Intracrystalline diffusivity of lignin-derived benzene derivatives in silicalite-1 crystal in aqueous-phase system

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ABSTRACT

Lignin is a renewable resource that can generate a variety of value-added benzene derivatives during hydrothermal and/or chemical hydrolysis treatment; the crucial task is to separate the targeted derivatives from the hydrolysate. This study aims to investigate the adsorption kinetics of lignin-derived benzene derivatives onto silicalite-1 crystal in an aqueous-phase system to examine the potential applicability of silicalite-1 to aqueous-phase kinetic separation. Functional groups substituted to benzene include –OH, –CH$_3$, –CH$_2$–CH$_3$, –OCH$_3$, –CHO, –COOH, and –CH$_2$=CH$_2$–COOH. First, the corrected diffusivity was compared among cresol isomers. Critical diameter of the isomers was found to be a key parameter, giving rise to significant differences in diffusivity. Interestingly, we also discovered a considerable difference (maximum over 4 orders of magnitude) in corrected diffusivity, even among *mono-* and *para-*substituted derivatives, although these sorbates have the same critical diameter. In particular, the carboxylic derivatives tended to exhibit extremely low diffusivities and to show S-shaped isotherms. The diffusivities were strongly affected by the melting point of the sorbates. These results indicate a strong sorbate-sorbate interaction (e.g., hydrogen-bonding between carboxylic groups) that considerably limits molecular mobility in the narrow channel. Our findings are relevant to research on silicalite-1 to aqueous-phase kinetic separation.

1. Introduction

Lignin, an aromatic polymer, is a renewable natural resource contained in plant biomass. Hydrothermal and/or chemical hydrolysis treatment can depolymerize lignin into value-added benzene derivatives such as phenol [1,2], cresol isomers [1,2], *p*-hydroxybenzaldehyde [3–5], vanillin [3–5], benzoic acid [3], *p*-hyroxybenzoic acid [3,5], *p*-coumaric acid [4–6], and ferulic acid [4–6]. However, the by-production of other benzene derivatives is unavoidable during the depolymerization of lignin [3,6], and thus it is a crucial and challenging task to selectively recover the targeted compounds from the hydrolysate [6].

Silicalite-1, the all-silica MFI-type zeolite, has been extensively applied as an adsorbent in both gas- and liquid-phase systems, due to its extremely strong hydrophobicity and precise molecular sieving property [7–11]. Silicalite-1 has two types of orthogonal channels: straight (0.53 × 0.56 nm in channel diameter [12]) and sinusoidal (0.51 × 0.55 nm in channel diameter [12]). It is a sorbent that preferably adsorbs *mono-* and *para-*substituted benzene derivatives like toluene, ethylbenzene, and *p*-xylene, due to a molecular sieving effect [13,14]. There is some information in the literature regarding the adsorption equilibrium of benzene derivatives in aqueous-phase systems

[15,16]. Wilkenhöner et al. [17] reported the intracrystalline diffusivity of hydroxybenzenes in MFI-type titanosilicate (TS-1). However, there has been little study of the adsorption kinetics of benzene derivatives onto silicalite-1 crystal in an aqueous-phase system.

The diffusion mechanism in zeolite has been well established in a gas-phase system. There are also abundant data regarding the intracrystalline diffusivity of benzene derivatives in silicalite-1 in a gas-phase system. It has been empirically demonstrated for silicalite-1 that intracrystalline diffusivity in the gas-phase system is primarily governed by the critical diameter of the sorbate (the diameter of the cylinder that just circumscribes the molecule in its most favorable equilibrium conformation [18]), although a few exceptions have been observed [13,14,19]. Specifically, intracrystalline diffusivity of *o*-xylene, with a larger critical diameter, is one order of magnitude smaller compared to that of *p*-xylene (critical diameter ≈ 4.8 Å [20]) [13,21]. Intracrystalline diffusivities of benzene, toluene, ethylbenzene, and *p*-xylene are on the same order of magnitude, due to the same critical diameter (≈ 4.8 Å [20]) [13].

Adsorption from the gas phase proceeds via transport diffusion through vacant micropores. In contrast, adsorption from the liquid phase generally involves a counter-diffusion exchange process, since

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sorbates displace solvents in the micropores [18]. Hence, Kärger and Ruthven [22] claimed that, in the case of a rapidly diffusing solvent, intracrystalline diffusivity in silicalite-1 for liquid-phase systems was similar to that for gas-phase systems at the linear isotherm region. On the other hand, Boulicaut et al. [23] and Cherntongchai and Brandani [24] found that diffusivity in the hexane phase was generally 1–2 orders of magnitude larger than that in the gas phase for some branched alkanes [23] and aromatics [24]. Thus, information is still quite limited regarding intracrystalline diffusion mechanisms in liquid-phase systems, especially in aqueous-phase systems. In addition, lignin-derived benzene derivatives generally have high boiling points, due to polar functional groups like carboxylic, hydroxyl groups, etc. Hence, the intracrystalline diffusivity of these derivatives is basically immeasurable in a gas-phase system at around ambient temperature, even though the diffusivity in the liquid-phase system is similar to that in the gas-phase system.

Given these facts, in our previous study we systematically investigated the adsorption kinetics of lignin-derived benzene derivatives onto zeolite beta in a liquid-phase system [25]. We also observed the adsorption of some derivatives (*p*-coumaric acid and *p*-hydroxybenzoic acid) onto silicalite-1 occurring very slowly [25]. However, the kinetic mechanism underlying that phenomenon remains unclear. Hence, the objective of this study is to investigate intracrystalline diffusivity of lignin-derived benzene derivatives in silicalite-1 crystal by ultrasonication-based batch experiments in order to examine the potential applicability of silicalite-1 to aqueous-phase kinetic separation.

2. Experimental

2.1. Materials

All the reagents were purchased from Wako Pure Chemical Co. The molecular structures and physicochemical properties of sorbates employed are listed in Tables 1a and b. All the sorbates had high boiling points, and thus were non-volatile at around ambient atmosphere.

Crystalline powder of commercial silicalite-1 (HiSiv-3000, SiO_2/Al_2O_3 ratio > 1000) with a crystal diameter of approximately 1.5 µm was purchased from Union Showa. In addition, silicalite-1 with different crystal sizes (0.25, 0.58, and 2.4 µm in diameter) was synthesized by the dry-gel conversion (DGC) method [26]; we refer to these samples as DGC-0.25 µm, DGC-0.58 µm, and DGC-2.4 µm, respectively. Fig. 1 shows SEM images of silicalite-1 samples (SEMS-4500; Hitachi). The BET surface areas were 400, 410, 355, and 376 m^2/g for DGC-0.25 µm, DGC-0.58 µm, DGC-2.4 µm, and HiSiv-3000, respectively. The total pore volumes (N_2 adsorption amount at relative pressure of 0.9) were 0.190, 0.191, 0.165, and 0.186 cc (liquid)/g for DGC-0.25 µm, DGC-0.58 µm, DGC-2.4 µm, and HiSiv-3000, respectively. Details regarding the synthesis procedure for DGC samples and other characterization data (XRD pattern, ^{29}Si MAS NMR spectrum, adsorption isotherms of

nitrogen, hexane, and water, and adsorption isotherm of *p*-coumaric acid on the DGC samples) are included in Section S1 in the Supplementary Material.

2.2. Adsorption experiments

2.2.1. Single-component adsorption

Almost all of the sorbates employed in this study have carboxyl and/ or hydroxyl groups (p$K_{a, COOH}$ = 3.9–4.6 and p$K_{a, OH}$ = 7.7–10.3, respectively), and hence are proton-dissociative in aqueous solution. This means that two species of sorbates (i.e., those in dissociating and non-dissociating states) can exist in the solution at relatively high pH value. This is quite troublesome in terms of the analysis and interpretation of the adsorption phenomena observed. Hence, the adsorption experiments were basically carried out at pH 2 in order to avoid the proton-dissociation of sorbate in the aqueous solution. This enabled us to interpret the adsorption phenomena of only non-dissociating sorbates. Also, all the adsorption experiments were carried out at 30 ˚C.

A series of batch experiments were carried out to obtain the adsorption isotherm. Dried silicalite-1 (30–150 mg) was mixed with 40 ml of aqueous solution containing 2–200 mg/L of sorbate. The pH of the solution was adjusted in advance to 2 by the addition of HCl solution. The solution was shaken at 100 rpm using an incubator shaker (Excella E24; New Brunswick Scientific) for 1–30 days after ultrasonication for 10 min. The supernatant was filtered with a syringe filter unit (aperture: 0.2 µm; Advantec), followed by an adequate dilution (1–100 fold) with HCl solution of pH 2, so that the absorbance of the sorbate in the solution ranged almost from 0.1 to 1.0. Subsequently, the equilibrium concentration of the diluted solution was measured with a UV spectrophotometer (UV mini-1240; Shimadzu) at an adequate wavelength. The wavelength for each sorbate is listed in Tables 1a and b. The amount adsorbed was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W_s} \tag{1}$$

where q_e is the equilibrium adsorption amount (mg/g), C_0 is the initial concentration of sorbate in the solution (mg/L), C_e is the equilibrium concentration of sorbate in the solution (mg/L), V is the volume of solution (L), and W_s is the weight of the sorbent (g).

Time-elapsed uptake was also measured by batch experiments to investigate the adsorption kinetics. The dried sorbent was added to 100 ml of aqueous solution containing 100 mg/L of sorbate in an ultrasonic bath (FU-80C; TGK Station) circulated with water medium at 30 ˚C. The sorbent dosage ranged from 0.8 to 4.5 g/L. Ultrasonication was stopped after 30 min, followed by stirring with a magnetic stirrer at a rate of 500 rpm in the water bath at 30 ˚C. The ultrasonication is essential to eliminate the large concentration gap between the particle surface and bulk solution that occurs at the initial stage of adsorption (see Section S2 in the Supplementary Material). At each sampling time,

Table 1a

Molecular structures and physicochemical properties of *mono*- and *para*-substituted benzene derivatives.

sorbate	phenol	*p*-cresol	*p*-ethyl phenol	*p*-methoxy phenol	benzoic acid	*p*-toluic acid	*p*-hydroxy benzaldehyde	*p*-hydroxy benzoic acid	*p*-coumaric acid
molecular structure	OH	OH / CH₃	OH / H₃C	OH / OCH₃	COOH	COOH / CH₃	OH / CHO	OH / COOH	OH / COOH
melting point [˚C]	40	34	47	54	122	183	117	216	207
boiling point [˚C]	181	201	219	243	250	275	310	336	389
p$K_{a,COOH}$	–	–	–	–	4.2	4.3	–	4.5	4.6
p$K_{a,OH}$	9.8	10.2	10.2	10.0	–	–	7.7	9.1	9.4
wave-length [nm][a]	269	276	275	287	230	240	283	255	308

[a] Wavelength of maximum absorbance for ultraviolet and visible spectroscopy measured at pH 2.