Effect of Phenyl-substituted Ethoxysilane on Gas Permeation Characteristics of a Silica Membrane

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Abstract: The present study attempts to control the micropore size of silica membrane by varying a substituent group in silane precursors. An amorphous silica membrane was produced by thermal decomposition of phenylethoxysilane (PTES) on a γ-alumina coated α-alumina tube with pore size of 6-8 nm. For the gas molecules of CO₂, N₂, CH₄ and C₂H₆, the PTES-derived membrane exhibited higher molecular-sieving property than the membrane formed with tetraethoxysilane (TEOS). Controlling of micropores of silica membrane using phenylethoxysilane as the Si-source was conjectured to result in performance improvements.

Keywords: membrane separation, gas permeation, molecular-sieving, silica, phenylethoxysilane

Introduction

Porous inorganic membranes which contain angstrom range pores represent an attractive approach for separating gas mixtures. Among membranes developed to date, the most promising is an amorphous silica membrane, formed on a porous support tube by sol-gel or chemical vapor deposition (CVD) process [1-4]. These silica membranes were able to separate hydrogen from other gases larger than CO₂ with selectivities of 100-1000. However, Molecules larger than CO₂ permeated the silica membranes by the Knudsen diffusion mechanism through a small number of mesopores left in membrane coating process. In order to improve permselectivities of larger molecules, strict control of micropore size is required.

The size of micropore is more successfully controlled by the sol-gel process than by the CVD method. Raman and coworkers [5] demonstrated that a sol-gel process with organic templates lead to a microporous silica membrane, which exhibited both high permeance and permselectivity for mixtures of carbon dioxide and methane. The sol-gel process is attractive for multilayer deposition which can lead to a controlled structure, composition and activity for the membrane. Gas permeation rate and selectivity through these sol-gel derived membranes are usually high. However, these membranes calcined or sintered at relatively low temperature for a short time show the thermal and hydrothermal instability due to pore growth, grain coarsening and defect development above 400-500°C [6]. CVD method is fundamentally much simpler and easier than wet processes such as sol-gel process and hydrothermal synthesis. As stated above, amorphous silica membranes formed by the CVD method are hydrogen permselective but often not useful for the separation of larger molecules. In this study, we attempt to make the best use of the simplicity of the CVD process as well as to enlarge the micropore size of silica membrane using phenyl-substituted ethoxysilane as the Si-source. The prepared membrane was characterized by permeation test of gases with various molecular size.

Experimental

A porous α-alumina tube manufactured by NOK Corp. (Japan) was used as the membrane support. γ-Alumina was coated onto the porous support tube by dipping-drying-firing procedure with a boehmite sol (γ-AlOOH) prepared by the procedure of Yoldas [7]. The thickness of the γ-alumina layer was 3-4 μm, and the top surface was smooth and defect free. The average pore size of the γ-alumina coated α-alumina support tube was determined by N₂-adsorption isotherm using Micromeritics,
Phenyl-substituted ethoxysilane

Figure 1. Schematic illustration for pore size control by phenyl-substituted ethoxysilane.

ASAP 2200 and was about 6-8 nm in diameter. A silica membrane was produced onto the γ-alumina coated α-alumina support tube by pyrolysis of tetraethoxysilane (TEOS, Si(OC₂H₅)₄, Aldrich) or phenytriethoxysilane (PTES, PhSi(OC₂H₅)₃, Aldrich) at 773-873K. Details of membrane preparation have been reported previously [8-10]. When PTES was used as the Si-source, organic fragments remaining in the membrane were completely removed by the subsequent calcination in air at 673 K for 5 h. Figure 1 shows the synthesis scheme for micropore controlling by phenyl-substituted ethoxysilane.

Modified membranes were observed with a field emission scanning electron microscope (SEM, JEOL JSM-840A). Gas permeation experiments were performed at 523 K using single-component of hydrogen, carbon dioxide, nitrogen, methane and propane. Argon was used as the sweep gas on the permeate side, and ambient pressure was maintained on both sides of the membrane. The flow rate was measured with a soap-film flow meter, and gas compositions were analyzed using a gas chromatograph (Shimazu, GA-14) with a thermal conductivity detector. Gas permeance is defined as a transport flux per unit transmembrane driving force, partial pressure difference, and is given in unit of mol m⁻² s⁻¹ Pa⁻¹.

Results and Discussion

Morphology of a silica membrane was not greatly affected by the Si-precursor, TEOS or PTES. The silica modified layer was expanded to a depth of 200-500 nm, and the top surface contained no pinholes. The mechanism of pore plugging and membrane morphology during chemical vapor deposition with cross-flow have been reported previously [8-10].

Figure 2 shows the results of the gas permeation test for the silica membranes prepared with TEOS and PTES. In the case of TEOS-derived membrane, hydrogen selectivities to \( \text{N}_2 \), \( \text{CO}_2 \), \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \) were in the range of 10-15, but selectivities among the gases except hydrogen remained at the level of theoretical values by Knudsen diffusion, lighter gas being permeated preferentially. Molecules larger than hydrogen leaked through a small number of mesopores, which were left unplugged in the membrane. On the other hand, the PTES-derived membrane exhibited molecular sieving property. The gas permeance values followed the exact order of the kinetic diameters of the gas molecules. Hydrogen, which has the smallest kinetic diameter (0.29 nm), carbon dioxide (0.33 nm), nitrogen (0.36 nm), methane (0.38 nm) and finally propane (0.43 nm) (Kinetic diameters are cited from the literature [11]). Permeselectivity values for the membrane were also well above the Knudsen diffusion values. The selectivities of carbon dioxide to methane and propane were 5.8 and 13.2, respectively, compared to the Knudsen diffusion values of 0.6 and 1.0. This result is quite different from the permeation of the membrane prepared with TEOS. In addition, the hydrogen permeance was dramatically improved: hydrogen permeance of PTES-derived membrane was 4.5 times higher than that of TEOS-derived membrane maintaining a high hydrogen/nitrogen selectivity of 59.5.

The PTES-derived membrane thus is believed to have micropores larger than those of the TEOS-derived membrane and all the mesopores were virtually plugged. In addition, the PTES-derived membrane consisted of abundant sub-micropores through which only hydrogen is permeable and a few micropores through which \( \text{CO}_2 \) and \( \text{N}_2 \) are barely able to pass one another. This suggests that micropore size in the amorphous silica membranes was well controlled by varying the substituents on silanes. Under the present deposition condition of 773 K, phenyl groups of PTES remained unreacted and decreased the crosslink density, thus leading to a loose amorphous structure after calcination. The BET surface areas of calcined silica powders were, respectively, 193 m²/g and 365 m²/g for TEOS and PTES used as the Si source. Therefore, it is presumed that micropores were more abundant in the membrane formed with PTES than
with TEOS. Although there is currently no direct method to measure the pore size distribution of the supported submicron-thick membrane layer in the silica-based membranes [12], we believe that the large observed differences in the permeance values for gases with only relatively small differences in kinetic diameters indicate that the diameter of most of the pores is below 0.5 nm.

Conclusions

A defect free silica membrane was synthesized in a mesoporous \( \gamma \)-alumina film coated on the \( \alpha \)-alumina tube by chemical vapor deposition of phenyltriethoxysilane (PTES) at 773 K. Carbonaceous matters that remain in the membrane were removed by subsequent calcination. The PTES-derived membrane showed molecular-sieving characteristics differentiating \( \text{CO}_2 \), \( \text{N}_2 \), \( \text{CH}_4 \), and \( \text{C}_3\text{H}_6 \) by molecular size, while TEOS-derived membrane separated the gases by Knudsen diffusion, lighter gas being permeated preferentially. The PTES-derived membrane had abundant sub-micropores, which is larger than those of the TEOS-derived membrane and no mesopores of Knudsen diffusion regime. Improved membrane performance was obtained by using PTES as a CVD precursor, presumably via fine-tuning of micropores with successful removal of mesopores.

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References