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LETTER

Hydrothermally stable aluminosilicate mesostructures prepared from zeolite ZSM-5

**Shan Wang · Tao Dou · Yuping Li · Zhirong Dou ·
Ying Zhang · Xiaofeng Li · Zichun Yan**

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Significant advances have been made recently in improving both the hydrothermal stability and acidity of MCM-41 and SBA-15 mesostructures through the use of protozeolitic aluminosilicate nanoclusters or ‘‘zeolite seeds’’ as framework precursors [1–8]. These nanoclusters contain the secondary building blocks of the zeolite structures that they nucleate. Since the first demonstration of this approach to stable aluminosilicate mesostructures successfully utilized faujasitic zeolite seeds (FAU) to construct the walls of a hexagonal MCM-41 structure [1], many efforts have been made to assemble hydrothermally stable mesopores that are structurally analogous to MCM-41 and SBA-15 from different zeolite seeds solutions such as zeolite L, Beta and ZSM-5 seeds [2–8]. All of these mesoporous materials show highly hydrothermal stability and good activity in catalytic conversion of organic compounds, as compared with conventional mesopores such as MCM-41 and SBA-15. However, to the best of our knowledge, researchers are still not able to prepare every type of zeolite seeds at the present time, which means that many types of zeolites haven’t their own seeds. Therefore, it is impossible to synthesize hydrothermally stable mesoporous aluminosilicates containing the five-ring subunits characteristic of zeolites other than those reported previously. We report here a general approach to more acidic and hydrothermally stable mesostructures based on the direct assembly of zeolite precursors which were obtained by the dissolution of preformed zeolite into strongly basic solutions.

We describe here the synthesis and properties of a typical hexagonal aluminosilicate mesostructure (Si/Al = 40) derived from precursors that were produced by dissolving zeolite ZSM-5 in strongly basic solution of NaOH via a two-step procedure. First, 1.9 g of zeolite ZSM-5 was dispersed in 10 mL of a solution of NaOH (4 M aqueous solution) and stirred for 30 min at room temperature. To this solution was added 22 g solution of CTAB (hexadecyltrimethylammonium bromide, 10 wt.% aqueous solution). After additional stirring for about 30 min the mixture was transferred into stainless steel autoclaves for hydrothermal treatment at 373 K for 20 h. Second, the pH value of the reaction mixture was adjusted to 8.5 by dropwise addition of 2 M HCl solution with vigorous stirring, which followed by an additional aging period of 24 h at 373 K and afforded a hexagonal aluminosilicate mesostructure, which we denote as MCM-41$_{Z}$. Treatment of the as-made mesostructure with 0.1 M NH_4NO_3 at 373 K displaced exchangeable sodium ions, as well as 50% of the surfactant from the mesostructure. The product then was calcined at 823 K for 6 h to remove the remaining surfactant and to convert NH_4^+ at exchange sites to protons. Chemical analysis indicated a Si/Al molar ratio of 40 which is in agreement with the ratio contained in the initial dissolved zeolite.

S. Wang · T. Dou (✉) · Y. Li · Z. Dou ·
X. Li · Z. Yan
Institute of Special Chemicals, Taiyuan University
of Technology, No. 79 West Yingze Street, Taiyuan 030024,
P.R. China
e-mail: dtao1@yeah.net

T. Dou · Y. Zhang
The CNPC key laboratory
of Catalysis, University of Petroleum (Bei Jing), Fuxue
Road, Changping, Beijing 102249, P.R. China

The structures and properties of resultant materials were investigated by XRD diffractograms, N_2 adsorption istherms, ^{27}Al NMR spectroscopy, IR spectroscopy and catalytic tests. The XRD patterns of the samples were recorded using a Rigaku D/max-2500 X-ray powder diffractometer, which employed Ni-filtered Cu Kα radiation (40 kV, 100 mA). The nitrogen adsorption isotherms at 77 K were measured using a Micromeritics ASAP2010 system and the pore-size distribution for mesopore was analyzed from the desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method. IR spectra of the samples were recorded on a BIO-RAD FT-IR spectrometer (FTS165) with a resolution of 2 cm^{-1}. ^{27}Al NMR spectrum was recorded on a Varian $^{\text{Unity}}$Inova 300 spectrometer, and the chemical shifts were referenced to $\text{Al(H}_2\text{O)}_6^{3+}$. Catalytic tests for the dealkylation of C10^{+} aromatic hydrocarbon were carried out using a conventional flow reactor, and the analyses of the catalytic products were carried out with an SP-2100 gas chromatograph (Beijing Analytic Instrumental Co.) equipped with an FID detector. H_2 was used as the carrier gas immediately after removal of air from the reactor for 2 h in flowing pure N_2. The catalytic reaction was performed according to the following standard conditions: the mass catalyst was 0.4996 g; reaction temperature and pressure were 823 K and 5.0 MPa, respectively; the flow rate of reactants was 0.5 mL/h.

The XRD patterns (Fig. 1A) of the MCM-41$_{\text{Z}}$ sample show that MCM-41$_{\text{Z}}$ has ordered hexagonal arrays of mesopores and the result of no distinguishable peaks in the wide angle region in the XRD pattern (8–40°, not shown) suggests that the product is a pure mesoporous phase without zeolite crystals. Also included in Fig. 1 are the corresponding patterns for MCM-41 prepared under exactly the same conditions as MCM-41$_{\text{Z}}$ sample except that the alkaline solution of zeolite ZSM-5 was replaced by an equivalent amount of TEOS (tetraethyl orthosilicate) and NaAlO_2 (sodium aluminate). The XRD results clearly indicate that the MCM-41$_{\text{Z}}$ mesostructure assembled from precursors of zeolite ZSM-5 retains a well-ordered hexagonal structure upon being treated in boiling water for 120 h. In comparison, the mesostructures prepared from conventional silicate and aluminate precursors are almost totally destroyed after the same treatment by boiling water.

The above observations are supported by a comparison of the N_2 sorption isotherms shown in Fig. 2. The surface areas, framework pore sizes, and pore volumes for MCM-41$_{\text{Z}}$ are provided in Table 1 and are compared with those for MCM-41 formed under equivalent conditions. The calcined MCM-41$_{\text{Z}}$ shows the surface area and pore volume of 954 m^2/g and 0.69 cm^3/g, respectively (Fig. 2A (a) and Table 1). After treatment in boiling water for 120 h, we find that the MCM-41$_{\text{Z}}$ aluminosilicate mesostructure retains long-range hexagonal order (cf., Fig. 1) and substantial mesoporosity (cf., Fig. 2B (a) and Table 1) which gives the surface area and pore volume of 649 m^2/g and 0.48 cm^3/g, respectively. In contrast, MCM-41 assembled from conventional aluminosilicate anions retains its surface area of only 50 m^2/g, indicating the complete destruction of its mesostructure (Fig. 2B (b) and Table 1). These results confirm that MCM-41$_{\text{Z}}$ is much more hydrothermally stable than MCM-41.

It is very interesting to note that the *d*(100) value of MCM-41$_{\text{Z}}$ is much larger than that of MCM-41 prepared from the same condition. Combining the results of N_2 adsorption isotherms that both samples have very similar pore size distributions (Table 1), we can conclude that the pore wall of MCM-41$_{\text{Z}}$ is much

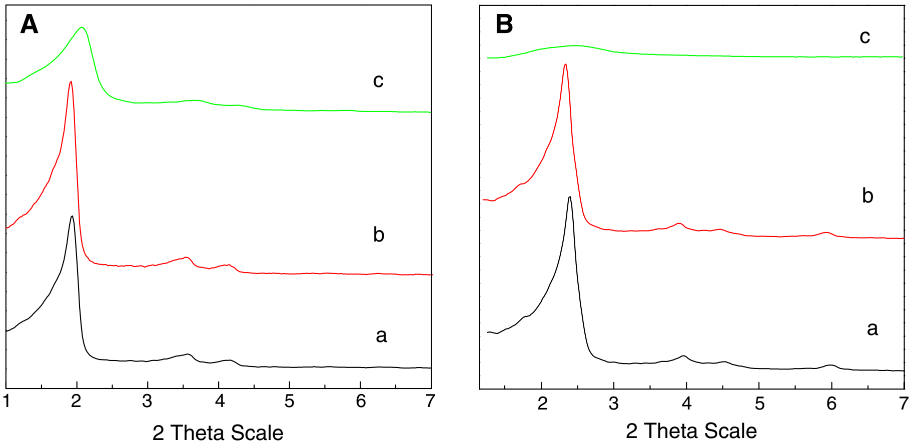

Fig. 1 XRD patterns of (a) as-synthesized, (b) calcined and (c) treated (**A**) MCM-41$_{\text{Z}}$ and (**B**) MCM-41 (treated the samples in boiling water for 120 h)

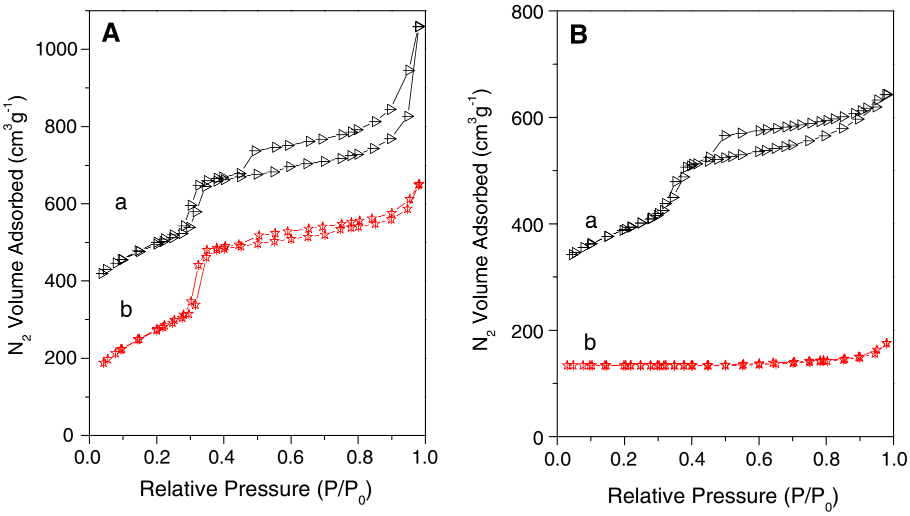

Fig. 2 N_2 adsorption/desorption isotherms for calcined samples before (**A**) and after (**B**) treated in boiling water for 120 h: (a) MCM-41$_Z$; (b) MCM-41. The isotherms are offset by 200 cm^3 g^{-1} for clarity

Table 1 Textural and catalytic properties of the samples of MCM-41$_Z$ and MCM-41

Samples[a]	Unit cell dimension[c] a_0 (nm)	Pore diameter D (nm)	Surface area S_{BET} (m^2/g)	Pore volume (cm^3/g)	Wall thickness[d] t (nm)	Conversion of reactant (%)
MCM-41$_Z$						
Calcined	5.31	2.79	954	0.69	2.52	51.8
Treated[b], 120 h	4.76	3.09	649	0.48	1.67	–
MCM-41						
Calcined	4.35	2.87	1040	0.71	1.48	10.9
Treated[b], 120 h	–	–	50	–	–	–
H-ZSM-5	–	–	–	–	–	40.8

[a] The Si/Al ratio in all samples is 40; [b] treatment in boiling water for 120 h; [c] unit cell dimension calculated as $a_0 = 2d_{100}/\sqrt{3}$; [d] pore wall thickness (t) calculated as $t = a_0 - D$

thicker than that of MCM-41 prepared from the same conditions. This phenomenon is attributed to the assumption that the zeolite ZSM-5 was not dissolved completely into nonstructured silica–alumina species but produced a lot of secondary building units characteristic of zeolite ZSM-5; the nanoclustered zeolite subunits used in the synthesis of MCM-41$_Z$ have much stronger rigidity and larger volume than the amorphous silicon species used in the conventional synthesis of MCM-41, therefore the assembly of these secondary building units needs more space to connect to each other.

^{27}Al NMR spectroscopy (Fig. 3) indicates that more than 90% of the aluminum centers in calcined MCM-41$_Z$ are in tetrahedral siting of aluminum, the strong acidity of the hydrothermally stable mesostructures was verified through experiments for the dealkylation of C10$^+$ aromatic hydrocarbon. The conversions of reactants for calcined forms of MCM-41$_Z$, MCM-41 and ZSM-5 are 51.8%, 10.9% and 40.8%, respectively (provided in Table 1). The conversion for the H-ZSM-5 (40.8%) is somehow lower than that for the H-MCM-41$_Z$ (51.8%) due to its relatively small pore size and the large diameter of the reactant molecules. Still, the conversion for the H-MCM-41$_Z$ (51.8%) is much higher than that for the H-MCM-41 (10.9%) sample, and this result would be ascribed to the introduction into the MCM-41$_Z$ mesopore wall a lot of secondary building units characteristic of zeolite ZSM-5 which gives rise to the higher hydrothermal stability and more strong acid sites. In a word, the MCM-41$_Z$ combines the advantages of both ZSM-5 (strong acidity) and MCM-41 (large pores), which makes it far more active acid catalysts than the equivalent MCM-41 prepared from conventional aluminosilicate precursors. All these results, together with the hydrothermal stability properties, suggest that the MCM-41$_Z$ may be suitable acid catalysts for the processing of high molecular weight petroleum fractions that cannot be adequately refined over microporous zeolites.

We attribute the extraordinarily hydrothermal stability and catalytic activity of MCM-41$_Z$ at least in part

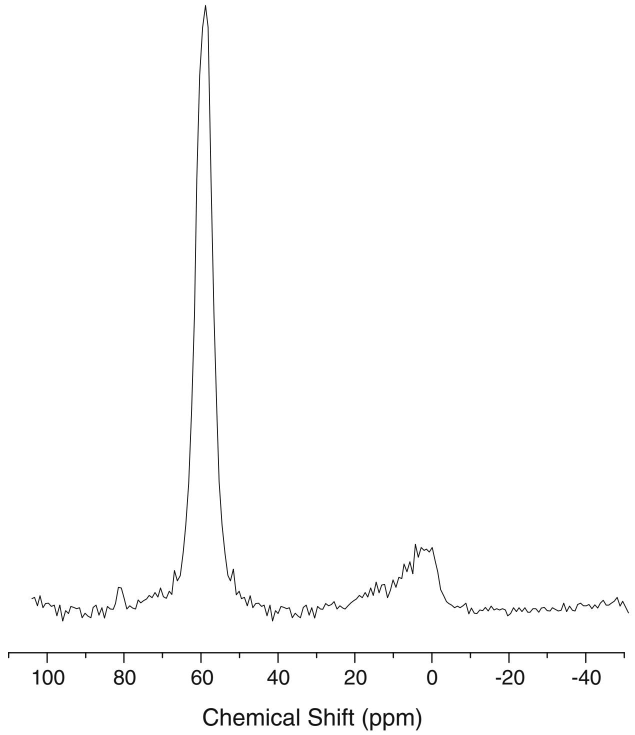

Fig. 3 ^{27}Al NMR spectrum of calcined MCM-41$_Z$

to the zeolite-like subunits of AlO_4 and SiO_4 tetrahedra in the framework walls of the mesostructure. Evidence for the retention of a protozeolitic connectivity of tetrahedral was provided by IR spectroscopy. In addition to a few sharp bands at 430–480 cm^{-1}, the band (558 cm^{-1}) in the 550–600 cm^{-1} region, which is characteristic of five-membered ring subunits [9, 10], is well-expressed in the spectrum of MCM-41$_Z$ but not for the MCM-41 derivative (Fig. 4).

The syntheses of composite molecular sieves containing mixtures of zeolite ZSM-5 and mesostructure MCM-41 have been reported by several research groups [11, 12, 13]. These products show X-ray reflections in the wide angle region, which indicates the existence of ZSM-5 crystals in them. However, the XRD pattern of MCM-41$_Z$ shows no wide range Bragg X-ray reflections, which verifies the lack of ZSM-5 zeolite crystals in MCM-41$_Z$. Based on the speculation that aluminosilicate species with corresponding zeolitic structure could be obtained by the alkaline treatment of certain zeolite, the S. Inagaki research group first reported the synthesis of MCM-41 type mesoporous materials containing fragments of the structure of ZSM-5 zeolite from the filtration of alkaline dissolution of ZSM-5 [14]. However, this approach did not make full use of the zeolite and the resultant Si/Al ratio was approximately 30 times larger than the initial zeolite. Aiming at providing a more effective and general approach to the incorporation of certain zeolite secondary building units into the framework walls of mesoporous materials, our research group carried out the assembly of MCM-41 type mesopores from the solutions containing zeolitic subunits originated from a two-step hydrolysis process of zeolites including Beta, MOR [15], ZSM-5 etc., which was a short-time alkaline treatment of zeolite followed by another long-period hydrolysis in the presence of a cationic surfactant (CTABr) which stabilized the zeolitic fragments by ion pairing. Similar research work has been reported by H. Wang et al. most recently [16]. It has been confirmed that the step of the surfactant-mediated hydrolysis of zeolite ZSM-5 makes far more effective the preparation of mesostructures with high levels of five-ring subunits than the direct zeolite hydrolysis.

The use of zeolite to produce precursors for the assembly of hydrothermally stable aluminosilicates mesostructures is not limited to compositions with Si/Al molar ratio of 40. We also have used zeolite ZSM-5 to prepare MCM-41$_Z$ with Si/Al molar ratio varied from 20 to 45 with retention of the structural, hydrothermal stability, and acidic properties found for MCM-41$_Z$ described above. In addition, our approach is not limited to the use of ZSM-5 to obtain precursors. Using MOR and Beta etc. zeolites with higher Si/Al molar ratio (normally larger than approximately 12),

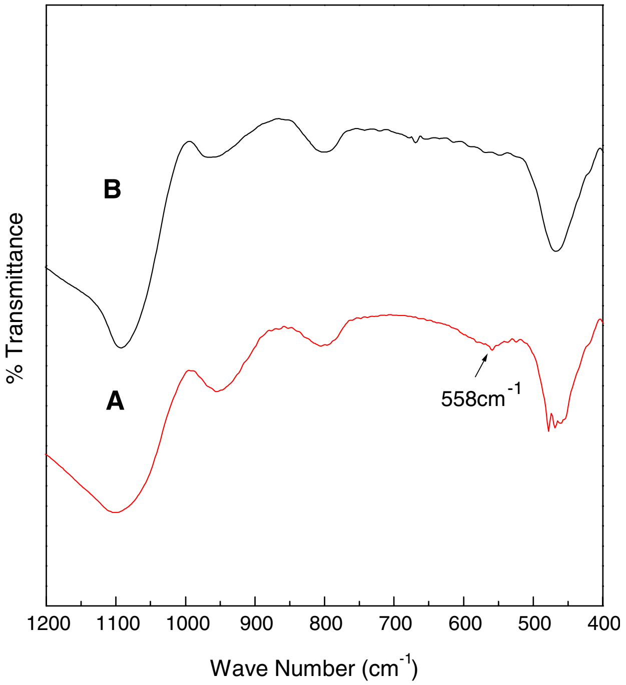

Fig. 4 IR spectra of calcined samples: (**A**) MCM-41$_Z$ (**B**) MCM-41

we also have prepared related hexagonal aluminosilicate mesostructures. Future studies will report on such hydrothermally stable mesostructures derived from various zeolites in both basic and acidic media.

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