

## Tailor and Control of Acidic Strength in Ordered Mesoporous Aluminosilicates by Using Preformed Zeolite Precursors

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The acidic strength of ordered mesoporous aluminosilicates of MAS-2, MAS-3, MAS-7 and MAS-9 and microporous crystals of Y, L, beta, and ZSM-5 zeolites was systemically investigated by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD). Due to the use of preformed zeolite precursors of Y, L, beta and ZSM-5, the ordered mesoporous aluminosilicates with distinguished acidic strength were obtained, being dependent on the type of preformed zeolite precursors. Therefore, the acidic strength of these mesoporous aluminosilicates could be tailored and controlled.

**Keywords**    NH<sub>3</sub>-TPD, acidic strength, ordered mesoporous aluminosilicate, preformed zeolite precursor

### Introduction

Microporous crystals of zeolites with uniform and molecular-pore size are currently being used as industrial catalysts on a large scale. However, they can not effectively catalyze large molecules due to the limitation of microporous size.<sup>1</sup> The discovery of ordered mesoporous materials such as MCM-41 and SBA-15 offers an opportunity for silicate and aluminosilicate as versatile catalysts and catalyst supports for catalytic conversion of large molecules, but the relatively low acidity of these mesoporous materials, as compared with that of microporous crystals, greatly limits their catalytic applications in industry.<sup>2-5</sup>

Many efforts have been made to improve the acidity of ordered mesoporous materials.<sup>6-10</sup> The HPAs-incorporation approach has successfully generated those exhibiting good catalytic performance in paraffin isomerization and isobutane/butene alkylation. However, the success is limited because some pores are blocked by HPAs and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and surface area of the materials is reduced significantly.<sup>11,12</sup> Therefore, ordered mesoporous materials with strong acidity and uniform pore size as well as large surface area are still being sought. More recently, through the grafting route<sup>13-15</sup> and post-synthesis<sup>16</sup> as well as zeolite seeds solution<sup>17</sup> or zeolite nanoclusters,<sup>18</sup> some mesoporous aluminosilicates with relatively strong acidity have been successfully obtained, but their acidic strength is not easily designed and controlled.

On the other hand, it is well known that various

types of microporous crystals of aluminosilicates such as zeolite Y, ZSM-5, beta, and L, exhibit distinguishably acidic strength, which is very important for industrial application in various catalytic reactions. For example, zeolite Y is the most important FCC catalyst,<sup>19-21</sup> ZSM-5 is an effective catalyst in highly shape-selective catalysis,<sup>22-24</sup> beta exhibits high activity and selectivity in catalytic alkylations,<sup>25</sup> and zeolite L is a good catalyst for aromatization reactions.<sup>26</sup>

Here we report that the acidic strength of ordered mesoporous aluminosilicates can be designed and controlled by the assembly of preformed aluminosilicate precursors containing various types of zeolite primary and secondary building units with surfactant micella.

### Experimental

#### Synthesis

Four ordered mesoporous aluminosilicates are designed as MAS-2, MAS-3, MAS-7 and MAS-9, respectively. MAS-2 and MAS-3 were synthesized from the assembly of cetyltrimethylammonium bromide (CTAB, Shanghai Chemical Co.) cationic surfactant with preformed zeolite Y and zeolite L precursors in basic media, respectively. As a typical example, synthesis of MAS-3 is as follows: (1) Preformed zeolite L precursor was crystallized at 35 °C for 3 d with molar ratio of Na<sub>2</sub>O : K<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : H<sub>2</sub>O at 7.2 : 10.8 : 1 : 30 : 540, as reported previously;<sup>27</sup> (2) CTAB (0.003 mol) was dissolved in 1.44 mol of H<sub>2</sub>O (under stirring

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and heating; (3) 12 mL of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  solution was added into CTAB solution and followed by the addition of 4.5 mL of the preformed zeolite L precursor, then 10% sulfuric acid was added into the mixture and pH value of the solution was altered to 9–10; (4) The mixture was stirred for 3–4 h and transferred into the autoclave for additional crystallization at 100 °C for 3 d. Finally, the product was collected by filtration, washed with distilled water, dried at ambient temperature and calcinated at 550 °C for 5 h to remove the surfactant.

Preparation of MAS-2 was similar to that of MAS-3, except for the substitution of preformed zeolite Y precursors. The zeolite Y precursors were crystallized at 25 °C for 24 h with molar ratio of  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$  at 15.6 : 1 : 19 : 369.

MAS-7 and MAS-9 were synthesized from the assembly of triblock polymer surfactant (P123, BASF Co.) with zeolite beta and zeolite MFI precursors in strongly acidic media, respectively.<sup>18</sup>

AL-SBA-15 was prepared with molar ratio of  $\text{TEOS} : \text{H}_2\text{O} : \text{HCl} : \text{P123} : \text{NaAlO}_2$  at 35 : 6944 : 250 : 0.69 : 1. Al-MCM-41 was prepared with molar ratio of  $\text{TEOS} : \text{H}_2\text{O} : \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} : \text{C}_2\text{H}_5\text{NH}_2 : \text{CTAB}$  at 1 : 100 : 0.0065 : 1.4 : 0.14.

The preformed zeolite aluminosilicate precursors were prepared from hydrothermal crystallization of aluminosilicate gel. Preformed zeolite Y precursors were prepared from molar ratio of  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$  at 15.6 : 1 : 19 : 369. Preformed zeolite L precursors were prepared from molar ratio of  $\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$  at 7.2 : 10.8 : 1 : 30 : 540. Preformed zeolite Beta precursors were prepared from molar ratio of  $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{Na}_2\text{O} : \text{TEAOH} : \text{H}_2\text{O}$  at 1.0 : 60 : 2.5 : 800. Preformed zeolite MFI precursors were prepared from molar ratio of  $\text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{Na}_2\text{O} : (\text{TPA})_2\text{O} : \text{H}_2\text{O}$  at 1.0 : 50 : 1.0 : 7 : 1800. Addition of a small amount of these aluminosilicate precursors ( $w=0.03$ ) into alumina-silica gel leads to formation of zeolites of Y, L, beta and ZSM-5 with high crystallinity, respectively.<sup>18,28-31</sup> The aluminosilicate precursors appear to serve as seeds for the formation of zeolites.<sup>21,28</sup> IR characterization of these aluminosilicate precursors shows clear bands assigned to characteristic of zeolite primary building units. For example, characterization of preformed ZSM-5 precursors exhibits an IR band at 520–600  $\text{cm}^{-1}$ , which is due to 5-membered rings.<sup>24</sup>

All samples were turned to H-form and by ion-exchanged with 0.1 mol/L of  $\text{NH}_4\text{NO}_3$  solution at 60 °C, followed by calcination at 550 °C.

### Characterization

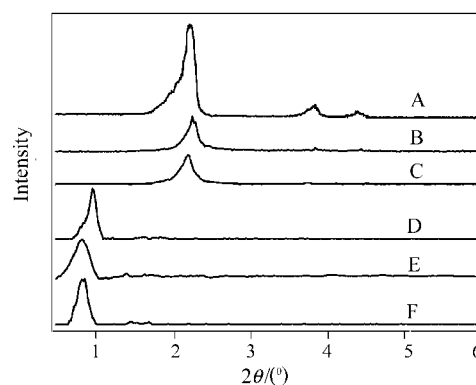
XRD patterns of MAS-2, MAS-3, MAS-7 and MAS-9 were obtained with a Siemens D5005 diffractometer using  $\text{Cu K}\alpha$  ( $\lambda=0.154$  nm) radiation. The nitrogen isotherms at  $-196$  °C were measured using a Micromeritics ASAP 2010M. The samples were outgassed for 2 h at 400 °C before the measurements. The pore-size distributions for mesopores were calculated using

Barrett-Joyner-Halenda (BJH) model. Si/Al ratio of the samples was measured by Perkin-Elmer 3300 DV ICP. The  $\text{NH}_3$ -TPD of the sample was carried out as follows: 100 mg of a sample was placed in a sample cell and pre-heated at 600 °C for 1 h in flowing nitrogen (99.999%) at a flow rate of 100  $\text{cm}^3/\text{min}$ . After being cooled to room temperature, the sample was saturated in adsorbed ammonia for 120 min in order to confirm the equilibrium adsorption, followed by removal of physical adsorption of ammonia at 120 °C for 1 h in pure nitrogen flow. Finally, temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD) curves were obtained in the range of 120–600 °C at a temperature-increasing rate of 10 °C/min.

## Results and discussion

### X-ray diffraction

The small-angle X-ray diffraction (XRD) patterns of samples (Figure 1) show well-resolved peaks indexed as (100), (110) and (200) reflections associated with the hexagonal symmetry. The  $d(100)$  values of MAS-2 and MAS-3 synthesized in basic media are 3.95 and 3.97 nm, and the  $d(100)$  values of MAS-7 and MAS-9 synthesized in acidic media are 11.2 and 11.1 nm, respectively.



**Figure 1** XRD patterns of mesoporous aluminosilicates of (A) Al-MCM-41, (B) MAS-2, (C) MAS-3, (D) Al-SBA-15, (E) MAS-7 and (F) MAS-9.

Furthermore, no diffraction peak was observed in the region of  $10^\circ$ – $40^\circ$  for these samples, indicating the absence of large microporous crystals in the sample, and it is suggested that all samples are pure phase.

### Isotherms for $\text{N}_2$

Table 1 presents the parameters of various mesoporous aluminosilicates and microporous crystals. Interestingly, the isotherms of these ordered mesoporous aluminosilicates exhibit typical adsorption curve of type IV. A steep rise occurs in the curve at a relative pressure  $0.33 < p/p_0 < 0.40$  or  $0.50 < p/p_0 < 0.80$  due to the mesoporous structures. Additionally, the surface area, pore volume, and pore size of the mesoporous aluminosilicates are much larger than those of microporous crystals. For example, the surface area of MAS-9 is at

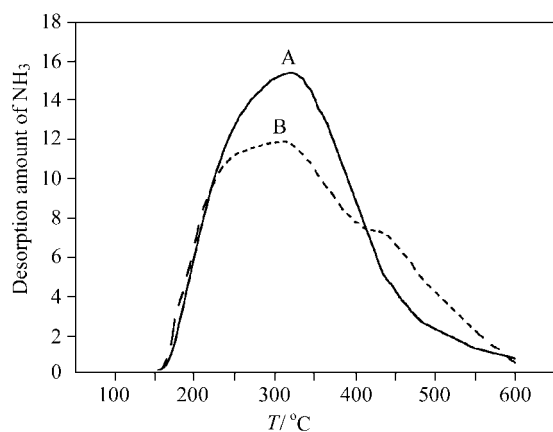
1019 m<sup>2</sup>/g, and the surface area of zeolite ZSM-5 is at 454 m<sup>2</sup>/g.

**Table 1** Properties of mesoporous aluminosilicates of MAS-2, MAS-3, MAS-7, MAS-9, Al-SBA-15 and Al-MCM-41 and microporous crystals of zeolites Y, L, beta and HZSM-5

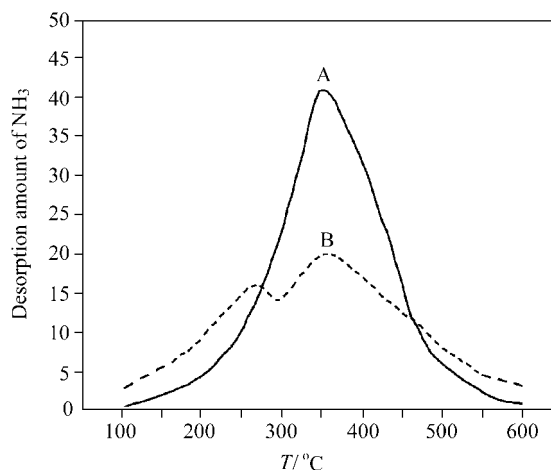
Sample	Surface area/ (m <sup>2</sup> · g <sup>-1</sup> )	Pore volume/ (cm <sup>3</sup> · g <sup>-1</sup> )	Pore size/ nm	Si/Al
MAS-2	946	0.82	3.6	11
MAS-3	919	0.8	3.4	14
MAS-7	958	1.24	7.6	59
MAS-9	1019	1.41	8.0	90
Al-SBA-15	925	1.5	7.2	40
Al-MCM-41	884	0.88	2.8	89
Y	621	0.32	0.78	5.6
L	605	0.29	0.72	11.9
Hbeta	581	0.21	0.69	60
HZSM-5	454	0.17	0.57	50

### NH<sub>3</sub>-TPD

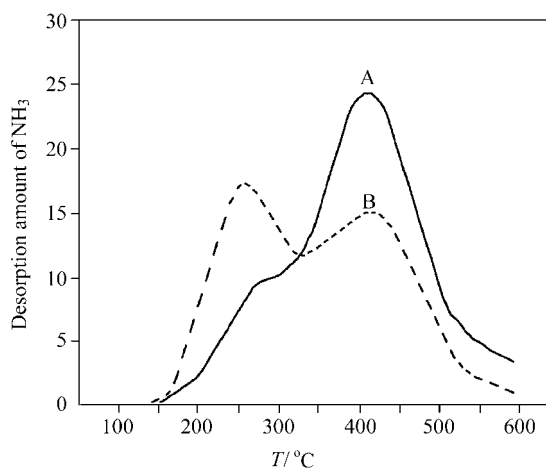
Figures 2—5 show NH<sub>3</sub>-TPD curves of microporous crystals of zeolite L, Y, beta and ZSM-5 and mesoporous aluminosilicates of MAS-2, MAS-3, MAS-7 and MAS-9, respectively. Zeolite L exhibits a broad peak centered at 320 °C (Figure 2A), and MAS-3 prepared from the assembly of zeolite L nanoclusters with CTAB surfactant gives a broad peak at 316 °C and a weak shoulder peak at 430 °C (Figure 2B). Zeolite Y exhibits a peak centered at 350 °C (Figure 3A) and MAS-2 assembled from zeolite Y nanoclusters gives a weak peak at 266 °C and a strong peak at 350 °C (Figure 3B). Zeolite beta gives two peaks at 275 and 415 °C (Figure 4A), and MAS-7 assembled from zeolite beta nanoclusters gives two peaks at 260 and 420 °C (Figure 4B). Zeolite ZSM-5 gives two peaks at 265 and 445 °C (Figure 5A), and MAS-9 assembled from zeolite ZSM-5 nanoclusters gives two peaks at 265 and 450 °C



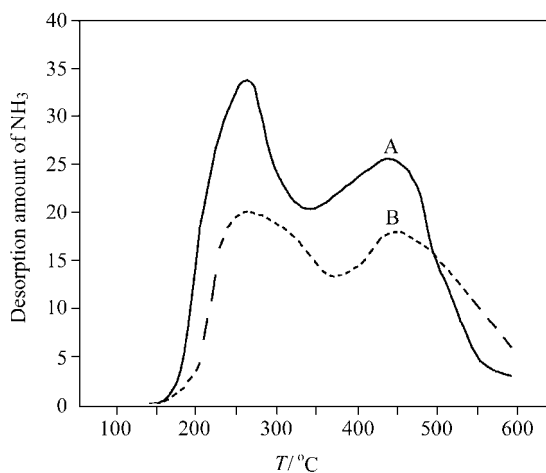
**Figure 2** NH<sub>3</sub>-TPD curves of (A) microporous crystal of zeolite L and (B) mesoporous aluminosilicate of MAS-3.



**Figure 3** NH<sub>3</sub>-TPD curves of (A) microporous crystal of zeolite Y and (B) mesoporous aluminosilicate of MAS-2.

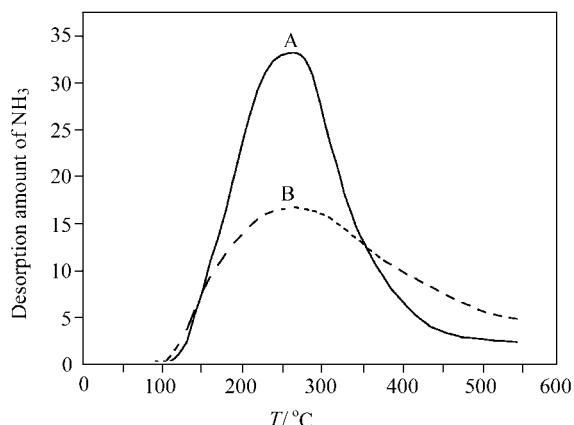


**Figure 4** NH<sub>3</sub>-TPD curves of (A) microporous crystal of zeolite beta and (B) mesoporous aluminosilicate of MAS-7.



**Figure 5** NH<sub>3</sub>-TPD curves of (A) microporous crystal of zeolite ZSM-5 and (B) mesoporous aluminosilicate of MAS-9.

(Figure 5B). Figure 6 shows the NH<sub>3</sub>-TPD curves of the mesoporous aluminosilicates of Al-MCM-41 and Al-SBA-15, exhibiting a peak centered at near 265 °C.



**Figure 6**  $\text{NH}_3$ -TPD curves of mesoporous aluminosilicates of (A) Al-MCM-41 and (B) Al-SBA-15.

Generally, the temperature of desorbed ammonia is related to the strength of acidic sites. Higher  $\text{NH}_3$ -desorbed temperature indicates stronger acidic sites in the samples.

As observed in Figures 2—5, the obvious features are shown in the following: (1) Acidic strength of various microporous crystals of zeolites is distinguishable, which has been reported previously.<sup>1</sup> For example, ZSM-5 exhibits the strongest acidic strength, and zeolite L shows relatively weak acidic strength. The order of acidic strength is as follows: ZSM-5 > beta > Y > L. (2) Acidic strength of various mesoporous aluminosilicates assembled from various zeolite precursors is also distinguishable. The order of acidic strength is as follows: MAS-9 > MAS-7 > MAS-2 > MAS-3, which is the same as that order of microporous crystals. These results suggest that acidic strength of these mesoporous aluminosilicates is related to the preformed zeolite precursors. (3) As compared with that of Al-MCM-41 and Al-SBA-15, the acidic strength of mesoporous aluminosilicates is highly enhanced. For example, the desorption temperature of ammonia over Al-SBA-15 is at near 265 °C, and in contrast the desorption temperature of ammonia over MAS-9 shows at 450 °C.

There is currently great interest in preparation of ordered mesoporous materials assembled from zeolite nanoclusters.<sup>18,28-33</sup> Pinnavania *et al.*<sup>17</sup> have successfully prepared steam-stable MSU-S by using zeolite Y, MFI and beta seeds solution; Xiao *et al.*<sup>18</sup> have synthesized hydrothermal stable MAS samples by using MFI, beta, and TS-1 zeolite precursors. Unfortunately, the acidic strength is not systemically investigated yet. In this work, we carefully compare the acidic strength of mesoporous aluminosilicates assembled from preformed zeolite Y, L, beta, and MFI precursors, respectively.

MAS-3 is a novel mesoporous aluminosilicate assembled from preformed zeolite L precursors, and the preformed zeolite Y precursor for preparation of MAS-3 was synthesized by a new route (aluminosilicate gel crystallized at room temperature for 24 h). Preformed zeolite beta and MFI precursors were synthesized according to our patents.<sup>18</sup>

$\text{NH}_3$ -TPD of microporous crystals of zeolites have been investigated carefully in the early literature,<sup>1</sup> and it was found that microporous crystals of zeolites basically exhibited two peaks at 250—280 °C and 300—480 °C, which were assigned to weak acidic and strong acidic sites in the samples, respectively. The weak acidic sites are related to defects of  $\text{TO}_4$  (T=Si and Al), zeolite type, and ion type of zeolites, and the strong acidic sites are strongly dependent on zeolite type, Si/Al ratio, and ion type of zeolites. Because the strongly acidic sites play major roles in acidic catalysis, only strongly acidic sites are discussed in this paper.

Interestingly, as observed in Figures 2—5, the acidic strength of ordered mesoporous aluminosilicates of MAS series is much higher than that of Al-MCM-41 and Al-SBA-15 (Figures 2—6). By assembly of the preformed zeolite precursors containing zeolite primary and secondary building units (PBSU) with surfactant micella, the preformed zeolite nanoclusters are fixed in the wall of mesoporous aluminosilicates. Since the preformed zeolite nanoclusters have similar zeolite primary and secondary building units (PBSU) with those of microporous crystals of zeolites, the acidic strength of mesoporous aluminosilicates is closed to that of microporous crystals of zeolites. Therefore, mesoporous aluminosilicate of MAS-9 assembled from ZSM-5 zeolite nanoclusters exhibits stronger acidic strength than that of MAS-3 assembled from zeolite L nanoclusters. These results may be potentially important for industrial application by using mesoporous aluminosilicates as new acidic catalysts for catalytic conversion of larger molecules.<sup>18</sup> In contrast, the mesoporous walls of Al-MCM-41 and Al-SBA-15 are amorphous, and their acidic strength is not easy to design and control. Generally, Al-MCM-41 and Al-SBA-15 show relatively weaker acidic strength than microporous crystals of zeolites.

## Conclusion

The acidic strength of ordered mesoporous aluminosilicates assembled from preformed zeolite precursors is systemically investigated by temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD). The results show that the ordered mesoporous aluminosilicates exhibit distinguishable acidic strength, being dependent on the use of preformed zeolite precursors. Therefore, the acidic strength of ordered mesoporous aluminosilicates could be designed and controlled.

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