

Ordered mesoporous membranes: Effects of support and surfactant removal conditions on membrane quality

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Abstract

Ordered mesoporous MCM-48 membranes with cubic pore structure were prepared by solution growth method and characterized by XRD, SEM/EDS and unsteady-state gas permeation. The membranes were fabricated on symmetric α -alumina supports of different pore sizes under hydrothermal conditions using cetyltrimethylammonium bromide (CTAB) as a surfactant. The surfactant was removed by calcination and Soxhlet extraction at 100 °C using ethanol/HCl mixture. The X-ray diffraction showed that these membranes possessed a cubic MCM-48 pore structure. The N₂ adsorption studies at 77 K indicated high pore volumes and pore size distribution in the mesoporous regime with an average pore diameter of ~2.6 nm. The membranes prepared on the A15 α -alumina support (0.3 μ m average pore size) exhibited the presence of pinhole defects. The single gas N₂ and CO₂ permeation experiments showed that the best quality membranes were synthesized on the α -A16 alumina supports (average pore size ~0.2 μ m) when the surfactant was removed by Soxhlet extraction. For these membranes the N₂ and CO₂ permeation was found to be governed by Knudsen diffusion. The permeance was independent of the feed pressure, indicating the absence of viscous flow contribution to gas transport.

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1. Introduction

Porous inorganic membranes are highly promising for separation processes under severe conditions, such as high temperatures and corrosive environments encountered in many process streams because of their rigid and uniform structure. The development of new fabrication techniques, e.g. sol–gel deposition and hydrothermal synthesis, has made it possible to synthesize chemically resistant, thermally stable and robust inorganic membranes. Recently, both amorphous and structured silica membranes have been under intense investigation for a variety of applications including gas and liquid separations [1,2]. The reported membranes were microporous or mesoporous depending on the application.

High quality microporous zeolitic membranes, e.g. ZSM-5 have been synthesized on various supports via in situ crystallization [2,3], secondary growth [4] and vapor transport methods [5].

Extensive studies of gas and liquid separations have been conducted using zeolite membranes. The results obtained for these separations have been interpreted on the basis of adsorption, diffusion and molecular sieving mechanisms [6]. High performance of the membranes has been observed for water/ethanol, isomer separation (e.g. xylene isomers) and pervaporation based on adsorption diffusion mechanism [7].

The M41S family of ordered mesoporous molecular sieves discovered in 1992 [8,9] has attracted a great deal of interest in recent years from the catalysis [10] and separations communities [11]. Significant progress has been made in the preparation of various ordered mesoporous materials with uniform pore sizes. Recently, there has been increasing interest in the synthesis of inorganic membranes based on ordered mesoporous silicas [1,8,11–16]. Such ordered mesoporous thin films and membranes are highly promising because of high fluxes expected for larger molecules. Ordered mesoporous membranes can also be utilized in membrane reactors [17,18]. Furthermore, the pore surfaces of mesoporous membranes can be modified with hydrophobic groups to enable separation of hydrophobic/hydrophilic molecules, such as ethanol from water [7]. The

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mesoporous MCM-41 and MCM-48 silica membranes and films have been recently reported [19,20]. Their pore size can be adjusted to achieve the desired separation efficiency by using surfactants of different hydrocarbon chain lengths, hydrocarbon expanders, or post-synthesis hydrothermal treatments [21]. Zhao et al. [22] fabricated mesoporous silica films with three-dimensional cubic ($Pm3n$) pore structure and varying pore sizes (18–25 Å) on silicon wafers. Free-standing silica films with unidimensional hexagonal pore channels with ~ 1.6 nm pores have been prepared by templating silicates with surfactant micelles at the air–water [23,24] and oil–water [25] interfaces.

Our studies focused on the preparation of MCM-48 membranes, because MCM-48 possesses three-dimensional interconnected cubic pore structure, which decreases diffusion limitations and is, therefore, more attractive than MCM-41. Park et al. [1] and Nishiyama et al. [12] reported formation of MCM-48 membranes on alumina supports by hydrothermal solution growth method, which were permeable to gases after the surfactant removal. Various research groups have also obtained mesoporous MCM-48 membranes by sol–gel deposition on alumina supports [14,15]. All of these studies reported the surfactant removal by calcination at ~ 500 °C. However, the MCM-48 structure experiences $\sim 20\%$ contraction of the silica framework at 300–400 °C during surfactant decomposition [3,9,26,27]. Such large lattice contraction is expected to result in significant mechanical stresses in the MCM-48 membranes and the formation of macroscopic defects in the MCM-48 membrane layer, such as large cracks.

In the present study we investigate surfactant removal methods from as-synthesized MCM-48 membranes and examine the effect of support pore size on the preparation of defect-free MCM-48 membranes.

2. Experimental

2.1. Support preparation

Porous α -alumina supports with average pore diameters of 0.2 and 0.3 μm were prepared from alumina powders, A16SG and A15SG (Alcoa World Chemicals) containing two average particle diameters. These two alumina supports were used to study the effect of the support pore size on the membrane quality. The alumina powders were mixed with 8 wt.% water in a crystal mortar and thoroughly mixed. Then 2.1 g of the mixture was placed in a mold and compressed at 5000 psi for 30 s followed by compression at 20,000 psi for 2 min. The supports were subjected to a sintering treatment at 1500 °C for 30 h to strengthen the support structure and increase its density. The final average pore size for these supports was ~ 0.2 μm for the A16 supports and 0.3 μm for the A15 supports, respectively, measured by the steady-state He permeation [28].

2.2. Synthesis of MCM-48 membranes

The MCM-48 membranes were prepared by a solution growth method. Porous alumina supports were placed in neat tetraethylorthosilicate (TEOS) for 30 min. Cetyltrimethylammonium bro-

mid (CTAB), $\text{C}_{19}\text{H}_{42}\text{NBr}$ (Aldrich), NaOH (Aldrich) and deionized water were stirred at room temperature to obtain a homogeneous solution. This solution was then added to the α -alumina support in TEOS and the combined solution was further stirred for 2 h. The final molar composition of the mixture was 1.0 TEOS:0.59 CTAB:0.5 NaOH:61 H_2O . This mixture was transferred to an autoclave and the alumina support was placed at the bottom of the autoclave. After 4 days at 90 °C, the membrane was removed and washed with deionized water. The synthesis of the bulk MCM-48 silica was conducted under similar experimental conditions in the absence of α -alumina support.

2.3. Surfactant removal from MCM-48 membranes

Two different methods were used to remove the surfactant from the MCM-48 membranes. In the first method, they were heated at 1 °C/min and calcined at 500 °C for 4 h. In the second method, the surfactant was extracted using an EtOH/HCl solution containing 250 ml EtOH and 3.5 g 37% HCl at 100 °C for 24 h. After surfactant extraction, the MCM-48 membranes were further calcined at 350 °C to study the effect of additional calcination step on the membrane quality.

2.4. Physico-chemical characterization of MCM-48 membranes

The unsteady-state gas permeation experiments were carried out using N_2 and CO_2 at room temperature (25 °C) and 90 °C. The permeate side of the membrane was maintained at atmospheric pressure (14.7 psi), while three different pressures (10–30 psig) were used on the feed side. A schematic representation of the unsteady-state permeation system is shown in Fig. 1.

The gas permeance was calculated from the slope of the pressure versus time plot, which gave the dP''/dt value according to Eq. (1):

$$\text{Permeance} : \frac{F}{L} = \frac{V_c}{RTA_m(P' - P'')} \frac{dP''}{dt} \quad (1)$$

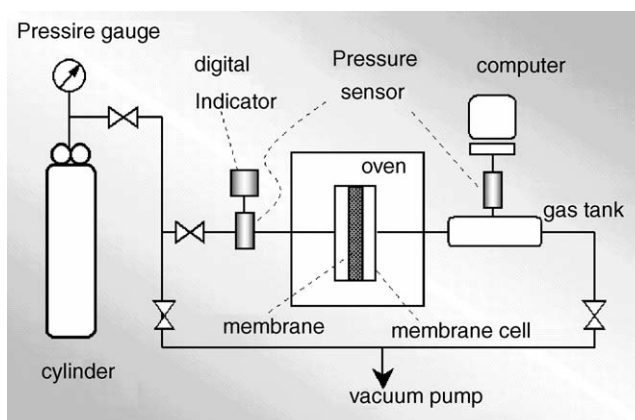


Fig. 1. Schematic diagram of single gas unsteady-state permeation system.

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