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Short Communication

Synthesis of highly regular mesoporous Al-MCM-41 from metakaolin

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ABSTRACT

Mesoporous molecular sieve Al-MCM-41 with Si/Al ratio = 5, was in situ synthesized under hydrothermal condition using tetraethylorthosilicate (TEOS) and metakaolin as silica and aluminum sources and cetyl trimethylammonium bromide as structure directing agent. Powder X-ray diffraction (XRD), solid-state magic-angle spinning (MAS) NMR spectroscopy, Fourier transform infrared spectroscopy (FT-IR), N_2 isothermal adsorption–desorption, SEM and TEM are used to characterize the samples. Metakaolin used as source of aluminum and silicon allowed the formation of well-ordered Al-MCM-41 mesoporous materials. Thus, inexpensive metakaolin is probably a better Al and Si source for MCM-41 samples with low Si/Al ratios than other aluminum sources.

1. Introduction

Use of mesoporous molecular sieves (MCM-41) (Kresge et al., 1992) has attracted considerable attention due to their unique properties, specially catalysis involving large molecules.

Incorporation of metal cations into the silicate framework, such as tetrahedral coordinated Al, which can generate Brönsted acid sites, has been the focus of much recent research. In the last few years, there were many reports of synthesis and characterization of Al-MCM-41 with different Si/Al ratios and with different alumina sources such as sodium aluminates, aluminium sulfate, aluminium nitrate, metakaolin and aluminium isopropoxide or silica sources including sodium silicate and silicon alkoxides (Corma et al., 1994; Luan et al., 1995; Kim et al., 1997; Eimer et al., 2003; Fang et al., 2005; Kang et al., 2005). These synthesis methods not only consume various expensive chemicals and also cause environmental contamination.

Here we present an in situ synthesis route of Al-MCM-41 with high structural order with metakaolin as silica and aluminum sources and cetyl trimethylammonium bromide (CTAB).

2. Experimental

Metakaolin was obtained from Anhui Xuena nonmetal Co. Ltd. Major composition (mass %) of the starting metakaolin was SiO_2 (54), Al_2O_3 (43), TiO_2 (1.2), Fe_2O_3 (0.6), CaO (0.5), MgO (0.3), Na_2O (0.2) and K_2O (0.05). The other reactants used in this experiment were CTAB (A. R.), TEOS (A.R.), NaOH (A.R.).

For the synthesis of the Al-MCM-41 (Si/Al = 5) material, 5.0 g of metakaolin were dissolved in NaOH solution and the mixture was stirred for half an hour at ambient temperature. Then 10 mL of TEOS, which was dispersed in 20 mL deionized water, was added dropwise under stirring and the mixture was vigorously stirred for about half an hour until gel formation (pH = 11) at ambient temperature. Then, 3.6 g of CTAB, dispersed in a small amount of water, was added dropwise with strongly stirring so that the gel changed into dispersion after further vigorously stirring for 1 h at ambient temperature. The gel composition $1SiO_2{:}0.1Al_2O_3{:}0.3NaOH{:}\ 0.2CTAB{:}80H_2O$. The dispersion was heated in a Teflon-line steel autoclave to 403 K for 24 h or 373 k for 48 h. After cooling to room temperature, the material was recovered by filtration, washed with deionized water, dried in air at 333 K overnight and calcined at 813 K for 6 h.

The low angle XRD patterns of Al-MCM-41 (Si/Al = 5) samples were obtained with Rigaku D/max-2500 X-ray diffractometer in the range of 2θ between 0.6° and 10° using nickel filtered CuKα. ^{27}Al MAS NMR spectra were performed on a Varian Infinity Plus 300 MHz spectrometer. The FT-IR spectra of KBr pellets were recorded in a Nicolet 470 spectrometer, resolution 4 cm^{-1}. Surface area measurements were carried out on a Nova 2000*e* Instrument following the BET procedure using N_2 as adsorptive at liquid nitrogen temperature. Prior to adsorption the calcined samples were degassed at 473 K for 16 h. The pore size distribution in the mesopore region was determined by applying the BJH method to the adsorption branch of the isotherms. The SEM images were obtained on a KYKY-2800B scanning electron microscope equipped Thermo energy dispersion spectra (EDS). TEM

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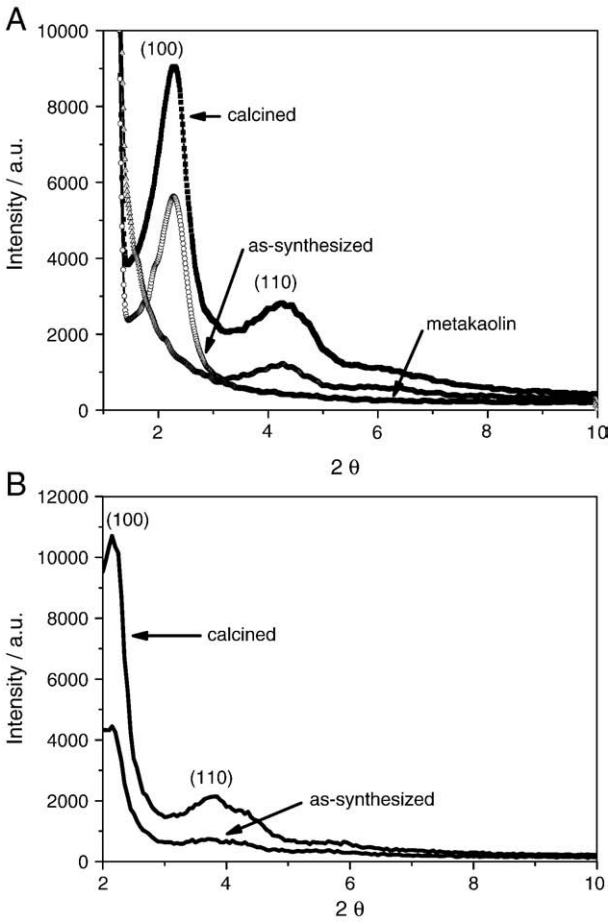

Fig. 1. XRD pattern A: Al-MCM-41 (403 K); B: Al-MCM-41 (373 K).

images were obtained using a Phillips EM 400ST transmission electron microscope.

3. Results and discussion

The XRD diffraction patterns of as-synthesized and calcined samples are given in Fig. 1 (A: Al-MCM-41 (403 K); B: Al-MCM-41 (373 K)). Metakaolin shows no reflection between 0.6° and 10°. A strong reflection at $2\theta = 2.12–2.30$ corresponded to the molecular sieve with $a_0 = 4.43–4.75$ nm. The unit cell parameters and d spacing values of the Al-MCM-41 samples are given in Table 1. The hexagonal (P6mm space group) unit cell parameter a_0 was calculated from the equation $a_0 = 2d_{100}\sqrt{3}$. May be due to the high Al content and low of crystallinity that the (110) and (200) reflections overlapped and the (210) reflection was absent as reported before (Corma et al., 1994; Luan et al., 1995; Kim et al., 1997; Eimer et al., 2003). However, no reflection was observed for the material with a Si/Al ratio of 5 (Luan et al., 1995; Kim et al., 1997). The patterns of samples calcined at 813 K (to remove the surfactant) are much better resolved than the as-

Table 1
XRD and lattice parameter and textural characteristics of the samples.

Samples	*d*-spacing value (nm)		Unit cell parameter	Surface area	Pore diameter	Pore volume
	As-synthesized	Calcined	a_0 (nm)	(BET) (cm^2/g)	(nm)	(BJH) (cm^3/g)
Al-MCM-41 (403 K)	4.11	4.11	4.75	753	3.33	0.63
Al-MCM-41 (373 K)	3.89	3.84	4.43	647	3.06	0.55

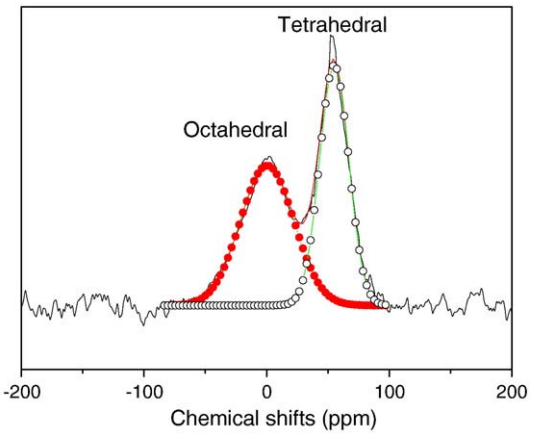

Fig. 2. ^{27}Al MAS NMR spectra of calcined Al-MCM-41 (403 K).

synthesized samples. The (100) reflection becomes sharper and more intense upon calcination, although the (110) and (200) reflections are still ill-defined and overlap to give a single broad band. On calcination of as-synthesized mesoporous materials, a lattice contraction is commonly observed due to the removal of the surfactant and the condensation of silanol (SiOH) groups in the walls. In our case, the unit-cell contractions that was only 1.3% for Al-MCM-41 (403 K) and zero for Al-MCM-41 (373 K). Thus, mineral metakaolin is probably a better Al source for the synthesis of MCM-41 samples with low Si/Al ratios (Table 1).

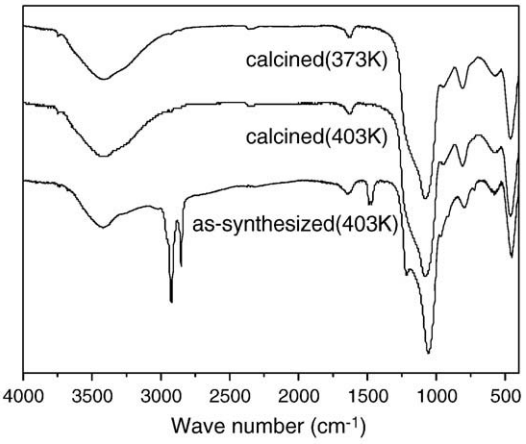

Fig. 3. FT-IR spectra.

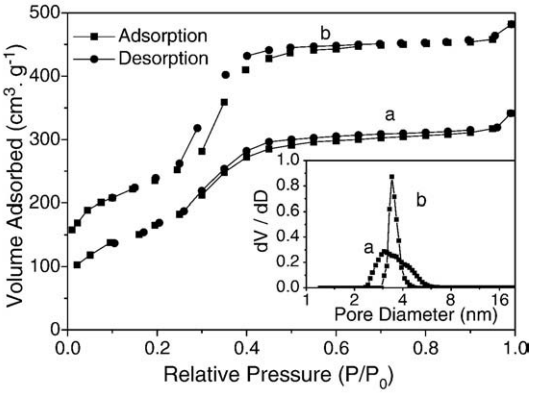

Fig. 4. N_2 adsorption–desorption isotherms and pore size distribution. a: Al-MCM-41 (373 K); b: Al-MCM-41 (403 K).