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学位論文内容の要旨

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学位論文題名

Diffusion Mechanism of aromatic hydrocarbons within zeolites in liquid phase and sub-and super-critical fluids
(液相・亜臨界・超臨界流体中のゼオライトの芳香族炭化水素の拡散機構)

Zeolites are important catalysts in the field of petrochemistry, fine chemical, and chemical biomass conversion. Because the zeolites exhibit unique shape selective catalysis caused by molecular sieving effect, the materials are exploited as adsorbents, catalysis, and separation membrane. In an industrial reaction, observed reaction rates of zeolites-catalyzed reactions can be controlled by diffusion resistance of reactants and products inside the zeolite. Moreover, the pore size and structure sometimes strengthen limitations to the mass transport processes that affect activity and selectivity of the reaction. Because the diffusion coefficient of the hydrocarbon substrate depends on its size relative to the size of catalyst pores and the physicochemical features of the fluid where the catalysts and the substrate exist. Therefore, understanding diffusion mechanisms of molecules in the porous catalysts under different conditions are very critical for designing the catalysis and supply more useful information on reaction processes using those catalysts, since the degree of the diffusion limitations are observed differently by depending on molecular size and circumstance around the catalysts, such as gas, liquid, sub-critical and supercritical fluids. This research measures the diffusivity of aromatic hydrocarbons within zeolites in liquid, sub- and super-critical fluids and clarifies the diffusion mechanisms.

This paper consists of six chapters. The chapter 1 is the introduction that describes research background including the general characteristics of zeolites, intralystalline diffusion phenomenon within zeolite and the general characteristics of supercritical fluids, and finally introduces the purpose of this study and the structure of this paper.

Chapter 2 focuses on measuring the adsorption and intracrystalline diffusivities of phenolic compounds (phenol, p-propylphenol and m-cresol) and toluene within silicalite-1 and H-MFI in the liquid phase (solvent: mesitylene) in the temperature range from 313 to 353 K by using the constant volumetric method. The amounts of m-cresol showed lower adsorbed amount compared with those of other diffusion substances ($Q_{phenol} \approx Q_{p-propylphenol} \approx Q_{toluene}$ onto silicalite-1) at 313, 323 and 353K due to its larger kinetic diameter. Unlike adsorbed toluene, phenol have stronger interactions in H-MFI than in silicalite-1, indicating that hydrogen bonding between the OH group of phenol and Brønsted acid sites within H-MFI enhanced the adsorption of phenol. Whereas the intracrystalline diffusivity of m-cresol exhibited lower intracrystalline diffusivity as compare with those of other diffusion substances ($D_{phenol} \approx D_{p-propylphenol} \approx D_{toluene}$ within silicalite-1), indicating that the intracrystalline diffusivity was governed by geometrical limitation. The

intracrystalline diffusivity of phenol was lower within H-MFI with acid sites than within silicalite-1. The residence time of phenol on the acid sites became longer than that of toluene.

Chapter 3 described the intracrystalline diffusivities of phenol and toluene within H-Y-type zeolite in the mesitylene, cyclohexane and 2-propanol in the temperature range from 313 to 353 K. The activation energy for the intracrystalline diffusivity of toluene within H-Y in the liquid phase was larger than that in the gas phase, indicating that the solvent coexisting within the H-Y pores affected the diffusion mechanism of toluene. The intracrystalline diffusivity of phenol within H-Y in mesitylene was smaller than that of toluene, because the phenol molecule was more strongly adsorbed on the acid sites of H-Y as compared with toluene. The intracrystalline diffusivities of phenol within H-Y for the three solvents were in the following order: 2-propanol > cyclohexane > mesitylene. The amount of adsorbed phenol on H-Y in 2-propanol as solvent was smallest relative to the amounts of phenol adsorbed on H-Y in the other solvents. The results indicated that the adsorption of phenol on H-Y in the different solvents affected the intracrystalline diffusivity of phenol and its activation energy.

Chapter 4 clarified diffusion mechanism of 1-Methylnaphthalene or toluene within Si-beta or silicalite-1 and K-ZSM-5 in the sub- and super-critical fluids. The intracrystalline diffusivity of 1-Methylnaphthalene or toluene in the sub- and super-critical fluids was much larger than that in the gas phase, because solvent molecules coexisted inside the pores. During 313 ~ 473 K, the intracrystalline diffusivity increased with increasing the temperature. Above 473 K, the intracrystalline diffusivity of 1-Methylnaphthalene or toluene within Si-beta or silicalite-1 was decreased, and the almost minimum value at critical temperature was obtained in the supercritical fluids. Because solvent molecules gather around diffusion molecules near the critical point to forming clusters. For this point, the resistance at the pore mouth of the Si-beta or silicalite-1 increases and the apparent intracrystalline diffusivity decreases. In contrast, intracrystalline diffusivity of toluene within K-ZSM-5 in the sub- and super-critical of cyclopentane showed much higher value than that within silicalite-1 as well as the diffusivity of toluene was reduced with decreasing Al content in K-ZSM-5. Because of toluene concentration at outer surface of the K-ZSM-5 was increased, formation of the cluster may be suppressed and decreased diffusion resistance at pore mouth, leading to increase the diffusivity.

Chapter 5 investigated intracrystalline diffusivities of toluene, xylene isomers, p-propylphenol, propylbenzene, and p-cresol within silicalite-1, K-ZSM-5, and K-Y in sub-, and super-critical fluid of cyclopentane (473-543 K, 5 MPa). The Arrhenius plots of the intracrystalline diffusivity of p-xylene, p-cresol and p-propylphenol within silicalite-1 under 5 MPa shows similar values and made the almost minimum value at critical temperature (513 K). This result suggest that formation of cluster between solvent and diffusion substance near the critical point of solvent. In addition, the intracrystalline diffusivities of toluene and propylbenzene within K-ZSM-5, and K-Y showed almost the same value, and p-cresol exhibited lower intracrystalline diffusivity. It is attributed that the hydroxy group in p-cresol was adsorbed strongly on K^+ of K-ZSM-5 (or K-Y) and this led to a lower intracrystalline diffusivity. The diffusion mechanism of p-xylene within K-ZSM-5 and K-Y are different may be due to the different pore structure of K-ZSM-5 and K-Y. The intracrystalline diffusivity for three xylene isomers within silicalite-1, K-ZSM-5 and K-Y in sub-critical and super-critical fluids follow the order of o-xylene < m-xylene < p-xylene, which shows the values as expected according to their molecular kinetic diameter.

Chapter 6 contained summary of chapter 2 to chapter 5 and outlook.