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Catalysis Today 25 (1995) 209–212

CATALYSIS TODAY

Silicalite-1 zeolite composite membranes

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Abstract

This review paper discusses the preparation of silicalite-1 zeolite membranes, the experimental procedures used for gas separation measurements and the results of single gas and gas mixture experiments. Silicalite–alumina composite membranes were prepared by an in-situ zeolite synthesis method using an alumina membrane tube with a 5-nm-pore-diameter, γ-alumina layer as a substrate. Single gas permeances of H_2, Ar, n-C_4H_{10}, i-C_4H_{10} and SF_6 were measured and mixtures of H_2/i-C_4H_{10} and H_2/SF_6 were separated to characterize the silicalite membrane. These measurements were made from 300 to 737 K. Transport through the silicalite membrane appeared to be controlled by molecular size and adsorption properties. Permeances of all components studied were activated, and activation energies ranged from 8.5 to 16.2 kJ/mol. The ratio of single gas permeances was as high as 136 for H_2/SF_6 and 1100 for H_2/i-C_4H_{10} at 298 K. Separation selectivities at elevated temperatures were significantly above Knudsen diffusion selectivity and were larger than ratios of pure gas permeances at the same temperature. The largest permeance ratio for the separation of mixtures was 12.8 for H_2/SF_6 at 583 K. Separation selectivities were higher when a pressure drop was maintained across the membrane than when an inert sweep gas was used because of counter diffusion of the sweep gas.

1. Introduction

Because of their unique thermal, structural, and chemical stabilities, inorganic membranes have found potential applications in high temperature and high pressure separation, filtration, and catalytic membrane reactors [1–6]. Inorganic membranes can be divided into two categories: porous inorganic membranes and dense counterparts. Porous membranes, such as microporous silica glass and alumina, have high permeances, but relatively low separation selectivities that are usually limited by Knudsen diffusion. Dense membranes, such as palladium alloys and dense silica, show the opposite characteristics: high selectivities, but low permeances. In recent years, improvements have been made to develop high permeability and high selectivity microporous membranes [5–7]. Continuous separations have also been reported for zeolite membranes [8–14], which have the potential to exhibit both high separation selectivities and high permeances. The zeolite pores, which are of molecular dimensions, allow the possibility of separating molecules based on their size.

Bakker et al. [13] synthesized a 50-μm thick, continuous layer of silicalite-1, a Si-rich ZSM-5 zeolite, on a porous, sintered, stainless steel substrate. They observed more than two orders of magnitude difference in steady-state permeation rates at room temperature for the gases studied. Increasing the temperature increased the permeability for most of the gases studied. At room temperature, permeation of weakly adsorbing molecules such as mixtures was governed mainly by differences in adsorption strengths. Separation

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0920-5861/95/$09.50
SSDI 0920-5861(95)00109-3

selectivities greater than 100 were obtained with the strongly adsorbing molecule preferentially permeating.

We recently [14] reported the preparation of a composite membrane that consisted of a 5–10 μm continuous layer of silicalite-1 zeolite on an alumina membrane substrate. X-ray diffraction and SEM confirmed the presence of a silicalite phase. The silicalite layer decreased the N_2 permeance through the membrane by a factor of 5, but it decreased the CH_3OH permeance a factor of 190. At 373 K and pressures from 100 to 1100 kPa, CH_3OH permeated through the zeolite membrane faster than H_3 and CH_4 because CH_3OH adsorbed and blocked the pores for H_2 and CH_4 permeation. The highest separation selectivities were 190 for CH_3OH/CH_4 and 1000 for CH_3OH/H_2.

In this study [15], silicalite composite membranes were prepared by the same method described by Jia et al. [14]. Both single gas permeations and mixture gas separations were carried out to characterize the silicalite membrane. The temperature dependencies of single gas permeances through the alumina and silicalite membranes were studied. Separations of gas mixtures were performed by either maintaining a pressure drop across the membrane or using an inert sweep gas.

2. Experimental procedures

2.1. *Zeolite preparation*

Silicalite membranes were prepared by growing silicalite from a gel onto a 0.65-cm ID alumina membrane tube. The alumina membrane had a composite structure consisting of several layers of different pore sizes and thickness [5]. The tubes are available commercially from US Filter. The final inside layer was approximately 5-μm thick and had a narrow pore size distribution centered around 5-nm diameter pores. To prevent bypass during permeation measurements, the ends of the 8.5 cm long alumina tube were sealed with a glazing compound (GL 611A, Duncan), which was heat cured for 2 h at 1013 K.

A gel for synthesis of silicalite-1 was prepared according to the procedure by Grose and Flanigen [16]. The components (0.95 g NaOH, 2.1 g tetrapropylammonium bromide (TPABr), and 10 g silica (Aerosol 130, Degussa) were dissolved in 125 g of distilled water and mixed thoroughly with a magnetic stirrer. The gel was allowed to age for at least one day before it was transferred to the inside of an alumina tube. Both ends of the tube were plugged with Teflon caps and the tube was placed vertically in a Teflon-lined autoclave. The autoclave was placed in a temperature-controlled oven and the synthesis was carried out at 453 K under autogenous pressure for 12 h. The membrane was washed with distilled water after being removed from the autoclave. The procedure was repeated with the tube inverted from its previous orientation to obtain a more uniform coating. After the second synthesis, the membrane was washed with distilled water, dried at 383 K overnight, and tested for N_2 permeance. A well-synthesized membrane was impermeable before calcination because the silicalite pores were blocked by TPABr molecules. Extensive studies have shown that at least two synthesis steps were needed to obtain a nonpermeable membrane, and occasionally three synthesis steps were required.

The membrane was then calcined in air to remove TPABr from the silicalite. To avoid developing cracks in the membrane during calcination, the calcination procedure was carried out in a computer-controlled muffle furnace using the temperature ramp given in Ref. [15]. This slow heating required 3 days. The highest temperature was 738 K, where the membrane was held for 8 h. After cooling, the membranes were stored at 373 K to avoid water adsorption in the pores.

2.2. *Permeation measurements*

A stainless steel flow system was used for both single gas permeation and binary gas separation measurements. Gas flow rates were controlled by Tylan mass flow controllers. For measurements at elevated temperatures, the gases were preheated and fed into a stainless steel module, where the membranes were mounted. This module has gas inlets and outlets for both the tube and shell sides of the membranes. Single gases or gas mixtures were fed to the tube side of the membrane. Gaskets were used to seal the tube and shell sides from each other and to seal the membrane in the module from the outside. Graphite strings were wrapped around the tube to serve as gaskets for experiments to 723 K. Silicone O-rings were used for experiments to 623 K since they were easier to seal without damaging the membrane. The silicone was limited to 643 K, however. The module was heated by high-temperature heating tapes and insulated so that temperature measurements from four thermocouples located at different positions were within 2 K of each other. Further details are in Ref. [15].

3. Results

3.1. Single gas permeation

The data for the results described below is given in Ref. [15]. The addition of a silicalite zeolite layer onto the alumina substrate decreased the permeances of all gases studied compared to the alumina support. At room temperature, the H_2 and Ar permeances in the zeolite membrane were 13–14% of those for the alumina membrane. The permeance of SF_6 decreased a factor of 170, and that of n-C_4H_{10} decreased a factor of 270. The permeance of i-C_4H_{10}, however, was a factor of about 6000 lower through the silicalite layer, and the n-C_4H_{10}/i-C_4H_{10} permeance ratio was 22 at room temperature.

Permeances in the silicalite membrane showed a complicated dependence on temperature. Below 400 K, the H_2 and Ar permeances decreased as temperature increased and above 400 K these permeances increased. Permeances for the other gases were activated at all temperatures and they increased faster with temperature than H_2 and Ar. Thus, the ratios of pure gas permeances changed significantly with temperature. Whereas the H_2 permeance approximately doubled from 298 to 583 K, the SF_6 permeance increased a factor of 27 and i-C_4H_{10} permeance increased a factor of almost 450 over the same temperature range. Even though the plots of permeation versus temperature were not exponential over the entire temperature range, they were fit reasonably well by Arrhenius plots. The deviations were mostly for SF_6 and i-C_4H_{10} at low temperatures.

3.2. Gas mixture separations

Separation selectivities for the silicalite membrane were greater than Knudsen diffusion values. H_2/i-C_4H_{10} separation selectivities were 6.2–6.5 with Ar or SF_6 sweep gases; the value expected for Knudsen flow is 5.4. When Ar sweep gas was used, permeances of H_2 and i-C_4H_{10} were only 16–23% of the pure gas permeances. Moreover, when SF_6 was used as a sweep gas, permeances were almost a factor of 3 lower than when Ar was used, though the separation selectivity was essentially the same. Ar and SF_6 were used as sweep gases since they are inert and could also be used as molecular probes of the silicalite membrane.

Separation selectivities were almost twice as high when a pressure drop across the silicalite membrane was used instead of a sweep gas. Moreover, the H_2 permeances were similar to the pure gas permeances at the same temperature. The i-C_4H_{10} permeances did not increase as rapidly with temperature during the separation experiments as they did for the single gas measurements. At 583 K, the i-C_4H_{10} permeance in the mixture was only 30% of the single gas permeance. Thus, the separation selectivities increased slightly as temperature increased, and the highest separation selectivity of 12.8 was obtained at 583 K.

The selectivities were lower with the sweep gas present due to the counter diffusion of the sweep gas. Collisions of the sweep gas with the larger feed gas molecule are favored which will slow it relative to the smaller feed gas molecule. This is why the permeances of the feed gases were lower when SF_6 was used.

4. Conclusions

A continuous, silicalite zeolite membrane was synthesized as a thin layer on an alumina membrane. Transport through the silicalite membrane was controlled by molecular size and adsorption properties, as expected for a zeolite membrane, indicating the defect concentration was low. Transport of all gases was activated, with activation energies of 8.5–16.2 kJ/mol. Single gas permeances differed by as much as three orders of magnitude for different gases. Separation factors for binary mixtures at elevated temperature were similar to or larger than ratios of pure gas permeances. Higher separation factors were obtained with a pressure drop across the membrane than when a sweep gas was used; counter diffusion of the sweep gas significantly decreased gas permeances. The alumina membrane itself exhibited permeances expected for Knudsen or Knudsen plus surface diffusion.

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