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Rapid synthesis of faujasite/polyethersulfone composite membrane and application for CO_2/N_2 separation

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ABSTRACT

Rapid growth of faujasitic membranes on polyethersulfone support was investigated. The membrane growth occurred in a novel zeolite reactor, where the extent of supersaturation of the synthesis gel 8.5 Na_2O: 1 Al_2O_3: 10.9 SiO_2: $487H_2O$ was controlled by removal of water from the reaction system. The gel remaining after removal of half the water from the reaction was isolated and used as a coating on the polymer support. Along with this reactive gel, coating of a uniform film of nanozeolite seed deposition on the porous polymer support was also investigated. Eight variations of the gel-seed combinations were examined for membrane growth. The optimal membrane synthesis condition was defined as coating of the PES support by a nanozeolite seed layer of 250–300 nm thickness, and then introduction into the reactor after water is removed, and continuing the reflux process with reintroduction of the water for another hour. Further characterization included X-ray diffraction, optical microscopy and detailed scanning electron microscopy. Leak test of a dye through the membrane and the mechanical stability of the membrane via a tape test were performed. The transport properties of these membranes for CO_2/N_2 separation were evaluated. There were three ways the membrane samples were prepared and handled for transport measurements. Prior to transport measurements, all samples were covered with PDMS. Initial attempts placed the seeded PES support into the growth reactor. These samples all exhibited poor transport properties with CO_2/N_2 selectivities less than 10. For the second group, the seeded PES supports were placed in a holder that ensured flatness during the zeolite growth process. There was significant improvement in the transport properties, with half of the membranes exhibiting CO_2/N_2 selectivity greater than 20. With the third group of membranes also grown in the flat geometry, care was taken to keep them flat through all the subsequent steps including washing, drying and putting on the PDMS layer. Transport properties improved further. The twelve membranes in this group exhibited CO_2/N_2 separation factor in the range of 16–110 with CO_2 permeance in the range of 180–2000 GPU ($1\ \text{GPU} = 3.3 \times 10^{-10}\ \text{mol/m}^2 \cdot \text{Pa}$).

1. Introduction

Zeolites are microporous crystalline aluminosilicates, with well-defined pore sizes at the sub-nanometer level [1–4]. Because of the narrow pore size, thermal and chemical stability, zeolite membranes are attractive for pervaporation, gas and liquid separations [2,4–10]. There is currently great urgency in removal of CO_2 from flue gas emanating from coal-fired power plants, followed by sequestration to decelerate global warming effects. Selective CO_2 removal also can benefit other industries, such as in natural gas purification and in water gas shift reactions for hydrogen production [2,11]. Compared with traditional absorption-based separation, membrane separation is significantly more energy efficient [12].

The faujasite framework, with its three-dimensional architecture and 7.4 Å pore opening is attractive for gas separations, and has been extensively studied [1]. Because of its large pore size, there is no steric hindrance for CO_2, N_2 or other similarly sized gas molecules to enter the zeolite framework. However, CO_2, because of its higher quadrupole moment exhibits preferential interaction with the zeolite framework and the extraframework cations [13]. Aided by such interactions, CO_2 molecules preferentially permeate through zeolite framework by surface diffusion, while N_2 is blocked

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due to pore constriction caused by CO_2 adsorption, and forms the basis for gas separation [14,15].

Even though zeolite membranes have been studied for gas separation, [16,17] factors such as long synthesis time, membrane defects, high cost and poor reproducibility in zeolite membrane manufacture have limited their commercial use [4]. The only commercial use of zeolite membranes is in solvent purification by pervaporation [7,18–22]. Zeolite membranes are typically grown on α-alumina or metal supports [14,16,17,22–29]. These supports are expensive, mechanically rigid and difficult to fabricate in large-scale production. An alternative is using polymer supports, which if successful, can use all of the advances in polymer membrane fabrication to lower cost. However, a major technical hurdle is the long time it takes to synthesize zeolites, which is incompatible with polymer membrane manufacturing methods. A second issue is that inter-particle defects appear during the zeolite growth process, no matter what the support, which leads to low performance reproducibility [4]. Multiple strategies have been proposed to fix mesoporous defects, and some of these strategies can be adapted to the zeolite polymer system [4]. There have been recent reports of synthesis of zeolite A membranes on polymer hollow fibers and examined for pervaporation applications [21]. New strategies of synthesis of ultrathin zeolite membranes is an active area of research [30].

In this paper, we address two issues, accelerating zeolite membrane growth on polymer supports, and sealing of defects to enhance transport properties. Ultra-thin (250–300 nm) faujasite zeolite membranes on porous polyethersulfone (PES) supports has been synthesized in 1 h, following the rapid crystallization synthesis procedure described previously [31]. This is amongst the thinnest faujasite membrane that has been reported in the literature. Structural characteristics of this membrane are evaluated. We have investigated the use of silicone rubber (PDMS) to heal the defects on the grown zeolite membrane. Transport properties of these membranes for CO_2/N_2 separation are explored.

2. Experimental procedure

2.1. Chemicals

Aluminum hydroxide ($Al(OH)_3$, 76.5%) was obtained from Alfa Aesar, and sodium hydroxide pellets from Fisher Scientific (NaOH, 99.0%). Ludox SM-30 colloidal silica (SiO_2, 30%), Ludox HS-30 colloidal silica (SiO_2, 30%), aluminum isopropoxide ($Al(O{-}CH(CH_3)_2)_3$, 98%) and tetramethylammonium bromide ($(CH_3)_4NBr$, TMA), 98%) were obtained from Aldrich (Milwaukee, WI, USA). Tetramethylammonium hydroxide (25% aqueous) was obtained from SACHEM Inc. All chemicals were used as received. Polyethersulfone (PES) 300 kDa supports were purchased from MILLIPORE Biomax. Water was purified by a Millipore ultrapure water system.

2.2. Synthesis

2.2.1. Nanocrystalline zeolite Y seeds

Nanocrystalline zeolites were synthesized by a procedure reported in the literature [32]. The gel composition was: 0.048 Na_2O: 2.40 $(TMA)_2O(2OH)$: 1.2 $(TMA)_2O(2Br)$: 4.35 SiO_2: 1.0 Al_2O_3: 249H_2O (TMA^+ is tetramethylammonium). Typically, the silicon source, Ludox HS-30 (26.2 g) and TMAOH (10.46 g) were mixed in a Teflon bottle, sealed with parafilm and stirred at room temperature for 30 min. Aluminum isopropoxide (12.5) g was dissolved in 76.5 g H_2O and TMAOH (52.3 g) at 70 °C until the suspension became clear. TMABr (11.3 g) was added to the clear solution of aluminate and stirred at room temperature for 15 min. Finally, the silicon and aluminum solutions were mixed and aged at room temperature with stirring for 3 days, followed by heating at 100 °C in an oil bath with stirring for 4 days. The product was isolated by dialysis and ultracentrifugation, followed by ion-exchange with 0.2 M NaCl solution for 2 h. The ion exchanged product was washed with DI water and stored as a 1 wt% aqueous stock solution.

2.2.2. Zeolite Y seed layer

Zeolite Y seed layer on PES support was prepared by vacuum dip-coating. Before dip-coating, zeolite Y stock solution was put in an ultrasonic bath for 1 h and then diluted with DI water to the required concentration. Vacuum-assisted dip-coating involved evacuation of the PES support with zeolite seed dispersion on the top of the support for 3 s. The coated support was stored in a plastic sample bag.

2.2.3. Zeolite Y membrane synthesis

The gel composition used for membrane growth was 8.5 Na_2O: 1 Al_2O_3: 10.9 SiO_2: 488H_2O, (note that the previous composition reported in Reference 31 was in error by a factor of two) which was prepared by mixing 85.24 g H_2O, 2.208 g of $Al(OH)_3$ and 7.29 g NaOH with 13.85 g Ludox SM-30 followed by aging for 4 h at room temperature. Then the opaque gel was moved to round bottom flask, brought to reflux, 40–45 mL of H_2O was removed from the gel during 1 h of heating under reflux. During the next hour with the flask still under reflux, 40–45 mL H_2O was added back. The support was introduced in the flask at different stages during the synthesis, as described in results section.

2.2.4. PDMS coating

Zeolite membranes were spin coated with 3.5 wt% polydimethylsiloxane (PDMS) monomer solution. PDMS monomer solution was prepared by adding PDMS monomer, crosslinker and catalyst in the ratio of 100:1:0.5 to heptane. For spin coating of PDMS onto a zeolite membrane, the membrane was first taped on the flat plate of the spin coater and PDMS monomer dispersion was added to cover the whole membrane. Spinning process consisted of 2000 rpm spin for 5 s and then 4000 rpm spin for 1 min. After spin coating, the membranes were kept at room temperature overnight for crosslinking of the PDMS.

2.3. Characterization

2.3.1. X-ray diffraction

A Bruker D8 X-Ray Diffractometer using CuKα ($\lambda = 1.5405$ Å) radiation was used to characterize the phase composition of zeolite membranes.

2.3.2. Size and zeta potential

Size and zeta potential of nanocrystalline zeolite Y was characterized with Malvern Zetasizer.

2.3.3. Optical microscope

Surface morphology of membrane samples were studied with OLYMPUS PME3 optical microscope.

2.3.4. Scanning electron microscopy

Membrane samples were taped on a SEM holder with conductive carbon paste and gold coated at 40 mA for 20 s. Electron beams with 30 kV voltage and 41 pA current were typically used. A FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) was employed for cross sectional measurements.