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QUARTERLY PROGRESS REPORT

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Project Title: Hydrogen Separation by Ceramic Membranes in Coal Gasification

Identification Number: DE-AC21-90MC26365

Institution: California Institute of Technology

Principal Investigator: G. R. Gavalas

I. Project Objectives

Develop hydrogen-permselective ceramic membranes for water-gas shift membrane-reactor suitable for hydrogen production from coal gas. Evaluate the technical and economic potential of the membrane-reactor.

II. Work Performed During Reporting Period

Task 1 and 2. Membrane Deposition and Stability Testing

During the reporting period exploratory experiments begun on a membrane preparation technique aimed at providing higher membrane permeance. The new preparation technique involves two stages. The first stage is the formation of a layer of silica gel by a two-phase interfacial reaction within the pores of the substrate. The gel is then dried and calcined yielding a microporous (pore diameter below 10 Å) silica layer within the pores of the substrate tube. The second stage involves one-sided chemical vapor deposition using the $SiCl_4$-H_2O reaction to close up the micropores of the gel layer and produce the final hydrogen permselective membrane.

The concept underlying this new preparation technique is the following. Chemical vapor deposition of SiO_2 using the $SiCl_4$-H_2O reaction is relatively slow allowing penetration of the reactants about 20 μm within the porous support. The resulting deposit layer consists of a thin region (perhaps about 1 μm) of high selectivity just below the surface of the substrate and a thick region (about 20 μm) of diminished porosity gradually blending with the unmodified substrate. The thick region is not uniform, with porosity varying from its low percolation threshold at the one end to the original value of the untreated support at the other side. This region reduces substantially the gas permeance without contributing much to the selectivity. To improve the membrane permeance it is essential to reduce the thickness of the deposit layer, both the highly selective region, and the thicker partially constricted region. The deposit layer thickness can be reduced by reducing the penetration of the $SiCl_4$ reactant, (by increasing the Thiele modulus) either by increasing the reaction rate parameters, or decreasing the effective diffusion coefficient, or both. The technique chosen is based on the reduction of the diffusion coefficient by

decreasing the pore size of the support. This pore size reduction must apply over a thin region of the support, otherwise it will contribute to the overall resistance. These considerations provide the rationale for the two-stage nature of the new deposition technique. The first stage involves interfacial reaction to form a thin silica gel layer resulting in a region of reduced pore size. The interfacial reaction provides the possibility of producing very thin layers of reduced porosity, as will be explained below. The second stage involves the usual CVD treatment and does not need further discussion other than to note that it acts to finally close the pores in the layer already formed by the first stage of liquid phase interfacial reaction.

The liquid-phase interfacial reaction is carried out by the following sequence of steps:

i) The porous space of the support tube is filled with water, either by relying on natural capillary condensation from the surrounding air, or by actually contacting the tube with liquid water.

ii) The support tube is contacted from the bore side or the outside with a solution of $SiCl_4$-CCl_4 at ambient temperatures for a specified length of time.

iii) The tube is dried, brought slowly to about 700°C, and then subjected to the second stage treatment by CVD.

In view of the immiscibility of the aqueous phase and the $SiCl_4$-CCl_4 solution, reaction takes place only at the interface between the two phases which is at the geometric surface (bore or outside) of the support. The reaction involves a sequence of hydrolysis and condensation steps similar to those involved in the conventional sol-gel process:

$$SiCl_4 \xrightarrow{H_2O} SiCl_3OH \xrightarrow{H_2O} SiCO_2(OH)_2 \longrightarrow \ldots \longrightarrow Si(OH)_4$$

$$SiCl_x(OH)_{4-x} + SiCl_y(OH)_{4-y} = H_2O + SiCl_x(OH)_{3-x}\text{-}O\text{-}SiCl_y(OH)_{3-y}$$

$$SiCl_x(OH)_{4-x} + SiCl_y(OH)_{4-y} = HCl + SiCl_{x-1}(OH)_{4-x}\text{-}O\text{-}SiCl_y(OH)_{3-y}$$

As the species lose chlorine and gain silanols or form siloxane bonds, they become increasingly soluble in water and diffuse away from the interface into the aqueous phase occupying the pores of the substrate. However, the diffusion of the product species slows down with increasing degree of polymerization. Eventually condensation leads to gel formation and suppresses further penetration into the aqueous phase. The thickness of the gel layer clearly depends on the balance among the rates of hydrolysis, condensation and diffusion. Several means can be used to influence this balance in order to prepare thin gel layers. At this time we have only obtained some preliminary results summarized below. More work will be required to exploit the full potential of this technique.

Results

In the first few experiments after the completion of gel formation and drying, the tubes cracked during heating when the temperature exceeded 500°C. The procedure was subsequently modified so that the gel would form near the bore surface rather than near the

outside surface. In addition, the heating rate during calcination was reduced to 2°C/minute. Table 1 below shows the results of the first two successful preparations.

The permeances of membranes No. 7 and No. 10 are lower by a factor of approximately 1.5 than those of the membranes prepared by single stage CVD. As we are very early on the learning curve of the two-stage technique, however, we hope that significant improvements are possible with further work.

Task 4. Economic Evaluation

The subcontractor KIT has completed their final report, a copy of which has been forwarded to the DOE program manager. The KTI report will be incorporated in the final report of this project.

Table 1. Preparation conditions and permeation properties of two membrane prepared by the two-stage technique.

Membrane Code	Interfacial Reaction[a] Time (min)	Drying Time (hours)	CVD Time[b] (min)	Permeances at 700°C (cm_3/cm_2-min-atm)					
				Before Treatment		After Liquid Phase Reaction and Drying		After CVD	
				H_2	N_2	H_2	N_2	H_2	N_2
7	15	24	11	0.460	0.123	0.313	0.079	0.254	0.009
10	7.5	1	14	0.442	0.118	0.379	0.068	0.303	0.0008

[a] the interfacial reaction was carried out at ambient temperature using a 50-50 $SiCl_4$-CCl_4 solution as the one phase and water as the other phase.

[b] CVD was carried out at 700°C in one-sided geometry using a stream containing 10% $SiCl_4$, 22% H_2O balance N_2.

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