Development of Membrane Materials for Advanced Reactors for Carbon-Free Fossil Fuel Conversion

K. Stoitsas, T.H.Y Tran, A. Weibel, J. Schoonman

Delft University of Technology, Faculty of Applied Sciences, Department DelftChemTech, Delft, The Netherlands

Introduction

The steam-reforming and the water-gas shift equilibria are key reactions for the production of hydrogen from fossil fuels, i.e.,

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

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

The use of a membrane reactor, that can effectively separate hydrogen from H_2O, CO or CO_2, will shift the equilibrium to the product side.

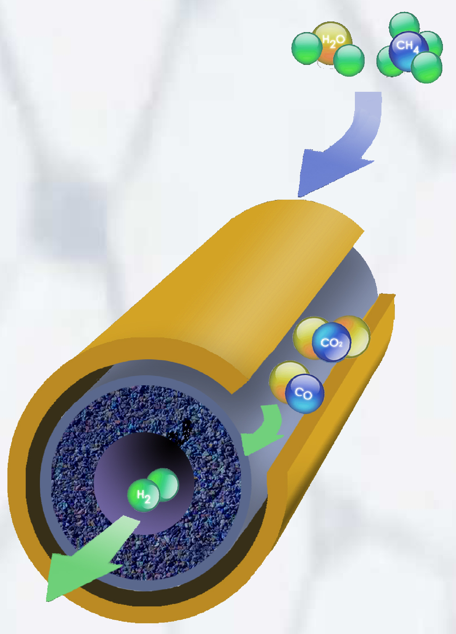

Figure 1. Schematic diagram of separation-enhanced membrane reactor

The combination of reaction and separation for the natural gas reforming can lower significantly the operation temperature while the efficiency increases from 70%, using conventional reactors, to 90%.

Aim of the research

Aim of this work is the development of a novel ceramic membrane for separating selectively hydrogen from carbon dioxide and carbon monoxide. The membranes will be used in membrane reactors for the above mentioned carbon conversions.

Mesoporous membranes will be developed on macroporous supports via the sol-gel method. In turn these membranes will be modified via the Atomic Layer Deposition technique to synthesize microporous structures (pore size smaller than 2nm) that will achieve, due to molecular sieving effects, high separation factors for hydrogen.

Experimental

Synthesis

Mesoporous γ-alumina membranes are being developed using the sol-gel technique. According the sol-gel technique, a nanocolloidal boehmite sol is prepared by hydrolysis of aluminum-tri-sec-butylate. After hydrolysis, peptization follows by the addition of HNO_3.

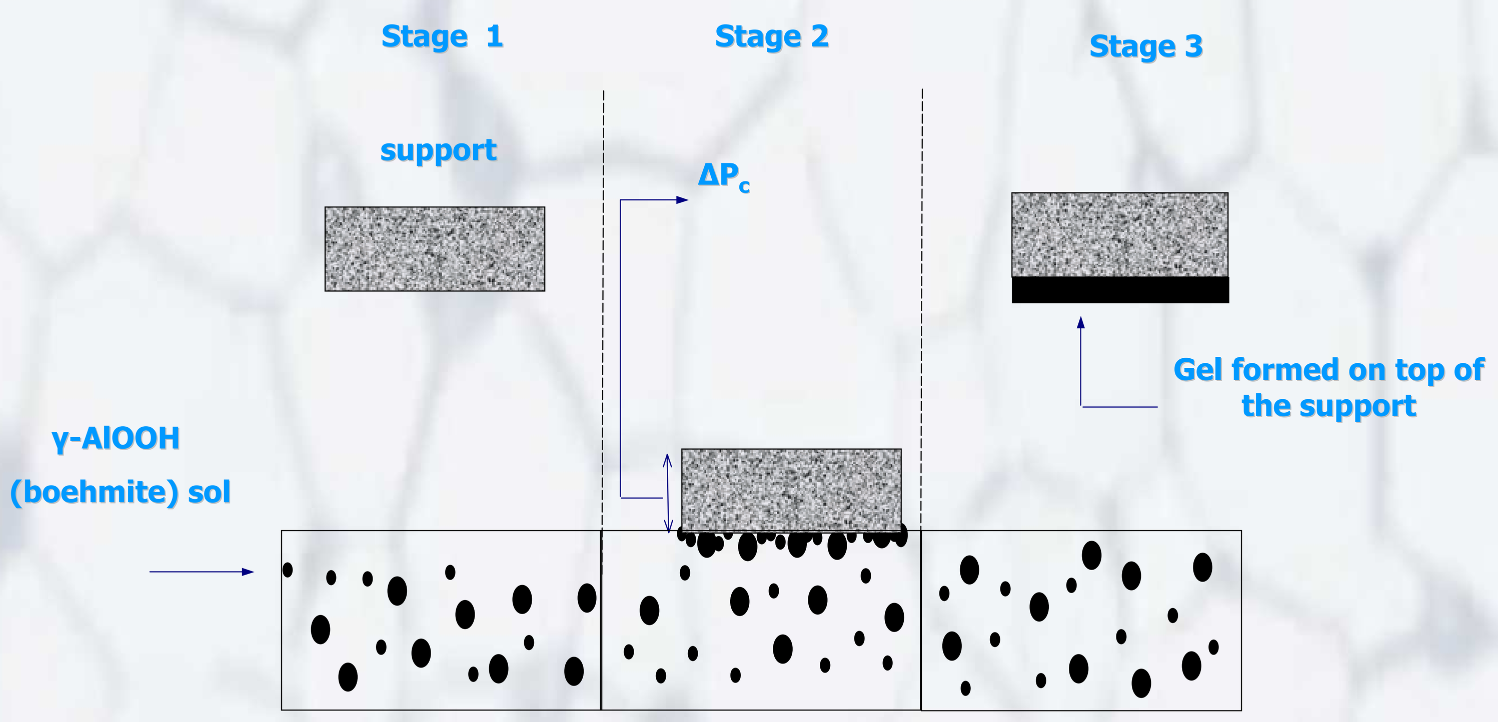

Figure 2. Schematic diagram of the slip-casting technique

Characterization

The thickness of the γ-Al_2O_3 film is on average 1.3 μm after the first dipping while the surface of the membrane shows no cracks. The nitrogen adsorption-desorption diagram is type IV, characteristic for mesoporous solids with typical hysteresis. The mean pore size of the membranes is 5.5 nm.

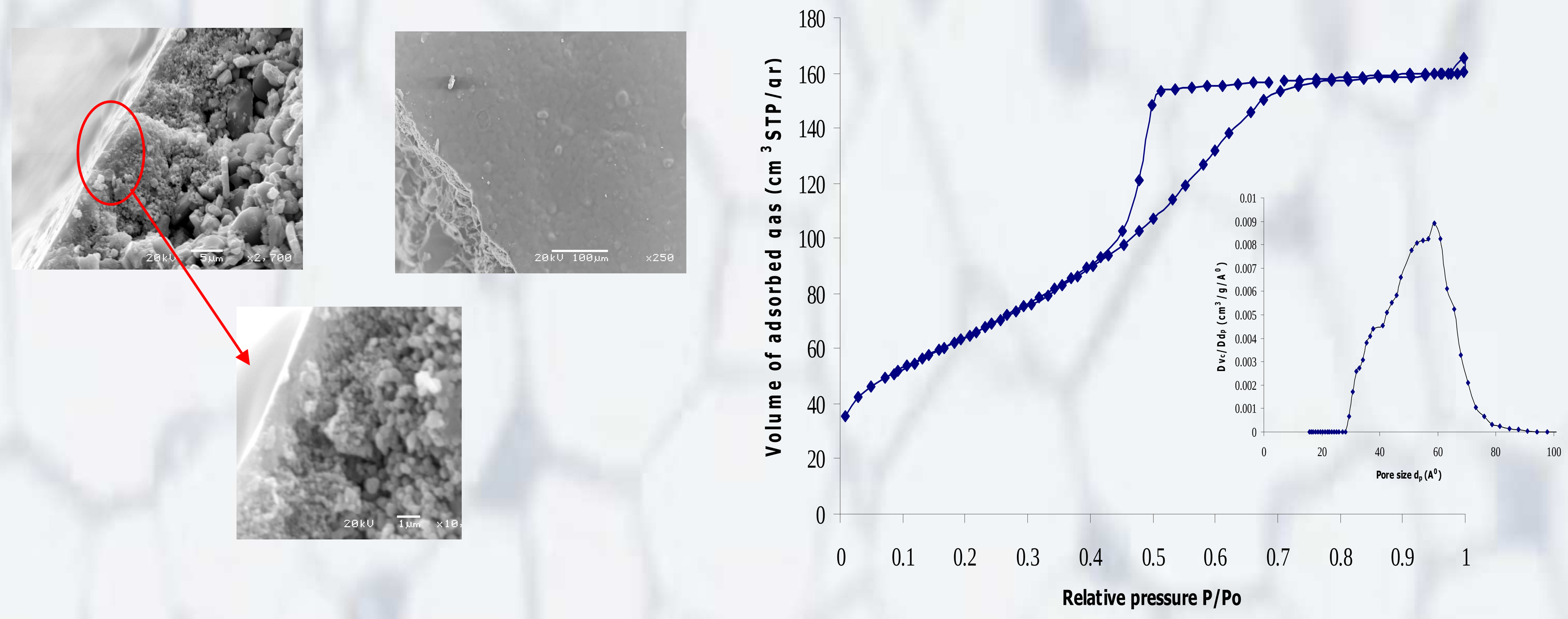

Figure 3. Scanning electron micrograph of a supported γ-Al_2O_3 membrane and the N_2 adsorption-desorption isotherm with the respective pore size distribution for γ-Al_2O_3 films

The quality of the supported membranes is tested by gas permeability measurements with inert gases.

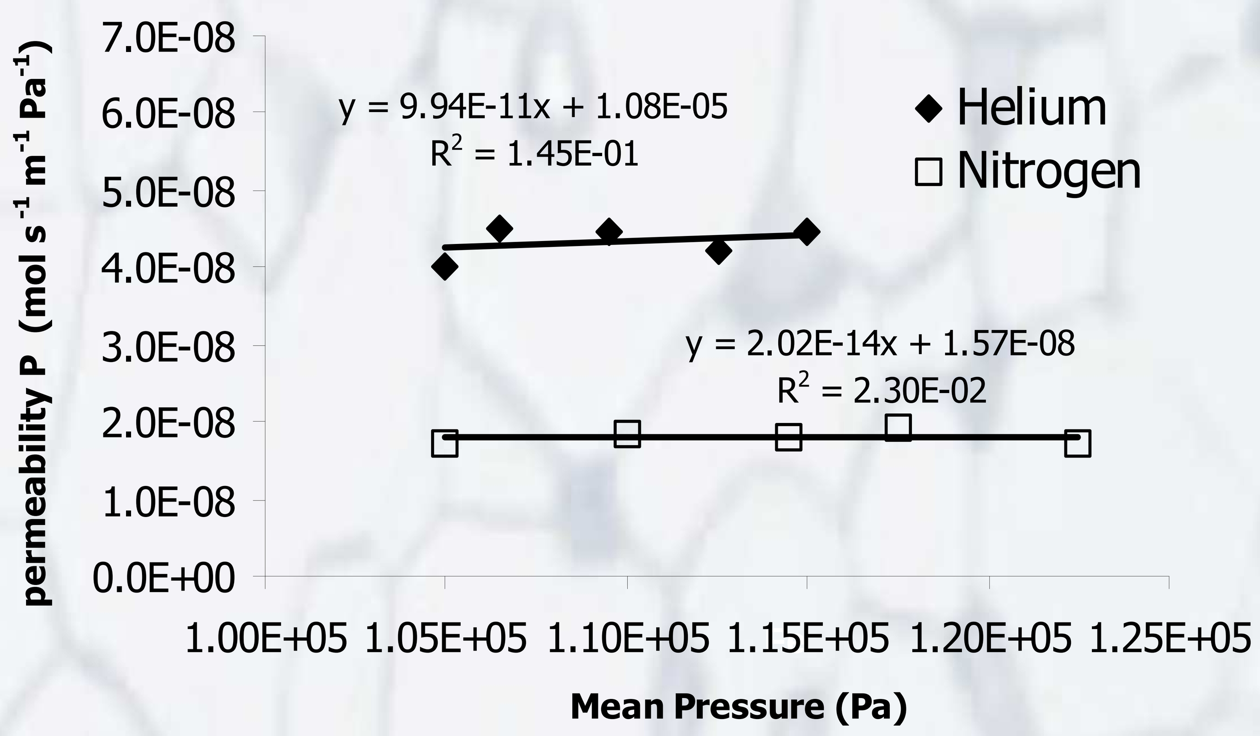

Figure 4. He and N_2 permeability measurements for the supported membrane system at 25°C

The He permeability for the macroporous systems has a value of $2.5 \cdot 10^{-7}$ mole·m^{-1}·s^{-1}·Pa^{-1} at a mean pressure of 1.25 bar. The permeability ratio of He/N_2 for the a-alumina supports is between 1.53 and 1.61, which is 58 and 61% corresponding to the ideal selectivity that the Knudsen law predicts. In the case of γ-Al_2O_3 membranes the respective permeability ratio is 90% of the ideal Knudsen selectivity, indicating the smaller pore size of these systems.

Future Plans

- ❖ It is planned to synthesize membranes with a narrower pore size distribution and improved temperature stability
- ❖ Transmission Electron Microscopy measurements have been planned in order to acquire a complete picture of the nanostructure of γ-Al_2O_3 membranes
- ❖ Atomic Layer Deposition equipment is being modified in order to accept disc-shaped membranes

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