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Concetta Ruocco, Eugenio Meloni, Vincenzo Palma, Martin van Sint Annaland, Vincenzo Spallina, Fausto Gallucci

Abstract

This work reports the preparation and characterization of a novel catalyst for ethanol reforming especially designed for use in a fluidized bed membrane reactor (FBMR). The catalyst was tested under fluidization conditions and the results show good attrition resistance of the catalyst and no chemical interaction with the membrane material. Furthermore, the catalyst was studied in more details for kinetics. The results of catalytic tests suggested different pathways for steam and oxidative reforming of ethanol. It was found that at the studied conditions ethanol is completely converted. A simplified kinetic model was thus proposed and kinetic parameters were evaluated.

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Introduction

Hydrogen has for long time now been indicated as a preferred energy carrier of the future. Indeed hydrogen can also be seen as storage media for peak renewable electricity production. However, at the moment hydrogen is still being produced mainly by fossil fuels conversion. Although almost all hydrogen is generated from fossil fuels today (by either reforming or gasification), hydrogen can be produced from bio-renewable feedstocks via thermo-chemical conversion processes such as pyrolysis, gasification, steam gasification, supercritical water gasification of biomass and steam reforming of bio-fuels. The term biofuel is referred to liquid, gas and solid fuels predominantly produced from biomass.

According to Demirbas, the transition to biofuels (either bio-gas, bio-alcohols and FTS fuels) is dictated by a combination of “energy security reasons, environmental concerns, foreign exchange savings and socioeconomic issues related to the rural sector” [1].

It is projected that the biofuel economy will grow rapidly during the 21st century; in the most biomass-intensive scenario, biomass energy would contribute by 2050 about one half of total energy demand in developing countries.

Among the various feedstocks, ethanol is one of the preferred renewable source for hydrogen production thanks
to its unique features. Its hydrogen capacity is relatively high; it easier to handle than hydrogen gas, being liquid and non-toxic; and even better, it is produced at global scale. Presently, the US is the leading country in ethanol production. In 2012, the ethanol industry produced 1317.9 million gallons. This is more than double of the Brazilian production (5557 million gallons) and ten times more than the production in the European Union (1139 million gallons) [2].

The conversion of ethanol to a gas mixture (containing hydrogen) is relatively easy. However, one of the products of this conversion is methane, which reduces the hydrogen yield. Due to its endothermicity, the ethanol steam reforming (ESR) reaction is promoted at high temperatures (>600 °C), in order to increase the H₂ concentration and lower the CH₄ concentration [3]. Only at temperatures above 800 °C, the equilibrium H₂ selectivity is nearly 100%.

The catalytic performance of supported noble metal (Ru, Rh, Pd, Pt, Ir, Au) catalysts for the steam reforming of ethanol has been investigated in the temperature range of 600–850 °C with respect to the nature of the active metallic phase, the nature of the support (Al₂O₃, MgO, TiO₂) and the metal loading. Different authors [4–6] used Rh, Pd, and Pt on different supports such as alumina and ceria: the noble metals activity decreased in the order of Pt-loaded catalyst, Rh-loaded catalyst, Pd-loaded catalyst. However, several studies reported the promising performances of bimetallic systems, which exploit the synergistic effect related to the presence of two active species [7–10]. Moreover, also the choice of support strongly affects the catalyst activity and stability. Dehydration of ethanol to ethylene was noted on alumina-supported noble metal catalysts [11]. On the contrary, CeO₂ have been extensively investigated as support for ethanol reforming due to its high oxygen storage and release capacity, which increases the metal-support interactions and promote carbon gasification reactions, thus resulting in improved catalyst stability [12,13]. In particular, the catalyst stability was also monitored with and without the presence of oxygen [14,15].

An improvement in the hydrogen yield at lower temperatures can be achieved by integrating hydrogen production and hydrogen recovery in a single multifunctional unit. The application of membrane reactors (generally packed bed membrane reactors) has been proposed for this reaction system, and it has been shown that indeed a higher ethanol conversion per pass and pure hydrogen production can be achieved in membrane reactors [16–19]. All these membrane reactor studies used relatively thick (and low flux) membranes. However, thin and high flux membranes are nowadays available on the market that make the use of membrane reactors more industrially attractive [20–23].

However, when the hydrogen flux is very high and in the presence of active catalysts (as the ones used for ethanol reforming), external mass transfer limitations from the catalyst bed to the membrane surface (also known as concentration polarization) become limiting in the hydrogen production capacity and affect the reactor performances, thereby undesirably increasing the required membrane area.

To overcome these limitations different membrane reactors have been proposed in literature ranging from micro-reactors to fluidized bed reactors. Micro-reactors are very interesting for their increase in the rate of mass and heat transfer, however, the amount of catalyst that can be used is very limited to avoid excessive pressure drop. Moreover, manifolding and gas distribution in membrane micro-reactors was demonstrated to be a big challenge. Membrane assisted fluidized beds seem to hold the solution to the problems of mass transfer, pressure drop and catalyst mass.

The main advantages of the fluidized bed membrane reactors over other types of reactors can be listed as:

- Negligible pressure drop, which allows using small particle sizes resulting in no internal mass and heat transfer limitations.
- (Virtual) isothermal operation even in case of highly endothermic/exothermic reactions or in case of liquid fuel injection.
- Flexibility in membrane and heat transfer surface area and arrangement of the membrane bundles.
- Improved fluidization behavior.

While the advantages of fluidized bed reactors are clearly stated and demonstrated by many authors, recently it was reported that components of catalysts and membranes can interact reducing dramatically the efficiency of the membranes [49].

For the application of thin membranes in fluidized bed membrane reactors for ethanol reforming it is thus very important to develop a catalyst that on the one hand can survive under fluidization conditions and, on the other hand does not chemically interact with the membranes.

In this work we will discuss the preparation and characterization of a new catalyst for ethanol reforming for application in fluidized bed (membrane) reactors. First, the catalyst preparation will be discussed, followed by tests under fluidization conditions. The permeation test for the membrane will be carried out in an empty bed and in presence of the catalyst and the H₂ flux presented for both cases to demonstrating the feasibility of the current material in a membrane assisted fluidized bed reactor. Finally, a simplified kinetic model will be presented along with the kinetic parameters derived from detailed kinetic experiments.

Catalyst preparation and characterization

The Pt-Ni/CeO₂/SiO₂ catalyst (with a CeO₂/SiO₂ weight ratio of 20%) was prepared via the wet impregnation method developed by the ProCEED laboratory at the University of Salerno. Silica powder (Sigma–Aldrich, pore size 60 Å) was calcined in a muffle furnace at 600 °C for 3 h prior to be used. The silica was impregnated with an aqueous solution of Ce(NO₃)₂·6H₂O for 1 h at 80 °C, then dried at 120 °C for 12 h to remove water excess. The resulting solid was thermally calcined at the same conditions reported for SiO₂. The optimal Ni and Pt loadings on CeO₂/SiO₂ were previously determined [24] to be respectively 10 and 3 wt% referred only to the CeO₂ support. The desired loadings were reached by sequential impregnation stages. Required amounts of Ni(NO₃)₂·6H₂O were dissolved in bi-distilled water and impregnated on the CeO₂/SiO₂ support. Then, drying and calcination were performed to complete Ni deposition. Finally, the catalyst was mixed to an aqueous

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solution of PtCl₄, salt precursor of the noble metal, which was impregnated by the same procedure described above. The Ce(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O and PtCl₄ salts were supplied by Strem Chemicals. The benefits, in terms of activity and stability of the final catalyst, linked to nickel deposition on the support surface earlier than platinum were reported in previous studies [24].

Elemental analysis to determine the final loading percentages of ceria, nickel and platinum was performed with the Energy Dispersive X-Ray Fluorescence (EDXRF) technique (Thermo-Scientific QUANT™X). The B.E.T. (Brunauer Emmett Teller) surface area was calculated from nitrogen adsorption at −196 °C. Prior to the adsorption measurement, a pretreatment step of the prepared catalysts was conducted at 120 °C for 1 h. X-ray diffraction (XRD) measurements were performed on fresh catalysts with 20 values ranging between 5 and 80 using a D8 Brooker diffractometer graphite-filtered Cu Kα radiation (λ = 1.5406 A). The Scherrer equation was used to estimate the mean Ni and CeO₂ crystallite size based on full width at half maximum (FWHM). Raman spectra were obtained with a Dispersive MicroRaman (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 200–1200 cm⁻¹ Raman shift.

To study the reducibility of the prepared catalyst, H₂-TPR (Temperature Programmed Reduction) measurements were carried out under a 5%H₂/N₂ stream from ambient temperature to 600 °C (heating rate of 10 °C/min). In particular, 3 g of the sample was treated at 600 °C for 1 h in the laboratory apparatus described elsewhere [25].

**Structural properties of the catalyst and the support**

Table 1 presents the measured metals and CeO₂ weight loadings as well as the support and catalyst specific surface area (SSA).

The ceria loading in the final catalyst agrees well with the theoretical content (20 wt%). The bulk elemental composition of the metals is also consistent with the expected values, as 2.2 and 0.6 wt% correspond to 10.7 and 2.9% on weight basis referring only to the CeO₂ content, respectively.

The impregnation of CeO₂ and active species resulted in a decrease in the specific surface area of the pure support. This effect can be linked to pore blockage [26] by the added species, which is more pronounced in the case of CeO₂ due to its higher loading with respect to Ni and Pt.

The XRD patterns of the prepared samples are reported in Fig. 1. The diffraction patterns clearly show the presence of an amorphous peak at 20 = 23°, ascribable to SiO₂ support [27–29].

![Fig. 1 – X-ray diffraction patterns of the prepared catalyst and the CeO₂/SiO₂ support.](image)

After the addition of 20% of CeO₂, the main peaks [30,31] of the ceria fluorite structure are visible (at 28.6, 33.1, 47.1, 56.5, 58.9 and 69.2°). Moreover, the final catalyst showed the diffraction peaks of NiO [32] at 37.4, 43.5 and 63.2°. No peaks relevant to the presence of PtO₂ species were identified, probably due to its low loading or amorphous state [33]. The crystallite sizes of CeO₂ and NiO, as calculated by the Scherrer equation, were ca. 7 nm and 11 nm, respectively (Table 1).

Moreover, the average dimension of the CeO₂ crystallite was not affected by active species deposition.

![Image](image)

**Table 1 – Characteristic of support and fresh catalyst: specific surface area and chemical composition.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m²/g)</th>
<th>SiO₂ (wt%)</th>
<th>CeO₂ (wt%)</th>
<th>Ni (wt%)</th>
<th>Pt (wt%)</th>
<th>dCeO₂ (Å)</th>
<th>dNiO (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>400</td>
<td>100-</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CeO₂/SiO₂</td>
<td>281</td>
<td>78.6</td>
<td>21.4</td>
<td>–</td>
<td>–</td>
<td>67</td>
<td>–</td>
</tr>
<tr>
<td>Pt-Ni/CeO₂/SiO₂</td>
<td>232</td>
<td>76.5</td>
<td>20.7</td>
<td>2.2</td>
<td>0.6</td>
<td>68</td>
<td>114</td>
</tr>
</tbody>
</table>
The second peak is attributed to the reduction of NiO species [43] interacting with the support. The quantitative results of TPR analysis, reported in Table 2, suggest that the dissociation of hydrogen on the Pt particles and its successive spillover [44,45] to NiO and CeO2 leads to hydrogen uptakes higher than the expected consumption, due to the higher reactivity of atomic hydrogen compared to molecular hydrogen.

Moreover, the easy occurrence of redox phenomena, typical of rare earth oxides, provide a number of surface oxygen sites on CeO2 support, which are reactive towards spillover [46,47].

**Test under fluidization conditions**

The bimetallic catalyst was tested under fluidization conditions at both low and high temperature. The particle size distribution after the fluidization tests has been compared with the one of the catalyst as received. The results are reported in Fig. 4, as particle size distribution (measured by laser diffraction in wet conditions with Fritsch Analysette 22) of fresh support and after fluidization at 25 and 400 °C for 24 h. Most of the studies on fluidization resistance are carried out at low temperature and for shorter time. The reason we carried out tests at higher temperatures (up to 400 °C) is because at temperatures higher than 300 °C the catalyst or support in fluidization conditions could chemically react with the membrane surface as reported in a previous work (see Ref. [48]) and this occurs in the first hrs of fluidization. Furthermore, also the particle size distribution of the samples after the reactive tests has been reported. As evident from Fig. 4, the catalyst shows a very good mechanical resistance to fluidization, since its particle size distribution was hardly affected by fluidization at different temperatures and conditions (the fines lost after all tests combined were less than 3% of the initial catalyst mass). In addition, after the reactive test and in presence of a membrane the particle size distribution did not change, while also the hydrogen permeation of the membrane was unaffected (see section below) confirming that the new catalyst can be used in fluidized bed membrane reactor.

### Catalyst – membrane interaction

H2 permeation tests have been carried out in the permeation setup at the TUE described in Ref. [49] where also reactive permeation was performed under fluidization conditions. An ultra-thin (~1 μm thick) Pd-based supported on a ceramic porous tube of 7/10 mm (I.D/O.D) prepared by a combination of PVD magnetron sputtering and electroless plating techniques has been tested [23]. The permeation tests were carried out in a 11 cm membrane feeding 3500 Nml/min of H2 and increasing the N2 flow rate in order to change the H2 mol fraction. The total pressure of the feed/retentate side has been varied from 1 to 4 bar. At the permeate side no sweep gas was used and the pressure was maintained at atmospheric conditions.

The results shown in Fig. 5 show that the presence of the catalyst (fluidized bed configuration) does not affect the permeation rate and the membrane was reaching the same H2
flux than in the case of empty bed. Moreover, after the permeation test with catalyst, the permeation test were repeated in an empty bed and the results were reproduced as in first experiment without catalyst (empty bed configuration). This results demonstrate that the current catalyst does not interact with the membrane and the membrane performance are not affected. This demonstrates the current catalyst can be safely integrated with the membrane in a fluidized bed membrane reactor.

**Kinetic experiments**

The experiments to determine the catalytic activity of Pt-Ni/CeO₂ for ethanol reforming were carried out in a quartz micro fixed-bed reactor (µ-PBR). The experimental setup (Fig. 6) is divided in a gas feeding system including a controlled evaporator mixer (CEM) for liquid feeding and evaporation, a U-shaped quartz reactor of 7 mm I.D. placed in an electric furnace, and a gas analysis device. The catalytic bed consisted of 503 mg of Pt-Ni/CeO₂ (50 < dₚ < 150 μm). The bed was loaded over a layer of quartz wool, and the section before and after the bed was filled with quartz particles (0.1 < dₚ < 0.3 mm) to decrease as much as possible gas phase reactions. Experiments in the same configuration without catalyst showed no conversion, thus the gas phase reactions can be neglected. The temperature was measured by a thermocouple that was located in the radial center of the reactor, about 2 cm downstream the catalytic bed. After water condensation, the outlet gas composition was analyzed by a GMS815P Extractive gas
Kinetic test

Kinetic tests have been carried out in the kinetic setup described above to determine which kinetic model better describes the reaction of ethanol autothermal reforming. The operating conditions in terms of S/C and O/C have been selected according to Foresti et al. [50] in which the overall thermal balance of the plant has been assessed and compared with conventional ethanol reforming including also the presence of the PEM fuel cell. The S/C ratio used would circumvent the carbon formation on the catalyst, although independent study on a similar catalyst (see Ref. [51]) show that at low S/C ratios coke selectivities of this catalyst were among the lowest found in the recent literature.

Ethanol conversion

Different experiments have been carried out in order to investigate the ethanol conversion at different conditions, particularly to confirm earlier results by Palma et al. [52], who showed that the ethanol is completely converted into other gases after 15–150 ms using 480 °C and 340 °C. In order to reproduce similar conditions, the reactor was filled with 50.28 mg of Pt-Ni/CoO2 catalyst with a volume of 1.07 cm3. The tests were carried out at 480 °C, 520 °C and 550 °C by feeding a steam/ethanol mixture with a molar feed ratio steam/ethanol of 6. For each temperature, two different flow rates were considered, viz. a GHSV of 72,000 h−1 and 115,000 h−1 corresponding to gas residence times of 30 and 50 ms, respectively.

For each experiment the amount of ethanol (EtOH) converted was calculated according to the C–H–O balance. In particular, in absence of carbon deposition and formation of other hydrocarbons (confirmed for all tests in this work) the carbon in the ethanol is converted into CH4, CO and CO2, thus the conversion is calculated as:

\[ x_{\text{EtOH}} = \frac{\text{mol CO} \text{out} + \text{mol CO2} \text{out} + \text{mol CH4} \text{out}}{2\text{mol EtOH} \text{in}} \]  

Fig. 7 shows that indeed the ethanol conversion is always higher than 95% and, especially at higher temperatures (around 520–550 °C) where the catalyst would be used in a fluidized bed (membrane) reactor, the conversion of ethanol is complete even for very low gas residence times. These results also confirm that no other by-products have been formed during the experiments (also confirmed by HPLC tests). It should be also highlighted here that in a fluidized bed reactor with membranes the contact time would be one order of magnitude higher than the one used in these experiments and thus one can safely assume that ethanol will be completely converted. For a detailed kinetic modeling it is thus important to study the behavior of methane and CO as function of the contact time over this new catalyst.

Steam methane reforming

In order to evaluate the effects of steam and reaction products on the ethanol reforming reaction rate, the effects of CH4, CO, H2O and H2 were investigated in detail separately.

The methane conversion rate was calculated as:

\[ r_{\text{CH4}} = \frac{\text{mol/}(s \text{ kgcat})}{\text{CH4 in} - \text{CH4 out}} \]  

As this reaction is part of ethanol reforming, the reaction is expected to occur at high steam content, thus a steam-carbon molar ratio always higher than 5 has been used in the experiments. This also resulted in absence of carbon deposition during the experiments (also checked by oxidation after the kinetics tests). Experiments were carried out varying the composition of one component (shown in bold in the table) by balancing this with N2 while all other compositions are held constant.

Table 3 summarizes all the gas inlet compositions used in this work. The total flow rate and temperature were kept constant in all the experiments. The tests were first carried out at 500 °C with a total volumetric gas flow rate of 1000 ml(STP)/min, which corresponds to a GHSV of 14,154 h−1. The gas inlet composition 7.9% CH4, 3.5% CO, 3.9% H2, 64.2% H2O and 20.6% N2 was used as base case. β is the approach to equilibrium of the methane reforming, as described in the kinetic model below. The content of the reactive gases was varied in order to determine the reaction order of each gas in the steam reforming reaction.

In order to determine the pre-exponential factor (k0,SMR) and apparent activation energy (Eact,SMR) for the steam reforming of methane other experiments were carried out with a gas flow rate of 1000 ml/min using a gas mixture of 4.5% CH4, 4.5% CO, 4.5% H2, 27.3% H2O and 59.1% N2, at three different temperatures: 480 °C, 500 °C and 520 °C. From the Arrhenius-plot the pre-exponential factor and apparent activation energy has been determined (the slope of the line reported in Fig. 8 represents −Eact,SMR/β).

Water gas shift

In the previous experiments the steam reforming of methane occurred in parallel with the water gas shift reaction, but analyzing the previous experimental results, it is evident that the WGS reaction was at equilibrium at each temperature and composition. To better assess this point, several experiments have been carried out using the μ-PBR with 543 mg of catalyst for the WGS reaction alone. The catalyst has been mixed with

**Fig. 7 – Ethanol conversion as a function of temperature and residence time.**
inert material (520 mg of quartz). The reactor length is therefore 0.6 cm.

The inlet composition of each experiment and the results are presented in Fig. 9. The results show also the expected syngas composition in case of chemical equilibrium which was predicted using a Gibbs reactor type from Aspen Plus (the red bars). The experiments were carried out using a gas hourly space velocity (GHSV) of 14,154 h\(^{-1}\).

As can be observed from the experiments reported in Fig. 9 the WGS reaction is at equilibrium. At these temperatures, and with this very active catalyst, it was not possible (nor necessary) to achieve low conversion and determine the WGS reaction kinetics separately.

Table 3 – Experimental conditions and CH\(_4\) conversion rate obtained (T = 500 °C).

<table>
<thead>
<tr>
<th>F(_{\text{CH}_4}) (ml min(^{-1}))</th>
<th>F(_{\text{H}_2\text{O}}) (ml min(^{-1}))</th>
<th>F(_{\text{H}_2}) (ml min(^{-1}))</th>
<th>F(_{\text{CO}}) (ml min(^{-1}))</th>
<th>F(_{\text{N}_2}) (ml min(^{-1}))</th>
<th>(\beta)</th>
<th>(r_{\text{CH}_4}) (mol kg(^{-1}) cat s(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>98.69</td>
<td>592.15</td>
<td>59.22</td>
<td>16.30</td>
<td>215.40</td>
<td>1.28 \times 10^{-2}</td>
<td>2.49 \times 10^{-2}</td>
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<td>59.22</td>
<td>592.15</td>
<td>59.22</td>
<td>16.30</td>
<td>254.87</td>
<td>1.60 \times 10^{-2}</td>
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<td>59.22</td>
<td>16.30</td>
<td>235.13</td>
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<td>592.15</td>
<td>72.09</td>
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<td>215.40</td>
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<td>592.15</td>
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<tr>
<td>78.95</td>
<td>592.15</td>
<td>34.88</td>
<td>27.65</td>
<td>230.20</td>
<td>8.11 \times 10^{-3}</td>
<td>1.74 \times 10^{-2}</td>
</tr>
<tr>
<td>78.95</td>
<td>592.15</td>
<td>34.88</td>
<td>20.84</td>
<td>245.00</td>
<td>6.08 \times 10^{-3}</td>
<td>1.83 \times 10^{-2}</td>
</tr>
<tr>
<td>78.95</td>
<td>592.15</td>
<td>34.88</td>
<td>14.03</td>
<td>259.81</td>
<td>4.05 \times 10^{-3}</td>
<td>1.72 \times 10^{-2}</td>
</tr>
</tbody>
</table>

Fig. 8 – Arrhenius plot for the SMR reaction over the Pt/Ni – CeO\(_2\) catalyst.

Fig. 9 – Outlet gas composition of the test on WGS over the catalyst and corresponding composition at the chemical equilibrium.
**Kinetic model**

The results of these tests (and additional tests with oxygen addition, not reported here) suggested us to describe the autothermal reforming of ethanol with the following set of reactions as illustrated in Fig. 10. Two different pathways have been considered for the ethanol autothermal reforming. In the first pathway the ethanol is instantaneously converted into a mixture of gas corresponding to equivalent ethanol, \( (C_2H_5OHeq = CH_4 + H_2 + CO) \) and after that the methane partial oxidation occurs followed by the SMR and WGS. In the second pathway, the ethanol first reacts with \( O_2 \), the remaining ethanol is converted into equivalent ethanol \( (C_2H_5OHeq) \) and after that followed by SMR and WGS.

For each reaction (case a) the rate of conversion is calculated as follow:

1) \( C_2H_5OH \rightarrow CH_4 + H_2 + CO \): full conversion of \( C_2H_5OH \) into \( C_2H_5OHeq \) assumed with an infinite reaction rate
2) \( CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \): the reaction rate has been assumed at chemical equilibrium
3) \( CH_4 + H_2O \leftrightarrow CO + 3H_2 \): the reaction rate of the steam reforming reaction has been determined experimentally
4) \( CO + H_2O \leftrightarrow CO_2 + H_2 \): water gas shift reaction has been assumed at chemical equilibrium.

For each reaction (case b) the rate of conversion is calculated as follow:

1) \( C_2H_5OH + 3.5aO_2 \rightarrow (1 - a)C_2H_5OH + 2aCO_2 + 3aH_2O \): the reaction has been assumed at chemical equilibrium
2) \( C_2H_5OH \rightarrow CH_4 + H_2 + CO \): full conversion is assumed with an infinite reaction rate
3) \( CH_4 + H_2O \leftrightarrow CO + 3H_2 \): the reaction rate of the steam reforming reaction has been determined experimentally
4) \( CO + H_2O \leftrightarrow CO_2 + H_2 \): water gas shift reaction has been assumed at chemical equilibrium.

The set of equations and the variables used for the kinetic model are reported below.

**Oxidation reactions**

Methane and ethanol oxidation reactions are assumed to be at chemical equilibrium and therefore, due to the very high equilibrium constant, the oxygen is assumed to be instantaneously completely converted. This has also been experimentally verified.

**Steam methane reforming**

An empirical power-law expression is used to describe the kinetics of SMR. The power-law expression generally used for the SMR is:

\[
R_{\text{SMR}} = k_{\text{SMR}} \left( \frac{p_{\text{CH}_4}}{p_{\text{H}_2}} \cdot \frac{p_{\text{H}_2O}}{p_{\text{C}_2\text{H}_5\text{OH}}} \right) \left( \frac{p_{\text{CO}}}{p_{\text{H}_2O}} \right) (1 - \beta) \quad (3)
\]

\[
\beta = \left( \frac{1}{K_{eq}} \right) \left( \frac{p_{\text{H}_2}}{p_{\text{C}_2\text{H}_5\text{OH}}} \right) \quad (4)
\]

\[
k_{\text{SMR}} = k_{0,\text{SMR}} \exp \left( \frac{-\Delta G_{\text{SMR}}}{RT} \right) \quad (5)
\]

\[
k_{\text{SMR}} = k_{0,\text{SMR}} \exp \left( \frac{-E_{\text{act,SMR}}}{RT} \right) \quad (6)
\]

where \( \beta \) is a measure related to the extent of the reverse reaction or approach to equilibrium, and \( a,b,c,d \) are the reaction orders in \( \text{CH}_4, \text{H}_2O, \text{H}_2 \) and \( \text{CO} \) respectively and \( K_{eq} \) is the equilibrium constant for the SMR reaction. The parameters have been determined from the experimental data previously presented in Table 3.

**Water gas shift**

Based on the experimental results the water gas shift reaction has been assumed at chemical equilibrium and therefore a kinetic model is not required. Thus, for the specific case the following equations have been added to the model.
Different experiments (at various temperatures) have been carried out on ethanol steam reforming (E-SR) and ethanol autothermal reforming (E-ATR), using 0.59 mg of catalyst in a reactor of 3 cm diameter and 1 cm length.

In the first case (E-SR), two different conditions have been compared (see Table 4):

1) Ethanol + steam (using a steam-to-ethanol ratio of 5 and 6) and \( N_2 \) (adjusted in order to have a dilution-ratio \( r.d. \) equal to 1.86) have been fed in the reactor using respectively 50 and 100 ml/min of ethanol.

2) The same experiments have been carried out where the ethanol has been replaced by the equivalent gas \((H_2 + CO + CH_4)\) and therefore the composition and volumetric flow rate is different.

The results of these experiments were fitted together with the results of the experiments presented above for SMR. The corresponding values for the exponents for the methane reforming are:

\[
a = 0.85, \quad b = 0.35, \quad c = d = 0.
\]

The comparison between the experimental results of case 1, case 2 and the fitting of the model is reported in Fig. 11. The WGS reaction has been kept at chemical equilibrium as previously discussed.

A second comparison was carried out for ethanol autothermal reforming. In the second case (E-ATR) several conditions have been compared (see Table 5):

![Fig. 11 — Comparison between the experimental results and model for ethanol steam reforming.](image-url)
feeding ethanol

\[ \text{Equivalent ethanol reforming} \]

1) Ethanol + steam + air (using a steam-to-ethanol ratio of 5 and 6), with air in order to have an oxygen-to-ethanol \((\text{O}/\text{EtOH})\) of 0.84 and 0.5) and \(\text{N}_2\).

2) Equivalent ethanol + steam + air, where the ethanol was replaced with the equivalent methane/syngas (\(\text{CH}_4 + \text{CO} + \text{H}_2\)).

3) In this case we have assumed that the amount of \(\text{O}_2\) reacted with ethanol by producing \(\text{CO}_2\) and \(\text{H}_2\)O and the remaining ethanol was converted into equivalent ethanol.

The experimental comparison of the three different inlet compositions is shown in Fig. 12.

From the results, we can conclude that:

- The ethanol auto-thermal reforming (blue bars) is better described when it is assumed that the ethanol is first oxidized with the reacting oxygen and after that, the remaining part is converted into equivalent ethanol (red bars).

- In case the conversion pathway considers first the conversion of ethanol into equivalent gas and after that, the oxidation and the other reactions occur (green bars) the results differ significantly: in particular, the \(\text{CH}_4\) in the products is always overestimated and therefore the produced \(\text{H}_2\) is well below to the expected mole fraction.

From the results shown in this experimental comparison, the ethanol autothermal reforming can be assumed to follow the pathway as illustrated in Fig. 10b.

For the steam methane reforming reaction the component reaction orders \((a, b, c, d)\) have been determined by minimizing the squared difference between the experimental results (when feeding ethanol + steam + air) and the model predictions. The obtained values are: \(a = 0.96\), \(b = 0.28\) and \(c = d = 0\).

A comparison between the two experiments and the model predictions are plotted in Fig. 13. The results show that the modeling is predicting the outlet composition with a very low error.

### Comparison with other kinetic models

The kinetic expressions determined in this work have been compared with a different steam reforming model proposed in the literature [53] as a function of the partial pressure (expressed in Pa). This reaction scheme has been selected because it was derived in excess of water as was the case for all the experiments reported in this paper. In this model the ethanol was assumed to be converted into equivalent ethanol as in Fig. 10a.

\[
R_{\text{MOX}} = \frac{k_{\text{(CH}_4\text{)}} p_{\text{CH}_4} p_{\text{O}_2}}{(1 + K_{\text{CH}_4}^\text{eq} p_{\text{CH}_4} + K_{\text{O}_2}^\text{eq} p_{\text{O}_2})^2} + \frac{k_{\text{(H}_2\text{)}} p_{\text{H}_2} p_{\text{O}_2}}{(1 + K_{\text{H}_2}^\text{eq} p_{\text{H}_2} + K_{\text{O}_2}^\text{eq} p_{\text{O}_2})^2} \exp(\frac{-E_{\text{act,i}}}{RT(K)})
\]

\[
K_{\text{OX}}^\text{i} = A_{\text{OX}}^\text{i} \exp(\frac{-\Delta H_{\text{OX}}^\text{i}}{RT(K)})
\]

where:

<table>
<thead>
<tr>
<th>Pre-exponential factor</th>
<th>(E_{\text{act,i}}) (kJ/mol)</th>
<th>(\Delta H_{\text{OX}}^\text{i}) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
<td>8.11 \times 10^{-5}</td>
<td>86</td>
</tr>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
<td>6.82 \times 10^{-5}</td>
<td>86</td>
</tr>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
<td>1.26 \times 10^{-6}</td>
<td>-27</td>
</tr>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
<td>7.82 \times 10^{-12}</td>
<td>20</td>
</tr>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
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<td>106.9</td>
</tr>
<tr>
<td>(A_{\text{H}}) [mol/(Pa(^2)kg(_{\text{cat}})])</td>
<td>2.45 \times 10^{-3}</td>
<td>54.5</td>
</tr>
</tbody>
</table>

From the results (see Fig. 14) it is possible to notice that the methane conversion and the CO conversion calculated with the model proposed by Numaguchi and Kikuchi are significantly lower than the one observed in the experiments and therefore the correct composition cannot be predicted with the model proposed by Numaguchi and Kikuchi for the catalyst developed in this work.

A second comparison has been carried out with a kinetic model for ethanol steam reforming at low temperature proposed in Ref. [52]. In this case the pathways for the ethanol conversion is based on the following reactions:

1) \(\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2\) ethanol dehydrogenation
2) \(\text{C}_2\text{H}_5\text{OH} \rightarrow 1.5 \text{CH}_4 + 0.5 \text{CO}\) ethanol decomposition
3) \(\text{C}_2\text{H}_4\text{O} \rightarrow \text{CH}_4 + \text{CO} \) acetaldehyde decomposition
4) \(\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 3\text{H}_2\) acetaldehyde reforming
5) \(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\) water gas shift

In this case the comparison cannot be carried out for the ethanol autothermal reforming since no reaction with \(\text{O}_2\) was
Fig. 12 – Experimental results and comparison for the ethanol autothermal reforming reaction at different operating conditions.

Fig. 13 – Model comparison with experimental results.
provided. Therefore, the model presented in Ref. [52] was compared with the experimental results for ethanol steam reforming reactions with a steam/ethanol ratio of 6, in the temperature range of 480–550 °C and using two different flow rates (respectively 50 and 83 ml/min of ethanol) (see Fig. 15).

The comparison shows that:

- The ethanol conversion is complete as observed also in the experimental tests of this work
- No acetaldehyde has been detected with the experimental tests and the model correctly predicts its conversion into gas species
- The CH₄ conversion calculated with the model proposed in literature is lower than the one obtained from the experiments
- The differences in the CO composition at the reactor outlet (lower in case of model) are mostly related to discrepancies in the CH₄ conversion
- As a consequence, the H₂ content in the gas at the reactor outlet is not correctly estimated.

Conclusions

A new catalyst was developed and tested for steam reforming and autothermal reforming of ethanol that can be used in fluidized beds also in presence of membranes. The catalyst is stable under fluidization conditions and does not chemically interact with the membrane. An extensive number of kinetic experiments have been carried out to investigate the reaction mechanism. The results confirm that for both steam reforming and autothermal reforming reactions, in the investigated temperature range relevant for fluidized bed membrane reactors, the ethanol is completely converted, indicating that the catalyst is very active for both reforming and water gas shift reactions. The WGS was found to be always at equilibrium in all the experiments carried out. The methane reforming reaction is much faster when compared with literature models for this reaction over different catalysts. Based on the experimental data, a simplified kinetic model has been proposed assuming that instantaneously all oxygen present oxidizes ethanol to CO₂ and H₂O and the remaining ethanol to methane and syngas. With the determined kinetic parameters the model could well describe the experimental results within 5% error. Based on the results of the kinetics for EtOH to H₂ conversion, the mass transfer limitation due to the H₂ permeation are the limiting factor to enhance the fuel conversion, therefore the amount of catalyst can be limited (about 1 kg of Catalyst is necessary for a reactor that produces 3.5 Nm³/h of pure H₂) which can be diluted (about 80% of dilution using the CeO₂ + SiO₂ support material) in order to ensure that the membrane are immersed in the bed. The membrane arrangement is made so that the mass transfer limitation between bubble and emulsion phase are reduced by limiting the bubble diameter.
of the reactor (in fact membranes acts as internals). The fluidization regime will ensure uniform temperature profile along the bed and therefore the membranes do not experience any thermal stress in the axial direction. All these information will be used to design the integrated membrane reactor for the pilot plant.

Acknowledgement

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Fig. 15 – Comparison between the experimental results and the model proposed in Ref. [52] (blue bar) at three different temperatures and, respectively, two different gas flow rates (and residence time). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

References


