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Innovative Methods for the Characterization of Ceramic Nanofiltration Membranes Modified by TEOS/O3 Chemical Vapor Deposition

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1. Introduction

The chemical vapor deposition (CVD) technique is successfully used for the deposition of thin films of several oxides on porous substrates [1]. In the most frequently applied CVD the two reactants are flowing at the opposite sides of the membrane (counter diffusion CVD). In this mode of operation the two reactants diffuse opposite to each other through the pores and react at the pore entrance or near the top layer surface to form a thin oxide film [2,3].

2. Experimental , Results and Discussion

The reactor cell consisted of an outer non-porous glass tube accommodating the tubular composite ceramic membranes. The membranes were composed of a macroporous α- and γ-alumina support (outer layer) and an inner thin nanoporous silica layer. Each membrane was positioned at the center of the reactor tube and was mechanically sealed at both ends with inner non-porous glass tubes.

At the first CVD process a stream of nitrogen was introduced into a tetraethoxysilane (TEOS) bubbler kept at temperatures between 40 and 80°C. The N_2/TEOS stream was fed through the inner side of the membrane. The air/O_3 stream was introduced into the outer side of the membrane and from the opposite side of the reactor. The temperature during the CVD process varied between 300-350°C. The ratio of O_3/TEOS flow rates in the gas streams varied between 16 and 30. A different CVD process was also attempted in which membranes were first equilibrated with TEOS vapors at different temperatures and subsequently subjected to the aforementioned O_3/TEOS reaction

During the CVD process, membrane-permeating oxygen was enriching the inner N_2/TEOS stream. An Electrolytic Oxygen sensor (on line with N_2 stream) continuously monitored the oxygen concentration decrease due to SiO_2 deposition inside the pores. The pressure difference between the two ceramic tube sides has been also continuously monitored in order to asses its contribution to the deposition rate and deposition layer morphology. Three segments of the membrane derived from the first CVD process have been tested for single gas permeance of He, N_2, and CH_4 at 293, 323, 343 and 373K. The results were corrected for support contribution and the resulting thin layer permeance was evaluated. For the segments derived from the two ends, the top layer permeance was pressure dependent for both He and N_2, revealing the existence of defects. In the case of the middle segment, the top layer permeance decreased slightly for both He and N_2, compared to the unmodified membrane and showed no tendency for increase with increasing pressure, in the range of 50-100kPa. Additionally, temperature dependence of permeance was of Knudsen type.

The top layer He and N_2 single gas permeance was pressure independent at 293, 323, 343 and 373K and was one order of magnitude lower compared to the unmodified membrane (~ $1.0\text{-}1.2 \cdot 10^{-8}$ mol/m$^2 \cdot$sec$\cdot$Pa for He and ~ $3.9\text{-}4.4 \cdot 10^{-8}$ mol/m$^2 \cdot$sec$\cdot$Pa for N_2). Moreover, diffusion was activated in the temperature range examined and the corresponding apparent activation energies for He and N_2 were 2.6 and 2.7 kJ/mol.

All membranes were also investigated for defects (down to 20Å) by a specially developed mercury intrusion technique. The membrane support surface was sealed with an epoxy resin (Varian), exposing only the thin layer surface to mercury penetration. This technique was validated, by performing blank tests in which the whole membrane area was covered with resin.

Permporometry (H2O/He, 31°C) as well as differential permeability experiments were applied in order to define the pore size distribution of the two modified and one unmodified membrane.

3. Conclusions

SiO_2 film growth at the feed sites of the reactor is inadequate, as indicated by the pressure dependence of the corresponding segment permeance for each modified membrane.

In the contrary, the middle segment permeance of both modified membranes was independent of pressure, indicating gas transport by Knudsen diffusion. Furthermore, the central segment of the membrane modified by the second CVD process showed activated diffusion for both He and N_2 implying the existence of nanopores in the separation layer.

A new technique based on mercury intrusion was developed and validated as a tool for the investigation of possible defects or macropores existence. Finally, it was also observed by SEM microscopy that the existence of pressure of the air/O_3 stream during the deposition results in the formation of a silica thin film on top of the membrane's top layer.

References

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