reactant product molecules and heavy coke precursors. Whereas, the *precipitation* catalyst possesses randomly small distributed pores, trapping coke precursors to form coke particles that deactivate the catalyst (Figure I-12).

Coating Ni/Al₂O₃ catalysts with *alumina*

ALD overcoats have proved resistance to sintering and coking with higher stability compared to the uncoated material attributed to the formation of NiAl₂O₄ species that preserves the small nickel particle size [85]. However, most of the initial active sites were encapsulated by the *ALD alumina* resulting in lower initial activity in DRM. Recently, attention was directed towards synthesizing *mesoporous* Al₂O₃ supports that can boost activity and stability. Several methods were applied such as the nanocasting method (SBA-15 or Carbon as hard templates) or the modified sol-gel self-assembly

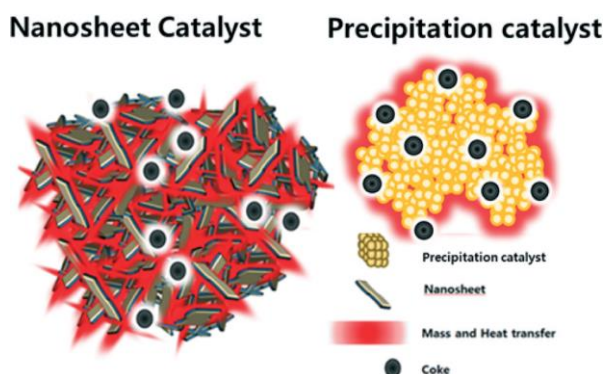


Figure I-12: Schematic illustrating the catalyst morphology effect on coke catalyst deactivation [86]

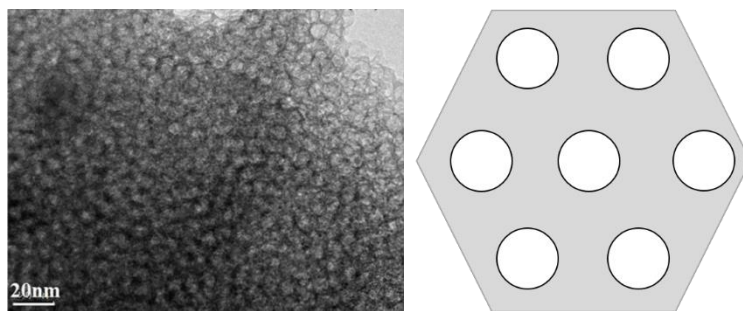


Figure I-13: Porous alumina structure [77]

process with the presence of a soft template (CTAB or P123) as structuring agent (Figure I-13) [87,88]. Compared with the first pathway requiring more than one impregnation and calcination steps, the evaporation-induced self-assembly (EISA) method was the most successful one with Al_2O_3 support carrying ordered hexagonal pores and high surface area ($225 \text{ m}^2\cdot\text{g}^{-1}$) available for Ni species during impregnation. This structure formed rigid, stable and high dispersion of Ni metals inside the mesoporous cage of alumina limiting the nickel sintering to reach a cluster size of 15 nm and resulting in highly active amorphous carbon.

I.4.2.3. Doped Ni- Al_2O_3 catalyst

Besides developing monometallic catalysts with different support modifications and Ni deposition methods, studies were done also on alloying nickel with a second metal to alter the catalyst surface properties (not presented in the Table Appendix). This second metal forms bimetallic materials where Ni is alloyed to a noble [37,89–103] or a transition metal [104–112] having distinctive bi-functional assets when in contact with Al_2O_3 support. However, the bimetallic systems are outside the scope of this thesis, where Ni is the focus since it has better performance than any other transition metal even when used alone and it is way cheaper than noble metals that is being avoided. Same reasoning goes for tri-metallic Ni-alumina catalysts [113–128] that make the system more complex, expensive and far from the purpose required. Adding dopants to reduce and remove carbon deposition on Ni- Al_2O_3 is an interesting approach. Thus, we focused on basified dopants and magnesium specifically since it is less expensive than other dopants seen in literature like Ce [82,129–136], La [137–143], and Mn [144,145].

Basic metal oxides have received a great attention in DRM because of their high Lewis basicity that enhances chemisorption of CO_2 (acidic gas) and improves coke resistance. Barium, calcium and magnesium were applied in dry reforming [146–150]. However, Ba has been barely used because Ni tends to sinter in presence of Barium forming big aggregates and barium carbonates. It may also lead to nickel re-oxidation during handling of catalyst and carbon deposition with large particle size of 20 nm [149]. Ni-doped calcium alumina catalyst revealed in a study an important role in inducing high basicity but did not eliminate the occurrence of carbon and the Ni nanoparticle size obtained was quite large (21 nm) resulting in catalyst deactivation [150]. Ni alloyed with Mg on commercial alumina sample provided the highest CH_4 and CO_2 conversions compared to Ba and Ca supported samples [151,152].

The author explained the difference in performances by a study done on Ni supported on MgO, CaO, and BaO [153]. CO temperature programmed desorption results (TPD) showed in this study that Mg promoted sample produces less amount of CO₂ from CO compared to Ba and Ca samples. This means that the Mg-containing sample is more resistant to the disproportionation side reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ over Ni sites implying higher stability. In addition, MgO is the only face-centered cubic type promoter with lattice parameter ($a= 4.21 \text{ \AA}$, $A-B= 2.11 \text{ \AA}$) and bond distance close to NiO ($a= 4.19 \text{ \AA}$, $A-B= 2.10 \text{ \AA}$) [153,154]. Due to this similarity, a solid solution can be formed retarding reduction of NiO to Ni strengthening the interaction with the Al₂O₃ support and reducing Ni segregation. It is also important to deem in mind that NiO amount should not be too low compared to Mg since only a very small amount of Ni will segregate at the solid-gas interface during reduction curtailing the catalyst activity. Ni-Mg-Al₂O₃ used so far in DRM still faces certain deficiencies that are elaborated in Chapter III.

I.5. Thesis objectives and methodology

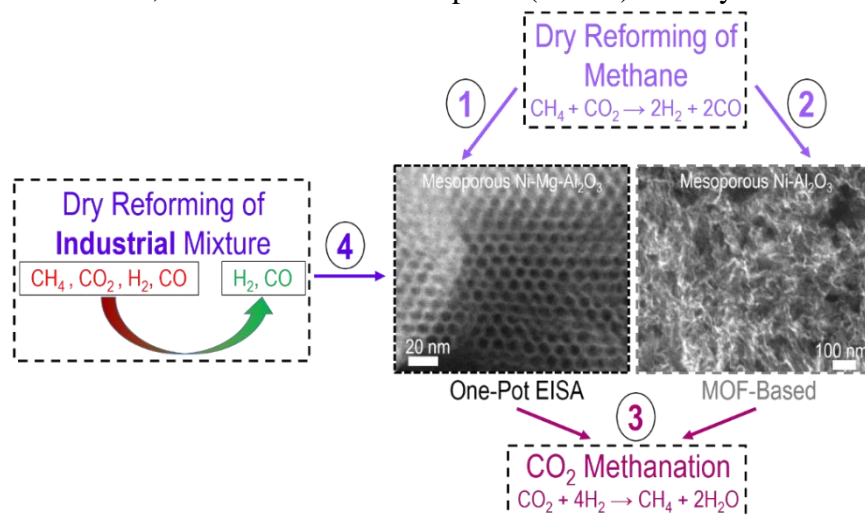
Based on this review on dry reforming of methane and on recent advances of Ni-alumina, obtaining highly active and stable catalyst has not been reached. Studies have demonstrated that different parameters during the material preparation can greatly influence its behavior during catalytic test. Needless to say, the one-pot method seems to be the best solution for Ni addition within Al₂O₃ support. The shape of alumina has to be constructed in a way that ensures occlusion and confinement of nickel particles within the support structure to avoid sintering as much as possible. MgO is the most suitable basic dopant to Ni-Al₂O₃ suppressing carbon formation. In this context, the objectives of this thesis is to take advantage of the different positive routes described above to go even further in the elaboration of highly active and stable catalyst for DRM. The proposed approaches are the following:

1. In *chapter 3*: To combine Mg-dopant with Ni precursors by one-pot within the synthesis of mesoporous alumina catalyst. Altering the EISA method, Ni, Mg and Al precursors are all mixed together to synthesize highly uniform dispersed Ni and Mg among the mesoporous framework of alumina. This technique takes advantages of two features: first, Ni is trapped within the parallel ordered mesopores that cease particle sintering, and second, the presence of MgO suppresses carbon formation by enhancing the chemisorption and activation of CO₂. A target will be also to find the

optimum Mg loading that seems from bibliography (as will be introduced in the chapter) to play a determining role.

- In **chapter 4**: To adopt a novel technique derived from one-pot and different type of alumina support as a new way of occluding Ni inside the pores. Thus, we chose an Al-containing Metal-organic framework (MOF) as sacrificial precursor to prepare the catalysts. This route combines the advantages of high porosity, high surface area and intimate mixing between the nickel and support components to synthesize highly stable and active Ni/alumina catalysts for DRM.
- In **chapter 5**: To extrapolate the study of the catalytic performances of the most interesting synthesized mesoporous Ni-alumina based materials (tested in chapters 3 and 4 in DRM) to another reaction of potential interest as well, namely CO₂ methanation reaction.
- In **chapter 6**: To move to extended and more realistic reactant mixtures for methane reforming reaction after finishing from the conventional model mixtures. Treatment of biomass wastes do not only result in CH₄ and CO₂ formation but includes H₂ and CO. As a result, a product gasification mixture composition from a Lebanese industry containing CH₄, CO₂, H₂ and CO was treated under Ni-Mg-Al₂O₃ based catalysts in reforming reaction to investigate the efficiency of our catalysts under harsh conditions.

To achieve our purpose, many characterization techniques were applied and used in order to analyze the materials prepared. They will be presented first, in **chapter 2** where the equipment and experimental conditions for characterizations in addition to the set-up of both DRM and CO₂ methanation catalytic tests and considerations on thermodynamic equilibrium are elaborated. Then, above-mentioned chapters (3 to 6) will systematically recall some



bibliographic elements specific to the treated topic, then introduce the conditions of preparation of the studied samples, analyze (if relevant) their physicochemical properties (both in calcined and reduced states) and finally discuss catalytic features.

II. Chapter 2: Technical Part



The methods adopted for synthesizing the materials employed in this thesis will be presented in the respective chapters where these materials will be studied. The aim of the present chapter is to give a rigorous explanation about the characterization techniques used to determine the physico-chemical properties of the samples prepared embracing the structure, the texture, the reducibility and the state of the active phase in the catalyst system. After explaining each technique used, the catalytic schemes of both dry reforming and CO₂ methanation will be elaborated in details along with the appropriate conditions used in each reaction. This last part will also include a discussion on thermodynamic equilibrium which has to be considered to estimate catalysts performances.

II.1. Characterization techniques

II.1.1. Physicochemical techniques

II.1.1.1. N₂-Sorption

Principle of the technique: This technique provides information about surface area, pore volume and pore diameter. It is based on a gas-solid adsorption phenomenon involving intermolecular forces (Van der Waals), analysed on a volumetric basis at constant temperature. The volume of adsorbed gas (nitrogen in our case) is measured as a function of partial pressure (P/P_0). The adsorption process is followed by a desorption that coexists to represent the opposite operation in which the amount of adsorbed species decreases. The recorded values at increasing and decreasing P/P_0 allow for the plotting of adsorption-desorption isotherms. If the adsorption and desorption curves do not coincide, a hysteresis loop appears. The shape of the isotherms informs on the types of pores present in the materials that can include macropores (pore width

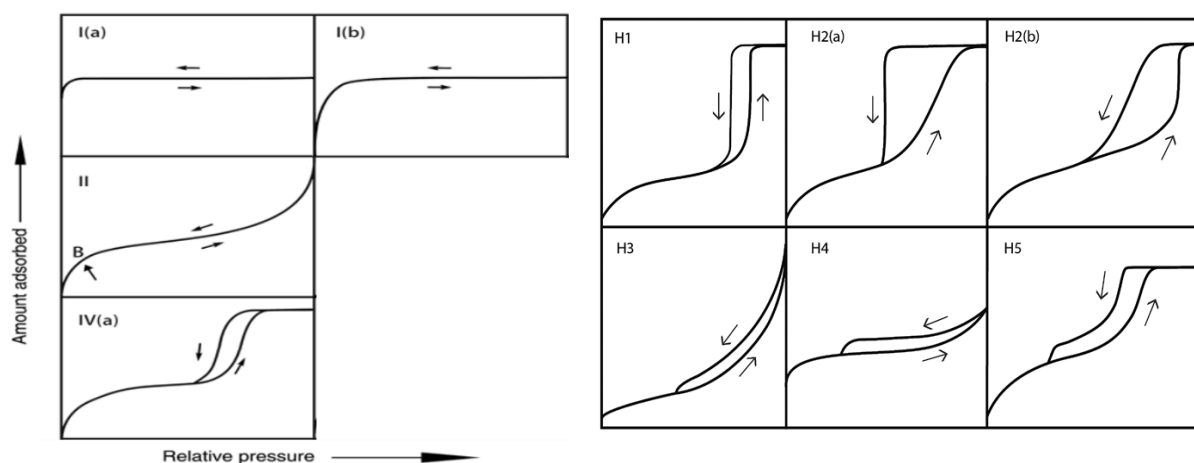


Figure II-1: Classification of physisorption isotherms (left graphs) and hysteresis loops (right graphs) [157]

> 50 nm), mesopores (2 < pore width < 50 nm) and micropores (pore width < 2nm) [155,156]. There exist 6 distinct types of isotherms identified by IUPAC (International Union of Pure and Applied Chemistry), among which three of them only will be of interest in our study (Figure II-1): type I is dedicated to microporous materials with (a) narrow micropores (< 1 nm in diameter) and (b) wide micropores (with diameter between 1 and 2.5 nm) giving capillary condensation at very low pressure, type II is typical of nonporous/macroporous adsorbents characterized by monolayer then multilayer adsorption on surfaces, and type IV is related to mesoporous samples with the presence of capillary condensation in the mesopores giving a hysteresis. For this latter type, many different kinds of hysteresis loops have been reported where the main ones are illustrated in Figure II-1. To elaborate, H1 loop is given by materials with a narrow range of uniform mesopores, H2 loop is found in more complex pore structure where network effect is crucial associated to pore blocking, and the unusual type H5 hysteresis could be found in plugged hexagonal template silica having open and partially blocked mesopores. H3 resembles a type II isotherm that belongs to plate-like particles such as clays or to macropore networks not fully filled with pore condensate. H4 loop possesses an adsorption branch that is a composite of types I and II and is found in zeolites and micro-mesoporous carbons.

Procedure: Nitrogen adsorption-desorption experiments were conducted on an ASAP 2020 Micromeritics apparatus that contains degas and analysis ports. 70-80 mg of the sample (support, materials calcined and reduced) to be analysed was enclosed in a glass tube and degassed under vacuum for 2 hours at 250 °C with a rate of 10 °C.min⁻¹ in order to remove all impurities (H₂O, CO₂) from the surface of the sample prior to N₂-sorption analysis. After degassing, the sample was placed in a liquid nitrogen bath (-196 °C). The adsorption isotherms were obtained by introducing stepwise known volumes of N₂ into the cell (adsorption) then evacuating the cell progressively (desorption), and plotting the volumes as a function of the equilibrium pressure P/P₀ at each step in the range of 0 to 1.

Derived results: The values of surface area, pore volume and pore diameter were obtained directly from the machine software that did automatically the calculations:

a) Surface area (Brunauer-Emmet-Teller method): The conventional linear equation applied is the following:

$$\frac{\frac{P}{P_0}}{n \times (1 - \frac{P}{P_0})} = \frac{1}{n_m \times C} + \frac{C-1}{n_m \times C} \times \frac{P}{P_0}$$

where,

- n is the volume of gas adsorbed at relative P/P_0 at standard temperature and pressure (0 °C, 760 mmHg) and is deduced from the isotherm curve (y-axis)
- P/P_0 is the total pressure over the vapor pressure of the adsorbate at experimental temperature conditions and is deduced from the isotherm curve (x-axis)
- n_m is the specific monolayer capacity, calculated as specified below
- C is the BET constant related to heat of adsorption and this parameter is exponentially related to the energy of monolayer adsorption.

A convenient way to derive n_m is to plot $P/P_0/(n \times (1-P/P_0))$ as a function of P/P_0 to form a linear relation expressed by BET plot. The y-intercept of this line corresponds to $1/n_m C$ and its slope is $C-1/n_m C$. This linearity of the BET plot is restricted to a range of $\frac{P}{P_0}$ of 0.05-0.3. The

second part in the BET method is to calculate the BET surface area from the monolayer capacity based on the equation: $a_{S\text{ BET}} = \frac{n_m * NA * \sigma_m}{m}$

where, σ_m is the molecular cross sectional area taken by the adsorbate molecule in the complete monolayer (σ_m (N₂): 0.162 nm²), a_s (BET) is the BET specific of the adsorbent (catalyst) of mass m (g), NA is the Avogadro's number ($6.023 * 10^{23}$ molecules.mol⁻¹) and n_m is the volume adsorbed at monolayer coverage (ml) [155].

b) Pore volume: The total pore volume is determined from the amount of vapor adsorbed at a relative partial pressure close to unity ($P/P_0 = 0.95-0.99$) and taking into consideration that the pores are filled with the adsorbate in the bulk liquid state. The microporous volume is determined by t-plot method using: $t = t_m * (V_{exp}/V_m)$ where t is the thickness of adsorbed multilayer, t_m is the thickness of each layer ($t_m = 3.54 \text{ \AA}$ (N₂)). The low linear region intercept with the y-axis corresponds to microporous volume [156].

c) Pore size: The pore size distribution curves are applied on the desorption branches of the adsorption-desorption curves by applying the Kelvin equation: $r_k = \frac{-2\sigma v}{RT \ln(\frac{P}{P_0})}$ where, r_k is the Kelvin radius, σ is the surface tension of the liquid condensate, v is the molar volume of the liquid condensate. The pore radius (r_p) for the cylindrical pores is calculated by the sum of Kelvin radius (r_k) and the film thickness of adsorbed multilayer (t): $r_p = r_k + t$ [156].

II.1.1.2. X-ray diffraction (XRD)

Principle of the technique: This technique determines the crystalline structure and size of crystalline domains in the catalyst. An incident X-ray beam is directed towards the solid

material used in which the intensity of the diffracted X-ray is collected (Figure II-2). Diffraction occurs when the angle between the incident rays and a crystallographic plan is identical to the angle

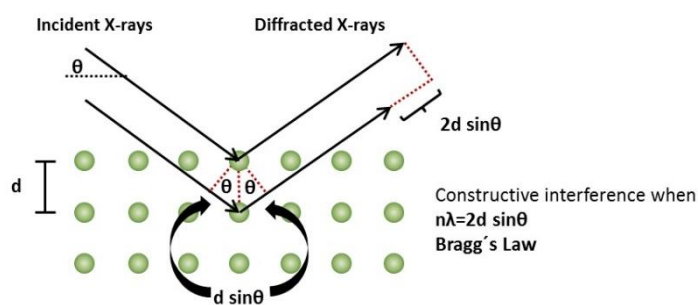


Figure II-2: Mode of X-ray diffraction

between this plan and the diffracted rays. The resulting constructive interference of the diffracted beam enhances the diffracted intensity following what is called the Bragg's law $2d\sin\theta=n\lambda$ [157] where, θ is half the diffraction angle, n is the order of diffraction (equal to 1), λ is the wavelength of the radiation, d is the distance between two planes of the same crystallographic family (\AA) with indices hkl .

Procedure: The small angle XRD patterns were measured in the 2 Theta range between 0.5 and 5° on a Brüker D8 diffractometer (available at LRS, Paris) operating at 30 kV and 10 mA, using the $\text{CuK}\alpha$ wavelength (1.5418 \AA) and a step size of 0.01° (1 s per step). These patterns were recorded for the calcined and reduced Ni-based materials. The wide angle XRD measurements were conducted on a PANalytical XPert³ diffractometer in Lebanon ($\text{Cu K}\alpha$, $\lambda=1.5405 \text{ nm}$) in a 2 Teta range between 5 and 90° . A voltage of 30 kV was used with a current of 10 mA and a step size of 0.02° at 2 seconds time per step.

Derived results: The nature of the nano-crystalline phases in the samples are determined by a direct comparison of the obtained diffraction patterns to standard powder XRD files found in the International Center for Diffraction Data (ICDD). The particle size of the crystal domains is calculated based on the full width at half maximum using Scherrer equation: $D = K \cdot \lambda / \beta \cdot \cos \theta$ where, D is the average nanocrystals size (\AA), K is the shape factor (0.9 for spherical particles), λ is the X-ray wavelength (1.5405 \AA), β is the full width at half maximum (FWHM) calculated from the Warren equation: $\beta = \sqrt{(\beta_{\text{measured}}^2 - \beta_{\text{reference}}^2)}$ with $\beta_{\text{reference}} = 0.18^\circ$, and θ is the peak position (radians).

II.1.1.3 X-ray fluorescence (XRF)

Principle of the technique: X-ray fluorescence (XRF) is a technique of non-destructive chemical analysis (Al and Ni in our case). This is made possible by the respond of atoms to the interacted X-radiation. When the sample is illuminated by an intense X-ray beam (incident beam), the sample is excited by the primary X-radiation and emits X-rays along a spectrum of wavelengths which characteristics depend on the type of atoms present in the material. To

elaborate, when the atoms in the sample absorb X-ray energy by ionization, electrons from the inner electron shells (K) are knocked and ejected. The resultant void is replaced by electrons from an outer higher energy orbital (L or M shell) releasing energy (fluorescence radiation) due to the decreased energy of the inner electron orbital compared with the outer one. This energy released generates emission

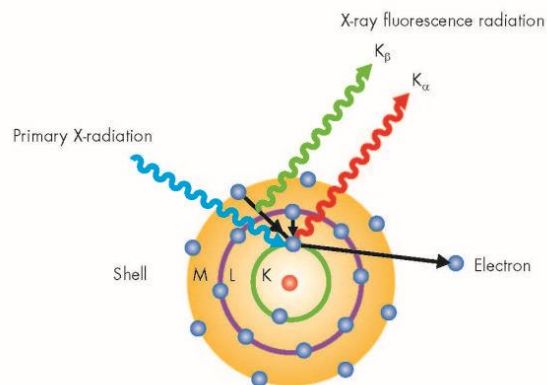


Figure II-3: Principle of X-ray fluorescence

X-rays in the form of K α and K β radiation that is a characteristic of a particular material evaluated by a detector [158] (Figure II-3).

Procedure: XRF was performed on an XEPOS spectrometer (Spectro Ametek). Quantitative data were obtained using the MicroPowder method combining the well-established fundamental parameters approach to XRF spectrometer calibration (calibration curve previously established from NiO and alumina mixtures with known chemical compositions) with automatic correction for matrix effects by using the Compton backscatter information from the sample to calculate the matrix interference.

Derived results: The content in elements obtained by the analyses were used to calculate the chemical compositions of the material studied (Al, Ni, Si).

II.1.2. Electron microscopies

II.1.2.1. Transmission electron microscopy (TEM)

Principle of the technique: Information about the support morphology and nickel nanoparticles dispersion will be trivially identified in this technique. The electron beam passes through the sample where the electrons are absorbed as a function of sample density, thickness, and chemical nature. The electrons interaction forms an image on Ni-Al₂O₃ material morphology with Ni particles appearing as black dots since it is thicker than Al₂O₃ support. This technique can be used also in diffraction mode opening the feature of determining reticular distances and crystalline zones that facilitates identifying the nature of the particle present in correlation with the International Center for Diffraction Data (ICDD) sheets. The chemical composition can be also determined when enough energy is present in the electron beam ejecting a core-level electron energy from an atom that is further filled by a higher-level electron energy. The difference between these two energy levels emits an X-ray energy that is a

characteristic of an element. Combined scanning transmission electron microscopy-High angular annular dark field (STEM-HAADF) and energy dispersive X-ray (EDX) mapping visualize further the Ni distribution in ultra-thin sections of a selected sample. The response of the signals in HAADF mode depends on the contrast of atomic number of the elements present in the sample. It detects heavy elements (in our case Ni ($Z=28$) dispersed on supports (Al_2O_3 in this report, $Z=19$) and make it clearer to visualize occlusion of Ni inside the pores compared to normal TEM mode [159,160]. Using the EDX mapping complements HAADF experiment by chemically analyzing the elements present on the catalyst that also gives an indication about the homogenous distribution of each of them.

Procedure: A JEOL-JEM 2010 electron microscope operating at 200 keV (LaB₆ gun) was used for transmission electron microscopy (TEM) experiments. The observations were done on ultrathin sections of the samples prepared by mixing a few milligrams of the powder embedded in a resin, and heated at 60 °C for 48h to provoke polymerization. The polymerized blocks were cut by an ultra-microtome so we could obtain slices (50-70 nm in thickness) deposited on copper grids covered with a carbon membrane layer. Combined STEM-HAADF and EDX Mapping was performed on a JEOL-JEM 2100Plus microscope. The analysis was performed on areas of diameter between 100-250 nm.

Derived results: For the mesoporous materials, when the organized alumina grains are parallel to the electron beam, organized parallel channels are detected, whereas, the perpendicular orientation of the grain to the beam shows hexagonal pore apertures at high magnification. Average sizes of nickel particles (calcined, reduced and spent materials), when visible, were estimated using the ImageJ software and taking at least 500 particles into consideration. This technique also allows for visualization of carbon deposits if present.

II.1.2.2. Scanning electron microscopy (SEM)

Principle of the technique: SEM provides information on the external surface topology of the grains. A specimen is scanned with a focused beam of electron that interacts with the electrons of the material observed generating pictures to study the surface topography (secondary electrons imaging) but also to check existence of external nano-metal particles (backscattered electrons imaging).

Procedure: Scanning Electron Microscopy (SEM) images were taken on a Hitachi SU-70 SEM-FEG microscope (LaB₆ Gun) with an electron acceleration tension of 7 kV. The samples were deposited on the analysis Al support and observed in mixed mode (70% of secondary electrons and 30% of retro-diffused signals).

Derived results: The grain morphology and external surface of the sample are visualized with depiction of external Ni particles if present and visualization of carbon species over spent catalysts.

II.1.3. Spectroscopies

II.1.3.1. X-ray photoelectron spectroscopy (XPS)

Principle of the technique: It allows for a clear understanding of the nature and chemical states of the elements present on a material surface. Photoelectrons are ejected from core energy levels of different atoms in the sample after X-ray bombardment. They are then collected and their kinetic energy (E_k) measured is transformed to binding energy (E_B) by a given incident energy of the X-ray beam ($h\nu$): $h\nu = E_k + E_B$ [161]. The XPS curve is plotted using the emitted photoelectron intensity as a function of the binding energy.

Procedure: An Omicron (ESCA+) X-ray photoelectron spectrometer with Al $K\alpha$ ($h\nu = 1486.6$ eV) X-ray source having a 300 W electron beam power was used to visualize the XPS spectra. The sample was first evacuated under a vacuum of less than 10^{-10} mbar, then a monochromatic X-ray (Al $K\alpha$) irradiated the sample and excited the electrons.

Derived results: The surface composition of the material is determined by attributing the observed energy peaks to a specific element and quantifying their area using the Casa XPS software.

II.1.3.2. Raman spectroscopy

Principle of the technique: The sample is illuminated with a monochromatic laser beam that creates a scattered light upon interaction with the sample molecules. The strike monochromatic radiation scatters in all direction after the collision with the sample. Most of the scattered radiation acquire similar frequency to that of the incident one (Rayleigh scattering) A very small fraction of the scattered light has a distinct frequency than that of the incident light which allows the construction of the Raman spectrum. With higher incident frequency than that of the scattered one, Stokes lines are seen in the Raman spectrum whereas anti-stokes lines appear when the frequency of the scattered radiation is higher. Conventional Raman spectroscopy measures Stokes bands because they are more intense than anti-stokes bands at normal temperature. The latter are usually used to measure fluorescing samples that interfere with Stoke bands. The Raman spectrum appears in the form of intensity as a function of wavenumber shift that is a characteristic of a chemical component. The Raman spectrum

provides further information about the quantity of the component present inferred from the intensity of the spectrum, stress and strain states identified from the peak shift, the degree of crystallinity revealed by the width of the peak and crystal symmetry and orientation detected from the polarization state [162].

Procedure: Raman measurements were conducted on a Kaiser microscope optical system (RXN1) containing a charge-coupled detector. The laser beam ($\lambda = 785$ nm) was focused by adjusting the microscope to an objective of 50X long working distance (8 mm) lens. The spectra obtained were collected over a range of $150\text{--}3200$ cm^{-1} with a 10 mW laser power, 10 seconds acquisition time and 30 accumulation per each spectrum.

Derived results: In our case, Raman was adopted to identify the presence of carbon and its properties on the spent catalysts after DRM reaction. Graphene and graphite in particular have stacks of sp^2 bonded planar graphene sheets that give a Raman spectrum with a main G band at around 1585 cm^{-1} . Carbon nanotubes are composed of rolled up graphene sheets in the form of hollow tubes that induce an additional D band that is located at 1350 cm^{-1} . The presence of this latter peak depicts a defect in the structure of carbon formed and lessen its degree of crystallinity. This assumption is more estimated by the calculation of the intensity ratio between these 2 bands. For instance the lower the I_D/I_G ratio, the higher is the degree of crystallinity of the carbon and the more difficult becomes its removal.

II.1.4. Thermal techniques

II.1.4.1. Temperature programmed reduction (TPR)

Principle of the technique: Temperature programmed reduction (TPR) is a technique used to characterize the reducibility and amount of reducible species in a sample. A flow of H_2 diluted in Ar passes through the sample that is progressively heated. The composition of the gas is continuously compared to a reference gas and any consumption of hydrogen by the studied material can be detected based on the variation of a thermal conductivity detector (TCD). Before

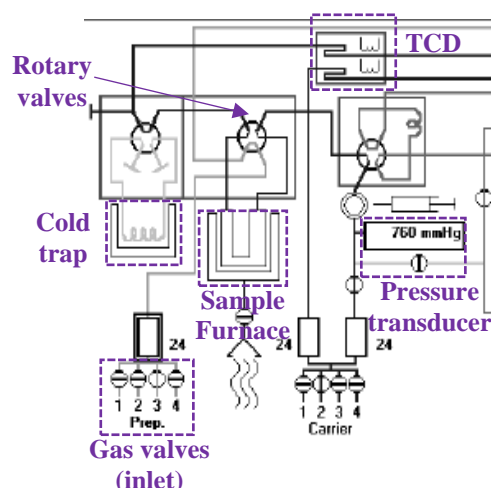


Figure II-4: TPR schematic

reaching the detector, the gas flow is circulated into an ice bath in order to trap any water

produced during the reduction reaction (in our case $\text{NiO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Ni}_{(s)}^0 + \text{H}_2\text{O}_{(g)}$) and to guarantee the detection of the sole H_2 component (Figure II-4).

Procedure: Measurements were performed on an Autochem 2920 equipment (Micromeritics) (Figure II-4). The calcined samples (80 mg) were deposited on a quartz wool inside a U-shaped quartz reactor and the H_2 consumption profiles were registered during heating from 25 °C till 900 °C with a rate of 10 °C.min⁻¹ and a 5 vol% H_2/Ar flow of 30 ml.min⁻¹ at 1 atm.

Derived results: The amount of hydrogen consumed by each material was evaluated by integrating the area under the TCD curve over the reduction temperature range. Different reduction peak temperatures could give an idea about the interaction between the active phase (Ni) and the alumina support used with higher reduction temperature triggering stronger metal-support interaction.

II.1.4.2. Thermo-gravimetric analysis (TGA) coupled with differential thermal analysis (DTA)

Principle of the technique: Thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA), depicts weight changes (TGA) and exothermic or endothermic heat flow (DTA) as a function of both time and temperature during heating. The increase in temperature decomposes components that their corresponding weight loss/gain can be calculated and the components nature can be as well identified by mass spectrometry (MS).

Procedure: Experiments were performed on a TA SDT Q600 instrument working in horizontal mode. One of the two alumina crucibles was filled with about 10 mg of sample while the other (reference) crucible was kept empty. Both were located in the heating chamber and equipped with thermocouples to follow simultaneously weight and heat flow changes during heating, carried out in air flow (50 ml.min⁻¹) from room temperature to 900 °C with a ramping rate of 5 °C.min⁻¹. A capillary placed at the exit of the chamber and connected to a Fisons VG Thermolab Mass Spectrometer was also used to perform continuous mass spectrometry (MS) analysis of the exhaust gases.

Derived results: We used this technique for the detection in our samples of carbon and nitrate species able to be oxidatively decomposed upon heating in air accompanied by a weight loss. When present, the associated exothermic behavior was detected by the positive increase of the heat flow and MS was used to identify the nature of the evolved gaseous products.

II.1.4.3. Hydrogen chemisorption

Principle of the technique: H₂-chemisorption measurements allow for the estimation of the number of metal surface sites which is used in the calculation of turn over frequency (TOF) for any metal-containing catalyst for a specific reaction. This method is of peculiar interest when the optimization of a catalytic formulation is targeted as it estimates the available metal surface area of samples resulting from various preparation procedures and conditions (temperature,

type of support), and thus provides an indirect information about the catalytic reactivity of the catalyst. Metal adsorption sites must be accessible in large amount to the probe molecule. Weakly adsorbed species “R” (reversible adsorption) are most often present on the surface of the support, whereas more strongly chemisorbed species “I” (irreversible adsorption) are usually bound to metals [163] (Figure II-5). To

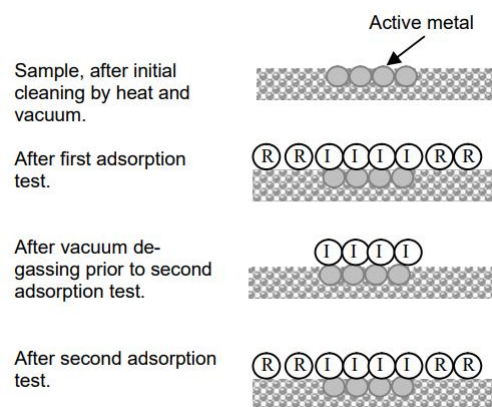


Figure II-5: Steps required to determine chemisorption isotherm

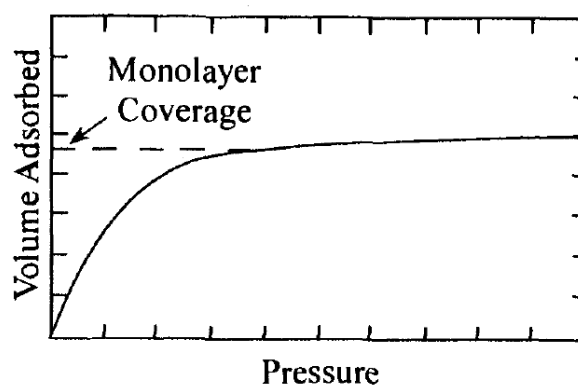


Figure II-6: Chemisorption isotherm

distinguish between reversible and irreversible adsorption, a second chemisorption isotherm is run after the sample is evacuated following the first chemisorption isotherm to remove the weakly adsorbed molecules. In this 2nd chemisorption isotherm measurement, the surface metal sites are already covered by a monolayer of chemisorbed species and thus the recorded H₂ uptake is only related to the reversibly adsorbed species. The isotherm due to irreversible adsorption of the probe (Figure II-6) is obtained by subtracting the uptake of the reversibly adsorbed species (2nd isotherm) from the total uptake (reversible + irreversible, 1st isotherm). The dissociative adsorption of H₂ occurs onto 2 surface metal sites ($H_2 + 2M_s \rightarrow 2H-M_s$, M_s is a surface metal atom (Ni)).

Procedure: H₂-chemisorption measurements were conducted on BELsorp-max (MicrotracBEL) apparatus. The samples (~ 200 mg) were firstly reduced under hydrogen for 2 hours at 650/800 °C with a heating rate of 10 °C.min⁻¹ before evacuation at 620/770 °C for 1h. Then the H₂-chemisorption experiments were performed at 298 K in the 0-50 kPa domain with intermediate evacuation of the samples for 2 h at 298 K between the first and the second isotherm.

Derived results: The fraction of metal exposed (dispersion) was estimated from the H₂ chemisorption measurements using the following equation: Dispersion (%) = N_S/N_T, where, N_S represents the number of surface metal atoms obtained from the chemisorption data and N_T is the total number of metal atoms present in the sample. TOF can be then calculated by the following formula: $TOF = \frac{(CH_{4,in} - CH_{4,out}) \times AB_{Ni} \times F}{D_{Ni} \times W \times X_{Ni}}$ (CH_{4,in} and CH_{4,out} are the inlet and outlet concentrations of CH₄ respectively, AB_{Ni} is the atomic weight of Ni, F is the total flow rate (mol.s⁻¹), W is the mass of the catalyst (g), X_{Ni} is the Ni content (g_{Ni}.g_{cat}⁻¹), D_{Ni} is the Ni dispersion).

II.2. Experimental catalytic tests set-ups

This part describes the equipment and conditions used to perform the methane reforming reaction (both dry reforming of methane alone, and reforming of waste pyrolysis mixture) and the CO₂ methanation reaction. Before doing that, thermodynamic equilibrium is calculated for each type of reaction and the employed procedure is explained. This is important to understand the choice of experimental conditions (temperature) and to properly evaluate latter catalysts performances.

II.2.1. Conditions for Dry Reforming of Methane

II.2.1.1. Thermodynamic equilibrium curves for standard DRM

Thermodynamic equilibrium was estimated based on the HSC (H, S and C stand for enthalpy, entropy and heat capacity respectively) 7.1 chemistry software using the Gibbs free energy principle. As a first step, CH₄ and CO₂ are inserted in the software as initial reactants with CH₄:CO₂ ratio of 1 and H₂O, H₂, and CO as expected components products. The temperature is varied between 100 and 1000 °C at a constant atmospheric pressure. Figure II-7

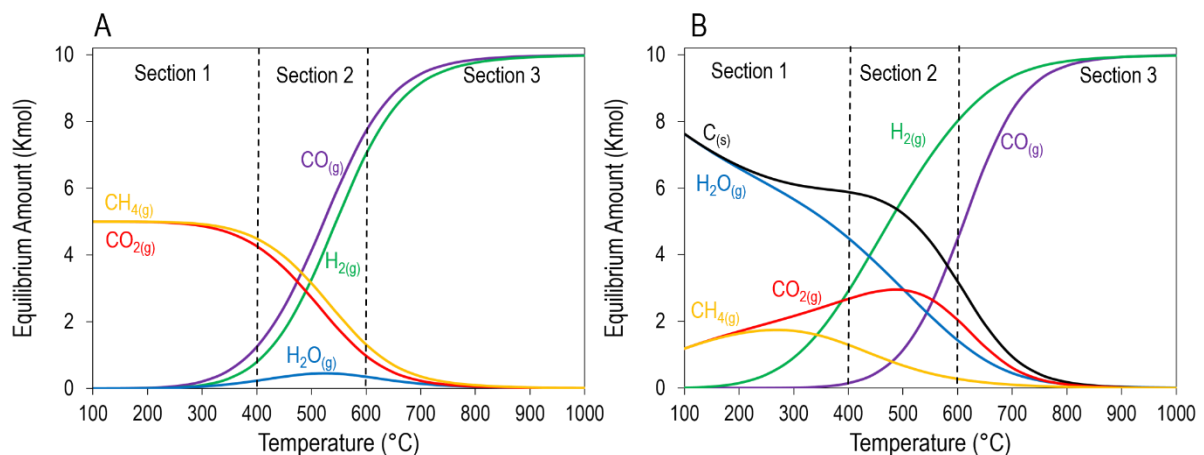


Figure II-7: Thermodynamic equilibrium curve for DRM (CH₄:CO₂ = 1:1) reactants and products at P= 1 atm (A) without and (B) with carbon as side product and Argon as diluent

A illustrates the results obtained under such parameter conditions showing the evolution of concentrations of all gaseous components as a function of temperature. In this figure, CH₄ and CO₂ concentrations remain constant and no products (H₂, CO) are formed at low temperatures (section 1). DRM starts to occur at temperatures above 400 °C with maximum CH₄ and CO₂ conversions attained at 800 °C (section 3), confirming indeed the endothermic behavior of this reaction. The expected H₂:CO ratio at high reaction temperature is 1. The only possible side reaction in this case is the RWGS dominating in section 2 producing H₂O and lowering the H₂:CO ratio (<1). In the experiments 650 °C was used instead of 800 C because it favors lower energy consumption and still limits carbon formation favoring the main DRM reaction.

In the second step, carbon is allowed to take place in DRM and therefore was added as an additional product component to H₂, CO and H₂O. Figure II-7 B illustrates the thermodynamics calculations results in presence of carbon. It clearly shows that carbon influences the DRM reaction by retarding its occurrence. For instance, at low to moderate reaction temperatures (sections 1, 2) side reactions prevail like CO dehydrogenation and CO disproportionation producing C(s) and H₂O, thus hampering the main reaction. DRM prevails at temperatures above 600 °C (section 3) shifting the maximum CO₂ and CH₄ conversions to 900 °C.

Thermodynamics equilibrium curves for reforming of waste pyrolysis product mixture are presented and discussed in details in chapter VI.

II.2.1.2. Equipment for reforming reactions

Dry reforming experiments were performed in Lebanon at the University of Balamand using a **Microactivity-Reference catalytic reactor MAR** (PID Eng. and Tech., Spain) unit,



Figure II-8: MAR equipment and Micro-GC

(Figure II-8). This unit encompasses a hot box, a reaction system and valves control elements. A Gilson high performance liquid chromatography (HPLC) pump is present on the top of the unit to generate water if needed (not used in our case). A computer equipped with remote control system can be seen next to the MAR including communications through Ethernet capable of following continuously all variable parameters including pressure, temperature, hot box temperature, and gas flow rates. This MAR is connected online to an Inficon3000 gas chromatograph Micro-GC unit to analyze the reactor outlet (reactant and product gases). This Micro-GC is composed of thermal conductivity detectors (TCD) and two columns for gas composition detection: molecular sieve column (column A) adsorbs CH_4 (retention time (RT): 2.2 min), CO (RT: 3.2 min) and H_2 (RT:0.8 min) gases and plot U column (column B) adsorbs CO_2 (RT: 0.65 min) gas. CH_4 is detected as well on Plot U column but the Mol Sieve column has been used for CH_4 .

The PID (Process Integral Development) diagram (Figure II-9) provides a detailed description of the interior operation, divided into 3 main parts. The first one includes the gas delivery system including in our case CH_4 , CO_2 , H_2 and Ar gases connected each to a mass flow controller to obtain the required flow rate before being mixed together in a gas mixer. The 2nd part of the scheme involves the hot box inside which the main reactor is settled. Thus, the mixed gas reactants are entered into the hot box that is equipped with an electric forced convection heater to control the temperature (between 160 and 180 °C) to restrict any possible condensation. The preheated streams then merge into a 6-port valve controlled to direct the flow path either towards the reactor or rerouting it towards the system bypassing the reactor. Reaching the fixed bed tubular reactor (Hastelloy X), the gas flow inside is up-down where the reactants are fed from the upper part and the products are collected from the lower part of the reactor. The reactor is equipped with a thermocouple in contact with a catalyst bed placed inside a porous plate deposited between 2 layers of quartz wool, it has a length of 305 mm, an external diameter of 14.5 mm, an internal diameter of 9 mm, a maximum recommended temperature of 1200 °C and a maximum pressure of 100 bar. The product gases at the reactor outlet pass through the hot box to the 6-port valve reaching the liquid-gas separator (Peltier) to condense the liquid at low temperature. The remained gases are again directed to the hot box under controlled pressure (micrometric regulating valve) before being analyzed online by micro gas chromatography.

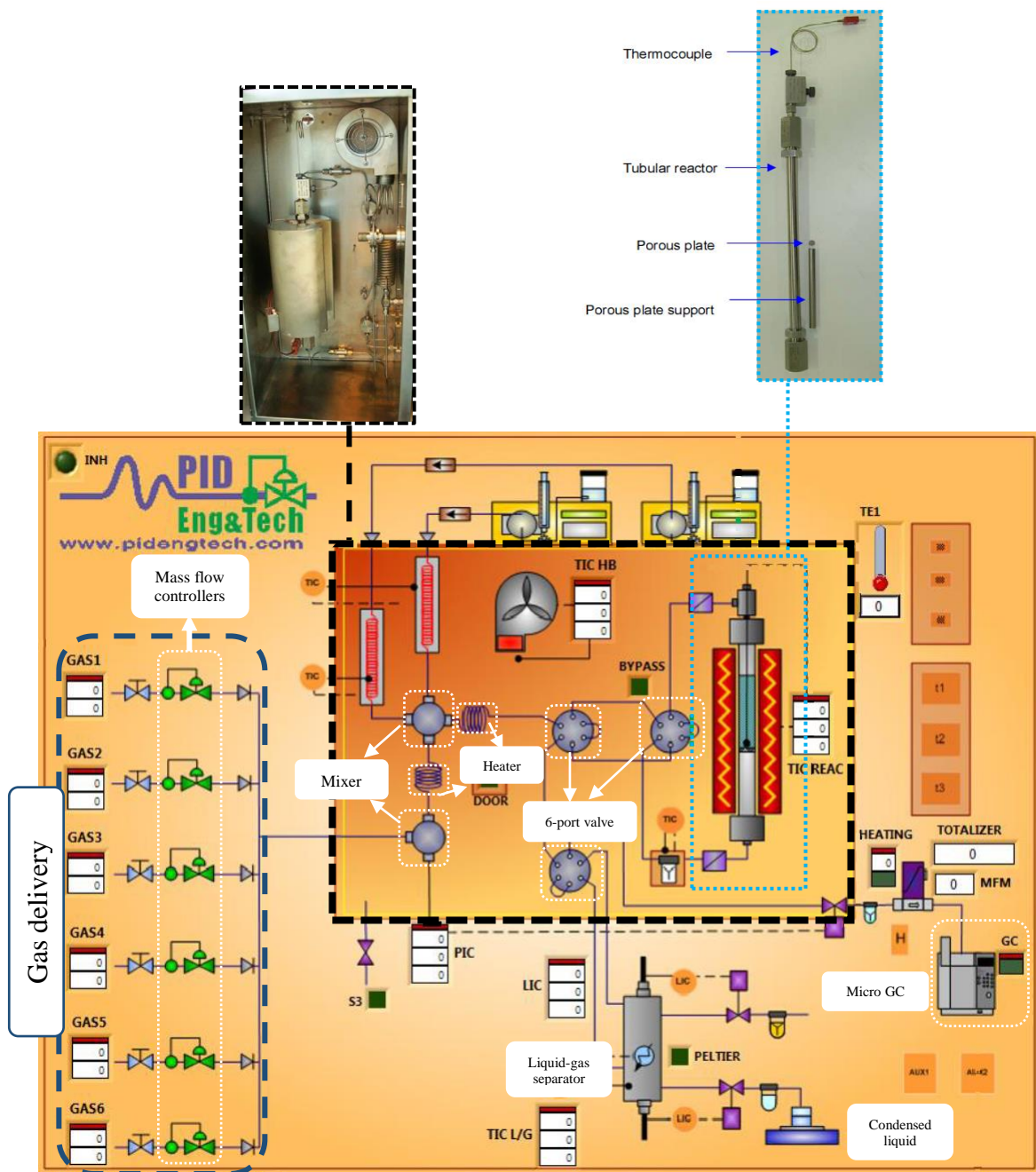


Figure II-9: General scheme of dry reforming system

II.2.1.3. Explanation of procedure adopted

Any calcined sample is first introduced inside the Hastelloy-X reactor and a leak test is performed prior to the reaction. It is done by using argon as an inert gas with a flow rate of $50 \text{ ml}\cdot\text{min}^{-1}$ that contributes to a continuous increase of pressure until reaching a set value of 5 bar (otherwise a leak is present in the line connections). After attaining 5 bar, the gas inlet (Ar) is closed, and the maintaining of the pressure for a sufficient period of time (5 minutes) is

controlled to ensure the absence of leak after positioning the tubular reactor. Then, the catalyst is reduced *in-situ* at 650/800 °C for 2 h (after heating at a rate of 10 °C.min⁻¹) in a 30 ml.min⁻¹ flow of 5 vol% H₂/Ar (Figure II-10) to convert all NiO species into active metallic Ni⁰ needed for the reaction to occur ($\text{NiO}_{(s)} + \text{H}_{2(g)} \rightarrow \text{Ni}^0 + \text{H}_2\text{O}_{(g)}$). Then, the flow is switched to the reactant mixtures, chosen as CH₄/CO₂=1/1 or CH₄/CO₂/H₂/CO= 0.75/1/1.57/0.85 in this work, with a gas hourly space velocity (GHSV) of 180 or 72 L.g⁻¹.h⁻¹ (for 20 or 50 mg of catalyst, respectively). The activity is then measured while increasing the temperature from 250 °C till 800 °C at a rate of 5 °C.min⁻¹. Also, stability measurements were done at 650°C for 13/40/100 h time on stream (Figure II-10). The reactants (CH₄, CO₂) and the products (H₂, CO) are quantified by Micro GC analysis. The results obtained as concentrations are converted to CH₄ and CO₂ conversions and H₂/CO ratio using the following equations:

$$\text{CH}_4 \text{ conversion \%} = \frac{(\text{CH}_4(\text{in}) - \text{CH}_4(\text{out}))}{\text{CH}_4(\text{in})} \times 100$$

$$\text{CO}_2 \text{ conversion \%} = \frac{(\text{CO}_2(\text{in}) - \text{CO}_2(\text{out}))}{\text{CO}_2(\text{in})} \times 100$$

$$\text{H}_2/\text{CO} = \frac{\text{H}_2 \text{ generation rate}}{\text{CO generation rate}}$$

II.2.2. CO₂ methanation reaction

II.2.2.1. Thermodynamic equilibrium curves for CO₂ methanation

Similar to DRM, HSC chemistry software is used to see the behavior of CO₂ reactant under equilibrium conditions. H₂ and CO₂ are inserted in the software as initial reactants with H₂:CO₂ ratio of 4:1, and H₂O and CH₄ as expected components products. The temperature is varied between 250 and 600 °C and the pressure was increased from 1 to 100 bars. Figure II-11 illustrates the results obtained by showing the variation of CO₂ conversion as a function of pressure and temperature. As seen, the conversion of CO₂ increases with increasing pressure

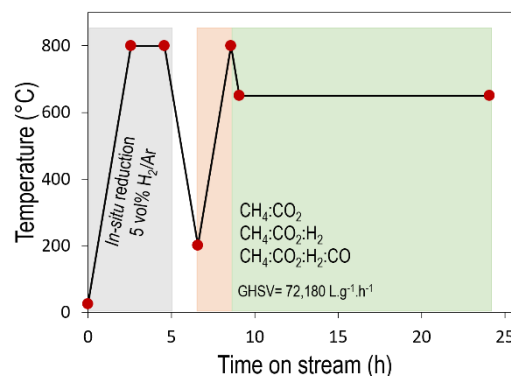


Figure II-10: Temperature profile during *in-situ* reduction (grey area), activity (orange area), and stability (green area) tests in DRM

and decreasing temperature. Consequently, elevated conversions can only be achieved at low temperatures or high pressures. However, a very high operating pressure does not lead to a significant increase of the methane yield [164]. Performing the reaction at high temperature, above 400 °C, results in the formation of CO as a by-product because the reverse water gas shift reaction becomes more favorable and CH₄ formation is banned. This phenomenon prevails at temperatures above 550 °C. Thermodynamically, there is no carbon accumulation under mild operation conditions (100-400 °C) [165,166].

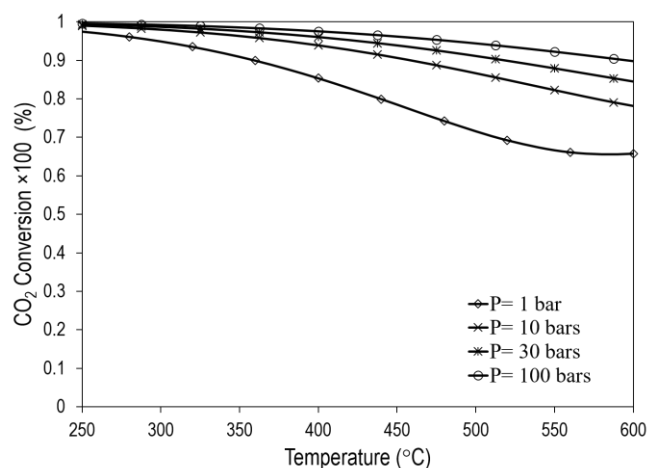


Figure II-11: Thermodynamic CO₂ conversion as a function of temperature and pressure obtained from HSC chemistry software.

II.2.2.2. Equipment for catalytic methanation

CO₂ methanation experiments were performed in Portugal at Instituto Superior Tecnico (University of Lisbon) using a quartz reactor placed inside a **TermoLab** electric vertical oven

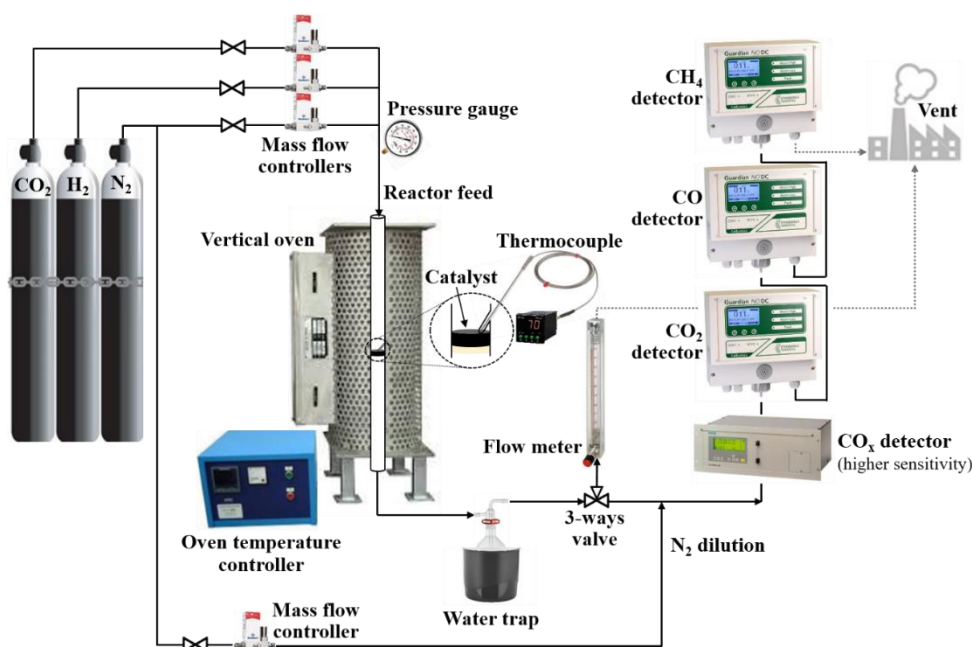


Figure II-12: General scheme of the CO₂ methanation system

unit (Figure II-12). Inside the reactor lies the catalytic bed on a porous plate that is in contact with a thermocouple to control the temperature. Similar to the DRM reaction, the reactants flow

from the upper part of the reactor and the products are collected from the bottom of the reactor. The products obtained go to a water trap placed next to the quartz reactor to condensate the H₂O produced ($\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$) and the remaining gas passes through a 3-ways valve either to an in-line flow meter to measure the outlet flow or to several gas detectors to analyze the product gas (dry base results). To this end, four gas IR detectors are available: the Ultramat 23 Siemens one is used to detect low amount of CO_x gases (<1 vol% CO₂, CO) and three Guardian NG Edinburg sensors are available for higher ranges of CO₂, CH₄, and CO (<10 vol%). CO usually has a low selectivity, thus the low concentrations detector is needed. Concerning the CO₂ component, its concentration will be always higher than 5 vol% and therefore the reading is sufficient from the Guardian sensor only. The reactant gases (H₂ and CO₂) are regulated with mass flow controllers (Brooks) with 99.99% purity before reaching the reactor inlet. N₂ gas (purity: 99.99%) is used as a diluent at the exit of the reactor to dilute the product gases before reaching the detectors in order to reach a concentration and a flow (500 ml.min⁻¹) suitable for the apparatus sensitivity.

II.2.2.3. Explanation of procedure adopted

200 mg of catalyst is used for the CO₂ methanation reaction. As for DRM, the catalyst is first pre-treated *in-situ* at 650/800 °C for 1 h with a heating rate of 5 °C.min⁻¹ and an 80 vol% H₂/N₂ flow of 250 ml.min⁻¹ at atmospheric pressure to reduce nickel oxide species to metallic Ni⁰ which is also the active phase for methanation (Figure II-13). After reduction, the reactor is cooled down to 250 °C and the feed gas is switched to CO₂ methanation reactants containing H₂, CO₂ and N₂ with a molar ratio of 36:9:10 respectively. The activity is then followed while increasing the temperature gradually from 250 °C till 450 °C (50 °C step size) with a heating rate of 5 °C.min⁻¹ and a total flow of H₂ and CO₂ equal to 288 ml.min⁻¹. At each temperature, CO₂ conversion and CH₄ selectivity are measured for 3 successive times after stabilization. The stability test was conducted at 300 °C

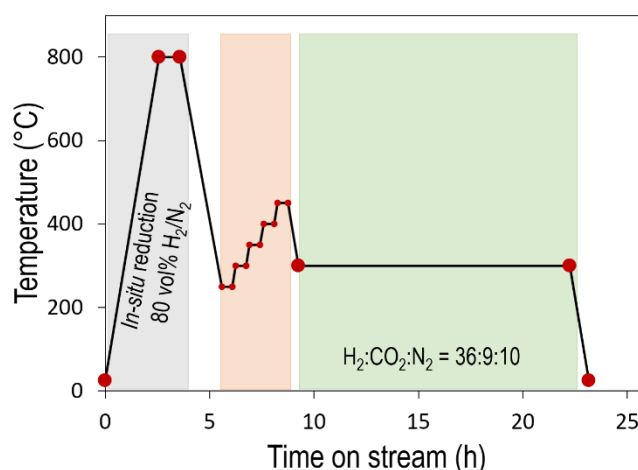


Figure II-13: Temperature profile during *in-situ* reduction (grey area), activity (orange area), and stability (green area) tests in CO₂ methanation

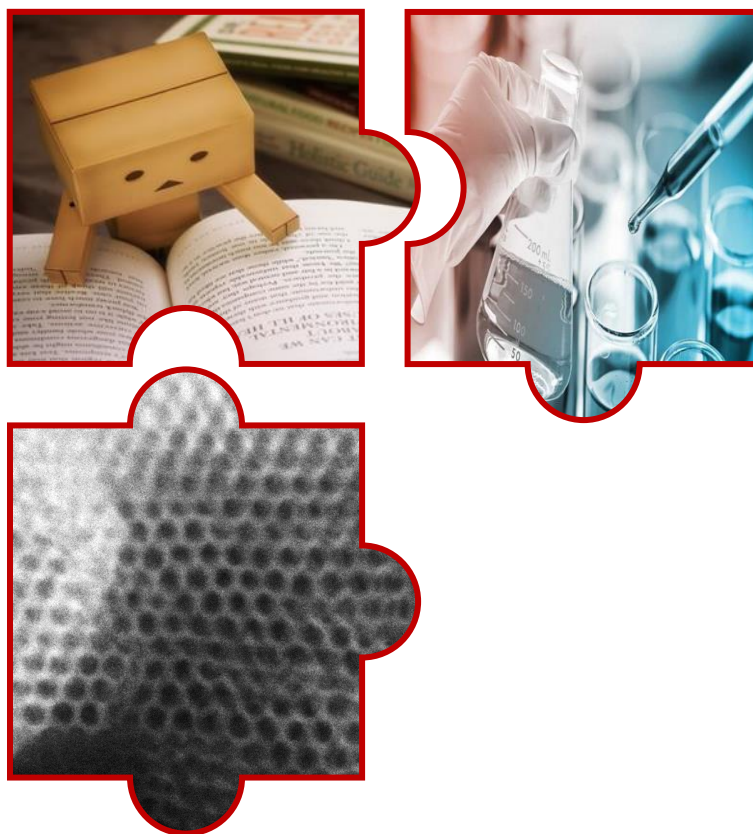
for 10/20 h time on stream (Figure II-13). The conversion of CO₂ as well as selectivity to CH₄ and CO are calculated relying on the inlet and outlet molar flow rates following the formulas:

$$\text{CO}_2 \text{ conversion (\%)} = \frac{F_{\text{CO}_2, \text{inlet}} - F_{\text{CO}_2, \text{outlet}}}{F_{\text{CO}_2, \text{inlet}}} \times 100$$

$$\text{CH}_4 \text{ selectivity} = \frac{F_{\text{CH}_4, \text{outlet}}}{F_{\text{CO}_2, \text{inlet}} - F_{\text{CO}_2, \text{outlet}}} \times 100$$

$$\text{CO selectivity} = \frac{F_{\text{CO}, \text{outlet}}}{F_{\text{CO}_2, \text{inlet}} - F_{\text{CO}_2, \text{outlet}}} \times 100$$

III. Chapter 3: Effect of magnesium loading over ordered mesoporous Ni₅-Mg_y-Al₂O₃ DRM catalysts



This chapter is an elaboration of one of the thesis aim that is to improve the stability of ordered Ni-alumina mesoporous catalyst for dry reforming of methane by addition of an appropriate amount of Mg to increase the basicity. Mg can act as a promoter by increasing the number of basic sites in the catalyst that strengthen chemisorption of CO₂ and boost catalytic performances. The state of the art specific to mesoporous Ni-Mg-Al₂O₃ materials used for reforming reactions will be recalled and compared with the present work. Our methodology was to fix the nickel content and vary the MgO one in order to understand the origin of the existence of an optimum magnesium content, so it has been varied from 0 to 26 wt%. The method of preparation will be explained in details, followed by the physicochemical characterizations of the obtained materials. The resulting catalytic performances will be presented and explained in accordance with the physico-chemical properties.

III.1. Literature review

Several preparation methods have been used in the literature for the preparation of alumina-based catalysts containing both nickel and magnesium and were applied in DRM reaction with a CH₄:CO₂ ratio of 1: sol-gel [148], two-step hydrothermal [167], impregnation [168–170] and co-precipitation [171–173]. Table III-1 summarizes some of these studies by specifying the method of preparation, the Ni and Mg amounts along with their order of addition. Some of the textural and structural properties are also summarized among with the catalytic conditions and performances of each catalyst. In brief:

- The impregnation, a method used to deposit Ni and Mg on an already existing alumina support, resulted in large Ni particle sizes up to 24 nm with a huge decrease in catalytic activity (~50%). Arbag H. [170] reported in his study the influence of Ni and Mg impregnation sequence on alumina. He concluded that the simultaneous impregnation of Ni and Mg on an Al₂O₃ support (Mg-Ni@MA) led to the best catalytic stability due to the strong metal-support interaction triggered

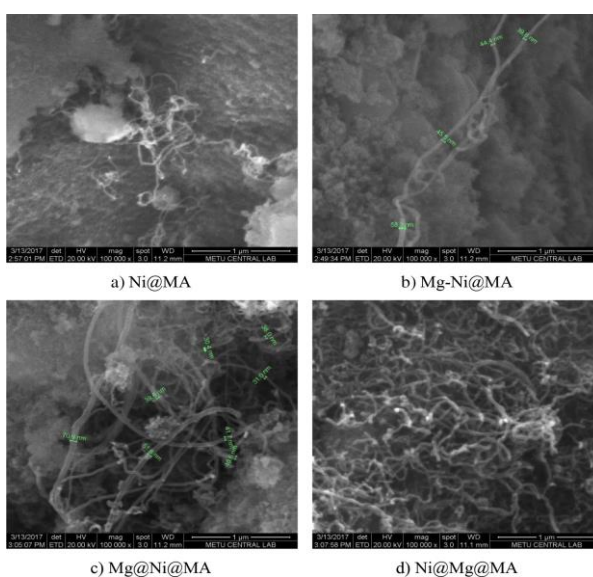


Figure III-1: SEM images of spent Ni/Mg/Al₂O₃ catalysts [170]

Table III-1: Bibliographic listing of Ni-MgO-Al₂O₃ catalysts synthesized by different techniques and their performances in DRM

Sample	Method of Preparation	Ni(wt%)	Order of Ni/Mg addition	MgO(wt%)	Al ₂ O ₃ (wt%)	Particle Size (nm)	BET SA (m ² .g ⁻¹)	PD (nm)	PV (cm ³ .g ⁻¹)	T(°C), P(atm)	C _w (mg), GHSV,CH ₄ :CO ₂ :N ₂	TOS (hr)	Conversions (%)		C _(s) (%)
													XCH ₄	XCO ₂	
Ni-MgO-Al ₂ O ₃ ^[148]	Sol-gel	15	Together with Al precursor	-	85	15.1	140	2.5	n.m.	800, 1	100,36,1:1:1	40	56-44	61-50	n.m.
				5	80	13.7	133	3.6					76-71	84-79	n.m.
				24	61	6.6	115	4.3					82-79	88-86	n.m.
				37	48	8	147	6.1					90-87	93-91	n.m.
				52	33	8.5/15.5 ^s	177	6.2					84-84	89-89	20
				65	20	8.8	193	4.9					83-82	88-88	n.m.
				80	5	6	99	11.3					88-85	92-90	n.m.
				45	45	11.6/15 ^s	162	3.4					0.45	35	40
Ni/MgO-Al ₂ O ₃ ^[167]	Two-step hydrothermal	10	Mg and Al precursors added to Ni(OH) ₂ nanoparticles	70	30	10.6/14 ^s	149	3.3	0.34	650,1	100,60,49:49:2	10	40	50	54
				75	15	6.8/7.2 ^s	135	3.8	0.28				52	63	37
				79	12	8.8/13 ^s	117	5.6	0.35				45	55	60
				82	8	8.9/13 ^s	50	6.4	0.36				30	45	51
				90	0	11.1/13 ^s	39	6.6	0.21				8	20	32
				2	40	24	105	n.m.	n.m.				800,1	n.m.,36, 1:1:1	25
4	40	17	99	97-55	97-45										
5	40	14	94	95-50	95-50										
Ni/MgO-Al ₂ O ₃ ^[168]	Impregnation	7	After Al Commercial Al ₂ O ₃	2	40	24	105	n.m.	n.m.	800,1	n.m.,36, 1:1:1	25	99-85	99-85	n.m.
4	40	17	99	97-55	97-45										
5	40	14	94	95-50	95-50										
Ni/MgO-Al ₂ O ₃ ^[170]	Co-impregnation	5	Same time	3	92	11.8	56	30	0.49	750, 1	100, 36, 1:1:1	4	42-40	60-59	5
Ni-Mg-Al ^[172]	Co-precipitation	11 mol%	A solution of Ni, Mg, Al with solution of NaOH added in 50 ml H ₂ O	0 mol%	89	7.8/10 ^s	150 ^r	4.1 ^r	0.45 ^r	750,1	50,28,1:1	60	70-40	72-45	35
				5 mol%	84	6.7/7.8 ^s	124 ^r	4.7 ^r	0.35 ^r				82	84	17
				10 mol%	79	6.2 ^r /7.6 ^s	143 ^r	5.5 ^r	0.42 ^r				87	91	10
				20 mol%	69	6.4 ^r /7.5 ^s	131 ^r	5.9 ^r	0.37 ^r				80	82	12
				30 mol%	59	6.5 ^r /7.8 ^s	125 ^r	5.6 ^r	0.33 ^r				73	82	15
				Ni-Mg-Al ^[173]	Co-precipitation	10	A solution of Ni, Mg, Al added to Na ₂ CO ₃	Mg/Al:0.25	-				16.8/19 ^s	145	8
Mg/Al:0.43	15.3/18 ^s	179	6.9					0.43		85-86 (85)	86-87	5			
Mg/Al:0.67	11.6/15 ^s	223	4.6					0.42		84-85 (84.7)	86-86	-			
Mg/Al:1	11.9/13 ^s	218	4.2					0.46		83-84 (83.6)	85-86	-			
Mg/Al:4	9.4/11 ^s	190	3.9					0.36		82-83 (82.7)	85-85	-			
Ni/MgO-Al ₂ O ₃ ^[174]	Impregnation	5	Ni impregnated on one-pot Mg Al	1	99	n.m.	208	6.6	0.31	700,1	100,15,1:1	100			
				2	98		184	7.8	0.37						
				3	97		188	4.9	0.27						
				5	95		163	7.8	0.28				77-73	77-73	8
				8	92		159	5.6	0.27						
				10	90		163	7.8	0.33						

SA : surface area, PD : pore diameter, PV : pore volume, C_w : catalyst weight, GHSV : gas hourly space velocity in L.g⁻¹.h⁻¹, TOS : time in stream, XCH₄/XCO₂ : conversions of CH₄ and CO₂ respectively, ^{r,s}: reduced and spent materials

by the formation of a NiO-MgO solid solution. However, it still resulted in the formation of carbon filaments even if in less amount compared to the other impregnation sequences. The authors suggest that the formation of carbon is due to the occurrence of a partial phase transformation of alumina from γ -Al₂O₃ to α -Al₂O₃ and MgAl₂O₄ spinel phase during calcination and reduction which alters the porous structure of the catalyst leading to a decrease in the surface area (56 m².g⁻¹) and altering the Ni-support interaction.

- The co-precipitation method led to catalysts with acceptable surface areas and Ni particle sizes ranging between 6.5 and 17 nm. Again, the method did not prevent the formation of whiskers carbon, oxidation of metallic Ni and sintering thus affecting the stability in long term tests [171–173].
- The 2-step hydrothermal technique giving non-porous materials was the least efficient (lower catalytic activity) with sintering and large amounts of carbon deposition were observed on all the catalysts after only 10 h reaction independently from the Mg amount added [167].
- The sol-gel pathway came up with porous materials having non ordered mesoporosity. The catalysts were somehow stable through time with little deactivation, but, even the best catalyst with 52 wt% MgO encountered carbon nanotubes formation with sintered Ni crystallites from 8 to 15 nm.
- Leilei Xu et al. compared the deposition of Ni by incipient wetness impregnation on mesoporous and non-porous Mg-Al₂O₃ support. As mentioned earlier, using Al₂O₃ support with ordered mesoporosity serves as a good way to confine nickel inside the pores resisting sintering and subsequent coke deposition. Thus, non-porous Ni/Mg-Al₂O₃ was less stable with 28.3% carbon formation compared to 8 wt% for the mesoporous Ni/Mg-Al₂O₃ sample [174].

Studies have been tackled also on hydrotalcite catalysts since they are cheap with basic properties that showed good activity in DRM. However, these catalysts suffer from fast sintering and coke formation due to their poor texture disturbing Ni dispersion [175–177]. For example, in a recent study done by Bruna Rego de Vasconcelos et al., a hydrotalcite catalyst needed 70 wt% of Mg to enhance its stability. However, even with this high amount of Mg, core-shell carbon and carbon nanotubes were inevitably present [178].

Based on the above-mentioned literature, a lack is still present in synthesizing a stable porous Ni-Al₂O₃ catalyst taking advantage of the Mg basic properties in casting carbon. In

addition, all the aforementioned ways of doping Ni with Mg suffer from certain deficiencies like the need of a long preparation time (i.e. several impregnations/calcinations) [108,167,168,171,173], tough conditions as high temperature [148,167], hard operation steps [167,171,173], and expensive substrates.

More interestingly, it can be noted from the data in Table III-1 that, regardless of the preparation protocol used, there is always an intermediate optimum amount of magnesium that leads the highest activity and stability of CH₄ and CO₂ conversions. To illustrate this, Figure III-2 reports the conversion of CH₄ as a function of Mg amount (expressed as Mg/Al molar ratio) for the representative work taken from the table. The scale applied for these studies is not always the same because of the distinct preparation methods used, shifting the trends in Mg contents. Nevertheless, all examples in Figure III-2 show an optimum in Mg content giving the best conversion level. An explanation of such specific behavior has to our knowledge not been detailed yet and will be targeted in this chapter. Thus, the current work aims in producing a

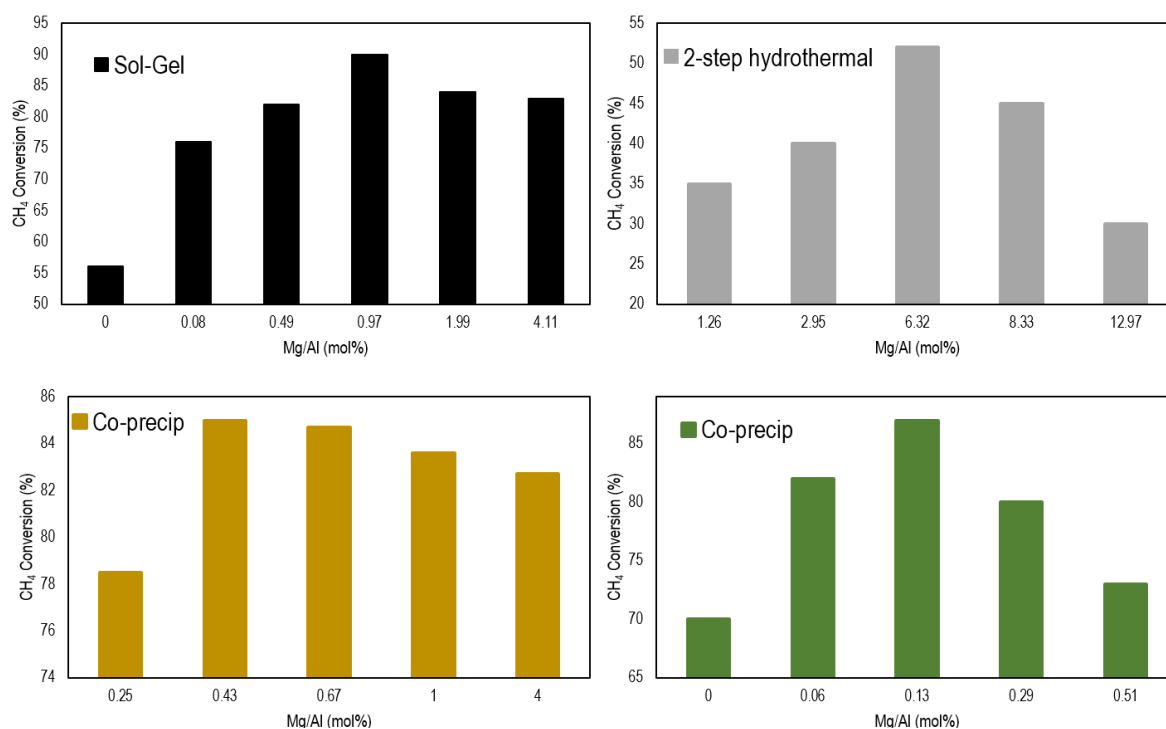


Figure III-2: Variation of CH₄ conversion as a function of Mg content in different methods of Ni-Mg-Al₂O₃ preparation present in literature: Sol-gel [148], 2-step hydrothermal [167], co-precipitation [172], and co-precipitation [173]

defined catalyst porosity, using fewer preparation steps than the previous mentioned ones. Moreover, an inspection on Mg content influence regarding the physicochemical properties and the catalytic performance of Ni-Mg-Al₂O₃ material that resembles a parabola (volcano-shape curve) is constructively demonstrated.

III.2. Synthesis of mesoporous one-pot Ni₅-Mg_y-Al₂O₃ materials

III.2.1. Synthesis principle

Nickel-based mesoporous alumina promoted by MgO was prepared using an alteration of the evaporation induced self-assembly (EISA) method. Figure III-3 represents the principle of EISA route. P123, used as surfactant, is mixed with absolute ethanol and metal precursors to form a micelle solution. P123 surfactant stabilizes Al and other metal species (Mg, Ni) through complexation bonds and inhibits agglomeration of alumina nanoparticles. Aluminum isopropoxide was used as Al metal precursor because it is assigned as a base and extra oxygen donor with no acid generated when reacting slowly with ethanol. It is also crucial for achieving homogeneous composition in the entire framework. Ethanol is a polar solvent which presence improves the proton transfer in the system donating oxygen and promoting the inorganic-inorganic interaction necessary for the polymerization of mesostructured oxide materials. HNO₃ acid is added to the mixture to influence the polymerization of the inorganic metal precursor of the hydrolysis and condensation rates. This acid has a larger aqueous ionic radius compared to other acids leading to weak complexation ability protecting the balance between organic/inorganic interfaces [179–181]. During the evaporation of ethanol, the composite mesostructure with ordered arrays of surfactant micelles embedded within the alumina matrices are formed. Then, the unidimensional materials are obtained after thermal decomposition of the template micelles.

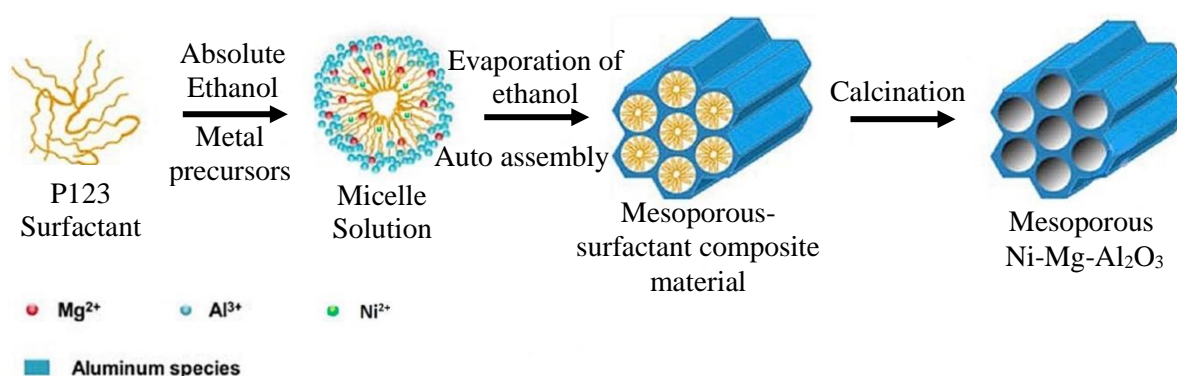


Figure III-3: A representative schematic of the mechanism involved in the synthesis of mesoporous Ni-Mg-Al₂O₃ catalyst

The one-pot EISA is an alteration of the EISA that embraces a direct addition of a second metal within the synthesis of mesoporous alumina. This method of preparation was tried by our group in a previous PhD thesis, where Ni was added simultaneously to Al precursor. The

obtained material confined Ni inside the alumina walls leading to excellent dispersion and good catalytic performance in bi-reforming of methane [65] compared to impregnated alumina samples that face calamitous sintering and coke deposition. In our case, this preparation is extended and several Mg weight percent were added during the synthesis to produce in one shot ordered mesoporous Ni-Mg-Al₂O₃ catalysts where the effect of Mg amount is investigated in details.

III.2.2. Synthesis procedure

A series of alumina based samples with 5 wt% nickel and different magnesium loading was prepared. The method used is the well-known one-pot evaporation induced self-assembly (EISA) method [180,181] applied for synthesis of mesoporous Ni-Al₂O₃ materials. In our case, we modified this method to include magnesium within the synthesis. The procedure of the catalysts preparation steps is described in Figure III-4. First, 7 g of P123 Pluronic triblock copolymer (EO₂₀PO₇₀EO₂₀, M_n=5800, Sigma-Aldrich, 435465) was dissolved in 140 ml of absolute ethanol (CH₃CH₂OH, M_n=46.07, Sigma-Aldrich, 64175) at ambient temperature (25 °C) under intense stirring. During the stirring process (Figure III-4 A), 11.63 ml of 65 wt% nitric acid (HNO₃, M_n=63.01, Johnson Matthey S.A) was added simultaneously with **A mmol** of aluminum isopropoxide (Al[OCH(CH₃)₂]₃, M_n=204.24, Sigma-Aldrich, 220418), **B mmol** of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, M_n=290.79, Sigma-Aldrich, 72253), and **C mmol** of magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, M_n=256.41, Sigma-Aldrich, 203696) to the solution, where A, B and C vary depending on the desired molar composition of

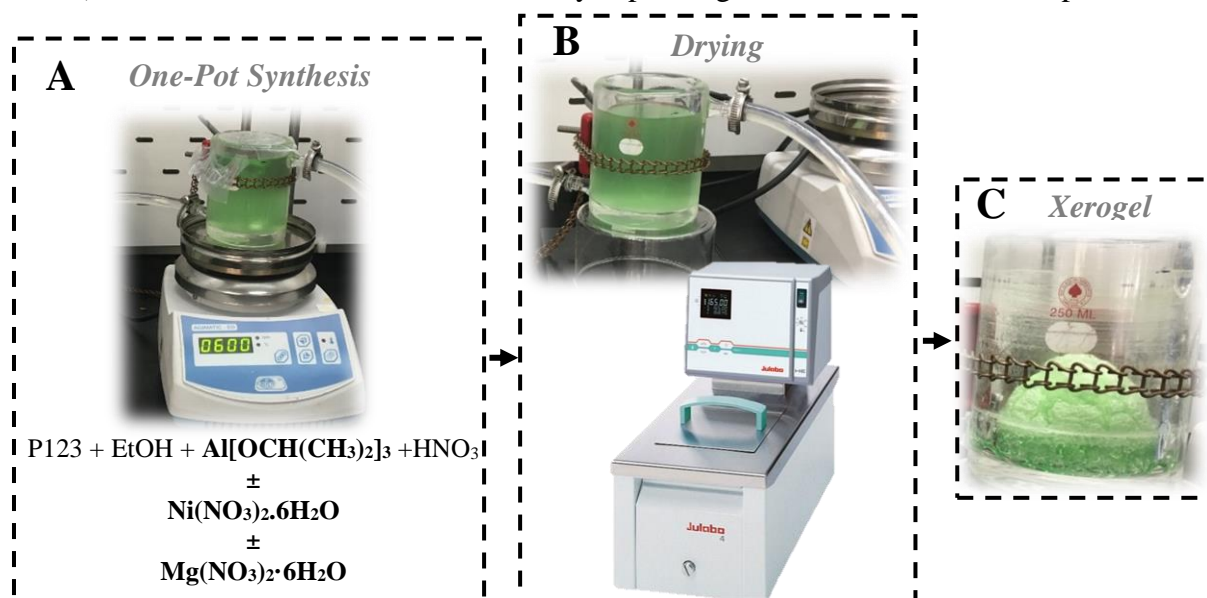


Figure III-4: Chronological steps summary of preparing mesoporous one-pot Ni_x-Mg_y-Al₂O₃ following EISA route

the solid but keeping the total (**A**+ **B**+ **C**) value constant at 10 mmol (details in Table III-2). All mentioned chemicals were employed in the catalysts preparations as received and without additional purifications. The obtained mixture was then covered with a polyethylene film (PE) and stirring was kept overnight to reach a complete dissolution of the chemicals added. Then, the solution was dried at 60 °C for 48 h to slowly evaporate ethanol and HNO₃ with the aid of a Julabo that circulates water to regulate and control the temperature (Figure III-4 B). The resulting Xerogel (Figure III-4 C) was calcined in a muffle furnace under air at 600 °C for 5 h with a heating rate of 0.5 °C.min⁻¹ (thin bed conditions). The samples obtained were denoted as Ni_x-Mg_y-Al₂O₃ where x and y correspond to the molar percentage of Ni and Mg, respectively calculated as follows: $x = n_{Ni} / (n_{Ni} + n_{Al} + n_{Mg}) * 100$ and $y = n_{Mg} / (n_{Ni} + n_{Al} + n_{Mg}) * 100$; n represents the number of atoms of each element.

Note that the “y” numbers of Mg 0, 5, 10, 15, 30 and 50 are mole contents. They correspond to Mg weight percentage detailed in Table III-2 and that are 0, 2.5, 5, 7, 15, and 26 wt%, respectively.

Table III-2: Summary of the synthesis conditions of the Ni₅-Mg_y-Al₂O₃ mesoporous materials prepared by one-pot EISA route

Sample code	Metal contents (wt%)		Ni _x Mg _y Al _z atomic formula *	Weight of chemical added (g)			
	Ni	Mg		P123	Al[OCH(CH ₃) ₂] ₃	Ni(NO ₃) ₂ · 6H ₂ O	Mg(NO ₃) ₂ · 6H ₂ O
Al ₂ O ₃	-	-	Ni ₀ Mg ₀ Al ₁₀₀	7	14.3	0	0
Ni ₅ -Al ₂ O ₃		0	Ni ₅ Mg ₀ Al ₉₅		13.6	1.02	0
Ni ₅ -Mg ₅ -Al ₂ O ₃		2.5	Ni ₅ Mg ₅ Al ₉₀		12.9	1.02	0.9
Ni ₅ -Mg ₁₀ -Al ₂ O ₃	5	5	Ni ₅ Mg ₁₀ Al ₈₅		12.2	1.02	1.8
Ni ₅ -Mg ₁₅ -Al ₂ O ₃		7	Ni ₅ Mg ₁₅ Al ₈₀		11.5	1.02	2.7
Ni ₅ -Mg ₃₀ -Al ₂ O ₃		15	Ni ₅ Mg ₃₀ Al ₆₅		9.3	1.02	5.4
Ni ₅ -Mg ₅₀ -Al ₂ O ₃		26	Ni ₅ Mg ₅₀ Al ₄₅		6.5	1.02	9
Mg ₅₀ -Al ₂ O ₃	0	26	Mg ₅₀ Al ₅₀		7.1	0	9

* Atomic formula does not take into account oxygen

III.3. Textural and structural properties of the calcined Ni₅-Mg_y-Al₂O₃ materials

III.3.1. Porosity by N₂-sorption technique

The nitrogen physisorption isotherms of the calcined Ni₅-Mg_y-Al₂O₃ samples as well as their corresponding pore size distributions are displayed in Figure III-5. All the materials exhibit

a type IV isotherm with H1 hysteresis loop attributable to mesoporous solids [155]. All samples with a magnesium weight percent between 0 and 7 wt% (Figure III-5 A) exhibit capillary steps of very steep hysteresis loop, which suggests the presence of uniform mesopores carrying cylindrical shaped patterns [155] [180,182]. Further increase in magnesium weight (Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ samples) leads to a decrease in the steepness of capillary condensation step and alteration in the hysteresis loop (Figure III-5 B) indicative of some loss of mesopores ordering.

Simultaneously, a shift of the condensation step to a higher relative pressure is seen, revealing the formation of larger mesopores [180]. This is indeed confirmed by the BJH curves derived from the desorption part of the N₂-sorption presented as insets in Figure III-5. For instance, Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ exhibit broader pore size distribution leading to larger mean pore diameter compared to the other samples with narrow pore size distribution and eventually a smaller pore diameter.

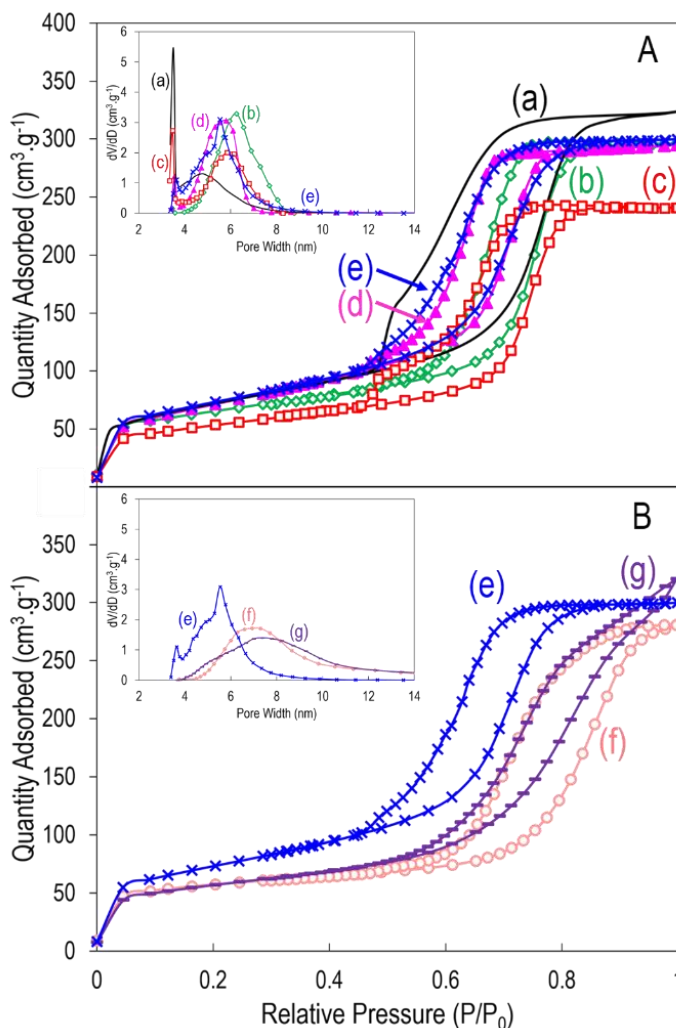


Figure III-5: Nitrogen adsorption/desorption isotherms and pore size distribution profiles (insets) of Ni₅-Mg_x-Al₂O₃ catalysts calcined at 600 °C: (a) Al₂O₃, (b) Ni₅-Al₂O₃, (c) Ni₅-Mg₅-Al₂O₃, (d) Ni₅-Mg₁₀-Al₂O₃, (e) Ni₅-Mg₁₅-Al₂O₃, (f) Ni₅-Mg₃₀-Al₂O₃, (g) Ni₅-Mg₅₀-Al₂O₃

Table III-3 reports the values of surface areas (SA) and pore volumes (PV) of all the prepared materials. For the sake of easy comparison, the Table reports the data obtained for calcined samples (this section) but it also includes those measured in a next section for reduced (section III.5) materials. An increase in Mg content up to 7 wt% did not have a significant effect or change on the BET surface area and pore volume of the solids in comparison with pure alumina. They all demonstrate high SA between 230 and 262 m².g⁻¹ with comparable PV (0.47-0.52 cm³.g⁻¹). Whereas, Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ have lower surface area of about 25% less than Al₂O₃ support confirming the presence of irregular mesopores with probably blocking parts (plugs).

It can be also noted on Figure III-5 that the physisorption curve of pure Al₂O₃ shows a second small desorption step at lower partial pressures (P/P₀=0.5) unlike the nickel-magnesium based catalysts. This could be attributed to the presence of plugs in the mesopores creating inkbottle sections within the channels which is absent in Ni and Mg enriched samples having only one desorption step at P/P₀=0.8 corresponding to open pores [183,184]. Similar behavior has been seen in literature, where scientists proposed that the addition of nickel nitrate could ameliorate the ordered mesoporosity of the alumina support [180] and contribute to larger mesopores by acting as sustained-released agents to maintain an acidic equilibrium environment. According to these authors, the nickel nitrate precursor contains crystallographic water that hydrolyzes and produces in-situ H⁺ by being transformed into free water in nitrate. The hydrolysis process of the nitrates can be also affected by the trace water in ethanol and the relative humidity in the air above the solution.

Table III-3: Porous characteristics of calcined and reduced Ni₅-Mg_y-Al₂O₃ materials

Sample	Ni content ^a (wt%)	S.A. ^b (m ² .g ⁻¹)	V _{tot} ^b (cm ³ .g ⁻¹)	Mean ^b (nm)
Al ₂ O ₃	-	258 (127)	0.52 (0.28)	4.8 (5.3)
Ni ₅ -Al ₂ O ₃	5.0	229 (246)	0.49 (0.54)	6.2 (6.6)
Ni ₅ -Mg ₅ -Al ₂ O ₃	5.0	235 (207)	0.40 (0.62)	5.8 (8.5)
Ni ₅ -Mg ₁₀ -Al ₂ O ₃	4.52	258 (207)	0.47 (0.40)	5.8 (5.1)
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	4.91	262 (229)	0.49 (0.38)	5.5 (5.7)
Ni ₅ -Mg ₃₀ -Al ₂ O ₃	4.93	196 (144)	0.48 (0.36)	6.9 (7.6)
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	4.96	200 (172)	0.52 (0.42)	7.4 (8.0)

a: Ni amount determined by XRF, b: total surface area (S.A.), total pore volume (V_{tot}) and mean pore diameter (mean) calculated from the N₂ sorption isotherms for calcined (normal font) or reduced (in brackets) materials properties

III.3.2. Structural properties and crystallite type/size by small and wide angle XRD

The influence of the metal loading was also investigated using small angle XRD as seen in Figure III-6 A. Small angle X-Ray Diffraction has been widely applied on ordered mesoporous materials such as SBA-15 [185], MCM-41 [186] and Al₂O₃ [180] to prove the presence of two-dimensional structure. Pure Al₂O₃ exhibits a strong diffraction peak around 0.7-0.9° and a weak diffraction peak around 1.5-1.7° characteristic of [100] and [110] plane

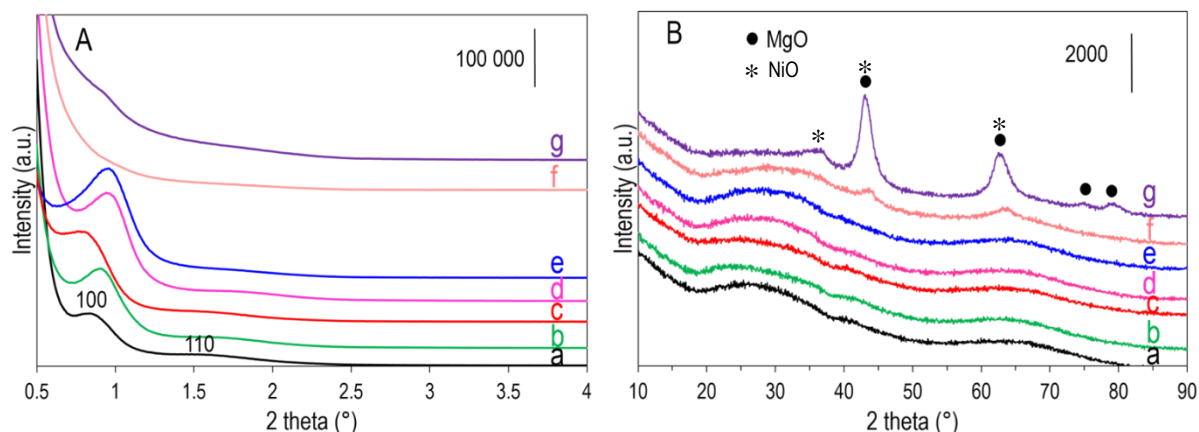


Figure III-6: (A) low and (B) wide angles XRD patterns of Ni₅-Mg_x-Al_y catalysts calcined at 600 °C: (a) Al₂O₃, (b) Ni₅-Al₂O₃, (c) Ni₅-Mg₅-Al₂O₃, (d) Ni₅-Mg₁₀-Al₂O₃, (e) Ni₅-Mg₁₅-Al₂O₃, (f) Ni₅-Mg₃₀-Al₂O₃, (g) Ni₅-Mg₅₀-Al₂O₃

reflections, respectively. This behavior is an evidence of the presence of hexagonally ordered mesopores with *p6mm* symmetry [180,181]. These reflection peaks are also detectable in Ni₅-Mg_y-Al₂O₃ samples having an Mg wt% range from 0 to 7 wt% and are more intense in the case of Ni₅-Mg₁₀-Al₂O₃, and Ni₅-Mg₁₅-Al₂O₃ which means that the hexagonal arrangement is highly uniform in the latter samples [187]. Magnesium (dissolution of magnesium nitrate into Mg²⁺) triggers certain interaction between non-ionic surfactant P123 and metal ions (Ni²⁺), leading to a better ordered structure than Ni effect [188–190]. An appropriate amount Mg²⁺ ions play a key role in accelerating the coalescence of surfactant to form micelles preserving the Al-OH concentration species needed to form 2D-hexagonal structure. Contrarily, this better uniformity is lost in Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ catalysts that show no visible peaks in the small angle XRD patterns suggesting the absence of ordered porosity. This could be due to Mg²⁺ incorporation into mesoporous alumina framework and production of Mg-O bonds with longer lengths than those of Al-O bonds. Thus, the mesostructure faces an expansion since the ionic radius of Mg²⁺ is larger than that of Al³⁺, hindering the merge of the micelle composite. This is the reason why it was not possible to calculate the pore thickness for these samples, contrarily to the previous more ordered samples for which the thickness is usually close to 5 nm for Ni-

based samples and slightly higher (7.3 nm) for Al₂O₃ (Table III-4) shifting the peaks to lower angles as seen in Figure III-6 A.

Note that Ni₅-Mg₅-Al₂O₃ sample is always out of the trend followed by the other Mg-based materials. This could be due to the fact that this sample was firstly prepared and the preparation procedure was not fully optimized by that time, and it will be excluded from the rest of the comparison.

Table III-4: Interplanar spacing and unit cell parameter of calcined and reduced Ni₅-Mg_y-Al₂O₃ samples

Samples	Calcined			Reduced		
	d ₁₀₀ [*] (nm)	a ₀ [*] (nm)	t [*] (nm)	d ₁₀₀ [*] (nm)	a ₀ [*] (nm)	t [*] (nm)
Al ₂ O ₃	10.5	12.1	7.3	10.3	11.9	6.6
Ni ₅ -Al ₂ O ₃	9.8	11.3	5.1	9.7	11.2	4.7
Ni ₅ -Mg ₅ -Al ₂ O ₃	10.9	12.5	6.7	n.d.	n.d.	n.d.
Ni ₅ -Mg ₁₀ -Al ₂ O ₃	9.4	10.8	5.0	8.4	9.7	4.6
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	9.5	10.7	5.2	8.7	10.1	4.4
Ni ₅ -Mg ₃₀ -Al ₂ O ₃	-	-	-	-	-	-
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	-	-	-	-	-	-

d₁₀₀^{*}: host Al₂O₃ periodicity (interplane distance) derived from low-angle XRD

a₀^{*}: lattice parameter, a₀= 2d₁₀₀^{*}/√3

t^{*}: pore wall thickness, t= a₀ - D_{BJH}

n.d. not determined

The wide angle XRD curves with different magnesium content are presented in Figure III-6 B. Mesoporous alumina support (curve a) has no visible diffraction peak indicating an amorphous Al₂O₃ walls oxide. Ni₅-Mg_y-Al₂O₃ samples having Mg content of 7 wt% or less, exhibit no apparent NiO, MgO, and even Al₂O₃ diffraction peaks as well. This observance means that NiO, MgO, and Al₂O₃ crystallites are either lower than the detection limit in XRD (smaller than 3 nm) or that the nickel and Al₂O₃ present are not crystalline (amorphous phase). The absence of crystallite domains suggests homogeneous elements distribution and high metal dispersion. Compared to other nickel-magnesium mesoporous alumina prepared using different methods [108,148,167,168,171,173] (Table III-1), the nickel particle size is here much smaller which assures that the one-pot method plays a crucial role in ensuring high nickel dispersion. Adding higher amount of Mg (15-26 wt%) contributes to the appearance of MgO (JPCDS: 01-079-9866) diffraction peaks. The size of the crystal domains is around <3 and 5 nm for Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃, respectively (Table III-5) at 2θ= 63°. This reveals a disturbance in the Mg dispersion in the samples with high Mg loadings. NiO species with mean sizes high enough to become detectable might be also present as deduced from the peaks at 2θ equal to 37, 43 and 63° but they however superpose those of MgO having similar positions, making their identification questionable.

Table III-5: Ni average particle size for calcined, reduced and spent materials

Sample	Particle size (nm) ^a		
	Calc. Φ NiO	Red. Φ Ni ⁰	Spent Φ Ni ⁰
Al₂O₃	n.d. (<i>n.d.</i>)	-	-
Ni₅-Al₂O₃	n.d. (<i>n.d.</i>)	4 (4.6)	n.p.
Ni₅-Mg₅-Al₂O₃	n.d. (<i>n.d.</i>)	4.3 (<i>n.p.</i>)	n.p.
Ni₅-Mg₁₀-Al₂O₃	n.d. (<i>n.d.</i>)	5.6 (5.3)	n.p.
Ni₅-Mg₁₅-Al₂O₃	n.d. (<i>n.d.</i>)	4.4 (4.5)	4.2 (5)
Ni₅-Mg₃₀-Al₂O₃	<3* (<i>n.p.</i>)	4.7 (7.4)	n.p.
Ni₅-Mg₅₀-Al₂O₃	5.0* (<i>n.p.</i>)	7.7 (8.8)	9.7

a: mean size values estimated from XRD (normal font) by applying the Scherrer equation considering the Ni⁰ reflection at $2\theta = 51.9^\circ$, and from the histograms obtained from representative TEM images (in brackets), n.d.: not detectable, * MgO crystalline domains, n.p. not performed

III.3.3. Visualization of porosities by TEM

High resolution transmission electron microscopy (HRTEM) and high angular annular dark field (HAADF) observations were performed on selected samples using ultra-thin microtomic sections for higher quality and better identification of porosity. Figure III-7 shows typical micrographs obtained for the calcined mesoporous Ni₅-Al₂O₃ sample. Sticking to the HRTEM mode when the alumina grains are parallel to the electronic beam, arranged and parallel channels are intelligible and clear (Figure III-7 A). Moreover, Figure III-7 A' is the result of a perpendicular orientation of the grain to the beam and depicts very regular hexagonal pore apertures at high magnification (2D p6mm hexagonally structured mesoporous channels) confirming N₂-sorption results. Both orientations show absence of Ni particles to the naked eye, in line with the absence in section III.3.2 of any XRD detection of NiO crystals for this sample. In order to have more precise and clearer observations, STEM-HAADF images (Figure III-7 B-B') were performed on the same sample since it plays more on the atomic contrast and could help differentiate between Ni and Al species. However, again, the pictures did not contribute to detection of any Ni-based particles distinct from the alumina. These results, in coherence with XRD ones, insist on the excellent dispersion of Ni with a size of nano-clusters undetectable or inserted inside the wall of the mesoporous alumina framework.

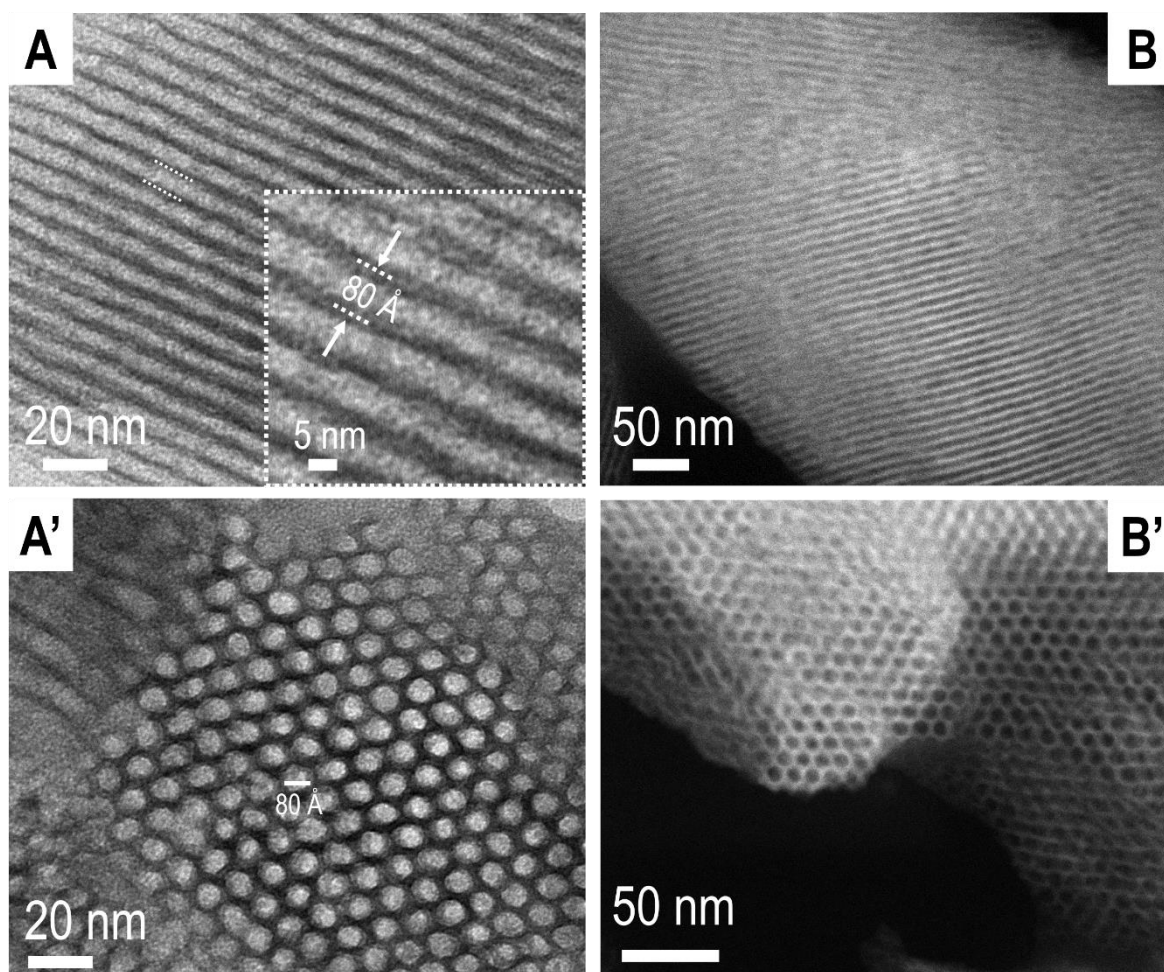


Figure III-7: Representative HRTEM (A-A') and STEM-HAADF (B-B') micrographs of calcined mesoporous Ni₅-Al₂O₃ showing the intimate mixing between Ni and its alumina support after synthesis; (B-B') are pictures for preliminary experiments done on MPQ-Paris Diderot microscopy (JEOL ARM 200F, coll. J. Nelayah)

In agreement with textural properties discussed above (section III.3.1), the successive increase of MgO content till 7 wt% does not alter the well-organized parallel channels and the honeycomb orientation of the alumina pores (Figure III-8 A-A'). Again, no Ni-based particles are detected by HRTEM and Ni remains homogeneously spread on the alumina support. On the contrary, further magnesium increment (Figure III-8 B-B') confirms the deterioration of the structured channels and pores (suspected in N₂-sorption), and formation of ill-defined pore morphology. Few nickel oxide particles start to appear at this stage, indicating a less homogeneous distribution of Ni, and Ni-based (NiO) particles become clearly distinct when 26 weight percent of magnesium is present in the sample. In addition, Figure III-8 B' depicts a darker zone over alumina support that could be due to magnesium segregation justifying the MgO peaks observed in XRD experiments that are superposing those of NiO peaks. This hypothesis cannot be confirmed without making mapping and HAADF on the same area of the

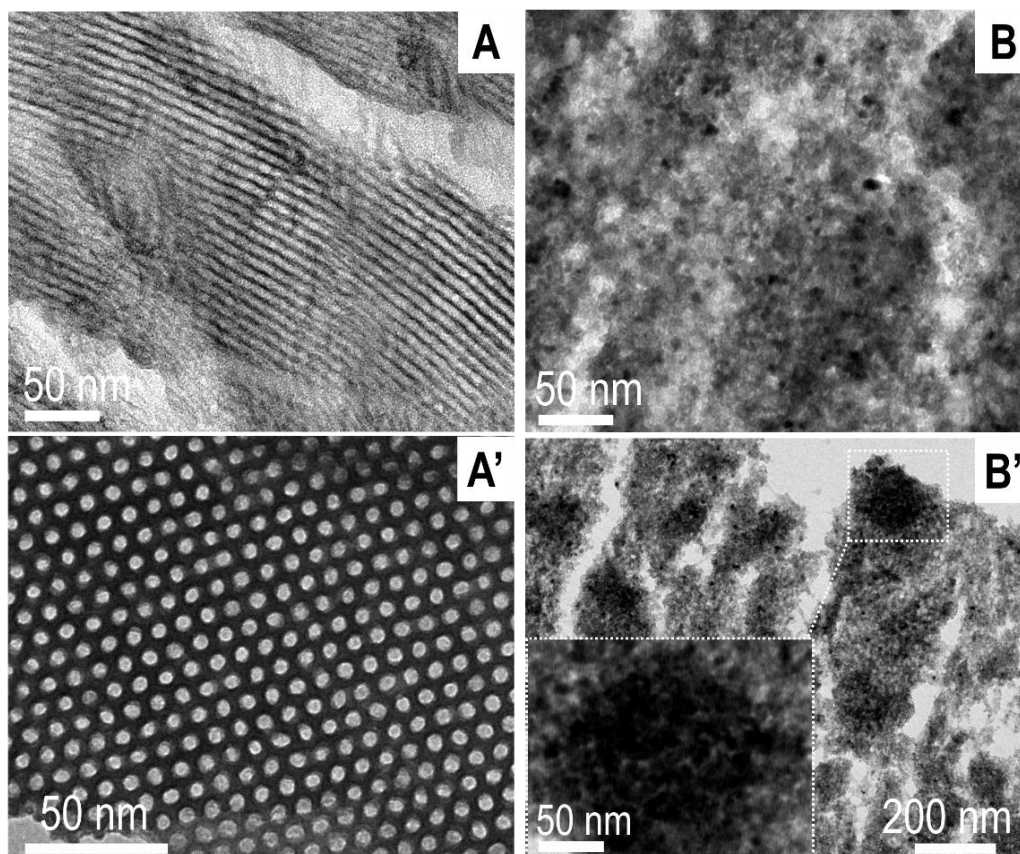


Figure III-8: Representative STEM micrographs of calcined mesoporous (A-A') Ni₅-Mg₁₅-Al₂O₃ and (B-B') Ni₅-Mg₅₀-Al₂O₃ catalysts

calcined sample. This experiment was not done on the calcined material, but was performed on the reduced one confirming in the upcoming paragraphs the assumption made.

III.3.4. Additional collaborative experiments to characterize samples basicity

Infra-red measurements were done to verify how the addition of Mg affects the basicity of the sample. These experiments were performed in collaboration with Politecnico University in Torino that is also a part of the ERANETMED European project SOL-CARE. The five evaluated samples are: Al₂O₃ (black curve), Ni₅-Mg₅-Al₂O₃ (pink curve), Ni₅-Mg₁₅-Al₂O₃ (red curve), Ni₅-Mg₃₀-Al₂O₃ (green curve) and Ni₅-Mg₅₀-Al₂O₃ (blue curve). The CO₂ adsorption was done at room temperature on calcined samples outgassed directly at 500 °C followed by desorption at room temperature. Figure III-9 presents Infra-red spectra for all the tested materials. The bands centered around 1560 and 1415 cm⁻¹ are attributed to unidentate carbonates, and those around 1650 and 1375 cm⁻¹ are assigned to bidentate carbonates. As the Mg amount increases from 0 to 7 wt%, the intensities for all bands progressively increase indicating a small enhancement of CO₂ affinity with the surface. This process is strongly accentuated when going from 7 to 15 wt% Mg (Ni₅-Mg₃₀-Al₂O₃), especially for bands of

unidentate carbonate species (1560 and 1415 cm⁻¹). This shows a sudden increase in basicity that is in line with the formation of stronger basic O²⁻ sites generated by some MgO segregation. When the segregation becomes more important (Ni₅-Mg₅₀-Al₂O₃), the Mg dispersion is extremely diminished (prevalence of bulk MgO) providing less accessible

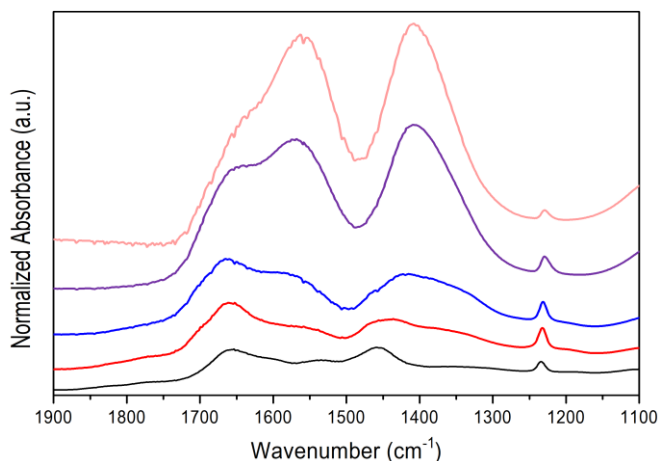


Figure III-9: CO₂ adsorption by Infra-red measurements on mesoporous: Al₂O₃ (black curve), Ni₅-Mg₅-Al₂O₃ (pink curve), Ni₅-Mg₁₅-Al₂O₃ (red curve), Ni₅-Mg₃₀-Al₂O₃ (green curve) and Ni₅-Mg₅₀-Al₂O₃ (blue curve)

basic sites and therefore the intensities of unidentate carbonate are decreased due to strong decrease in the amount of adsorbed CO₂. More studies obtained by Infra-red spectroscopy have been analyzed confirming the results observed (TEM, XRD, EDS mapping) on these materials but are not detailed in the thesis.

III.4. Reducibility of mesoporous Ni₅-Mg_y-Al₂O₃ catalysts

Figure III-10 displays the TPR (temperature-programmed reduction) profiles of calcined Ni₅-Mg_y-Al₂O₃ materials with different Mg contents. Beginning with the Al₂O₃ support, no reduction peak is observed confirming that the support does not play a role in H₂-consumption. Ni₅-Mg_y-Al₂O₃ materials with Mg content up to 7 wt% show a single hydrogen reduction peak at a temperature range between 640 and 710 °C. For all these samples, the H₂-uptake calculated from the area under the curve (Figure III-10) is close to the theoretical value (860 μmol.g⁻¹) confirming the sole Ni reduction and the expected 5 wt% Ni content (Table III-6). The absence of a reduction peak in the range of 300-400 °C reveals that there is no free NiO species [88,169,191] and that

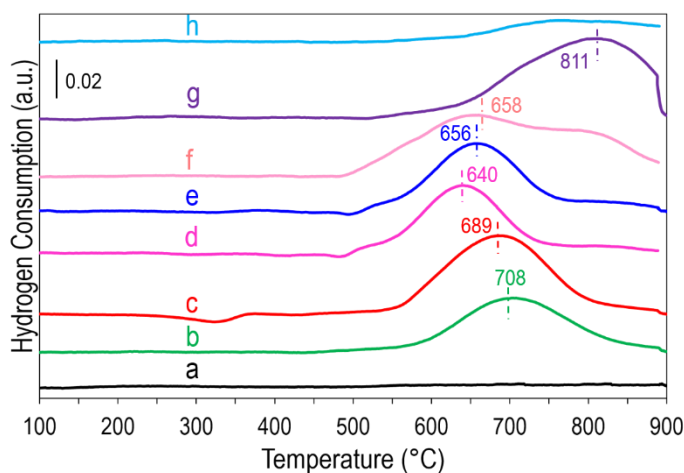


Figure III-10: H₂-TPR profiles of mesoporous Ni₅-Mg_x-Al₂O₃ catalysts calcined at 600 °C: (a) Al₂O₃, (b) Ni₅-Al₂O₃, (c) Ni₅-Mg₅-Al₂O₃, (d) Ni₅-Mg₁₀-Al₂O₃, (e) Ni₅-Mg₁₅-Al₂O₃, (f) Ni₅-Mg₃₀-Al₂O₃, (g) Ni₅-Mg₅₀-Al₂O₃, (h) Mg₅₀-Al₂O₃

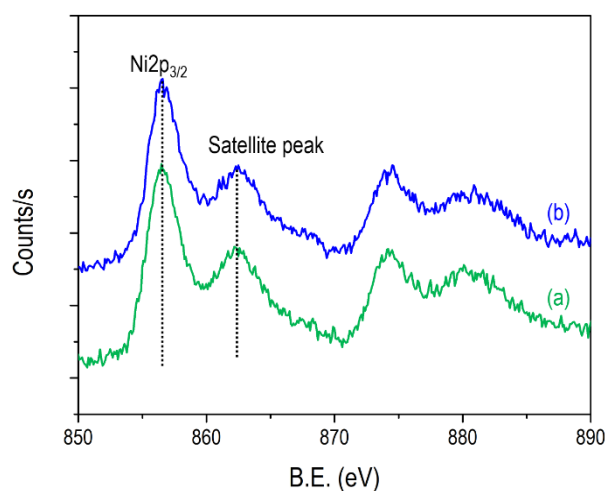
Ni is strongly interacting with the alumina support at high temperatures, revealing high dispersion of Ni particles. This behavior is similar to surface spinel mixed-phases nickel aluminate species [180]. In our case, it could be explained by the fact that in one-pot synthesis nickel atoms replace tetrahedral coordinated alumina atoms forming solid solutions in the form of Ni-O-Al structures. This species could be a stoichiometric NiAl₂O₄ phase or a surface Ni in alumina-mixed layers as demonstrated by XPS measurement [88] (Figure III-11). For instance, for both Ni₅-Al₂O₃ and Ni₅-Mg₁₅-Al₂O₃ samples, the position of the Ni2p_{3/2} peak centered at 856 eV and accompanied with a shake-up satellite peak around 862 eV excludes the presence of pure NiO which binding energy is expected at 853 eV.

Table III-6: H₂-uptake of calcined Ni₅-Mg_y-Al₂O₃

Sample	H ₂ consumption (μmol.g ⁻¹)	(T-E)/T (%)
Al ₂ O ₃	-	-
Ni ₅ -Al ₂ O ₃	815	5
Ni ₅ -Mg ₅ -Al ₂ O ₃	921	7
Ni ₅ -Mg ₁₀ -Al ₂ O ₃	863	0.34
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	905	5
Ni ₅ -Mg ₃₀ -Al ₂ O ₃	1125	30
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	1175	35

T: Theoretical value of expected H₂-consumption, E:

Experimental value of H₂-consumed

Figure III-11: XPS spectra of the Ni2p in calcined (a) Ni₅-Al₂O₃ and (b) Ni₅-Mg₁₅-Al₂O₃ materials

Another important feature can be also observed in Figure III-10. The reduction peak is shifted to a slightly lower temperature from Ni₅-Al₂O₃ to Ni₅-Mg₁₅-Al₂O₃ when increasing Mg amount to 7 wt%. This behavior could be attributed to a competitive formation of NiAl₂O₄ or MgAl₂O₄ clusters. Increasing the Mg content gradually would inhibit the formation of NiAl₂O₄ spinel and boost the appearance of MgAl₂O₄ species, which facilitates the reduction of nickel oxide particles, lowers the interaction towards alumina, and shifts the reduction peak to a lower temperature [169,174,192].

Increasing further the amount of Mg (Ni₅-Mg₃₀-Al₂O₃) induces a small deviation of the reduction peak towards a higher temperature with an additional peak shoulder noticeable at around 800 °C. This phenomenon is more pronounced in the case of Ni₅-Mg₅₀-Al₂O₃ with 26 wt% Mg where the reduction temperature for the whole single peak position is shifted to about

810 °C. The big amount of Mg compared to Ni can increase the bond strength for Ni-O in the close vicinity of Mg²⁺ cations, forming NiO-MgO solid solution, thus hindering and retarding the reduction of the NiO species [171,193]. Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ also exhibit around 30% higher H₂-consumption than the theoretical value. As the Ni content is confirmed by fluorescence (Table III-3), and Al₂O₃ support does not consume hydrogen (curve a in Figure III-10), TPR was performed on Mg₅₀-Al₂O₃ free of nickel. Curve h of the TPR profile in Figure III-10 shows a small reduction peak at a very high temperature corresponding to 277 μmol.g⁻¹ of H₂ consumed. Thus, the additional H₂ amount induced in Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ materials is possibly indicative of some Mg derived species.

III.5. Textural and structure properties of reduced Ni₅-Mg_y-Al₂O₃ materials

Similar to the calcined samples, the reduced (650 °C/2h) Ni₅-Mg_y-Al₂O₃ materials were characterized by N₂-sorption, XRD, and TEM to follow their structural and textural behavior in presence of metallic Ni⁰, the active phase in DRM.

III.5.1. Porosity by N₂-sorption technique

The N₂-sorption isotherms (Figure III-12) of the Ni₅-Mg_y-Al₂O₃ samples examined after reduction display similar isotherm shapes and pore size distribution profiles as their calcined counterparts. They conserve a type IV isotherm with H1 hysteresis loop, preserving their porous characteristics after reduction. Their pore size

distribution remains narrow for the catalysts containing 7 wt% Mg and wide for Ni₅-Mg₃₀-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃. Nevertheless, the surface area and pore volume were somehow smaller for all the treated catalysts regardless the amount of Mg present (Table III-3). The loss in S_{BET} values is equal to 50 % for Al₂O₃, 26 % for Ni₅-Mg₃₀-Al₂O₃, and 7-15 % for all the

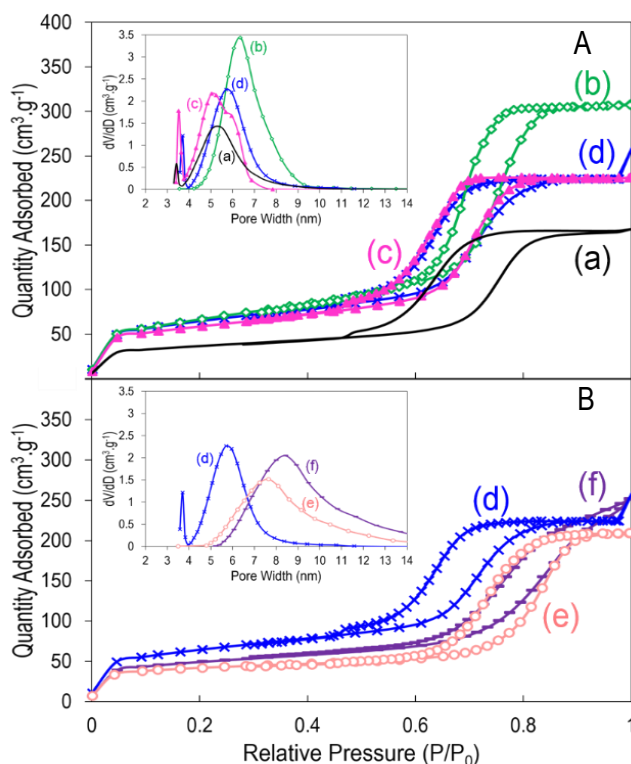


Figure III-12: Nitrogen adsorption/desorption isotherms and pore size distribution profiles (insets) of Ni₅-Mg_x-Al₂O₃ catalysts reduced at 650 °C for 2 hours: (a) Al₂O₃, (b) Ni₅-Al₂O₃, (c) Ni₅-Mg₁₀-Al₂O₃, (d) Ni₅-Mg₁₅-Al₂O₃, (e) Ni₅-Mg₃₀-Al₂O₃, (f) Ni₅-Mg₅₀-Al₂O₃

others. This observed decline in the textural properties could arise from a shrinkage of the material skeleton (Al₂O₃ framework) due to the high reduction temperature (650 °C).

III.5.2. Porosity properties and Ni particle size by small and wide angle XRD

Paying attention to the small angle XRD curves (Figure III-13 A), the two diffraction peaks, at circa 0.90° and 1.5°, ascribed to the [100] and [110] plane reflections respectively, are still visible after reduction for all mesoporous Ni₅-Mg_y-Al₂O₃ with Mg content below 15 wt%. Such observation indicates again that the one-pot ordered mesoporous Ni₅-Mg_x-Al₂O₃ catalysts with limited Mg content have a good thermal stability, and the high reduction temperature did not strongly affect their 2D hexagonal alumina structure that conserves its *p6mm* symmetry. However, the peak intensities are slightly lower and shifted to higher angles identifying pore

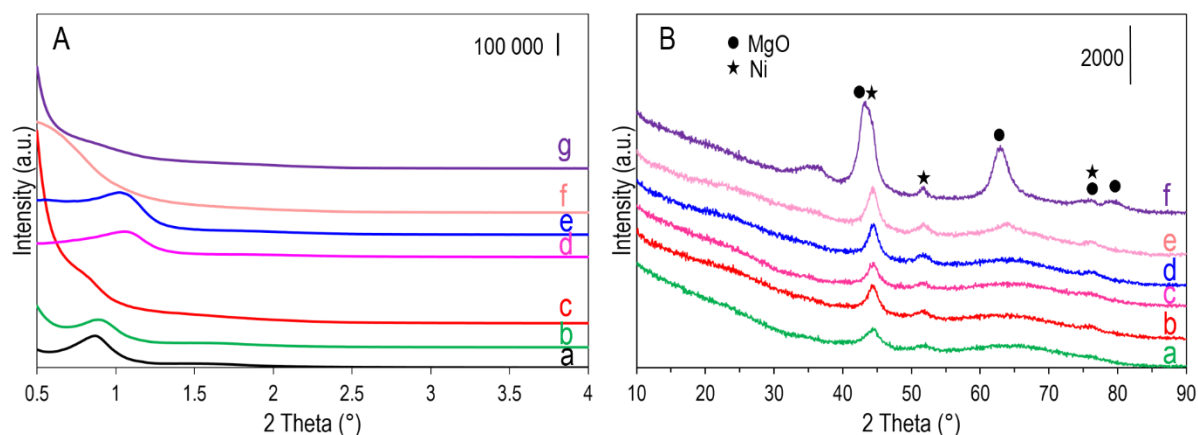


Figure III-13: (A) small angle and (B) wide angle XRD patterns of in-situ H₂-reduced Ni₅-Mg_x-Al₂O₃ catalysts: (a) Al₂O₃, (b) Ni₅-Al₂O₃, (c) Ni₅-Mg₅-Al₂O₃, (d) Ni₅-Mg₁₀-Al₂O₃, (e) Ni₅-Mg₁₅-Al₂O₃, (f) Ni₅-Mg₃₀-Al₂O₃, (g) Ni₅-Mg₅₀-Al₂O₃

shrinkage as shown in physisorption. Indeed, the lattice parameter (Table III-4) decreases slightly from 12.1 (Al₂O₃), 11.3 (Ni₅-Al₂O₃), 10.8 (Ni₅-Mg₁₀-Al₂O₃) and 10.7 (Ni₅-Mg₁₅-Al₂O₃) nm at calcined states to 11.9, 11.2, 9.7 and 10.1 nm for reduced samples, respectively.

Concerning the influence of reduction on the dispersion and location of Ni species, the wide angle XRD (Figure III-13 B) for all Ni₅-Mg_y-Al₂O₃ reduced catalysts exhibit different curves shape compared to the calcined ones. Ni⁰ species appear in all samples with a broad peak (indexed as a star on the graph) and face centered cubic (FCC) unit cell (Ref. code:03-065-0380) at 2θ equal 44°, 52° and 76° highlighting on a phase transition from clusters in spinel structures (Ni-O-Al) invisible by XRD to metallic Ni⁰. This phase transition could have also contributed to the loss in textural properties (surface area, pore volume), but at a limited extent in view of the limited Ni content. In the Ni₅-Mg₅₀-Al₂O₃ catalyst MgO peaks, still appear

simultaneously with Ni⁰ species stressing on the presence of NiO-MgO solid solution as demonstrated before in TPR experiments. Subsequently, all catalysts except the one containing 26 wt% Mg, exhibit small Ni⁰ nanoparticles size in the range of 4-5 nm (Table III-5), much below than those classically reported in literature for Ni-Mg-alumina catalysts (Table III-1). When very high amount of Mg is added (26 wt%), the nickel particles are larger (mean size 7.7 nm).

III.5.3. SEM and TEM for reduced Ni₅-Mg_y-Al₂O₃ catalysts

Representative SEM images (not performed for calcined materials) are done on three chosen in-situ reduced samples. Mesoporous Ni₅-Al₂O₃ (Figure III-14 A) and Ni₅-Mg₁₅-Al₂O₃

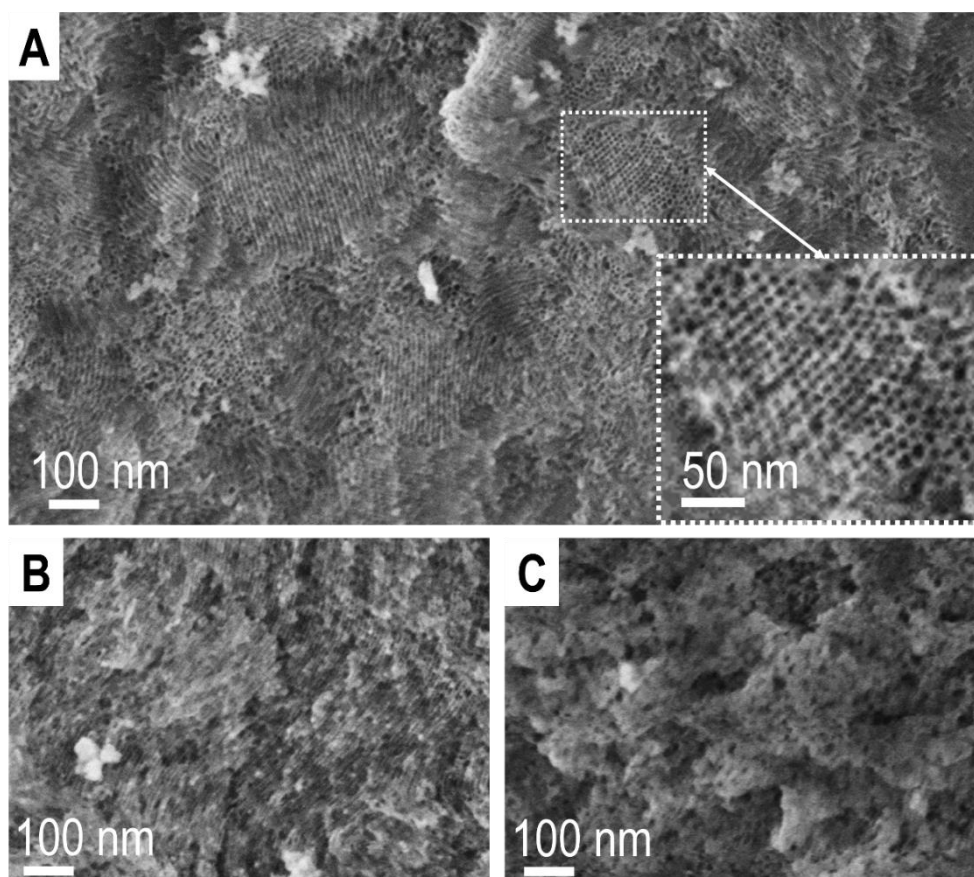


Figure III-14: SEM micrographs of in-situ reduced (650 °C/2h, H₂/Ar) (A) Ni₅-Al₂O₃, (B) Ni₅-Mg₁₅-Al₂O₃, (C) Ni₅-Mg₅₀Al₂O₃

(Figure III-14 B) catalysts reveal that the grains appear in a bulk mass having a smooth homogenous external topography without any cracks or defects. Moreover, the periodic porous organization is intelligible displaying ordered hexagonal arrangement of pores along the [001] direction with honeycomb mesoporous structure (inset in Figure III-14 A) and linear porous channel along the [110] direction. On the other hand, and in agreement with the textural

properties obtained in N₂-sorption Ni₅-Mg₅₀-Al₂O₃ (Figure III-14 C) presents amorphous porosity with random distribution and disappearance of parallel channels. Besides, there is no evidence of external Ni or Mg nano-particles in all the three samples, with no bright color on the alumina surface that could diffuse due to their high electronic density elements. Thus, the metals are embedded inside the alumina framework after reduction as will be demonstrated in TEM results.

Consistently, the high dispersion in the reduced materials seen by XRD in Ni₅-Al₂O₃ and Ni₅-Mg₁₅-Al₂O₃ is confirmed by STEM-HAADF observations (Figure III-15, Figure III-16 A-A''). It was focused on this technique for further implication on Ni and Mg position and distribution over Al₂O₃ support. All of the Ni⁰ nanoparticles population appear either as very small dark spots (TEM) or as white dots (HAADF) on the grey alumina matrix and are located inside the regular hexagonal arrangement of the porous structure or embedded and anchored inside the alumina framework wall. These pictures also reveal an average particle size of 4.6 and 4.5 nm for mesoporous Ni₅-Al₂O₃ and Ni₅-Mg₁₅-Al₂O₃ respectively in line with results obtained in wide angle XRD measurements (Table III-5). Thus, the one-pot EISA method

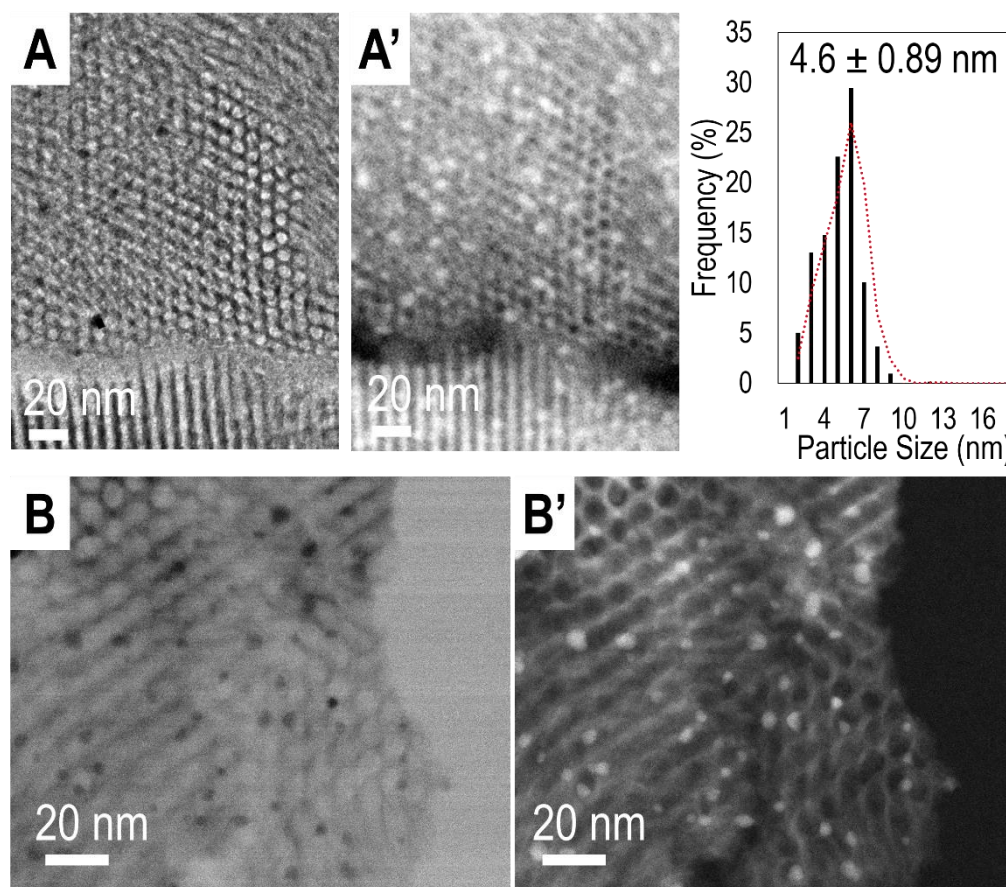


Figure III-15: Representative (A-A'), (B-B') STEM-HAADF micrographs of reduced mesoporous Ni₅-Al₂O₃ showing presence of Ni nano-species after reduction

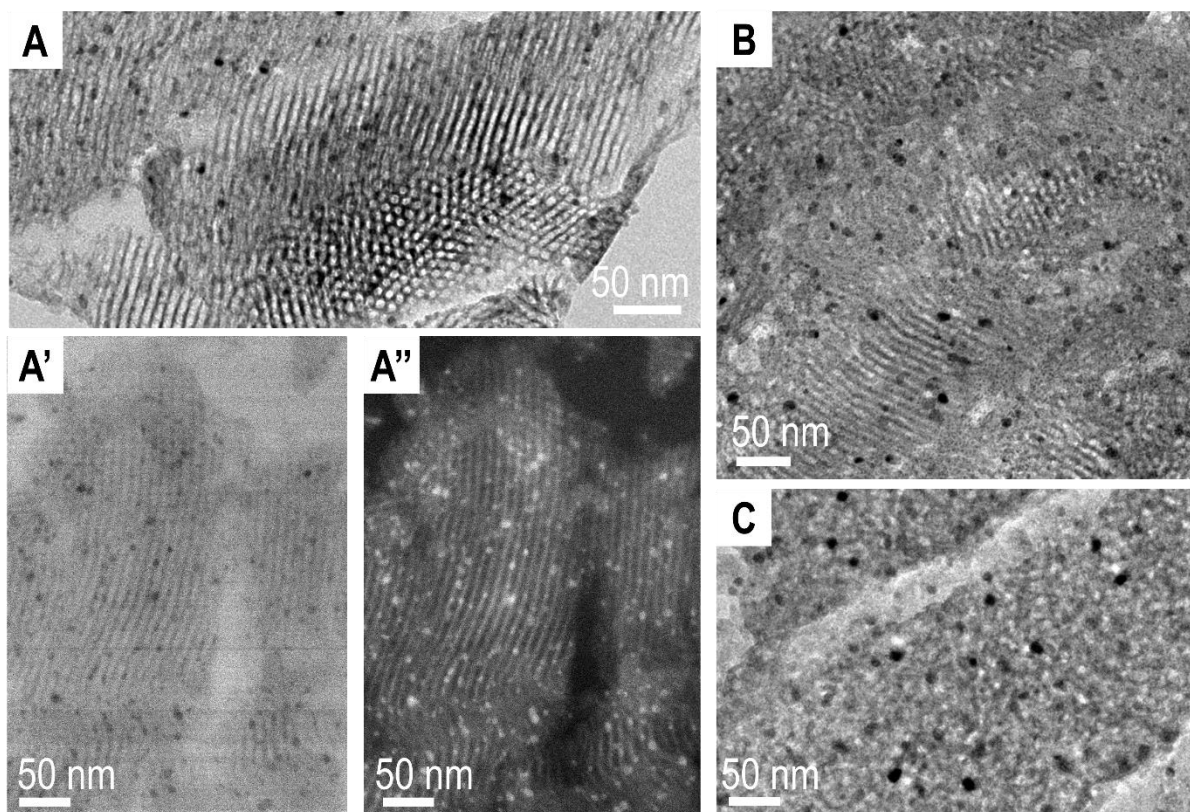


Figure III-16: Representative standard HRTEM micrographs of reduced (650 °C/2h) mesoporous (A) Ni₅-Mg₁₅-Al₂O₃, (B) Ni₅-Mg₃₀-Al₂O₃ and (C) Ni₅-Mg₅₀-Al₂O₃ and STEM-HAADF (A'-A'') of Ni₅-Mg₁₅-Al₂O₃ showing presence of Ni nano-species after reduction

proved to be very efficient in withstanding harsh thermal conditions (calcination, reduction) with 5 wt% Ni and up to 7 wt% Mg content. This route starts to lose its ordered mesoporosity impact when higher amount of MgO is added. For example, Figure III-16 B shows HRTEM image of Ni₅-Mg₃₀-Al₂O₃ with part of the sample featuring parallel channels and another part with complete random porosity. The influence of MgO on the pore size and morphology is confirmed by Ni₅-Mg₅₀-Al₂O₃ (Figure III-16 C) catalyst that still shows its total disordered porosity as its calcined form. In the high Mg% samples, the nickel particles formed are no longer present inside the mesostructured skeleton and are randomly scattered with larger Ni⁰ particle sizes of 8.8 nm for Ni₅-Mg₅₀-Al₂O₃ sample (Table III-5).

Confirmation about metallic Ni⁰ occlusion and dispersion within the alumina matrix after reduction is provided by locally pointed EDS mapping analyses (Figure III-17) performed over selected alumina grains. This method locates Ni or MgO existence that is not clearly visible by TEM what drove us to go further in our study and understand the good/bad dispersion of nickel/magnesium. The EDS mapping supports the earlier XRD and TEM findings and assert on the homogeneous and excellent dispersion of nickel particles on mesoporous alumina parent

for Ni₅-Al₂O₃ and its preservation in Ni₅-Mg₁₅-Al₂O₃ (Figure III-17 A, B). Additional feature was noticeable in this type of experiment is the presence of Mg element all over the alumina matrix that accentuates on the fact that magnesium particles are as dispersed as nickel and superposed. Figure III-17 C, demonstrates, as mentioned before, that when Mg content is increased up to 26 wt% it triggers a detrimental disturbance in Ni repartition. This disturbance is also seen for Mg element where Al₂O₃ support shows some areas more enriched in magnesium than other places with a driven segregation as indicated by the white arrows on EDS maps.

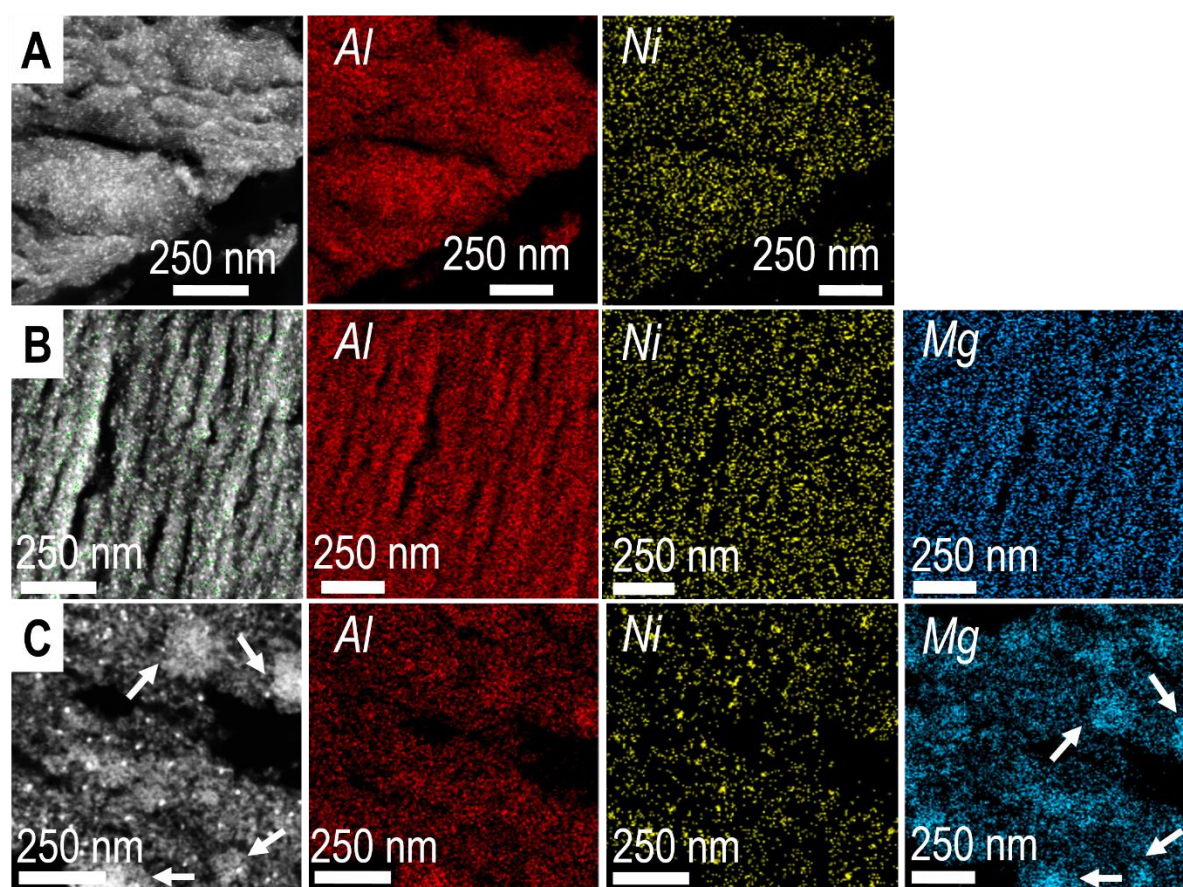


Figure III-17: HAADF with EDS mapping images of (A) Ni₅-Al₂O₃, (B) Ni₅-Mg₁₅-Al₂O₃, and (C) Ni₅-Mg₅₀-Al₂O₃. Atoms of Al (red), Ni (yellow), and Mg (blue) were identified within EDS maps

III.5.4. Ni dispersion derived from H₂-TPD and H₂-chemisorption

The H₂-TPD experiments performed over reduced catalysts provide further information about the metal dispersion determined from the amount of desorbed hydrogen. The related profiles displayed in Figure III-18 show two distinct desorption domains independent from the

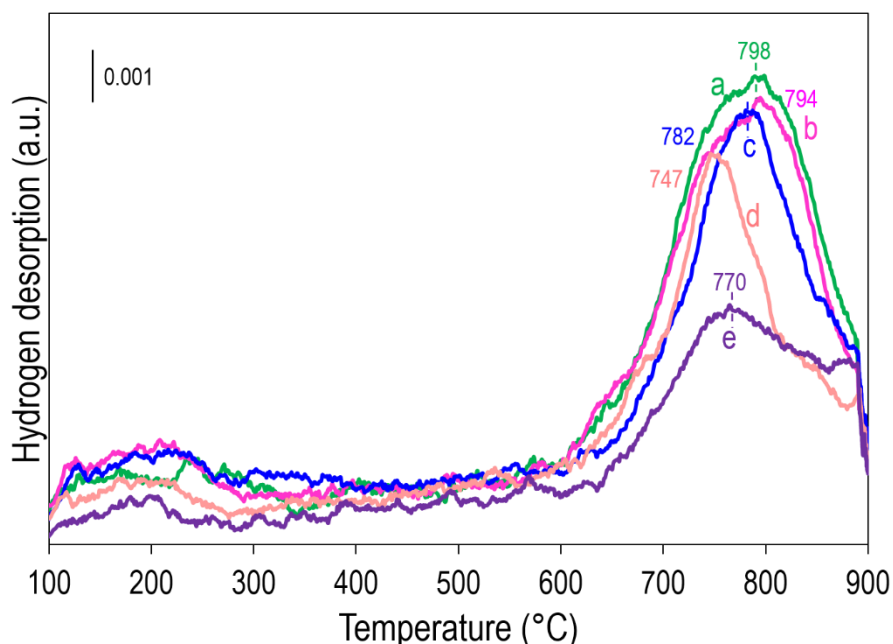


Figure III-18: H₂-TPD profiles of alumina based-materials: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₀-Al₂O₃, (c) Ni₅-Mg₁₅-Al₂O₃, (d) Ni₅-Mg₃₀-Al₂O₃, and (e) Ni₅-Mg₅₀-Al₂O₃

amount of MgO present. Hydrogen atoms desorbed at temperatures below 450 °C, represent exposed surfaces of low dispersed Ni⁰ nanoparticles. The domain with the higher desorption temperature above 600 °C is due to surfaces of Ni⁰ particles immersed in the alumina layer. The relative surface area of the high temperature desorption peak is much larger than that at low temperature for all Ni₅-Mg_y-Al₂O₃ catalysts asserting on the strong metal support interaction seen in TPR and the occlusion of Ni species within the alumina matrix as assumed in TEM of calcined samples. However, the integrated areas of Ni₅-Mg₃₀-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃ are somehow smaller than the others because MgO species could cover some surface Ni particles [194]. A good dispersion is achieved following the one-pot strategy and it is conserved with magnesium-based samples up to 7 wt% (Ni₅-Al₂O₃: 18%, Ni₅-Mg₁₀-Al₂O₃: 17%, Ni₅-Mg₁₅-Al₂O₃: 16.5%, Ni₅-Mg₃₀-Al₂O₃: 11.8% and Ni₅-Mg₅₀-Al₂O₃: 10%). The results obtained are somehow close to dispersion obtained from H₂-chemisorption method except for Mg-free mesoporous Ni₅-Al₂O₃ sample (Ni₅-Al₂O₃: 9.8%, Ni₅-Mg₁₀-Al₂O₃: 16.7%, Ni₅-Mg₁₅-Al₂O₃: 15.3%, Ni₅-Mg₃₀-Al₂O₃: 8.9% and Ni₅-Mg₅₀-Al₂O₃: 12.8%).

III.7. Dry reforming of methane reaction

The above characterization properties of the calcined and reduced samples, clearly indicate that there exists an optimal magnesium content in our series of samples with regard to their structural and porous properties. Indeed, the incorporation of Mg up to a certain extent (7

wt%) preserves the mesoporous alumina framework and leads to samples with high repartition of both Ni and Mg species. In contrary, a higher amount of magnesium leads to non-homogeneous and less ordered samples having lower surface area and pore volume, and in which the oxide Al₂O₃ and MgO phases are segregated. This seen trend resembles the “volcano-shape” curve seen at the beginning of this chapter for catalytic performances taken from bibliography and that will be also seen below for our series of catalyst tested in DRM.

III.7.1. Activity in DRM of Ni₅-Al₂O₃ and Ni₅-Mg₁₅-Al₂O₃ at a GHSV of 36 L.g⁻¹.h⁻¹

Catalytic tests in DRM were first carried out on two of the prepared catalysts, Ni₅-Al₂O₃ and Ni₅-Mg₁₅-Al₂O₃, using 100 mg of sample each time, giving a GHSV of 36 L.g⁻¹.h⁻¹ as often applied in the literature (see Table III-1). The CH₄:CO₂ ratio of used reactants was 1 and the conversions were measured for 50 hours time on stream (Figure III-19). In such conditions, both catalysts exhibited somehow similar performances with high CH₄ and CO₂ conversions close to thermodynamic equilibrium curve (estimated from the HSC software, as explained in chapter II), much better than literature catalysts presented in Table III-1 prepared by other techniques. For example, if we take the Ni-Mg-Al₂O₃ sample synthesized by the 2-step hydrothermal method [167], having the closest experimental test conditions as ours, we see that the conversions obtained are almost half of those of the current results with very high percentage of coke produced (37%). This reveals a very high activity for both of our catalysts, in line with the excellent Ni dispersions deduced above from physicochemical characterizations on both samples.

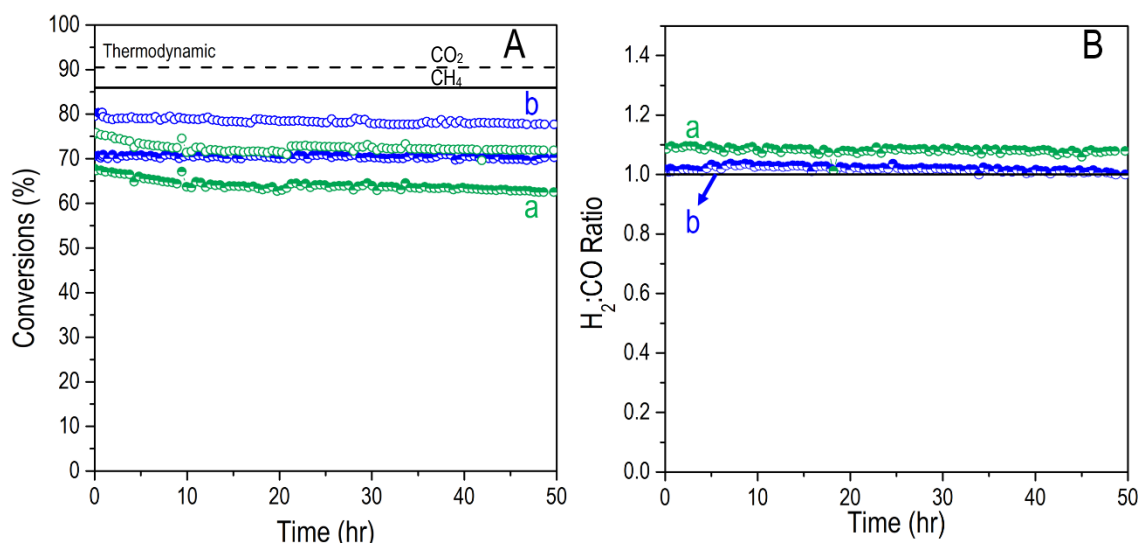


Figure III-19: Variation of (A) CH₄ (filled circle) and CO₂ conversion (empty circle), and (B) H₂:CO ratio as a function of time on stream during DRM (T= 650 °C, P=1 atm, CH₄:CO₂=1:1, GHSV= 36 L.g⁻¹.h⁻¹) over (a) Ni₅-Al₂O₃ and (b) Ni₅-Mg₁₅-Al₂O₃

Looking in more details, Ni₅-Mg₁₅-Al₂O₃ leads to slightly higher conversions (by 4 wt% in CO₂ conversion) as well as a slightly higher stability than Ni₅-Al₂O₃ that faces around 5% loss of its activity after 50 hours, attributable to higher coke deposition since the H₂:CO value is higher than 1 (Figure III-19 B). This agrees well with the proposal discussed in chapter I that adding a moderate amount of Mg boosts the creation of basic sites that favor CO₂ chemisorption on the catalyst, and hence its reaction with formed carbon species, thus reducing carbon deposition. Nevertheless, the promoting effect of Mg is not clearly intelligible, and cannot be analyzed with great accuracy, because of the operating conditions (limited GHSV) that lead to conversions close to equilibrium.

III.7.3. Performances of the Ni₅-Mg_y-Al₂O₃ catalysts at a GHSV of 180 L.g⁻¹.h⁻¹

III.7.3.1. Light off curves

Higher GHSV (180 L.g⁻¹.h⁻¹) was applied to lower the conversions and allow for a correct comparison of performances between the prepared Ni₅-Mg_y-Al₂O₃ catalysts. Figure III-20 shows results of light off curves (conversions followed while increasing the temperature) for four chosen catalysts (Ni₅-Al₂O₃, Ni₅-Mg₁₅-Al₂O₃, Ni₅-Mg₃₀-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃). Both CH₄, and CO₂ conversions in graphs A and B increase with temperature no matter what is the amount of MgO indicative of an endothermic DRM as demonstrated in the thermodynamics graphs in chapter II. Conversions on mesoporous Ni₅-Mg₁₅-Al₂O₃ are always the highest compared to the other three samples, and by more than 20% for instance at the temperature of 750 °C. Increasing further the amount of Mg (Ni₅-Mg₃₀-Al₂O₃) is no longer beneficial and leads to a catalyst with similar activity to that of the Mg-free Al₂O₃ based sample.

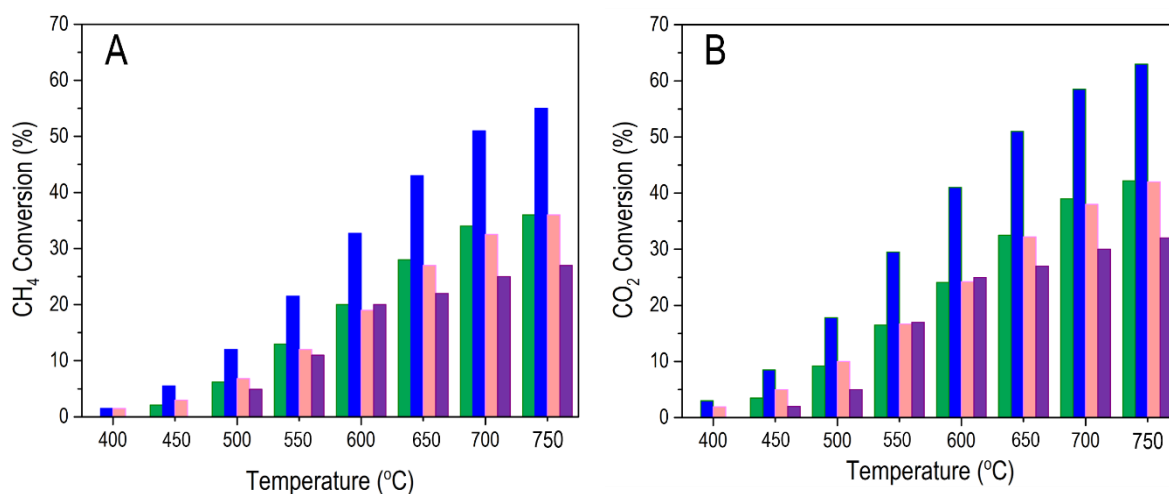


Figure III-20: Variation of (A) CH₄ and (B) CO₂ conversion levels as a function of temperature (400-800 °C) during DRM (P=1 atm, CH₄:CO₂=1:1, GHSV=180 L.g⁻¹.h⁻¹) over (green) Ni₅-Al₂O₃, (blue) Ni₅-Mg₁₅-Al₂O₃, (pink) Ni₅-Mg₃₀-Al₂O₃, (purple) Ni₅-Mg₅₀-Al₂O₃

Moreover, Ni₅-Mg₅₀-Al₂O₃ with the highest Mg content shows a continuous decline in conversion.

The H₂:CO product ratios obtained over the 4 catalysts as a function of temperature is presented in Figure III-21. As the temperature increases, the H₂:CO ratio in mesoporous Ni₅-Mg_y-Al₂O₃ increases to reach values close to 1 at 650 and 750 °C as expected thermodynamically. However with 26 wt% of Mg (Ni₅-Mg₅₀-Al₂O₃) the H₂:CO ratio is lower than 1 highlighting on the probable appearance of reverse water gas shift reaction.

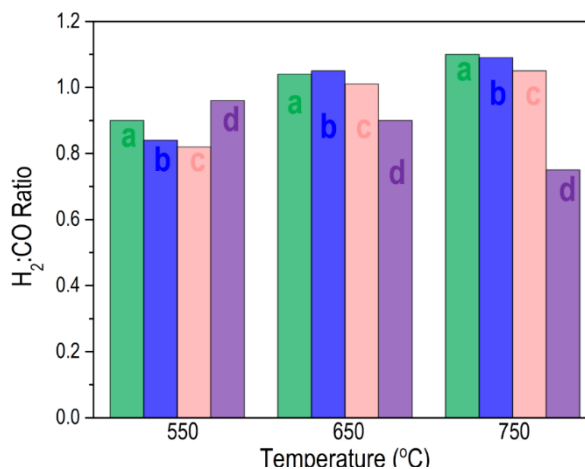


Figure III-21: Variation of H₂:CO ratio as a function of temperature during DRM (P=1 atm, CH₄:CO₂=1:1, GHSV=180 L.g⁻¹.h⁻¹) over (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, (d) Ni₅-Mg₅₀-Al₂O₃

III.7.3.2. Stability of Ni₅-Mg_y-Al₂O₃ catalysts

Stability tests of the aforementioned samples were done at 650 °C and the catalytic results are shown in Figure III-22 as a function of time on stream. Ni₅-Mg₁₅-Al₂O₃ (curve b) was the most stable catalyst through time with 0% loss in activity compared to 2% loss for both Ni₅-Al₂O₃ (curve a) and Ni₅-Mg₃₀-Al₂O₃ (curve c), and 6% loss for Ni₅-Mg₅₀-Al₂O₃ (curve d) after 12 hours test. The H₂:CO ratio was also very close to 1 for the 7 wt% Mg alumina based catalyst

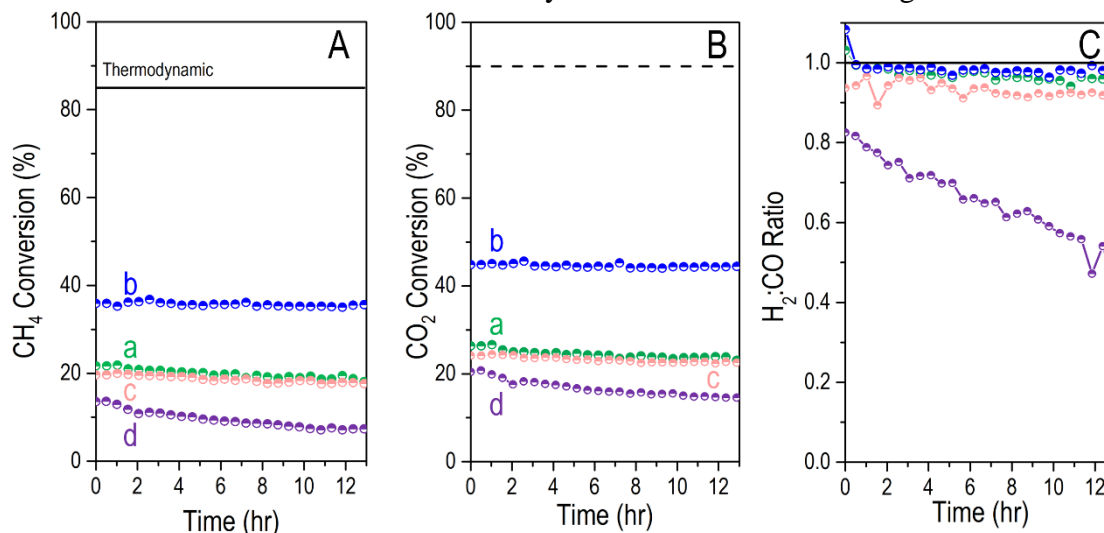


Figure III-22: Variation of (A) CH₄ conversion, (B) CO₂ conversion, and (C) H₂:CO ratio as a function of time on stream during DRM (T= 650 °C, P=1 atm, CH₄:CO₂=1:1, GHSV=180 L.g⁻¹.h⁻¹) over (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, (d) Ni₅-Mg₅₀-Al₂O₃. Thermodynamic values of CH₄ and H₂:CO (straight black line) and CO₂ (dashed black line) are calculated using the HSC 7.1 software

in contrast to the sample carrying the highest amount of Mg (26 wt%) that exhibits a much lower value of 0.82 and decreases through time indicating a strong influence of RWGS reaction over this sample. This difference in catalytic behavior can be explained by the influence of Mg loading on the structural and textural properties of the samples. Indeed, the moderate amount of Mg (7 wt%) contributed to well-ordered alumina walls support with equal repartition of Mg and Ni species and small Ni nanoparticles. In addition, the Mg present helps in enhancing CO₂ chemisorption and activation that cast any source of carbon formed during CH₄ activation. However, increasing a lot the amount of Mg, as in the case of Ni₅-Mg₅₀-Al₂O₃, degrades the uniform porosity (as seen in the previous sections), weakens Ni dispersion, and strengthens MgO segregation. The extensive amount of Mg triggers tremendous CO₂ sites that help in directing the reverse water gas shift reaction retarding and hindering the activity of the main reaction [195].

The XRD for the spent samples (Table III-5) agree well with the catalytic test results. Ni₅-Mg₁₅Al₂O₃ has a 4.2 nm Ni⁰ particle size that is quite similar to its reduced value and therefore no sintering has occurred under the harsh reaction conditions imposed. On the other hand, the nanoparticle size of Ni₅-Mg₅₀-Al₂O₃ increased from 8.8 nm in its reduced form to 9.7 nm after reaction implying some sort of sintering and growth of metallic Ni⁰ that could also boost deactivation.

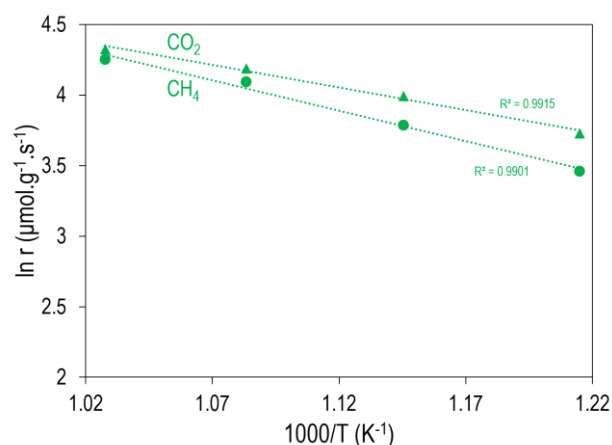
III.7.4. Turn over frequency and activation energy of Ni₅-Mg_y-Al₂O₃ catalysts

Turn over frequency (TOF) are used to make a direct comparison between the samples since they consist of normalized values taking into account the dispersion and number of metallic active sites. The TOF of each sample was calculated by taking an average value of the conversion at 650 °C after 2 hours reaction and presented in Table III-7. The TOF value increased from 5.77 s⁻¹ in Ni₅-Al₂O₃ to 6.64 s⁻¹ in Ni₅-Mg₁₅-Al₂O₃ that is the maximum value achieved, then decreased to reach 3.03 s⁻¹ in Ni₅-Mg₅₀-Al₂O₃.

Table III-7: Apparent activation energies (E_a) for the prepared Ni₅-Mg_y-Al₂O₃ catalysts

Sample	TOF (s ⁻¹)	E _a CH ₄ (kJ.mol ⁻¹)	E _a CO ₂ (kJ.mol ⁻¹)	Reference
Ni ₅ -Al ₂ O ₃	5.77	35.92	26.32	This work
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	6.64	28.14	22.30	This work
Ni ₅ -Mg ₃₀ -Al ₂ O ₃	6.23	34.30	26.22	This work
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	3.03	36.59	28	This work
Ni ₇ -Ce _y -Al ₂ O ₃	-	41.40	-	[134]
Ni ₇ -Ce _y -Al ₂ O ₃	-	38.93	-	[82]
Ni ₁₃ -La _y -Al ₂ O ₃	3.45-5.77	44.38	-	[196]
Ni-Pt-Al ₂ O ₃	-	104.67	-	[195]
Ni ₅ -CaO ₂₁ -Al ₂ O ₃	-	108.85	98.74	[197]
Ni-Al ₂ O ₃	0.6	70.60	69.00	[198]
Ni-γAl ₂ O ₃	-	51.9	56.1	[199]
Ni-K/CeO ₂ -Al ₂ O ₃	-	46.1	46.2	[200]

To further understand the promotion effect of MgO for DRM, the activation energy (E_a) of all the catalysts was obtained based on Arrhenius formula over a temperature range of 550-700 °C with much higher space velocity of 666 L.g⁻¹.h⁻¹ guarantying both low conversion levels (<15%) and absence of transport effect necessary for obtaining kinetics information. The relationship between

Figure III-23: Example of Arrhenius plot in DRM of Ni₅-Al₂O₃ catalyst

natural logarithm of CH₄ consumption rate and reciprocal of temperature is depicted in Figure III-23 and the values of E_a are presented in Table III-7. The intrinsic experimental data of each catalyst are taken after 60 minutes time on stream to ensure stable performance.

As estimated from literature, the methane apparent activation energies in DRM for all Ni based catalysts is in the range of 20-360 kJ.mol⁻¹. This wide range of values is dependent on the type of support, the nature of promoters, and the catalytic tests conditions applied. It can be mentioned that our results of E_a are in the same order of magnitude compared to literature [196,197]. As shown in Table III-7, regardless of the amount of Mg added, the E_a of CH₄ consumption for all catalysts studied is higher than that of CO₂. This means that the E_a of CH₄ is more sensitive to temperature change than CO₂ [195,199–202], consequently higher CO₂

conversions compared to CH₄ are obtained. In addition, Ni₅-Mg₁₅-Al₂O₃ has the lowest activation energy for CH₄ and CO₂ consumption (28.14 and 22.30 kJ.mol⁻¹, respectively) and the trend is in good agreement with what was obtained in the activity of those catalysts. Thus, the addition of a proper amount of magnesium promoter can remarkably reduce the energy consumption of the system by lowering adsorbed CH₄ and CO₂ species E_a in DRM. However, with a very high amount of Mg (15-26 wt%), the activation barrier becomes higher and the E_a value increases. Not to mention, that the values of E_a obtained in this study are lower than several Ni-Al₂O₃ based catalysts studied in literature (Table III-7) independent of the amount of promoter present.

III.7.5. Power law rate expression for Ni₅-Al₂O₃ catalyst

The influence of the partial pressures of CH₄ and CO₂ on the DRM rate was studied over mesoporous Ni₅-Al₂O₃ catalyst. A constant CH₄ partial pressure of 0.05 atm was used as the CO₂ partial pressure was varied between 0.01 and 0.05 atm and vice versa. The CH₄ consumption rates in the kinetics measurements ($-r_{\text{CH}_4} = \frac{X_{\text{CH}_4} \times F_{\text{CH}_4}}{W_{\text{cat}}}$; X_{CH₄} is CH₄ conversion, F_{CH₄} is the initial flow rate of CH₄ (mmol.s⁻¹) and W_{cat} is the catalyst weight (g)) are calculated from the slopes of the conversions versus residence time plots. The empirical power law $-r_{\text{CH}_4} = K \times P_{(\text{CH}_4)}^a \times P_{(\text{CO}_2)}^b$ was used to estimate the reaction orders (a, b) and the apparent rate constant (K) by applying the non-linear regression analysis in POLYMATH 6.1 software choosing Levenberg-Marquardt algorithm. The obtained rates in Table III-8 and their corresponding partial pressure values obtained at 650 °C were utilized in order to calculate and provide the values of the reactants orders presented. Results of the regression analysis give the following values: a= 0.75, b= 0.99 and K= 13.48 (mmol.g⁻¹.s⁻¹.atm^{-(a+b)}) with a variance (σ²) of 6.242E⁻⁰⁶. Both CH₄ and CO₂ orders were close to 1, similar to a study done by Wang S. et al. who demonstrated that when the partial pressure of CO₂ is below 8.4 kPa, the reaction order of CO₂ is almost 1 [203]. On the other hand, the power constant for CO₂ is higher than the order of CH₄ suggesting that the reaction is more sensitive to CO₂ partial pressure than CH₄ partial pressure. This dependence of Ni-Al₂O₃ on CO₂ partial pressure might be probably due to the utilization of oxygen coming from CO₂ to clean deposited carbon in agreement with the deactivation seen in stability results. As for the Ni₅-Mg₁₅-Al₂O₃, the amount of basic sites present could enhance the chemisorption of CO₂ that provides the oxygen needed in removing carbon, hence limiting CO₂ dependency [204]. However, this is just a hypothesis that needs to be justified by similar kinetics experiments on the Mg-based material. The kinetics of DRM as

the simple power-law model is a simple model that provides rough estimation of the parameters, but is insufficient under a large extent of partial pressure data. Description of the mechanistic steps is needed by using Langmuir-Hinshelwood model to describe DRM kinetics. This process was also tackled in the core of the thesis but is not presented because it has not finished yet.

Table III-8: Initial rates of DRM at 650 °C over mesoporous Ni₅-Al₂O₃ catalyst

Partial pressures (atm)		CH ₄ /CO ₂	Reaction rate (mmol.g ⁻¹ .s ⁻¹)
CH ₄	CO ₂		
0.01	0.05	0.2	0.0188
0.02	0.05	0.4	0.0363
0.03	0.05	0.6	0.0548
0.04	0.05	0.8	0.0645
0.05	0.05	1	0.0701
0.05	0.04	1.2	0.0576
0.05	0.03	1.6	0.0441
0.05	0.02	2.4	0.0284
0.05	0.01	4.8	0.0159

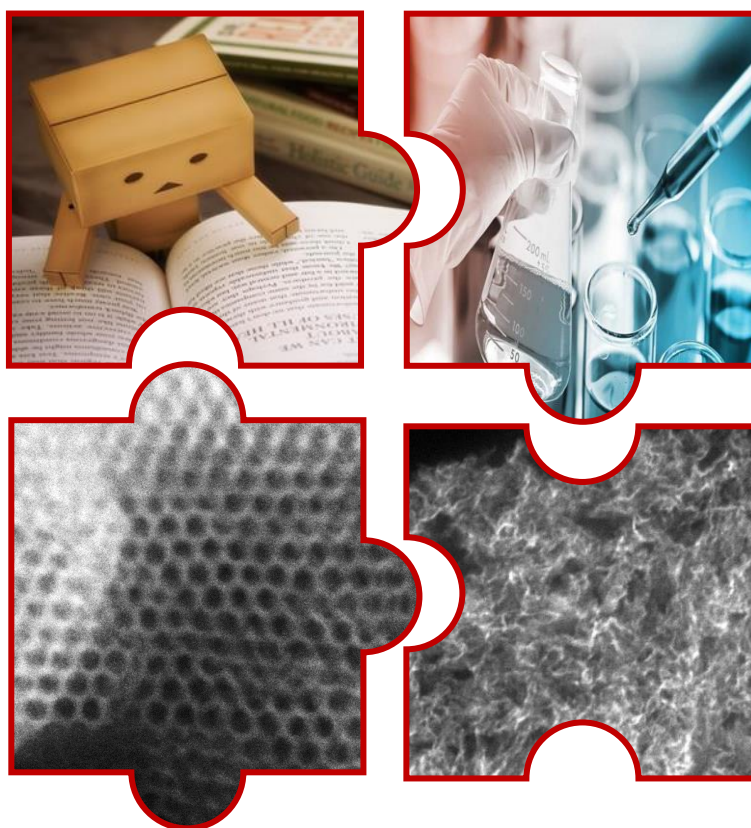
III.8. Conclusion

Ni₅-Mg_y-Al₂O₃ ordered mesoporous catalysts containing a wide range of Mg wt% (0-26 wt%) were synthesized using the evaporation induced self-assembly procedure associated to a “one-pot” methodology. Based on extensive physicochemical properties seen through the chapter, the inclusion of a maximum of 7 wt% Mg loading preserves high and homogenous Ni dispersion with simultaneous excellent Mg repartition. Mesoporous Ni₅-Mg₁₅-Al₂O₃ acquired also organized porosity that is even better than Al₂O₃ and Ni₅-Al₂O₃. For instance, Mg²⁺ ions facilitate the rate of hydrolysis of P123 and aluminum precursor especially that some AlO_x sites in the mesoporous alumina are preferable doping sites for Mg atoms. These good structural and textural characteristics, in addition to the enhanced basicity seen by infra-red (creation of basic sites) that accelerates CO₂ chemisorption, contributed to superior catalytic performances (lowest activation energy) with the best activity and stability among the rest of the samples.

On the contrary, if we continue to increase the amount of Mg (15-26 wt%), Ni species lose their excellent repartition over the alumina support and MgO is segregated. The organized

mesoporosity also disappears forming Mg-O bonds with longer length than those of Al-O bonds expanding the Al₂O₃ structure. As a result, the catalytic performance faces a calamitous decrease (increase in activation energy) especially that the excessive number of basic sites can lead to CO₂ coverage of active Ni sites. Hence, this chapter has justified the reason behind observing a “volcano-shape” curve in most of the Ni-Mg-Al₂O₃ studies.

IV. Chapter IV: Porous nickel-alumina derived from metal-organic framework (MIL-53): a new approach to achieve active and stable catalysts in methane dry reforming



This chapter tackles a second strategy of synthesizing a material that combines the features of high porosity, high surface area and intimate mixing between Ni metal and Al₂O₃ support with high activity and stability in DRM. A short literature review about MOF materials will be elaborated specifying the selected type in this thesis. The preparation steps will be then described in details along with the proper textural and structural properties of the novel obtained Ni-Al₂O₃ materials that were then treated in DRM reaction to compare their performance to those of a commercial-based catalyst.

IV.1. Literature review

MOFs (Metal Organic Framework) are highly porous hybrid materials made by a regular assembly of metal clusters connected to one another's by multifunctional organic linkers. For example, MOF structures can be synthesized using common organic ligands like 1,4-benzenedicarboxylic acid, its functionalized forms and 1,3,5-benzenedicarboxylic acid in conjunction with metal nodes of Zn²⁺, Cu²⁺, Cr³⁺, Al³⁺, Fe³⁺ and Zr⁴⁺ [205]. MOF abbreviation is usually used as a general name of a class of compounds, however there are many MOFs named according to the place of their discoveries such as UiO (Universitetet i Oslo), MIL (Materials of Institut Lavoisier), and HKUST (Hong Kong University of Science and Technology). Other MOFs have zeolites topology with metal ions surrounded by tetrahedra made of nitrogen atoms and connected through imidazole rings that are designated as ZIF (Zeolite Imidazole Framework). MOFs, in general, are characterized by extremely high specific surfaces and pore volumes that make them of great interest as host materials as was

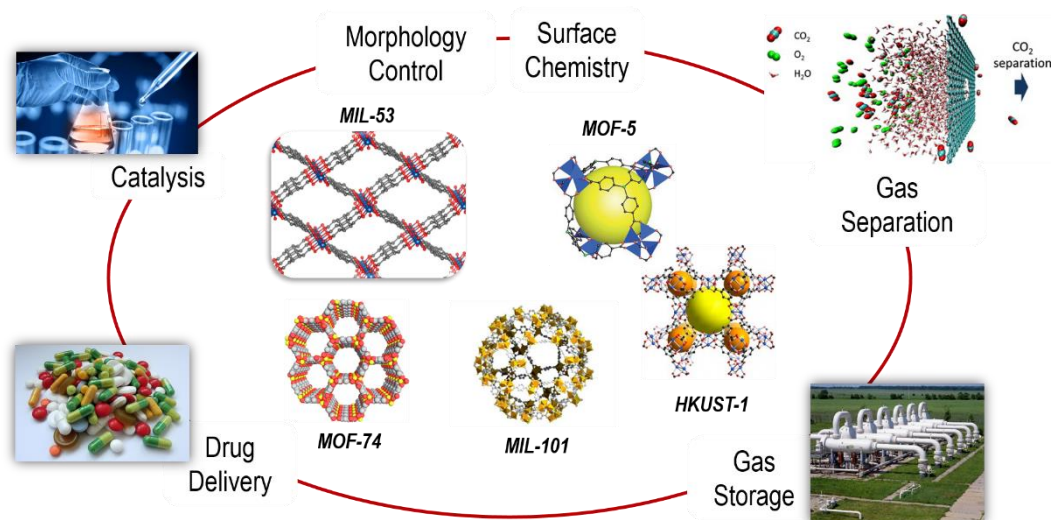


Figure IV-1: Types of several MOFs and their applications

already demonstrated in many applications such as gas storage, molecular separation, sensing, drug delivery or magnetism (Figure IV-1) [206]. In the field of catalysis, the high accessibility of their metal nodes and their reactivity have started to be exploited as well, even if stability issues in the conditions of catalysis still often remain to be solved.

Besides, the scope of MOF application was recently broadened to another level. Indeed, these hybrid materials are used as sacrificial templates to synthesize either carbonaceous or purely inorganic materials with unique textural properties depending on the thermal treatment used for their transformation [207–210]. Starting with the carbon-based supports, there is quite abundant literature about it. The first 8 lines in Table IV-1 summarize the reported Ni/C-based catalysts doped with nickel derived from MOF and details the treatment conditions applied as well as surface areas obtained and types of applications. In all cases, to obtain a carbon support from the MOF, the sample was thermally treated in an inert gas (N₂, Ar). The Ni particle size ranged from 5 nm when coupled with Pt to 50 nm when present alone. The surface area could be as small as 7 m².g⁻¹ and as large as 750 m².g⁻¹.

As our main interest in the present work concerned metal oxides (more specifically alumina) derived from MOFs, Table IV-1 also embraces the different existing bibliographic examples on such systems. To obtain metal oxide, the MOF structure has then to be thermally treated under air or pure O₂. As seen in the table, in the case of alumina, no active metal phase was added and the prepared materials, with surface areas varying from 50 to 270 m².g⁻¹, were not tested in any application. For these samples, Table IV-2 details the differences between the type of the parents MOF used, the ligand nature, the Al source and the thermal treatment applied. Despite the fact that these alumina were already reported, they were not chosen in our study because they have expensive ligand or Al source in addition to the high temperature and long time required for the preparation of the MOF that is later calcined to obtain the Al₂O₃ oxide.

In this thesis, the selected MOF is instead an aluminum-based MIL-53(Al) composed of aluminum hydroxyl chains connected by terephthalate organic linkers and running along one-dimensional channels. The benefit of this MIL-53(Al) is that it is synthesized using a microwave within 30 minutes reaction only, the linker and Al source are cheaper than the ones mentioned in Table IV-2. Moreover, MIL-53(Al) is made from the assembly of relatively inexpensive components, namely hydroxyl-aluminum species and terephthalate linkers, which can be extracted from natural or recycled feedstock [211,212] making this MOF-derived strategy economically and ecologically viable.

Table IV-1: Summary about Ni/C and oxides-MOF-derived materials and their applications

Sample	Derived MOF	Treatment	Particle size (nm)	Surface area (m ² .g ⁻¹)	Application
Ni@C-N ^[213]	MOF	Ar	17.4	100-200	Alkanes oxidation
Ni/C ^[214]	MOF	N ₂	19-40	7, 51, 389	4-nitrophenol reduction
Ni/C ^[215]	NiOF	N ₂	11	130	Super capacitors
Ni-Zn/C ^[216]	ZIF-8	N ₂	n.m.	750	CO ₂ capture and separation
Ni/C ^[217]	MOF	Ar	18-50	18-165	H ₂ evolution reaction Furfural
CuNi/C ^[218]	MOF	N ₂	15	91	Conversion to cyclopentanone
Ni/C ^[219]	MOF	N ₂	n.m.	460-600	Super capacitors
Pt-Ni/PC ^[220]	MOF-5	Ar	5	234	Fuel cells
Mn ₃ O ₄ ^[221]	Mn-MOF	Air	-	108-160	No Application
Co ₃ O ₄ ^[210]	ZIF-67	Air	8-28	22-120	Gas sensing
ZnO/Co ₃ O ₄ ^[222]	ZIF-8@ZIF67	Air	n.m.	2-25	CO ₂ photo reduction
Cr ₂ O ₃ /Al ₂ O ₃ ^[207]	MIL-101	O ₂	30	102	Isobutane dehydrogenation
ZrO ₂ ^[209]	UiO-66	Air	3.1	174	No Application
Cu/ZnO ^[223]	HKUST-1	Air	24	5.5	Hydrogenolysis of glycerol
Au/TiO ₂ ^[224]	MIL-125	O ₂	n.m.	20	CO ₂ reduction
Al ₂ O ₃ ^[225]	MOF A520	Air	-	205	No Application
Al ₂ O ₃ ^[226]	MIL-110	Air	-	138	No Application
Al ₂ O ₃ ^[226]	MIL-100	Air	-	123	No Application
Al ₂ O ₃ ^[227]	MIL-96	Air	-	56	No Application
Al ₂ O ₃ ^[228]	MIL-53	O ₂	-	88	No Application
Al ₂ O ₃ ^[228]	DUT-5	O ₂	-	270	No Application

Table IV-2: Differences in the synthesis of Al-based MOFs

Al-based MOFs	Ligand Type	Al source	Method of preparation
MOF A520	Fumaric acid	Al ₂ (SO ₄) ₃ .18H ₂ O	Glass container/60 °C, 4h
MIL-110	Trimethyl-1,3,5-benzenetricarboxylate	Al(NO ₃) ₃ .9H ₂ O	Autoclave/210°C,72h
MIL-100	Trimethyl-1,3,5-benzenetricarboxylate	Al(NO ₃) ₃ .9H ₂ O	Autoclave/210°C,3.5h
MIL-96	Trimethyl-1,3,5-benzenetricarboxylate	Al(NO ₃) ₃ .9H ₂ O	Autoclave/210°C,24h
DUT-5	<i>Biphenyl-4,4'-dicarboxylic acid</i>	Al(NO ₃) ₃ .9H ₂ O	Autoclave/180°C,24h
MIL-53	Benzene-1,4-dicarboxylic acid	Al(NO ₃) ₃ .9H ₂ O	Autoclave/220°C,72h

This MIL-53(Al) will be impregnated for the first time with nickel precursor and used as a source of porous Ni-Al₂O₃ catalyst that will be applied in dry reforming of methane reaction. The MIL-53(Al) host gathers the attributes required to obtain a porous nickel-alumina solid solution after its calcination: on one hand, it possesses a high porosity and metal-cluster accessibility expected to favor the homogeneous dispersion of nickel species within the oxide structure; on the other hand, it contains organics whose decomposition enables the formation of porosity in the obtained alumina [228]. An additional benefit is the occurrence in this structure of aluminum bridging hydroxyl groups lying along the inorganic chains that can interact with the nickel precursors and hence act as anchorage sites.

IV.2. Synthesis of mesoporous Ni-Al₂O₃ derived from MOF (MIL-53(Al))

The parent Al-containing MIL-53(Al) material was synthesized according to a known microwave-based procedure reported to provide nanocrystallites of homogeneous distribution in shape and size [229]. Figure IV-2 describes in details the step of MIL-53 preparation. It consists in mixing 1.21 g of AlCl₃.6H₂O (M_n=241.43, Sigma-Aldrich, 237078) and 0.42 g of benzene-1,4-di-carboxylic acid (M_n=166.13, Sigma-Aldrich, 185361) with 3 ml water and 5 ml of dimethylformamide (DMF) (M_n=73.09, Sigma-Aldrich, PHR1553) (Figure IV-2 A), then transferring the mixture into a 50 ml reactor and heating it in a microwave oven for 30 minutes at 125 °C at a heating ramp of 2 °C.min⁻¹ and with a power of 200 W (Figure IV-2 B). The stability of these parameters are followed through synthesis on the screen of the microwave displaying a graph for example of power and temperature as a function of time (inset Figure IV-2 B). The solid obtained was recovered by centrifugation and washed six times in 10 ml of

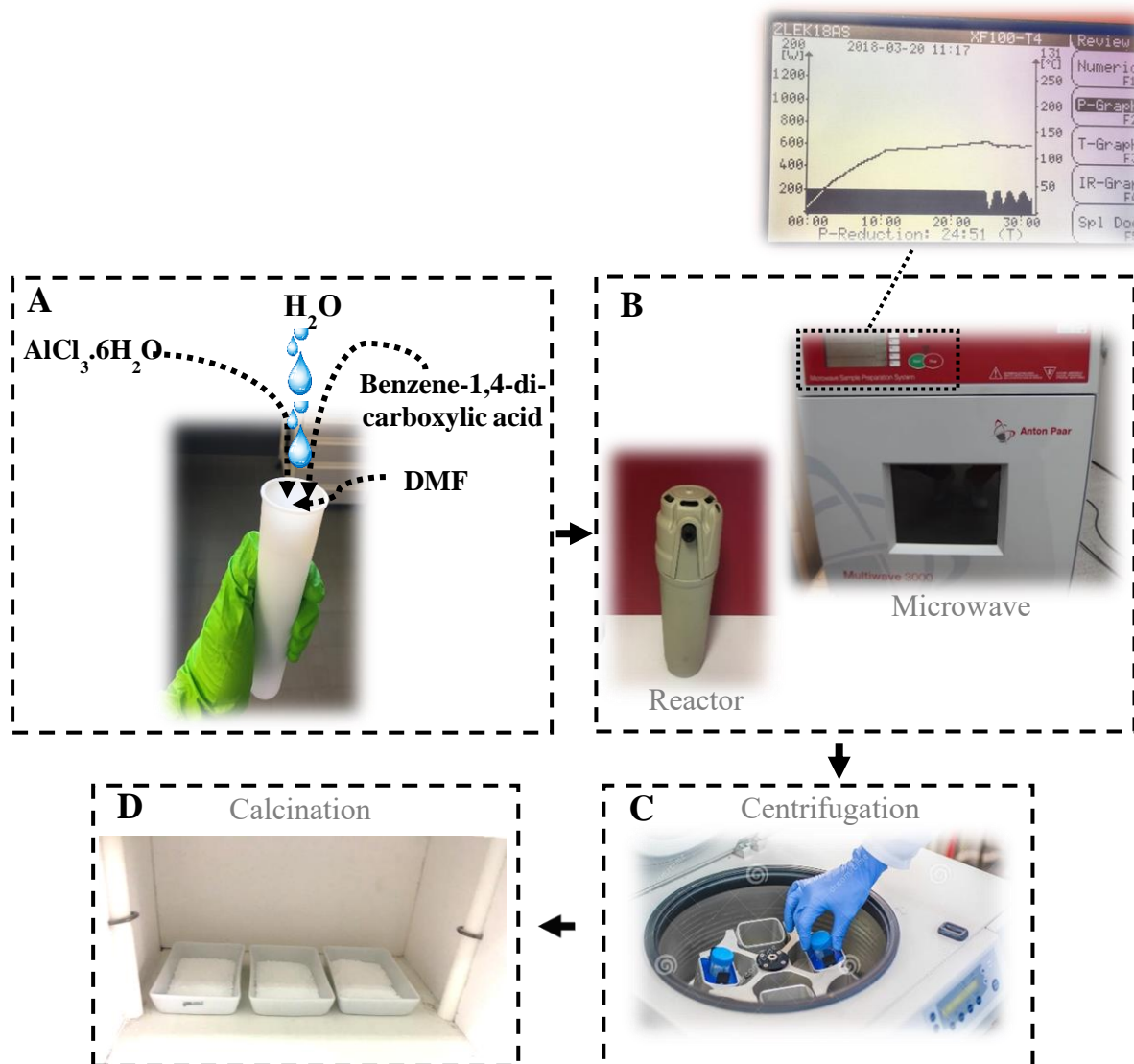


Figure IV-2: Chronological steps summary of preparing mesoporous $\text{Ni-Al}_2\text{O}_3$ with 5wt% nickel following the new metal organic framework route

DMF then in 10 ml of deionized water to ensure full removal of unwanted residues (Figure IV-2 C). After the last centrifugation, the white powder was dried for 24 h at 70 °C and heated in air (Figure IV-2 D) at 220 °C for 72 h to remove the structuring agent and obtain activated **MIL-53** sample.

Nickel introduction was carried out by incipient wetness impregnation performed on the **MIL-53** sample freshly dehydrated at 80 °C in an oven overnight. The procedure consisted in adding dropwise a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution with a volume equal to the pore volume of the MOF support (as estimated from N_2 -sorption analysis) and a Ni concentration established as to correspond to a Ni/Al atomic ratio in the sample of 0.07 (i.e. final Ni content in the dry catalyst of 5 wt%). The solid obtained after drying at room temperature for 24 h is hereafter denoted **Ni/MIL-53** (Figure IV-3). Part of it was kept as such to perform hydration-dehydration

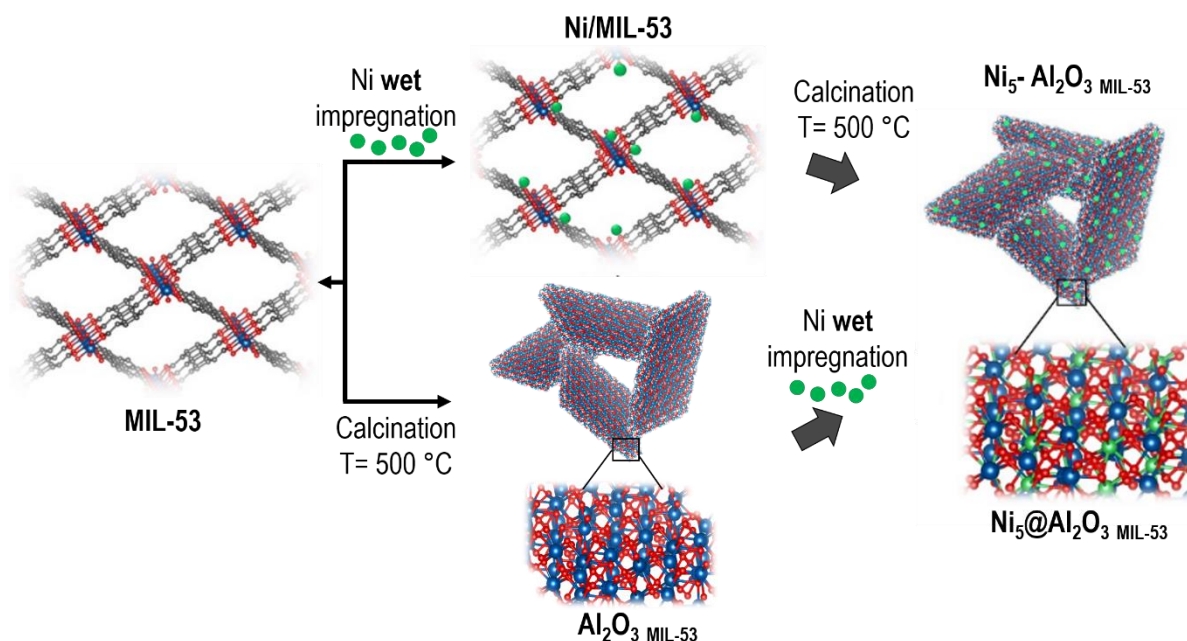


Figure IV-3: Schematic representing two types of Ni-Al₂O₃ catalyst derived from MIL-53 framework based on the order of Ni impregnation with respect to calcination tests and the other part was submitted to calcination in air for 5 h at 500 °C (thin bed conditions, heating rate 0.5 °C.min⁻¹) to give Ni₅-Al₂O₃ MIL-53.

For comparison purposes, a reference sample was also prepared to check the influence of calcination order. To elaborate, MIL-53 material was first placed in a ceramic plate and heated in static air at 500 °C (heating rate 0.5 °C.min⁻¹) for 5 h to remove the organic linkers and lead to an alumina material (Al₂O₃ MIL-53). Then, the alumina support obtained was impregnated by 5 wt% Ni using same conditions as above (pre-calcined MIL-53) followed by a second calcination in air at 500 °C (Figure IV-3). To distinguish between these two nickel-based alumina catalysts, the latter sample was denoted as Ni₅@Al₂O₃ MIL-53. These two alumina-based materials derived from MOF were compared to a distinct commercial alumina support. It is a conventional γ -alumina support obtained by calcination at 500 °C in air of a commercial bohemite (Sasol Plural, alumina hydrate AlOOH). The obtained alumina was impregnated with 5wt% Ni following the same incipient wetness impregnation strategy mentioned previously and labeled as Ni₅@Al₂O₃ com. The materials involved in this chapter are summarized in Table IV-3.

Table IV-3: Summary of the mesoporous Ni-Al₂O₃ catalysts prepared by the MIL-53 route

Sample	Support	Mode of Ni insertion	Ni content (wt%)
MIL-53		-	-
Ni ₅ -Al ₂ O ₃ MIL-53	Synthesized	I.W.I Prior MIL calc.	5
Ni ₅ @Al ₂ O ₃ MIL-53		I.W.I After MIL calc.	
Ni ₅ @Al ₂ O ₃ COM	Commercial	I.W.I	

IV.3. Physicochemical Characteristics of the parent MIL-53, activated MIL-53 and impregnated Ni₅-Al₂O₃ MIL-53 materials

IV.3.1. Structure of the as-synthesized and activated MIL-53 materials

After synthesis in microwave conditions, the parent MIL-53 sample was first characterized by X-ray diffraction (Figure IV-4 a). The pattern is similar to that reported in the literature for a MIL-53 material synthesized with the same microwave procedure (MW) [229]. This validates the formation of the targeted MIL-53 framework, even if small differences can be observed between this XRD pattern and the ones reported after synthesis under conventional heating [229]. This can be due to the dynamic properties of the MIL-53 structure which pore

size is strongly sensitive to guest adsorption (so-called “breathing behavior”) [230]. Hence,

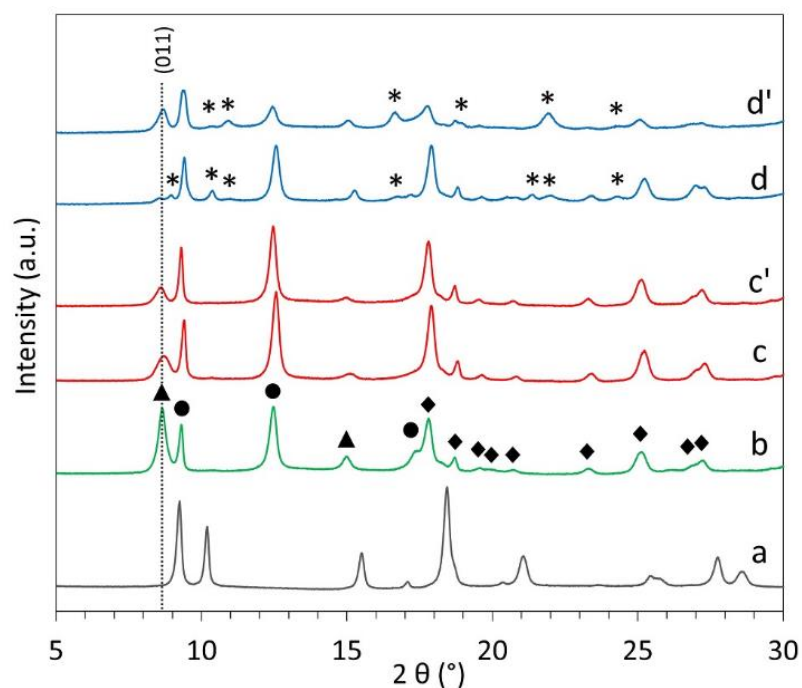


Figure IV-4: X-ray diffraction patterns of: (a) as synthesized MIL-53(Al), (b) activated MIL-53, (c) rehydrated MIL-53 dried in room atmosphere or (c') at 200 °C, (d) impregnated Ni/MIL-53 dried in room atmosphere or (d') at 200 °C. Triangles and spheres indicate the peak positions corresponding to the open and closed forms of the MIL-53 structure, respectively (as reported in [230]). Diamonds show unattributed reflections that may correspond to an intermediate state. Stars indicate peaks appearing after nickel impregnation. The dot vertical line shows the position of the 011 reflection characteristic of the MIL-53 large-pore phase.

different synthesis methods could lead to variations in the amounts of molecules (solvent and unreacted linkers) trapped within the pores due to different crystal formation rates.

After activation at 220 °C in air (to remove all adsorbates from the pores), the diffractogram changes to a completely different one (sample MIL-53, Figure IV-4 b), in accordance with the dynamic nature of the MIL-53 structure mentioned above. One can note however that the new XRD pattern is not composed only of peaks belonging to the large pore form of MIL-53 (indicated by black triangles, typical of empty pores), but it also contains peaks related to the narrow pore form (indicated by black spheres) as well as reflections characteristic of an intermediate state between the open and closed forms (indicated by black diamonds). This multiphasic structural state is related to the thermal history of the sample as already described by others for MIL-53 [231] and can be taken as representative of the “activated form”.

IV.3.2. Structural properties of impregnated Ni/MIL-53

As shown in Figure IV-4 d, all the peaks corresponding to this activated form are still present after Ni impregnation (Ni/MIL-53), even if slightly shifted and with distinct relative intensities for some of them. More importantly, new tiny peaks appear at unusual positions and they are visible both after drying in room atmosphere and at 200 °C (identified by stars, Figure IV-4 d and d', respectively). Such new reflections were to our knowledge never reported for MIL-53, strongly suggesting that nickel cations are inserted within the pores where they provoke structural deformation by interacting with the framework as in the case of adsorbed organic guest molecules [232].

In order to confirm the origin of these new reflections, a series of experiments was done with the aim to demonstrate that they appear only in the presence of Ni and do not simply come from different hydration states generating cell volumes and symmetry changes in response to the above-mentioned “breathing behavior”. We prepared to this end a nickel free hydrated MIL-53 sample to be compared to freshly impregnated Ni/MIL-53. This was done by immersing the freshly activated MIL-53 powder into a volume of pure water equivalent to the one used for Ni impregnation. XRD patterns were then taken, after submitting both rehydrated MIL-53 and impregnated Ni/MIL-53 to the same successive drying treatments consisting first in natural drying in room atmosphere (Figure IV-4 c and d) then in drying at 200 °C for 24h (Figure IV-4 c' and d'). Whatever the treatment, the additional tiny peaks (indicated by black stars) were present for Ni/MIL-53 (Figure IV-4 d and d') but not for MIL-53 (Figure IV-4 c and 2c').

Together with the limited intensity of these peaks that fits well the limited Ni content in the samples, this systematic difference is in line with a local framework distortion due to interaction with nickel cations occluded within the pores. Such distortion also agrees with the small shift to higher angle of the (011) reflection (at $2\theta = 8.7^\circ$) of the large-pore phase pattern, which is particularly disturbed after nickel impregnation (Figure IV-4 d).

IV.3.3. Effect of the addition of Ni on porous characteristics

The presence of nickel within the pores is further supported by the strong decrease of the saturation volume of N_2 adsorbed at low relative pressure ($P/P_0 = 0.2$) in Ni/MIL-53 (Figure IV-5 c) compared to both activated MIL (Figure IV-5 a) and rehydrated MIL (Figure IV-5 b), which corroborates a pore hindrance linked to the presence of Ni^{2+} . Accordingly, the microporous volume drops from $0.40 \text{ cm}^3 \cdot \text{g}^{-1}$ (activated MIL-53) to $0.09 \text{ cm}^3 \cdot \text{g}^{-1}$ upon nickel impregnation (Ni/MIL-53) and the BET specific surface simultaneously diminishes from $1130 \text{ m}^2 \cdot \text{g}^{-1}$ (MIL-53) to $300 \text{ m}^2 \cdot \text{g}^{-1}$ (Ni/MIL-53). By comparison, the pore volume is much less affected ($0.32 \text{ cm}^3 \cdot \text{g}^{-1}$) upon simple MIL rehydration without nickel. In such case, a small decrease is also noted, probably due to some (but limited) loss of structural integrity after water adsorption. This could also explain the XRD peak broadening seen for both rehydrated (MIL-53) and impregnated (Ni/MIL-53) series of samples ((011) reflection at $2\theta = 8.7^\circ$ mainly, Figure IV-4). Noteworthy, the N_2 adsorption-desorption isotherms of all materials (MIL-53, rehydrated MIL-53 and Ni/MIL-53, Figure IV-5 a-c) also display a marked step at relative

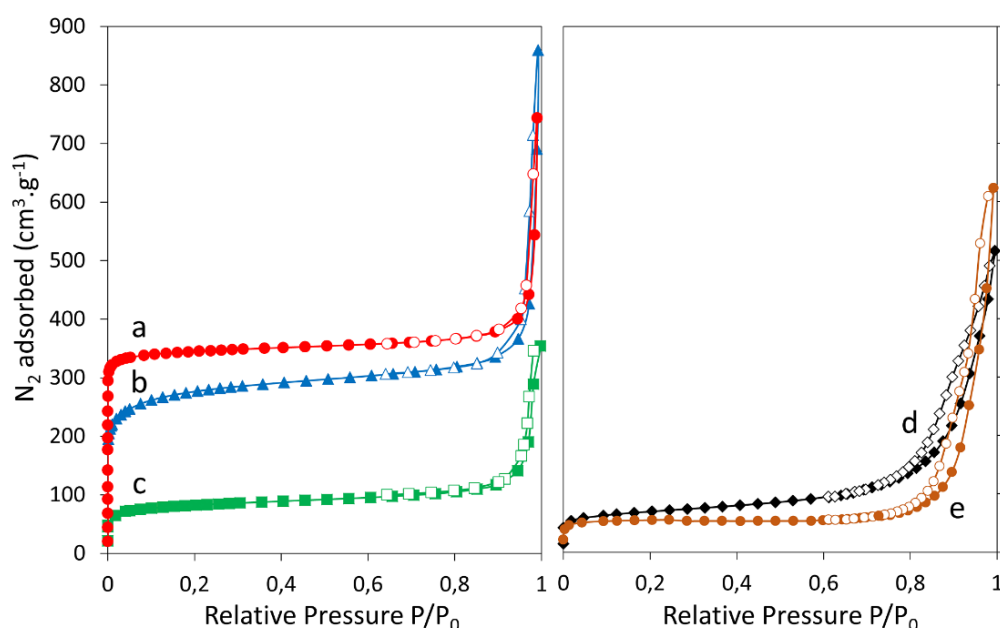


Figure IV-5: N_2 physisorption isotherms after degassing at 120°C of: (a) freshly activated MIL-53, (b) rehydrated MIL-53, (c) Ni/MIL-53, (d) $Ni_5\text{-Al}_2\text{O}_3$ MIL-53 and (e) $Ni_5^0\text{-Al}_2\text{O}_3$ MIL-53. Filled and empty symbols correspond to adsorption and desorption isotherms, respectively.

pressures above $P/P_0 = 0.9$ characteristic of a substantial intercrystalline meso-macro porosity occurring between aggregated nanocrystals.

IV.3.4. Organic linkers removal followed by thermogravimetric analysis

Another evidence of the intimate mixing between the nickel precursor species and the porous network in Ni/MIL-53 is given by thermogravimetric analyses as discussed in this paragraph. This technique was applied to study the decomposition in air of the carbonaceous (terephthalate) linkers constitutive of the parent MIL-53, the aim being to form the oxide alumina matrix.

Figure IV-6 A shows the TGA profiles obtained on freshly activated MIL-53, rehydrated MIL-53 and impregnated Ni/MIL-53 (curves a to c, respectively). A weight loss of about 15 % between 200 °C and 420 °C is distinctly seen for impregnated Ni/MIL-53 (Figure IV-6 A c) but not for the Ni-free materials. As confirmed by the simultaneous MS detection of NO (mass 30) in the exhaust gas (Figure IV-6 B, bottom, blue curve), this weight loss

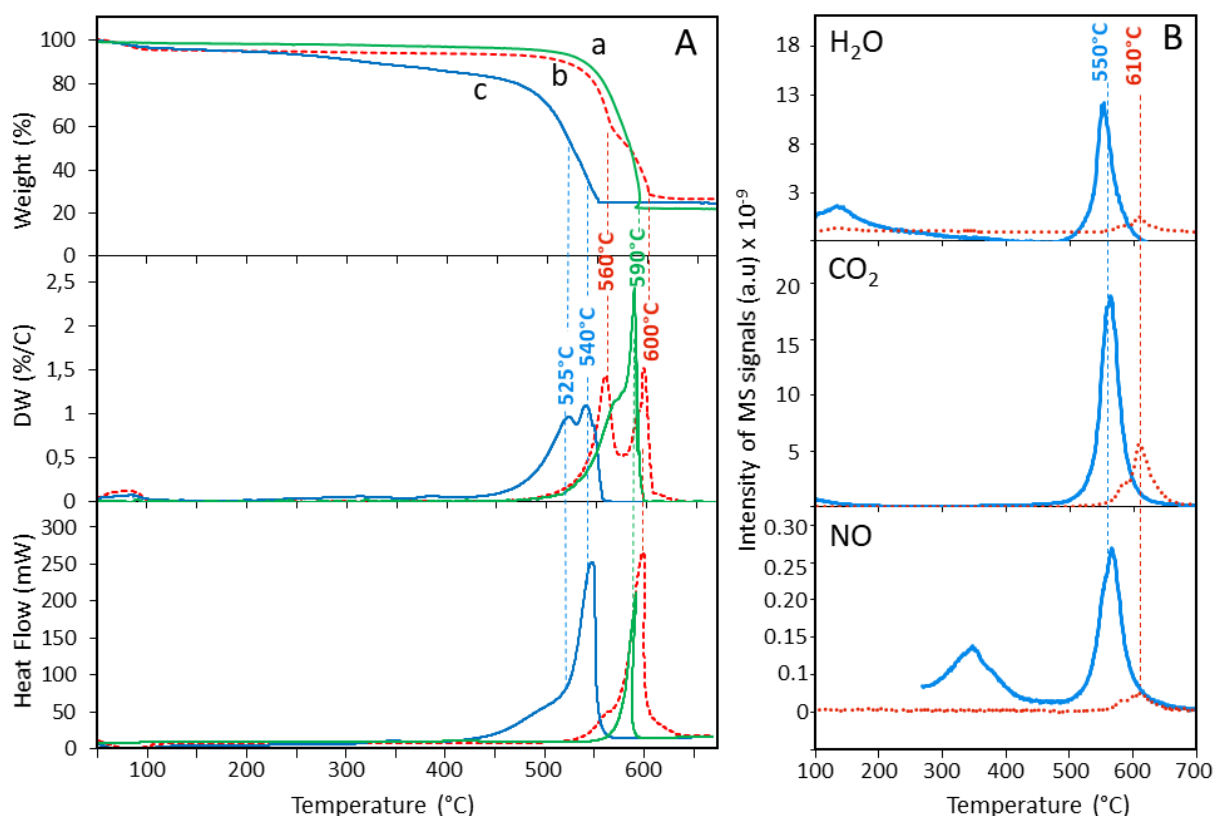


Figure IV-6: (A) TGA (top curves), DTG (middle curves) and DTA (bottom curves) profiles for samples: (a) freshly activated MIL-53, (b) rehydrated MIL-53 and (c) impregnated Ni/MIL-53. (B) Mass spectrometry profiles corresponding to the detection of H₂O (mass 18), NO (mass 30) and CO₂ (mass 44) for hydrated MIL-53 (red dotted lines) and impregnated Ni/MIL-53 (blue lines). The temperatures of peak maxima in B are slightly higher than in A due to the delay for the exhaust gases to reach the MS analysis chamber.

corresponds to the thermal decomposition of nitrates introduced together with nickel during the impregnation step.

From the curves in Figure IV-6, it can be also seen that the oxidizing nitrogen oxide species (such as NO) formed within the pores of Ni/MIL-53 during the heating induce a lowering by more than 60 °C of the temperature at which the linkers degradation occurs (important weight loss between 400-550 °C, Figure IV-6 c, top) compared to both freshly activated and rehydrated MIL-53 (process shifted to 500-650 °C for both of them, Figure IV-6 a and b). The DTG profiles (Figure IV-6 B, middle curves) reveal that the degradation takes place in two steps, as previously reported for the amino-terephthalate MIL-125(Ti) [233]. The second step is accompanied by an evolution of CO₂ for both MIL-53 and Ni/MIL-53 and also of NO for Ni/MIL-53 (see respective curves in Figure IV-6 B), and the process is strongly exothermic as seen from the DTA profiles (Figure IV-6 A, bottom curves). Hence, all data indicate that the linkers degradation is displaced towards a significantly lower temperature after nickel impregnation, giving the following scenario during heating of Ni/MIL-53: (1) the temperature increase up to 150 °C leads to the dehydration of the hexahydrate nickel nitrate used as nickel precursor according to the equation $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$, the theoretical mass loss of 59% for this event being close to the 50% measured by TG; (2) this is followed between 200 and 400 °C by nitrates decomposition into NO_x (NO, NO₂, etc.) [234] with simultaneous formation of a NiO-based phase (for the sake of neutrality preservation); (3) then, strongly adsorbed NO_x oxidizers remaining within the pores in close proximity (or in contact) with the organic linkers promote their decomposition, decreasing the temperature at which it occurs [235].

In view of these TG profiles, we decided to set the calcination temperature of Ni/MIL-53 during sample preparation (to form Ni₅-Al₂O₃ MIL-53) at 500 °C, a temperature high enough to degrade the linkers but guaranteeing as well the development of the porosity and the large surface area of the pure mineral final phase. Indeed, it was recently reported that a temperature close to the onset of the parent MOF calcination temperature is optimal for the preparation of inorganic structures with preserved morphology and dimensions [210], which is important for preserving an intercrystalline porosity and large surface area in the obtained catalyst.

IV.4. Physicochemical properties of the calcined $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, $\text{Ni}_5@Al_2O_3$ MIL-53, and $\text{Ni}_5@Al_2O_3$ COM

IV.4.1. Morphologies, porous characteristics and Ni location in calcined $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53

Figure IV-7 and Figure IV-8 show typical SEM and TEM micrographs of the parent (MIL-53) and impregnated then calcined ($\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53) materials. In both scanning (Figure

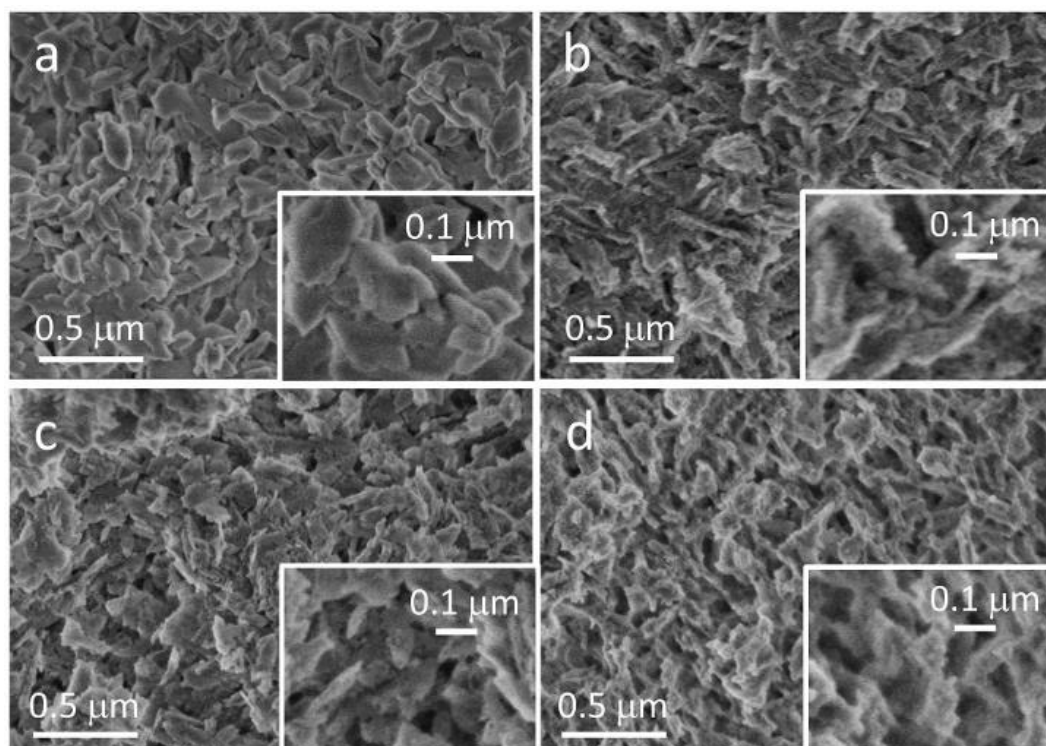


Figure IV-7: Representative SEM images of (a) MIL-53, (b) $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, (c) Al_2O_3 MIL-53 and (d) $\text{Ni}_5@Al_2O_3$ MIL-53

IV-7 a) and transmission (Figure IV-8 a) modes, MIL-53 appears as slightly elongated aggregated nanocrystallites with uniform sizes of approximately 20 nm in length. Such morphology is coherent with the high intercrystalline volume identified above from N_2 physisorption. After calcination at 500 °C (sample $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, Figure IV-7 b and Figure IV-8 b), the size and shape of the nanograins are globally preserved although they tend to become thinner, forming fused ill-defined and more defective alumina flakes that are actually composed of several randomly interwoven nanosheets (inset in Figure IV-8 b). This is in line with the N_2 isotherm of this sample that displays features typical of layered mesoporous materials, namely (i) a progressive increase of the adsorbed N_2 volume, observed here at P/P_0 higher than 0.75 and (ii) a slit-type hysteresis spread over P/P_0 values, ranging here from 0.75 to 1 (Figure IV-5 d) and revealing a relatively polydisperse size distribution of large mesopores. The BET specific surface of $239 \text{ m}^2\cdot\text{g}^{-1}$ is still high, even if much smaller than in the parent

MIL-53 material (Table IV-4) due to the organic linkers removal, and the microporous volume is close to that in Ni/MIL-53 (Figure IV-5 d and c, respectively).

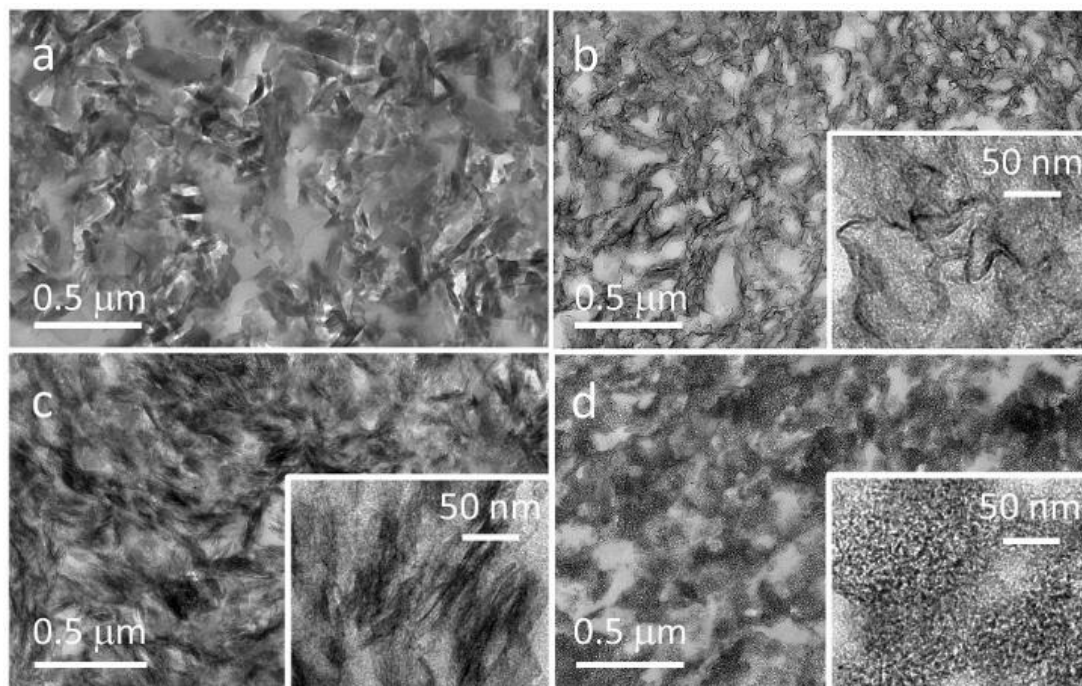


Figure IV-8: Representative HR-TEM images of (a) MIL-53, (b) Ni₅-Al₂O₃ MIL-53, (c) Al₂O₃ MIL-53 and (d) Ni₅@Al₂O₃ MIL-53

Table IV-4: Textural characteristics, reduction temperature and nickel content

Sample names	Textural properties of calcined samples ^a			Reduction temperature (°C)	Ni content ^b (wt%)	Ni ⁰ nanoparticle size after reduction (nm) ^c		Ni ⁰ nanoparticle dispersion after reduction (%) ^d
	S.A. (m ² .g ⁻¹)	V _{tot} (cm ³ .g ⁻¹)	Φ mean (nm)			reduced	spent	
MIL-53	1130	0.80	n.d					
Ni ₅ -Al ₂ O ₃ MIL-53	239	0.82	10	830	5.1 (5.2)			
Ni ₅ ⁰ -Al ₂ O ₃ MIL-53	200	1.02	16			6.8 (5.3)	7.5	19 (18.3)
Al ₂ O ₃ MIL-53	318	1.19	6.2					
Ni ₅ @Al ₂ O ₃ MIL-53	244	0.94	5.1	700/820	4.7 (4.6)			
Ni ₅ ⁰ @Al ₂ O ₃ MIL-53	130	0.55	5.6			10.2 (8.0)	11.0	12 (11.8)
Al ₂ O ₃ COM	185	0.51	9.2					
Ni ₅ @Al ₂ O ₃ COM	168	0.47	9.9	630/800	5 (5)			
Ni ₅ ⁰ @Al ₂ O ₃ COM	125	0.43	10.3			22 (18)	29	5.6 (9.6)

a: total surface area (S.A.), total pore volume (V_{tot}) and mean pore diameter (mean) calculated from the N₂ sorption isotherms.

b: Ni content from TPR taking into account that the theoretical amount is 860 μmol.g⁻¹, In brackets: values determined by XRF.

c: mean size values calculated from the histograms of TEM, In brackets: values estimated from XRD by applying the Scherrer equation of the Ni⁰ reflection at 2θ = 51.9°. The particle sizes could not be identified by XRD after test because of the lack of sufficient sample amount.

d: nanoparticle dispersion calculated from the formula $D = 6 \times 10^9 \times (V_{Ni}/A_{Ni}) \times (1/d)$ where d is the particle size (estimated from XRD), V is the volume of Ni atom in the bulk metal and A is the area of the Ni surface atom [236,237]. In brackets: nanoparticle dispersion calculated from H₂-chemisorption

According to XRD (Figure IV-9 a), these nanosheets structurally correspond to a cubic spinel NiAl_2O_4 phase with (400) and (440) planes giving main peaks at $2\theta = 45.0^\circ$ and 65.6° [238–240]. They do not contain any peak attributable to crystalline NiO, confirming the intimate mixing between Ni and the oxide support. This is also demonstrated by the temperature program reduction profile of $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 that displays only one peak centered at a high temperature of about 830°C (Table IV-4 and Figure IV-10 a) typical of the formation of the spinel NiAl_2O_4 phase [241,242].

The high and homogeneous Ni dispersion throughout the sample is also visible from STEM-HAADF and EDX elemental mappings that show the superimposed Ni and Al distributions on a representative $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 grain (Figure IV-11). Analysis of the selected area electron diffraction (SAED) patterns was also done on the calcined sample showing reticular distances (Figure IV-12) in the diffraction ring at $d_1 = 1.8 \text{ \AA}$ and $d_2 = 1.3 \text{ \AA}$ close to reticular distances $d = 2 \text{ \AA}$ and

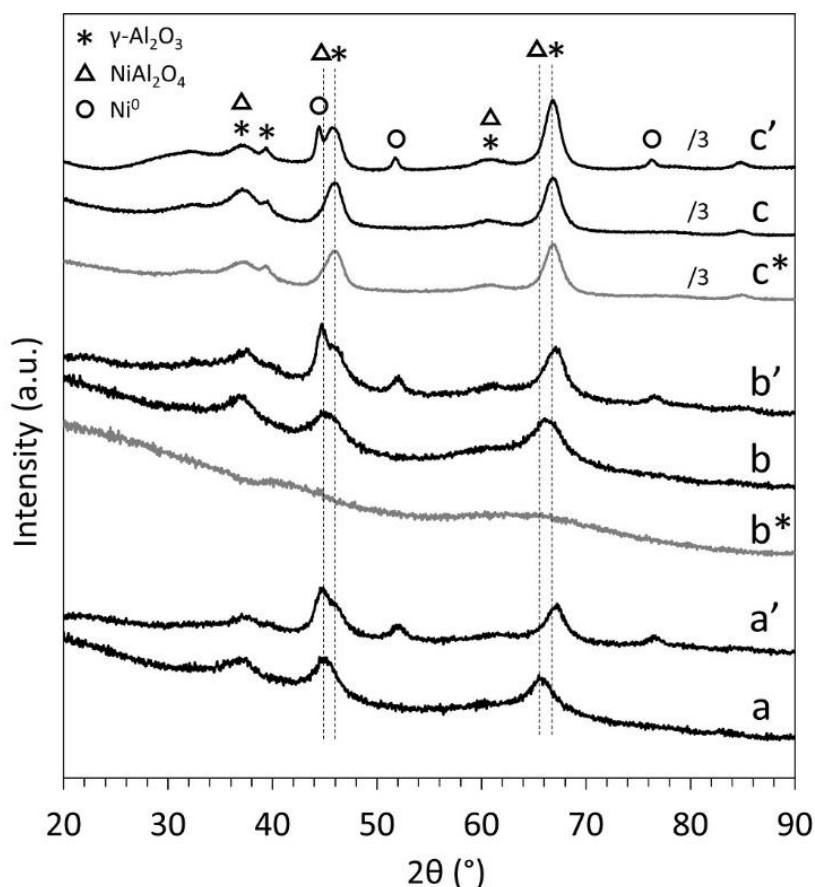


Figure IV-9: Diffractograms of the Ni containing samples: (a) $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, (a') $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, (b) $\text{Ni}_5@Al_2O_3$ MIL-53, (b') $\text{Ni}_5^0@Al_2O_3$ MIL-53, (c) $\text{Ni}_5@Al_2O_3$ COM, (c') $\text{Ni}_5^0@Al_2O_3$ COM. The diffractograms of the preformed alumina supports (light grey lines) are shown for comparison: (b*) Al_2O_3 MIL-53 and (c*) Al_2O_3 COM. Intensities are divided by 3 in patterns c*, c and c'.

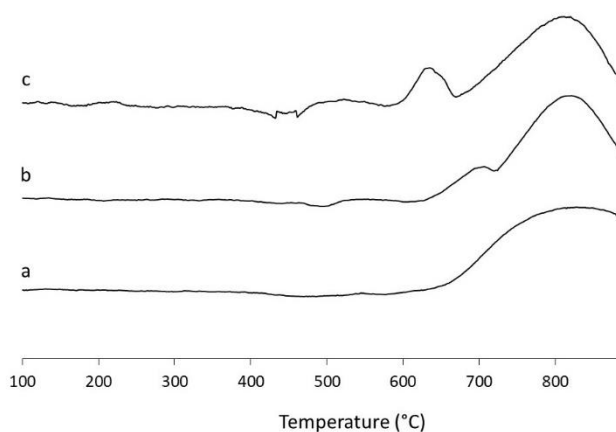


Figure IV-10: Temperature program Reduction analyses of the samples (a) $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, (b) $\text{Ni}_5@Al_2O_3$ MIL-53, and (c) $\text{Ni}_5@Al_2O_3$ COM.

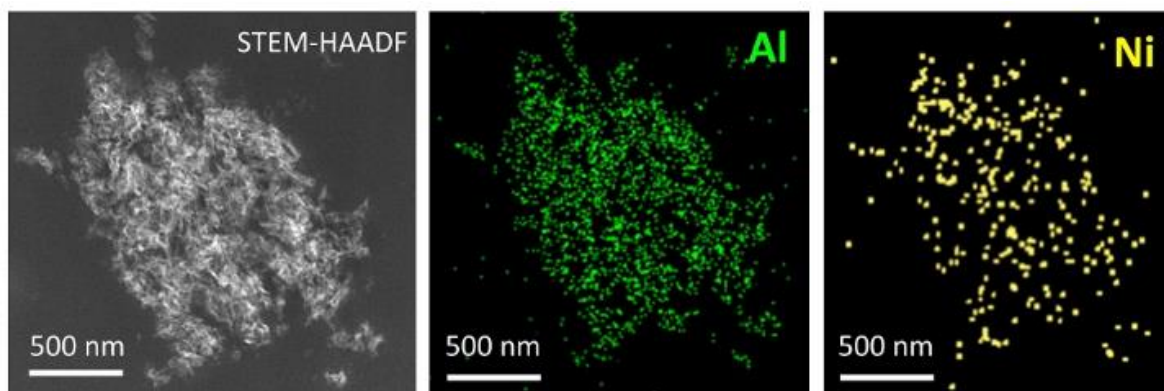


Figure IV-11: STEM-HAADF image of $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ (left) and EDX elemental mappings of the same area for Al (in green) and Ni (in yellow).

1.4 Å that can be estimated above from XRD for NiAl_2O_4 and also not far from those typical of $\gamma\text{-Al}_2\text{O}_3$ ($d = 1.4$ Å and 1.98 Å attributed to (440) and (400) planes, respectively). On the contrary, the lattice spacing expected around 2.4 Å and 2.1 Å for (111) and (200) crystal planes of NiO [243] are not distinguished confirming the absence of such phase as discussed above.

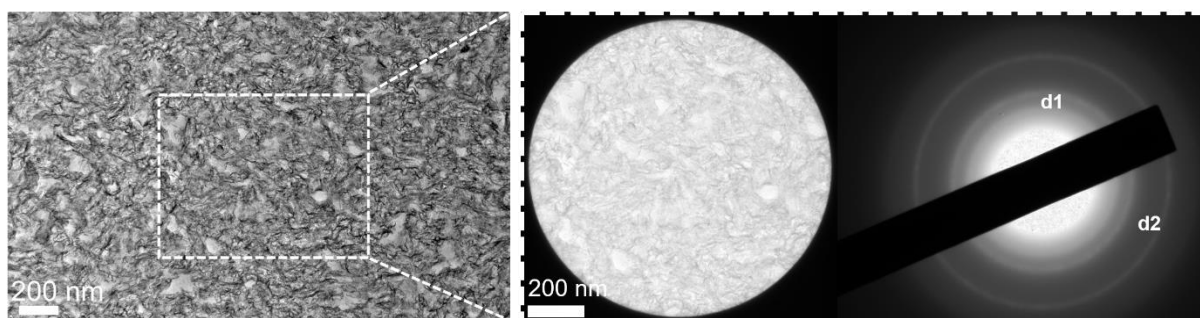


Figure IV-12: Representative TEM micrographs with its corresponding local SAED image over selected grain zones of calcined $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$

IV.4.2. Comparative properties of calcined $\text{Ni}_5\text{@Al}_2\text{O}_3_{\text{MIL-53}}$ prepared by impregnation of $\text{Al}_2\text{O}_3_{\text{MIL-53}}$

In order to evaluate the impact on the material properties of the adopted preparation procedure (i.e. impregnating first the activated MIL-53 with nickel then calcining it), a different order was applied by first calcining the activated MIL-53 (to obtain $\text{Al}_2\text{O}_3_{\text{MIL-53}}$) then impregnating and calcining it at 500°C (to remove adsorbed nitrates and water molecules). This second sequence order, in which the impregnation is done on a preformed alumina support (here $\text{Al}_2\text{O}_3_{\text{MIL-53}}$), resembles a conventional preparation route.

From XRD, the structure of $\text{Al}_2\text{O}_3_{\text{MIL-53}}$ is typical of an amorphous alumina (Figure IV-9 b*). It changes after Ni impregnation and calcination (sample $\text{Ni}_5\text{@Al}_2\text{O}_3_{\text{MIL-53}}$, Figure IV-9 b) to a crystalline phase very similar to that in $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ except for two reflections

(2θ at 45.8° and 66.5°) that appear broadened and subtly shifted towards positions typical of $\gamma\text{-Al}_2\text{O}_3$ ($2\theta = 46.2^\circ$ and 67.0°). This suggests a coexistence of both phases, as also supported by the TPR profile that contains two peaks, (i) a main one at high temperature (with maximum at $T = 820^\circ\text{C}$, Figure IV-10 b) indicative of some inclusion of nickel within the oxide matrix as in $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$, and (ii) a smaller one centered at about 700°C characteristic of nickel interacting less strongly with the alumina support (most probably nickel oxo-clusters on the external surface of the alumina grains).

In term of morphology, the preformed alumina support appears as nanograins composed of both packed and interwoven nanosheets (sample $\text{Al}_2\text{O}_3_{\text{MIL-53}}$, Figure IV-7 c, Figure IV-8 c) and this amorphous two-dimensional aspect is lost after nickel impregnation and calcination, turning to aggregates of tiny nanocrystals with ill-defined shapes (sample $\text{Ni}_5@\text{Al}_2\text{O}_3_{\text{MIL-53}}$, Figure IV-7 d, Figure IV-8 d). This final morphology significantly differs from the lamellar shape seen above for $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$. Moreover, the grains appear assembled, forming a polycrystalline structure with polymodal porosity, in line with the three well defined steps observed in the N_2 adsorption isotherm of this sample (Figure IV-13 a), typical of the coexistence of micro, meso and macropores.

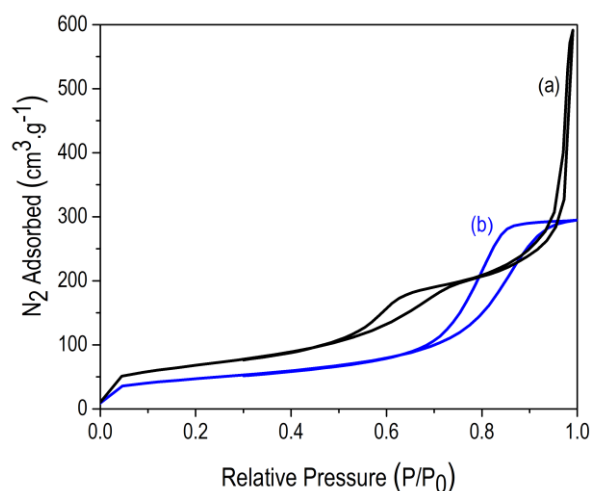


Figure IV-13: N_2 physisorption isotherms of the samples: (a) $\text{Ni}_5@\text{Al}_2\text{O}_3_{\text{MIL-53}}$ and (b) $\text{Ni}_5@\text{Al}_2\text{O}_3_{\text{COM}}$

Therefore, the order of the “calcination / Ni^{2+} impregnation” sequence, which affected the temperature of degradation of the MIL organic linkers (TG/SM data, Figure IV-6), also impacts the structure, texture and reducibility of the final material. To sum up, impregnation of the nickel cations within the activated MIL-53 to position them along the aluminum chains of the framework before the calcination step ($\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$) allows for a somewhat better dispersion (Table IV-4) and stabilization of nickel through their insertion into interwoven 2-dimensional alumina nanosheets. Notably, another advantage of this sequence order is to

require only one calcination step during material preparation instead of two for conventionally impregnated $\text{Ni}_5@Al_2O_3_{MIL-53}$.

IV.4.3. Physicochemical properties of conventional $Al_2O_3_{COM}$ and $Ni_5@Al_2O_3_{COM}$

For the sake of comparison, a last material ($Ni_5@Al_2O_3_{COM}$) was prepared by conventional nickel impregnation of a commercial γ -alumina ($Al_2O_3_{COM}$) and tested as traditional reference catalyst. Both $Ni_5@Al_2O_3_{COM}$ and its support $Al_2O_3_{COM}$ show four main diffraction peaks, which are typical of crystalline γ - Al_2O_3 (Figure IV-9 c^* and c , respectively). No evidence of spinel phase can be observed on the diffractogram of $Ni_5@Al_2O_3_{COM}$, although diffraction peaks corresponding to a small fraction of this phase might be masked by those of the γ - Al_2O_3 phase. The TPR trace of this material displays two peaks, as for $Ni_5@Al_2O_3_{MIL-53}$, but centered at lower temperatures than previously (630 °C and 800 °C, Figure IV-10 c), indicating a weaker Ni-support interaction than in both MOF-based samples, especially $Ni_5-Al_2O_3_{MIL-53}$. Similarly to $Ni_5@Al_2O_3_{MIL-53}$, a fraction of the nickel in $Ni_5@Al_2O_3_{COM}$ is probably existing in the material as amorphous NiO, as revealed by the TPR signal observed at relatively low temperature ($T < 700^\circ\text{C}$).

The significantly higher dispersion and stabilization of Ni in $Ni_5-Al_2O_3_{MIL-53}$ sample can be explained as follows: the impregnation of nickel nitrate on the parent MIL-53 with especially high surface area enables the initial occlusion of the nickel precursors along the organic linkers and $[Al(OH)O]_n$ clusters decorating the pores, leading after the MOF calcination step (organic removal) to the formation of an Al_2O_3 - $NiAl_2O_4$ phase in which nickel and aluminum cations are intimately mixed in a homogenous oxide phase. In contrast, impregnation of a preformed alumina (obtained by calcination of either MIL-53 or boehmite) then impregnation and calcination leads to a mixture of alumina, $NiAl_2O_3$ and NiO with an overall weaker interaction between nickel and the alumina matrix. Interestingly, the presence of nickel at the very first step of the preparation seems to direct the formation of the crystalline spinel $NiAl_2O_4$ phase during calcination (giving $Ni_5-Al_2O_3_{MIL-53}$), while no spinel phase is formed when starting from pure MIL-53 (giving amorphous $Al_2O_3_{MIL-53}$).

IV.5. Physicochemical properties of reduced $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53, $\text{Ni}_5@ \text{Al}_2\text{O}_3$ MIL-53, and $\text{Ni}_5@ \text{Al}_2\text{O}_3$ COM

Previous to catalytic tests, all the prepared nickel-alumina materials were treated under a flowing H_2 atmosphere to obtain reduced Ni^0 , the active phase for DRM. The H_2 consumption during TPR was used to estimate the amount of reducible Ni^{2+} in all nickel containing samples, considering the consumption of one H_2 molecule per Ni^{2+} cation. For all samples, the Ni content is in accordance with that measured by X-fluorescence and close to the expected 5 wt% Ni, even if slightly lower, by less than 10%, for sample $\text{Ni}_5^0@ \text{Al}_2\text{O}_3$ MIL-53 (Table IV-4).

The XRD patterns of the samples reduced at 800 °C are shown in Figure IV-9 and compared to those before reduction. The reduction of $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 to $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 leads to the formation of new diffraction peaks assignable to the (111), (200) and (220) planes of crystalline Ni^0 (at $2\theta = 44.5^\circ$, 51.9° and 76° , respectively, Figure IV-9 a'). Bands attributable to an alumina-based phase are still present but they are slightly shifted (compared to those before reduction) towards positions characteristic of pure $\gamma\text{-Al}_2\text{O}_3$ which attests of Ni extraction from the oxide matrix towards the pore surface.

The reduction of the sample was followed by H_2 in-situ XRD techniques (done at University of Lille in collaboration with “unité de catalyse et chimie du solide” (UCCS)) in the temperature range of 25-850 °C (Figure IV-14). In good agreement with XRD and TPR measurements, the reduction does not start before 700 °C and it is at this temperature also that we start to see disappearance of NiAl_2O_4 spinel and presence of metallic Ni^0 species and $\gamma\text{-Al}_2\text{O}_3$ phase.

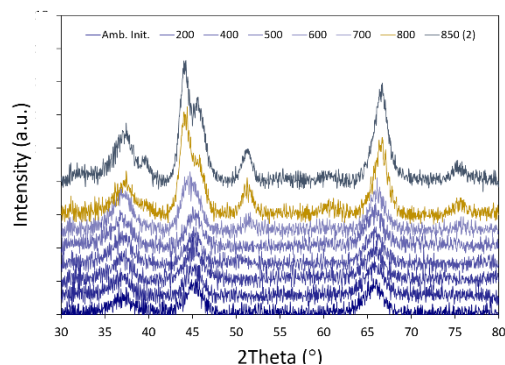


Figure IV-14: In-situ XRD patterns of $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 during reduction by hydrogen (5% H_2 in Ar) up to 850 °C

Application of the Scherrer equation (Figure IV-9) to the Ni^0 reflection at $2\theta = 51.9^\circ$ leads to a mean Ni^0 nanoparticle size of 5.3 nm, slightly smaller than the value estimated by HR-TEM after measuring the sizes of at least 500 nanoparticles (Table IV-4). Considering the TEM image of $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 shown in Figure IV-15 a and the non-symmetrical shape of the histogram of particles sizes for this sample (Figure IV-16), it can be assumed that this average size discrepancy comes from contrast issues making uneasy the detection of the smallest

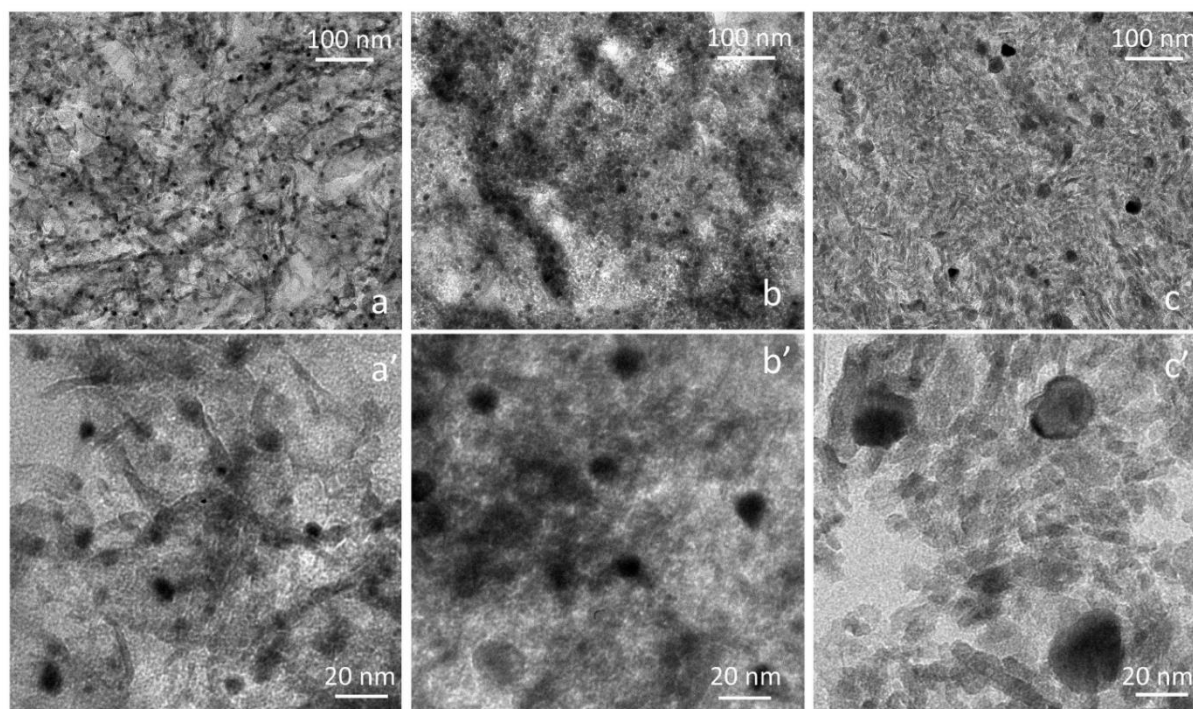


Figure IV-15: HR-TEM images of the reduced samples: (a and a') $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, (b and b') $\text{Ni}_5^0@\text{Al}_2\text{O}_3$ MIL-53, (c and c') $\text{Ni}_5^0@\text{Al}_2\text{O}_3$ COM.

nanoparticles (from 2 to 4 nm) on the alumina grains, in spite of the good resolution of HR-TEM images. In this sample, all detected nickel nanoparticles are homogeneously distributed all over the support which still appears as interwoven alumina sheets (as in $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 before reduction).

The preservation of the morphology after reduction is also attested by textural features, the N_2 physisorption isotherm of $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 still showing a slit-like hysteresis typical of a layered material composed of poorly organized interlayered pores (Figure IV-5 e). The amount of N_2 adsorbed at $P/P_0 > 0.8$ is however higher than that before reduction (Table IV-4), indicating the formation of

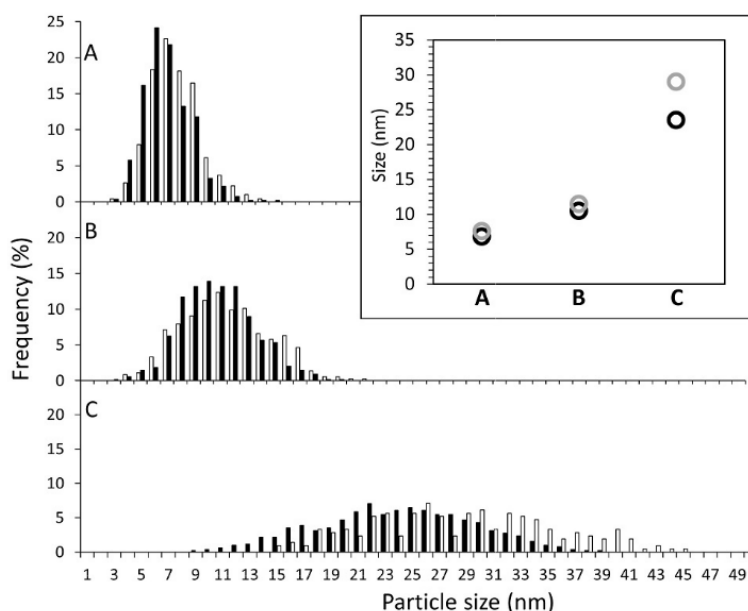


Figure IV-16: Histograms established from at least 500 Ni_5^0 nanoparticles in typical HR-TEM images of (A) $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, (B) $\text{Ni}_5^0@\text{Al}_2\text{O}_3$ MIL-53 and (C) $\text{Ni}_5^0@\text{Al}_2\text{O}_3$ COM before and after 13h of catalytic test (black and white bares, respectively). Related mean sizes are shown in (D) for the catalysts before (black circles) and after (grey circles) test

additional large mesopores within the material. This increase of the total pore volume and mean pore size upon reduction is likely due to the exfoliation of the packed nanosheets through (i) the transformation of the NiAl_2O_4 spinel phase into $\gamma\text{-Al}_2\text{O}_3$ and (ii) the formation of the Ni^0 nanoparticles that may tend to further space apart the nanosheets one from another.

The reduction of nickel impregnated on the two preformed alumina supports ($\text{Al}_2\text{O}_3_{\text{MIL-53}}$ and $\text{Al}_2\text{O}_3_{\text{COM}}$) led similarly to the appearance of homogeneously dispersed Ni^0 nanoparticles (Figure IV-15 b and c, respectively), but the particles and their size distributions were systematically larger than on $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ (Table IV-4), especially in the case of $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$ (size = 22 nm) (Figure IV-16). Hence, the homogeneous NiAl_2O_4 -based spinel nanophase formation seen during the first steps of preparation of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ and issued from initial nickel insertion within the pores of the MOF with high surface area before linker decomposition seems to play an important role towards metal stabilization with a positive effect that remains after partial extraction from the alumina matrix upon reduction.

IV.6. Catalytic activity and stability in dry reforming of methane

VI.6.1. Catalytic activity of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ and $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$

Figure IV-17 A, B illustrates the activity test for both $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ and $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$ catalysts in addition to the expected thermodynamic values at different temperatures (light off measurements). A slightly higher CO_2 than CH_4 conversion is also depicted over the entire temperature range accounting for the RWGS reactions that consumes CO_2 and increases its

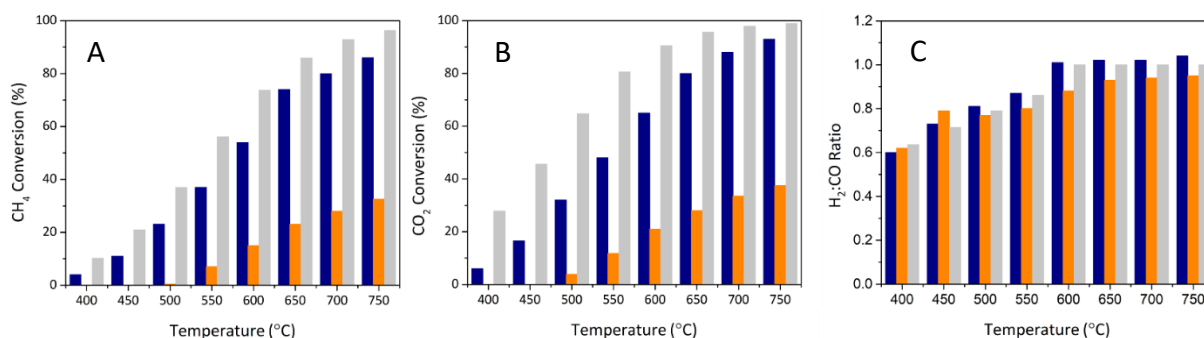


Figure IV-17: (A) CH_4 , (B) CO_2 conversions, and (C) $\text{H}_2\text{:CO}$ product ratio during DRM upon continuous increase of temperature from 400 °C till 750 °C over in-situ reduced (800 °C/2h): (blue) $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$, and (orange) $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$. Grey columns are the calculated values at the thermodynamic equilibrium for the CO_2 , CH_4 conversions and $\text{H}_2\text{:CO}$ ratio

conversion level. This trend is seen over both catalysts. However, the conversions of $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$ catalyst starts at higher temperature (450 °C) compared to those of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ (390 °C) with 25% less conversion values. This difference in conversions and the superior

performance of the MOF-based sample over the commercial one is due to the large particle size (22 nm) and the lower dispersion acquired by the latter (5.6 %) decreasing the available Ni⁰ active sites for CH₄ and CO₂ reactants. As for the H₂:CO molar ratio presented in Figure IV-17 C as a function of temperature, they appear to be always less than the thermodynamic values for Ni₅⁰@Al₂O₃ COM suggesting the occurrence of RWGS, whereas for Ni₅⁰-Al₂O₃ MIL-53 it is always close to 1 showing a selective DRM operation, with limitation to a great extent of side products (C_(s) and H₂O).

V.6.2. Catalytic stability of Ni₅⁰-Al₂O₃ MIL-53, Ni₅⁰@Al₂O₃ MIL-53 and Ni₅⁰@Al₂O₃ COM

Finally, the stability test experiments of Ni₅⁰-Al₂O₃ MIL-53 were tested at 650 °C in the reaction of dry reforming of methane and compared to those of Ni₅⁰@Al₂O₃ MIL-53 and Ni₅⁰@Al₂O₃ COM (Figure IV-18 and Table IV-5). Temperature of 650°C was selected as seen in chapter III in order to be able to compare the performances of the three different catalysts at conversion of reactants below 100%. Stability over a longer reaction time (100h) was also investigated for Ni₅⁰-Al₂O₃ MIL-53. Figure IV-18 A and B show that the CO₂ and CH₄ conversions on both MOF-derived catalysts (a and b) are high, close to thermodynamic

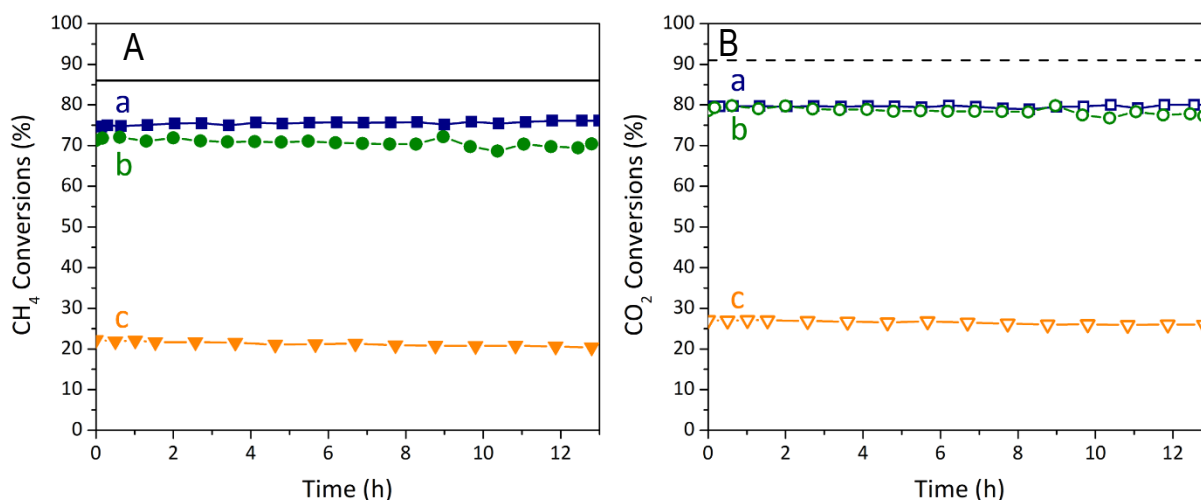


Figure IV-18: Comparison of the catalytic performances in DRM of (a) Ni₅⁰-Al₂O₃ MIL-53, (b) Ni₅⁰@Al₂O₃ MIL-53 and (c) Ni₅⁰@Al₂O₃ COM as a function of (A) CH₄ and (B) CO₂ conversions measured during 13h of reaction. Black continued and dashed lines are the calculated values at the thermodynamic equilibrium for the CH₄ and CO₂ conversions, respectively

equilibrium, and much higher (2 to 3 times) than those on Ni₅⁰@Al₂O₃ COM. The selectivity to DRM on Ni₅⁰-Al₂O₃ MIL-53 is also remarkable, as attested by two features that indicate limited occurrence of side reactions: (i) the close CH₄ and CO₂ conversions that differ by only 7% and

(ii) the H₂:CO ratio very close to 1 (Figure IV-19). A rather good selectivity to DRM is also observed on Ni₅⁰@Al₂O₃MIL-53 but with a H₂:CO ratio higher than 1 that suggests the occurrence of some CH₄ decomposition (CH₄(g) → C(s) + 2H₂(g)). Noteworthy Ni₅⁰-Al₂O₃ MIL-53 is not

Table IV-5: Catalytic test results for all the prepared catalysts

Catalyst	Conversion (%)						Molar composition of main products (H ₂ /CO)			Coke content (%)	
	t=0.5h		t=13h		t=100h		t=0.5h	t=13h	t=100h	t=13h	t=100h
	X _{CH4}	X _{CO2}	X _{CH4}	X _{CO2}	X _{CH4}	X _{CO2}					
Ni ₅ -Al ₂ O ₃ MIL-53	75	79	76	79	74	80	1.02	1.01	1.03	0	0
Ni ₅ @Al ₂ O ₃ MIL-53	71	79	70	77	n.p.	n.p.	1.12	1.09	n.p.	5	n.p.
Ni ₅ @Al ₂ O ₃ COM	22	27	20	26	n.p.	n.p.	0.93	0.89	n.p.	7	n.p.

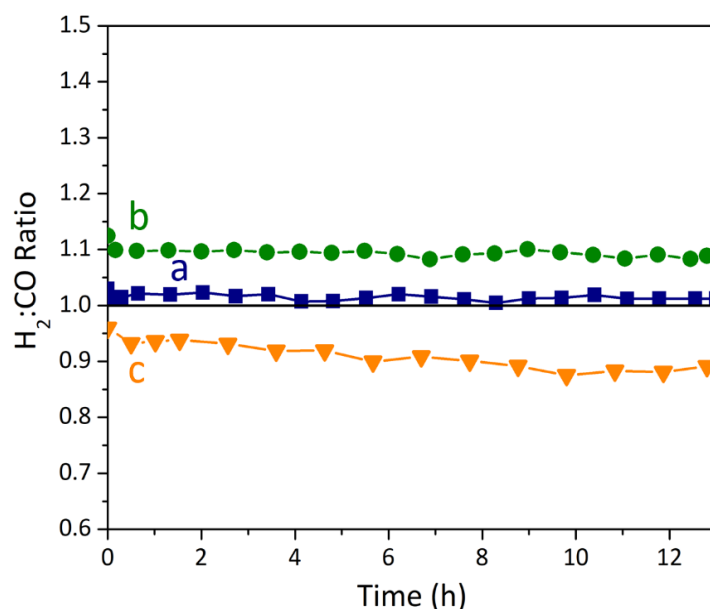


Figure IV-19: H₂:CO ratios in DRM (a) Ni₅⁰-Al₂O₃ MIL-53, (b) Ni₅⁰@Al₂O₃ MIL-53 and (c) Ni₅⁰@Al₂O₃ COM

only the most active catalyst but it is also very stable as its performance after the prolonged 100 h on stream remains nearly equal to that measured at the early stage of the reaction (Figure IV-20).

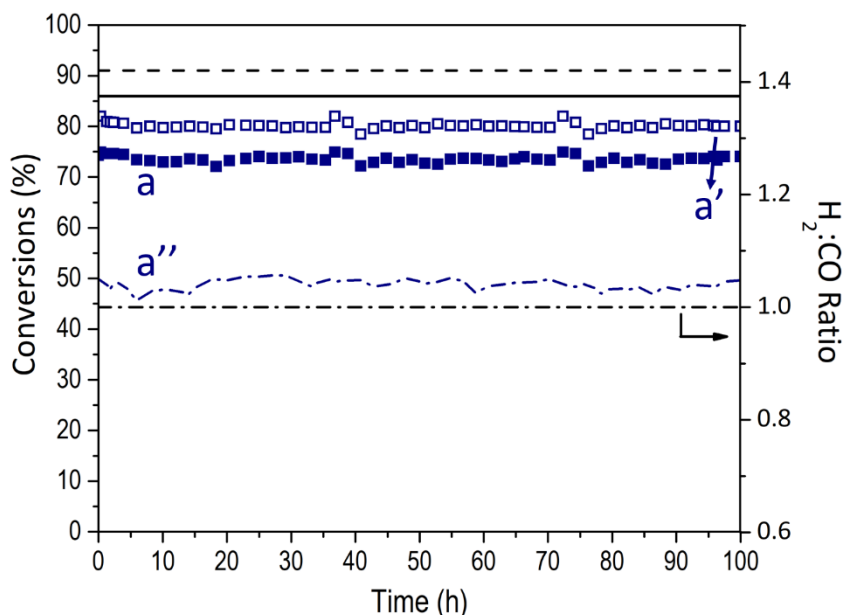


Figure IV-20: Catalytic performances in DRM of $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, as a function of (a) CH_4 and (a') CO_2 conversions measured during 100h of reaction. Black continued and dashed lines are the calculated values at the thermodynamic equilibrium for the CH_4 and CO_2 conversions, respectively

VI.6.3. Characterization of spent catalysts after DRM

VI.6.3.1. Carbon formation

The formation of carbon deposits on the surface of the spent $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 material is indeed confirmed by the 5 % weight loss detected at $T = 600^\circ\text{C}$ when submitted to the D and G bands visible by Raman spectroscopy (Figure IV-21) as well as by TGA analysis (Figure IV-22) [27] and by the observation of carbon nanotubes on the catalyst surface by scanning electron microscopy (Figure IV-23 b and b').

Regarding the Raman signals, the two main bands (D and G) are typical of the doubly degenerated phonon mode of C atoms in the sp^2 carbon networks with high degree of symmetry and of order (graphitic carbon, G-band, 1600 cm^{-1}) and of a disordered structural mode of carbon species (D-band, 1300 cm^{-1}). The

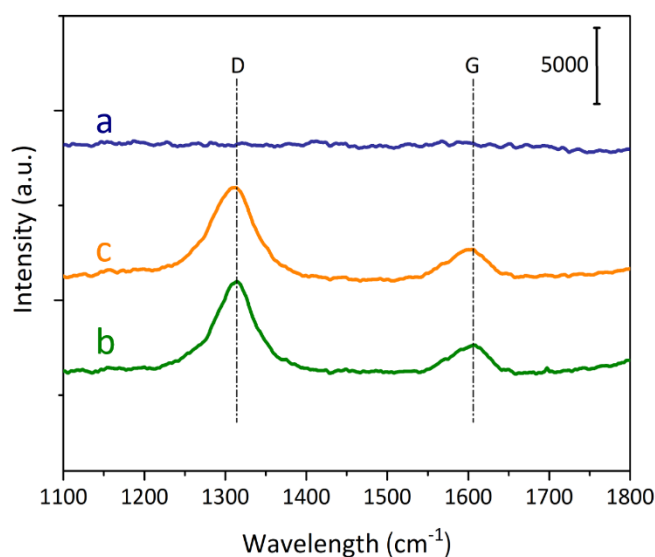


Figure IV-21: Raman spectroscopy profiles of the spent catalysts: a) $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, (b-) $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53, and (c) $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ COM

intensity ratio between these two bands can be used as an indicator of the crystalline degree and of the presence of defects in the carbon species; the smaller the ratio (<1) the higher the structural order. Here, both $\text{Ni}_5^0@Al_2O_3_{MIL-53}$ and $\text{Ni}_5^0@Al_2O_3_{COM}$ have a ratio significantly higher than 1 (4.6 and 4.2 respectively) which indicates the disordered character of the carbon deposits, in line with the occurrence of carbon nanotubes observed on these samples by electron microscopy.

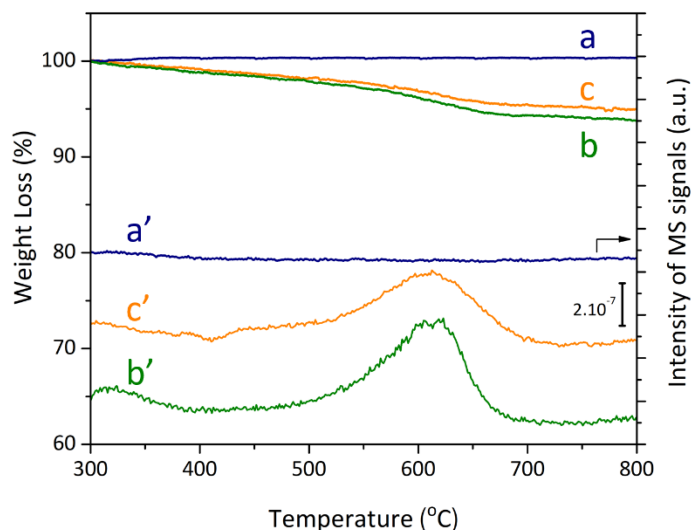


Figure IV-22: TGA profiles (at the top) associated to MS signals corresponding to CO_2 (at the bottom) of the spent (a-a') $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{MIL-53}$, (b-b') $\text{Ni}_5^0@Al_2O_3_{MIL-53}$, and (c-c') $\text{Ni}_5^0@Al_2O_3_{COM}$

Such deposits are similarly clearly identified on the spent $\text{Ni}_5^0@Al_2O_3_{COM}$ catalysts, with a TGA weight loss (7 %) even higher (Figure IV-22) in spite of the low activity of this

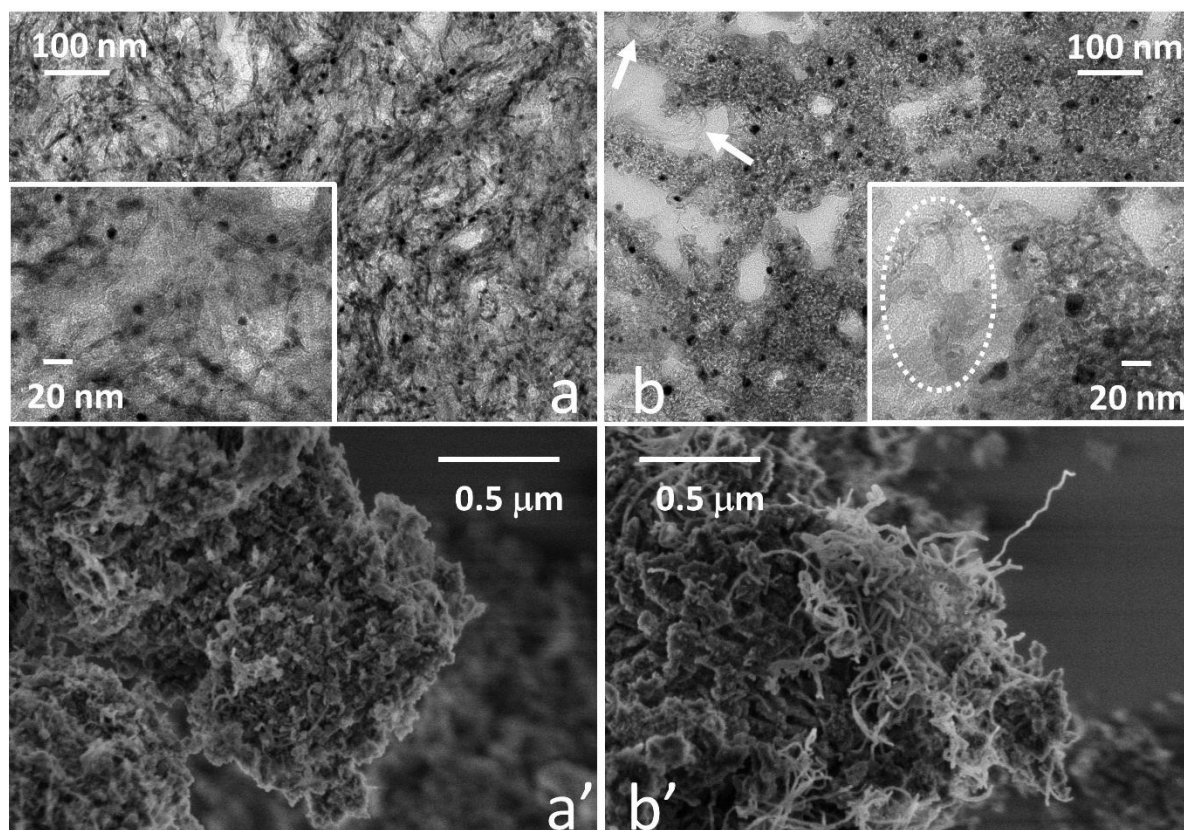


Figure IV-23: TEM (a,b) and SEM (a',b') images of spent (a,a') $\text{Ni}_5\text{-Al}_2\text{O}_3_{MIL-53}$ and (b,b') $\text{Ni}_5@Al_2O_3_{MIL-53}$. The dashed oval and white arrows in (b) highlight the presence of carbon nanotubes

catalyst (low conversion level) and with D and G bands still clearly displayed on the Raman spectrograph (Figure IV-21 c). In contrast, such deposits are not detected on the most active $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ material, even after the 100 h test, neither by TGA, nor by Raman spectroscopy or electron microscopy (Figure IV-23 a and a').

VI.6.3.2. Side reactions

The occurrence of side reactions on the reference $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$ material is confirmed by the products $\text{H}_2\text{:CO}$, which is initially below 1 and decreases with time (Figure IV-19 c), indicating some H_2 consumption through reverse water-gas shift (RWGS) reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) and/or direct reduction of CO_2 ($\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$) that consumes a part of the produced H_2 although this reaction is not possible being rather encountered in the 100-400 °C temperature range.

VI.6.3.3. Ni dispersion

These results demonstrate the superior performances of the catalysts prepared from MIL-53, especially of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ over $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$. The superiority of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ in term of conversion is in line with the better Ni^0 dispersion in this sample (Figure IV-23 a and Table IV-4). It moreover reveals, together with the remarkable selectivity of $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ to DRM all along the run (higher than on $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{MIL-53}}$ also prepared from MIL-53), a preservation of the active sites and hence a persistent strong nickel-support interaction even in the harsh conditions of reaction. This is seen by the high and comparable nickel dispersion both after reduction (Figure IV-15 a, a' and Figure IV-16 a) and after reaction (Figure IV-16 a and Figure IV-23 a). In contrast, a significant sintering takes place in $\text{Ni}_5^0\text{@Al}_2\text{O}_3_{\text{COM}}$ which the mean nickel particle size increases by about 30% after test (Table IV-5 and Figure IV-23 c,d). The formation in $\text{Ni}_5^0\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ of the stable spinel nickel aluminate phase, favored by the initial proximity between the nickel cations and the aluminum carboxylate clusters within the pore of MIL-53 during the calcination step, is believed to be at the origin of the stability of the dispersed Ni^0 nanoparticles. It could result from the presence of a remaining nickel aluminate spinel nanophase at the interface between the support and the metal nanoparticles after reduction that might insure a strong anchorage of the nanoparticles onto the resulting alumina support. One can also speculate that the layered texture of the material, which is remarkably well preserved during the 100h of reaction (Figure IV-23 a), contributes to the stability of the active phase as well by isolating and enhancing the occlusion of the nanoparticles, each of them being caught between two alumina sheets. This nanoparticle

confinement effect may also explain the absence of carbon production on this sample. This explanation is in line with previous data showing that the occlusion of nickel nanoparticles within the mesopores of alumina supports prevent the catalysis of carbon nanotube formation, which occurs only from the nickel nanoparticles located on the external surface of the support [244].

IV.7. Comparison of $\text{Ni}_5^0\text{-Al}_2\text{O}_3$ MIL-53 with other materials in literature

It is worth adding that although the nickel nanoparticles reported here are not the smallest reported in the literature so far (the application of atomic layer deposition recently afforded nanoparticle size below 3 nm [245]), this study demonstrates the potential of MOFs as sacrificial hosts for preparing highly dispersed nickel nanoparticles whose size is below than those prepared by employing other type of oxides as stable nickel cation hosts, such as alkaline earth metal substituted $\text{MZr}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ perovskites [246] or the lanthanum zirconate pyrochlore $\text{La}_2\text{Zr}_{2-x}\text{Ni}_x\text{O}_{7-\delta}$ [247]. Noteworthy, the use of MOF results in materials with a relatively high surface area (S. A. = $240 \text{ m}^2\cdot\text{g}^{-1}$) compared to that obtained with other types of purely inorganic sacrificial nickel host cited above (S.A. < $20 \text{ m}^2\cdot\text{g}^{-1}$), which can be seen as an additional benefit of this strategy in view of catalysis applications.

To end, and as a comparison $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 showed superior performance than an organized mesoporous based alumina catalyst. Organized mesoporous Al_2O_3 was prepared following the EISA route and impregnated with 5wt% Ni ($\text{Ni}_5\text{-Al}_2\text{O}_3$ Meso). The latter exhibited lower surface area than that of the MOF-based catalyst by 25% accompanied with a lower reduction temperature emphasizing on the less Ni-support interaction. This leads to larger particle size with retarded activity and appearance of carbon at the end of the reaction (Table IV-6).

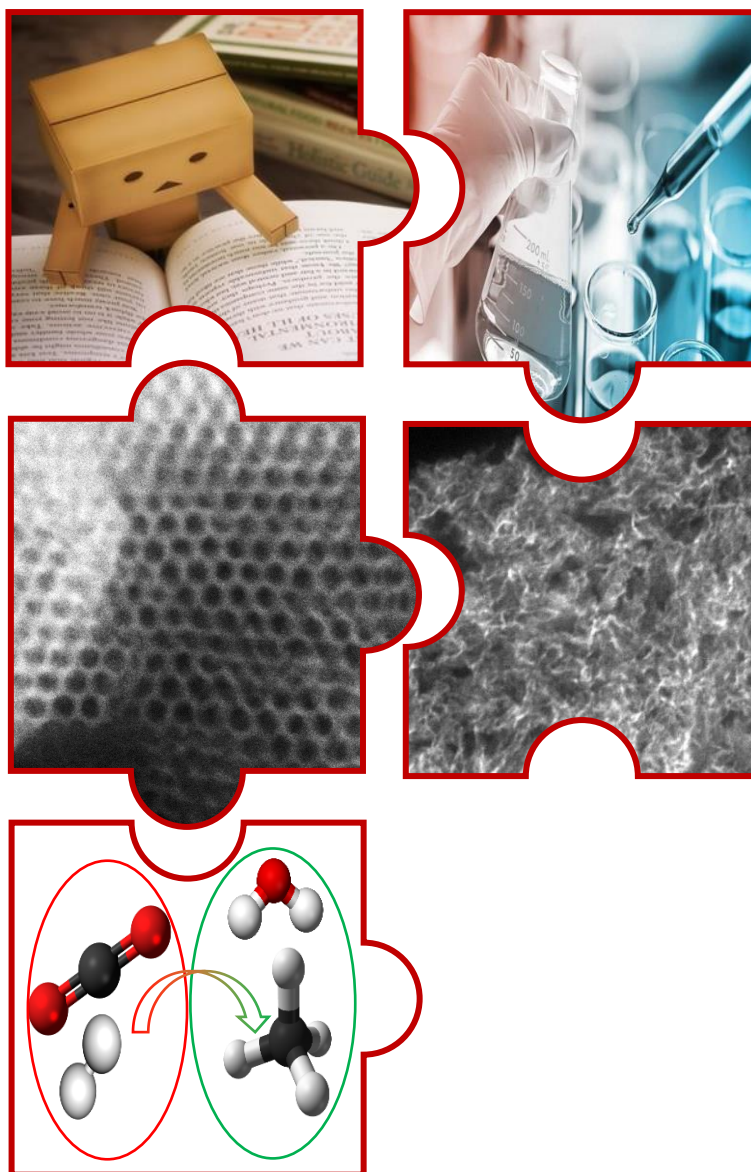
Table IV-6: Comparison between $\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53 and $\text{Ni}_5\text{-Al}_2\text{O}_3$ Meso

Catalyst	Maximum reduction temperature (°C)	Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Particle size (nm)		Activity at 650 °C		C(s)
			reduced	spent	t=0.5h	t=13h	
$\text{Ni}_5\text{-Al}_2\text{O}_3$ MIL-53	830	239	6.8	7	75-79	76-79	No
$\text{Ni}_5\text{-Al}_2\text{O}_3$ Meso	708	182	8.5	10	41-46	41-47	Yes

IV.8. Conclusion

In this work we highlighted on the benefit of using aluminum carboxylate MIL-53 as a sacrificial nickel precursor host to prepare a dry methane reforming catalyst composed of nickel nanoparticles dispersed within a porous γ -Al₂O₃ lamellar phase. The higher surface area of this metal-organic framework compared to preformed porous alumina supports allows for a more efficient dispersion of the nickel precursors and, in turn, for a superior dispersion and uniformity of the nickel nanoparticles obtained after the MOF calcination and subsequent reduction steps. Consequently, the performances in terms of activity, selectivity and stability of this new catalyst for dry reforming of methane within the reaction conditions applied in this study are higher than those of comparative nickel@alumina catalysts prepared by conventional nickel impregnation of preformed alumina supports. The results displayed in this report demonstrate that MOF can be considered as a promising hybrid alternative to the sacrificial inorganic and non-porous hosts (perovskite, hydrotalcites) used so far to stabilize nickel species towards the synthesis of catalysts based on nickel metal nanoparticles.

V. Chapter V: Mesoporous nickel-alumina catalysts for CO₂ methanation



The objective of chapter V is to check if the good materials seen in the previous chapters are efficient in another reaction of strong interest in the energy domain, CO₂ methanation. The principle of this application is to produce methane by converting CO₂ (greenhouse valorization) together with H₂ (generated by electrolysis from renewable energy surplus (wind/sun)). A brief summary about CO₂ methanation process and the Ni-Al₂O₃ based catalysts state-of-art are first reported. Then the preparation method and the composition of the Ni-Al₂O₃ materials used are described including different Ni loading and other classical Ni-based support (for comparison), before presenting their physicochemical properties and catalytic performances in this specific reaction. Note that this work was done in collaboration with the Portuguese team (University of Lisbon) in the core of the ERANETMED project providing me with the opportunity to do a 1 month internship in their laboratory and using the available facilities (i.e. CO₂ methanation equipment).

V.1. Literature Review

V.1.1. General definition

CO₂ methanation is the hydrogenation of CO₂ to methane, also known as Sabatier reaction. This process is receiving great attention because it is based on the production of CH₄ (chemical and energy production) from CO₂ (valorization of greenhouse gas) and H₂ that can be generated by electrolysis of water using excess of renewable electric energy (from solar and wind) produced in low consumption periods [28,248–250]. This wind to natural gas (CH₄) concept frequently called power-to-gas (P2G) relies on the existing gas grid infrastructures for storing and converting the generated fuel to electricity as seen in Figure V-1[28]. CO₂ methanation projects are dominant in Germany due to the transformation of its energy system to a 100% renewable one, triggered by the huge demand to chemically store the electric energy and the need to compensate the intermittency of wind and solar energy provision. The produced methane can be applied in the chemical industry, lowering

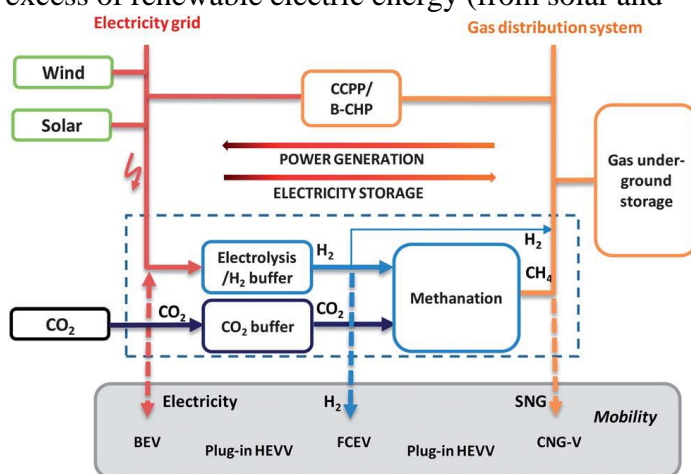


Figure V-1: Schematic describing wind to natural gas concept for bidirectional coupling of the electricity and gas grids [28]

the carbon footprint and the energy requirements. Complementary, this CH₄ can be also reused in DRM reaction. Moreover, an additional advantage in terms of energy saving is, as illustrated in Figure V-2, is that the energy produced during methanation (exothermic reaction) can be used to provide heat to perform DRM (endothermic reaction) (Modification of Eva-Adam process) [28,250,251].

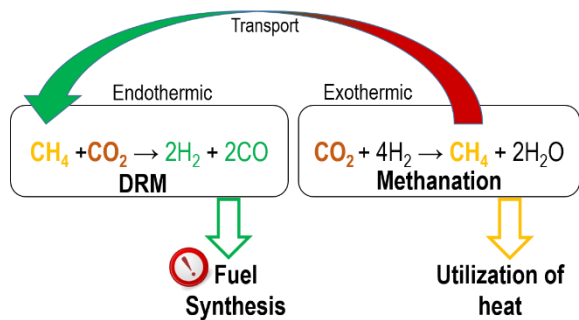


Figure V-2: Chemical energy storage using heat from renewables and DRM and methanation as energy carriers [251]

As already presented in chapter II, thermodynamic analysis demonstrates that, with a stoichiometric feed gas H₂/CO₂ of 4 and a temperature range of 200-350 °C, the main products will be only CH₄ and H₂O. As a result, the assumed methanation reaction is the following: CO₂ + 4H₂ ↔ CH₄ + 2H₂O. Since this reaction is an eight-electron process to fully reduce carbon dioxide to methane with significant kinetic limitations, a catalyst is mandatory to achieve acceptable rates and selectivity. Despite the difference in operating temperatures between DRM and CO₂ methanation, the catalysts used for both reactions have many similarities and the good catalysts found for DRM could be also suitable for methanation.

V.1.2. Catalysts applied in literature

In the state of the art regarding CO₂ methanation catalysts, many studies are based on nickel due to its high activity, selectivity and comparatively low price [248,252–254]. However, the operating temperatures should be high enough to avoid the potential formation of highly toxic nickel carbonyls from carbon monoxide, which defines the possible temperatures range between 200 and 550 °C [164]. Table V-1 illustrates some of the newest research studies that applied Ni-Al₂O₃ based catalysts in CO₂ methanation, summarizing the preparation method, nickel amount, some of the physicochemical properties of the reported materials and their performances towards CO₂ methanation. This table shows that, as observed in dry reforming of methane, Ni nanoparticles were also deposited on Al₂O₃ support using different insertion methods. However, a direct comparison between the reported catalysts is difficult due to the differences in the operating conditions used. Needless to say, Ni/Al₂O₃ materials prepared by standard impregnation methods [253,254] lead to relatively large particle sizes (10-30 nm), weakening the interaction with the support and favoring agglomeration processes during the course of the reaction. Ni/Al₂O₃ materials prepared by deposition-precipitation resulted in

smaller particle sizes (e.g. 3.2 nm) [255] but, the Ni interaction with Al₂O₃ was poor, leading to low activity (CO₂ conversion of 22%). The occurrence of deactivation during the test was attributed to the oxidation of the most active Ni sites in the presence of O₂ impurities. Moreover, as observed for DRM in chapter III, some reported studies on methanation also revealed that the addition of a basic additives such as Mn, CaO, Mg, Sr, Ba, or La ameliorate performances [256–258] due to an enhancement of the chemical adsorption of CO₂ that decreases in turn its activation energy [257].

Table V-1: Bibliography of some of the current Ni-Al₂O₃ based catalysts applied in CO₂ methanation

Catalyst	Preparation method	Ni amount (wt%)	S.A. (m ² .g ⁻¹)	Particle size (nm)	GHSV (L.g ⁻¹ .h ⁻¹)/ T(°C)	XCO ₂ (%)	SCH ₄ (%)	TOF (CO ₂ , s ⁻¹)
Ni/Al ₂ O ₃ ^[255]	DP ^a	10	200	3.7	26700*/300	22	85	8.10 ⁻²
Ni/Al ₂ O ₃ ^[259]	<i>In-situ</i> growth	20	143	5	2.4 / 265	90	99	2.4.10 ⁻³
Ni/Al ₂ O ₃ ^[253]	I.W.I ^b	15	260	n.m.	2400* / 260	17	15	6.57.10 ⁻³
Ni/Al ₂ O ₃ ^[254]	W.I.	125	n.m.	10-30	52300* / 500	71	86	n.m.
Ni-Al ₂ O ₃ ^[260]	EISA	15	206	4	91 ^c / 400	82	97	n.m.
Ni/Al ₂ O ₃ ^[261]	Microwave	20	163	10	4.2 / 325	85	90	n.m.
Ni-Ru-Mn-Al ₂ O ₃ ^[262]	I.W.I	60	47	n.m.	0.5 / 400	100	72	n.m.
Ni-CaO/Al ₂ O ₃ ^[256]	I.W.I	15	7	n.m.	n.m. / 450	66	92	n.m.
Ni-Ru-CaO -Al ₂ O ₃ ^[194]	EISA	10	308	5	30 / 380	84	100	2.15.10 ⁻³
Ni-CaO/Al ₂ O ₃ ^[257]	I.W.I	20	144	11.2	16000*/500	70	42	n.m.
Ni-Mg/Al ₂ O ₃ ^[257]	I.W.I	20	170	10.8	16000*/500	67	35	n.m.
Ni-Sr/Al ₂ O ₃ ^[257]	I.W.I	20	157	9.3	16000*/500	72	50	n.m.
Ni-Ba/Al ₂ O ₃ ^[257]	I.W.I	20	161	11.1	16000*/500	67	55	n.m.
Ni-La/Al ₂ O ₃ ^[258]	I.W.I	13.6	100	10	55000*/377	n.m.	78	n.m.

a: deposition-precipitation, b: incipient wetness impregnation, c: H₂:CO₂ = 5:1

*: unit in h⁻¹, n.m.: not mentioned, S.A.: surface area, XCO₂: CO₂ conversion, SCH₄: CH₄ selectivity

Some reports on preparation methods, similar to ours, involving *in-situ* growth (one-pot Ni addition), microwave or EISA techniques can also be found in literature for methanation, but not numerous. They resulted in better catalytic performance with improved CO₂ conversion and CH₄ selectivity, but still suffered from deactivation due to sintering (from 5 to 8.5 nm) [259], oxidation [260], or little carbon formation [261].

The use of MOF-based catalysts is also not null in CO₂ methanation as it was in DRM, but it is very new and introduced, to our knowledge, to few research studies involving expensive noble metals [263–265], cobalt [266], and nickel [267,268] nanoparticles with different size. However, even for Ni-MOF, the catalysts were very distinct from ours since they were mostly

used in non-calcined form. In the example given by Zhen et al. [267] MOF-5 was used to disperse 5 to 12.5 wt% Ni. The best catalyst, with 10 wt% Ni, gave 75% CH₄ yield at 320 °C (GHSV=125 ml.min⁻¹.g⁻¹, P= 1atm) and had a metal Ni average size of 9 nm. The same authors showed that, under similar catalytic test conditions, the activity of 20 wt% Ni deposited on MIL-101 [268] was better than other nickel-supported materials (γ -Al₂O₃, SiO₂, TiO₂). Even though these MOFs displayed good catalytic performances in CO₂ methanation, they are unstable at high temperature and thermally decompose.

For this reason, MOFs can be used instead as a sacrificial template resulting in carbonaceous or purely inorganic materials depending on the thermal treatment adopted. This route has not been applied so far, to our knowledge, for Ni-based MOF and the catalyst prepared following this method in CO₂ methanation is a Co metal [266]. In this study the MOF used is ZIF-67 pyrolyzed under N₂ atmosphere, and later reduced with H₂ to obtain Co-based porous carbon (PC) with Co nanoparticles between 7-20 nm in size. This catalyst had a high surface area of 346 m².g⁻¹ with a CH₄ yield of 52 % at 270 °C (GHSV=1200 ml.min⁻¹.g⁻¹, P= 30 atm) and no sintering of Co nanoparticles which make them enticing compared to Co supported on commercial activated carbon catalyst.

From this aspect, and attracted by the high surface area and metal dispersion that our mesoporous Ni-Mg-Al₂O₃ synthesized by one-pot method (chapter III) and Ni-Al₂O₃ derived from MIL-53(Al) (chapter IV) have, and their encouraging results in DRM, we thought that these new materials can also bring new outcomes to the field of CO₂ methanation.

V.2. Synthesis of mesoporous one-pot Ni_x-Mg_y-Al₂O₃ and Ni_x-Al₂O₃ derived from MIL-53(Al) materials

The preparation methods followed for the two sets of materials studied in this chapter are similar to the elaborated explanation in section III.2 for mesoporous Ni_x-Mg_y-Al₂O₃ and section IV.2 for mesoporous Ni_x-Al₂O₃ derived from MIL-53(Al). The only difference that might reside between the samples from this chapter and the previous ones is the amount of Ni added. Table V-2 and Table V-3 summarize all the mesoporous magnesium-based alumina and MOF derived samples, respectively. Some of the obtained Ni-Al₂O₃ samples (MOF-based materials specifically) were also compared to other more classical materials used in the Portuguese partner team as listed at the bottom of Table V-3. They all contain 15 wt% Ni

deposited by incipient wetness impregnation on Cs-USY zeolite (Si/Al_{global} of 38) [269,270], mesoporous commercial SBA-15 [271], and one-pot EISA alumina supports.

Table V-2: Summary of the prepared one-pot mesoporous Ni_xMg_y-Al₂O₃ samples

Sample code	Ni _x Mg _y Al _z atomic formula	Metal contents (wt%)		Weight of chemical added (g)			
		Ni	Mg	P123	Al[OCH(CH ₃) ₂] ₃	Ni(NO ₃) ₂ ·6H ₂ O	Mg(NO ₃) ₂ ·6H ₂ O
Al ₂ O ₃	Ni ₀ Mg ₀ Al ₁₀₀	-	-	7	14.3	0	0
Ni ₅ -Al ₂ O ₃	Ni ₅ Mg ₀ Al ₉₅		0		13.6	1.02	0
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	Ni ₅ Mg ₁₅ Al ₈₀	5	7		11.5	1.02	2.7
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	Ni ₅ Mg ₅₀ Al ₄₅		26		6.5	1.02	9
Ni ₁₀ -Mg ₁₅ -Al ₂ O ₃	Ni ₁₀ Mg ₁₅ Al ₇₅	10			10.7	2.03	2.7
Ni ₁₅ -Mg ₁₅ -Al ₂ O ₃	Ni ₁₅ Mg ₁₅ Al ₇₀	15	7		10.0	3.05	2.7
Ni ₂₀ -Mg ₁₅ -Al ₂ O ₃	Ni ₂₀ Mg ₁₅ Al ₆₅	20			9.3	4.07	2.7

Table V-3: Summary of mesoporous Ni_x-Al₂O₃ materials derived from MIL-53 framework

Sample	Support	Mode of Ni insertion	Ni contents (wt%)
MIL-53		-	-
Ni ₅ -Al ₂ O ₃ MIL-53	Synthesized	I.W.I Prior MIL calc.	5
Ni ₁₅ -Al ₂ O ₃ MIL-53			15
Ni ₂₀ -Al ₂ O ₃ MIL-53			20
Ni ₁₅ @Al ₂ O ₃ MIL-53		I.W.I After MIL calc.	15
Ni ₁₅ @USY	Commercial	I.W.I	15
Ni ₁₅ @SBA-15			
Ni ₁₅ -Al ₂ O ₃ One-Pot	Synthesized	One-pot	

The following results are divided into two parts. The first part tackles the magnesium-based mesoporous alumina materials and the effect of nickel and magnesium amount on CO₂ methanation. The second part includes the MOF based alumina samples with different nickel contents that are in turn compared to other Ni-based samples and evaluated also in CO₂ methanation reaction.

V.3. Physicochemical properties followed by CO₂ methanation over mesoporous Ni_x-Mg_y-Al₂O₃ materials

V.3.1. Variation of Mg content and its influence on CO₂ methanation

V.3.1.1. Physicochemical properties

In this part, three samples were chosen for comparison: Ni₅-Al₂O₃, Ni₅-Mg₁₅-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃. To avoid repetition, their physicochemical properties results are not presented here since they are detailed in Chapter III, and Table V-4 summarizes certain values. Note that the values in brackets and italic font for the surface area and pore volume as well as the italic font for the nickel nanoparticles size correspond to the reduced form of the materials.

Table V-4: Physicochemical properties of calcined and reduced (*in italic*) Ni_x-Mg_y-Al₂O₃ materials

Catalyst code	h index ^a	V _{tot} ^b (cm ³ /g)	S.A. ^b (m ² /g)	ΦNi ⁰ ^c (nm)	Dispersion ^d (%)
Ni ₅ -Al ₂ O ₃	0.55	0.49 (0.32)	234 (173)	4.6	21
Ni ₅ -Mg ₁₅ -Al ₂ O ₃	0.45	0.56 (<i>n.d.</i>)	240 (<i>n.d.</i>)	4.5	21
Ni ₅ -Mg ₅₀ -Al ₂ O ₃	0.38	0.54 (<i>n.d.</i>)	205 (<i>n.d.</i>)	8.8	11
Ni ₁₀ -Mg ₁₅ -Al ₂ O ₃	0.41	0.57 (0.52)	247 (219)	5.85	17
Ni ₁₅ -Mg ₁₅ -Al ₂ O ₃	0.46	0.54 (0.45)	203 (160)	6.37	15
Ni ₂₀ -Mg ₁₅ -Al ₂ O ₃	0.45	0.47 (0.48)	197 (198)	9	11

^a determined from TGA-DSC experiments; ^b total surface area (S.A.) and total pore volume (V_{tot}) calculated from the N₂ sorption isotherms, in brackets: reduced materials; ^c value estimated from the histograms obtained from representative TEM images of each reduced sample; ^d nanoparticle dispersion calculated from TEM of reduced samples

V.3.1.2. Surface adsorption properties

The interaction with water was evaluated since H₂O is a reaction product that could have an eventual relevant inhibitory role in the methanation reaction [166,269,272–278]. In addition, and in the specific case of zeolites (crystalline alumina-silicate materials) water could be chemically adsorbed on CO₂ activation sites, playing another inhibitory role in the reaction [269,279,280]. The strength of the water interaction with the catalysts was estimated by determining the h index by TGA-DSC experiments that were done in Portugal. Briefly, an h index value close to 1 indicates that the samples are not strongly interacting with water (most of the water molecules will be easily desorb below 150 °C) while indexes close to 0 indicate stronger interaction between water and the catalysts (only a small fraction of water molecules desorb below 150 °C). As seen in Table V-4, increasing the Mg loading strengthens the interaction between water and the samples with h index decreasing from 0.55 in Ni₅-Al₂O₃ to

0.38 in Ni₅-Mg₅₀-Al₂O₃. This decrease can lead to a higher water concentration over the catalysts during the reaction and higher inhibitory effect.

The interaction of the samples with CO₂ was also characterized by collecting CO₂ isotherms (experiments performed in Portugal by degassing the calcined samples then adsorbing CO₂ at 0 °C). This technique, was adopted in the present study for comparing the affinity of the samples towards CO₂. Results, illustrated in Figure V-3, present the same CO₂ uptake for all the three materials at high pressures but, in terms of affinity (low relative pressure points), Ni₅-Mg₅₀-Al₂O₃ presents significantly enhanced CO₂ uptakes. This agrees with the higher content of CO₂ adsorbed on this sample compared to those containing 0 and 7 wt% Mg as seen by Infra-red data in chapter III (Figure III-9).

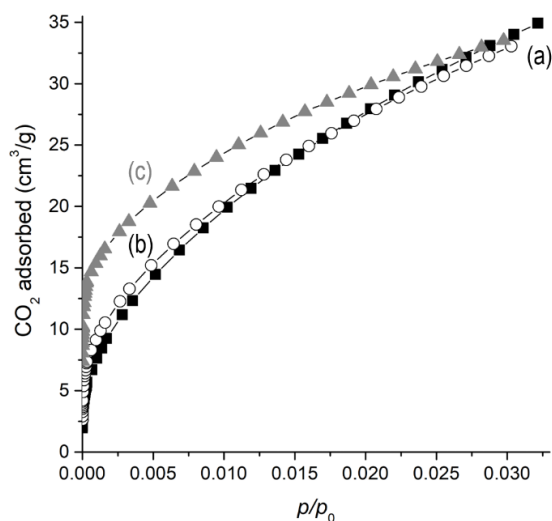


Figure V-3: CO₂ isotherms obtained for (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃ and (c) Ni₅-Mg₅₀-Al₂O₃ samples

V.3.1.3. CO₂ methanation on Ni₅-Mg_y-Al₂O₃ mesoporous materials

Catalytic test results of these materials are depicted in Figure V-4. CO₂ conversions increase with temperatures, and do not follow the trend of the theoretical CO₂ conversion curve that starts at very high value (97 %) and decrease with temperatures. This difference is due to the presence of a barrier in the kinetics that limits CO₂ activation. As for the variation in Mg content, mesoporous Ni₅-Mg₁₅-Al₂O₃ catalyst has higher CO₂ conversions than Ni₅-Al₂O₃ over all temperatures range. This behavior resembles what was seen for DRM reaction and solidifies the efficiency of Mg in enhancing performances of the catalyst by increasing the surface basicity that

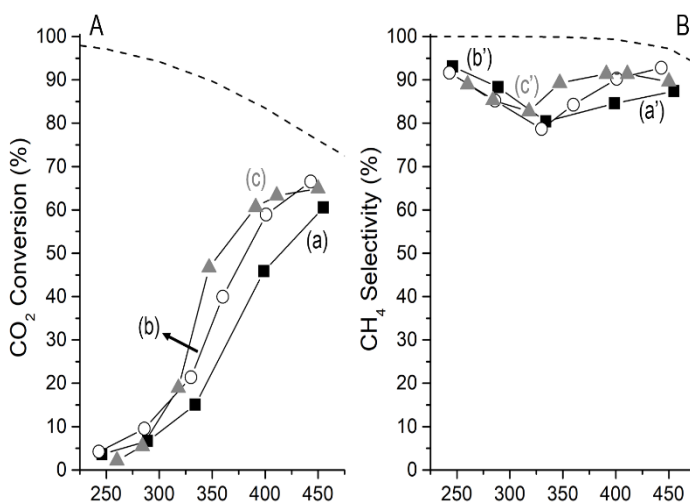


Figure V-4: (A) CO₂ conversion and (B) CH₄ selectivity of (a-a') Ni₅-Al₂O₃, (b-b') Ni₅-Mg₁₅-Al₂O₃, and (c-c') Ni₅-Mg₅₀-Al₂O₃

intensifies CO₂ chemisorption and, subsequently, activates CO₂ during the course of the reaction [182,281–287]. A suggested mechanism can explain the difference: on Ni₅-Al₂O₃ catalyst, CO₂ methanation is expected to be indicated by dissociation of CO₂ into carbon species (CO_{ads}) and an oxygen species (O_{ads}) over the catalyst surface. CO_{ads} then reacts with H atoms to generate CH₄ through several reaction mechanism steps on Ni active sites, responsible for dissociating H₂ into H atoms. When Mg is added to the sample, the formation of CO_{ads} is increased suppressing its desorption process into CO leading to higher CH₄ selectivity. Reaching 26 wt% of Mg (Ni₅-Mg₅₀-Al₂O₃), CO₂ conversion is not improved and its behavior looks similar to the 7 wt% Mg sample. This unimproved activity could be related to the lower Ni dispersion (11%), higher interaction with water (h index: 0.38) and damage in the structured mesoporosity. In addition, excessive Mg basic promoter would firmly adsorb CO₂ as seen in CO₂ adsorption curves, making its desorption step more difficult covering Ni neighbor active sites and hindering H₂ activation. The results agree well with the performance of the materials in DRM reaction. For further investigation on the effect of Ni content in the mesoporous alumina samples in the next paragraphs, Ni₅-Mg₁₅-Al₂O₃ was selected as having the best compromise between Mg promoter content (7 wt%), metallic dispersion (21 %), catalyst reducibility and CO₂ affinity.

V.3.2. Influence of Ni content in Ni_x-Mg₁₅-Al₂O₃ catalysts with constant Mg loading

V.3.2.1. Ni_x-Mg₁₅-Al₂O₃ structural, textural, and surface properties

The Ni amount was varied from 5 to 20 wt% keeping a constant Mg content of 7 wt%.

Till a Ni content up to 10 wt%, no diffraction peaks are observed in the XRD patterns (Figure V-5) similarly to the behavior seen in Chapter III, stressing on the high dispersion achieved in this type of sample when adding a low to moderate nickel amount. Reaching 15 wt% Ni (Ni₁₅-Mg₁₅-Al₂O₃), new diffraction peaks appear at different diffraction angles ($2\theta = 37^\circ, 43^\circ, \text{ and } 63.5^\circ$) and become more intense in the case of Ni₂₀-Mg₁₅-Al₂O₃

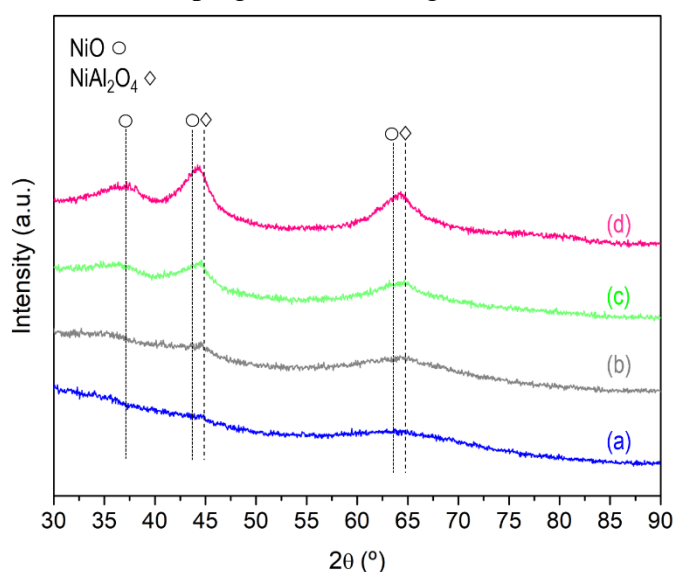


Figure V-5: XRD patterns of calcined (a) Ni₅-Mg₁₅-Al₂O₃, (b) Ni₁₀-Mg₁₅-Al₂O₃, (c) Ni₁₅-Mg₁₅-Al₂O₃, and (d) Ni₂₀-Mg₁₅-Al₂O₃ samples

(curve d). The peaks are broad and no fully symmetrical revealing a possible simultaneous presence of two species (NiAl₂O₄ and NiO), and disturbing repartition of Ni particles in response to the increase of Ni loading.

The water strength affinity (Table V-4) was not affected by the change of Ni content with comparable h values of 0.41-0.46. Thus, the inhibitory effect of water in the reaction is not expected to vary from one sample to another.

Regarding the textural properties, these materials also present the characteristics of mesoporous materials with type IV isotherm and H1 hysteresis loop (Figure V-6 A) accompanied with narrow pore size distribution and average pore diameter of 6-9 nm. As the Ni loading increases from 5 to 20 wt%, a gradual decrease in both pore volumes and surface areas occurs (Table V-4), due to more nickel species filling the pores of alumina support and limiting N₂ accessibility.

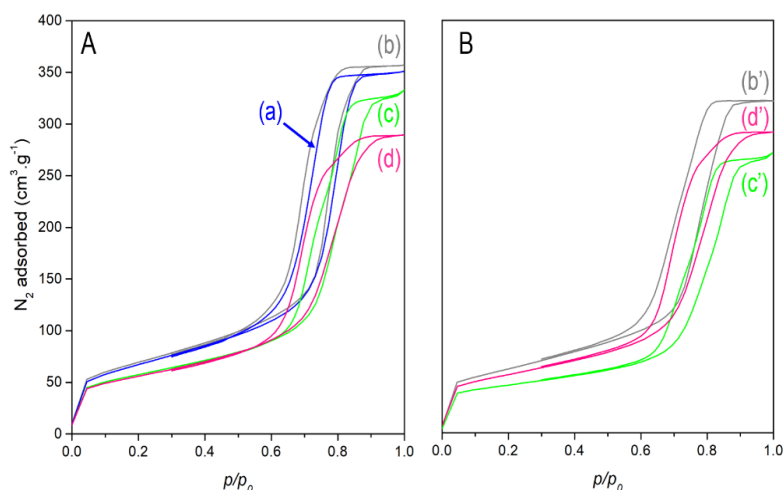


Figure V-6: N₂-sorption curves of (A) calcined and (B) reduced (a-a') Ni₅-Mg₁₅-Al₂O₃, (b-b') Ni₁₀-Mg₁₅-Al₂O₃, (c-c') Ni₁₅-Mg₁₅-Al₂O₃, and (d-d') Ni₂₀-Mg₁₅-Al₂O₃ samples

due to more nickel species filling the pores of alumina support and limiting N₂ accessibility.

V.3.2.2. Surface properties and reducibility of Ni_x-Mg₁₅-Al₂O₃ samples

CO₂ affinity (Figure V-7 A) profiles vary as follows: Ni₅-Mg₁₅-Al₂O₃ >> Ni₁₅-Mg₁₅-Al₂O₃ > Ni₁₀-Mg₁₅-Al₂O₃ > Ni₂₀-Mg₁₅-Al₂O₃. This means that when Ni is present in lower quantity compared to Mg, the interaction with CO₂ increases. In contrast, similar or higher Ni loading than Mg in the alumina samples limits the accessibility of CO₂ to the adsorption sites.

The reducibility of these samples (Figure V-7 B) behaves similarly to the samples in Chapter III with a unique reduction peak between 600 and 800 °C, asserting on the strong metal support interaction even with high Ni loadings. Reduction peaks of both Ni₁₅-Mg₁₅-Al₂O₃ and Ni₂₀-Mg₁₅-Al₂O₃ samples are shifted to a slightly higher temperature than Ni₅-Mg₁₅-Al₂O₃, in agreement with XRD measurements, showing presence of Ni as NiAl₂O₄ [287–289], retarding their reduction. The H₂-uptake was in agreement with the Ni percentage present in each sample

with around 800 $\mu\text{mol.g}^{-1}$ H₂ consumed for Ni₅-Mg₁₅-Al₂O₃, 1600 $\mu\text{mol.g}^{-1}$ for Ni₁₀-Mg₁₅-Al₂O₃, 2400 $\mu\text{mol.g}^{-1}$ for Ni₁₅-Mg₁₅-Al₂O₃, and 3300 $\mu\text{mol.g}^{-1}$ consumed for Ni₂₀-Mg₁₅-Al₂O₃.

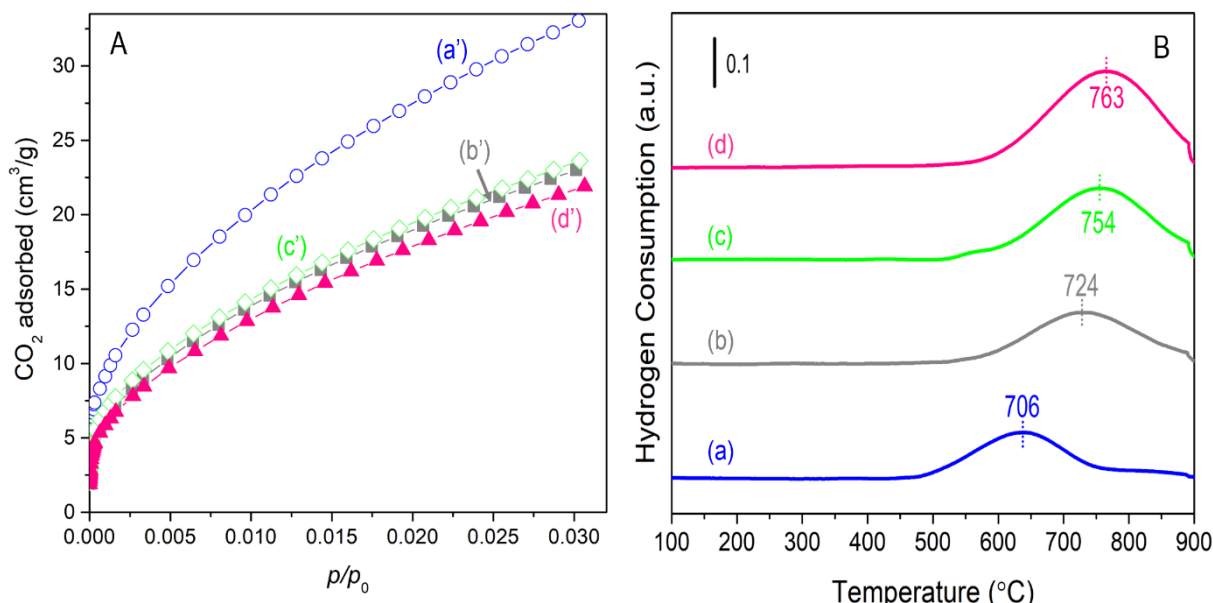


Figure V-7: (A) CO₂ isotherms and (B) H₂-TPR profiles of calcined (a-a') Ni₅-Mg₁₅-Al₂O₃, (b-b') Ni₁₀-Mg₁₅-Al₂O₃, (c-c') Ni₁₅-Mg₁₅-Al₂O₃, and (d-d') Ni₂₀-Mg₁₅-Al₂O₃ samples

Reduced Ni_x-Mg₁₅-Al₂O₃ samples exhibit an increment of metallic nickel particle size from 4.5 to 9 nm in the Ni content range of 5-20 wt% as demonstrated by TEM (Table V-4).

V.3.2.3. CO₂ methanation on mesoporous Ni_x-Mg₁₅-Al₂O₃ catalysts

All the reduced samples were tested in CO₂ methanation (Figure V-8). When going from the Ni₅-Mg₁₅-Al₂O₃ to Ni₁₀-Mg₁₅-Al₂O₃ then Ni₁₅-Mg₁₅-Al₂O₃ catalysts the activity (CO₂ conversion) progressively increases in line with the increment in Ni content, each metal site being active for the dissociation of H₂ into H atoms [290–294]. This increase is however not totally proportional to Ni content due to slight changes in the metal dispersion (Table V-4). When moving from Ni₁₅-Mg₁₅-Al₂O₃ to Ni₂₀-Mg₁₅-Al₂O₃, the CO₂ conversion is no longer

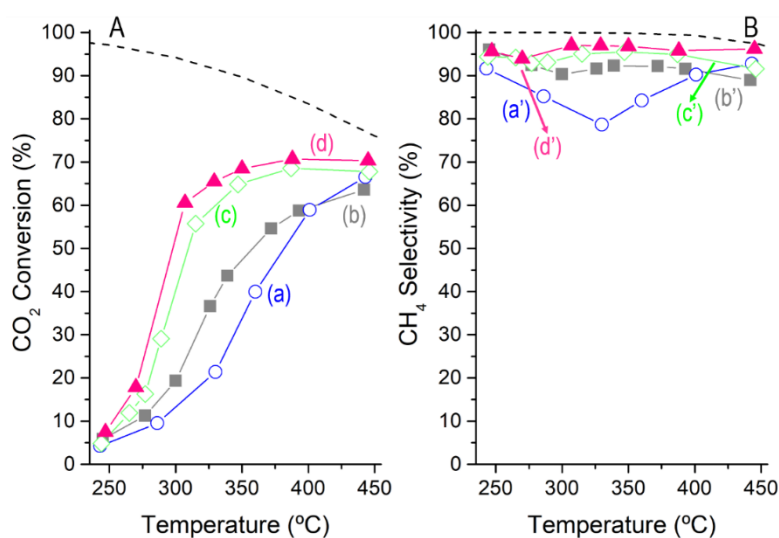


Figure V-8: (A) CO₂ conversion and (B) CH₄ selectivity of (a-a') Ni₅-Mg₁₅-Al₂O₃, (b-b') Ni₁₀-Mg₁₅-Al₂O₃, (c-c') Ni₁₅-Mg₁₅-Al₂O₃, and (d-d') Ni₂₀-Mg₁₅-Al₂O₃ samples

improved because of the significantly lower Ni dispersion. In the frame of this work, we were not able to perform H₂-TPD and TOF calculations on the series of samples with varying Ni content that would be necessary to reach a better quantification of activities as was done in chapter III for DRM.

Stability tests carried out on both Ni₅-Mg₁₅-Al₂O₃ and Ni₁₅-Mg₁₅-Al₂O₃ at 315 °C for 10 hours (Figure V-9) demonstrate high stability of the samples through time with no evidence of any deactivation. This performance suggests the absence of sintering of nickel nanoparticles. Note also that the selectivity to methane is close to 100% on Ni₁₅-Mg₁₅-Al₂O₃ while it is 10 % less on Ni₅-Mg₁₅-Al₂O₃ on which some side product (notably CO) is formed due less sites for H₂ dissociation.

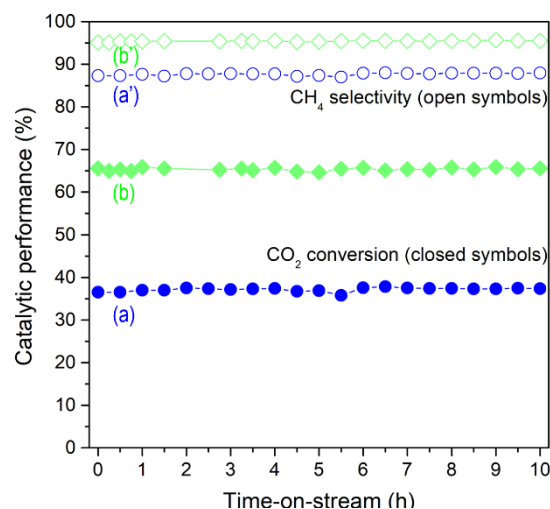


Figure V-9: Stability test in terms of (a-b) CO₂ conversion and (a'-b') CH₄ selectivity of (a-a') Ni₅-Mg₁₅-Al₂O₃ and (b-b') Ni₁₅-Mg₁₅-Al₂O₃

To conclude this part, the results of the most promising sample (Ni₁₅-Mg₁₅-Al₂O₃) were compared to other Ni-based prepared by conventional or by one-pot method in literature (Table V-5). All the presented studies used much more favorable contact times (almost six times higher than the one used in this work) and milder conditions than ours. Therefore, a direct comparison is complicated, but, with the harsh conditions used, in our case, the results obtained for mesoporous Ni₁₅-Mg₁₅-Al₂O₃ are comparable and even better (first 2 rows) than those shown in the table, indicating promising future for these materials in the CO₂ methanation reaction.

Table V-5: Comparison of the performances revealed by the most promising Ni-Mg-Al₂O₃ material from the present work with other traditional (first two rows) and one-pot Al₂O₃ samples reported in the literature

Catalyst	Catalytic tests conditions			Best catalytic performances achieved			Ref.
	<i>P</i> (bar)	<i>H</i> ₂ :CO ₂	<i>GHSV</i> (ml.min ⁻¹ .g ⁻¹)	<i>T</i> (°C)	CO ₂ conversion (%)	CH ₄ selectivity (%)	
15Ni-20Ca/Al ₂ O ₃	1	4:1	-	450	66	92	[256]
10Ni-8Mg/Al ₂ O ₃	1	4:1	16000 h ⁻¹	500	67	35	[257]
10Ni-8Ca-Al ₂ O ₃	1	4:1	250	350	76	98	[284]
10Ni-3Pr-Al ₂ O ₃	1	4:1	250	350	74	98	[295]
10Ni-1Ru-2Ca-Al ₂ O ₃	1	4:1	500	380	84	>99	[194]
Ni ₁₅ -Mg ₁₅ -Al ₂ O ₃	1	4:1	1440	350	65	95	This work

V.4. Physicochemical properties followed by CO₂ methanation over mesoporous Ni_x-Al₂O₃ materials derived from MIL-53 framework

V.4.1. Textural and structural properties of calcined samples

Figure V-10 A (curves a-b) shows the XRD patterns of Ni₅-Al₂O₃ MIL-53 (same sample as in chapter IV) and Ni-enriched (15 wt% Ni) Ni₁₅-Al₂O₃ MIL-53 calcined materials derived from MIL-53. Both samples exhibit the same three main peaks seen at $2\theta = 37^\circ$, 45.0° and 65.6° in chapter IV that structurally correspond to a cubic spinel NiAl₂O₄ phase with (220), (400) and (440) planes (JCPDS: 001-1299) [28,48,49] with higher intensity in Ni₁₅-Al₂O₃ MIL-53 sample. The absence of NiO crystalline peaks confirms the assumption of an intimate mixing between Ni and the oxide support even with higher nickel loading (15 wt%). For instance, NiO species reacts with alumina during the high temperature calcination to form a new stable crystal phase

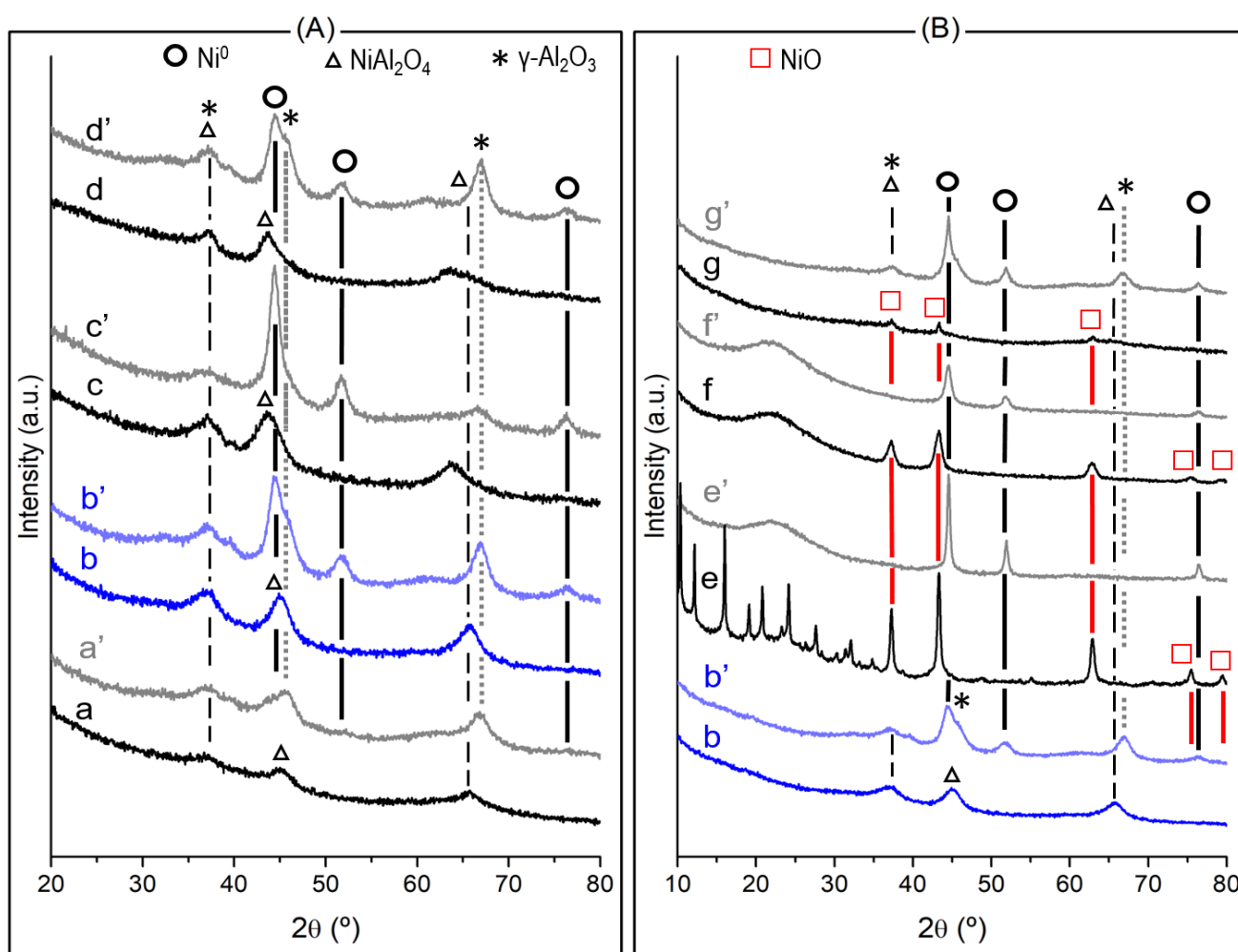


Figure V-10: XRD patterns of calcined (a-g) and reduced (a'-g') samples respectively: a-a') Ni₅-Al₂O₃ MIL-53, b-b') Ni₁₅-Al₂O₃ MIL-53, c-c') Ni₂₀-Al₂O₃ MIL-53, d-d') Ni₁₅@Al₂O₃ MIL-53, e-e') Ni₁₅@USY, f-f') Ni₁₅@SBA-15, and g-g') Ni₁₅-Al₂O₃

that belongs to a cubic system with Fd-3 m space group. The spinel structure consists of an ensemble of tetrahedral coordination occupied with bivalent Ni²⁺ and octahedral coordination filled with trivalent Al³⁺ cations. This scattering can be altered when Ni²⁺ partially adopts the octahedral site while the tetrahedral site hosts Al³⁺ together with Ni²⁺ ions resulting in a family of compounds of inverse spinel structure known as Ni_{1-x}[Ni_xAl_{2-x}]O₄ where 0 < x < 1. This structure flexibility could enhance the interaction between Ni and the support, restrict the aggregation of metallic Ni sites, and increase their dispersion [169,173,296].

The diffraction peak ($2\theta = 65.6^\circ$) of Ni₂₀-Al₂O₃ MIL-53 containing 20 wt% Ni is shifted slightly to the left, which could reveal the presence of a small fraction of NiO species in addition to NiAl₂O₄. Same observation was detected for Ni₁₅@Al₂O₃ MIL-53 where nickel is impregnated after MIL-53 calcination suggesting a lower degree of interaction with the support and confirming that the order of nickel impregnation with respect to calcination has an influence towards nickel dispersion [297,298].

Ni₁₅-Al₂O₃ MIL-53 was compared to other materials prepared with different support type having a fixed 15 wt% Ni percentage (Figure V-10 B). Ni₁₅@USY (e), Ni₁₅@SBA-15 (f), and Ni₁₅-Al₂O₃ (g) show diffraction peaks at $2\theta = 37.2^\circ$, 43.1° and 62.8° attributed to NiO species that correspond respectively to the planes (111), (200) and (220) with face centered cubic cell (JCPDS: 01-071-4750) suggesting lower interaction with the support and larger particle size. Table V-6 indicates NiO average particle size of 17.2 nm, 8.6 nm, and 8 nm for Ni₁₅@USY, Ni₁₅@SBA-15, and Ni₁₅-Al₂O₃ respectively.

Table V-6: Ni-nanoparticle sizes of the calcined and reduced materials, and metallic Ni dispersion on reduced samples

Catalyst code	Φ NiO ^a (nm)	Φ Ni ⁰ ^b (nm)	Ni ⁰ dispersion ^c (%)
Ni ₅ -Al ₂ O ₃ MIL-53	-	- (7.0)	14
Ni ₁₅ -Al ₂ O ₃ MIL-53	-	5.6 (8.6)	12
Ni ₂₀ -Al ₂ O ₃ MIL-53	-	7.1 (9.4)	11
Ni ₁₅ @Al ₂ O ₃ MIL-53	-	6.2 (9.2)	11
Ni ₁₅ @USY	17.2	18.9 (25)	4
Ni ₁₅ @SBA-15	8	9.7 (17.1)	6
Ni ₁₅ -Al ₂ O ₃ one-pot	8.6	8.8 (9.0)	11

a: value of NiO particle size estimated from XRD diffractograms of calcined materials; b: value of metallic Ni⁰ nanoparticle estimated from XRD of reduced materials, in brackets: nanoparticle size from the histograms obtained from representative TEM images of each samples; c: nanoparticle dispersion calculated from TEM

Increasing the Ni amount from 5 to 20 wt% does not alter the shape of the isotherm in all Ni-Al₂O₃ materials derived from MIL-53 and all of them resembles the shape already seen and discussed in chapter III. Ni₅-Al₂O₃ MIL-53, Ni₁₅-Al₂O₃ MIL-53, and Ni₂₀-Al₂O₃ MIL-53 have close values of surface area (230-250 m².g⁻¹, Table V-7) and pore volume (0.97-1.09 cm³.g⁻¹) indicating that this method is adequate for a wide range of nickel loadings (5-20 wt%). Regarding Ni₁₅@Al₂O₃ MIL-53 sample that is calcined then impregnated, its surface area (156 m².g⁻¹) and pore volume (0.42 cm³.g⁻¹) are lower by 30 and 50% respectively than the samples that are firstly impregnated by Ni on MIL-53(Al) framework and later calcined.

The textural properties obtained by physisorption are well confirmed by HRTEM images. For instance, both Ni₅-Al₂O₃ MIL-53, and Ni₁₅-Al₂O₃ MIL-53 present a fused ill-defined and defective alumina flakes composed of several randomly interwoven nanosheets with approximately 20 nm in length (Figure V-11 A, A' and B, B'). Ni₁₅-Al₂O₃ MIL-53 (Figure V-11 B, B') has no detection of nickel particles confirming the results of XRD that reveal the presence of NiAl₂O₄ instead of NiO. This accentuates on the efficiency of MIL-53(Al) derived method to highly and homogeneously distribute Ni throughout the samples even if higher Ni amount is used.

Table V-7: Main textural properties of the calcined and reduced samples prepared in the present work

Catalyst code	h index ^a	V _{micro} ^b (cm ³ .g ⁻¹)	V _{meso} ^b (cm ³ .g ⁻¹)	S.A. ^b (m ² .g ⁻¹)
MIL-53	-	0.4	0.4	1130
Al ₂ O ₃ MIL-53	-	-	1.19	318
Ni ₅ -Al ₂ O ₃ MIL-53	0.64	-	0.97 (0.85)	230 (225)
Ni ₁₅ -Al ₂ O ₃ MIL-53	0.60	-	1.09 (1.02)	251 (150)
Ni ₂₀ -Al ₂ O ₃ MIL-53	0.58	-	1.05 (0.71)	245 (175)
Ni ₁₅ @Al ₂ O ₃ MIL-53	0.54	-	0.42 (0.29)	156 (81)
USY	-	0.208	0.271	298
Ni ₁₅ @USY	0.87	0.16 (0.01)	0.20 (0.25)	259* (261)*
SBA-15	-	-	1.02	701
Ni ₁₅ @SBA-15	0.98	0.11 (0.07)	0.66 (0.62)	487 (422)
Al ₂ O ₃ One-Pot	-	-	0.52	258
Ni ₁₅ -Al ₂ O ₃ One-Pot	0.38	-	0.13 (0.11)	60 (44)

^a determined from TGA-DSC experiments; ^b total surface area (S.A.), microporous (V_{micro}) and mesoporous (V_{meso}) pore volume calculated from the N₂ sorption isotherms, in brackets: reduced materials *S_{ext} determined using t-plot method for the zeolite sample after calcination and reduction

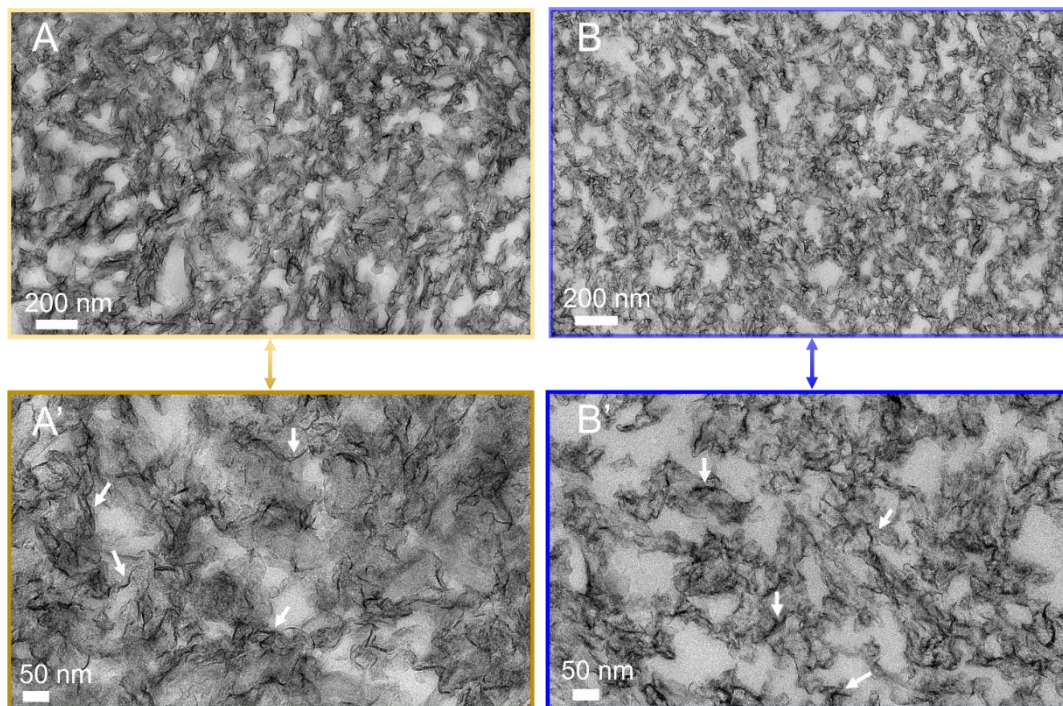


Figure V-11: HR-TEM Micrographs of fresh Ni-Al₂O₃ MIL-53 catalysts: (A-A') Ni₅-Al₂O₃ MIL-53, (B-B') Ni₁₅-Al₂O₃ MIL-53.

The h indexes determined for the different Ni_x-Al₂O₃ MIL-53 samples are somehow quite similar (~0.6 in all cases, Table V-7) neglecting any impact of this parameter on the catalytic performances.

V.4.2. Reducibility of Ni_x-Al₂O₃ MIL-53 materials

The reducibility of all calcined Ni_x-Al₂O₃ MIL-53 materials (Figure V-12 A) with different Ni wt% (5-20 wt%) present similar reduction profiles with one reduction curve occurring at temperatures above 500 °C. The absence of a second reduction peak at lower temperature indicates that the Ni species present in these sample are all strongly interacting with the support [271], as in spinel mixed phases with no weakly bounded Ni species [287–289]. These results agree well with what has been seen in XRD and TEM. Thus, the impregnation of nickel nitrate on the parent MIL-53 allows the formation of an Al₂O₃-NiAl₂O₄ phase in which nickel and aluminium cations are intimately mixed in a homogenous oxide phase over a wide range of Ni loading (5-20 wt%). Note that a small displacement in the maximum reduction temperature towards lower temperatures was observed for Ni₂₀-Al₂O₃ MIL-53 (Figure V-12 A, c) insisting on the formation of small fraction of easier reducible Ni species that is in good agreement with XRD results showing a shift of the peak from 2θ of 65° to 63°.

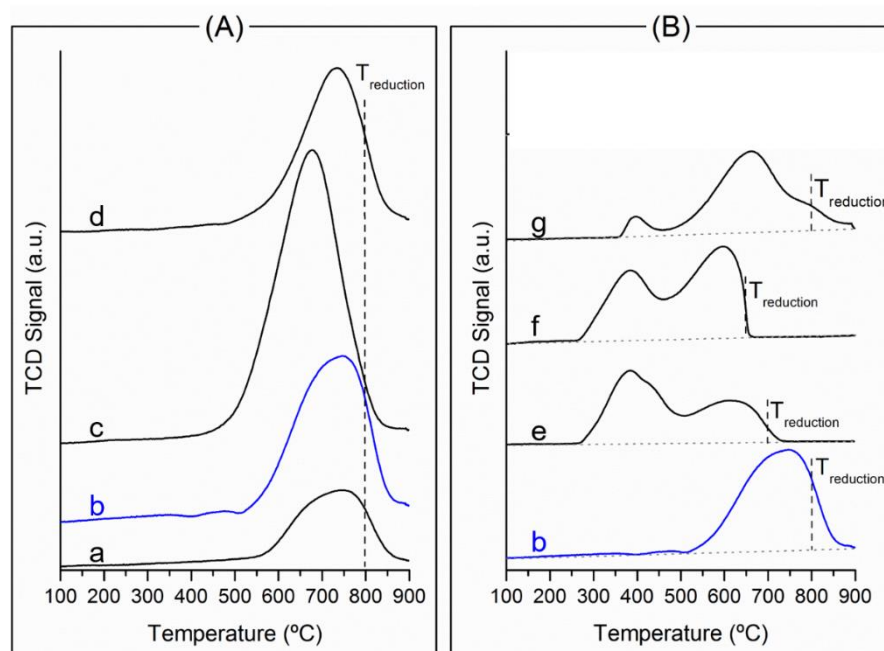


Figure V-12: H₂-TPR profiles for calcined (A) MOF-derived samples: (a) Ni₅-Al₂O₃ MIL-53, b) Ni₁₅-Al₂O₃ MIL-53, c) Ni₂₀-Al₂O₃ MIL-53, and d) Ni₁₅@Al₂O₃ MIL-53 and (B) other Ni-based materials: (e) Ni₁₅@USY, f) Ni₁₅@SBA-15, and g) Ni₁₅-Al₂O₃

Compared to other non-MOF samples, microporous (Ni₁₅@USY) or mesoporous (Ni@SBA-15, Ni₁₅-Al₂O₃_{One-pot}) in texture, non-Al₂O₃ based materials Ni₁₅@USY and Ni₁₅@SBA-15 acquire the highest h index of 0.87 and 0.98, respectively due to the presence of silica that makes them more hydrophobic compared to alumina-based sample that is known to be hydrated when in contact with H₂O.

On the other hand, the non-MOF based materials present two reduction peaks at low ($T < 500$ °C) and high ($T > 500$ °C) temperatures, asserting the existence of different types of nickel species with distinctive metal-support interactions. Ni₁₅@USY (Figure V-12 B e) contains Ni species that are present mainly as NiO and whose reduction processes occur at ~320 °C (NiO in the zeolite external surface) and 400 °C (NiO in the zeolite supercages) as demonstrated elsewhere [269,287,299–301]. A smaller additional reduction peak occurred at a temperature above 600 °C attributed to the reduction of NiO species present in the mesoporous cavities of this specific commercial zeolite [287,293,300,301]. Ni₁₅@SBA-15 (Figure V-12 B f) presents also two reduction peaks, one at ~400 °C and the second one is at ~600 °C, attributed to NiO species weakly (external surface) and strongly (mesoporous channels) interacting with the silica support, respectively [185,293,302]. Ni₁₅-Al₂O₃ One-pot (Figure V-12 B g) presents a main reduction peak at ~700 °C, as in the case of the MOF-derived material, due to reduction of Ni strongly interacting with Al₂O₃ [303,304]. However, this sample presents also a less

relevant reduction process at ~400 °C corresponding to the reduction of NiO species weakly interacting with Al₂O₃ matrix. These results are compatible with XRD measurements that showed clear peaks of NiO species.

V.4.3. Textural and structural properties of reduced materials

XRD patterns of the Ni_x-Al₂O₃ MIL-53 samples reduced at 800 °C are shown in Figure V-10 (A) along with those before reduction. The reduction of all MIL-53 based materials contributed to the formation of new diffraction peaks attributed to (111), (200) and (220) planes of crystalline Ni⁰ at 2θ of 44.5°, 51.9° and 76°, respectively (JCPDS: 03-065-0380). In addition, bands corresponding to gamma-alumina appear clearly in the reduced materials asserting on the Ni extraction from NiAl₂O₄ oxide phase to metallic Ni⁰ on the pore surface. Scherrer equation was applied at 2θ of 51.9° for all the samples and it leads to a mean Ni particle size of <5 nm, 5.6 nm, 7.1 nm and 6.2 nm for Ni₅-Al₂O₃ MIL-53, Ni₁₅-Al₂O₃ MIL-53, Ni₂₀-Al₂O₃ MIL-53 and Ni₁₅@Al₂O₃ MIL-53 respectively (Table V-6). These particle sizes are systematically smaller than the ones between 9 and 20 nm reported in literature on other MOF materials [266,267]. Thus, these data highlight again that this new strategy of occluding nickel inside the pores of alumina following MIL-53 route is very efficient and capable of producing small nickel particles even for high nickel loading.

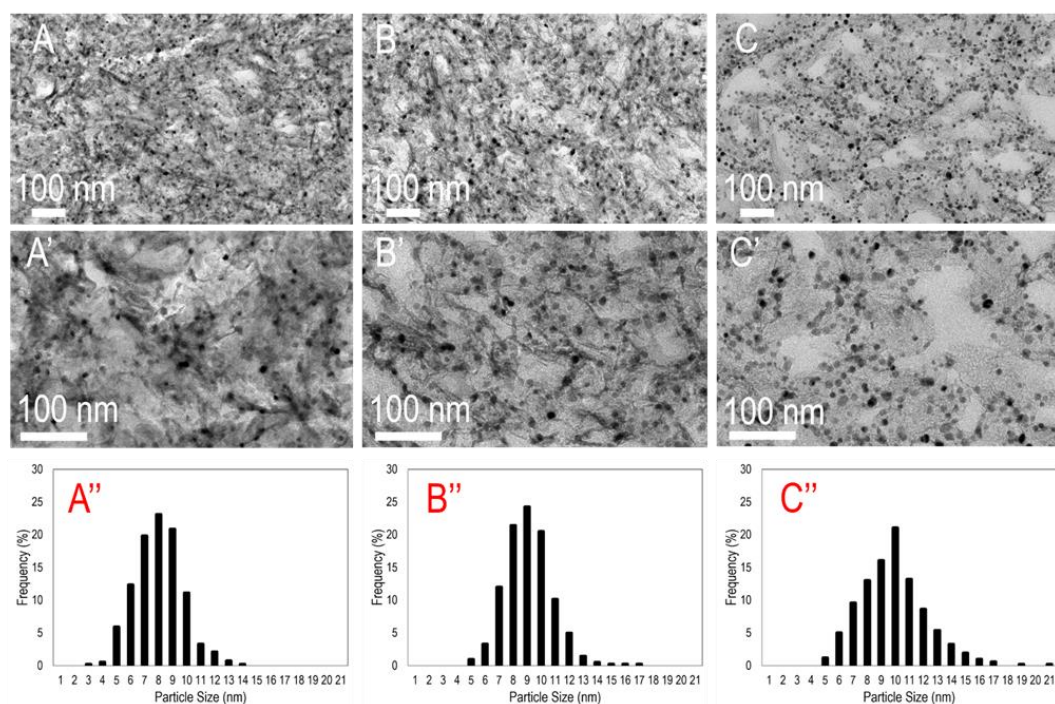


Figure V-13: HR-TEM Micrographs and Ni⁰ particle size distribution of reduced catalysts: (A-A'') Ni₅-Al₂O₃ MIL-53, (B-B'') Ni₁₅-Al₂O₃ MIL-53, and (C-C'') Ni₂₀-Al₂O₃ MIL-53

Particle sizes obtained from TEM (Table V-6) confirm further the trend seen in XRD even if the mean values are slightly higher in TEM (due probably to the difficulty to detect very small particles). Detected nickel particles (Figure V-13), independent from Ni loading, are homogeneously distributed all over the support, which still appears as interwoven alumina sheets. This morphology was also preserved in the physisorption shape of the reduced Ni_x-Al₂O₃ MIL-53 samples showing a slit-like hysteresis typical of a layered material with unorganized interlayered pores. The surface area decreased due to shrinkage of material after harsh reduction temperature at 800 °C or to growth of Ni particles due to phase transformation of NiAl₂O₄ into gamma-alumina and metallic Ni⁰ nanoparticles spacing apart the nanosheets one from another (Table V-6).

Compared with the non-MIL-53(Al) based materials, their particle size was larger with eventually lower dispersion (Table V-6). Ni₁₅@SBA-15 (9.7 nm (XRD)/ 17 nm (TEM)) and Ni₁₅@USY (19 nm (XRD)/ 25 nm (TEM)) had the lowest dispersion compared to other alumina-based samples. They demonstrated the weakest metal-support interactions with negative impact on the particle size, easily inducing sintering. These results confirm what was mentioned in literature about the importance of Al₂O₃ support in enhancing the metal-support interaction, increasing dispersion and enhancing stability compared to ZrO₂, TiO₂ and SiO₂ [59].

V.4.4. Catalytic performances of Ni-based catalysts

Ni_x-Al₂O₃ MIL-53 catalysts derived from MIL-53 framework showed that increasing Ni content enhances the catalytic performances in terms of both CO₂ conversion and CH₄ selectivity as function of temperature (Figure V-14). The conversion of CO₂ increased when passing from 5 to 20 wt% Ni. This enhancement in methanation performances, could be attributed to the increase in the number of Ni⁰ active sites available for H₂ dissociation [275,294,301,305–307].

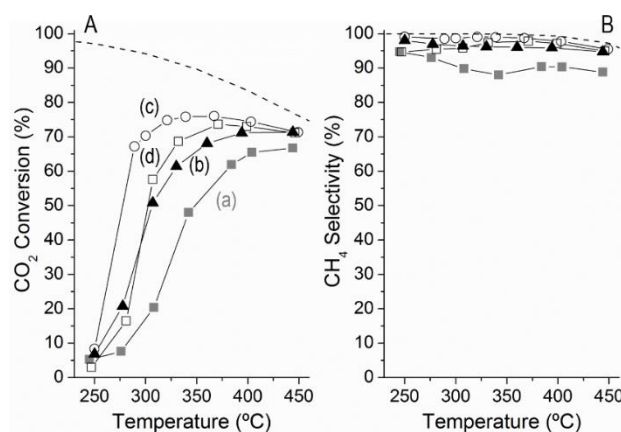


Figure V-14: (A) CO₂ conversion and (B) CH₄ selectivity of a) Ni₅-Al₂O₃ MIL-53, b) Ni₁₅-Al₂O₃ MIL-53, c-) Ni₂₀-Al₂O₃ MIL-53, and d) Ni₁₅@Al₂O₃ MIL-53

Ni₁₅-Al₂O₃ MIL-53 with 15 wt% Ni was tested over a long period of 20 h at 350 °C (Figure V-15). It showed excellent stability proving resistibility towards any deactivation. The conversion of CO₂ was high about 72% with an outstanding selectivity of 98% that is constant during the time. These results affirm that Ni-Al₂O₃ catalysts derived from MOF framework are

new and interesting materials for this environmental catalytic application, proving their efficiency in terms of both activity and stability. This excellent performance is further affirmed by TEM of the spent Ni₁₅-Al₂O₃ MIL-53 catalyst after reaction (Figure V-16). The catalyst textural properties were preserved with high nickel dispersion and an average Ni particle size of 7.3 nm (confirmed by XRD) casting any chance of sintering. TGA experiment was also applied on the spent materials showing no weight loss at a temperature range of 200 and 900 °C confirming as well the absence of carbon.

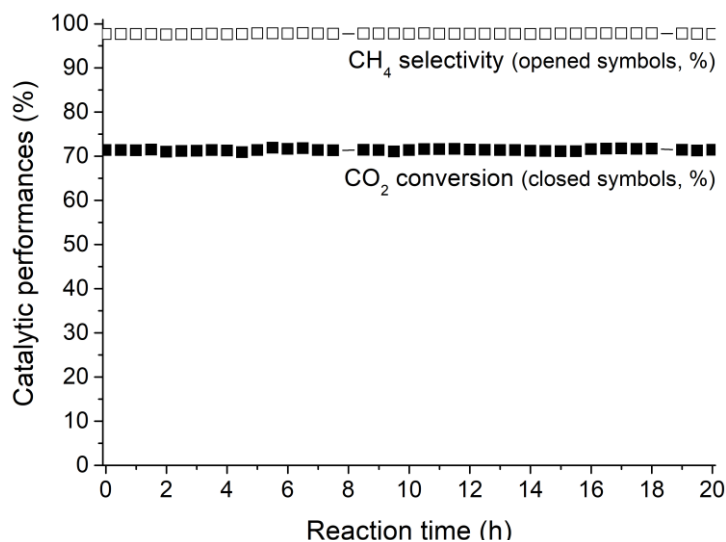


Figure V-15: Stability test of Ni₁₅-Al₂O₃ MIL-53 over 20 h time on stream

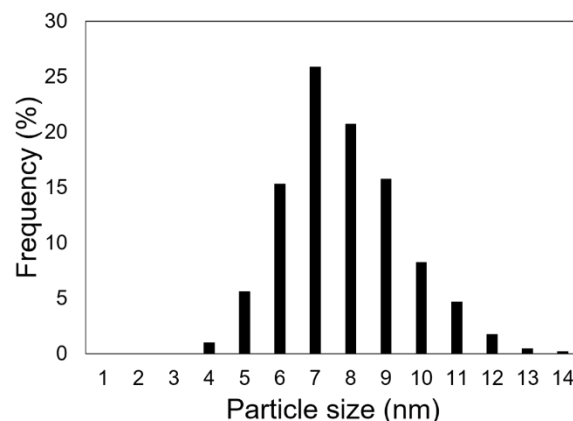
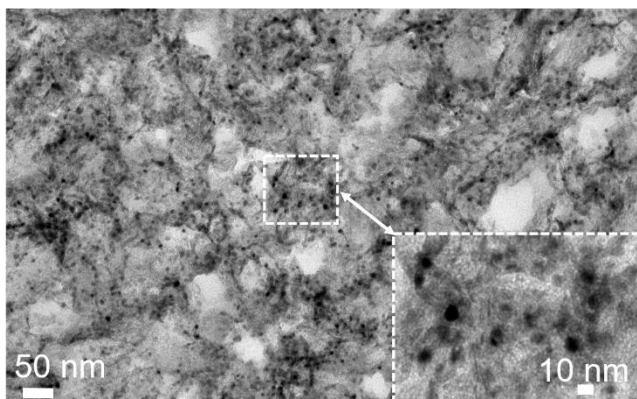


Figure V-16: TEM micrograph of spent Ni₁₅-Al₂O₃ MIL-53 after CO₂ methanation reaction. Conditions: T=350 °C, GHSV=1440 ml.g⁻¹.min⁻¹, H₂:CO₂= 4:1

Again, Ni₁₅-Al₂O₃ MIL-53 was compared to other non-MIL-53 materials (Figure V-17), this time with the catalytic performance. It is clear that Ni₁₅-Al₂O₃ MIL-53 acquires the highest activity among all the presented samples over all temperature range. This behavior is expected since Ni₁₅-Al₂O₃ MIL-53 possesses the

strongest interaction between Ni active phase and Al₂O₃ support, the highest dispersion, and the smallest particle size (7 nm) avoiding possibilities of Ni sintering that decreases in turn the number of active metal sites. Note that Ni₁₅@USY should have the lowest activity since it has the worst parameters in terms of Ni particle size and Ni-support interaction. The reason behind such unexpected trend, could be due to some better CO₂ adsorption on this sample especially that zeolite can play a role in the catalytic test enhancing the interaction between its compensating cations and carbon dioxide. Similar phenomenon has been seen in one of the literature [269] showing that sintering in zeolites does not change catalytic performance.

Ni₂₀-Al₂O₃ MIL-53 was compared at the end to the catalytic performance test of a commercial Ni@γ-Al₂O₃ (25 wt% Ni). Figure V-18 A shows that Ni₂₀-Al₂O₃ MIL-53 presents better activity than the commercial catalyst tested under the same conditions. This is due to the higher metallic surface area available in the MOF sample for the reaction and to the higher metal-support interactions, enhancing dispersion and boosting catalytic performance. Both samples were however stable over time (Figure V-18 B), with a CO₂ conversion of 75% and a CH₄ selectivity of 99% for Ni₂₀-Al₂O₃ MIL-53 compared to 60% CO₂ conversion and 95% CH₄ selectivity for Ni@γ-Al₂O₃.

Finally, Ni₂₀-Al₂O₃ MIL-53 was compared to other MOFs (as support or template) based materials applied in CO₂ methanation reaction (Table

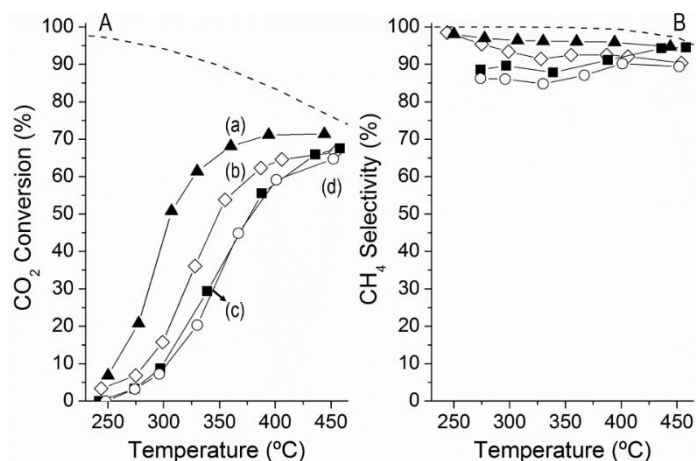


Figure V-17: (A) CO₂ conversion and (B) CH₄ selectivity of (a) Ni₁₅-Al₂O₃ MIL-53, (b) Ni₁₅@USY, (c) Ni₁₅@SBA-15, d) Ni₁₅-Al₂O₃

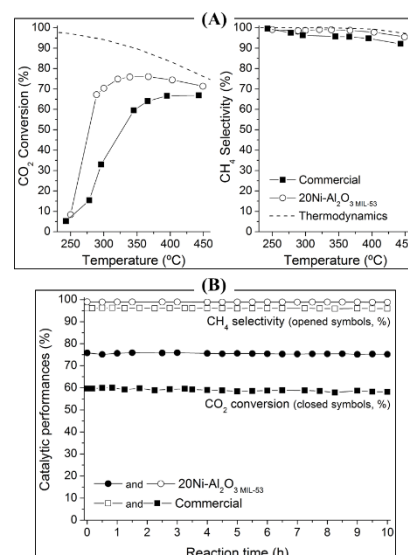


Figure V-18: (A) CO₂ conversion and CH₄ selectivity and (B) stability at 350 °C of Ni₂₀-Al₂O₃ MIL-53 and Ni@γ-Al₂O₃

V-8). Needless to say, the contact times used in the present work are less favorable than the ones reported in other studies. However, results indicate that using an Al-based MOF as precursor results in better outcomes in terms of both CO₂ conversion and CH₄ selectivity. Consequently, the presented work constitutes a great advance in the use of active, selective and stable Ni-MOF-derived materials for CO₂ methanation, especially when taking into account that few studies have been reported till the moment in this area.

Table V-8: Comparison of the performances revealed by the best MOF-derived material from the present work with similar reported catalysts in the literature.

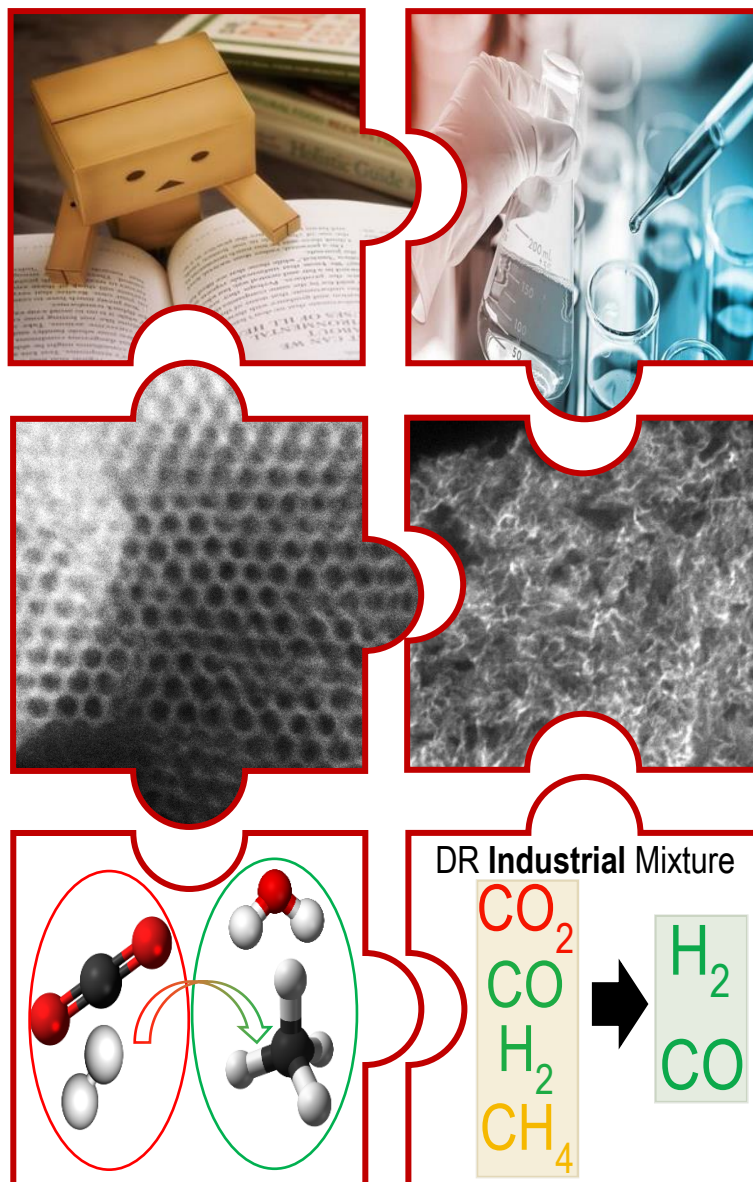
Catalyst	MOF	Metal amount (wt%)	Catalytic tests conditions			Best catalytic performances achieved			
			<i>P</i> (bar)	<i>H</i> ₂ :CO ₂	<i>GHSV</i> (ml.min ⁻¹ .g ⁻¹)	<i>T</i> (°C)	CO ₂ conversion (%)	CH ₄ selectivity (%)	TOF (s ⁻¹)
1%Ru-ZrO ₂ ^[263]	UiO-66	1	30	4:1	317	350	96	99	n.a.
32.5%Co-PC ^{a[266]}	ZIF-67	32.5	30	4:1	1200	270	53	99	n.a.
10%Ni/MOF-5 ^{b[267]}	MOF-5	10	1	4:1	125	320	75	>99	n.a.
Pd@UiO-66 ^{b[264]}	UiO-66	6	40	4:1	250	340	56	97	n.a.
Pt/UiO-66 ^{b[265]}	UiO-66	3		5.2:1	110	350	49	36	n.a.
20%Ni/MIL-101 ^{b[268]}	MIL-101	20	1	4:1	125	320	>99	>99	1.41 · 10 ⁻³
20%Ni-Al ₂ O ₃ [*]	MIL-53	20	1	4:1	1440	300	70	>99	2.67 · 10 ⁻¹

^a PC: Porous carbon; ^bMOF-5, UiO-66, MIL-101 structures not collapsed during the preparation nor the pre-activation, ^{*} This work

V.5. Conclusion

In summary, mesoporous Ni₅-Mg_y-Al₂O₃ and Ni₅-Al₂O₃ derived from MIL-53 framework, good in DRM (chapters III-IV), also exhibit good performances in CO₂ methanation reaction. As for DRM, in the Ni₅-Mg_y-Al₂O₃ series of catalysts, an optimum amount of 7 wt% Mg favors both CO₂ conversions and CH₄ selectivity avoiding MgO segregation and keeping sufficient basic sites to activate CO₂ species and enhance the reaction mechanism. This chapter also shows that Ni loading can be increased up to 15 wt% conserving to a certain extent very good dispersions in both the proposed one-pot EISA and MOF routes. This leads to enhanced conversion of carbon dioxide and high selectivity to methane provided by the high metallic surface area available for the dissociation of hydrogen. The obtained Ni₁₅-Al₂O₃ MIL-53 catalyst has superior performances than USY zeolite, SBA-15 material and Ni-Al₂O₃ commercial or synthesized by a different method. Ni-Al₂O₃ derived from MIL-53 framework led to superior results compared to the few existing MOF-based materials already used in CO₂ methanation. Needless to say, the promising activity, selectivity and stability of the synthesized materials turn them into potential catalysts for a large-scale application of power-to-gas as in DRM.

VI. Chapter VI: Promotion of mesoporous nickel-alumina based catalysts by magnesium addition for reforming of waste gasification products



This chapter ends the thesis report by tackling dry reforming over a more complex mixture containing not only CH_4 and CO_2 in the feed, but also H_2 and CO . The addition of the product within the feed mixture makes the reaction more challenging, but more realistic. The non-conventional model mixture was taken from a pyrolysis product unit after treatment of biomass wastes in a Lebanese industry partner of the SOL-CARE project. A thermodynamic study was done on the obtained mixture in dry reforming to check the expected behavior. Then, the reaction was applied on mesoporous $\text{Ni}_5\text{-Mg}_y\text{-Al}_2\text{O}_3$ materials to investigate the efficiency of these catalysts, with good performance in standard DRM, under harsh conditions.

VI.1. Literature Review

As mentioned earlier in Chapter I of this report, biomass is one of the alternative sources of energy that can be used to limit the dependency on fossil fuels and their impact on the global environment. The process of conversion of biomass to energy encompasses a wide range of different renewable sources. The organic biomass wastes are derived from garbage, animal manure and biodegradable materials. This technology consists a thermochemical route to convert biomass. This method divided into 2 options which choice depends on the desired form of energy and on the type and quantity of biomass feedstock available [308–310]:

1. Combustion: It is the direct burning of biomass into air where the chemical energy stored inside it will be converted to heat, mechanical power and electricity that can be used for example in furnaces, boilers (heating water, cooking), and steam turbines. This method is wasteful of resources (low conversion efficiency, less than 25% chemical energy of the solids converted to thermal and electrical energy).

2. Pyrolysis and gasification: It is the partial oxidation of biomass in absence of O_2 or presence of air at around 500-800 °C [311]. Gaseous products mostly contain a mixture of CH_4 , CO_2 , H_2 , and CO gases, some light hydrocarbons (chars), tars, ash and minor contaminants (NH_3 , H_2S , SO_2) [312]. The produced gas can be burnt directly or used as a fuel for gas turbines and engines if it has low calorific value. Otherwise the gaseous mixture (CH_4 , CO_2 , H_2 , CO) can be transformed under suitable reactions to syngas (H_2 and CO) and used as feedstock in the production of liquid fuels (Fischer-Tropsch synthesis) and methanol, each of which may be served as fuels for transportation.

It is recommended, for time saving and environmental considerations, to carry out gasification/pyrolysis in a unique one-stage reactor [313–316]. Nevertheless, no satisfactory production of clean syngas (H_2 , CO) was obtained and formation of tar can block the reactor in

such conditions. A two-stage reactor [317–319] was developed where the waste is first pyrolyzed to produce a range of pyrolysis gases that pass directly to a second-stage catalytic reactor where catalytic reforming takes place to generate higher yield of hydrogen or syngas. Even if very attractive, such type of combined reactor will not be considered in this work because efforts are still needed to improve each individual step, and the focus will remain targeted towards the reforming stage to find a good catalyst that can handle the complex product mixture of the pyrolysis reaction.

As seen in chapter I, a great effort has been made in literature on developing reforming catalysts conducted using model compounds (CH_4 , and CO_2 only), whereas those involving real raw material are still limited. Few studies worked on reforming of gasification/pyrolysis products using different type of catalysts. The final reforming product also had distinct syngas ratio (probably due to the type of waste used). For example, Juniza MD Saad et al. [320] performed catalytic dry reforming on evolved gas from pyrolysis of plastics. The composition of the pyrolysis product gas was not specified. Ni-Co-Al catalyst used increased syngas yields with an $\text{H}_2:\text{CO}=0.5$. However, carbon formation occurred during reaction deactivating the catalyst. Katsuya Kawamoto et al. [321] performed reforming after gasification on a wood feedstock sample. The complex mixture used was composed of 9% CH_4 , 32% CO_2 , 23% H_2 and 32% CO . In this study, mesoporous Ni/SBA-15 was applied playing on the mode of Ni insertion on the SBA-15 support which was either by impregnation or direct synthesis. Maximum concentrations were achieved when 20 wt% of NiO were added over SBA-15 with an $\text{H}_2:\text{CO}$ ratio of 2.2. Yeshui Zhang [322] investigated four different Al_2O_3 -based catalysts ($\text{Co}/\text{Al}_2\text{O}_3$, $\text{Cu}/\text{Al}_2\text{O}_3$, $\text{Fe}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$) prepared by incipient wetness impregnation and their effect in dry reforming of waste tires pyrolysis product. The composition of the reforming feed was not detailed. The highest gas yield and hydrogen production was achieved in $\text{Ni}/\text{Al}_2\text{O}_3$ with an $\text{H}_2:\text{CO}$ ratio of 3.6 and the least amount of carbon nanotubes deposition.

Few other researchers relied on modeling and theoretical paths to evaluate the influence of H_2 or CO addition to CH_4 and CO_2 in the feed mixture [323,324]. Liu L. 328 et al. suggests that the addition of H_2 ($\text{CH}_4:\text{CO}_2:\text{H}_2$: 1:2:1) or CO ($\text{CH}_4:\text{CO}_2:\text{CO}$: 1:2:1) to the initial feed blocks the conversions of CH_4 and CO_2 directing different reactions. H. Hublot stated that CO_2 addition promotes DR reaction while CO had no kinetic effect 327. These studies did not rely on any experiment, and therefore no catalyst was synthesized and tested.

In our case, the realistic mixture to be applied in reforming was taken from a pilot plant pyrolysis product. The model gas composition provided from a Lebanese industry (INDEVCO) containing $\text{CH}_4:\text{CO}_2:\text{H}_2:\text{CO} = 0.75:1:1.57:0.85$ will be tested theoretically (HSC software) and experimentally (DRM on $\text{Ni}_5\text{-Mg}_y\text{-Al}_2\text{O}_3$ catalysts seen in chapter III). Before applying such mixture directly in reforming, the standard feed ratio was changed progressively from a standard reforming with a $\text{CH}_4:\text{CO}_2=1$ to $\text{CH}_4:\text{CO}_2=0.75$, till the addition of H_2 ($\text{CH}_4:\text{CO}_2:\text{H}_2=0.75:1:1.57$) and CO ($\text{CH}_4:\text{CO}_2:\text{CO}=0.75:1:0.85$) in the initial feed mixture. The results are then compared to the overall composition with the inclusion of CH_4 , CO_2 , H_2 and CO initially as reactants. Altering the initial feed composition to meet or be closer to realistic conditions make the reaction itself more complicated and more prone to side reactions (production of water and carbon deposition) which diminish the conversions compared to classical DRM.

VI.2. Thermodynamic analysis

Before doing the catalytic tests, we performed thermodynamic simulations to check the changes in the feed mixture going from the case of $\text{CH}_4:\text{CO}_2$ of 0.75:1 to $\text{CH}_4:\text{CO}_2:\text{H}_2:\text{CO} = 0.75:1:1.57:0.85$. Moreover, the regions of side reactions are specified in order to select the conditions where these reactions are limited. Table VI-1 summarizes the cases of inlet feed composition used and the obtained $\text{H}_2:\text{CO}$ ratios by the software considering or not the presence of carbon $\text{C}_{(s)}$.

Table VI-1: The molar composition applied to the inlet feed mixture of DRM reaction and the thermodynamic values of $\text{H}_2:\text{CO}$ ratio obtained in each case

Cases	Inlet feed Composition				$\text{H}_2:\text{CO}$ HSC values					
	CH ₄	CO ₂	H ₂	CO	Sec.1		Sec.2		Sec.3	
					No C	With C	No C	With C	No C	With C
Case 1	●	●			0.18-0.77	13000-10	0.77-0.9	10-0.96	0.9-0.8	0.96-0.8
Case 2	●	●	●		4700-5.9	55000-23	5.9-1.9	23-2	1.9-1.7	2-1.7
Case 3	●	●		●	0-0.2	6800-7.6	0.2-0.6	7.6-0.7	0.6-0.5	0.7-0.6
Case 4	●	●	●	●	1065-2	27000-17	2-1.2	17-1.5	1.2-1.15	1.5-1.15

VI.2.1. Thermodynamic analysis in absence of $\text{C}_{(s)}$

Figure VI-1 A simulates case 1 with $\text{CH}_4:\text{CO}_2$ ratio of 0.75:1. No reforming reaction takes place below 400 °C in region 1 (absence of products (H_2 , CO) formation) stimulating the high temperature needed for the DR reaction to occur no matter what the feed composition is. Formation of the syngas is further promoted at higher temperatures. However, in this case

(excess of CO_2 with respect to CH_4), H_2O is formed even at high reaction temperature (650 - 1000 °C) with more CO product compared to H_2 . This means that more CO_2 present in the feed mixture boosts the occurrence of the RWGS ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) reaction consuming CO_2 and H_2 to produce CO and H_2O that leads to H_2 : CO ratio always less than 1 (Table VI-1, case 1).

In case 2, H_2 is added to the initial feed mixture (Figure VI-1 B, CH_4 : CO_2 : $\text{H}_2 = 0.75$: 1 : 1.57). As a result, CO_2 methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) side reaction is promoted at low temperatures (section 1) prevailing the production of H_2O and CH_4 . As the temperature increases, a small increase in CO_2 production is noticed in section 2 stressing on the occurrence of WGS reaction making CO reacts with H_2O to form CO_2 and H_2 . Section 3 is the region where the reforming reaction dominates with an H_2 : CO ratio of 1.9 at 600 °C and 1.7 at 1000 °C.

When CO is added to the feed mixture (case 3, CH_4 : CO_2 : $\text{CO} = 0.75$: 1 : 0.85), no reaction occurs at temperature below 400 °C as CO_2 , CH_4 , and CO equilibrium amount remains constant (Figure VI-1 C). Dry reforming starts to occur at temperature higher than 400 °C reaching an H_2 : CO ratio of 0.6 at 600 °C and 0.5 at 1000 °C. The amount of H_2O reached at 1000 °C is slightly lower than that in case 1. This might be due to the excess of CO that can play a role in triggering WGS consuming H_2O and CO to form H_2 and CO_2 .

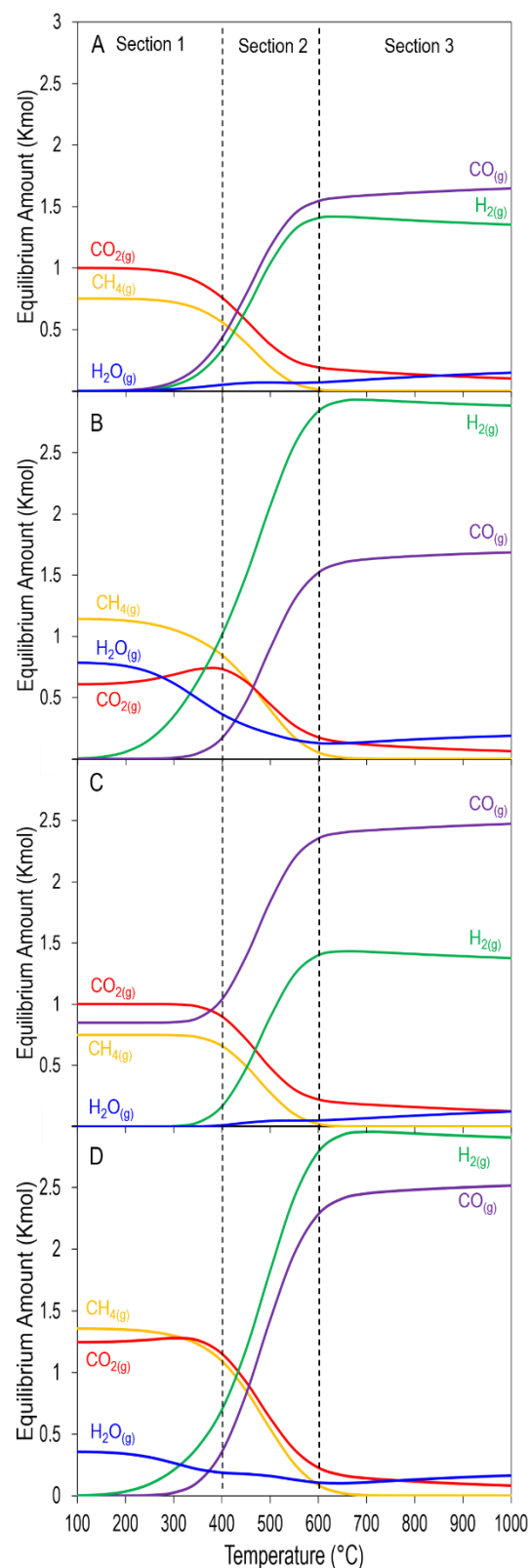


Figure VI-1: Thermodynamic equilibrium curves for DR reactants and products at $P= 1$ atm excluding carbon from the calculations

Case 4 involves the final pyrolysis product mixture ($\text{CH}_4:\text{CO}_2:\text{H}_2:\text{CO} = 0.75:1:1.57:0.85$), and is presented in Figure VI-1 D. At temperatures lower than 400 °C (section 1), the reactant mixture is more influenced by the presence of H_2 than CO inducing CO_2 methanation reaction. DR starts to occur in section 2 and prevails in section 3 with an inevitable presence of H_2O . In this case, the $\text{H}_2:\text{CO}$ ratio is 1.2 at 600 °C and 1.15 at 1000 °C.

VI.2.2. Thermodynamic analysis in presence of $\text{C}_{(s)}$

Considering carbon as reactant and/or product in the thermodynamic calculations affect the shape of the curves especially in the low temperature region (Figure VI-2). For instance, in the case of $\text{CH}_4:\text{CO}_2 = 0.75:1$ (Figure VI-2 A), CO hydrogenation and CO disproportionation are dominant in section 1 and 2. In section 3, the profile becomes similar to the free-carbon case since the aforementioned reactions cannot occur at elevated temperatures.

When H_2 is added in addition to CH_4 , and CO_2 (Figure VI-2 B), CO_2 hydrogenation is more common to occur in section 1 increasing the amount of carbon and H_2O , and CO disproportionation along with WGS reaction in section 2.

The presence of CO with CH_4 and CO_2 triggers CO disproportionation and hydrogenation reactions in section 1 and again WGS reaction in section 2 (Figure VI-2 C).

Figure VI-2 D, contains all the feed mixture combining the side reactions seen in the cases of B and C. The inhibition effect of carbon on the main reaction is noticed from the $\text{H}_2:\text{CO}$ ratio achieved in Table VI-1 for all reactant conditions that are very high. Section 3, the favorable temperature range for reforming reaction, shows similar trend in the 4 cases as the carbon-free

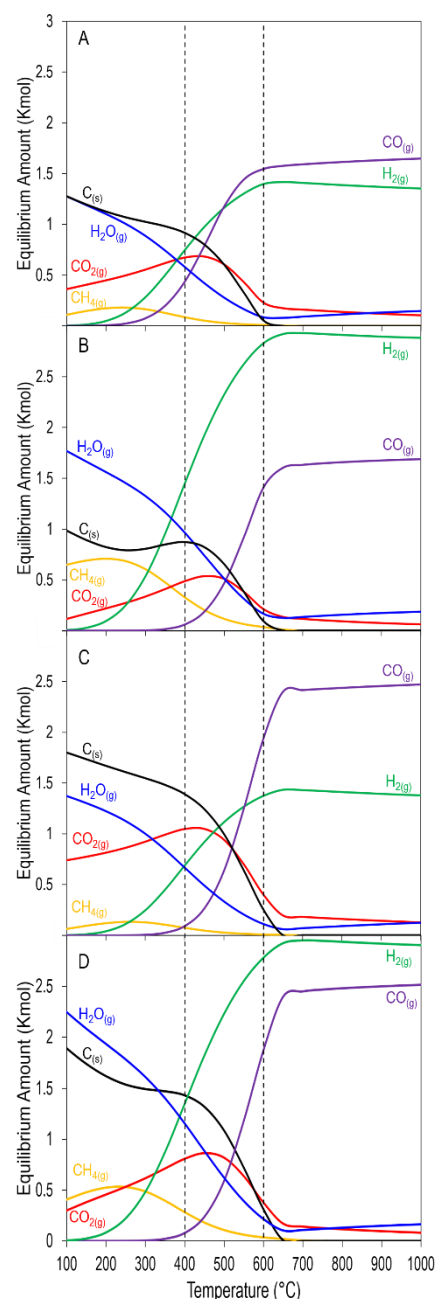


Figure VI-2: Thermodynamic equilibrium curves for DR reactants and products at $P= 1$ atm including carbon as side product

thermodynamic curves. This is explained by the fact that carbon forming reactions do not occur at elevated temperature above 600 °C which avoid the occurrence of side reactions seen in section 1 and 2. The only possible side reaction producing carbon at such elevated temperature is the CH₄ decomposition. However, it is seen from all the profiles that this reaction does not have an important influence under the reactant conditions applied, since C_(s) formation is very little with H₂:CO values (Table VI-1) slightly higher than those of the free-carbon case.

The change in the reactant feed affects the selectivity with different values seen in each case for H₂:CO ratio. The presence of the complex mixture does not cast water production with a possibility of carbon formation making such realistic conditions more challenging than standard ones. The next paragraphs focus on the evaluation of the performances of mesoporous Ni₅-Mg_y-Al₂O₃ catalysts under similar reaction conditions.

VI.3. Catalytic performance of Ni₅-Mg_y-Al₂O₃ mesoporous catalysts

To measure the catalytic test in each reactant mixture case, the total gas hourly space velocity (GHSV) was set at 180 L.g⁻¹.h⁻¹. The reactant feed ratio was changed four times to check the influence of each stoichiometric mixture on the catalytic activity. Mesoporous Ni₅-Al₂O₃, Ni₅-Mg₁₅-Al₂O₃, and Ni₅-Mg₃₀-Al₂O₃ catalysts are tested in all feed mixture compositions. The aim is to estimate if these materials could withstand the harsh realistic conditions applied.

VI.3.1. Effect of methane to carbon dioxide ratio

In the case of a feed mixture of CH₄:CO₂ = 0.75:1 (Figure VI-3) CH₄ and CO₂ conversions as well as H₂:CO ratio increase with increasing temperature resembling more the

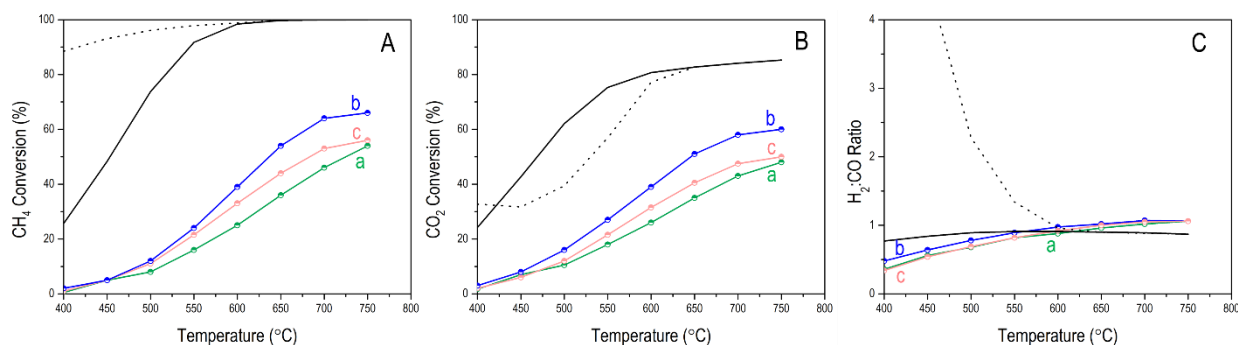


Figure VI-3: (A) CH₄ and (B) CO₂ conversions with (C) H₂:CO ratio as a function of temperature of: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, and (c) Ni₅-Mg₃₀-Al₂O₃; black line and black dashed line correspond to thermodynamic values without and with C_(s); Initial feed mixture: CH₄:CO₂=0.75:1

thermodynamic curve in absence of $C_{(s)}$. This means that the dry reforming operation is done in a free-carbon formation or that the amount of carbon formed is very little. Moreover, the conversions for all catalysts (highest activity for $Ni_5-Mg_{15}-Al_2O_3$) were enhanced compared to standard dry reforming results ($CH_4:CO_2 = 1:1$) due to the presence of more CO_2 amount that shifts the reaction towards production of H_2 and CO . The excess of CO_2 also contributed to lower CO_2 conversions than CH_4 because some unreacted CO_2 will be left at the end of reaction. However, this difference between both conversions was not big since CO_2 plays the role of oxidant and could react with C deposits to form CO , but can also be further consumed by favoring the occurrence of RWGS producing more H_2O than the standard case ($CH_4:CO_2 = 1:1$) [325–327].

VI.3.2. Effect of H_2 addition to CH_4 and CO_2 feed stream

In process of adapting the mixture to the industrial case, hydrogen was added to the feed mixture with a stoichiometric ratio of $CH_4:CO_2:H_2=0.75:1:1.57$. Figure VI-4 shows the light off curves of the three tested catalysts. Both CH_4 and CO_2 conversions increase with

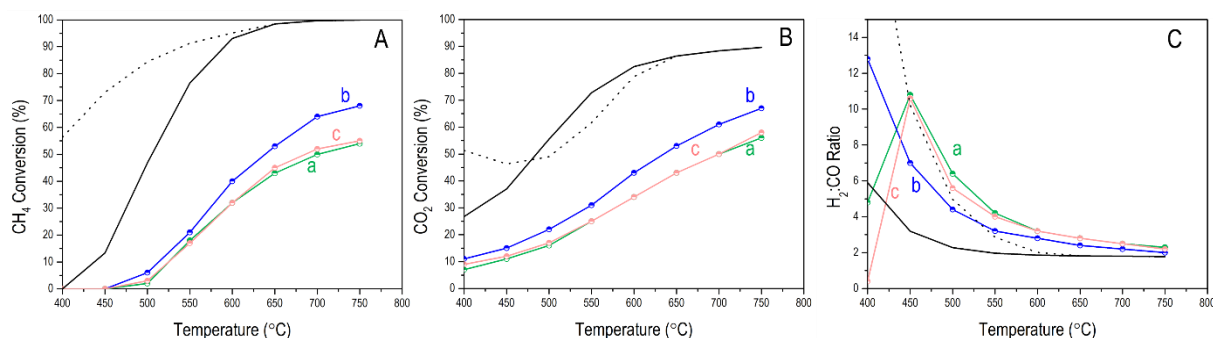


Figure VI-4: (A) CH_4 and (B) CO_2 conversions with (C) $H_2:CO$ ratio as a function of time of: (a) $Ni_5-Al_2O_3$, (b) $Ni_5-Mg_{15}-Al_2O_3$, and (c) $Ni_5-Mg_{30}-Al_2O_3$; black line and black dashed line correspond to thermodynamic values without and with $C_{(s)}$ respectively; Initial feed mixture: $CH_4:CO_2:H_2=0.75:1:1.57$

temperature (Figure VI-4 A, B), however the CO_2 conversions start at higher values than CH_4 that was always negligible between 400-500 °C. This is due to the presence of H_2 initially in the feed that blocks CH_4 conversion by favoring the CO_2 methanation reaction consuming CO_2 to produce CH_4 and H_2O (hydrogen consumption exceeds the production from hydrocarbon reforming). The main dry reforming reaction dominates then in the high temperature region (550-750 °C) showing consumption of both CH_4 and CO_2 (hydrogen formation from methane balances the oxidation of H_2 by CO_2).

Performing the test over 48 h time on stream (Figure VI-5), all 3 catalysts deactivate slowly through time with the following increasing order of stability: $\text{Ni}_5\text{-Al}_2\text{O}_3 < \text{Ni}_5\text{-Mg}_{30}\text{-Al}_2\text{O}_3 < \text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$. CO_2 conversion was higher for all catalysts than CH_4 conversion unlike thermodynamics, because the addition of H_2 promotes the RWGS [324], however the $\text{H}_2:\text{CO}$ ratio did not decrease a lot. This could be due to a competitive side reactions effect

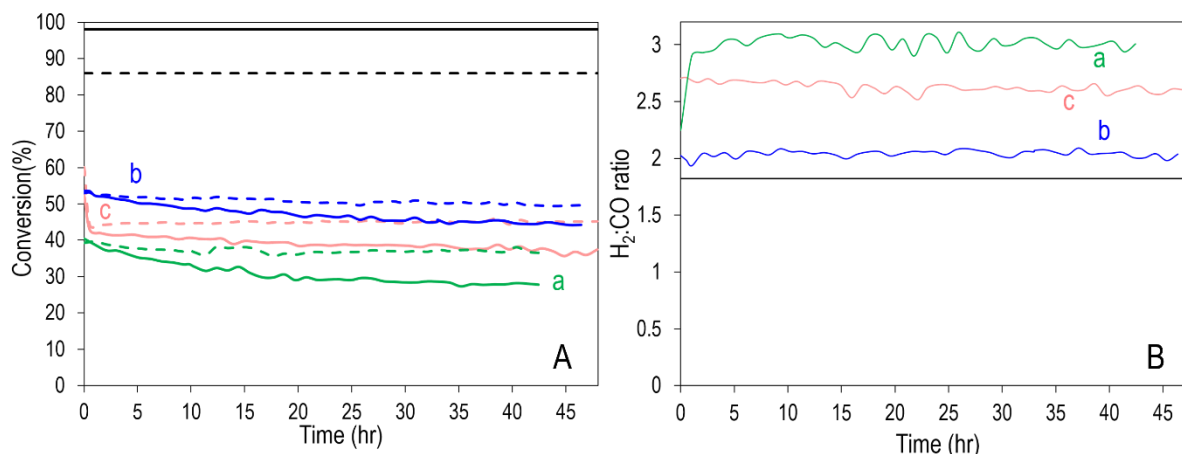


Figure VI-5: (A) CH_4 and (B) CO_2 conversions with (C) $\text{H}_2:\text{CO}$ ratio as a function of time of: (a) $\text{Ni}_5\text{-Al}_2\text{O}_3$, (b) $\text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$, and (c) $\text{Ni}_5\text{-Mg}_{30}\text{-Al}_2\text{O}_3$; black line and black dashed line correspond to thermodynamic values of CH_4 and CO_2 conversions, respectively; Initial feed mixture: $\text{CH}_4:\text{CO}_2:\text{H}_2=0.75:1:1.57$ ($T=650^\circ\text{C}$)

between RWGS and CH_4 decomposition [328]. Moreover, it has been mentioned in other studies [329,330] that the presence of additional amount of H_2 to the reaction can prevent the surface of metal Ni crystallite from deactivation by reacting with carbon deposits formed by CH_4 dissociation. This is true in the case of $\text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$. The presence of both H_2 and moderate amount of Mg leads to an equilibrium between methane adsorption, dissociation, diffusion and desorption of hydrogen, with CO_2 chemisorption and activation. This equilibrium induces higher CH_4 and CO_2 conversions in $\text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$ with sustained stability because the carbon formed are removed from two sides reaching a syngas mixture of $\text{H}_2:\text{CO}$ ratio around 2 close to the expected value.

On the other hand, when higher amount of Mg ($\text{Ni}_5\text{-Mg}_{30}\text{-Al}_2\text{O}_3$) is present, the number of basic sites becomes excessive that the adsorbed CO_2 could cover some of the Ni active sites of the catalyst and desorption from the active sites become difficult due to the strong alkaline sites among the framework of the catalysts. As a result, CH_4 and CO_2 conversions are restrained from further increase, decreasing stability [172]. In $\text{Ni}_5\text{-Al}_2\text{O}_3$, the presence of an excess of H_2 is not sufficient to cast the carbon formed, and thus it was the least stable acquiring the highest $\text{H}_2:\text{CO}$ ratio of around 2.8.

VI.3.3. Effect of CO addition to CH₄ and CO₂ feed stream

Adding CO to the reactants blocked the conversion of CH₄ and CO₂ at low temperatures (< 500 °C, Figure VI-6) due to the inhibition of the main dry reforming reaction. Dry reforming of methane is favored at high temperatures contributing to higher values of CH₄ conversions compared to CO₂ conversions since CO₂ is present in excess and will act as an oxidant with a positive effect on CH₄ conversion. H₂ and CO are the major products at high temperatures, but the simultaneous occurrence of the reverse reduction of CO₂ by H₂ (RWGS reaction) and reforming of methane to CO make its production predominant achieving low values of H₂:CO ratios.

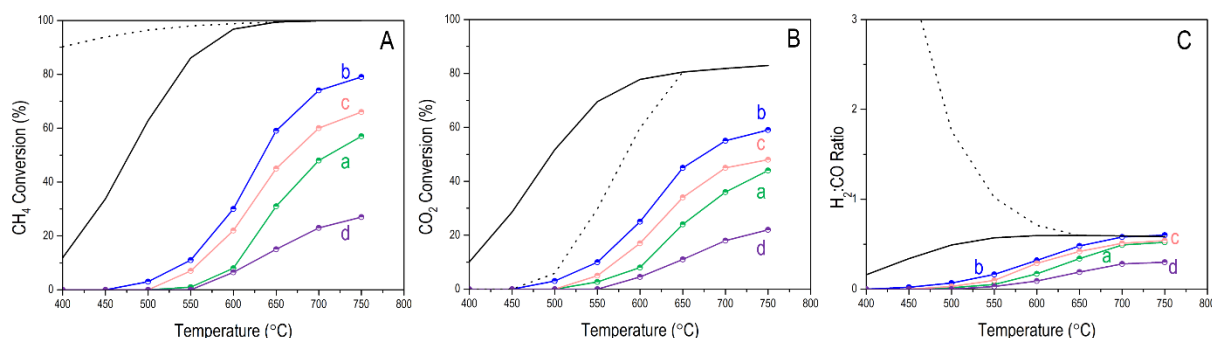


Figure VI-6: (A) CH₄ and (B) CO₂ conversions with (C) H₂:CO ratio as a function of time of: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃; black line and black dashed line correspond to thermodynamic values without and with C_(s) respectively; Initial feed mixture: CH₄:CO₂:CO=0.75:1:0.85

As for the stability of the studied materials, Ni₅-Mg₁₅-Al₂O₃ proved again to be the most stable catalyst (Figure VI-7). The higher Mg content catalysts (Ni₅-Mg₃₀-Al₂O₃, Ni₅-Mg₅₀-Al₂O₃) create an excess number of basic sites with more CO₂ adsorbed, leading to occurrence of RWGS producing CO and H₂O and decreasing the H₂:CO ratio.

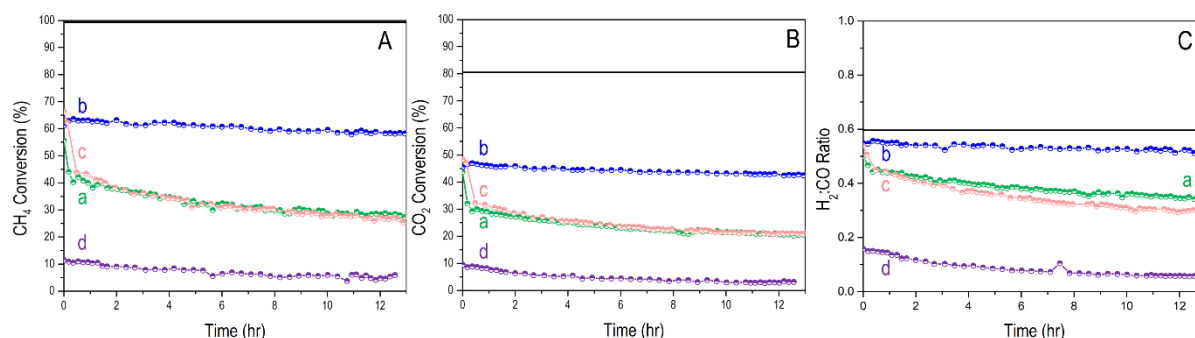


Figure VI-7: (A) CH₄ and (B) CO₂ conversions with (C) H₂:CO ratio as a function of time of: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃; black line corresponds to thermodynamic values without C_(s); Initial feed mixture: CH₄:CO₂:CO=0.75:1:0.85 (T= 650 °C)

VI.3.4. Effect of H₂ and CO addition to CH₄ and CO₂ feed stream

The light off curves of a model pyrolysis product mixture are presented in Figure VI-8. The results are somehow a combination of the three previous cases. CO₂ conversions start at lower temperature than that of CH₄ due to the presence of H₂ that stimulates the CO₂ methanation reaction. As the temperature is increased, both conversions are enhanced reflecting the appearance of the main dry reforming of methane reaction. The trend of these conversions resemble the free-carbon thermodynamic curves and the H₂:CO ratio fluctuates around 1.2-1.3.

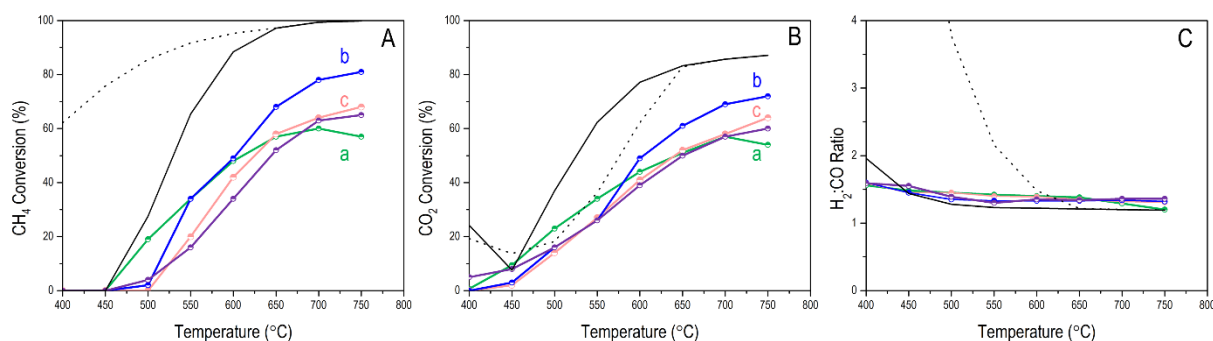


Figure VI-8: (A) CH₄ and (B) CO₂ conversions with (C) H₂:CO ratio as a function of time of: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃; black line and black dashed line correspond to thermodynamic values without and with C_(s) respectively; Initial feed mixture: CH₄:CO₂:H₂:CO=0.75:1:1.57:0.85

Concerning the stability of the mesoporous Ni₅-Mg_y-Al₂O₃ materials, Ni₅-Mg₁₅-Al₂O₃ seems to be the most stable with the highest activity through time (Figure VI-9). The other materials face small deactivation (CH₄ conversion loss as follows: 3% in Ni₅-Al₂O₃, 2% in Ni₅-Mg₃₀-Al₂O₃, and 6% in Ni₅-Mg₅₀-Al₂O₃). This means that the prepared sample (Ni₅-Mg₁₅-

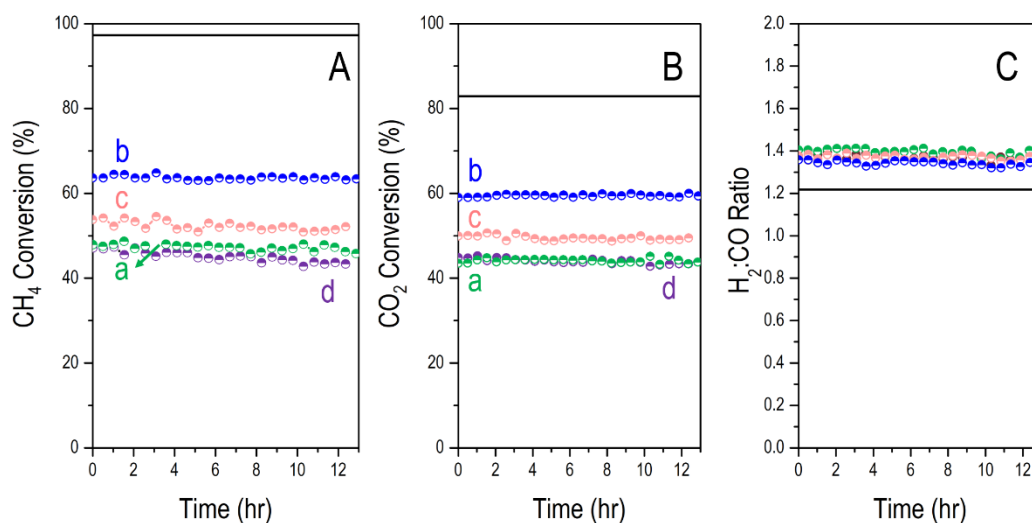


Figure VI-9: (A) CH₄ and (B) CO₂ conversions with (C) H₂:CO ratio as a function of time of: (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, (c) Ni₅-Mg₃₀-Al₂O₃, and (d) Ni₅-Mg₅₀-Al₂O₃; black line corresponds to thermodynamic values without C_(s); Initial feed mixture: CH₄:CO₂:H₂:CO=0.75:1:1.57:0.85 (T= 650 °C)

Al₂O₃) is capable to withstand the harsh dry reforming conditions imposed by the complex pyrolysis products. This will be further confirmed by the physicochemical comparison of the spent catalysts presented in the next paragraph.

Spent Ni₅-Al₂O₃, Ni₅-Mg₁₅-Al₂O₃, and Ni₅-Mg₅₀-Al₂O₃ catalysts are characterized by XRD, TEM, TGA and Raman spectroscopy. Regarding TEM microscopy, Figure VI-10 shows that the materials tested are affected to a great extent by the complex dry reforming reaction. Ni₅-Al₂O₃ revealed sintering by showing large particle sizes of nickel and deposition of carbon nanotubes (Figure VI-10 A, A'). The Ni⁰ average particle size was increased from 4.5 nm in its reduced state to 11 nm after reforming. Ni₅-Mg₁₅-Al₂O₃ that exhibited the best catalytic performance preserves its textural and structural properties showing no carbon deposition over the support with a small nickel nanoparticles of 4 nm (Figure VI-10 B, B'). Ni₅-Mg₅₀-Al₂O₃ catalyst (Figure VI-10 C, C') does not show carbon nanotubes on its surface, but it faces a high degree of sintering increasing the reduced metallic Ni⁰ from 7.7 nm (reduced form) to 15 nm after test. The average Ni⁰ particle size of the spent materials were in good trend agreement with XRD measurements with smaller values than those estimated by TEM: 8 nm for Ni₅-Al₂O₃, below detection limit (< 4 nm) for Ni₅-Mg₁₅-Al₂O₃ and 9.3 nm for Ni₅-Mg₅₀-Al₂O₃.

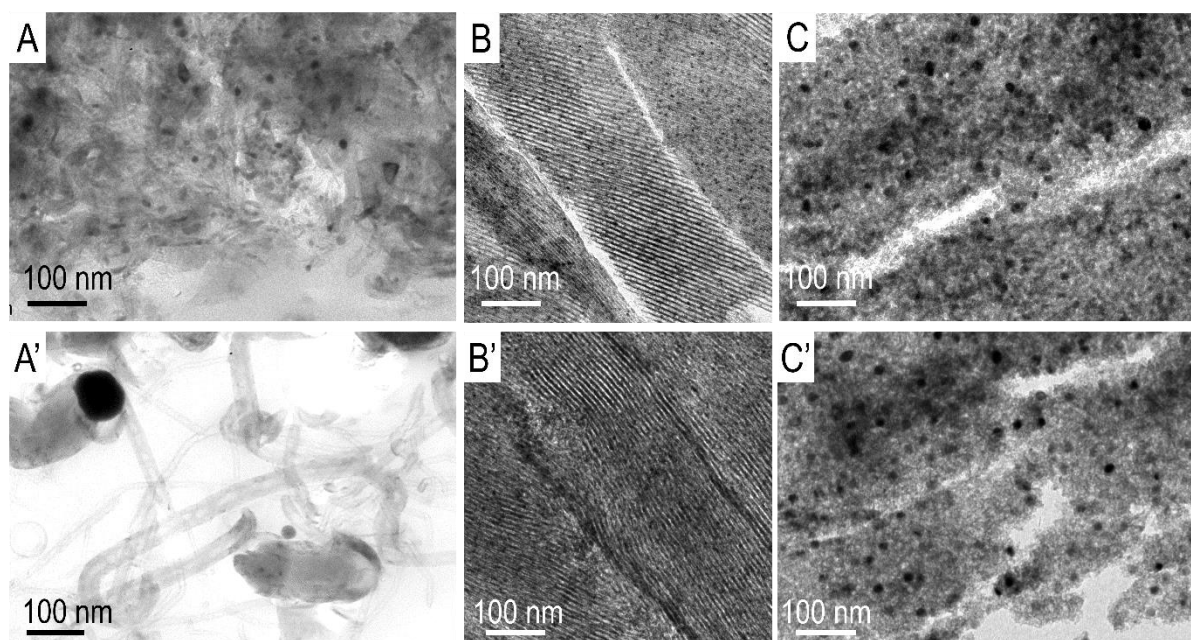


Figure VI-10: TEM images of spent (A, A') Ni₅-Al₂O₃, (B, B') Ni₅-Mg₁₅-Al₂O₃, and (C, C') Ni₅-Mg₅₀-Al₂O₃.

The presence of carbon on spent catalysts is confirmed by TGA analysis as well as to the D and G bands visible by Raman spectroscopy (Figure VI-11). Regarding the TGA analysis,

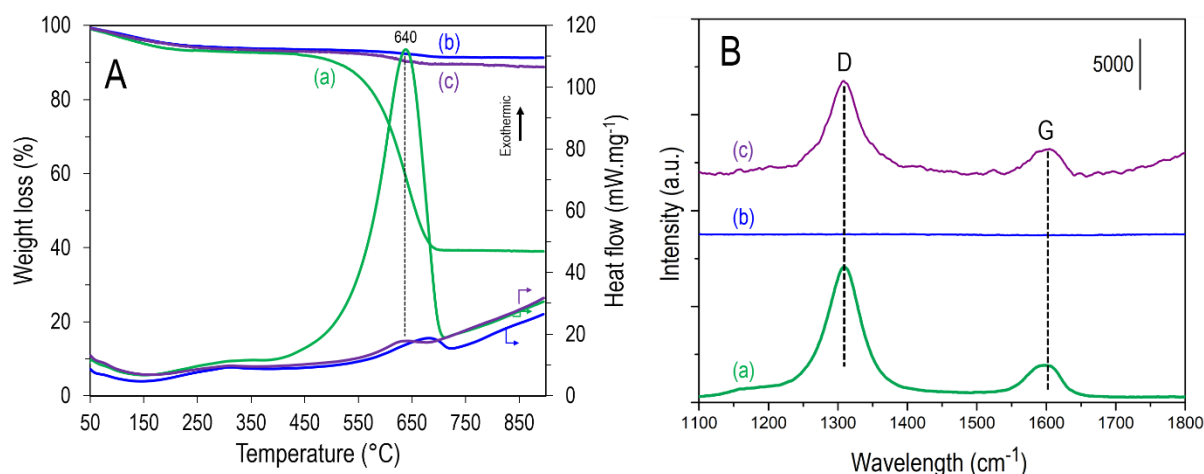


Figure VI-11: (A) TGA profiles (at the top) associated to heat flow signals (at the bottom) and (B) Raman spectroscopy signals of the spent (a) Ni₅-Al₂O₃, (b) Ni₅-Mg₁₅-Al₂O₃, and (c) Ni₅-Mg₅₀-Al₂O₃. all spent catalysts depict a small decrease in weight (around 9-10 %) at temperatures below 150 °C attributed to desorption of water from the alumina support. An additional loss in weight is noticed at a temperature of 640 °C indicating carbon oxidation with matching exothermic peak. This loss is more important in the case of Ni₅-Al₂O₃ catalyst (40 %) than Ni₅-Mg₁₅-Al₂O₃ (2 %) and Ni₅-Mg₅₀-Al₂O₃ (6 %). As for the Raman spectroscopy, the two main bands (D and G) are typical of the doubly degenerated phonon mode of C atoms in the sp² carbon networks with high degree of symmetry and of order (graphitic carbon, G-band, 1600 cm⁻¹), and of a disordered structural mode of carbon species (D-band, 1300 cm⁻¹). The intensity ratio between these two bands can be used as an indicator of the crystalline degree and of the presence of defects in the carbon species; the smaller the ratio (<1) the higher the structural order. Here, both Ni₅-Al₂O₃ and Ni₅-Mg₅₀-Al₂O₃ have a ratio significantly higher than 1 (4.77 and 4.15 respectively) which indicates the disordered character of the carbon deposits, in line with the occurrence of carbon nanotubes observed on Ni₅-Al₂O₃ by electron microscopy. Note that the intensities of the two bands are higher in Ni₅-Al₂O₃ than in Ni₅-Mg₅₀-Al₂O₃ in good agreement with TGA results. The absence of any band in Ni₅-Mg₁₅-Al₂O₃ confirms the absence or the presence of a negligible amount of carbon nanotubes not detectible by Raman spectroscopy contributing to a fluorescence background.

VI.4. Conclusion

As a conclusion of this chapter, it is evident that alteration of the initial DR feed mixture influences the products behavior and the selectivity of the reaction. Briefly, a CH₄:CO₂ ratio of 0.75:1 has a positive effect on the reaction due to CH₄ present as limiting reactant, and thus the

more CO₂ available helps in oxidizing carbon formed during reaction. Adding H₂ to the feed blocks CH₄ conversions at low temperatures to direct CO₂ methanation instead. In such condition, DR is dominated at elevated temperatures, but the presence of high H₂ amount shows occurrence of RWGS. The H₂:CO ratio achieved in this case was around 2. When CO is initially added to CO₂ and CH₄ no side reaction takes place at low reaction temperatures (<400 °C), but its presence retards conversions of CH₄ and CO₂ for DRM. The selectivity achieved in this case is as low as H₂:CO of 0.5. The complex model mixture (CH₄, CO₂, H₂, CO) is a combination of the above mentioned mixtures with a selectivity of H₂:CO of 1.3.

Results also revealed that Ni₅-Mg₁₅-Al₂O₃, similar to the case of standard dry reforming of methane (CH₄:CO₂ = 1:1), had the best catalytic performance among all the other tested materials. This confirms the importance of high order mesoporous structure and the presence of an optimum amount of basic modifier to highly disperse nickel particles restricting sintering and carbon formation. Thus, Ni₅-Mg₁₅-Al₂O₃ proved to be a good candidate in reforming of complex and realistic mixtures with a great stability for a long period of time (50 hrs).

General conclusion and perspectives

Despite the enormous studies tackled on dry reforming of methane reaction, this reaction still faces obstructions regarding the utilized catalysts. The problems encountered are mainly related to the sintering of nickel active sites or/and to the formation of carbon species deactivating the catalyst and hindering DRM reaction.

In this work, stable and selective Ni-based alumina material were designed by taking into consideration different key factors: 1) Simultaneous addition of Ni precursors within the synthesis of Al_2O_3 support, 2) mutation in the shape of the alumina support for better trapping and confinement of nickel nanoparticles inside the support structure (pores/walls) preventing sintering, and 3) modification of the material basicity by adding MgO as a basic dopant to enhance reactivity by annealing coke deposition

First, $\text{Ni}_5\text{-Mg}_y\text{-Al}_2\text{O}_3$ ordered mesoporous catalysts were synthesized combining the three aforementioned approaches. Mg loading was varied between 0 and 26 wt%. $\text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$ with intermediate Mg content (7 wt%) has the best catalytic performances with as superior activity and stability among all the other Mg amounts. This was explained by several combined features: i) the high, homogenous and simultaneous dispersion of both Ni and Mg species, ii) the high surface area and ordered channels for Al_2O_3 support and iii) the enhancement of material basicity that accelerates CO_2 chemisorption reducing the activation energy. Further increment of Mg loading (15-26 wt%) has negative catalytic response due to a strong MgO segregation in the material that disturbs the structure and pores ordering, and strongly affects Ni dispersion.

Second, and inspired by approaches one and two, a deep explanation was given about the benefit of using metal-organic framework (MIL-53(Al)) as a sacrificial nickel precursor host to highly disperse nickel nanoparticles within a porous $\gamma\text{-Al}_2\text{O}_3$ lamellar phase. Indeed, $\text{Ni}_5\text{-Al}_2\text{O}_3_{\text{MIL-53}}$ synthesized by impregnation of Ni on the MOF prior to calcination resulted in high surface area, with superior dispersion and uniformity of nickel nanoparticles leading to high activity, selectivity and stability in DRM. Under similar test conditions, this new material was even better than $\text{Ni}_5@\text{Al}_2\text{O}_3_{\text{MIL-53}}$ and traditional $\text{Ni}_5@\text{Al}_2\text{O}_3_{\text{COM}}$ prepared by conventional nickel impregnation over preformed alumina supports that acquired larger nickel nanoparticles with eventually lower dispersion.

Third, the application of $\text{Ni}_5\text{-Mg}_y\text{-Al}_2\text{O}_3$ and $\text{Ni}_x\text{-Al}_2\text{O}_3$ MIL-53 catalysts was extended to CO_2 methanation reaction where their behavior was as outstanding as in dry reforming of methane. This proves the efficiency of these materials to be applied in versatile energy applications ranging from low to high reaction temperatures. $\text{Ni}_5\text{-Mg}_y\text{-Al}_2\text{O}_3$ catalyst ($\text{Ni}_5\text{-Mg}_{15}\text{-Al}_2\text{O}_3$ specifically) showed also good resistance in dry reforming of pyrolysis gaseous products towards sintering and carbon formation. This further highlights on the capability of the synthesized materials to withstand and operate in realistic conditions.

As for the perspectives, starting first with the materials synthesis, it could be a good idea to work on following same strategies but with cheaper and more “eco-friendly” templates. In the case of one-pot mesoporous $\text{Ni}_x\text{-Mg}_y\text{-Al}_2\text{O}_3$ P123 commercial organic surfactant was used and is applied commonly to many mesoporous materials of Al_2O_3 and silica. But it was recently revealed to have poor biodegradability and toxic to several biological organisms at high concentrations in addition to its high relative cost. The trend should be towards using more environmentally friendly surfactants derived from renewable sources. For instance, chitosan polymers, derived from the shell of crustaceans such as shrimps and crabs, can be used. A basic trials on using such template in the following thesis was tried but it yielded to poorly ordered mesoporous material. So the parameters of synthesis are suggested to be optimized. In the MOF case for example, the terephthalic acid used in the synthesis produce can be obtained from PET (polyethylene terephthalate) that is an industrially important waste stream and consists of more than 85% of terephthalic acid. Moreover, PET hydrolysis can be achieved at 200 °C in water, which is close to the synthesis conditions of MIL-53(Al). This idea took a part in my PhD work (training of an Italian masters student as internship in the frame of SOL-CARE project) where MIL-53(Al) was successfully synthesized by in-situ/ex-situ generation of linkers from PET hydrolysis. The obtained MIL-53(Al) followed later the same strategy as the seen samples and was impregnated with Ni and calcined.

For industrial application, even though the catalysts used in this work showed very good activity and stability, they need to be further tested at high pressures and for longer period of time (more than two weeks). It is also important to obtain kinetic and mechanistic information to design any reactor and predict products flow rate of the scaled-up operation. A fair part of the kinetics and mechanistic aspects are exploited on mesoporous $\text{Ni}_5\text{-Al}_2\text{O}_3$ catalyst but they still need to be optimized and applied on the other materials for comparison.

Appendix

Table: Recent development in the synthesis of Ni-Al₂O₃ catalysts in DRM

Ref.	Ni amount (wt%)	Type of Al ₂ O ₃	Ni insertion	Ni (nm)	Ni ^δ (nm)	Test conditions	X(CH ₄) _i	X(CO ₂) _i	X(CH ₄) _f	X(CO ₂) _f	H ₂ :CO	Deactivation reason
[71]	26	Commercial α	W.I.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	Filamentous C _(s)
[73]	20	Commercial	W.I.	n.m.	n.m.	Fixed bed (h:400 mm, d=14mm), 750 °C, 9 h	45	n.m.	25	n.m.	n.m.	C _(s)
[74]	15	Commercial	W.I.	n.m.	n.m.	Tubular U-shaped, 300 mg, 650 °C, 10 h, 45 L.g ⁻¹ .h ⁻¹	40	50	30	45	n.m.	C _(s)
[75]	26	Commercial α	I.W.I.	n.m.	n.m.	Tubular U-shaped	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
[64]	10	Commercial	I.W.I.	4	n.m.	Fixed bed (d:9 mm), 200 mg, 800°C, 50h, 48 L.g ⁻¹ .h ⁻¹	80	85	50	65	0.8	C _(s)
[72]	8	Commercial γ	EDF	12	n.m.	Fixed bed, 750 °C, 120 L.g ⁻¹ .h ⁻¹	14.5	32	n.m.	n.m.	0.4	C _(s)
[76]	10	Commercial	electrospinning	6.5	n.m.	Fixed bed (d:8 mm), 100 mg, 700 °C, 300 min, 48 L.g ⁻¹ .h ⁻¹	55	82	50	80	0.8	C _(s)
[77]	12	Al precursor	EISA	15	n.m.	Fixed bed, 50 mg, , 800 °C, 80 h, 72 L.g ⁻¹ .h ⁻¹	90	90	88	88	n.m.	C _(s)
[78]	20	Al precursor	aerogel	9	20	Quartz, (d:18 mm), 200 mg, 800 °C, 30 h	95	95	90	90	n.m.	Amorphous C _(s) and S
[79]	10	Al precursor	combustion	4.6	16.8	Fixed bed, 100 mg, 700 °C, 24 h	40	52	35	47	n.m.	Whiskers C _(s) and S
[80]	10	Meso-Al ₂ O ₃	One-pot	11	15	Fixed bed, 100 mg, , 800 °C, 500 min, 52 L.g ⁻¹ .h ⁻¹	62	75	52	62	0.78	Nanotubes C _(s)
[81]	10	Al precursor	2-step hydrothermal	7	n.m.	100 mg, , 800 °C, 50 h, 21 L.g ⁻¹ .h ⁻¹	95	90	95	90	0.92	Amorphous C _(s)
[83]	35	γ nanoflakes	Hydrothermal	5.5	8.5	Fixed bed quartz, 100 mg, , 800 °C, 50 h	82	n.m.	80	n.m.	0.90	Nanotubes C _(s)
[84]	10	Nanosheets γ	I.W.I.	6.7	7	Quartz (d=8mm), 100 mg, 700 °C, 300 min, 48 L.g ⁻¹ .h ⁻¹	55	n.m.	55	n.m.	n.m.	-
[86]	10	Nanosheets	Hydrothermal	12	14	Quartz (d=8mm), 100 mg, 800 °C, 100 h, 108 L.g ⁻¹ .h ⁻¹	95	94	90	92	0.95	35% C _(s)
[87]	5	Meso-Al ₂ O ₃	Hydrolysis deposition	5.5	20	Fixed bed s.s.(d= 6 mm), 500 mg, , 800 °C, 10 h, 14.4 L.g ⁻¹ .h ⁻¹	92	97	90	92	0.85	C _(s) and S
[88]	10	Al precursor	I.W.I.	14	15	Fixed bed Quartz (d=8mm), 100 mg, 700 °C, 100 h, 15L.g ⁻¹ .h ⁻¹	80	80	78	78	0.8	Graphitic C _(s)

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4. Porous nickel-alumina derived from metal-organic framework (MIL-53): a new approach to achieve active and stable catalysts in methane dry reforming, L. Karam, J. Reboul, S. Casale, P. Massiani, N. El Hassan, *under revision*
5. Comprehensive study on the effect of magnesium loading over Nickel-ordered mesoporous alumina in dry reforming of methane, L. Karam, P. Massiani, N. El Hassan, *under preparation*
6. Mesoporous nickel-alumina catalysts derived from MIL-53(Al) metal organic framework: a new path for achieving promising activity for CO₂ methanation, L. Karam, M.C. Bacariza, J.M. Lopes, C. Henriques, J. Reboul, N. El Hassan, P. Massiani, *under preparation*

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1. Reforming kinetics over highly dispersed nickel nanoparticles supported on mesoporous silica prepared by a facile method, L. Karam*, N. El Hassan, LIRA Program, (December 2016, Beirut, Lebanon), Poster
2. Dry reforming of methane over porous alumina materials derived from metal organic framework, L. Karam*, J. Reboul, N. El Hassan, P. Massiani, Premier congrès français des MOFs, COFs et polymères poreux (May 2018, Paris, France), Poster
3. Reforming of waste gasification products to syngas on nickel-magnesium mesoporous alumina catalysts, L. Karam*; N. El Hassan; P. Massiani, Groupe d'étude en catalyse-GECAT, (May 2018, Trégunc, France), Poster
4. Promotion of mesoporous nickel-alumina based catalysts by magnesium addition for reforming of waste gasification products, L. Karam*; N. El Hassan; F. Launay; P. Massiani, International symposium on heterogeneous catalysis, (August 2018, Sofia, Bulgaria), **Oral**
5. Advanced Catalytic Materials with Well-Defined Nanostructures for Energy & Fuel, L. Karam*; J. Reboul; S. Casale; N. El Hassan; P. Massiani; ACS National Meeting & Exposition, (August 2018, Boston, USA), **Oral**
6. Mesoporous Ni-Al₂O₃ derived from metal organic framework: A promising catalyst for CO₂ methanation, L. Karam*, J. Reboul, M.C. Bacariza, J.M. Lopes, C. Henriques, N. El Hassan, P. Massiani, EuropaCat (August 2019, Aachen, Germany), Poster

Abstract :

Dry reforming of methane is a process that converts CH_4 and CO_2 gases, emitted from burning of fossil fuels or decomposition of biomass, into syngas gaseous mixture of H_2 : CO ratio equal to 1. Ni based catalysts proved to be suitable candidates for the reaction due to their good activity, wider availability and lower cost than noble-based materials. However, these catalysts still face sintering of Ni active phase and coke deposition decreasing the catalytic stability. In this thesis we developed two different synthesis routes of mesoporous Ni- Al_2O_3 based catalysts that can occlude Ni inside the pores achieving high activity and stability in reforming. A set of complimentary physicochemical techniques was systematically applied to thoroughly investigate the materials properties at all steps of preparation and activation. The first approach embraced synthesis of mesoporous Ni-Mg- Al_2O_3 materials by one-pot strategy. Results demonstrated that 7 wt% Mg (optimum loading) based sample contribute to high and homogenous Ni dispersion with simultaneous excellent Mg repartition, preserving ordered mesoporous Al_2O_3 walls. The good structural and textural characteristics in addition to the enhance basicity reinforce activity and stability. The second method involved synthesizing new mesoporous Ni- Al_2O_3 materials using metal-organic framework as sacrificial template. This procedure results in small Ni^0 nanoparticles homogeneously dispersed and stabilized within the high surface area support resisting sintering and inhibiting carbon nanotubes formation during reforming reaction. Based on catalytic tests completed by thermodynamics calculations, the synthesized materials proved to be efficient not only for dry reforming of methane, but also for CO_2 methanation reaction and dry reforming of waste pyrolysis products.

Keywords: methane reforming, CO_2 methanation, nickel nanoparticles, mesoporous Al_2O_3 , metal-organic framework