Synthesis of Highly Ordered, Extremely Hydrothermal stable SBA-15/Al-SBA-15 under the Assistance of Sodium Chloride

Changlin Li, Yanqin Wang,* Yanglong Guo, Xiaohui Liu, Yun Guo, Zhigang Zhang, Yunsong Wang, and Guanzhong Lu

Lab for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P. R. China

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In this paper, highly ordered, extremely hydrothermal stable SBA-15/Al-SBA-15 has been synthesized using mixed surfactants (triblock copolymer, P123, and semifluorinated surfactant, FSO-100) as a template at a high aging temperature (140−180 °C) with the assistance of NaCl. Thus - synthesized SBA-15 maintained the well-resolved SXRD patterns and high surface area, large pore size, and high pore volume after being hydrothermally treated at 100 °C for 300 h or 600 °C for 6 h, whereas less-ordered SBA-15 was synthesized at such high temperatures without the addition of NaCl. Furthermore, highly hydrothermal stable Al-SBA-15 has been synthesized with tetrahedral Al totally incorporated in the framework.

Introduction

Since the discovery of M41S by Mobil's scientists in 1992,[1] ordered mesoporous silicate materials have attracted considerable attention for their potential applications, such as catalysts, catalyst supports, adsorbents, and so on. To date, a series of ordered mesoporous silica (M41S,[1] SBA,[2,3] MSU,[4] HMS,[5] etc.) has been successfully synthesized. However, these materials have not been widely used in industry because of their relatively poor hydrothermal stability and the lack of acidity or redox properties.

To improve the hydrothermal stability of the mesoporous materials, several approaches have been employed, including the post-treatment with organosilane,[6,7] incorporation of heteroatoms by doping or post-grafting,[8,9] pH adjusting,[10] assembly of zeolite precursors,[11,12] carbon propping,[13] and the addition of salt.[14,15] The post-treatment of MCM-41 with methylchlorosilane has been used just at the discovery of the M41S family,[6] the assembly of preformed zeolite seed also exhibited remarkable hydrothermal stability,[11,12] and the addition of inorganic salts (such as KCl, NaCl) during the aging process or post-hydrothermal treatment also effectively improved the hydrothermal stability in boiling water.[14,15] Extensive studies have demonstrated that increasing the thickness and condensation of the mesoporous walls are effective strategies for enhancing the hydrothermal stability.

SBA-15, a mesoporous silica, was synthesized by the coassembly of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) and tetraethyl orthosilicate (TEOS) in acidic conditions. It has a larger pore diameter, thick pore wall, and relatively high hydrothermal stability and shows great advantages in applications. But its hydrothermal stability is still unsatisfactory. In general, increasing the aging temperature would be a good way to enhance the hydrolysis and condensation of silicon precursors and finally improve the hydrothermal stability. However, the thermal stability of hydrocarbon surfactants is so low that the increased aging temperature may cause a distortion of the micelle and impact the ordering of the mesostructure, and even decompose the surfactants. Han et al.[16,17] demonstrated the synthesis at high temperature and obtained hydrothermal stable mesoporous silica with a mixture of fluorocarbon and hydrocarbon surfactants as templates. Fluorocarbon surfactant has a higher thermal stability than hydrocarbon surfactant, so the mixed surfactants (fluorocarbon−hydrocarbon surfactant) may lead to high hydrothermal stability.

To create acidic sites in mesoporous materials, much effort has been focused on the incorporation of heteroatoms, such as Al atoms in the framework of mesoporous silica by post

* Corresponding author. Tel: 86-21-64253824. Fax: 86-21-64253703. Email: wangyanqin@ecust.edu.cn.

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grafting or doping (one-pot synthesis). In the one-pot synthesis of Al-SBA-15, the low synthetic pH value is not favored for the incorporation of Al atoms in the framework, and thus the "pH-adjusting" method was developed to incorporate much higher Al content in SBA-15.[18] To further increase the hydrothermal stability of thus synthesized Al-SBA-15, the use of mixed surfactants of fluorocarbon and hydrocarbon surfactant may be a good method, but the hydrophobicity of fluorocarbon surfactant prevents Al atoms from going into the framework.[19] Semifluorinated surfactant FSO-100 ($CF_3(CF_2)_4(EO)_{10}$) is a polyether surfactant and has been used as a template to synthesize mesoporous silica[20] (JLU-14, 15) and enhance the ordering by using an organic agent.[21] But thus synthesized JLU-14, 15 has a smaller pore size (similar to MCM-41) and poor hydrothermal stability (similar to SBA-15).

To enhance the ordering of the mesostructures and the hydrothermal stability, we have used the mixtures of semifluorinated surfactant (FSO-100) and hydrocarbon surfactant (P123) to synthesize SBA-15 under the assistance of NaCl at high aging temperatures. Furthermore, Al-SBA-15 with 4-coordinated states and high hydrothermal stability has also been successfully synthesized by the pH-adjusting method.

Experimental Section

Chemicals. Pluronic Triblock copolymer P123 (MW = 5800, $EO_{20}PO_{70}EO_{20}$) and semifluorinated surfactant (FSO-100, $CF_3(CF_2)_4(EO)_{10}$) were purchased from Aldrich and DuPont, respectively. Tetraethyl orthosilicate (TEOS), $NaAlO_2$, hydrochloric acid, ethanol, and sodium chloride were obtained from Shanghai Chemical Co. All chemicals were used as received without further purification.

Synthesis of Highly Ordered Hydrothermal Stable SBA-15. In a typical synthesis, 1.74 g of P123, 1.20 g of FSO-100, and 2.92 g of NaCl were dissolved in 100 mL of a 1.0 M HCl aqueous solution, and 5.6 mL of TEOS was then added under stirring. After further stirring at 40 °C for 30 h, the mixture (with a molar composition of 0.012:0.068:1:2:4:214 P123:FSO-100:TEOS:NaCl:HCl:H_2O) was transferred into an Teflon-lined autoclave for further condensation at various temperatures (140−180 °C) for 48 h. The products were collected by filtration, washed with deionized water and then ethanol, and dried at 100 °C overnight. The as-synthesized materials were calcined in air at 550 °C for 5 h to remove the template. Samples without the addition of NaCl were also synthesized with a similar procedure.

Synthesis of a Highly Hydrothermal Stable Al-SBA-15 by a pH-Adjusting Method. A required amount of $NaAlO_2$ was dissolved in 30 mL of 1 M HCl aqueous solution and added to the prehydrolyzed silicate sol (the same composition as that above, stirring at 40 °C for 6 h after adding TEOS). After further stirring at 40 °C for 24 h, the mixture was aged at 100 °C for 48 h and then cooled to room temperature; the pH was adjusted to 5 using ammonia (28%), and the mixture was finally aged at 160 °C for 48 h. The following steps are the same as those described in the synthesis of highly ordered hydrothermal stable SBA-15.

Hydrothermal Stability Evaluation. The hydrothermal stability was investigated by treating SBA-15 and Al-SBA-15 in a closed bottle at 100 °C for 300 h under static conditions.

The high-temperature hydrothermal stability was tested by treating the sample at 600 °C for 6 h in a flow of nitrogen saturated with water vapor at 100 °C.

Characterization. Small-angle X-ray diffraction patterns (SXRD) were recorded with a Rigaku D/max-2550VB/PC diffractometer using Cu K_α radiation. Transmission electron microscope (TEM) images were obtained with TECNAI 20S-TWIN. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2010 sorption analyzer. Before the measurements, the samples were outgassed at 300 °C in a vacuum for 6 h. The Brumauer−Emmett−Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett−Joyner−Halanda (BJH) method. The total pore volume (V_p) was estimated at a relative pressure of 0.975. The ratios of Si/Al and remaining chloride were determined by energy-dispersive X-ray spectroscopy (EDX). ^{27}Al MAS NMR spectra were recorded on a Bruker DRX-400 spectrometer equipped with a magic angle spin probe at room temperature. NH_3−TPD measurements were carried out in a flow reactor. Ammonia was introduced by a N_2 stream containing 10 vol % ammonia at 100 °C. The physically adsorbed NH_3 was removed by purging it with a nitrogen flow at 100 °C until the baseline was flat. The reactor temperature was then raised at a rate of 10 °C/min.

Results and Discussion

Highly Ordered, Hydrothermal Stable SBA-15. The synthesis was done in a 1.0 M HCl solution and the mixture of triblock copolymer P123 and semifluorinated surfactant FSO-100 was taken as the template. Semifluorinated surfactant FSO-100 is composed of the hydrophobic fluorinated hydrocarbon chain and the hydrophilic polyethylene oxides blocks, whose structure is partially similar to that of triblock copolymer P123. Therefore, semifluorinated surfactant FSO-100 and triblock copolymer P123 could form a stable mixed micelle in a broad range. In our case (the mass ratio of P123/FSO-100 is 1.45), the mixed micelle can be easily achieved at room temperature. Surface tension measurements revealed that only one break point existed on the curve, suggesting that they formed a mixed micelle rather than separate micelles. After calcination, both surfactants decomposed completely, and the EDX measurements revealed that no detectable chlorine remained in the calcined products, which indicated the complete elimination of chloride upon washing and calcination.

Figure 1A shows the SXRD patterns of SBA-15 synthesized at 160 °C with and without the addition of NaCl. It clearly shows that the addition of NaCl remarkably enhances the ordering of the mesostructures; this phenomenon has been found and discussed before.[22−25] Figure 1B gives the SXRD patterns of SBA-15 synthesized at various aging temperatures in the presence of NaCl. It clearly shows 3−4 well-resolved peaks that can be indexed as (100), (110), (200), and (210)

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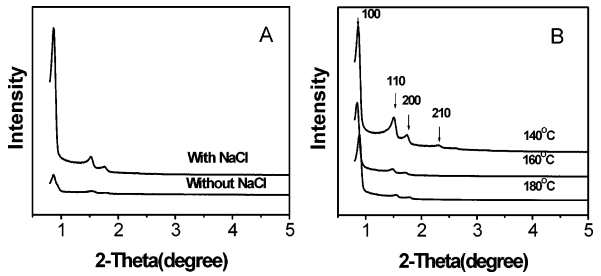

Figure 1. (A) SXRD patterns of SBA-15 synthesized at 160 °C with and without NaCl, (B) SXRD of SBA-15 synthesized with the addition of NaCl at different temperatures (140−180 °C).

diffractions associated with the *p6mm* hexagonal symmetry at the aging temperature of 140 °C. This is an indication of a good long-range hexagonal ordering. But at the higher aging temperature (180 °C), the higher-order reflections ((110), (200)) became weaker, indicating the lesser ordering of the mesostructures, but they are still good enough. This may be due to the lower stability of the template (P123), and TG/DTA measurements (unshown here) confirmed it. The weight loss decreased and the exothermic peak shifted to higher temperatures (187, 220, 248, and 279 °C for normal SBA-15 and SBA-15 aging at 140, 160, and 180 °C, respectively) with increasing aging temperature, which finally led to the lesser ordering of the mesostructures at high aging temperature. It is also interesting to note that with the increase in the aging temperature, the diffraction intensity decreases slightly and the peak positions shift a little bit. The latter is attributed to the nearly complete dehydration of the EO chains at higher aging temperature, so the unit-cell parameter is similar at high aging temperatures. The peak position shifted slightly to lower angles when the aging temperature increased from 140 to 160 °C, which is in accord with the previous results synthesized at relatively low temperatures.[20] But when the aging temperature increased further (from 160 to 180 °C), the reflection positions shifted to higher angles, indicating the shrinkage of the unit cells, which is due to the high condensation of the framework and similar to Xiao's work.[17]

The high ordering of the mesostructures synthesized above can be further confirmed by TEM analysis. The TEM images of SBA-15 synthesized at different temperatures are given in Figure 2. All of them show highly ordered hexagonal arrays of the mesopores with large uniform pore size. Judging from the dark contrast in the TEM images, the distance between mesopores is estimated to be ca.11 nm, in good agreement with the value measured from SXRD. Furthermore, the relatively thicker mesoporous walls, which are responsible for the high hydrothermal stability, are obvious.

Figure 3 depicts the N_2 adsorption−desorption isotherms and the corresponding pore size distributions of the calcined samples. The structural properties of the samples are summarized in Table 1. It can be seen from Figure 3 that all samples exhibit type IV isotherms with a typical capillary condensation step at the relative pressure (p/p_0) range of 0.6−0.8, which confirms that they are typical ordered mesoporous materials with large uniform pore size. With the increase in the aging temperature, the relative pressure of capillary condensation is slightly shifted toward a lower value, indicating a decrease in pore size as shown in the corresponding pore size distribution. Meanwhile, it is worthy to note that all the samples have relatively low surface area; this may be due to the lack of the micropores in the walls and high density of thick walls, which are caused by the combination of salt effect and high aging temperature. But the surface area of samples synthesized with FSO-100 is larger than the that of samples with fluorocarbon−hydrocarbon surfactant,[16,17] because FSO-100 is more hydrophilic than FC-4 and the latter has nearly no micropores.

Figure 4A is the SXRD patterns of SBA-15 after being treated in boiling water for 300 h. Three main peaks, indexed as (100), (110), and (200) reflections of the mesostructures, are obvious. And there were no significant changes in 2θ positions, peak intensities, and linewidths compared with those of calcined SBA-15, indicating that the highly ordered mesostructures were still maintained after hydrothermal treatment. The SXRD patterns of steam-treated SBA-15 (600 °C, 6 h) synthesized at different temperatures are displayed in Figure 4B. The patterns also show a very intense (100) diffraction peak and two additional higher-order peaks, which means that the mesostructures weren't destroyed even under such severe conditions. These results demonstrate that the synthesized samples have remarkable hydrothermal stability.

After being treated in boiling water or steamed, the samples still exhibit type IV isotherms (Figure 5, left), except for the sample aged at 180 °C and steam-treated for 6 h; there is just a little distortion of the hysteretic loops, validating a good maintenance of the mesostructures. From the pore size distribution (Figure 5, right), we can find that the samples after treatment possess a slightly broadened pore size distribution, especially for the sample aged at 180 °C and steam-treated for 6 h. The latter could be attributed to the fewer micropores and the lesser-ordering in the original sample. Zhang[13] found that the microporosity of the mesostructured silica SBA-15 is a very important factor for the hydrothermal stability. According to the data presented in Table 1, the treated samples maintained most of the BET surface area and pore volume. For example, the treated sample synthesized at 160 °C maintained 74% of the specific surface area and 80% of the pore volume. All of the results further demonstrate that the samples (except the one aged at 180 °C) have good mesostructural ordering and remarkable hydrothermal stability.

Hydrothermal Stable Al-SBA-15 Synthesized by the pH-Adjusting Method at High Temperature. Al-SBA-15 was synthesized in a 1.0 M HCl solution, using TEOS and $NaAlO_2$ as the precursors and mixed surfactants as the template. First, the mixture was aged at 100 °C for 48 h; the pH was then adjusted to 5 with ammonia, and the mixture was finally aged at 160 °C for 2 days.

Figure 6 shows the XRD patterns of Al-SBA-15 and the corresponding hydrothermally treated samples. All of the SXRD patterns show three well-resolved peaks, indicating

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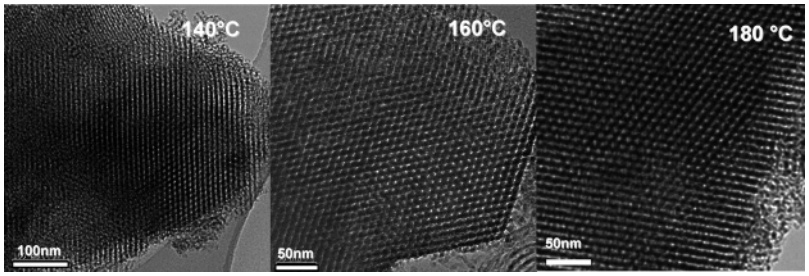

Figure 2. TEM images of the SBA-15 synthesized at different aging temperatures.

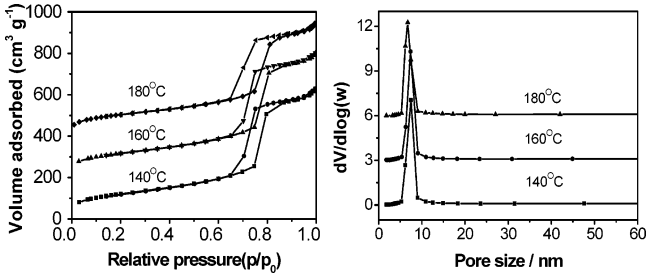

Figure 3. N_2 adsorption−desorption isotherms (left column) and the corresponding pore size distribution (right column) of calcined SBA-15.

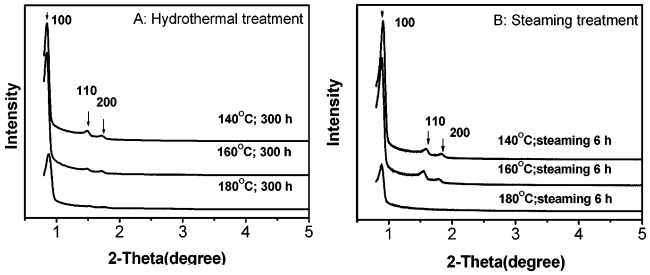

Figure 4. SXRD patterns of SBA-15 after being (A) treated in boiling water for 300 h or (B) steamed at 600 °C for 6 h.

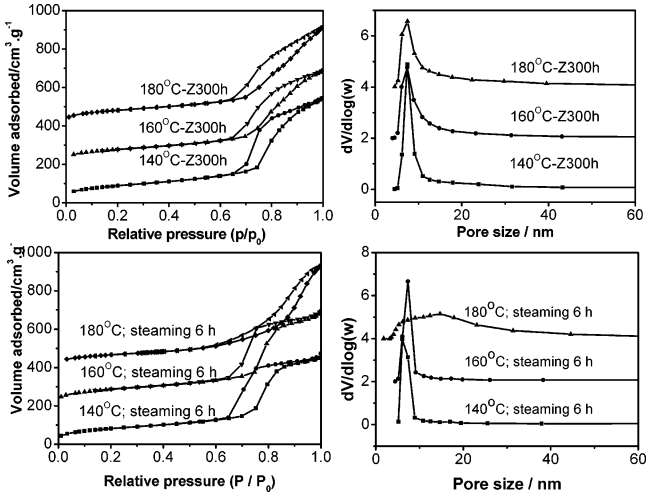

Figure 5. N_2 adsorption−desorption isotherms (left column) and corresponding pore size distribution (right column) of SBA-15 hydrothermal treated in boiling water for 300 h and steamed at 600 °C for 6 h.

that the samples exhibit good long-range 2D hexagonal pore ordering and high hydrothermal stability. The well-ordered hexagonal arrays can be easily seen from the TEM images displayed in Figure 7.

The porosity of Al-SBA-15 and the hydrothermal treated samples were measured by N_2 sorption. Figure 8 gives the N_2 adsorption−desorption isotherms and the corresponding pore size distribution. The isotherms are typical type IV with a H_1 hysteretic loop and all the samples display a narrow pore size distribution, which won't be affected by even the hydrothermal treatment. The specific structural parameters are given in Table 2. It can be seen that there is only a 3.2% decrease in BET surface area after treatment in boiling water and a 15.2% decrease after steam treatment. It is notable that the Al-SBA-15 exhibits much better hydrothermal stability than SBA-15 synthesized at high temperature.

It is reported by Wu and his co-workers[18] that mesoporous silica SBA-15 high heteroatom content can be easily synthesized by the pH-adjusting method. However, in our study, there is only partial Al incorporated into the products. Compared with the initial Si/Al ratio of 5, the EDX analysis shows that the final Si/Al ratio of the calcined sample is 30, indicating that most of the Al was leached out during filtration. This may be due to the relatively low pH value, which is not high enough to lead all Al^{3+} species into oxo form and incorporate it into the framework. The ^{27}Al MAS NMR spectrum given in Figure 9 shows that there is a sharp resonance peak at 53 ppm, which is assigned to 4-coordinated Al species in its framework. Beside this peak, there are no signals related to other Al species. It is clear that all of the Al atoms incorporated in the sample are located at 4-coor-

Table 1. Structural Properties of the Calcined and Hydrothermally Treated Samples[a]

sample	d_{100} (nm)	a_0 (nm)	S_{BET} (m^2g^{-1})	D_p (nm)	W (nm)	V_p ($cm^3\,g^{-1}$)	V_m ($cm^3\,g^{-1}$)	S_{BET} reduced (%)
S−140	10.2	11.8	438	7.4	4.4	0.983	0.015	
S−140−H	10.4	12.0	320	7.5	4.5	0.848	0.012	26.9
S−140−600	9.7	11.2	298	6.5	4.7	0.738	0.006	32.0
S−160	10.4	11.9	422	7.3	4.6	0.941	0.013	
S−160−H	10.5	12.1	312	7.5	4.6	0.832	0.009	26.0
S−160−600	9.9	11.4	313	7.3	4.1	0.764	0.007	25.8
S−180	10.0	11.5	377	6.8	4.7	0.851	0.006	
S−180−H	10.1	11.7	294	7.6	4.1	0.797	0.011	22.0
S−180−600	10.0	11.5	243	7.0 + 14.7[b]	4.5	0.821	0.001	35.5

[a] a_0 = Cell dimension; D_p = pore diameter; W = pore wall thickness; V_p = total pore volume. [b] Pores come from the aggregation of particles (void space).

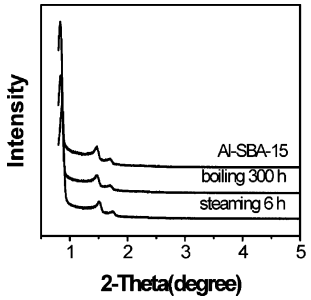

Figure 6. SXRD patterns of Al-SBA-15, treated in boiling water for 300 h, steamed at (600 °C) for 6 h.

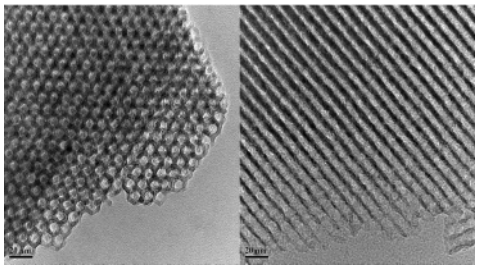

Figure 7. TEM images of Al-SBA-15 in the direction along (left) and perpendicular (right) to the pore axis.

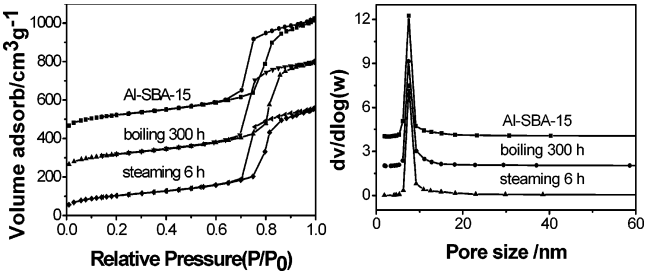

Figure 8. N_2 adsorption−desorption isotherms (left column) and the corresponding pore size distribution (right column) of Al-SBA-15. As-calcined, treated in boiling water for 300 h, or steamed at 600 °C for 6 h.

dinated sites. At these conditions (100 °C, 48 h; pH 5, 160 °C, 48 h), with the decrease in the initial molar ratio of Al/Si (1/20), the molar ratio in the product was still close to 1/30, indicating that the amount of Al incorporated in the framework is related to the pH value. With the increase in the pH value (e.g., pH 7), a higher Al/Si ratio could be achieved, but the ordering of the mesostructures decreased in our case and other species, such as the 6-coordinated Al, appeared.

The NH_3−TPD profile of Al-SBA-15 is displayed in Figure 10; it exhibits two peaks at 200 and 375 °C, respectively. The first peak corresponds to the weak acid sites, and the broad peak at 375 °C suggests that the Al-SBA-15 possesses a large amount of medium acid sites. Generally speaking, the acidity of Al-SBA-15 is still weaker

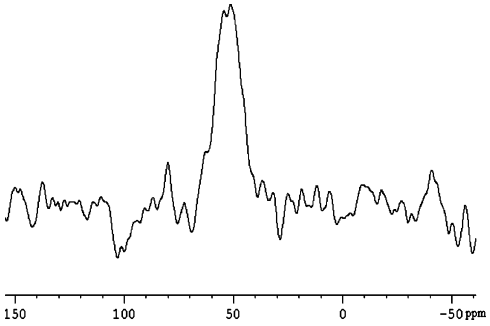

Figure 9. ^{27}Al MAS NMR spectrum of calcined Al-SBA-15.

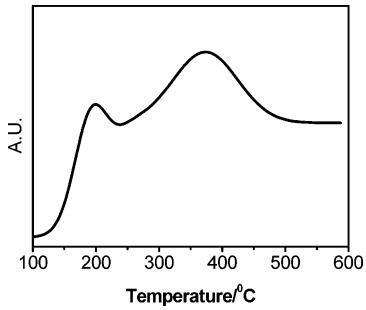

Figure 10. NH_3−TPD of Al-SBA-15 synthesized with an extended second aging time.

than that of zeolite but is strong enough for some catalytic reactions that only need a medium acid strength.

It is shown in this work that both the ordering and the hydrothermal stability of mesoporous materials have been significantly enhanced by increasing the aging temperature, and by the addition of inorganic salt. Pluronics show an anomalous temperature behavior; a rise in temperature can lead to phase separation, and this phenomenon happens easily in the mixed system under high temperature. Additional NaCl can create a nonpolar environment in the solution by dehydrating the polyethylene units. This nonpolar circumstance may favor the formation of stable mixed micelles and local arrays, which could finally induce the ordered arrangement. In addition, the salt could increase the interaction between surfactant headgroups and the silicon precursor by additive electrolyte effect,[26] resulting in an enhanced self-assembly action.

Conclusion

In conclusion, highly ordered and highly hydrothermal stable mesoporous silica SBA-15 has been synthesized in a simple one-step procedure using mixed surfactants as template under the assistance of NaCl. After being treated in boiling water for 300 h or steamed at 600 °C for 6 h, the mesostructures obviously haven't changed in ordering, and they've maintained a 70% excess of the BET surface area and 80% excess of the pore volume. As-synthesized Al-

Table 2. Structural Properties of Calcined and Treated Samples of Al-SBA-15[a]

sample	d_{100} (nm)	a_0 (nm)	S_{BET} (m^2g^{-1})	D_p (nm)	W (nm)	V_p ($cm^3\,g^{-1}$)	V_m ($cm^3\,g^{-1}$)	S_{BET} reduced (%)
S	10.6	11.8	440	7.5	4.4	0.975	0.023	
S−H	10.5	12.1	426	7.5	4.6	0.936	0.019	3.2
S−600	10.2	11.2	373	7.5	4.7	0.870	0.015	15.2

[a] a_0 = Cell dimension; D_p = pore diameter; W = pore wall thickness; V_p = total pore volume.

substituted SBA-15 exhibits more excellent hydrothermal stability and a large number of medium acid sites. Such materials may have extensive potential applications in catalysis and separation. It is proposed that the addition of NaCl can promote the stability of mixed micelle, boost the arrangement of the channels, and accelerate the hydrolysis of the silicon precursor and condensation of the silicate wall. This method may be extended to fabricate many other materials.

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