

Communications

Stable Tetrahedral Aluminum Sites in Hexagonal Mesoporous Aluminosilicates

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A unique templating approach for the synthesis of hexagonal mesoporous aluminosilicates via self-assembly of pre-formed aluminosilicate nanoclusters with the templating micella formed by cetyltrimethylammonium bromide (CTAB) is described. The obtained materials of MAS-5 are hydrothermally stable, which is shown by X-ray diffraction (XRD) analysis. Furthermore, as characterized by NMR technique, MAS-5 has stable tetrahedral aluminum sites that is the major contributions to the acidity of aluminosilicate molecular sieve, and on non-framework aluminium species in the samples was observed.

Keywords ordered mesoporous aluminosilicates, thermal and hydrothermal stability, X-ray diffraction (XRD), ²⁷Al NMR spectroscopy

The stability of mesoporous silica such as hexagonally ordered MCM-41 has attracted much attention since they are potentially used as versatile catalysts and catalyst supports,¹⁻¹⁷ and recently some stable mesoporous silica has been obtained. For examples, stable mesoporous SBA-15 with thick pore walls has been prepared using triblock copolymers as templates.³ The synthesis of stable MSU materials has been achieved using neutral gemini surfactants as templates.⁴ The preparation of stable KIT-1 involves the use of inorganic salts as additives.¹⁵

However, of greater importance is the stability of mesoporous aluminosilicates, because the mesoporous alu-

minosilicates show stronger acidity than mesoporous silica.^{1,8} Recently the stable mesoporous aluminosilicates was able to obtain. For examples, the ultrastable mesoporous aluminosilicates have been prepared from the grafting route.⁶⁻⁸ The steam-stable aluminosilicate mesostructure is assembled from zeolite Y seeds.¹⁷

The stability of these mesoporous materials is usually characterized by X-ray diffraction (XRD) analysis under the thermal and hydrothermal treatments. The XRD technique is very sensitive to characterize mesostructures, but it is difficult to distinguish the framework (4-coordinated) from non-framework (6-coordinated) aluminium in mesoporous aluminosilicates. The aluminium in the framework is the source of acidic sites, and the non-framework aluminium in the porous materials is not a major contribution to acidity.¹⁸ The stability of aluminum sites in the framework of mesoporous materials is one of the most important factors for the use of acidic catalysts, which strongly influences the catalytic activity and selectivity in catalytic reactions.¹ In some cases, although the mesoporous aluminosilicates show perfect XRD peaks, the dealumination from the sample framework occurs significantly.¹ Additionally, although the mesoporous aluminosilicates are stable, there is still non-framework aluminium in the samples.⁸ Therefore, stable mesoporous aluminosilicates

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without non-framework aluminium are always desirable.

On the other hand, microporous zeolites have very stable aluminium sites in the framework and are widely used in commercial catalysts. Recently, there are several interesting reports on the synthesis of zeolites with primary and secondary structural building units using structure-directing agents such as aluminosilicate nanoclusters.¹⁹⁻²¹

More recently, we present a unique templating approach for the synthesis of hexagonal mesoporous aluminosilicates via self-assembly of pre-formed aluminosilicate nanoclusters obtained by heating alumina-silica gels at 100–140 °C in the presence of tetraethylammonium hydroxide (TEAOH), with the templating micella formed by cetyltrimethylammonium bromide (CTAB)^{22,23} and triblock copolymers (P123).²⁴⁻²⁶ The results show that these new materials are hydrothermally stable, but we still do not know the stability of the tetrahedral aluminum species in the mesoporous aluminosilicates. Here the stable tetrahedral aluminum sites in the framework are shown, and no non-framework aluminium species in the samples was observed.

The hexagonal mesoporous aluminosilicates (denoted as MAS-5) with stable tetrahedral aluminum in the framework were hydrothermally synthesized from starting materials consisting of silica and sodium aluminate (Shenyang Chemical Co., China) in the presence of co-templates, *i.e.*, tetraethylammonium hydroxide (TEAOH, Sinopec, China) and cetyltrimethylammonium bromide (CTAB, Shanghai Chemical Co.) cationic surfactant at Al₂O₃/SiO₂/TEAOH/CTAB/H₂O molar ratios of 1.0/70.0–350/10.0–33.0/12.0–32.0/500–2000. The molar ratio of SiO₂/Al₂O₃ in the final products was varied from 10 to 350.^{22,23}

A general procedure for preparing MAS-5 is as follows: (1) 0.236–1.360 g of sodium aluminate, 0.110–0.400 g of sodium hydroxide, and 26.000–36.000 g of tetraethylammonium hydroxide (20 wt% aqueous solution) were mixed in a plastic vessel. Then 10.086 g of fume silica were added and the reaction mixture was stirred for several hours till a homogeneous solution was formed. The solution was transferred to Teflon-lined stainless-steel autoclaves and heated to 100–150 °C for 2–5 h, yielding aluminosilicate precursors. (2) A mixture of 1.180–1.920 g of CTAB and 25.000 g of deionized water was added into 9.8 g of the aluminosilicate precursors. The resulting mixture was transferred to Teflon-lined stainless-steel autoclaves, again, heated at

100–150 °C in an oven. (3) After crystallization for 48 h, the solid product was filtered, washed with water, and dried at 80 °C in air for 12 h. (4) Calcination of the sample was carried out at 550 °C for 6 h in oxygen flow to remove the templates of TEAOH and CTAB. (5) Protonized form of the sample was prepared by ion-exchange with NH₄Cl, followed by calcination at 500 °C for 2 h.

XRD patterns were obtained with a Siemens D5005 diffractometer using Cu K α radiation. Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were recorded on a Philips CM200FEG with an acceleration voltage of 200 kV. ²⁷Al NMR spectra were recorded on a Bruker MSL-300WB spectrometer, and chemical shifts were referenced to Al(H₂O)₆³⁺. Infrared (IR) spectra of the samples were recorded on a Perkin-Elmer FT-IR spectrometer (PE 430) with a resolution of 1 cm⁻¹.

Fig. 1A(a) shows the small-angle XRD patterns of as-synthesized MCM-41 sample, exhibiting three well-resolved peaks that can be indexed as (100), (110), and (200) reflections associated with the hexagonal symmetry. After calcination in air at 550 °C for 4 h, the sample XRD pattern [Fig. 1A(b)] shows that the three diffraction peaks are still present, indicating that hexagonal MCM-41 is thermally stable.

Fig. 1B(a) shows ²⁷Al NMR spectra of as-synthesized and calcined MCM-41 samples. The as-synthesized sample exhibits only one peak at δ 55, which is assigned to tetrahedral aluminum in the framework of mesoporous aluminosilicates.¹ However, after calcination in air at 550 °C for 4 h, the sample NMR spectrum [Fig. 1B(b)] shows a new peak at δ 0 assigned to 6-coordinated aluminium,¹ in addition to the peak at δ 55. The formation of 6-coordinated aluminium in the sample is possibly from dealumination of the sample. These results suggest that the thermal stability of tetrahedral aluminum in the framework of MCM-41 sample is relatively low, and even at calcination temperature of 550 °C for 4 h partial tetrahedral aluminum are dealuminated, forming the non-framework aluminum species.

Fig. 2A shows the small angle XRD patterns of as-synthesized, calcined, and hydrothermally treated MAS-5 samples. The as-synthesized MAS-5 sample shows three well-resolved peaks [Fig. 2A(a)] that can be indexed as (100), (110), and (200) reflections associated with the hexagonal symmetry. The (100) peak reflects a *d* spacing of 4.441 nm (*a*₀ = 5.133 nm). No diffraction peak

was observed in the region of higher angles 10° – 40° , which indicates the absence of large microporous crystals in the sample, suggesting that MAS-5 sample is a pure phase.

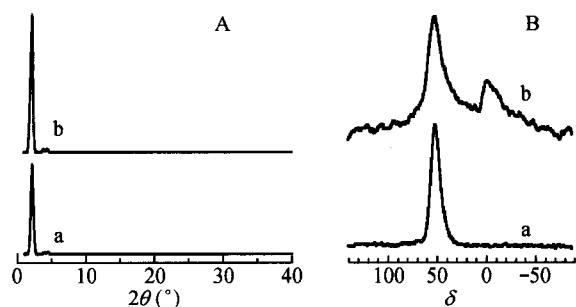


Fig. 1 [A] XRD patterns of (a) as-synthesized MCM-41 and (b) calcined MCM-41 at 550 °C for 4 h. [B] ^{27}Al NMR spectra of (a) as-synthesized MCM-41 and (b) calcined MCM-41 at 550 °C for 4 h.

After calcination in air at 550 °C for 4 h, the sample XRD pattern [Fig. 2A(b)] shows that the three diffraction peaks are still present, confirming that hexagonal MAS-5 is thermally stable. After treatment at 600 °C for 4 h in flowing water steam, the calcined sample still shows XRD pattern [Fig. 2A(c)] that can be assigned to the hexagonal symmetry. These results suggest that MAS-5 has a remarkable thermal and hydrothermal stability.

Fig. 2B shows ^{27}Al NMR spectra of as-synthesized, calcined, and hydrothermally treated MAS-5 samples. Interestingly, the three samples give only one peak at δ 61 assigned to tetrahedral aluminum sites in the framework of mesoporous aluminosilicates. The results indicate that the tetrahedral aluminum in the MAS-5 is thermally and hydrothermally stable, even if calcination at 550 °C for 4 h and steaming at 600 °C for 4 h.

As compared with those of MCM-41 (Fig. 1B) whose full width half-height (FWHH) is about δ 15, the FWHH of MAS-5 (Fig. 2B) is much narrower (about δ 7), suggesting the order of Al species in MAS-5 sample is better than that of MCM-41. Furthermore, we observed the peak position of ^{27}Al NMR for MAS-5 appears at δ 61, which is close to that of Beta zeolite. In contrast, MCM-41 exhibits this peak at δ 55. On the basis of relationship between ^{27}Al chemical shift and the bond angle in the framework of aluminosilicate zeolites,²⁷ it is suggested that Al-O-Si angle in MAS-5 is similar to that in Beta, which is smaller than that in MCM-41.

IR characterizations of MCM-41 and MAS-5 at the similar Si/Al ratio show that MAS-5 exhibits the bands at 520–600 cm^{-1} , which are similar to those of 5-membered rings of T–O–T (T = Si or Al) in microporous zeolites, while these bands could not be observed in the sample of MCM-41.²⁸ These results suggest that MAS-5 has zeolite primary and secondary building units, because the characteristic bands assigned to zeolite primary and secondary building units have been shown by IR spectroscopy, but in XRD no peaks were observed in 6° – 40° .

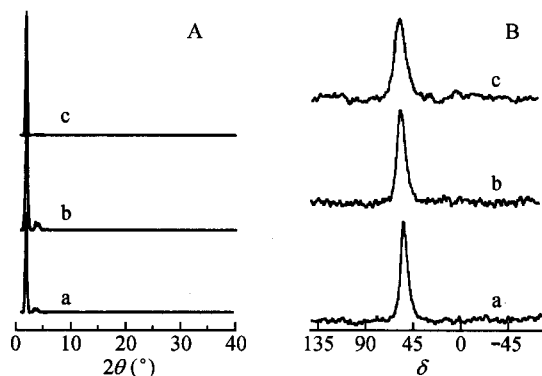


Fig. 2 [A] XRD patterns of (a) as-synthesized MAS-5, (b) calcined MAS-5 at 550 °C for 4 h and (c) MAS-5 after treatment with 100% water vapor at 600 °C for 4 h. [B] ^{27}Al NMR spectra of (a) as-synthesized MAS-5, (b) calcined MAS-5 at 550 °C for 4 h and (c) MAS-5 after treatment with 100% water vapor at 600 °C for 4 h.

Based on all these observations, we propose a tentative mechanism that the formation of mesoporous MAS-5 materials was via the self-assembly of aluminosilicate precursors (nanoclusters with zeolite building units of primary and secondary structure) with CTAB micella. Thus the stable tetrahedral aluminum sites in the framework were obtained.

Incorporation of tetrahedral aluminum into mesoporous materials is generally from directing addition of aluminum compounds in starting gels^{1,2} or post-synthesis.⁵⁻⁸ The former shows relatively low stability of tetrahedral aluminum in the framework of mesoporous materials such as MCM-41,^{1,2} and the latter shows both 4- and 6-coordinated aluminum in the mesoporous materials.⁵⁻⁸ In our case, by the self-assembly of pre-formed aluminosilicate precursors with CTAB micella, we have prepared stable tetrahedral aluminum sites in hexagonal mesoporous

aluminosilicates without formation of 6-coordinated aluminum species.

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