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Hydrogen Separation by Ceramic Membranes in Coal Gasification

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Hydrogen Separation by Ceramic Membranes in Coal Gasification

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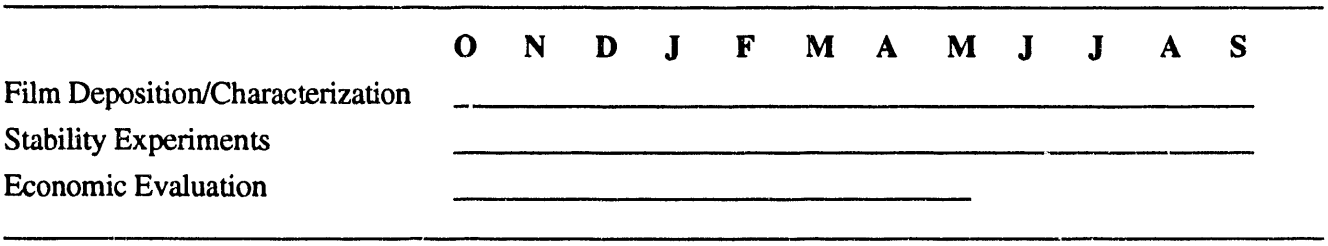
Period of Performance	1/9/90 to 8/31/92

Schedule and Milestones

FY92 Program Schedule



OBJECTIVES

The general objective of this project is to develop inorganic membranes for separation of hydrogen from coal gas at high temperatures. The project includes the following tasks: (i) membrane development by chemical vapor deposition of dense silica layers within the pores of support tubes, (ii) membrane characterization, (iii) tests of membrane stability to extended operation in contact with a simulated coal gas, (iv) development of a model for combined shift reaction and membrane hydrogen separation, and (v) comparative economic analysis of membrane-based hydrogen production and a conventional process of hydrogen production from coal.

BACKGROUND INFORMATION

Coal gasification is a promising alternative to steam reforming of natural gas as a source of hydrogen for the synthesis of ammonia and other chemicals. The hydrogen consumed in coal conversion to liquid fuels could also be derived from the gasification of coal or coal residues. In either of these uses of coal the separation of hydrogen from coal gas can be carried out by established processes like acid gas removal and pressure swing adsorption. However, membrane separation is a promising alternative having the potential of higher energy efficiency and simpler process flowsheet. To realize these potential advantages the separation must be carried out at elevated temperatures necessitating the use of inorganic membranes. Separation of hydrogen sufficiently pure for ammonia or other chemical synthesis requires membranes of very high selectivity, while separation of less pure hydrogen for use in coal liquefaction is feasible with less selective membranes.

Among various inorganic materials amorphous oxides (glass) such as SiO_2 and B_2O_3 are known to be very highly selective to hydrogen (and helium) permeation. For example, at 500°C, the permeability coefficient of oxygen through amorphous SiO_2 is lower than that of hydrogen by more than four orders of magnitude, and the permeability of nitrogen is even lower. Diffusion through the dense glass network is activated and even for hydrogen the permeability becomes significant only at elevated temperatures. Because of the low permeability, separation membranes based on SiO_2 or other amorphous oxides must be of an asymmetric or composite type, i.e. they must consist of a thin layer of the selective material deposited on a porous tube providing mechanical support. Deposition of the selective layer on the porous support can be carried out by liquid phase or gas phase techniques, but gas phase techniques, i.e. chemical vapor deposition (CVD), seem to be more suitable for depositing dense layers. The advantage of dense layers, in contrast to mesoporous or microporous layers, is the high selectivity, essential for the separation of high purity hydrogen.

The present project was initiated in early 1990 to develop hydrogen permselective SiO_2 membranes, test membrane stability under conditions simulating application to hydrogen separation from coal gas, and perform economic evaluation of a membrane-based process versus a conventional process. Membrane preparation has been carried out by CVD of SiO_2 on porous Vycor support tubes. The CVD reaction was the hydrolysis of silicon tetrachloride ($SiCl_4 + H_2O$). Earlier in the project we had also prepared and studied TiO_2 and Al_2O_3 membranes. Although TiO_2 and Al_2O_3 also exhibit hydrogen permselectivity, they are inferior in both permeability and selectivity to SiO_2 and, hence, our recent work has been devoted exclusively to SiO_2.

In last year's proceedings, we described two CVD geometries, the two-sided or opposing reactants geometry, and the one-sided geometry. For CVD of SiO_2 the one-sided geometry provides thinner, therefore more permeable, layers with only a small sacrifice in selectivity. In addition to permeance and selectivity, membrane stability to the process environment is a critical issue. It turns out that the permeance of the SiO_2 membranes decreases upon extended exposure to elevated temperatures and high pressures of water vapor. In our previous conference paper we reported stability tests showing that the membrane permeance decreases by a factor of 3-5 and seemingly stabilizes at that lower value after one to two weeks of exposure to 550°C and 3 atmospheres of water pressure. The membranes prepared by one-sided CVD were found superior in terms of stability than those prepared by two-sided CVD. These previous results have been published in two recent papers (Tsapatsis et al. 1991, 1992).

During the last year our experimental work on SiO_2 membranes focused on modifications of the preparation technique intended to increase membrane permeance. In addition, a series of extended stability testing was carried out. In parallel, Kinetics Technology International, under subcontract to this contract, carried out process flowsheeting and economic evaluation of a membrane-assisted process for ammonia production from coal.

PROJECT DESCRIPTION

Materials

Porous Vycor tubes supplied by Corning Inc. were used as the membrane support. Most of the work was carried out with tubes of 5 mm ID, 1.1 mm wall thickness and 40 Å mean pore diameter. In a few experiments tubes of 5 mm ID, 0.33 mm wall thickness and 25 Å mean pore diameter were used. Silicon precursors for the CVD included $SiCl_4$, $Cl_3SiOSiCl_3$, and $Cl_3SiOSiCl_2OSiCl_3$ which we shall refer to as the monomer (M), dimer (D) and trimer (T), respectively. These variations in the support and the CVD reactants were undertaken in the hope of increasing membrane permeance. By going from $SiCl_4$ to the dimer and further to the trimer the reaction rate with surface-

OH groups is increased, simply by having more Si-Cl bonds (4 in the monomer $SiCl_4$, 6 in the dimer, and 8 in the trimer), while the Knudsen diffusion coefficient is decreased as the molecular weight increases from 170 for $SiCl_4$ to 285 for the dimer and 400 for the trimer. Likewise, decreasing the pore size results in an increase of the reaction rate (because of the larger surface area) and a decrease of the diffusion coefficient. The increased reaction rate coefficient and reduced diffusion coefficient was expected to result in shallower pore penetration, thinner deposit layer and, hence, higher permeance.

Apparatus and Procedure

The apparatus for one-sided CVD was described in last year's conference paper and in the paper by Tsapatsis et al., 1991. Briefly, a porous Vycor support tube with nonporous quartz sections welded on its two ends was placed concentrically within a quartz cylinder and connected to lines for inlet and outlet of reactants, and to a vacuum line. The concentric cylinder reactor was placed in a hinged electrical furnace to maintain the specified temperature (650-750°C). The two reactant streams $SiCl_4$-N_2 and H_2O-N_2 generated using bubblers were introduced in the bore of the Vycor tube upstream of the porous section. The reactant flow was interrupted every 2 to 5 minutes to measure the H_2 and N_2 permeance of the membrane. The CVD was terminated after the N_2 permeance decreased by a factor of about 200 from its initial value.

Stability Experiments

After CVD the membrane tubes were left for a few hours under N_2 flow at 700-750°C and then were enclosed in a pressure cylinder (5 cm ID, 1 m long). In a typical stability test, three or four membrane tubes were placed and secured in the cylinder. The cylinder was then loaded with the appropriate amount of N_2 and H_2O such that after the temperature was raised to 550°C the partial pressures of H_2O and N_2 were 3 atm and 7 atm respectively. After approximately two weeks of this hydrothermal treatment the cylinder was cooled, depressurized and opened up, and the membranes were once more placed in the concentric reactor apparatus for measurement of H_2 and N_2 permeances.

RESULTS

Table 1 lists the support tubes and the deposition reactants and other conditions used to prepare seven membranes. The permeances of these membranes immediately after deposition, after twelve hours of thermal treatment at 700-750°C, and after thirteen days of additional hydrothermal treatment at 550°C under 3 atm of water vapor are listed in Table 2. Figure 1 is an Arrhenius plot of the hydrogen permeance of membrane D25 (dimer reactant, 25 Å pore support) before and after the hydrothermal treatment.

The following conclusions can be drawn from the results of Tables 1 and 2. All membranes prepared in this series underwent hydrothermal treatment with the expected decrease of hydrogen permeance. Using the dimer and trimer precursors resulted in a slight improvement in hydrogen permeance and had no consistent effect on the H_2:N_2 selectivity. Using the 25 Å pore tubes improved moderately the hydrogen permeance but seemingly reduced the selectivity from about 500-1000 to about 200-300. The best permeance was obtained with membrane D25 made with 25 Å pore size tubes using the dimer precursor. This tube had hydrogen permeance 0.13 cm^3/cm^2-min-atm and H_2:N_2 selectivity of 200 at 500°C, after the thirteen-day hydrothermal treatment. It must be noted that the measurement of the very small nitrogen permeance is subject to considerable error, especially if there is some small leak in the system. Hence the true N_2 permeances may be considerably lower than the measurements indicate, and the reported selectivities probably significantly underestimate the true selectivities.

Figure 1 shows a sharp increase in the activation energy of hydrogen permeance following deposition and hydrothermal treatment. The permeance of the untreated tube has negative activation energy in accordance with Knudsen diffusion (permeance inversely proportional to $T^{1/2}$). After deposition and annealing, the activation energy increases to a value about 10 kJ. This value is the result of the series combination of

Table 1. One-Sided Deposition of Membranes Using Different Substrate Tubes and Different Precursors

Code	Substrate Tubes[a] Pore Diameter (Å)	Reactants (%) Precursor[b]	H_2O	Temperature (°C)	Time (min)
M40	40	M, 2	6	750	3.75
D40A	40	D, 0.05	5	700	11
D40B	40	C, 0.7	22	700	5
T40	40	T, c	22	700	11
M25A	25	M, 2	3	750	3
M25B	25	M, 2	6	750	0.83
D25	25	D, 0.045	5	700	2.3

[a] 40 Å pore diameter tubes have 5 mm ID and 1 mm wall thickness; 25 Å pore diameter tubes have 5 mm ID, 0.33 mm wall thickness

[b] M denotes $SiCl_4$, D denotes $Cl_3SiOSiCl_3$, T denotes $Cl_3SiOSiCl_2OSiCl_3$

[c] vapor pressure of trimer unknown; bubbler maintained at 125°C

the deposit layer resistance and the resistance of the untreated tube. After the hydrothermal treatment, the resistance is dominated by the deposit layer, whence the much higher activation energy (~30 kJ/mol).

ECONOMIC EVALUATION

Kinetics Technology International carried out analysis and economic evaluation of a membrane-assisted and a conventional process of ammonia from coal. A schematic of the hydrogen production parts of the two processes is shown in Figure 2. The coal gasifier and the ammonia plant are excluded from this Figure as being identical in both processes. The coal gas is assumed to be produced in a KRW oxygen-blown gasifier converting about 1000 ton per day low sulfur (0.4%) coal. Both processes use the same amount and composition of coal gas and produce purified hydrogen equivalent to 560 ton per day ammonia. Both processes produce electric power as well as ammonia by using part of the feed coal gas in a gas turbine-steam turbine dual cycle. Much of the power generated is used for the internal needs of the process, most of it for driving the ammonia compressors and the combustion air compressors. However, there is some net power produced by both processes. Although the two processes receive the same amount of coal gas and produce the same amount of ammonia they differ in net power production and in capital cost because they employ different unit operations and equipment. The economic evaluation was limited to the hydrogen production units, for the coal gasifier and ammonia plant were identical in the two processes.

The conventional process adds a large amount of steam to the coal gas such that after two successive catalytic shift stages (high temperature and low temperature) the conversion of CO is 99+%. Pure hydrogen with only traces of CO, CO_2, CH_4 and H_2S is produced by pressure swing adsorption (PSA) and conducted to the ammonia plant. The net power production in this process was estimated to be 36.6 MW.

The membrane-assisted process requires a much smaller amount of steam to achieve high conversion for the shift reaction. The membrane reactor used in this process consists of three high temperature shift reactor units, each followed by a membrane unit and a heat exchanger. The permeate gas is high purity hydrogen which after methanation (to convert the few tens of a percent of

Table 2. Membrane Permeance to Hydrogen and Nitrogen under Various Treatments (Treatment II: 12 Hours under N_2 at 700-750°C; Treatment II: 13 Days at 550°C under 3 atm of Water and 7 atm N_2)

Membrane[a]	Temperature of Measurement (°C)[b]	Membrane Permeance ($cm^3(STP)/cm^2$-min-atm)							
		Before Deposition		Immediately After Deposition		After Treatment I		After Treatment I&II	
		H_2	N_2	H_2	$N_2 \times 10^3$	H_2	$N_2 \times 10^3$	H_2	$N_2 \times 10^3$
M40	450	0.41	0.11			0.22	0.86	0.06 (404)	0.18 (404)
	600	0.37	0.10			0.25	0.96	0.11	0.21
	750	0.35	0.094			0.27	1.00	0.15 (684)[b]	0.23 (684)
D40A	450	0.41	0.11			0.21	0.4	0.06 (400)	0.14 (400)
	600	0.37	0.10			0.21	0.3	0.13	0.16
	700	0.35	0.095			0.26	0.3	0.17	0.16
D40B	700	0.471	0.126	0.322	5.6	0.299	0.22		
T40	415							0.06	0.17
	591							0.15	0.3
	700	0.57	0.154	0.465	1.3	0.447	0.55	0.20 (684)	0.51(684)
M25B	450	1.05	0.31			0.26	3	0.03 (420)	0.4 (420)
	600	0.98	0.29			0.34	2	0.11 (596)	0.7 (596)
	700	0.91	0.27			0.40 (750)	1.6	0.16 (684)	0.8 (684)
D25	450	1.05	0.31			0.52	1.3	0.08 (408)	0.8 (408)
	600	0.98	0.29			0.59	1.3	0.20 (592)	0.9 (592)
	700	0.91	0.27			0.63	1.8	0.27 (684)	1.0 (684)

[a] Membrane codes defined in Table 1

[b] Certain permeances were measured at different temperatures given in parentheses

CO and CO_2 to methane) can go to the ammonia plant. The nonpermeate gas containing significant fractions of hydrogen, carbon dioxide and methane (deriving from the coal gas) is fed directly to the combined cycle power generation. The net power production in the membrane-assisted process was estimated as 44.4 MW.

For the purpose of economic evaluation it was necessary to obtain a cost estimate for the membrane. For this purpose it was assumed that each of the three membrane units consists of series-parallel combination of several thousand membrane modules. Each membrane module in turn consists of several thousand membrane capillaries sealed in parallel to an endplate and enclosed in a metal casing. The capillaries were assumed to have 0.5 mm ID, 0.7 mm OD and hydrogen permeance at 500°C of 0.1 cm^3/cm^2-min-atm in accordance with the values measured after hydrothermal treatment.

On the basis of the above parameters, the membrane area required by the process was calculated to be 150,000 m^2, or 19.3 tons of capillaries. The cost of the membrane units is difficult to estimate because Vycor tubes below 5 mm ID are not produced commercially. However, some very crude estimates made by Corning Inc. placed the cost at 300-600 dollars per pound. Using the figure of $500/lb and including some additional cost for the CVD treatment and the fabrication of modules and larger units, we arrived at a cost of about $24 million for the membrane units. Compared to this membrane cost, the conventional process has only $6 million for the PSA unit. All other equipment are the same for both processes. Thus, the membrane-assisted process has 24 – 6 = $18 million extra cost while producing 7.8 MW extra power. With the price of power between 2 ct and 5 ct per kWhr, the extra power would generate $1.36 million to $3.4 million annually. With these figures the extra cost for the membrane would require 5 to 13 years to be recovered, which is too long.

The membrane process would become competitive if the hydrogen permeance could be increased by a factor of 3 to (0.3 cm^3/cm^2-min-atm) so that the extra membrane cost would be reduced to 8 – 6 = $2 million and the recovery period to 0.6-1.5 years. The above estimates are subject to considerable uncertainty due to the lack of reliable costs for the individual membrane capillaries and the fabrication of membrane modules. Further work is clearly indicated on increasing membrane permeance, developing techniques for making multi-tube modules, and generating reliable cost estimates for tubes and modules.

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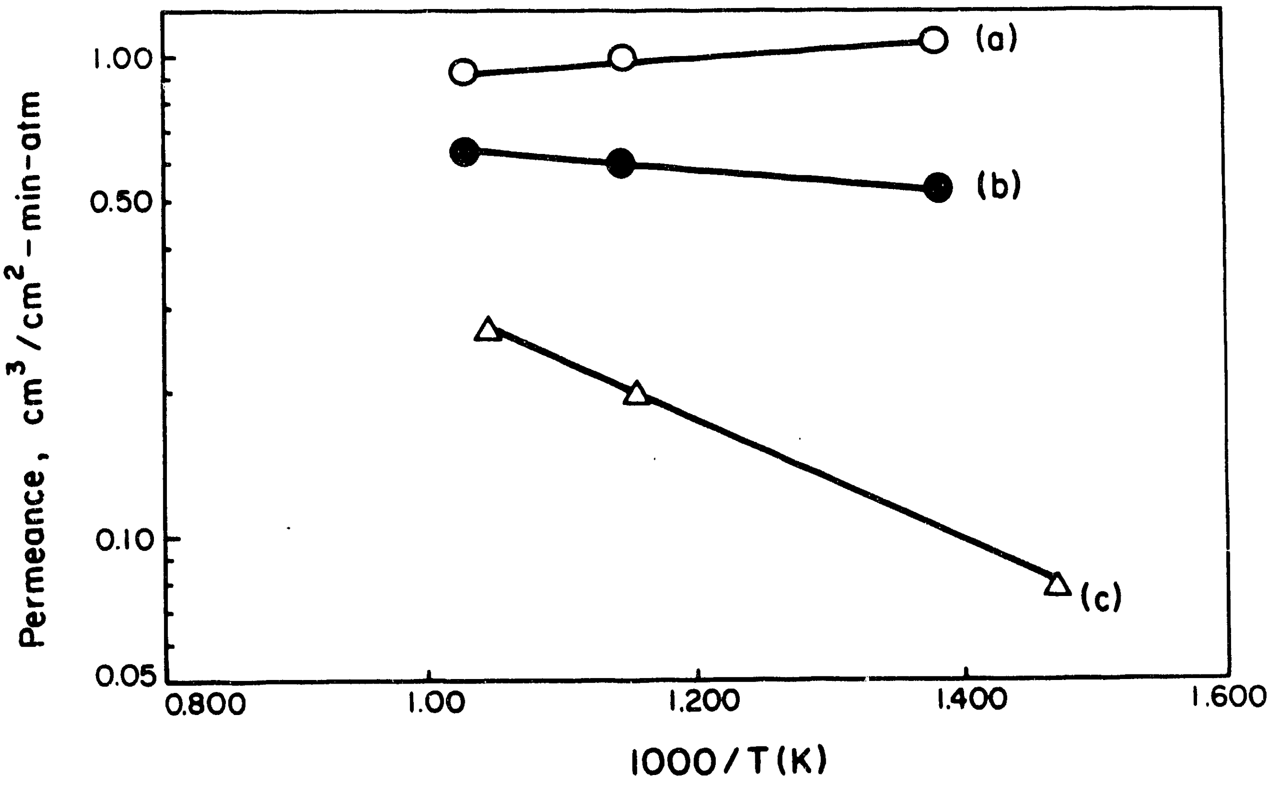

Figure 1. Arrhenius Diagram of the Permeance of a SiO_2 Membrane (a) before Deposition, (b) After Deposition, and (c) After 13 Days at 550°C, 3 atm H_2O

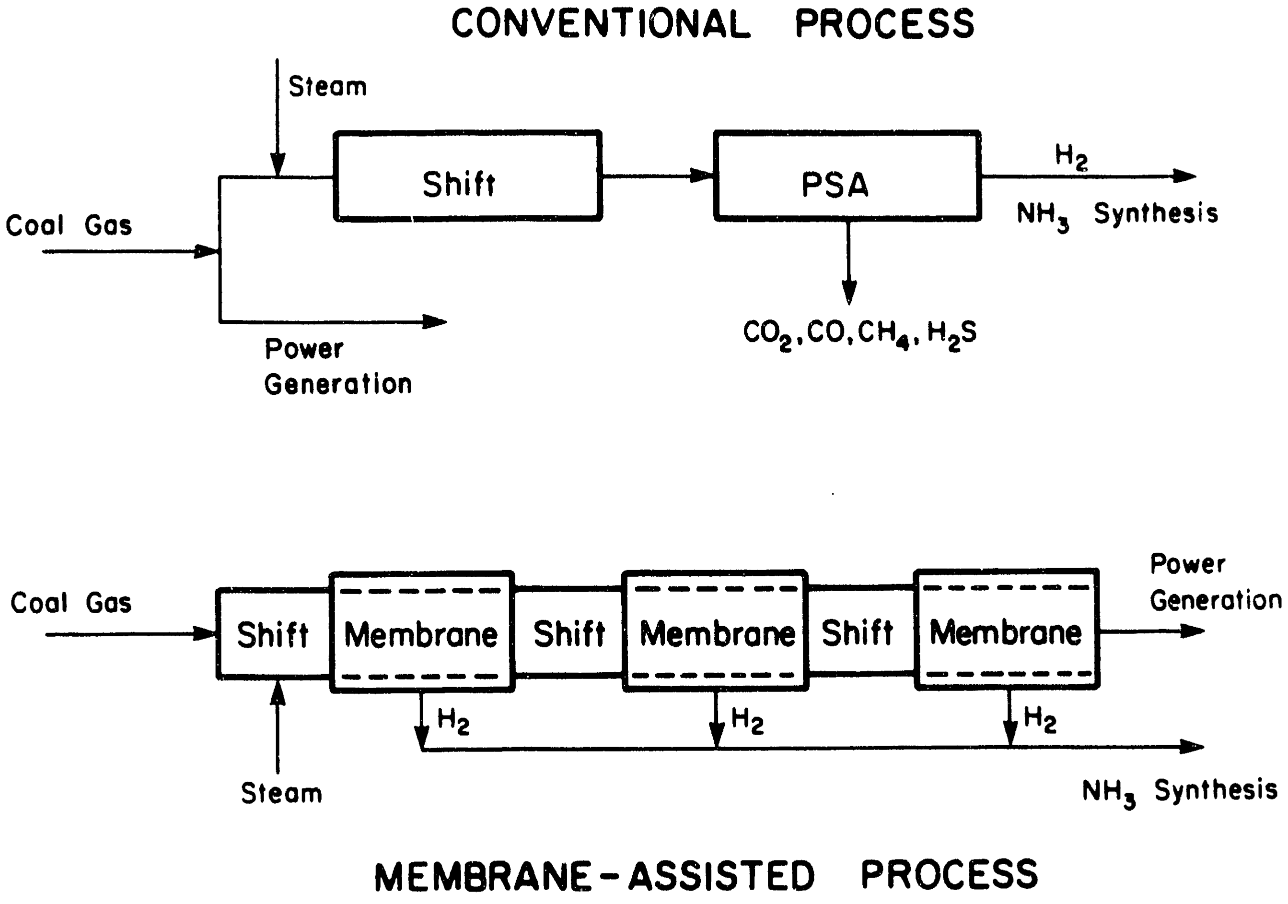

Figure 2. Schematic Block Diagram of a Conventional (top) and a Membrane-Assisted Process for Ammnia Production from Coal

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