Global Climate and Energy Project
Advanced Membrane Reactors in Energy Systems;
A carbon-free conversion of fossil fuels

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K. Stoitsas
T.H.Y Tran
J. Schoonman

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Investigators
Joop Schoonman, Professor of Inorganic Chemistry; Konstantinos Stoitsas, post-doctoral researcher, Thi Hoang Yen Tran, PhD student.

Abstract
Mesoporous and microporous membranes are developed via the sol-gel technique in supported and unsupported form. Primary mesoporous $\gamma$-Al$_2$O$_3$ membranes in supported form were characterized by permporometry technique and have a pore size of 2-3 nm with a rather sharp and narrow pore size distribution. The membranes exhibit rather good temperature stability at 600°C, making these membranes excellent candidates for further modification with Atomic Layer Deposition Technique. Membranes doped with La show a better performance with regard to thermal stability. Supported $\gamma$-Al$_2$O$_3$ membranes are crack free and the dominant diffusion mechanism of inert gases through the structure is Knudsen diffusion as obtained from permeability measurements. TEM micrographs of the layer of $\gamma$-Al$_2$O$_3$ reveal a card-pack structure of the membrane.

Mixing a colloidal boehmite sol and a polymeric silica sol in different proportions allow to develop mesoporous and microporous composite Al$_2$O$_3$-SiO$_2$ thin films. The pore size of the microporous films is 0.5 nm with a rather broad pore size distribution. The films are homogeneous according to preliminary SEM-EDX studies.

Introduction
Steam reforming (1) and water gas shift (2) are key reactions for the production of H$_2$ from fossil fuels. The use of membrane reactors for these conversions will shift the equilibrium to the product side giving higher methane conversions whilst the purity of the H$_2$ is improved.

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad (1)$$
$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (2)$$

Pd-alloy membranes are totally selective for H$_2$ and have already achieved much higher conversions compared to those defined by the equilibrium [1,2]. However, the high cost of palladium, the relatively low hydrogen permeation capacity and the stability problems by the deposition of carbon or poisoning of impurities, like sulfur or carbon monoxide, do not allow the commercialization of this type of membranes on a large scale [3,4]. The use of porous ceramic membrane reactors is another attractive option for the steam reforming and water gas shift conversions due to the permeable character of these membranes and due to the high resistance of these materials in harsh environments [5]. This report describes the experimental work done on the synthesis and the characterization of porous ceramic membranes designed specifically for the separation of H$_2$ from CO$_2$ and CO.
Results

Characterisation of primary γ-Al₂O₃ membranes

In the previous Progress Report (March-August 2006) the chemistry and the synthesis of thin films of γ-Al₂O₃ membranes were described. Also preliminary permeability results confirmed the crack free character of the thin films. The pores of the unsupported samples had a size of 3 to 7 nm.

Further characterization of the supported γ-Al₂O₃ samples was performed with the permporometry technique in order to determine the pore size distribution of these membranes. Permporometry is a new characterization method that can discriminate between the open pores called “active” pores and the dead-end pores called “inactive pores” [6]. Permporometry is based on the controlled stepwise blocking of pores by condensation of a vapour, present as a component of a gas mixture and the parallel measurement of the gas flux through the membrane (Figure 1).

The relative pressure of water is controlled by the flow of Helium at the feed side.

Figure 1: Permporometry separation unit

<table>
<thead>
<tr>
<th>P_{rel}</th>
<th>State Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>All pores are open</td>
</tr>
<tr>
<td>0 &lt; P_{rel} &lt; 1</td>
<td>Small pores are filled with condensate</td>
</tr>
<tr>
<td>1</td>
<td>All pores are blocked</td>
</tr>
</tbody>
</table>

Figure 2: Blockage of the pores as a function of the relative pressure
By applying a pressure drop of 200-500 mbar along the membrane, a mixture of He/H$_2$O is forced to pass through the membrane. As the relative pressure of the condensable gas increases capillary condensation follows the adsorption mode blocking the pores for the diffusion of the non-condensable gas (Figure 2). The relative pressure at which pore filling starts depends on the radius of the capillary and can be calculated from the Kelvin relation.

$$\ln\left(\frac{p}{p_o}\right) = -\frac{2\gamma V_M}{rRT} \cos(\theta)$$

(3)

Where $p$ is actual vapour pressure, $p_o$ is the saturated vapour pressure, $\gamma$ is the surface tension, $V_M$ the molar volume, $R$ the universal gas constant, $T$ the temperature, $r$ the radius of the capillary and $\theta$ the contact angle of the liquid on the solid.

The flux of He through $\gamma$-Al$_2$O$_3$ membranes, synthesized as described in the previous report, is shown in Figure 3 during the desorption and adsorption of H$_2$O vapour.

This typical flux-relative pressure plot can be divided into three main areas. At low relative pressures the flux of He decreases slightly. In this region all the pores are empty and available for transport but still the available space for the diffusion of He decreases due to monolayer adsorption of H$_2$O. At pores with size 2nm < dp < 4nm the flux of He decreases with relative pressure because multilayer diffusion and capillary condensation takes place. For pores larger than 5nm the flux of He is almost zero indicating that all the pores are blocked and no cracks or pores larger than 5nm are present in the structure of this type of membranes.

The pore size distribution of the $\gamma$-Al$_2$O$_3$ membranes is shown in Figure 4 for the adsorption and desorption mode. For the determination of the pore size of the active pores the desorption branch is used due to the fact that the equilibrium of the
adsorption process is more difficult to reach. Therefore, the quantitative analysis of the desorption process is preferred [7].

The pore size distribution for the active pores of the $\gamma$-$\text{Al}_2\text{O}_3$ membranes is rather sharp and narrow with a mean pore size of 2.5 nm according to the desorption branch. It is clear that membranes exhibit a very well defined structure, which is almost in agreement with results found with N$_2$ physisorption. Small differences between the pore size of unsupported and supported samples arise from the fact that during drying and calcination, stresses created by the presence of the support result in a more closed structure for the supported samples [8].

SEM and TEM pictures of the supported samples confirm the absence of cracks or larger pores (Figure 5).

The interface between the membrane and the support reveals that the structure of the membrane is composed by primary particles which are stacked in a way that the large planes are parallel to each other. The final structure of the membranes is a card-pack structure with slit-shaped pores [9,10].
The temperature stability of $\gamma$-$\mathrm{Al}_2\mathrm{O}_3$ films was studied having in mind that these membranes are going to be modified with ALD technique at high temperatures. In addition membranes are going to be used in the steam reforming reaction and will be exposed to high temperatures necessary for substantial CH$_4$ conversion. In Table I the most important structural properties of samples heated in air for different times are presented.

**Table I:** Structural properties of the $\gamma$-alumina films by N$_2$ Physisorption

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m$^2$/gr)</th>
<th>Pore volume (cm$^3$/gr)</th>
<th>Porosity (%)</th>
<th>Mean pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$/$600^\circ\mathrm{C}$/3h</td>
<td>198</td>
<td>0.23</td>
<td>46</td>
<td>5.88</td>
</tr>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$/$600^\circ\mathrm{C}$/1 week</td>
<td>176</td>
<td>0.26</td>
<td>49</td>
<td>6.56</td>
</tr>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$/$600^\circ\mathrm{C}$/3 weeks</td>
<td>184</td>
<td>0.28</td>
<td>51</td>
<td>6.56</td>
</tr>
</tbody>
</table>

All the samples remain mesoporous with a pore size smaller than 10 nm. Significant differences start appearing when the samples are heated for 1 week at $600^\circ\mathrm{C}$. The pore size increases almost 11% of the initial pore size while the surface area is decreasing due to sintering effects. Longer times (3 weeks) at $600^\circ\mathrm{C}$ does not seem to affect the structure, as the mean pore size remains constant.

In order to improve the stability of the films, an amount of aqueous La(NO$_3$)$_3$ was added to the initial boehmite sol [11,12]. The concentration of La(NO$_3$)$_3$ in the final sol is 1.18 wt. %. Higher concentrations of La(NO$_3$)$_3$ cause flocculation of the boehmite sol. The structural characteristics of the doped films were examined using N$_2$ physisorption and are presented in Table II.

**Table II:** Structural properties of the La doped-$\gamma$-alumina films by N$_2$ Physisorption

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m$^2$/gr)</th>
<th>Pore volume (cm$^3$/gr)</th>
<th>Porosity (%)</th>
<th>Mean pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$ doped with 1.18 wt% La/ $600^\circ\mathrm{C}$/3h</td>
<td>183</td>
<td>0.18</td>
<td>40</td>
<td>5.88</td>
</tr>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$ doped with 1.18 wt% La/ $600^\circ\mathrm{C}$/1 week</td>
<td>143</td>
<td>0.19</td>
<td>40</td>
<td>6.08</td>
</tr>
<tr>
<td>$\gamma$-$\mathrm{Al}_2\mathrm{O}_3$ doped with 1.18 wt% La/ $600^\circ\mathrm{C}$/1 week</td>
<td>172</td>
<td>0.22</td>
<td>45</td>
<td>6.08</td>
</tr>
</tbody>
</table>

* The concentration of lanthanum is rather low, for this reason it is not taken into account in the calculations of porosity.

In the case of the lanthanum doped membranes, the increase of the pore size when heated at $600^\circ\mathrm{C}$ for 1 week is only 3% of the initial pore size. Lanthanum in this case decreases the rate of the surface diffusion during sintering resulting in more stable structures with temperature than the undoped one.
The sharp and narrow pore size distribution of the $\gamma$-Al$_2$O$_3$ membranes in combination with the very good temperature stability make these membranes ideal candidates for modification with Atomic Layer Deposition Technique.

**Synthesis of microporous membranes**

Microporous membranes (with pore size smaller than 2nm) are synthesized via the sol-gel technique by hydrolysis of Tetra-Ethyl-Ortho-Silicate under acidic conditions. A mixture of acid and water is carefully added to a mixture of TEOS and C$_2$H$_5$OH under vigorous stirring. The final mixture has a standard molar ratio of TEOS-H$_2$O-HNO$_3$-C$_2$H$_5$OH in the range of 1(TEOS)-6.4(H$_2$O) –0.085(HNO$_3$) –3.8 (C$_2$H$_5$OH). After the addition is complete the reaction mixture is refluxed for 3 hours at 70ºC under continuous stirring. For the synthesis of thin films small amounts of silica sol are poured into petri dishes and subsequently dried for 4-5 days under ambient conditions. After drying, calcination in air follows at 600ºC for 3 h with a heating rate of 60ºC/h [13].

N$_2$ porosimetry has been employed in order to verify that the developed alumina-silica membranes have a microporous pore size. The N$_2$ physisorption isotherms of unsupported silica membranes are shown in [Figure 6](#) below. The isotherm for pure SiO$_2$ is type I, which is characteristic for microporous materials. At low relative pressure the N$_2$ molecules are adsorbed in the space within the micropores (micropore filling) in monolayer or in bilayer form. Hysteresis is not present for this material due to the non-development of liquid phase in the micropores.

It is known that the hydrophilic surface of the silica membranes leads to pore blocking by H$_2$O and especially at higher temperatures this can seriously degrade the microstructure [14]. For this reason composite SiO$_2$-Al$_2$O$_3$ membranes were synthesized with various ratios, which are mesoporous, microporous or a combination of both. Composite membranes were synthesized by mixing colloidal boehmite and polymeric silica sols in different proportions.

![Figure 6: N$_2$ adsorption-desorption isotherms for $\gamma$-Al$_2$O$_3$, SiO$_2$ and composite films calcined at 600ºC for 3hr in air](#)
From Figure 6 it is clear that upon reducing the concentration of SiO₂ in the composite samples the micro porosity of the materials is reduced. The samples with low SiO₂ concentration (until 20% mole) comprise a mesoporous structure with a mean pore size of 2.5 nm. On the other hand samples with SiO₂ concentration between 20 and 50 % mole exhibit a bimodal pore size distribution. The micropores have a size of 0.55 nm and a rather broad pore size distribution. At the mesoporous regime the pores have a size of 2.5 nm. The isotherms of these samples show the characteristic hysteresis of the mesoporous solids. Increasing the concentration of SiO₂ the hysteresis starts to vanish and the isotherms tend to become type I. Thin films with concentrations of SiO₂ higher than 50% mole have a totally microporous character without mesopores, however, the micropore size remains 0.55 nm.

![Figure 7: Pore size distributions by applying the DFT model (left) and the HK model (right)](image)

The pore size distribution of the thin films is estimated by the nitrogen desorption isotherm applying Density Functional Theory (DFT) theory for the mesopores that takes into account the interactions of nitrogen with the specific material. For the micropores the Horvath Kowazoe model is applied for the determination of its pore size.

Preliminary EDX experiments show that the samples are homogeneous without segregation of phases of Al₂O₃ or SiO₂.

Supported composite membranes are synthesized by dip coating of α-Al₂O₃ supports, with a mean pore size of 100 nm, in a sol containing 53 % mole SiO₂. Permporometry measurements for a sample dipped one time with a sol containing polyvinyl alcohol 1.5 wt.% are presented in Figure 8.
The permeation curve in this case is characteristic for microporous membranes (pore diameter smaller than 2 nm). At small relative pressures a small reduction of the He permeance is observed due to the blocking of micropores. At higher relative pressure the permeance of He reaches a plateau. The density of the defects of this membrane is high which explains the high final permeability of He around \(1 \cdot 10^{-5} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}\). Mesopores are not present in this membrane, which actually is in agreement with the \(\text{N}_2\) physisorption results for the unsupported flakes. Another interesting remark is that desorption curve does not follow the adsorption possibly due to strong adsorption of \(\text{H}_2\text{O}\) at the hydrophilic surface of \(\text{SiO}_2\).

**Conclusions**

- Mesoporous supported \(\gamma\)-\(\text{Al}_2\text{O}_3\) membranes with a sharp and narrow pore size distribution and a mean pore size of 2.5 nm are synthesized via the sol-gel method
- \(\gamma\)-alumina membranes exhibit very good temperature stability. Specifically membranes doped with La exhibit better stability than the undoped membranes when treated for 1 week at 600ºC.
- Microporous silica and alumina-silica composite membranes are synthesized via the sol-gel method. Microporous membranes have a pore size of 0.5 nm.

**Future Plans**

- The project efforts will be focused on the development of supported microporous membranes.
- Transmission Electron Microscopy measurements have been planned in order to acquire a picture of the nanostructure of silica membranes.
- A study about the hydrothermal stability of the membranes is in progress.
- Modification experiments with Atomic Layer Deposition and Sputtering for the development of microstructures with tailored pore size that will yield high separation factors for \(\text{H}_2\).

**Figure 8:** Permporometry adsorption and desorption curve for an Al-Si composite membrane with 53% mole \(\text{SiO}_2\)
References

Contacts
Joop Schoonman: J.Schoonman@tudelft.nl
Konstantinos Stoitsas: K.Stoitsas@tudelft.nl

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