

Ceramic Membranes for Hydrogen Production from Coal

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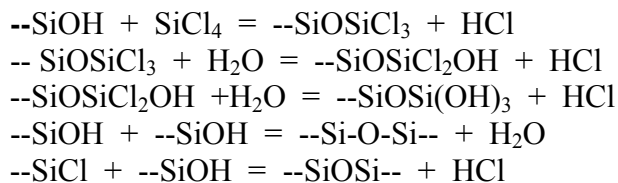
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The objective of this project is to develop ceramic membranes for hydrogen separation from coal gas or other fuel gas during or immediately after the steam reforming step. The membrane considered in this project is dense silica coated on a porous support by chemical vapor deposition (CVD). At elevated temperatures dense silica is highly selective to hydrogen but its permeability is low. An effective membrane must, therefore, be very thin, on the order of 0.1 μm or less which is possible only if the support has predominantly pores below about 5 nm in diameter. The support elements used in the experiments were MFI zeolite (ZSM-5 or Silicalite) films grown on $\alpha\text{-Al}_2\text{O}_3$ tubes of mean pore size 1 μm and wall thickness 0.6 mm. The role of the zeolite in this case is to narrow down the pore size of the support from 1 μm to below 5 nm. Although the MFI zeolite pores are only 0.55 nm in diameter, zeolite membranes also contain nonzeolitic pores of nm size at the intercrystalline boundaries. Membrane preparation, therefore, consists of two major steps: growth of a zeolite layer on $\alpha\text{-Al}_2\text{O}_3$ and CVD of silica on the zeolite layer.

The MFI zeolite layer was deposited by the usual hydrothermal route. Conditions of relatively low solution alkalinity were used to favor zeolite layers of high gas permeance. In some preparations, the $\alpha\text{-Al}_2\text{O}_3$ supports were pretreated by impregnation with a colloidal suspension of 0.1 μm MFI particles made in a separate hydrothermal reaction. The impregnation was repeated once (with an intermediate drying) to reach a weight gain of about 0.2% of the alumina support. Zeolite growth on the seeded supports was conducted by holding the support tubes in a clear solution of composition SiO_2 : 0.1TPAOH: 0.2NaOH: 98H₂O at 95°C for 20 hours. The seeding pretreatment on the internal pore surface and the relatively low reaction temperature results in zeolite growth inside the pores of the support in a region about 20 μm below the surface as determined by SEM-EDS of the tube cross section. Alternatively, unseeded $\alpha\text{-Al}_2\text{O}_3$ tubes of 0.15 μm mean pore diameter were treated in the same solution at 150°C for only 4 hours. Under these conditions the zeolite grew on the external surface of the support although some internal growth was also observed. In either case two or three growth periods were needed to obtain a gas-tight layer. The tubes were subsequently heated in air to a final temperature of 500°C at a heating rate 5-10°C to decompose and burn out the organic template (TPA+) occluding zeolitic and small nonzeolitic pores. The quality of the MFI/alumina composites was evaluated by gas permeation measurements and by nitrogen adsorption. Single gas permeation measurements were carried out by the pressure rise technique while mixture measurements were carried out by a flow technique using a sweep gas. In the latter case the permeate gas was analyzed by gas chromatography. Single gas measurements gave the following permeances (permeance is transmembrane flux normalized by the corresponding partial pressure difference) in MPU (1MPU= 10^{-8} mol/m²-s-Pa) at 150°C: about 40 for n-butane, 30 for H₂ and CO₂, 17 for N₂, and 0.5 for isobutane. These numbers indicate that transport is controlled by a combination of adsorption and molecular sieving.

The second step in membrane preparation was deposition of silica on the MFI layer. In previous work in our laboratory silica deposition was carried out by a series of cycles each of which consisted of 1 minute exposure to SiCl_4 followed by 1 minute exposure to H_2O with evacuation after each exposure. These two half-reactions take place via OH groups (silanols) that are continuously regenerated on the surface of silica:



where -- represents three bonds with one of the following entities: OH, OSi, or Cl.

The above reactions can take place at a temperature as low as 50°C in the presence of a base like ammonia or pyridine, which binds HCl and suppresses the reverse reactions. However, our initial experiments showed that the silica deposited at $50\text{--}90^\circ\text{C}$ was thermally unstable and collapsed when heated at 400°C . Hence, the bulk of the CVD experiments were carried out at $450\text{--}500^\circ\text{C}$. Every 5 cycles the progress of deposition was monitored by permeation measurements at 150°C with several gases using the pressure rise technique. It was found that the permeance of hydrogen declines very slowly, while the permeance nitrogen declines faster such that after about 25 reaction cycles the single gas selectivity of hydrogen over nitrogen increased from about 2 to about 80. At that point the permeance of hydrogen was about 8 MPU and that of CO_2 was 0.8 MPU. During the same time the permeance of n-butane had decreased by a factor of over 1000 from 40 MPU to 0.02 MPU while that of isobutane declined from 0.5 MPU to 0.03 MPU.

The permeation results summarized above suggest that transport prior to deposition proceeded through two pathways: zeolitic channels responsible for the bulk of the flux of H_2 , N_2 , and n-butane, and nonzeolitic pores between the crystals. The second route is responsible for the flux of isobutane and larger molecules before deposition, and for the residual flux of nitrogen after deposition. After 25 cycles of deposition the zeolitic channels were blocked to all gases except hydrogen and, to a smaller extent, CO_2 . The flux of nitrogen and butanes took place through the larger pathways between the crystals. Some of these pathways are in the range of tens of nanometers since they were not blocked after 25 reaction cycles. Measurements of the nitrogen adsorption isotherm at 77 K revealed a substantial change at very low relative pressures (below 10^{-4}) suggesting that silica CVD modified the internal zeolitic channels. It is concluded that the changes in the flux of H_2 , N_2 , and CO_2 are due to a narrowing of the zeolitic channels rather than to the formation of an external silica layer which after 25 cycles was estimated to be on the order of only 2 nm.