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Preparation of mesoporous Al-MCM-41 with stable tetrahedral aluminum using ionic liquids as a single template

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Abstract

Mesoporous Al-MCM-41 materials were synthesized using room temperature ionic liquid 1-cethyl-3-methylimidazolium bromide ([C_{16}mim]Br) as a single template and characterized by X-ray diffraction, N_2 adsorption–desorption, ICP-AES, ^{27}Al MAS NMR and TEM technique. These mesoporous materials exhibit hexagonal *p6m* pore architectures, and possess high surface area and narrow pore distribution. All aluminum in as-synthesized samples exists in tetrahedral coordination. Upon calcination nearly all aluminum still remains the tetrahedral coordination even when the Si/Al ratio is as low as 15. This indicates that the tetrahedral aluminum of Al-MCM-41 is stable.

Keywords: Al-MCM-41; Ionic liquid; Characterization; Preparation

1. Introduction

The discovery of mesoporous molecular sieves M41S by Mobil workers [1,2] has caused a booming research in this field. This type of mesoporous materials consists of uniform hexagonal arrays of linear channels that are constructed with a honeycomb-like silica matrix, as well as possesses large pore openings and high surface area. The materials exhibit 2D symmetry. Each pore surrounded by six neighbors. The continuous mesopores arrange parallelly through the entire length of the particles.

The purely siliceous mesoporous MCM-41 has been conventionally synthesized using cetyltrimethylammonium bromide (CTAB) [3–5], and also recently using room temperature ionic liquid [C_{16}mim]Br as template [6], but this material has a chemically inert silicate framework and consequently no acid sites. The acid sites for catalysis can be generated when aluminum heteroatoms are incorporated into the framework of mesoporous MCM-41 by isomorphous substitution of aluminum for silicon during hydrothermal synthesis [7,8].

Among various procedures for the preparation of Al-MCM-41, CTAB is conventionally used as template [9,10]. The studies of ^{27}Al MAS NMR indicate that the use of CTAB as a single template for Al-MCM-41 synthesis (Si/Al ratio < 100)

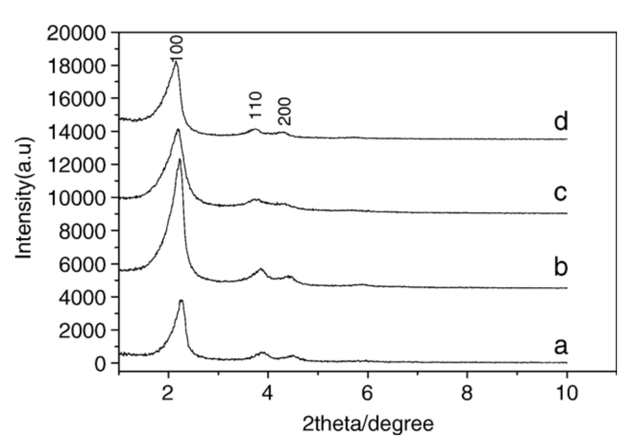

Fig. 1. The XRD patterns of calcined samples: a. AM-IL-100; b. AM-IL-50;c. AM-IL-20; d. AM-IL-15.

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Table 1
Structural and physicochemical properties of the Al-MCM-41 samples with different Si/Al ratios after calcination at 550 °C for 4 h

Sample code	Si/Al ratio		XRD		BET			^{27}Al MAS NMR	
	Gel	Calcined	d_{100} (nm)	a_0 (nm)	S.A[a] (m^2/g)	P.D[b] (nm)	P.V[c] (cm^3/g)	Tetrahedral / (tetrahedral and octahedral) × 100%[d]	
								As-synthesized	Calcined
AM-CTAB-15	15	14	4.16	4.78	1010	3.04	1.10	100%	88.9 +/− 0.1%
AM-IL-15	15	14	4.15	4.80	867	3.16	1.09	100%	98.9 +/− 0.1%
AM-IL-20	20	19	4.10	4.73	1122	2.98	1.42	100%	99.4 +/− 0.1%
AM-IL-50	50	47	3.95	4.56	1202	2.96	1.26	100%	99.8 +/− 0.1%
AM-IL-100	100	89	3.81	4.40	1083	2.72	1.20	100%	100%

[a]Surface area.
[b]Pore diameter.
[c]Pore volume.
[d]Calculated from the integrated intensities of peaks assigned to tetrahedral and octahedral species respectively.

leads to a significant dislodgement of aluminum from the framework upon calcinations [11,12]. However, much of the activity of this type of material stems from the presence of stable tetrahedral aluminum in the silica framework but not the octahedral, and dealumination on calcination reduces the effectiveness of the material. Therefore, the preparation of Al-MCM-41 with stable tetrahedral aluminum has become the subject of much attention.

In this work, we report a novel method for the synthesis of mesoporous Al-MCM-41 with stable tetrahedral aluminum in the framework using room temperature ionic liquid as a single template. Room temperature ionic liquids are salts with low melting point, sometimes as low as −96 °C [13]. Most of the investigated room temperature ionic liquids consist of the organic cation 1-alkyl-3-methylimidazolium (abbreviated $[C_n mim]^+$, where n = number of carbon atoms in a linear alkyl chain) and either organic or inorganic anions. Long-chain room temperature ionic liquids have been shown to display the behaviors of both lyotropic [14] and thermotropic liquid-crystals [15], and this provides a partially ordered environment and a better selectivity for organic reactions [16]. Herein, we choose room temperature ionic liquid $[C_{16}mim]Br$ as a single template for the preparation of mesoporous Al-MCM-41 with stable tetrahedral aluminum.

2. Experimental

All reagents such as sodium silicate, aluminum sulphate, dichloromethane and sulfuric acid were of AR grade and used as received. 1-methylimidazole and 1-bromohexadecane were used for the synthesis of $[C_{16}mim]Br$ [17].

Mesoporous Al-MCM-41 samples with various molar ratios of Si/Al were synthesized from the gels with the following gel composition: $1SiO_2$: xAl_2O_3:0.5 $[C_{16}mim]Br$: $0.77H_2SO_4$: $120H_2O$ (x varies with the molar ratios of Si/Al). The resulting gels were transferred to a Teflon-linered steel autoclave for crystallization at 80 °C for 7 days. The obtained samples were filtered, washed with distilled water and dried at 80 °C for 8 h in air. Calcination of the samples was carried out at 550 °C for 4 h in air to remove template. Samples with different Si/Al molar ratios were designated as AM-IL-y (y = Si/Al molar ratio, $15 \leq y \leq 100$). To compare with $[C_{16}mim]Br$, the conventional template CTAB was singly used for the synthesis of the samples of Al-MCM-41. The samples were designated as AM-CTAB-y (y = Si/Al molar ratio).

The X-ray diffraction (XRD) patterns of the samples were obtained with a Bruker D8 Advance diffractometer using Cu K_α radiation. The Si/Al molar ratios of the samples were recorded on an allied analytical ICAP 9000 atomic emission spectrometer.

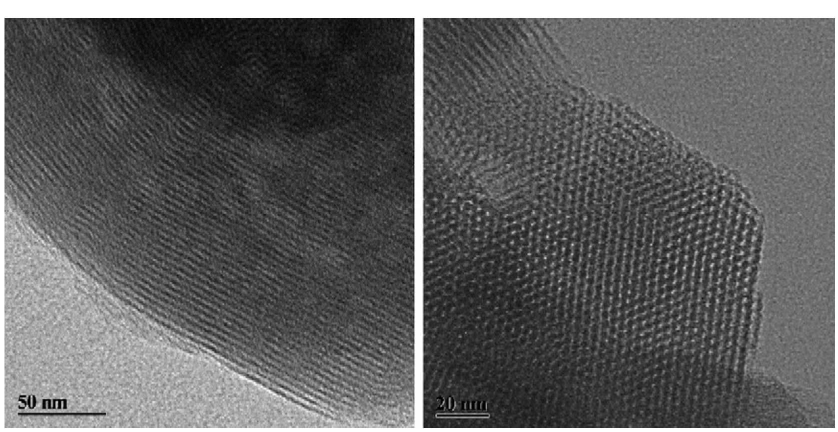

Fig. 2. TEM spectra of the calcined samples (Si/Al = 15).