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H_2 Separation Using Defect-Free, Inorganic Composite Membranes

Miao Yu,* Hans H. Funke, Richard D. Noble, and John L. Falconer

Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309-0424, United States

S Supporting Information

ABSTRACT: Defect-free, microporous Al_2O_3/SAPO-34 zeolite composite membranes were prepared by coating hydrothermally grown zeolite membranes with microporous alumina using molecular layer deposition. These inorganic composite membranes are highly efficient for H_2 separation: their highest H_2/N_2 mixture selectivity was 1040, in contrast with selectivities of 8 for SAPO-34 membranes. The composite membranes were selective for H_2 for temperatures up to at least 473 K and feed pressures up to at least 1.5 MPa; at 473 K and 1.5 MPa, the H_2/N_2 separation selectivity was 750. The H_2/CO_2 separation selectivity was lower than the H_2/N_2 selectivity and decreased slightly with increasing pressure; the selectivity was 20 at 473 K and 1.5 MPa. The high H_2 selectivity resulted either because most of the pores in the Al_2O_3 layer were slightly smaller than 0.36 nm (the kinetic diameter of N_2) or because the Al_2O_3 layer slightly narrowed the SAPO-34 pore entrance. These composite membranes may represent a new class of inorganic membranes for gas separation.

Zeolite membranes have been studied for separations[1−6] because of their molecular-sized pores, adsorption properties, and high thermal and chemical stabilities. Their ability to separate mixtures depends on the size and number of defects, which are intercrystalline pathways in these polycrystalline membranes that are larger than the zeolite pores and thus typically nonselective. Various post-treatment methods[7−9] to eliminate or reduce these defects in order to improve separation selectivities have been investigated. Although the separation performance was improved to some extent after these treatments, a large flux drop was typically seen because the sealing materials were not selectively deposited in nanometer-sized defects.

Molecular layer deposition (MLD)[10−12] is a technique that can form ultrathin, conformal coatings of inorganic−organic hybrid materials on a variety of substrates. The layers are produced by sequentially conducting a series of half-reactions on the surface. Each set of half-reactions deposits a layer that conforms to the surface, and multiple cycles yield a layer of desired thickness. The film thickness is controlled at the subnanometer level because each half reaction is self-limiting. This technique has been used to form ultrathin, hybrid aluminum alkoxide (alucone) films on nonporous silica nanoparticles using alternating reactions of trimethylaluminium (TMA) and ethylene glycol (EG).[13] The dense hybrid layers can be subsequently converted into porous inorganic coatings by removing the organic component. Two previous studies have used MLD to deposit thin porous oxide layers for separations. Jiang et al.[14] deposited sub-10 nm thick organic/inorganic dense membranes on the surface of a nanoporous support by plasma-defined atomic layer deposition, which is essentially the same as MLD, on a mesoporous support. They used UV/ozone exposure to remove the bridging organic template to open the pores. After 200 deposition cycles, their membranes had He/N_2 ideal selectivities greater than 1000 at room temperature. They reported separations only at room temperature, however, and indicated that changes in the preparation were needed for use at higher temperatures. Liang et al.[13] deposited a 45 nm thick, dense alucone layer on a 5 nm γ-alumina support using 150 MLD cycles at 373 K. Pores were formed in the dense MLD layer by both water vapor etching at room temperature and calcination at 673 K in air. However, the H_2/N_2 and H_2/CO_2 ideal selectivities were similar to Knudsen selectivities at 295 K, and the H_2 permeance was 1.3×10^{-8} mol m^{-2} s^{-1} Pa^{-1} after 20 h of water etching, which was almost 3 orders of magnitude lower than the permeance of the original support.

In the current study, MLD was used to deposit aluminum alkoxide on and between hydrothermally synthesized SAPO-34 crystals in the polycrystalline membrane layer, as shown schematically in Figure 1a. Subsequent oxidation formed a microporous Al_2O_3/SAPO-34 composite membrane with pores that were ∼0.36 nm, as indicated by single-gas permeation measurements (Figure S1 in the Supporting Information); the H_2/propane ideal selectivity increased from 52 (before MLD) to 925 (after MLD). A focused ion beam (FIB) scanning electron microscopy (SEM) image of the cross section of a SAPO-34 membrane coated with an MLD layer after oxidation (Figure 1b) showed a uniform and continuous MLD coating (∼10 nm thick) on the SAPO-34 zeolite surface. This thickness is similar to that from previous alucone MLD growth rates.[13] The surface of the MLD membrane was first coated with a 15−20 nm thick Au/Pd layer by sputtering to improve the surface conductivity. Next, a protective Pt layer (∼200 nm thick) was deposited to facilitate FIB cutting to obtain a sharp edge without destroying the multilayer structure. The slightly smaller pores in the composite membranes in comparison with the SAPO-34 crystal pores (0.38 nm) had a dramatic effect on the membrane separations. These membranes separated H_2 from N_2 and CO_2 over a range of temperatures and at high feed pressures, whereas SAPO-34 membranes had low selectivities for these separations.

Two SAPO-34 membranes (M1 and M2), with CO_2/CH_4 separation selectivities of 75 and 69, respectively, at 295 K with a 4.6 MPa pressure drop, were used to prepare the composite membranes in this study. They were synthesized using the same autothermal procedure, but membrane M1 was calcined in air and membrane M2 was heated in vacuum at 673 K for 4 h (see

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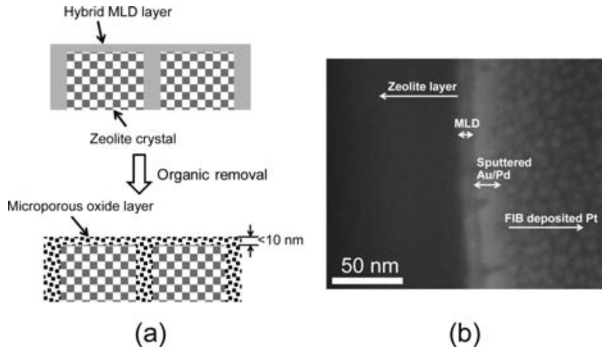

Figure 1. (a) Schematic illustration of the inorganic composite membrane preparation process. The hybrid material is first deposited on and between zeolite crystals, and subsequent removal of the organic component generates a porous composite membrane. (b) FIB SEM image showing a cross section of a SAPO-34 zeolite layer coated with an MLD layer.

the Supporting Information for details) to remove the structure-directing templates. Their H_2/N_2 separation selectivities increased from 4 to 11 as the temperature increased from 295 to 473 K (Figure S2a,b). Their H_2 permeances were almost constant over this temperature range, but the N_2 permeances decreased significantly as the temperature increased. The composite membranes prepared from these two SAPO-34 membranes had much higher H_2/N_2 separation selectivities (Figure S2c,d). The maximum H_2/N_2 selectivities for a feed pressure of 0.33 MPa obtained between 390 and 400 K were 580 and 315 for composite membranes M1 and M2, respectively.

The composite membranes were selective for H_2 at feed pressures of up to 1.5 MPa, the highest pressure possible in the permeation system. The permeances and selectivities had similar pressure dependences at 398 and 473 K, as shown in Figure 2 for membrane M1. The H_2 permeances did not change much as the feed pressure increased, and the H_2/N_2 separation selectivities had maxima at feed pressures of ~1 MPa. The maximum selectivities were 1040 at 398 K and 970 at 473 K. The selectivities increased as the feed pressure increased from 0.4 to ~1.0 MPa because both the N_2 and H_2 permeances decreased but the N_2 permeances decreased faster. The selectivities decreased at higher feed pressures, as the N_2 permeances increased while the H_2 permeances remained constant. The N_2 permeances were dominated by flow through micropores and viscous flow through defects, but these pathways make a negligible contribution to the total H_2 flux.

The composite membranes also had higher H_2/CO_2 separation selectivities at elevated temperature and high pressure. Previous studies[15,16] showed that the H_2/CO_2 separation selectivities of SAPO-34 membranes were only ~2 at 473 K with a 0.14 MPa pressure drop. The H_2/CO_2 separation selectivity for membrane M1 at 473 K and a feed pressure of 0.35 MPa was only 1.3. The H_2/CO_2 separation selectivity at 473 K for composite membrane M1 was 23 at 0.35 MPa and 20 at 1.5 MPa (Figure 3). The H_2 permeance decreased as the feed pressure increased, but the CO_2 permeance did not change. The constant CO_2 permeance as the pressure increased could be due to its weak adsorption in the microporous MLD layer at 473 K, causing the CO_2 adsorption to be in the Henry's regime. The H_2 permeance may have decreased because additional CO_2 adsorption at the higher pressure blocked some of the H_2 permeation. In contrast, N_2 had a negligible effect on H_2 permeance even at high pressure (Figure 2). This may be because N_2 could not enter most of the pores in the MLD layer.

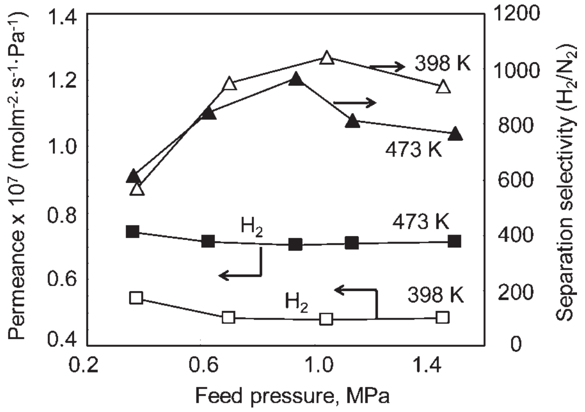

Figure 2. Permeance and separation selectivity of a 50/50 H_2/N_2 mixture as a function of feed pressure for composite membrane M1 (permeate pressure = 84 kPa).

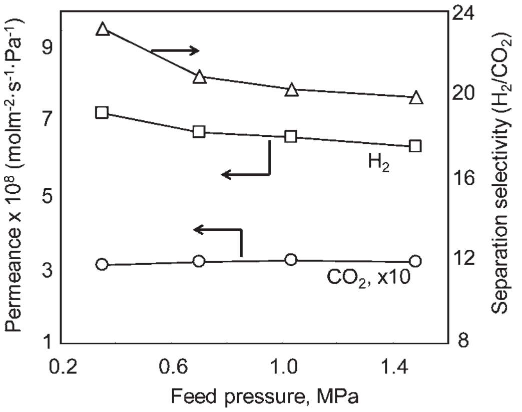

Figure 3. Permeance and separation selectivity of a H_2/CO_2 mixture at 473 K as a function of feed pressure for composite membrane M1 (permeate pressure = 84 kPa).

Small-pore zeolite membranes have been studied for H_2 separation, but the separation selectivities were found to be low.[17−19] Zeolite A membranes had H_2/N_2 separation selectivities of 4.8 between 308 and 398 K, with H_2 permeances from 10^{-8} to 10^{-7} mol m^{-2} s^{-1} Pa^{-1};[17] after ion exchange, the highest H_2/N_2 separation selectivity was 9.9 for KA zeolite membranes.[18] The selectivities were not high in these membranes, even though the zeolite A pores are only 0.3 nm, because these membranes had nanometer-sized defects. Guan et al.[20] measured H_2/N_2 and H_2/CO_2 separation selectivities of 6 and 9.7, respectively, at 308 K for $AlPO_4$-5 membranes. van den Bergh et al.,[21] using DDR zeolite membranes, reported H_2/isobuyltene separation selectivities of ~400 from 303 to 673 K, but the highest H_2/N_2 and H_2/CO_2 separation selectivities were ~10 and 2, respectively at 673 K.

Microporous silica membranes prepared by sol−gel or chemical vapor deposition (CVD) were selective for high-temperature H_2 separation,[22−24] and more recent membranes had high selectivities and permeances at lower temperatures. Ohta et al.[25] controlled the pore sizes in silica membranes using different CVD precursors. Silica membranes prepared from dimethoxydiphenylsilane had the highest H_2 permeance (1.5×10^{-6} mol/(m^2·s·Pa)), but their H_2/N_2 ideal selectivities were only about

150 at 573 K; in contrast, those prepared from phenyltrimethoxysilane had H_2 permeances of 2×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and the highest H_2/N_2 ideal selectivity was ~1000 at 573 K. Gopalakrishnan et al.[26] obtained pure H_2 permeances of 5.1–7.0 × 10^{-7} mol m^{-2} s^{-1} Pa^{-1} for silica membranes prepared by CVD over the temperature rage 373–673 K. Their membranes had H_2/N_2 and H_2/CO_2 separation selectivities of 57 and 36, respectively, at 673 K. The sol–gel method can control the pore size of silica membranes, and H_2 permeances from 1×10^{-7} to 1×10^{-6} mol m^{-2} s^{-1} Pa^{-1} have been reported with H_2/N_2 separation selectivities of ~100 at 473 K.[27,28]

At 473 K, the H_2 separation selectivities at 1.5 MPa in the MLD-modified SAPO-34 membranes were similar to those of high-quality silica membranes at low pressure.[25] Higher pressure drops are expected to the decrease separation performance of silica membranes because viscous flow permeation through nonselective defects increases with the pressure drop. The hydrogen permeances were slightly lower than those of silica membranes with similar selectivities.[25] The properties of the MLD layers were not optimized, however, and the H_2 permeances could potentially be increased significantly by using supports with higher fluxes, optimizing the MLD layer oxidation, and depositing thinner layers. In addition, MLD could be used to prepare ultrathin membranes with other chemical compositions and pore sizes.

In summary, defect-free, porous Al_2O_3/SAPO-34 zeolite composite membranes were prepared by depositing a thin porous alumina layer onto hydrothermally grown SAPO-34 polycrystalline zeolite membranes using molecular layer deposition (MLD). These composite membranes have significantly higher H_2 separation selectivities at elevated temperature and high pressure than SAPO-34 membranes. The composite membranes have smaller pore sizes (0.36 nm) than SAPO-34 pores (0.38 nm) and negligible flow in larger pores/defects. The composite membranes have H_2/N_2 separation selectivities as high as 1040, and these membranes were H_2-selective from 298 to 473 K for pressure drops from 0.1 to 1.5 MPa. The H_2/CO_2 separation selectivities were 23 and 20 at feed pressures of 0.33 and 1.48 MPa, respectively, at 473 K. The separation performance of these composite membranes could likely be improved by modifying the MLD growth conditions and organic oxidation conditions. These porous oxide/zeolite composite membranes may represent a new class of gas-separation membranes.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental methods, single-gas permeation, mixture separation at low pressure, and comparison of inorganic composite membranes with polymer membranes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

miao.yu@colorado.edu

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