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Microporous and Mesoporous Materials 91 (2006) 85–91

MICROPOROUS AND MESOPOROUS MATERIALS

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Mesoporous aluminosilicates synthesized with single molecular precursor (*sec*-BuO)$_2$AlOSi(OEt)$_3$ as aluminum source

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Received 7 September 2005; received in revised form 4 November 2005; accepted 11 November 2005
Available online 28 December 2005

Abstract

Single molecular precursor bis(*sec*-butoxy)aluminoxytriethoxysilane [(*sec*-BuO)$_2$AlOSi(OEt)$_3$] was used as aluminum source for the synthesis of mesoporous aluminosilicates with low Si/Al ratios from 1.0 to 10.0 via a template-assisted method. The samples with Si/Al ratios of 1.0 and 3.0 have wormhole-like pore structure, while the samples with Si/Al ratios of 5.0 and 10.0 have ordered hexagonal mesoporous structures with extensive void defects amid the nanochannels. IR spectra of pyridine adsorption and NH$_3$-TPD characterizations suggest that the mesoporous aluminosilicates have both Brönsted and Lewis acid sites with medium strength. The amounts of acid sites of the mesoporous aluminosilicates do not run parallel with the concentration of the tetrahedrally coordinated aluminum in the mesoporous framework.

Keywords: Mesoporous aluminosilicates; Void defects; Low Si/Al ratios; Acidity

1. Introduction

Mesoporous aluminosilicates with high surface area and well-defined pore structure have attracted great attention in the fields of separation and catalysis, especially for the reactions involving large molecules [1–3]. Since the discovery of MCM-41 [4], a key scientific objective has been the synthesis of mesoporous materials with higher content of tetrahedral Al in the mesoporous framework because the tetrahedrally coordinated trivalent aluminum atoms are considered to be the major interaction sites for guest molecules and the origin of acidity [1,5,6]. Previous attempts for the synthesis of mesoporous aluminosilicates have employed various aluminum salts as precursors [5,7]. However, due to the big difference in the hydrolysis and condensation rates between aluminum and silica precursors, it is difficult to obtain ordered mesoporous aluminosilicates with high content of aluminum tetrahedrally coordinated in the framework [5]. Many efforts have been made to overcome these difficulties, such as hydrolyzing the silica precursors in advance, decreasing the hydrolysis rate of aluminum precursors by complexing them with chelating agents, forming the mixed metaloxane Si–O–Al bonds at the precursor stage [8–10]. It also might be possible to increase the content of aluminum in mesoporous silica by using the mixed surfactant and two-step pH adjusting method [11–13]. However, it is very difficult to obtain the mesoporous aluminosilicates with Si/Al ratio as low as 1.0. Moreover, MCM-41 type mesostructure consisting of mainly one-dimensional nanochannels is dominant for most mesoporous aluminosilicates with low Si/Al ratio [5,6,14], which make the interchannel transportation of guest molecules ineffective, especially for large molecules [15–17]. Therefore, to synthesize mesoporous aluminosilicates with low Si/Al ratio and open mesoporous structure remains a challenge. Moreover, there are almost no detailed studies on the acidic and catalytic properties of the mesoporous aluminosilicate with Si/Al ratio as low as

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doi:10.1016/j.micromeso.2005.11.021

1.0. The necessity of the existence of high content of tetrahedrally coordinated aluminum for the generation of high acidity for the mesoporous aluminosilicate remains a question.

Single source molecular precursors based on –OSi(O^tBu)$_3$ ligand were employed for the synthesis of multicomponent oxide materials [18–26]. However, only $(EtO)_nM[OSi(O^tBu)_3]_4$ ($M = Zr, Fe, Ta$; $n = 0, 2$) have been tried for the synthesis of mesoporous materials [22]. In this article, the mesoporous aluminosilicates with high content of framework aluminum and extensive void defects were synthesized by using the single source molecular precursor [(*sec*-BuO)$_2$AlOSi(OEt)$_3$] via a template-assisted approach. It is possible to precisely control the structure and active site in the materials by using the above mentioned single molecular precursor.

2. Experimental sections

2.1. Reagents

Di-*sec*-butoxyaluminoxytriethoxysilane ((*sec*-BuO)$_2$AlO Si(OEt)$_3$) was purchased from Gelest. Tetramethyl orthosilicate (TMOS) was purchased from Aldrich. The surfactant cetyltrimethylammonium bromide (CTAB) was obtained from Aldrich. All chemicals were used directly without further purification.

2.2. Synthesis of mesoporous aluminosilicates with Si/Al ratio of 1.0

7.77 g of di-*sec*-butoxyaluminoxytriethoxysilane was added to the aqueous solution containing 4.5 g of cetyltrimethylammonium bromide, 0.45 g of NaOH and 50 mL of H_2O with stirring at 30 °C. The mixture was vigorously stirred for 20 h and transferred into an autoclave. After aging for 72 h at 110 °C, the resultant solid was filtered, washed, and dried at 60 °C for 15 h. The molar gel ratio for the synthesis is Si:Al:0.56CTAB:0.51NaOH:126H_2O. The sample was denoted as as-synthesized AS-1.

2.3. Synthesis of mesoporous aluminosilicates with Si/Al ratios of 3.0, 5.0 and 10.0

To prepare the materials with Si/Al ratio of 10.0, a homogeneous mixture of 4.5 g of TMOS and 1.16 g of di-*sec*-butoxyaluminoxytriethoxysilane was added to the solution containing 2 g of CTAB, 0.38 g of NaOH and 49 mL of water at 30 °C. The mixture was vigorously stirred at 30 °C for 20 h and transferred into an autoclave. After aging for 72 h at 110 °C, the resultant solid was filtered, washed, and dried at 60 °C for 15 h. The sample was donated as the as-synthesized AS-10 (Si/Al = 10.0). AS-3 (Si/Al = 3.0) and AS-5 (Si/Al = 5.0) were prepared with the same procedures as AS-10. The molar ratio for the synthesis of mesoporous materials is $(1.1 - x)$Si:xAl: 0.17CTAB:0.29NaOH:82H_2O.

2.4. Transformation of Na-type materials to H-type materials

The H-type materials were generated by stirring 1 g of as-synthesized samples in ethanol solutions (1 g NH_4NO_3/100 mL EtOH (95%)) at 80 °C for 4 h [27]. The powder products were recovered by filtration. The above procedures were repeated for three times to ensure a complete exchange of Na^+. After drying at 80 °C, the samples were calcined at 550 °C for 10 h to get the calcined H-type materials.

2.5. Characterizations

XRD patterns were recorded on a Rigaku D/Max 3400 powder diffraction system using Cu Kα radiation (40 kV and 30 mA) over the range $0.5° \leqslant 2\theta \leqslant 8°$. Nitrogen sorption experiments were performed at −196 °C on ASAP 2000 system in static measurement mode. The samples were out gassed at 300 °C for 10 h before the measurement. The pore size distribution curves were obtained from the analysis of the adsorption branch of the isotherms using BJH (Barrett–Joyner–Halenda) method. Transmission electron microscopy (TEM) measurements were made on a JEM-3010 electron microscope (JEOL Japan) with an acceleration voltage of 300 kV. Scanning electron micrographs (SEM) were taken on JEM-6360 electron microscope with an acceleration voltage of 29 kV. The samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold prior to imaging. ^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a Bruker DRX-400 spectrometer equipped with a magic angle spin probe at room temperature. $AlCl_3 \cdot 6H_2O$ was used as reference.

IR spectra of adsorbed pyridine were taken on a Thermo Nicolet NEXUS 470 FT-IR spectrometer. The samples were made into self-supporting wafers and were evacuated in an IR cell at 400 °C for 100 min. IR background spectra were recorded after the samples were cooled down to room temperature. Pyridine was then admitted into the IR cell and the IR spectra of adsorbed pyridine were recorded after a degassing at 150 °C for 30 min.

NH_3-TPD measurements were carried out in a flow reactor. Samples were activated at 700 °C for 1 h in a flow of helium, subsequently, ammonia was introduced by a He stream containing 10 vol% of ammonia at 100 °C. The physically adsorbed NH_3 was removed by purging with a helium flow at 100 °C until the baseline was flat. Then the reactor temperature was ramped at a rate of 10 °C/min.

3. Results and discussion

3.1. Structural characterizations

The XRD patterns of the calcined aluminosilicates with Si/Al ratios of 1.0–10.0 are given in Fig. 1. Three