

DEFECT-FREE ZEOLITE THIN FILM MEMBRANES FOR H₂ SEPARATION

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Introduction

Much effort has recently been devoted to the synthesis of inorganic zeolite membranes because of their potential applications in the domains of gas separation, pervaporation, reverse osmosis or in the development of chemical sensors and catalytic membranes.^{1,2,3,4,5} Specifically, development of new technologies for H₂ separation and purification has a high priority for the future of H₂ as a fuel source. H₂ is commonly produced by the reformation of hydrocarbons and must be purified. Zeolite membranes in particular combine pore size and shape selectivity with the inherent mechanical, thermal, and chemical stability necessary for long term separations.

The effective pore size distribution of the zeolite membrane, and hence its separation performance, is intrinsically governed by the choice of the zeolitic phase.^{6,7,8,9} This applies when molecular size exclusion sieving is dominant and no other diffusion pathways bypass the network of well defined zeolitic channels; otherwise viscous flow through grain boundaries prevails. Zeolite membranes are typically synthesized on porous substrates by two different methods,¹⁰: one step hydrothermal reaction on a pristine substrate from an aluminosilicate gel or by seed-promoted hydrothermal crystallization of the zeolitic layer. In both cases, the synthesis is affected by many complex interrelated factors such as the overall composition, concentration and viscosity of the gel, its pH, the source of silica and its degree of polymerization, the temperature and duration of the reaction. The optimization of these parameters is crucial to obtaining reliably "defect free" membranes. We report here on the synthesis of ZSM-5 and silicalite membranes¹¹ on porous alumina disk supports, their characterization and their permeation performance for pure He, SF₆, H₂, CO₂, O₂, CH₄, N₂, and CO gases. We also show the reproducibility of the permeation values and the durability of a number of these films.

Experimental

Gases: Reagent grade pure gases were purchased from Trigas. H₂, CO₂, O₂, CH₄, N₂, CO were used to test the permeation of the membranes for reforming gases. SF₆ was used to detect defects, He was used to purge and clean the unit.

Permeation Measurements: The membrane permeations were measured at room temperature using pure gases and a constant trans-membrane pressure of 16 PSI controlled by a backpressure regulator. The membrane was sealed in a Swagelok fitting using Viton O-rings. The gas flow through the membrane was measured using an acoustic displacement flowmeter (ADM 2000 from J&W) and a digital bubble flowmeter (HP-9301). Between permeation measurements with different pure gases (SF₆, H₂, CO₂, O₂, CH₄, N₂, CO), the whole system is purged, flushed with Helium and evacuated several times. The ideal gas selectivity was calculated as the ratio of the permeances in the steady regime.

Characterization Techniques: The zeolite membranes and seeds were characterized by X-ray diffraction (Siemens D500 diffractometer, Cu K α radiation, Bragg-Brentano geometry) and by Scanning Electron Microscopy (JEOL-6300V equipped with a Link Gem Oxford 6699 EDAX attachment).

Membrane Synthesis: In this work, the growth of both the ZSM-5 and silicalite (Al-free ZSM-5) membrane on the porous

support is achieved by hydrothermal synthesis on supports seeded by rubbing.

The α -alumina substrates supplied by Inocerme Gmbh have a 1.8 micron average pore size, a diameter of 13 mm and a thickness of 1mm. The alumina substrates were first cleaned ultrasonically in acetone, rinsed in DI water and calcined at 1000°C overnight to remove any contaminants. All membranes in this work were obtained using seeded substrates to promote the nucleation and growth of the zeolite layer.

Tetra Propyl Ammonium (TPA) templated silicalite seeds were prepared under mild hydrothermal conditions in order to limit the size of the crystallites.¹² A rubbing method of seeding was used. The seeded alumina substrates were then heated in air to 500°C for 6 hours, and then cooled to room temperature using a ramp rate of 4°C/min to remove the TPA template and attach the seeds to the substrate. They were then stored in a desiccator for later use.

The difference in zeolite type resulted from the type of gel used for the hydrothermal synthesis. For ZSM-5, water, sodium hydroxide and alumina sulfate were mixed together and stirred until all reactants dissolved. Ludox-30 (Aldrich) was added to the mixture, which was then aged hours at room temperature for 24 hours. For Silicalite, the silicon source for the membrane synthesis is colloidal silica Ludox SM-30 (Aldrich); the organic template used is Tetra Propyl Ammonium (TPA) from TPAOH and TPABr (both from Alfa Aesar), and NaOH is the alkalinity source. Each gel was aged while being stirred at room temperature for 24 hours.

The seeded substrates were held vertically in the Teflon lined Parr reactor using Teflon holders to prevent sedimentation on top of the membrane. The homogenous gel was then poured in the reactor until the membrane was fully immersed. The hydrothermal syntheses were carried out in Parr reactors with a 23ml Teflon liner at temperature ranging from 160°C to 180°C and reaction time from 12 hours to 48 hours.

After synthesis, the membrane was washed with DI water and dried in air at 50°C for few hours. A permeation test on the as synthesized membrane allows the rapid assessment of its quality before the time-consuming calcination step. At that stage, a good quality membrane should be gas-tight, or impermeable, for SF₆. The SF₆ kinetic diameter of 5.5 Å is slightly larger than the pores of the ZSM-5 zeolite (minimum diameter 5.1 Å) thus SF₆ diffusion indicates the presence of membrane defects.¹³ Any existing defects (partial coverage of the substrate and micro-cracks) can be repaired by a second hydrothermal synthesis step, using a shorter reaction time and more diluted starting gel. These modifications to the original synthesis parameters help to avoid the growth of columnar zeolite crystals (or agglomerates of crystals) on top of the first layer, as they would not contribute to the plugging of the existing cracks or voids in the film. The silicalite membranes presented here were gas-tight prior to calcination and did not require a second hydrothermal treatment.

Once the adequacy of the membrane was established, the organic template was removed from the membrane pores by calcination in air. The calcined membranes are whitish in color, indicating that no carbon deposit is present on the surface.

Results and Discussion

Examination of the membranes by SEM showed dense coverage of zeolite crystals on the alumina support. The thickness of the crystalline layer is on average 10 microns and was found to be fairly uniform throughout the individual membranes. Selectivity values are listed in Tables 1 and 2.

ZSM-5: For H₂ purification, ZSM-5 membranes were synthesized on flat α -alumina disks. They were tested for selectivities toward the pure gases. Much as expected, the permeation preferences were dictated by size selectivity; He > H₂ > CO₂ > O₂ > N₂ > CO > CH₄. In particular, these membranes have separations of H₂/N₂ \geq 61, H₂/CO₂ \geq 80, H₂/CH₄ = 7, CH₄/CO₂ \geq 11. Although these membranes required additional secondary growth procedures to produce a “defect-free” membrane, the flux through the films was extremely high, on the order of 10⁻⁶ mole/(m²Pa sec).

Investigation of the performance and longevity at room temperature of the ZSM-5 membranes showed a moderate decrease over time. After more than 60 hours of continuous measurement under H₂, the flow rate was about 85% of its peak flow value. Calcination to 500°C restores the ZSM-5 membrane to its original flow value. Most likely, water vapor that was not removed from the permeation unit during the He gas purge and evacuation step is responsible for this decrease in flow. Longevity tests continue with other pure gases as well as industrially important mixed gases.

Silicalite: An interesting feature of these membranes is that the permeance with CO₂ is higher than that of any other gas tested, including He or H₂, even though the kinetic diameter of CO₂ is significantly larger than that of He or H₂. This property is observed reproducibly for every silicalite membrane synthesized and tested in our lab. As the CO₂ to air permeance ratios we observed are between 2 and 3, and CO permeances up to 6x10⁻⁷ [mole/m² s Pa] our membranes could at room temperature separate CO₂ from air. The higher permeance of CO₂ than other gases is likely due to surface diffusion of the CO₂ (coexisting with Knudsen diffusion), which has apparently a good affinity for this zeolite surface.

We tested a broad series of light gases (He, SF₆, H₂, CO₂, O₂, CH₄, N₂, and CO), targeting those associated with methane reforming for H₂ production. Results show that methane exhibits a behavior similar to that of CO₂, diffusing faster than both He and H₂, although the enhancement is less pronounced. CO does not seem to interact strongly with the membrane, with permeance values very similar to those of O₂ or N₂.

Investigation of the performance durability and longevity of the silicalite membranes showed that the permeance for CO₂ decreases slowly with time. After more than 60 hours of continuous measurement under CO₂, one of the membranes (22B) showed only about a third of the initial flow value. The non-interacting gases such as He do not show a marked reduction in permeance over time. Importantly, the membrane could be partially “regenerated” by heating it with a temperature profile similar to that employed for the initial calcinations. The gas flow increased to about half the starting values. This gradual decrease of permeance with time observed with pure gas will likely occur over a longer time scale when gas mixtures are used.

Conclusions

“Defect-free” ZSM-5 and Silicalite membranes have been grown reproducibly through experimentation with the synthetic parameters. The membranes are of uniform thickness and good quality as shown by the consistency and quality of the permeation data and the low SF₆ permeance. Although ZSM-5 and Silicalite are structurally identical (ZSM-5 has substituted aluminum into a portion of the silicon framework sites), they show remarkably different permeation properties. The permeation characteristics of silicalite membranes show an interesting preference for pure CO₂ gas, which flows through the silicalite membranes faster than He gas or H₂ gas, despite the larger kinetic diameter of CO₂. Modifications of the permeation unit to allow the use of gas mixtures at different temperatures are in progress and will allow the determination of the best regime for these membranes.

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Table 1. ZSM-5 and Silicalite Single Gas Selectivities. Trans-membrane pressure: 16 PSI.

SNL TPA/Si (Silicalite 2-sided) \approx 10⁻⁶ – 10⁻⁷ mole/(m² Pa sec)

H ₂ /N ₂ = 1.4	
H ₂ /CH ₄ = 0.625	CO ₂ /N ₂ = 4.2
He/N ₂ = 1.1	CO ₂ /O ₂ = 4.9
CH ₄ /N ₂ = 2.28	CO ₂ /H ₂ = 3.0
H ₂ /CO ₂ \geq 0.34	CO ₂ /CO = 4.2
H ₂ /O ₂ = 1.7	CO ₂ /CH ₄ = 1.8
CH ₄ /CO ₂ = 0.54	
H ₂ /CO = 1.43	

SNL Na/Al/Si (ZSM-5 2-sided) Knudsen Selectivity Lit. (values for Al/Si) \approx 10⁻⁶ mole/(m² Pa sec) \approx 10⁻⁷-10⁻¹⁰ mole/(m²Pa*s)

H ₂ /N ₂ \geq 61	H ₂ /N ₂ = 3.73	H ₂ /N ₂ = 3.91
H ₂ /CH ₄ = 7	N ₂ /CO ₂ = 1.00	N ₂ /CO ₂ = 0.625
He/N ₂ \geq 7	He/N ₂ = 2.64	H ₂ /N ₂ = 100; 150°C
CH ₄ /N ₂ \geq 1.4	CH ₄ /N ₂ = 1.32	10 ⁻¹⁰ perm.
H ₂ /CO ₂ \geq 80		
H ₂ /O ₂ \geq 11		
CH ₄ /CO ₂ \geq 11		

Table 2. Silicalite Single Gas Permeance (10⁻⁷ mole/ m² s Pa). Trans-membrane pressure: 16 PSI.

Gas / (Kinetic \varnothing (Å)) Membrane	He (2.6)	SF ₆ (5.5)	H ₂ (2.8)	CO ₂ (3.3)	O ₂ (3.5)	CH ₄ (3.8)	N ₂ (3.6)	CO (3.7)
18A	1.8	<0.05	2.4	2.9	1.4	-	-	1.6
21A	1.2	<0.04	1.6	3.0	1.3	1.7	1.1	-
22A	1.5	<0.02	2.0	5.9	1.2	3.2	1.4	1.4
22B	1.5	<0.03	2.9	4.9	-	-	-	-
22B regenerated	1.1	-	1.4	2.9	-	-	-	-
28A	0.8	<0.03	1.9	5.1	1.3	2.6	1.6	1.6

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