1064 Chemistry Letters Vol.38, No.11 (2009)

Effects of the Affinity between the Pore Wall and Solvent on the Intracrystalline Diffusivities of Benzene within Porous Materials in the Liquid Phase

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The intracrystalline diffusivities of benzene within porous materials in isopropanol solution were measured by the conventional constant volume method. The diffusivities within mesoporous silicas in isopropanol solution were smaller than those in cyclohexane solution. This means the effective pore diameter for the benzene diffusion in the presence of isopropanol is small, because isopropanol are preferentially adsorbed on the pore surface with silanol group due to the hydrophilic affinity.

In the past 20 years, mesoporous materials have gained considerable interest as heterogeneous catalysts and adsorbents. Mesoporous materials have a huge surface area (ca. 1000 $m^2 g^{-1}$) and a large pore diameter (2–50 nm) compared with zeolites, the pore diameters of which are almost the same as the molecular diameters of hydrocarbons. Thus, there have been many reports regarding the synthesis of new mesoporous materials[1,2] and reactions using mesoporous materials as catalysts.[3] In the catalytic reaction using these porous materials, reactant molecules diffuse into the pore of the catalyst to the active site where the chemical reactions proceed. The products then diffuse back to the bulk phase from the porous catalyst. Because the diffusivities of reactant and product molecules strongly affect the activities and selectivity of the catalytic reactions, the diffusivities are important for catalytic design. There have been many reports concerning the diffusivities of hydrocarbons within zeolite in the gas phase.[4] We have also reported the intracrystalline diffusivities of hydrocarbons within zeolite in the gas phase based on a constant volumetric method.[5] There have been few reports, however, regarding the diffusivities within pores in the liquid phase under high-temperature and high-pressure conditions, despite the fact that some reactions carried out under these conditions are utilized for commercial production. We have previously succeeded in measuring the intracrystalline diffusivity of benzene within silicalite-1 crystal in cyclohexane solution using Raman spectroscopy.[6] In this study, the intracrystalline diffusivities of benzene within porous silicas in isopropanol and cyclohexane solution were measured, and the effects of the affinity between the silica pore wall and the solvents on the benzene intracrystalline diffusivities were investigated.

Table 1. Adsorbents used in this study and their pore diameters

Adsorbent	Pore diameter/nm
Silicalite-1	0.55
MMSS-10	2
MMSS-16	2.7
MMSS-18	3.1
Silica gel	10
γ-Al_2O_3	190
SiO_2–Al_2O_3	680

These porous silicas used in this study are listed in Table 1. Silicalite-1 was used as a microporous material. MMSS (monodispersed mesoporous silica spheres)-10, 16, 18,[2] and silica gel (GL Sciences Inc. Intersil SIL-100A) were employed as mesoporous materials. Moreover, γ-Al_2O_3 and SiO_2–Al_2O_3 were used as macroporous materials. Benzene was used as a diffusion molecule. Isopropanol and cyclohexane were used as solvents. The diffusion measurements were conducted at benzene concentration in the range from 0 to 500 $mol\,m^{-3}$. The intracrystalline diffusivities of benzene within porous silicas in these solvents were measured by the conventional constant volume method using Raman spectroscopy. The transient change in benzene concentrations in solution due to its adsorption and diffusion onto porous materials are expressed by the following theoretical equations[7] for porous materials with a hexagonal slab shape (MFI-type zeolite; silicalite-1) and a spherical shape (MMSS-10, MMSS-16, MMSS-18, silica gel, γ-Al_2O_3, and SiO_2–Al_2O_3).

[hexagonal slab shape]

$$\frac{M_t}{M_\mathrm{e}} = \frac{C_0 - C_t}{C_0 - C_\mathrm{e}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n{}^2} \exp\left(-\frac{D_\mathrm{ad} q_n{}^2 t}{L^2}\right) \quad (1)$$

where $\alpha = V/(a_\mathrm{m} WHL)$ and q_n are nonzero positive roots of $\tan q_n = -\alpha q_n$.

[spherical shape]

$$\frac{M_t}{M_\mathrm{e}} = \frac{C_0 - C_t}{C_0 - C_\mathrm{e}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)}{9+9\alpha+\alpha^2 q_n{}^2} \exp\left(-\frac{D_\mathrm{ad} q_n{}^2 t}{R_0^2}\right) \quad (2)$$

where $\alpha = V/(a_\mathrm{m} WHR_0)$ and q_n are nonzero positive roots of $\tan q_n = 3q_n/(3+\alpha q_n{}^2)$. M_t is the amount adsorbed at a time t, M_e is the M_t value at equilibrium, and D_ad is the intracrystalline diffusivity of benzene in the adsorption process. C_t is the benzene concentration in the solution at a time t, and C_0 and C_e are the C_t values in the initial state and at equilibrium, respectively. L and R_0 are the half-thickness of the hexagonal slab shape and the radius of the spherical shape, respectively, and these correspond to the diffusion distance, and a_m is the outer surface area of the crystal. W and V are the weight of the porous silicas and the volume of the liquid phase, respectively. H is the partition factor. By comparing the change in the benzene concentration in the solution with time to the numerical results, the intracrystalline diffusivity can be obtained. We have previously described the apparatus and measurement procedure in detail.[6]

Figure 1 shows the intracrystalline diffusivities of benzene within porous silica-based materials in the liquid phase (benzene/isopropanol and benzene/cyclohexane) as a function of

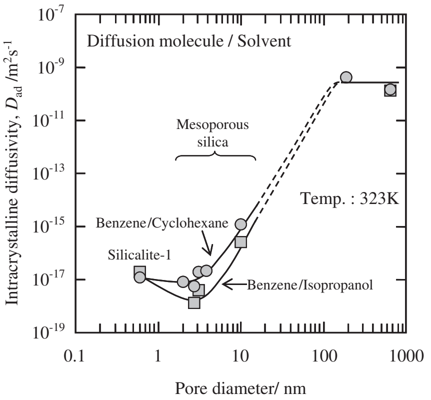

Figure 1. The intracrystalline diffusivities of benzene within pores in the isopropanol solution and in the cyclohexane solution in relation to the pore diameter.

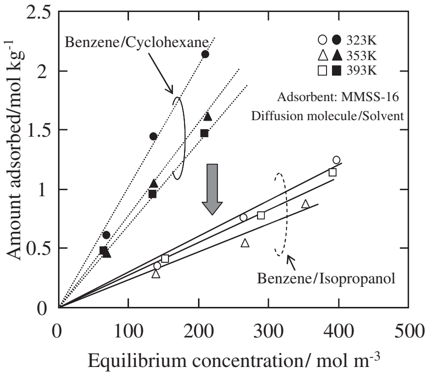

Figure 2. Adsorption isotherms of benzene onto the MMSS-16 in isopropanol solution (open symbols) and in cyclohexane (closed symbols).

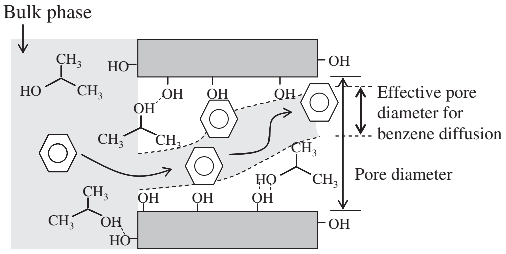

Figure 3. Image of the benzene diffusion mechanism within mesoporous silica in isopropanol solution.

the pore diameter. The results show that the pore diameters of these porous materials strongly affect the intracrystalline diffusivity of benzene in the liquid phase. The intracrystalline diffusivities of benzene within porous materials decreased with increasing pore diameter, and the diffusivities exhibited a minimum value around a pore diameter of approximately 3 nm, at which point the diffusivities began to increase again. The small diffusivities in the mesopore region (pore diameter of materials was 2–4 nm) were attributed to the adsorption of solvent molecules onto the pore surface, which was clearly observed in benzene/isopropanol solution. In the micropore region (here, silicalite-1), the intracrystalline diffusivities of benzene showed almost the same values, regardless of the different solvents, isopropanol, and cyclohexane. From this result, it can be considered that the benzene molecules independently diffuse within the pore of silicalite-1 in accordance with the configurational diffusion, because the pore diameter of silicalite-1 is almost the same as the molecular diameter of benzene. In contrast, the intracrystalline diffusivities of benzene within mesoporous silica in those solutions were the same and/or smaller than that within the silicalite-1. Moreover, the intracrystalline diffusivities of benzene within mesoporous silicas in the isopropanol solution were smaller than those in the cyclohexane solution. Because these mesoporous silicas have silanol groups on their pore surface, it is considered that the isopropanol molecules are preferentially adsorbed onto their pore surface due to hydrophilic affinity. Therefore, the adsorbed isopropanol molecules decrease the effective pore diameter for benzene diffusion, leading to the small intracrystalline diffusivity of benzene, as compared with benzene/cyclohexane solution. Figure 2 shows typical adsorption isotherms of benzene onto the MMSS-16. The linear relationship between the amounts of benzene adsorbed onto MMSS-16 and the equilibrium benzene concentration indicates that the adsorption isotherm can be expressed by a Henry-type equation, regardless of the solvent, under the concentration conditions used in this study. It was observed that the amount of adsorbed benzene within the mesoporous silicas in isopropanol solution was smaller than that in the cyclohexane solution. This result also confirmed the isopropanol adsorption on the pore surface, which restrained the benzene diffusion and adsorption within the mesoporous materials in the liquid phase. From this result, a schematic image of the benzene diffusion within mesoporous silicas in isopropanol solution can be described, as shown in Figure 3.

In summary, when hydrophilic molecules are used as solvents in the liquid phase, the hydrophilic molecules are preferentially adsorbed onto the mesoporous silica wall due to the hydrophilic affinity between silanol groups and hydrophilic groups such as C–OH, which reduce the effective pore diameter for the benzene diffusion. Moreover, the preferential adsorption of isopropanol on the pore wall causes a decrease in the amount of adsorbed benzene, as shown in Figure 2.

This work was supported in part by the Industrial Technology Research Grant Program in 2006, 06B44702a from New Energy and Industrial Technology Development Organization (NEDO) of Japan and by the Global COE Program (Project No. B01: Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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