Development of Nanostructured Catalysts
for H₂ Production and Purification

(SETTORE SCIENTIFICO-DISCIPLINARE: CHIM/03)

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A.A. 2007-2009
There are only two possible conclusions:
if the result confirms the hypothesis,
you made a measurement;
if the result is contrary to the assumptions,
you made a discovery.

(Ci sono soltanto due possibili conclusioni:
se il risultato conferma le ipotesi,
hai fatto una misura;
se il risultato è contrario alle ipotesi,
hai fatto una scoperta.)

(E. Fermi)
## Contents

**Abstract** (Italian version) 11

**Abstract** (English version) 13

### Chapter I

**Introduction**

1.1 Energy and environmental problems 16

1.2 Hydrogen as energy vector 19

1.2.1 Hydrogen for fuel cell applications 20

1.3 Heterogeneous catalysis in the nanotechnology context 24

1.4 Industrial collaboration and aim of the thesis 26

References 27

### Chapter II

**Experimental section**

2.1 Catalysts synthesis 35

2.1.1 Bimetallic catalyst for alcohols steam reforming 35

- *Method A: oxalate co-precipitation* 35
- *Method B: Oxalate gel-coprecipitation* 35
- *Method C: Carbonate gel-coprecipitation* 36

2.1.2 Pt based catalysts for glycerol reforming 37

2.1.3 Ru embedded catalysts for ammonia decomposition 37
• DP (Deep Purple) Method

• NaBH₄ Method

2.1.4 Fe/Mo based catalysts for ammonia decomposition

2.2 Characterization techniques

2.2.1 Physisorption and Chemisorption measurements

2.2.2 X-Ray Diffraction (XRD) measurements

2.2.3 Temperature Programmed Reduction (TPR)

2.2.4 Thermo-Gravimetric Analysis (TGA)

2.2.5 Temperature Programmed Oxidation (TPO)

2.2.6 Temperature Programmed Surface Reaction (TPSR)

2.3 Catalytic activity measurements

2.3.1 Alcohols steam reforming

2.3.2 Glycerol reforming measurements

2.3.3 Ammonia decomposition measurements

References

Chapter III
Alcohols Reforming

3.1 Introduction

3.2 Characterization of fresh catalysts

• Physisorption- and Chemisorption

• Temperature Programmed Reduction (TPR)

• Powder X-Ray Diffraction (XRD)
3.3 Catalytic activity results

3.3.1 Methanol Steam Reforming Reaction (MSR) 63

3.3.2 Ethanol Steam Reforming Reaction (ESR) 66

3.4 Characterization of exhaust catalysts 69

- Powder X-Ray Diffraction (XRD) 69

- Thermo-Gravimetric Analysis (TGA) and Temperature Programmed Oxidation (TPO) 71

3.5 Conclusions 72

References 73

Chapter IV

Glycerol Reforming

4.1 Introduction 79

4.2 Catalytic activity results 81

4.2.1 Glycerol steam reforming reaction 81

4.2.2 Catalysts stability evaluation 86

4.3 Characterization of fresh catalysts 88

- Temperature Programmed Reduction (TPR) 88

- Physisorption- and Chemisorption 89

- Powder X-Ray Diffraction (XRD) 90

- Ammonia Temperature Programmed Desorption (NH₃-TPD) 94

4.4 Effect of CeO₂ and La₂O₃ doping on the catalysts stability and origin of catalyst deactivation effect 95

4.4.1 Characterization of exhaust catalysts 95
• Physisorption - and Chemisorption
• Powder X-Ray Diffraction (XRD)
• Thermo Gravimetric Analysis (TGA)
• High Resolution- Transmission Electron Microscopy (HR-TEM)

4.5 Conclusions

References

Chapter V
Ammonia decomposition

5.1 Ru based catalysts

5.1.1 Introduction
5.1.2 Catalytic activity results
5.1.3 Catalysts stability evaluation
5.1.4 Catalysts characterization

• Temperature Programmed Reduction (TPR)
• Powder X-Ray Diffraction (XRD)
• XRD characterization of exhaust catalysts
• Textural characterization: Physisorption measurements
• Static and dynamic H₂-Chemisorption
• Temperature Programmed Surface Reaction (TPSR)

5.1.5 Conclusions

5.2 Fe/Mo based catalysts: preliminary results

5.2.1 Introduction
5.2.2 Catalysts characterization

- **Textural characterization: Physisorption measurements**
- **Temperature Programmed Reduction (TPR)**
- **Powder X-Ray Diffraction (XRD)**

5.2.3 Catalytic activity: preliminary results

References

Chapter VI

Conclusions

Acknowledgements
Abstract

La richiesta mondiale di energia è in costante crescita a causa di diversi fattori tra cui incremento della qualità della vita, incremento della popolazione, l’industrializzazione, la crescita economica dei Paesi in via di sviluppo, etc. Saranno quindi essenziali importanti cambiamenti nelle tecnologie utilizzate per la produzione di energia per soddisfare la crescente domanda energetica nel rispetto delle severe limitazioni ambientali richieste per uno sviluppo sostenibile.

In questo contesto viene riconosciuto all’idrogeno l’importante ruolo di vettore energetico (in concomitanza con lo sviluppo della tecnologia delle celle a combustibile) oltre che di molecola essenziale per un vasto numero di processi industriali.

L’obiettivo di questo lavoro è stato lo sviluppo di catalizzatori nanostrutturati per la produzione di idrogeno a partire da risorse alternative, siano esse rinnovabili (etanolo e glicerolo) o facilmente trasportabili (metanolo ed ammoniaca).

Lo scopo di questa tesi è quello di migliorare le prestazioni dei catalizzatori impiegati nei processi di produzione dell’idrogeno attraverso la comprensione dei meccanismi di reazione e ottimizzate modulando la fase attiva a livello di nanoscala. In particolare sono stati sviluppati catalizzatori per la reazione di reforming in fase gas di metanolo e etanolo (Cu/Ni/Co supportati su ZnO/Al2O3), per la reazione reforming in fase gas di glicerolo (Pt supportato su MOx/Al2O3 con MOx = CeO2 o La2O3) e per la reazione di decomposizione dell’ammoniaca (nanoparticelle di Ru incapsulate in una matrice di ZrO2 drogata La e Fe/Mo supportati su variamente drogata ZrO2 o su Al2O3 modificata).

Abstract

Worldwide energy requirement is steadily increasing because of many reasons, such as enhancement of the quality of life, population increase, industrialization, rapid economic growth of developing countries, etc. Important changes in the energy production technologies will be essential to fit the increased energy demand with the stringent environmental limitations required by a sustainable development.

In this context, H₂ is recognized as an important energy vector (in combination with fuel cells) and as an essential molecule required by a large number of industrial processes.

The aim of this work was the development of nanostructured catalysts for hydrogen production starting from alternative sources, such as renewable materials (ethanol and glycerol) or easily transportable liquids (methanol and ammonia).

This thesis is aimed at improving the performances of catalysts involved in H₂ production processes by understanding the reaction mechanisms and by tuning the nature of the catalysts’ active phase at the nanoscale level. In particular, nanostructured catalysts were developed for methanol and ethanol steam reforming (Cu/Ni/Co supported on ZnO/Al₂O₃), glycerol steam reforming (Pt supported on MOₓ/Al₂O₃ with MOₓ = CeO₂ or La₂O₃) and NH₃ decomposition (Ru nanoparticles embedded into La-doped ZrO₂ and Fe/Mo supported on doped ZrO₂ or modified Al₂O₃).

This work was part of a fruitful collaboration with ACTA S.p.A.. Remarkably, part of the results obtained from this collaboration has been recently the subject of a recent world patent (WO/2009/016177).
# Chapter I

**Introduction**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Energy and environmental problems</td>
<td>16</td>
</tr>
<tr>
<td>1.2 Hydrogen as energy vector</td>
<td>19</td>
</tr>
<tr>
<td>1.2.1 Hydrogen for fuel cell applications</td>
<td>20</td>
</tr>
<tr>
<td>1.3 Heterogeneous catalysis in the nanotechnology context</td>
<td>24</td>
</tr>
<tr>
<td>1.4 Industrial collaboration and aim of the thesis</td>
<td>26</td>
</tr>
</tbody>
</table>

References 27
1.1 Energy and environmental problems

World energy consumption is steadily increasing for a variety of reasons, which include enhancements in quality of life, population increase, industrialization, rapid economic growth of developing countries, increased transportation of people and goods, etc. There are many types of fuel available worldwide, the demand for which strongly depends on application and use, location and regional resources, cost, “cleanness” and environmental impact factors, safety of generation and utilization, socioeconomic factors, global and regional politics, etc.\[1\]

According to the recently released 2008 BP Statistical Review of World Energy, the world’s total proven oil, natural gas and coal reserves are respectively 169 billion tons, 177 trillion cubic meters and 847 billion tons by the end of 2007. With current consumption trends, the reserves-to-production ratio of world proven reserves of oil lower than that of world proven reserves of natural gas and coal—42 years versus 60 and 133 years, \[2-4\] respectively.

Even if the rate of increase of per capita fossil energy consumption is slowed by conservation measures, rapid population growth is expected to speed fossil energy depletion and intensify global warming.\[5\] Therefore, the projected availability of all fossil energy reserves probably has been overstated. Substantially reducing use of fossil fuels through an efficient use of energy and the adoption of solar energy technologies will extend the life of fossil fuel resources and could provide the time needed to develop and improve renewable energy technologies.\[6\] Renewable resources are often located in remote areas, and it is expensive to build power lines to the cities where the electricity they produce is needed. The use of renewable sources is also limited by the fact that they are not always available (cloudy days reduce solar power; calm days reduce wind power; and droughts reduce the water available for hydropower.)

The production and use of renewable fuels has grown more quickly in recent years (Fig. 1.1) as a result of higher prices for oil and natural gas, and a number of State
and Federal Government incentives, including the Energy Policy Acts of 2002 and 2005.\[7\] The use of renewable fuels is expected to continue to grow over the next years, although we will still rely on non-renewable fuels to meet most of our energy needs.

All fossil fuels are nonrenewable, and as such they will eventually be depleted. Since they are based on finite resources localized in certain areas of the world, they will become expensive. Further, fossil fuel combustion, especially that based on oil and coal, is the major contributor to increasing carbon dioxide concentration in the atmosphere, thereby contributing to probable global warming.\[8,9\] The climate change is considered one of the most serious environmental threats throughout the world because of its potential impact on food production and processes vital to a productive environment.\[10\] Therefore, concerns about carbon dioxide emissions may discourage widespread dependence on coal use and encourage the development and use of renewable energy technologies.\[11\]

Certainly there is no easy and single solution to the enormous problems of energy demand and environmental protection. In this contest, the use of renewables, such as biomasses, is certainly one of the possible solutions which will allow future development of our society. The conversion of renewable resources into either clean
fuels or chemicals is attracting growing interests due to the continuous reduction of fossil hydrocarbons supplies.\textsuperscript{[12]}

Renewable energy technologies will however introduce new conflicts. For example, a basic parameter controlling renewable energy supplies is the availability of land. In fact, with approximately 75\% of the total land area exploited for agriculture and forestry, there is relatively little land available for other uses, such as biomass production and solar technologies. Population growth is expected to further exacerbate the demand for land. Therefore, future land conflicts could be intense.\textsuperscript{[13]}

In fact, depending on the starting biomass-based material, the fuel production can result sustainable or not. First generation bio-fuels are essentially composed by ethanol and bio-diesel, obtained from sugar fermentation and transesterification of animal fats or vegetable oils, respectively.\textsuperscript{[14,15]}

Unfortunately, the production of these bio-fuels is not sustainable on a long term period because it can seriously compromise both food supplies and biodiversity.\textsuperscript{[16]}

The use of biomasses consisting of residual non-food parts of current crops represents a challenging goal for the sustainable production of second generation bio-fuels whose production can start from the extraction of complex molecules, such as lignin or cellulose, from woods or fibrous biomasses.\textsuperscript{[17,18]}

To this purpose, several catalytic processes for the production of useful chemicals and feedstocks via hydrolysis of lignocellulose residues have been already investigated.\textsuperscript{[19,20]}

Finally, third generation bio-fuels can be finally produced from marine biomasses, such as algae, with higher energy balances than those obtained from land crops.\textsuperscript{[21,22]}

Nowadays, it is generally accepted that simultaneous employment of different energy resources could be a possible solution of the energy problem.\textsuperscript{[23,24]} The ‘‘hydrogen economy’’ is being promoted as one of the solutions of the world’s energy problems.\textsuperscript{[25]}
1.2 Hydrogen as Energy Vector

Hydrogen is not only a fundamental chemical for important industrial processes but it is also considered an attractive and clean energy vector in the timely fuel cells technology. Nowadays hydrogen is mostly used for fuel purification from sulfur and nitrogen (HDS and HDN steps), ammonia synthesis, cracking/refining processes, methanol production, hydrogenation reactions, fuel production via Fisher-Tropsh synthesis. In the energy field, hydrogen is more properly conceived as an energy vector rather than an energy source as its production requires energy from other sources. One of the principal attraction of hydrogen as energy carrier is the possibility to produce it from a variety of primary energy sources by many different technologies (Fig. 1.2). Conventionally produced hydrogen costs about twice than natural gas or oil and about 3 times more than coal. At present only the space industry seems to be willing to pay the high cost of hydrogen energy. These industrial methods mainly consume fossil fuels as energy source and are considered to be energy intensive and not always environmental friendly.

![Diagram of hydrogen production methods and applications](image)

Figure 1.2: Central role of hydrogen as an energy carrier linking multiple hydrogen production methods and various user applications
Currently, approximately 96% of the hydrogen is produced from fossil fuel-based processes (48% from natural gas, 30% from oil, and 18% from coal). The remaining 4% is produced through water electrolysis, photolytic splitting or high-temperature thermochemical cycles and from biomasses.[29]

Such a diversity of production sources contribute significantly to ensure energy supply.

The production of hydrogen from renewable biomass has several advantages and limitations compared to that of fossil fuels. The yield of hydrogen that can be produced from biomass is relatively low, 16–18% based on dry biomass weight.[31]

Two types of biomass feedstock are available to be converted into hydrogen[32]: (1) biomass dedicated from crops[33] and (2) less expensive residues, such as organic waste from regular agricultural farming and wood processing (biomass residues). Biomass, especially organic waste, offers an economical, environmental friendly way for renewable hydrogen production.[34]

1.2.1 Hydrogen for fuel cell applications

The importance of hydrogen as a potential energy carrier has increased significantly over the last decade, owing to the rapid advances in fuel cell technology. Fuel cells, operating using hydrogen or hydrogen rich fuels, have the potential to become major factors in catalyzing the transition to a future sustainable energy system with low carbon dioxide emissions.[35] Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side.[36] A representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is schematically reported in Fig. 1.3. In a typical fuel cell, gaseous fuels are fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment; the electrochemical reactions take place at the electrodes to produce electricity. A fuel cell, although having components and characteristics similar to
those of a typical battery, differs in several respects. The battery is an energy storage device. The maximum energy available is determined by the amount of chemical reactants stored within the battery itself. The battery will cease to produce electrical energy when the chemical reactants are consumed. In a secondary battery, the reactants are regenerated by recharging, which involves putting energy into the battery from an external source. The fuel cell, on the other hand, is an energy conversion device that theoretically has the capability of producing electrical energy for as long as the fuel and oxidant are supplied to the electrodes. Actually, degradation, primarily corrosion, or malfunction of components limit the practical operating life of fuel cells.

![Figure 1.3: Schematically representation of an individual fuel cell](image)

While the ultimate goal is to use renewable resources to generate hydrogen for use in a fuel cell stack to produce power, there are currently many barriers to the hydrogen economy because the issue of efficient storage and transport of hydrogen is not yet resolved. For this reason, there is considerable interest in utilizing fuel processing
technologies to generate hydrogen in situ on an “as needed” basis. Fuel processing technologies convert a hydrogen containing material into a hydrogen rich stream. Several types of fuel cell operating on a variety of fuels and suitable for different energy applications have been developed, but all share the basic design of two electrodes (anode and cathode) separated by a solid or liquid electrolyte or membrane. Hydrogen (or hydrogen-containing fuel) and oxygen are fed into the anode and cathode of the fuel cell and the electrochemical reactions assisted by catalysts take place at the electrodes. A variety of fuel cells are in different stages of development. They can be classified by use in diverse categories, depending on the combination of type of fuel and oxidant, whether the fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, the type of electrolyte, the temperature of operation, whether the reactants are fed to the cell by internal or external manifolds, etc. The most common classification of fuel cells is by the type of electrolyte used in the cells and includes 1) polymer electrolyte membrane fuel cell (PEM-FC), 2) alkaline fuel cell (AFC), 3) phosphoric acid fuel cell (PAFC), 4) molten carbonate fuel cell (MCFC), 5) intermediate temperature solid oxide fuel cell (ITSOFC), and 6) tubular solid oxide fuel cell (TSOFC). These fuel cells are listed in the order of approximate operating temperature, ranging from ~80°C for PEM-FC, ~100°C for AFC, ~200°C for PAFC, ~650°C for MCFC, ~800°C for ITSOFC, and 1000°C for TSOFC. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermomechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnections, current collectors, etc.). Aqueous electrolytes are limited to temperatures of about 200°C or lower because of their high water vapor pressure and/or rapid degradation at higher temperatures. The operating temperature also plays an important role in dictating the type of fuel that can be used in a fuel cell. The low-temperature fuel cells with aqueous electrolytes are, in most practical applications, restricted to hydrogen as a fuel. In high-temperature fuel cells, CO and even CH₄ can be used because of the inherently rapid electrode kinetics and at high temperature.
In particular, the development of power systems based on polymer electrolyte membrane fuel cells (PEM-FC) that utilize hydrogen to produce power can provide thermodynamic and environmental advantages.[46]

Fuel processing technologies convert a hydrogen containing material into a hydrogen rich stream.[38] One popular fuel processing technology involves steam reforming of hydrocarbons (see chapters III and IV) and there is a considerable amount of literature in this area which describes the fabrication of small reactors for mobile applications.

The use of hydrocarbons for producing hydrogen typically leads to the production of carbon monoxide, which poisons the PEM fuel cell catalyst. Furthermore, sulfur compounds in the hydrocarbons also present operational difficulties in the fuel cell. To alleviate these problems, it is necessary to add multiple processing steps such as water–gas shift reactions, methanation, oxidation and desulfurization.

A possible alternative is to use ammonia as a source of hydrogen (see chapter V). On-site or on-board H₂ production by NH₃ decomposition can produce hydrogen without concomitant COₓ release; unfortunately, the performances of Polymer Electrolyte Membrane Fuel Cells (PEM-FC) are strongly reduced by the presence of even very low amounts of NH₃ in the gas stream fed at the anode (also 1ppm of NH₃ has detrimental effects).[47] Since the NH₃ decomposition is an equilibrium reaction, it is practically impossible to avoid the presence of traces of NH₃ in the effluents and some purification steps are required (such as filters to trap NH₃ or separation of H₂ by membranes). Solid Oxide Fuel Cells (SOFC) can operate using directly ammonia as fuel,[48,49] although some problems must be solved. NH₃ is decomposed to N₂ and H⁺ releasing electrons at the anode, H⁺ migrate through the electrolyte to the cathode, where they react with gaseous O₂ and the electrons (from the electrical circuit) producing H₂O.[50]

The major applications for fuel cells are as stationary electric power plants, including cogeneration units; as motive power for vehicles; and as on-board electric power for space vehicles.[36]
In transportation, hydrogen fuel cell engines operate at an efficiency of up to 65%, compared to 25% for present-day petrol-driven car engines. When heat generated in fuel cells is also used in combined heat and power (CHP) systems, an overall efficiency in excess of 85% can be achieved.\textsuperscript{[51]} Unlike internal combustion engines or turbines, fuel cells demonstrate high efficiency across most of their output power range. This scalability makes fuel cells ideal for a variety of applications from mobile phone batteries through vehicle applications to large-scale centralized or decentralized stationary power generation.

1.3 Heterogeneous catalysis in the nanotechnology context

Heterogeneous catalysis is of vital importance to the world’s economy, allowing us to convert raw materials into valuable chemicals and fuels in an economical, efficient, and environmentally benign manner. Heterogeneous catalysis is also finding new applications in emerging areas such as fuel cells,\textsuperscript{[52-54]} green chemistry,\textsuperscript{[55-57]} nanotechnology\textsuperscript{[58]} and biorefining/biotechnology.\textsuperscript{[59-63]} Indeed, continued research into heterogeneous catalysis is required to allow us to address increasingly complex environmental and energy issues facing our industrialized society.

Generally it is possible summarize the key attributes of a good catalyst as following:\textsuperscript{[64]}

- The catalyst should exhibit good selectivity for production of the desired products.
- The catalyst should achieve adequate rates of reaction at the desired reaction conditions of the process (remembering that achieving good selectivity is often more important than achieving high catalytic activity).
- The catalyst should show stable performance at reaction conditions for long periods of time, or it should be possible to regenerate good catalyst performance by appropriate treatment.
- The catalyst should have good accessibility of reactants and products to the active sites such that high rates can be achieved per reactor volume.
Industrial catalysis generally takes place at the nanoscale (or sub-nanoscale): most of the catalysts are made of metal particles of a few nanometers in size and all the elementary reaction steps occur at the atomic (or molecular) scale. Thus, catalysis seems to be intrinsically a nanoscale phenomenon.[65]

Nanocatalysis is one of the most exciting subfields of nanoscience. Unlike the common practice in catalysis, where the catalytic performance scales with the surface to volume ratio of the dispersed catalytic agent, nanocatalysts are distinguished by their unique and non-scaleable properties that originate from the highly reduced dimensions of the active catalytic aggregates.[66] Consequently, the central aim of nanocatalysis is the promotion, enhancement, steering and control of chemical reactions by changing the size, dimensionality, chemical composition, morphology, or charge state of the catalyst or the reaction center, and/or by changing the kinetics through nanopatterning of the catalytic reaction centers.[67-69]

The goal, therefore, is not an ideal catalyst but the optimum, which may be defined by economic feasibility studies concerning not only the catalyst but also the rest of the process. And when the catalytic process is established and the catalyst in question must compete as a replacement, the replacement catalyst's cost and method of manufacture predominate in arriving at the optimum formula. Depending on the use and the economic competition, therefore, the optimization studies establish an hierarchy among the properties and characteristics of a catalyst; and knowledge of this hierarchy helps to better orient the efforts of the research team responsible for creating and developing the catalyst and its process. Even when the hierarchy is not fixed at the start, it can evolve in the course of developing the catalyst, sometimes even after industrialization.[64]

It is exactly the main topic in this work.
1.4 Industrial collaboration and aim of the thesis

The main objective of this thesis concerns the development of nanostructured catalysts for hydrogen production from renewable sources. This work was carried out in collaboration with ACTA s.p.a. [http://www.acta-nanotech.com], an Italian Firm, which focuses its attention on three important and fast-growing markets: i) renewable energy, ii) portable power and iii) waste to energy.

In the range of this collaboration catalysts were developed to be used to obtain hydrogen through two different reactions: alcohols reforming and ammonia decomposition.

In particular, the results obtained from the development of non-noble metal based catalysts for ethanol steam reforming reaction (see chapter III) lead to the publication of an International Patent (P. Bert, S. Catanorchi, P. Fornasiero, M. Graziani, B. Lorenzut, H. Miller, T. Montini, M. Ragnoli, A. Scaffidi, A. Tampucci, “Catalysts supported on ZnO for syngas production by alcohols reforming and their use.”, PCT/EP2008/059937); the high catalytic activity and the economic advantage, due to the employment of non-noble metal, made these catalysts interesting in the industrial applications.

In this work, we developed and characterized many different catalytic systems, which were tested on different reactions (ethanol steam reforming, methanol steam reforming, glycerol steam reforming and ammonia decomposition) with the intent to obtain hydrogen starting from renewable sources.

We demonstrated that applying a synthesis approach focused on the control of the particles dimensions it is possible to obtain more active and stable catalysts with respect to those prepared by conventional methods; in particular the embedded approach (see chapter V), which consists in the encapsulation of the metal nanoparticles into a metal oxide matrix, leads to the formation of very small nanoparticles, which demonstrated itself very active and very stable.
References


[64] “*Handbook of heterogeneous catalysis*”, Edited by G. Ertl, H. Knozinger, F. Schuth, J. Weitkamp, Weiley-VCH, **2007**.


Chapter II

Experimental section

2.1 Catalysts synthesis

2.1.1 Bimetallic catalyst for alcohols steam reforming

- Method A: oxalate co-precipitation
- Method B: Oxalate gel-coprecipitation
- Method C: Carbonate gel-coprecipitation

2.1.2 Pt based catalysts for glycerol reforming

2.1.3 Ru embedded catalysts for ammonia decomposition

- DP (Deep Purple) Method
- NaBH₄ Method

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2.2 Characterization techniques

2.2.1 Physisorption and Chemisorption measurements

2.2.2 X-Ray Diffraction (XRD) measurements

2.2.3 Temperature Programmed Reduction (TPR)

2.2.4 Thermo-Gravimetric Analysis (TGA)
2.2.5 Temperature Programmed Oxidation (TPO) 44

2.2.6 Temperature Programmed Surface Reaction (TPSR) 45

2.3 Catalytic activity measurements 45

2.3.1 Alcohols steam reforming 45

2.3.2 Glycerol reforming measurements 48

2.3.3 Ammonia decomposition measurements 50

References 52
2.1 Catalysts synthesis

2.1.1 Bimetallic catalysts for alcohols steam reforming

The catalyst preparation was designed in order to optimize the performances of the systems in the alcohols reforming, especially in the case of ethanol. All the catalysts have the molar composition of M/Zn/Al = 45/45/10 (M = Cu, CuNi, CuCo). A typical procedure used to prepare this type of catalysts consists in the oxalate coprecipitation method.

The three different methodologies adopted are summarized as follow:

Method A: Oxalate coprecipitation

A 1M aqueous solution of oxalic acid (excess 20%) is rapidly added to aqueous solution of Cu(NO$_3$)$_2$$\cdot$3H$_2$O, Zn(NO$_3$)$_2$$\cdot$6H$_2$O and Al(NO$_3$)$_3$$\cdot$9H$_2$O (total metal concentration: 0.1M) under vigorous stirring and left at room temperature for 1h. A precipitate is formed and the solid was collected by filtering and washed with bidistilled water. Then the precipitates was dried at 110°C overnight. The solid was finally calcined in a muffle at 150°C for 1h, 200°C for 1h, 250°C for 1h, 300°C for 1h and 360°C for 8.5h (heating rate 3°C min$^{-1}$).

Method B: Oxalate gel-coprecipitation

This procedure is similar to the previous one, but the solvent in this case is ethanol. A 1M ethanol solution of oxalic acid (excess 20%) is rapidly added to ethanol solution of Cu(NO$_3$)$_2$$\cdot$3H$_2$O, Zn(NO$_3$)$_2$$\cdot$6H$_2$O and Al(NO$_3$)$_3$$\cdot$9H$_2$O (total metal concentration: 0.1M) under vigorous stirring and left at room temperature for 1h. The precipitate was filtered and dried at 110°C overnight. The solid was finally calcined in a muffle at 150°C for 1h, 200°C for 1h, 250°C for 1h, 300°C for 1h and 360°C for 8.5h (heating rate 3°C min$^{-1}$).
**Method C: Carbonate gel-coprecipitation**

A 1M water/ethanol (1:1 v/v) solution of Na$_2$CO$_3$ (excess 20%) is rapidly added to a water/ethanol (1:1 v/v) solution of Cu(NO$_3$)$_2$$\cdot$3H$_2$O, Zn(NO$_3$)$_2$$\cdot$6H$_2$O and Al(NO$_3$)$_3$$\cdot$9H$_2$O (total metal concentration: 0.1M) under vigorous stirring. The precipitate was left for 1.5h at 40 °C and then recovered by filtration, followed by washing with bidistilled water. The solid product was dried at 90°C overnight and then calcined in a static oven at 400°C for 12h (heating rate 3°C min$^{-1}$).[1]

The effect of the preparation methodology was evaluated on Cu-based samples while the effect of the addition of a second metal (Ni or Co) was evaluated preparing the samples following the Method C.

The prepared samples and the abbreviations are summarized in Tab. 2.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>preparation method</th>
<th>abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$</td>
<td>oxalate co-precipitation – method A</td>
<td>Cu/ZnO/Al$_2$O$_3$-A</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$</td>
<td>oxalate gel co-precipitation – method B</td>
<td>Cu/ZnO/Al$_2$O$_3$-B</td>
</tr>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$</td>
<td>carbonate gel co-precipitation – method C</td>
<td>Cu/ZnO/Al$_2$O$_3$-C</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al$_2$O$_3$</td>
<td>carbonate gel co-precipitation– method C</td>
<td>Co/Cu/ZnO/Al$_2$O$_3$-C</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al$_2$O$_3$</td>
<td>carbonate gel co-precipitation– method C</td>
<td>Ni/Cu/ZnO/Al$_2$O$_3$-C</td>
</tr>
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</table>

The resulting powders were diluted in a commercial Al$_2$O$_3$ (Grace Davison MI 407 pre-calcined at 1100°C for 24h), pelletized, crushed and sieved to collect the fraction smaller than 250 µm.
2.1.2 Pt based catalysts for glycerol reforming

All studied catalysts have been supported on Al₂O₃ beads to reduce the overpressure inside the reactor during activity tests. Al₂O₃ (Puralox TH100) beads have been kindly provided by SASOL in the form of spheres (diameter ~ 1.0mm) and have been calcined at 900°C for 24h before their use in order to remove all organic binders and stabilize their texture.

The beads were modified by introducing either La₂O₃ or CeO₂ in order to reduce the acidity and to evaluate (in the case of CeO₂) the effects of the presence of a redox active component. La₂O₃ (5 wt%) was introduced by impregnation of the Al₂O₃ spheres using a solution of La(NO₃)₃•9H₂O in water. Afterwards, the solvent was removed by evaporation at reduced pressure and the resulting material was dried at 120°C overnight and calcined in static air at 700°C for 5h, respectively. CeO₂ (20 wt%) was introduced by impregnation of the Al₂O₃ spheres (previously degassed at 225°C overnight) using an isooctane solution of Ce(OC₈H₁₇)₄. The latter was prepared according to literature procedures [5] After soaking of the Al₂O₃ spheres, the solvent was removed by evaporation at reduced pressure and the resulting material was dried at 120°C overnight and calcined in static air at 700°C for 5h, respectively. Pt (in the amount of 3 wt%) was loaded on the bare or modified Al₂O₃ spheres by impregnation using a water solution of Pt(NO₃)₂. After drying at 120°C overnight, the products were calcined at 500°C for 5h.

2.1.3 Ru embedded catalysts for ammonia decomposition

The catalyst preparation was designed in order to optimize the performances of the systems in the ammonia decomposition reaction. A nominal metal loading of 3 wt% is used for all the samples. The preparation of Ru embedded samples, schematically illustrated in Fig 2.1, begins with the preparation of colloidal Ru nanoparticles. Lanthana-Stabilized Zirconia (LSZ) is deposited around them by a precipitation technique. Two preparation methods were used to synthesize colloidal Ru nanoparticles.
Preparation of colloidal Ru suspension

Preparation of LSZ hydroxide matrix by co-precipitation method

Calcination

Ru@LSZ

Figure 2.1: Schematic representation of Ru@LSZ synthesis

Preparation of Ru@LSZ-DP: DP (Deep Purple) Method

Colloidal Ru nanoparticles were prepared by a refluxing method using Poly (N-Vynil-2-Pyrrolidone) (PVP) as protecting agent. The chosen methodology allows to modulate the mean dimension of Ru nanoparticles changing the experimental conditions, such as Ru concentration, the PVP/Ru molar ratio and (most important) the molecular weight of the alcohol used as solvent. In fact, the increase of the molecular weight and of the boiling point of the solvent alcohol results in a decrease of the mean dimension of the Ru nanoparticles obtained with this method. On the other hand, high boiling alcohols are hardly removable by evaporation and the solubility of metal oxide precursors is low. For the preparation of this samples, ethanol was selected as solvent, even obtaining very small colloidal Ru nanoparticles as a deep purple (DP) suspension.

In a 250 mL bottom flask, PVP K30 (0.989 g, 8.9 x 10⁻³ mol as monomeric unit) and RuCl₃•xH₂O (0.233 g, 8.9 x 10⁻⁴ mol Ru) were dissolved in ethanol (120 mL) under stirring to form a dark red solution. After refluxing for 24h, a deep purple colloidal suspension is obtained, according to the procedure reported by Zhang et al. Under the experimental conditions adopted (VP/Ru = 10, PVP molecular weight ~ 40000 g/mol, ethanol as solvent and reducing agent, refluxing time 24h), Ru nanoparticles with a mean diameter of 2.5 nm can be obtained. Before the deposition of LSZ
around the nanoparticles, ethanol was evaporated at reduced pressure and the PVP-protected nanoparticles were re-suspended in 50 mL of water.

The \( \text{La}_2\text{O}_3 \) – stabilized \( \text{ZrO}_2 \) (LSZ) was deposited by a co-precipitation method. The aqueous Ru nanoparticles suspension was added under vigorous stirring to an aqueous solution of 5.77 g of \( \text{ZrO(NO}_3\text{)}_2\times\text{H}_2\text{O} \) (99%, Aldrich) and 1.01 g \( \text{La(NO}_3\text{)}_3\times6\text{H}_2\text{O} \) (99.9%, Aldrich) in 250 mL of water. The metal solution comprising the protected Ru nanoparticles was added dropwise to 220 mL of an aqueous solution of NaOH (2.5 M). The obtained precipitate was stirred for 2h and then filtered and washed with water. The solid obtained was suspended in 300 mL of 2-propanol and refluxed for 4h in order to stabilize the texture of the oxide matrix. After filtration, the solid was dried at 120°C overnight and calcined in a static oven at 500°C for 5h with heating and cooling rates of 1°C min\(^{-1}\).

**Preparation of Ru@LSZ-NaBH\(_4\), NaBH\(_4\) Method**

Metal nanoparticles can be easily synthesized by reduction with NaBH\(_4\) in an aqueous solution of RuCl\(_3\)\(\times\text{H}_2\text{O}\) containing cationic surfactants. The Ru nanoparticles are protected to their aggregation being entrapped inside the hydrophobic environment of the micelles form by the surfactants (Fig. 2.1). In this method, N-hexadecyl-N-(2-hydroxyethyl)-N,N-dimethyl ammonium bromide (HEAC16Br) as protecting agent was used. The use of HEAC16X (\(X = \text{Cl}^-\text{ or Br}^-\)) as protecting agent for metal nanoparticles preparation was extensively reported for different noble metals, such as Rh,\(^{[9,10]}\) Ir,\(^{[11]}\) Pt,\(^{[12]}\) Pd,\(^{[13]}\) and Ru.\(^{[14]}\) Moreover, Rh nanoparticles protected by HEAC16Br have already been used as building blocks for the preparation of embedded catalysts.\(^{[15-17]}\)

The cationic surfactant HEAC16Br was prepared by reaction of 1 – bromohexadecane (99%, Fluka) with a 30% excess of N,N – dimethylethanolamine (99%, Fluka) in absolute ethanol (Aldrich) under reflux for 1h,\(^{[18]}\) and purified by crystallization in absolute ethanol \(^{[19]}\) (Yield 70 – 80%, m.p. 200 – 210°C, \(\text{H}-\text{NMR}\) and \(\text{C}-\text{NMR}\) spectra in agreement with that reported in Ref. [10]).
The preparation of HEAC16Br-protected Ru nanoparticles was as follow. A solution of HEAC16Br (3.262 g, 8.3 x 10^{-3} mol) and NaBH₄ (84 mg, 2.2 x 10^{-3} mol) in 210 mL of water and a solution of RuCl₃•xH₂O (0.233 g, 8.9 x 10^{-4} mol Ru) in 52 mL of water were thermostated at 20°C. Then, the solution containing HEAC16Br and NaBH₄ was quickly added under vigorous stirring to the RuCl₃•xH₂O solution to obtain an aqueous Ru colloidal suspension. The reduction occurs instantaneously, revealed by the immediate color change from yellow-brown to black. The suspension is then stirred for 2h to decompose the excess of the reducing agent. Ru nanoparticles with a mean dimension of 3.0 nm are reported following this preparation.\(^{[14]}\)

The La₂O₃ – stabilized ZrO₂ (LSZ) has been deposited around the metal nanoparticles by a co-precipitation method, in a similar manner than previously reported. The aqueous Ru nanoparticles suspension was added under vigorous stirring to a solution of 5.77 g of ZrO(NO₃)₂•xH₂O (99%, Aldrich) and 1.01 g La(NO₃)₃•6H₂O (99.9%, Aldrich) in 250 mL of water. The metal solution comprising the protected Ru nanoparticles was added dropwise to 220 mL of an aqueous solution of NaOH (2.5 M). The precipitate was stirred for 2h and then filtered. In this case, the precipitate was washed suspending the solid into 200 mL of a NH₄NO₃/NH₄OH buffer solution (pH = 10), in order to remove bromide ions. Finally, the solid obtained was suspended in 300 mL of 2-propanol and refluxed for 4h in order to stabilize the texture of the oxide matrix.\(^{[7,8]}\) After filtration, the solid was dried at 120°C overnight and calcined in a static oven at 500°C for 5h with heating and cooling rates of 1°C min⁻¹.

For comparison, conventional impregnated samples Ru/LSZ were prepared as reference catalysts. The bare LSZ supports were synthesized using the above described procedures, however without the presence of Ru nanoparticles. After calcination at 500°C for 5h, Ru was deposited by conventional impregnation. The support was dispersed in an ethanolic solution containing the appropriate amount of RuCl₃•xH₂O. After stirring for 1h and evaporation of the solvent at reduced pressure,
the samples were dried at 120°C overnight and finally calcined at 400°C for 5h (heating rate 3°C min⁻¹).

The prepared samples and their abbreviation are summarized in Tab. 2.2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation method</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(3%)@LSZ</td>
<td>Deep Purple</td>
<td>Ru@LSZ-DP</td>
</tr>
<tr>
<td>Ru(3%)@LSZ</td>
<td>NaBH₄</td>
<td>Ru@LSZ-NaBH₄</td>
</tr>
<tr>
<td>Ru(3%)@LSZ</td>
<td>impregnation on LSZ-DP</td>
<td>Ru/LSZ-DP</td>
</tr>
<tr>
<td>Ru(3%)@LSZ</td>
<td>impregnation on LSZ-NaBH₄</td>
<td>Ru/LSZ-NaBH₄</td>
</tr>
</tbody>
</table>

2.1.4 **Fe/Mo based catalysts for ammonia decomposition**

The catalyst preparation was designed in order to optimize the performances of the systems in the ammonia decomposition reaction. Fe and Mo precursors were impregnated on different supports, previously calcined at 900°C for 5h. Commercial stabilized ZrO₂ (provided by MEL Chemicals, UK) and modified Al₂O₃ (prepared by impregnation of commercial Al₂O₃, provided by SASOL, Germany) were used as supports. ZrO₂ doped with Y, La or Ce (denoted as YSZ, LSZ and CSZ, respectively) were chosen as supports since the doping stabilize the texture of the materials and decrease its acidity. Commercial Al₂O₃ were modified with 10wt% of La₂O₃ by impregnation with La(NO₃)₃•9H₂O dissolved in ethanol (La-Al₂O₃) or with a 10wt% of Ce₀.₆Zr₀.₄O₂ by impregnation with an aqueous citrate-gel comprising Ce and Zr (CZ-Al₂O₃) to decrease the acidity of the bare support. In fact, it is well known that the NH₃ decomposition reaction is favoured when supports with basic characteristics are used to disperse the active phase.

The samples were prepared by co-impregnation using bis (acetylacetonato) dioxomolybdenum(VI) ([CH₃COCH=C(O-)CH₃]2MoO₂, >99.9% Aldrich) and
Iron(III) acetylacetonate (Fe(C₅H₇O₂)₃, >99.9% Aldrich) as metal precursors. Briefly, an appropriate amount of precursors was dissolved in acetone under vigorous stirring for 1h; at the same time, a suspension of the support (doped ZrO₂ or Al₂O₃) in acetone was prepared. Subsequently, the metals solution was added to the suspension containing the support under vigorous stirring. The final suspension was stirred for 1h and then the solvent was evaporated under vacuum. The solid residue was dried overnight at 120°C in air. The material was further calcined in static oven at 400°C in air for 5h (heating rate 1°C min⁻¹, cooling rate 4.5°C min⁻¹).

The obtained materials (Tab. 2.3) are designated as FeₓMoᵧ/Support, where x and y represent the iron and molybdenum loading (wt%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (wt%)</th>
<th>Mo (wt%)</th>
<th>Support composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₁₀Mo₁₀/YSZ</td>
<td>10%</td>
<td>10%</td>
<td>Y₂O₃(7-9%)-ZrO₂</td>
</tr>
<tr>
<td>Fe₅Mo₅/YSZ</td>
<td>5%</td>
<td>5%</td>
<td>Y₂O₃(7-9%)-ZrO₂</td>
</tr>
<tr>
<td>Fe₅Mo₅/LSZ</td>
<td>5%</td>
<td>5%</td>
<td>La₂O₃(8-12%)-ZrO₂</td>
</tr>
<tr>
<td>Fe₅Mo₅/La-Al₂O₃</td>
<td>5%</td>
<td>5%</td>
<td>La₂O₃(10%)-Al₂O₃</td>
</tr>
<tr>
<td>Fe₅Mo₅/CZ-Al₂O₃</td>
<td>5%</td>
<td>5%</td>
<td>Ce₀.₆Zr₀.₄O₂(13%)-Al₂O₃</td>
</tr>
</tbody>
</table>

### 2.2 Characterization techniques

#### 2.2.1 Physisorption and Chemisorption measurements

H₂ chemisorption and physisorption measurements were conducted using a Micromeritics ASAP 2020 analyzer. N₂ physisorption isotherms were collected at -196°C on 0.1 g of sample, after evacuation at 350°C overnight. Surface area and pore distribution were obtained applying the BET and BJH methods, respectively.[²⁰] H₂ chemisorption experiments are conducted at -94°C (solid/liquid acetone bath) on 0.2 g of catalyst.[²¹] The calcined samples were subjected to a standard cleaning
procedure (flow of O₂ (5%) / Ar (35 mL min⁻¹) at a heating rate of 10°C min⁻¹ up to 500°C) to remove adsorbed species (water and carbonates). Subsequently, the samples were pre-reduced in a flow of H₂ (5%) / Ar (35 mL min⁻¹) at a heating rate of 10°C min⁻¹ up to the desired temperature (500°C for Pt based samples and 800°C for Ru based samples). After 5 h at those temperature, the samples were evacuated at 400°C for 4h, and cooled under vacuum to the adsorption temperature (-94°C). Typically, an equilibration time of 10 min was employed. Adsorbed volumes were determined by extrapolation to zero pressure of the linear part of the adsorption isotherm (100 - 400 torr) after elimination of the reversible adsorbed hydrogen. A chemisorption steechiometry H : Metal = 1:1 was assumed. The aged samples (recovered after catalytic activity experiments) were not subjected to standard pretreatments to avoid metal re-dispersion and/or removal of carbonaceous species. These samples were only pre-reduced for 1 h in a flow of H₂ (5%) / Ar (35 mL min⁻¹) at a heating rate of 10°C min⁻¹ up to 100°C, evacuated at 400°C for 4h and subjected to chemisorption measurement at -94°C.

2.2.2 X-Ray Diffraction (XRD) measurements

A Philips X’Pert vertical goniometer with Bragg-Brentano geometry, connected to a highly stabilized generator, was used for the XRD measurements. A focusing graphite monochromator and a proportional counter with a pulse-height discriminator were used. Nickel-filtered Cu Kα radiation and a step-by-step technique are employed (steps of 2θ = 0.05°), with collection times of 10 s step⁻¹. Line broadening analysis (LBA) was carried out using a previously published method. The quantitative phase analysis by X-ray diffraction was performed using the Rietveld method (DBWS9600 computer program written by Sakthivel & Young and modified by Riello et al.)

2.2.3 Temperature Programmed Reduction (TPR)
Temperature Programmed Reductions (TPR) were performed on the calcined materials. The samples were pre-treated at 500°C for 1h by pulsing 100 µL of O₂ in an Ar flow every 75 s, then purged with Ar at 150°C for 15 min and cooled to room temperature. H₂ (5%) / Ar was admitted into the reactor and the flow allowed to stabilize for 30 min before increasing the temperature to 1000°C at 10°C min⁻¹. After TPR, the samples were outgassed under an Ar flow at 1000°C for 15 min and cooled to 427°C, at which temperature oxidation was carried out with pulses of O₂ in an Ar flow for 1h. H₂ consumption was monitored using a Thermo Conductivity Detector (TCD).

### 2.2.4 Thermo-Gravimetric Analysis (TGA)

The carbon deposits on the aged catalysts were characterized using Thermo-Gravimetric Analysis (TGA). TGA analysis were performed using a EXSTAR Thermo Gravimetric Analyzer (TG/DTA) Seiko 6200 coupled with a mass spectrometer ThermoStar™ GSD 301 T for the analysis of the exhaust gases. Typically, 20 mg of the aged samples were loaded in the instrument and the TGA was performed in flowing air (flow rate 100 mL min⁻¹) with a heating rate of 10°C min⁻¹.

### 2.2.5 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) experiments were performed using a Hiden HPR 20 quadrupole mass spectrometer. Typically, 10mg of the aged samples after ESR experiments were treated in O₂ (15%) / Ar (60 mL min⁻¹) and heated to 900°C at 10 °C min⁻¹.
2.2.6 Temperature Programmed Surface Reaction (TPSR)
Temperature Programmed Surface Reaction (TPSR) of ammonia was conducted in a home-made flow apparatus using a mass spectrometer Hiden HPR20 as analyzer. In a typical NH₃-TPSR experiment, about 0.25 g of the sample was loaded in U-shaped quartz microreactor. The samples were reduced flowing H₂ (35 mL min⁻¹) at 800°C for 3h. After the treatment, the adsorbed H₂ was removed by flowing the system with Ar at 800°C for 30min. Afterwards, the samples were cooled at 110°C under the inert gas flow. For NH₃ adsorption, the reduced samples were saturated flowing NH₃ (10%) / Ar (50 mL min⁻¹) at 110°C for 30min. After NH₃ adsorption, the sample was flushed in Ar flow at 110°C for 1h to remove physically adsorbed NH₃. The NH₃-TPSR profile for each sample was recorded by increasing the temperature from 110 to 800°C with a heating rate of 20°C min⁻¹ under flow of Ar (50 mL min⁻¹). The desorbed products were analyzed by means of a mass spectrometer operating in the electron impact mode with a ionization energy of 35 eV. The desorbed species were identified on the basis of the intensity of various mass fragments: m/z = 2 for H₂, m/z = 28 for N₂ and m/z = 16 for NH₃ (the parent peak – m/z = 17 – is influenced by the desorbed water).

2.3 Catalytic activity measurements

2.3.1 Alcohols steam reforming
All catalytic tests were conducted at atmospheric pressure in a conventional fixed bed reactor (U shape quartz microreactor with internal diameter of 4 mm). The temperature of the catalyst was measured with a K-type thermocouple. Before the catalytic test the samples were pre-activated by reduction in H₂(5%)/Ar at 360°C for 1h (40 mL min⁻¹, 10°C min⁻¹). In alcohols steam reforming experiments ~45 mg of catalyst were typically used. EtOH/H₂O 1:5 and MeOH/H₂O 1:1 mixtures were injected into an Ar flow with a Hamilton Gastight syringe using a INSTECH Model 2000 syringe pump. All the transfer lines between the syringe, reactor and GC were
kept at 120°C. Gas flow rates were ~29 ml min\(^{-1}\) to ensure GHSV values of 120000 ml·g\(^{-1}\)·h\(^{-1}\). On line GC analysis were performed using a Hewlett-Packard 5890 Series II gas chromatograph. A Molsieve 5A column with Ar carrier was connected to a thermal conductivity detector (TCD) to analyze H\(_2\), O\(_2\), N\(_2\), CH\(_4\) and CO. A Select Permanent Gases/CO\(_2\) PLOT column (parallel PoraPLOT 50 m x 0.53 mm ID and Molsieve 5A 10 m x 0.53 mm ID column) with He carrier and connected in series to a methanator and to a flame ionization detector (FID) was used to analyze the carbon containing compounds. C balance was always within ± 2%. (Fig. 2.2)

The gaseous mixture was first introduced in the reactor at 150°C, before ramping the furnace a temperature to 700°C at 0.7°C·min\(^{-1}\).
H₂ yields were calculated according to the methanol steam reforming (MeOH-SR) and ethanol steam reforming (EtOH-SR) reactions which include the water gas shift reaction:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2
\]

\[
\text{H}_2 \text{ yield} = \frac{1}{3} \cdot \frac{\text{mol(H}_2\text{) produced}}{\text{mol(MeOH) in the feed}}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} + 3 \text{H}_2\text{O} \rightarrow 3 \text{CO}_2 + 6 \text{H}_2
\]

\[
\text{H}_2 \text{ yield} = \frac{1}{6} \cdot \frac{\text{mol(H}_2\text{) produced}}{\text{mol(EtOH) in the feed}}
\]

However, many side reactions, in particular during EtOH-SR reaction, leading to the production of hydrogen rich compounds like \(\text{CH}_4\), \(\text{CH}_3\text{CHO}\), \(\text{CH}_2\text{CH}_2\) reduced the expected hydrogen yield (Fig. 2.3).[24]

Some of these compounds act as coke precursors leading to the formation of carbonaceous deposits.

\[\text{Figure 2.3 : Schematic representation of reaction network involved in the ethanol steam reforming}\]
2.3.2 Glycerol steam reforming measurements

In a typical procedure 1 g of the fresh catalyst was loaded over fused SiO₂ granules (-4+16 mesh; Sigma-Aldrich), in the middle of a ¼-inch outer diameter stainless-steel reactor placed in an electrical furnace. Fused SiO₂ granules were then used to cover the catalytic bed to favor the vaporization of the liquid reagents injected from the top of the reactor. Type-K thermocouple was finally attached to the outside of the reactor to measure the reactor temperature. Fresh catalysts were reduced before each catalytic test by treatment with pure H₂ (25 mL min⁻¹) at 500°C for 5h. After purging the reactor with Ar and cooling to the desired temperature, a mixture water/glycerol (30 wt%) was introduced at its top by means of a KNF pump (Model STEPDOS 03 RC) which allows for a constant flow rate of 0.32 mL/min throughout the catalytic process. The outlet effluents were cooled through a water-condenser to remove all liquid fractions. Volatiles were analyzed on-line by GC using a Hewlett Packard 6890 gas chromatograph and then vented. A Molsieve 5A column, using Ar as carrier, connected to a thermal conductivity detector (TCD) was used to follow the H₂, O₂, N₂, CH₄ and CO production. A PoraPLOT Q column, using He as carrier, connected to both a methanator and a flame ionization detector (FID) was used to analyze all carbon-containing compounds.(Fig. 2.4)

After reduction at 500°C, the catalytic systems are cooled to 250°C and the liquid injection starts. The catalyst temperature is maintained at 250°C for 1h before starting the GC analysis. Afterwards, the catalyst temperature is increased step-by-step up to 600°C (step 50°C), and volatiles produced at the reactor outlet are systematically analyzed throughout the whole temperature range. For stability tests, after the reduction step, the systems are cooled to the final temperature (350°C), at which stage the injection of the glycerol solution and the GC analysis of volatiles produced at the reactor outlet, start.
Glycerol can be converted into hydrogen by steam reforming (SR) according to the following reaction:

\[ \text{C}_3\text{H}_8\text{O}_3 + 3 \text{ H}_2\text{O} \rightarrow 3 \text{ CO}_2 + 7 \text{ H}_2 \]

Typically, the glycerol SR is a catalytic process that occurs in vapor phase at atmospheric pressure and temperatures up to 900 °C. Due to its endothermicity, high temperatures, low pressures and a high steam glycerol ratio are generally required to get high substrate conversions.\[^{25}\]
2.3.3 Ammonia decomposition measurements

Catalytic experiments were conducted in a U-shaped 8 mm ID quartz reactor under atmospheric pressure. Pure ammonia (transistor grade purity) was used as reactant. Mass of catalysts and gas flow rates were adjusted in order to test the samples under different conditions: GHSV = 4000 mL g⁻¹ h⁻¹ (100 mg of catalysts and 51.0 mL min⁻¹ of NH₃) and GHSV = 30000 mL g⁻¹ h⁻¹ (250 mg of catalyst and 16.1 mL min⁻¹ of NH₃).

Before testing, the calcined materials were activated by reduction in H₂ flow (35 mL min⁻¹) at 800°C for 3h. After reduction, H₂ was removed by Ar flow (35 mL min⁻¹) for 30 min and the temperature was decreased to 250°C. Then NH₃ was introduced in the reactor, stabilizing the system for 30 min before starting catalytic activity measurements. Catalytic activity were evaluated at every 50°C from 250°C to 800°C.

Three analysis of the gaseous mixture were performed at each temperature. The catalyst was subjected to two activity cycles, to verify the stability after reaction at high temperature. For the stability test, after activation by H₂ reduction at 800 °C, the samples were cooled at 500°C under Ar flow (35 mL min⁻¹). After stabilization of the temperature NH₃ was introduced in the reactor and the gaseous mixture exiting from the reactor was analyzed every hour.

On-line GC analysis was performed using a Shimadzu 2010 gas-chromatograph equipped with a TCD (AGC Instruments) mounting Au filaments in order to avoid corrosion by NH₃. Two packed columns with Ar as carrier were used. A Molsieve 5A column was used for the separation of H₂ and N₂ while a Porapak Q column was used for the separation of NH₃ from permanent gases (H₂ and N₂). The analysis of the gases was performed by the alternative injection of the mixture into the columns by the use of a 10 way valve equipped with 2 loops.(Fig. 2.5)
NH$_3$ conversion was calculated on the bases of the following reaction:

$$2 \text{NH}_3 = \text{N}_2 + 3 \text{H}_2$$

H$_2$ yields was calculated according to the ammonia decomposition reaction

$$2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$$

$$H_2 \text{ yield} = \frac{\text{mol(H}_2\text{) produced}}{3 \cdot \text{mol(NH}_3\text{) in the feed}}$$

Although the assessment of relevant elementary steps and structure sensitivity in NH$_3$ decomposition have been widely reported, the kinetics of NH$_3$ decomposition over Ru is not well established and many contradictory findings still remain unresolved.$^{[26]}$
References


Chapter III

Alcohols Reforming

3.1 Introduction 56

3.2 Characterization of fresh catalysts 57
  • Physisorption- and Chemisorption 57
  • Temperature Programmed Reduction (TPR) 59
  • Powder X-Ray Diffraction (XRD) 60

3.3 Catalytic activity results 63
  3.3.1 Methanol Steam Reforming Reaction (MSR) 63
  3.3.2 Ethanol Steam Reforming Reaction (ESR) 66

3.4 Characterization of exhaust catalysts 69
  • Powder X-Ray Diffraction (XRD) 69
  • Thermo-Gravimetric Analysis (TGA) and Temperature Programmed Oxidation (TPO) 71

3.5 Conclusions 72

References 73
3.1 Introduction

In the energy area, the interest in the alternative fuels has increased rapidly in recent years due to the drivers for cleaner air and less dependence upon foreign oil. Due to the ever-growing world energy demand, diversification of energy sources is foreseen.\cite{1,2}

Among the various efforts being made to meet global energy needs, the energy carried by hydrogen has become an attractive option in terms of sustainability and low environmental impact. Hydrogen can store energy and delivery it to where it is needed.\cite{3,4}

Different raw materials and reactions can be proposed for hydrogen production.\cite{3,5-7} The selection of hydrogen source for a particular application depends on technical, economic and political factors. Commercially, methane steam reforming is the primary method to produce hydrogen. However, for mobile applications, it is preferable to have a hydrogen source in liquid form that can supply H$_2$ when needed, because it does not require gaseous hydrogen storage and distribution. Therefore, alcohols like methanol and ethanol are promising candidates. The advantages for both methanol and ethanol include their easiness to handled and to transport with respect to gaseous fuels and their low cost. Furthermore, these compounds can be synthesized not only from fossil fuels but, more importantly, from syn-gas obtained from biomass and they can be used in steam reforming reactions under mild operative conditions.

Catalysts based on copper-zinc composite oxides are the most frequently studied systems in the methanol steam reforming due to their high selectivity and activity \cite{3,8-11} and as an outgrowth of their extensive use in methanol synthesis. It is generally accepted that copper dispersion plays a key role in the catalytic performance of these materials while the role of ZnO is to obtain and maintain the catalytically active copper in optimal dispersion and to improve reducibility of CuO.\cite{12-14} The addition of small amount of Al$_2$O$_3$ further inhibits thermal sintering of copper particles and, therefore, imparts chemical and thermal stability to the catalyst.\cite{15,16}
On the contrary, few works are presented in literature about the application of Cu/ZnO-based catalysts in ethanol steam reforming process.\cite{17-20} With respect to methanol, ethanol requires higher reforming temperatures due to the presence of the C-C bond. However, at high temperature Cu-based catalysts undergo a relatively fast deactivation mainly due to thermal sintering of metallic Cu particles.

We examined hydrogen production by steam reforming of methanol and ethanol over Cu/ZnO/Al₂O₃ catalysts. The influence of the synthesis method on the chemical and physical properties and the catalytic activity were investigated. Moreover, the effect of the introduction of a second metal (Co or Ni) in the catalyst formulation was also examined, with the aim to improve activity and stability. Temperature Programmed Reduction (TPR) and BET surface area measurements were used to characterize the catalyst surfaces. X-ray diffraction (XRD) was used to study the bulk structure of the catalysts and thermal analysis was adopted to study the carbon deposits.

3.2 Characterization of fresh catalysts

*Physisorption and Chemisorption*

Cu/ZnO/Al₂O₃ catalysts, with a molar ratio of copper, zinc and aluminum 45:45:10, were prepared by different methods (see chapter II) referred as: i) oxalate coprecipitation (method A),\cite{21} ii) oxalate gel-coprecipitation (method B)\cite{21} and iii) carbonate coprecipitation (method C – adapted from Ref.\cite{21}). Briefly, methods A and B comprise the coprecipitation of the cations as oxalates. The two methods differ for the used solvent: water for method A and ethanol for method B. Finally, method C comprises the coprecipitation of the cations using sodium carbonate. With respect to the procedure reported in the literature,\cite{21} in our case a water/ethanol 1:1 by volume was used as solvent. Cu/ZnO/Al₂O₃ materials with a molar ratio Cu/Zn/Al = 45/45/10 were prepared using the three methodologies. Using the latter approach, two bimetallic samples were also synthesized: Co/Cu/ZnO/Al₂O₃ and Ni/Cu/ZnO/Al₂O₃ with a molar ratio M/Cu/Zn/Al = 22.5/22.5/45/10 (with M = Co or Ni).
The results of the textural characterization of the calcined samples are summarized in Table 3.1. All the samples present type IV isotherms with hysteresis loop typical of mesoporous materials. The t-plot analysis reveals that the microporous volume is always negligible, while the BJH analysis confirms the presence of an wide mesoporous network of pores with ink-bottle shape.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA[^a] (m² g⁻¹)</th>
<th>dM[^b] (nm)</th>
<th>CPV[^c] (mL g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al₂O₃-A</td>
<td>30</td>
<td>29</td>
<td>0.22</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-B</td>
<td>89</td>
<td>14</td>
<td>0.32</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-C</td>
<td>106</td>
<td>56</td>
<td>0.84</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al₂O₃-C</td>
<td>122</td>
<td>22</td>
<td>0.46</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al₂O₃-C</td>
<td>123</td>
<td>14</td>
<td>0.36</td>
</tr>
</tbody>
</table>

[^a]: Specific Surface Area from the BET analysis;  
[^b]: Maximum of the BJH pore distribution calculated on the desorption branch;  
[^c]: Cumulative Pore Volume;

Comparing the samples with the same composition (Cu/ZnO/Al₂O₃), the use of ethanol as precipitation solvent (method B) results in a higher surface area with respect the similar sample prepared using water (method A), in agreement with the original preparation method.[21] Moreover, the materials prepared using oxalic acid present a highest surface area within the Cu/ZnO/Al₂O₃ samples, contrary to the result reported.[21] This result could be related with the use of an ethanol/water mixture in our case. Since the preparation method C leads to material with higher surface area, this synthesis was adopted to investigate the effect of catalyst doping with Co and Ni. The replacement of Cu with a second metal results in a slightly increase of surface area, while the mean pore diameter and the pore volume are significantly reduced.
Temperature Programmed Reduction (TPR)

The reduction properties of the different samples were examined by TPR using H₂. Figure 3.1 presents the TPR profiles for the samples investigated in this study. As a general feature, both monometallic and bimetallic samples reveal a main reduction peak at low temperature, in the 200 – 300°C temperature range. Moreover, some features attributable to Bouyancy’s effect can be recognized at temperatures higher than the calcination treatment. Regarding the Cu/ZnO/Al₂O₃ samples, the reduction of CuO-species takes place at lower temperature than bulk CuO (maximum at 250°C with a shoulder at 320°C - data not reported). The maximum of the reduction peak for the Cu/ZnO/Al₂O₃-A sample is around 240°C and shifts to 225 and 210°C in the Cu/ZnO/Al₂O₃-B and Cu/ZnO/Al₂O₃-C samples, respectively. The reducibility of CuO strongly depend from its dispersion onto a support: the higher the dispersion, the lower the reduction temperature.²²-²⁶ In agreement with this interpretation, the TPR results suggest differences in the dispersion of CuO-species on the monometallic samples.

Figure 3.1: Temperature Programmed Reduction (TPR) profiles for Cu/ZnO/Al₂O₃-A (a), Cu/ZnO/Al₂O₃-B (b), Cu/ZnO/Al₂O₃-C (c), Co/Cu/ZnO/Al₂O₃-C (d) and Ni/Cu/ZnO/Al₂O₃-C (e).
The partial substitution of Cu with Co or Ni results in a modest shift to high temperature of the main reduction peak and the appearance of additional features at higher temperatures: in the case of Co/Cu/ZnO/Al₂O₃-C the maximum is around 210°C with a shoulder at 280°C while a maximum at 225°C with a broad peak centered around 370°C are observed for Ni/Cu/ZnO/Al₂O₃-C. These results suggest that the introduction of Co or Ni in the formulation of the material has only a marginal effect on the reduction of Cu-species while the new reduction peaks could be associated with the reduction of Co- or Ni-species. Similar results has been obtained on materials with analogous composition prepared from layered double hydroxides [27,28] or by co-precipitation. [29] Finally, based on the TPR results, a pre-reduction at 360°C for 2 h was selected as a pre-treatment before catalytic activity tests.

**Powder X-Ray Diffraction (XRD)**

The composition and the morphology of the calcined and reduced materials was evaluated using powder XRD (Figure 3.2 and Table 3.2). As a general comment, no indications of Al-related phases (such as transitional Al₂O₃) were evidenced, mainly due to the relatively low Al content and the mild calcination treatment which avoid strong material crystallization. Similarly, no evidences of ZnAl₂O₄ formation are obtained.

The XRD pattern of Cu/ZnO/Al₂O₃-A sample evidenced the presence of well developed reflections of ZnO (31.8°, 34.4° and 36.2°) and CuO (35.5° and 38.7°). The mean crystallite size of ZnO and CuO are quite large (Table 3.2), in agreement with the low surface area of the material (Table 3.1) and the its catalytic behavior similar to that of bulk CuO (see below). In the case of Cu/ZnO/Al₂O₃-B and Cu/ZnO/Al₂O₃-C samples, broad XRD patterns are observed, with a partial overlapping of the reflection of ZnO and CuO. Similar crystallite sizes for the two phases were estimated (Table 3.2). The crystallite sizes are lower with respect to those of Cu/ZnO/Al₂O₃-A sample.
Figure 3.2: Powder XRD patterns of the calcined (A) and reduced in H₂(5%)/Ar flow at 360°C for 2h (B) for Cu/ZnO/Al₂O₃-A (a), Cu/ZnO/Al₂O₃-B (b), Cu/ZnO/Al₂O₃-C (c), Co/Cu/ZnO/Al₂O₃-C (d) and Ni/Cu/ZnO/Al₂O₃-C (e).

Table 3.2. Mean crystallite size (nm) determined applying the Scherrer’s equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcined</th>
<th>Reduced</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO</td>
<td>ZnO</td>
<td>Co-spinel</td>
<td>(Ni,Cu)O</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-A</td>
<td>16</td>
<td>15</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-B</td>
<td>8</td>
<td>8</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cu/ZnO/Al₂O₃-C</td>
<td>7</td>
<td>6</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al₂O₃-C</td>
<td>---</td>
<td>---</td>
<td>2</td>
<td>---</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al₂O₃-C</td>
<td>---</td>
<td>5</td>
<td>---</td>
<td>2</td>
</tr>
</tbody>
</table>
The higher dispersion of the CuO crystallites justifies the lower reduction temperature observed during TPR experiments. After reduction at 360°C for 2h, all the samples present a well developed reflections related to metallic Cu (43.3° and 50.4°) and ZnO. The crystallite size of the latter is almost unaffected by the reduction treatment. In the Cu/ZnO/Al2O3-B and Cu/ZnO/Al2O3-C samples, traces of CuO are detected (reflection at 38.7°), although the TPR characterization suggests that the reduction of Cu-species is complete at 360°C. The amount of CuO is higher in the Cu/ZnO/Al2O3-C sample. Although the XRD patterns of reduced samples were acquired immediately after the pre-treatment, the presence of CuO can be attributable to an easy reoxidation of highly dispersed nanosized Cu particles during exposure to air.

The XRD pattern of Co/Cu/ZnO/Al2O3-C (recorded few times on different aliquots of sample) indicates very low crystallinity. The observed pattern could be related to the presence of a Co-based spinel phase, with Cu(II) distributed as a dopant of these structures. ZnCo2O4, ZnAl2O4 and Co3O4 could be candidate as host phase with the spinel structure, since these materials present a very similar XRD patterns (same space group and similar cell parameters). After reduction, the spinel structure is decomposed and the on-set of the reflections of highly dispersed ZnO is observed. A very broad reflection is present in the region of 2θ = 40 – 45°. The broadness of the reflection do not allow for a clear attribution to a metallic phase, suggesting that metal Co and Cu should be widely dispersed.

In the case of Ni/Cu/ZnO/Al2O3-C material, the introduction of Ni(II) leads to the formation of a Ni-Cu mixed oxide(main reflection at 42.9°), with the cubic structure of NiO and a very small crystallite size. After reduction, a Ni-Cu alloy is formed, as revealed by the single reflection at 43.8°, between those of pure Ni and pure Cu (44.5° and 43.3°, respectively). A cell parameter of 0.357nm can be calculated from the position of the main reflection of the alloy, value is very good agreement with the theoretical one calculated on the basis of the Vegard’s law. For an equimolar Ni/Cu metal phase, the presence of two alloys is expected on the basis of previous reports on Ni/Cu catalysts.[30] The presence of a single alloy could be related with the
relatively low reduction temperature and/or with the formation of the mixed oxide in the calcined material, which allow to avoid metal segregation after reduction. Notably, the reduction induces a deep crystallization of both ZnO and (Ni,Cu) particles (Table 3.2).

3.3 Catalytic activity results

3.3.1 Methanol Steam Reforming (MSR)

Figure 3.3 (a, b, c) shows the results of the steam reforming of methanol over Cu/ZnO/Al₂O₃ prepared according to the three different coprecipitation methods. On all the samples, methanol conversion starts above 150°C. Below 300°C, the main products are CO₂ and H₂, indicating that the water gas shift (WGS) reaction is operative even at low temperature. The formation of small quantities of CO is observed only above 300°C, consistently with the fact that, increasing the temperature, the equilibrium of the exothermic WGS shifts towards the reactants. The three synthetic procedures do not seem to significantly influence the catalytic performance, despite the fact that lead to materials with different Cu metal dispersion and total surface area. Indeed, rather small changes in product distribution are observed. All the catalysts are able to convert 100% methanol already above 250°C and promote WGS reaction in the same range of temperatures. These experimental results are in agreement with the data reported in literature on analogous systems.[8,11,13,16,21]

The catalytic activity changes with the introduction of a second metal component (Co or Ni) as displayed in Figure 3.3 (d, e). In particular, although the activity in methanol decomposition remains high, WGS does not reach the equilibrium. Moreover, CH₄ is also detected, as a product of CO and CO₂ hydrogenation. CO is observed among the products already at low temperatures (< 300°C). The CO yield reaches a maximum around 270°C, after which it decreases while CO₂ formation increases.
Cu/Zn-based catalysts were extensively studied since they are the more active non-precious metal catalyst for methanol reforming. Methanol conversion on these materials greatly depends on the status of copper, such as the dispersion, metal surface area and particle size.\textsuperscript{[21,22,24,31-33]} Shen et al.\textsuperscript{[34]} examined the effect of preparation method on the catalytic behavior of Cu/Zn/Al catalysts finding that it significantly affects the dispersion of copper particles and thus, the catalyst performance in terms of methanol conversion, H\textsubscript{2} yield and CO concentration. A correlation between the observed catalytic activity and the presence of highly dispersed Cu metal particles, obtained by an appropriate synthetic procedure, was also proposed by Shishido et al.\textsuperscript{[35]} and Li et al.\textsuperscript{[36]}

A very high catalytic activity for methanol steam reforming at low temperature was reported by Zhang et al.\textsuperscript{[21]} on Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst synthesized by a gel-coprecipitation approach with respect to the catalysts prepared by conventional
coprecipitation technique. This superior catalytic performance was attributed not only to the generation of highly dispersed copper and zinc components but also to the creation of catalytically active copper species with a much higher metallic copper specific surface and a stronger Cu-Zn interaction.

Similarly, Zhang et al. \cite{37} attributed the better performance of a Cu/ZnO/Al2O3 catalyst obtained from a CuO/ZnO/Al2O3 sample, prepared by conventional carbonate coprecipitation method and aged under microwave irradiation, to the creation of highly strained copper nanocrystals in the active catalyst. Finally, Kurr et al. \cite{8} found that on various Cu/ZnO/Al2O3 catalysts, prepared by hydroxycarbonate coprecipitation procedure, the catalytic activity and thermal stability under methanol steam reforming conditions are influenced not only by specific copper surface area but also by defects in the bulk structure.

In this work, the three coprecipitation procedures lead to three catalysts, Cu/ZnO/Al2O3-A, B and C, with different surface area as well as different copper dispersion as suggested by TPR and XRD measurements. Nevertheless, the catalytic activity does not seem to be greatly influenced by these properties. Notably, as indicated by XRD data (Table 3.2), the reduction leads to an increase in Cu and ZnO crystallite sizes. The effect is more pronounced on the Cu/ZnO/Al2O3-A sample with the low surface area. However, it has also to keep in mind the intrinsic characteristics/limitations of X-ray diffraction technique: XRD signal is more sensitive to the contribution of the large and more crystalline particles, with respect to the small and amorphous one which can give a key contribution to the activity.\cite{38}

To explain activity observations, another aspect has to be taken into account: the adsorption properties of the support. It was reported that the adsorption capacity of the oxides used as support affects catalytic performances, because spillover effects can play a key role in reaction mechanisms for these systems. In fact, hydrogen species were shown to be mobile over both Cu and ZnO phases of these catalysts and can be stored on the surface,\cite{39} whereas oxygen species move from ZnO to Cu, most likely in the form of hydroxides.\cite{40} It was also proposed by Peppley et al. \cite{41,42} a mechanism scheme for methanol steam reforming on Cu/ZnO/Al2O3 catalyst
according to which the active sites for the methanol decomposition and for the direct methanol-steam reaction and WGS are different. Moreover, hydrogen adsorption does not seem to compete for the active sites on which the oxygen-containing species adsorb. On the basis of these considerations, it is clear that several factors can influence positively or negatively the catalytic activity and they work together. Due to a compensation effect, thus, the global results could not lead to substantial differences in experimental observations.

Only a few reports on the use of the addition of a second metal to Cu-based catalysts employed in the steam reforming of methanol. Liao et al. [43] reported that Ni-Cu alloys supported on carbon nanotubes (CNT) show better activity than the single metals, with the best performances with a Ni/Cu composition of 20/80 on a molar basis. No indications on CH$_4$ formation are reported. Gadne et al. [44] studied the steam reforming of methanol under supercritical conditions catalyzed by the reactor wall made by Inconel (a Ni-Cr-Fe alloy). The CH$_4$ formation can be reduced by alloying the internal wall of the reactor with Cu. No data regarding the use of Co-Cu bimetallic system are reported, at the best of our knowledge.

### 3.3.2 Ethanol Steam Reforming (ESR)

Figure 3.4 (a, b, c) presents typical activity profiles for Cu/ZnO/Al$_2$O$_3$ (-A, -B, -C) catalysts under ethanol steam reforming reaction. The behavior is very similar at low temperature while, differences can be observed for temperatures higher than 400°C. In particular, on all samples, ethanol conversion starts above 150°C producing essentially acetaldehyde and H$_2$, which are the main products up to 400-450°C. Increasing the temperature, on Cu/ZnO/Al$_2$O$_3$-A the acetaldehyde yield decreases while CH$_3$COCH$_3$ and CO$_2$ start to be formed up to 600°C. Small amounts of CH$_4$ are also monitored. Above this temperature, the only detected products are CH$_3$CHO and H$_2$. On Cu/ZnO/Al$_2$O$_3$-B, the formation of CH$_3$COCH$_3$, CO$_2$ and CH$_4$ is shifted towards higher temperatures (> 450°C) and they remain the main products together with H$_2$ up to 650°C, after which their yields decrease while acetaldehyde is again observed.
Figure 3.4: Ethanol Steam Reforming results on Cu/ZnO/Al₂O₃-A (a), Cu/ZnO/Al₂O₃-B (b), Cu/ZnO/Al₂O₃-C (c), Co/Cu/ZnO/Al₂O₃-C (d) and Ni/Cu/ZnO/Al₂O₃-C (e). Reaction conditions: CH₃CH₂OH (1.0%) + H₂O (5.0%) in Ar, GHSV = 120000 mL g⁻¹ h⁻¹.

The performance of Cu/ZnO/Al₂O₃-C is very similar to Cu/ZnO/Al₂O₃-B. Noteworthy, significant amounts of CO are not observed. Moreover, ethylene is not detected for all the catalysts. The dehydration of ethanol to ethylene is well known to proceed on the strong acidic sites of oxide supports.\textsuperscript{[30,45,46]} In the case of Cu/ZnO/Al₂O₃, the inhibition of ethylene production can be related to the small amount of alumina with respect to the Cu and Zn content of the samples and/or to the partial coverage of the alumina surface by copper and ZnO (basic oxide), with consequent reduction of the acidic sites. However, the activity of Cu/ZnO-based materials in the reforming of ethylene cannot be completely excluded.

The product distribution described above differs from the few data presented in literature on similar Cu/ZnO/Al₂O₃ systems. Cavallaro \textit{et al.} \textsuperscript{[47]} investigated the steam reforming of ethanol over CuO/ZnO/Al₂O₃ prepared by coprecipitation procedure and found that the catalyst exhibited good
activity with CO, CO₂ and H₂ as the main products above 360°C. The formation of oxygenated by-products like acetaldehyde, acetic acid and ethyl acetate, is favored only by low temperatures (< 330°C). Notably, acetone formation which was observed in this work for temperatures higher than 400-450°C, was not described by the same authors.

The suppression of acetone production in the catalysts presented here, can be achieved introducing Co and Ni in the catalyst formulation with a consequent improvement in the reforming activity as showed in Figure 3.4 (d, e).

On Co/Cu/ZnO/Al₂O₃-C, ethanol conversion starts immediately. Up to 250°C, the main products are acetaldehyde and hydrogen. Above this temperature, CO and CH₄ are formed while acetaldehyde yield decreases. The yield of hydrogen grows in all the temperature range investigated. CO₂ is also observed for temperatures higher than 350°C. On Ni/Cu/ZnO/Al₂O₃-C, ethanol conversion becomes significant above 200°C. The product distribution is similar to Co/Cu/ZnO/Al₂O₃-C with some differences. The formation of CH₄ is inhibited, due to the ability of Ni to promote the steam reforming of methane [48] and CO is detected only above 300°C.

The observed enhancement in ethanol reforming activity was also documented in literature over similar bimetallic catalysts. Homs et al., for instance, studied bimetallic Co-Ni and Co-Cu samples containing 0.7 wt.% sodium promoter. In the 250-450 °C temperature range, a remarkable improvement in H₂ yield and stability was observed when Ni is added to Co/ZnO sample. The same positive effect instead, was not detected with the introduction of Cu in the catalyst formulation.

Galetti et al. [17] described a quaternary mixed oxide Cu/Co/Zn/Al, which exhibited high activity and stability in the temperature range 400-600°C producing mainly H₂, CO₂ and CO and minor amounts of CH₄. The catalytic behavior was correlated to the structure of the catalyst composed by a spinel matrix (i.e. ZnAl₂O₄) with a high dispersion of oxidized Cu and Co species.

Zhang et al. [49] presented a promising Ni(30 wt.%)/Cu(5 wt.%)/Al₂O₃-ZnO catalyst which showed complete conversion of ethanol at the temperature ranging from 250-600°C. Acetaldehyde was only observed below 350°C, while for higher temperatures
CO, CO₂, CH₄ and H₂ are the only detected products. No ethylene was monitored in all the temperature range investigated and the coking amount is very low. The effect of Ni and Co introduction in Cu/ZnO/Al₂O₃ commercial catalyst was also studied by Grzegorczyk et al. [50]. The major differences were observed below 480°C, where methane formation slightly decreases while H₂ selectivity and yield increase. The effect is more significant for Co with respect to Ni.

A dependence of the reforming activity from the precursor used was discussed by Llorca et al. on Co/ZnO-based catalysts. [51-53] The sample prepared with Co₂(CO)₈ precursor showed the best performance at 350°C producing only small amounts of CH₄ as by-products without CO formation. The results confirm the key role of metal dispersion of the active phase in determining the desired reforming activity.

The stability of catalytic activity under isothermal conditions was tested at 600°C since at this temperature, H₂ production reaches a maximum while CH₄ formation is negligible. Although no significant deactivation for all the samples was observed for 24 h.

### 3.4 Characterization of exhaust catalysts

**Powder X-Ray Diffraction (XRD)**

XRD data recorded on exhaust catalysts suggest that a significant increase of crystallite sizes occurs for all the samples (Figure 3.5), as a result of the thermal treatment at high temperature. Table 3.3 summarizes the mean crystallite sizes of the different phases revealed by XRD diffraction. The presence of ZnAl₂O₄ is evidenced in the oxide supports, together with ZnO. In the case of Co/Cu/ZnO/Al₂O₃-C, two distinct metal phases are observed. On the contrary, the alloy formed by Ni and Cu during the initial reduction pre-treatment remains unperturbed for Ni/Cu/ZnO/Al₂O₃-C sample (cell parameter of the alloy: 0.3579 nm). The reflection near 26.6° observed in XRD spectra of both Co/Cu/ZnO/Al₂O₃-C and Ni/Cu/ZnO/Al₂O₃-C can be attributed to graphite, indicating that the deposition of large amounts of graphitic coke occurs.
Figure 3.5: XRD patterns of the aged Cu/ZnO/Al$_2$O$_3$-C (a), Co/Cu/ZnO/Al$_2$O$_3$-C (b) and Ni/Cu/ZnO/Al$_2$O$_3$-C (c). Reaction conditions: CH$_3$CH$_2$OH (1.0%) + H$_2$O (5.0%) in Ar, GHSV = 120000 mL g$^{-1}$ h$^{-1}$, aging during run-up experiment up to 600°C followed by isothermal treatment at 600°C for 24 h.

Table 3.3: Mean Crystallite sizes of the phases observed in the XRD patterns of the aged samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO</th>
<th>ZnAl$_2$O$_4$</th>
<th>Graphite</th>
<th>Cu</th>
<th>Co</th>
<th>NiCu alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/ZnO/Al$_2$O$_3$-C</td>
<td>44</td>
<td>12</td>
<td>---</td>
<td>26</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Co/Cu/ZnO/Al$_2$O$_3$-C</td>
<td>88</td>
<td>13</td>
<td>6</td>
<td>32</td>
<td>25</td>
<td>---</td>
</tr>
<tr>
<td>Ni/Cu/ZnO/Al$_2$O$_3$-C</td>
<td>55</td>
<td>13</td>
<td>5</td>
<td>---</td>
<td>---</td>
<td>23</td>
</tr>
</tbody>
</table>
Thermo-Gravimetric Analysis (TGA) and Temperature Programmed Oxidation (TPO)

The amount of carbon deposited on catalysts was estimated by TGA (Figure 3.6 d) while the species evolved during carbon removal were analyzed separately during Temperature Programmed Oxidation experiments (Figure 3.6 a, b and c).

Figure 3.6: TPO profiles of the aged Cu/ZnO/Al$_2$O$_3$-C (a), Co/Cu/ZnO/Al$_2$O$_3$-C (b) and Ni/Cu/ZnO/Al$_2$O$_3$-C (c) and TGA analysis of the same samples. Triangles indicates the weight corrected for the oxidation of the metal phases. Aging conditions: CH$_3$CH$_2$OH (1.0%) + H$_2$O (5.0%) in Ar, GHSV = 120000 mL g$^{-1}$ h$^{-1}$, aging during run-up experiment up to 600°C followed by isothermal treatment at 600°C for 24 h.
Generally, TGA experiments show a slight initial increase of the weight, followed by a decrease related to carbon species removal. The initial weight increase could be related with the oxidation of the metal phases to the corresponding oxide. Assuming the formation of CuO, Co₃O₄ and NiO as metal oxide phases (similarly to the phases observed in the calcined samples), the exact weight loss due to carbon removal can be calculated. The results showed that coke deposition is strongly reduced on Ni/Cu with respect to Co/Cu system. Indeed, on Co/Cu/ZnO/Al₂O₃ sample the amount of carbon was 0.5765 g/g_cat while 0.3804 and 0.0974 g/g_cat was calculated for Ni/Cu/ZnO/Al₂O₃ and Cu/ZnO/Al₂O₃, respectively.

The small coking tendency of Cu/ZnO/Al₂O₃ sample is consistent with its poor reforming activity at 600°C as displayed in Figure 3.4c. On the other hand, the higher resistance of Ni/Cu system towards coke deactivation with respect to that of Co/Cu system can be correlated to the Ni/Cu alloy formation. The Cu atoms in the alloy can occupy preferentially either flat terrace sites, or edge and kink Ni sites which are mainly responsible for carbon formation. As indicated by XRD data, the alloy formation between Co and Cu does not take place.

Notably, the higher CO₂ evolution temperature observed during TPO experiments on aged Ni/Cu/ZnO/Al₂O₃-C is an indication of the presence of a more graphitic carbonaceous deposit with respect to the aged Ni/Cu/ZnO/Al₂O₃-B.

### 3.5 Conclusions

The main results of this work can be summarized as follow:

1. Active and cheap catalysts, comprising of base metals (Cu, Co and Ni) as active phase and ZnO as promoter, can be prepared following simple ways, demonstrating good performances in the hydrogen production through the steam reforming of alcohols.

2. The preparation methodology of Cu/ZnO/Al₂O₃ has a strong influence on the surface area and metal dispersion of the catalysts. Nevertheless, methanol steam
reforming reaction is in our case marginally affected, as a combination of structural factors.

3. Cu/ZnO/Al₂O₃ is active for the dehydrogenation of ethanol, producing quantitatively acetaldehyde at moderate temperature, being Cu not able to activate the C-C bond. The ethanol steam reforming is enhanced introducing Ni and/or Co in the formulation of the active phase.

4. Coke deposition occurs significantly on Co/Cu/ZnO/Al₂O₃ while, alloy formation between Ni and Cu, significantly reduce these deactivation phenomena.

References


Chapter IV

Glycerol Reforming

4.1 Introduction 79

4.2 Catalytic activity results 81

4.2.1 Glycerol steam reforming reaction 81

4.2.2 Catalysts stability evaluation 86

4.3 Characterization of fresh catalysts 88

- Temperature Programmed Reduction (TPR) 88
- Physisorption- and Chemisorption 89
- Powder X-Ray Diffraction (XRD) 90
- Ammonia Temperature Programmed Desorption (NH₃-TPD) 94

4.4 Effect of CeO₂ and La₂O₃ doping on the catalysts stability and origin of catalyst deactivation effect 95

4.4.1 Characterization of exhaust catalysts 95

- Physisorption - and Chemisorption 95
- Powder X-Ray Diffraction (XRD) 96
- Thermo Gravimetric Analysis (TGA) 98
• High Resolution- Transmission Electron Microscopy (HR-TEM)

4.5 Conclusions

References
4.1 Introduction

Glycerol is the main by-product of biodiesel production and its exceeding production derives from the more and more increasing biofuels demand.\cite{1} The use of renewables, such as biomasses, is essential for a sustainable development of our society. The conversion of renewable resources into either clean fuels or chemicals is attracting growing interests due to the continuous reduction of fossil hydrocarbons supplies.\cite{2} Recent reviews account for a large variety of catalytic and enzymatic transformation of glycerol into high-value chemical derivatives.\cite{1,3-8}

The use of this feedstock to obtain hydrogen has gained a lot of attention due to the increasing hydrogen demand, mainly for fuel cells applications.\cite{9}

Therefore, glycerol conversion to H₂-rich mixtures is not only an interesting research topic but more importantly an attractive way towards a sustainable biodiesel production.

Glycerol can be converted into syn-gas by steam reforming (SR) according to the following reaction:

\[
C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7 H_2 \quad \text{Eq. 4.1}
\]

This process can be formally written as a combination of two separate reactions: glycerol decomposition into H₂ and CO (Eq. 4.2) followed by the Water Gas Shift (WGS) equilibrium (Eq. 4.3):

\[
C_3H_8O_3 \rightarrow 3CO + 4 H_2 \quad \text{Eq. 4.2}
\]

\[
CO + H_2O = CO_2 + H_2 \quad \text{Eq. 4.3}
\]

Typically, the glycerol SR is a catalytic process that occurs in vapor phase at atmospheric pressure and temperatures up to 900°C. Due to its endothermicity, high temperatures, low pressures and a high steam glycerol ratio are generally required to get high substrate conversions.\cite{10} When compared with the Aqueous Phase Reforming (APR) protocol, SR requires higher energy to vaporize the biomass
solutions. In spite of this general disadvantage, SR could be preferred to the APR protocol because of the lower amount of contaminating side-products produced. Indeed, under SR conditions, the amount of methane and higher hydrocarbons can be significantly reduced with respect to the APR conditions,\[11,12\] just running the reaction at atmospheric pressure instead of higher pressure (as required by the APR process).\[9\] In addition, the APR process, in case of concentrated solutions, still needs to be optimized.\[11,13\]

Many metal catalysts have been scrutinized for the glycerol SR among which Ru,\[14-16\] Rh,\[15,17\] Ir,\[15,18,19\] Pd,\[15,20,21\] Pt,\[15,17,22-25\] Co,\[18\] and Ni\[15,18,21,24,26-30\] are the most representative ones. Pt is a good candidate for the glycerol SR allowing for efficient C-C, O-H and C-H bond cleavages with high activity and selectivity levels. On the contrary, other metals need some promoters to ensure similar performances.\[20,29,31\]

A wide variety of supports for the metal active sites have also been tested in the glycerol SR reaction, from acidic\[15\] to basic,\[27\] in many cases without paying attention to the non-innocent role of these materials on the catalytic process.

An efficient catalyst for H\(_2\) production from glycerol is expected to break-up the substrate through C-C, O-H and C-H bond cleavages, promoting at the same time the elimination of the metal-passivating carbon monoxide via the WGS reaction. Finally, such a catalyst should not promote either the C-O cleavage or the CO or CO\(_2\) hydrogenation to form alkanes and more polar compounds, respectively.\[32\]

Many research efforts are required to scale-up the glycerol SR from lab to industry. Indeed, some important properties of the catalytic system, such as stability and selectivity towards H\(_2\) production, must be carefully considered before this step. Moreover, catalyst deactivation due to coke deposition on the catalyst surface represents one of the most important limitations to the industrial glycerol SR. It is well known that CeO\(_2\) can act as a non innocent support, preventing, to some extent, coke deposition at the catalyst active sites.\[18,33,34\]

Furthermore, CeO\(_2\) can efficiently catalyze the WGS reaction,\[18,35-37\] favoring carbon monoxide elimination and preventing the catalysts from passivation/deactivation.
It should be pointed out that acidic catalyst supports, such as Al₂O₃, can promote the occurrence of side reactions during the SR process basically leading to saturated[^3] or unsaturated hydrocarbons[^38] products. One possible alternative to control the acidic sites density in these supports is their impregnation with basic oxides such as La₂O₃ or CeO₂.

We prepared new Al₂O₃/CeO₂ and Al₂O₃/La₂O₃-supported Pt nanoparticles and studied their use as efficient catalytic systems for the H₂ production via glycerol SR. We have demonstrated that the support acidity is reduced by means of basic additives such as CeO₂ and La₂O₃, improving the catalyst stability and selectivity and reducing, at the same time, the formation of undesirable products and coke depositions.

A complete characterization of the new catalytic systems is provided, with the aim of rationalizing the fundamental role of the support composition on the catalytic performance of the Pt nanoparticles.

### 4.2 Catalytic activity results

#### 4.2.1 Glycerol steam reforming reaction

Running-up experiments under SR conditions have shown a strong influence of the composition of the catalyst support on the conversion of glycerol into syn-gas. Fig. 4.1 shows the conversion of glycerol to gaseous products, calculated on the basis of their flow at the outlet of the reactor (after condensation of the non-volatile compounds), as a function of the catalyst temperature, while Fig. 4.2 illustrates the composition of the gas phase produced throughout the catalytic process as revealed by GC analysis.

A typical Pt/Al₂O₃ catalyst exhibits a poor activity in the glycerol SR at low temperature with a minimum in the glycerol conversion to syn-gas in the range of
350 – 400°C. At the same time, very low gas flows are generally recorded (~ 25 mL min⁻¹) and a significant amount of hydrocarbons (CH₄, C₂H₄ and C₂H₆) is detected in the effluents. Finally, the collected liquid fraction presents a typical yellow – brownish colour, suggesting the formation of heavy oxygenated hydrocarbons produced by condensation side-reactions. A qualitative GC-MS analysis of the liquid fractions collected during the reaction at 350 – 400°C confirmed the presence of high quantities of unreacted glycerol and evidenced the presence of a large number of by-products. The most abundant are hydroxyacetone, 1,2-propandiol, ethylene glycol and their monoesters with acetic acid. The presence of acrolein or acrilic acid cannot be excluded, since the unequivocal attribution of all the peaks in the chromatogram is not possible, because of the large number of by-products (present in traces).

Other authors\cite{1} have observed a similar low activity for catalytic Pt nanoparticles over carbon supports. This effect has been ultimately attributed to a rapid carbon monoxide passivation of the catalyst active sites already at low temperatures. The metal sites passivation by CO favors glycerol dehydration at the acidic sites of the support,\cite{39} ultimately increasing the amount of undesired by-products.
Figure 4.2: Gas phase composition as a function of the catalyst temperature on Pt/Al₂O₃ (a), Pt/L₆O₃/Al₂O₃ (b) and Pt/CeO₂/Al₂O₃ (c). Condition: 1.00 g catalyst, 0.32 mL min⁻¹ of C₃H₈O₃ (30 wt%) water solution.

A strong increase in the glycerol conversion to syn-gas is observed on the same catalyst by increasing the reaction temperature, although the complete conversion is never reached. H₂ and CO₂ are produced above 450°C with the presence of a small amount of CH₄ and traces of CO (over 550°C).

The poor activity of the Pt/Al₂O₃ catalyst in the glycerol SR can be ascribed to the occurrence of a complex network of side-reactions, including dehydration / condensation / polymerization reactions, promoted by the acid sites of the support, as well as dehydrogenation / hydrogenation reactions promoted by the Pt nanoparticles. Comparable results have been recently reported for the SR of glycerol using Al₂O₃ –
supported Ni catalysts\textsuperscript{[24]} as well as for aqueous-phase reforming over Al\textsubscript{2}O\textsubscript{3} – supported Pt catalysts.\textsuperscript{[38,40]}

Notably, Pt/Al\textsubscript{2}O\textsubscript{3} catalysts doped with either CeO\textsubscript{2} or La\textsubscript{2}O\textsubscript{3} exhibit very different catalytic activity and selectivity. Although a trend similar to that recorded for Pt/Al\textsubscript{2}O\textsubscript{3} is observed for temperature lower than 300°C, a sharp increase is reached for the doped systems between 350 – 400°C, leading to glycerol conversions close to the maximum (Fig. 4.1). While temperatures up to 300°C generate H\textsubscript{2} and CO (suggesting the glycerol decomposition as the main operative process – Eq. 4.2), over 350°C a significant increase in H\textsubscript{2} and CO\textsubscript{2} production is observed, which indicates that the WGS equilibrium (Eq. 4.3) is also operative (Fig. 4.2). CH\textsubscript{4} is the major by-product observed, while only traces of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} are present.

A decrease in the gas flow is observed for temperatures over 400°C. A similar effect of La\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2} has been already reported by Iriondo et al.\textsuperscript{[29]} studying the effect of various doping agents on the activity of Ni/Al\textsubscript{2}O\textsubscript{3} catalyst in the glycerol SR and APR. While Pt/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} shows a decrement up to 500°C, where the glycerol conversion stabilizes around 50%, the Pt/La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} system is characterized by a second maximum around 550°C, which affects the final gas stream composition only marginally. For both doped catalysts, only a slight increase in the CO concentration is observed at high temperatures, which is reasonably attributed to the WGS exothermic equilibrium. The gas stream profile for Pt/La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} (two relative maxima in the glycerol conversion) is perfectly reproducible and it is maintained for different batches of fresh catalyst. Such a profile is probably associated to a progressive deactivation / reactivation of the catalytic sites with the catalyst temperature with no apparent modification of the catalyst selectivity. Accordingly, detectable amounts of unreacted glycerol and by-products are invariably identified by GC-MS analysis of the liquid fractions collected from the reactor working at temperature higher than 450°C with doped Pt/Al\textsubscript{2}O\textsubscript{3} catalysts.

Table 4.1 presents the evolution of relative ratios between the main gaseous products for the various catalysts at different temperatures. For Pt/Al\textsubscript{2}O\textsubscript{3}, the highest CH\textsubscript{4}/H\textsubscript{2} is observed, confirming that this catalyst presents the highest selectivity to the
<table>
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<tr>
<th>Sample</th>
<th>Temperature °C</th>
<th>H₂/CO</th>
<th>H₂/CO₂</th>
<th>CO/CO₂</th>
<th>CH₄/H₂</th>
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<tr>
<td>Pt/CeO₂/Al₂O₃</td>
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<td>1.78</td>
<td>4.97</td>
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</tr>
<tr>
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<td>4.15</td>
<td>2.26</td>
<td>0.095</td>
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<td>0.09</td>
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<td></td>
<td>450</td>
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<td>1.82</td>
<td>0.09</td>
<td>0.094</td>
</tr>
<tr>
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<td>1.86</td>
<td>0.14</td>
<td>0.094</td>
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<tr>
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<td>0.083</td>
</tr>
<tr>
<td></td>
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<td>12.62</td>
<td>2.13</td>
<td>0.17</td>
<td>0.024</td>
</tr>
</tbody>
</table>

[a] Condition: 1.00 g catalyst, 0.32 mL min⁻¹ of C₃H₆O₃ (30 wt%) water solution
hydrocarbon production. For Pt/La$_2$O$_3$/Al$_2$O$_3$, the analysis of the molar ratios confirms that below 300°C the glycerol decomposition (Eq. 4.2) is operative (H$_2$/CO ratio close to the theoretical 1.33 value). When the temperature is increased, the WGS is also involved, approaching the complete steam reforming process (Eq. 4.1) with a H$_2$/CO$_2$ ∼ 2.33; at the same time, the CO/CO$_2$ ratio is strongly reduced. Finally, for Pt/CeO$_2$/Al$_2$O$_3$, the occurrence of the WGS reaction at low temperature is confirmed by H$_2$/CO > 1.33 already at 250°C.

### 4.2.2 Catalysts stability evaluation

The preservation of the catalyst stability throughout a catalytic process represents one of the most important goals to be addressed while designing new catalytic systems. To assess the practical use of our Pt-based catalysts, long term stability tests were performed. The catalyst stability for the doped samples has been studied in the glycerol SR process at 350°C (Fig. 4.3), the lowest temperature at which the complete conversion of glycerol to H$_2$ and CO$_2$ is achieved. Notably, at the same temperature, the plain Pt/Al$_2$O$_3$ catalyst shows its lowest catalytic performance. Both doped catalysts present a good stability for at least 20h. While the Pt/CeO$_2$/Al$_2$O$_3$ system exhibits a very fast decrease in the glycerol conversion to syn-gas after 20h, the La$_2$O$_3$-doped catalyst maintain a high stability over a period of 50h. Notably, the selectivity in the different products remains almost constant throughout the reaction. The sharp decrease observed for the Pt/CeO$_2$/Al$_2$O$_3$ was also previously reported in the case of Pt/Al$_2$O$_3$.[39] The process was interpreted on the bases of the fact that the reactor initially operates at 100% conversion and glycerol is present only in the upstream portion of the catalyst bed in the tubular reactor. Therefore, the deactivation front moves from the reactor inlet to the outlet as olefinic species are formed from glycerol on the Al$_2$O$_3$ acid sites, followed by deposition of coke from these species covering the Pt surface sites.[39]

Despite the relatively high ceria loading (20 wt%), the catalyst surface still presents a significant amount of acidic sites (see NH$_3$-TPD section below). This may be due to a partial ceria agglomeration into relatively small but appreciable nanoparticles.
caused by the calcination at 700°C. Indeed, the formation of ceria particles with idealized cubic shape having a ∼ 4.3 nm edge (see XRD section below), its resulting

Figure 4.3: Stability test over doped Pt/Al₂O₃ catalyst. Upper part: Percentage glycerol conversion to gas phase products. Lower part: Gas phase composition using Pt/La₂O₃/Al₂O₃ (a) and Pt/CeO₂/Al₂O₃ (b). Condition: 1.00 g catalyst, 0.32 mL min⁻¹ of C₃H₆O₃ (30 wt%) water solution, T = 350 °C.

surface area would be around 7 m² g⁻¹, which corresponds to less than 8% of the catalyst total surface area. On the contrary, in the case of the La₂O₃ based system, the very high dispersion of this basic oxide results in a more significant alumina acidic sites reduction.
4.3 Characterization of fresh catalysts

Temperature Programmed Reduction (TPR)

Temperature Programmed Reduction (TPR) profiles of the investigated samples are presented in Fig.4.4. All samples containing Pt are featured by a broad reduction process with a maximum around 120°C, related to the reduction of PtO$_X$ species formed during the calcination treatment. While Pt/CeO$_2$/Al$_2$O$_3$ shows an important H$_2$ consumption over 500°C due to the bulk reduction of CeO$_2$, the Pt/Al$_2$O$_3$ and Pt/La$_2$O$_3$/Al$_2$O$_3$ samples do not show any reduction process over 400°C.

![Figure 4.4: Temperature Programmed Reduction (TPR) profiles for (a) Pt/Al$_2$O$_3$, (b) Pt/La$_2$O$_3$/Al$_2$O$_3$, (c) Pt/CeO$_2$/Al$_2$O$_3$ and (d) CeO$_2$/Al$_2$O$_3$.](image)

Different types of PtO$_X$ species can be obtained from the oxidation of the Pt/Al$_2$O$_3$ catalyst,\textsuperscript{[41]} from oxygen passivated Pt particles (when the oxidation is performed at room temperature) to the formation of PtAl$_2$O$_4$ species (by heating Pt nanoparticles
in the presence of Al₂O₃ over 600°C). In our systems, the calcination step at 500°C is expected to generate basically PtO₂ although the high nanoparticle dispersion does not allow for a definitive structural confirmation of the Pt-species (XRD data not shown). The PtO₂ reduction should occur almost quantitatively under a stream of H₂ between 100 and 300°C, depending on the metal loading, the support nature and the metal dispersion.\(^{[41-44]}\)

A catalyst pre-treatment in a flow of H₂ at 500°C has been carried out on all our catalytic systems before their characterization and use in the glycerol SR. Such a treatment is expected to completely reduce all Pt species present in the samples.

**Physisorption and Chemisorption**

The results of N₂ physisorption and H₂ chemisorption experiments on the reduced samples are summarized in Table 4.2 All samples show high surface area and similar pore dimensions, consistent with the texture of the Al₂O₃ support.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA(^{[a]}) (m² g⁻¹)</th>
<th>dM(^{[b]}) (nm)</th>
<th>CPV(^{[c]}) (mL g⁻¹)</th>
<th>H/Pt(^{[d]})</th>
<th>PS(^{[e]}) (nm)</th>
<th>CS(^{[f]}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>97</td>
<td>11</td>
<td>0.367</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>96</td>
<td>11</td>
<td>0.349</td>
<td>0.78</td>
<td>1.4</td>
<td>1.5</td>
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<tr>
<td>La₂O₃/Al₂O₃</td>
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<td>12</td>
<td>0.338</td>
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<tr>
<td>Pt/La₂O₃/Al₂O₃</td>
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<td>11</td>
<td>0.323</td>
<td>0.71</td>
<td>1.6</td>
<td>1.5</td>
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<td>CeO₂/Al₂O₃</td>
<td>100</td>
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<td>0.292</td>
<td>0.50</td>
<td>2.3</td>
<td>nd (^{[h]})</td>
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<tr>
<td>Pt/CeO₂/Al₂O₃</td>
<td>96</td>
<td>11</td>
<td>0.281</td>
<td>0.72 (^{[e]})</td>
<td>1.6 (^{[e]})</td>
<td>nd (^{[h]})</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Specific Surface Area from the BET analysis; \(^{[b]}\) Maximum of the BJH pore distribution calculated on the desorption branch; \(^{[c]}\) Cumulative Pore Volume; \(^{[d]}\) H/Pt ratio obtained from H₂ chemisorption at -94 °C of the samples previously reduced at 500°C for 5h; \(^{[e]}\) Average Pt Particle Size obtained from H₂ chemisorption assuming a spherical geometry; \(^{[f]}\) Average Pt Crystallite Size determined by XRD technique; \(^{[g]}\) After reduction at 500°C, the sample was oxidized at 427°C flowing O₂ (5%) / Ar (30 mL min⁻¹), then reduced at 100°C flowing H₂ (5%) / Ar (30 mL min⁻¹) and finally evacuated at 400°C for 4h, accordingly to Ref. \(^{[45]}\); \(^{[h]}\) Not determined.
The introduction of doping oxides onto the Al₂O₃-support results in a slight decrease of the cumulative pore volume, which is more pronounced in the case of CeO₂ because of a higher doping oxide loading. Such a trend together with no significant variation of either the specific surface area (SSA) or the pore diameters accounts for a good dispersion of the doping agents onto the support surface. H₂ chemisorption has finally revealed a high dispersion of the Pt nanoparticles onto the supports. A lower H/Pt ratio is observed for Pt/CeO₂/Al₂O₃ sample after reduction at 500°C, probably due to a partial electronic deactivation of the Pt nanoparticles, as previously reported for related CeO₂-based systems.[45] A mild oxidative treatment was then applied to the latter sample in order to re-oxidize CeO₂ without modifying the Pt dispersion and making the H/Pt ratio comparable with that observed for the other samples.

**Powder X-Ray Diffraction (XRD)**

The XRD pattern of each sample shows the typical θ-Al₂O₃ signals of the catalyst support (Fig. 4.5).[46]

While the Pt/CeO₂/Al₂O₃ catalyst (Fig. 4.5c) contains new reflections ascribable to the cubic CeO₂ phase, the Pt/La₂O₃/Al₂O₃ system (Fig. 4.5b) does not show any reflection clearly attributable to specific La-containing species, probably because of either a low amount of La₂O₃ or a high oxide dispersion onto the support, or a combination of both.

Crystallite sizes of 4.3 ± 0.4 nm can be calculated for the activated Pt/CeO₂/Al₂O₃ catalyst from the XRD profile fitting of the CeO₂ phase. Such a result indicates that the catalyst activation protocol does not affect the structural characteristics of the doping agent.

The XRD characterization of the supported Pt nanoparticles is generally a difficult task when complex support patterns are combined with a low and broadened pattern of the metal phase. In any case, an accurate study can be done by comparing the support and catalyst patterns within a Rietveld procedure.[47]
In order to separate the platinum scattering from that of the support, the air-corrected diffraction pattern of the catalysts was fitted through Rietveld methods using platinum fcc structure and the experimental diffraction pattern of the support. This analytical method allows for a quantitative evaluation of the metal phase as well. In this way, an additional internal validity test of the line broadening analysis is performed\(^\text{[48]}\) (Figs. 4.6 – 4.8).

The main Pt crystallite sizes are listed in Table 4.2. Pt crystallite sizes of 1.5 ± 0.2 nm has been calculated for both Pt/Al\(_2\)O\(_3\) and Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\), in good agreement with the H\(_2\) chemisorption experiments. As for Pt/CeO\(_2\)/Al\(_2\)O\(_3\), the low quality of separation of XRD pattern of the metallic phase from the CeO\(_2\)/Al\(_2\)O\(_3\) support does not allow for an accurate determination of the Pt nanoparticle distribution (Fig. 4.8).
Figure 4.6: (a) XRD patterns of Pt/Al₂O₃ after reduction at 500°C for 5h. After subtraction of the signal for the Al₂O₃ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.

Figure 4.7: (a) XRD patterns of Pt/La₂O₃/Al₂O₃ after reduction at 500°C for 5h. After subtraction of the signal for the La₂O₃/Al₂O₃ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.
Figure 4.8: XRD patterns of Pt/CeO$_2$/Al$_2$O$_3$ after reduction at 500°C for 5h. After subtraction of the signal for the CeO$_2$/Al$_2$O$_3$ support, the quality of the contribution of Pt is not enough to allow a good estimation of the Pt particle size distribution.

Moreover, the Rietveld refinement of the XRD pattern for the reduced Pt/CeO$_2$/Al$_2$O$_3$ species accounts for a ~ 5.5 wt% of Pt loading, which is almost the double of the nominal Pt amount. This is a further proof of the low quality of the evaluation of the XRD pattern of platinum in this material. In contrast, Pt contents of 2.7 wt% and 2.3 wt% have been obtained for the Pt/Al$_2$O$_3$ and Pt/La$_2$O$_3$/Al$_2$O$_3$, respectively, which fits well with the nominal Pt loading (3 wt%). The low quality of the XRD diffractograms of the active phase of Pt/CeO$_2$/Al$_2$O$_3$ could be attributed to high scattering factors of CeO$_2$, the reflections of which dominate the XRD pattern. Finally, the lack of clear reflections ascribable to metallic Pt in all samples suggests a very high dispersion of Pt nanoparticles (dimension < 1nm) on the surface of the catalyst, in agreement with the H$_2$ chemisorption results.
**Ammonia Temperature Programmed Desorption (NH₃-TPD)**

The acidity of the different catalysts were determined by NH₃-TPD. NH₃ desorption from Al₂O₃-based materials is usually reported in the range between 100 – 500°C for NH₃ adsorbed on the Brønsted acidic sites (OH groups).[^49]

As Fig. 4.9 shows, the influence of La₂O₃ or CeO₂ doping results in a strong effect on the population of acidic sites and consequently on the amount of adsorbed NH₃. Pt/Al₂O₃ presents the highest amount of NH₃ adsorbed. At least two superimposed desorption peaks can be identified (~ 220 and ~ 325°C), related to weakly and medium/strongly adsorbed NH₃. The introduction of La₂O₃ and CeO₂ results in a high reduction of the amount of desorbed NH₃, together with a significant shift to lower temperatures for both desorption maxima. Since comparable surface areas were measured for all samples, these results indicate that the addition of basic promoters reduce the acidic sites number and strength. The significantly lower acidity of the La₂O₃-based system can be associated with the very high dispersion of the doping oxide on the alumina surface.

![Figure 4.9: NH₃-TPD profiles recorded for the samples reduced at 500°C: Pt/Al₂O₃ (a), Pt/La₂O₃/Al₂O₃ (b) and Pt/CeO₂/Al₂O₃ (c).](image-url)
The reduced acidity of the materials promoted by the La$_2$O$_3$ and CeO$_2$ doping justifies their better performance in the glycerol SR. The worst reforming activity observed with Pt/Al$_2$O$_3$ is therefore ascribed to the occurrence of the undesired side-reaction of dehydration / condensation catalyzed by the acid sites of the support.

4.4 Effect of CeO$_2$ and La$_2$O$_3$ doping on the catalysts stability and origin of catalyst deactivation effect

4.4.1 Characterization of exhaust catalysts

Exhaust catalysts, as obtained after aging under glycerol SR conditions, have been fully characterized in an attempt of highlighting possible eventual structural catalyst modifications as well as deactivation phenomena occurring during the catalytic process.

Physisorption and chemisorption

Table 4.3 summarizes the results of N$_2$ physisorption and H$_2$ chemisorption experiments on the aged samples. A significant reduction of the accessible Pt active sites is clearly evident. This effect may be due to the concomitant occurrence of several processes:
- partial sintering of the Pt nanoparticles
- deposition of carbonaceous residues onto the Pt active sites (coke)
- progressive occlusion of the pores onto the catalyst support

The latter point is confirmed by the N$_2$ physisorption experiments where a progressive decrease of the specific surface areas and pore volumes is recorded for all aged samples.
Table 4.3: Physisorption and chemisorption results on aged samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA(^a) (m(^2) g(^{-1}))</th>
<th>dM(^b) (nm)</th>
<th>CPV(^c) (mL g(^{-1}))</th>
<th>H/Pt(^d) (nm)</th>
<th>PS(^e) (nm)</th>
<th>CS(^f) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al(_2)O(_3) run-up at 600°C.</td>
<td>78</td>
<td>15</td>
<td>0.268</td>
<td>0.35</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Pt/La(_2)O(_3)/Al(_2)O(_3) run-up at 600°C.</td>
<td>69</td>
<td>17</td>
<td>0.161</td>
<td>0.32</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Pt/La(_2)O(_3)/Al(_2)O(_3) Stability at 350°C</td>
<td>80</td>
<td>16</td>
<td>0.270</td>
<td>0.21</td>
<td>5.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Pt/CeO(_2)/Al(_2)O(_3) run-up at 600°C.</td>
<td>78</td>
<td>15</td>
<td>0.234</td>
<td>0.42</td>
<td>2.7</td>
<td>nd(^g)</td>
</tr>
<tr>
<td>Pt/CeO(_2)/Al(_2)O(_3) Stability at 350°C</td>
<td>95</td>
<td>16</td>
<td>0.276</td>
<td>0.48</td>
<td>2.4</td>
<td>nd(^g)</td>
</tr>
</tbody>
</table>

\(^a\) Specific Surface Area from the BET analysis; \(^b\) Maximum of the BJH pore distribution calculated on the desorption branch; \(^c\) Cumulative Pore Volume; \(^d\) H/Pt ratio obtained from H\(_2\) chemisorption at -94 °C of the samples previously reduced at 500°C for 5h; \(^e\) Average Pt Particle Size obtained from H\(_2\) chemisorption assuming a spherical geometry; \(^f\) Average Pt Crystallite Size determined by powder XRD; \(^g\) Not determined.

**Powder X-Ray Diffraction (XRD)**

Calculation of the Pt nanoparticle sizes from the XRD patterns (Fig. 4.10) of the aged catalysts (after subtracting the contribution of the support) has shown an appreciable increase in the Pt nanoparticle dimensions for both Pt/Al\(_2\)O\(_3\) and Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\) (Figs. 4.11 and 4.12). This result fits well with the H\(_2\) chemisorption experiments. The H/Pt values decrease can be explained by the occurrence of the following effects:

- sintering of the Pt nanoparticles
- active sites passivation due to formation of coke deposits.
Figure 4.10: Powder XRD patterns for the aged samples: Pt/Al₂O₃ (a), Pt/La₂O₃/Al₂O₃ (b) and Pt/CeO₂/Al₂O₃ (c) after run-up activity up to 600°C and Pt/La₂O₃/Al₂O₃ (d) and Pt/CeO₂/Al₂O₃ (e) after stability tests at 350°C for 52 and 27h, respectively. The reflections of CeO₂ are marked with diamonds.

Figure 4.11: (a) XRD patterns of Pt/Al₂O₃ after glycerol steam reforming up to 600°C. After subtraction of the signal for the Al₂O₃ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.
Figure 4.12: (a) XRD patterns of Pt/La$_2$O$_3$/Al$_2$O$_3$ after glycerol steam reforming up to 600°C. After subtraction of the signal for the La$_2$O$_3$/Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.

_Thermo Gravimetric Analysis (TGA)_

A Thermo Gravimetric Analysis (TGA) performed on the exhaust catalysts has allowed for the assessment of both amount and type of carbonaceous compounds deposited onto the catalyst surface. Coupling the TGA with a quadrupole for the MS gas analysis of the volatiles has finally provided a clear identification of the decomposition products (basically H$_2$O and CO$_2$). The TGA profiles and the curves related to CO$_2$ evolution are reported in Fig. 4.13. From a perusal of Table 4.2, Table 4.3 and Fig. 4.13, it is possible to conclude that both metal sintering and coke deposition are operative in all catalytic tests.

H$_2$O evolution due to the humidity adsorbed at the catalyst surface (unreported data) with no concomitant CO$_2$ formation, and responsible for the initial catalyst weight loss, is observed below 200°C for all the analyzed samples. Above 200°C, carbonaceous deposits start to burn, with the production of only marginal amounts of H$_2$O.
As Fig. 4.13 shows, after running up experiments, Pt/Al₂O₃ exhibits the highest weight loss (6.4 wt%), with a significant CO₂ evolution between 250 and 600°C. This observation is perfectly in line with its lower catalytic activity. A high amount of carbonaceous compounds actually covers the catalyst surface during the reforming process, as a consequence of the higher acidity of the catalyst support. On the contrary, Pt/La₂O₃/Al₂O₃ and Pt/CeO₂/Al₂O₃ show a significantly lower amount of adsorbed organic residues (4.1 wt% and 1.9 wt%, respectively).

The reduced amount of carbonaceous deposits can be ultimately related to the lower acidity of the catalyst supports. Similar CO₂ evolution profiles and comparable temperature ranges for Pt/La₂O₃/Al₂O₃ and Pt/Al₂O₃ suggest a similar nature of the carbonaceous deposits. In contrast, the Pt/CeO₂/Al₂O₃ sample shows a symmetric
CO\textsubscript{2} evolution peak in a lower temperature range. This result can be reasonably ascribed to either a less graphitic nature of the coke deposits and/or to a cooperative effect of CeO\textsubscript{2} in the combustion of the carbonaceous materials. In fact, it is well known that the introduction of CeO\textsubscript{2}-based additives to a reforming catalyst can prevent the deposition of coke-based materials or favor their elimination during oxidative treatments.\textsuperscript{[15,18]}

Prolonged reactivity tests at 350°C with both Pt/La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and Pt/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} reveal the formation of a low amount of carbonaceous deposits thus suggesting that the higher the catalyst temperature the higher the amount of the coke deposits. For the Pt/La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst, the lower reaction temperature reduces the polymerization reaction (weight loss 3.3 wt%), leading to carbonaceous deposits which are easily removed during TGA (Fig. 4.13d). Finally, despite the deep and sudden loss of reforming activity, very low amount of carbonaceous deposits were removed during the TGA analysis (~ 0.5% of weight loss) around 600 – 700°C (Fig. 4.13e).

\textit{High Resolution- Transmission Electron Microscopy (HR-TEM)}

Fig. 4.14 shows representative HR-TEM images acquired for the spent Pt/La\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} after stability test under glycerol SR conditions at 350°C for 52h. Pt nanoparticles can be easily recognized in the images as dark particles and by the spacing between the lattice planes. The dimensions of the Pt nanoparticles are in the range of 2 – 3 nm, in good agreement with XRD and the size of the nanoparticles is only marginally affected by the prolonged use under glycerol SR conditions.

EDX analysis confirms the presence of lanthanum although no clear attribution to a particular phase is possible (as revealed by XRD too). The Al\textsubscript{2}O\textsubscript{3} support appears in the HR-TEM images as well defined crystallites with dimensions of 15 – 20 nm. Some examples of relatively clean particles of the support are present in the upper part of Fig. 4.14, where the lattice plane of 0-Al\textsubscript{2}O\textsubscript{3} can be observed.

Some carbonaceous amorphous regions of few nanometers have been observed on the surface of the used catalyst. However, suitable information about the spatial
distribution of carbon species on the active particles cannot be unambiguously determined. Despite this, the reduction of the H/Pt ratio measured by H₂ chemisorption suggests that the amorphous carbon deposits partially cover the Pt nanoparticles, since the real dimension of the nanoparticles is only marginally affected by their prolonged use under glycerol SR (as evidenced by XRD and HR-TEM).

![HR-TEM image](image)

Figure 4.14 Representative HR-TEM images of Pt/La₂O₃/Al₂O₃ after stability tests at 350°C for 52h.

### 4.5 Conclusions

The present study deals with the effects deriving from the addition of basic oxides (La₂O₃ and CeO₂) to Pt/Al₂O₃ catalysts for the H₂ production through glycerol Steam Reforming. The most relevant conclusions of this work can be summarized as follows:

1. Pt/Al₂O₃ catalyst promotes the H₂ production only at high temperature (> 500°C), which is ascribed to the occurrence of side reactions promoted by the acidic sites
on the Al₂O₃ support. A lot of undesired by-products formed by dehydration / polymerization reactions were detected in the liquid effluent from the reactor.

2. La₂O₃ and CeO₂ deposited onto Al₂O₃ improve the catalytic performances of the Pt nanoparticles, decreasing the acidity of the support, as evidenced by NH₃-TPD. Such a metal oxide doping allows glycerol to be completely converted into syngas already at 350°C efficiently promoting, at the same time, the Water-Gas Shift reaction. Finally, little amounts of CH₄ are produced as a result of concomitant hydrogenation reactions.

3. The addition of La₂O₃ and CeO₂ significantly improves the catalyst stability as a consequence of the reduced acidity of the Al₂O₃ support. Moreover, the amount of carbon deposits is significantly reduced when compared with the plain Pt/Al₂O₃ sample. Despite these positive effects, the CeO₂-doped catalyst deactivates quickly after 20 hours at 350°C while a higher stability is shown by the La₂O₃-doped sample (over 50h).

4. The detailed characterization of the fresh and spent catalysts allows a better understanding of our doped catalysts behavior under glycerol SR conditions. The slight deactivation observed for Pt/La₂O₃/Al₂O₃ catalyst can be related to coke deposition on the catalyst surface, resulting in a significant Pt coverage (as assessed by H₂ chemisorption and HR-TEM) The effect of Pt sintering or surface area decrease is only marginal.

References


Chapter V

Ammonia decomposition

5.1 Ru based catalysts

5.1.1 Introduction
5.1.2 Catalytic activity results
5.1.3 Catalysts stability evaluation
5.1.4 Catalysts characterization

• Temperature Programmed Reduction (TPR)
• Powder X-Ray Diffraction (XRD)
• XRD characterization of exhaust catalysts
• Textural characterization: Physisorption measurements
• Static and dynamic H₂-Chemisorption
• Temperature Programmed Surface Reaction (TPSR)

5.1.5 Conclusions

5.2 Fe/Mo based catalysts: preliminary results

5.2.1 Introduction
5.2.2 Catalysts characterization
• Textural characterization: Physisorption measurements 133
• Temperature Programmed Reduction (TPR) 134
• Powder X-Ray Diffraction (XRD) 137

5.2.3 Catalytic activity: preliminary results 141

References 143
5.1 Ru based catalysts

5.1.1 Introduction

The interest for non conventional fuels has significantly increased in the last years because of the environmental pollution problem generated by the use of fossil fuels and for the progressive difficulty in the supply of the large demand of energy.[1] Many alternatives to fossil fuels are under investigation worldwide. The most promising seem to be (i) renewable fuels obtained from second and third generation biomasses and (ii) H₂ in combination with fuel cells, but also other possibilities are considered. Between these latter, ammonia (NH₃) is investigated as a possible fuels in some applications. In fact, it is an interesting energy vector because it could be used for the production of H₂ (NH₃ has an H₂ content of 17.7wt%, higher than that of methanol). Ammonia production is a well known technology (large scale plants exist since many decades) and its capillary distribution could be easily achieved using the existing infrastructures.[2-4] On-site or on-board H₂ production by NH₃ decomposition can produce hydrogen without concomitant COₓ release. Finally, ammonia can be used as fuel for Internal Combustion Engines (ICE). However, the toxicity and flammability concerns of ammonia could constitute serious limits for its utilization. To compensate these problems, efforts have been made to fix ammonia into less dangerous compounds, to be reversibly released and stored on-board for vehicular applications, preventing any risks related to a crash. In this respect, a number of publications describes H₂ release from amine boranes (such as H₃NBH₃),[5-8] although these materials are difficult to be regenerated.[9-11] As an alternative, ammonia can be reversibly stored in other solid compound, such as Mg(NH₃)₆Cl₂[12-14]

H₂ can be produced by the endothermic NH₃ decomposition following the equilibrium:

\[ 2\text{NH}_3 = \text{N}_2 + 3\text{H}_2 \quad \Delta H^\circ = 92 \text{ KJ mol}^{-1} \quad \text{Eq. 5.1} \]
NH\(_3\) conversion is therefore favored at high temperature and low pressure operating conditions. Unfortunately, the performances of Polymer Electrolyte Membrane Fuel Cells (PEM-FC) are strongly reduced by the presence of even very low amounts of NH\(_3\) in the gas stream fed at the anode (even 1ppm of NH\(_3\) has detrimental effects).\(^{[15]}\) Since the NH\(_3\) decomposition is an equilibrium reaction, it is practically impossible to avoid the presence of traces of NH\(_3\) in the effluents and some purification steps are required (filters to trap NH\(_3\) or separation of H\(_2\) by membranes). On the contrary, Solid Oxide Fuel Cells (SOFC) can operate using directly ammonia as fuel,\(^{[16,17]}\) although some problems must be solved. The use of oxide ion conductors (doped ZrO\(_2\) or doped CeO\(_2\)) as electrolyte results in the oxidation of NH\(_3\) by O\(^+\) ions, resulting in a significant production of NO\(_X\). In this case, a DeNO\(_X\) system (using the same NH\(_3\) as reducing agent) must be mounted to purify the exhaust gases. More interesting is the use of a proton conducting electrolytes (such as doped BaCeO\(_3\)).\(^{[18,19]}\) NH\(_3\) is decomposed to N\(_2\) and H\(^+\) releasing electrons at the anode, H\(^+\) migrate to the cathode, where they react with gaseous O\(_2\) and the electrons (from the electrical circuit) producing H\(_2\)O. In this context, the decomposition of ammonia to H\(_2\)/N\(_2\) mixture before reaching the SOFC’s anode is advantageous because the endothermic NH\(_3\) decomposition removes heat from the cell, decreasing the performances.\(^{[20]}\)

The use of ammonia as fuel for ICE is an old but promising technology, although in this case moderate amounts of NO\(_X\) are also produced and an abatement system is required to reduce the pollutant emissions with the exhausts.\(^{[21]}\) Ammonia fueled engines could be obtained by slightly modifying the conventional spark ignition engines. Due to the high autoignition temperature (651°C), ammonia needs a flame accelerator, such as hydrogen in order to burn efficiently. Therefore, also in the case of ICE, ammonia should be at least in part decomposed to H\(_2)/N\(_2\) mixtures, in order to maintain an acceptable combustion in the engine. A minimum of 5vol% of H\(_2\) is required in gas stream for the normal operation of the ICE, while a higher H\(_2\) content is beneficial during the starting procedure.\(^{[21]}\) In this context, the development of
heterogeneous catalysts active in the temperature range of 400 – 500°C is a must. The waste heat (from the SOFC or the ICE) can be used to sustain the endothermic reaction of H₂ production needed for the operation of the system.

Many different metals have been tested as active component for ammonia decomposition, in particular group VIII metals (Fe, Ni, Ru, Ir, Co, Pt). However the catalytic activities reported were very low below 600°C. Ru is reported as the most active. The performances of Ru-based catalysts are strongly affected by the nature of the support and by the mean crystallite size of Ru nanoparticles, with an optimum around 2 nm. Unfortunately, Ru-based catalysts usually present a quite low metal dispersion and efforts have been made in order to reduce the metal particle size with the careful control of the preparation conditions.

Among the studied supports, graphitic carbon and carbon nanotubes (CNTs) are the most suitable support for Ru catalysts. However, the high cost of CNTs still constrains their large scale use. NH₃ could be completely decomposed over K-promoted Ru (5wt%)/CNT catalyst at relatively low temperature (450 – 500 °C) and even at high space velocity. The good performance of Ru/CNT catalyst is related with (i) the presence of –COOH and –OH groups on the CNT surface responsible for anchoring of Ru entities and (ii) the confinement effect of Ru nanoparticles inside the CNT pores (with a inner diameter of 3 – 10 nm). Although the catalyst shows a relatively good stability of the catalytic activity, carbon stability against gasification is still an open question.

Basic oxides are more efficient as supports for Ru catalysts with respect to acidic oxides. Zheng et al. reported that Ru (5wt%)/Al₂O₃ catalyst leads to the complete conversion of ammonia at 550°C, while Choudhary et al. obtained the complete conversion of NH₃ only at 650°C using Ru (10wt%)/SiO₂ under similar reaction conditions. Zhang et al. reported that Ru (2.8wt%)/MgO catalyst prepared by a polyol reduction method (obtaining a material similar to our embedded catalysts – see below) shows approximately 80% of NH₃ conversion at 500°C. The complete conversion was achieved by the use of Cs as promoter deposited by impregnation. Yin et al. reported that high NH₃ conversion can be achieved using a superbasic
support, such as ZrO(OH)$_2$ gel digested by refluxing in a KOH aqueous solution (denoted as K-ZrO$_2$-KOH). This support is amorphous and contains significant amount of K$^+$. Ru (loading ~5wt%) was deposited with a high metal dispersion from Ru(acac)$_3$ or RuCl$_3$, evidencing the poisoning effect due to residual chlorides.$^{[32]}$ Ru/K-ZrO$_2$-KOH from Ru(acac)$_3$ presents a very good stability at 350°C under severe reaction conditions (high space velocity) within a 300h period, with rapid aging at higher temperature (up to 600°C) in between.

We present the results regarding the preparation and the functional and structural/morphological characterization of an active and stable Lanthanum Stabilized Zirconia (LSZ)-based catalysts containing 3wt% of Ru. The catalysts were prepared by an innovative synthetic methodology which allows the encapsulation of the active metal phase inside the oxide matrix, with the aim to avoid sintering of the metal and the catalyst deactivation during the reaction (see chapter II). The adopted embedding strategy is largely reported in the literature for the preparation of heterogeneous catalysts with peculiar activity and stability.$^{[33]}$ Heterogeneous catalysts comprising embedded Ru nanoparticles have been previously reported in the literature, with a variety of supports, preparation method and test reactions.$^{[34-37]}$ The embedding methodology was successfully employed by our group in other processes involved in the H$_2$ production, such as methane partial oxidation$^{[38,39]}$ and ethanol steam reforming.$^{[40,41]}$

Two different embedding strategies were adopted in this study to prepare Ru@LSZ catalysts. Ru nanoparticles were synthesized by reduction of RuCl$_3$ in the presence of two different protecting agents. In the first case, Ru nanoparticles were prepared by alcohol reduction in the presence of a polymer (Poly Vynil Pyrrolidone – PVP), obtaining a deep purple metal nanoparticles suspensions (method DP).$^{[42]}$ In the second case, Ru nanoparticles formed by NaBH$_4$ reduction were protected by N-hexadecyl-N-(2-hydroxyethyl)-N,N-dimethyl ammonium bromide, a cationic surfactant denoted as HEAC16Br (method NaBH$_4$).$^{[43]}$ Around the nanoparticles, mixed La/Zr hydroxides were deposited. After various post synthesis treatments, embedded Ru nanoparticles into the ZrO$_2$-based oxides were obtained. The
performances of the embedded catalysts were compared with those of catalysts prepared by conventional impregnation (Ru/LSZ).

5.2.2 Catalytic activity results

Fig. 5.1 shows the activity for NH$_3$ decomposition of pre-reduced embedded and impregnated Ru(3wt%)-LSZ catalysts. Catalytic tests were performed under atmospheric pressure and with pure NH$_3$. Both high and low space velocities were investigated. It is evident that the samples prepared by the embedding methods show better activity with respect to the samples prepared by classical impregnation.

Figure 5.1: Catalytic activity on NH$_3$ decomposition for Ru-LSZ catalysts. Pretreatment: reduction in-situ in flowing H$_2$ (35 mL min$^{-1}$) at 800°C for 3h. Conditions: (a) GHSV = 4000 mL g$^{-1}$ h$^{-1}$; (b) GHSV = 30000 mL g$^{-1}$ h$^{-1}$.

Over the embedded catalysts, NH$_3$ conversion starts above 300°C, while over the impregnated ones at 400°C. The NH$_3$ conversion over Ru@LSZ-DP is slightly higher than that obtained for Ru@LSZ-NaBH$_4$. Significant differences in the
ammonia conversion in all the range of temperature is observable: the light-off temperatures (T50 – defined as the temperature corresponding to a 50% NH₃ conversion) for the embedded catalysts is at least 200°C lower than those of the corresponding impregnated samples. Two reactivity cycles were performed on the various catalysts, without evidencing any appreciable deactivation.

Tests on other Ru-based catalysts are reported in the literature under the same reaction conditions (GHSV = 30000 mL g⁻¹ h⁻¹). [25,26,31] Under similar conditions, Ru@LSZ-DP presents the same ammonia conversion than K-promoted Ru(5wt%)/CNTs of Yin et al.[25], the most active catalysts reported in literature data. Notably, the metal loading in our embedded catalysts is lower than that of the catalysts usually reported.

5.2.3 Catalysts stability evaluation

An important issue on the development of any new heterogeneous catalysts is the stability of the materials under prolonged exposure to the reaction mixture. The performances of the embedded Ru@LSZ catalysts and of the corresponding reference impregnated Ru/LSZ-NaBH₄ were studied for ammonia decomposition at 500°C over a period of 120h (Fig. 5.2) Such a temperature represents the technical limit to the operation of the NH₃ decomposition in combination with an ICE. The stability of the Ru/LSZ-DP catalyst was not studied because of its very low activity. All the catalysts present NH₃ conversion comparable to that observed during the run-up experiments at this temperature (Fig. 5.1). Fig. 5.2 shows that NH₃ conversion remains almost constant for all the catalysts over the period of the stability test.
To investigate more realistic conditions for a widespread utilization of ammonia as energy vector, reactivity tests were also performed using technical ammonia, that contains approximately 300 ppm of hydrocarbons. Identical activity and stability results were obtained, indicating that the small impurities of the feedstock have a negligible effect on the catalysts’ performances.

5.1.4 Catalysts characterization

Temperature Programmed Reduction (TPR)
The reduction properties of the as prepared samples were examined by Temperature Programmed Reduction (TPR) under flowing H₂ (5%)/Ar (Fig. 5.3). As a general feature, all the samples, both embedded and impregnated, reveal multiple reduction processes at low temperature (below 250°C). The positions of the
reduction maxima are strongly dependent on the reaction conditions (mass of catalysts, gas flow and composition, heating rate).

![Figure 5.3: Temperature Programmed Reduction (TPR) profiles for Ru@LSZ-DP (a), Ru@LSZ-NaBH₄ (b), Ru/LSZ-DP (c) and Ru/LSZ-NaBH₄ (d).](image)

However, it is usually accepted that the reduction at low temperature is ascribable to highly dispersed RuOₓ species while at higher temperature the reduction of well crystallized RuO₂ particles is operative. Moreover, the reduction temperature is effected by the nature of the support. Consistently, the different low temperature H₂ consumption of the samples based on identical supports can be justified mainly considering a different size and distribution of RuOₓ particles. Significantly, a reduction peak at high temperature (600 – 700°C) is observed, especially with the samples prepared by the DP method. The reduction of RuOₓ species was never reported in the literature in this temperature range. Although this reduction process could be partially ascribed to such extent of Buoyancy effect, the reduction of RuOₓ species strongly interacting with the support or almost fully embedded into the oxide matrix appears as more reasonable explanation for the H₂
consumption at high temperatures. In fact, the high temperature peak is more pronounced in the samples having lower specific surface area (see below), where the contribution of the Buoyancy effect should be minimal. The presence of metal oxide species strongly interacting with the support have already been reported for catalysts prepared by the embedding approach.\textsuperscript{[38]}

Consistently with the TPR results, in order to fully reduce the metal species before the reactivity tests, a pretreatment in H\textsubscript{2} flow (35 mL min\textsuperscript{-1}) at 800°C for 3h was applied to all the materials. This pre-treatment serves as activation treatment (to fully reduce RuO\textsubscript{X} species) and as an aging protocol, since the samples were not yet subjected to any thermal treatment above 500°C.

\textit{Powder X-Ray Diffraction (XRD)}

Powder XRD analysis of the samples after different thermo-chemical treatments evidences great differences among the various materials studied.

Fig. 5.4 presents the XRD patterns of the samples after calcination at 500°C. The XRD patterns of the calcined samples are dominated by broad reflections attributable to LSZ support. The presence of amorphous materials can not be excluded (especially in Fig. 5.4, traces b and c). Weak and very sharp reflections of RuO\textsubscript{2} were generally observed, indicating the presence of very large RuO\textsubscript{2} particles (crystallite size 30 – 100 nm). In the case of the Ru/LSZ-DP sample, the presence of NaCl is evidenced, likely originated during the synthesis of the catalyst by reaction of the chlorides from RuCl\textsubscript{3} with impurities of sodium.

XRD patterns of the samples after standard activation in H\textsubscript{2} (800°C for 3h) and after aging under NH\textsubscript{3} decomposition conditions (2 run-up cycles at GHSV = 30000 mL g\textsuperscript{1} h\textsuperscript{-1}) are reported in Fig. 5.5. Depending on the preparation method and treatment, different crystalline phases were observed. The analysis of each XRD pattern allows for a semi-quantitative determination of the structure and composition of the various phases present. Table 5.1 summarizes the crystal phases identified and the mean crystallite size for each phase.
Figure 5.4: Powder XRD patterns of the calcined samples: Ru@LSZ-DP (a), Ru@LSZ-NaBH$_4$ (b), Ru/LSZ-DP (c) and Ru/LSZ-NaBH$_4$ (d).

Figure 5.5: Powder XRD patterns of Ru@LSZ-DP (a), Ru@LSZ-NaBH$_4$ (b), Ru/LSZ-DP (c) and Ru/LSZ-NaBH$_4$ (d) after activation pre-treatment (reduction in H$_2$ flow at 800°C for 3h).
Table 5.1: Results from the analysis of the XRD patterns of embedded (Ru@LSZ) and impregnated (Ru/LSZ) samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activated [a]</th>
<th>After run-up [b]</th>
<th>After stability tests [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase</td>
<td>Wt %</td>
<td>CS [d] (nm)</td>
</tr>
<tr>
<td>Ru@LSZ-DP</td>
<td>Tetragonal LSZ</td>
<td>46.5</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Cubic LSZ</td>
<td>14.9</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Na₂ZrO₃</td>
<td>38.6</td>
<td>42</td>
</tr>
<tr>
<td>Ru@LSZ-NaBH₄</td>
<td>Tetragonal LSZ</td>
<td>99.5</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>0.5</td>
<td>120</td>
</tr>
<tr>
<td>Ru/LSZ-DP</td>
<td>Tetragonal LSZ</td>
<td>44.7</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Cubic LSZ</td>
<td>10.2</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Monoclinic ZrO₂</td>
<td>41.7</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>3.4</td>
<td>70</td>
</tr>
<tr>
<td>Ru/LSZ-NaBH₄</td>
<td>Tetragonal LSZ</td>
<td>96.8</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>3.2</td>
<td>78</td>
</tr>
</tbody>
</table>

[a] After standard activation pre-treatment (reduction in H₂ flow at 800°C for 3h). [b] Activated sample after 2 cycles under NH₃ decomposition conditions (GHSV = 30000 mL g⁻¹ h⁻¹). [c] Activated sample after stability tests under NH₃ decomposition conditions (GHSV = 30000 mL g⁻¹ h⁻¹) for 110h at 500°C. [d] Crystallite Size calculated applying the Scherrer’s equation. [e] The Rietveld results for this sample is semi-quantitative, since the exact composition of the phases is not known and some reflections are not clearly identified.
The samples prepared by the DP method (embedded and impregnated) are composed of a complex mixture of phases. The XRD pattern of the reduced Ru@LSZ-DP sample is dominated by the tetragonal structure (space group P4_2/nmc) of the LSZ. The increase in the cell parameters with respect to those of pure tetragonal ZrO_2 (JCPDS n° 50-1089: a = 0.35984 nm, c = 0.51520 nm) and the very low tetragonal distortion (from the cell parameters, \(a^2/(a^2c)\) of 1.005 can be calculated) clearly evidences the incorporation of La into the ZrO_2 oxide, as a result of the larger ionic radius of La(III) with respect to Zr(IV) (for a 8-fold coordinates site, 0.130 nm and 0.098 nm, respectively). The XRD pattern of the reduced Ru@LSZ-DP evidenced also the presence of monoclinic Na_2ZrO_3 and of a cubic LSZ phase with fluoritic structure. The cell parameters of Na_2ZrO_3 are close to those of the pure monoclinic phase (JCPDS n° 35-0770: a = 0.56233 nm, b = 0.97491 nm, c = 1.11270 nm, \(\beta = 99.983^\circ\)). The formation of Na_2ZrO_3 is an indication of the presence of large amounts of Na^+ adsorbed on the solid material as a consequence of the precipitation of the La/Zr mixed hydroxides with NaOH. The presence of Na^+ in the material could also affect the structure of the tetragonal LSZ phase, reducing the tetragonal distortion. Finally, accordingly to the empirical formula proposed by Kim, from the value of the cell parameter (0.5309 nm) of the cubic LSZ phase it is possible to calculate the composition of Zr_{1-x}La_xO_{2-x/2}. (x = 0.385). This is an indication of an enrichment in La with respect to the nominal composition of the LSZ oxide. However, the inclusion of Na^+ as impurity in the La/Zr mixed hydroxides can not be ruled out. Notably, no reflection clearly related to Ru-based phases were observed, suggesting that Ru is present as highly dispersed nanoparticles. This is in good agreement with the high catalytic activity demonstrated by this sample. Consistently, Zheng et al. reported that the maximum in the reaction rate for NH_3 decomposition is observed when Ru nanoparticles of \(\sim 2\) nm are present. Moreover, Na_2ZrO_3 or Na^+ could act as promoters for the reaction. In fact, it is well known the beneficial effect of basic oxides as supports and/or of the presence of alkali metals as promoters on Ru catalysts. To demonstrate the effect of the presence of Na^+ or Na_2ZrO_3 on the catalytic performances of our Ru@LSZ-DP catalyst,
attempts were done to (i) reduce the presence of Na⁺ by washing the gel with diluted HNO₃ (1%) and (ii) to re-introduce sodium by impregnating the washed material with NaNO₃ (soaking the catalyst powder into an aqueous solution of NaNO₃ 2M). After washing, a lower catalytic activity was observed (Fig 5.6).

![Figure 5.6: Catalytic activity on NH₃ decomposition for Ru@LSZ catalysts after modification of the synthesis procedure in order to evaluate the effect of Na⁺ impurities. Pre-treatment: reduction in-situ in flowing H₂ (35 mL min⁻¹) at 800°C for 3h. Conditions: (a) GHSV = 4000 mL g⁻¹ h⁻¹; (b) GHSV = 30000 mL g⁻¹ h⁻¹.](image)

The XRD pattern of the reduced sample (Fig. 5.7) shows the formation of a solid solution La₂O₃ – ZrO₂ with tetragonal structure and of large Ru crystallites (167 nm). This latter observation can be a result of the possible Ru re-dispersion during the washing treatment. After impregnation of the washed material with NaNO₃, a further decrease of the catalytic activity was observed (Fig 5.6). The XRD pattern of the activated sample show the presence of tetragonal LSZ, monoclinic ZrO₂, metallic Ru (mean crystallite size of 124 nm) and a cubic phase with patterns compatible with
those of Na₂O (although its cell parameter is strongly reduced with respect to the theoretical value of Na₂O – 0.5392 vs 0.555 nm).

![Figure 5.7: Powder XRD patterns of Ru@LSZ-DP-Washed and Ru@LSZ-DP-Washed + NaNO₃; (b) Rietveld analysis of the Ru/LSZ-DP-Washed sample after standard activation (reduction in H₂ flow at 800°C for 3h); (c) Rietveld analysis of the Ru/LSZ-DP-Washed + NaNO₃ sample after standard activation (reduction in H₂ flow at 800°C for 3h).]

The situation of the activated Ru/LSZ-DP (prepared by impregnation) is more complex than that of the corresponding embedded sample. The oxide support is composed of a mixture of tetragonal LSZ (major phase), monoclinic ZrO₂ and cubic LSZ. This latter phase has a cell parameter shorter than that of the corresponding phase observed for the reduced Ru@LSZ-DP, suggesting a different degree of substitution of Zr with La and/or Na. Un-identified reflections in the Rietveld analysis indicate the presence of at least one other abundant compound. The most
intense un-identified reflections resemble the XRD patterns of cubic NaCl, although with a significant lengthening of the cell parameter. Notably, in this case clear and sharp reflections related to metal Ru are observed, indicating the presence of very large Ru particles (~70nm). Presence of unknown amount of Na – based compound do not allow quantification of the others species.

The XRD analysis of the samples prepared following the NaBH\(_4\) method is significantly less complex. A solid solution between ZrO\(_2\) and La\(_2\)O\(_3\) with a tetragonal structure (designed as tetragonal LSZ) constitute the oxide support. No reflections related to cubic LSZ, monoclinic ZrO\(_2\) or monoclinic Na\(_2\)ZrO\(_3\) are observed. This result suggest that the washing procedure adopted to remove bromide ions and the excess of surfactant used for the preparation of Ru nanoparticles is also effective in the elimination of the Na\(^+\) impurities. Notably, the catalytic activity of Ru@LSZ-NaBH\(_4\) is only a slightly lower than that of Ru@LSZ-DP, indicating that the promotional effect of Na\(_2\)ZrO\(_3\) is not essential to obtain high ammonia conversions. Weak but very sharp reflections assigned to metallic Ru are also observed. In the case of the impregnated Ru/LSZ-NaBH\(_4\) sample, the Rietveld analysis accounts for a 3.2 wt% of Ru (instead of the nominal 3 wt%) with very large crystallites (~78 nm). On the contrary, the amount of Ru estimated for the embedded Ru@LSZ-NaBH\(_4\) is quite low (0.5 wt%). Furthermore, very large Ru crystallites were observed (~120 nm). The low amount of Ru estimated by Rietveld analysis, in combination with the good catalytic activity and the acceptable Ru accessibility (see H\(_2\) chemisorption section) suggests the presence of a large number of highly dispersed Ru nanoparticles, not detectable by XRD. A partial re-dissolution of some small Ru nanoparticles during the washing procedure can not be excluded. The re-deposition of Ru on the external surface of the material could account for the presence of these large Ru particle. In fact, a significant sinterization of the noble metal re-deposited on the external surface of the support and, therefore, not protected can occur during the calcination and reduction steps.
**XRD characterization of exhaust catalysts**

After aging under NH₃ decomposition, only minor modification of the structural properties of the catalysts were evidenced. Fig. 5.8a shows the XRD patterns of the samples after aging under run-up experiments while after stability test the samples present the XRD pattern reported in Fig. 5.8b. Notably, no significant differences in the Ru crystallite size is observed. The only significant difference observed regards with the Ru@LSZ-DP sample. After run-up experiments (up to 800°C), the amount of Na₂ZrO₃ decreases forming tetragonal and pyrochlore-like LSZ. On the contrary, after stability test (prolonged exposure to NH₃ at 500°C), the amount of tetragonal LSZ decreases forming Na₂ZrO₃ and pyrochlore-like LSZ. Nevertheless, the activity and stability results suggest that the evolution of the phases in the oxide do not appreciably influence the catalytic activity and the dimension of the Ru nanoparticles.

![Figure 5.8: Powder XRD patterns of Ru@LSZ-DP (a), Ru@LSZ-NaBH₄ (b), Ru/LSZ-DP (c) and Ru/LSZ-NaBH₄ (d) after aging under NH₃ decomposition after run-up experiments (left part) and after stability tests (right part).](image)
Textural characterization: Physisorption measurements

The results of the textural characterization of the calcined samples are summarized in Table 5.2. All the samples present type IV isotherms with hysteresis loop typical of mesoporous materials.\textsuperscript{[50]} The t-plot analysis reveals that the microporous volume is always negligible. After all the thermo-chemical treatments considered, the samples prepared following the DP method present lower surface area and pore volume and larger pores than those prepared by the NaBH\textsubscript{4} method. The last ones are homogeneous and the better textural properties (Table 5.2) are the result of the stabilizing effect of the formation of ZrO\textsubscript{2}-La\textsubscript{2}O\textsubscript{3} solid solution. Moreover, in the preparation of the NaBH\textsubscript{4} samples, the precipitate is carefully washed to remove Br\textsuperscript{-} and Na\textsuperscript{+} ions and the excess of surfactant, while in the DP method the excess of PVP is removed only by filtration of the mother liquor. The deep sinterization of the DP materials could be the result of the presence of a various crystallographic phases and of a possible local over-heating consequent to the polymer combustion. Finally, in the NaBH\textsubscript{4} preparation method, the large amount of a cationic surfactant (HEAC16Br) can act as directing agent during the gel formation, leading to a material with high surface area similarly to that previously reported for ZrO\textsubscript{2}-based material preparation.\textsuperscript{[51,52]}

After standard activation pre-treatment (reduction in H\textsubscript{2} flow at 800°C for 3h), all the samples undergo a significant decrease of surface area and pore volume, as a result of the sintering phenomena provoked by the reduction at high temperature. Despite its good catalytic activity (Fig. 5.1), the embedded Ru@LSZ-DP sample exhibits a low surface area (Table 5.2). On the other hand, the embedded Ru@LSZ-NaBH\textsubscript{4} sample shows a smaller decrease of surface area and pore volume as a result of the better thermal stability of the tetragonal ZrO\textsubscript{2}-La\textsubscript{2}O\textsubscript{3} solid solution. Comparable surface areas were observed between the embedded catalysts and the respective impregnated samples. These results suggest that the catalytic activity is mainly influenced by the Ru crystallite size, not by the surface area of the support.
Table 5.2. N$_2$ physisorption results for embedded (Ru@LSZ) and impregnated (Ru/LSZ) samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Calcined $^{[a]}$</th>
<th>Activated $^{[b]}$</th>
<th>After run-up $^{[c]}$</th>
<th>After stability tests $^{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SSA $^{[e]}$ (m$^2$ g$^{-1}$)</td>
<td>d$_M$ $^{[f]}$ (nm)</td>
<td>SSA $^{[e]}$ (m$^2$ g$^{-1}$)</td>
<td>d$_M$ $^{[f]}$ (nm)</td>
</tr>
<tr>
<td>Ru@LSZ-DP</td>
<td>56</td>
<td>15/26 $^{[h]}$</td>
<td>0.46</td>
<td>12</td>
</tr>
<tr>
<td>Ru@LSZ-NaBH$_4$</td>
<td>171</td>
<td>-</td>
<td>0.35</td>
<td>57</td>
</tr>
<tr>
<td>Ru/LSZ-DP</td>
<td>45</td>
<td>10</td>
<td>0.15</td>
<td>5</td>
</tr>
<tr>
<td>Ru/LSZ-NaBH$_4$</td>
<td>144</td>
<td>7</td>
<td>0.35</td>
<td>50</td>
</tr>
<tr>
<td>LSZ-DP</td>
<td>46</td>
<td>10</td>
<td>0.15</td>
<td>2</td>
</tr>
<tr>
<td>LSZ-NaBH$_4$</td>
<td>144</td>
<td>7</td>
<td>0.35</td>
<td>62</td>
</tr>
</tbody>
</table>

$^{[a]}$ After calcination in air at 500 °C for 5 h. $^{[b]}$ After standard activation pre-treatment (reduction in H$_2$ flow at 800°C for 3h). $^{[c]}$ After 2 cycles under NH$_3$ decomposition conditions (GHSV = 30000 mL g$^{-1}$ h$^{-1}$). $^{[d]}$ After stability tests under NH$_3$ decomposition conditions (GHSV = 30000 mL g$^{-1}$ h$^{-1}$) for 110h at 500°C. $^{[e]}$ Specific Surface Area. $^{[f]}$ Maxima of the pore distribution calculated by BJH analysis of the desorption branch of the N$_2$ isotherm. $^{[g]}$ Cumulative Pore Volume. $^{[h]}$ Bimodal distribution.
Finally, the textural properties of the samples are only marginally affected by the aging under NH₃ decomposition reaction, both during run-up tests or long term stability tests.

**Static and dynamic H₂ chemisorption**

H₂ chemisorption experiment were performed with the aim of further investigating the accessibility of the metal nanoparticles. The measurements were performed both under static and dynamic conditions in order to better evaluate the accessibility of Ru. It is important to underline that, among all the metals, the determination of Ru dispersion by chemisorption is particularly tricky, since H₂ adsorption kinetic is quite slow. Many efforts are reported to establish the best experimental conditions for the determination of the Ru dispersion by chemisorption.[53-55] Okal et al.[53] demonstrated that, operating at 100°C and with an equilibration time of at least 1h, static H₂ chemisorption provides reliable values of the Ru dispersion. Similar experimental conditions were used in this study. The results are summarized in Table 5.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Static H₂ chemisorption [a]</th>
<th>Dynamic H₂ chemisorption [b]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H/Ru [c]</td>
<td>Area [d] (m² g⁻¹)</td>
</tr>
<tr>
<td>Ru@LSZ-DP</td>
<td>0.262</td>
<td>2.87</td>
</tr>
<tr>
<td>Ru@LSZ-NaBH₄</td>
<td>0.190</td>
<td>2.08</td>
</tr>
<tr>
<td>Ru/LSZ-DP</td>
<td>0.026</td>
<td>0.29</td>
</tr>
<tr>
<td>Ru/LSZ-NaBH₄</td>
<td>0.040</td>
<td>0.44</td>
</tr>
</tbody>
</table>

[a] Static chemisorption was measured on the samples at 100°C in the 25 – 400 torr pressure range. The reversible adsorption was subtracted by the double isotherm method. [b] Dynamic chemisorption was measured on the samples at 100°C injecting by pulse known doses of reactive probe gas. The reversible adsorption was subtracted by the double isotherm method. [c] Calculated using a H:Ru = 1:1 stoichiometry. [d] Metal Surface Area per gram of catalyst. [e] Particle size.
The sample Ru@LSZ-DP shows relatively high static H₂ chemisorption capability, suggesting the presence of small Ru nanoparticles. This is in agreement with the absence of reflections related to Ru in the XRD pattern of this sample (Fig. 5.5, trace a). Nevertheless, by dynamic H₂ chemisorption a lower H/Ru value is evidenced. In all the other cases, the results obtained using the two techniques are comparable and in good agreement with the indication obtained from the XRD patterns of the corresponding reduced samples. The relatively high H/Ru obtained for the activated Ru@LSZ-NaBH₄ is another indication of the presence of an appreciable amount of small Ru nanoparticles, partially embedded into LSZ, together with a fraction of large Ru particles evidenced by XRD.

The static H₂ chemisorption experiments demonstrated that the Ru nanoparticles are accessible to the gas phase reagents, evidencing that the embedding preparation does not result in a complete occlusion of the metal phase. Furthermore, the embedded catalysts present the highest Ru dispersion and the highest catalytic activity. On the other hand, the impregnated samples present a very low metal surface area (Table 5.3), large Ru crystallites (from XRD) and the worst catalytic performances.

In the case of the Ru@LSZ-DP sample, where static H₂ chemisorption suggest the presence of the smallest Ru nanoparticles, dynamic H₂ chemisorption reveals a H/Ru significantly lower than that obtained by the static technique. Although presence of large pores is evidenced in this sample, this result could be at least partially related to gas diffusional limitations. Moreover, an effect of the small Ru particle size in the H₂ adsorption kinetic can not ruled out. In fact, a better agreement between the two techniques is obtained when very large Ru particles are present as in the impregnated samples. In the case of the Ru@LSZ-NaBH₄ sample, where H₂ could be easily adsorbed on the large particles and transferred to the smaller by spillover through the support, enabling a realistic determination of the Ru particle size also by dynamic H₂ chemisorption.
Temperature Programmed Surface Reaction (TPSR) of adsorbed ammonia were conducted to further investigate the differences in the samples investigated (Fig. 5.9). After saturation of the surface with NH₃ at 110°C, the desorption of various species were observed. The main species revealed during the heating ramp are H₂, N₂, NH₃ and H₂O (from the support).

No significant evolution of species different other than H₂O (not reported) is observed for the Ru/LSZ-DP sample, that possess low surface area (5m² g⁻¹) and very low metal dispersion (H/Ru = 0.026 by static H₂ chemisorption). This results suggests that the amount of NH₃ adsorbed on this material is negligible, in agreement with the very low activity of this catalyst. On the contrary, the samples with high surface area (Ru/LSZ-NaBH₄) or high metal dispersion (Ru@LSZ-DP) or both (Ru@LSZ-NaBH₄), show significant desorption of H₂, N₂ and NH₃.

Figure 5.9: Temperature Programmed Surface Reaction (TPSR) experiments after NH₃ adsorption at 110°C on Ru@LSZ-DP (a), Ru@LSZ-NaBH₄ (b), Ru/LSZ-DP (c) and Ru/LSZ-NaBH₄ (d).
The amounts of desorbed species from the embedded catalysts is larger than those observed for the correspondent impregnated ones, in agreement with the better activity of the materials prepared by the embedding procedures. Moreover, the samples following the NaBH₄ method desorb a larger amount of products, in agreement with their larger surface area.

The trend in the peak temperature of the different species (corresponding to the maximum of the desorption peak) well agrees with the catalytic performances of the materials and with their morphological characteristics. The samples prepared following the NaBH₄ method show peak temperatures of 385°C for H₂, 325°C for N₂ and 250°C for NH₃. The highest intensity observed for the Ru@LSZ-NaBH₄ can be related to the highest metal dispersion, which favors NH₃ adsorption. On the other hand, the Ru@LSZ-DP sample, which demonstrated the best catalytic activity, shows lower peak temperatures (345°C for H₂, 270°C for N₂ and 260°C for NH₃).

The lowering of desorption temperatures for the Ru@LSZ-DP catalyst with respect to those of the Ru@LSZ-NaBH₄ could be related to the presence of Na₂ZrO₃. In fact, it is well known the promotional effect of basic supports[^31,^32] or alkali metal as promoters[^25,^30-^32] of the activity of Ru catalysts. A study of the dissociative chemisorption and associative desorption of N₂ on Ru/MgO catalysts, Hinrichsen et al.[^56] showed that, after impregnation with CsNO₃, the temperature for N₂ desorption from a surface previously saturated with N atoms (from N₂ dissociation) strongly decreased. Moreover, studying Ru/CNT catalysts for NH₃ decomposition, Wang et al.[^57] reported that the promotional effect of a modifier is a combined result of (i) enhancing combinative desorption of nitrogen atoms and (ii) decreasing of apparent activation energy of the decomposition reaction. The best promoters for Ru/CNT catalysts are K, Na and Li from nitrates, hydroxides or carbonates[^57] and their action is an electronic effect on the Ru nanoparticles, in a similar manner that that reported on catalysts for NH₃ synthesis[^58-^63] On the contrary, electron-withdrawing groups (such as halogens or sulfates) act as inhibitors.[^57] Consistently, the Ru/LSZ-DP, which comprises a very complicated mixtures of phases among
which the presence of chloride ions can not be excluded, presents a very low activity and no H₂ and N₂ desorption is observed in the TPSR experiments.

5.1.5 Conclusions

The influence of the synthesis method on the catalytic activity of Ru-based catalysts on the ammonia decomposition reaction were studied. Active and stable catalysts were prepared by embedding of pre-formed Ru nanoparticles (protected by a polymer or a cationic surfactant) into La-doped ZrO₂ (LSZ) support formed by co-precipitation. The activity of the embedded catalysts is significantly higher than that of reference catalysts prepared by impregnation of similar supports. Depending on the preparation method, the oxide support is composed of a ZrO₂ – La₂O₃ solid solution, with tetragonal structure and high surface area, or as a complex mixture of phases (such as tetragonal and cubic LSZ, monoclinic ZrO₂ and Na₂ZrO₃), with small surface area, deriving from the presence of considerable amounts of Na-based impurity as a result of the precipitation step with NaOH. Notably, the factor governing the activity of the catalysts is the dispersion for the Ru nanoparticles. Catalysts prepared by embedding pre-formed nanoparticles present small Ru nanoparticles (as evidenced by XRD and chemisorption). As expected, the catalysts prepared by impregnation undergo a deep sinterization of the metal phase leading to significantly lower conversions. Temperature Programmed Surface Reaction experiments using ammonia well agree with the catalytic activity results, indicating that high H₂ and N₂ desorption are obtained only if Ru is dispersed in very small nanoparticles.
5.2  Fe/Mo based catalysts: preliminary results

5.2.1  Introduction

It is well known that Ru based catalysts on different supports are the most active systems in the ammonia decomposition reaction.\cite{25} However the limited availability of noble metal and their high costs makes it necessary to develop less expensive catalysts based on non precious metals.

Many different non noble metals have been tested; for example, Zheng et al.\cite{31,64} reported an high ammonia conversion (60%) at 500°C (GHSV = 30000) on Ni (~ 45 wt%) based catalysts doped with La supported on Al$_2$O$_3$ synthetized by co-precipitation method; the same group demonstrated also the improvement of catalysts activity and stability due to the introduction of CeO$_2$ into the Ni/Al$_2$O$_3$ system\cite{65}; iron based catalysts supported on different metal oxides were also reported in literature data as active catalysts both in the ammonia synthesis and in the ammonia decomposition reaction.\cite{66,67}; finally, vanadium carbide and molybdenum carbide and nitride were also investigated as possible alternative to precious metal based catalysts in the ammonia decomposition reaction.\cite{68} In particular, Choi\cite{68} reported that early transition metal carbides and nitrides exhibit catalytic properties similar to those of platinum-group metals; it was reported that vanadium films were not very active in the ammonia decomposition reaction but become activated after bulk nitridation.\cite{69} From these results it appears that nitridation or carburization of the bulk metals (vanadium and molybdenum) might have caused catalytically inert parent metals to posses the catalytic behaviors similar to those of platinum group metals.\cite{70}

Moreover it is also reported that Fe and Mo are involved as active components in many different biological processes in which NH$_3$, N$_2$ and others N-based compounds are involved.\cite{71,72} Applying a biomimetic approach, we decided to investigate and develop Fe- and Mo- based bimetallic systems supported on different metal oxides in order to verify both a possible synergic effect due to the
contemporary presence of two metal phases and the influence of the support interaction.

In this thesis we present the preliminary results regarding Fe(5wt%)/Mo(5wt%) deposited on different supports by classical impregnation method starting from acetyl acetonate precursors (see chapter II). The functional and structural/morphological characterization of these systems were investigated.

Fe(10wt%)/Mo(10%) based catalyst was used as reference to better justify the choice of metal loading.

5.2.2 Characterization of the catalysts

Textural characterization: Physisorption measurements

The results of the textural characterization of the calcined samples are summarized in Table 5.4. All the samples present type IV isotherms with hysteresis loop typical of mesoporous materials. The t-plot analysis indicates that the microporous volume is negligible. The BJH analysis reveals that the materials have a pore distribution centred approximately between 10 and 30 nm. The catalysts prepared using modified-Al₂O₃ as support show higher surface area and larger pore volume with respect to those prepared using doped-ZrO₂ as support.

The materials calcined after impregnation with Fe/Mo precursors shows a slightly lower surface area and pore volume with respect to the corresponding bare supports, as a result of the partial pore blocking or covering of the internal surface of the pores. Finally, the reduction applied to all the samples as activation pre-treatment do not affect significantly the textural characteristics of the samples.
Table 5.4: Catalysts textural properties after calcinations at 400°C for 5h and standard activation pre-treatment (reduction in H$_2$ flow at 800°C for 2h).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Calcined $^{[a]}$</th>
<th>Activated $^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SSA $^{[c]}$ (m$^2$ g$^{-1}$)</td>
<td>$d_m^{[d]}$ (nm)</td>
</tr>
<tr>
<td>YSZ</td>
<td>29</td>
<td>18/37</td>
</tr>
<tr>
<td>LSZ</td>
<td>59</td>
<td>11/38</td>
</tr>
<tr>
<td>CSZ</td>
<td>34</td>
<td>16/57</td>
</tr>
<tr>
<td>CZ-Al$_2$O$_3$</td>
<td>95</td>
<td>39</td>
</tr>
<tr>
<td>La-Al$_2$O$_3$</td>
<td>90</td>
<td>28</td>
</tr>
<tr>
<td>Fe$<em>{10}$Mo$</em>{10}$/YSZ</td>
<td>27</td>
<td>9/13</td>
</tr>
<tr>
<td>Fe$_5$Mo$_5$/YSZ</td>
<td>30</td>
<td>11/38</td>
</tr>
<tr>
<td>Fe$_5$Mo$_5$/LSZ</td>
<td>52</td>
<td>10/38</td>
</tr>
<tr>
<td>Fe$_5$Mo$_5$/CSZ</td>
<td>30</td>
<td>8/56</td>
</tr>
<tr>
<td>Fe$_5$Mo$_5$/CZ-Al$_2$O$_3$</td>
<td>89</td>
<td>27</td>
</tr>
<tr>
<td>Fe$_5$Mo$_5$/La-Al$_2$O$_3$</td>
<td>92</td>
<td>28</td>
</tr>
</tbody>
</table>

$^{[a]}$ Bare supports calcined at 900°C for 5h; Fe-Mo-based catalysts calcined in air at 400°C for 5h after impregnation. $^{[b]}$ After standard activation pre-treatment (reduction in H$_2$ flow at 800°C for 2h). $^{[c]}$ Specific Surface Area. $^{[d]}$ Maxima of the pore distribution calculated by BJH analysis of the desorption branch of the N$_2$ isotherm. $^{[e]}$ Cumulative Pore Volume

**Temperature Programmed Reduction (TPR)**

The reduction properties of the different samples were examined by Temperature Programmed Reduction (TPR) in a flow of H$_2$(5%)/Ar. Figure 5.10 presents the TPR profiles of selected samples. As a general feature, the samples present various reduction processes, operative at low and high temperature ($T > 600°C$).
Figure 5.10: TPR of calcined samples after a standard cleaning procedures: Fe_{10}/YSZ (a), Mo_{10}/YSZ (b), Fe_{10}Mo_{10}/YSZ (c), Fe_{5}Mo_{5}/YSZ (d), Fe_{5}Mo_{5}/LSZ (e) and Fe_{5}Mo_{5}/CSZ (f). The subscript below Fe and Mo indicates the nominal wt % of the corresponding metal.

It is well-known that the reduction processes of Fe_{2}O_{3} and MoO_{3} are multi-step processes. In fact, both Fe and Mo are in their highest oxidation state and the full reduction passes through all the other states as follow:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 & \to \text{Fe}_3\text{O}_4 \to \text{FeO} \to \text{Fe} \\
\text{MoO}_3 & \to \text{MoO}_2 \to \text{Mo}
\end{align*}
\]

Consistently, the TPR profile of Fe_{2}O_{3} and MoO_{3} are characterized by a multiple number of H_{2} consumption peaks, as previously reported in the literature. Brown et al.\textsuperscript{[73]} studied the reducibility of bulk iron oxide materials employed as ammonia...
synthesis catalysts. Their TPR study showed that the reduction of Fe$_2$O$_3$ proceed in steps, the first of which is its reduction to Fe$_3$O$_4$.

A study of MoO$_3$ on γ-Al$_2$O$_3$\cite{74} showed that the reducibility of MoO$_3$ catalysts prepared by impregnation method was correlated to the surface coverage of the support. This implies either that (i) the interaction between the Mo species and the Al$_2$O$_3$ is greatest at lower coverages or (ii) the effect is caused by differences in the degree of aggregation, which increases with surface coverage. It is not possible to easily differentiate between the two possibilities.

The TPR profile of Fe(10%)/YSZ sample (Fig. 5.10, trace a) is characterized by three different contributes (300, 450 and 620°C) in agreement with the presence of Fe$_2$O$_3$. The TPR profile for Mo(10%)/YSZ sample (Fig. 5.10, trace b) evidenced an hydrogen uptake below 600°C and a high temperature contribute (about 900°C), suggesting the presence of MoO$_3$ entities.

The nature of the support and the presence of both the active components in the same system affect the TPR results. Multiple reduction processes are observed, suggesting that Fe and Mo are present in their higher oxidation states (Fe$_2$O$_3$ and MoO$_3$). The reduction processes operative below 600°C are shifted to higher temperature with respect to the corresponding processes in the monometallic systems. On the contrary, the reduction processes operative above 600°C are promoted, with the peak temperatures comprised in between those observed in the case of the monometallic samples. These results are probably related with the interaction between the two different reducible species – Fe(III) and Mo(VI). The formation of mixed oxides could also by considered, although no clear indications of their presence can be presented because of the even low metal loading and the mild calcination temperature after impregnation (see XRD section). In fact, many iron-molybdenum mixed oxides are reported in the literature, such as Fe$_2$Mo$_3$O$_8$, Fe$_2$Mo$_3$O$_{12}$, Fe$_2$MoO$_4$ and FeMoO$_4$\cite{75}. The reduction properties of these materials are widely investigated for the preparation of Fe-Mo alloys\cite{76-79}. The shift towards higher temperatures of the reduction peaks in the sample Fe$_{10}$Mo$_{10}$/YSZ could be explained with the different aggregation of metal nanoparticles correlated with the higher metal loading.
Finally, the total H₂ consumption for the Fe₅Mo₅/CSZ sample is higher than the other samples with the same Fe/Mo amounts due to the contribution of the CSZ reduction. In fact, the TPR profile of the CSZ support shows two reduction processes in the same temperature ranges that the Fe/Mo oxides reduction (data not shown). Therefore, the reduction of the support superimposes with that of the active phase precursors deposited by impregnation.

In order to fully reduce the metal species before the reactivity tests, an *in-situ* pretreatment in H₂ flow (35 mL min⁻¹) at 800°C for 2h was applied to all the materials.

**Powder X-Ray Diffraction (XRD)**

Powder X-Ray Diffraction (XRD) has been used to study the evolution of the active phase (comprising Fe and Mo) after different treatments. XRD patterns of the calcined samples present only the reflection related with the used supports. Commercial zirconias, doped with Yttrium (YSZ), Lanthanum (LSZ) or Cerium (CSZ) are homogeneous solid solutions with a tetragonal structure (space group P4₂/nmc), accordingly with the amount of the dopant cations present (between 10 and 20 mol%). The cell parameters changes accordingly with the ionic radius of the dopant cations. A mean crystallite size of 24, 20 and 21 nm is calculated for YSZ, LSZ and CSZ respectively. In the case of Al₂O₃-based supports, the broad reflections due to transitional Al₂O₃ complicates a clear attribution of the crystalline phase. Nevertheless the reflections of the CZ phase (in Fe₅Mo₅/CZ-Al₂O₃) and of LaAlO₃ (in Fe₅Mo₅/La-Al₂O₃) can be distinguished. A mean crystallite size of 6 and 14 nm can be calculated for the CZ and LaAlO₃ phases, respectively. Notably, no reflection related to Fe and/or Mo-containing species have been observed in all the calcined samples. This result well agrees with the low temperature calcination treatment applied to the samples after impregnation (400°C). Fe and Mo oxides are well dispersed on the surface of the support and, because of the quite low loading, the broad reflections can not be distinguished.
The XRD patterns of the samples supported on doped-ZrO$_2$ after activation pre-treatment are presented in Fig. 5.11

Figure 5.11: XRD patterns of the samples after standard activation (reduction in H$_2$ at 800°C for 2h): Fe$_{10}$Mo$_{10}$/YSZ (a), Fe$_5$Mo$_5$/YSZ (b), Fe$_5$Mo$_5$/LSZ (c) and Fe$_5$Mo$_5$/CSZ (d).

After activation, in addition to the reflections of the supports, the features of the metallic phases of Fe and Mo are present in the XRD patterns of the catalysts supported on commercial zirconia (YSZ, LSZ and CSZ). Table 5.5 summarizes the mean crystallite sizes calculated applying the Scherrer’s equation to the main reflection of each phase. Notably, in agreement with the physisorption results, the crystallite sizes of the supports are almost unaffected by the reduction treatment.
Due to the quite low amount of the active phase, only the most intense (111) reflections of metallic Fe and/or Mo can be appreciated. All the samples supported on doped-ZrO$_2$ exhibit the characteristic reflections of metallic Fe. The (111) reflection of Fe in the Fe$_5$Mo$_5$/LSZ sample is particularly broad, suggesting a very high dispersion of Fe in this sample. The main reflection of metallic Mo is present only in the XRD pattern of the Fe$_{10}$Mo$_{10}$/YSZ sample, due to the higher metal loading. Moreover, a very broad reflection is present in between the main reflections of metallic Fe and Mo, as evidenced in the magnification of the $2\theta = 32.5 - 52.5^\circ$
range (Fig. 5.11, left part). This broad reflection is attributable to the (111) reflection of a Fe-Mo alloy with a very small crystallite size (~3nm). Since Fe and Mo present the same crystal structure (space group Fm$\bar{3}$m), the composition of the alloy could be calculated from the Vegard’s law. The broadness of the reflection and its very low intensity do not allow for a correct determination of the cell parameter, leading to not reliable results. Nevertheless, the absence of the reflections of metallic Mo in the samples containing the 5wt% of the metals suggests that the alloy should contain all the Mo present in the sample and part of Fe.

Fig. 5.12 shows the XRD patterns of the reduced Fe$_5$Mo$_5$/CZ-Al$_2$O$_3$ and Fe$_5$Mo$_5$/La-Al$_2$O$_3$ in comparison with those of the correspondent supports. The XRD analysis of the samples supported on modified-Al$_2$O$_3$ is much more complicated due to the low crystallinity degree of the supports. Moreover, the presence of a significant amounts of amorphous material resulting from the incomplete stabilization of transitional aluminas due to the quite short treatment at 900°C.

![Figure 5.12: XRD patterns of the samples after standard activation: Fe5Mo5/CZ-Al2O3 (a) and Fe5Mo5/La-Al2O3 (b). The grey lines show the XRD patterns of the correspondent supports.](image-url)
From the comparison of the patterns, only the main reflection of metallic Fe can be appreciated. From the fitting of the profile, a crystallite size of ~ 12 nm can be calculated. No phases containing Mo can be clearly observed.

5.2.3 Catalytic activity: preliminary results

Fig. 5.13 shows the activity for NH\textsubscript{3} decomposition of reduced Fe-Mo-based catalysts. Catalytic tests were performed under atmospheric pressure and pure NH\textsubscript{3}. Two reaction conditions, in terms of Gas Hourly Space Velocity (GHSV) have been investigated. The low GHSV value (4000 mL g\textsuperscript{-1} h\textsuperscript{-1}) is more representative of a catalytic system employed to produce a gaseous mixture used as feed for an internal combustion engine, where a quite low H\textsubscript{2} concentration is needed. On the other hand, the higher GHSV (46000 mL g\textsuperscript{-1} h\textsuperscript{-1}) is representative of a catalytic system working in combination with a NH\textsubscript{3}-fed SOFC, where a higher operative temperature can be reached.

At GHSV = 4000 mL g\textsuperscript{-1} h\textsuperscript{-1}, NH\textsubscript{3} starts to be converted over Fe-Mo-based catalysts above 400°C, while its complete conversion is reached at 700°C. Between the two catalysts studied, no significant differences were observed changing the total metal loading. Therefore, a total metal loading of 10wt% (Fe\textsubscript{5}Mo\textsubscript{5}-based catalysts) has been chosen to study the effect of the support composition on the catalytic activity. Minor differences in the ammonia conversion are evidenced: a light-off temperatures (T50 – defined as the temperature corresponding to a NH\textsubscript{3} conversion of 50%) of about 625°C is obtained for the Fe\textsubscript{5}Mo\textsubscript{5}-catalysts supported on YSZ, LSZ, CSZ and CZ-Al\textsubscript{2}O\textsubscript{3}. T50 of Fe\textsubscript{10}Mo\textsubscript{10}/YSZ and Fe\textsubscript{5}Mo\textsubscript{5}/La-Al\textsubscript{2}O\textsubscript{3} is at 600°C. In the case of Fe\textsubscript{10}Mo\textsubscript{10}/YSZ, this improvement could be related to the higher metal loading while, in the case of Fe\textsubscript{5}Mo\textsubscript{5}/La-Al\textsubscript{2}O\textsubscript{3}, the higher activity could be an effect of the lower acidity of the support. Two ru-up cycles were performed on the investigated catalysts, evidencing no appreciable deactivation.
The stability of the catalytic activity under NH$_3$ decomposition were evaluated for all the catalysts at 650°C, evidencing that the NH$_3$ conversion is constant over a period of time of at least 120 hours.

Finally, to investigate more realistic conditions for a widespread utilization of ammonia as energy vector, reactivity tests were also performed using technical ammonia, that contains approximately 300 ppm of hydrocarbons. Very similar activity and stability results were obtained, indicating that the slightly lower purity of the feedstock has a negligible effect of the catalysts’ performances.

The preliminary catalytic activity results confirmed our idea regarding the use on non noble metals as active phase for hydrogen production from ammonia, on the basis of the microscopic reversibility concept. In fact, iron is the active component of the well known industrial catalysts for ammonia synthesis.$^{[80,81]}$ Moreover, Mo-based catalysts also demonstrated significant results in the same process.$^{[82-84]}$
References


Worldwide energy requirement is steadily increasing because of many reasons, such as enhancement of the quality of life, population increase, industrialization, rapid economic growth of developing countries, etc. Important changes in the energy production technologies will be essential to fit the increased energy demand with the stringent environmental limitations required by a sustainable development. In particular, the diversification of the energy sources and fuels, including large use of renewables, is a must. The choice of an appropriate fuel different from oil strongly depends on application and use, location and regional resources, cost, environmental impact factors, safety of generation and utilization, socioeconomic factors, global and regional politics, etc.

In this context, H\textsubscript{2} is recognized as an important energy vector (in combination with fuel cells) and as an essential molecule required by a large number of industrial processes. H\textsubscript{2} is actually produced by steam reforming of methane. The diversification of the sources and processes for H\textsubscript{2} production will be fundamental for the future, especially including renewable raw materials (such as ethanol, glycerol or other biomass-derived materials) or energy sources (such as solar light). Moreover, serious problems are connected with H\textsubscript{2} distribution and/or transportation. Therefore, the delocalized H\textsubscript{2} production from easily transportable fuels (such as liquid ammonia or methanol) is a interest solution.

The aim of this thesis is the development of nanostructured catalysts for hydrogen production starting from alternative sources, such as renewable materials (ethanol and glycerol) or easily transportable liquids (methanol and ammonia). Different
catalytic systems were prepared and tested in various reactions. The synthesis approaches adopted in this thesis focused on the control of the particles dimensions, demonstrating that the nanostructured catalysts show an improvement of the catalytic performances with respect to similar catalysts prepared by conventional methods.

Active and cheap catalysts, comprising of base metals (Cu, Co and Ni) as active phase and ZnO as promoter were developed for hydrogen production through the steam reforming of alcohols (methanol and ethanol). Cu/ZnOAl₂O₃ system is very active in hydrogen production through methanol steam reforming. On the contrary, it mainly promotes the dehydrogenation of ethanol, producing quantitatively acetaldehyde at moderate temperature since it is not able to activate the C-C bond. Ethanol steam reforming is enhanced introducing Ni and/or Co in the formulation of the catalyst. Moreover, while coke deposition occurs significantly on Co/Cu/ZnO/Al₂O₃, alloy formation between Ni and Cu reduce these deactivation phenomenon.

Glycerol steam reforming reaction was investigated as an alternative way to produce hydrogen valorizing a biodiesel by-product. In particular, the effects of the addition of promoter oxides (La₂O₃ and CeO₂) to a conventional Pt/Al₂O₃ catalyst were studied. La₂O₃ and CeO₂ deposited onto Al₂O₃ improve the catalytic performances of the Pt nanoparticles, decreasing the acidity of the support as evidenced by NH₃-TPD. While Pt/Al₂O₃ catalyst promotes the H₂ production only at high temperature (> 500°C), the introduction of La₂O₃ or CeO₂ allows glycerol to be completely converted into syn-gas already at 350°C and, at the same time, efficiently promote the Water-Gas Shift reaction. Furthermore, the addition of La₂O₃ and CeO₂ significantly improves the catalyst stability, The amount of carbon deposits is significantly reduced on the promoted catalysts in comparison with the bare Pt/Al₂O₃, as a consequence of the inhibition of side-reactions promoted by the acid sites of the Al₂O₃ support. Despite these positive effects, the CeO₂-doped catalyst deactivates quickly while a higher stability is shown by the La₂O₃-doped material. The slight deactivation observed for Pt/La₂O₃/Al₂O₃ catalyst can be once more
related to coke deposition on the catalyst surface, resulting in a significant coverage of the catalyst surface (as assessed by H₂ chemisorption and HR-TEM).

Finally, the hydrogen production through the ammonia decomposition were studied with the aim to produce a H₂/N₂/NH₃ mixture suitable to feed an Internal Combustion Engine. Highly active and stable catalysts were prepared following an embedding approach, consisting in the encapsulation of preformed metal nanoparticles into a porous oxide support. The accurate design of the preparation protocol allows the development very active and stable catalytic systems with an careful control of the metal nanoparticle dimensions. Active and stable catalysts were prepared by embedding of pre-formed Ru nanoparticles (protected by a polymer or a cationic surfactant) into La-doped ZrO₂ (LSZ) support formed by co-precipitation. The activity of the embedded catalysts is significantly higher than that of reference catalysts prepared by impregnation of similar supports. Depending on the preparation method, the oxide support is composed of a ZrO₂ – La₂O₃ solid solution, with tetragonal structure and high surface area, or as a complex mixture of phases (such as tetragonal and cubic LSZ, monoclinic ZrO₂ and Na₂ZrO₃), with small surface area, deriving from the presence of considerable amounts of Na-based impurity as a result of the precipitation step with NaOH. Notably, the factor governing the activity of the catalysts is the dispersion for the Ru nanoparticles. Catalysts prepared by embedding pre-formed nanoparticles present small Ru nanoparticles (as evidenced by XRD and chemisorption). As expected, the catalysts prepared by impregnation undergo a deep sinterization of the metal phase leading to significantly lower conversions. Temperature Programmed Surface Reaction experiments using ammonia well agree with the catalytic activity results, indicating that high H₂ and N₂ desorption are obtained only if Ru is dispersed in very small nanoparticles.

We investigate also non precious metal free catalysts for ammonia decomposition reaction and preliminary studies indicates that Fe/Mo based systems can be promising non noble metal catalysts for this reaction.

Summarizing this thesis demonstrated that, tuning the nature of the catalysts’ active phase at nanoscale level, it is possible to successfully optimize the performances of
various catalytic processes involving the production of hydrogen from sources available in large quantities, such as ethanol, glycerol or ammonia.
Acknowledgements

First of all, I would like to acknowledge Acta S.p.A. for financially supporting my Ph.D. thesis and for precious scientific collaboration.

I would like to express my gratitude to my supervisor, Prof. Paolo Fornasiero and my tutor Dr. Tiziano Montini, for giving me the opportunity to carried out an interesting and challenging research project.

I’m sincerely grateful to all the members of the MEE research group, for their friendship, scientific and emotional support: dr. Loredana De Rogatis, dott. Valentina Gombac, dott. Matteo Cargnello, dr. Nicolàs M. Bertèro, dr. Gabriele Balducci and dr. Manuela Bevilacqua.

A special and warmly thank to Prof. Mauro Graziani for his continuous and precious support during all my Ph.D period.

Finally, special thanks to my Father for always be there.