Short communication

Dynamic adsorption of toluene on pore-size tuned supermicroporous silicas

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A B S T R A C T

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.

1. 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 Fig. 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—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—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 (Fig. 2)
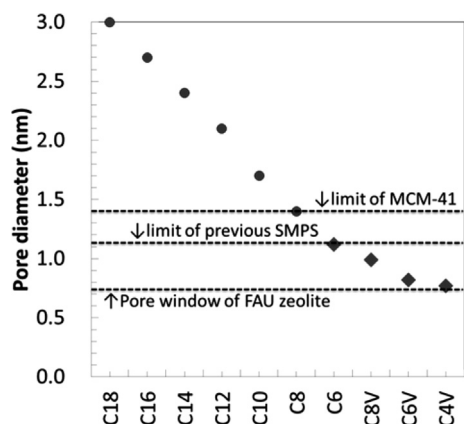
Fig. 1. The correlation between the surfactant chain length and the average pore diameter of MPSs and SMPSs ("V" represents the use of TEVS).

[13,14]. Synthesis of SMPSs 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 SMPSs 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 Fig. 1, the uncontrollable region of porous materials has been bridged entirely by the SMPSs produced by solvent-free techniques.

In the present study, we utilized the SMPSs 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.

2. Experimental section

2.1. 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 Cn-MPS and Cn-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 CnV-SMPS.

2.2. 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 cm^3 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 dm^3/ 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.

2.3. 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
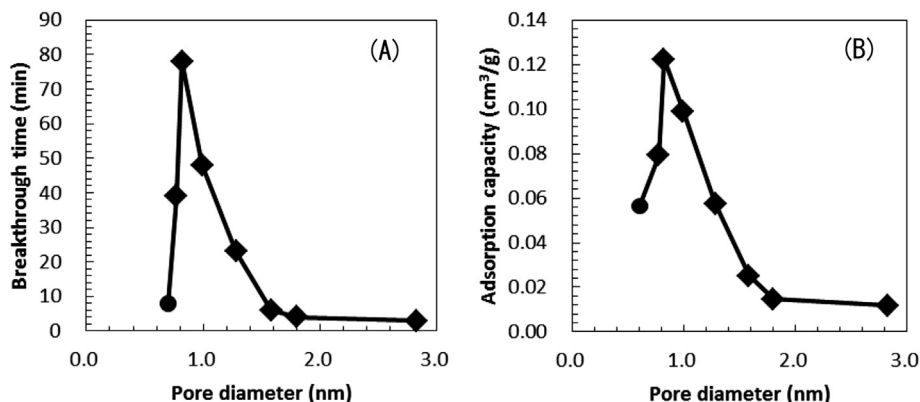

Fig. 2. The correlation between the pore diameter of adsorbents and (A) the breakthrough time, (B) the dynamic adsorption capacity (diamonds: MPSs and SMPSs, circle: zeolite).