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CO selective oxidation using catalytic zeolite membranes

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HIGHLIGHTS

● High CO conversions and selectivities have been measured with Pt-zeolite membranes.
● Na-Y zeolite membranes were synthesized by secondary growth method.
● Pt/Na-Y membranes were prepared by cationic exchange.
● Low exchange times provide better Pt\textsuperscript{2+} reductions inside the zeolite channels.

ARTICLE INFO

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CO SelOx
Membrane reactors
Zeolite catalytic membranes

ABSTRACT

Traces of CO in hydrogen rich gas streams poison the anode of proton exchange membrane fuel cells reducing their power output and decreasing the cell life. This paper investigates the CO selective oxidation in simulated reformate gas by using catalytic zeolite membranes. In particular, the CO removal efficiency was explored using catalytic membranes characterized by different permeation properties (prepared using different protocols) and loaded with the catalyst by means of cationic exchange and reduction process. The most promising experimental results are obtained with membranes prepared with small crystals and low concentration of zeolite suspension (during the seeding step) and with a hydrothermal treatment of 90 °C for 24 h. These membranes are characterized by lower permeance and showed interesting catalytic performance in terms of CO reduction and selectivity.

1. Introduction

Fuel cells represent an alternative to existing power conversion technologies due to their high fuel efficiency and low-environmental impact [1]. The most promising fuel cell technology for transport and residential applications are the proton exchange membrane fuel cell (PEMFC) fueled by hydrogen, due to the fast start-up, high power density and low-temperature operation [2]. The hydrogen rich gas, generally produced by reforming of hydrocarbons, contains CO which is a poison for the anode (Pt electrode) of the PEMFC. This degradation can be avoided by keeping the CO amount in the H\textsubscript{2} feed stream below 10 ppm (depending on the fuel cell temperature) [3].

Selective CO oxidation (CO SelOx) is the most promising and economical approach for the removal of CO from H\textsubscript{2}-rich gas streams. Considering that this reaction involves oxygen that can react towards both hydrogen and CO oxidation, a selective catalyst is required to avoid H\textsubscript{2} consumption [4,5]. The conventional catalysts used for this reaction are Pt, Pd, Rh, Au, CuO and Co\textsubscript{3}O\textsubscript{4} supported on CeO\textsubscript{2}, SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} [6–13].

Pt-based catalysts require relatively high temperatures (≥ 170 °C). Besides, the presence of water vapor improves their catalytic properties, while the CO\textsubscript{2} is detrimental for their performance [14,15].

Au-based catalysts are more active than platinum catalysts at relatively low temperatures (< 117 °C); However, they are more prone to deactivation in presence of CO\textsubscript{2} and H\textsubscript{2}O in the gas stream [15].

An improvement of the Pt catalytic properties was also investigated in the open literature by using Rh and Ru as promoters. As an example, a very high conversion of CO was achieved by using a reactor with Pt-Ru catalyst [16]. Interesting catalytic performance were also exhibited by CuO-CeO\textsubscript{2} catalysts; however, the presence of water and carbon...
dioxide led to a significant decrease in their activity [17,18]. Recently, it was demonstrated that the use of cheaper catalytic materials (as for example Co3O4/CoO2/ZrO2) exhibit high conversion (90%) at the expenses of low selectivity at 200 °C. On the other hand, if CO SelOx is to be performed at lower temperatures (125 °C) these materials show an important gain in selectivity (greater than 80%) at lower CO conversions [19]. Besides, experimental results indicate that the catalytic activity depended on the Co3O4 amount.

Although alumina is the most common support used for noble metal-base catalysts, different studies demonstrated that the use of zeolite as support for Pt catalysts improved the catalytic performance due to the high Pt dispersion in the zeolite pores [20–22]. In the past years, a novel trend in CO selOx is the use of zeolite membranes as support material for the catalytic particles. In particular, a zeolite catalytic membrane allows a high dispersion of the catalyst in a very thin zeolite layer leading to a gas-through configuration. In this configuration, the contact between reactant and catalytic phase is improved, by-pass problems are reduced and the contact time between the gas phase and the catalysts is very short (preventing high H2 loss). Bernardo et al. [23,24] investigated all these aspects. In particular, they used different Pt/NaY membranes demonstrating the possibility to reduce the CO content by using the membrane with the lowest permeance. Hasegawa and coworkers [25], the first who used zeolite membranes for carrying out the SelOx, reduced the CO content below 8 ppm with a feed stream containing 97–98% of hydrogen and 1% of CO, with a molar ratio O2/CO = 1.2 at 200 °C.

In this study, a zeolite catalytic membrane reactors for the CO SelOx were investigated. In particular, the Pt catalyst was dispersed on faujasite (FAU) type zeolites deposited in the inner part of porous alumina tubes. The use of FAU zeolites was considered because of their characteristic topology, whose crystals present pores of 0.74 nm and cavities of 1.38 nm and so small gases can easily pass through and react with the catalysts. The CO removal efficiency was investigated using catalytic membranes characterized by different permeation properties (prepared using different protocols). Besides, the effect of temperature, pressure and feed mixture composition was also investigated. Finally, the physico-chemical membrane characterization was carried out.

2. Materials and methods

2.1. Materials

The silica source used for FAU membranes preparation was sodium silicate solution (26.5% SiO2, 10.6% Na2O, 62.9% H2O, Sigma-Aldrich), while the alumina source used was sodium aluminate (54% Al2O3, 46% Na2O, VWR chemicals) in pellets. Sodium hydroxide (NaOH pellets, VWR chemicals) and distilled water were also employed. Pt-salt ([Pt(NH3)4]Cl2; Sigma-Aldrich) was used for the ion exchange. These data were obtained by means of atomic absorption spectrometry (GBC Avanta PM Instrument) and the calculated Pt loadings on each membrane are reported in Table 4. Finally, the membranes were calcined at 210 °C for four hours and in presence of H2 (feed flow rate = 500 ml min−1) for the platinum reduction and ammonia removal.

During the seeding step, the slurry, having neutral pH, was stirred for preventing the agglomerate formation and, subsequently, it was fed into the tubular alumina support by using a peristaltic pump. During the seeding, the crystals used had the same topology but different Si/Al ratio (NaX and NaY) and size compared with FAU zeolites (see Table 1) for investigating the effect of the crystals characteristics on the membrane performance. An overview of the operating conditions of the seeding step is reported in Table 1.

After the seeding step, the supports were dried in air overnight at room temperature under rotation for favoring the removal of water. The growth step was carried out pouring the synthesis solution on the inner support, located in a Teflon-lined autoclave. The formation of crystals on the outer surface of the support was avoided wrapping it with Teflon tape. The autoclave was vertically placed in the pre-heated furnace for the hydrothermal treatment under autogenous pressure. During this step, different times and temperatures were considered for evaluating their influence on the membrane performance. The operating conditions used are reported in Table 2. After the membrane preparation, the membranes were washed with distilled water to remove amorphous materials until a pH of 7 was reached. After that, they were dried in air for 24 h and in a furnace at 130 °C for 12 h.

In particular, up to seven different zeolite membranes were prepared depending on the seeding and growing conditions, and their properties are reported in Table 3.

The membranes were Pt-loaded by means of cationic exchange methods. In particular, the zeolite membranes were immersed in a Pt-salt ([Pt(NH3)4]Cl2) solution, having a concentration of 2.5 mmol L−1, at 80 °C for 4 h [28] except for the membrane ZM-Y4, which was kept in contact with the solution for two hours. During the ionic exchange, the platinum salt solution was continuously stirred for avoiding concentration gradients.

The Pt (II) amount in the membranes was evaluated considering the concentrations difference between the initial and final solutions used for the ion exchange. These data were obtained by means of atomic absorption spectrometry (GBC Avanta PM Instrument) and the calculated Pt loadings on each membrane are reported in Table 4. Finally, the membranes were calcined at 210 °C for four hours and in presence of H2 (feed flow rate = 500 ml min−1) for the platinum reduction and ammonia removal.

Table 1

<table>
<thead>
<tr>
<th>Operating conditions used during the seeding procedure.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeds</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>α-Al2O3 support pore size</td>
</tr>
<tr>
<td>Zeolite concentration in the suspension</td>
</tr>
<tr>
<td>pH suspension</td>
</tr>
<tr>
<td>Rotation</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Time</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Operating conditions used for the hydrothermal treatment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals</td>
</tr>
<tr>
<td>Molar composition</td>
</tr>
<tr>
<td>Solution aging</td>
</tr>
<tr>
<td>Time and Temperature</td>
</tr>
</tbody>
</table>
In this work is presented in Fig. 1 calculated. A schematic representation of the experimental facility used towards the selective CO oxidation according to Eqs. (1) and (2) were to measure the gas composition, thus the conversion and selectivity to -wards the vessel, two coolers avoided water in the analysis section and a back-pressure regulator was installed to control the reaction pressure. Part of the dry gas mixture was selected in order to cover a wide range of operating conditions as stated in Table 3, where an overview of all the experiments carried out is given. Downstream the vessel, two flow controllers, supplied by Bronkhorst, and it was introduced from inside the membrane. Different gas mixtures were selected in order to cover a wide range of operating conditions as stated in Table 5, where an overview of all the experiments carried out is given. Downstream the vessel, two cooler-water avoided water in the analysis section and a back-pressure regulator was installed to control the reaction pressure. Part of the dry gas products was sent to a micro-GC analysis (model Varian CP-4900) to measure the gas composition, thus the conversion and selectivity towards the selective CO oxidation according to Eqs. (1) and (2) were calculated. A schematic representation of the experimental facility used in this work is presented in Fig. 1.

Before and after the loading of Pt on the membranes, N2 permeation tests were carried out following a common pressure drop method [27].

### 2.3. Catalytic membrane reaction tests

Before starting the experiments, the membranes were properly sealed and connected to stainless steel tubing to ensure that all the gases feed pass through the zeolite membranes. In all the membranes one of the ends was sealed using standard Swagelok plugs and graphite ferrules to avoid membrane breakage due to different thermal expansion, thus leading to a dead-end membrane configuration. The other side of the membrane was connected to a 6 mm stainless steel tube using a similar ceramic/metallic sealing approach, and this tube was in its turn connected to a 4.5 cm inner diameter stainless steel reactor. This reactor was placed inside an electrical oven to control the reaction temperature. The gas feed was controlled by mass flow controllers, supplied by Bronkhorst, and it was introduced from inside the membrane. Different gas mixtures were selected in order to cover a wide range of operating conditions as stated in Table 5, where an overview of all the experiments carried out is given. Downstream the vessel, two coolers avoided water in the analysis section and a back-pressure regulator was installed to control the reaction pressure. Part of the dry gas products was sent to a micro-GC analysis (model Varian CP-4900) to measure the gas composition, thus the conversion and selectivity towards the selective CO oxidation according to Eqs. (1) and (2) were calculated. A schematic representation of the experimental facility used in this work is presented in Fig. 1.

### 2.4. Membrane characterisation

Membranes were characterized after use, by means of different techniques, to better understand the behavior showed during the experiments as well as the differences existing in the results between the experiments. After the experiments, the membranes were cut and cross-section and surface SEM images were obtained using a JEOL JSM-6330F Quanta SEM/EDX machine using secondary electrons. An Atomic Force Microscope (AFM) was used to obtain high resolution images of the samples surface. The AFM, a MultiMode 8 equipped with a Nanoscope V controller (Bruker), was operated in tapping mode in air and at room temperature using levers with a resonance frequency of 150 kHz (TAP150, Bruker).

### 3. Results and discussion

#### 3.1. Catalytic tests

The membrane performance was evaluated before and after cationic exchange by single gas (N2) permeation tests at room temperature and in absence of sweep gas. The membranes with lower permeance values were those prepared with NaY crystals (during the seeding step) as reported in Table 6. From the permeation values it is observed that the FAU membranes prepared with a slurry concentration of 0.014 wt% and a hydrothermal treatment at 90 °C for 24 h showed the best performances in terms of decrease in permeance compared with the bare alumina support tube. These two parameters, lower concentration and smaller crystals size of the suspension, lead to a more uniform crystals layer on the inner support surface. In addition, the hydrothermal treatment carried out for 24 h permitted to achieve a better growth of the zeolite layer than that formed after only 5 h. A prolonged thermal treatment also allows the formation of more stable zeolite layer chemically bounded on the support surface [29]. The synthesis time was restricted to 24 h because a more prolonged treatment leads to the formation of another zeolite topology (P-type), as reported by lassinatti et al. [29]. After cationic exchange, the permeance values remained almost the same (see Table 6).

The behavior of the catalytic membranes at different temperatures, pressures and feed flow rates was investigated by keeping constant the feed molar composition as reported in the reference case in Table 5.

The catalytic tests were performed in the temperature range of 180–250 °C for all the prepared membranes. In the range investigated, an increase in the CO conversion was measured when varying the reaction temperature from 180 °C to 215 °C. However, a further increase in temperature (up to 250 °C) hardly influenced the measured conversion. On the other hand, the CO2 selectivity remained constant in the whole temperature range considered. Hasegawa et al. [30] found the same trend with an increase of the conversion passing for a maximum. Besides, they detected a decrease in the CO conversion for

### Table 3

Operating conditions used for the different prepared membranes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystals type</th>
<th>Zeolite Suspensions concentration (wt.%)</th>
<th>T (°C)</th>
<th>t (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM-X1</td>
<td>X</td>
<td>0.032</td>
<td>110</td>
<td>5</td>
</tr>
<tr>
<td>ZM-X2</td>
<td>X</td>
<td>0.032</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>ZM-X3</td>
<td>X</td>
<td>0.014</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>ZM-Y1</td>
<td>Y</td>
<td>0.014</td>
<td>110</td>
<td>5</td>
</tr>
<tr>
<td>ZM-Y2</td>
<td>Y</td>
<td>0.032</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>ZM-Y3</td>
<td>Y</td>
<td>0.014</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>ZM-Y4</td>
<td>Y</td>
<td>0.014</td>
<td>90</td>
<td>24</td>
</tr>
</tbody>
</table>

### Table 4

Amount of platinum loaded in the membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Amount of platinum loaded (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM-X1</td>
<td>24</td>
</tr>
<tr>
<td>ZM-X2</td>
<td>19</td>
</tr>
<tr>
<td>ZM-X3</td>
<td>18</td>
</tr>
<tr>
<td>ZM-Y1</td>
<td>17</td>
</tr>
<tr>
<td>ZM-Y2</td>
<td>18</td>
</tr>
<tr>
<td>ZM-Y3</td>
<td>19</td>
</tr>
<tr>
<td>ZM-Y4</td>
<td>10</td>
</tr>
</tbody>
</table>

### Table 5

Set of experimental conditions investigated in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference case</th>
<th>Conditions tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed gas composition</td>
<td></td>
<td>1% CO, 1% O2, 60% H2, N2 balance (A)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>215</td>
<td>180–250</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>2</td>
<td>2–4</td>
</tr>
<tr>
<td>Inlet gas flow rate (Nml/min)</td>
<td>515</td>
<td>250–800</td>
</tr>
</tbody>
</table>

\[
X_{CO} = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}} \tag{1}
\]

\[
S_{CO_2} = \frac{CO_2_{outlet} - CO_2_{inlet}}{2(O_2_{inlet} - O_2_{outlet})} \tag{2}
\]

Prior to starting the experiments, the catalytic membrane was activated at 210 °C in 20% H2 in N2 for 3 h. Subsequently, the desired gas mixture was selected and the reaction was maintained for 45 min where steady state operation was assessed according to gas analysis. Selected experiments were repeated to verify reproducibility of the measured data. Before and after the reaction tests, the gas was fed to the external vessel to measure the gas permeation through the membrane as a function of the vessel pressure for H2 and N2. In all the cases a Knudsen selectivity was observed, thus the zeolite structure was not affected after being exposed to several hours at reaction conditions.
temperatures higher than 250 °C. Considering these data, all the experiments hereafter were carried out at 215 °C. An example of the effect of temperature on the CO conversion and the CO2 selectivity is reported for the samples ZM-X3 and ZM-Y3 in Fig. 2.

Once fixed the operating temperature for the remaining experiments, the influence of pressure (2–4 bar) and feed flow rate on the CO conversion and CO2 selectivity was also investigated. Regarding the effect of pressure, the experimental results evidenced that the CO conversion and the selectivity to CO2 remained almost constant. Therefore, in further experiments it was decided to operate at 2 bar. An illustrative example of the effect of pressure on the reaction performance for the membrane ZM-X1 is presented in Fig. 3. Bernardo et al. [24] demonstrated that the feed pressure can have an influence on the CO removal depending on the gas passing slow through the zeolite pores and defects. The CO molecules passing through the zeolite channels (narrow space) have high probability to interact with the metal catalyst. In this case, the effect of the pressure is negligible. On the other hand, when the CO flows through the support pores (defects) an improved CO removal was obtained by increasing the pressure. Therefore, considering the negligible effect of the pressure on the catalytic performance for the different prepared samples, it is possible to assert that the cross-flow filtration seeding permits to prepare membrane with a low concentration of defects.

Regarding the different feed flow rates considered in this study (261 ml min⁻¹; 565 ml min⁻¹; 804 ml min⁻¹), neither the CO conversion, nor the selectivity to CO2 were hardly changed when the membranes were exposed to different residence times, showing that we are not limited by catalytic activity.

The different Pt/Na-Y membranes were tested at 215 °C, 2 bar and 565 ml min⁻¹ using different gas mixtures (see Table 5). When using the reference condition (mixture A), all the membranes exhibited good catalytic performance as reported in Fig. 4. In particular, the best catalytic membranes were ZM-X3 and ZM-Y4, where the CO conversion was about 99% with a selectivity to CO2 of around 60%. These membranes were prepared by using the lower concentration of crystals during the seeding step and the longer hydrothermal treatment (90 h instead of 5 h). These results evidenced that the preparation of membranes with good properties requires low concentration of the slurry and a hydrothermal treatment of 24 h at 90 °C in order to have a more uniform and compact zeolite layer.

In a real SelOx process, the gas stream from the water gas shift contains around 20–25% of CO2. Therefore, another possibility would be to carry out the CO SelOx downstream the water gas shift reactor instead of after H2 recovery in the common Pressure Swing Adsorption unit (PSA). In Fig. 5 the CO conversion and the CO2 selectivity are reported using a feed gas mixture with a composition containing 20% of

---

**Table 6**

Gas permeance before and after cationic exchange.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal type used in the seeding step</th>
<th>$\Pi_{\text{N}_2}$ (µmol m⁻² s⁻¹ Pa⁻¹) before ion exchange</th>
<th>$\Pi_{\text{N}_2}$ (µmol m⁻² s⁻¹ Pa⁻¹) after ion exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃ Support</td>
<td>–</td>
<td>20.0</td>
<td>–</td>
</tr>
<tr>
<td>ZM-X1</td>
<td>X</td>
<td>15.4</td>
<td>15.1</td>
</tr>
<tr>
<td>ZM-X2</td>
<td>X</td>
<td>13.0</td>
<td>12.8</td>
</tr>
<tr>
<td>ZM-X3</td>
<td>X</td>
<td>12.1</td>
<td>11.7</td>
</tr>
<tr>
<td>ZM-Y1</td>
<td>Y</td>
<td>10.2</td>
<td>9.87</td>
</tr>
<tr>
<td>ZM-Y2</td>
<td>Y</td>
<td>10.2</td>
<td>9.70</td>
</tr>
<tr>
<td>ZM-Y3</td>
<td>Y</td>
<td>6.30</td>
<td>6.13</td>
</tr>
<tr>
<td>ZM-Y4</td>
<td>Y</td>
<td>7.10</td>
<td>6.56</td>
</tr>
</tbody>
</table>

---

Fig. 1. Schematic representation of the experimental facility used in this work.
For all the catalytic systems, the CO conversions and CO₂ selectivity decreased (see Fig. 5). This behavior was explained considering the presence of the reverse water gas shift that limited the CO oxidation at high temperature. As also presented in Fig. 5 (right), the oxygen conversion decreased when the CO₂ was in the feed. Thus, the CO₂ slowed the oxidation of both CO and H₂. These aspects were deeply investigated by Manasilp and Gulari [14]. The authors demonstrated the presence of the reverse water gas shift using as feed mixture only CO₂ (25%) and H₂ (70%). Their experimental results evidenced that an increase in the reaction temperatures led to an increase in the CO formation (1200 ppm at 170 °C and 2400 ppm at 210 °C).

When analyzing in detail all the data (for instance to the membrane ZM-X1) it is evidenced that the oxygen conversion remains similar when CO₂ is added in the feed as compared with a case without CO₂ in the feed and at the same operating conditions. However, the CO conversion is decreased in case of CO₂ addition. This decrease is associated to the fact that, even if CO is consumed by oxidation, the reverse water gas shift is playing a role in the process producing extra CO.

Finally, the influence of a higher concentration of CO (from 1% to 2%) in the feed stream was investigated. The obtained experimental data were reported in Fig. 6.

When using a stoichiometric amount of oxygen for selective CO oxidation, a decrease in the CO conversion is evidenced as compared with previous measurements (see Figs. 4 and 5). This is explained by the fact that the selectivity towards CO oxidation is not 100% and part of the oxygen is consumed by H₂ combustion. The conversion obtained with each membrane follows a similar trend as with other feed gas mixtures and operating conditions, which give an indication on the accessibility and the loading of the Pt catalyst. In particular, the membranes ZM-X1 and ZM-Y3 show the lowest conversions, while the membrane ZM-Y4 has the highest one.

On the other hand, the selectivity towards CO oxidation shows an increase compared to other gas feed mixtures with excess of oxygen in the feed. This indicates that at lower oxygen partial pressures, the selective CO oxidation is favored compared to the H₂ oxidation, although still not enough for complete CO conversion.

A comparison with literature data is reported in Table 7, better results were obtained in terms of conversion and selectivity with the Pt/Na-Y membranes. It is possible to explain these results considering that a catalytic membrane reactors can be seen as a “nano-engineered” catalyst because catalytic nanoparticles are entrapped in a thin zeolite layer. Consequently, an efficient reactor/catalyst contact is ensured with a reduction of the by-pass problem present in a packed bed reactor.
3.2. Membrane characterization

After catalytic tests, the zeolite layers grown on the alumina supports were analyzed by using SEM. SEM micrographs of four membranes are shown in Fig. 7.

Put in comparison the ZM-Y1, ZM-Y2 and ZM-Y4 membranes with the bare support the formation of a uniform zeolite layer on the support was evident (see Fig. 7a-h). Besides, it is possible to observe as the thickness of the zeolite layer changed by varying the synthesis protocol. Prolonged thermal treatment ensured the formation of a thicker layer. In fact, the ZM-Y1 sample (synthesized for 5 h) showed a layer of about 9 μm, whilst the other samples (synthesized for 24 h) exhibited a layer almost twice thicker (see Fig. 7g). In addition, the concentration of the zeolite slurry, used during the seeding step, influenced to a lesser extent the membrane thickness. For example, ZM-Y2 and ZM-Y4 seeded with different zeolite suspension concentration (see Table 3) showed different thickness (see Fig. 7h and l).

EDX analyses were also carried out on the membrane cross section of the FAU layer. The Si/Al ratio calculated from the element concentration for the different samples was of about 1.5 indicating the presence of the NaX zeolite. By way of example, the EDX analyses of the samples ZM-Y1 and ZM-Y4 were reported. The platinum concentration is in agreement with those found by atomic absorption spectrometry (see Fig. 8).

In Fig. 9 is shown the surface topography measured on an area of 1×1 μm² of some samples. Imaging on larger areas was difficult to achieve due to the large variations in height of the samples that were beyond the working possibilities of the AFM. Sample ZM-Y1 shows a granular and disordered structure due to the very short synthesis time (5 h) during the growth treatment. On the contrary, images acquired on samples ZM-X3 and ZM-Y4 point to, in both cases, the presence of big crystalline domains owing to the longer synthesis time (24 h) during the growth step.

4. Conclusions

CO SelOx can be efficiently carried out by using catalytic zeolite membranes synthesized by secondary growth method. This method permitted to produce mechanically stable films with interesting catalytic performance. In particular, better membranes are those prepared with small crystals and low concentration of zeolite suspension (during the seeding step) and with a hydrothermal treatment of 90 °C for 24 h.

The presence of the CO₂ in the feed stream determined a decrease in CO conversions and CO₂ selectivity for all the catalytic systems. This behavior is owing to the presence of the reverse water gas shift that limited the CO oxidation at high temperature. In addition, a higher concentration of CO (from 1% to 2%) in the feed stream resulted in a decrease in the CO conversion as part of the oxygen was consumed by

### Table 7
Comparison with literature data of CO selective oxidation in different reactors.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feed (mol%)</th>
<th>CO conversion</th>
<th>Selectivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>O₂</td>
<td>H₂</td>
<td>N₂</td>
</tr>
<tr>
<td>0.4%Co1%Pt</td>
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<td>0.49</td>
<td>73.98</td>
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<td>10</td>
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<td>5%Pt/Al₂O₃</td>
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<td>60</td>
<td>-</td>
<td>This work</td>
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Fig. 5. CO conversion and selectivity to CO₂ (left) using a gas mixture containing 20% CO₂ (gas mixture B) and the comparison in terms of O₂ conversion with the reference mixture (A) for all the Pt/Na-Y membranes (Mixture A = CO₂:H₂:N₂ = 1:1:60:38; Mixture B: CO₂:H₂:CO₂:N₂ = 1:1:60:20:18; P = 2 bar; T = 215 °C).

Fig. 6. CO conversion and CO₂ selectivity for the Pt/Na-Y membranes using a feed composition of CO₂:H₂:N₂ = 2:1:60:37, P = 2 bar and T = 215 °C.

Fig. 7.
Fig. 7. SEM micrographs: (a) cross section and (b) top-view of bare support; (c) cross section and (d) top-view of the membrane ZM-Y1; (e) cross section and (f) top-view of the membrane ZM-Y2 (g) cross section and (h) top-view of the membrane ZM-Y4.

Fig. 8. EDX analyses for the samples: a) ZM-Y1 and b) ZM-Y4.

Fig. 9. AFM analyses of the samples: a) ZM-Y1, b) ZM-X3, c) ZM-Y4.
H₂ oxidation. However, at such conditions, the selectivity towards CO₂ is increased. This indicates that at low oxygen partial pressures the CO oxidation is favored compared to the H₂ oxidation.

The best catalytic system is the ZM-Y4 sample exchanged for a reduced number of hours (2 instead of 4). A reduced time, during the ion exchange, permitted the reduction of the Pt³⁺ particles into the zeolite and produced number of hours (2 instead of 4). A reduced time, during the ion exchange, permitted the reduction of the Pt³⁺ particles into the zeolite membrane.

References


