초청강연

Porous Ceramic Membranes for Separation of Molecular Mixtures
-Fabrication methods, Separation performance and Stability-

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1. Introduction

About 20 years ago, inorganic porous membranes were found quite effective also for separation of some kinds of molecular mixtures. Since then many researchers have been engaged in developing various kinds of inorganic membranes. Some of them are dense membranes such as perovskite type membranes for O_2 separation, metal membranes for H_2 separation and dense silica membranes for separation of H_2 or He, for example. Most of the inorganic membranes, however, are porous membranes of fine pore size less than 1nm such as various kinds of zeolite membranes, porous carbon membranes and sol-gel derived ceramic membranes.

The molecular sizes of many chemicals of ordinary molecular weights are usually less than around 1 nm and thus porous separation membranes should require pores of the same order for high selectivity. Several methods have been proposed for fabrication of inorganic porous membranes of his kind: thermal hydrolysis, CVD method, phase separation and leaching, sol-gel method, pyrolysis etc. Each method has its own merits and demerits just as the membrane materials do.

Here in this presentation I would like to introduce one of the most flexible methods or the sol-gel method with some examples of the observed characteristics for separation of molecular mixtures with the so-gel derived membranes.

2. Membrane Fabrication

There are at least four requirements for the developments of practical separation membranes:

(a) high flux

• thin membrane thickness, • highly porous material, • sufficiently small pore size, • specific membrane (pore) structures, etc.

(b) high selectivity

• defects-free membrane, • sufficiently small pore size, • sharp pore size distribution, • selective interaction with pore wall, etc.

(c) high stability

• stability against (hot) water, acids, alkali and organic chemicals, • stability against high temperature and mechanical load, etc.

(d) low cost.

• low price of substrate, • easy fabrication procedures
• easy handling etc.

In order to develop practical inorganic separation membranes it will be crucially important to search for membrane materials of high porosity and of high stability against chemicals. Especially stability against water is quite important to every kind of membranes because otherwise the membrane may change its pore structures or separation characteristics due to the capillary condensation of water vapor while left in the atmosphere.

2.1 Sol-gel methods

The sol-gel methods provide one of the most flexible techniques to fabricate inorganic porous membranes of various pore sizes and of various single and composite inorganic materials. Moreover, sol-gel derived ceramic membrane generally comprises an extremely thin active top layer on a coarse layer or porous support. The asymmetric membrane structures hopefully make the permeation flux quite large as shown in the following sections. *The methods comprise two stages: sol* preparation and membrane coating.

2.2 Sol preparation

The particle size control in addition to the narrow size distribution is quite essential. In case of multi-components colloidal sol preparation the preparation procedures should be well studied to obtain highly composite colloidal sols. Figure 1 shows an example of preparation method of SiO_2-ZrO_2 composite colloidal sols. The average particle sizes can be controlled by the sol concentration at the boiling step and by pH of the sol.

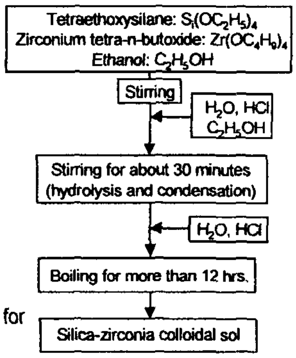


Fig.1 Example of preparation procedures for colloidal SiO_2-ZrO_2 sols

2.3 Membrane coating

The conventional method of the membrane coating is the slip coating or dip coating, where sols are usually coated at room temperature and dried slowly, then fired with careful temperature controlling (heating and cooling). 'The hot coating method' is much more rough, quick and efficient at *the same time. The procedures are shown in Fig.2, for* example.

By these fabrication procedures we can obtain porous ceramic membranes of thin active layers for separation as shown in Fig.3. An example of pore size estimation by the gas permeation of various kinetic diameters is shown for

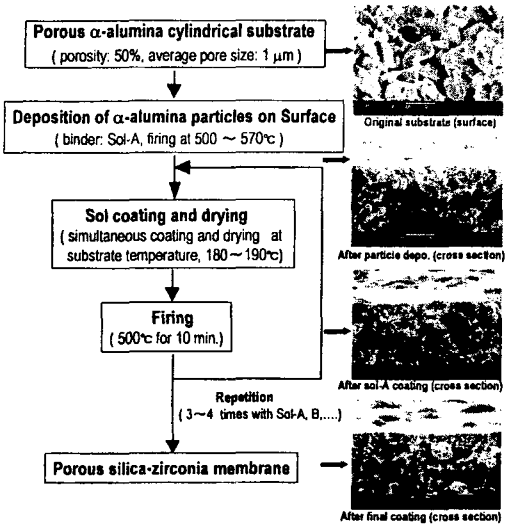


Fig.2 Membrane coating by hot coating methods

silica membranes (pore size < 0.55 nm), for example. The dynamic method of humid gas permeation based on the Kelvin's capillary condensation theory is also quite helpful to estimate the pore size larger than around 1 nm.

3. Some Examples of Separation Performance

Here in this section are shown some examples of separation performance or characteristics observed for gas separation and pervaporation of liquid mixtures such as aqueous solutions of organic chemicals.

3.1 Gas permeation and separation

Silica membranes show quite efficient separation characteristics for gas separation. Figure 5 shows a separation example of H_2/N_2 mixtures at 270°C. The pore size of this kind of silica membrane is less than a few Angstrom, and the activated permeation prevails only for H_2 and He. The observed ideal separation ratio for He/N_2 for this membrane is 326. The silica membrane in Fig.5 was prepared not by the hot coating procedures but by the conventional dip coating method. The permeance and the selectivity can be improved by the hot coating method.

The following simple mass balance gives an equation of separation performance, assuming complete mixing on both sides of the membrane (Fig.6).

Permeation rates of components A, B:

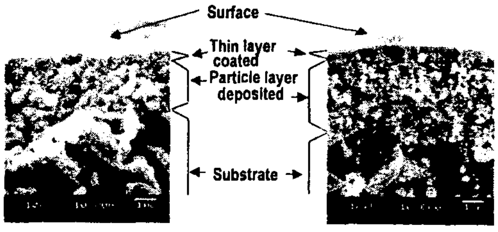
$$N_A = K_A(P_u x_A - P_d y_A), \qquad N_B = K_B(P_u x_B - P_d y_B)$$

From these equations and mass balance, we can obtain

$$y_A = \gamma - [\{\gamma^2 - 4\,\alpha\,\beta(\alpha-1)\,x_A\}]^{1/2} / \{2\beta\,(\alpha-1)\}$$

here α : **permeability ratio** K_A/K_B
β : **total pressure ratio** P_d/P_u
$\gamma = (\alpha-1)(x_A+\beta)+1$

Some calculated examples are shown in Fig.7 with various permeability ratios, α.



SiO₂-ZrO₂membrane **SiO₂ membrane**

Fig.3 Examples of SEM photograph of membrane cross-section

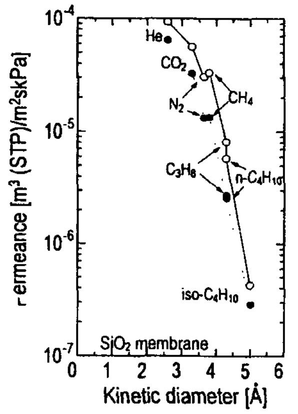


Fig.4 Examples of permeance vs. kinetic diameter of gases

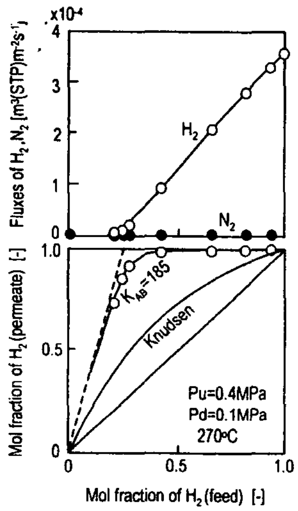
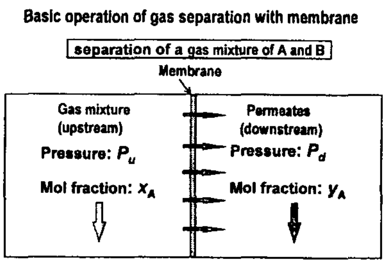


Fig. 5 Example of H_2/N_2 separation at 270°C

Fig.6



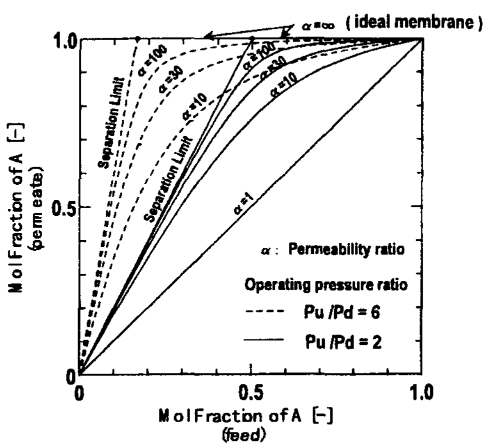


Fig.7 Some calculated separation performance

A porous silica membrane of pore size around 4-6 Angstrom is quite interesting for separation of organic gases such as propylene from its propane mixture (Fig.8). This kind of porous membrane is quite stable in dry conditions, but not stable against water or water vapor.

Gas permeation mechanisms

The gas permeation mechanisms depend on the interactions between the permeating gas molecules and the pore wall (fig.9). Potential energy *ΔEp* (or pore size) can define the permeation mechanism.

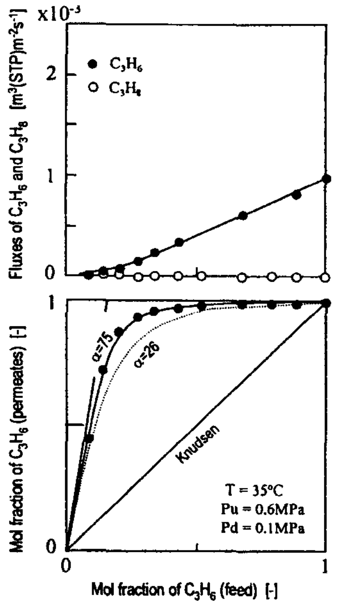


Fig.8 An example of C_3H_6/C_3H_8 separation

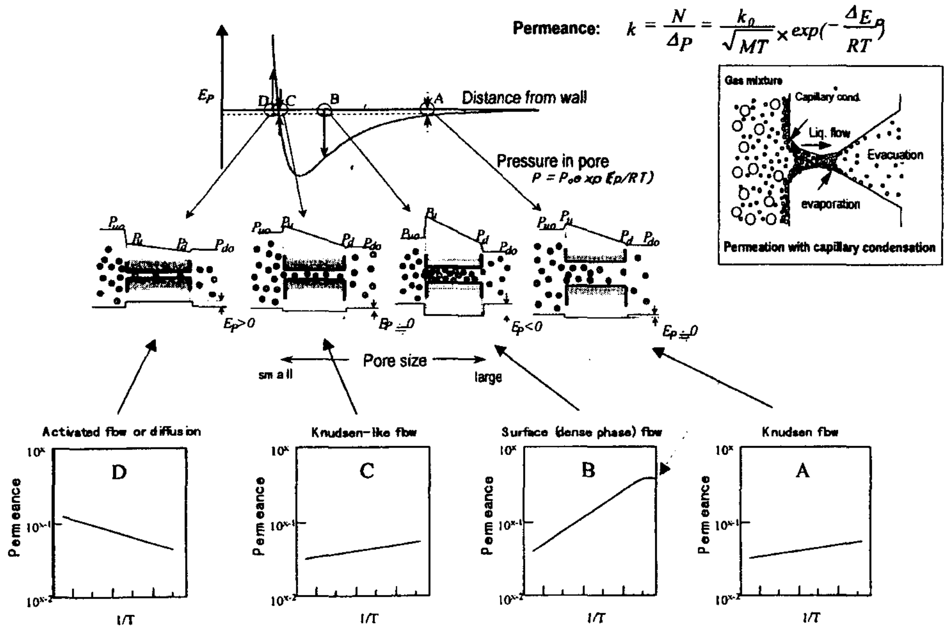


Fig.9 Permeation mechanisms of gasses in fine pore

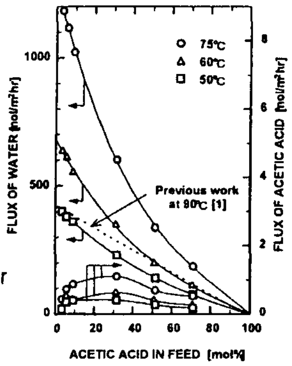


Fig.10 Separation results for acetic acid/water mixture

3.2 Pervaporation performance

Silica membranes

Silica membranes are relatively stable against aqueous solutions of organic acids. They can be used for separation of acetic acid/water mixture. Some separation results are shown in Fig.10. This kind of silica membrane can be applied to a membrane-aided reactor for esterification (Fig.11). If the pore size is well controlled, silica membranes are quite effective for separation of ethanol/benzene, toluene, cyclohexane mixtures, etc.

Silica-zirconia membranes

Also silica-zirconia(10%) porous membrane shows good separation performance for methanol/MTBE mixtures (Fig.12). A larger content of zirconia makes silica-zirconia membranes quite stable against hot water (Fig.13). The water flux at 72mol% of IPA (10 wt% H_2O) is around 9 kg/m²/h with a separation factor of larger than 2500.

A model of pervaporation mechanism

The separation mechanism seems to depend on some kinds of interaction of the participating molecules and pore wall besides the pore size. Adsorption of IPA molecules at low IPA concentration and reaction between IPA and -OH group on the pore wall in the higher concentration region seem to make the silica-zirconia membrane in Fig.13 a molecular sieving-like membrane for the mixture.

A permeation mechanism for pervaporation has been proposed as shown in Fig.14. A conical pore structure in the active separation layer is assumed with the smaller opening to the feed mixture. The pure liquid water can be drown out of the mixture by the difference between the capillary suction pressure and the osmotic pressure. The former is usually larger than the latter since the pore size is mostly less than several Angstrom. The liquid water evaporates at the meniscus in the pore due to the evacuation in the permeate side. Some rate equations assuming the pore structures can allow numerical simulations to obtain good discriptions of the phenopmena.

4. Concluding remarks

Because of their high selectivity, high flux and high stability inorganic membranes can hopefully be applied in various fields such as pervaporation, gas (vapor) separation, senser, membrane-aided reactor, catalytic membrane reactor, etc.

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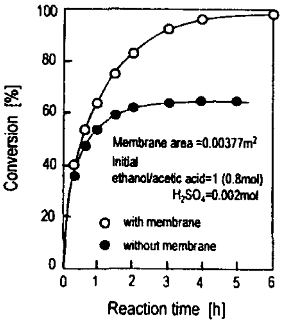

Fig.11 Esterification with and without membrane

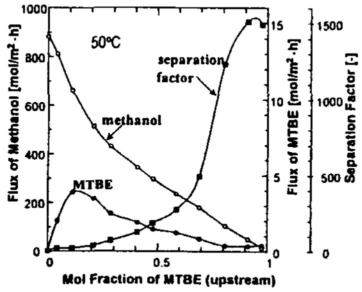

Fig.12 Pervaporation of methanol/MTBE mixture at 50 °C

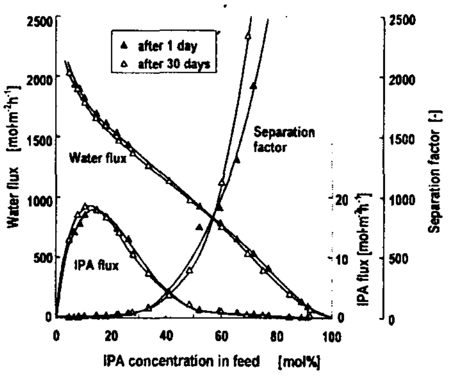

Fig.13 Pervaporation of IPA/water mixtures at normal boiling points

(SiO_2-ZrO_2(40%) membrane fired at 400°C)

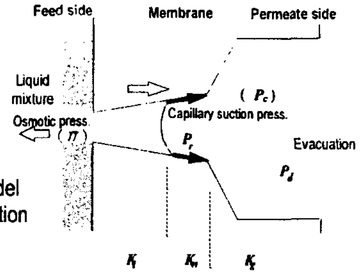

Fig.14
A simple model of pervaporation mechanism