Improvement of Surface Transport Property by Surface Modification

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Porous glass is a kind of borosilicate glass characterized by a sharp pore size distribution and a large specific surface area. The pores, only a few nanometers wide, are the smallest found in inorganic membrane materials. In addition, porous glass is thermally and chemically stable, and so seems promising as a separation membrane for use under severe conditions. In several research studies made in recent years, however, the poor selectivity of porous glass was pointed out. The effects of operating conditions on the permeation rate and the selectivity were carefully studied in these investigations, and yet few improvements of the selectivity by membrane modification have been achieved (Schnabel and Vaulont, 1978). Our intent in this work was therefore to improve the selectivity of this inorganic material.

The transport mechanisms of gas molecules through porous materials are gas phase flow, adsorbed phase flow (surface flow), condensed flow, and their combinations. For gas phase flow, the mechanism has been clarified well enough to estimate parameters, and the selectivity is shown to be poor in the absence of a large molecular weight difference. On the other hand, there still remain unclarified points about surface flow, in spite of its importance in such fields as membrane separation, adsorption, catalysis, and drying.

The surface flow rate is controlled by the product of adsorbability (in this case Henry's constant) and mobility (surface diffusivity) of an adsorbed molecule on the surface. In a previous paper, the authors presented a correlation of surface diffusivity with a dimensionless heat of adsorption, considering a surface structural effect (Okubo and Inoue, 1987). In this communication, the possibility of improving the selectivity by surface modification is presented, and two factors that govern surface transport are discussed.

Experimental Methods

A porous glass surface is covered with hydrophilic silanol groups $\geq$SiOH, which interact with the adsorbed molecules (Hair, 1967). As the surface is a field of surface flow, the modification of the surface by reaction of the surface silanol group is expected to be effective in changing the surface flow property. The silanol group can react with alcohols, chlorides, fluorides, organosilicon compounds, and others. In this work, surface silanol groups were esterified with three kinds of alcohols, methanol, ethanol, and 1-propanol, by the method for silica gel of Utsugi (1973). Porous glass pipes were heated in an autoclave with the alcohols up to the alcohols' critical temperature.

$$\geq \mathrm{SiOH} + \mathrm{ROH} \rightarrow \geq \mathrm{SiOR} + \mathrm{H_2O}$$

Single-gas permeation experiments using carbon dioxide (CO_2), propane (C_3H_8), Freon 22 (R-22, $CHClF_2$), and Freon 114 (R-114, $CClF_2$—$CClF_2$) were carried out at 308, 318, and 328 K. A small surface coverage region (gas phase pressure = 10–1,000 Pa) was chosen to clearly evaluate the effect of surface conditions on surface flow. The experimental procedure was the same as previously described (Okubo and Inoue, 1987).

Results

Physical properties of the original and modified porous glasses, determined by the method of Dollimore and Heal (1964), are shown in Table 1. After modification, pore radii were found unchanged, while surface areas and pore volumes were lower, a result of partial pore closure. Carbon content and calculated modified group concentration are summarized in Table 2. The original silanol group concentration was determined from the weight loss in thermal analysis (Young, 1958). As the size of the alcohol molecule increased, the modified group concentration decreased. According to a model presented by Utsugi (1973), one modified group can cover some unmodified silanol groups by its rotation. Considering the size of the modified group with Utsugi's model, these surfaces were expected to be completely covered with modified groups (Okubo and Inoue, 1987).

Table 1. Physical Properties of Original and Modified Porous Glasses

Alcohols	Pore Radius nm	Surface Area $m^2 \cdot kg^{-1}$	Pore Volume $m^3 \cdot kg^{-1}$
Original	1.5	3.01×10^5	2.31×10^{-4}
MeOH	1.5	2.52	2.06
EtOH	1.5	2.11	1.69
1-PrOH	1.5	2.11	1.60

The changes in effective diffusivities defined in Eq. 1 are illustrated in Figure 1, where K_s is Henry's constant.

$$D_e = \frac{NL}{A(C_1 - C_2)} = \frac{\epsilon}{k_g^2} D_g + \frac{\rho S_p}{k_s^2} K_s D_s \qquad (1)$$

The abscissa indicates the carbon number per modified group. The tendency of the change was different for each gas. That is, the effective diffusivity of propane increased, while that of R-22 and R-114 decreased after modifications. For example, the effective diffusivity of propane at 308 K through the glass modified with 1-propanol was 1.3 times that through the original glass, compared to 0.39 times for R-22. These results indicate a possibility of changing membrane properties and of achieving better selectivity by suitable modifications.

Discussion

Structural parameters (porosity, tortuosity, surface area, and apparent density), which were also changed by modifications, are included in effective diffusivity as defined in Eq. 1. To clarify the effect of surface conditions on surface transport, the product of surface diffusivity D_s and Henry's constant K_s is discussed here. Each was presented and discussed in the previous paper (Okubo and Inoue, 1987). The product, K_sD_s, corresponds to the surface flow rate on a flat surface with unit gas concentration difference per unit distance. The changes in this product are shown in Figure 2. The difference in tendency of change among the gases displayed in Figure 1 disappeared, and the product increased similarly with increasing surface carbon number for all gases except R-22.

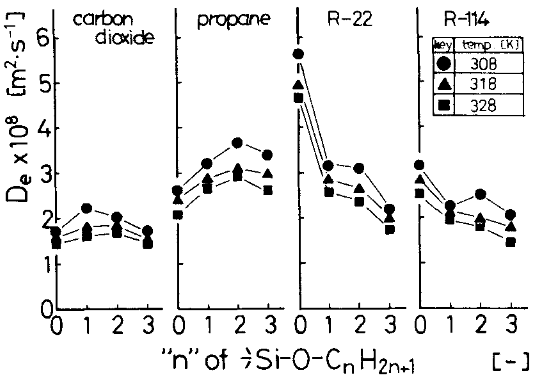

Figure 1. Changes in effective diffusivities by surface modifications.

Table 2. Properties of Original and Modified Porous Glass Surfaces

Alcohols	Carbon Content wt. %	Concentration of Group nm^{-2}
Original	—	7.0 ($\equiv$SiOH)
MeOH	2.22	4.53 ($\equiv$SiOMe)
EtOH	2.96	3.62 ($\equiv$SiOEt)
1-PrOH	3.85	3.17 ($\equiv$SiOPr)

To interpret the similar tendency evident in Figure 2, the intermolecular force between one adsorbed molecule and one surface group is considered. Intermolecular forces include dispersion, induction, and orientation forces. Dispersion forces are operative even between nonpolar molecules, and generally increase as the molecular weight increases. Induction and orientation forces are caused by interactions with permanent dipole moments. Permanent dipole moments of the permeating species in the present study other than R-22 are very small. The molecular weight of the surface groups increases with increasing carbon number while the permanent dipole moment decreases. So, except for R-22, the dispersion force is expected to play the most important role in the interaction between one adsorbed molecule and one surface group. Consequently, the interaction between the sorbate and the surface is expected to increase as the carbon number increases. Because of its large permanent dipole moment, the interaction of R-22 with the original silanol groups is expected to be no less than those with modified groups. Thus the tendency in Figure 2 is accounted for as follows. The surface transport product, K_sD_s, is increased as the interaction between one adsorbed molecule and one surface group increases. This is caused by a greater relative increase in the Henry's constant, which offsets any decrease in the surface diffusivity (Okubo and Inoue, 1987).

Conclusions

The results of single-gas permeation experiments through surface-modified porous glasses suggest the possibility of improving the separation property by surface modification. It was shown that surface modification increased surface transport. The transport rate correlates with the degree of interaction between one adsorbed molecule and one surface group.

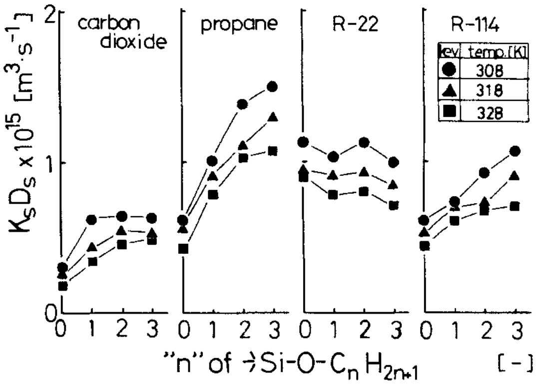

Figure 2. Changes in products of Henry's constants and surface diffusivities by surface modifications.

Notation

A = apparent cross-sectional area, m^2
C_1 = gas phase concentration in upstream side, $mol \cdot m^{-3}$
C_2 = gas phase concentration in downstream side, $mol \cdot m^{-3}$
D_e = effective diffusivity, Eq. 1, $m^2 \cdot s^{-1}$
D_g = gas diffusivity, $m^2 \cdot s^{-1}$
D_s = surface diffusivity, $m^2 \cdot s^{-1}$
K_s = Henry's constant of adsorption, m
k_g^2 = tortuosity factor for gas phase flow
k_s^2 = tortuosity factor for surface flow
L = thickness of membrane, m
N = total flux through membrane, $mol \cdot s^{-1}$
S_p = specific surface area of porous glass, $m^2 \cdot kg^{-1}$
ϵ = porosity of porous glass
ρ = apparent density of porous glass, $kg \cdot m^{-3}$

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