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Dynamic Adsorption of Toluene on Pore-Size Tuned Supermicroporous Silicas

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Abstract:

The dynamic adsorption of toluene was investigated using supermicroporous silicas (SMPSs) synthesized through a solvent-free route by using tetraethoxysilane and conventional alkyltrimethylammonium halides as a structure-directing agent. The adsorption capacity of SMPSs depended on their pore diameters, which were precisely tuned in a range from 0.7 to 2.0 nm at single-angstrom intervals. The micropore filling of the molecule that is highly enhanced with micropores smaller than 1 nm improves the dynamic adsorption performance.

Keywords: Supermicroporous silica, Dynamic adsorption, Mesoporous silica, Solvent-free synthesis, Volatile organic compound

Introduction:

The removal of volatile organic compounds (VOCs) by using an adsorption technique is important in industrial processes for environmental and health conservation.[1,2] The dynamic adsorption [3] process using an adsorption agent is generally applied to removal of VOCs at a low concentration below 0.1% from stream gases at a high flow rate (see Figure S1).

Activated carbons are commonly used as an adsorbent having a high capacity for dynamic adsorption. [4] However, there has been a recent interest in alternative inorganic materials for removing large amounts of VOCs because carbon is basically flammable. Mesoporous silicas [5-10] (MPSs) with a diameter in the range from 2.0 to 10 nm have attracted an attention as a new class of adsorbents due to their high surface area and thermal stability. In previous works, however, the adsorption capacity of MPSs was reported to be relatively low for the dynamic adsorption of VOCs. [10] It indicates that the adsorption based on the capillary condensation of molecules is not effective for removal of VOCs from gas streams.

Since the range of supermicropores [11,12] ($d = 0.7\text{--}2.0$ nm) corresponds to the size of various organic molecules, the confined molecules are strongly trapped due to the overlap of the attractive force from opposing pore walls (micropore filling). Thus, supermicroporous materials are beneficial for dynamic adsorption. Although zeolites, which have micropores, are commonly used for dynamic adsorption, sluggish diffusion of adsorbates in the micropores degrades their performance. [10] The typical pore-window sizes of zeolites ($0.6\text{--}0.7$ nm) are generally too small for efficient diffusion. Moreover, the specific adsorption of VOC molecules to the acidic sites of zeolites also restricts diffusion. Kosuge *et al.* demonstrated the importance of micropores for

dynamic adsorption using SBA-15 types of MPSs. [10] Although the dynamic adsorption capacity depended on the micropore volume, the influence of the micropore sizes is still unclear. Therefore, supermicroporous silicas with a tunable pore diameter and an inert surface have been desired for fundamental research of micropore filling and development of a high performance adsorbent for the dynamic adsorption system.

In general, the pore diameter of MPSs can be controlled in the range from ~1.5 to ~10 nm by varying the size of the surfactant micelles that are used as a structure-directing agent (SDA). [8,9] In the case of alkyltrimethylammonium halides (C_nTAX , X: Cl or Br), the alkyl chains from C_8 to C_{18} are utilized for the production of a pore diameter from 1.5 to 3.0 nm with an ordered assembly (Figure 2). [13,14] Synthesis of SMPs with C_6TAX and shorter surfactants is fundamentally difficult due to a lack of micelle formability of the short-chain surfactants in an aqueous medium. Recently, our research group reported SMPs with a tunable pore diameter below 1 nm by using enhanced micelle formability in a solvent-free system. [15] The pore diameters in the supermicropore region were estimated by the nitrogen adsorption-desorption isotherms. Direct observation of WO_3 nanodots stuffed in the pores by transmission electron microscopy supported the estimation of their diameter. As shown in Figure 1, the uncontrollable region of porous materials has been bridged entirely by the SMPs

produced by solvent-free techniques.

In the present study, we utilized the SMPSSs as adsorbents for the removal of VOCs. The effect of pore size for the dynamic adsorption of toluene was examined in the range from the meso- to the supermicropore regions. Finally, the capacity for the dynamic adsorption of toluene was found to be dramatically increased in pores with a diameter below 1 nm.

Experimental Section

Solvent-free syntheses of supermicroporous silica

7.5 mmol of long-chain surfactants ($C_{18}TACl$, $C_{16}TACl$, $C_{14}TABr$, $C_{12}TABr$, $C_{10}TABr$) or 22.5 mmol of short-chain surfactants (C_8TABr , C_6TABr , C_4TACl) was suspended in 37.5 mmol of tetraethyl orthosilicate (TEOS) in a closed polypropylene vessel. Then, 152 mmol (4 equivalents versus TEOS) of water acidified to pH 2 by using hydrochloric acid was added to the suspension. The mole composition of $TEOS/H_2O/C_nTAX$ was set to 1.0 : 4.0 : 0.2 for the long chain surfactants or 1.0 : 4.0 : 0.6 for the short-chain surfactants. After stirring for 1 h, the suspension turned to a homogeneous solution with the hydrolysis of TEOS. The solution was continuously stirred at room temperature to complete gelation for several days. The gelation time depends on the chain length of the

SDA. The obtained transparent gel was dried at 333 K and calcined at 873 K to remove the organic templates. After calcination, colorless, transparent, and monolithic porous silica was obtained. The obtained porous silica was crushed and sieved into 1.0-1.7-mm grains for dynamic adsorption experiments. Mesoporous and supermicroporous silica samples prepared with C_nTAX are denoted by the terms C_n-MPS and C_n-SMPS, respectively. For pore-size reduction, 1.93 mmol (5 mol% versus TEOS) of triethoxyvinylsilane (TEVS) was used as an additional silica source. The samples prepared with TEVS are denoted as C_nV-SMPS.

Dynamic adsorption of toluene

The dynamic adsorption experiments were carried out by using toluene as a model VOC with a dynamic adsorption system RVOC-6301 (Ohkura Riken). A 6.4 cm³ of adsorbents was packed into a glass tube (inner diameter : 15 mm) with glass wool and steel clips. The adsorbents were heated at 473 K for 2 h in a dry airflow to remove pre-adsorbed species. The adsorbents were then cooled to 298 K before the experiments. The concentration of toluene was fixed at 100 ppm in dry air, and the flow rate was fixed at 10.6 dm³/h. This condition simulated a typical removal process of VOCs from exhaust in conventional small factories. The output gas concentration of toluene was continually

monitored by a 3000A Micro-GC (Agilent) equipped with a Stabilwax column in 1-min intervals until the output gas concentration reached that of the input gas.

Characterization

The nitrogen adsorption-desorption isotherms were obtained at 77 K with a TriStar 3000 (Micromeritics) using samples pretreated under a vacuum at 433 K for 5 h. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore-size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method and the Grand Canonical Monte Carlo (GCMC) method. For the GCMC method, the BELSORP-max system (Nihon BEL, Inc.) was used for recording the isotherm, and BEL-Master software was used for analyses assuming a cylindrical pore structure with an oxygen-exposed surface as a pore model and a single Gaussian peak for pore-size distribution. The small angle X-ray diffraction patterns were recorded on a D8 Advance (Bruker) with Cu K α radiation.

Results and Discussion

Table 1 summarizes the pore structures of meso- and supermicroporous silicas synthesized by a solvent-free reaction. The pore diameter was monotonically decreased

from ca. 3.0 to 0.77 nm by decreasing the alkyl chain-length of the surfactant used as an SDA (Figure 1). The specific surface area and the total pore volume were decreased with shrinkage of the pores. These trends are consistent with other types of porous silicas, i.e. the MCM-41 series.

In the mesopore region, the average pore diameters were estimated by the Barrett-Joyner-Halenda [16] (BJH), Horvath-Kawazoe [17] (HK), and Grand Canonical Monte Carlo [18] (GCMC) methods, respectively. The HK and the GCMC methods give almost consistent value, however the BJH method gives slightly underestimated values. For the pore size distribution, the BJH method gives reliable distribution. In contrast, the HK and the GCMC methods give severely overestimated distributions. In the supermicropore region below 1.5 nm, pore diameters were estimated using the GCMC method. Thus, the reliability of the present GCMC analyses was confirmed by direct TEM observation of WO₃ nanodots synthesized in SMPSs.[15] 1.11, 0.89, and 0.77 nm dots were observed with narrow size distribution in the micropores of C6-SMPS, C4-SMPS, and C4V-SMPS, respectively. (see supporting information) Therefore, we have realized the size-tunable production of supermicropores in the range from 0.7 to 2.0 nm at single-angstrom intervals using conventional surfactants with short alkyl chains using the solvent-free method.

The successful production of SMPSSs was attributed to the enhancement of cooperative self-assembly [19-21] which provides an additional driving force for micellization. Self-assembly of the surfactants and aggregation of silicate species proceed cooperatively in the system because of the strong ionic interaction between the head groups. This interaction is stronger than that in the conventional solution phase due to the absence of solvent molecules. Therefore, the micellization of short-chain surfactants, such as C₆TABr and C₄TACl, was achieved. For further pore-size control, we utilized the pore-size-reduction effects of the co-condensation of triethoxyvinylsilane (TEVS). [22] The addition of 5mol% TEVS with TEOS as a silica source reduced the pore diameters 0.15–0.3 nm for C₈V-SMPS, C₆V-SMPS, and C₄V-SMPS.

We performed the dynamic adsorption experiment using MPSs, SMPSSs, and a commercial zeolite as an adsorbent. One of the important parameters for determining the performance of the adsorbents is the breakthrough time, which is the period from the start to the time when VOCs are detected in the output gas. The adsorption capacity, which is the specific amount of adsorbed total toluene evaluated from an integrated area of breakthrough curves, is also essential for dynamic adsorption. Table 1 and Figure 2 summarizes the breakthrough time and the adsorption capacity of all of the adsorbents. The MPS samples with a pore diameter above 1.5 nm exhibit quite low

performance, with a breakthrough time shorter than 6 min and an adsorption capacity lower than 0.025 cm³/g due to a weak adsorption force for the capillary condensation. In the series of SMPs with having a pore diameter below 1.5 nm, the breakthrough time and the adsorption capacity steeply increased up to 80 min and 0.12 cm³/g, respectively, by decreasing the pore diameter to 0.8 nm. The highest adsorption capacity is more than three times greater than that of SBA-15 types of MPSs and is comparable to that of activated carbon. [10] However, the breakthrough time and the capacity of the samples with pores smaller than 0.8 nm (C4V-SMPS and zeolite) were remarkably decreased. Figure 3A shows the correlation between the average pore diameter and the total pore volume of the samples. The total pore volume of the present samples was decreased by reducing the pore diameter due to increasing pore-wall thickness. The decreases in the breakthrough time and the adsorption capacity were mainly attributed to the decreased pore volume. Moreover, the breakthrough time would also be reduced due to the restricted diffusion of the adsorbate in pores smaller than 0.8 nm because the pore size becomes smaller than the molecular length of toluene. The specific adsorption to the acidic sites on the pore wall of zeolite limited the diffusion of the adsorbate. Therefore, a fatal decrease in the breakthrough time was observed for zeolite, whereas it has a moderate adsorption capacity

Figure 3B shows the filling fraction, which was calculated from the dynamic adsorption capacity divided by the total pore volume of the adsorbents, as a function of the pore diameter. The filling fraction was steeply increased by decreasing the pore diameter in the supermicropore region below 1.5 nm. In contrast to the breakthrough time and the adsorption capacity, the filling fraction was simply increased by decreasing the pore diameter below 0.8 nm. These results indicate that the strength of the micropore filling is enhanced by decreasing the pore diameter in the region close to the size of the adsorbate.

The large pore volume, the strong adsorption force, and fast diffusion in the pore are required to achieve efficient dynamic adsorption. The adsorption force increases by reducing the pore size, although pore volume and diffusion efficiency decrease simultaneously. In the present study, we found that the SMPS with a pore size that corresponding to the molecular length of the adsorbate involved well-balanced parameters. Therefore, the fine pore-size optimization is important for the dynamic adsorption of various VOCs. The solvent-free method, which exhibits pore controllability for SMPSs is a strong tool for designing tailor-made adsorbents for wide range of VOCs.

Conclusions:

The effect of pore size in meso- to supermicropore regions for dynamic adsorption of toluene was evaluated for porous silicas as an adsorbent. We used finely tuned pores of the porous silicas prepared by the solvent-free method for a detailed investigation. An importance of strong adsorption force in the supermicropore was demonstrated for the dynamic adsorption. The optimum pore diameter of SMPS for sufficient removal of toluene was determined to be 0.8 nm, which corresponds to the molecular size of toluene. Therefore, the fine-tunings in the pore diameter is peculiarly important along with increment of micropore volumes for achieving efficient adsorption performance. The high controllability of the pore size of SMPSs would enable the design of excellent adsorbents for the dynamic adsorption of various molecules.

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Tables:

Table 1. The textual properties and the dynamic adsorption performance of various adsorbents.

Sample	Pore diameter ^(a)	Pore volume	Specific surface area ^(b)	Break through time	Adsorption capacity ^(c)	Filling fraction
	(nm)	(cm ³ /g)	(m ² /g)	(min)	(cm ³ /g)	(%)
C16-MPS	2.82	0.79	1450	3	0.01	2
C12-SMPS	1.80	0.53	1060	4	0.02	3
C10-SMPS	1.58	0.45	920	6	0.03	6
C8-SMPS	1.28	0.41	810	23	0.06	14
C6-SMPS	1.12	0.32	630	51	0.08	26
C8V-SMPS	0.99	0.26	520	48	0.10	38
C6V-SMPS	0.82	0.20	400	78	0.12	61
C4V-SMPS	0.77	0.14	300	39	0.08	57
Silicagel (Q3)	-	0.33	590	18	0.03	9
Zeolite	~0.7	0.10	250	8	0.06	57

(a) The average pore diameter determined by using the GCMC method. (b) The specific surface area calculated from the BET method. (c) calculated from integrated area of the breakthrough curves.

Figure Captions

Figure 1. The correlation between the surfactant chain length and the average pore diameter of MPSs and SMPSs. (“V” represents the use of TEVS)

Figure 2. The correlation between the pore diameter of adsorbents and (A) the breakthrough time, (B) the dynamic adsorption capacity. (diamonds: MPSs and SMPSs, circle: zeolite)

Figure 3. The correlation between the pore diameter of SMPSs and (A) the total pore volume, (B) the filling fraction.

Graphical Abstract

Figures:

Figure 1. The correlation between the surfactant chain length and the average pore diameter of MPSs and SMPSs. (“V” represents the use of TEVS)

Figure 2. The correlation between the pore diameter of adsorbents and (A) the breakthrough time, (B) the dynamic adsorption capacity. (diamonds: MPSs and SMPSs, circle: zeolite)

Figure 3. The correlation between the pore diameter and (A) the total pore volume, (B) the filling fraction of SMPs.