Gas permeation characteristics of γ-alumina Membranes Modified by Atomic Layer Deposition

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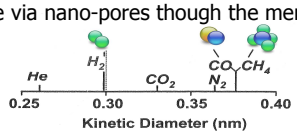
Aim of research

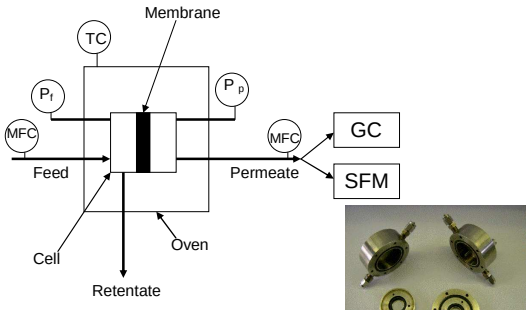
γ-alumina substrates made via the sol-gel technique are modified by Atomic Layer Deposition (ALD) in order to tune the size of the pores to the kinetic diameter of hydrogen. Gas permeation and separation properties of these membranes in single and mixed gases, e.g. H_2/CO_2, are experimentally studied at different temperatures and pressures revealing the impact of the ALD modification on the gas permeation of the membrane. The membrane will be used for the development of a membrane reactor for carbon free fossil fuel conversion in which the gases are separated on the basis of their molecular size via nano-pores though the membrane.



Preparation steps of Al_2O_3 membranes

Boehmite Sol
(Hydrolysis of aluminum butylate)
⇩
Dip coating on α-alumina supports — Sol-gel technique
Drying ⇩ Calcination
γ-alumina substrates
⇩ Al_2O_3 Coating — ALD technique
Alumina membranes

Gas pemeation results



The schematic diagram of the gas permeation equipment

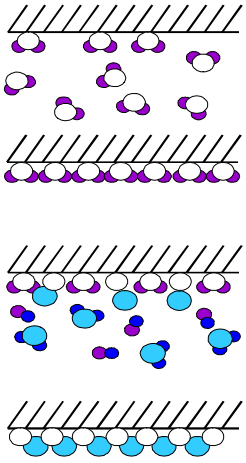
MFC: mass flow controller
TC: temperature controller
P_f: pressure in the feed side
P_p: pressure in the permeate side
GC: gas chromatograph
SFM: soap flow meter

Permeance

$$F = \frac{J}{\Delta P * A}$$

F: gas permeance of the membrane (mol.m^{-2}.s^{-1}.Pa^{-1})
J: gas flow through the membrane (mol.s^{-1})
ΔP: pressure drop across the membrane (Pa)
A: exposed area of the membrane (m^2).

Principle of Atomic Layer Deposition Technique



Precursor A is introduced into the reactor

One monolayer of precursor A adsorbs at the surface

Precursor B is introduced into the reactor and reacts with the adsorbed precursor A

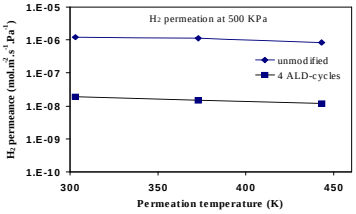
A monolayer of compound AB is formed

$$\mathbf{AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_n^* + CH_4 \ or \ 2CH_4} \quad (1)$$

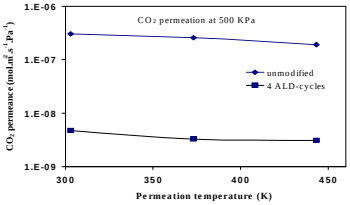
$$\mathbf{AlOAl(CH_3)_n^* + nH_2O \rightarrow AlOAl(OH)_n^* + nCH_4} \quad (2)$$

n=1 or 2

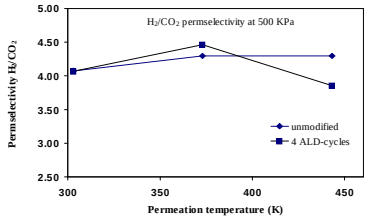
Binary reaction sequence for Al_2O_3 in which the surface species are designated by asterisks



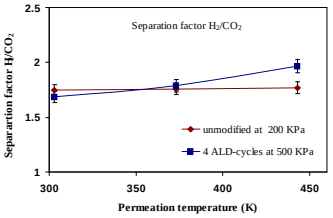
H_2 permeance for unmodified and ALD-modified γ-alumina membranes.



CO_2 permeance for unmodified and ALD-modified γ-alumina membranes.



H_2/CO_2 permselectivity at 500 kPa for unmodified and ALD-modified γ-alumina membranes



Separation factor for H_2/CO_2 (mixture 50/50 : v/v) for unmodified and ALD-modified γ-alumina membranes.

Separation factor

$$\alpha_{H_2/CO_2} = \frac{y_{H_2}/y_{CO_2}}{x_{H_2}/x_{CO_2}}$$

x , y : molar fractions at the retentate and the permeate streams.

Summary

✓ γ-alumina substrates have a pore size of 2-3 nm without cracks or defects.

✓ The ALD can be used to modify the γ-alumina substrate structure by infiltration of Al_2O_3 in the pores. After 4 cycles of Al_2O_3 deposition on the membrane, the H_2/CO_2 selectivity (4.06) is smaller than the theoretical one (4.69) predicted by the Knudsen diffusion mechanism. The results are very promising.

Future work

➢ Optimization of experimental ALD process parameters in order to have more effective in reducing of the pore size of the membrane.

➢ Optimization of the substrate synthesis for ALD in order to obtain a mesoporous structure with a monodisperse pore size distribution based on silica and zirconia.

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