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## CATALYTIC MATERIALS FOR BIOMASS-DERIVED SECONDARY RAW MATERIALS TRANSFORMATIONS

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Ελαβε Κυριος ο Θεός τον άνθρωπον, τον οποίον εδημιούργησε, και έθεσεν αυτόν στον παράδεισον της χαράς και της τέρψεως, δια να εργάζεται εις αυτόν και να τον φυλάσση.

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#### List of publications

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#### List of abbreviations

COP21	21 <sup>st</sup> UN Conference of the Parties
GHG	Global Emission of Greenhouse Gases
SR	Steam Reforming
APR	Aqueous Phase Reforming
XRPD	X-ray Powder Diffraction
XAS	X-ray Absorption Spectroscopy
RESPES	Resonant Photoemission Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
HAADF	High-Angle Annular Dark Field
EDX	Energy Dispersive X-ray
FEG	Field Emission Gun
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
FT-IR	Fourier Transform Infrared
ATR-IR	Attenuated Total Reflectance Infrared
UV-Vis	Ultraviolet-Visible
TGA	Thermogravimetric Analysis
DTGA	Differential Thermogravimetric Analysis
TPR	Temperature Programmed Reduction
TPD	Temperature Programmed Desorption
HPLC	High Pressure Liquid Chromatography
GC	Gas Chromatography
BAS	Brønsted Acid Site
LAS	Lewis Acid Site
TOF	Turnover Frequency

T <sub>R</sub>	Temperature of Reforming
WHSV	Weight Space Hourly Velocity
GHSV	Gas Hourly Space Velocity
GLY	Glycerol
AA	Acetic Acid
Ру	Pyridine
EG	Ethylene Glycol
HMF	5-(hydroxymethyl)-2-furaldehyde
NBP	Niobium Phosphate
PEA	Phenylethylamine
CEL	Cellobiose
GLC	Glucose
FRU	Fructose
CP1	Condensation Products
TTIP	Titanium Isopropoxide
t.o.s.	Time on Stream
NPs	Nanoparticles
Ea	Activation Energy
А	Pre-exponential Factor
$C_R$	Inlet Concentrations
$C_F$	Outlet concentrations
k	Rate Coefficient
<i>k</i> <sub>obs</sub>	Observed Rate Coefficient
θ	Contact Time
v	Volume of the Catalytic Bed
u	Flow rate
V	Volume of the Reservoir
LSPR	Localized Surface Plasmon Resonance

PRET	Plasmon-induced Resonant Energy Transfer
V <sub>O</sub> s	Oxygen Vacancies
СВ	Conduction Band
VB	Valence Band
DOS	Density of States
λ	Wavelength
DFT	Density Functional Theory

## . Introduction

#### 1.1 The challenge of sustainability

The first industrial revolution marked the beginning of a completely new era for mankind by putting the constant seeking of cheap energy and new raw materials at the center of our lives. This led entire regions of Europe and the world to assume a different relevance, according to the energy source available. Areas that once were considered deserted and with very few chances of development, became in short time the fulcrum of the energy supply to the world, like the Arabic peninsula and the polar regions. Along with the wealth generated by the industrialization of the economies, environmental issues arose, but only in the very recent years a true consciousness about sustainability has been developed. The public opinion has come to realize that if the climate changes will not be stopped the consequences might be drastic and irreversible. The most famous example is the constant increasing of CO<sub>2</sub> concentration in the atmosphere due to anthropogenic activities, which is likely the cause of the rapid rise of the average global temperature [1].

Fortunately, many countries have pledged to minimize their carbon emissions and to promote the implementation of new and cleaner energy technologies, making sustainability the pivot of the new development policies. Sustainability was defined as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" at the Burtland conference in 1987 [2]. As a very preliminary result of these policies, for the first time, the economic growth and energy-related emission are starting to decouple. Day by day always more countries are adhering to the 21<sup>st</sup> UN Conference of the Parties (COP21) held in Paris in 2015 that sets new targets for the reduction of the carbon emissions and encourages a wider exploitation of renewable resources [3].

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If renewables represent the long-term solution, for the short- to middle-term period a continuous improvement of the energy efficiency seems to be more realistic [4]. Utilization of locally-produced energy (possibly sustainable), reduction of the wastes, as well as recovery of the low-grade heat [5], have been proposed as ways to improve the overall efficiency not only of the transformation processes, but also of buildings, houses, factories, etc. [4.] Some resistance has been encountered when trying to implement these new policies. The relatively high costs of implementation are, however, compensated by the economical return in terms energy saving. Thus, the parallel development of both renewable-based technologies and increasing the energy efficiency is probably the most viable solution to meet the environmental and economical requirements at the same time.

As previously introduced, the development of suitable, "green" technologies is not a sudden process, but on the contrary it requires important investments and long-time plans. [1,6] The rapid depletion of fossil fuels, which are the sources of most of our energy and chemicals, is swiftly reducing the available time, making the next few years crucial for our future. Although many claim that reducing emissions by using new technologies and renewables would cost too much, resulting in loss of competitiveness, the reality is quite the opposite: The necessary investments would be manageable and even profitable by stimulating the growth with the creation of millions of "green" jobs and by increasing the technological innovation [6]. Besides the beneficial impact on human health, the exploitation of renewable local resources is also an opportunity to promote the economies of those countries suffering from the lack of fossil fuels, therefore having high energy-related costs. For instance, countries with high solar irradiation could gain much benefits from the exploitation of the sun for both energy and fuels production. Speaking more generally, our practically total dependence on fossil fuels, and particularly on oil and coal, puts in real danger our way of living even in the near future [2,3]. Hence, the transition to a productive system, where always more chemical commodities are produced starting from renewable resources, like biomass, as well as the development of transport networks, where only clean energy is admitted, are primary goals of this century [3,6].

Besides the development challenge, renewable-based technologies are, however, not devoid from intrinsic drawbacks. For instance, when talking about wind energy, the winds are sometimes hard to predict and not always constants. Another example, which will be discussed in more detail in the next paragraph, is the very complex composition of the biomass, that makes the industrial production of molecules with high interest as chemical building blocks quite tricky [7,8]. Despite these and other problems, an actual transition to a "green" economy is possible also by starting from the technologies already available, and the related costs must be seen as investments that will pay off the generations to come, just like the investments of the past have brought us here.

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#### 1.1.1 Sustainable raw materials and clean energy vectors

The reasons behind the reckless use of fossil raw materials and fuels for almost every application is that they are very easy to process, have a high energy density, and are (still) abundant. While abundance is the key factor that would make the renewables very appealing, the relatively low energy density and sometimes the difficulties in their management are issues that are hindering their real use. Among others, like water, there is a high interest in biomass since is carbon-neutral. This means that when biomass is used, the net contribution to the carbon emissions in the atmosphere is theoretically zero. However, the effective contribution of biomass to carbon emissions must take into account also all the additional costs, both in terms of energy consumption and emissions. Life cycle assessment approaches are powerful tools that try to predict the overall benefits when using biomass, from the production, the transportation, and finally to the utilization. Surprisingly, it was found that the global emission of greenhouse gases (GHG) using renewables could be comparable, or in some cases, even higher than those of fossil fuels using the current technologies [9,10]. A sensitive case is energy production from wastes, where purification- and transportation-related energy requirements are not negligible. Moreover, GHG are highly variables, mostly depending on the kind of biomass considered and the distance between production and final utilization sites. Wind energy for local use is considered to be one of the most overall "green" ways for energy production, while optimized lowtemperature transformations should be preferred to improve the energy efficiency and, thus, contain the emissions.

Nonetheless, biomass exploitation is one of the most promising ways for both sustainable energy and chemicals production. It is practically ubiquitous because it can be derived by an endless list of plants, animal residues, by-products of other processes, algae, agricultural crops, wastes, etc. Crops and agricultural residues represent the most exploited ones, owing to their low cost and ease-to-produce [11,12].

This huge list of sources of biomass may be a problem when trying to predict its exact final composition, which ranges from simple molecules, such as alcohols, to heavy oxygenates, such as sugars or lignocellulose, but it is also a unique opportunity for the production of an equally endless list of chemical commodities [8]. Furthermore, molecules with high interest as energy vectors can be produced from biomass, with hydrogen being the most important one [1,13]. The choice of the proper kind of biomass to be exploited becomes then crucial. Besides that, an excessive use of agricultural-derived raw materials could become competitive with the food production. The solution is to use only byproducts of other processes or wastes, which would be otherwise disposed in incinerators or landfills. However, the low purity and danger in their handling are currently slowing their use [11-14].

Despite these issues, many technologies for the processing of raw biomass have been developed. For example, catalytic supercritical water gasification, known also as hydrothermal gasification, is a promising technology for the production of sustainable hydrogen from non-edible biomass, such as lignocellulosic materials and algae. More generally, pyrolysis, gasification, reforming reactions, partial oxidations, electrolysis, photocatalytic, photo-electrocatalytic water splitting, and fermentations, all represent interesting processing for raw biomass transformation. Issues still remain, particularly regarding product selectivity and coking [7,8,12-18]. Importantly, studies carried out on single model molecules, such as acetic acid, glycerol, ethanol, etc., showed promising results, and maybe could provide useful insights for the development of more active and selective technologies [7,8,12-18].

As mentioned previously, also hydrogen can be produced from biomass. In fact, in order to replace natural gas as main source, an enormous scientific effort is focused on the development of technologies using biomass as feedstock [12-16,18]. The potentialities of hydrogen as the future energy vector depend a lot on the way it is produced, because it can be considered "green" and sustainable only as long as the entire production chain is "green" and sustainable. Otherwise, it would be "brown", that is just another fuel derived from fossil raw materials (i.e., steam reforming of natural gas) [1,13]. Apart from the production challenge, there are other problems concerning hydrogen, like heavy corrosion, losses and low energy density by volume [13]. Nevertheless, the carbon neutrality and the possibility to use hydrogen in already existing devices, like fuels cells or even combustion engines, as well as reactant for refining industries and ammonia synthesis, are pushing the scientific research and, more importantly, the public opinion towards the creation of a real hydrogen economy [1].

In this broad scenario of renewable resources and new clean energy vectors, catalysis plays a fundamental role, and its importance has never been so fundamental as nowadays. Indeed, practically all the technologies for biomass processing need catalytic materials to work and/or to achieve industrial-relevant production rates [7,8,12-18]. The reason is that catalysis allows to dramatically increase the reaction rates and/or to optimize the selectivity towards the desired products, which is crucial for the limitation of the by-products, and thus for the cleanness of the process. Homogeneous catalysts have demonstrated excellent catalytic properties for the biomass valorization, such as high yields and high selectivity. However, the difficulties encountered in removing possible metals in trace and separating the catalysts from the reaction media have limited their use. The most logic solution is to use something easy to remove from the reactors but that still ensures high catalytic performances, that is, heterogeneous catalysts. These materials are typically composed by high surface area supports, such as silica or alumina, on which is anchored or deposited a catalytically active phase, such as metal

nanoparticles in the range of 1-20 nm, or grafted molecules. Thermal and chemical stability are important features for the supports, as high turnover frequency is for the active sites. In the next section the impact of catalyst nanostructuring on the catalytic activity will be discussed

#### 1.1.2 The role of nanocatalysis

Ideally, industrial-grade catalysts should feature all the positive peculiarities of homogeneous catalysts, like high conversion levels and high selectivity, but with the ease in separation and handling proper of heterogeneous catalysts. When the dimensions fall in the nanometric scale, materials show unique features that can be tuned to enhance the catalytic performances and, thus, meet all the aforementioned requirements [19]. Many different ways of nanostructuring catalysts have been proposed in the last years, mostly thanks to the development of powerful characterization tools, like HRTEM with the aberrations corrected and synchrotron light-based technologies, that allow scientists to investigate the materials even at the atomistic scale. As a very representative example, a Pt dispersion so high that practically all the surface of the support is decorated with very stable Pt atoms, has been achieved by smart synthesis procedures and thermal treatments. The so-prepared catalyst featured, in terms of available active phase, Pt atoms that resemble those of a homogeneous catalyst, while being anchored and stabilized on a support [20].

For many years supports were considered only as mere carriers, with the only task of supporting the active phase, but it has become clear that their role is far more important than that. In fact, in many cases, supports actively participate into the reaction, sometimes by activating the reactant molecules and/or by providing fundamental acidic/basic functionalities, as well as spillover centers for the intermediates [21]. The smart use of such peculiarities, proper of the supports, could result priceless for the development of active catalysts that must show high production rates and resistance over time while having low preparation costs. A good example is the addition of ZnO to a Co/CeO<sub>2</sub> catalysts for ethanol steam reforming investigated by Davidson *et al.* [22], which resulted in enhanced water activation and oxygen mobility, leading to increased resistance against coking.

In order to reduce or at least contain costs of supported catalysts, which is fundamental for their commercialization, many routes have been proposed. The most straightforward is the use of non-noble metals or, when that is not feasible, to use very low metal loadings. This implies that the few active phase available must show the best performances possible, both in terms of productivity and stability. Improving the active phase stability by means of promoters or working on the shape of metal nanoparticles are only few examples of ways to address this challenge. There is, in fact, a strong dependence of the catalytic activity and stability with the size and the shape of the nanoparticles. For

instance, a lower defectivity of the nanoparticles has a positive effect on catalyst stability by reducing the coking rates [23]. Advanced preparation procedures designed to both ensure high active phase dispersions and shape control have been developed. For instance, Benito *et al.* [24] studied the impact of two preparation procedures on the catalytic activity of a low-loading bimetallic Rh-Ni catalyst, namely chemical vapor deposition and coprecipitation methods. The bimetallic catalysts were also compared to the monometallic ones. The Rh-Ni catalyst prepared by coprecipitation showed the best catalytic performances among all the tested catalysts, owing to the stronger Rh-Ni interaction, which increased the Ni reducibility and dispersion.

As just shown, the addition of a second metal, referred to as promoter, is a good strategy to contain manufacturing costs while improving the activity. Noteworthy, bimetallic catalysts often show completely new characteristics, which would not be available by using the single metals alone. Such improved features arise from the electronic interactions between the two metals and/or by the introduction of new powerful functionalities in close proximity to the main metal. All these new features may result, for example, in new pathways followed by the reaction, as well as in outstanding resistance to coking and poisoning [19,21,25,26].

Always in the scenario of cost containment, the production of relatively high amounts of active and stable catalyst is fundamental. Besides the classical preparation procedures, many novel methodologies have been proposed to prepare optimized catalysts. Just an example, the preformation of ligand-free nanoparticles via evaporation technologies has proven to be highly promising for the preparation of active bimetallic catalysts, obtainable even in higher amount than with the more classical gas-phase methods [27].

The list of the possibilities offered by nanostructuring catalytic materials for the development of industrial-grade catalysts could continue practically forever. Great improvements in catalytic activity have been achieved thanks to nanostructuring. However, without a deep understanding of the actual reaction mechanisms involved in the processes, further improvements are rather unlikely to be achieved. The use of *in-situ* and/or *in-operando* characterization techniques, as well as novel computational modelling, could open new possibilities for the rational design of the new, powerful catalysts. Such characterizations should be used also because detailed information on the features of the catalyst surfaces under real working conditions are critical to the development of reliable predictive computational methodologies [28]. There is, in fact, a strong connection between the catalytic performances and the surface structure/properties of the catalyst, which are in turn highly dependent on the reaction conditions. However, it is sometimes hard to investigate the catalytic materials at the atomistic scale under *operando* conditions, due to the modification phenomena and/or the presence of adsorbed reactants/intermediates [29]. As an example of structure-dependent activity,

is worthy a mention the case of ammonia synthesis on single-crystal Fe surfaces. It was found a correlation between the ammonia production rates and the exposed face of Fe crystals, which depends strongly on the activation treatment. The following activity ranking was evidenced: Fe(111) > Fe(100) > Fe(110). [30] Moreover, Li *et al.* [31] showed by *ab-initio* calculation, fully supported by experimental observations, that the lattice mismatch and the lack of strong electronic interactions between the spinel (111) surface oxygens of the Mg(Al)O support and Ru nanoparticles were the cause behind the poor catalyst stability. These findings, but of course not only them, could be very important to the choice of more suitable compatible materials for the preparation of more stable catalysts.

Thanks to advanced characterization techniques and the support of theoretical calculations, some monometallic catalysts were found to be actually bimetallic catalysts. As an example, Karim *et al.* [32] revealed that a high temperature pretreatment of a Pd/ZnO catalyst in hydrogen facilitates the formation of a surface intermetallic Pd-Zn, which is essential for low CO selectivity, due to the lower methanol decomposition, in the steam reforming reaction of methanol. The steam reforming reaction of ethanol was used by Wang *et al.* [33] as probe to investigate the support effect on a Pt-Ni catalyst, and the results were fully supported by DFT calculations. Compared to other supports, the higher activity of the TiO<sub>2</sub>-supported catalyst was ascribed to the lower binding energy of TiO<sub>2</sub> toward Ni, with the consequent formation of Ni segregates in the form of Ni-terminated surfaces, which are the most active in reforming reactions.

In conclusion, it has become evident that the technologies now available need to be improved to meet the environmental requirements and develop completely sustainable economies. Bimetallic catalysts offer promising opportunities, but much must still be discovered about the actual structure of the catalysts under real working conditions. Nanostructuring and deep investigations of the reaction mechanisms, as well as computational predictive tools, may allow to further rationalize the materials design for specific applications up to, hopefully, developing industrial-relevant grade catalysts.

#### 1.2 Aim of the thesis

The broad aim of the present thesis work is to exploit biomass-derived compounds as raw materials for the sustainable production of hydrogen and chemicals through chemical transformations. Specifically, the focus of the work is the nanostructuring of the catalytic materials in order to improve their performances, both in terms of productivity and selectivity, in reforming and biomass valorization reactions. The impact of the nanostructuring is investigated and correlated to the reaction pathways as well. For the sake of this work, two different biomass-derived model molecules and one by-product of a well-known industrial process are considered.

Acetic acid, which is one of the most abundant components of the bio-oil derived from the pyrolysis of biomass, and glycerol, which is a by-product of the biodiesel industry, are used as model molecules for hydrogen production via steam and aqueous phase reforming. The role of the defectivity of supported Ru and Rh nanoparticles in the reaction of the steam reforming of acetic acid is highlighted and tuned by controlling nanoparticles shape and size. Particular emphasis is given to the impact of their reduced defectivity on the catalyst stability and coke deposition rates. On the other hand, the addition of Mn as promoter to a Pt-based catalyst is studied and tested in both the steam and aqueous phase reforming reaction of glycerol. The new surface properties of the prepared bimetallic catalyst are investigated by mimicking the real working conditions, and correlated with the reaction pathways.

Finally, the direct conversion of cellobiose, a model molecule of the saccharidic-derived biomass, to 5-hydroxymethyl-2-furaldehyde (HMF), which is a platform molecule for the sustainable production of many compounds with high commercial interest, is deeply studied. In detail, the surface acidic properties of a series of niobium phosphate-modified catalysts are thoroughly characterized by spectroscopic infrared technique by mimicking the actual working conditions, and correlated to the reactivity.

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#### Chapter 1

# **2**. Well-formed, size-controlled ruthenium nanoparticles active and stable for acetic acid steam reforming

#### 2.1 Introduction

Hydrogen is often thought as future clean and efficient energy vector. However, hydrogen is mainly produced by steam reforming of natural gas, making the development of processes both economically and environmentally friendly fundamental for the creation of a real hydrogen-based society. Several processes based on renewable resources/wastes and energy sources have been proposed, such as water electrolysis (using electricity obtained from sustainable resources) [1,2], and water photo-splitting [3,4]. Even though these technologies are theoretically completely sustainable and feasible, there are still several issues to be addressed, mostly regarding the scaling up and the maximum amount of hydrogen that can be produced, which are hindering their implementation for real applications in the short timescale. Conversely, reforming reactions are a well-established technology, easy to scale up, and as such is highly promising for industrial-relevant hydrogen production from biomass.

There are already few known examples of real applications, at least at the pilot plant stage, such as Linde plant for glycerol pyro-steam reforming in Leunde, able to produce up to 50 m<sup>3</sup> h<sup>-1</sup> of hydrogen [5], or BTG Biomass Technology Group BV pilot plant for the conversion of wet biomass and residues in supercritical water to produce substitute natural gas or hydrogen (5-30 L h<sup>-1</sup> of liquids) [6]. Pyrolysis oils have attracted much attention among renewables or waste raw materials because they can be produced from a large variety of sources and are a way to compact biomass to increase the energy density and reduce the content of water, thus making their transportation, storage and delivery more economically competitive. They are composed by a complicate mixture of different compounds, such as acids, alcohols, ketone, aldehydes, esters, sugars, phenol, and others, which is appealing for the production of a variety of biomaterials, chemicals, bio-fuels, and energy. Hydrogen and syngas are typical commodities that can be produced from steam reforming of whole bio-oils, or principally from their hydro-soluble light fraction. The former can be used as energy vector or for upgrading the heavier compounds of non-water soluble fraction of bio-oil, whereas syngas is a key intermediate for the production of biofuels and other chemicals. Around the 4-15 % of the whole bio-oil is made of carboxylic acids [7], with the acetic acid being of the main components. It represents around 6-10% of whole bio-oils [8], and reaches up to 12% of water soluble fraction.

Many catalysts have been investigated so far both based on noble metals and non-noble metals, but also mixtures of them. Among the noble metals, Rh is known for its excellent catalytic properties, [9,10] while ceria and zirconia are renowned as supports due to their high oxygen mobility. Lemonidou and co-workers reported on the optimized performances of a low loaded Rh catalyst supported on (La-doped) CeO<sub>2</sub>-ZrO<sub>2</sub> [11,12]. Another metal that showed remarkable catalytic activity in reforming reactions and low coke deposition rates, is Ru [13-16]. Conversely, Pt-based systems have been reported to be less active than Rh, Pd, and Ru [17]. Among non-noble metals, Ni is the most widely used, alone [18,19], or in bimetallic systems [20-24]. Contrary to noble metal catalysts, Ni and Co catalysts exhibited relevant coke deposition rates, which is probably one of the most important issues of all reforming catalysts [25,28]. Hu *et al.* [29] reported a coke deposition rate of 12.5 mg<sub>coke</sub> g<sub>cat</sub> h<sup>-1</sup> for a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after 20 h time-on-stream (t.o.s.) carried out at stoichiometric steam-to-carbon (S/C) ratio and at a reaction temperature of 600 °C.

Many strategies have been studied trying to overcome this issue, such as the addition of a second metal known to limit coke deposition rates, like Cu [30], and/or choosing the proper support materials able to stabilize the metal nanoparticles, with high the oxygen mobility and the suitable balance between acidic and basic surface features. In this scenario Mg(Al)O mixed oxides are well established support materials in SR reactions of CH<sub>4</sub>, ethanol, glycerol, acetic acid, due to their ability in stabilizing supported metal NPs, and limiting coke formation [14,31-39]. The development of catalysts featuring high stability and low coke deposition rates is of primary importance. Moreover, limiting or at least reducing the amount of noble metals in the catalysts is fundamental to contain the costs. The synthesis of stabilized metal nanoparticles in solution by suitable preparation methods offers the possibility to finely control the size and the shape of final supported particles [40]. Here we report, for the first time, the application of size- controlled metal nanoparticles (SCMNPs) deposition method [41-45] for the preparation of low loaded Mg(Al)O mixed oxide supported Rh and Ru catalysts and their application in acetic acid steam reforming. Ru was chosen as active metal due

to its well-known activity in reforming reactions, resistance to coking, and, if compared to other noble metals, low cost. Mg(Al)O mixed oxides are promising supports for many applications including steam reforming, also with Ru [37,46-48]. On the other hand, Rh catalysts were taken as references owing to their known remarkable activity.

Ru and Rh nanoparticles were prepared by reduction of the corresponding metal salts with molecular hydrogen in organic solvent in the presence of long-chain aliphatic amines (trioctylamine). The so prepared colloids were then deposited on the supports leading to size-controlled supported Rh and Ru nanoparticles, respectively. Compared to other preparation procedures, as will be discussed, this method results in catalysts showing superior catalytic activity, stability, and resistance to coking. Moreover, SCMNPs deposition method here described can be easily scaled up making it interesting for the preparation of real industrial catalysts.

#### 2.2 Experimental

#### 2.2.1 Catalysts preparation

A commercial Pural MG70 hydrotalcite (Sasol, Germany) was calcined in air overnight at 900 °C to obtain the Mg(Al)O mixed oxide support (hereinafter called MG70). A wet impregnation procedure [37] was used to prepare a first set of catalysts starting from MCl<sub>3</sub> (Sigma Aldrich) aqueous solutions (M: Ru and Rh), hereinafter referred to as M/MG70, followed by calcination in air at 500 °C for 1 h.

A second set of catalysts, hereinafter called M(TOA)/MG70 was prepared by size-controlled metal nanoparticles (SCMNPs) deposition method [41,42,44]. The SCMPs THF solutions  $(1.7 \times 10^{-3} \text{ M})$  were obtained by reduction of the metal chloride with trioctylamine (TOA) in a slight molar excess (3:1 TOA:M molar ratio) under static hydrogen atmosphere (1.0 bar, T = 25 °C) for 24 h. The SCMNPs were deposited on MG70 by contacting the solutions with the support under inert atmosphere for 1 h, the catalysts were then filtered, washed with THF (3 times, 20 mL) and finally dried in vacuo overnight. The catalysts were then pelletized with a 45-35 mesh, and before the catalytic tests were reduced *in situ* at 700 °C in a H<sub>2</sub> flow (50 mL min<sup>-1</sup>).

#### 2.2.2. Materials characterization

Inductively coupled plasma-optical spectroscopy (ICP-OES) (ICAP 6300 Duo, Thermo Fisher Scientific) was used after digestion of the catalysts to determine the metal loadings. The reduced Ru catalysts (approximately 15 mg) were digested in 5 mL of NaOCl 13%, and then acidified with 5 mL of HCl 37%. Rh catalysts (approximately 15 mg) were microwave digested in aqua regia. After digestion all solutions were diluted with high purity deionized (18 M cm) water (MilliQ Academic, Millipore) until they reached 20 g. Finally, support residues, eventually present, were eliminated by filtration with a PTFE syringe filter (0.20  $\mu$ m).

 $N_2$ -physisorption isotherms at 77 K were performed to measure the specific surface areas of the catalysts with a ASAP 2020 apparatus using the BET equation. Prior to each measurement the catalysts were outgassed at 200 °C for 2h.

The acid properties of the Ru catalysts were studied by fast Fourier infrared spectroscopy (FT-IR) (Biorad FTS-60A) using pyridine as probe molecule. First, the reduced samples were pressed in self-supporting disks of about 13 mm in diameter, and transferred into the IR cell, and reduced *in situ* in static hydrogen at 500 °C for 30 min. Then, the samples were contacted with pyridine vapours for 10 min at room temperature, followed by 30 min in high vacuum to eliminate the excess of pyridine. Finally, a series of spectra were collected every 50 °C starting from room temperature until 250 °C. Acidic surface sites were determined integrating the peak at 1448 cm<sup>-1</sup>, corresponding to Lewis acidity (Brønsted acid sites were not detected), according to Emeis [49]. The values are expressed as micromoles of adsorbed pyridine per gram of catalyst ( $\mu$ mol  $g_{cat}^{-1}$ ).

#### 2.2.3 XRPD

X-ray powder diffraction (XRPD) patterns were recorded in the  $5^{\circ} \le 2\theta \le 70^{\circ}$  range employing the Cu-K radiation at room temperature. Rietveld analysis was performed using the GSAS software suite of programs. [50] Structural models were taken from [51] for cubic MgAl<sub>2</sub>O<sub>4</sub> (space group Fd-3m), from [52] for cubic MgO (Fm-3m) and from [53] for rhombohedral Mg<sub>6</sub>Al<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4H<sub>2</sub>O (hereafter HT) (space group R-3m).

The background was subtracted using the shifted Chebyshev polynomials, while the diffraction peak profiles were fitted with a modified pseudo-Voigt function. In the last refinement cycles, scale phase factors, and cell parameters, as well as isotropic thermal parameters, were allowed to vary as well as back- ground, zero diffractometer position and line profile parameters.

#### 2.2.4 H<sub>2</sub>-TPR

A PulseChemisorb 2700 (Micromeritics) device was used to perform the hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) experiments, by ramping the temperature until 750 °C at 8 °C min<sup>-1</sup> in an 8 vol.% H<sub>2</sub>/Ar flow. The amount of hydrogen consumed during was measured by TCD. Prior to the analysis, the M/MG70 samples were treated at 130 °C for 1 h under Ar flow (20 mL min<sup>-1</sup>), while M(TOA)/MG70 samples were calcined at 500 °C for 2 h in O<sub>2</sub> (40 mL min<sup>-1</sup>).

#### **2.2.5 HRTEM**

Electron micrographs were carried out with a Zeiss LIBRA 200FE, equipped with: 200 kV FEG, in column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), HAADF STEM facility, EDS probe for chemical analysis. Before introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a holey carbon gold grid (300 mesh).

The histograms of the metal particle size distribution for the samples were obtained by counting at least 500 particles onto the micrographs. The mean particle diameter (d<sub>m</sub>) was evaluated by using the formula  $d_m = \sum d_i n_i / \sum n$  where  $n_i$  is the number of particles with diameter  $d_i$ . Metal dispersion was evaluated from mean particle diameter according to the procedure reported by Borodzínski and Bonarowska [54].

#### 2.2.6 TG analysis

Thermal gravimetric analysis were performed on a NETZSCH STA 409 PC/PG apparatus in order to estimate the amount of coke deposited on the catalysts after the catalytic tests. About 40 mg of sample were loaded in a platinum crucible and heated in a 40 mL min<sup>-1</sup> air flow up to 900 °C at a constant rate of 5 °C min<sup>-1</sup>.

#### 2.2.7 CO-DRIFTS

Diffuse reflectance infrared Fourier transformed spectroscopy experiments using CO as probe molecule (CO-DRIFTS) were performed on a Biorad FTS-60A apparatus, which is described elsewhere [55,56]. Before CO adsorption the samples were reduced in situ in hydrogen flow (20 mL min<sup>-1</sup>) at 500 °C for 1 h, then cooled down to RT in He flow (20 mL min<sup>-1</sup>). Pure CO flow (20 mL min<sup>-1</sup>) was then admitted to the DRIFTS reaction chamber and after 30 min the cell was purged with He until CO adsorption bands stability.

#### 2.2.8 Catalytic tests

A home-made test unit [37] was used to perform the acetic acid steam reforming experiments. The catalysts were placed in a fixed-bed tubular quartz reactor operating at atmospheric pressure and the reactant mixture was fed by means of a dosing pump (KNF LAB SIMDOS 02). He was used as carrier gas (30 mL min<sup>-1</sup>). Prior to each experiment, the pelletized catalysts were reduced *in situ* at 700 °C for 1 h in H<sub>2</sub> flow (30 mL min<sup>-1</sup>). The reactant mixture was vaporized by a dedicated furnace at 250 °C on a quartz chunks bed placed before the catalytic bed. Gaseous products (H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub>) were analysed by an online double column GC-TCD (Agilent 6890N), one analysis per hour (20 analysis). The overall reaction and the equations used for the calculation of the hydrogen yield, carbon conversion and selectivity towards the products are as follows:

 $CH_{3}COOH + 2H_{2}O \rightarrow 2CO_{2} + 4H_{2}$   $H_{2} \text{ Yield (\%)} = \frac{H_{2} \text{ mol produced}}{(\text{mol AA in the feed}) \times 4} \times 100$   $Carbon \text{ Conversion (\%)} = \frac{(CO_{2} + CO + CH_{4}) \text{ mol produced}}{(\text{mol AA in the feed}) \times 2} \times 100$   $Selectivity \text{ of } i (\%) = \frac{i \text{ mol produced}}{(\Sigma i \text{ species}) \text{ mol produced}} \times 100$   $(i \text{ species} = CO_{2}, CO, CH_{4})$ 

The catalysts reactivity was evaluated for 20 h t.o.s. at a reforming temperature ( $T_R$ ) of 700 °C using a S/C ratio of 3 (mol/mol), fed at 60 µL min<sup>-1</sup>. The weight hourly space (WHSV) was 6 h<sup>-1</sup> (defined as mass of acetic acid in the feeding mixture per mass of catalyst per hour), but stress tests were performed at WHSV of 12 h<sup>-1</sup> and/or  $T_R$  of 600 °C. TOF values were calculated according to the following equation:

 $\text{TOF}(h^{-1}) = \frac{\text{mol AA converted to CO}_2, \text{CO}, \text{CH}_4}{\text{mol of metal} \times \text{dispersion} \times \text{h}}$ 

Metal: Ru and Rh

#### 2.3 Results

#### 2.3.1 General features

The metal loadings of the catalysts determined by ICP-OES analysis were found to be close to the theoretical ones (0.5 wt.%), ranging from 0.4 to 0.6 wt.% for the SCMNPs derived and impregnated catalysts, respectively. Specific surface area of catalysts shows a small decrease with respect to parent bare support, and data suggest dependence on metal content and on calcination times (24 h for MG70 and 48 h for MG70-48, respectively) (see Table 1).

Elemental analysis was used to evaluate the amount of nitrogen deriving from the decomposition of TOA in the SCMNPs derived samples. Only the fresh (i.e., as synthesized) Rubased catalysts so prepared showed residual presence of nitrogen, with Ru(TOA)/MG70 and Ru(TOA)/MG70-48 having 1.64 and 1.89 wt.% of N content, respectively. However, the reduction treatment completely resulted in the removal of all the N present.

The acidic surface features of all the catalysts were investigated by FT-IR using pyridine as probe molecule. Upon pyridine adsorption bands located around 1600-1613 cm<sup>-1</sup> and 1440-1449 cm<sup>-1</sup> appear in FTIR spectra (not shown) due to pyridine adsorbed on  $Mg^{2+}$  and  $Al^{3+}$  sites. More in detail band at 1600-1613 cm<sup>-1</sup> originates from  $Mg^{2+}$  c.u.s. sites, while that at 1440-1449 cm<sup>-1</sup> derives from octahedral and tetrahedral  $Al^{3+}$  sites [57]. No Brønsted acid centres were detected, and Lewis acid sites (LAS) were present in comparable amounts on the bare support and on all the reduced Ru and Rh catalysts, regardless the metal and/or the preparation procedure (see Table 1).

Sample	M (Rh, Ru) Loadings (wt.%)	$\frac{SSA_{BET}}{(m^2 g^{-1})}$	N content Fresh / Reduced (wt.%)	Lewis acid sites (µmol g <sub>cat</sub> <sup>-1</sup> )
MG70	-	87	0 / 0	16
Rh/MG70	0.51	75	0 / 0	19
Rh(TOA)/MG70	0.37	81	0 / 0	13
Ru/MG70	0.59	70	0 / 0	17
Ru(TOA)/MG70	0.38	82	1.64 / 0	15
Ru(TOA)/MG70-48	0.46	58	1.89 / 0	14

 Table 1. Metal loadings, specific surface area (SSA), N content and Lewis acid sites (LAS) of bare MG70 support and of Rh and Ru catalysts.

#### 2.3.2 H<sub>2</sub>-TPR

Figure 1 shows the H<sub>2</sub>-TPR profiles of the Ru and Rh catalysts. SCMNPs (M = Ru and Rh) deposited samples show lower reduction temperatures if compared with traditional wet impregnated ones: 304 °C and 122 °C for Rh/MG70 (trace a) and Rh(TOA)/MG70 (trace b), respectively. Rubased catalysts show a similar behaviour, but with a little more complex reduction patterns. Ru/MG70 sample (trace c) has a main peak centred around 204 °C and a small, broad shoulder at 267 °C; Ru(TOA)/MG70 catalyst (trace d) displays two sharp peaks at 125 °C and 145 °C (with also two minor peaks at 90 °C and 233 °C).

In the oxidized catalysts, a lower degree of reduction of the Ru and Rh cations dissolution in Mg Al spinel lattice or, in other words, a lower interaction of the oxide species with the support, was suggested by the location of the reduction peaks of SCMNPs samples (traces b, d and e in Fig. 1) [37,58]. Interestingly, an increase in reduction temperature of Ru oxide nanoparticles occurred, with the appearance of an "high" temperature main peak located at 174 °C in the TPR profile, as the content of the residual hydrotalcite decreased in the Ru(TOA)/MG70-48 sample (trace e).



**Figure 1.** Hydrogen consumption profiles (TPR) of Rh/MG70, trace (a); Rh(TOA)/MG70 trace (b); Ru/MG70, trace (c); Ru(TOA)/MG70, trace (d); Ru(TOA) /MG70-48, trace (e) catalysts.

#### 2.3.3 XRPD

X-ray powder diffraction was used to investigate the phase composition of commercial MG70 hydrotalcite before and after the annealing treatment. In Figure 2(a) is reported the XRPD pattern collected on pristine hydrotalcite MG70. The diffraction peaks are consistent with rhombohedral polymorph (space group R- 3m). In Figure 2(b) the Rietveld refinement related to MG70 sample annealed overnight is shown as an example. All the peaks in the diffractrograms are indexed according to the following phases: MgAl<sub>2</sub>O<sub>4</sub> (space group Fd-3m), MgO (Fm-3m) and residual HT. No diffraction signals ascribable to supported metal nanoparticles were detected. The same pattern indexing holds for XRPD related to Ru/MG70 and Ru(TOA)/MG70 samples.

In Table 2, selected structural parameters along with phase fractions estimated by Rietveld method obtained for all samples are listed. The presence of MgO and spinel-type phases is in agreement with previous studies on annealing of HT at 900 °C [59]. The different approaches used to prepare the catalysts did not affect the composition of the support, in fact all the samples obtained from MG70 annealed overnight at 900 °C showed the same phase composition. Conversely, the annealing time had a profound impact on the phase composition, in particular on both the MgO and the residual hydrotalcite percentage. With longer annealing times, a lower amount of hydrotalcite was found.



**Figure 2.** (a) X-ray powder diffraction pattern of MG70 before annealing. The indexing is related to main peaks of HT phase. (*b*) Measured (dots), calculated (line) powder diffraction patterns and residuals (bottom line) for MG70 after annealing. Markers indicate the peaks related to the identified phases.

	MG70	MG70-48	Ru/MG70	Ru(TOA)/MG70
Phase 1 - MgAl <sub>2</sub> O <sub>4</sub>				
a (Å)	8.105(1)	8.099(1)	8.095(1)	8.097(8)
V (Å <sup>3</sup> )	532.5(2)	531.9(2)	530.5(2)	531.1(2)
Phase Fraction (%)	32.61	34.1	33.72	32.60
Phase 2 - MgO				
a (Å)	4.2090(6)	4.2099(5)	4.2051(6)	4.2086(5)
V (Å <sup>3</sup> )	74.57(3)	74.62(3)	74.36(3)	74.54(2)
Phase Fraction (%)	52.74	59.3	51.53	52.31
Phase 3 - Hydrotalcite				
a (Å)	3.053(2)	3.054(3)	3.058(1)	3.033(8)
c (Å)	23.78(2)	23.26(4)	24.04(1)	24.18(3)
V (Å <sup>3</sup> )	191.9(2)	187.9(3)	194.7(2)	192.7(3)
Phase Fraction (%)	14.65	6.3	14.75	15.09

Table 2. Selected Rietveld refinement results for annealed MG70, MG70-48, Ru/MG70 and Ru(TOA)/MG70.

#### 2.3.4 CO-DRIFTS

The presence of isolated Rh<sup>*n*+</sup> and Ru<sup>*n*+</sup> sites and the surface properties of metals NPs (exposed facets, corners, etc.), as well as their defectivity, were investigated by DRIFT spectra of adsorbed CO reported in Fig. 3. The CO-DRIFT spectra of Ru and Rh samples exposed to pure CO flow and then briefly purged in He flow showed peculiar features of both CO linearly adsorbed on zero-valent metal nanoparticles in the wavelengths range 2100-1950 cm<sup>-1</sup> and on isolated Rh<sup>*n*+</sup> and Ru<sup>*n*+</sup> sites. Bands centred at around 1830 cm<sup>-1</sup> ascribable to bridge CO were detected in Rh samples. Moreover, upon CO adsorption carbonates and hydrogenocarbonates absorption bands appear at 1600-1400 cm<sup>-1</sup> (not shown) [60]. A fitting procedure was used to analyse the convoluted bands located at 2100-1950 cm<sup>-1</sup>, the complete list of selected parameters of the resulting bands (location, height, width, area) being reported in Table 3.

The band due to linearly adsorbed CO on Rh<sup>0</sup> species (2060 cm<sup>-1</sup>) appeared with about the same intensity in both the spectra of the Rh catalysts [61]. The formation of dicarbonyl species on oxidized Rh sites, that is Rh<sup>I</sup>-(CO)<sub>2</sub>, can be inferred in both the spectra by the presence of three bands related to the symmetric (2095 cm<sup>-1</sup>) and antisymmetric (2041 cm<sup>-1</sup>) stretching modes [62]. The sample Rh(TOA)/MG70 displayed the highest intensity. The broad bands centred around 1820, 1645, 1520 and 1410 cm<sup>-1</sup> (not shown) can be ascribed to carbonates and hydrogenocarbonates.

Both Ru/MG70 and Ru(TOA)/MG70 samples showed bands corresponding to CO species linearly adsorbed on metallic Ru nanoparticles, located at 2033-2035 cm<sup>-1</sup>, very similar to those found in Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 2030 cm<sup>-1</sup> [63]. In addition, the presence of bands centred at 1998-2001 cm<sup>-1</sup> indicate the presence of CO adsorbed on highly reactive Ru<sup>0</sup> species, that is very small Ru clusters or atomically dispersed Ru on the support. However, these bands can also be ascribed to  $Ru^{n+}$  dicarbonyl species, which is also corroborated by the presence of tricarbonyl species,  $Ru^{n+}$ -(CO)<sub>3</sub>, detectable at 2135 cm<sup>-1</sup> and 2069-2073 cm<sup>-1</sup> [57]. These Ru species can result from the oxidative rupture of small Ru NPs [64] by a mechanism similar to the well-known one occurring for Rh [62]. The only band having the same intensity in both the samples was the one assigned to dicarbonyl species, in fact in fact in Ru(TOA)/MG70 the intensity of the band related to Ru<sup>0</sup>-(CO) species was higher and the bands of  $Ru^{n+}$ -(CO)<sub>3</sub> species were weaker. On the other hand, the band assigned to linearly adsorbed CO on  $Ru^{n+}$  species at 2114 cm<sup>-1</sup> and to bridged CO species, that is  $Ru_2$ -(CO), at 1925 cm<sup>-1</sup>, appeared only in the spectrum of Ru/MG70. A similar pattern was reported by some of us [46] for Ru/MG70 catalysts obtained by CVD of  $Ru(TMHD)_3$  (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate). Interestingly, while the band located at 2045 cm<sup>-1</sup> completely disappeared upon exposure to prolonged He flow, all the bands at 2130, 2070, and 2000 cm<sup>-1</sup> resulted stable.



**Figure 3.** CO-DRIFT spectra of Rh(TOA)/MG70, trace (a); Rh/MG70, trace (b); Ru(TOA)/MG70-48, trace (c); Ru(TOA)/MG70, trace (d); Ru/MG70, trace (e) catalysts.

Table 3. Most significant CO infrared absorption bands resulting from CO-DRIFT spectra deconvolution,
with their assignment.

Sample	Center	Height	Area	Assignment / [61,63]
	$(cm^{-1})$	(K.M. units)	(ratio)	
Rh/MG70	2095	0.013	0.16 (0.05)	sym-Rh <sup>I</sup> -(CO) <sub>2</sub>
	2060	0.135	3.25 (1.00)	Rh <sup>0</sup> -CO
	2040	0.065	2.52 (0.77)	as-Rh <sup>I</sup> -(CO) <sub>2</sub>
Rh(TOA)/MG70	2095	0.048	0.67 (0.15)	sym-Rh <sup>1</sup> -(CO) <sub>2</sub>
	2059	0.156	4.38 (1.00)	Rh <sup>0</sup> -CO
	2030	0.082	2.51 (0.57)	as-Rh <sup>I</sup> -(CO) <sub>2</sub>
Ru/MG70	2071	0.014	0.63 (0.46)	$\operatorname{Ru}^{n+}$ -(CO) <sub>3</sub>
	2033	0.084	0.27 (0.20)	Ru <sup>0</sup> -CO
	2001	0.018	1.37 (1.00)	$\operatorname{Ru}^{0^*}$ -CO / $\operatorname{Ru}^{n^+}$ -(CO) <sub>3</sub>
Ru(TOA)/MG70	2069	0.009	0.15 (0.10)	$\operatorname{Ru}^{n+}$ -(CO) <sub>3</sub>
	2035	0.036	1.48 (1.00)	Ru <sup>0</sup> -CO
	1998	0.017	1.37 (0.93)	$\operatorname{Ru}^{0^*}$ -CO / $\operatorname{Ru}^{n^+}$ -(CO) <sub>2</sub>
Ru(TOA)/MG70-48	2073	0.043	0.94 (0.18)	$\operatorname{Ru}^{n+}$ -(CO) <sub>3</sub>
	2034	0.081	5.24 (1.00)	Ru <sup>0</sup> -CO
	1987	0.015	0.58 (0.11)	$Ru^{0*}$ -CO / $Ru^{n+}$ -(CO) <sub>2</sub>
# 2.3.5 Catalytic performances

Rh based catalysts showed stable and high performances irrespective of metal deposition method (Figure 4A), with carbon conversion values comprised between 90 and 100% and hydrogen yield ranging from 65% to 70%. Conversely, Ru based catalysts performances strongly depended on the preparation method. In fact, Ru/MG70 activity decreased rapidly reaching, at 20 h t.o.s., 60% of carbon conversion, and 40% of hydrogen yield values, while Ru(TOA)/MG70 showed high performances, comparable with the reference Rh based systems (Figure 4B). As will be discussed in the next sections, coke deposition and/or nanoparticles sintering phenomena can be the responsible for these different behaviours.

Selectivity toward carbon-containing products (i.e., CO, CO<sub>2</sub> and CH<sub>4</sub>) are shown in Figure 5, and generally remained stable along t.o.s., with Ru based catalysts showing a slightly higher selectivity toward CO<sub>2</sub> and CH<sub>4</sub> if compared to the Rh-based ones. Finally, Ru(TOA)/MG70-48 sample showed good starting performances (H<sub>2</sub> yield = 58% and carbon conversion = 95%), but it deactivated at longer t.o.s. (H<sub>2</sub> yield = 55% and carbon conversion = 86%). Ru(TOA) catalysts were further tested under more severe reaction conditions, as reported in Figure 6, increasing the WHSV to 12 h<sup>-1</sup>, and their good performances were substantially confirmed, with the carbon conversion being almost complete, while observing only a 7% decrease in H<sub>2</sub> yield, and even minor variations in selectivity to CO, CO<sub>2</sub> and CH<sub>4</sub>.

Conversely, when a reaction of 600 °C was used, both carbon conversion and hydrogen yield dropped to 84% and 48%, respectively, while selectivity to  $CO_2$  and  $CH_4$  increased to 77% and 5%, respectively, and CO selectivity decreased to 17.8%. In Table 4 are reported the specific activity, expressed as turnover frequency, of all the Rh and Ru catalysts. Ru(TOA)/MG70 and Rh(TOA)/MG70 showed comparable specific activities (ranging 2100-2500 h<sup>-1</sup>), stable throughout the reaction, and higher than those measured for Rh/MG70 and Ru/MG70. The latter showed deactivation, passing from a TOF of 1500 h<sup>-1</sup> to 1170 h<sup>-1</sup>. Ru(TOA)/MG70-48 tested at double WHSV (i.e., 12 h<sup>-1</sup> vs. 6 h<sup>-1</sup>) revealed good activity even if some deactivation occurred at 20 h t.o.s..



**Figure 4.** Catalytic performances measured as H<sub>2</sub> yield (dashed line) and carbon conversion (continuos line) of Rh/MG70 (empty squares); Rh(TOA)/MG70 (full squares) catalysts (Fig. 4 A) and of Ru/MG70 (empty circles); Ru(TOA)/MG70 (full circles) (Fig. 4 B) catalysts, as measured at  $T_R = 700$  °C, WHSV = 6 h<sup>-1</sup>, S/C = 3.



**Figure 5.** Selectivity to CO<sub>2</sub> (dark gray bar), CO (light gray bar), and CH<sub>4</sub> (black bordered) of Rh; Rh(TOA); Ru; Ru(TOA) /MG70 catalysts, as measured at 20 h t.o.s.,  $T_R = 700$  °C, WHSV = 6 h<sup>-1</sup>, S/C = 3, and Ru(TOA)/MG70-48 at WHSV = 12 h<sup>-1</sup>.



**Figure 6.** Catalytic performances of Ru(TOA)/MG70 catalyst (H<sub>2</sub> Yield, black bar; C conversion, dashed bar; CO<sub>2</sub> sel., dark grey bar; CO sel., light grey bar; CH<sub>4</sub> sel., white bordered bar) as measured at S/C = 3 and t.o.s. = 20 h under different reaction conditions:  $T_R = 700$  °C, WHSV = 6 h<sup>-1</sup>;  $T_R = 700$  °C, WHSV = 12 h<sup>-1</sup>,  $T_R = 600$  °C, WHSV = 6 h<sup>-1</sup>.

Sample	Dispersion (%)	t.o.s (h)	TOF <sup>a</sup> (h <sup>-1</sup> )		
		5	1690		
Rh/MG70	39	20	1740		
	42	5	2140		
Kn(TOA)/MG/0	42	20	250		
<b>Pu/MG70</b>	31	5	1500		
Ku/WIO70	51	20	1170		
$R_{\rm H}(TOA)/MG70$	38	5	2350		
Ku(10A)/W070	56	20	2470		
Ru(TOA)/MG70-48	39	5	3770 <sup>b</sup>		
$\operatorname{Ku}(10A)/\operatorname{WIO}/0-40$	59	20	3420 <sup>b</sup>		

**Table 4.** Specific activities at 5 and 20 h t.o.s. for Rh- and Ru-based catalysts at  $T_R = 700$  °C, WSHV = 6 h<sup>-1</sup>.

<sup>a</sup> TOF based on carbon conversion to gaseous products (CO<sub>2</sub>, CO, and CH<sub>4</sub>).

<sup>b</sup>  $T_R = 700 \text{ °C}$ , WSHV = 12 h<sup>-1</sup>.

# 2.3.6 Coke characterization (TGA)

A mass loss in the temperature range of 350-550 °C due to the combustion of coke deposited on the samples' surfaces was revealed in all the TGA analysis of the Rh and Ru spent catalysts (Figure 7). The lowest coke deposition occurred on TOA derived systems (Table 5), regardless of metal (i.e., 2.0 and 1.9 mg<sub>coke</sub>  $g_{cat}^{-1}$  h<sup>-1</sup> for Ru(TOA) and Rh(TOA) respectively). Conversely, the highest coke amount was found to be deposited on Ru/MG70 sample. Notwithstanding, only a slight increase of catalyst coking occurred in the stress tests at double WHSV (Table 5).



**Figure 7.** TGA profiles of bare MG70, trace (a); Rh(TOA)/MG70, trace (b); Rh/MG70, trace (c); Ru(TOA)/MG70 ( $T_R = 600 \text{ °C}$ ), trace (d); Ru(TOA)/MG70-48, trace (e); Ru(TOA)/MG70 (WHSV = 12 h<sup>-1</sup>), trace (f); Ru(TOA)/MG70 (WHSV = 6 h<sup>-1</sup>), trace (g); Ru/MG70, trace (h) catalysts.

Table 4. Coke integral deposition rates on Rh and Ru catalysts. Coke amount measured on used catalysts
after 20 h t.o.s., $T_R=700$ °C, WHSV = 6 h <sup>-1</sup> ; * $T_R=700$ °C, WHSV = 12 h <sup>-1</sup> ; <sup>§</sup> T = 600 °C, WHSV = 12 h <sup>-1</sup>

Sample	$(\mathrm{mg}_{\mathrm{coke}}  \mathrm{g}_{\mathrm{cat}}^{-1}  \mathrm{h}^{-1})$				
Rh/MG70	3.4				
Rh(TOA)/MG70	1.9				
Ru/MG70	4.9				
Ru(TOA)/MG70	2.0				
Ru(TOA)/MG70*	3.1				
Ru(TOA)/MG70 <sup>§</sup>	2.6				
Ru(TOA)/MG70-48*	3.3				

#### Chapter 2

#### 2.3.7 Catalysts stability (HRTEM, XRPD)

HRTEM micrographs were collected on fresh catalysts prior to catalytic run and on the used ones after 20 h of catalytic experiments. Rh-supported Mg(Al)O samples (Figures 8A and B), prepared following both the two different synthetic approaches, present metal particles highly dispersed on the solid support with very similar sizes. In both samples a narrow particle size distribution, mainly ranging 0.5-2.5nm, with a comparable mean diameter (1.4 nm and 1.5 nm for Rh(TOA)/MG70 and Rh/MG70, respectively) was observed.

Conversely, HRTEM micrographs of the Ru samples (Figures 9A-C) revealed for SCMNs deposition-derived Ru catalysts (both Ru(TOA)/MG70 and Ru(TOA)/MG70-48) smaller metal particles' sizes with a narrower size distribution when compared to traditionally impregnated ones. Ru NPs in Ru(TOA)/MG70 and Ru(TOA)/MG70-48 have a mean size of 1.6 and 1.5 nm, respectively with a s.d. of 0.5 nm, whereas in Ru/MG70 Ru nanoparticles are larger (mean size of 2.6 nm) and the distribution is slightly broader (s.d. of 1.2 nm). Interestingly, no aggregation of the metal particles occurred in the deposition step was evidenced by the comparison between the HRTEM analysis of Rh(TOA) and Ru(TOA) soluble nanoparticles (Figures 10A and B) with the corresponding deriving supported systems samples.

Once employed in SR reaction Rh catalysts revealed some sintering, more evident in impregnated sample, with an increase of mean particle size from 1.4 to 1.8 nm and from 1.5 to 2.0 nm for Rh(TOA)/MG70 and Rh/MG70, respectively; while size distribution continued to be sharp, with s.d. = 0.4 (Fig. 11A and B). On the other hand, Ru catalysts supported on MG70, showed only a small increase in mean particle size: from 1.6 to 1.8nm and from 2.6 to 2.7 nm for Ru(TOA)/MG70 and Ru/MG70, respectively, but size distribution of the latter was still broad and a very low amount of larger particles ranging 10-15nm in diameter, was also detected in the used sample (Figure 12A and B). Conversely, Ru(TOA)/MG70-48 catalyst shows a different behaviour. Specifically, after the catalytic test nanoparticles size increases from 1.5 (Fig. 9C) to 2.6 nm (Fig. 12C), likely due to the lower amount of residual HT phase in MG70-48 support. Actually, the structural phases after the catalytic tests was studied by XRPD the analysis of Ru(TOA)/MG70 and Ru(TOA)/MG70-48. A low angle magnification of the Rietveld refinements related to the samples is shown in Figure 13. Diffraction signals related to hydrotalcite phase were not detected in Ru(TOA)/MG70-48, whereas Ru(TOA)/MG70 is composed by MgO 54.4%, Mg Al<sub>2</sub>O<sub>4</sub> 30.6% and HT 15.0%. MgO and MgAl<sub>2</sub>O<sub>4</sub> phase fractions are 70.4% and 26.0%, respectively, in Ru(TOA)/MG70-48 sample. Again, no diffraction scattering from the supported metal was detected in both samples.



**Figure 8.** HRTEM micrographs and particle size distributions of freshly prepared Rh(TOA)/MG70 (A) and Rh/MG70 (B).



**Figure 9.** HRTEM micrographs and particle size distributions of freshly prepared Ru(TOA)/MG70 (A), Ru/MG70 (B) and Ru(TOA)/MG70-48 (C).



Figure 10. HRTEM micrographs of freshly prepared Rh(TOA) (A) and Ru(TOA) (B) colloids.



**Figure 11.** HRTEM micrographs and particle size distributions of Rh(TOA)/MG70 (A) and Rh/MG70 (B) after catalysis (20 h).



**Figure 12.** HRTEM micrographs and particle size distributions of Ru(TOA)/MG70 (A), Ru/MG70 (B) and Ru(TOA)/MG70-48 (C) after catalysis (20 h).



**Figure 13.** Measured (dots), calculated (line) powder diffraction patterns for (1) Ru(TOA)/MG70 and (2) Ru(TOA)/MG70-48 MG70 after catalytic tests. Vertical dashed line marks the main diffraction peak related to HT phase.

#### **2.4 Discussion**

The catalytic performances showed by Rh, Rh(TOA), and Ru(TOA) are comparable with those reported with similar Ru-based systems [14], and also with more diffuse Ni-based systems, under similar reaction conditions [10,65-67]. Steam reforming (Eq. (1)) and reforming (Eq. (2)) reactions typically produce hydrogen, carbon dioxide, carbon monoxide as main products, while at temperature above 400-500 °C the ketonization reaction (Eq. (5)) is almost zero. Noteworthy, the hydrogen yield close to 65% and the CO<sub>2</sub> selectivity around 70%, at total carbon conversion, are direct proof of the importance of reforming reaction at low S/C ratios, like the one used in the current study (i.e., 3).

Compared to the Rh catalysts, the Ru catalysts displayed a slightly higher  $CO_2/CO$  ratio, with the former being 2.5 and the latter 3.0, which that can be ascribed to the WGS activity peculiar of Ru-based systems. The observed small decrease in hydrogen yield and in  $CO_2$  selectivity as a consequence of the space velocity (WHSV) increase from 6 to 12 h<sup>-1</sup> for Ru(TOA) can be accounted by a decrease of steam reforming and WGS activity.

$CH_3COOH + 2 H_2O \rightarrow 4 H_2 + 2 CO_2$	Steam reforming	(1)	
$CH_3COOH \rightarrow 2 H_2 + 2 CO$	Reforming	(2)	

$\rm CO + H_2O \rightarrow \rm CO_2 + H_2$	WGS	(3)
$CH_3COOH \rightarrow CH_4 + CO_2$	Decarboxylation	(4)
$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O$	Ketonization	(5)
$\rm CO + 3~H_2 \rightarrow CH_4 + H_2O$	CO methanation	(6)
$\mathrm{CO}_2 + 4 \mathrm{~H}_2 \rightarrow \mathrm{CH}_4 + 2 \mathrm{~H}_2\mathrm{O}$	CO <sub>2</sub> methanation	(7)
$CH_3COOH \rightarrow C_2H_4, C$	Decomposition	(8)
$2CO \rightarrow CO_2 + C$	Boudard reaction	(9)
$C + H_2O \rightarrow CO + H_2$	C gasification	(10)

The decrease in steam reforming and WGS activity for Ru(TOA) can be the reason behind the observed small decrease in hydrogen yield and CO<sub>2</sub> selectivity as the WHSV was increased from 6  $h^{-1}$  to 12  $h^{-1}$ . On the other hand, as the reaction temperature was brought from 700 °C to 600 °C, an appreciable decrease in reforming activity, more evident for reforming reactions, was evidenced, while the WGS activity was promoted by the lower temperature along with some decarboxylation (Eq. (4)), leading to 5.3% methane selectivity. Methanation reactions cannot be excluded and could provide methane in CO<sub>2</sub>, CO, H<sub>2</sub> rich environment (Eqs. (6) and (7)) [60]. Because of the high combustion temperature ranging from 450°C to 600 °C, it can be deduced that the coke deposited on all the catalysts during the reaction was mainly of aromatic nature (graphitic). Interestingly, filamentous carbon was not detected due to the low carbon solubility in Rh and Ru small nanoparticles.

Its formation can occur both by acetic acid decomposition (Eq. (8)) and Boudard reaction (Eq. (9)), and is generally quite low for all the catalysts under all the investigated conditions. This behaviour is in agreement with the well-known properties of both  $MgAl_2O_4$  [14] and MgO [60] to promote  $H_2O$  adsorption and OH and O spillover from support to metal thus promoting carbon gasification (Eq. (10)) even at low S/C ratios. It is worth noting that the amount of coke detected is independent from the nature of the metal, but only on the preparation method, as the catalysts prepared

by SCMNPS showed lower coke deposition rates if compared with traditionally impregnated catalysts. Finally, except for Ru/MG70, which suffered an evident deactivation with its performances already decreasing at the beginning of the reaction, all the catalysts showed good stability with t.o.s. The poor stability of Ru/MG70 can be accounted by the observed increase in coke amount since Ru NPs are stable against sintering as revealed by TGA and HRTEM measurements.

Conversely, Ru(TOA)/MG70-48 showed a similar deactivation, even though in less extent, which could be ascribed mainly to Ru NPs sintering (coke deposition is comparable to the one of stable catalysts), as evidenced by HRTEM micrographs and size distribution data. In fact, nanoparticles sintering and coke deposition are generally the main causes behind the deactivation of the catalysts in steam reforming reactions.

Coke is mainly deposited by surface reactions on acidic sites of support oxides [64] or by decomposition occurring at defects on metal nanoparticles [68], and nanoparticles sintering is a more complex phenomenon since it depends on several parameters. Some of these parameters can be related to the metal, such as its nature (i.e., its melting point temperature), reducibility, ionic radius/charge ratio for the inclusion in support lattice. Others are ascribable to the support, such as nature of the lattice, ease of ions substitution and formation of mixed oxides with metal ions, metal-support interactions, etc. Steam reforming reactions are generally carried out under harsh conditions, like high temperatures, in presence of steam, in oxidative and reductive conditions, and in presence of species able to promote metals oxidative breakup such as CO. With all these conditions in mind, the optimal catalyst should possess some peculiar features: Low concentration of surface acidic and basic sites, ability to interact with supported metal NPs (to limit sintering) but low tendency to form mixed oxides and to host and stabilize isolated oxidized metal sites.

As far as metal NPs stability against sintering is concerned, usually Ru NPs show high stability that can be ascribed to the properties of Mg(Al)O spinel phase [37,64], which is however in apparent contrast with a recent report by Li *et al.* [69] where the authors ascribed the poor stability to the lattice mismatch and to the lack of strong electronic attractions between the spinel (111) surface oxygens and metals/metal oxides. Nevertheless, in our case, Ru nanoparticles are much smaller even from the beginning of the synthesis, and the support used in the present study consists not only of MgAl<sub>2</sub>O<sub>4</sub> phase but contains also MgO and unconverted hydrotalcite. The latter can play a significant role in stabilizing the metal nanoparticles. Moreover, metal nanoparticles can interact with each one of these phases with different adhesion energies, which also depend on the metal itself and the size of the nanoparticles [70]. Assuming a significant fraction of residual hydrotalcite located preferentially on the external surface of support grains, it is reasonable that metal NPs have major interaction with hydrotalcite itself rather than with MgAl<sub>2</sub>O<sub>4</sub> and MgO.

The occurrence of sintering only in Ru(TOA)/MG70-48 sample, with the mean particles size increased from 1.5 nm to 2.6 nm, confirmed the contribution to the metal nanoparticles stabilization by the residual hydrotalcite phase. On the other hand, Ru(TOA)/MG70 showed only a negligible increase from 1.6 to 1.8 nm. This behaviour is reflected also by the catalytic performances of Ru(TOA)/MG70-48 sample, which showed a decrease of conversion, hydrogen yield and CO<sub>2</sub> selectivity yet after 5 h of t.o.s. These evidences are also in agreement with XRPD data showing a residual amount of hydrotalcite, after catalytic runs, only in Ru(TOA)/MG70, whereas it is undetectable in Ru(TOA)/MG70-48 sample.

As far as coking is concerned, only low surface Lewis-type acidity was revealed in all the samples by FT-IR experiments with pyridine. This evidence is consistent with previous reports on Mg(Al)O mixed oxide supports and LAS is mainly due to  $Mg^{2+}$  c.u.s. sites and octahedral and tetrahedral Al<sup>3+</sup> sites present on MG70 surface. Moreover, the acidity generally induced by the presence of very small nanoparticles, even occurring on non-acidic supports [71], was not active in our catalysts, even for very small Rh(TOA) and Ru(TOA) nanoparticles, since all of them and the bare support showed totally comparable Lewis acid sites concentrations. Consequently, the differences in coke integral deposition rates, which follow the order Ru/MG70 > Rh/MG70 > Rh(TOA)/MG70 ~ Ru(TOA)/MG70, found onto our catalysts (measured under the same reaction conditions) cannot be related only to surface reactions occurring on surface acid sites.

The presence of very few, or even the absence, of defects (i.e., kinks, steps, edges, etc.) of the supported metal nanoparticles exerts an important role on the catalytic performances. In fact, well-formed Rh nanoparticles were reported to catalyse more selectively carbon-reforming rather than carbon-forming reactions in CH<sub>4</sub>-CPO, thus avoiding coke accumulation, and improving activity and selectivity [62,72,73]. Similarly, coordinatively unsaturated sites/steps sites acting as nucleation centres promoting the growth of filamentous carbon where reported for Ag/Ni catalysts [74]. A perusal of our characterization data clearly shows how ruthenium nanoparticles present in Ru(TOA) catalysts are more well-formed with respect to Ru impregnated ones.

The present results recall the behaviour of Rh-based  $CH_4$ -CPO catalysts previously studied by some of us [62,73]. In that work, the presence of isolated oxidized sites and the resulting low  $Rh^0/Rh^1$ ratio, which is a clear indication of defective, not well-formed metal nanoparticles, were detected in the catalysts prepared by conventional nitrates impregnation. Conversely, Rh nanoparticles obtained by a peculiar multi-step OM-CVD showed an opposite behaviour, ascribed to the presence of wellformed, less defective metal nanoparticles. Since  $Rh^1$ -(CO)<sub>2</sub> sites derive by the oxidative disgregation reactions of Rh clusters, rafts and defective particles (Eq. (11)), a low  $Rh^0/Rh^1$  ratio indicates an higher amounts of defective rhodium nanoparticles with respect to "stable" ones [75].

$$1/nRh_{n}^{0} + 2CO + xOH \rightarrow (O^{2-})_{x}Rh^{1-}(CO)_{2} + 0.5xH_{2}$$
  $x = 1 - 2$  (11)

On the other hand, a higher fraction of CO linearly bonded to the metallic nanoparticles was evidenced by CO-DRIFTS experiments in Ru(TOA), Rh(TOA), and Rh/MG70 if compared to Ru/MG70. Specifically, in the latter sample a higher amount of di- and tri-carbonyls ruthenium species (Ru<sup>*n*+</sup>-(CO)<sub>m</sub> with m = 2, 3) were detected that can result from small ruthenium clusters formed by CO disgregation of defects-rich ruthenium nanoparticles. The easiest formation of isolated oxidized surface carbonyls, such as Rh<sup>1</sup>(CO)<sup>2</sup> and Ru -(CO)<sub>x</sub> (x = 2, 3), occurring on impregnated Rh and Ru MG70 catalysts, cannot be simply ascribed to the high number of surface metal atoms in low coordination. In fact, they are the most reactive in the reaction with CO, leading to Rh<sup>1</sup> and Ru<sup>*n*+</sup> dior tri-carbonyls, usually present in low dimension metal nanoparticles (i.e., the number of coordinatively unsaturated surface atoms on corners and edges is expected to increase as the size of metal NPs decreases) as already reported by some of us [43,45].

The TPR data further corroborate this interpretation. The profiles of co-precipitated samples, which show well-dispersed RuO<sub>x</sub> and bulk RuO<sub>2</sub> reduction peaks around 200-250 °C, resulted comparable to the ones of our traditionally impregnated samples. Notably, strongly interacting species that usually are reduced at higher temperatures, for instance at 400 °C for alumina supported Ru, are totally absent in our samples. The even lower reduction peaks exhibited by SCMNPs-derived systems confirm the very low presence of species interacting with the support, which, upon reduction, can lead to the formation of Ru<sup>*n*+</sup> or small clusters in close proximity to the metal nanoparticles, thus enhancing their defectivity.

#### 2.5 Conclusions

SCMNPs deposition method was employed to easily prepare Rh- and Ru-based catalysts by H<sub>2</sub>reduction of the corresponding metal chlorides in presence of trialkylamine. Low metal loadings were obtained by SCMNPs procedure on Mg-Al mixed oxide support. Ru catalysts showed good performances, as activity and selectivity are concerned, (73% H<sub>2</sub> yield, 74% CO<sub>2</sub> selectivity and total carbon conversion at 700 °C, WHSV = 6 h<sup>-1</sup>, S/C = 3) in the steam reforming of acetic acid, fully comparable with those obtained with Rh-based systems.

Ru SCMNs derived catalysts showed also high stability under reaction conditions (100% carbon conversion; 65% H<sub>2</sub> yield, 72% CO<sub>2</sub> selectivity, after 20 h t.o.s. at 700 °C, WHSV = 12 h<sup>-1</sup>, S/C = 3) superior to that of traditionally impregnated catalysts. Well-formed, crystalline metal nanoparticles with uniform size distribution were the responsible for the enhanced performances and stability, able to keep the coke deposition rate as low as 2.0 mg<sub>coke</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. In addition, the presence of unconverted hydrotalcite phase in the support resulted to be critical for the nanoparticles stabilization against sintering due to enhanced strong metal-support interactions.

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# Chapter 2

# **3**. Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol

# **3.1 Introduction**

Sustainable hydrogen production will probably play a decisive role in future economies, due to the need of clean energy vectors to meet the modern environmental requirements, and to minimize our dependence on fossil fuels [1-4]. Water and biomass are emerging as valuable candidates to replace natural gas as main feedstock for the hydrogen production, owing to their abundance, relatively low cost, and carbon neutrality. Besides promising routes such as photoelectrochemical water-splitting and enzymatic and microbiological-based technologies, which are however in a too early stage of development for an economically sustainable implementation, reforming of biomass-derived compounds could be a viable way for the medium-term future, since it couples a well-known technology with sustainable feedstocks [2-5].

Among others, steam reforming (SR) and aqueous phase reforming (APR) have been extensively studied in the past years, showing that high hydrogen production rates can be achieved using a large variety of organic substrates, from simple model molecules to complicated mixtures, like bio-oil and bio-oil derivate mixtures [3,5-13].

In this scenario, glycerol will become one of the most important commodities as it is the main byproduct from the transesterification of vegetable oils and fats to produce biodiesel, and is a good model compound for polyols in biomass catalytic conversion processes [14-16]. A wide number of works have been published on SR and APR of glycerol for the hydrogen production, using a variety of catalysts based on both precious and non-precious metals [11,17-23]. Ru catalysts have shown good catalytic performances because of their high C-C cleavage ability and coke resistance [18], while among non-precious metals, Ni is generally preferred [24]. In order to achieve good conversion levels with these catalysts, high temperatures are generally required. On the other hand, Pt-based catalysts can be very active even at relatively low temperature (< 300 °C), while retaining good C-C cleavage activity [24].

With the aim of further increasing the hydrogen production up to industrial-relevant rates, among others, Re and Mo have been investigated as promoters. Dietrich *et al.* had studied with an *in operando* XAS technique a Pt-Mo catalyst supported on carbon black for the aqueous phase reforming of glycerol, and found an increased glycerol conversion, but a lower hydrogen selectivity. The latter was ascribed to the partial oxidation of Mo in aqueous phase reforming conditions, which led to increased C-O cleavage activity through acid catalyzed reactions [21].

As one of the early effective industrial promoters used in particular for the naphtha reforming, Re has attracted much attention also for the reforming of glycerol, ethylene glycol, and sugars [11,13,17,25]. Generally, the catalytic performances of the Pt-Re catalysts increased with all the substrates, both in SR and APR. Besides the acidity induced by the partial oxidation of Re in hydrothermal conditions, which as in the case of Mo led to higher conversion levels but lower selectivity toward hydrogen, Wang and co-workers found that the enhanced performances of Pt-Re catalysts were mostly due to the facile CO desorption from the catalyst surface by spillover from Pt to adjacent ReO<sub>x</sub> sites [11,17,26,27].

In order to develop cheap industrial-grade catalyst, new promoters are required. In the last years, manganese has been proposed as effective promoter for Pt- and Ni-based catalysts, both in the SR and APR of oxygenates, showing remarkable performances in terms of improved hydrogen production rates [10,28]. Noteworthy, Mn is an effective promoter for the CO oxidation reaction due to its good redox properties and high oxygen storage capability. This peculiar features could be useful for the production of hydrogen with lower levels of CO, which is poisonous for many noble metals, and in particular Pt [29,30].

There is, however, a lack of understanding of the actual promotion mechanism of Mn in reforming reactions, and about the impact of water on the bimetallic catalyst whether it is fed in the vapor or liquid phase. In this research work, a Pt-Mn catalyst supported on activated carbon is tested in both SR and APR of glycerol and compared to monometallic Pt/C. The catalysts were characterized by CO chemisorption, hydrogen temperature programmed reduction, HRTEM and STEM together with EDX analysis. In order to investigate the surface properties of the catalysts under simulated reforming conditions, with particular focus on the acidic properties, pretreatments with steam were carried out before ATR-IR with pyridine as probe molecule and NH<sub>3</sub>-TPD experiments.

#### **3.2 Experimental**

#### **3.2.1 Catalysts preparation**

The catalysts were prepared by incipient wetness impregnation method using an activated carbon as support (TA60, PICATAL), previously dried overnight at 110 °C. Tetrammineplatinum (II) nitrate hexahydrate ( $(NH_3)_4Pt(NO_3)_2$ '6H<sub>2</sub>O, Sigma-Aldrich) and manganese nitrate tetrahydrate ( $(Mn(NO_3)_2$ '4H<sub>2</sub>O, Sigma-Aldrich) were used as metal precursors. The impregnated samples were dried overnight at room temperature, and then calcined at 260 °C for 2 h in air. The bimetallic catalyst (Pt-Mn/C) was prepared by co-impregnation of the two metal salts, followed by the same drying and calcination steps. The Pt/Mn molar ratio was 1, with the Pt being the 2 wt.%.

#### 3.2.1 Physical adsorption and chemisorption

Specific surface areas were measured by nitrogen physisorption isotherms at 77 K using the BET method (Tristar II, Micromeritics), outgassing the samples at 110 °C for 2 h before each measurement. The metal loadings were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after microwave digestion of the samples in aqua regia.

CO-pulse chemisorption was performed on an Autochem II (Micromeritics). The samples were reduced with 10 vol.%  $H_2/Ar$  at 280 °C for 1 h, and then purged for 30 min with He before being cooled to 40 °C. A series of CO pulses were then introduced until saturation. Platinum dispersion was calculated by processing the thermal conductivity detector (TCD) signals, assuming a Pt/CO stoichiometry of 1.

H<sub>2</sub>-TPR experiments were carried out on the same apparatus. Prior to each analysis, the samples were pretreated in flowing He for 1 h at 110 °C, and then cooled down to room temperature. The temperature ramp used in all the experiments was 10 °C min<sup>-1</sup> with a 10 vol.% H<sub>2</sub>/Ar flow.

CO- and NH<sub>3</sub>-TPD experiments were performed again by using the Autochem II (Micromeritics) apparatus. The samples were reduced at 280 °C with a 10 vol.% H<sub>2</sub>/Ar flow, then cooled to 225 °C under He flow. After this first step, steam pulses were introduced for about 1 h by flowing He through a water bubbler, followed by cooling to 40 °C, and then purged for 1 h. After 1 h under CO or NH<sub>3</sub> flow (50 mL min<sup>-1</sup>), the samples were purged with He for 1 h at room temperature. Finally, the samples were heated up with a ramp rate of 10 °C min<sup>-1</sup> to 500 °C in He flow. CO desorption curves were obtained by processing the TCD signals, while the amount of desorbed ammonia was calculated by integrating the mass signals (ThermoStar Quadropole Mass Spectrometer from Pfeiffer Vacuum).

#### **3.2.2 Electron microscopy**

Electron micrographs were collected with a Zeiss LIBRA 200FE, equipped with: 200 kV FEG, in-column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), HAADF-STEM facility and EDX probe for chemical analysis. Before introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol, and then a drop of the suspension was deposited on a holey carbon gold grid (300 mesh). The histograms of the metal particle size distribution for the samples were obtained by counting at least 500 particles onto the micrographs. The mean particle diameter (d<sub>m</sub>) was calculated by using the formula  $d_m = \sum d_i n_i / \sum n$ , where  $n_i$  is the number of particles with diameter  $d_i$ .

### **3.2.3 ATR-IR**

In order to run the ATR-IR experiments, the equipment described by Ref. [17] was used. The Internal Reflection Element (IRE) was coated by suspending 5 mg of catalyst in 1 mL of Milli-Q water, and sonicating the solution for 30 s. 400  $\mu$ L of solution were then deposited on the surface of the IRE. Finally, the solution was dried for 1 h at 90 °C using a heating rate of 10 °C min<sup>-1</sup>. The acidity of the catalyst was probed mimicking the reaction conditions, that is reduction of the catalyst followed by treatment with steam.

The procedure was as follows: 1) The ATR cell was heated to 280 °C under helium at a heating rate of 5 °C min<sup>-1</sup>. 2) Once at 280 °C, the catalyst was reduced by flowing 10% H<sub>2</sub>/Ar (40 mL min<sup>-1</sup>) for 30 min. 3) Residual hydrogen was removed by purging with helium for 30 min (40 mL min<sup>-1</sup>). 4) The ATR cell was cooled to 225 °C, and 10 pulses of steam were injected by flowing helium into a water bubbler at room temperature in order to fill a 50  $\mu$ L loop. The time between pulses was about 2 min. 5) After the last pulse, the remaining steam was flushed for 30 min using helium (40 mL min<sup>-1</sup>). 6) The ATR cell was cooled down to 40 °C under helium, and a background was taken. 7) 10 pulses of pyridine were injected as described in 4). 8) Spectra were collected after He purging at a temperature of 40 °C. The equipment used was a Bruker Tensor 27. The resolution of the scans was 4 cm<sup>-1</sup> and 128 scans were averaged for each spectrum.

#### 2.3 Catalytic tests

For the steam reforming reactions, a lab-scale test unit with a fixed-bed reactor was used [31]. In a typical experiment, a certain amount of catalyst diluted with SiC (60-100 mesh, five times dilution in weight) was held in place by quartz wool in a quartz tube. To prevent condensation, both the vaporizer and the downstream line were heated with heating tape, while the low boiling-point reaction products were condensed in a cold trap at 0 °C. Prior to the reaction, the catalysts were reduced *in situ* at 280 °C for 1 h with 10 vol.% H<sub>2</sub>/Ar flow (50 mL min<sup>-1</sup>), purged for 30 min with N<sub>2</sub> (50 mL min<sup>-1</sup>), and then cooled to the reaction temperature (225 °C). A syringe pump was used to introduce a 10 wt.% glycerol/water solution using nitrogen as carrier. The Gas Hourly Space Velocity (GHSV) was varied by adjusting the liquid and gas flow rates, keeping constant the partial pressure of the reactants. The outlet gases were dried by passing through an anhydrous CaSO<sub>4</sub> drierite drying column, and then analyzed with an online Agilent 490 micro GC with four independent modules equipped with a TCD, using nitrogen as internal standard.

Aqueous phase reforming reactions were carried out in a stainless steel bench reactor (Parr 4848). Typically, a certain amount of catalyst was first reduced *ex situ* at 280 °C for 1 h with 10 vol.%  $H_2/Ar$  flow (50 mL min<sup>-1</sup>), and then transferred into the reactor containing the same reaction mixture of the steam reforming experiments. The mixture was continuously stirred at about 200 rpm. The reactor was purged for 30 min with nitrogen flow and pressurized with an initial pressure of 30 bar which served also as internal standard for the quantification of the gaseous products. The reactor was then heated at 225 °C, and held at this temperature for 1 h. Finally, the reactor was cooled down to room temperature. The gaseous products were collected in an Agilent sampling gas bag (0.5 L capacity, Tedlar), and analyzed offline with the same Agilent 490 micro GC used for the steam reforming experiments. After depressurization, the liquid products were collected and filtered with a 0.45 µm PTFE filter.

The condensed liquid products of both the SR and APR reactions were analyzed with Agilent 7890A GC, with their composition being calculated by external calibration curves. The equations used for the calculation of the conversion, the turnover frequency (TOF) of hydrogen, and the selectivity towards the reaction products are the following:

Conversion (%) = 
$$\frac{C \text{ moles in the products}}{C \text{ moles in the feed}} \times 100$$

H<sub>2</sub> Selectivity (%) =  $\frac{H_2 \text{ moles produced}}{C \text{ moles in the products } \times 7} \times 100$ 

Selectivity of *i* (%)= $\frac{i \text{ moles produced}}{C \text{ moles in the products}} \times 100$ 

TOF of  $H_2(\min^{-1}) = \frac{H_2 \text{ production rate}}{Pt \text{ dispersion}}$ 

### **3.3 Results**

# **3.3.1 General features**

The metal loadings of the catalysts resulted close to the theoretical ones (Table 1), except for the Mn/C catalyst where the Mn loading was found 1.79 wt.%. The specific surface area of the Mn-based catalyst resembled the one of the bare support, whereas the Pt-based catalysts showed slightly lower values, likely due to partial pore plugging.

The Pt dispersion was calculated by CO-pulse chemisorption, assuming a stoichiometry of CO/Pt of 1. As can be seen in Table 1, the co-impregnation procedure for the preparation of the Pt-Mn/C sample had almost no influence on the Pt dispersion, meaning that in both the monometallic and bimetallic samples the Pt is highly dispersed (> 92%). Considering that the Mn/C sample showed no CO uptake, a simultaneous adsorption by the two metals in the bimetallic sample is improbable.

Sample	Mn	Pt	Dispersion*	SSA <sub>BET</sub>		
	(wt.%)	(wt.%)	(%)	$(m^2 g^{-1})$		
С	-	-	-	1075		
Pt/C	-	1.41	94.5	957		
Pt-Mn/C	0.51	1.21	92.1	992		
Mn/C	1.79	-	-	1093		

Table 1. Metal loadings, Pt dispersions, and specific surface areas of the samples.

\*Calculated by CO-pulse chemisorption.

# 3.3.2 H<sub>2</sub>-TPR

H<sub>2</sub>-TPR experiments were used to investigate the effect of the addition of Mn on the reducibility of the Pt-Mn/C catalyst (Figure 1). The TPR profile of Mn/C showed only one weak peak centered at around 270 °C, probably due to the reduction of non-stoichiometrically dispersed MnO<sub>x</sub> species [32,33], and a broad peak over 500 °C, which is attributed to the support gasification [34,35]. Pt/C showed a uniform reduction peak centered at 167 °C, which corresponds to a hydrogen consumption of 0.09 mmol g<sup>-1</sup>, consistent with the reduction of Pt<sup>+2</sup> to Pt<sup>0</sup>. The addition of Mn (i.e., Pt-Mn/C catalyst) caused a shift of the reduction peak to a higher temperature (186 °C), along with an increased hydrogen consumption up to 0.15 mmol g<sup>-1</sup>.



Figure 1. H<sub>2</sub>-TPR profiles of Pt-Mn/C, Pt/C, and Mn/C.

# 3.3.3 Catalytic reactivity

# 3.3.3.1 Steam reforming

Steam reforming of glycerol over the three samples was performed at 225 °C using a 10 wt.% aqueous solution. The product selectivity was evaluated at the same conversion level (~25%) by adjusting the GHSV. The main gaseous reaction products were  $H_2$ , CO, CO<sub>2</sub>, and CH<sub>4</sub>, with only traces of ethylene and ethane. Besides unreacted glycerol, the liquid phase consisted mostly in ethylene glycol (EG), acetol, alcohols (methanol and ethanol), acetic acid, and acetaldehyde.

The results are summarized in Table 2. A blank test with activated carbon gave negligible activity, as well as with the Mn/C catalyst (conversion <1%). In Figure 2 are reported the catalytic performances of the Pt/C and Pt-Mn/C catalysts in terms of conversion and TOF of H<sub>2</sub>. The results obtained with the Pt/C are consistent with previous studies reported in the literature [17,36], with a

conversion of 26 % and a TOF of  $H_2$  of 6 min<sup>-1</sup>. As expected, CO and EG, along with the alcohols, were the main products in the gaseous and liquid phase, respectively.

The addition of Mn to Pt significantly enhanced both the TOF of hydrogen, which was increased of about a factor of 5, and the conversion up to 78.2%. The conversion towards the gaseous products doubled, reaching almost the 45%, with CO and hydrogen being always the main products. The presence of Mn also drastically changed the selectivity of the products. Specifically, in the gaseous products, the selectivity toward CO and H<sub>2</sub> dropped to 40% and 25%, respectively, while the liquid phase consisted basically of hydroxyacetone (that is acetol). Little difference in selectivity of CO<sub>2</sub> and alcohols was observed between Pt/C and Pt-Mn/C (Table 2). Although the hydrogen selectivity resulted lower, the Pt-Mn/C showed higher conversion and TOF of hydrogen compared to Pt/C.



**Figure 2.** Conversion and TOF of  $H_2$  (A) and product selectivity (B) in SR of 10wt.% glycerol aqueous solution at 225 °C and ambient pressure. GHSV was held at 30,000 h<sup>-1</sup> for Pt/C and 90,000 h<sup>-1</sup> for Pt-Mn/C for comparison at similar conversion (~25%).

Conversion (%)				Product selectivity (C-based, %)*								
Catalyst	Liquid product	Gas product	Total	H <sub>2</sub>	СО	CO <sub>2</sub>	$\mathrm{CH}_4$	EG	Acetol	Alcohol	Acetic acid	Acetaldehyde
Pt/C	5.9	20.1	26.0	36.9	60.5	2.3	0.5	13.0	8.5	12.3	2.0	0.9
Pt-Mn/C	34.6	43.6	78.2	25.2	39.0	3.0	0.9	4.4	39.8	10.2	0.7	2.0

Table 2. Conversion and product selectivity data of SR of glycerol over Pt/C and Pt-Mn/C.

\*Product selectivity evaluated at 30,000 h<sup>-1</sup> and 90,000 h<sup>-1</sup> of GHSV for Pt/C and Pt-Mn/C, respectively.

#### 3.3.3.2 Aqueous phase reforming

The catalytic performances of the catalysts were evaluated in the aqueous phase reforming of 10 wt.% glycerol at 225 °C. The reactions were carried out in a batch reactor with an initial pressure of 30 bar of nitrogen. As in the case of steam reforming, the catalytic activity of Pt/C resulted comparable to previous studies reported in the literature (Figure 3) [26,37]. The main reaction products were H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> in the gaseous phase, and ethylene glycol (EG), acetol, alcohols (methanol and ethanol), acetic acid, and acetaldehyde were collected in the liquid phase along with unreacted glycerol.

In contrast to SR, the addition of Mn had a minor impact on the catalytic activity and product distribution. In particular, the conversion and TOF of hydrogen were improved by a factor of 1.3 and 1.4, respectively (Table 3). Practically no difference in products selectivity was found over Pt/C and Pt-Mn/C, with the exception of the selectivity toward hydrogen, which increased from 51.3% to 58.0%.



**Figure 3.** Conversion and TOF of  $H_2$  (A) and product selectivity (B) in APR of 10 wt.% glycerol aqueous solution at 225 °C and 30 bar of initial pressure.

Conversion (%)				Product selectivity (C-based, %)									
Catalyst	Liquid product	Gas product	Total	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	EG	Acetol	Alcohol	Acetic acid	Acetaldehyde		
Pt/C	1.0	7.6	8.6	51.3	57.7	4.9	17.1	10.7	8.3	1.0	0.3		
Pt-Mn/C	1.2	9.4	10.6	58.0	58.0	5.8	18.3	8.4	8.4	0.5	0.3		

Table 3. Conversion and product selectivity data of APR of glycerol over Pt/C and Pt-Mn/C.

# 3.3.4 Electron microscopy

In order to study the morphological and structural features of the Pt-based mono- and bimetallic catalysts, HRTEM, STEM and EDX analyses were performed (Figure 4). STEM micrographs collected on fresh Pt/C and Pt-Mn/C showed in both cases the carbonaceous support densely populated by monodispersed metal particles with very small particle sizes (mean diameter less than 1.0 nm) (Figures 4A and 4B).

STEM-EDX maps of the bimetallic Pt-Mn/C catalysts revealed the presence of both Pt and Mn homogeneously dispersed all over the carbonaceous support (Figures 4C and 4D). These results agree well with the high Pt dispersion (> 92%) calculated by CO pulse chemisorption analysis. However, a lower amount of Mn was detected as larger aggregates mainly as  $MnO_2$  crystalline structure, as revealed by electron diffractions (not shown).



Figure 4. Representative STEM micrographs of Pt/C (A), Pt-Mn/C (B). The scale bar is correspondent to 20 nm. EDX-maps of Pt (C) and Mn (D) of Pt-Mn/C.

STEM analysis of the Pt-Mn/C catalyst after steam reforming revealed the presence of Pt nanoparticles with a slightly higher mean particle size (1.5 nm) (Figure 5A). A comparable Pt nanoparticle distribution was obtained in Pt-Mn/C catalyst after aqueous phase reforming (1.7 nm) (Figure 5B). Both Pt and Mn EDX signals were detected in both Pt-Mn/C after SR and after APR. However, in the former both the signals were similar in intensity to those found in the fresh catalyst, whereas in the latter the signal of Mn was significantly lower, thus indicating a significant decrease of Mn content respect to the parent fresh sample (not shown).



**Figure 5.** Representative HAADF-STEM micrographs of Pt-Mn/C after SR (A) and APR (B). The scale bar is correspondent to 20 nm.

# 3.3.5 CO- and NH<sub>3</sub>-TPD

In order to rule out any possible promoting action due to CO spillover from the Pt sites promoted by Mn, as for the case of Re over Pt-Re/C [11,17], CO-TPD experiments were performed (Figure 6A). Prior to the adsorption of CO, the samples were treated with steam pulses at 225 °C in order to mimic the reforming conditions. Similar to CO-pulse chemisorption experiments, the Mn/C sample gave negligible CO adsorption. No significant difference was found in the CO-TPD profiles of Pt/C and Pt-Mn/C, with only one maximum at 102 °C.

The total acidity and the relative strength of the catalysts were evaluated by ammonia TPD experiments (Figure 6B). As per the CO-TPD analysis, the samples were treated with steam at 225 °C. A base line was established with only the activated carbon support (not shown), which gave a negligible amount of adsorbed ammonia. Both Pt/C and Mn/C catalysts exhibited comparable acid strength with a singular peak centered at around 129 °C, whereas the ammonia desorption profile of Pt-Mn/C showed a peak at lower temperature (111 °C) with a shoulder at 169 °C. The total number of acid sites was calculated by integrating the desorption peaks, giving 149  $\mu$ mol g<sup>-1</sup> of ammonia adsorbed on Pt-Mn/C, while less acid sites were found on Pt/C and Mn/C, with 55 and 118  $\mu$ mol g<sup>-1</sup>, respectively.



**Figure 6.** CO-TPD on Pt/C and Pt-Mn/C (A), and NH<sub>3</sub>-TPD on Pt/C, Mn/C and Pt-Mn/C (B). All catalysts were reduced at 280 °C and saturated with steam at 225 °C prior to the experiments.

#### **3.3.6 ATR-IR**

Due to the strong IR absorption of carbon based materials, an ATR-IR technique with *in situ* capability was used to investigate the nature of the acid sites of the catalysts. Before the adsorption of pyridine, the samples were reduced at 280 °C, and then treated with steam at 225 °C. All the experiments were repeated to make sure that the observed signals were not due to spectrum noise.

Figure 7 shows the spectra obtained, while the experiment carried out with only the support gave only a background signal (not shown) [38]. The bands located in the region around 1440 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> are peculiar of pyridine interacting with Lewis acid sites (L), while the interaction with Brønsted acid sites (B) gives bands at 1540 cm<sup>-1</sup> and 1640 cm<sup>-1</sup>. The band at 1480 cm<sup>-1</sup> is originated by the simultaneous interaction of pyridine on coupled Lewis and Brønsted acid sites [39].

Differently from Re/C, which showed no pyridine adsorption even after harsh pretreatments like with hot liquid water [11], Mn/C exhibited two broad features centered at around 1550 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> that can be assigned to pyridine coordinated to Brønsted acid sites. Moreover, a weak band at about 1430 cm<sup>-1</sup> and a shoulder at 1575 cm<sup>-1</sup> are also resolved, which can be assigned to pyridine coordinated to strong Lewis acid sites [11,40].

Only Lewis type acidity was observed on Pt/C, with a peak resolved at 1440 cm<sup>-1</sup> and a broader feature centered at around 1600 cm<sup>-1</sup>, due coordinately unsaturated  $Pt^{\delta+}$  sites. The spectrum of Pt-Mn/C resembled that of Mn/C, showing both the broad features around 1550 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> due to protonated pyridine along with the peaks assigned to Lewis sites located at 1430 cm<sup>-1</sup> and 1575 cm<sup>-1</sup>. However, the intensity of all the peaks, and particularly of those due to the Lewis acid sites, were much more intense than Mn/C.



**Figure 7.** Pyridine adsorption on Mn/C, Pt/C, and Pt-Mn/C investigated by ATR-IR spectroscopy (L: Lewis acid sites; B: Brønsted acid sites). All catalysts were reduced at 280 °C and saturated with steam at 225 °C prior to the experiments.

#### **3.4 Discussion**

One of the most important key features of supported metal catalysts for heterogeneous reactions is the metal dispersion [41]. It is widely accepted that a proper metal dispersion, as well as a sharp size distribution, must be achieved in order to maximize the catalytic performances. While not always smaller metal nanoparticles mean higher catalytic activity, like in the case of Rh nanoparticles for the methane steam reforming where particles below 2.5 nm showed fast deactivation due to coking [42], in the steam reforming of glycerol very small nanoparticles of noble metals are desirable [11,17,43,44].

In the present work, Pt particles sizes homogeneously distributed below 1.0 nm in diameter (HRTEM) were obtained by simple incipient wetness impregnation in both the Pt-based catalysts. Pt dispersions as high as 94.5%, calculated by CO pulse chemisorption, confirmed that most of the Pt atoms are exposed, assuming completely shelled polyhedron-nanoparticles [45]. More importantly, the co-impregnation procedure for the preparation of Pt-Mn/C had a negligible impact on the Pt dispersion (Table 1), indicating again the presence of well dispersed Pt nanoparticles and no surface coverage by Mn-based species. The very similar Pt dispersions of Pt/C and Pt-Mn/C make the comparison of the catalytic results, in particular as concerns the TOF of hydrogen, easier and significant.

Besides dispersions, the location and the interaction between the two metals are critical for the activity of a bimetallic catalyst [46,47]. In this work, an interaction of Pt with Mn, which is probably in the oxidized form considering that no reduction peaks were observed in the H<sub>2</sub>-TPR profile of Mn/C below 300 °C, can be reasonably inferred by the presence of a unique peak at a higher temperature than that of Pt/C (Figure 1). In addition, assuming that the average oxidation state of Pt remains unchanged, it has been already reported that the almost double hydrogen consumption shown by Pt-Mn/C compared to Pt/C is due to Pt nanoparticles interacting with well dispersed MnO<sub>x</sub> centers [29].

A further evidence of the proximity of the two metals derives from the EDX maps (Figures 4C and 4D) that show a homogeneous distribution of the two metals, with the signals of Pt and Mn always homogeneously covering the entire surface of the catalyst. Another key point in a bimetallic catalyst is the ratio between the two metals.

In this research work a Pt to Mn molar ratio of 1 was chosen according to the work by Kim *et al.* [10], where among a series of Pt-Mn catalysts tested in the aqueous phase reforming of ethylene glycol, the molar ratio of 1 showed the highest catalytic activity both in terms of hydrogen production rates and carbon conversion. The different Pt precursor (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) and the higher reduction temperature (350 °C) used in that study resulted in a low Pt dispersion (43.0%) and, more importantly,
in the formation of a bulk alloy between Pt and Mn, as revealed by the peak at 40.3° in the X-ray diffraction (XRD) pattern, indeed attributed to Pt alloyed in bulk [10]. The very small Pt nanoparticles size obtained in this study in the Pt-Mn/C sample made impossible the resolution of any X-ray diffraction peaks. Although the Pt-Mn/C investigated in this work has many similarities with other catalysts previously described, like Pt-Re/C, its reactivity in steam and aqueous phase reforming presents some differences, probably because of the presence of Mn in the oxidized form.

All the catalytic tests were performed with a 10 wt.% of glycerol at 225 °C. In the steam reforming, the Pt/C catalyst exhibited catalytic performances in line with previous works at comparable experimental conditions, with a TOF of hydrogen of about 6 min<sup>-1</sup> [17,24,26]. As expected, the main reaction products were mainly due to reaction pathways where the C-C bonds cleavage is favored, such as ethylene glycol in the liquid phase, with only a minor part of products derived by the scission of the C-O bonds, like acetol [48]. The low amount of carbon dioxide produced in the steam reforming reaction is due to the poor water gas shift activity of Pt supported on carbon even at relatively low temperatures [49].

The addition of Mn to Pt/C had a different impact on the catalytic performances of steam reforming with respect to aqueous phase reforming of glycerol. In fact, in the first case, the Pt-Mn/C catalyst showed improved TOF of hydrogen and glycerol conversion of about factors of 5 and 3, respectively. Conversely, only a slight increase in hydrogen production and conversion was found in the aqueous phase reforming reaction.

A careful analysis of the reaction products, which are correlated to the reaction pathway, could provide insights on the improved catalytic activity of Pt-Mn/C in steam reforming of glycerol. A reported in Table 2, while the conversion of Pt/C was prevalently directed toward the gaseous products, Pt-Mn/C, exhibited a high conversion level also to liquid products, in particular acetol, which is formed by dehydration of glycerol, reflecting the higher selectivity toward the C-O bond cleavage of Pt-Mn/C. Another indication of the preferential dehydration pathway followed by the Pt-Mn/C catalyst comes from the lower selectivity toward hydrogen and carbon monoxide, which are formed by dehydrogenation followed by decarbonylation of glycerol, as in the case of Pt/C (Table 2). Both ethanol and methanol can be formed via both pathways as final products of the dehydrogenation of ethylene glycol and/or acetol, therefore they are less indicative of the reaction pathway followed by the catalysts [17,26].

The different reaction pathways taken by Pt/C and Pt-Mn/C in the steam reforming of glycerol can be explained by the higher acidity of the Mn-promoted catalyst, while is less likely a mechanism involving CO spillover from Pt sites to MnO<sub>x</sub> because otherwise differences in the product selectivity should have been observed [17,26]. However, in order to rule out any possible CO spillover effect,

CO-TPD experiments were performed by pretreating the samples with steam at 225 °C in order to simulate steam reforming conditions. As expected, no difference in the desorption profiles were found, with both Pt/C and Pt-Mn/C showing a singular desorption peak centered at 102 °C (Figure 6A).

The same pretreatment was used in the ammonia TPD experiments to investigate the acid character of the samples again simulating steam reforming conditions. Based on the location of the desorption peaks, Pt/C and Mn/C had the same acid strength, which is in accordance with several authors who had reported similar results on similar systems, showing that supported Mn oxides catalysts have generally a quite low acid strength, due to both Lewis- and Brønsted-type sites [50-52]. A detailed investigation of the nature of the acid sites present in all the catalysts was made possible thanks to an *in-situ* ATR-IR technique with pyridine as probe molecule. Pt/C exhibited only Lewis-type acidity, as revealed by the peaks resolved at 1599 cm<sup>-1</sup> and 1440 cm<sup>-1</sup>, probably due to electron deficient Pt<sup> $\delta+$ </sup> centers formed as consequence of the steam pretreatment. Both Lewis and Brønsted acid sites were present in Mn/C, with the broad feature centered at 1550 cm<sup>-1</sup> ascribed to protonated pyridine, suggesting a prevalence of Brønsted sites in this sample (Figure 7) [29]. Importantly, two barely resolved bands centered at lower frequency than those assigned to Lewis acid sites in Pt/C were observed, indicating the presence of strong Lewis-type acidity [11]. These strong sites were probably too few in number to be revealed and then quantified by the NH<sub>3</sub>-TPD.

After adding Mn to Pt, a shoulder at high temperature was observed in the ammonia desorption profiles, along with a shift to a lower temperature of the main reduction peak. Moreover, in the ATR-IR spectrum of Pt-Mn/C the bands assigned to strong Lewis acid sites increased in intensity (Figure 7). Since the same low-frequency peaks, although very weak, were also found in Mn/C, they can be reasonably assigned to exposed oxidized  $Mn^{\delta+}$  centers. As suggested by the H<sub>2</sub>-TPR experiments (Figure 1), where Pt-Mn/C showed a higher hydrogen consumed than Pt/C, the increased number of strong Lewis acid sites could be the product of the interaction between the two metals [37]. It has been recently demonstrated that the increased formation of acid-catalyzed products in the reforming of glycerol is indeed associated to the presence of strong Lewis acid sites [11,53-55].

However, the negligible catalytic activity of Mn/C indicates that the decomposition of glycerol initiates on the Pt sites, and subsequently proceeds towards acid-catalyzed reactions on exposed oxidized  $Mn^{\delta^+}$  sites, shifting the product selectivity toward acetol. Brønsted acid sites on Pt-Mn/C, whose presence was evidenced by the broad feature at 1599 cm<sup>-1</sup>, had a minor influence on the reaction, since no products derived by proton-catalyzed reaction were found [55]. The retained selectivity toward CO<sub>2</sub> with respect to Pt/C is probably due to the CO oxidation capability of Mn oxides [29].

As far as the aqueous phase reforming reactions is concerned, Pt-Mn/C and Pt/C showed comparable catalytic performances, as well as the same products selectivity. A mildly higher TOF of H<sub>2</sub> and conversion level were, however, shown by Pt-Mn/C. ICP-OES analysis on used Pt-Mn/C revealed that most of all the Mn leached out from the catalyst, thus explaining the similarity with Pt/C, in particular in terms of products selectivity. The lower amount of Mn was also confirmed by EDX analysis (not shown).

Wang and co-workers had deeply studied similar systems (i.e., Pt-Re/C) for aqueous phase reforming reactions, and found that although around 50% of Re leached out, the catalyst maintained its superior catalytic activity compared to Pt/C. The presence of both oxidized Re and an Pt-Re alloy was revealed by *in-situ* XPS and Raman measurements [26].

Similarly, the formation of an alloy between Pt and Mn in the Pt-Mn/C catalyst studied by Kim *et al.* in the aqueous phase reforming of ethylene glycol was evidenced by XRD patterns, and attributed for the increased activity [10].

Comparable conclusions were also formulated by Dietrich *et al.* for a Pt-Mo catalyst in the aqueous phase reforming of glycerol [21]. It seems that the enhanced reforming performances of a bimetallic catalyst in aqueous phase reforming reactions is correlated to the presence of an alloy between the noble metal and the promoter, stabilizing the latter against dissolution.

In the Pt-Mn/C investigated in the present study, the amount of Pt alloyed with Mn was reasonably considered negligible, or at least not enough to have a major impact on the reactivity. The slightly improved TOF and selectivity of hydrogen might be explained by the presence of a small amount of Mn alloyed with Pt that did not leach into the reaction medium, and by considering a promotional mechanism similar to that reported for Pt-Re/C catalyst (vide supra). Indeed, ICP-OES analysis on the spent catalyst revealed a residual presence of Mn (< 5% of the fresh sample). Contrary to aqueous phase reforming, neither Pt nor Mn loss were evidenced by the spent Pt-Mn/C used in the steam reforming reactions.

#### **3.5 Conclusions**

The catalytic performances of a bimetallic Pt-Mn/C catalyst were investigated in the steam and aqueous phase reforming of glycerol. In the first case, with water fed as steam, the catalyst showed enhanced TOF of hydrogen and conversion compared to Pt/C, whereas with liquid water only a mild improvement was found.

In steam reforming, upon addition of Mn, the product selectivity shifted toward acetol at expense of CO and hydrogen, suggesting that the dehydration of glycerol (that is the C-O bond scission) was more favored than the dehydrogenation pathway (that is the C-C bond scission). This behavior could be due to the increased acidity of Pt-Mn/C, and in particular to the presence of strong Lewis acid sites, which have been reported to be responsible for the dehydration of glycerol.

Under aqueous phase reforming conditions most of the Mn leached into the reaction medium, but the residual metal still present on the catalyst might be responsible for the slight increase in catalytic activity, suggesting that an alloy formation might be fundamental for the stabilization of the promoter under such harsh reaction conditions.

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# Chapter 3

# . Cooperative action of Brønsted and Lewis acid sites of niobium phosphate catalysts for cellobiose conversion in water

# 2.1 Introduction

Niobium is a very interesting catalytic species that has attracted much attention owing to its redox and acidic properties, and that is currently used in many catalytic applications, such as selective oxidations and acid-demanding reactions [1-3]. Niobium phosphate (NbOPO<sub>4</sub> hereafter called NBP) has a texture, acidic and catalytic properties similar to the most popular niobium oxide catalyst, but it has the advantage of conserving these characteristics even at high temperatures [1,4]. In fact, Osazaki *et al.* showed that amorphous niobium phosphate does not crystallize prior to 800 °C, and exhibits remarkable catalytic activity even after heat treatments at temperatures as high as 500 °C [5,6].

Due to these peculiarities, it has been used in some reactions were acidic functionalities are required, such as 3,3-dimethyl-1-butene isomerization [7]. Moreover, niobium phosphate has shown promising catalytic performances in reactions where water is concerned as reactant, product, or solvent, such as fructose dehydration to 5-hydroxymethyl-2-furaldehyde (HMF) and other reactions of biomass conversion [8-12].

Differently from many conventional LAS-containing catalysts, these materials are resistant to water since the isolated Nb Lewis acid sites present at the surface maintain lively catalytic activity in polar and protic solvents [4,13]. Recently [13], it has been confirmed that the presence of water-tolerant acidic sites in hydrated niobic acid (Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O) originates from the presence of the NbO<sub>4</sub>-

 $H_2O$  adducts, still having a residual positive charge and thus acting as LAS. NBP is a higher protonic solid than the most well-known niobic acid catalyst [10,14]. NBP materials show the presence of medium to strong Brønsted acid sites at the surface, as well as medium to strong Lewis acidity, as revealed by acetonitrile FT-IR investigations. Lewis acid sites are generated by unsaturated Nb<sup>+5</sup> sites, while Brønsted acidity is mainly due to P-OH groups, and in lesser extent to Nb-OH sites [14].

Interestingly, a similar behaviour was reported also for TiO<sub>4</sub> tetrahedra dispersed on mesoporous silica [15] and for anatase [16], the latter showing an even higher density of water-tolerant LAS than niobic acid. Various catalytic and characterization experiments have demonstrated the *effective* acidity in water of NBP and niobic acid, along with other Nb-based catalysts, which has been exploited for biomass valorisation using water as solvent [9-12,17,18].

In general, these catalysts are active and selective in reactions of hydrolysis, isomerization and dehydration of the saccharidic biomass. Unfortunately, due to severe deposition on the surface of the so-called *humins* [19], which are insoluble in water, these materials rapidly deactivate [12,18,20]. Saccharidic biomass, which is derived mostly from agricultural wastes and/or forestall residues, can be converted into interesting platform molecules such as HMF, from hexose polymers, or furfural, from pentose polymers [21-27].

As a matter of facts, HMF is attracting great attention in the industrial world. Many versatile chemical intermediates can be generated from HMF by large scale transformations, such as 5-hydroxymethylfuranoic acid, 2-5-furandicarboxylic acid, 2,5-bis(hydroxymethyl)furan, and 2,5-furandicarboxaldehyde, among other compounds [28-30]. All the molecules can be used as six-carbon atoms monomers for the replacement of other oil-derived compounds. For example, 2,5-furandicarboxylic acid is able to replace terephthalic, isophthalic, and adipic acids in the manufacture of polyamides, polyesters, and polyurethanes [31,32].

The present study provides evidences that NBP and NBP-modified materials, obtained from acidic treatment of NBP, can be successfully used as catalysts for the production of HMF starting from cellobiose, which was chosen as model molecule of cellulose polymers. Cellobiose molecule is constituted by glucose units linked by  $\beta$ ,1-4-glycosidic bonds. Because of the presence of such a strong bond, cellobiose is much harder to hydrolyse than other disaccharides (for example, sucrose and maltose) [33].

The unique characteristics of the acidic catalysts used in this work have permitted to realize the conversion of cellobiose to HMF in water under mild conditions of temperature. The acidity of the samples has been characterized by liquid-solid titrations carried out in a modified liquid-chromatograph (HPLC) by basic solutions of phenylethylamine (PEA) in different solvents. Cyclohexane, an aprotic and non-polar solvent that does not interact with the surface, was used for

the determination of the *intrinsic* acidity, while the *effective* acidity was evaluated in water. The nature and concentration of the acid sites were further investigated by spectroscopic analysis also in the presence of water, mimicking the reaction environment.

#### 4.2 Experimental

#### 4.2.1 Materials

NBP was kindly supplied from Companhia Brasileira de Metalurgia e Mineração (CBMM). It contains 66.7 wt.% of Nb<sub>2</sub>O<sub>5</sub>, 15.9 wt.% of P<sub>2</sub>O<sub>5</sub> 2.1 wt.% of K<sub>2</sub>O, and 15.3 wt.% of H<sub>2</sub>O. The catalysts NBP01, NBP1, and NBP10 were prepared by pretreating the as-received NBP material with HCl at 0.1, 1, and 10 M concentrations, respectively. Briefly, weighted amounts of dried NBP (at 120 °C overnight) were soaked in 25 mL of HCl aqueous solution at fixed concentrations (0.1, 1, and 10 M), and vigorously stirred for 1 h at room temperature. Successively, the samples were filtered and thoroughly washed with 25 mL of fresh water, maintaining the suspension under vigorous stirring for another hour. The rinsing operation was repeated at least three times, until neutrality of the collected waters. Finally, the samples were dried overnight at 120 °C.

All the NBP-derived samples did not contain any chloride species possibly due to the preparation procedure, as revealed by EDX analysis (TM-1000 Tabletop Microscope, Hitachi Science Systems Ltd). Prior to all the experiments, the NBP, NBP01, NBP1, and NBP10 were reduced in powder with defined size after tableting. Specifically, the samples were pressed and sieved to 20-40 mesh for the catalytic tests, 45-60 mesh for the morphological analysis, while an 80-200 mesh was used for the acidity titrations. 2-Phenylethylamine (PEA), pyridine (Py), hydrochloric acid (37%) were purchased from Sigma-Aldrich. Cyclohexane and water (VWR, HPLC grade), were used for the liquid-solid acid titrations. D-(+)-cellobiose ( $\geq$ 99%, Fluka), glucose (RPE, Carlo Erba), D-(+)-maltose ( $\geq$ 98%, Sigma-Aldrich), and D-(–)-fructose ( $\geq$ 99%, Sigma) were used as substrate and standards for the various analyses.

The acidic resin (Amberlite IR-120 (H), Carlo Erba, referred as A120) is a styrenedivinylbenzene copolymer with sulfonic acid (-SO<sub>3</sub>H) groups. A120 (a gel type resin) was supplied in the acidic form. Before the use, the acidic resin was rinsed with distilled water to remove any traces of mineral acids, repeating the procedure until complete absence of colour and acidity in the wash water. It was employed as particles of 0.3-1.1 mm size. The acid characteristics of A120 have been previously studied. It carries 2.27 meq/g of acidic centres, as measured in water by PEA titration. [34]

#### 4.2.2 Catalysts characterization

Nitrogen physisorption isotherms, measured at the liquid nitrogen temperature with an automatic surface area analyser (Sorptomatic 1900 instrument), were performed in order to calculate the specific surface areas and the pore volumes of all the samples. The BET and BJH methods were used to compute the collected data. Prior to the measurement, the sample (ca. 100-150 mg), crushed and sieved as 45-60 mesh particles, was thermally activated at 120 °C for 2 h under vacuum. The pore volume was determined from the total amount of N<sub>2</sub> adsorbed at P/P<sub>0</sub> = 0.99 using the N<sub>2</sub> density in the normal liquid state ( $\rho = 0.8081$  g cm<sup>-3</sup>). N<sub>2</sub> molecular area was taken as 16.2 Å<sup>2</sup>.

PEA was used as basic probe in the acidity measurements of the samples in liquid. The *intrinsic* acidity (I.A) and the *effective* acidity (E.A) were determined by using cyclohexane and water as solvents, respectively. A recirculation chromatographic line (HPLC), comprising a pump (Waters 515) and a monochromatic UV detector (Waters, model 2487, = 254 nm) were used. The sample (ca. 0.1 g crushed and sieved as 80-200 mesh particles) was placed on a sample holder (stainless steel tube, 2 mm i.d. and 12 cm of length), between two sand pillows.

Prior to the measurement, the sample was activated at 150 °C for 3 h in flowing air (8 mL min<sup>-1</sup>), and then filled with the liquid (cyclohexane or water). The sample holder was mounted in place of the chromatographic HPLC column and maintained at constant temperature ( $30.0 \pm 0.1$  °C). Successive dosed amounts of PEA (50 L, ca. 0.10 M) were injected into the line in which the solution continuously circulated, until adsorption equilibrium was achieved. After the collection of the first adsorption isotherm of PEA on the fresh sample (I run), pure solvent was allowed to flow through the PEA-saturated sample up to the zero signal of the UV detector (this operation lasted between 40 and 60 min). Finally, a new adsorption of PEA on the same sample was repeated (II run). The collected data were interpreted according to the Langmuir model (Eq. (1)).

$$PEA_{ads} / PEA_{ads,max} = b_{ads} \left[ PEA \right]_{eq} / (1 + b_{ads} \left[ PEA \right]_{eq})$$
(1)

From the conventional linearized equation, reporting  $[PEA]_{eq} / PEA_{ads}$  vs.  $[PEA]_{eq}$ , the values of  $PEA_{ads,max}$  (meq g<sup>-1</sup>) could be obtained. The values of  $PEA_{ads,max}$  of the I run isotherm corresponded to the number of total acid sites  $PEA_{tot}$ , assuming a stoichiometry of 1 : 1 for the PEA absorption on the acid site, while the value of  $PEA_{ads,max}$  (meq g<sup>-1</sup>) obtained from the II run isotherm corresponded to the number of weak acidic sites,  $PEA_{weak}$ . From the difference of the number of the total and weak acid sites the number of strong acid sites was obtained,  $PEA_{strong}$ . Previous tests of PEA adsorption showed that it was adsorbed in negligible amount on samples without any acid and basic sites (sand, Fluka).

Fourier Transform Infrared Spectroscopy (FT- IR) (Biorad FTS-60A) using pyridine as probe molecule both in vapour phase and aqueous solution was employed to investigate the nature of the acid sites of the catalysts [35]. All the samples were pressed into 10-15 mg self-supporting disks (0.65  $\text{cm}^2$  of geometrical area), and before each analysis they were calcined for 2 h at 150 °C in air. After outgassing for 30 min in high vacuum, the samples were contacted with pyridine vapours at room temperature for 10min or, alter- natively, a  $1 \times 10^{-3}$  M pyridine aqueous solution was dropped on self-supporting disks under argon flow. After pyridine adsorption, the samples were outgassed for 30 min in high vacuum at different temperatures (i.e. RT, 50, 100, 150, 200, 250 °C).

By integrating the peaks at 1540 cm<sup>-1</sup> and 1448 cm<sup>-1</sup> of the spectra outgassed at 150 °C, according to the procedure reported by Emeis [36], the BAS and LAS concentrations were determined, respectively, and expressed as milliequivalent of absorbed pyridine per gram of sample  $(meq_{Py}g_{cat}^{-1})$ . In order to evaluate the amount of carbonaceous residues deposited after the catalytic tests on the catalysts, thermogravimetric analysis were performed with a TGA7 from Perkin Elmer instrument [37]. Prior to the analysis, the sample discharged from the reactor was dried at 80 °C for 2 h. Finally, an amount of 10-20 mg was put on the pan of the TGA and the temperature was allowed to increase from 50 °C to 800 °C at 10 °C min<sup>-1</sup> under air flowing.

#### 4.2.3 Catalytic tests

A total recirculation reaction line schematically shown in Figure 1 was used for the tests of catalytic conversion of cellobiose. The line can withstand pressures as high as 10 bar. The apparatus comprises: A liquid-chromatographic pump (Merck-Hitachi, L-6200 Intelligent Pump), a stainless steel pre-heater, a fixed-bed flow reactor (172 mm long, 4.7 mm internal diameter and 6.4 mm external diameter) thermostated at the reaction temperature inserted into a thermostated oven, and a jacketed reservoir maintained at 17 °C by cold water circulation.

The line worked in total recirculation, that is the feeding solution in the reservoir (typically 50 mL) was continuously sent to the reactor, and the outlet flow from the reactor was sent back again to the reservoir. The total volume of the circulating solution was 78 mL. At the exit from the reactor, a cooling system with a coil immersed in cold water (17 °C) allowed the solution to cool down, followed by a double micrometric valve that allowed the regulation of the pressure in the line. The catalyst sample (ca. 1 mL, 20-40 mesh particles) was held in the middle of the reactor between two sand pillows. The initial cellobiose aqueous solution (50 mM concentration) was continuously circulated (3 mL min<sup>-1</sup>) through the reaction line and on the solid catalyst, at constant temperature in a range 80-130 °C, up to 100 h.

Through this operative procedure, kinetic study could be realized by withdrawals of given amount of solution (ca. 0.1 mL) from the reservoir, and the catalyst stability could be investigated as well. The reaction products (20 L) were analysed by a liquid chromatograph (HPLC) with an injector (Waters U6 K), a pump (Waters 510), an oven for the thermoregulation of the column (Waters, model CHM), a refractive index detector (Waters 410) operating at 40 °C, and a Hewlett Packard interface (model 35900). Two columns were employed for qualitative and quantitative analyses: a Sugar-Pak-I (Waters), operating at 90 °C and eluted with a solution of Ca-EDTA 10<sup>-4</sup> M in water (0.5 mL min<sup>-1</sup>), and a Carbohydrate Analysis (Waters), suitable for volatile compounds and organic acids, operating at room temperature and eluted with acetonitrile / water 80:20 (0.5 mL min<sup>-1</sup>). Standard solutions of cellobiose, glucose, fructose, HMF, furfural, levulinic and formic acids at different concentrations in the range of concentrations used in the activity tests were used for the calibration.

In all the catalytic tests, the unreacted cellobiose and the formed reaction products (glucose, fructose, HMF, and a soluble condensation product not yet identified and indicated as CP1) were quantified and expressed in terms of mono-saccharides equivalents. It was not possible to quantify a small amount of other soluble by-products formed, corresponding to less than 5% on average. The quantification of the formed insoluble products was performed by comparing the total chromatographic areas of the soluble products of cellobiose analysed during the reaction with the initial area of cellobiose.



**Figure 1.** Scheme of the catalytic reaction line used for the catalytic tests of cellobiose transformation to HMF working in complete recirculation of the liquid aqueous solution; the catalytic reactor worked between 80 °C and 130 °C under pressure.

# 4.2.3 Kinetic interpretation

The hydrolysis of cellobiose in water excess can be considered as a *pseudo*-first order reaction, and when the reactor works as an ideal plug flow reactor, the following kinetic equation holds:

$$C_{\rm F} = C_{\rm R} \cdot \exp(-k\theta) \tag{2}$$

$$\theta = \nu / u \tag{3}$$

where  $C_R$  and  $C_F$  are the inlet and outlet concentrations of cellobiose into and from the catalytic bed, respectively, *k* the rate coefficient,  $\theta$  the contact time, *v* the volume of the catalytic bed and *u* the flow rate. When the flow rate is sufficiently high and the reaction rate is sufficiently low, the influent ( $C_R$ ) and effluent ( $C_F$ ) substrate concentrations to and from the reactor, respectively, are practically equal to the effluent and influent concentrations of the reservoir.

Additionally, the substrate concentration ( $C_R$ ) in the exit stream from the reservoir is the same of that within the stirred reservoir. The variation of the mole-number of cellobiose in the reservoir of volume *V* in the time interval d*t* is:

$$-dn = -VC_{R} = (C_{R} - C_{F}) \cdot u dt$$
(4)

Considering the Equations 2 and 3, it can be obtained:

$$-dC_{R} = C_{R} \cdot (1 - \exp(-k\theta)) \cdot \frac{u}{V} dt$$
(5)

$$-\frac{\mathrm{d}C_{\mathrm{R}}}{\mathrm{C}_{\mathrm{R}}} = \frac{1 - \exp(-k\theta)}{k\theta} \frac{k\nu}{V} \,\mathrm{dt} \tag{6}$$

If k and  $\theta$  values are sufficiently low, being the reaction rate low and the flow rate high, as above supposed, it can be considered that:

$$1 - \exp(-k\theta) \approx k\theta \tag{7}$$

Then, Equation 6 can be rewritten as:

$$-\frac{\mathrm{d}C_{\mathrm{R}}}{\mathrm{C}_{\mathrm{R}}} = \frac{k\nu}{V} \,\mathrm{dt} \tag{8}$$

and

$$-\frac{\mathrm{d}C_{\mathrm{R}}}{\mathrm{d}t} = k_{obs}C_{\mathrm{R}} \tag{9}$$

where:

$$k_{obs} = \frac{k\nu}{V} \tag{10}$$

A linear dependence of  $\ln C_R vs.$  t can be obtained by integrating Equation 9:

$$\ln C_{\rm R} = \ln C_{\rm R}^0 - k_{obs} \cdot t \tag{11}$$

Once  $k_{obs}$  has been obtained, the rate coefficient (*k*) can be easily computed by Equation 10. It can be evaluated that the approximation deriving by Equation 7 causes an error  $\leq 5\%$  for a ratio  $k/SV \leq 0.1$ , being  $SV = 1/\theta$  the space velocity [33].

#### 4.3 Results and discussion

#### 4.3.1 Catalysts characterization

NBP is known to be an acid solid with a high ratio of BAS to LAS, higher than, for example, niobium oxide. Considering that we wanted to use NBP as catalyst for the cellobiose hydrolysis, which is a reaction that requires protonic acidity, we increased the protonicity of its surface by hydrolysing the Nb-O, Nb=O, and P=O bonds with HCl solutions. The aim was to increase the surface hydroxyl groups concentration with positive consequences on the catalytic activity.

The amorphous property of NBP is well-known and reported in the literature [38,39]. A well crystallized phase of NbOPO<sub>4</sub> (the  $\beta$  form) is formed only after a heat treatment at 1100 °C. The studied NBP sample and those obtained by acidic treatment of NBP had all amorphous character (Figure 2). The elemental composition of all the NBP-modified materials did not differed significantly from that of the parent NBP (Table 1). However, a slight decrease in Nb and P concentrations if compared to the so-received NBP suggested that leaching could have occurred during the acidic treatment (Table 1). The values of surface area of the NBP samples, measured by nitrogen adsorption and thermally treated at 120 °C before the analysis, are listed in Table 2.

The acidic treatment of NBP did not result in remarkable morphologic modifications of the obtained samples. The values of surface area of all the samples are comprised in the 105-115 m<sup>2</sup> g<sup>-1</sup> interval and those of pore volume between 0.28-0.30 cm<sup>3</sup> g<sup>-1</sup>, except NBP10 that has little higher surface and pore volume, likely due to some decrease of particle size following the strong acid treatment (10 M in HCl). All these findings indicate that NBP and NBP-modified samples are resistant materials, withstanding severe chemical pretreatments without any important structural or morphologic modifications.



Figure 2. XRD patterns of NBP and one derived sample from acidic treatment (NBP1).

Element	NBP01 (wt %)	NBP10 (wt %)	
Р	16.5	16.6	
Cl	0.0	0.0	
K	3.2	2.0	
Nb	80.3	81.4	

Table 1. Element Analysis of NBP1 and NBP10 Evaluated by EDX<sup>a</sup>

<sup>a</sup> EDX: TM-1000 Tabletop Microscope, Hitachi Science Systems Ltd.

NBP composition (from CBMM): 66.7 wt.% of Nb<sub>2</sub>O<sub>5</sub>, 15.9 wt.% of P<sub>2</sub>O<sub>5</sub>, 2.1 wt.% of K<sub>2</sub>O, and 15.3 wt.% of H<sub>2</sub>O.

Normalized composition on Nb, P, and K: 89.97 wt.% Nb, 6.68 wt.% P, 3.36 wt.% K.

# 4.3.2 Intrinsic and effective surface acidic properties

Different methods under different conditions have been employed in the present study to investigate the acidic properties of NBP and related materials. The total surface acid sites of the samples was titrated with a basic probe (PEA) dissolved in two solvents: cyclohexane and water, to determine the intrinsic and effective acidity, respectively [18]. The quantification of the well-known water-tolerant acidic properties of the acid sites of NBP was performed by comparison of the results collected with the two different solvents.

Moreover, more sound correlations between the catalyst activity and *effective* catalyst acidity (i.e., acidity measured in water) can be obtained. The full comprehension of the acid properties must for sure pass through also the understanding of the nature of the acid sites present on the catalysts. The NBP and related samples studied are known to have both BAS and LAS at their surfaces. In addition, it is known that the catalytic activity and selectivity in any given reactions are affected by the nature, strength, and distribution of the different acid sites on the surface.

Spectrophotometric experiments of base adsorption and desorption at increasing temperatures can be made in order to control the presence of Brønsted- and Lewis-type acidity, as well as their relative amount and acid strength. In this case, the experiments of base adsorption-desorption have been also carried out in the presence of water.

### 4.3.3 Acidity measurements by PEA titrations in liquid

As apolar and aprotic solvent, cyclohexane was chosen due to these features for the determination of the *intrinsic* acidity of NBP. The results show a very high acidity both in terms of amount of total acid sites and of strength (Table 2). From the I run adsorption of PEA (Figure 3, right side), the total amount of acid sites (PEA<sub>tot</sub> in meq g<sup>-1</sup>) could be determined by applying the Langmuir equation (Eq. (1)) to the adsorption data. The total amount of the titrated sites (Table 2) is in perfect agreement with our previous measurements [10]. A comparable amount of acid sites was revealed by all the NBP-modified materials (namely, NBP01, NBP1, and NBP10), with just a very slight increase found. The acidity ranking, written in terms of PEA<sub>tot</sub>, follows the sequence: NBP < NBP01 < NBP1 < NBP10.

Apparently, the acidic treatment with HCl led only to a samples with modest higher acidity. The II run adsorptions of PEA in cyclohexane (Figure 3, left side) were very low on all the samples. In this case, the amount of acid sites determined from the adsorption data by Eq. (1) corresponded only to the weak acid sites (PEA<sub>weak</sub>, in meq g<sup>-1</sup>). The values of PEA<sub>weak</sub> corresponded to the amount

of PEA desorbed following the pure cyclohexane elution (see Experimental). Therefore, the acid strength of these sites was very high. The strong acid sites ( $PEA_{strong}$ , in meq g<sup>-1</sup>) corresponded, on average, to 87% of all sites titrated.

Figure 3 shows for all the samples the measured adsorption isotherms of PEA in cyclohexane; the I run adsorptions, in particular, have a well Langmuirian shape, typical of chemisorption, in agreement with the high acid strength of the sites. The measurement carried out in water, that is the determination of the *effective* acidity, showed a completely different scenario. It is known that water (polar compound, with solvating ability as well) reacts with Brønsted sites and decreases the acid site strength by solvating effects and H-bond formation.

Moreover, water can coordinate Lewis acid sites, thus hindering their acidic function [40,41]. It is reasonable to say that in presence of water the acidity of solid acid is excepted to decrease, as indeed already demonstrated on several catalytic materials [10,17,18]. This is due to the solvating action of water which allows the creation of strong bonds with acidic centres. Water has to be displaced by the basic probe in order to be adsorbed, and this is only possible if a strong acid-base bond is formed. It is also possible that water and the probe can find simultaneously an allocation in the coordination sphere of the acid centre, as it has been demonstrated for Nb centres in several catalytic materials [16]. The data reported in Table 2 show in presence of water only a marginal decrease of the amount of acid sites occurred if compared to the titrations performed in cyclohexane (NBP retained in water around 87% of its *intrinsic* acid sites while NBP01, NBP1, and NBP10 maintained in water around 75% of their *intrinsic* acid sites).

The water-tolerant characteristic of Nb acid sites of niobium phosphate samples was confirmed by the mild decrease of the acidity observed in all the samples. In water, the acid strength of the catalysts was much lower in comparison to the ones measured in cyclohexane (that is, the *intrinsic* acidity). For NBP, only 31% of the effective acid sites are strong sites, while only 15%, on average, for NBP0.1, NBP1, and NBP10. As a general trend, the surface acid strength of the samples in water was lowered in comparison with that intrinsically possessed by the samples. In Figure 4 are reported the isotherms runs of PEA absorption in water for all the samples.

By comparing these results with the ones collected in cyclohexane (Figure 3), it appears clear that in presence of water a decrease of strength of the *effective* acidity occurred in all the samples. The only slight differences of the results of intrinsic and effective acidities of NBP and related samples demonstrated that NBP is a very robust catalyst that does not suffer too much the hydrolytic effect of acidic solutions. The comparison of acidity between NBP and niobic acid led to interesting insights, as emerged from Ref. [10]. Specifically, NBP has twice the number of total acid sites possessed by niobic acid in terms of *intrinsic* acidity (measured in cyclohexane), with a greater

percentage of strong acid sites. Moreover, NBP manifests almost the double acid sites compared to niobic acid, while the acid strength of them was very similar.

Sample	SSA <sup>a</sup>	Pore Volume <sup>b</sup>	Total Acid Sites ( <b>I.A.</b> ) <sup>b</sup>	Strong Acid Sites (I.A.) <sup>b</sup>	Total Acid Sites (E.A.) <sup>b</sup>	Strong Acid Sites (E.A.) <sup>b</sup>	
	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$PEA_{tot} (meq g^{-1})$	PEA <sub>strong</sub> (meq g <sup>-1</sup> )	$PEA_{tot} (meq g^{-1})$	$PEA_{strong} (meq g^{-1})$	
NBP	115	0.30	0.403	0.353 (88%) <sup>c</sup>	0.350	0.108 (31%) °	
NBP01	105	0.29	0.437	0.378 (87%)	0.344	0.0430 (12%)	
NBP1	110	0.28	0.439	0.379 (86%)	0.313	0.0496 (16%)	
NBP10	144	0.35	0.450	0.395 (88%)	0.349	0.057 (16%)	

### Table 2. Main properties of the catalyst.

<sup>*a*</sup> Thermal treatment of activation: 120°C for 2 h under vacuum (10<sup>-3</sup> mbar).

<sup>b</sup> Adsorption temperature, 30°C; solvent, cyclohexane for *intrinsic* acidity (I.A.), and water for *effective* acidity (E.A.) measurements.

<sup>c</sup> Percent of strong acid sites.



**Figure 3**. Isotherms at 30 °C of PEA adsorption in cyclohexane (*intrinsic* acidity) on all the catalyst samples; I run adsorption (right) and II run adsorption (left).



**Figure 4.** Isotherms at 30 °C of PEA adsorption in water (*effective* acidity) on all the catalyst samples; I run adsorption (right) and II run adsorption (left).

#### 4.3.4 Nature of the acid sites studied by FT-IR spectroscopy

The presence of both terminal P-OH and Nb-OH groups was confirmed by FT-IR spectroscopy on the niobium phosphate catalysts, with the former leading to mildly stronger Brønsted-type acidity than Nb-OH sites. Lewis acidity is also present on the surface and it has been associated with coordinatively unsaturated Nb<sup>+5</sup> sites [14,42], like recently revealed by acetonitrile adsorption followed by FT-IR spectroscopy [43].

In the present work, the FT-IR characterization was carried out with pyridine both in vapour phase and in aqueous solution with the aim of better understanding the reaction and deactivation mechanisms. In Figures 5 and 6 the FT-IR desorption spectra at 150 °C in the range of 1400-1700 cm<sup>-1</sup> of pyridine contacted both in vapour phase and aqueous solution on NBP, NBP01, NBP1 and NBP10 catalysts are shown.

Although with different intensities, all the spectra exhibited the same bands associated to the presence of both Brønsted- and Lewis-type acidity. Specifically, the sharp bands due to pyridine interacting with Lewis acid sites 1448 cm<sup>-1</sup> ( $v_{19b}$  mode) and 1610 cm<sup>-1</sup> ( $v_{8a}$  mode) can be clearly observed, while the broad bands at 1540 cm<sup>-1</sup> ( $v_{19b}$  mode) and 1637 cm<sup>-1</sup> ( $v_{8a}$  mode) are assigned to Brønsted acid sites [35]. The bands located at 1448 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> were used for the quantitative determination of Lewis and Brønsted acid sites, respectively, according to the procedure reported by Emeis [36]. The attribution of the band at 1480 cm<sup>-1</sup> is more difficult but it is likely related to the simultaneous interaction of pyridine on coupled Brønsted and Lewis sites.

In addition to these bands, all the samples showed a weak band located at 3665 cm<sup>-1</sup> (not shown) before outgassing, reasonably attributable to the -OH stretching mode of surface hydrogenphosphate species, that became sharper with outgassing until 250 °C [19]. The band relative to the -OH stretching mode of free Nb-O sites at 3708 cm<sup>-1</sup> was almost never observed until high pyridine desorption temperatures. These findings suggest that the main responsible for the Brønsted acidity are the surface P-OH groups. On the other hand, low-coordinated Nb sites in tetrahedral coordination could be responsible for the Lewis acidity, as proposed for very similar water-tolerant acid materials such as niobic acid (Nb<sub>2</sub>O<sub>5</sub>'*n*H<sub>2</sub>O) and H<sub>3</sub>PO<sub>4</sub>-reated niobic acid [13].

Pyridine in aqueous solution was purposely employed to investigate the acidic properties of the catalysts mimicking the real working conditions (i.e., in aqueous solutions). In order to confirm the co-absorption of pyridine with water molecules, the band due to the scissoring mode of absorbed water molecules located at 1620 cm<sup>-1</sup> was followed all over the desorption experiments (Figures 7 and 8). In all the samples contacted with pyridine in aqueous solution, in fact, this peculiar band was considerably more intense at 150 °C than that of the samples contacted with pyridine vapours, confirming the higher presence of water.

The results of the determination of the nature of the acid sites of all the catalysts using both the two ways of investigation are reported in Table 3. From data collected with pyridine in vapour phase on NBP, the concentration of Brønsted and Lewis acid sites was found 0.047 meq  $g^{-1}$  and 0.080 meq  $g^{-1}$ , respectively, in line with previous reports in the literature with comparable material pretreatment [44]. In the samples treated with HCl an increase of the overall acidity was observed, in particular it was found twice the amount of Lewis acid sites and about three time the amount of Brønsted acid sites. The only exception to this trend was shown by the sample NBP10 which showed twice the concentration of Brønsted acid sites. Moreover, the molar ratio between the two types of acid sites remained practically unchanged even after the treatment with the 10 M HCl solution. The observed differences could be justified at the light of the modification of the Nb and P surface composition (Table 1).

The situation changed when pyridine was contacted in aqueous solution. Specifically, the concentration of Lewis acid sites of NBP slightly decreased to 0.0058 meq g<sup>-1</sup>, whereas no major differences were evidenced in the Brønsted-type acidity (0.0045 meq g<sup>-1</sup>). On the other hand, the samples treated with HCl showed a quite different behaviour. Lewis acid sites showed remarkable tolerance to water, suffering only a negligible decrease, while the Brønsted acid sites decreased deeply. Only for the NBP10 catalyst, the concentration of Lewis acid sites was almost the half, but in any case, it was almost the twice the amount of the parent NBP catalyst. The acidic treatment on NBP material had also an impact on the Brønsted population, with their concentration being higher (when

measured in vapour phase) compared to the values found for NBP. These new Brønsted acid sites have low acid strength and only a limited amount (on average 40%) was detected in the presence of water (Table 3).

The different impact of water on the LAS and BAS population can be rationalized considering that in presence of water the hydrogenphosphate groups responsible for the Brønsted-type acidity undergo partial re-hydration, thus decreasing in number, whereas the Nb sites responsible for the Lewis-type acidity, even though re-hydrated, can coordinate simultaneously both water and probe molecules [45]. As previously reported, the peculiar ability of Nb sites to coordinate simultaneously both water molecules and probes can be ascribed to the positive charge on Nb centres in tetrahedral coordination, as demonstrated by FT-IR investigation with carbon monoxide as probe molecule on niobic acid [13].



**Figure 5.** FT-IR desorption spectra at 150 °C of pyridine on NBP (a), NBP01 (b), NBP1 (c) and NBP10 (d,) with pyridine adsorbed in vapor phase. BAS and LAS peaks at 1540 and 1448 cm<sup>-1</sup>, respectively.



**Figure 6.** FT-IR desorption spectra at 150 °C of pyridine on NBP (a), NBP01 (b), NBP1 (c) and NBP10 (d), with pyridine adsorbed in aqueous solution. BAS and LAS peaks at 1540 and 1448 cm<sup>-1</sup>, respectively. Scissoring mode band (W) of adsorbed water molecules at 1620 cm<sup>-1</sup>.



**Figure 7.** FT-IR desorption spectra in the region from 1550 cm<sup>-1</sup> to 1710 cm<sup>-1</sup> of NBP01 from room temperature (RT) to 250 °C with pyridine adsorbed in vapor phase. BAS and LAS bands at 1637 cm<sup>-1</sup> and 1610 cm<sup>-1</sup>, respectively. Band related to the scissoring mode of the adsorbed water molecules (W) at 1620 cm<sup>-1</sup>.



**Figure 8.** FT-IR desorption spectra in the region from 1550 cm<sup>-1</sup> to 1710 cm<sup>-1</sup> of NBP01 from room temperature (RT) to 250 °C with pyridine adsorbed in aqueous solution. BAS and LAS bands at 1637 cm<sup>-1</sup> and 1610 cm<sup>-1</sup>, respectively. Band related to the scissoring mode of the adsorbed water molecules (W) at 1620 cm<sup>-1</sup>.

		Py <sub>(vap)</sub> <sup>a</sup>			Py <sub>(aq)</sub> <sup>b</sup>	
Sample	LAS	BAS	LAS/BAS	LAS	BAS	LAS/BAS
Sample	$(\text{meq g}^{-1})$	(meq $g^{-1}$ )		$(\text{meq g}^{-1})$	(meq $g^{-1}$ )	
NBP	0.080	0.047	1.69	0.058	0.045	1.30
NBP01	0.151	0.123	1.23	0.121	0.029	4.25
NBP1	0.157	0.118	1.33	0.121	0.052	2.35
NBP10	0.159	0.093	1.72	0.095	0.040	2.40

**Table 3.** Determination of the nature of the acid sites determined by FT-IR with pyridine (Py) as probe molecule in absence and in presence of water.

<sup>*a*</sup> Pyridine contacted in vapor phase.

<sup>b</sup> Pyridine contacted in aqueous solution.

#### 4.3.5 Catalytic conversion of cellobiose in water

From our past activity on the hydrolysis of the disaccharides, among the organic catalysts, the acidic resin A120, and NBP, among the inorganic catalysts, have shown the most interesting performances towards the hydrolysis of cellobiose under mild conditions (80 °C) [33]. In general, NBP showed higher activity than niobic acid in the hydrolysis of disaccharides (sucrose, maltose, and cellobiose). For example, the values of rate constants for the sucrose hydrolysis were 0.33  $h^{-1}$  and 0.045  $h^{-1}$  on NBP and niobic acid, respectively [33].

Cellobiose hydrolysis is a simple and clean reaction that leads selectively to glucose formation. The option of increasing the reaction temperature can have interesting consequences on the NBP catalyst. In first place, higher hydrolysis rates, and secondly, the activation of consecutive reactions from the formed glucose, thus allowing the formation of highly appealing final products, such as HMF.

With this aim, we have deepened the study of cellobiose conversion on the NBP acid catalysts, and we compared the results with the catalytic activity of A120, working in the temperature interval of 110-130 °C and 80-110 °C, respectively. The results showed, as expected, that A120 has better catalytic activity than NBP; at temperature of 110 °C, its coefficient rate is ca. ten times higher (Table 4). A120 showed also appreciable activity at lower temperatures. At 80 °C, the obtained rate coefficient (0.08 h<sup>-1</sup>) is in agreement with that already reported for the same reaction [33].

Temperature had a positive action on the catalytic performances of the two catalysts. On A120 after 50 h of reaction, cellobiose conversion was 9%, 60%, and 87% at 80 °C, 100 °C, and 110 °C, respectively, while on NBP after 50 h of reaction, cellobiose conversion attained 24%, 46%, and 70% at 110 °C, 120 °C, and 130 °C, respectively. The temperature dependence of the reaction of cellobiose conversion was evaluated by the classical Arrhenius approach in order to obtain the activation energy (Table 4). Comparable values of the activation energy have been calculated for A120 and NBP. This differs from what had been obtained working with the disaccharide sucrose (substrate very easy to hydrolyse), in fact in that case the value of  $E_a$  of A120 was about half that of NBP catalyst [33].

The product-distributions showed by A120 and NBP differed significantly. In Figures 9 and 10 are reported for both catalysts the distribution trends of reactant and products (in terms of milliequivalents of monosaccharide) as a function of reaction time at 110 °C. Similar trends were observed for the other temperatures investigated. The conversion of cellobiose to glucose was the only reaction observed using A120, in fact only glucose and very little amount of soluble by-products (<5 meq L<sup>-1</sup> only at 110 °C) were formed until almost total cellobiose conversion (Figure 9). The decrease of cellobiose concentration showed by NBP at 110 °C was not only much slower than on A120, but during the reaction course other products accompanied the glucose formation, such as

fructose, HMF, and CP1. Selectivity to glucose was about the 35%, while selectivity to fructose was not higher than 3%. This indicated that the peculiar acidity of NBP (co-presence of lively BAS and LAS in water) was able to isomerize in some part glucose to fructose, and the latter was involved in the subsequent reactions.

This behaviour was also observed on NBP at reaction temperatures of 120 °C and 130 °C. In detail, fructose selectivity was not higher than 3.5-4%, while glucose selectivity attained 38-42%. It is well-known that fructose is more reactive than glucose and it can be easily converted in HMF by cyclo-dehydration reactions [46,47].

Moreover, evidences similar to those above discussed were recently reported by Zhang *et al.* [9] that demonstrated the role of Lewis acids in aqueous solution in the isomerization of glucose to fructose, followed by fructose dehydration to HMF. On NBP, the observed HMF was formed with selectivity of 15%, 26%, and 31% at 110 °C, 120 °C, and 130 °C, respectively.

Besides HMF, which constitutes a final stable product of cellobiose conversion, the formation of a heavier soluble condensation product (CP1) was detected, likely an oligomer of HMF, as our first analytical evidences seem to indicate. CP1 was revealed in the HPLC chromatogram at the lowest retention time, in the zone in which soluble oligosaccharides are typically observed. However, considering that CP1 was successfully extracted from the aqueous solution containing the reaction products with methyl isobutyl ketone, it should be associated to a compound different from oligosaccharides. CP1 was completely absent on A120, where any HMF was not formed, but it was observed on NBP with high yield (from 8% to 20% in the temperature interval 110-130 °C after 50 h of reaction). Only at reaction temperature of 120 °C and 130 °C, other soluble by-products were formed that in total gave a total concentration around 5-7 meq L<sup>-1</sup>.

The catalytic performances of NBP01, NBP1, and NBP10 were also tested under the same conditions in the temperature interval of 110-130 °C. Cellobiose conversion and product distributions did not significantly differ from those observed on NBP, as the sample surfaces are not highly different from NBP. As a general trend, glucose was formed in a high amount, while a low amount of fructose was always observed. HMF and CP1 were the two final stable products. All the other by-products ranged from 4% to 10% of the total product formed. Figure 11 shows the values of cellobiose conversion and yields to glucose, fructose, HMF, and CP1 obtained at 120 °C after 24 h of reaction obtained with all four samples. Cellobiose conversions ranged from 30% to 40%, and the yields of HMF were always similar to that of CP1.

Interestingly, NBP01 displayed the most peculiar results in terms of cellobiose conversion and yield to HMF. The activity ranking of the NBP-samples was evaluated on the basis of the rate coefficients of the reaction of cellobiose conversion at 120  $^{\circ}$ C, and was the following: NBP01 >

NBP10 > NBP  $\approx$  NBP1 (Table 5). The rate coefficient of NBP01 is almost double than that of NBP, even though it showed intrinsic and effective acidity similar to NBP. It is worth noting that the effective acid strength of the sites of NBP01 is lower than that possessed by NBP, as well as the LAS population (Table 3). These differences should account for the highest activity of NBP01 among the other NBP-samples.

The  $E_a$  values of NBP, NBP01, and NBP10 are comprised in a short interval (115-126 kJ mol<sup>-1</sup>), as well as the ln A values (35-38), as reported in Table 5. As excepted, these low values of  $E_a$  have been obtained for the most active catalysts. Due to compensation effect often observed in the derivation of the activation parameters, ln A values are low, too [48]. On the contrary, NBP1 exhibited high  $E_a$  and ln A values associated with the lowest rate coefficient for the studied reaction of cellobiose conversion to HMF. This could be due to a non-balanced presence of LAS and BAS on its surface, which causes a lower reaction rate if compared to the other NBP-modified catalysts. In the recent literature, the correlation between a balanced population of Lewis and Brønsted sites and the catalytic activity of niobium oxide and niobium phosphate catalysts used in the conversion of biomass-derived carbohydrates to HMF in water has been discussed [9].

It is known that the reaction of fructose to HMF, which was observed with all the NBP-catalysts during cellobiose conversion, leads to catalyst deactivation due to the formation of insoluble *humic* materials that precipitate on the catalyst surface, being highly insoluble in water [20,49-51]. The consequent subtraction of active catalytic sites results in lower reaction rates.

The recent review of I. Sádaba *et al.* [52] discusses extensively various phenomena responsible of catalyst deactivation in liquid media, in particular in reactions of biomass conversion, with attention to the possibility of reusing the solid catalysts affected by deactivation.

During the kinetic interpretation of the data to obtain the rate coefficients of all the NBPcatalysts, deactivation was considered. As shown in Figure 12, not perfectly linear trends (in particular, at the highest reaction temperature, 130 °C) were obtained when plotting the linearized first order rate equation up to about 100 h of reaction. Focusing on the results obtained at 130 °C, the computed values of the coefficient rates ( $k_{obs}$ ) are 1.81 h<sup>-1</sup> in the time interval 0-10 h, and 0.94 h<sup>-1</sup> in the time interval 20-30 h. The decreasing trend of the  $k_{obs}$  values with reaction time suggest partial deactivation of the catalyst surface.

An evaluation of the formation of insoluble products during the reaction was made possible by the comparison of the total chromatographic areas obtained analysing the samples collected at the different reaction times with the initial area of cellobiose. The insoluble products, expressed in terms of mono-saccharides equivalents, were < 5% of the fed cellobiose for the total reaction time (100 h) at 110 °C, and up to 70 h and 30 h at 120 °C and 130 °C, respectively. The insoluble products were

roughly 9-10% in 50 h of reaction at 130 °C. In order to study the catalysts deactivation, the adsorbed organic species were investigated by thermo-gravimetric analysis (TGA) after drying the samples at 80 °C.

Following the method described by Sahoo *et al.* [53], the thermogravimetric profiles can be divided in three-sub-intervals of temperature: Volatile organic compounds (VOCs, 50-180 °C), soft-coke (180-330 °C), and hard coke (330-800 °C). Figure 13 shows the TGA profiles and the relative first derivative curves (DTGA) as a function of temperature for NBP after reaction at 110 °C, 120 °C, and 130 °C, taken as example. VOCs are present in the highest amount on NBP (DTGA peak at 170 °C with a shoulder at 150 °C) at all the temperatures, while hard-coke (DTGA peak at 450 °C) was only detected on the catalyst after reaction at 120 °C and, in particular, at 130 °C. This means that the insoluble organic species formed during fructose dehydration reaction can convert and grow on the catalyst surface as a function of the reaction temperature, leading to the formation of coke. The so-formed coke could be removed by simple oxidative thermal treatments, allowing the reuse of the catalyst. The same experimental TGA evidence were observed on all the other NBP-modified catalysts.

<u>Camar 1</u> -	Temperature	Rate coefficient <sup><i>a</i></sup>	Ea	$\ln A^b$
Sample	(°C)	$(h^{-1})$	(kJ mol <sup>-1</sup> )	
	80	0.077		
A120	100	0.856	$119 \pm 2$	38 ± 1
	110	1.966		
	110	0.291		
NBP <sup>c</sup>	120	0.759	$115 \pm 6$	$35 \pm 2$
	130	1.811		

 Table 4. Rate coefficients and kinetic parameters for the reaction of conversion of cellobiose in water on the catalysts A120 and NBP.

<sup>*a*</sup> k (for calculation, see 4.2.3. paragraph).

 ${}^{b}A(h^{-1})$ 

<sup>*c*</sup> Evaluated in the first part of the reaction.



**Figure 9.** Distribution trends of CEL ( $\Box$ ) and GLC ( $\Diamond$ ) in the reaction of conversion of cellobiose in water on A120 catalyst at 110 °C (concentration in terms of mequivalent of monosaccharide).



Figure 10. Distribution trends of CEL ( $\Box$ ), GLC ( $\Diamond$ ), FRU ( $\Delta$ ), HMF (O), and CP1 (+) in the reaction of conversion of cellobiose in water on NBP catalyst at 110 °C (concentration in terms of mequivalent of monosaccharide).



**Figure 11.** Comparative results of the reaction of conversion of cellobiose on NBP, NBP01, NBP1, and NBP10 catalysts: conversion and yield to the reaction products evaluated at 120 ° C after 24 h of reaction.



**Figure 12.** Deactivation trend in the reaction of cellobiose transformation on NBP at 110°C ( $\Box$ ), 120°C ( $\Delta$ ), and 130°C ( $\circ$ ) as a function of reaction time. (cellobiose concentration in meq L<sup>-1</sup>).



**Figure 13.** TGA (red) and DTGA (black) profiles in air atmosphere as a function of temperature (10°C min<sup>-1</sup>) of used NBP after reaction at 110°C (A), 120°C (B), and 130°C (C).

	Samula	Rate coefficient <sup><i>a</i></sup>	Ea	$\ln A^b$	Rate coefficient ratio
Sample		(h <sup>-1</sup> )	(kJ mol <sup>-1</sup> )		$(k_{cat}/k_{NBP})$
	NBP	0.759	$115 \pm 6$	$35 \pm 2$	-
	NBP01	1.441	$125 \pm 32$	$38 \pm 10$	1.90
	NBP1	0.699	$166 \pm 3$	$50 \pm 1$	0.92
	NBP10	1.079	$126 \pm 10$	$38 \pm 3$	1.42

**Table 5.** Rate coefficients and kinetic parameters for the reaction of conversion of cellobiose in water onNBP and derived catalysts 120 °C.

# 4.4 Conclusions

The good water-tolerant acid properties of niobium phosphate have been confirmed by basetitrations in water by comparison with those collected in cyclohexane. In addition, the prevalent Lewis acidity of niobium phosphate catalysts in water has been proved by spectrophotometric evidence. The key to successfully realizing the conversion of carbohydrate biomass to HMF is the balanced presence on the catalyst surface of both Brønsted and Lewis acid sites with lively acidity in the chosen reaction solvent. The cooperative action of the BAS and LAS can combine the first hydrolysis step with the isomerization and dehydration steps in a one-pot reaction system.

The effective acidity of the NBP-modified samples is high, while the effective acid strength can be suitable for the activation of substrates in given reactions. The catalytic production of HMF directly from polysaccharides can take advantage of catalysts having both Lewis and Brønsted acid sites on the surface, like NBP.

These peculiarities allow the hydrolysis of the polysaccharide by Brønsted acid sites, the isomerization of the monomer sugars formed by Lewis acid sites, and finally their dehydration to the final HMF target molecule. In order to increase the HMF yield, the optimization of the acid catalyst with balanced LAS and BAS populations and the selection of a suitable solvent mixture with water would be the two actions to perform.

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## Chapter 4

## **5**. General conclusions

As pointed out in the first chapter, the aim of this thesis work was to harness biomass-derived compounds for the sustainable production of hydrogen and chemicals. So far, many catalytic materials have been tested and investigated in the open literature. High performances and stability under harsh reaction conditions are fundamental requirements for an industrial relevant catalyst for the conversion of biomass or biomass-derived compounds. Generally, only noble metal-based catalysts and/or material prepared by expensive techniques feature these characteristics. In the optics of upgrading the reactions studied at the laboratory scale to industrial grade, however, cheaper and easier-to-prepare materials are needed. The use of *in-situ* characterization techniques to investigate the catalysts under real working condition is crucial as well.

In the second chapter of the present thesis, the catalytic performances in the steam reforming of acetic acid of a Ru-based catalyst were improved by reducing the defectivity of the metal nanoparticles. A novel preparation procedure was adopted, which basically consisted in the controlled pre-formation of the nanoparticles in a colloidal suspension followed by their deposition on a hydrotalcite-derived support. Although this procedure might seem expensive and therefore not suitable for a real industrial catalyst, no thermal treatments were used. Of course, the nanoparticles were reduced prior to their deposition on the support, but this was achieved just by using a static hydrogen atmosphere at room temperature. The controlled size and shape of the metallic active phase led to a Ru catalyst featuring a higher resistance to coke deposition, which is one of the first causes of deactivation during reforming reaction, especially when using acidic molecules in the feed. More importantly, the catalytic performances shown by this novel Ru catalyst were practically identical to those of a reference Rh-based catalyst, which was chosen for its the well-known activity. In fact, both

the catalysts exhibited a total conversion of acetic acid and high hydrogen selectivity, as well as a comparable low coke deposition rates. A control Ru sample prepared by simple wet impregnation underwent rapid deactivation due to severe coking within few hours. Such a remarkable result could be extremely useful for the future preparation of catalysts based also on non-noble metals that typically lack of stability in reforming conditions, particularly if employed in the reforming of hard-to-treat mixtures like bio-oil.

The strategies to improve the activity of catalyst are multiple and involve different aspects of the materials, like the surface properties of the supports, doping, etc. In the third chapter, a Pt-based catalyst supported on activated carbon was modified by Mn and tested in steam and aqueous phase reforming of glycerol, which was chosen since it has industrial relevance as by-product of the biodiesel industry. The addition of a second metal is a common way to introduce new functionalities to the parent catalyst, very often resulting in completely different catalytic behavior, but always with the general goal of improving the activity. Pt is a noble metal featuring excellent performances in reforming reactions, owing to its high C-C bond cleavage activity at low temperature. The addition of Mn by simple wet co-impregnation was performed with the aim of improving the hydrogen production while reducing the cost of the catalyst. As expected, the bimetallic catalyst exhibited superior activity compared to the monometallic Pt catalyst, both in terms of glycerol conversion and hydrogen production rate in the steam reforming reaction. A higher selectivity to dehydration products was also evidenced. The reason of this improvement was found to be the peculiar acidic surface properties, as revealed by ammonia desorption experiments and ATR-IR analysis using pyridine as probe molecule. In particular, strong Lewis acid sites were formed upon addition of Mn, which are considered responsible for the dehydration of glycerol. In reforming reactions acidity is generally seen as a detrimental factor, often leading to undesired polymerization and eventually to coking. In this case, however, the peculiar acidic properties of the Pt-Mn catalysts, with few, strong Lewis acid sites, resulted to be beneficial to the reaction. The low amount of strong acid sites probably activated the glycerol molecules, which then reacted on the Pt sites. A part of the glycerol underwent dehydration, as witnessed by the higher amount of dehydration products compared to the Pt sample, suggesting that a fine tuning of the type of acidity and relative strength could be used to further increase the catalytic activity. These important results were obtained thanks to pretreatments with steam at the reaction temperature prior to the experiments, highlighting the importance of characterization performed under simulated reaction conditions. On the other hand, in the aqueous phase reforming only a minor increase of activity was shown by the Pt-Mn catalysts. The reason of such a difference was ascribed to the leaching of most of the Mn into the aqueous media. Nonetheless, the remaining Mn was probably alloyed to the Pt, leading to increased conversion and hydrogen yield

by enhanced CO spillover from the Pt centers. However, these conclusions were formulated solely on the basis of the analysis of the reaction products and previous literature works. The lack of availability of instruments capable of withstanding high pressures and high temperature, such those of APR, made impossible any characterization simulating the reaction conditions. Many literature works also draw conclusions only on the basis of speculations and with no direct evidences of the actual situation of the reaction and of the catalyst. This further evidences that without *in-situ* characterizations or by simulating the working conditions, no truly helpful information can be gathered, thus making difficult the design of always more active catalysts.

Sustainable hydrogen production is for sure one of the most relevant applications of biomassderived compounds, but not the only one. The production of platform molecules for the sustainable production of materials with high interest for the market, such as plastics, has had always great attention and much has been achieved in the last decades. As per many other processes, the direct conversion of raw biomass into these platform molecules is still a challenge, therefore model compounds are more often used. Cellobiose is a model for the cellulose polymers, and it is widely recognized as possible source of many other interesting molecules. The classical transformations of cellobiose involve acid-catalyzed reactions, typically using first a Brønsted acid, primarily aimed at hydrolyzing the  $\beta$ -1,4-glycosidic bonds between the two monomers of glucose, followed by treatments with mineral acids to convert the so-formed glucose to the target molecules. Obviously, all these steps are not fully sustainable under an industrial point of view. The development of onepot reactions using cheap catalytic materials is thus important to make possible the large-scale production of sustainable materials. In the third chapter, a series of niobium phosphate-modified materials with HCl were tested in the direct conversion of cellobiose to HMF. Acidic treatments were performed in order to enhance the acidic surface features of the parent niobium phosphate, which is known to have both Lewis and Brønsted acid sites. What marks the difference of niobium phosphate compared to other solid acids is its tolerance towards polar solvents, that is, it shows acidic behavior even in water. Having in mind the importance of *in-situ* characterization, the surface acid sites of all the catalysts were studied in the presence of liquid water at the reaction temperature. Specifically, FTIR analysis were carried out by contacting the pyridine in aqueous solution. The results evidenced that a proper balance of the type of acid sites and their relative abundance, as well as their strength, is important to achieve high productivity and selectivity towards HMF. In fact, the catalyst with the higher Lewis-to-Brønsted acidity ratio and a total acid strength comparable to that of the parent, unmodified niobium phosphate showed the best catalytic activity. Also in this case, the fine tuning of the surface acid properties was fundamental, and modifications with different acidic treatments is worth to be further explored to enhance the catalytic activity.