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EFFICIENT NANOCATALYSTS FOR HYDROGEN PRODUCTION BY STEAM REFORMING OF OXYGENATED COMPOUNDS

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SÍNTESIS DE CATALIZADORES PARA PRODUCCIÓN DE HIDRÓGENO MEDIANTE REFORMADO CON VAPOR DE COMPUESTOS OXIGENADOS

EFFICIENT NANOCATALYSTS FOR HYDROGEN PRODUCTION BY STEAM REFORMING OF OXYGENATED COMPOUNDS

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Luis J. Alemany Arrebola, Catedrático de Ingeniería Química de la Universidad de Málaga, e Izabela Stefanowicz-Pieta, Investigadora Instituto de Química Física (Academia de Ciencias Polaca), en Varsovia (Polonia)

ACREDITAN que la Memoria de Tesis titulada 'SÍNTESIS DE CATALIZADORES PARA PRODUCCIÓN DE HIDRÓGENO MEDIANTE REFORMADO CON VAPOR DE COMPUESTOS OXIGENADOS' presentada por D. Rafael González Gil, ha sido realizada bajo su dirección y reuniendo, a nuestro juicio, los requisitos necesarios para que su autor pueda aspirar al grado de DOCTOR, autorizando su presentación para su defensa en la Facultad de Ciencias de la Universidad de Málaga.

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Abstract

Hydrogen is widely used in petrochemical industries as a feedstock for the production of chemicals. However, the current hydrogen production method via natural gas steam reforming is unsustainable due to the depletion of natural gas resources and associated pollutant emissions. This Thesis focuses on the steam reforming of oxygenated model compounds, which are the main components of raw bio-oil (a liquid product of biomass fast pyrolysis) and can serve as hydrogen carriers or alternative fuels. The valorization of these compounds through their conversion into hydrogen, an increasingly important energy vector, is proposed. The objective of this work is to compare different routes for hydrogen production to establish the optimal operating conditions for its valorization. Acetone, ethanol and DME/MeOH couple were selected as oxygenated model compounds.

Active catalysts have been developed for the studied processes based on the monometallic Ni/Al_2O_3 system, which is widely used in industrial natural gas reforming. The system was modified according to the process and the oxygenated compound used, allowing adaptation to the specific conditions of each case. Bimetallic catalysts were prepared by incipient wetness impregnation of noble (RhNi) and transition metals (VNi) on an Al_2O_3 support, with different metal-to-Ni relative ratios. These catalysts were thoroughly characterized, and their activity, selectivity and stability were evaluated. Additionally, the mechanistic aspects of metal addition to Ni-based catalysts and the interaction and behavior of *M*-Ni pair were studied, combining activity and spectroscopic data.

Overall, the addition of a second metal to the Ni-based catalyst significantly modified its properties, improving Ni stability and distribution on the support surface, and enhancing catalytic activity by increasing selectivity in the promoted reactions. Acetone and ethanol steam reforming processes were studied with the RhNi bimetallic system, also examining the influence of the support on ethanol reforming due to its sensitivity to carbon deposition on the catalyst surface. Rh incorporation (at a Ni/Rh atomic ratio of 100/1) affects Ni metal size. Moreover, carbon deposited after reaction seems to be dependent not only on the Rh incorporated but also on the properties of alumina support, by reducing the amount of carbon deposited onto catalysts surface after reforming tests. The Ni/Al_2O_3 system was modified by adding V at different V/Ni ratios to study the steam reforming of the DME/MeOH couple. V incorporation to Ni/Al_2O_3 increased the relative contribution of NiO, suggesting an interaction between V and Ni that prevents the formation of spinel $NiAl_2O_4$. TPR analysis showed a decrease in the signal associated with spinel in bimetallic VNi systems, indicating that V addition modified surface characteristics and prevented undesirable Ni-support interaction Consequently, Ni-O-Ni and V-O-Ni species determined the reaction selectivity in DME-SR.

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The catalysts' activity in the studied processes was evaluated at atmospheric pressure operating under plug flow conditions across a temperature range of 423 and 973 K (depending on the oxygenated tested). Liquid reactants, in the cases of acetone, ethanol, and methanol-SR, were fed as mixtures with water using a HPLC pump at stoichiometric steam-to-oxygenated molar ratios. Reaction products were characterized using chromatographic techniques, analyzing the gaseous product stream composition. This work demonstrated that a high hydrogen yield and selectivity could be achieved with *M*-doped Ni/Al_2O_3 catalyst compared to the typical Ni/Al_2O_3 system.

Acetone and ethanol can be efficiently reformed into a hydrogen-rich stream. Rh plays a crucial role in acetone steam reforming, allowing complete acetone conversion and promoting H_2 production with minimal carbon deposition. Ethanol reforming primarily occurs via ethanol decomposition into acetone, acetaldehyde, and ethylene, followed by steam reforming and decomposition of these intermediates. Ethanol reforming showed higher hydrogen selectivity than acetone-SR. A structured catalyst was designed to analyze its performance at pilot scale in ethanol reforming, producing an H_2 stream suitable for feeding a PEM fuel cell. A multimetallic RhCeNi (0.0009:5:9 atomic ratio) in pellet form demonstrated activity in the pilot plant process, where H_2 and CO_2 were the main components detected with a molar ratio H_2/CO_2 close to 3.0, achieving 98 % ethanol at 923 K.

Alternatively, DME offers the advantages of easy storage and transportation, with the potential to use existing LPG infrastructure due to similar physical properties. This makes DME not only an H_2 source but also an alternative fuel for diesel engines or as a diesel blend. The mechanism of hydrogen recovery via DME steam reforming was further studied, analyzing the reactions and catalyst interactions using FTIR to understand and improve the process. It was shown that water and DME compete for active sites on the catalyst surface, requiring a temperature of 773 K to promote the SR reaction, which proceeds via DME hydrolysis followed by methanol steam reforming. The presence of Lewis acid sites with high acid strength in this catalyst enhances the DME conversion through immediate hydrolysis and direct methanol reforming.

Overall, this Thesis contributes to a better understanding of the processes involved in hydrogen production from different oxygenated compounds with varying properties and characteristics. It aids in the design of catalytic systems for the valorization of raw bio-oil, whose main components were represented and modeled in this work. It also highlights the potential use of these molecules as a H_2 carrier for advanced storage, transport, and distribution, supporting the development of decarbonized industry and transport models with hydrogen as a key ally.

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A Guillermo y Alberto

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“No es verdad que las personas dejen de perseguir sueños porque se hacen viejas, sino que se hacen viejas porque dejan de perseguir sus sueños”

Gabriel García Márquez

"...y lo que me hace levantarme por las mañanas sigue siendo la espera de lo que está por llegar y no se anuncia, es la espera de lo inesperado, y no ceso de fantasear con lo que ha de venir"

Javier Marías

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Chapter 1

Introduction

1. The energy supply context

Non-renewable fuels such as coal, oil and natural gas currently account for more than 80% of the world's energy demand, with no major changes expected in the coming years. Although the Covid-19 pandemic has caused more disruption to the energy sector than any other event in recent history, its impacts will be felt for years to come [1]. The large-scale consumption of these natural resources has allowed our society to reach unprecedented levels of development; however, it has also created a high dependence on them. One sector that exemplifies this dependence is transportation, which relies almost exclusively on oil. In 2012, the transportation sector accounted for 25 % of total world energy consumption, with energy use in transportation increasing by 1.4 % per year from 2012 to 2040. This growth is responsible for almost a third of the total energy consumed globally [2].

As shown in **figure 1**, while consumption of non-fossil fuels is expected to grow faster than that of fossil fuels, fossil fuels are still projected to account for 75 % of energy use by 2040 [2]. An increase in global demand is predicted, where 60% coming from China, India and the Near East [1]. In 2012, global energy consumption was 511 EJ, with energy reserves estimated at 39,910 Exajoule (EJ) and resource estimates of 533,526 EJ [3] for the same year. Despite these reserves and resources potentially covering current demand for 78 and 1,044 years, respectively, fossil fuels are not inexhaustible as they require millions of years to form. Various factors, including economic and environmental repercussion,

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underscore the need for a shift away from fossil fuels.

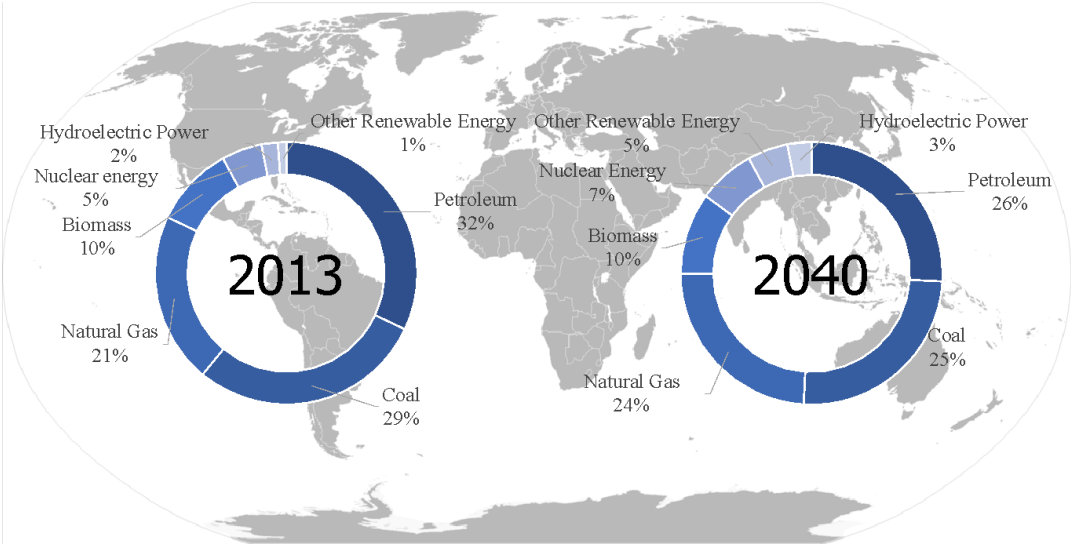

Figure 1: Perspectives of growth in world demand for primary energy. Data adapted from international energy agency **[1]** and Repsol (www.repsol.com).

The first concern is the finite nature of fossil fuel reserves. The current rate of consumption increases each year to meet the growing demands of industrialized countries and rapidly developing economies such as China and India. Economically, the high prices of fossil fuels are due to the concentration of production in certain areas of the world, many of which are conflict-prone, putting supply at constant risk. The Near East controls over 60 % of the world's oil reserves and 40 % of the natural gas. Additionally, three countries - China, Russia, and the USA - hold two-thirds of the world's coal deposits. Rising oil prices in the long term lead many energy users to adopt more energy energy-efficient technologies and to move away from liquid fuels when feasible [2].

From an environmental perspective, the use of these fuels is accompanied by emissions of *greenhouse gases* that are harmful to the environment. The combustion of fossil fuels to produce energy generates emissions as CO_2 and CO, contributing to the greenhouse effect, acid rain and the contamination of soil, air, and water. Scientific analyses since the mid-19th century industrial revolution have established that the growth in emissions of CO_2 and other gases with global warming potential has led to a rapid increase in global temperatures [4].

Given the growing energy demand and unsustainable situation, a transition to new forms of energy production and consumption is necessary. Expecting a significant

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change in energy consumption habits and population needs is unrealistic; thus, the solution lies in developing alternative and renewable energy sources. Achieving a global energy transition that aligns with climate goals is essential. Current pledges by governments to reduce emissions to net zero cover around 70 % of global economic activity and CO_2 emissions. The Net-Zero Emissions by 2050 Scenario (NZE) outlines what is needed across various sectors to achieve net-zero energy-related and industrial process CO_2 emissions by 2050 [5].

Renewable energies contribute to increasing a country's energy security by diversifying its energy matrix, mitigating greenhouse gas emissions, and reducing dependence on external supplies. In contrast to conventional sources, renewables are clean and inexhaustible resources with minimal and reversible impact. They also promote technological development and job creation.

As mentioned, the transport sector significantly influences society and the economy, generating greenhouse gases and air pollutants that adversely affect the environment, global climate, and human health. It is the only main European economic sector whose GHG emissions have increased since 1990; transport emissions have risen by 19.4 % during this period [6]. The Directive 2009/28/EC [7] aims for approximately 10 % of fuel used in transport to come from renewable sources. New approaches are necessary to eliminate barriers to the market penetration of alternative fuel vehicle technologies, such as battery electric vehicles (BEV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and extended-range electric vehicles (EREV) However, using these alternatives in transport is not free from polluting emissions, as the electricity must be generated with zero emissions [8].

Giving the limitations of fossil energy and environmental concerns, clean and renewable energy is globally recognized for its sustainability. Solar, wind, and hydro energies are promising but generally site-specific and intermittent, thus not sufficient to meet the entire economy's needs. One major obstacle to using renewable energies on a larger scale is proper electricity storage and transmission [9]. Recent trends in energy storage technologies show that hydrogen, as an energy carrier, is a promising alternative for energy storage. According to recent

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International Renewable Energy Agency (IRENA) report, hydrogen has the potential to decarbonize sectors such as industry, shipping, aviation, and heating, which are traditionally harder to electrify [10]. The International Energy Agency (IEA) also sees hydrogen's versatility and compatibility with renewables as integral to our clean energy future [11].

Therefore, it is necessary to search for future zero-emission technologies, such as vehicles with fuel cells powered by hydrogen produced from renewable resources [12]. Hydrogen, as a versatile, efficient, and sustainable clean energy carrier and strategic feedstock in chemical industries, can replace fossil fuels due to its high energy yield compared to traditional hydrocarbon fuels. It has been identified as an ideal sustainable resource for a near future [13].

2. **Hydrogen**

Hydrogen is an alternative fuel that supports energy development due to its cleanness and high combustion efficiency. Recognized as a potential energy source since the early 19th century, hydrogen has garnered significant attention in recent years. **Figure 2** illustrates the current hydrogen value chain, detailing the main hydrogen production processes and its most widespread uses.

Currently, the global demand for 'pure' hydrogen exceeds 70 million tons per year (equivalent to 8 EJ, which is less than 2 % of the world's total primary energy supply). This hydrogen is primarily used for industrial purposes in chemical and petrochemical applications. Major uses include ammonia and methanol synthesis, Fischer-Tropsh (F-T) synthesis, and refinery and petrochemical processes such as hydrotreatment and hydrocracking. Additionally, there is a demand for 45 million tons of hydrogen as part of gas mixtures, such as synthesis gas, uses for fuel or feedstock. The main applications for hydrogen in gas mixtures are methanol production and steel production [11,14].

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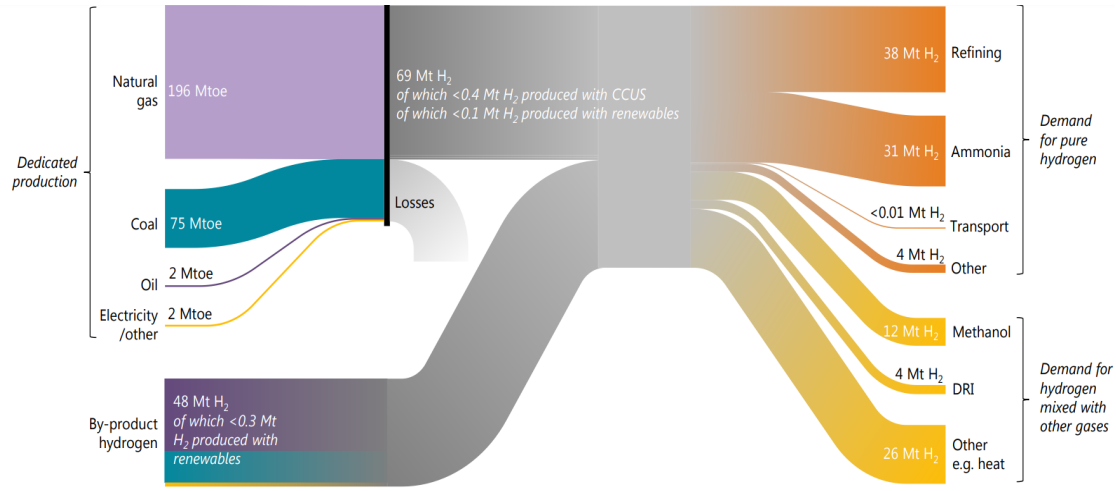

Figure 2: Current hydrogen value chain. Source: IEA (2019a) **[11].**

Hydrogen is considered as an *energy carrier* rather than a primary energy source. Despite being one of the most abundant elements in nature, hydrogen does not exist in its pure state and must be produced from hydrogen-contain raw materials. Therefore, it is used to store and transport energy efficiently [15]. Coupling renewable energy with hydrogen production offers a promising pathway to produce 'green hydrogen', which has a minimal environmental impact. In the 2019 European Green Deal [16] the European Commission designated green hydrogen as a priority industrial sector for commercialization by 2030.

Hydrogen's use as fuel is based on its high energy density, containing the same amount of energy as 2.6 kg of natural gas (methane, CH_4) or 3.1 kg of gasoline. Moreover, hydrogen's wide range of inflammability in dry air (1 atm, 25ºC, 4-75 %) compared with other fuels (diesel: 0.6-5.5 %; methane: 5-15 %) allows for better control of combustion.

As shown in **Table 1**, hydrogen can store approximately three times more energy per unit mass than other fuels, but its low density results it the lowest energy storage per unit volume [11]. This poses challenges in the transport, storage, and distribution of hydrogen compared to gasoline or butane, especially for transport and portable applications.

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Table 1: Energy densities of various fuels.

		Stored Energy		
	Density [kg/m^3]	Volume [kWh/m^3]	Volume [kWh/Nm^3]	Mass [kWh/kg]
H_2 liquid (1 bar; -252.8ºC)	70.71	2375	3	33.59
H_2 gas (300 bar; 25ºC)	20.55	690	3	33.59
H_2 gas (700 bar; 25ºC)	47.96	1611	3	33.59
Natural Gas (1 bar; 25ºC)	0.65	9.1	10	13.93
Liquid Butane (25ºC)	550	7000	33	12.73
Gasoline	750	9270	-	12.36

On the other hand, hydrogen possesses the quality of being combustible, meaning it can oxidize in the presence of oxygen or air, releasing energy in the form of heat. It combustion value with oxygen is $14.19 \cdot 10^4$ kJ/kg. Unlike other fuels, hydrogen reacts with oxygen to produces only steam, making it a clean combustion fuel. However, it is important to qualify this statement since the majority of current commercial hydrogen production methods involve the use of fossil fuels. In fact, natural gas is the primary source of hydrogen production, accounting for around three-quarters of the annual global dedicated hydrogen production. Consequently, hydrogen production is responsible for approximately 830 million tonnes of CO_2 emissions per year, highlighting the urgent need for alternative production methods [17].

Interest in hydrogen as an energy vector has significantly increased for vehicle fuel and production of stationary energy from fuel cells. These modern applications are currently under extensive research due to due to their high efficiency and lack of harmful emissions, contrasting conventional electricity production methods [18]. Fuel cells have undergone significant technological advancements recently, and their efficiency is no longer a major obstacle to the future development of commercial hydrogen-powered vehicles. By leveraging these technological advancements and strategic implementations, hydrogen fuel cells offer a promising alternative to traditional combustion engines. Their efficiency and environmental benefits position them as a critical component in the transition cleaner solution.

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Additionally, hydrogen emerges as a promising solution to address challenges associated with fossil fuel dependency and greenhouse gas emissions. It opens a wide range of options for decarbonizing processes, sectors, and uses that are difficult to electrify. Hydrogen can serve both as a raw material for the synthesis of other compounds and as a direct fuel, enhancing its role in achieving a sustainable energy future.

2.1. **Novel Applications of Hydrogen**

The utilization of hydrogen as a fuel presents various alternative applications, including internal combustion engines and fuel cell vehicles (FCVs). There is a concerted effort towards increasing the adoption of FCVs due to their provision of clean renewable energy sources, along with their demonstrate safety, reliability, cleanliness, and efficiency. Fuel cells, particularly those reliant on hydrogen, exhibit higher energy efficiency compared to internal combustion engines, with fuel cell-based power plants achieving superior system efficiencies [18–20]. Specifically, fuel cell-based power plants can achieve efficiencies ranging from 70 to 80 %, in contrast to the 30 % to 37 % efficiency of combustion-bases systems [21]. These advancements in technology have alleviated concerns regarding the efficiency of hydrogen-powered commercial vehicles in the near future.

As electrochemical devices, fuel cells convert chemical energy directly into electrical energy, enabling continuous electrical energy production while providing fuel and oxidant to the electrodes [22]. This process, not subject to the Carnol limit, occurs via the combustion reaction of hydrogen, where oxygen and hydrogen combine to form water, generating electrical energy and releasing heat. This clean reaction yields only water vapor, posing no threat to the environment. Fuel cells are primarily classified bases on the type of electrolyte they employ, affecting the electrochemical reactions, catalyst requirements, operating temperature, fuel types, and other factors, consequently influencing their most suitable applications. The predominant classification method categorizes fuel cells by electrolyte type, including polymer electrolyte membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs), alkaline fuel cells (AFCs), solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), phosphoric acid fuel cells (PAFCs), and reversible

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fuel cells. Additionally, they can be classified by operating temperature into low (work at about 80ºC), intermediate (they work at about 200ºC), and high-temperature (working temperature between 650 and 1100ºC) fuel cells. Due to their high-energy efficiency, low pollution emissions, and operating temperature, proton exchange membrane fuel cells (PEMFCs) are considered promising portable power sources. Their rapid startup time and favorable power-to-weight ratio make them particularly suitable for applications in passenger vehicles, such as cars and buses. In the transportation sector, PEMFCs or high-temperature fuel cells, notably solid oxide fuel cells (SOFCs), achieve efficiencies of 40 % to 50 %, surpassing the efficiency of internal combustion engines (IC), which typically operate at 20 % to 35 % efficiency [21].

Hydrogen also finds application in internal combustion engines, which, alongside fuel cells, represent sustainable and clean energy sources for the transport sector. While fuel cells are considered the future, advances in hydrogen internal combustion engines and engines utilizing hydrogen/hydrocarbon mixtures are also progressing. Hydrogen, as an additive to traditional fuel, enhances gasoline engine performance, particularly under lean operating conditions, and holds potential for reducing emissions from internal combustion engines, thereby displacing a fraction of fossil fuel [23–25]. The exploration of alternative fuels, primarily for diesel engines, has been accompanied by investigations into hydrogen's impact on combustion characteristics, engine performance, and pollutant emissions. Due to the growing interest in the use of alternative fuels like Biodiesel, studies have also been carried out to investigate the impact of Biodiesel and different energetic fractions of hydrogen content on the mixture formation, combustion characteristics, engine performance and pollutant emission formation [26].

Direct hydrogen combustion, in both internal combustion engines and gas turbines, poses challenges due to hydrogen's properties and the emissions produced during combustion. Although hydrogen combustion primarily yields water vapor without toxic by-products, it also generates NO_x when burned in air. Consequently, controlling combustion temperature and gas residence time at high temperatures is essential. Hydrogen's combustion properties, including its wide flammability range and low ignition energy, significantly influence its performance as an engine fuel [27–29].

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Until a hydrogen infrastructure established, hydrogen/natural gas fuel blends provide a logical transition to fully hydrogen-powered vehicles. Blending hydrogen with natural gas enhances the operation parameters of combustion systems, particularly in specialized energy applications involving natural gas. The blending of hydrogen with natural gas can serve as a particularly cost-effective transitional option, particularly in European or regions lacking dedicated hydrogen infrastructure,

The integration of hydrogen into the existing natural gas grid offers a significant reduction in investment costs associated with the development of new transportation and distribution infrastructures. However, current limits on hydrogen blending in natural gas networks are subject to various constraints. Natural gas transportation networks can accommodate blends of up to 50 %, while distribution networks can tolerate blends of up to 15 % without requiring significant modifications. Due to hydrogen's lower energy density (approximately one-third that of natural gas), blending reduces the energy content of the supplied gas. Therefore, it is necessary to carefully assess the tolerance of equipment connected to the gas network in each case to establish the upper limit for hydrogen blending [30,31].

Furthermore, hydrogen can be used to produce by-products such as ammonia or methanol, which are key to the decarbonization of maritime, air, and heavy land transport as well as some industrial sectors. The core of Power-to-Fuel (PtF) concept is H_2 gas, termed as power-to-hydrogen (PtH_2), which is considered as the main intermediate for converting power to hydrogen-based synthetic fuels.

Ammonia and methanol are key industrial chemicals with strong demand in the agriculture, manufacturing, and construction sectors. Conventional ammonia and methanol production processes contribute significantly to carbon emissions. As governments around the world implement various decarbonization strategies, it has become imperative to curb emissions from these processes. The evolution of low-carbon hydrogen, a key feedstock for both ammonia and methanol, can help decarbonize these chemicals [32].

Green methanol (CH_3OH) is a synthetic fuel called e-methanol if it is produced

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using green hydrogen and non-fossil carbon captured from the atmosphere. Methanol can be used as a raw material in some of the most challenging sectors to decarbonize, such as maritime and aviation transportation or the chemical industry. In maritime transportation, it is considered one of the renewable fuels of the future [33,34]. Its use will require the construction of new ships or adapting the engines of existing ones, as well as modifying storage and distribution systems in ports. In aviation transportation, it can be used to produce e-SAF, sustainable synthetic aviation fuel. The methanol pathway can be divided into the actual methanol synthesis, and the subsequent conversion of methanol into a hydrocarbon fuel mixture rich in kerosene components (Methanol-to-Kerosene (MtK), also Methanol-to-Jet (MtJ)). This e-SAF can be blended with traditional kerosene without the need to modify aircraft engines [35].

On the other hand, green ammonia is a product derived from green hydrogen that can be used as sustainable marine fuel and as a carrier of green hydrogen for transportation, as well as in the production of nitrogen fertilizers. Both its production, combining green hydrogen and atmospheric nitrogen, and its use as a fuel are carbon-neutral [36,37]. It is easier to transport ammonia than hydrogen because its storage does not require temperatures as low as those of hydrogen, and because there have been ships and infrastructure dedicated to its transportation for decades.

The ammonia and methanol market segments can be more easily decarbonized by using low-carbon hydrogen for their production, also helping to mitigate emissions from end-use applications that rely on these two chemicals [32]. The transition to a hydrogen-based economy offers a promising pathway to achieve significant reductions in carbon emissions across various sectors. By integrating hydrogen into existing energy infrastructures and leveraging it for the production of critical industrial chemicals, we can advance towards a more sustainable and carbon-neutral future. However, this transition requires careful consideration of technological, economic, and regulatory factors to ensure the safe and efficient blending of hydrogen into natural gas grids, as well as the development of infrastructure and policies that support the widespread adoption of green hydrogen and its derivatives.

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2.2. **Overviews of Hydrogen Production Technologies**

Technically, hydrogen can be used in many different sectors, as previously discussed. However, despite hydrogen's great potential, it must be kept in mind that its production, transport and conversion all require energy, as well as significant investment [38]. Since hydrogen is not found in nature in free form, it must be extracted from other raw materials through certain transformation processes. One of the advantages of using hydrogen as an energy vector is that it can be obtained from all primary resources, including fossil fuels such as natural gas, oil, and coal, as well as renewable energy sources and nuclear power [39]. An overview of the strategies for hydrogen manufacture from various hydrogen-containing feedstocks is shown in **Figure 3**, where all possible production technologies are related to their different resource options.

The methods of obtaining H_2 are varied and, depending on the raw material, can be classified into: i) reforming of fossil sources (natural gas, oil derivatives, coal); ii) routes from biomass; and iii) electrochemical separation from water. Depending on the raw material required and the CO_2 emissions generated to obtain it, hydrogen is generally classified into the following types:

- **Renewable hydrogen or green hydrogen**. Hydrogen generated from renewable electricity, using water as the raw material, by means of an electrolysis process. Likewise, hydrogen obtained by reforming biogas or biochemical conversion of biomass, provided that the established sustainability requirements are met, will be of a renewable nature. Green hydrogen is now recognized as a promising solution for improving renewable energy generation. However, green hydrogen (produced by renewables) has historically contributed a negligible proportion of total hydrogen production; in 2018 green hydrogen made up only 11 % of the total. To meet decarbonization goals, this proportion must be greater, and for this to occur, green hydrogen costs need to be more competitive.

- **Grey hydrogen**: hydrogen produced from natural gas or other light hydrocarbons such as methane or liquefied petroleum gases through

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reforming processes. Currently, 99 % of the hydrogen consumed in Spain is of this type.

- **Blue hydrogen**: hydrogen obtained in a similar way to gray hydrogen, but to which carbon capture, utilization, and storage techniques (CCUS: carbon capture, utilization, and storage) are applied, thus reducing CO_2 emissions generated during the process by up to 95 %.

In addition to the above, there are other types with a very diverse environmental impact, such as **black** or **brown** hydrogen, whose raw material is coal, nuclear energy or electricity from the grid. These are not included in the above classification because it is difficult to quantify the environmental impact of their production and consumption.

Starting from fossil and renewable raw materials, a mixture of hydrogen and CO, known as synthesis gas or *syngas*, can be produced by reforming or gasification. This *syngas* is normally used in the synthesis of liquid fuels through the Fischer-Tropsch (F-T) process or can be subsequently treated by the water-gas shift (WGS) reaction followed by preferential oxidation of CO to obtain a hydrogen-enriched stream. On the other hand, hydrogen could be **produced directly from water**, the most abundant source of hydrogen in the world, by **electrolysis**, **thermochemical cycles**, or **photocatalytic division**, although this process is in the initial stage of laboratory research.

With solid feedstock such as coal, petroleum coke or biomass, there are various gasification processes that involve endothermic steam gasification and exothermic oxidation reaction to provide the heat *in situ* to sustain the reaction process. Today, natural gas and coal still account for almost 95 % of the worldwide hydrogen production [40]. Reforming is a well-developed technology for converting hydrocarbons into molecular hydrogen, and carbon dioxide or syngas (H_2 + CO) at a high temperature. Nearly 50 % of the hydrogen produced worldwide is derived from natural gas, primarily by steam reforming, which is currently the most widely used technology for H_2 production on an industrial scale [41,42].

Serval main reactions occur during the reforming process, but it is important to note that this technology is highly dependent on the type of reactant used. Other

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contributions to H_2 production are mainly form partial oxidation of refinery oil (30 %) and coal gasification, whereas only 4 % comes from the electrolysis of water, because the production processes from fossil material are much cheaper than the electrolysis [43].

The clean and non-polluting character of hydrogen as a fuel depends on the raw material and process used to obtain it, as well as the origin of the required energy. The evolution towards sustainability generates a transition scenario from obtaining H_2 from natural gas and water electrolysis. In this transition, the **emerging raw material** is **lignocellulosic biomass**, which is of unquestionable interest for obtaining H_2 on a large scale due to its nature as a renewable source, universal availability, net zero CO_2 generation, and advanced recovery technology.

Hydrogen can typically be produced in vapor phase from **hydrocarbons** and **oxygenates hydrocarbons** by means of three different chemical processes based on the type of oxidant used: steam reforming (SR), partial oxidation (POX), dry reforming (DR), or combination of them, such as autothermal reforming (ATR) or mixed reforming (DR+SR). Moreover, the routes for obtaining H_2 from lignocellulosic biomass can be grouped in:

- **Direct routes**, such as gasification, high-temperature pyrolysis, catalytic pyrolysis, and biological processes.

- **Indirect routes**, with intermediate stages of obtaining oxygenates (ethanol, methanol, dimethyl ether, bio-oil, etc.) for subsequent reforming. Among the oxygenates that can be recovered to obtain H_2 on a large scale through reforming, interest has focused mainly on methanol, DME, and bioethanol obtained through hydrolysis-fermentation, and on glycerol as a by-product of biodiesel production.

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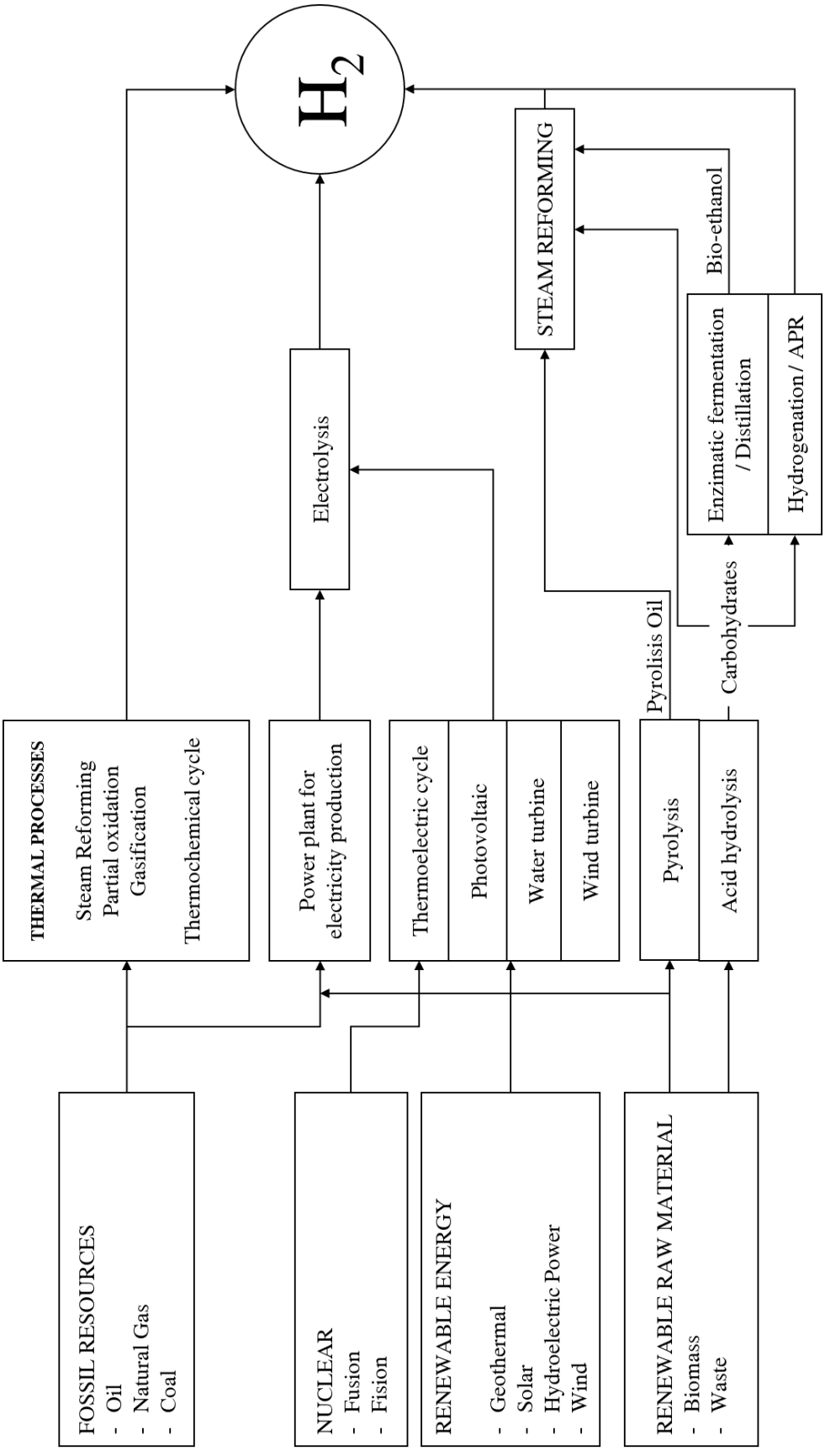

Figure 3: Flowsheet of a summary of main hydrogen production routes.

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2.2.1. Steam reforming

Steam Reforming (SR) is the most common and well-established reforming technology, widely developed in the petrochemical industry to convert natural gas into hydrogen. This technology is favored due to its high H_2-yield and the production of a H_2/CO ratio of about 3:1 [44]. The general equation for the steam reforming process for a hydrocarbon, and specifically for methane steam reforming, are presented as follows, together with the Wayer Gas Shift reaction (WGS-r):

$$C_mH_n + mH_2O \leftrightarrow mCO + (m + \frac{n}{2})H_2$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

This reaction is strongly endothermic, resulting in gas volume expansion and requiring an external heat supply, making it favorable under low pressure. Additionally, hydrogen can be obtained by reacting the CO with water via WGS-r, a mildly exothermic reaction. Steam reforming of natural gas is approximately 65 – 75 % efficient. Industrially, this process requires a several reactor tubes filled with reforming catalyst and a furnace that provides the necessary heat. The reformer operates in the temperature range between 500 and 900ºC and at pressure above 20 atm. Moreover, formation of coke and the production of undesirable secondary reactions, listed below might, might lead to catalyst deactivation.

$$CH_4 \leftrightarrow C + 2H_2$$

$$2CO \leftrightarrow C + CO_2$$

Steam reforming of natural gas has been performed at high temperatures over Ni - based catalysts. Ni has been the favored active metal because of its sufficient activity and low cost. The commonly used support has been alumina, a refractory and highly stable material. This support is acidic and favors hydrocarbon cracking and polymerization, promoting catalyst deactivation. To prevent coke deposition and improve Ni stability, the incorporation of a second metal has been studied [45]. García-Diéguez et al. found that, on alumina-supported Pt-Ni bimetallic catalysts, the addition of Pt also decreased the formation of nickel aluminate, which is a non-reducible inert species [46].

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2.2.2. Partial oxidation

Partial Oxidation (POX) converts hydrocarbons to hydrogen in the presence of oxygen and can be represented by the following equation. Through partial oxidation, hydrogen can be obtained from a wide variety of raw materials or by-products from other reactions, including hydrocarbons, industrial waste, biomass, methane, etc. By means of partial oxidation with oxygen at temperatures between 1150-1350 °C, a crude gas composed of H_2, CO, CO_2 and CH_4 is produced. The impurities contained in the raw gas depend on the composition of the raw material and the process conditions (pressure and temperature), with sulfur coming from the raw material present almost entirely in the form of H_2S. subsequently, purification and conditioning stages are carried out to obtain hydrogen-enriched streams.

$$C_mH_n + \frac{m}{2}O_2 \leftrightarrow mCO + \frac{n}{2}H_2$$

This process is exothermic in nature, depending on the amount of oxygen added, and does not require any external heating other than the supply of air or pure oxygen. Complete oxidation (air supply in excess) will burn the fuel or reactant completely, thereby reducing the amount of hydrogen produced. POX allows a fast start-up and has a short response time, which makes it attractive for applications involving frequent transient operations. Through this process, a H_2-to-CO molar ratio in the range of 1 to 2 can be produced, accompanied by a lower CH_4 concentration than in steam reforming (SR) due to the combustion of CH_4 in the presence of O_2. Coke formation is not favored compared to the SR process, but problems with catalyst deactivation appear due to metal sintering [47].

2.2.3. Dry Reforming

Dry Reforming of Methane (DRM) has received increased interest because it is an attractive process for converting greenhouse gases into synthesis gas (syngas) or as a pre-production process for many chemicals. In this way, water can be replaced by CO_2 to produce syngas through an endothermic process with lower H_2/CO ratio values; i.e. 1:1 for complete conversion. This ratio is appropriate for the synthesis of valuable oxygenated chemicals via Fischer-Tropsch process. When a source of CO_2 is available, CO_2 reforming is likely to become a promising industrial process, reusing greenhouse effect gases as CO_2 and CH_4. The equation for the DRM process

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is presented as follow:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$$

This process is favored by high temperatures and low pressures. Thermodynamically, it can occur at temperatures around 640ºC, although values higher than 800ºC are required to achieve acceptable conversion [48]. The selectivity is determined by the occurrence of side reactions depending on the temperature. The reverse water gas shift reaction (RWGS-r) and carbon deposition forming from Boudouard reaction can occur at temperature lower than 700ºC. In this sense, DRM requires the use of stable and effective catalysts resistant to coking, with Ni-based catalysts being the most commonly used, often modified with noble metal for this purpose [46,49,50].

2.2.4. Mixed processes

The reforming processes can be combined to take advantage of the benefits they offer. Autothermal Reforming (ATR) was developed and used in commercial applications to provide synthesis gas for ammonia and methanol synthesis. In this process, organic feedstock (natural gas and steam/carbon dioxide) is mixed directly with oxygen and air in the reformer [51]. The reaction takes place in a single chamber where methane is partially oxidized, making the process exothermic due to the oxidation. When an autothermal reformer uses CO_2, the H_2/CO ratio produced is 1:1, and when it uses steam, this ratio is over 2.5:1. The reactions can be described in the following equations:

$$2CH_4 + CO_2 + O_2 \leftrightarrow 3CO + 3H_2 + H_2O + heat$$

$$4CH_4 + 2H_2O + O_2 \leftrightarrow 4CO + 10H_2$$

ATR operates in a temperature range between 900-1150ºC and under a pressure range from 1 to 80 bar. The key feature of autothermal reforming is that the thermal energy generated by POX is absorbed by SR, resulting in a thermo-neutral process. Moreover, by using steam, coke formation, which occurs in partial oxidation, is reduced, and it also takes advantage of the high hydrogen yield in steam reforming. In addition to the combinations already described, such as ATR, tri-reforming or mixed reforming has also been studied. In this process, two endothermic reactions, steam reforming and dry reforming, are combined with partial oxidation.

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3. **Oxygenated hydrocarbons**

The growing interest in oxygenated hydrocarbons is driven by their potential as a fuel source for reforming technology, complementing the utilization of natural gas. Oxygenates, a large group of chemical compounds containing oxygen in their chemical structure, range from simple monoalcohols to carbohydrates and are produced from various sources, including raw biomass and platform chemicals. The types and sources of major oxygenates are listed in **table 2**. In this context, steam reforming of aqueous bio-oil fractions presents an interesting alternative for producing hydrogen in a renewable manner[52–55].

Raw bio-oil is unsuitable for direct use as fuel because of its high oxygen content, low heating value, immiscibility with petroleum fuels, and high acidity. Consequently, significant research efforts have focused on upgrading the quality of raw bio-oil [56] and developing technologies to convert bio-oil into value-added products, thus reviving the interest in reforming renewable oxygenated hydrocarbons for hydrogen production. Biomass, an abundant and carbon-neutral renewable energy resource, can be converted through thermal and catalytic processes into various gaseous and liquid products for producing alternative liquid fuels and a variety of chemicals [56–59]. Biomass typically consist of 38-50 % cellulose, 23-32 % hemicellulose, 15-25 % lignin, and other components (5-13 %) [56,60,61]. Numerous experimental and modeling studies have explored converting biomass to hydrogen using different thermochemical pathways, primarily involving gasification or pyrolysis of biomass at various temperatures and pressures [62]. Gasification of biomass produces syngas (H_2+CO), which can subsequently be used to generate a wide range of fuels (methanol, DME, various alcohols, and high-grade diesel through Fischer-Tropsch synthesis) [63,64]. Flash pyrolysis of biomass is another promising method for producing primarily liquid products (bio-oil). This method is currently of particular interest because the liquid can be stored, transported, and used for energy, chemicals, or as an energy carrier. Pyrolysis of biomass yields a liquid "bio-oil" composed of oxygenated compounds and water, notable for being renewable, having low sulfur and nitrogen content, and being CO_2-neutral upon combustion [61]. The bio-oil obtained through pyrolysis can also be reformed.

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Flash pyrolysis is typically conducted at temperatures between 400 – 600ºC, with a low residence time (1-2 s) and a high heating rate (1000 – 10000 K/s), followed by rapid cooling of the products upon exiting the reactor. Under these conditions, the liquid yields are around 75 %, with gas and char yields between 10-20 wt.% and 10-15 wt.%, respectively [65]. Recent advancements in pyrolysis technologies have enabled efficient conversion of biomass into a bio-oil, a mixture of oxygenated compounds including acids, alcohols, ketones, esters, ethers, aldehydes, phenols, and their derivatives, carbohydrates, and a significant proportion of lignin-derived oligomers.

For this doctoral research, particular attention is focused on four main oxygenated compounds, each representing different functional groups: acetone (ketone), ethanol (C_2 monoalcohol), dimethyl ether (ether) and methanol (C_1 monoalcohol).

3.1. **Valorization route: reforming of the aqueous phase of bio-oil**

The availability of biomass and the advantages of obtaining bio-oil through pyrolysis, compared to other biomass-derived oxygenates, presents bio-oil as a promising vector for large-scale H_2 production. Moreover, steam reforming is a suitable route that avoids the need to separate water from the bio-oil. The development of appropriate catalysts and the establishment of process conditions have been significantly influenced by the complexity and instability of bio-oil, particularly the complete bio-oil. Therefore, extensive experience in pure oxygenate reforming is essential [66]. As discussed earlier, catalytic reforming of oxygenates can occur under various operating conditions in either the vapor or liquid phase, utilizing different processes and energy inputs as shown in **table 3**. Recent efforts in hydrogen production via steam reforming of bio-oil have been hindered by severe catalyst deactivation due to coke/oligomer deposition, even in the presence of excess steam ($H_2O/C > 5$). A lower steam-to-carbon ratio (<2) is essential for the economy viability of the process. These operating conditions depend on the type of reactants, with higher hydrocarbon chains requiring higher reaction temperatures for better conversion. In this subsection, a brief summary of typical operational conditions and the most accepted mechanisms for the steam reforming of typical oxygenated compounds is presented.

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Table 2: Types and sources of oxygenates.

Type	Model compound	Source/production
mono-alcohol	methanol	synthesis from syngas
	ethanol	ethylene dehydration; sugars fermentation
aldehyde	formaldehyde	methanol oxidation
	acetaldehyde	ethylene oxidation
polyol	ethylene glycol	hydration of ethylene oxide; synthesis from syngas; synthesis from biomass derived glycerol and cellulose
	glycerol	Byproduct of biodiesel production via trans-esterification
ether	dimethyl ether	Methanol dehydration; synthesis from syngas
carboxylic acid	formic acid	Naphta partial oxidation; methanol carbonylation; biomass and CO_2 hydrogenation
	acetic acid	Methanol carbonylation; bacterial fermentation of sugars and alcohols
ketone	acetone	Cumene process (benzene is alkylated with propylene to produce cumene, followed by oxidation by air to produce phenol and acetone)
aromatics	phenols	Cumene process
carbohydrate	sugars	Hydrolysis of lignocellulosic biomass
bio-oil	raw bio-oil	Fast pyrolysis of lignocellulosic biomass
	aqueous phase of bio-oil (APB)	Fractionation of bio-oil

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Table 3: Hydrogen production from oxygenated compounds reforming: operating conditions.

	feedstock	equation	*[a] T_r (ºC)	P (bar)	*[b] ratio	Ref.
SR	acetone	$C_3H_6O + 5H_2O \rightarrow 3CO_3 + 8H_2$				[67,68]
	ethanol	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$	300-700	1	1.5-8	[69,70]
	DME	$CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 6H_2$				[20,71]
	methanol	$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$	150-400	1		[72,73]
	glycerol	$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2$	350-550	1	3-14	[74,75]
	Acetic acid	$CH_3COOH + H_2O \rightarrow H_2 + CO_2$				[76,77]
OSR	ethanol	$C_2H_5OH + \frac{3}{2}O_2 \rightarrow 2CO_2 + 3H_2$	300-700	1	0-3	[78]
	DME	$C_2H_5OH + H_2O + O_2 \rightarrow 2CO_2 + 4H_2$	600-750	1		[79]
DR	ethanol	$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2$	600-800	1	2	[80]
APR	ethylene glycol	$C_2H_6O_2 + 2H_2O \rightarrow 2CO_2 + 5H_2$	177-267	34-56	0-10 (wt%)	[81]
APR	glycerol	$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$	374-800	221	0-50 (wt%)	[82]
PR	oxygenates	$C_xH_yO_z + (2x-k)H_2O \rightarrow \left(2x + \frac{y}{2} - z\right)H_2 + xCO_2$	RT	1		[83]

*a Common Reaction Temperature

*b S/C; O_2/C; CO_2/C molar ratios

*SR: Steam Reforming; OST: Oxidative Steam Reforming; DR: Dry Reforming; APR: Aqueous Phase Reforming; PR: Photocatalytic Reforming.

3.1.1. *Steam Reforming.*

The availability of lignocellulosic biomass and the advantages offered by obtaining bio-oil through pyrolysis, compared to other biomass-derived oxygenates, presents bio-oil as an interesting vector for large-scale H_2 production. Steam reforming is the process where hydrocarbons react with steam at high temperatures, converting into CO and H_2. To address issues of activity, selectivity, and catalyst lifetime, a better understanding of both the catalytic steam reforming mechanisms and the thermally induced cracking decomposition reactions of oxygenates is needed. The steam reforming of oxygenated hydrocarbons with the chemical formula of $C_nH_mO_k$ can generally be described by Eq. (1) as presented by Czernik et al. [84]. In a complete conversion of an oxygenated hydrocarbon, the reforming reaction is typically accompanied by the Water Gas Shift (WGS) reaction, Eq. (2), and its reverse, with the extent of these reactions depending on the operating conditions

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influencing the yield of the process. The overall reforming reaction can be represented by Eq. (3), which combines steam reforming (Eq, 1) and WGS (Eq. 2). Steam reforming is usually carried out at high temperatures (400 – 800ºC) and atmospheric pressure, through it is sometimes conducted at elevated pressure in industrial practice. Eq. (3) is often used to describe the SR reaction of oxygenates, although at high temperatures the WGS shifts to the left, resulting in significant amounts of CO.

Additionally, unwanted side reactions occur during steam reforming, decreasing hydrogen production and potentially leading to coke formation. Few of the primary products of biomass pyrolysis are thermally stable at the typical temperatures of a hydrocarbon reformer. Thus, there is significant competition between catalytic reforming reactions and thermal decomposition for most oxygenates [85]. Thermal decomposition (cracking) of most oxygenates can result in the formation of mainly coke and/or a mixture of gases (Eq. 4-6). This reaction should be minimized due to the coke formation, as coke production is one of the major issues in the reforming reaction of hydrocarbons [86].

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + \left(n + \left(\frac{m}{2}\right) - k\right)H_2 \qquad \Delta H^0 > 0 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0 = -41.2\ KJ/mol \qquad (2)$$

$$C_nH_mO_k - (2n-k)H_2O \rightarrow nCO_2 + (2n + \left(\frac{m}{2}\right) - k)H_2 \qquad \Delta H^0 > 0 \qquad (3)$$

$$C_nH_mO_k \rightarrow C_xH_yO_z + gas(H_2, CO, CO_2, CH_4 \ldots) + coke \qquad \Delta H^0 < 0 \qquad (4)$$

$$C_nH_mO_k \rightarrow CO + H_2 \qquad \Delta H^0 < 0 \qquad (5)$$

$$C_nH_mO_k \rightarrow CO_2 + CH_4 \qquad \Delta H^0 < 0 \qquad (6)$$

$$2CO \rightarrow C + CO_2 \qquad \Delta H^0 = -172.0\ kJ/mol \qquad (7)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H^0 = -206.0\ kJ/mol \qquad (8)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0 = +206.0\ kJ/mol \qquad (9)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H^0 = +165.0\ kJ/mol \qquad (10)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0 = +247.0\ kJ/mol \qquad (11)$$

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Utilizing different reaction conditions and reforming catalysts can help reduce the number of secondary reactions, thus favoring H_2-selectivity. Consequently, the final concentration of the reaction products (CO, H_2, CO_2, and CH_4) will depend on the equilibrium constants of the reactions involved in the reforming, as well as the transformations of these products according to the co-side reactions. Additionally, the Boudouard reaction, metanation of CO, and/or steam/dry reforming (Eq. 7-11) of methane will also influence the product distribution, especially at low temperatures and/or high pressures.

a. Acetic Acid Steam Reforming (HOAc-SR)

Acetic acid is a major component of bio-oil, which a content of up to 32 wt.% [87]. Additionally, acetic acid can be produced in large quantities from biomass through fermentation [88]. Therefore, acetic acid (HOAc) is recognized as an important and representative derivative of biomass, useful for establishing correlations between the physicochemical characteristics of catalysts and their reforming performance for hydrogen production. Moreover, because acetic acid contains all the types of carbon bonds (C-C, C-O, C=O, C-H) and O-H bonds, it has been extensively used as a probe molecule in various catalytic reactions.

The chemical reactions involved in the catalytic reforming of HOAc are very complex, with some of the main reactions described as follow. H_2, CO, CO_2 and CH_4 are the major products in HOAc-SR from catalytic steam reforming (Eq. 12 and/or 13). Acetone can be formed via acetic acid ketonization (Eq. 14), following the route described below. Furthermore, H_2 can be produced directly from HOAc-SR (Eq. 12 and 13), or from thermal decomposition and water gas shift reaction (Eq. 15 and 13 respectively), as well as from steam/dry reforming of methane (Eq. 9-11) produced by acid decomposition [67,85].

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2 \qquad \Delta H^0 = +184.0\ kJ/mol \quad (12)$$

$$CH_3COOH + H_2O \rightarrow CO + CO_2 + 3H_2 \qquad \Delta H^0 = +145.0\ kJ/mol \quad (13)$$

$$2CH_3COOH \rightarrow C_3H_6O + CO_2 + H_2O \qquad \Delta H^0 = -42.0\ kJ/mol \quad (14)$$

$$CH_3COOH \rightarrow CO_2 + CH_4 \qquad \Delta H^0 = -17.0\ kJ/mol \quad (15)$$

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Previous research has shown that, through thermodynamic analysis of HOAc-SR process, the optimal operating conditions were found to be S/C = 3, T = 627°C, and 1 atm, demonstrating that the conversion of acetic acid is not limited by equilibrium and, therefore, complete conversion can be achieved. Temperature and the S/C ratio are key factors in the products distribution, where an increase in temperature favors decomposition reactions, and an increase in the S/C ratio favors the steam reforming (SR) and water gas shift (WGS) reactions [89,90].

b. Acetone Steam Reforming (SRA)

Taking acetone as an example of the ketones, the steam reforming reaction generally follows the stoichiometric reaction (Eq. 16). Acetone is a cheap by-product of the phenol production process via the *cumene* peroxidation route. Utilizing acetone for hydrogen production via steam reforming can be considered a way to enhance its value.

$$C_3H_6O + 5H_2O \rightarrow 3CO_2 + 8H_2 \qquad \Delta H^0 = +346.0\ kJ/mol \quad (16)$$

However, this is not a straightforward reaction, as several intermediates are formed during the process depending on the catalyst used and the thermodynamic properties. Many researches have focused on acetone reforming. Sanchari Basu *et al.* [91] report that the conversion of acetone in the steam reforming process requires a temperature of up to 500ºC, achieving 80 % selectivity to hydrogen when operating under an optimal steam-to-acetone molar ratio close to 8/1. Apart from H_2, CO, and CO_2, common by-products of acetone reforming include CH_4, C_2H_4, ethanol, acetaldehyde, acetic acid, and isopropanol, especially at temperatures higher than 620ºC [68]. Additionally, acetone decomposes according to an endothermic apparent overall reaction into ketene and methane (Eq. 17) at temperatures above 773 K [92–94]. Under this conditions, ketene decomposition or ketene coupling can occur as a parallel processes, with ethylene and CO as the principal products (Eq.18)[95].

$$CH_3COCH_3 \rightarrow CH_2CO + CH_4 \qquad \Delta H^0 = +166.0\ kJ/mol \quad (17)$$

$$CH_2CO \rightarrow 1/2C_2H_4 + CO \qquad \Delta H^0 = +63.0\ kJ/mol \quad (18)$$

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c. *Ethanol Steam Reforming (EtOH-SR)*

Ethanol steam reforming for H_2-enriched streams has gained significant attention because it is a renewable resource, easy to handle and transport, and thermodynamically feasible to decompose, offering smaller environmental pollution as a sustainable energy source. More importantly, ethanol is CO_2 neutral since the amount of CO_2 produced by steam reforming is consumed by the biomass growth, providing a nearly closed carbon loop. Extensive research on ethanol steam reforming has been conducted over years to achieve higher efficiency and greater H_2 production [69,96,97]. Ethanol is an ideal raw material for hydrogen production and can be obtained from biomass, extensively studied due to its obtainability from the fermentation process of various renewable sources [98]. Furthermore, ethanol can be considered as a model C_2 mono-alcohol compound in the aqueous phase of bio-oil [98–100]. The process follows the stoichiometric reaction (Eq. 19) or an alternative with insufficient steam supply (Eq. 20).

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad \Delta H^0 = +174.0\ kJ/mol \qquad (19)$$

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2 \qquad \Delta H^0 = +256.0\ kJ/mol \qquad (20)$$

The temperature range for operating ethanol steam reforming is quite wide, from 300 – 650ºC, allowing for the complete conversion of ethanol at 350ºC and atmospheric pressure in the presence of a catalyst, requiring a much lower temperature than methane reforming. The reaction mechanism of the ESR process depends on the metal catalyst used, which promotes the scission of C-C and C-H bonds [99]. Additionally, the support may participate in the WGS reaction and its reverse, as well as in the occurrence of secondary parallel reactions like acetone formation (Eq. 21). Depending on the catalyst's acidity, two major but undesirable routes should also be considered: ethanol is highly favored to undergo dehydrogenation to form acetaldehyde (Eq. 22), since dehydrogenation, an endothermic reaction, has a lower energy requirement compared to the endothermic SR process. Acetaldehyde undergoes steam reforming to CO and H_2 (Eq. 23) or further decomposes to form CH_4 and CO (Eq. 24). Additionally, ethylene may be formed via ethanol dehydration (Eq. 25*)*; ethylene can easily polymerize to form coke (Eq. 26). Ethanol decomposition pathways also contribute to the final

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products, as shown in (Eq. 27) and (Eq. 28), leading to methane and acetone formation, respectively [101–103]. If methane is produced in high selectivity, it can also be reformed to produce hydrogen with CO_2 and/or CO, as shown in subsequent reactions; and acetone can follow the route detailed above

$$2C_2H_5OH \rightarrow CH_3COCH_3 + 2H_2 \qquad \Delta H^0 = +116.0\ kJ/mol \qquad (21)$$

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad \Delta H^0 = +68.0\ kJ/mol \qquad (22)$$

$$C_2H_4O + H_2O \rightarrow 2CO + 3H_2 \qquad \Delta H^0 = +81.0\ kJ/mol \qquad (23)$$

$$CH_3CHO \rightarrow CO + CH_4 \qquad \Delta H^0 = -6.0\ kJ/mol \qquad (24)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad \Delta H^0 = +45.0\ kJ/mol \qquad (25)$$

$$nC_2H_4 \rightarrow polymers \rightarrow C \qquad \Delta H^0(depends\ on\ the\ form\ of\ coke) \qquad (26)$$

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad \Delta H^0 = +83.0\ kJ/mol \qquad (27)$$

$$2C_2H_5OH \rightarrow CH_3COCH_3 + 2H_2 \qquad \Delta H^0 = +116.0\ kJ/mol \qquad (28)$$

d. DME and Methanol Steam Reforming (DME-SR, MeOH-SR)

DME has recently attracted attention as a hydrogen carrier since, unlike methanol (which is used in reforming with PEMFC), DME is harmless, non-corrosive, has a high energy density and high H/C ratio, with no C-C bonds. Different processes for obtaining hydrogen from DME have been studied, including partial oxidation (POX), steam reforming (SR) and autothermal reforming (ATR). Obtaining H_2 by partial oxidation of DME has the advantage of not requiring external energy input, as it is an exothermic process. However, the hydrogen yield is low in comparison with the rest of the processes. DME steam reforming (DME-SR) is presented as the H_2-production process from DME with the highest theoretical hydrogen yield [20,104]. The steam reforming of DME has been demonstrated to occur through two reactions in series, where the first reaction is DME hydrolysis (DME-HYD) (Eq. 30), followed by methanol steam reforming (MeOH-SR) (Eq. 3), to produce a hydrogen-rich stream [105,106]. Eq. (29) represents the DME steam reforming (DME-SR), a linear combination of Eq. (30) and (31) respectively. The integrated system of DME-SR also contains products from the WGS-r (Eq. 2), and its reverse.

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Thermodynamically, DME-HYD to methanol is an equilibrium-limited reaction [107,108] and can be considered as the limiting step in DME-SR process, so total conversion of DME cannot be achieved considering this reaction alone. Coupling this reaction with MeOH-SR, an important increase of DME conversion can be achieved by shifting the equilibrium of reaction (Eq. 30) in the forward direction. Under these considerations, it is important to note that steam reforming of methanol occurs at temperatures of 200–300 °C but the hydrolysis of DME to methanol occurs in the temperature range of 300–400 °C [109]. Other reactions such as DME decomposition (DME-DEC) (Eq. 33), direct CO_2 formation (Eq. 34), methanation reactions (Eq. 35-36) or methane reforming (Eq. 9-11), showed as follow can be considered in the DME-SR process, in addition to those relating to MeOH-SR described below.

In this context, it is important to note that the study of parallel reactions and particularly of methanol steam reforming requires a previous study to find the optimal conditions and for a better understanding of DME-SR process.

$$CH_3OCH_3 + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \qquad \Delta H^0 = +35.0\ kJ/mol \qquad (29)$$

$$CH_3OCH_3 + H_2O \leftrightarrow 2CH_3OH \qquad \Delta H^0 = +36.3\ kJ/mol \qquad (30)$$

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad \Delta H^0 = +49.7\ kJ/mol \qquad (31)$$

$$CH_3OCH_3 + H_2O + O_2 \leftrightarrow 4H_2 + 2CO_2 \qquad \Delta H^0 = ??\ kJ/mol \qquad (32)$$

$$CH_3OCH_3 \leftrightarrow CH_4 + H_2 + CO \qquad \Delta H^0 = -1.0\ kJ/mol \qquad (33)$$

$$CH_3OCH_3 + H_2O \leftrightarrow CH_4 + CO_2 + 2H_2 \qquad \Delta H^0 = -42.0\ kJ/mol \qquad (34)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H^0 = -206.0\ kJ/mol \qquad (35)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \Delta H^0 = -165.0\ kJ/mol \qquad (36)$$

According to the literature on the Methanol Steam Reforming (MeOH-SR) process, it can be described by the chemical reactions shown below [67,72,73]. Methanol transformation into gaseous mixtures rich in hydrogen can be performed in two ways, by methanol steam reforming (Eq. 31) or by methanol decomposition (Eq. 37) principally. Since methanol decomposition is the reverse of methanol synthesis

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reaction, the commercial catalysts for methanol synthesis are active in this reaction. Methanol steam reforming over Cu-based catalysts was originally thought to have involved Methanol - Decomposition (MeOH-Dec, Eq. 37) followed by WGS-r (Eq. 3). However, there is evidence to suggest another pathway including direct MeOH-SR (Eq. 31) depending on operating conditions and catalysts used. Further, it is important to study the possibility of the formation of small amount of dimethyl ether (Eq. 38, 39) and formaldehyde (Eq. 40).

$$CH_3OH \leftrightarrow CO + 2H_2 \qquad \Delta H^0 = +90.2 kJ/mol \quad (37)$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta H^0 = kJ/mol \quad (38)$$

$$3CH_3OH \leftrightarrow CH_3OCH_3 + CO_2 + H_2 \qquad \Delta H^0 = kJ/mol \quad (39)$$

$$CH_3OH \leftrightarrow CH_2O + H_2 \qquad \Delta H^0 = kJ/mol \quad (40)$$

$$2CH_3OH \leftrightarrow HCOOCH_3 + 2H_2 \qquad \Delta H^0 = kJ/mol \quad (41)$$

$$HCOOCH_3 + H_2O \leftrightarrow CH_3OH + HCOOH \qquad \Delta H^0 = kJ/mol \quad (42)$$

$$HCOOH \leftrightarrow H_2 + CO_2 \qquad \Delta H^0 = kJ/mol \quad (43)$$

$$2CH_3OH \leftrightarrow CH_4 + 2H_2 + CO_2 \qquad \Delta H^0 = kJ/mol \quad (44)$$

$$2CH_3OH \leftrightarrow CH_4 + CO + H_2 + H_2O \qquad \Delta H^0 = kJ/mol \quad (45)$$

$$CH_3OH \leftrightarrow C + H_2O + H_2 \qquad \Delta H^0 = kJ/mol \quad (46)$$

Another mechanism deals with the formation of methyl formate intermediate through methanol dehydrogenation to methyl formate and hydrogen (Eq. 41) [110,111]. This methyl formate can react with water to produce methanol and formic acid. After that, this acid formic can descompose to CO_2 and H_2 (Eq. 42 and 43), among other secondary direct decomposition reactions (Eq. 44-46).

As can be seen, the process of Oxygenated-SR process leads to the appearance of numerous secondary reactions that complicate the mechanism. In the case of DME-SR, it is interesting to study the MeOH-SR process to understand the mechanism under the catalysts used, considering this process as the second stage in DME-SR.

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4. Catalysts for reforming of oxygenated compounds

The choice of the catalyst plays a fundamental role in catalytic process reforming with vapor oxygenated compounds and an optimized formulation is essential to achieve the desired conversion, product selectivity and H_2-yield. The most important disadvantages found in the design of these catalysts is deactivation due to the sintering of the metal and the formation of coke. In addition, the nature of the catalyst can take the reaction through one mechanism or another, favoring some reactions or others, so that different results can be obtained[112]. There are a few reports on reforming model compounds of bio-oil or water separated bio-oils [74,113–115], reforming multicomponent mixtures [116,117] and even the whole bio-oil [52,53,118] making clear the great diversity in by-products obtained and the complexity present in the raw bio-oil reforming process. Understanding the reaction behaviors, the derivatives products during bio-oil production process and steam reforming is of importance for optimization of the process for steam reforming of bio-oil and the catalyst design.

4.1. ***Supports***

According to literature, numerous supports have been investigated in reforming reactions covering a wide range from basic to acidic supports and been used in the steam reforming of oxygenated compounds. The selection of a suitable support is one of the key points to improve the activity and stability of the catalyst. In consequence, utilizing supports with a high surface area may create more dispersion of active sites on the support pores. In addition, oxygen storage capacity, porosity of the materials, redox properties and thermal stability need to be carefully evaluated. The commonly catalyst system used for reforming reactions has been Ni-based materials. The most used support for the synthesis of Ni-based catalysts has been Al_2O_3, due to its mechanical properties and because it favours the good dispersion of Ni on its surface. This support is widely used in reforming reactions of numerous components found in biomass-derived bio-oil, such as acetic acid, methanol and acetone steam reforming [67]. However, due to the acidic properties of Al_2O_3, it promotes the deactivation of the catalyst by the formation and deposition of coke on its surface. Accordingly, the modification of Ni-Al_2O_3

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catalysts by incorporating metal oxide promoters with basic properties (MgO, ZrO_2, CeO_2, CaO, La_2O_3…) has been widely studied in the literature in order to increase their activity, reducibility, stability and regenerability in the reforming of oxygenated compounds in addition to promoting methane steam reforming as well as WGS-reaction [119–121]. MgO is a basic oxide that has the same crystalline structure as NiO; as a result, the combination of MgO and NiO produces solid solution catalysts with basic surface properties, which is favourable for the inhibition of coke formation. Moreover, the addition of alkali elements is also used to neutralize acid sites and, in consequence, reduce carbon deposition over catalyst surface [122,123]. The modified Al_2O_3, Al_2O_3-ZrO_2, Al_2O_3-ZrO2-La_2O_3 and Olivine with different metal content, were tested in a continuous flow fixed bed reactor to produce hydrogen from glycerol by steam reforming process [123]. The catalyst Ni-Pd/Al_2O_3-ZrO_2 showed the smaller particles of Ni in comparison with the rest of catalysts tested; moreover, this material presents the highest hydrogen yield (73'84 %), although a high temperature over 800ºC was needed.

Ceria and mixed oxide ceria have been widely used as catalytically active systems for ethanol reforming processes due to CeO_2 has shown excellent properties to improve thermal stability of the alumina by promoting Ni dispersion favoring metal-support interactions [80]. In this sense, CeO_2 is a partially reducible oxide that is characterized by a synergy with the metal phase, finding, for example, a better catalytic activity when Pt is supported on CeO_2 instead of Al_2O_3 testing in ethanol steam reforming [124]. Moreover, ceria has the capacity to store and release oxygen and decrease the activation energy, which makes it very attractive in hydrogen production processes[125,126]. On the other hand, CeO_2 has been extensively employed as support and catalytic promoter in ethanol steam reforming due to tis oxide improves catalytic activity by decreasing the carbon deposition, due to the high amount of mobile lattice oxygen induced by the CeO_2 [127]. Zirconia is also considered as a partially reduced oxide, like CeO_2 and is also used as a catalyst in reforming reactions. In this sense, the role of ZrO_2 and ZnO has also been investigated intensively. ZrO_2 and ZnO were tested in oxidative SR of methanol and volatiles derived from biomass [128,129]. However, comparing Pt/ZrO_2 and Pt/CeO_2, the activity is still superior using CeO_2 as a support. Martinelli et al. probed that Na-promoted ZrO_2 catalyst improve product yield, increasing CO_2

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content, when tested in ethanol steam reforming [130]. K.F.M. Elias et al. studied the effect of CeO_2 addition to Ni/ZnO-based catalysts for hydrogen production from Acetone Steam Reforming, finding an increase in H_2-yield comparing to unmodified system, as well as a reduction in carbonaceous deposits as a result of improved the oxygen storage capacity (OSC) of the catalyst after ceria incorporation into structure [131].

In addition, the incorporation of Mg and Ca favors the reduction of particle size, which increases the dispersion of the active phase and, therefore, the interaction between the metal and the support [119,121]. On the other hand, it has also been published that the addition of these elements favors the reforming of methane and reduces the formation of ethylene, which is a precursor of the formation of coke. Accordingly, the effectiveness of the incorporation of alkali metal oxides such as MgO in Ni/Al has been demonstrated, since it favors the adsorption of H_2O and the mobility of the OH groups by inducing the gasification of the coke formed, in addition to reducing the residual acidity of the alumina [132].

On the other hand, other systems have been probed in SR-reactions. The mesoporous carbon can be used as a support since its large volume and specific area make it suitable for embedding nanoparticles. In this sense, this material has been used for ESR showing high H_2-yield in stream products accompanied by low content of unwanted by-products, presenting itself as a promising system in reform reactions [122]. Pd/Ni-Co catalyst derived from a hydrotalcite-like material was proposed for steam reforming reactions. Esteban-Díez et al. studied this system on reforming of acetic acid, acetone and their blends, using dolomite as sorbent CO_2 to improve the WGS process [133], achieving H_2 selectivity values around 99.8–99.9 % at 575ºC.

The existing literature on the steam reforming reaction of DME can be divided into two large groups: those articles that study different acid catalysts and their effect on the DME hydrolysis reaction and on the overall reforming reaction, and those articles that study the effect of variation in the composition of the active phase. The common approach in DME-SR is to use acid catalyst for the hydrolysis of DME to methanol. An acidic function is important for the development of catalysts active

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in DME-SR given than hydrolysis is the process-limiting step [134,135]. The typical catalyst used in the reforming reaction of DME is the $Cu/ZnO/Al_2O_3$ catalyst (CuZnAl) [136]. It is well known that this catalyst has been a benchmark catalyst in methanol synthesis and is active for the methanol reforming reaction. In addition, CuZnAl system is one of the most important catalyst in low-temperature water-gas shift reaction (LT-WGS-r) [137]. Cu is commonly regarded as the active phase, but the role of ZnO and Al_2O_3 is more than that of an inert support. The combination of Cu with ZnO particles leads to a synergic effect that improve Cu-sites activity [138–140]. ZnO has been identified as a textural promoter to segregate Cu and its presence is indispensable in CuZnAl materials focused on maximizing Cu-Zn contact. The mechanism of this synergistic effect has been debated and widely studied for a long time. On the one hand, it has been proposed that ZnO acts as a hydrogen reserve facilitating the reduction of adjacent Cu surfaces [141,142]. Furthermore, the so-called Strong Metal-Support Interaction (SMSI) mechanism was proposed, where morphological changes in Cu-particles are proposed, due to a wetting of ZnO in reducing atmosphere or the supply of Zn atoms to Cu surface, acting as dispersive agent [141]. In line with these studies, the addition of Zr to the Cu-Zn system has been proven to improve copper dispersion as well as the surface basicity, thus reducing sintering [143,144].

But not only these ZnO_2 bases supports have been used in DME-SR. Faungnawakij et al. have extensively studied the reforming reaction of DME, using a copper-iron spinel of CuB_2O_4 formula as an active catalyst for the methanol reforming reaction [145] and have investigated the effect of different acid supports for the hydrolysis of DME, such as the use of H-mordenite, Y or ZSM-5 zeolites, -Al_2O_3, V_2O_5 and TiO_2 [146,147].

Al_2O_3 is commonly used in spite of high temperatures (at least 350 – 400ºC) are needed due to its low acidity [20,148]; nevertheless, this acidic characteristics of the alumina can hydrolyze the DME, so it is a good candidate for the DME reforming reaction. It could be either a physical mixture of a DME hydrolysis catalyst and a methanol steam reforming catalyst or a single dual-function catalyst. Acid site density, strength of the acid sites and hydrophobicity have been suggested to influence the activity of the hydrolysis catalysts [149,150]. In this respect it is necessary to take into account that zeolites may generate long-chain hydrocarbons

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at temperatures above 300ºC through the methanol to olefins reaction influencing the desired performance. As compared to strong acids such as H-ZSM5 and morderite, γ-Al_2O_3 possesses relatively weak acid sites and therefore provides lower hydrolysis activity. However, weak acids are beneficial from the point of view of catalyst durability and side reaction inhibition [108]. According to literature, higher activity is observed for HZSM-5 zeolite than for γ -Al_2O_3 in DME hydrolysis, with insignificant formation of hydrocarbons as secondary products [151]. Although zeolites, such as ZSM-5 and mordenite provided better activity than alumina, they were rapidly deactivated due to coking problems [152,153]. Taking into account these limitations, alumina is the most suitable and commonly used catalyst for DME hydrolysis, showing a high activity at temperatures above 300ºC due to its moderate acidity. However, it is not clear what the effect of the acid strength on alumina over activity of DME hydrolysis is and how hydrolysis occurs. Some studies propose that the DME hydrolysis on the hydroxylated surfaces of γ-Al_2O_3 at temperatures around 250-350ºC is likely to occur at the -OH groups [154].

Among all of them, alumina remains a suitable support in steam reforming of oxygenated compounds because it provides a large surface area, mechanical resistance and stability, although its acidity promotes the formation of coke, which can be inhibited with the appropriate formulation of the catalyst.

4.2. ***Active Phase: monometallic and bimetallic formulation***

An appropriate metal-support interaction is also needed to produce catalysts with outstanding stability and reducibility properties. Catalysts for the steam reforming of oxygenated compounds are mainly based on supported nickel. As we know nickel has been extensively used for steam reforming of hydrocarbons since it is inexpensive and easily available. Ni-based catalysts have been widely used for the reforming of bio-oil, due to its high C–C bond-breaking activity, relatively low cost and its well-known catalytic behavior in WGS-r [155]. Reforming of bio-oil light fraction compounds involves the cleavage of C – H and C – C bonds, which, compared to methane, are easier to activate and require lower temperatures. The pathway to reforming these compounds is different from the one extensively

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described for CH_4 steam reforming. In ethanol steam reforming for example, activation of the -OH group is required for cleavage of O – H bond forming acetaldehyde; this activation is favored on more oxophilic metals (e.g., Ni, Co and Rh) while less oxophilic metals (eg., Pt and Pd) facilitate C – H cleavage [156]. On Ni/Al_2O_3 catalysts at low temperatures (<350ºC), the decomposition of ethanol occurs via the acetaldehyde intermediate, which decomposes to species such as CHx and CO, leading to the formation of equimolar mixtures of CH_4 and CO. At high temperatures, the steam reforming of ethanol occurs via oxidation of CO and decomposition of CHx to C and H_2 [99]. Moreover, Ni-based catalysts have been extensively used in other oxy-compounds steam reforming reactions (acetone, methanol, glycerol, alcohols…), in gas and liquid phase obtaining H_2-rich stream with high conversions [157]. However, Ni-based supported catalysts suffer deactivation due to carbon deposition, because methane formation from steam reforming of oxygenated, formation that is a serious problem when reforming bio-oils. Moreover, the acid-basic sites on the surface of the catalysts affect the dehydration of alcohols and the deposition/gasification of coke [158,159]. Addition of cobalt has been found to reduce the methane formation reaction and hence carbon deposition. Moretti et al. explained the improvement in the activity of Ni-Co catalysts due to a reducibility of both metal oxide phases, showing a synergic effect between Co and Ni [160]. On the other hand, Fe and Cu are used [70,111,161] as well as noble metals such Pt, Pd and Rh and the bimetallic Ni-based catalysts or metal alloys employing Ni have been also reported [162,163].

Rh has been widely examined as the active metal for SR due to its superior activity toward C – H and C – C bond cleavage. On the other hand, Rh have presented the higher resistance to coke formation because it is also capable of reforming ethylene, making it one of the most studied active phases for the reforming reactions. Furthermore, the addition of Rh to conventional Ni-based catalysts is regarded as an active system due to its high activity and its capacity to diminish the intermediate products. The addition of Rh to Ni-based systems promotes a lower reducibility of NiO for bimetallic catalysts compared with monometallic ones [164]. The improved stability and activity of the Ni-base catalyst with the Rh incorporation is assumed to be due to a cooperative effect of Rh and Ni activities, to the fact that it promotes the WGS reaction; moreover, the addition of Rh improve the capacity to

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gasify the methyl group and prevent the accumulation of acetate. On the other hand, the bimetallic Rh-Ni catalyst presents a strong inhibition of filamentous carbon and a very low amount of amorphous carbon over the catalyst surface, in comparison with monometallic ones [165]. As for the support, different supports have been used for their combination with Rh, both in mono and bimetallic systems [45,80]. Introducing small amounts of Rh can significantly improve activity and stability of Ni-based catalyst reducing the deposition of carbonaceous species, and with same metal loading, Rh doped nickel catalyst performs even better than nickel and Rh alone, needing just 0.1 wt.% Rh to Ni-based catalyst [45]. C.H. Campos et al. found that the incorporation of 1%p/p Rh to Ni/Al_2O_3 doped with La_2O_3-CeO_2 enhances the activity and stability compared to the monometallic 1.0%Rh or 10%Ni [165]. As mentioned before, Ce presents particular redox properties in the presence of transition or noble metals; so Ni–Ce and Rh–Ce bimetallic combinations were tested in reforming processes. Rh/CeO_2 catalyst showed excellent catalytic behavior for oxidative ethanol reforming and presumably for ethanol steam reforming [166].

Only limited studies have reported the use of Ni-Pt bimetallic catalysts for steam reforming of oxygenated hydrocarbons. Almost all of these studies have concluded that bimetallic Ni-Pt samples have better catalytic performance compared with the monometallic catalysts [124,130,162]. The improvement in the catalytic activity and reactivity of Ni/Al_2O_3 systems with the incorporation of Pt has already been demonstrated, producing high hydrogen yields through dry methane reforming [46,49]. Claudio-Piedras et al. studied the influence on methanol steam reforming of Pt-nanocatalyst employing CeO_2-NR as support, finding that, when Pt is incorporated to CeO_2-NR, MeOH-Conversion increase from 20% to almost 100%, reaching this maximum value at 350ºC. On the other hand, bimetallic PtNi catalysts have been used in hydrogen production through ethylene glycol steam reforming; the addition of Pt enhanced both activity and H_2 selectivity [167]. However, the high cost of noble metals has shifted attention to other promoters effective in breaking C – C bonds and highly active in steam reforming. In this sense, Braga et al. studied the effect of Ni-, Ni-Co and Co on $MgAl_2O_4$ supported in Acetone-SR studying the effect of metal addition [68].

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As mentioned before, Cu-based catalysts have been considered promising catalysts for steam reforming of DME because copper catalysts are widely known to have high activity for methanol steam reforming [168,169]. The influence of the oxidation state of Cu on catalytic reactivity has always been a focus of research in many Cu-catalyzed reactions. Cu^{2+} is the predominant Cu species in fresh catalysts, and undergoes a two-step reduction process to Cu^0 via the Cu^+ intermediate state. Cu^0, Cu^+ and Cu^{2+} could coexist in the catalytic system, and reduction of Cu^{2+} and reoxidation of Cu^0 occurred through the formation of Cu^+ intermediate species. It has been shown that metallic Cu^0 is necessary for methanol steam reforming (MSR) whereas oxidized Cu^+ and Cu^{2+} favor the formation of water and CO/CO_2. Moreover, both Cu^+ and Cu^0 are proven to be the active sites for MeOH-SR, promoting HCOO- and COO- species formation by Cu^+ and the contribution of Cu^0 to the CH_3O- species formation. On the other hand, the oxidation state of Cu have been found to be closely associated with Cu–ZnO and has been widely used in MeOH-SR, finding the importance of a strong Cu/ZnO interaction on the reactivity of the catalyst, finding that doping copper to zinc results in enhanced catalytic activity with increased selectivity towards hydrogen [136,138,139].

However, copper-based catalysts have intrinsic drawbacks, for example, sintering susceptibility at high temperatures and pyrophoric issue upon air exposure; in this sense, these catalysts suffer an irreversible deactivation exceeding 300ºC due to the trend of Cu species to form aggregates [170–172]. This reaction occurs at temperatures of 200-300ºC but the hydrolysis of DME needs a temperature range of 300-400ºC and therefore the durability of copper will be a concern. However, with Al_2O_3 as support, MeOH-SR activity decreases because it inhibits CuO reduction due to a strong interaction between Al_2O_3 and CuO. Highly reducing atmosphere is reported to cause a phase change in the catalyst structure that results in thermal agglomeration phenomenon (sintering) [128]. It has also been proven that Ni addition attenuates Cu sintering, given that it improves surface dispersion and strengthens the interaction between Cu and γ-Al_2O_3 [173]. The effect of copper incorporation over Ni/Al_2O_3 catalysts has been investigated for hydrogen production steam reforming of alcohols. Fierro et al. reported that the interaction of Cu-Ni and the support seem to play an important role in the reaction network, achieving higher H_2-yields with an increased Cu-content of up to 3% in ethanol

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oxidative steam reforming [174].

The 8-10 groups of periodic table elements present thermal stability compared with copper, although have low activity and produce more CO in comparison with Cu-based [73]. It seems very appropriate to use elements from these groups along with copper to overcome the low stability of Cu-based catalysts. The most used catalyst in this group is the palladium-based catalyst [175]. Palladium catalysts have also been shown to exhibit high activity for DME-SR, however associated with the formation of large amount of CO, due to its used for methanol decomposition ($CH_3OH \leftrightarrow CO + 2H_2$) [176]. It has been demonstrated that Pd catalysts with ZnO or Ga_2O_3 as support and supported over Cu-based catalysts were effective in MeOH-SR process, among which Pd/ZnO catalyst presented high activity and selectivity towards H_2 and CO_2, although addition of Pd led to poorer selectivity, due to a significant increase in the selectivity to CO [177–179].

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5. Objective

In view of the current increase in the demand for energy and the imperative need to decarbonize the global energy system and further avoid the worst of a climate change that has become a crisis, hydrogen is a promising energy alternative. The use of oxygenated compounds in the hydrogen production is favored by the energetic contribution of the oxygen atoms contained in the molecules tested, hence enhancing the steam reforming reaction, which is energy intensive. The main objective of this Doctoral Thesis is to contribute to the development of efficient nano-catalysts in the reforming processes of oxygenated compounds with steam, as well as the establishment of the operational conditions for each of them.

In detail, the following individual objectives are proposed:

- Design of a bifunctional nanocatalyst efficient in H_2 production by steam reforming, comparison with commercial industrial catalysts and the establishment of the development of the improved catalyst synthesis protocol.

- Comparative evaluation on the hydrogen yield of oxygenated model molecules with different functional groups based on operating temperature, yield and product distribution.

- FTIR-in situ study to establish the mechanistic route and the stages involved in the steam reforming process and prediction of the operating regions, based on the experimental results, by means of simulation.

- Finally, the development of a reaction microdevice and the testing of the microreformer for hydrogen production from dimethyl ether (DME)/methanol.

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Chapter 2

Experimental Procedure

In this chapter, we offer a description of the materials used in the synthesis of the catalysts and reactivity studies. In a second section, the equipment and the instruments used are described as well as the experimental methodology used in the preparation and characterization of the catalysts together with the performance of the reactivity tests and the data procedure. Lastly, the mathematical model developed for the thermodynamic study of processes is described.

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1. Materials

1.1. Reagents

The chemicals used in this work for the synthesis and characterization of catalysts and to carry out the catalytic reactions are displayed as follows, listing the reactants used for the synthesis of catalysts and for the catalytic tests, and summarizing the gasses utilized for characterization and catalytic activity.

- **γ-Alumina Puralox TH**: γ-Alumina supplied by *Sasol*, with a total pore volume of 1 $cm^3.g^{-1}$ and surface area value of 144 $m^2.g^{-1}$.

- **Aluminum oxide extruded in cylindrical pellets**: Aluminum oxide extruded in cylindrical pellets supplied by *Alfa Aesar*, with a total pore volume of 0.47 $cm^3.g^{-1}$ and surface area value of 107 $m^2.g^{-1}$; with a diameter of 3 mm and a length of between 4 and 6 mm long (medium value = 5.2 mm).

- ***Nickel (II) nitrate hexahydrate*** ($Ni(NO_3)_2 \cdot 6H_2O$): salt employed as Ni precursor, with a molecular weight of 182.70 $g.mol^{-1}$.

- ***Rhodium (III) nitrate hydrate*** ($Rh(NO_3)_3 \cdot xH_2O$): salt employed as Rh precursor, with a molecular weight of 288.92 $g.mol^{-1}$.

- ***Cerium(III) nitrate hexahydrate*** ($Ce(NO_3)_3 \cdot 6H_2O$): salt employed as Ce precursor, with a molecular weight of 434.22 $g.mol^{-1}$.

- ***Copper (II) nitrate trihydrate*** ($Cu(NO_3)_2 \cdot 3H_2O$): salt employed as Cu precursor, with a molecular weight of 241.60 $g.mol^{-1}$.

- ***Ammonium metavanadate*** (NH_4VO_3): salt used as V precursor, with a molecular weight of 116.98 $g.mol^{-1}$.

- ***Oxalic acid*** ($C_2H_2O_4$): acid used to improve vanadium solubility forming corresponding vanadium (V^{4+}) oxalate salt, with a molecular weight of 90.03 $g.mol^{-1}$.

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1.2. **Liquids**

The liquid reactants used in the experiments for both *in situ* and flow reactivity are detailed as follows.

- ***Acetone (CH_3COCH_3)***: acetone for synthesis with a molecular weight of 58.08 $g.mol^{-1}$, supplied by *PanReac*, with 99.5 % of purity.

- ***Ethanol (CH_3CH_2OH)***: ethanol absolute PA with a molecular weight of 46.07 $g.mol^{-1}$, supplied by *PanReac*.

- ***Methanol (CH_3OH)***: methanol for analysis, ACS, ISO, with a molecular weight of 32.04 $g.mol^{-1}$ supplied by *PanReac*.

1.3. **Gasses**

The gasses used in the experiments are detailed below.

- ***Dimethyl Ether, DME (CH_3OCH_3)***: with a molecular weight of 74.12 $g.mol^{-1}$, supplied by *Abelló Linde*, with 10 % of DME in He, used in experiments for both *in situ* and flow reactivity.

- ***Ammonia (NH_3)***: with a molecular weight of 15 $g.mol^{-1}$ was supplied by *Abelló Linde* as a cylinder of pure gas for probe molecule adsorption experiments.

- ***Hydrogen (H_2)***: with a molecular weight value of 2 $g.mol^{-1}$ supplied by *Abelló Linde* with 3 % of Hydrogen and 3000 ppm of Ar in He.

- ***Hydrogen (H_2)***: with a molecular weight value of 2 $g.mol^{-1}$ supplied by *Abelló Linde* with 20 % of Hydrogen in He.

- ***Helium (He)***: with high purity and a molecular weight of 4 $g.mol^{-1}$, provided by *Abelló Linde*.

- ***Nitrogen (N_2)***: with a molecular weight of 28 $g.mol^{-1}$, provided by *Air Liquide*.

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2. Equipments

The equipment and instruments used in the experimental part of this PhD Thesis are described in this section.

2.1. Furnace

A tubular Carbolite-CST1000 model furnace, from *Heareus* was employed in order to thermally treat the materials and consisted of a refractory inner tube that can reach a temperature of 1000ºC. The temperature can be adjusted by a Eurotherm 808 controller.

2.2. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared studies were carried out in different conditions and with different equipment depending on the purpose of the experiment. DME interactions with the catalysts and the thermal evolution of surface space were studied by *in situ* infrared spectroscopy experiments. Samples were activated in H_2 (3 torr) at 500ºC. DME or DME+H_2O pulses (3 torr) were admitted into the IR cell at room temperature, leaving a contact time of 10 min. In every case, 100 scans were registered in the range between 4000 and 400 cm^{-1} with a resolution of 1 cm^{-1}. Each sample was pressed into a self-supporting disk (~ 20 mg, surface area of 1.5 cm^2) placed in an IR cell, equipped with KBr windows, connected to a conventional gas handling system. Probe molecule adsorption was carried out in an IR cell connected to a conventional outgassing/gas manipulation apparatus and spectra were recorded by a Nicolet Nexus 6700 spectrometer with MCT detector. The system was composed of a vertical furnace that allowed the thermal treatment of the samples. The samples were pressed into 13 mm disks using a hydraulic press and placed in the sample holder of a quartz cell with KBr windows, permanently connected to a conventional vacuum line ($\approx 1 \cdot 10^{-4}$ torr).

Thermal evolution of the interaction between the probe molecule and the catalytic surface under static conditions was characterized, i.e., without evacuation of the reaction atmosphere. The temperature was increased to 500 ºC in 100ºC intervals. At each temperature, the IR spectra of the gas phase and the catalyst's surface were

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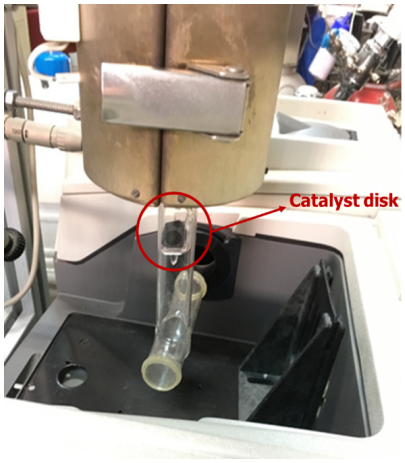
recorded. presented spectra are the spectra subtractions of the activated sample (500ºC under outgassing) and gas phase.



2.3. **Flow reaction system**

Catalytic tests in the flow reaction system were carried out where the feed gases flowed down through a fixed catalytic bed. The equipment consisted of a quartz tubular fixed bed reactor, with no radial diffusion and with a narrowing after the bed in order to prevent the occurrence of secondary reactions, located inside an electric furnace that was regulated by a PID controller (TIC, TOHO TTM-0005), where 60 mg of powder catalyst was placed. The feed steam was adjusted by the PID 1831 mass flow controller, specifically calibrated for each gas and connected to a mixing box. The total flow was 100 $cm^3.min^{-1}$, corresponding to a Gas Hourly Space Velocity (GHSV) of $3 \cdot 10^4$ h^{-1}. The Pfeiffer Prima^{TM} Quadrupole Mass Spectrometer QMS 200 was used to analyze the product distribution. The following mass/charge ratios were used to monitor the evolution of the involved species concentration during the reactions: 2 (H_2), 4 (He), 18 (H_2O), 28 (CO or N_2), 32 (MeOH or O_2), 40 (Ar), 44 (CO_2), 46 (DME). The analysis of the mass/charge ratio 12 (C) and 14 (N) were registered to differentiate the lines in which the two compounds coincide. The quantification of the QMS data was carried out using experimental factors that had been obtained during the calibration process, performed with calibration mixtures.

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2.4. **Activity tests in continuous flow reaction system. MicroActivity.**

Laboratory 1 (PROCAT-UMA): The experiments were performed at atmospheric pressure in a MicroActivity PID Eng&Tech system consisting of a fixed-bed flow reactor (i.d. 9 mm) and a mass flow controller unit. A HPLC pump (Gilson 307) was used to feed the liquid reactants (a mixture of the liquid oxygenated and water) to the reactor. The fixed bed reactor was equipped with a coaxial thermocouple placed at the center of catalyst bed to monitor the reactor temperature. Separation and quantification of the products were attained by on-line gas chromatograph (Agilent 7820A GC) equipped with a thermal-conductivity detector (TCD) and a flame ionization detector (FID).

Laboratory 2 (Institut Energetyky-Warsaw): The experiments were performed at atmospheric pressure in a system consisting of a quartz tube reactor (O.D.:50 mm), where 10 g of the sample was loaded. Gas mixtures were prepared from cylinder gases and controlled by mass flow controllers (Bronkhorst), the water steam was provided by a steam generator equipped with precision evaporator and superheater (Cellkraft). The Hiden QGA mass spectrometer (MS) was used to control product distribution at reactor outlet.

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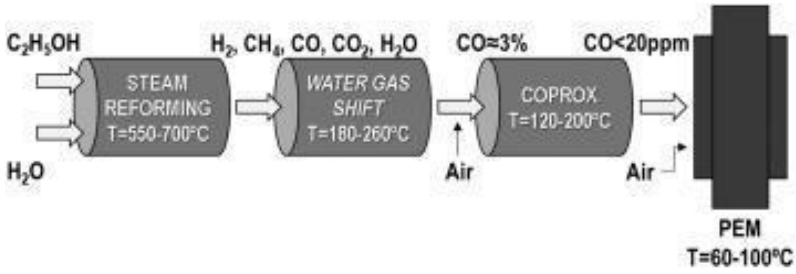
Laboratory 3 (University of Buenos Aires-Argentina): Pilot scale ethanol steam reforming tests were performed at atmospheric pressure in a semi-industrial plant. The configuration consists of a catalytic hydrogen production unit (steam reformer) followed by a purification step consisting of Water Gas Shift units (HT-WGS and LT-WGS) and a CO preferential oxidation (CO-PROX) reactor. The plant is connected to a 2.5 kW PEM-FC from Ballard, and other equipment is needed, such as heat exchangers, a metering pump, a reservoir for the water–ethanol mixture, an evaporator, mass flow controllers and automatic valves. The reformer unit consists of 316 stainless steel tubing Sch 40 1″ in diameter and 110 cm long, heated by electric furnaces, packed with an inert bed and a catalytic bed diluted with inert pellets. The reaction feed consisted of an optimized mixture (ethanol/water); the mixture was evaporated in a vaporization unit upstream of the reformer. The reactor was equipped with a coaxial thermocouple placed at the center of the catalytic-bed to monitor the reactor temperature. Separation and quantification of the products were attained by on-line gas chromatograph (Agilent 6820 GC System) equipped with a thermal-conductivity detector (TCD) and a flame ionization detector (FID).



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3. Catalysts synthesis

3.1. Powder catalysts

The Steam reforming *M*Ni catalysts were prepared in powder form by wetness impregnation method through a multi-stage synthesis with nickel and second-metal salts as precursors using a commercial alumina as support (γ-Al_2O_3 Puralox TH 100/150 from Sasol, A_{BET} = 144 $m^2.g^{-1}$ and V_p=0.97 $cm^3.g^{-1}$). $Ni(NO_3)_2 \cdot 6H_2O$, NH_4VO_3 ($Rh(NO_3)_3 \cdot xH_2O$), ($Cu(NO_3)_2 \cdot 3H_2O$), were used as Ni, V, Rh, and Cu precursors respectively for all catalysts. In the first step, the alumina support was impregnated with an aqueous nickel precursor solution in order to obtain a Ni content of 20%wt. (9 at. per nm^2 of support). After first impregnation, the material was dried at 105ºC for 12 h and calcined at 450ºC for 4 h in order to decompose the nickel nitrate. Next, the system was impregnated with the solution of salt in distilled water and of vanadium salt in oxalic acid (to improve solubility forming corresponding vanadium (V^{4+}) oxalate). Afterwards the catalysts were dried at 105ºC for 12 h and calcined at 500ºC for 4 h.

3.2. Catalyst in *pellet* form / conformed catalysts

Structured commercial (New Chemical) catalysts **for DME-SR**. Methodology: Multi-stage impregnation with nickel and vanadium precursors. Porous Al_2O_3 (A_{BET}=2 m_2/g) in the form of 7-hole rings and in powder form (for laboratory tests) were used. In the first step, the alumina support was double impregnated with an aqueous nickel (II) nitrate (V) solution ($Ni(NO_3)_2$, Stanlab). After each impregnation, the materials were dried at 378 K for 12 h and calcined at 723 K for 4 h in order to decompose the nickel nitrate. Next, the system was impregnated with vanadium salt solution to obtain 0.5, 1 and 3 wt.% of V in the final catalysts, obtained in industrial form, are denoted as 0.5V-Ni, 1V-Ni, 3V-Ni.

The commercial Ni and Cu catalysts (New Chemical), denoted as 10NiWSP and Cu-CP-LTM respectively, were used as reference samples.

Structured synthesized catalysts for **Ethanol Steam Reforming**. Commercial aluminum oxide extruded in *cylindrical pellets* (A_{BET} = 107 $m^2.g^{-1}$; Vp = 0.47 $cm^3.g^{-1}$) was employed to prepare structured catalysts. Alumina pellets with a

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diameter of 3 mm and between 4 and 6 mm long (medium value = 5.2 mm), were dried before impregnation. The catalyst was prepared by incipient wetness co-impregnation method. Ni and Ce content were optimized at 9 and 5 at. per nm^2 for Ni and Ce, respectively (atomic ratio Ce/Ni = 0.55); Rh content was optimized at 1:10.000 atomic-ratio in respect to Ni content. $Ni(NO_3)_2 \cdot 6H_2O$ and $Rh(NO_3)_3 \cdot xH_2O$ salts used as precursors were dissolved simultaneously in distilled water.

The resultant mixture was magnetically stirred until complete homogenization and kept for 24 h. After that, $Ce(NO_3)_3 \cdot 6H_2O$ was added to the solution and the mixture was left stirring for another 24 h to ensure homogenization and interaction between metals. After impregnation, the catalyst was dried (80–100 °C) and calcined at 600 °C for 2 h and further denoted as structured multimetallic $RhCeNi/Al_2O_3$.

4. **Characterization techniques**

Characterization techniques were used to obtain the physicochemical properties of the catalysts, detailing structure, composition and detected species.

4.1. **Analysis of porous solids**

N_2 adsorption-desorption isotherms were obtained at 77 K 8-196ºC) using a Micromeritics ASAP 2020 Analyzer. Before the analysis, the samples were outgassed in vacuum ($1 \cdot 10^{-3}$ Pa) for 5 h at 473 K (180ºC). the specific surface area was obtained by the BET (Brunauer-Emmett-Teller) method, applying the lineal form of:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C}\right]\frac{P}{P_0}$$

where V is the adsorbed gas volume measured in normal conditions (760 mmHg and 0ºC) at each adsorbate partial pressure (P), P_0 is the saturation pressure of the nitrogen at 77K (-196ºC), V_m is the monolayer volume and C is a constant related to the adsorption energy. After having obtained the volume of the monolayer, the specific surface area (S_{BET}) was calculated with the equation ##, where N_A is the Avogadro number and σ corresponds to the area occupied by a nitrogen molecule.

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$$S_{BET} = \frac{V_m}{22414} \cdot N_A \cdot \sigma$$

The external superficial area and the micro-porosity were determined by the t-plot method, from the slope and the y-intercept of the representation of the adsorbed nitrogen quantity and the thickness of the adsorbed gas, t, applying the Harkins and Jura equation (eq. ##) for the estimation of the t:

$$t = \left(\frac{13.99}{0.034 - log\ (P/P_0)}\right)^{1/2}$$

The total pore volume was also calculated with the maximum quantity of adsorbed nitrogen and the density conversion factor. In addition, the microporous distribution was obtained by the MP method.

4.2. **X-Ray Photoelectron Spectroscopy (XPS)**

The XPS spectra were obtained in a Physical Electronic (PHI) 5701 spectrometer, equipped with a standard X-ray source with two Mg and Al anodes, PHI 04-548 model. The Precision Energy Analyzer/Multichannel Detector PHI 10-360 was employed to analyze in ultra-high vacuum the species presented in the powder catalysts that were supported in a stainless steel cylinder with a 0.5 cm^2 area. During the XPS spectra data processing, binding energy values were referenced to the C1s peak from the adventitious contamination layer, 284.8 eV of binding energy, to determine peak position within ±0.2 eV accuracy. All deconvolutions of experimental curves were done with Gaussian-Lorenzian line fitting of varying proportions (60-80 %), trying to minimize the X^2 value. This technique gave information about the surface atomic composition and the chemical or electronic state of each surface element. The following regions were analyzed; Al2p, O1s, N1s, Ni2p, V2p, Cu2p, CuLMM. The full spectra analysis was done using MultiPAck Software. Short acquisition time of 10 minutes was used to examine C1s, Cu2p, CuLLM and V2p XPS regions in order to minimize the photoreduction of species.

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4.3. **X-Ray Diffraction (XRD)**

X.Ray Powder Diffraction data were recorded with an EMPYREAN diffractometer (PANalytical), equipped with an automatic loader and a rotating sample holder, using Cu $K\alpha_{1,2}$ radiation ($\lambda = 1.54059$ Å). In the incident beam path, the optimal system consisted of a group of divergence and anti-divergence slits that were set at ½º Soller slits (incident and diffracted beam) of 0.04 rad was used. The PIXcel detector was employed. The X-Ray tube worked at 45 kV and 40 mA. The measurements were taken from 5º to 80º (Bragg angle, 2θ) for 30 minutes, with measurement steps of 0.017º. During the measurements, the intensity of the reflected X-rays was recorded and the diffraction pattern peaks appeared when the Bragg equation was fulfilled. This equation relates the X-Ray wavelength and the interatomic distance with the incidence angle of the diffracted beam:

$$n\lambda = 2dsin\theta$$

where λ is the wavelength, d is the distance between atomic layers and θ is the angle between the incident rays and the crystal surface. This data provided information about the crystallinity of the structures and allowed the identification of the phases.

4.4. **Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM)**

The acquisition of TEM images was carried out in a Philips CM200 (200 kV) microscope equipped with an Energy Dispersion X-ray Spectroscopy (EDX) analyzer that allows the analysis of the elements present in the sample. For this technique, the sample was dispersed in a volatile liquid (ethanol) and deposited on a carbon holder, which is transparent to radiation, and dried in air. A TalosTM F200X instrument from FEI was used for the high resolution TEM images and the EDX mapping.

4.5. **Fourier Transform Infrared Spectroscopy (FTIR)**

Superficial acidity and metal location**.** Fourier Transform Infrared (FTIR) spectra were recorded at a resolution of 1 cm^{-1} averaging 100 scans using a Thermo Nicolet

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6700 spectrometer. Each sample was pressed into a self-supporting disk (~20 mg, the surface area of 1.5 cm^2) placed in an IR cell, equipped with KBr windows, connected to a conventional gas handling system. NH_3 adsorption experiments were done with pretreated discs in the IR cell at 773 K under vacuum (10 - 5 Torr) for 2 h to remove surface contaminants. The pretreated samples were exposed to NH_3 at room temperature until saturation, i.e., until no further adsorbed species band growth was observed, after which the IR spectra of the surface species were collected between room temperature (RT)-773 K while outgassing in continuous evacuation.

5. **Catalytic study**

The reaction mechanism of the different reforming processes studied were addressed by a series of catalytic analyses, which are detailed in this section.

5.1. **Flow runs**

Laboratory 1 (PROCAT-UMA): The experiments were performed at atmospheric pressure in a MicroActivity PID Eng&Tech system consisting of a fixed-bed flow reactor (i.d. 9 mm) and a mass flow controller unit. A HPLC pump (Gilson 307) was used to feed in case of liquid reactants (a mixture of acetone, ethanol or methanol and water) to the reactor.

The fixed bed reactor was equipped with a coaxial thermocouple placed at the center of the catalyst bed to monitor the reactor temperature. Separation and quantification of the products were attained by on-line gas chromatograph (Agilent 7820A GC) equipped with thermal-conductivity detector (TCD) and flame ionization detector (FID). A temperature range from 150 and 550ºC at atmospheric pressure was used.

Acetone and ethanol steam reforming. A steam to carbon molar ratio (S/C) equal to 3 in case of acetone and S/C equal to 2 for ethanol reforming was used. The inlet flow of the alcohol-water mixture was set at 0'9 $cm^3.h^{-1}$ with a N_2 flow of 30 $cm^3.min^{-1}$ as diluent.

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The catalyst (0.1 g, 250 - 420 μm) diluted with an equal amount of quartz was placed in the reactor working at 9000 h^{-1}, operating under plug flow conditions. Before the reaction, catalysts were activated with a 20% H_2/80% He mixture at atmospheric pressure by raising the temperature slowly to 500 ºC and maintaining for 2 h.

Methanol and DME steam reforming. Experiments were carried out at atmospheric pressure with the total gas space velocity of 2000 h^{-1} in 80% of N_2 dilution and contact time of 6.26 $g \cdot h \cdot mol^{-1}$. The optimal steam/DME molar ratio is established around 3.5, taking into consideration the energy supply needed and in order to reduce the CO concentration; in this work a value close to 3 was used for DME-SR and MeOH-SR because of limitation of equipment. The total gas flow rate was kept constant at 6.5 $Ncm^3 \cdot min^{-1}$. The reactant DME and reducing gas H_2/He were controlled by mass flow controllers. The liquid reactant in the case of methanol steam reforming, a mixture of methanol and water, was fed using an HPLC pump (Gilson 307). Non-catalytic tests were carried out under same conditions, packing the reactor with quartz particles with the same size and weight, feeding DME and N_2.

Previous tests with different particle-size catalysts and dilution were performed to confirm the non-existence of heat or mass transfer limitations. Results are reported based on Oxygenate conversion and H_2-yield calculated according to the equilibrium reaction expressed with the equation as follows:

$$Y_{H_2} = \frac{F_{H_2 out}}{\#F_{OXY} in}$$

where $F_{H_2 out}$ is the hydrogen molar flow in the out stream and $F_{OXY\ in}$ the oxygenate inlet molar flow, according to stoichiometry of reforming reaction. The selectivity of main products on outlet stream were calculated using the equation:

$$S_i = \frac{n_i}{\Sigma n_i}$$

where n_i is the mole number of component *'i'* produced and Σn_i is the total mole number of products in the outlet stream. Conversion, selectivity and yield were

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calculated on dry basis and C, H and O balances were closed with deviations lower than 3%.

Laboratory 2 (Institut Energetyky-Warsaw): A pilot scale reactor was used to evaluate the DME-SR with catalysts in the form of 7-hole rings. The catalytic reactor used a cylindrical quartz tube of 50 mm inner diameter and 1000 mm length, with the catalysts in 7-hole ring form fixed to the center of the reaction tube. DME-SR was studied in a temperature range between 200 and 500ºC. 50 g of the sample was loaded into the reactor and exposed firstly to He flow when heated up to 500ºC. The mixture of DME and steam was fed and the reactor was subsequently heated to 500ºC with a temperature ramp of 10 K.min^{-1}. A S/C ratio close to 3 was used, with a total gas flow rate of 5 L·min^{-1} (GHSV = 2.12 · 10^3 h^{-1}, at 1 atm and 293 K). The VNi catalyst was studied, comparing it to conventional Cu-catalyst and commercial Ni-based catalyst.

Laboratory 3 (University of Buenos Aires-Argentina). The experiments were carried out under 650ºC and 700ºC during 78 h in order to study catalyst stability. The operating conditions used for these pilot plant studies are summarized in the following table:

Reaction conditions for ethanol steam reforming used in the pilot plant.

Reaction conditions	Value
Steam-to-ethanol molar ratio	7.0
Liquid mixed total flow (ml·min^{-1})	4.7
N_2 flow (Nm^3·h^{-1})	0.04
Gas flow (ethanol + steam) (Nm^3·h^{-1})	0.31
Molar flow (ethanol + steam) (mol·h^{-1})	13.0
Ethanol molar flow (mol·h^{-1})	1.6
Maximum overpressure (kg·cm^{-2})	2.5
Mass catalyst (g)	23.0
Pellets diameter (mm)	3
Pelltes length (mm)	5.2
Mass inert (g)	176.0
Dilution	1:7.7
Temperature (ºC)	650 – 700
Residence time ($g_{cal} \cdot h \cdot m_{ethanol}^{-3}$)	73.8

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6. Mathematical modeling.

This section addresses the implications of kinetics, mechanism, and thermodynamics on the steam reforming of oxygenated model compounds, based on acetone and ethanol steam reforming. This point deals with the modeling of the steam reforming process of the oxygenated compounds considered, through the development of a model implemented with the Matlab software capable of quantifying the effect of the reaction conditions (temperature, space time, molar S/C ratio and reaction time) on the distribution of products at the reactor outlet. We have taken as hypothesis about the system that the process takes place in an isothermal reactor of differential and pseudo homogeneous fixed bed, considering the absence of difussional problems in the axial and radial axes, so the system is considered to have an ideal piston flow behavior. The reaction system is an isothermal and one-dimensional fixed-bed reactor in which catalysts are packed. To represent the steady-state operation of the steam reforming, a pseudo-homogeneous model was adopted to develop the mathematical model subject to the assumption that the process occurs without axial dispersion. A Matlab subroutine function was used to numerically integrate the differential equations, mass balance of each component and energy balance, as follows respectively, thus determining the temperature and concentration profiles.

$$dF_i/_{dz} = f(r_i, T)$$

$$\frac{dT}{dz} = \frac{\left(\frac{4 \cdot U}{\rho_B}\right)(T_f - T) + \left(-\sum \Delta H_{r_i} \cdot r_i\right)}{\sum F_i \cdot Cp_i} \cdot \rho_B \cdot A$$

$$\sum \Delta H_{r_i}(T) = \left(\Delta H^0_{r_i}(T_R)\right) + \Delta C_p(T - T_R)$$

ΔH_{r_i} (i= 1 - 5 or 1 - 4) corresponds to the enthalpy of each reaction. The calorific capacities (ΔCp) are appraised for polynomial expressions in function of the temperature. Considering all boundary conditions are given at z=0, therefore, the set of ODEs constitutes the initial value problem. In the present study, the set of ODEs is solved by using the ODE solver “ode45” and “ode15s”, depending on the problem stiffness. The performance has been analyzed in terms of conversion of acetone or ethanol and H_2/CO molar ratios.

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Chapter 3

Production of hydrogen by catalytic steam reforming of oxygenated model compounds on Ni-modified supported catalysts Simulation and experimental results

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Production of hydrogen by catalytic steam reforming of oxygenated model compounds on Ni-modified supported catalysts. Simulation and experimental results.

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3.1. Abstract

Steam reforming of two representative components in the aqueous fraction of biooil, acetone and ethanol, was investigated over nickel based supported catalysts (Ni/Al_2O_3). The effect of Rh incorporation ($NiCeRh/Al_2O_3$) and the properties of different γ-Al_2O_3 used as support was tested. Hydrogen-rich gas is produced at temperatures higher than 673 K in both acetone and ethanol reforming with maximum mole fraction of 0.6-0.7. The reactions involved and the possible routes were studied. Rh incorporation and nanostructured alumina affect the Ni metal size and the amount of carbon deposited onto catalysts' surface after reforming tests; besides, acetone is also found as an important intermediate in ethanol reforming, and Rh improves hydrogen production with negligible intermediates presence. The effect of S/Acetone or S/Ethanol feed molar ratios, space velocity and temperature over acetone/ethanol conversion and over H_2/CO ratio were modeled using the Matlab software to find the regions and the optimal operating conditions in both processes. Simulation results are consistent with the experimental data.

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Chapter 4

Hydrogen production by ethanol steam reforming over multimetallic $RhCeNi/Al_2O_3$ structured catalyst. Pilot-scale study

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Hydrogen production by ethanol steam refroming over multimetallic $RhCeNi/Al_2O_3$ structured catalyst. Pilot-scale study.

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4.1. Abstract

A new multimetallic RhCeNi/Al_2O_3 catalyst structured in cylindrical pellet with an atomic ratio Ce/Ni=0.55 and minimal Rh content was developed and tested in ethanol steam reforming (ESR) at laboratory and semi-industrial pilot plant scales. A beneficial interaction for the major components, Ce-Ni, is noticed. Ce is mostly present as Ce^{4+} and Ce^{3+} and the incorporation of small amounts of Ni^{2+} species into the ceria fluorite-type structure is registered since an oxygen coordination disorder was induced by the Ni^{2+} dissolution that modifies the average size of particles. RhCeNi catalyst is active in the ESR even at different steam/ethanol ratio between 4 and 10 at laboratory scale and is also very active and stable at pilot-plant scale tested at S/EtOH ratio = 7, with a high H_2-yield (95% at 700ºC) and minimal presence of secondary products as acetone or ethylene and ethane. CO selectivity is maintained below 5-7% in the reformer gas-out stream, although it is further reduced to reach acceptable values after WGS and CO-PROX-units to feed the PEM located down-stream of the installation.

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Chapter 5

Hydrogen production by steam reforming of DME over Ni-based catalysts modified with vanadium

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Hydrogen production by steam reforming of DME over Ni-based catalysts modified with vanadium.

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5.1. Abstract.

Dimethyl ether steam reforming (DME-SR) for hydrogen production has been studied over VeNi/Al_2O_3 catalysts as part of an investigation aimed at the development of effective technology based on second generation of biofuels. Methanol steam reforming (MeOH-SR) was investigated as a step of the DME-SR process. High activity in the MeOH-SR was observed and two different mechanism depending on temperature and influenced by the vanadium content (0.5, 1 and 3%) was evidenced: direct methanol decomposition to CO and H_2 was observed at low temperature and low vanadium content and methanol steam reforming reaction occurs majorly to give an almost stoichiometric H_2/CO_2 ratio at moderate to high temperature (400ºC) over 3VNi. DME conversion is complete at 500ºC over VNi catalysts in DME-SR, as a two steps reaction: DME hydrolysis and MeOH-SR giving an H_2 rich gas reformate generated with a H_2 selectivity c.a. 60-70% over 0.5VNi and 3VNi, values maintained during 4.5 h of activity in the same reaction conditions with no signs of deactivation or significant coke formation over catalyst surface.

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Chapter 6

The role of Lewis acidic vanadium centers in DME steam reforming over V-Ni catalysts

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The role of Lewis acidic vanadium centers in DME steam reforming over V-Ni catalysts

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6.1. Abstract

Dimethyl ether (DME) as a potential chemical storage of renewable energy was studied for decomposition and steam reforming (DME SR) to produce hydrogen-rich streams over V-Ni/Al_2O_3 catalysts. The extent of DME decomposition, DME hydrolysis, and subsequent methanol steam reforming was examined during this study, focusing on the redox and acid/base properties of catalyst surface species. The results show that the DME SR performance depended on the acid-redox character of the Ni-O-Ni/V-O-Ni species dispersed onto alumina. For S/ C ratio close to 2.5, for relative V-rich catalysts, DME hydrolysis reaction over the Lewis acid sites was found a rate-determining step and then, metallic centers being responsible for H_2 and CO_2 production. For 3V-Ni/Al_2O_3 DME SR with low selectivity towards methane and direct H_2 and CO_2 production (H_2/CO_2 ratios close to 3), with near-complete DME conversion was obtained above 673 K.

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Chapter 7

General conclusions, limitations of studies and future work

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7.1. General Conclusion

Hydrogen has emerged as a promising alternative energy source due to its high energy density and potential for zero-emission applications. It is considered a promising fuel for fuel cell applications in portable devices and hydrogen fuel cell vehicles (FHCs). Steam reforming of hydrocarbons is a widely adopted method for large-scale hydrogen production. However, the integration of oxygenated compounds such as alcohols, ketones, and/or ethers into the steam reforming process has gained attention for its ability to enhance hydrogen production efficiency, mitigate carbon emissions, and improve overall process sustainability. The use of oxygenated compounds in hydrogen generation is favored by the energetic contribution of the oxygen atoms contained in the molecules tested, enhancing the steam reforming reaction, which is energy intensive. Specifically, for FCVs, hydrogen storage and supply infrastructure still need to be addressed and developed. In this sense, as an alternative, the possibility of on-board reforming of oxygenated hydrocarbons has been proposed.

Overall, from the results obtained in this Doctoral Thesis on Hydrogen production through steam reforming of some model oxygenated components of interest as H_2-carrier or as part of the bio-oil aqueous fraction, we can conclude the following: As a short-term technology for producing H_2-enriched streams, using nickel- modified alumina-supported catalysts has shown promising results. The outcomes fulfill the objectives of advancing towards the implementation of the steam reforming process of oxygenated compounds, leading the way towards the revalorization of waste from renewable sources in hydrogen production This allows for the analysis and design of an efficient catalytic system to reform the mixture of compounds resulting from the pyrolysis of biomass. Additionally, the results support proposing DME as an alternative fuel or as an efficient hydrogen carrier due to its ease and experience in storage and transport.

The use of a widely used catalyst for industrial-scale reforming, such as Ni/Al_2O_3, has been proposed and modified with the addition of a second metal in low content, depending on the oxygenated compound used. This approach creates significant and interesting opportunities in renewable hydrogen production. The systems

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analyzed allow for obtaining hydrogen-enriched streams with almost negligible content of unwanted by-products under typical reforming operating conditions.

7.2. Oxygenated Hydrocarbons Suitability

Although steam reforming of natural gas is the major route for hydrogen production for industrial needs, organics like alcohols, ethers, and ketones as feedstock for hydrogen generation also attract wide attention. These organics have higher volumetric energy density, making them ideal for on-site steam reforming for powering fuel cell-propelled vehicles. The use of oxygenated compounds provides flexibility in feedstock selection for steam reforming. By incorporating various oxygenated compounds, a broader range of renewable or waste-derived feedstocks can be utilized. The versatility reduces dependency on fossil fuels and opens avenues for sustainable hydrogen production from biomass, waste streams or renewable sources, promoting a circular economy by transforming waste into a valuable energy carrier.

In steam reforming, these compounds are exposed to high temperatures and steam in the presence of a catalyst to produce hydrogen gas. The choice of catalyst, temperature, and process conditions can significantly affect the efficiency and selectivity of hydrogen production from these oxygenated compounds. Each compound has its own set of advantages and challenges in terms of reforming for hydrogen production. Factors like cost, ease of production, efficiency, by-product formation, and catalyst requirements are crucial when selecting the most suitable oxygenated model compound for hydrogen production via steam reforming.

A comparison of the components used in the present work, described in previous chapters, can be made in terms of their properties, production, and suitability for hydrogen production via Steam Reforming.

Acetone has a high hydrogen-to-carbon ratio, making it a potential candidate for hydrogen production. It is produced through the oxidation of isopropyl alcohol or as a by-product in the cumene industry, especially used as solvent and in chemical production. Acetone has the advantage of availability from various sources widely used in industrial processes and can be derived from various biomass sources.

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However, reforming acetone for hydrogen production might require higher temperatures due to its chemical structure, and by-products like carbon monoxide (CO), coke and others could form during the process. Its propensity for decomposition at elevated temperatures might necessitate process adjustments or catalyst modifications during steam reforming.

In the case of **ethanol**, this compound can be produced through the fermentation of sugars in biomass or via chemical synthesis. Ethanol is a widely available biofuel with established and mature production methods. The advantage of using ethanol is that it can be obtained from renewable resources. However, although ethanol reforming can yield hydrogen, it might have lower hydrogen yields compared to simpler alcohols due to its larger molecular structure. Additionally, the process is complex and involves the production of numerous by-products.

Methanol has a higher hydrogen-to-carbon ratio compared to various other hydrocarbon-based fuels, making it an efficient source for hydrogen production via steam reforming. Methanol can be produced from various sources, including natural gas, biomass, and even carbon dioxide (via renewable energy sources in processes like Power-to-X). Its multiple production pathways contribute to its versatility as a feedstock for hydrogen generation.

Dimethyl ether (DME) is a promising choice for commercial hydrogen production via steam reforming to supply on-board hydrogen fuel cells. It has advantages such as non-toxicity, absence of C–C bonds, and high hydrogen-to-carbon ratio. In terms of energy density, DME performs moderately compared to other fuels. However, while it has a higher energy density compared to ethanol and methanol, it is lower than that of acetone. Moreover, acetone, ethanol, and methanol have established applications in the transportation sector, whereas DME is still in the early stages of commercialization for use in diesel engines, fuel cells, and potentially as a blending component in LPG.

In general, ethanol, acetone, and DME have their own advantages but might require specific reforming conditions or could produce lower yields of hydrogen or more undesirable by-products compared to methanol. The choice among these compounds would depend on factors like availability, cost, reforming efficiency,

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and byproduct management.

Interestingly, the search for alternative and sustainable substitutes to the current supply in the petrochemical industry for hydrogen production encourages this study. For the steam reforming of oxygenates, the critical point at this moment is the choice of a suitable catalyst. This study aims to determine if such catalysts demonstrate sufficient catalytic activity and stability for application, and which formulations and preparation methods are adequate. Most importantly, the findings disclosed that there was no need to drastically change the catalysts utilized for the steam reforming process; it has only been necessary to modify the Ni-based catalyst used for all processes by adding small amounts of a second metal to minimize by-products and avoid catalyst deactivation.

7.3. Catalysts Proposed

Using Ni/Al_2O_3 catalysts for hydrogen production via reforming of oxygenated model compounds derived from biomass is a prevalent approach in biofuel and renewable energy research. When dealing with oxygenated compounds derived from biomass such as ethanol, methanol, or various organic acids, these catalysts play a critical role in their conversion to hydrogen.

As can be seen from the results presented in the previous chapters and published in the various journals, a common base has been used for all the compounds proposed in this work. Given that the Ni-based catalyst on alumina have traditionally been used to produce hydrogen from natural gas reforming, and the benefits are well-known, it was decided to use this system to study the reforming processes of oxygenated compounds derived from organic waste or other renewable sources. This approach was chosen to homogenize the processes and take advantage of the knowledge generated from previous experience. It has been shown that this system is also effective for the reforming of the chosen oxygenates, serving as a common base for all of them but being slightly modified with the addition of small percentages of a second metal depending on the characteristics of the oxygenate used, the operating conditions and expected by-products.

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In the results obtained previously directly using the Ni/Al_2O_3 base system, although it is an active system, severe operating conditions are required to achieve almost complete conversion and activate the reforming with other undesired parallel reactions occurring. The use of compounds with different oxygen-containing functional groups makes the process more complex and induces numerous side reactions. Therefore, it was decided to dope the catalytic system with a second metal to improve the selectivity towards hydrogen-enriched streams, avoiding or reducing the occurrence of undesired reactions.

7.4. Acetone and Ethanol Steam Reforming

The transformation of two of the most important platform molecules, ethanol and acetone was address. Steam reforming of a ketone and short-chain bioalcohol was investigated over Rh-modified nickel catalysts on different alumina supports. Additionally, both experimental studies and simulations were conducted to understand the reaction mechanisms and optimize operating conditions for hydrogen production.

Hydrogen-rich gas is produced at temperatures higher than 673 K in both acetone and ethanol reforming, with maximum mole fraction of 0.6–0.7. The incorporation of Rh into the Ni/Al_2O_3 catalysts improved hydrogen production and reduced the presence of undesirable intermediates. Rh also influenced the size of Ni metal particles and the amount of carbon deposited on the catalyst surface. Nanostructured alumina also stabilize the Ni metal size and modify the nature and the carbon deposition rate.

Acetone is also found as an important intermediate in ethanol reforming, and the presence of Rh improves hydrogen production with negligible intermediates. The effect of Steam-to-Acetone or Steam-to-Ethanol feed molar ratios, space velocity and temperature over acetone/ethanol conversion and H_2/CO ratio were modeled and simulated using Matlab software to find the optimal operating conditions in both processes. Simulation results were coherent and fitted with the experimental data.

The study concludes that Ni-based catalysts, particularly those modified with Rh,

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are highly effective for the steam reforming of oxygenated compounds like acetone and ethanol to produce hydrogen. The research underscores the importance of optimizing catalyst properties and reaction conditions to achieve efficient hydrogen production, with both experimental and simulation studies providing valuable insights for practical applications.

7.5. DME/MeOH Stem Reforming

The production of hydrogen through the steam reforming of dimethyl ether (DME) using nickel-based catalysts modified with vanadium (V-Ni/Al_2O_3) was analyzed. The study focused on the two-step reaction process involving DME hydrolysis (DME-HYD) followed by methanol steam reforming (MeOH-SR). The impact of vanadium content on the reaction mechanisms and product distributions at different temperatures was analyzed. The research addresses the decomposition of DME, DME hydrolysis, and subsequent methanol steam reforming, with a focus on the surface redox and acid/base properties of the catalysts.

At 500°C, V-Ni catalysts achieved complete DME conversion, producing a hydrogen-rich gas with high selectivity. The catalysts exhibited stability over extended periods with minimal deactivation and coke formation. The research included the preparation, characterization, and performance testing of these catalysts in both laboratory and pilot-scale reactors.

It has been shown that the steam reforming of DME is comprised of two sequential steps: the hydrolysis of DME to methanol, which occurs on catalytic acidic-sites, and the steam reforming of intermediate methanol to form CO_2/CO and H_2, which occurs over metal or metal oxide centers. The DME hydrolysis, without methanol removal, is limited by a low equilibrium value of 15 % at 200ºC. Under these conditions, when methanol formed rapidly undergoes MeOH-SR, the hydrolysis is accelerated, resulting in higher DME-conversion. It has also been demonstrated that steam reforming of DME over a vanadium-doped nickel/alumina catalyst produces a high yield of hydrogen, although the required temperature is higher than expected. While temperatures above 500ºC are needed to carry out the reforming reaction and achieve complete conversion of DME, the resulting stream is devoid of unwanted

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by-products, yielding a stream where the main products are H_2 and CO_2 in a H_2/CO_2 molar ratio between 2 and 3.

Additionally, the studies on DME reforming identified that the hydrolysis of DME occurs over Lewis acid sites as the rate-determining step for vanadium-rich catalysts. This step is crucial for breaking down DME into methanol before further reforming. The performance of the catalysts was significantly influenced by the redox and acid-base properties of the Ni-O-Ni and V-O-Ni species on the alumina support. These properties need to be well-balanced to enhance hydrogen yield and minimize secondary reactions such as methanation and carbonation. Detailed mechanistic insights were provided through *in situ* FTIR studies, revealing the inhibition of the water-gas shift (WGS) reaction and the interactions between DME decomposition, hydrolysis, and methanol steam reforming.

7.6. Limitations and Future Improvements: Non-published data

In this line of research, we decided to continue in two related directions. First, we synthesized catalysts by adding different proportions of Cu to the Ni/Al_2O_3 system, applying these catalysts in both DME reforming and methanol reforming. Second, we worked on the design and study of a micro-reactor that could be incorporated on-board for mobile applications, generating hydrogen-rich streams in situ and co-fed with conventional fuel.

The most active catalysts for methanol reforming, which can also be used for DME reforming, are typically those based on combinations with ZnO, CeO_2, etc., to prevent copper sintering, which occurs at temperatures above approximately 300 ºC and is favored by the presence of steam. Previous publications have demonstrated improved activity and stability of copper in the presence of nickel, preventing copper agglomeration and deactivation. Following the basis of this thesis, we used the Ni/Al_2O_3 system and studied the effect of incorporating copper in different relative proportions (Ni/Cu). These unpublished studies have shown promising results for using these bimetallic CuNi systems with low copper loading. Regarding the Cu-Ni catalyst, preliminary non-published data demonstrated a synergistic effect in terms of catalytic activity and selectivity toward syngas products. Our study reveals that Cu enhances the selectivity of the Ni-based system

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towards CO and H_2 and reduces the operating temperature at which hydrogen-enriched streams are obtained compared to previously tested systems. It is noteworthy that, at medium-high temperatures, the bimetallic Cu-Ni catalyst surpasses the stability levels achieved with monometallic formulations, making it an interesting option for both DME reforming and directly obtaining high-purity hydrogen from methanol.

Based on all the obtained results, we worked on formulating a mixed catalytic system and incorporating it into a micro-reactor for steam reforming trials, specifically with methanol, with results currently under evaluation for publication. Preliminary studies have shown that using a Cu/Ni coating in the micro-reactor channels with the same relative proportion used in the previously discussed systems and feeding methanol at 400ºC with a space velocity close to 150,000 h^{-1}, nearly complete methanol conversion was achieved. The resulting stream was mainly composed of H_2 and CO_2 in near-stoichiometric proportions, with insignificant concentrations (< 2 %) of by-products detected.

Our ongoing research focuses on advancing the understanding and application of chemical hydrogen storage through the dehydrogenation of homocyclic liquid organic hydrogen carriers. We aim to conduct a comparative study of dimethyl ether (DME) steam reforming versus oxidative steam reforming using isothermal and electrically heated micro-reformers. These micro-reformers will be coated with a homogeneous layer of Cu-Ni-Rh catalyst prepared via a two-step process. Initially, a passivation layer using $Zr(i\text{-}PrO)_4/Al(i\text{-}PRO)_4$ will be applied and calcined to achieve a homogeneous and well-adhered ZrO_2 or Al_2O_3 layer on the channels' walls. Subsequently, the gel-catalyst will be impregnated. This method is expected to produce a thin catalyst layer of 80–100 nm, resulting in a catalyst load two orders of magnitude lower per surface area compared to conventional cordierite honeycombs (0.05 vs. 1–6 mg catalyst/cm^2). Our target is to achieve a hydrogen production rate of 100 NmL of H_2 per minute per cm^3 of reactor volume and ensure stable operation for nearly 2 hours, demonstrating the feasibility of on-site, on-demand hydrogen generation from DME for portable fuel cell applications.

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Chapter 8

Resumen

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Contexto y planteamiento de la Tesis

En el actual escenario de transición energética, uno de los más importantes retos que se plantea abordar es el aumento constante de la demanda energética mundial, como consecuencia del crecimiento de la población y el aumento del nivel de vida. Para alcanzar los objetivos de descarbonización se hace patente la necesidad de fomentar e impulsar el uso de energía eléctrica procedente de fuentes renovables, junto a la reducción progresiva del uso de combustibles fósiles, que va acompañado de emisiones de CO_2 y otros gases contaminantes. Las energías renovables ofrecen un futuro verde si los procesos de conversión se combinan de forma inteligente. En este sentido, el hidrógeno se presenta como el mejor aliado para construir un sistema energético descarbonizado. El hidrógeno se ha revelado como una prometedora fuente de energía alternativa debido a su elevada densidad energética y su potencial para aplicaciones de emisiones cero, considerándose además un combustible prometedor para aplicaciones en pilas de combustible en dispositivos portátiles o vehículos de pilas de combustible (FCV). Además, el hidrógeno se presenta como una manera eficiente de almacenar energía producida de manera renovable, como la solar o eólica, o mediante procesos de revaloración de residuos de origen biomásico, al considerarse un potente vector energético. Este proceso deberá ir adentrándose en sectores más allá del eléctrico, neutralizando las emisiones finales netas en todo el espectro, incluyendo el transporte e industria pesada, convirtiéndolo en un desafío en el que se necesita desplegar y desarrollar soluciones para un escalado de forma masiva.

El camino hacia la descarbonización de estos sectores para por la electrificación de los procesos donde sea posible, así como la sustitución de derivados del petróleo y combustibles fósiles por alternativas sin emisiones asociadas como puede ser el hidrógeno o los combustibles derivados de éste. El hidrógeno abre por tanto un amplio abanico de opciones no solo como materia prima en la síntesis de otros compuestos, sino como uso directo como combustible, uniendo su generación con energía renovable generando un ciclo energético sostenible.

En este contexto, se desarrollan los trabajos de la presente Tesis Doctoral, alrededor de un pilar fundamental basado en la generación renovable de este vector

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energético. Esta Tesis está centrada en el proceso de reformado con vapor, empleando para ello diversas moléculas oxigenadas con distintas propiedades y características que puedan obtenerse de manera eficiente en un contexto de **revalorización de residuos de origen biomásico**. Por una parte, los compuestos elegidos se presentan como modelos de la composición media del bio-oil obtenido mediante la pirólisis rápida de la biomasa. Esta ruta termoquímica posee positivas perspectivas para su implantación a gran escala. Por otro lado, se han elegido también compuestos que, por sí mismos, pueden ser usados directamente como combustibles o bien como portadores de hidrógeno, al contar con propiedades similares a otros combustibles convencionales facilitando su implantación y uso al no requerir grandes innovaciones en cuanto a su almacenamiento, distribución y transporte. Estos compuestos oxigenados elegidos presentan propiedades versátiles que los hacen potencialmente atractivos para su uso en estas actividades. El desarrollo por tanto de esta tesis se ha basado en distintas fases del proceso catalítico con vistas a un uso industrial o comercial: i) elección de componentes oxigenados modelo con diferentes aplicaciones en el sector energético; ii) discriminación y propuestas del catalizador adecuado; iii) estudio y desarrollo de catalizadores activos y selectivos en los procesos a estudiar, basándose en un sistema sencillo ampliamente usado en la industria; iv) estudio de actividad catalítica y de las propiedades físico-químicas y estructurales de los sistemas catalíticos sintetizados; v) aproximación a los procesos involucrados en el reformado de compuestos oxigenados; vi) establecimiento de condiciones óptimas de operación y propuesta de escalado.

Los compuestos presentes en el bio-oil generado en la pirólisis rápida de la biomasa proceden de la despolimerización de la celulosa, la hemicelulosa y la lignina, e incluyen fenoles, cetonas, ácidos, ésteres, aldehídos, alcoholes, entre otros. En esencia, es una micro-emulsión de estos compuestos en agua. A efectos de esta investigación doctoral, se presta especial atención a cuatro oxigenados principales que incluyen diferentes grupos funcionales: acetona (cetona), etanol (C2 mono-ol), dimetil éter (éter) y metanol (C1 mono-ol).

Por un lado, se ha estudiado el reformado con vapor de acetona y de etanol. La **acetona** es además un subproducto barato del proceso de producción de fenol por

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la ruta de peroxidación del cumeno. Esta ruta produce fenol y acetona en cantidades equimolares. La demanda de fenol crece día a día para satisfacer la expansión del mercado de resinas fenólicas, bisfenol-A para policarbonatos y otros, siendo la capacidad mundial de producción de acetona de 8,5 millones de toneladas. La utilización de acetona para la producción de hidrógeno mediante reformado con vapor puede considerarse una de las formas de aumentar su valor.

Además de estudiar el **etanol** como modelo de compuesto oxigenado alcohólico, el reformado con vapor de etanol para corrientes enriquecidas en H_2 ha suscitado gran interés al tratarse de un recurso renovable, fácil de manipular y transportar, y termodinámicamente factible de descomponer, por lo que ofrece una menor contaminación al medio ambiente como fuente sostenible de energía. Además, podría considerarse neutro en CO_2, ya que la cantidad de CO_2 producida por el reformado es consumida por el crecimiento de la biomasa, lo que ofrece un ciclo de carbono casi cerrado.

En un segundo bloque, se eligió el **DME** como compuesto oxigenado debido a múltiples ventajas y proyección futura en el campo de las renovables. Como alternativa, la posibilidad de realizar el proceso de reformado *on board* de hidrocarburos oxigenados como el DME o el metanol se presenta muy interesante y prometedora. El DME ha atraído la atención como portador de hidrógeno ya que es inofensivo, no corrosivo, tiene una alta densidad energética y una elevada relación H/C, no presentando además enlaces C-C. El reformado con vapor de DME es uno de los procesos de reformado con mayor rendimiento teórico de hidrógeno a temperaturas relativamente bajas. Además, el DME tiene la ventaja de que se puede almacenar y transportar fácilmente; la infraestructura existente de GLP se puede utilizar para el DME ya que sus propiedades físicas son similares, lo que convierte al DME no sólo en una fuente de H_2 sino también en un combustible alternativo para aplicaciones de motores diésel o como mezcla de diésel. El proceso de reformado de DME conlleva dos etapas en serie: una primera etapa de hidrólisis del DME, con formación de metanol; y una segunda etapa de reformado del metanol generado con vapor. Por esta razón, re requiere el uso de un catalizador bifuncional, que posea propiedades ácidas para promover el primer paso y propiedades *redox* para favorecer el reformado del metanol. También se consideró importante estudiar

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de manera independiente el reformado de **metanol**, con objeto de estudiar y profundizar en dicho mecanismo y poder emplear los resultados para un mejor diseño del catalizador y entendimiento del reformado de DME.

Los **catalizadores** empleados en el presente estudio tienen un nexo común: independientemente del oxigenado a estudiar, todos se basan en el catalizador convencional basado en níquel soportado sobre alúmina, Ni/Al_2O_3. Se ha ensayado dicho catalizador en el reformado con vapor de los compuestos oxigenados seleccionados, y, según las características particulares del proceso, se ha modificado mediante la adición de un segundo metal en distintas proporciones relativas Ni:*M*, que ha permitido estudiar los procesos y deducir la mejor configuración en cada caso. Los catalizadores basados en Ni se han empleado ampliamente en reacciones de reformado, incluido el reformado de bio-oil, debido a su elevada actividad frente a la ruptura del enlace C-C y a su coste relativamente bajo. Sin embargo, uno de los retos que se presentan ante su uso con los compuestos oxigenados es impedir o minimizar la desactivación del catalizador Ni/Al_2O_3 debido a su tendencia a la acumulación de coque, lo que se presenta común frente a las moléculas ensayadas. En este sentido, la incorporación de pequeñas cantidades de Rh al sistema basado en Ni se traduce en una mejora de la capacidad de reformado, promoviendo también la reacción de desplazamiento con vapor (WGS) y disminuyendo la formación y deposición de carbono en la superficie catalítica. La interacción Rh-Ni mejora la estabilidad del Ni, mejorando su difusión en la superficie del soporte e impidiendo la formación de espinelas estables.

Por otro lado, se ha publicado que las propiedades *redox* de las especies de vanadio y su capacidad como donantes de oxígeno para la oxidación del coque podrían hacer de este metal un componente interesante de los catalizadores convencionales de reformado. Además, se espera que la incorporación de vanadio en el sistema Ni/Al_2O_3 sea beneficiosa desde el punto de vista de la estabilidad y durabilidad del catalizador.

La naturaleza del **soporte** también desempeña un papel importante en la selectividad del producto y el comportamiento de desactivación del catalizador. Los soportes ácidos como el Al_2O_3 son más propensos a la desactivación debido a la

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formación de coque. En el presente estudio se ha empleado para todos los casos $\gamma - Al_2O_3(TH)$, siendo efectivo su uso como soporte. Sin embargo, su capacidad de dispersión, interacción superficial y reactividad general dependen de las condiciones operacionales del proceso. En el caso concreto del etanol, se estudió la posibilidad de emplear un soporte alternativo, una alumina nanofibrosa (Al_2O_3(N)), con el objeto de analizar las rutas de producción de etileno, principal precursor en la formación de carbón.

En base a los resultados que se fueron obteniendo y al interés para un posible escalado que pudiera generar cada uno de los procesos y compuestos ensayados, se analizó en profundidad, el **reformado de etanol**, proponiendo un sistema catalítico estructurado en forma de *pellets* para su uso en planta piloto. Se diseñó un catalizador multimetálico (RhCeNi) basado en el sistema empleado a escala de laboratorio, incorporando Ce, considerado soporte básico que limita la deshidratación del etanol y cuyas propiedades redox dificultan la formación de coque. Este sistema fue ensayado a escala de laboratorio y en una planta piloto constituida por un reactor tubular seguido de una unidad de *Water Gas Shift* y un reactor de CO-PROX, conectado en línea con una pila tipo PEM.

Por otro lado, debido al interés que el DME despierta tanto como su uso directo como combustible así como la posibilidad de plantear un sistema de reformado a bordo o su potencial como portador de hidrógeno, se profundizó en las reacciones y mecanismo sucedido bajo condiciones de reformado con vapor, desacoplando las etapas involucradas y analizando las reacciones sobre el soporte, con objeto de mejorar el sistema catalítico propuesto y avanzar en el establecimiento de las condiciones óptimas de operación.

El reformado de DME requiere de altas cantidades de vapor y del empleo de un catalizador bifuncional que responda a la necesidad de un sistema ácido que promueva la estable reacción de hidrólisis del DME para formar metanol, y de propiedades redox que activen el reformado de éste último, proponiendo para tal caso y presentando en el presente documento los resultados obtenidos con el sistema bimetálico VNi.

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Descripción de los capítulos de la Tesis

La presente memoria de Tesis se ha estructurado en siete capítulos donde se contextualiza la necesidad de contribuir al conocimiento en todo lo relacionado con la producción de hidrógeno renovable en un contexto energético de especial interés; se explica la metodología y el diseño de experimentos realizados así como los resultados correspondientes y las conclusiones principales derivadas. En el primer capítulo introductorio se expone el contexto energético actual y la necesidad de avanzar hacia una economía descarbonizada que presenta al hidrógeno como principal vector, analizando las diferentes opciones en cuanto a su producción partiendo de materia prima renovable. En el segundo capítulo se describen brevemente las técnicas experimentales y metodologías empleadas en el transcurso de los trabajos de la tesis, que sirve como introductorio a los cuatro capítulos posteriores. El contenido de cada uno de los cuatro capítulos referentes a los resultados y conclusiones obtenidos se corresponden con cada una de las publicaciones derivadas de los mismos. En un último capítulo se recogen las conclusiones generales derivadas del análisis de los resultados y conclusiones particulares resaltando los principales resultados recogidos en cada publicación citada, que ha permitido analizar de forma global los procesos abarcados y emitir los próximos pasos a seguir para avanzar en aquel o aquellos procesos prometedores de cara a un posible escalado y comercialización del proceso.

A continuación, se hace un breve resumen de cada capítulo, tanto Introducción como Experimental, así como los referentes a los resultados, los cuales atienden, como se ha mencionado, a cuatro publicaciones científicas, tres de ellas en la revista *International Journal of Hydrogen Energy* y una cuarta en la *Chemical Engineering Journal*, contando todas con una estructura similar: Introducción, apartado con descripción de metodología y experimental, exposición de resultados y conclusiones principales:

Capítulo 1: Introducción

En este primer capítulo se hace una introducción al estado energético actual, así como a la necesidad de diversificar las fuentes de producción energética, centrando

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el tema en el hidrógeno como vector energético. Se presentan las principales características del hidrógeno y sus aplicaciones más importantes, que lo convierten en un pilar fundamental en el escenario de transición energética en el que nos encontramos actualmente, así como vector clave en el proceso de descarbonización del transporte e industria impulsado por la mayoría de los países a nivel mundial. En este sentido, se hace un breve resumen de las diferentes alternativas en la producción de este gas combustible y se describen las diferentes rutas enfocadas en los procesos de reformado. Bajo esta premisa, se hace hincapié en la necesidad de partir de materiales renovables que permitan que la producción de este combustible gaseoso se lleve a cabo de forma sostenible, introduciendo por tanto las propiedades del biocrudo obtenido por pirólisis de residuos de origen biomásico y los componentes oxigenados modelo que lo componen. Con esta materia prima de partida, se describen los procesos de reformado de dichos compuestos orgánicos, así como los sistemas catalíticos ampliamente usados en este campo que permiten enfocar las directrices para el desarrollo de los trabajos de la tesis.

En este marco de contextualización de la tesis, se proponen a continuación los objetivos planteados para la misma, siendo el principal el de contribuir al desarrollo de nano-catalizadores eficientes en los procesos de reformado de compuestos oxigenados con vapor de agua, así como el establecimiento de las condiciones operacionales para cada uno de ellos. En detalle, se plantean los siguientes **objetivos individuales**:

Diseño de un nanocatalizador bifuncional eficiente en la producción de H2 mediante reformado con vapor, comparativa con catalizadores industriales comerciales y el establecimiento del desarrollo del protocolo de síntesis del catalizador mejorado.

Evaluación comparativa en el rendimiento a hidrógeno de las moléculas modelo oxigenadas, con distinto grupo funcional, en base a la temperatura de operación, rendimiento y distribución de productos.

Estudio de FTIR-in situ para establecimiento de la ruta mecanística y de las etapas involucradas en el proceso de reformado con vapor y predicción de las regiones de operación, en base a los resultados experimentales, mediante simulación.

Finalmente, el desarrollo de un microdispositivo de reacción y ensayos del microreformador para la producción de H2 alimentado por dimetil-éter (DME).

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Capítulo 2: Experimental

En este capítulo se listan los reactivos y materiales empleados tanto para la síntesis de catalizadores como para los estudios de actividad de los diferentes procesos analizados. Se describen los equipos empleados en los laboratorios en los que se ha trabajado a lo largo del desarrollo de la Tesis, así como la metodología y diseño de experimentos empleados en cada caso. También se describen las técnicas usadas para la caracterización de los sistemas catalíticos sintetizados. Todos estos aspectos son descritos de forma genérica en este capítulo 2 y en cada uno de los capítulos de resultados, en el correspondiente punto de las publicaciones relacionadas.

Capítulo 3: Production of hydrogen by catalytic steam reforming of oxygenated model compounds on Ni-modified supported catalysts. Simulation and experimental results.

Este capítulo recoge los resultados del estudio del reformado de acetona (SRA) y etanol (SRE), donde se analiza la influencia del catalizador empleado y se hace una comparativa con un modelo termodinámico diseñado para dichos procesos, comprobando que éste puede ser empleado para analizar las regiones operativas de operación de los procesos analizados. Estos resultados corresponden a la publicación: *International Journal of Hydrogen Energy,* ***40 (2015) 11217-11227***. De los resultados obtenidos se puede extraer que tanto la acetona como el etanol pueden emplearse para producir hidrógeno mediante el proceso de reformado con vapor, de una manera eficiente, empleando el sistema catalítico basado en Ni/Al_2O_3, y obteniendo una corriente con fracciones molares de hidrógeno del 60-70%, una vez alcanzados los 800 K. Se analizan en el trabajo aquellas reacciones y rutas paralelas que puedan dar lugar con el empleo de acetona y etanol como materia prima en el reformado, comprobando que, según las condiciones y catalizador empleados, el transcurso en mayor o menor medida de estas reacciones paralelas pueden repercutir negativamente tanto en la selectividad y rendimiento a hidrógeno

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como en la desactivación del catalizador por la formación de coque y su deposición sobre los centros activos del mismo. En este sentido, se decidió modificar el catalizador convencional Ni/Al_2O_3 con la incorporación de Rh en una razón atómica optimizada Ni:Rh = 100:1. Se observaron diferentes rutas en los resultados obtenidos para los procesos de reformado de acetona (SRA) y etanol (SRE) y se detectaron H_2, CO, CO_2 y CH_4 como los principales productos para los catalizadores Ni/Al_2O_3(TH) y $NiRh/Al_2O_3$(TH) en el SRA y el SRE. Además del reformado con vapor de la acetona (SRA), se produce la reacción de desplazamiento inverso del gas de agua (*Water Gas Shift Reaction – WGS*) y el reformado con vapor del metano. Comparando con los resultados obtenidos con el catalizador monometálico Ni/Al_2O_3, se comprueba que el Rh incorporado también desempeña un papel importante en el SRA, ya que permite la conversión completa de la acetona promoviendo la producción de H_2 con una deposición mínima de carbono tras las pruebas catalíticas. El reformado del etanol (SRE) se produce principalmente a través de la descomposición del etanol en acetona, acetaldehído y etileno, seguido del reformado con vapor y la descomposición de estos productos intermedios. La incorporación de Rh, incluso en carga mínima 1:100 (Rh:Ni) disminuye los productos intermedios promoviendo la reacción de descomposición del etanol.

Para el caso particular del etanol, considerando que una de las rutas es su descomposición a etileno, principal precursor en la formación de coque, se analizó la posibilidad de emplear un soporte distinto, alúmina nanofibrosa, debido a la diferencia en las propiedades ácidas del mismo. Con el empleo de este catalizador Ni/Al_2O_3(N) se destaca la ausencia de etileno en la corriente obtenida, influida por la naturaleza del soporte y principalmente por las propiedades ácidas. En este sentido, el contenido de Na en el soporte nanofibroso implica menor acidez en comparación con el soporte de alúmina TH, lo que se traduce en una menor selectividad hacia la formación de etileno.

La incorporación de Rh, incluso en una relación atómica baja en comparación con el Ni, mejora la actividad y estabilidad del Ni, disminuyendo el tamaño de partícula de Ni^0 y mejorando su distribución en la superficie catalítica. Además, la cantidad de carbón formada y depositada analizada después de reacción disminuye cuando se emplea el catalizador dopado con Rh, el cual promueve la gasificación de este.

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Además, el carbón depositado con el empleo del sistema monometálico basado en Ni es más estructurado, presentando un mayor grado de grafitización, por lo que afecta negativamente a la actividad y estabilidad del catalizador.

Capítulo 4: Hydrogen production by ethanol steam reforming over multimetallic RhCeNi/Al_2O_3 structured catalyst. Pilot-scale study.

Este capítulo se corresponde con la publicación: *International Journal of Hydrogen Energy* ***41 (2016) 16786-16796***. En este trabajo se explora la posibilidad de escalar el proceso de reformado de etanol con vapor, diseñando un sistema catalítico estructurado basado en los resultados obtenidos previamente, llevando a cabo el proceso en una planta piloto semi-industrial conectada en línea a una pila tipo PEM.

Se desarrolló un catalizador basado en Ni sobre un soporte de alúmina estructurado en forma de *pellets* cilíndricos. Se incorporó Rh, al igual que el sistema previamente ensayado, pero en una relación menor, incorporando Ce, con una formulación expresada como razón atómica en átomos por nm^2 **Rh:Ce:Ni=0.0009:5:9**. El CeO_2 se ha empleado como soporte y como promotor catalítico para la producción de hidrógeno a partir de etanol, encontrando que la adición de CeO_2 mejora la estabilidad del catalizador disminuyendo la formación de carbón, debido a la gran cantidad de oxígeno de red móvil. Además, la fuerte interacción entre el cerio y los otros metales activos debiera favorecer la actividad catalítica. Por otro lado, el Ce presenta propiedades redox particulares en presencia de metales de transición o nobles; por ello, las combinaciones bimetálicas Ni-Ce y Rh-Ce han sido testadas con resultados positivos en procesos de reformado. Además, se ha demostrado el excelente comportamiento catalítico del sistema Rh/CeO_2 para el reformado oxidativo del etanol, por lo que se decidió su empleo para el reformado con vapor de etanol en su escalado.

Se observó una interacción cooperativa para los componentes principales, Ce-Ni. El Ce está presente principalmente como Ce^{4+} y Ce^{3+} y destacar que parte de las

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especies de Ni^{2+} se integran en la estructura de tipo fluorita de la ceria, ya que la incorporación del Ni^{2+} provoca un desorden en la red de coordinación del oxígeno que modifica el tamaño medio de las partículas. El catalizador RhCeNi es activo en la *ESR* incluso a diferentes relaciones vapor/etanol entre 4 y 10 a escala de laboratorio y también es muy activo y estable a escala de planta piloto *testado* a una relación S/EtOH=7, con un alto rendimiento de H_2 (95% a 700ºC) y una presencia mínima de productos secundarios como acetona o etileno y etano. La selectividad a CO se mantiene por debajo del 5-7% en la corriente de salida de gases del reformador, aunque se reduce aún más para alcanzar valores aceptables después de las unidades WGS y CO-PROX para alimentar el PEM situado aguas abajo de la instalación.

Capítulo 5: Hydrogen production by steam reforming of DME over Ni-based catalysts modified with.

Este capítulo recoge los resultados del estudio realizado mediante el empleo de catalizadores comerciales de base níquel, modificados con vanadio e identificados como 0.5VNi, 1VNi y 3VNi, correspondiente el 0.5 %, 1 % y 3 % en peso de V respecto al Ni, para la producción de hidrógeno mediante reformado de dimetil éter (DME), publicado en *International Journal of Hydrogen Energy* ***41 (2016) 19781-19788***.

En este trabajo se estudia el proceso de reformado de DME con vapor de agua desde el punto de vista del proceso general, abordando las etapas involucradas, siendo las principales la hidrólisis de DME (identificada como DME-HYD) con la formación de metanol seguida del reformado del metanol generado (MeOH-SR), produciendo una corriente enriquecida en hidrógeno acompañada de CO_2. Ambas etapas se suceden en serie, por lo que una mayor activación de la etapa de reformado de metanol estaría encaminada hacia el desplazamiento y mayor conversión de la hidrólisis de DME. Paralelamente, se esperaría encontrar indicios de reacciones paralelas que pudieran alterar el equilibrio de los procesos, pudiendo ser, entre otras, la descomposición directa de DME, descomposición directa de metanol, que

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ambas harían posible encontrar metano (CH_4) en la corriente producto; y reacciones asociadas al reformado del metano generado, por encontrarse en las condiciones de operación requeridas y siendo el catalizador, en principio, activo a dicho proceso. Debido a estas consideraciones previas se planteó analizar el proceso de forma desacoplada, con el fin de determinar el comportamiento de los catalizadores frente a condiciones de reformado de metanol (MeOH-SR), Descomposición directa de DME (DME-Dec) en ausencia de agua y bajo condiciones propias de reformado (DME-SR).

Primeramente, se realizaron ensayos alimentando mezcla de metanol y agua en condiciones estequiométricas. Los resultados obtenidos tras dichos ensayos muestran que el CO y el hidrógeno se produjeron juntos como productos principales a baja temperatura (250 ºC), en una relación molar H_2/CO alrededor de 2, mientras que el CO_2 aparece a temperaturas más altas (>300 ºC). Estos resultados indican que a baja temperatura se promueve la descomposición directa del metanol, necesitando mayor temperatura para activar la reacción directa MeOH-SR. Los valores de rendimiento a H_2 obtenidos indican que con la incorporación de vanadio se produce una mejora de la actividad catalítica, obteniendo un mayor rendimiento con el catalizador 3VNi, generando hidrógeno a razón de 1,6-1,7 mol de H_2 por mol de metanol alimentado a partir de los 350ºC.

Por otro lado, alimentando exclusivamente DME, en ausencia de vapor de agua, con el objeto de analizar la posible contribución de la descomposición directa de DME (DME-Dec) y su interacción con los catalizadores comerciales empleados se obtuvo que la corriente producto presenta como composición principal una mezcla enriquecida en hidrógeno con presencia de CO_2, CO y metano (CH_4). Sobre el catalizador 0,5VNi, la conversión completa de DME se alcanza a los 350 ºC, donde el metano y CO_2 son los principales productos (70 % y 25 % respectivamente), obteniendo un comportamiento similar para el catalizador 3VNi. En ambos casos, dichas cantidades de CO_2 y CH_4 decrecen conforme aumenta la temperatura de operación a la vez que aumentan las concentraciones de CO e H_2, debido también a la contribución del reformado del metano formado. El máximo valor de hidrógeno se alcanza a una temperatura de ensayo de 550 ºC, con una razón H_2/CO_2 de 4 (550 ºC) para el sistema 0,5VNi; y razones H_2/CO de en torno a 1,87 (550 ºC). Se pudo

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comprobar que la ruta mecanística se desvía de la convencional encontrada empleando catalizadores convencionales de base cobre.

Finalmente, se estudió el proceso bajo condiciones de DME-SR, alimentado mezcla DME/H_2O estequiométrica, no encontrando actividad aparente hasta los 500ºC. Los resultados obtenidos apuntan a la ocurrencia de los dos pasos en serie considerados y descritos anteriormente. La ausencia de actividad por debajo de 500 ºC se asocia a la combinación de dos efectos distintos: el primero es que la reacción de hidrólisis del DME no se ve favorecida termodinámicamente a bajas temperaturas (<400ºC) y, como ya se ha mencionado, es la etapa determinante; además, se deduce un efecto inhibidor debido a la presencia de vapor en exceso ayudado por las muy bajas áreas superficiales de los catalizadores VNi (2 $m^2 \cdot g^{-1}$) ensayados. Los datos obtenidos a esta temperatura (500ºC) concuerdan con los resultados ya descritos para el reformado del metanol: plena conversión completa del metanol alimentado e H_2 y CO_2 como principales productos de reacción.

Como conclusión, se obtiene que la conversión de DME es completa a 500ºC sobre catalizadores VNi en DME-SR, que tiene lugar en dos pasos: Hidrólisis de DME y MeOH-SR, dando un reformado de gas rico en H_2 utilizando 3VNi con una selectividad de H_2 c.a. 60-70%.

Capítulo 6: The role of Lewis acidic vanadium centers in DME steam reforming over V-Ni catalysts.

Este capítulo se corresponde con la publicación realizada en *Chemical Engineering Journal* ***423 (2021) 129996***. En este trabajo se analiza el potencial del dimetiléter (DME) como portador de energía renovable como almacenamiento químico de hidrógeno y su reformado con vapor (DME-SR) para la producción posterior de corrientes ricas en hidrógeno sobre catalizadores V-Ni/Al_2O_3 sintetizados en el laboratorio, partiendo del catalizador convencional de base Ni empleado en los capítulos anteriores de la presente Tesis con los diferentes compuestos oxigenados ensayados. Durante este estudio se examinó el alcance de la descomposición del

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DME, la hidrólisis del DME y el reformado con vapor de metanol, centrándose en las propiedades redox y ácido/base de las especies superficiales del catalizador. Los resultados muestran que el rendimiento del DME-SR depende del carácter ácido-redox de las especies Ni-O-Ni/V-O-Ni dispersas sobre la alúmina. Para una relación S/C cercana a 2.5, para catalizadores relativamente ricos en V, se encontró que la reacción de hidrólisis del DME sobre los sitios ácidos de Lewis es un paso determinante de la velocidad y, a continuación, los centros metálicos son los responsables de la producción de H_2 y CO_2. Para el sistema 3V-Ni/Al_2O_3 se obtuvo en el proceso DME-SR una baja selectividad hacia metano y producción directa de H_2 y CO_2 (relaciones H_2/CO_2 cercanas a 3), con conversión casi completa de DME por encima de los 400ºC.

En este trabajo se emplean catalizadores sintetizados en el laboratorio, sobre la misma base Ni/Al_2O_3 que aquellos usados en los sistemas preparados para los procesos descritos en los capítulos anteriores, con el objeto de poder comparar el comportamiento de las diferentes moléculas de compuestos oxigenados seleccionados como reactivo de alimentación para la producción de hidrógeno. Se informa de los resultados correspondientes a la incorporación de cantidades crecientes de V; 0,5, 1 y 3 % respecto del Ni y se profundiza en las etapas involucradas en el proceso del DME-SR, con un estudio mediante FTIR-*in situ* con análisis de la fase gas y de la superficie, para establecer la ruta y etapas que condicionan el proceso global. En esta publicación se presentan además los resultados de una caracterización profunda de los catalizadores sintetizados, así como los datos obtenidos tras los ensayos realizados en reactor de flujo tanto para el proceso desacoplado de descomposición de DME (DME-Dec) y en condiciones propias de reformado (DME-SR), presentando la evolución de la selectividad productos generados y conversión de DME.

El trabajo se ha extendido a estudio de catalizadores bimetálicos Cu-Ni soportados en Al_2O_3 [Cu (*y* wt.%)Ni(*20* wt.%)/Al_2O_3] en la reacción de reformado con vapor de DME (DME-SR) mediante un estudio combinado de reactividad en estado estacionario e en régimen isotermo y de FTIR-in situ. Las pruebas de actividad de DME-SR van acompañadas de una caracterización de la superficie del catalizador para obtener una mejor comprensión de las especies de superficie evolucionadas,

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tanto en DME-HYD como en MeOH-SR posterior. Además del proceso SR, se evalúa el comportamiento del sistema catalítico en condiciones libres de agua para la descomposición del DME; así como el estudio de las rutas de reacción mediante FTIR *in situ* para sistemas monometálicos y bimetálicos. Esto resultados son objetivo de un artículo científico aún no publicado en el que se reporta que estos catalizadores han mostrado un efecto sinérgico en términos de actividad catalítica y selectividad hacia los productos de gas de síntesis ya que el tipo de interacción Cu-Ni altera la química de la superficie tanto en el comportamiento redox y equilibrio de acidez y, como resultado, se observa cómo las tendencias catalíticas están influenciadas por la razón atómica Cu/Ni de los catalizadores. Este estudio revela que el Cu mejora considerablemente la selectividad del Ni hacia CO y H_2 al prevenir la metanación de CO/CO_2 mediante el intermediario MeOH, mientras que los centros de cooperación Ni-Cu mejoran el rendimiento catalítico general del Ni a una razón H_2/CO próxima al termodinámico. Curiosamente, para temperaturas medias-altas, el catalizador bimetálico 3Cu-Ni supera los niveles de estabilidad alcanzados con cualquiera de las formulaciones monometálicas y algunas de las bimetálicas, presentándose como un catalizador que ha demostrado ser muy eficiente para operaciones isotérmicas en estado estacionario consideradas como prueba de experimentos catalíticos.

Se suma una aportación científica adicional, pendiente de publicación, sobre un estudio comparado de los catalizadores en la producción de hidrógeno mediante reformado con vapor de metanol. *A comparative Study of synthesized catalysts for hydrogen production by Methanol-Steam Reforming* (*Catalysts*-MPDI). El principal objetivo de este último trabajo es el estudio comparado del efecto de un segundo metal añadido a un catalizador a base de níquel en el proceso de reformado con vapor de metanol (MeOH-SR) dos sistemas bimetálicos, V-Ni y Cu-Ni, con diferente relación atómica M/Ni. Se estudiaron las propiedades catalíticas de los catalizadores investigados en el proceso MeOH-SR en un rango de temperatura entre 150–550ºC y se correlacionaron con sus propiedades fisicoquímicas y reactividad. Finalmente hay que mencionar que se desarrolló un microdispositivo de reacción que podría ser empleado como micro-reformador, como reactor catalítico de microcanales para la producción de hidrógeno a partir de oxigenados

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para la producción de H_2 y ensayado mediante alimentación de disolución acuosa de matenol. Se construyó un dispositivo de placas planas con 5 canales rectangulares con un volumen de 0,5 cm^3 en el que se depositó una capa catalítica de formulación NiCeRh, mediante impregnación.

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Appendix

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Production of hydrogen by catalytic steam reforming of oxygenated model compounds on Ni-modified supported catalysts. Simulation and experimental study

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ABSTRACT

Steam reforming of two representative components in the aqueous fraction of bio-oil, acetone and ethanol, was investigated over nickel based supported catalysts (Ni/Al_2O_3). The effect of Rh incorporation ($Ni–Rh/Al_2O_3$) and the properties of different γ-Al_2O_3 used as support was tested. Hydrogen-rich gas is produced at temperatures higher than 673 K in both acetone and ethanol reforming with maximum mole fraction of 0.6–0.7. The reactions involved and the possible routes were studied. Rh incorporation and nanostructured alumina affects the Ni metal size and the amount of carbon deposited onto catalysts' surface after reforming tests; besides, acetone is also found as an important intermediate in ethanol reforming, and Rh improve hydrogen production with negligible intermediates presence. The effect of S/Acetone or S/Ethanol feed molar ratios, space velocity and temperature over acetone/ethanol conversion and over H_2/CO ratio were modeled using the Matlab software in order to find the regions and the optimal operating conditions in both processes. Simulation results are consistent with the experimental data.

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Introduction

Development of clean, sustainable, and cost-competitive hydrogen production processes is essential to the market success of hydrogen-powered vehicles and fuel cells. Hydrogen is recognized as an important energy carrier and plays an important role in the future global economy [1,2]. The perspective of using hydrogen as a fuel in the future depends to a great extent on finding alternatives to the existing production technologies and feedstock. Most efforts are being dedicated to develop the utilization of renewable energy sources. Most hydrogen is currently produced from fossil fuels such as natural gas, naphtha and coal, and the traditional processes for hydrogen production are the catalytic steam reforming followed by water gas shift conversion [3–9].

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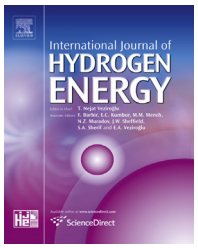

Hydrogen production by ethanol steam reforming over multimetallic RhCeNi/Al_2O_3 structured catalyst. Pilot-scale study

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ABSTRACT

A new multimetallic RhCeNi/Al_2O_3 catalyst structured in cylindrical pellet with an atomic ratio Ce/Ni = 0.55 and minimal Rh content was developed and tested in ethanol steam reforming (ESR) at laboratory and semi-industrial pilot plant scales. A beneficial interaction for the major components, Ce–Ni, is noticed. Ce is mostly present as Ce^{4+} and Ce^{3+} and the incorporation of small amount of Ni^{2+} species into the ceria fluorite-type structure is registered since an oxygen coordination disorder was induced by the Ni^{2+} dissolution that modifies the average size of particles. RhCeNi catalyst is active in the ESR even at different steam/ethanol ratio between 4 and 10 at laboratory scale and is also very active and stable at pilot-plant scale tested at S/EtOH ratio = 7, with a high H_2-yield (95% at 700 °C) and minimal presence of secondary products as acetone or ethylene and ethane. CO selectivity is maintained below of 5–7% in the reformer gas-out stream, although it is further reduced to reach acceptable values after WGS and CO-PROX-units to feed the PEM located downstream of the installation.

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Introduction

Renewable energy resources have shown a peculiar attention at present global scenario owing to growth of population and development, which leads to progressive depletion of conventional fossil fuels (coal, petroleum, natural gas). Among the renewable energy options, hydrogen (H_2) is considered an important energy carrier for the future because it is a clean and high efficient energy resource. H_2 production from bio-ethanol, coupled to fuel cells raised considerable attention in recent years [1,2]. Steam reforming of natural gas (methane), a non-renewable hydrocarbon, is the technology most commonly used for hydrogen production [3]. Nowadays there is a growing interest for hydrogen production from renewable sources such as ethanol [4], glycerol [5–7] or butanol [8]. Among the various feedstock alternatives, alcohols represent an emerging and alternative source of liquid fuels for hydrogen production since they can be produced renewably from biomass. In particular, bio-ethanol constitutes an important and very attractive source due to its relatively high

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Hydrogen production by steam reforming of DME over Ni-based catalysts modified with vanadium

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ABSTRACT

Dimethyl ether steam reforming (DME-SR) for hydrogen production has been studied over V–Ni/Al_2O_3 catalysts as part of an investigation aimed at the development of effective technology based on second generation of biofuels. Methanol steam reforming (MeOH-SR) was investigated as a step of the DME-SR process. High activity in the MeOH-SR was observed and two different mechanism depending on temperature and influenced by the vanadium content (0.5, 1 and 3%) was evidenced: direct methanol decomposition to CO and H_2 was observed at low temperature and low vanadium content and methanol steam reforming reaction occurs majorly to give an almost stoichiometric H_2/CO_2 ratio at moderate to high temperature (400 °C) over 3VNi. DME conversion is complete at 500 °C over VNi catalysts in DME-SR, as a two steps reaction: DME hydrolysis and MeOH-SR giving an H_2 rich gas reformate generated with a H_2 selectivity c.a. 60–70% over 0.5VNi and 3VNi, values maintained during 4.5 h of activity in the same reaction conditions with no signs of deactivation or significant coke formation over catalyst surface.

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Introduction

The on-board production of hydrogen from fossil fuels is challenging due to the needs of a fuel processor system that efficiently converts a hydrocarbon fuel into hydrogen for its use in fuel cells. The hydrogen-rich gas for fuel cell feeding can be produced by catalytic conversion of hydrocarbons and oxycompounds such as methane, propane, methanol, ethanol, propanol, acetone, and/or dimethyl ether (DME) [1–3]. Among these compounds, conversion of DME and methanol to hydrogen-rich gas proceeds with the best performance and selectivity at low temperatures (250–300 °C) [4–8]. The steam reforming of methanol (MeOH-SR) has received much attention for on-board hydrogen production [9] and steam reforming of DME (DME-SR) can be taken into account for the same purposes. Additionally, the use of DME for hydrogen production is accompanied by different advantages such as environmentally friendly, high heating value, ease of storage and transportation, and excellent self-ignition property with low particulate matter emission. DME presents high reactivity at low temperature, which is suitable for the reforming reactions with small amount of energy

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The role of Lewis acidic vanadium centers in DME steam reforming over V-Ni catalysts

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ABSTRACT

Dimethyl ether (DME) as a potential chemical storage of renewable energy was studied for decomposition and steam reforming (DME SR) to produce hydrogen-rich streams over V-Ni/Al_2O_3 catalysts. The extent of DME decomposition, DME hydrolysis, and subsequent methanol steam reforming was examined during this study, focusing on the redox and acid/base properties of catalyst surface species. The results show that the DME SR performance depended on the acid-redox character of the Ni-O-Ni/V-O-Ni species dispersed onto alumina. For S/C ratio close to 2.5, for relative V-rich catalysts, DME hydrolysis reaction over the Lewis acid sites was found a rate-determining step and then, metallic centers being responsible for H_2 and CO_2 production. For 3V-Ni/Al_2O_3 DME SR with low selectivity towards methane and direct H_2 and CO_2 production (H_2/CO_2 ratios close to 3), with near-complete DME conversion was obtained above 673 K.

1. Introduction

Green hydrogen is considered a promising fuel for fuel cell applications for portable devices or hydrogen fuel cell vehicles (FCVs) because of its high energy density and lack of CO_2 formed during combustion [1]. However, the major drawbacks preventing hydrogen-based efficient and environmentally friendly technologies applications are relatively costly hydrogen production, safety and storage issues [2,3]. Specifically for FCVs, hydrogen storage and supply infrastructure still need to be addressed and developed [4].

As an alternative, the possibility of on-board reforming of oxygenated hydrocarbons such as methanol, DME, or ethanol is being studied. Among them, DME has attracted attention as a hydrogen carrier since, unlike methanol, DME is harmless, not corrosive, has a high energy density and high H/C ratio, and no C–C bonds are present in DME molecule. In addition, DME steam reforming is one of the reforming processes with the highest theoretical hydrogen yield at relatively low temperatures [5–7]. Besides, DME has the advantages that it can be stored and transported easily; the existing LPG infrastructure can be used for DME since its physical properties are similar, making DME not only an H_2 source but also an alternative fuel for diesel engine applications or as a diesel blend [8,9]. However, DME may increase NOx emission levels, so after-treatment is still needed if used directly as a fuel [10].

DME reforming can occur with the participation of possible reactions listed in Table 1 Eqs. 1–13. Namely, steam reforming (Eq. 1) and oxidative steam reforming (Eq. 2) are accepted as the most suitable in terms of energy input, hydrogen yield, or operation conditions [11–16]. The steam reforming reaction is comprised of two steps in which DME hydrolysis to two molecules of methanol (Table 1, Eq. 5), which occurs over catalyst acid sites as the first step and then, methanol is transformed into a mix of CO_x and H_2 with the participation of the water–gas-shift (WGS) reaction over a metallic center (Table 1, Eqs. 6–8). To express the reaction mechanism (Eq. 6), methanol decomposition (Eq. 7) and reverse WGS reaction (Eq. 8) are commonly used. The appropriate balance between the acid and metal sites would be desirable to increase H_2 yield, and to minimize secondary reactions such as: DME and by-product decomposition, CO_2 mineralization (carbonation reaction where CO_3^{2-} is formed and energy released), and methanation, while also minimizing catalyst deactivation via metallic site sintering or carbon deposition [17]. Most of the literature regarding DME reforming has focused on Al_2O_3 or zeolites as supports for Cu, Zn, Pd, or Rh as the metal

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