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Development of pore size-controlled silica membranes for gas separation by chemical vapor deposition

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ABSTRACT

Silica membranes were prepared by chemical vapor deposition using oxygen and tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMS), or dimethoxydiphenylsilane (DMDPS) as the silicon source at 873 K. The pore size was successfully controlled by changing the number of phenyl groups on the silicon precursor. The permeation test of several gases revealed that larger pores were formed upon increasing the number of phenyl groups on the source. The DMDPS-derived membrane showed excellent hydrogen permeance at 573 K of the order of 10^{-6} mol m^{-2} s^{-1} Pa^{-1}, and a high hydrogen/sulfur hexafluoride permselectivity of over 6800, and this excellent performance was constant for 266 h even under moist conditions containing steam at 3.4 kPa and 573 K. Characterization with XPS indicated that the DMDPS-derived membrane was thinner than the TMOS membrane. Additionally, the bond energies of the silicon sources were estimated based on quantum chemical calculations with the CBS-QB3 method. The results showed a strong tendency for gas-phase conversion of TMOS or PTMS to dimethoxysilanone, $(MeO)_2Si{=}O$, and DMDPS to methoxyphenylsilanone, $Ph(MeO)Si{=}O$, transient intermediates that act as major precursors. It was suggested that whether the intermediate contained phenyl groups greatly influenced the enlargement of pore size of the silica membrane.

1. Introduction

Gas separation through a membrane is a valuable process because membrane separation makes an apparatus more compact with lower energy costs relative to many other conventional technologies. Target gases to be separated depend on the occasions, for example "hydrogen" should be separated in one case or "carbon dioxide" should be separated in another case, so the optimal membrane differs depending on the composition of each separation system. Polymeric membranes are now often used in such practical application in chemical industry. On the other hand, the separation system using inorganic membranes is also a promising technology because inorganic membranes are superior to organic membranes in terms of high-temperature- or chemical-resistance, separation in nonaqueous system, long-term operation, and so on. Generally, the typical principle of gas separation using inorganic membranes is the "molecular-sieve" mechanism; only gases that are smaller than the pore sizes can permeate through the membranes. Thus, the control of membrane structure is one of the most important techniques to be developed in inorganic membrane studies to take advantage of these features and broaden the application of inorganic membranes. Molecular sizes of gases are not more than 1 nm, so it is desirable to establish the methodology of controlling the pore size of the inorganic membranes in the subnanometer range to apply various gas separation system.

Hassan et al. [1] evaluated the permeation properties of a silica hollow fiber with micropores of 0.59–0.85 nm. The selectivity of carbon dioxide/methane was 156 at 298 K, but the permeance of carbon dioxide was only 10^{-10} mol m^{-2} s^{-1} Pa^{-1}. Several types of zeolite membranes such as DDR [2], LTA [3], MFI [4–6], and FAU [7–9] have been fabricated. Zeolite membranes have also been studied for various separation systems because of their properties of molecular sieving and sorption selectivity. On the other hand, zeolite membranes have a uniform structure and fixed pore size associated with each structure type, and therefore the control of membrane structure is impossible.

Amorphous silica membranes are attractive membranes because they are more economic and practical materials compared with any other inorganic membrane, and they can be prepared both by a sol–gel method [10–14] and by a chemical vapor deposition (CVD) method [15–19]. These reported silica membranes were able to separate hydrogen from other gases with a selectivity of

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100–1000, and so they have been studied for applications such as the methane–steam reforming reaction [20–22]. It was suggested that amorphous silica membrane prepared by the CVD method had micropores of approximately 0.3 nm because only hydrogen and helium were able to permeate through the membrane. However, there are many industrially important separation systems besides hydrogen separation. The development of silica membranes showing high selectivity among gases larger than hydrogen and the strict control of pore size are eagerly awaited.

Generally, the pore size of membranes is more successfully controlled by the sol–gel method than by the CVD method. Asaeda et al. [23] prepared a porous silica–zirconia membrane by the sol–gel process using tetraethoxysilane (TEOS) and zirconium tetra-*n*-butoxide. This composite membrane had micropores of about 0.5 nm and showed isopropyl alcohol/water selectivity of 40–2500. Raman and Brinker [24] fabricated silica membranes using a hybrid organic–inorganic sol, prepared by copolymerization of TEOS and methyltriethoxysilane. The carbon dioxide/methane selectivity of this membrane was 71.5 and the carbon dioxide permeance was of the order of 10^{-7} mol m^{-2} s^{-1} Pa^{-1}. Kim et al. [25] also prepared membranes using TEOS and methacryloxypropyltrimethoxysilane as the reactants in the sol–gel process. The pore size of the silica membrane prepared after calcinations at 673–973 K was estimated to be in the range of 0.6–0.7 nm. In addition, the membrane calcined at 873 K showed a hydrogen permeance of 2×10^{-7} to 7×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and the selectivity of hydrogen/sulfur hexafluoride was reported around 1000 at 573 K. Okui et al. [26] prepared porous organic/inorganic hybrid membranes via a sol–gel route using TEOS and phenyltrimethoxysilane (PTMS). The pore size of the membrane was so large that the molecular sieve effect was not shown.

On the other hand, the CVD process is simpler, and it is easier to prepare a membrane than with the sol–gel method. Sea et al. [27–29] prepared silica membranes by pyrolysis of phenyl-substituted ethoxysilanes, phenyltriethoxysilane (PTES) and diphenyldiethoxysilane (DPDES). Amorphous silica was deposited in the mesopores of an γ-alumina layer coated on an α-alumina tube, by evacuating the reactant through the porous wall. Carbon residues including the phenyl groups were removed by calcination after the CVD process. The permeance of hydrogen and selectivity of hydrogen/sulfur hexafluoride through PTES membrane were 5.7×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and 380 at 473 K. And the permeance of hydrogen and selectivity of hydrogen/sulfur hexafluoride through DPDES membrane were 5.0×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and 1200 at 473 K [28]. It was indicated by the permeation results of gases that the membranes produced from PTES and DPDES had looser structures than a TEOS-derived membrane and the DPDES membrane had larger micropores than the PTES membrane. In this way the methodology of pore size control by changing the functional groups of the silicon source is considered reasonable, but the analysis of the reaction or the mechanism of micropore formation has hardly been discussed.

Wróbel et al. [30,31] investigated the mechanism of silica film growth using TEOS in atomic oxygen-induced chemical vapor deposition (AOCVD) or in remote oxygen plasma chemical vapor depositions (ROP-CVD). In both reactions, the oligomeric products identified by GC/MS, and the chemistry involved in their formation, suggested the strong possibility that TEOS converted to diethoxysilanone, a highly reactive precursor for silica film growth. However, the reaction mechanism or the intermediates of the silicon source except for TEOS have seldom been studied. It is necessary to clarify why the functional groups of the silicon source determine the pore size of the membranes, for feeding back the results to improve membrane synthesis in the future.

In this study, silica membranes were prepared using tetramethoxysilane (TMOS), PTMS, and dimethoxydiphenylsilane (DMDPS) as the silicon sources not by pyrolysis but by two kinds of CVD methods with oxygen: a counter-diffusion CVD method and a one-sided diffusion CVD method. The three organosilanes, shown in Fig. 1, that have different numbers of phenyl groups were employed based on the concept that the pore size of the silica membrane was enlarged when the side chain groups in the silicon source were large atomic groups. We then report the permeation results of single gases through the silica membranes prepared from each silicon source, and characterization of the membranes using field emission-scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS) analysis. Moreover, possible intermediates in the CVD reactions are indicated based on the results of the bond dissociation energies calculated using quantum chemical calculations.

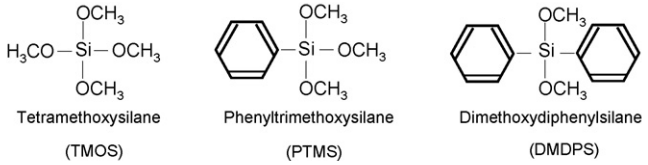

Fig. 1. Molecular structures of tetramethoxysilane, phenyltrimethoxysilane and dimethoxydiphenylsilane.

2. Experimental

A porous α-alumina capillary (Ø 3 mm, *L* 350 mm, supplied by NOK Co., Japan) with 100 nm pores was used as the substrate. A membrane was synthesized at the center of the substrate (50 mm) and the other parts were glazed with a sealant. The γ-alumina layer was coated to reduce the pore size according to the article by Yoshino et al. [32]. The outer surface of the effective area of the substrate was dipped in a boehmite sol (γ-AlOOH) for 5 s. After the dipping, the substrate was dried for 1 h in air and then calcined at 873 K for 3 h. The dipping–drying–calcination process was repeated twice. The pore size of the γ-alumina layer was found to be about 4 nm by permporometry measurements.

The silicon sources were TMOS, PTMS, and DMDPS, purchased from Shin-Etsu Chemical, Japan. Fig. 2 shows a schematic diagram of the CVD apparatus. All three silicon sources are liquids at room temperature. Their saturated vapors were introduced to a reactor using nitrogen gas as the carrier. As for the TMOS membrane, the counter-diffusion CVD method [19] was employed for membrane synthesis. TMOS was supplied through the outside of the substrate and oxygen supplied through the inside. On the other hand, when PTMS or DMDPS was used, a one-sided diffusion CVD method was employed. The silica source and oxygen were supplied concurrently through the outside of the substrate while controlling the pressure inside the substrate at 200 Pa using a vacuum pump. In both methods, the temperature of the substrate was maintained at 873 K, and the flow rates of both nitrogen and oxygen were controlled at 200 mL min^{-1} using a mass flow controller. The bubbler temperature for TMOS was maintained at 318 K, that for PTMS was at 423 K, and that for DMDPS was at 473 K. The CVD time was constant at 1 h.

Gas permeation measurements were carried out at 373–573 K using single-component hydrogen, oxygen, nitrogen, carbon tetrafluoride, and sulfur hexafluoride. The permeance tests of each gas were performed using the same apparatus. The permeance of hydrogen was measured using a bubble flow meter because of its high permeance, and that of the other gases was determined with the pressure difference method [19]. A steam test was also performed using the same apparatus. Nitrogen at a rate of 50 mL min^{-1} was bubbled through pure water controlled at 299 K, the vapor pressure of water being 3.4 kPa.