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Ship-in-a-bottle synthesis of a cobalt phthalocyanine/porous glass composite membrane for oxygen separation

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Abstract

A cobalt phthalocyanine/porous glass composite membrane for oxygen separation was prepared by ship-in-a-bottle synthesis where encapsulation of cobalt phthalocyanine into pores of porous glass was achieved by chemical vapour deposition using 1,2-dicyanobenzene. Formation of CoPc in the pores of porous glass was confirmed by UV-Visible spectroscopy. Single gas permeation through the membrane was measured at 298, 323 and 373 K using O_2 and N_2. Ratio of the permeances, O_2/N_2 through the membrane was about 3. This value was 3 times higher than the theoretical Knudsen value (O_2/N_2=0.94). This membrane indicates O_2-selectivity even at relatively high temperature.

Keywords

Ship-in-a-bottle synthesis; Oxygen separation; Cobalt phthalocyanine; Porous glass; Composite membranes

1. **Introduction**

Oxygen separation membranes are important in various fields such as medicine, oxygen-enriching combustion systems. With regard to oxygen-enriching membranes, considerable attention has been focused on the addition of an oxygen carrier into an organic polymer or inorganic-organic hybrid membrane. Some efforts have been made to facilitate transport using transition metal complexes (oxygen carriers) such as cobalt porphyrin complexes [1], cobalt Schiff base complexes[2, 3] and cobalt phthalocyanine complexes[4].

Recently, the encapsulation of transition-metal complexes within the pores of a porous material has been reported. Among these, the most common method utilizes a ship-in-a-bottle synthesis in which the final molecule is prepared inside the pores by reacting smaller precursors.[5, 6] After the synthesis, the large molecule remains ‘mechanically entrapped’ and encapsulated inside the pores with some restricted conformation and arrangement. Since this restricted conformation and arrangement can realize novel functionality (catalytic, electronic and optical properties), this method of preparing nanocomposite materials by ship-in-a-bottle has received considerable attention.

Here, we report the ship-in-a-bottle synthesis of a cobalt phthalocyanine/porous glass composite membrane for oxygen separation by chemical vapour deposition (CVD). Cobalt phthalocyanine (CoPc) has been used in the manufacture of dyes, electronics, photoactive materials, sensors and catalysts due to its electronic structure and stability in air. In addition, CoPc is known as a molecule with reversible oxygen-binding ability, and it can be used as an oxygen carrier in a facilitated oxygen transport membrane. However, it is difficult to fix it in the membrane. To solve this problem, we propose the application of ship-in-a-bottle synthesis by CVD using 1,2-dicyanobenzene (DCNB) as a small precursor. Co ions are fixed in the pores of porous glass by an ion exchange method, and then CoPc is synthesized with Co ions in the pores and gaseous DCNB introduced by CVD. Therefore, CoPc is encapsulated densely and deeply within the pores. Based on these concepts, we have prepared a novel porous glass composite membrane with CoPc as an oxygen carrier.

2. Experimental

Porous glass tubes with a mean pore diameter of 4 nm, outer diameter of 5 mm, inner diameter of 4 mm and length of approximately 5 cm were used as supports. Porous glass has silanol groups whose silanol protons can be replaced by metal ions. As a metal source, Co(II) ions were introduced into the porous glass by an ion exchange method, and cobalt-exchanged porous glass (Co-PG) was obtained. Before carrying out ion exchange, the porous glass tube was dried at 393 K for several hours in a vacuum to evaporate molecular water such that only the surface hydroxyl groups remained. The porous glass was immersed in a mixture of 12.5 mg of Co(II) acetate tetrahydrate and 10 ml ethanol (Co ion concentration: 5×10^{-3} mol•dm^{-3}). Ion exchange was then performed at room temperature for 24 h. To accelerate ion exchange, ultrasound was applied for the first 1 h. After a period of ion exchange, the porous glass tube was removed and re-immersed in ethanol at room temperature for 24 h to remove unexchanged Co ions. Co-PG was then re-heat treated at 453 K for 3 h in a vacuum to evaporate trapped ethanol. Dried Co-PG and DCNB were placed in a small glass tube. This tube was sealed in a vacuum and heated at 473 K for 24 h. During heating under vacuum, DCNB was sublimed and transferred into Co-PG, which became deep blue during this procedure. The final product, a cobalt phthalocyanine/porous glass composite membrane (CoPc-PG), was obtained on re-heat treatment at 623 K for 7 h in a vacuum to remove unreacted chemicals.

3. Results and discussion

In order to identify the products in the pores of the porous glass membrane, the CoPc-PG was treated with dimethylsulfoxide (DMSO) by Soxhlet extraction, and the UV-Visible absorption spectrum of the extract was measured (Fig. 1, spectrum a). Figure 1 includes a spectrum of pure CoPc dissolved in DMSO (spectrum b). The spectral shape and peak positions of CoPc-PG are consistent with those of CoPc. This agreement indicates that CoPc was exactly formed in CoPc-PG.

N_2 adsorption-desorption isotherms of PG and CoPc-PG at 77 K are shown in Fig. 2. These are type IV isotherms according to the BDDT classification originally proposed by Brunaer et al.[7] This isotherm is typical of adsorption-desorption on mesoporous solids, and it is characterized by a hysteresis loop. The amount of adsorption decreased with the introduction of CoPc. The specific surface areas based on the BET plots[8], pore volume and C constants of the membranes are presented in Table 1. The specific surface area and pore volume also decreased with the introduction of CoPc. The C constant for the CoPc-PG membrane was considerably different from that of the original porous glass membrane. It is known that the C constant is related to the heat of adsorption in the BET equation.[8] The difference is therefore considered to be due to a difference in the pore surface. The surface of the original porous glass (PG membrane) had OH groups, some of which were exchanged with Co(II) ions and the introduced CoPc during the ship-in-a-bottle synthesis, thereby altering the surface nature. These results indicate that molecules of CoPc were certainly encapsulated in the pores of the porous glass.

After drying at 373 K in a vacuum oven, single gas permeation (O_2 and N_2) through the membranes was measured at different temperatures by a variable pressure method.[9] One end of the tubular membrane was sealed, and the other was connected to a Pyrex glass tube with epoxy resin. The membrane modules were supported in a gas flow cell. Table 2 lists the permeances of O_2 and N_2 through the porous glass membrane and CoPc-PG membrane and shows the selectivity factor $\alpha = P_{O_2}/P_{N_2}$, where P_{O_2} and P_{N_2}

are the permeances of O_2 and N_2, respectively. The CoPc-PG membrane exhibited oxygen selectivity even at high temperature. The oxygen selectivity was found to increase slightly with temperature. At 373 K, the O_2/N_2 selectivity factor was 3.4, and the permeance of O_2 was 1.6×10^{-10} ($\mathrm{mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}}$). This selectivity factor is greater than the theoretical Knudsen value ($P_{O2}/P_{N2} = 0.94$), and it can be attributed to the affinity of CoPc for oxygen. This oxygen affinity is weakened with increasing temperature because oxygen adduct formation in CoPc is an exothermic reaction.[4] Therefore, CoPc effectively only releases oxygen at a higher temperature, that is strongly trapped by CoPc at low temperature and thus lowers the mobility of oxygen. The absence of oxygen selectivity in the porous glass membrane (without CoPc) confirms that oxygen selectivity is related to the presence of cobalt phthalocyanine.

4. Conclusion

A cobalt phthalocyanine/porous glass composite membrane for oxygen separation was prepared by ship-in-a-bottle synthesis using 1,2-dicyanobenzene (DCNB) as a reaction agent. The results indicate that CoPc is successfully synthesized in the pores of the porous glass membrane by ship-in-a-bottle synthesis using the CVD method. This membrane indicates O_2-selectivity even at relatively high temperature.

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Captions

Table 1 Specific surface area, pore volume and C constant of CoPc-PG and PG membrane.

Table 2 Permeances and selectivity factors of O_2 and N_2 through CoPc-PG and PG membranes at 298, 323 and 373 K.

Fig. 1 UV-Visible absorption spectra of (a) extraction from CoPc-PG membrane and (b) commercial CoPc in DMSO.

Fig. 2 N_2 adsorption-desorption isotherms of PG (○) and CoPc-PG (△) membrane; solid symbols: adsorption, open symbols: desorption

Table 1 Specific surface area, pore volume and C constant of CoPc-PG and PG membrane.

Sample	Specific surface area (m^2•g^{-1})	Pore volume (cm^3•g^{-1})	C constant
CoPc-PG	181	0.147	72.5
PG	243	0.177	286.3

Table 2 Permeances and selectivity factors of O_2 and N_2 through CoPc-PG and PG membranes at 298, 323 and 373 K.

Membrane	Temperature/ K	10^{-11} Permeance/ mol•m^{-2}•s^{-1}•Pa^{-1}		Selectivity factor
		O_2	N_2	PO_2/PN_2
CoPc-PG	298	7.97	2.78	2.9
	323	9.96	3.31	3.0
	373	15.6	4.57	3.4
PG	298	497	531	0.93
	323	466	509	0.92
	373	432	474	0.91

Theoretical selectivity factor based on Knudsen flow is 0.94.

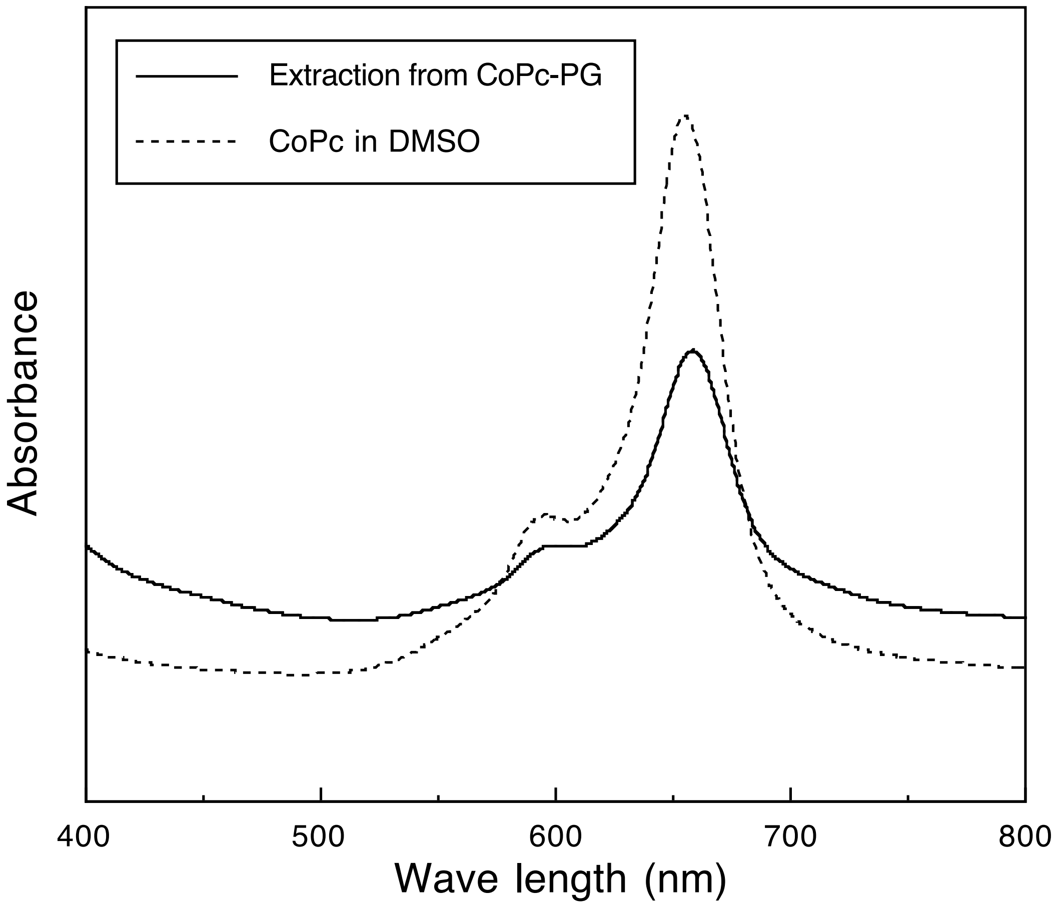

Fig. 1 Kuraoka et al.

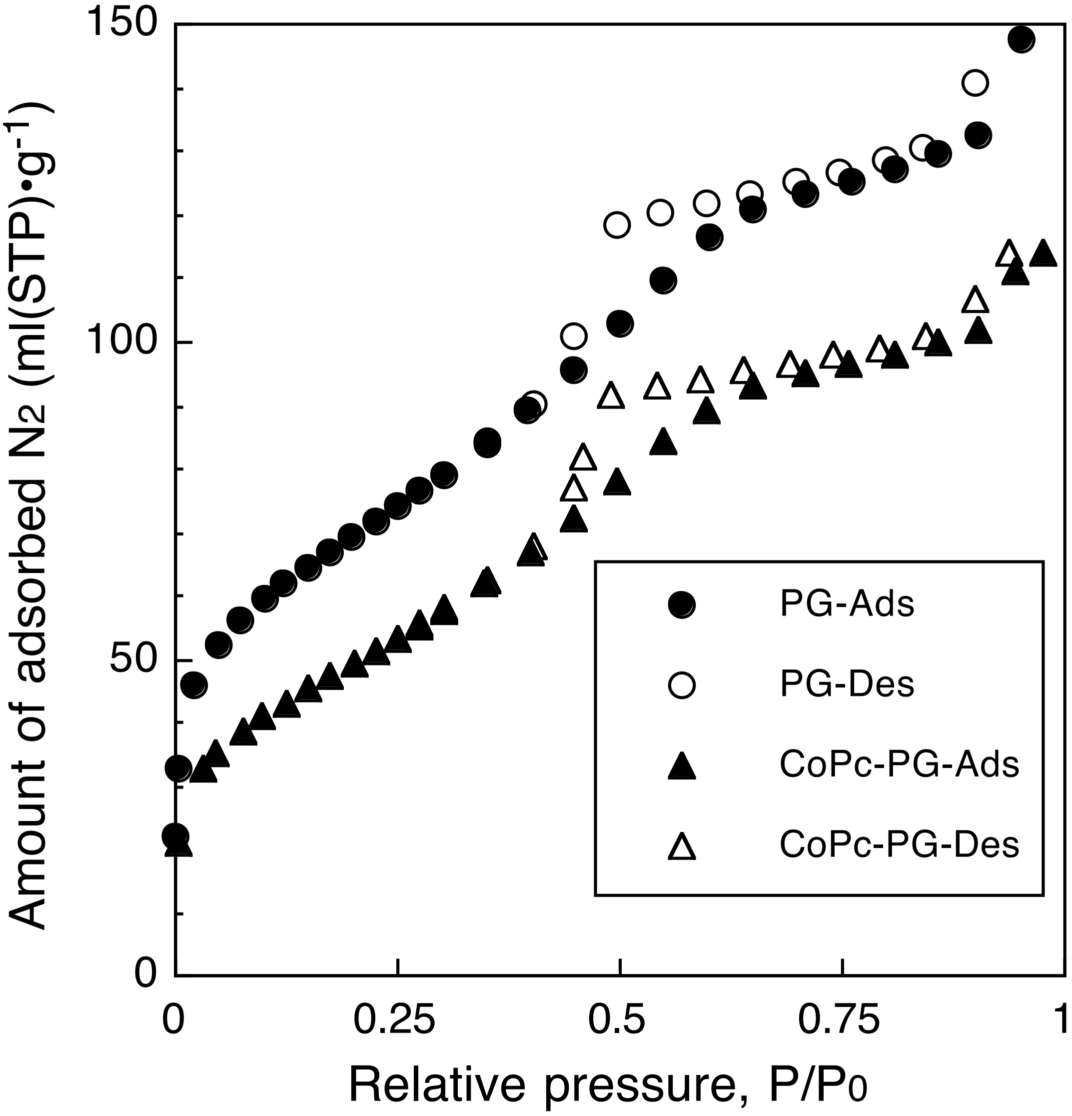

Fig. 2 Kuraoka et al.