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Diffusion phenomena of propane and propylene in colloidal zeolitic imidazolate Framework-8 particles

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ABSTRACT

Zeolitic imidazolate framework-8 (ZIF-8) enables a kinetic separation of propane and propylene with high efficiency, although the detailed mechanism has not yet been clarified. In the present study, we measure the adsorption rates of propane and propylene in ZIF-8 particles and *in-situ* X-ray diffraction patterns of ZIF-8 during the gas adsorption process to investigate the effect of the gas pressure and the flexibility of ZIF-8 framework on the diffusion process of propane and propylene in ZIF-8 particles. The adsorption rates of propane and propylene depend on the gas pressure, which would be due to the enlargement of the pore window diameter of the ZIF-8 framework during the gas adsorption as suggested by *in-situ* XRD measurements. This result is also supported by the calculation of interaction potential profiles between a gas molecule and the ZIF-8 framework, in which an energy barrier at the pore window limits the gas diffusion and the height of the barrier decreases with the increase in the pore window diameter. Furthermore, we find that the adsorption rates of propane and propylene depend on the particle size of ZIF-8, and the selectivity of propylene over propane increases with the particle size.

1. Introduction

Zeolitic imidazolate framework-8 (ZIF-8) [1,2], which is a family of the porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) [3,4], is a microporous material with a sodalite-type crystal structure consisting of zinc ions and 2-methylimidazolate (MIM) linkers. ZIF-8 is promising for various applications such as gas storages [5], electrical energy storage devices [6], and drug delivery systems [7–9] because of its high porosity, surface area, and remarkable chemical and thermal stabilities [1]. In addition to these features, ZIF-8 has intra-framework flexibility caused by the reorientation of MIM linkers [10,11]. The original structural configuration of ZIF-8 has narrow pore windows (ca. 0.31 nm) with a triangular shape, while the reorientation of the MIM linkers enlarges the window diameter to ca. 0.39 nm and changes the window shape into a circle. Due to the flexibility in the framework, ZIF-8 has been shown to adsorb molecules with kinetic diameters larger than its pore window diameters and to have peculiar molecular sieving properties that are different from those of zeolites with rather rigid frameworks. This feature of ZIF-8 enables a kinetic separation of molecules with similar sizes and boiling points [12–14], and the kinetic separation is a possible alternative to the conventional distillation in terms of cost and efficiency.

The first report on the molecular sieving property of ZIF-8 is made by Li et al. demonstrating a kinetic separation of propane and propylene with high efficiency [15]. A number of experimental and computational studies followed to investigate separation performances of ZIF-8 in the form of particles and membranes. ZIF-8 membranes supported on α-alumina discs have been demonstrated to show a selectivity up to ca. 50 for an equimolar mixture of propylene and propane [16–19]. Zhang et al. clarified that the effective aperture size of ZIF-8 for the molecular sieving is in the range from 0.40 to 0.42 nm, which is larger than the crystallographically determined aperture size of ZIF-8, through the measurements of the adsorption rate of molecules with varied sizes [20,21]. Molecular dynamics simulations for the self-diffusion process of ethane/propane in ZIF-8 demonstrated that gas molecules have to overcome an energy barrier existing at the entrance of pore windows and the MIM linker rotation helps them to pass through pore windows by enlarging the window diameter [22,23]. These results clearly suggest that the framework flexibility plays a crucial role in the diffusion phenomena in ZIF-8. However, to the best of our knowledge, there has been no direct evidence on the linker rotation during the diffusion process and also the relationship between the flexibility of ZIF-8 and the separation efficiency is unclear.

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Another important issue is the effect of the ZIF-8 size on the kinetic separation. Hara et al. synthesized ZIF-8 membranes with a counter diffusion method and found that the selectivity of propylene over propane depends on the membrane thickness [24,25]. Tanaka et al. revealed that the diffusion coefficient of n-butanol increases with the particle size of ZIF-8 [26], which is against a general trend that diffusion coefficients decrease with the particle size because of a longer diffusion distance in the particles. In addition, Chmelik et al. reported that the diffusion coefficients of ethene and ethane in ZIF-8 change depending on the loading of the gas molecules per cavity [27]. The particle size of ZIF-8 and the adsorbed amount of gases in ZIF-8 cavities are thus crucial for understanding and controlling the gas diffusion process, and detailed investigation on these factors is strongly required.

In the present study, we focus on the diffusion processes of propane and propylene molecules in ZIF-8 particles. We measure adsorption rates of propane and propylene separately and calculate diffusion coefficients. *In-situ* X-ray diffraction measurements of the ZIF-8 framework during the gas diffusion process are also conducted to clarify the structural change in the ZIF-8 framework. Furthermore, we measure the adsorption rates of propane and propylene in ZIF-8 particles with different sizes to explore the particle size dependence of the selectivity of propylene over propane.

2. Experimental methods

2.1. ZIF-8 synthesis

ZIF-8 particles were synthesized following our previous study [28] in which aqueous solutions of 2-methylimidazole (99%, Aldrich Chemical Co.) and zinc nitrate (98%, Aldrich Chemical Co.) were mixed using a central collision-type microreactor [29]. The detailed experimental procedure of the ZIF-8 synthesis is described in the supporting information.

2.2. Characterization

Adsorption isotherms and adsorption rates of propane and propylene in the synthesized ZIF-8 particles at varied temperatures were measured with an automated adsorption apparatus, BELSORP-18 (MicrotracBEL Corp., Japan), and an open system cooling water circulator, CL-80R (TAITEC Corp., Japan), to control the cell temperature. ZIF-8 particles were evacuated at 423 K for over 2 h under a pressure of less than 0.1 mPa before each measurement. In the adsorption rate measurements, after the gas was introduced to the sample chamber, which was under vacuum before the initial adsorption rate measurement, from the manifold chamber which was set at an arbitrary gas pressure, we calculated the time evolution of adsorbed amounts by monitoring the gas pressure decay in the manifold and sample chamber, and obtained an uptake curve during the process to reach the equilibrium pressure. We repeated this procedure by setting a higher pressure in the manifold chamber than the equilibrium pressure in the previous measurement, thereby obtaining a series of uptake curves at different equilibrium pressures. Separately from the sequential measurements of the adsorption rate, we also conducted a single-step rate measurement in which the gas was introduced to the sample chamber under vacuum from the manifold chamber with the gas pressure set at 110 kPa. The equilibrium pressure reached in the single-step measurement was ca. 70 kPa. We recorded *in-situ* X-ray diffraction patterns of the ZIF-8 framework during the adsorption of propylene using BELSORP-18 and an X-ray diffractometer, SmartLab (Rigaku Corp., Japan), with Cu Kα radiation (45 kV and 200 mA) at a scan rate of 2.5 °/min and a step size of 0.01°

2.3. Diffusion coefficients of gas in ZIF-8

For the calculation of diffusion coefficients of propane and propylene, we assume that the ZIF-8 particle shape is spherical and the gas concentrations in the ZIF-8 particles and the manifold chamber are uniform. The mass balance between the ZIF-8 particle and a sample chamber is given by

$$V\frac{dC_b}{dt} = -4\pi R_p^2 n\rho_p D_s\left(\frac{\partial N}{\partial r}\right)_{r=R_p} \quad (1)$$

where V is the volume of the sample chamber, C_b is the gas concentration in the chamber, t is time, R_p is the radius of a ZIF-8 particle, n is the number of ZIF-8 particles, ρ_p is the density of a ZIF-8 particle, D_s is the diffusion coefficient, N is the amount adsorbed in ZIF-8 particles, and r is the distance from the center of a ZIF-8 particle. D_s can be classified as the surface diffusion coefficient [30] because the diffusion in micropores is governed by a two-dimensional motion of adsorbed gases along a solid surface, which is different from a vapor-phase diffusion in pores such as the Knudsen diffusion of nonadsorbed gases. This is why the driving force for the diffusion in Eq. (1) is an adsorbed amount gradient instead of a gas concentration gradient. The relationship between N and D_s is given by the intra-particle diffusion equation as

$$\frac{\partial N}{\partial t} = D_s\cdot\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial N}{\partial r}\right) \quad (2)$$

After Eqs. (1) and (2) are nondimensionalized and Laplace transformed, we get the following equation (see the supporting information for the details) by performing the inversion of Laplace transformation.

$$\frac{N_t}{N_\infty} = 1-\sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp\left(-\frac{D_s b_n^2 t}{R_p^2}\right)}{9+9\alpha+\alpha^2 b_n^2} \quad (3)$$

where α and b_n are given by

$$\alpha = \frac{V}{\frac{4\pi R_p^3}{3}n\rho_p\frac{dN}{dC_b}} \quad (4)$$

$$\tan b_n = \frac{3b_n}{3+\alpha b_n^2} \quad (5)$$

N_t and N_∞ are the adsorbed amounts at a time, t, and at an equilibrium state. We obtained the diffusion coefficient by fitting Eq. (3) to the experimental results with the Marquardt method.

3. Calculation of interaction potential profiles

We calculated interaction potential profiles between a gas molecule (propane and propylene) and the ZIF-8 framework along a path through the center of a pore window by averaging over rotational configurations of a molecule at each position. An in-house code was used for the calculation of interaction potential profiles. We used an atomistic model of the ZIF-8 framework constructed based on the experimental crystallographic data by Moggach et al. [10], and rotated the MIM linkers around an axis connecting the two nitrogen atoms in the ZIF-8 frameworks to enlarge pore window diameters. Here, the rotation with the angle from 0° to 30° varied the pore window diameter from 0.31 to 0.40 nm. It should be noted that the pore window diameters agree with the experimental data [10]. The TraPPE-UA [31], which was originally developed for hydrocarbons and has been demonstrated to reproduce experimental vapor–liquid coexistence curves of various hydrocarbons, was applied in the present study for the Lennard-Jones (LJ) potential of a gas molecule (propane and propylene) and the corresponding parameters are summarized in Table 1. The interatomic

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