QUARTERLY PROGRESS REPORT

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Project Title: Silica Membranes for Hydrogen Separation from Coal Gas
Identification Number: DE-FG22-92PC92525
Institution: California Institute of Technology
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I. Project Objectives

The project objectives are (1) to explore new silylation reagents and reaction conditions with the purpose of reducing the thickness and increasing the permeance of silica membranes, (2) to delineate mechanism and kinetics of silica deposition, (3) to measure the permeability of silica layers at different extents of deposition and (4) to mathematically model the relationship of permeability and membrane structure.

II. Work Performed During Reporting Period

Fundamental Measurements in TGA-MS System

Experiments continued using the TGA-MS system. In each experiment the permeance of several gases is measured through a porous Vycor tube subjected to consecutive silylation-hydrolysis cycles which cause SiO2 deposition and narrowing of the pore size. Figures 1 and 2 show the results of one experiment that lasted 7 cycles. The points are at 0 cycles (untreated tube), 4 cycles and 7 cycles. Figure 1 compares normalized permeance ratios for CH4:N2 and SF6:N2 with the Knudsen value which is unity. There is a small but growing deviation from the Knudsen ratio with the selectivity changing in favor of the gas with the smaller kinetic diameter (N2). Figure 2 shows the absolute permeances of several gases versus weight gain (or cycle number). All gases show a gradual decrease of permeance with increasing deposition, as expected.

Computer Simulations

Considerable progress was achieved in the molecular dynamics simulation of diffusion in cylindrical capillaries. In prior simulations the capillary wall was simulated by a smooth potential in the perpendicular direction (Everett-Pohl, i.e. integrated Lennard-Jones) plus a periodic (sinusoidal) potential parallel to the walls. This soft periodic potential which has been used previously in surface diffusion studies did not allow adequate diffuse scattering and turned out to be unsuitable for MD calculations at elevated temperatures. We now have introduced...
discreet spherical clusters interacting with the gas molecules by a Lennard-Jones potential. These clusters are superimposed on the continuous Everett-Pohl potential and provide a mechanism for diffuse scattering. Figure 3 shows the results of one set of simulations. According to basic diffusion theory the mean square distance \( <r^2> \) traveled by a molecule should satisfy

\[
\lim_{t \to \infty} \frac{1}{2t} <r^2> = D
\]

The figure shows that with increasing time \( <r^2>/2t \) indeed tends to a limit. This limit is compared with the Knudsen diffusion coefficient for two values of the capillary radius. The graphs for the two radii are not directly comparable because the cluster densities used in the two cases were different.

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Deviation of Permeances from Knudsen Results

Figure 1. Normalized permeance ratios CH₄:N₂ and SF₆:N₂ at 500°C versus weight gain during alternating reactants deposition of SiO₂.
Figure 2. Permeance of several gases at 500°C versus weight gain during alternating reactants deposition of SiO₂.
Figure 3. Molecular dynamics simulation of Ar diffusion in a cylindrical capillary in the limit of low gas density. The capillary wall is modeled as a smooth Everett-Pohl potential plus a layer of discrete atoms.