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Featured Letter

Synthesis of ordered cubic smaller supermicroporous mesoporous silica using ionic liquid as template

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ABSTRACT

Ordered cubic smaller supermicroporous mesoporous silica has been successfully prepared using ionic liquid as template in acidic condition, where ionic liquid were produced from 1-dodecyl bromide and 1-methylimidazole ($\mathbf{I}_{12}$). Most importantly, MS-I_{12} exhibits two obvious pore size distribution at 1.7 nm attributed to supermicropores and 0.64 nm associated with micropores. Our present work is of importance because it not only provides a new methodology to synthesize supermicroporous mesoporous materials, but also opens a door for preparation of mesoporous silica with micropores.

1. Introduction

Since M41S materials first were reported by Mobil in 1990s, mesoporous silica materials have attracted considerable attention due to their excellent properties of high surface area, uniform pore size distribution, and tunable mesoporous structure [1–3]. Generally, such materials are divided into three categories: MCM-41 (hexagonal), MCM-48 (cubic) and MCM-50 (lamellar). Among them, cubic mesoporous silica has been considered as promising materials due to the fast transferring rate of guest molecules in mesopores [4]. However, considerable attention has been focused on synthesis and applications of hexagonal mesoporous silica, such as SBA-15, and MCM-41 [5]. Later, Huo et al. have reported the famous three-dimensional cubic mesoporous silica with space group *Pm*3n (named as SBA-1) [6]. Due to the excellent properties, mesoporous silica materials based on SBA-1 have attracted considerable interest.

Generally, SBA-1-based materials were prepared using cationic surfactants as templates, such as cetyltriethylammonium bromide (CTEABr) [7]. Although the researchers have tried to prepare SBA-1 with small pore size by using short-chain cationic surfactants as templates, the pore size of SBA-1 is normally larger than 2 nm.

On the other hand, ordered supermicroporous mesoporous materials with the pore size distribution ranging from 1 to 2 nm have attracted much attention due to their important application in industry [8]. It is deduced that the ordered mesoporous silica materials combining both three-dimensional (3D) cubic and supermicroporous could be used as promising materials for various practical applications. Therefore, development of an effective strategy for preparation of ordered cubic supermicroporous mesoporous silica is highly required.

Herein, we have demonstrated the preparation of ordered cubic supermicroporous mesoporous silica using ionic liquid as template in acidic condition. It is found that such cubic supermicroporous mesoporous silica exhibits two obvious pore size distribution at 1.7 nm attributed to supermicropores and 0.64 nm associated with micropores.

2. Experimental section

2.1. Materials

1-Hexadecyl bromide, 1-tetradecyl bromide, 1-dodecyl bromide, 1-decyl bromide, and 1-octyl bromide were purchased from Aldrich. 1-Methylimidazole, HCl and TEOS were purchased from Beijing Chemical Corp (Beijing, China). All chemicals were used without any further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of ionic liquids

Ionic liquids were prepared using 1-methylimidazole and alkyl bromide as precursors, according to the previous publication [9].

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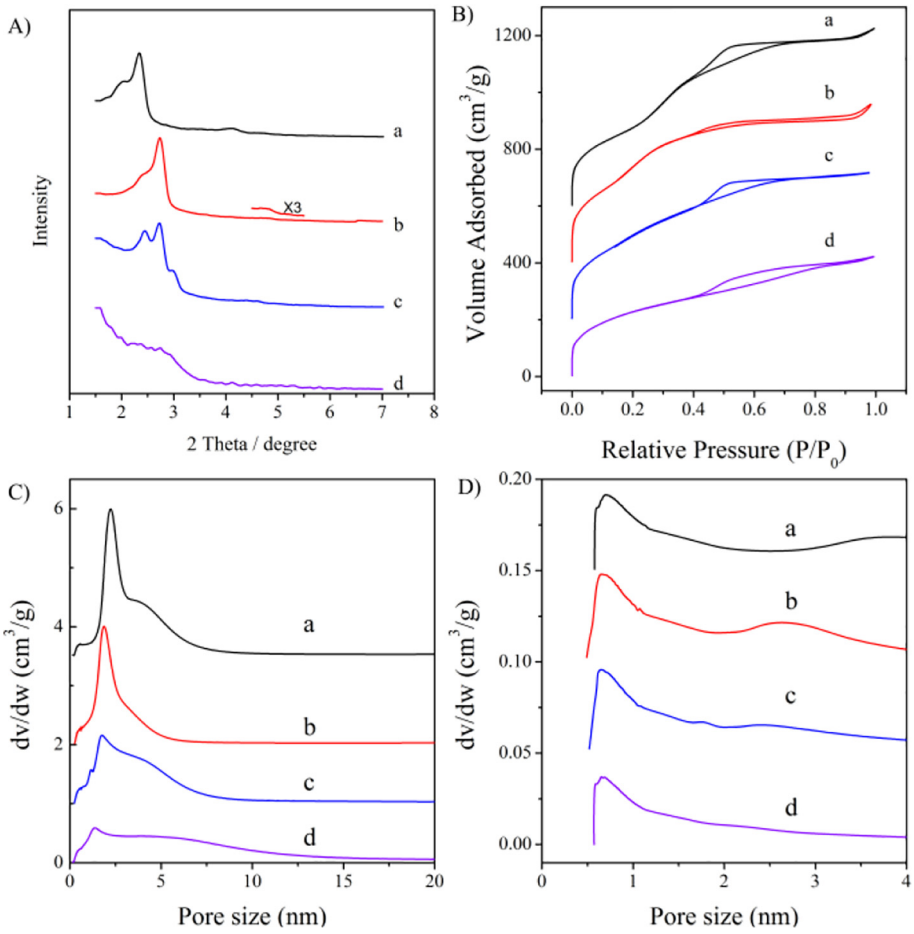

Fig. 1. (A) XRD patterns, (B) N_2 adsorption/desorption isotherms, (C) BJH pore sizes distribution and (D) HK pore size distribution of (a) MS-I_{16}, (b) MS-I_{14}, (c) MS-I_{12}, and (d) MS-I_{10}.

The ionic liquids thus obtained were designated as $\mathbf{I}_{16}$, $\mathbf{I}_{14}$, $\mathbf{I}_{12}$, and $\mathbf{I}_{10}$, when 1-hexadecyl bromide, 1-tetradecyl bromide, 1-dodecyl bromide, and 1-decyl bromide were used as precursors.

2.3. Preparation of mesoporous silica materials

Mesoporous silica materials were prepared using ionic liquids as templates in the presence of HCl. In a typical run, 0.64 g of $\mathbf{I}_{12}$ was added into 100 mL of water, followed by addition of 38.3 mL of HCl. After dissolution of $\mathbf{I}_{12}$, 2.25 mL of TEOS was added into the above mixture, followed by stirring for 1 h. After static for 24 h, the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave and then heated at 100 °C for 24 h. After calcination at 550 °C for 3 h, mesoporous silica materials were obtained (designated as MS-I_{12}). Other mesoporous silica materials were also prepared by using other ionic liquids as templates, including $\mathbf{I}_{16}$ (0.76 g), $\mathbf{I}_{14}$ (0.70 g), and $\mathbf{I}_{10}$ (0.58 g), which are designated as MS-I_{16}, MS-I_{12}, and MS-I_{10}.

2.4. Characterizations

Powder X-ray diffraction (XRD) data were recorded on a Siemens D5005 (40 kV, 30 mA) using nickel-filtered Cu Kα radiation with wavelength of λ = 1.5406 Å. Scanning electron microscopy experiments were performed on an S-5200 electron microscope (Hitachi, Japan).

Table 1
Textural parameters of MS-I_n samples.

Sample	S_{BET} (m^2/g)	V_{meso} (cm^3/g)	D_{meso} (nm)	D_{micro} (nm)
MS-I_{16}	1012	0.97	2.3	0.69
MS-I_{14}	1302	0.86	1.9	0.64
MS-I_{12}	1130	0.80	1.7	0.64
MS-I_{10}	842	0.65	1.4	0.66

3. Results and discussion

Fig. 1A shows the XRD patterns of mesoporous silica materials (MS-I_n samples). The MS-I_{16} exhibits a strong diffraction peak at 2θ of 2.35° and two weak diffraction peaks at 2θ of 2.01° and 4.08°. Notably, the ratio of diffraction peaks at high degree is 1:1.732, associated with characteristic reflections (1 0 0), and (1 1 0) hexagonal mesoporous silica with space group *p6mm*. Compared to the diffraction peaks in hexagonal mesoporous silica, another peak centered at 2θ of 2.01° is also observed, indicating that the sample may consist of hexagonal structure with another ambiguous structure. By decreasing the length of alkyl chain in ionic liquids, MS-I_{14} also exhibits three diffraction peaks similar to MS-I_{16}. The shift of diffraction peaks to high degree could be attributed to the decrease of template size, revealing *d* value from 4.37 nm (MS-I_{16}) to 3.71 nm (MS-I_{14}). Interestingly, three well diffraction peaks centered at 2θ of 2.44°, 2.73°, and 2.97° were observed on MS-I_{12} attributed to reflections (2 0 0), (2 1 0), and