Hydrothermally Stable Ordered Hexagonal Mesoporous Aluminosilicates Assembled from a Triblock Copolymer and Preformed Aluminosilicate Precursors in Strongly Acidic Media

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Mesoporous aluminosilicates (MAS-9) with ordered hexagonal struture have been prepared by assembly of preformed aluminosilicate precursors with a triblock copolymer in strongly acidic media by a two-step procedure. MAS-9 exhibits extraordinarily good hydrothermal stability and high catalytic activities for the cracking of both cumene and 1,3,5-tri-isopropylbenzene. Even after treatment in boiling water for 120 h, MAS-9 continues to show a large surface area (680 m^2/g) and high catalytic activities. Furthermore, this two-step strategy could be used as a new general method for the preparation of mesoporous aluminosilicate materials under strongly acidic conditions.

Introduction

Mesoporous molecular sieves such as MCM-41 have attracted much attention because of their potential use as versatile catalysts and catalyst supports for the conversion of large molecules.[1] However, as compared with conventional zeolites, these mesostructured materials have relatively low acidity and hydrothermal stability, which can be attributed to the amorphous nature of the pore walls.[1,2] Many efforts have been made to improve the hydrothermal stability of mesoporous materials.[3]

One might expect to improve both the stability and acidity of mesoporous materials by introducing zeolite structure building units into the pore walls.[3c−e] There have been some successful examples of the preparation of mesoporous aluminosilicates that have reasonably good hydrothermal stability and strong acidity by the assembly of zeolite seeds solution[4] or preformed aluminosilicate nanoclusters[5] with surfactants such as CTAB in alkaline media. For example, Pinnavaia et al. have prepared steam-stable aluminosilicate mesostructures (MSU-S) from nanoclustered zeolite Y seeds, zeolite Beta seeds, and zeolite ZSM-5 seeds solution.[4] Xiao et al. have prepared high-temperature hydrothermally stable mesoporous aluminosilicates (MAS-5) from zeolite Beta primary structure building units.[5] Notably, these syntheses are all carried out in alkaline media analogous to the MCM-41 system and there are still some problems to consider. On one hand, the wall thickness of the MCM-41-like mesoporous material is too thin to accommodate a complete zeolite primary unit. For example, the thickness of the mesoporous wall of MSU-$S_{(MFI)}$ prepared by the assembly of the MFI seeds solution with CTAB is only 9 Å;[4] however, de Moor et al. reported that the size of MFI primary units in the solution is 2.8 nm.[6] On the other hand, zeolite seeds easily grow into zeolite crystals under the alkaline conditions, and the preparations of MSU-S and MAS-5 materials are all under alkaline media. If the synthesis conditions are not controlled very well, a mixture of zeolite and MCM-41 would be obtained.

A new type of well-ordered hexagonal mesoporous silica designated as SBA-15 has been prepared by using triblock copolymers as templates in strongly acidic media (pH < 0).[7] Because it has much thicker walls (>3 nm), larger pores (5−30 nm), and higher stability than MCM-41, SBA-15 has attracted much attention in recent years.

We report here the preparation of a hexagonal, hydrothermally stable aluminosilicate mesostruture

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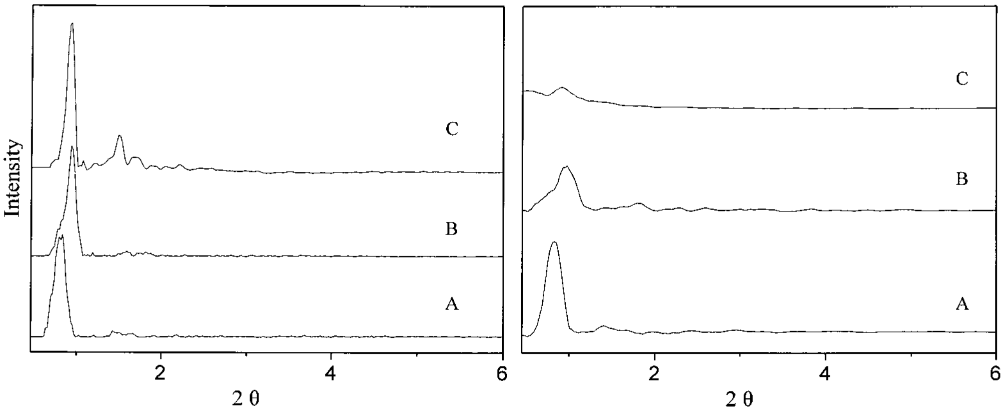

Figure 1. XRD patterns of calcined samples before (left) and after treatment (right) in boiling water for 120 h: (A) MAS-9, (B) SBA-15 prepared under the same conditions as MAS-9, and (C) Al−SBA-15 prepared according to the published procedure.[9]

(MAS-9) by a two-step synthesis procedure under strongly acidic media ($pH < 0$). First, precursors containing 2.8 nm sized MFI primary units (aluminosilicate nanoclusters) were prepared according to a published literature.[6] Second, the preformed precursors were used for the assembly with triblock copolymers in acidic media ($pH < 0$). In this way, the preformed MFI primary units were effectively introduced into the mesoporous walls and the obtained materials show high hydrothermal stability, strong acidity, and superior catalytic activities in the cracking of both small (cumene) and large molecules (1,3,5-tri-isopropylbenzene). Moreover, due to the strongly acidic conditions in the second step, the nanoclusters prepared in the first step would not grow continuously into large crystals and the products therefore would be pure mesoporous materials without zeolite crystals as byproducts.

Experimental Section

Synthesis. A typical synthesis for MAS-9 is as follows: (1) The zeolite precursor solution with zeolite ZSM-5 primary units was prepared by mixing 6 mL of tetrapropylammonium hydroxide (TPAOH) aqueous solution (20−25%), 0.12 g of $NaAlO_2$, and 5.6 mL of tetraethyl orthosilicate (TEOS) with 12 mL of H_2O under stirring ($Al_2O_3/SiO_2/Na_2O/(TPA)_2O/H_2O$ with molar ratios of 1.0/50/1.0/7/1800). The mixture is then aged at 100 °C for 2−3 h. The final product is a clear solution. (2) A portion of 0.8 g of $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was dissolved in 20 mL of H_2O with 5 mL of HCl (10 M/L), followed by the addition of 7.0 mL of precursor solution (containing 8 mmol of SiO_2) obtained in step one. The mixture was stirred at 40 °C for 20 h and then transferred into an autoclave for additional reaction at 100 °C for 36 h. (3) The product was collected by filtration, dried in air, and calcined at 550 °C for 5 h to remove the organic template.

For comparison, a SBA-15 sample was prepared under exactly the same conditions as the MAS-9 sample except that the aluminosilicate precursor solution was replaced by a corresponding amount of TEOS, $NaAlO_2$, and TPAOH solution. Two types of Al−SBA-15 were prepared by "postsynthesis" and "direct synthesis" according to the published procedures, respectively.[8,9]

Characterization. X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) images and electron diffraction (ED) patterns were recorded by a Philips CM200FEG with an acceleration voltage of 200 kV. The sample isotherms of nitrogen at the temperature of liquid nitrogen were measured by using a Micromeritics ASAP 2010 system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution was calculated by using the Barrett−Joyner−Halenda (BJH) model. ^{27}Al NMR spectra were recorded on a Bruker MSL-300WB spectrometer, and the chemical shifts were referenced to $Al(H_2O)_6^{3+}$. The Si/Al ratio of the samples was determined by the results of ICP (Perkin-Elmer 3300 DV) and chemical analysis. Temperature-programmed-desorption of ammonia ($TPD-NH_3$) curves were performed in the range of 120−600 °C at an increasing temperature rate of 15 °C/min. The adsorption of ammonia on the sample was performed at room temperature, followed by removal of physically adsorbed ammonia at 120 °C for 1 h in flowing pure nitrogen. Catalytic reactions were performed at 300 °C by pulse injections, and the data presented in this table are results after 10 injections. In each run, 50 mg of catalyst was used, the pulse injection of the reactant was 0.4 μml, and the reaction flow rate was 53.7 mL/min.

Results and Discussions

The XRD pattern (Figure 1A) and TEM image (not shown) of the MAS-9 sample show that MAS-9 has ordered hexagonal arrays of mesopores of uniform size. The result of no distinguishable peaks in the wide-angle region in the XRD pattern (10−40°, not shown) suggests that the product is a pure mesoporous phase without zeolite crystals. It is very interesting to note that the *d*(100) value of the MAS-9 sample is much larger than that of the SBA-15 sample (Figure 1B) prepared under the same conditions (116 and 95 Å, respectively). Combining the results of N_2 adsorption/desorption experiments (Figure 2) which show that they have almost the same pore-size distributions (80 and 76 Å, respectively), we can conclude that the mesoporous wall of the MAS-9 sample is 20 Å thicker than that of the SBA-15 sample prepared under the same conditions (Table 1). It is well-known that the wall thickness of SBA-15 can be adjusted by changing the reaction time and temperature; however, we found that MAS-9 samples always have much thicker walls than the SBA-15 samples prepared under the same conditions. This phenomenon is attributed to the assumption that the nanoclustered MFI primary units used in the synthesis of the MAS-9 have stronger rigidity and larger volume than the nonstructured silicon species used in the conventional synthesis of the SBA-15; therefore, the assembly of these nanoclusters needs more space to connect to each other. Furthermore, we observed that

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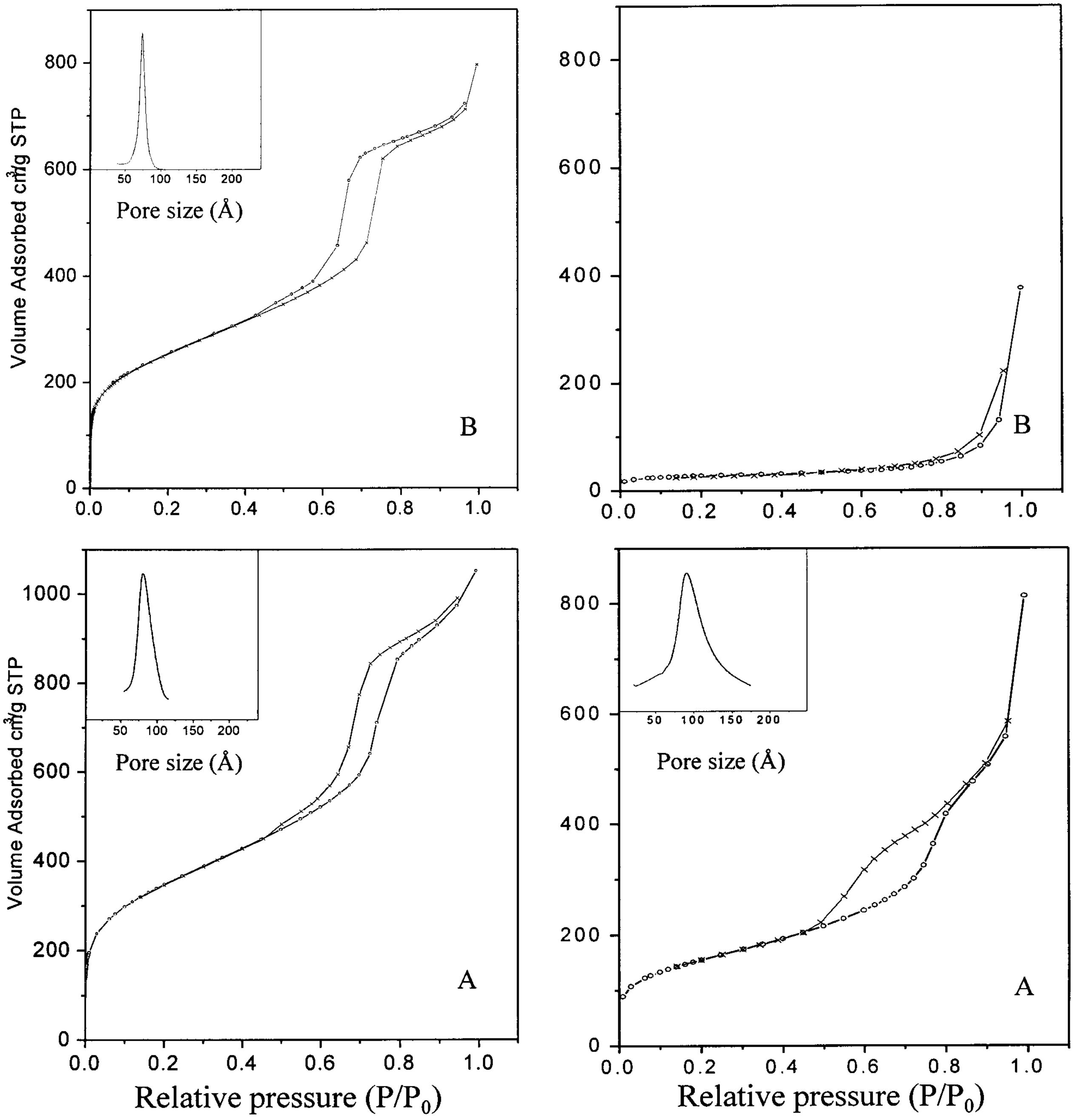

Figure 2. N_2 adsorption/desorption isotherms and pore-size distributions of calcined samples before (left) and after treatment (right) in boiling water for 120 h: (A) MAS-9 and (B) SBA-15 prepared under the same conditions as MAS-9.

both the samples of MAS-9 and SBA-15 give typical type IV isotherms (Figure 2), which indicates the presence of uniform mesopores. However, the pore-size distribution of the MAS-9 sample is somewhat broader than that of the SBA-15 sample, despite the fact that the maximum values are similar. It is proposed that this phenomenon can also be attributed to the difference between the nanoclustered zeolite primary units used for MAS-9 and the nonstructured silicon species used for SBA-15. The stronger rigidity and larger volume of the nanoclustered MFI units makes assembly with the template relatively difficult, and this results in some disorder in the products.

Notably, the results of XRD (Figure 1) and the isotherms for N_2 adsorption (Figure 2 and Table 1) clearly indicate that the MAS-9 sample assembled from ZSM-5 primary units retains an ordered hexagonal structure with a surface area of 680 m^2/g even after treatments in boiling water for 120 h. In comparison, SBA-15 and Al–SBA-15 prepared under the conventional method lose most of their mesostructure after the same treatments, with surface area less than 200 m^2/g. These results indicate that MAS-9 has much higher hydrothermal stability than SBA-15 and Al–SBA-15. Kawi et al. found that the small amount Al substituted in the framework of Si–MCM-41 gives great improvement in the hydrothermal stability.[10] In our case, MAS-9 is much more stable than Al–SBA-15 with similar Si/Al ratio. Therefore, the extra hydrothermal stability of MAS-9 should not be attributed to the Al substituted in the framework but to the presence of zeolite MFI primary units in the walls. MSU-G has been reported

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Table 1. Properties and Catalytic Activities in Cracking of Cumene and 1,3,5-Tri-isopropylbenzene of Various Samples before and after Treatment in Boiling Water for 120 h[a]

sample	*d* (100) (Å)	pore size (Å)	wall thickness (Å)	micropore vol (cm^3/g)	surface area (m^2/g)	conversion of cumene (%)	conversion of 1,3,5-tri-isopropylbenzene (%)
MAS-9	116	80	54	0.16	967	41.5	92.4
treated	121	96	43	0.08	680	12.7	34.6
SBA-15	95	76	34	0.05	910	inactive	inactive
treated				0	98	inactive	inactive
Al–SBA-15[b]					924	7.8	36.5
treated					85	<2.0	<5.0
Al–SBA-15[c]					1025	25.5	52.4
treated					167	<2.0	<5.0
H–ZSM-5						94.4	1.7

[a] The Si/Al ratio in all samples is 40 except for SBA-15 (pure silica). The MAS-9 sample and the SBA-15 sample were prepared under the same conditions. Pore-size distributions and pore volumes were determined from N_2 adsorption isotherms at 77 K. The wall thickness was calculated as: a_0 − pore size ($a_0 = 2 \times d(100)/3^{1/2}$). [b] Al–SBA-15 was prepared according to the method reported by ref 8. [c] Al–SBA-15 was prepared according to the method reported by ref 9.

with very high hydrothermal stabilities (more than 150 h in boiling water).[3b] However, MSU-G has relatively small surface area (less than 550 m^2/g) and is less ordered than MCM-41 or SBA-15. MAS-9 is well ordered with large surface area and remarkable hydrothermal stability, showing potential importance for catalytic applications.

Generally, the *t*-plots of conventional mesoporous materials should pass the zero of the axis, meaning that there are no micropores in them. Miyazawa et al. reported that there are some micropores smaller than 4 Å in the walls of SBA-15 formed by penetration of hydrophilic poly(ethylene oxide) chains of the triblock coplymer in the silica wall.[11] Ryoo et al. also found a network of micropores in the walls of SBA-15.[12] From the *t*-plots of SBA-15 and MAS-9 (not shown), we find that the SBA-15 sample prepared in this work also shows evidence of micropores contained in it. However, it is very interesting to note that the micropore volume of the MAS-9 sample (0.16 cm^3/g) is much more than that of the SBA-15 sample prepared under the same conditions (0.05 cm^3/g), as shown in Table 1. We even considered the fact that MAS-9 has thicker walls than SBA-15; the ratio of micropore volume to the thickness of the walls in MAS-9 is still much more than that in SBA-15. The larger micropore volume in MAS-9 may also be attributed to the existence of zeolite MFI primary units in the mesoporous walls.

IR spectrum of SBA-15 (Figure 3b) shows a broad band at 460 cm^{-1} in the region of 400–600 cm^{-1}, which is similar to those of amorphous materials. However, MAS-9 exhibits a few sharp bands at 410–480 cm^{-1} and an additional band at 556 cm^{-1} (Figure 3a), which are similar to those of the five-membered rings of T–O–T (T = Si or Al) in zeolite crystals.[13] These results also indicate that the mesoporous walls of MAS-9 contain the primary units of zeolite MFI.

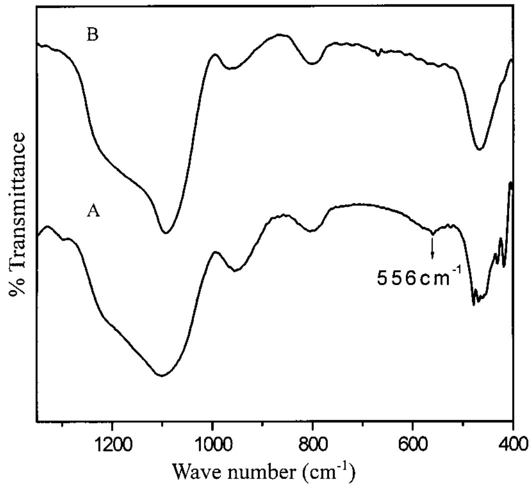

Figure 3. IR spectra of calcined samples: (A) MAS-9 and (B) SBA-15.

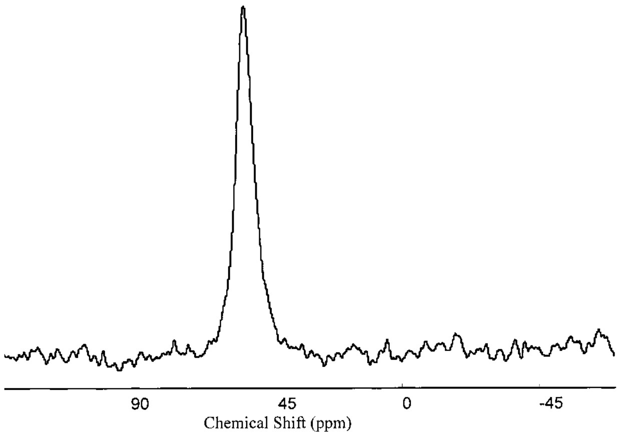

Figure 4. Al^{27} NMR spectrum of calcined MAS-9.

The ^{27}Al NMR spectra of MAS-9 (Figure 4) exhibit chemical shifts at 58 ppm assigned to four-coordinated Al, indicating that Al atoms are incorporated in the framework of MAS-9. As we know, under the synthesis conditions of SBA-15 (pH < 0), some metals will exist only in the cationic form other than their corresponding oxo species. Consequently, the synthesis of Al–SBA-15, which is more important in catalytic applications than the pure silica SBA-15, will be difficult. To prepare Al–SBA-15, some methods were invented including postsynthesis[8] and direct synthesis.[9] In our case, we directly introduce Al into the mesostructure in a strongly acidic media. On the contrary, the corresponding SBA-15 sample does not have any tetrahedral Al in the framework although the same amount of Al source was added to the initial gel. These results are explained by the assumption that Al species have already been fixed in the framework of the zeolite primary units in the first

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step of the preparation of MAS-9. With the self-assembly of the zeolite primary units surrounding the surfactant, Al species are directly introduced into the mesostructure. On the contrary, free aluminum (Al^{3+}) cannot enter the framework of SBA-15 in conventional synthesis.

Notably, the ^{27}Al chemical shift of tetrahedral aluminum in MAS-9 occurs at 58 ppm (similar to that in ZSM-5, ca. 60 ppm) rather than at 53 ppm as was previously reported for Al−SBA-15 that was prepared by different ways,[8,9] which suggests that the environment of aluminum in the MAS-9 is quite similar to that in the ZSM-5 crystal rather than that in amorphous Al−SBA-15. Moreover, the temperature-programmed-desorption of ammonia curves (TPD-NH_3, not shown) on the MAS-9, Al−SBA-15 and ZSM-5 samples with similar Si/Al ratio (40) indicate that acidic strength of MAS-9 is similar to that of ZSM-5 zeolite and much stronger than that of Al−SBA-15. All these results suggest that MAS-9 contains the primary structure units of ZSM-5.

The catalytic activities in the cracking of cumene and 1,3,5-tri-isopropylbenzene over various catalysts are summarized in Table 1. Although HZSM-5 shows strong acidity and gives very high conversion for cumene, it is almost inactive for 1,3,5-tri-isopropylbenzene due to its relatively small pore size and the large diameter of the reactant molecules. Under the same conditions, the Al−SBA-15 sample prepared by postsynthesis[8] shows relatively low activity, as a result of the amorphous nature of the Al species in its framework. The Al−SBA-15 sample synthesized by direct synthesis[9] shows catalytic activities (a conversion of 22.5 and 52.4% for cumene and 1,3,5-tri-isopropylbenzene, respectively) that are higher than that of the Al−SBA-15 prepared by postsynthesis but are still much lower than that of MAS-9. Only the MAS-9 sample shows high activities for both reactions (a conversion of 41.5 and 92.4% for cumene and 1,3,5-tri-isopropylbenzene, respectively) because it combines the advantages of both ZSM-5 (strong acidity) and SBA-15 (large pores). More significantly, after the treatment in boiling water for 120 h, the MAS-9 still shows a large surface area (680 m^2/g) and high catalytic activity (conversion of 12.7 and 34.6% for cumene and 1,3,5-tri-isopropylbenzene, respectively). In contrast, the Al−SBA-15 samples become almost inactive with a sharp decrease of the surface areas. All these results confirm that the MAS-9 is strongly acidic and highly hydrothermally stable, suggesting that it is a good candidate catalyst for industrial cracking of heavy oil (bulky molecules).

The precursors have been well characterized by de Moor et al. by small-angle X-ray scattering (SAXS), and two types of precursor particles were observed: 2.8 nm sized primary units and their aggregates (≈10 nm).[6] We think it is the 2.8 nm sized primary units that assemble with the copolymer surfactant to form the mesostructure. It is clearly difficult for the aggregates to assemble because of their large size. When negatively charged preformed zeolite nanoclusters were added into strongly acidic P123 solution, their surface charge quickly changed to positive. Then the positively charged protonated zeolite nanoclusters interact with hydrophilic PEO blocks through an $S^0(H^+)X^-I^+$ route[7] to promote the formation of the mesophase. With the consumption of 2.8 nm sized primary units, we suppose that the aggregates may separate into single 2.8 nm sized primary units to supply the need for assembly. We also notice that the Si/Al ratio of the MAS-9 sample prepared in this work is about 40 and therefore somewhat larger than that in the initial mixture (25), which means that not all of the Al species the initial reaction mixture are present in the final products. This may result from a dealumination effect due to the strongly acidic synthesis conditions.

Additionally, the aluminosilicate precursor solution exhibits an obvious band at 550 cm^{-1} in the IR spectrum, which is characteristic of five-membered rings in a ZSM-5 crystal. Furthermore, this precursor solution provides very good seeds for the synthesis of ZSM-5. All of these results suggest that the precursors contain ZSM-5 primary structure units.

Conclusions

Through a two-step procedure, mesoporous aluminosilicates (MAS-9) were successfully prepared by assembly of preformed aluminosilicate precursors with a triblock copolymer in strongly acidic media. We propose that the high hydrothermal stability and good catalytic activity of MAS-9 arise from the presence of ZSM-5 structure building units in the mesoporous walls. In addition, during the preparation of MAS-9, the Al species are fixed in the framework of the ZSM-5 nanoclusters in the first step and then introduced into the mesoporous structure along with the nanoclusters which self-assemble with the template in the second step. Thus, mesoporous aluminosilicates could be easily prepared in strongly acid media. Moreover, due to the strongly acidic conditions in the second step, the nanoclusters prepared in the first step would not grow continuously into large crystals. Therefore, the ordered mesoporous MAS-9 is generally a pure phase, and a mixture of mesoporous materials with zeolite crystals is avoided.

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