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QUARTERLY PROGRESS REPORT

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Project Title: Silica Membranes for Hydrogen Separation from Coal Gas

Identification Number: DE-FG22-92PC92525

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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

1. New Silylation Reagents and Reactions

A new reactor system was constructed which can be used for CVD of SiO_2 layers on porous Vycor tubes. The system is suitable for the usual one-sided deposition and for alternating (or layer-by-layer) deposition whereby the silylating agent and water are passed one at a time in alternating periods. The main advantage of alternating deposition is that it allows membrane deposition using silica precursors for which the homogeneous hydrolysis is fast. As we have demonstrated in earlier work, fast homogeneous reaction interferes with membrane formation. The disadvantage of alternating deposition is the longer time required for membrane formation.

Figure 1 is a schematic of the new reactor constructed for homogeneous deposition. In each silylation period the space inside and outside of the support tube is evacuated and a small and accurately controlled amount of reactant (e.g. $SiCl_4$) is allowed to flow from a storage glass flask 4 into the reactor annulus by opening valve 5 for a few seconds. The silylation reaction is allowed to proceed for the desired time interval (about one minute) after which the reactor is evacuated and flow of water vapor commences by opening valve 7. After the completion of one cycle of silylation and hydrolysis, the nitrogen permeance of the support tube is measured by the techniques used in our earlier work (bubble flow meter or pressure transducer). After the nitrogen permeance has decreased by a specified factor (about thirty) from its initial value, the reactions are terminated and the membrane is annealed at 700°C for about ten hours after which the nitrogen and hydrogen permeances are measured at several temperatures.

The new reactor system was constructed to carry out membrane preparation with new silylation reagents to be synthesized in our laboratory. One such reagent has already been synthesized and tested in the thermogravimetric analyzer to determine if and how fast it reacts with porous Vycor glass. The results obtained so far with this new reagent were not satisfactory but more experiments are planned for the near future. Several membrane synthesis experiments were performed with $SiCl_4$, $SiHCl_3$ and $Si_3O_2Cl_8$ using the new reactor. The results of these experiments are summarized in Tables 1-3. In all experiments the H_2 and N_2 permeance of the untreated tube at 700°C was 0.478 and 0.128 cm^3/cm^2-min-atm. Table 1 shows the results of deposition using $SiCl_4$. The hydrogen permeance is high (at 700°C it is only 13% below that of the untreated tube), but the selectivity (50-80) is lower than that achieved with the usual one-sided deposition. Table 2 shows the properties of the membrane obtained with the trimer $Cl_3SiOSiCl_2OSiCl_3$. The hydrogen permeance is very good, only 8% below that of the untreated tube. The selectivity is considerably higher (130-270) than that obtained with $SiCl_4$. Table 3 shows the properties of a membrane prepared with $SiCHCl_3$ after hydrothermal treatment. After 14 hours of hydrothermal treatment, the hydrogen permeance is below that obtained with the membrane of Table 1. After one week of hydrothermal treatment, the hydrogen permeance declined further as expected, but the final values are higher than those of the membranes previously prepared in our laboratory by one-sided deposition. The selectivity of the membrane is relatively low, however.

The hydrogen permeance of the membranes obtained with alternating deposition are equal or somewhat higher than those obtained in our previous membrane preparations. The H_2:N_2 selectivities are somewhat lower. The one week hydrothermal treatment of the tube of Table III carried out at 700°C with 10% H_2O was probably long enough to produce stable membrane properties.

2. Mechanism and Kinetics of SiO_2 Deposition

The kinetic studies outlined in our previous quarterly period have now been concluded and are summarized in the attached manuscript.

3. Membrane Characterization by TEM

Transmission electron micrographs of thin membrane sections are currently analyzed to obtain information about residual porosity in the separation layer of the membrane. The results will be presented in the next quarterly report.

Table 1. Silica membrane formed in 16 cycles of alternating reaction with 6% $SiCl_4$-N_2 and 10% H_2O-N_2 at 700°C. The length of each silylation and hydrolysis period was 1 minute and 5 minutes, respectively.

	Permeance (cm^3(STP)/cm^2-min-atm)	
Temperature (°C)	H_2	N_2
400	0.34	0.0063
500	0.38	0.0057
600	0.41	0.0056
700	0.41	0.0054

Table 2. Silica membrane formed in 50 cycles of alternating reaction with $Si_3O_2Cl_8$[a]-N_2, 10% H_2O-N_2. The length of each silylation and hydrolysis period was 1 minute and 5 minutes, respectively.

	Permeance (cm^3(STP)/cm^2-min-atm)	
Temperature (°C)	H_2	N_2
400	0.43	0.0016
500	0.43	0.0020
600	0.44	0.0026
700	0.44	0.0034

[a]The vapor pressure of this compound (Cl_3Si-O-$SiCl_2$-O-$SiCl_3$) is unknown. Vaporizer was maintained at 100°C.

Table 3. Silica membrane formed in 16 cycles of alternating reaction with 10% $SiHC_3$, N_2 and 10% H_2O-N_2 at 700°C. The length of each silylation and hydrolysis period was 0.5 minutes and 5 minutes, respectively.

	Permeance (cm^3(STP)/cm^2-min-atm)			
	after treatment I		after treatment II	
Temperature (°C)	H_2	N_2	H_2	N_2
450	0.22	0.0048	0.14	0.0048
600	0.30	0.0045	0.23	0.0045
700	0.33	0.0028	0.27	0.0043

Treatment I: 14 hours heating at 700°C in 10% H_2O-N_2.
Treatment II: 1 week heating at 700°C in 10% H_2O-N_2

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