Synthesis and hydrophobic adsorption properties of microporous/mesoporous hybrid materials

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ABSTRACT

Hybrid materials of silicalite-1 (Sil-1)-coated SBA-15 particles (MSs) have been successfully synthesized by crystallization process under hydrothermal conditions. These MSs materials were characterized by X-ray diffraction, nitrogen adsorption/desorption and TEM techniques, which illustrated that the silicalite-1-coated SBA-15 particles were successfully prepared and had large pore volume and hierarchical pore size distribution. Further experimental studies indicated that longer crystallization time under basic condition caused the mesostructure of SBA-15 materials to collapse destructively and higher calcination temperature tended to disrupt the long-range mesoscopic order while they had little influence on the phase of microcrystalline silicalite-1 zeolite. The resultant MSs materials were investigated by estimating dynamic adsorption capacity under dry and wet conditions to evaluate their adsorptive and hydrophobic properties. The hydrophobicity index (HI) value followed the sequence of silicalite-1 > MSs > SBA-15, which revealed that the SBA-15 particles coated with the silicalite-1 seeds enhanced the surface hydrophobicity, and also were consistent with FTIR results. Our studies show that MSs materials combined the advantages of the ordered mesoporous material (high adsorptive capacity, large pore volume) and silicalite-1 zeolite (super-hydrophobic property, high hydrothermal stability), and the presence of micropores directly led to an increase in the dynamic adsorption capacity of benzene under dry and wet conditions.

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1. Introduction

Zeolites have been widely used in industry as shape-selective catalysts and adsorbents due to their specific features (hydrothermal stability and many active sites and so forth) [1,2]. Their intricate channels and pores contribute to the development of the intracrystalline surface area at which a large number of catalytic and adsorptive sites can be generated [3]. Especially, the MFI type silicalite-1 (Sil-1) zeolite without cations and silanol defects exhibits high hydrophobic property during the adsorption of volatile organic compounds (VOCs) under wet conditions [4,5]. However, the sole presence of micropores (diameter < 20 Å) limits their use which involves diffusion of bulky molecule [6]. Ordered mesoporous silicates with enlarged pore diameters (20–500 Å) have been developed to overcome these difficulties.

SBA-15 [7], with tunable pore size and thick silica walls, has been chosen as an alternative to overcome the diffusion limitation of zeolites during the adsorption process. It has been widely used

as adsorbent for the removal of volatile organic compounds and toxic gases, and as substrate to synthesize organofunctionalized SBA-15 materials for the separation of bimolecular or adsorption of heavy metallic ions [8–10]. Unfortunately, SBA-15 materials with the amorphous silica wall exhibit low mechanical and hydrothermal stability compared to zeolitic materials (such as silicalite-1) [11,12]. Hence, attempts to combine the advantages of mesoporous material (large pore diameters and good accessibility) with zeolite (many active sites, hydrothermal stability and hydrophobic property) have attracted wide attentions and industrial interests [3].

The introduction of mesopores into zeolites has recently been achieved using several strategies to generate microporous/mesoporous hybrid materials [13,14]. In current approaches to obtain hybrid materials, prefabricated zeolite seeds are assembled into mesoporous materials upon addition of surfactant and heating [3,15–18] or pore walls of ordered mesoporous material restructured with the help of templates and recrystallization processes [19,20], and much attention has also been focused on the nanocasting method using various forms of carbon (CMKs) as template to replicate mesopore-containing zeolites [14,21–24]. Recently, Navascués et al. [5] synthesized hollow silicalite-1 spheres produced by liquid phase hydrothermal synthesis from

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mesoporous silica spheres seeded with silicalite-1 nanocrystals and used as an adsorbent for water, *n*-hexane, triisopropylbenzene and 2,2-dimethylbutane molecules to evaluate its hydrophobicity and pore accessibility. Other hybrid materials were synthesized that zeolitic particles were coated on spherical Pt/TiO₂ particles with a diameter of 0.5 μm under hydrothermal conditions and used in the application of catalyst particles coated with a permselective membrane to achieve reactant selectivities on a particle level successfully [25]. However, synthesis of microporous/mesoporous hybrid materials with mesoporous and zeolitic properties remains a challenge.

With the aim to combine advantages of the ordered mesoporous material and zeolite, we successfully synthesize microporous/mesoporous hybrid materials (MSs) with high pore volume, hydrophobic property, and good hydrothermal stability under a liquid phase hydrothermal process to coat silicalite-1 seeds onto SBA-15 particles. As both SBA-15 materials and silicalite-1 seeds are negatively charged [26], strong acid condition usually used in synthesis of SBA-15 mesostructures is not favorable for the incorporation of zeolitic subunits into the framework of SBA-15 particles. So the SBA-15 particles need to be modified by a mediator ion M⁺ to ensure interaction between the equally negatively charged silicalite-1 seeds via a I[−]M⁺S[−] pathway (I: inorganic species; M: cationic auxiliary; S: silicalite-1 seeds). The resultant MSs materials were used as adsorbents to study their dynamic adsorption capacity under dry and wet conditions and evaluate their adsorptive and hydrophobic properties.

2. Experimental

2.1. Material preparation

Chemicals used in this study include tetraethyl orthosilicate (TEOS), Pluronic P123 (MW: 5800, Aldrich), tetrapropylammonium hydroxide solution (TPAOH, 20%), silica sol (25%), and polyacrylamide (PAM, C498H).

Pure SBA-15 substrate was synthesized using a method reported by Zhao et al. [7]. The chemical composition of reaction mixture was

4 g P123: 0.041 mol TEOS: 0.24 mol HCl: 6.67 mol H₂O. The product obtained was subjected to crystallize at 100 °C for 48 h in Teflon bottles and calcined at 550 °C for 4 h. Then SBA-15 was dried at 383 K overnight under vacuum condition to remove water molecules and small organic impurities. Silicalite-1 seeds were prepared by a method described by Lechert and Kleinwort [27]. Homogenous solution with the molar composition of 1 TPAOH: 3.0 NaOH: 87.2 Silica Sol: 152.5 H₂O was aged for 16 h at 100 °C.

For a typical synthesis of MSs materials, 1 g of SBA-15 substrates was first dispersed in 10 ml of H₂O, and then 10 ml of NaCl (0.5 M) solution containing 20 mg cationic electrolyte C498H was added. Subsequently, the mixture was four times washed with distilled water and centrifuged at 3000 rpm for 10 min to remove excess C498H. Then, 80 ml of diluted NH₄OH solution (pH 9) with 3 g of silicalite-1 seeds, prepared as described above, was mixed and stirred. The excess silicalite-1 seeds were removed by water washing and then centrifuging. In the following steps, SBA-15 particles seeded with silicalite-1 were recrystallized under different synthesis conditions listed in Table 1. This procedure enables the silicalite-1 seeds coating with SBA-15 particles via electrostatic attraction to produce mesopore/silicalite-1 hybrid materials (MSs). The silicalite-1 was synthesized for the purpose of comparison using silicalite-1 seeds crystallized at 175 °C for 6 h, and calcined at 600 °C for 4 h with the heating rate of 5 K/min.

2.2. Material characterizations

Low angle X-ray diffraction (XRD) patterns of MSs were recorded on Siemens D5005 diffractometer at 40 kV and 40 mA using a Cu-Kα radiation ($\lambda = 0.15418$ nm) over the range 0.7–6.0°. High angle X-ray diffraction patterns of MSs were measured on a Rigaku power diffractometer (D/MAX-RB) using Cu-Kα radiation in a range of $2\theta = 10$ –70° at a scanning rate of 4°/min. Nitrogen adsorption/desorption were measured at liquid nitrogen temperature (77 K), using a NOVA 1200 gas sorption analyzer. Before the measurements, the samples were degassed under vacuum condition at 300 °C for 3 h. The Brunauer–Emmett–Teller (BET) surface

Fig. 1. Low angle X-ray diffraction (a) and high angle X-ray diffraction (b) of MSs patterns.

Table 1

Synthesis conditions of MSs patterns.

Sample	Compositions (molar ratio)	Crystallization conditions	Calcination conditions
MS-1	MS ^a :0.052TPAOH: 444H ₂ O	175 °C, 1 h	480 °C, 4 h
MS-2	MS:0.052TPAOH: 444H ₂ O	175 °C, 3 h	480 °C, 4 h
MS-3	MS:0.052TPAOH: 444H ₂ O	175 °C, 6 h	480 °C, 4 h
MS-4	MS:0.026TPAOH: 444H ₂ O	175 °C, 6 h	480 °C, 4 h
MS-5	MS:0TPAOH: 444H ₂ O	175 °C, 6 h	480 °C, 4 h
MS-6	MS:0.052TPAOH: 444H ₂ O	175 °C, 3 h	600 °C, 4 h
MS-7	MS:0.052TPAOH: 444H ₂ O	175 °C, 3 h	800 °C, 4 h
MS-8	MS: 0.026 TPAOH: 444 H ₂ O	175 °C, 3 h	600 °C, 4 h
MS-9	MS: 0.026 TPAOH: 444 H ₂ O	175 °C, 3 h	480 °C, 4 h

^a MS represents SBA-15 substrate.

areas were calculated based on the linear part of the BET plot ($P/P_0 = 0.05–0.25$). The total pore volumes were estimated according to nitrogen uptake at a relative pressure (P/P_0) of ca. 0.99. The pore size distribution was derived from the desorption branch of N₂ isotherms using Barrett–Joyner–Halenda (BJH) method [28]. The micropore volume and micropore surface area were estimated by a t-plot method. Transmission electron microscopy (TEM) images were collected on a Hitachi H-7500 operating at an accelerating voltage of 120 kV. Infrared spectra were recorded on a Bruker Tensor 27 using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) techniques.

2.3. Dynamic adsorption of VOCs

The dynamic adsorption processes of VOCs are associated with adsorption using a fixed bed in which adsorbents are packed. The samples were crushed and sieved between 40 mesh and 60 mesh, about 100 mg of pelletized sample was loaded in the adsorption bed. Before the adsorptive process, the samples were heated at 110 °C for overnight under vacuum condition to remove the physical adsorption of water molecules and small organic impurities adsorbed in pores. To investigate the hydrophobic property of MSs materials, a stream of VOC and nitrogen with a relative humidity of 13% water vapor was estimated to study the efficiency of the adsorbents under a more realistic environment. In our study, VOC (such as benzene) concentration is ca. 1000 ppm both under dry (without water vapors) or wet conditions.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1(a) and (b) shows low angle XRD and high angle XRD patterns of MSs materials, respectively. For MS-1, MS-2 and MS-3 with different crystallization time (see Table 1), only MS-2 sample with 3 h of crystallization time exhibits both peak of hexagonal symmetry of SBA-15 indexed as the (100) diffraction (Fig. 2(a)) and distinctive peaks of crystalline silicalite-1 structure at 7.8°, 8.8°, 23°, 23.6° and 24.4° (2θ) (Fig. 2(b)). However, the intensities of peaks for the MS-2 sample in Fig. 1 are considerably lower than those of SBA-15 substrate and silicalite-1, which indicates a strongly adverse effect of hydrothermal crystallization process on the MSs formation. MS-1 sample has three diffraction peaks (Fig. 2(a)) in low angle region but exhibits no characteristic diffraction peaks in high angle region (Fig. 1(b)), which indicates that short crystallization time (1 h) cannot lead to the formation of silicalite-1 zeolite structure. On the other hand, MS-3 with 6 h of crystallization time displays several distinctive peaks of silicalite-1 structure in Fig. 1(b) while no typical diffraction peak of order mesostructure of SBA-15 substrate appears (Fig. 1(a)). This indicates that mesostructure is seriously destroyed because long crystallization time under basic condition causes the mesostructure of SBA-15 substrate to collapse destructively. MS-3, MS-4 and MS-5 patterns with different molar ratios of TPAOH/MS in Fig. 1 indicate that smaller molar ratio of TPAOH/MS would hardly form the silicalite-1 zeolite structure.

To explore the effect of calcination temperature on structural and physical properties of MSs materials, samples of MS-2, MS-6 and MS-7 with the same composition and crystallization conditions but subjected to different calcination temperatures were compared. When calcination temperature increases to 800 °C, the crystallinity of mesoporous phase decreases which can be evidenced by the decrease in (100) peak intensity of the XRD patterns in Fig. 1(a). MS-7 shows only characteristics of silicalite-1 structure in Fig. 1(b)

Fig. 2. Nitrogen adsorption-desorption isotherms (a) and BJH pore size distribution (b) of SBA-15 and MSs patterns.

Table 2
Physico-chemical properties.

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Micropore area ($\text{m}^2 \text{g}^{-1}$)
MS-1	377.2	1.101	0.038	80.66
MS-2	178.7	0.857	0.017	19.19
MS-3	135.4	0.376	0.026	56.66
MS-4	113.9	0.671	0.015	32.34
MS-5	101.3	0.557	0.001	1.22
MS-6	211.6	0.744	0.022	45.87
MS-7	126.1	0.518	0.020	40.93
MS-8	199.6	0.873	0.018	39.58
MS-9	227.8	0.670	0.026	56.38
SBA-15	698.0	1.197	0.067	145.9
Silicalite-1	367.2	0.210	0.117	247.7

while MS-2 and MS-6 show both low angle and high angle diffraction peaks, indicating that higher calcination temperature (such as 800°C) tends to disrupt the long-range mesoscopic order while it has little influence on the phase of microcrystalline silicalite-1 zeolite. These observations indicate that silicalite-1 zeolite seeds which coated onto the mesopore surface of SBA-15 substrate grow up and disrupt the mesostructure under higher calcination temperature. On the other hand, amorphous silicas wall of SBA-15 substrate exhibits low hydrothermal stability compared to zeolitic materials (such as silicalite-1).

3.2. Nitrogen adsorption and textural properties

Fig. 2 shows nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution (b) of SBA-15 and MSs samples. The isotherms of the parent SBA-15 are of type IV in accordance to IUPAC nomenclature classification and possess type H1 hysteresis loops [29]. The isotherms of MSs samples in Fig. 2(a) displayed two sharp increases at the relative pressure $P/P_0 < 0.05$ and $P/P_0 > 0.8$. The amount of nitrogen adsorbed on MSs samples increases at partial pressure $P/P_0 < 0.05$ contributed to micropore filling [11,15]. The hysteresis loops located in the relative pressure $P/P_0 > 0.8$ associate with the presence of large mesopores arising from textural mesoporosity, which is attributed to interparticle voids and is complementary to the framework-confined mesoporosity [14].

It is also validated from the hierarchical BJH pore size distribution shown in Fig. 2(b) that MS-2, MS-6 and MS-8 samples all exhibit tri-modal of pores including micropores, small mesopores and large mesopores, which is similar to Yang et al.'s results [14]. As seen in Fig. 2(b), MS-2, MS-6 and MS-8 all remain mesopores of the SBA-15 substrate except a little shrinkage of the 2D hexagonal channels due to the recrystallization during the synthesis of MSs materials.

Table 2 summarizes the textural properties (S_{BET} , V_{total} , V_{Micro} and S_{Micro}) of the MSs samples synthesized under different conditions. The BET surface areas and total pore volumes decrease markedly in comparison with those of SBA-15 substrate. When the crystallization is performed under basic condition, the framework of SBA-15 substrate is eroded in the local range, which probably leads to the formation of larger pores or micropores during the reorganization process, as Fig. 2(b) displayed. Though MSs materials show lower BET surface areas than silicalite-1, they show relatively higher total pore volume. The increase in pore volume compared to normal silicalite-1 can be ascribed to the creation of mesoporosity arising from interparticle (void) mesopores and SBA-15 mesopores, as the proportion of pore volume contributed by micropores decreases.

3.3. Transmission electron microscopy

Though XRD diffraction patterns of MSs materials as described in Fig. 1 demonstrate the presence of the zeolite phase and mesostructure, it necessitates further exhaustive investigation by TEM to rule out the possibility that the materials are just a physical mixture of bulk zeolite and mesoporous solid. Fig. 3 shows the transmission electron microscopy images of the SBA-15 substrate at two different magnifications. As seen in Fig. 3(a), SBA-15 substrates consist of rod-like particles of about $1 \mu\text{m}$ in length. The magnified image of each rod viewed parallel to the mesopore channels are clearly observed in Fig. 3(b), which exhibits a uniform pore size with a highly ordered pore structure.

Fig. 4 shows the TEM images of MS-2, MS-6, MS-8 and MS-9 samples prepared under different conditions. It can be seen that the mesopores of MSs samples retain their size and morphology of rod-type (shown in Fig. 4) after crystallization process in the presence of TPAOH, which is consistent with the results

Fig. 3. TEM images of SBA-15 material at two different magnifications.

Fig. 4. TEM images of MSs materials.

of XRD and nitrogen adsorption–desorption isotherms analyzed above. TEM is further used to probe the nanostructure of silicalite-1 particle. Some agglomerates of segregated zeolite crystals, as seen from the dark field images in Fig. 4, indicate that the syn-

thesis procedure can be optimized to coat the silicalite-1 seeds onto the mesopore rods and generate hybrid products containing silicalite-1 nanocrystals. The TEM and XRD results are in good agreement in that the MSs samples contain a well-ordered meso-

Fig. 5. Breakthrough profiles for benzene on silicalite-1, MS-6 and SBA-15 adsorbent. The filled symbols are under dry conditions and the open symbols are under wet conditions (13% relative humidity).

pore system and domains of silicalite-1 coated on rod-like SBA-15 particles.

3.4. Dynamic adsorption of VOC behavior under dry and wet conditions

A breakthrough measurement is a direct method designed to clarify the dynamic performance of VOC adsorption. The dynamic adsorption behavior of benzene was evaluated on these MSs samples, and also on SBA-15 substrate and silicalite-1 for comparison. In order to compare the hydrophobicity, competitive adsorption of water and hydrocarbon was also studied. Fig. 5 shows the breakthrough profiles for benzene on silicalite-1, MS-6 and SBA-15 adsorbents under dry conditions and wet conditions at 13% relative humidity. The typical breakthrough curves give the evolution of the C/C_0 ratio as a function of time, where C is the concentration of benzene at the outlet of the adsorption bed and C_0 is the concentration of benzene at the inlet. In general, the longer the breakthrough time is, the higher the dynamic adsorption capacity obtains [30]. The adsorption behavior of high silica MFI type zeolite is greatly influenced by the presence of framework aluminum, cations and silanol defects [4]. The lack of heteroatom in silicalite-1 causes it to be shorter breakthrough time and exhibits low adsorption capacity under dry conditions as displayed in Fig. 5 and Table 3. The SBA-15 substrate has the largest dynamic adsorption capacity ($0.830 \text{ mmol/g}_{\text{adsorbent}}$) under dry conditions, while the MS-6 adsorbent has the middle adsorption capacity ($0.794 \text{ mmol/g}_{\text{adsorbent}}$) compared to the silicalite-1 and SBA-15 adsorbents.

When water vapor was taken as adsorbate together with VOC (benzene) to study hydrophobic properties of the samples under wet conditions, however, the dynamic adsorption capacity of

Fig. 6. FTIR spectra of: (a) silicalite-1, (b) MS-2, (c) MS-6, (d) MS-8 and (e) SBA-15.

SBA-15 decreases greatly ($0.586 \text{ mmol/g}_{\text{adsorbent}}$) due to lots of Si-OH groups on the surfaces of framework which induce the polar surface properties and hydrophilicity [31]. Compared to SBA-15 substrate, MSs and silicalite-1 adsorbents have less influence on the dynamic adsorption capacity under wet conditions. The hydrophobicity of MSs (MS-2, MS-6 and MS-8) is also characterized by FTIR technique shown in Fig. 6. The peaks that occur at about 1628 cm^{-1} and 3744 cm^{-1} are assigned to the vibrations of $\text{-H}_2\text{O}$ and free Si-OH [32]. As seen in Fig. 6, the intensities of peaks at 1628 cm^{-1} and 3744 cm^{-1} of MS-2, MS-6 and MS-8 samples decrease compared to SBA-15, which may confirm that SBA-15 substrates coated with silicalite-1 become more hydrophobic. Table 3 compiles the adsorption capacity for benzene of MSs, SBA-15 and silicalite-1 under dry and wet conditions. The hydrophobic/hydrophilic character is based on the interaction between the VOCs adsorbed and adsorbents. A hydrophobicity index (HI) has been introduced and simply defined as $Q_{\text{wet}}/Q_{\text{dry}}$, where Q_{wet} and Q_{dry} are the dynamic adsorption capacity per gram of adsorbent under wet (13% relative humidity) and dry conditions, respectively. As seen in Table 3, the HI value follows the sequence of silicalite-1 > MSs > SBA-15, which also represents the sequence of hydrophobicity. On the other hand, the SBA-15 particles coated with silicalite-1 seeds enhance the surface hydrophobicity. And to some extent, the MSs samples combine the advantages of the ordered mesoporous material and silicalite-1 zeolite to obtain high adsorptive capacity and super-hydrophobic property.

Fig. 7 depicts the relationship between the respective micropore volume and the total pore volume and dynamic VOC (benzene) adsorptive capacity for some selected MSs samples. Fig. 7(a) reveals that the presence of micropores in MSs samples directly causes an increase in the dynamic adsorptive capacity for benzene adsorption both under dry and wet conditions, where the micropore volume is therefore an essential factor in determining the dynamic capacity of MSs adsorbents, which is consistent with the result of the Kosuge et al.'s work [8]. Fig. 7(b) indicates that the MSs adsorbents with larger total pore volume do not have larger dynamic adsorptive capacity. However, no matter under dry conditions or wet conditions (13% relative humidity), the dynamic capacity is also in the order of MS-6 > silicalite-1. It is exploited that the MSs materials are interesting adsorbents for application under humid conditions, taking into account their hydrophobic and relative high adsorptive properties.

Table 3
Adsorption capacity for benzene under dry and wet conditions.

Samples	Dynamic adsorption capacity Q ($\text{mmol/g}_{\text{adsorbent}}$)		
	Q_{dry}	$Q_{13\% \text{ RH}}$	$Q_{13\% \text{ RH}}/Q_{\text{dry}}$
SBA-15	0.830	0.586	0.71
Silicalite-1	0.584	0.532	0.91
MS-2	0.676	0.589	0.87
MS-4	0.542	0.430	0.79
MS-6	0.794	0.689	0.87
MS-8	0.641	0.546	0.85

Fig. 7. Relationship between (a) the micropore volume and dynamic VOC (benzene) adsorptive capacity and (b) the total pore volume and dynamic VOC (benzene) adsorptive capacity for the MSs samples. The filled squares (■) are under dry conditions and the open squares (□) are under wet conditions (13% relative humidity).

4. Conclusions

Hybrid materials of silicalite-1-coated SBA-15 particles were synthesized by crystallization process under hydrothermal conditions. TEM studies, combined with XRD and nitrogen adsorption analyses, suggest that ordered mesoporous silica SBA-15 substrates coated with microcrystalline silicalite-1 zeolite were successfully synthesized and generate hybrid MSs materials. The influences of crystallization time and calcination time were investigated on the formation of MSs materials. It indicates that longer crystallization time under basic condition causes the mesostructure of SBA-15 substrate to collapse destructively and higher calcination temperature tends to disrupt the long-range mesoscopic order while it has little influence on the phase of microcrystalline silicalite-1 zeolite.

The resultant MSs materials were studied by estimating dynamic adsorption capacity under dry and wet conditions to evaluate their adsorptive and hydrophobic properties. The HI indicated that the SBA-15 particles coated with the silicalite-1 seeds enhance the surface hydrophobicity, and also are consistent with FTIR results. To some extent, the MSs samples combine the advantages of the ordered mesoporous material and silicalite-1 zeolite that obtain high adsorptive capacity and super-hydrophobic properties. In terms of the effect of pore structure on dynamic performance, it reveals that the presence of micropores in MSs materials directly causes an increase in the dynamic adsorptive capacity for benzene adsorption both under dry and wet conditions, where the micropore volume is therefore an essential factor in determining the dynamic capacity of MSs adsorbents. However, it also shows the challenge to increase the BET surface areas of MSs materials, which should be explored in the following step.

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