Synthesis and characterization of highly ordered MCM-41 in an alkali-free system and its catalytic activity

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MCM-41 mesoporous molecular sieve materials are synthesised using aqueous ammonia solution to adjust the pH of the reactant gel. Highly ordered MCM-41 with Si/Al ratio as low as 14 was obtained and characterised by ^{27}Al MAS NMR, XRD, N_2-adsorption, benzene sorption, and NH_3-TPD measurements. The acidity of MCM-41 materials obtained in this system was conveniently generated through straightforward calcination of the as-synthesised sample. More mild acidic sites generated could be due to the avoidance of the multiple calcination procedure and/or the trace sodium species which are the poisons to Brønsted acid. The catalytic activities for *n*-heptane cracking and isomerization of *m*-xylene were investigated, and these were in accordance with the known properties of MCM-41.

Keywords: MCM-41 synthesis; alkali-free gel; *n*-heptane cracking; NMR

1. Introduction

The mesoporous molecular sieve MCM-41 has attracted much attention because of its uniform mesopores, high surface area and thermal stability [1–3]. The acidity of this novel material was found to be similar to amorphous silica–alumina [3,4] due to its disordered wall structure [5,6]. It has also been found that MCM-41 is hydrothermally unstable compared to traditional zeolite [3,4]. Moreover, in order to generate acidity from the as-synthesised sample obtained from a sodium-containing system, calcination is required to remove the templates occluded in the channels. Subsequent ion exchange with ammonium salts and calcination again then results in the H-form of MCM-41. These procedures will inevitably lead to a certain degree of dealumination, as well as some structural collapse due to the hydrothermal unstability of MCM-41 [3].

On the other hand, Ti-containing MCM-41 has been found to be a very promising catalyst for production of fine chemicals [7]. Other transition metals, such as V, Mo, etc. incorporated into the framework of MCM-41 may find applications in oxidising organic molecules to valuable oxygenates [8] or to environmentally safe molecules [9]. It is known that these transition metals are very sensitive to the presence of sodium species [10]. In view of the above facts, it is of interest to synthesise MCM-41 in an alkali-free system.

Chen et al. [4] have reported the synthesis of aluminosilicate MCM-41 using aqueous ammonia solution (NH_4OH) to adjust the pH of the reactant gels, where another organic amine, e.g., tetramethylammonium hydroxide (TMAOH) and sodium species were also present in order to obtain highly ordered MCM-41. In the present paper, we report the synthesis of aluminosilicate MCM-41 using NH_4OH to adjust the pH of the gel mixture without any other organic amine in an alkali-free system. The products synthesised in this system exhibited highly ordered hexagonal structure characteristic of MCM-41 with a Si/Al ratio as low as 14 without observing any 6-coordinate aluminium as examined by ^{27}Al NMR. The acidity could be generated by straightforward calcination of the as-synthesised products. In this case, the occurrence of dealumination during calcination and trace sodium species which poison the Brønsted acid sites is avoided to a certain extent. Furthermore, some transition metal species (e.g., Ti, Mo) have been easily incorporated into the framework of MCM-41 [11].

2. Experimental

2.1. Synthesis

The synthesis of MCM-41 was carried out in a hydrothermal system with a molar composition of $7.2NH_4OH$–$30SiO_2$–xAl_2O_3–$5.1C_{16}H_{33}(CH_3)_3NBr$–$690H_2O$, where

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$x \leqslant 0.93$. The reaction gels were prepared using fumed silica (Cab-O-Sil M-5), aluminium sulfate, ammonium hydroxide (28%), cetyltrimethylammonium bromide, and dionised water as reactants without further purification. The following is a typical synthesis procedure: aluminium sulfate was dissolved in deionised water, then ammonia hydroxide and cetyltrimethylammonium bromide were added simultaneously to the above solution under constant stirring for 30 min. Fumed silica was finally added to the mixture under stirring for another 30 min to obtain a homogeneous supersaturated solution. The resulting gel was poured into a 800 ml autoclave and heated in a steady state for 72 h at 100°C. The solid product was filtered, washed extensively with deionised water and dried at 50°C. Samples synthesised from NH_4OH are denoted 41-A(*n*) where *n* represents the Si/Al ratio in the starting mixture. Samples obtained from sodium-containing gels, designated as 41-S(*n*), were synthesised according to Chen et al. [4]. The ZSM-5 zeolite with Si/Al ratio of 25 used as a catalytic activity reference was synthesised using 1,6-hexanediamine as a template in the same laboratory. Ion exchange of Na-form MCM-41 or ZSM-5 was carried out at 70 K for 24 h with 0.8 M NH_4NO_3 solution (solid/liquid = 1 g/150 ml). This procedure was repeated three times in order to substantially eliminate the sodium species. The NH_4-form MCM-41 was calcined in a muffle furnace, in dry air, from room temperature to 550 K at 10 K min^{-1} and held at this temperature for 24 h to obtain the H-form MCM-41. Catalysts were obtained from the protonic form of MCM-41 or ZSM-5. Powders were pelletised, crushed and sieved to obtain 15–30 mesh catalyst particles.

2.2. Characterisation

X-ray powder diffraction (XRD) data was collected on a Philips PW 1050 diffractometer using Ni filter, Cu Kα radiation. Nitrogen adsorption–desorption data was obtained at 77 K on an ASAP 2000 Micromeritics gas sorption analyser. The average pore sizes were calculated using the BJH method based on the desorption isotherm. Benzene adsorption capacities were measured at 298 K using a vacuum quartz spring balance (50 Torr). Solid-state nuclear magnetic resonance (NMR) was performed on a Bruker MSL 300 spectrometer operating at 59.627 MHz and 78.205 MHz for ^{29}Si and ^{27}Al, respectively. Samples were spun at the magic angle at 2.2 kHz for ^{29}Si and 8.0 kHz for ^{27}Al in Bruker double-air-bearing probes. Temperature programmed ammonium desorption (NH_3-TPD) was conducted in a home-built flow fixed-bed reactor. 100 mg of H-form samples were placed into a quartz tube located in an electric oven and heated from room temperature to 845 K at a heating rate of 10 K/min under a flow of helium, and held at this temperature for 30 min, then cooled to 425 K. Adsorbate was injected into the reactor until saturation of the adsorption sites at 425 K. Subsequently, the samples were heated again from 425 to 845 K at a heating rate of 10 K/min. During the entire process, the flow rate of helium was kept at 30 ml/min.

2.3. Catalysis

Catalytic activities for *n*-heptane cracking and *m*-xylene isomerization were performed on a flow fixed-bed reactor (5 ml) coupled with an on-line gas chromatograph. Prior to the test, catalyst particles were heated to 658 K and held at this temperature for 1 h in a helium flow of 60 ml/min at atmospheric pressure. The respective reaction parameters are mentioned in the related figure or table. The catalytic activities reported here were obtained after a reaction period of ca. 3 h at which time steady state was reached.

3. Results and discussion

Fig. 1 shows typical X-ray powder diffraction patterns of the sample 41-A(14) before and after calcination. It reveals that the mesophase obtained from NH_4OH-containing gels corresponds to MCM-41, as previously reported [1,2]. The as-synthesised sample exhibits poor-ordered wall structure as shown by the lower intensity at ca. 2° two theta compared to the calcined material which exhibits a higher intensity at about 2.2° two theta accompanied by two peaks at 4.5° and 5.5° two theta, respectively. This result indicates that the calcined MCM-41 material possesses a better-defined pore structure and slightly smaller pore size ($a_0 = 2d_{100}\sqrt{3}$) than that of the as-synthesised one, which is in good agreement with previous reports [1,2,4].

Table 1 lists the physical properties for samples 41-A(14), 41-A(∞) and 41-S(14) obtained using different preparation variables. The data indicates that samples with different Si/Al ratios or those obtained from differ-

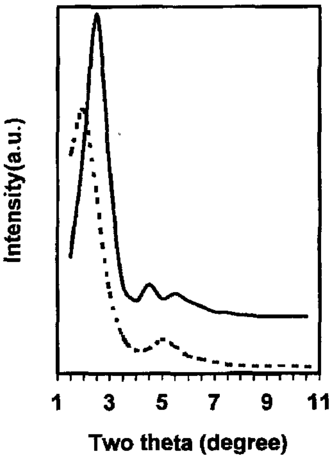

Fig. 1. X-ray powder diffraction patterns of the calcined 41-A(14) (——) and the as-synthesised 41-A(14) (- - -).

Table 1
Physicochemical properties of MCM-41

Sample	Si/Al ratio in the starting gel	BET surface area (m^2/g)	Pore size (Å)	Benzene uptake (wt%; 25°C, 50 Torr)
41-A(∞)	∞	1126.0	29.8	67.5
41-A(14)	14	996.9	29.0	60.0
41-S(14)	14	980.8	29.0	60.8

ent synthesis systems possess very high BET surface areas (about 1000 m^2/g), narrow pore size distributions centred at about 29 Å and large benzene sorption capacities (more than 60 wt%). This demonstrates that the mesophases synthesised using NH_4OH exhibit similar behaviour as MCM-41 obtained from sodium-containing systems. It can also be seen that the siliceous MCM-41 has the highest BET surface area and benzene sorption capacity. This suggests that the pore structure of siliceous MCM-41 is more regular than that of the aluminosilicate MCM-41. It can be deduced that incorporation of aluminium species into the framework of MCM-41 led to somewhat irregular pore arrangement. Such phenomena were also observed in the synthesis of MCM-41 from sodium-containing system and high silica zeolite ZSM-12 [12,13].

The ^{27}Al NMR spectra are shown in fig. 2. It can be seen that only one peak at 54.5 ppm attributed to tetrahedral aluminium [14] can be observed for sample 41-A(14) before and after calcination, thus indicating that the aluminium species added to the starting gels were thoroughly incorporated into the framework of MCM-41 in a 4-coordinated state. After calcination, the peak at 54.5 ppm becomes broader but no peak at 0–10 ppm was observed. The broadening of the peak may be an indication of the presence of some Al species in more distorted tetrahedral environments, without essentially damaging the pore structure of the material. However, the H-form 41-S(14) gives two peaks at 54.5 and 6.5 ppm, respectively. The peak at 6.5 ppm assigned to octahedral Al species [14] was not observed in the as-synthesised sample, indicating that dealumination of sample 41-S(14) must have occurred during the multiple calcination procedures [3]. This conclusion was further proven by the NH_3-TPD data as discussed below.

Fig. 3 shows the ^{29}Si NMR spectra of sample 41-A(14) before and after calcination and a comparison with amorphous silica (Cab-O-Sil M-5) which was used as the silica source. Four peaks at −92 ppm for Q_2, −101 ppm for Q_3, and −106 and −110 ppm for Q_4 can be observed with similar intensities for both the as-synthesised MCM-41 and the amorphous SiO_2, which suggests that the wall structure of MCM-41 may be amorphous [5,6]. The predominant Si species are Q_3 for both the amorphous SiO_2 [$Si(OSi)_3OH$] and the as-synthesised MCM-41 [$Si(OSi)_3OH$ or Si(3Si,1Al)]. However, after calcination, Q_2 disappeared, accompanied by the increasing intensities for Q_4 (−106 and −110 ppm). The Q_4/Q_3 silicon ratio was dramatically increased (> 0.4) after calcination, demonstrating that condensation of the hydroxyl groups pended on the silicate wall occurred via the loss of water and more regular wall structure

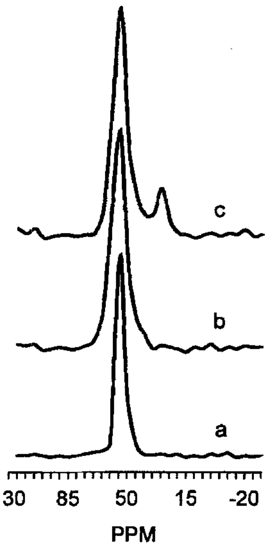

Fig. 2. ^{27}Al MAS NMR spectra for the MCM-41 materials of (a) the as-synthesised 41-A(14), (b) calcined 41-A(14) and (c) H-form 41-S(14).

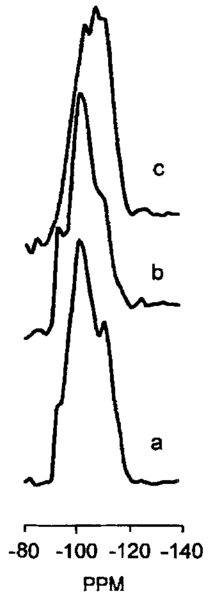

Fig. 3. ^{29}Si MAS NMR spectra for (a) as-synthesised 41-A(14), (b) amorphous SiO_2, and (c) calcined 41-A(14).

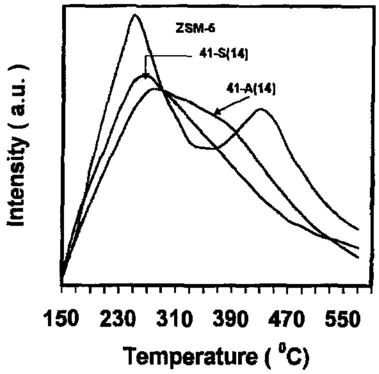

Fig. 4. NH_3-TPD profiles of H-form 41-A(14), H-form 41-S(14), and H-ZSM-5.

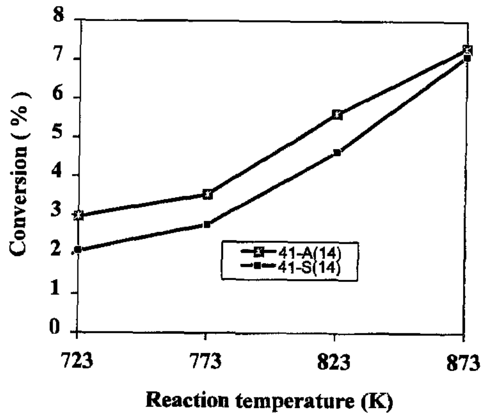

Fig. 5. Catalytic activity for *n*-heptane cracking over MCM-41 materials. Reaction parameters: pressure, 0.6 MPa; WHSV, 2 h^{-1}; N_2 dilution; molar ratio of *n*-heptane/N_2, 1.2.

was built up, which is in good agreement with the XRD results (see fig. 1).

The acidities of H-form 41-A(14) and 41-S(14) samples as examined by NH_3-TPD are shown in fig. 4, with H-ZSM-5 (Si/Al = 25) for comparison. It is clear that MCM-41 materials are aluminosilicate with weak (peak at 255°C) and mild acidity (peak at 335°C) compared to ZSM-5 zeolite. However, sample 41-S(14) possesses more weak acid sites associated with the extraframework Al species than that of the sample 41-A(14). This is consistent with the ^{27}Al NMR data as mentioned above. On the other hand, more mild acid sites can be found on sample 41-A(14) than with 41-S(14). This may be explained if either the multiple calcination procedures which result in a partial dealumination and/or the trace Na^+ species in 41-S(14) influence the mild acidic sites. MCM-41 synthesised from NH_4OH-containing gels, therefore, may be expected to be more catalytically active than that of the sample from sodium-containing gels.

Fig. 5 shows the catalytic activities for *n*-heptane cracking over different MCM-41 materials. 41-A(14) catalyst exhibits higher catalytic activity; while 41-S(14) catalyst shows lower catalytic activity due to its comparatively weak acidity. This means the mild acidic sites, rather than the weak ones, are the active sites for the reaction of *n*-heptane cracking. This is also in excellent agreement with the NH_3-TPD data.

m-xylene isomerization over 41-A(14) and H-ZSM-5 catalysts at a time-on-stream of 3 h is shown in table 2. The catalytic activity for MCM-41 materials is less than that of ZSM-5 zeolite because of its relatively low acid strength. The ratio of para- to ortho-xylene in the product is close to the thermodynamic equilibrium value for MCM-41 catalyst, indicating that MCM-41 does not have any product shape selectivity for *m*-xylene isomerisation.

4. Conclusion

Highly ordered MCM-41 has been synthesised using NH_4OH to adjust the pH of the reactant gels without any organic amine in an alkali-free system. The 4-coordinate aluminium could be incorporated into the framework of MCM-41 (Si/Al = 14–∞) without detecting any 6-coordinate aluminium in this study. MCM-41 materials obtained from this system can be activated by straightforward calcination of the as-synthesised sample, eliminating the conventional ion exchange and further calcination procedures. Importantly, the loss of acid sites caused by multiple calcination procedures and/or poisoning by sodium species is avoided. This conclusion is supported by both the NH_3-TPD and the catalytic activity for *n*-heptane cracking.

Table 2
Catalytic activity for *m*-xylene isomerization over 41-A(8) catalyst[a]

Catalyst	Temp. (°C)	Conv. (%)	Product distribution (%)					
			benzene	toluene	*p*-xylene	*m*-xylene	*o*-xylene	other aromatics
41-N(14)	400	17.4	0.0	0.3	8.3	82.6	8.0	0.8
	450	31.9	0.1	1.1	16.0	68.1	13.3	1.4
ZSM-5(25)	400	25.5	0.2	0.2	16.2	74.5	7.6	1.3
	450	34.0	0.3	0.7	19.3	66.0	11.9	1.8

[a] Reaction parameters: pressure, 0.6 MPa; WHSV, 4.6 h^{-1}; N_2 dilution; molar ratio of *m*-xylene/N_2, 2.

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