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Highly permeable mesoporous silica membranes synthesized by vapor infiltration of tetraethoxysilane into non-ionic alkyl poly(oxyethylene) surfactant films

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ABSTRACT

Mesoporous silica membranes were prepared on porous alumina substrates by a vapor infiltration of tetraethoxysilane (TEOS) into a non-ionic poly(oxyethylene) (Brij56) surfactant film. Periodic mesostructured silica membranes were formed on both α- and γ-alumina substrates pre-treated with polystyrene. The polystyrene polymer plugged the pores of the alumina substrates and inhibited the deposition of silica in the alumina pores, resulting in the formation of a very thin silica membrane without a silica/alumina composite layer at the interface between mesoporous silica and the alumina substrates. The calcined mesoporous silica membrane showed very high nitrogen permeance ($>10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}). The single gas permeation was governed by the Knudsen diffusion mechanism. The durability of the mesoporous silica membrane against moisture in air was improved by a silylation with trimethylethoxysililane.

1. Introduction

In the last decade, mesoporous silica membranes have been extensively studied because they are applicable to nanofiltration [1], ultrafiltration [2,3], pervaporation [4,5], membrane reactors [6] and supports for microporous materials based on their pore sizes [7–9]. The mesoporous silicas have a very narrow pore size distribution ranging from 2 to 10 nm. Their pore size can be controlled by using surfactants with different molecular sizes. In addition, the pore surface can be modified by organic groups [9–13] and metal nanoparticles [12,14–17] due to their large pore sizes compared to microporous materials such as zeolites. Whereas these modification techniques have been generally applied to catalysts [12,16,17] and adsorbents [9–11], an organo-functionalized mesoporous silica membrane was applicable for gas separations recently [13].

MCM-48, which has a cubic symmetry (*Ia*3*d*), has been often studied as a membrane material because of its 3D pore structure. The synthesis of the MCM-48 membrane on a porous support had been first reported in 1998 [18]. The MCM-48 membrane was successfully prepared by a hydrothermal synthesis under basic conditions through a self-assembled tetraethoxysilane (TEOS) and cethyltrimethylammonium bromide (CTAB) cationic surfactant. Then, several groups have reported the preparation of MCM-48 membranes [19–29] with respect to synthesis conditions [19–23], effect of supports [21–24], and removal conditions of surfactants [22,25].

After the reports on the synthesis of the MCM-48 membranes using ionic surfactant CTAB, preparations of mesoporous silica membranes using non-ionic block copolymers have been reported [3,30–32]. Xomeritakis et al. [30] synthesized mesoporous silica membranes by an aerosol deposition technique using polyoxyethylene(10) cethyl ether (Brij56). The synthesized mesoporous silica had a 3D cubic structure. Boissière et al. [3] demonstrated an interfacial growth mechanism for the preparation of an MSU-X type mesoporous silica membrane using a non-ionic polyethylene oxide (PEO)-based surfactant. The mesoporous silica membrane prepared using polystyrene-block-poly(ethylene oxide) (PS-b-PEO) was reported by Brinker et al. [31]. The use of the PS-b-PEO surfactant resulted in the formation of larger mesopores interconnected with micropores. Higgins et al. [32] prepared mesoporous silica membranes via micellar templating using a non-ionic ethylene oxide–propylene oxide–ethylene oxide tri-block copolymer sur-

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factant (EO–PO–EO, Pluronic P123). The membranes had a large pore size (ca. 5 nm) and showed high permeances for nitrogen ($>10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}).

As described above, mesoporous silica films and membranes have been prepared from precursor solutions including a silica source by hydrothermal synthesis [21–28], dip-coating [20], spin-coating [33], casting [34], aerosol-assisted deposition [32], solution growth [23], counter diffusion self-assembly [35] and interfacial growth [3]. On the other hand, recently, we have reported a formation of mesoporous silica films by an infiltration of a TEOS vapor into surfactant films [36,37]. A phase transition of surfactant–silicate nanocomposites occurs under the vapor infiltration. The mesostructured silica films with a 1D hexagonal [36] and 2D cage-like [37] pore structures have been synthesized so far using CTAB and non-ionic poly-(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) amphiphilic tri-block copolymer (Pluronic F127), respectively. More recently, a mesoporous silica thin film with a 3D pore structure (*Fmmm*) could be synthesized on the silicon substrate by the vapor phase method [38].

The obtained films were very thin and the thermal stability was high compared to the films prepared by the conventional sol–gel method. However, the mesoporous thin film had been synthesized only on the flat substrate such as a Si wafer and there is no report on preparation of mesoporous silica membranes by the vapor phase method on porous substrates. In the present study, we have developed the vapor phase method for the preparation of thin mesoporous silica membranes with a 3D pore structure on porous γ- and α-alumina substrates. To prepare thin mesoporous membrane with high gas permeance, the pre-treatment conditions of the porous substrates were optimized and single gas permeation properties and durability of the membranes against moisture in air were investigated.

2. Experimental

2.1. Materials

Brij56 ($C_{16}H_{33}(OCH_2CH_2)_{10}OH$) was purchased from Sigma–Aldrich, Japan. Polystyrene (MW = 2000), TEOS, sulfuric acid and hydrochloric acid were purchased from Wako Pure Chemical Industries Ltd. Trimethylethoxysilane (TMES) was purchased from Tokyo Chemical Industry Co. Ltd. All reagents were used without further purification.

A γ-alumina disk (mean pore diameter: 10 nm) and an α-alumina disk (mean pore diameter: 100 nm) were purchased from Noritake Co. Ltd. and NGK Insulaters Ltd., respectively. The substrates were cut into a square with 1 cm each, then washed by ethanol, dried and calcined at 773 K before used to remove organic impurities.

2.2. Polystyrene treatment of substrates

The surface of the porous alumina substrates was pre-treated using a solution containing a polystyrene polymer before the coating of mesoporous silica membranes. A 0.2-ml of 17 wt% polystyrene/toluene solution was spin-coated twice on the porous alumina substrates at 4000 rpm for 60 s. After the spin-coating, the treated alumina substrates were thermally treated at different temperatures (513–593 K) for 2 h.

2.3. Vapor phase synthesis of mesoporous silica membranes

The surfactant film was prepared on the porous alumina substrate by spin-coating at 4000 rpm for 60 s using a mixture of Brij56, sulfuric acid and ethanol with molar ratios of 0.16 Brij56:1.0 H_2SO_4:30 EtOH. The spin-coated surfactant film was placed vertically in a closed vessel with the volume of 50 ml along with a separate, 0.2 ml of both TEOS and hydrochloric acid. The vessel was then placed in an oven at 333 K for 15 min. Thus, the surfactant/H_2SO_4 film was exposed to saturated TEOS and HCl vapors under autogeneous pressure. The spin-coating and vapor phase treatment were repeated 3 times and then, the mesoporous membrane was calcined at 823 K in air for 5 h with a heating rate of 1 K/min to remove the surfactants and polystyrene polymers.

2.4. Silylation of mesoporous silica membranes by vapor phase treatment

The calcined mesoporous membrane was silylated with a TMES vapor. The calcined membrane was placed in a closed vessel separated from a small amount of TMES. The vessel was placed in an oven at 423 K for 2 h.

2.5. Characterization

The mesoporous silica membranes were identified by X-ray diffraction (XRD) patterns recorded on a Rigaku Mini-flex using Cu Kα radiation in the region of $2\theta = 1.1–8.0^\circ$ with a step size of 0.2° and a scan speed of 2.0°/min. The composition and thickness of the membranes were measured by scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis on Hitachi S-2250N. The mesostructure was observed by transmission electron microscopy (TEM) on FEI Tecnai 20 at 200 kV.

Permeation of pure nitrogen gas through the mesoporous silica membrane was performed at 293 K. In the permeation test, a total pressure on the feed side was kept constant in the range of 0.1–0.4 MPa and the permeate side was kept constant at atmospheric pressure. The permeate streams were analyzed with a soap meter.

3. Results and discussion

3.1. Effect of polystyrene treatment of the porous substrate

In the vapor phase synthesis, silica was deposited in the pores of the substrates, resulting in the formation of thick silica/alumina composite layers. In addition, the porous alumina substrates, especially α-alumina, have a rough membrane surface, on which the formation of periodic mesostructures often failed. In this study, the porous substrate was treated with a polystyrene polymer in order to inhibit the formation of the silica/alumina composite layer. The polystyrene polymer can be removed by calcination, which means that polystyrene polymer does not effect the gas permeation.

Fig. 1 shows SEM images of the cross-sectional views of the untreated and polystyrene-treated γ-alumina substrates. The polystyrene-treated γ-alumina substrate had a smooth surface compared to that of the untreated one. A polymer layer was not visible on the γ-alumina substrate. However, the single gas permeance of N_2 decreased from 3.4 to 2.0 μmol m^{-2} s^{-1} Pa^{-1} by the polystyrene treatment. These results suggest that the polystyrene polymer penetrated into the pores of the γ-alumina substrate and partially plugged the pores.

The mesoporous silica membranes were prepared by the vapor phase method on both the untreated and treated γ-alumina substrates. The XRD patterns of both the membranes are shown in Fig. 2. Regardless of with and without the pre-treatment, a periodic mesoporous layer could be synthesized on the γ-alumina substrates and the mesostructure on both the substrates remained