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Synthesis and characterization of ordered mesoporous silica membrane: Role of porous support and gas permeation study

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ABSTRACT

In this work, the supported silica membranes were synthesized on various self-made symmetrical α-alumina supports having different pore sizes by spin coating method. The final synthesized membranes were further characterized by XRD, FESEM and FTIR analysis. Gas separation properties of the resultant supported ordered mesoporous silica membranes were evaluated by single gas permeation experiments. The results showed that the lower pore sized α-alumina supports can effectively reduce the surface defects of the silica layer and enhance the gas permeation properties of the supported silica membranes. The orders of the silica structure were also improved by reducing the pore size of the α-alumina supports. Steady-state single gas permeation using CO_2, Ar, He and N_2 gases showed Knudsen diffusion mechanism for the membrane synthesized on the α-alumina support having lowest pore size of ~0.09 μm. The other membranes having higher pore sized supports obeyed both Knudsen as well as viscous diffusion mechanisms. In addition, mixed gas permeation (20% CO_2 and 80% N_2) studies were carried out using amino functionalized mesoporous silica membrane.

1. Introduction

Recently, ordered mesoporous silica membranes [1–10] have been widely investigated for use in nanofiltration, pervaporation, membrane reactors and also as support layers for micro porous gas separation membrane applications. Such ordered mesoporous thin film membranes are highly promising because of the higher flux. Also, the pore surfaces of the mesoporous membranes can be modified by using different functional groups such as, amino-silane for CO_2 separation from process steams or other required applications [11,12]. Synthesizing good quality ordered mesoporous silica membranes with controlled physical and chemical properties and also controlling the interface between various layers in multi-layered structures are very important. Simpler ways to synthesize mesoporous silica films by spin-coating [13,14] and dip coating [15,16] methods have been reported. These solvent-evaporation techniques have been utilized for the coating on glass supports [13,14] and on silicon wafers [15,16]. Various research groups have reported about the synthesis of mesoporous silica (MCM-48) membranes by sol–gel deposition on alumina supports [7,8]. However, the MCM-48 structure experiences ~20% contraction of the silica framework at (300–400) °C, during the surfactant decomposition [17–20]. 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. Depending on the pore size of the support, the crack in the membrane might vary. The large pore sized supports can also result into penetration of the membrane material inside the pores of the support [21,22]. Hence, the quality of the support is one of the important factors in synthesizing good quality silica membrane. Kumar et al. [23] synthesized MCM-48 membrane on different types of support for CO_2 separation by hydrothermal method. They reported that the membrane quality depends upon the pore size of the support. To the best of our knowledge, dependency of ordered mesoporous silica membrane formation on different supports by spin coating method has not been studied in the open literature so far. A good quality support of having smooth surface as well as narrow surface pore size are necessary for the formation of thin ordered mesoporous silica membrane by spin coating method.

A few other studies of ordered mesoporous silica films and membranes have been reported [5–11]. Huang et al. [5] has reported about the synthesis of MCM-41 and MCM-48 thin films on

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porous oxides, but gas permeance of these supported films were not reported. Chowdhury et al. [6] reported mesoporous silica membranes grown on top of macroporous α-alumina and mesoporous γ-alumina supports. However, gas permeances of these supports were not reported. High quality silica membranes were synthesized by de Vos and Verweij [2]. The membrane, fabricated for hydrogen separation, exhibited hydrogen over methane selectivity of over 5000 at 300 °C. The membrane also exhibited an extremely high hydrogen permeance of over 2×10^{-6} mol m^{-2} s^{-1} Pa^{-1}.

In the present work, ordered mesoporous silica membrane was synthesized by sol–gel technology using spin coating method on different types of self-made α-alumina supports of different pore sizes. The dependency on the support quality for synthesizing ordered mesoporous silica membrane by spin coating method was studied. A detailed characterization study was performed to evaluate the formation of ordered mesoporous silica membrane onto the different supports. Also, single gas permeation through the synthesized membranes using N_2, Ar, He and CO_2 gases were performed to know their efficiency and the mechanism of gas transport. In addition, mixed gas permeation (20% CO_2 and 80% N_2) studies were carried out using amino functionalized mesoporous silica membrane.

2. Experimental section

2.1. Materials

Poly (vinyl alcohol) (98–99 mol% hydrolyzed powder) was obtained from Loba Chemie Pvt. Ltd, Mumbai, India. α-Alumina powder (Alfa Aesar, 99.9% (metals basis), size < 1 micron APS powder, SA 6–8 m^2/g) was procured from Alfa Aesar, USA. Tetraethyl orthosilicate (TEOS), anhydrous toluene (EMPARTA^R ACS) and HCl (35%) were purchased from MERCK, India. N-hexadecyltrimethyl ammonium bromide (CTAB) and 3-aminopropyltriethoxysilane (3-APS) were supplied by Sigma Aldrich. Ethyl alcohol (EMSURE R ACS, ISO, Reag. PhEur) was obtained from Merck Germany.

2.2. Support synthesis

The membrane supports were prepared by dry compaction method using poly (vinyl alcohol) (PVA) as a binder. Preparation procedure was similar to that reported in our previous work [24]. In short, the binder solution was initially prepared by adding 2 wt % of solid PVA with distilled water followed by heating the mixture at 80 °C. The final powder was prepared by mixing ~10 wt% binder solution in dry α-alumina powder followed by sieving. A requisite amount of the mixed α-alumina powder was uniaxially pressed in a Compression Testing Machine (Aimil) by applying a certain amount of constant load for 5 min. A custom made stainless steel mould was used to make the circular disc membrane support. The supports thus obtained were carefully kept in a hot air oven at 150 °C for 24 h for drying. Thereafter, the sintering was done at different temperatures (1300 °C, 1400 °C and 1500 °C) using high temperature chamber furnace with P310 controller (Nabertherm, Germany). The supports were kept for 4 h at those temperatures. To obtain smooth surface as well as the required diameter for the gas permeation module (Fig. 1), sintered membranes were then polished using silicon carbide abrasive paper (No. C-320). The membrane supports thus obtained were cleaned ultrasonically (Elmasonic P-30H) in de-ionized water and dried at 150 °C overnight in a hot air oven to remove any contaminants. The final average pore size was measured by the N_2 permeation analysis and FESEM image analysis methods and these were described in our previous work [24].

2.3. Membrane synthesis

The silica sol for the spin coated membrane in this work was prepared as per the method described by Besson et al. [25]. A mixture of EtOH, TEOS and diluted HCl (0.056 M, pH = 1.67) was taken into a beaker and was stirred for 1 h at room temperature. Then a required amount of CTAB was added to the mixture at room temperature with continuous stirring to dissolve it completely. The final sol was stirred continuously for 24 h for aging. The final molar ratio of the silica sol was CTAB: TEOS: H_2O (HCl): EtOH = 0.1:1:0.28:22. Sufficient amount of silica sol was then taken from the beaker with the help of a micropipette and was added drop-wise onto the different α-Al_2O_3 supports for spin-coating. The coating was done at 4000 rpm for 180 s. The coated membranes were kept overnight in a laminar flow chamber (Dlab Tech, Clean Bench). Finally, the spin coated membranes were calcined in the chamber furnace (Nabertherm, Germany) at 550 °C for 6 h with the heating and cooling rate of 0.5 °C/min.

2.4. Functionalization of silica membrane by chemical grafting

The pores of the synthesized silica membrane were modified by 3-aminopropyltrimethoxysilirane (APS) to improve the CO_2 affinity of the pore walls. MR2 membrane was taken for the modification. The method was followed as described by Sakamoto et al. [11]. Calculated amount of 3-APS was dropped onto the ordered silica membrane MR2 which was previously taken into a beaker. The experiment was performed in Argon atmosphere. Before putting the silica membrane into the beaker, the membrane was dried at 120 °C in a vacuum oven for 24 h to remove the adsorbed water. The modification was performed for 24 h at around 150 °C with a condenser. Finally the modified membrane was washed with anhydrous toluene (Merck, India), several times and was also dried at 60 °C for 24 h in a hot air oven.

3. Membrane characterization

Structural analyses of the synthesized mesoporous silica membranes were conducted by (Bruke D8) advanced X-ray diffraction (XRD) measurement with Cu Kα radiation of wave length λ = 1.54056 Å for 2θ angles between 2° and 10° at a scanning rate of 0.02° s^{-1} and a step size of 0.5 s. Surface morphology, cross-sectional view and micro-structural analysis of the membrane supports were done by using field emission scanning electron microscope (FESEM) (Sigma- Zeiss). The FESEM analysis was carried out to find the defect on the membrane support surface and also to know about the surface morphology of the membranes. The EDX (OXFORD Instruments, X-Max^N) analysis was carried out at different location of the support and the membrane layer to confirm the presence of different elements. FTIR spectrum analyses (SHIMADZU, IR Affinity 1, Japan) in powder mode were carried out to resolve the organic chemical groups of the synthesized active layers. FTIR spectra were recorded in the 4000 – 500 cm^{-1} wave number region using spectroscopic-quality KBr powder with 40 scans per sample and 4 cm^{-1} resolution. The powder of the active membrane layer was scratched out by using a knife.

The steady-state gas permeation experiments were carried out using pure N_2, Ar, He and CO_2 at room temperature (298 ± 2 K). The permeate side of the membrane was maintained at atmospheric pressure (14.7 psi), while four different pressures (138–345 kPa) were used on the feed side. A schematic representation of the steady-state permeation system is shown in Fig. 1. Transport