Journal of Membrane Science 444 (2013) 384–393

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Improving SAPO-34 membrane synthesis

Rongfei Zhou, Eric W. Ping, Hans H. Funke*, John L. Falconer, Richard D. Noble

Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309-0596, United States

ARTICLE INFO

Article history:
Received 21 March 2013
Received in revised form
15 May 2013
Accepted 16 May 2013
Available online 28 May 2013

Keywords:
SAPO-34 membranes
High-temperature stability
Membrane preparation
CO_2/CH_4 separations
Spatial flux distributions

ABSTRACT

Previously, SAPO-34 membranes prepared using aluminum isopropoxide ($Al(O–i–Pr)_3$) and two templates (tetraethylammoniumhydroxide (TEAOH); dipropylamine (DPA)) were shown to separate CO_2/CH_4 mixtures with high fluxes at high pressures and room temperature. In this study, the synthesis was simplified, made safer, and modified to create less toxic waste by using only one template (TEAOH), but at twice the concentration, and $Al(OH)_3$ instead of $Al(O–i–Pr)_3$. However, some membranes prepared with the new procedure had low fluxes because they had impermeable regions. The impermeable regions were determined to be due to synthesis gel that remained in the support following a 15-min, post-synthesis rinse with water. Rinsing the membranes for at least 24 h in deionized water before calcination removed most of the residual gel and formed spatially-uniform membranes with high permeances (maximum of 1.2×10^{-6} mol/(m^2 s Pa)) and high CO_2/CH_4 separation selectivities (70) for 46-bar feed pressure. Additional benefits of these changes in membrane preparation include a 200-K increase in the temperature at which template could be removed, increased stability of calcined membranes contacted with liquid water, and better long-term stability during storage.

1. Introduction

Carbon dioxide must be removed from natural gas streams that are contaminated with high concentrations of CO_2, which decreases the energy content of the gas and is corrosive in the presence of moisture. Polymeric membranes are used for these separations [1], but the high CO_2 partial pressures in some natural gas wells can plasticize polymers and decrease the membrane separation performance [2]. The separations could be carried out at lower pressures, but this decreases the membrane driving force and introduces additional natural-gas recompression costs. Several types of zeolite membranes have been reported that separate CO_2/CH_4 mixtures: zeolite T [3,4], DDR [5,6], MFI [7,8], zeolite Y [9], AlPO-18 [10], and SAPO-34 [11–19]. Zeolite T membranes had CO_2/CH_4 selectivities of approximately 150, but their permeances were low (1.5×10^{-8} mol/(m^2 s Pa)), and the feed pressure used was only 0.5 MPa [3]. A DDR membrane was selective at higher pressures; at 3-MPa feed pressure, the CO_2/CH_4 separation selectivity was 80 with a CO_2 permeance of ~1.1×10^{-7} mol/(m^2 s Pa) [5]. Higher CO_2 permeances (~3×10^{-6} mol/(m^2 s Pa)) were obtained at 3-MPa feed pressure with MFI membranes, but the CO_2/CH_4 selectivity was only 3.5–4 [8]. Zeolite NaY [20] and KY [9] membranes were reported to have CO_2/CH_4 selectivities of 20 and 40 with permeances of about 2 and 9×10^{-7} mol/(m^2 s Pa), respectively, but these separations were carried out at a pressure of 101 kPa on both the feed and permeate side with helium sweep gas. AlPO-18 membranes had selectivities of ~60 for equimolar CO_2/CH_4 mixtures, but permeances were only 6.6×10^{-8} mol/(m^2 s Pa) [10].

Metal-organic frameworks (MOFs) membranes have also been used for CO_2/CH_4 separations, but their selectivities have been low, even at low feed pressures [21–23]. A CO_2/CH_4 selectivity of 3 was obtained for a MOF-5 membrane at a pressure drop of 100 kPa [21], and zeolite imidazolate framework-8 (ZIF-8) membranes [23] had a permeance of ~2.4×10^{-5} mol/(m^2 s Pa), but their selectivities were only 4 to 7 for a feed pressure of 140 kPa. Highly *c*-oriented ZIF-69 membranes had selectivities of 4.6 with a permeance of ~1.0×10^{-7} mol/(m^2 s Pa) [22].

We have previously reported SAPO-34 membranes with CO_2/CH_4 selectivities of 60 and CO_2 permeances of ~1×10^{-6} mol/(m^2 s Pa) for feed pressures of 4.6 MPa. For these high fluxes and high selectivities, concentration polarization decreased both the permeance and selectivity at high feed pressures, but its effect was minimized by using Teflon inserts in the center of the membrane tubes and by using high feed flow rates [24]. These membranes were prepared using two templates [tetraethylammonium hydroxide (TEAOH) and dipropylamine (DPA)] and aluminum isopropoxide as the aluminum source.

In the current study, the SAPO-34 membrane preparation was modified to decrease the cost of chemicals, reduce the environmental impact, and make the preparation safer for scale-up and commercial application. The aluminum isopropoxide ($Al(O–i–Pr)_3$)

* Corresponding author. Tel.: +1 303 492 3687.
E-mail address: funke@colorado.edu (H.H. Funke).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.05.048

used previously [11,12,14–19,24] hydrolyzes to form isopropanol, which is flammable. Thus, $Al(OH)_3$ was used instead because it does not form a flammable byproduct and it is also cheaper. In addition, the DPA template used in previous preparations was eliminated because it is flammable and toxic.

These changes in gel components required modifications in the synthesis in order to obtain selective membranes. Membranes prepared with $Al(OH)_3$ and two templates had higher selectivities than membranes prepared with $Al(O–i–Pr)_3$ but lower permeances because a large fraction of the membrane area was impermeable, as determined by spatial flux distribution measurements [25]. That is, some regions of the membranes had high permeances and selectivities, but no flux was detected through other regions of the membranes. The impermeable areas were eliminated when the membranes were rinsed in water for at least 12 h before calcination. Apparently, synthesis gel remained in the support pores when the membranes were rinsed for 15 min, and this caused impermeable areas to form during calcination. Previously, gels prepared with $Al(i\text{-}O\text{-}Pr)_3$ may have remained in the support after 15 min of rinsing but were not detrimental to the membranes. Whereas most membranes prepared with $Al(OH)_3$ and two templates had impermeable sections, only some of the membranes prepared with $Al(OH)_3$ and TEAOH as the only template and rinsed for short times before calcination had impermeable regions. In addition, membranes with impermeable regions were not stable in the presence of liquid water after calcination, but the thoroughly-washed membranes were. The change in membrane preparation also increased the temperature at which the template could be removed from 673 [19] to 873 K without introducing additional defects. Aluminum hydroxide apparently changed the membranes microstructure to make them more thermally stable. This was also observed with membranes that were washed for only 15 min, suggesting that the improved temperature stability was due to $Al(OH)_3$. The best SAPO-34 membrane prepared with $Al(OH)_3$ and a single template had a permeance of 1.2×10^{-6} mol/(m^2 s Pa) and a selectivity of 70 at a feed pressure of 4.6 MPa.

2. Experimental methods

2.1. Membrane seed preparation

SAPO-34 membranes were prepared by first seeding porous alumina supports with cubic SAPO-34 crystals, which were synthesized by microwave heating. The crystals had an average particle size of 300 nm. The seeds were prepared by stirring a mixture of $Al(O–i–Pr)_3$ (98%, Sigma-Aldrich), tetraethyl ammonium hydroxide (TEAOH) (35 wt% aqueous solution, Sigma-Aldrich), and deionized water for 2 h to form a homogeneous solution. Ludox AS-40 colloidal silica (40 wt% aqueous suspension, Sigma-Aldrich) was then added, and the resulting solution stirred for an additional 2 h before adding H_3PO_4 (85 wt% aqueous solution, Sigma-Aldrich), and then the solution was stirred for 3 d at room temperature. The final gel had a molar ratio of 1.0 Al_2O_3: 2.0 P_2O_5: 0.6 SiO_2: 4.0 TEAOH: 75 H_2O. The gel was transferred to a Teflon autoclave, which was heated in a microwave oven (CEM Mars Microwave Reaction System with XP-1500 plus reactor) to 453 K within 10 min and held at 453 K for 7 h. The reaction mixture was then cooled below 343 K, and the seeds were separated from the solution in a centrifuge at 7000 rpm for 30 min. The seeds were then re-suspended with DI water and centrifuged at 7000 rpm for 30 min to remove gel residues; this procedure was repeated four times, and the resulting SAPO-34 seeds were dried overnight at 323 K.

2.2. Membrane synthesis

Tubular alumina supports (11-mm OD, 7-mm ID, 100-nm average pore sizes, Inopor GmbH) were cut into 6-cm lengths, and the ends were glazed using Duncan ceramic glaze at 1223 K with heating and cooling rates of 1 K/min. The supports were then placed in boiling DI water for 30 min, removed from the water and placed in fresh boiling DI water (total of four times) and dried overnight at 373 K. Two membranes were prepared on porous stainless steel tubes with welded ends (Mott). The SAPO-34 seeds were deposited on the inside of the support tubes by either rub-coating or dip-coating. All membranes prepared with $Al(OH)_3$ and a single-template (TEAOH) were seeded by rub-coating, and all membranes prepared with two templates (TEAOH, DPA) were seeded by dip-coating unless indicated otherwise. We have previously shown that both seeding methods yielded membranes with similar separation properties; membrane performances were slightly more reproducible when dip-coating was used [26].

For dip-coating, the dry supports were first wrapped in 0.025-mm thick Teflon tape and then immersed for about 60 s in ethanol that contained 0.042 wt% SAPO-34 seeds and 0.003 wt% hydroxypropyl cellulose (Sigma-Aldrich), which was added as a colloidal stabilizer. The supports were lifted out of the seed suspension over a 25-s period and then dried at 373 K for 2 h. The Teflon tape was removed and the seeded supports were calcined in air at 673 K for 4 h with heating and cooling rates of 1 K/min. The outer surface of the alumina supports was then wrapped tightly with two layers of Teflon tape (0.13-mm thick tape for the first layer, 0.025-mm thick tape for the second layer).

Before rub-coating, the supports were tightly wrapped first with a layer of 0.13 mm thick Teflon tape and then with a layer of 0.025-mm thick tape. Rub-coating was then carried out by rubbing dry seeds evenly onto the inside surface of the alumina tubes for about 2 min with pipe cleaners covered with seed crystals.

Both seeding techniques only cover about 5–10% of the support surface with seed crystals as indicated by SEM (not shown). The dip-coated seeds are firmly attached to the support after calcination and appear to be distributed more uniformly than for rub-coating. However, the rub-coated seed crystals are loosely attached, and thus sample preparation for SEM likely affected their distribution, resulting in unreliable images.

After seeding, the membranes were prepared by using a single hydrothermal synthesis. Usually two seeded supports were placed in an autoclave, which was then filled with the synthesis gel to about 0.5 cm above the top of the supports. The autoclave was placed in a forced convection oven at 483 K for 5 h (two templates) or 493 K for 6 h (single template). The autoclaves were then cooled to room temperature with flowing tap water, and the membranes were removed and rinsed in flowing tap water for 15 min after unwrapping the Teflon tape. Some membranes were rinsed for an additional 24 or 48 h in stagnant DI water (500 mL, liquid exchanged several times) before drying them at 393 K overnight. For some syntheses, the gel pH was measured before and after synthesis using pH strips.

The membrane gels were prepared by mixing H_3PO_4 (85 wt% aqueous solution), an aluminum source ($Al(O–i–Pr)_3$, 98%, or $Al(OH)_3$, 55.7 wt% Al_2O_3) and DI water, and stirring the mixture for 2 h. The silica (Ludox AS-40 colloidal silica gel, 40 wt% aqueous solution) was added, and the mixture stirred again for 30 min. Then, TEAOH (35 wt% aqueous solution) was added and the mixture was stirred for an additional 30 min. When two templates were used, DPA (99%) was added 30 min after TEAOH and the mixture was stirred for an additional 30 min.

The synthesis gel for SAPO-34 membranes prepared with $Al(O–i–Pr)_3$ and two templates had a molar ratio of 1.0 Al_2O_3: 1.0 P_2O_5: 0.3 SiO_2: 1.0 TEAOH: 1.6 DPA: 155 H_2O, and the gel was aged for