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**Understanding of the High Hydrothermal Stability of the Mesoporous Materials Prepared by the Assembly of Triblock Copolymer with Preformed Zeolite Precursors in Acidic Media**

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Mesoporous pure silica (MPS-9) is prepared using an assembly of preformed Silicalite-I nanoclusters with a triblock copolymer surfactant. The results of X-ray diffraction, transmission electron microscopy, and N<sub>2</sub> adsorption show that MPS-9 has a mesostructure that is similar to that of other mesoporous materials prepared from preformed zeolite nanoclusters, such as mesoporous aluminum silicates (MAS-7, MAS-9) and titanium silicate (MTS-9). However, MPS-9 shows weaker hydrothermal stability, in comparison to those other mesoporous materials prepared from preformed zeolite nanoclusters. On the other hand, three Al-SBA-15 samples synthesized from various routes are all much more hydrothermally stable than pure silica SBA-15. The previously proposed factors, including thicker pore walls, a disordered structure, the “salt effect”, and zeolite-like connectivity, have been proven to be indeed favorable for the improvement of hydrothermal stability in this study. However, the introduction of heteroatoms (Al or Ti) in mesoporous materials is another favorable factor and can enhance the hydrothermal stability to a greater extent.

**Introduction**

The hydrothermal stability of ordered mesoporous materials is too weak to satisfy their potential applications as versatile catalysts and catalyst supports for the conversion of large molecules.<sup>1</sup> Many research efforts have therefore been focused on how to improve it.<sup>2–10</sup>

In the published progress, several reasons are associated with the enhanced hydrothermal stability of mesoporous silica. First, increasing the pore wall thickness and the extent of silica condensation within the pore wall can improve the hydrothermal stability. For example, pure silica SBA-15 is much more hydrothermally stable than MCM-41, which is due to its thicker wall.<sup>11a</sup> Mokaya has synthesized stable MCM-41 with thicker and highly condensed walls via secondary crystallization or long-time crystallization.<sup>11b,c</sup> Second, the “salt effect” can also help to improve the hydrothermal stability of mesoporous silica.<sup>2,12</sup> For example, the additions of various sodium salts into the gel mixture make MCM-41 stable in boiling water for > 12 h. Ryoo et al. suggested that the salt effect might cause a slow local reconstruction of the silica framework.<sup>12</sup> In addition, the hydrothermal stability of MCM-41 could be improved by adding tetra-alkylammonium ions, including TMA<sup>+</sup> or TEA<sup>+</sup>, in the gel mixture during the synthesis procedure.<sup>13</sup> It is explained that the presence of tetra-alkylammonium ions facilitates the condensation of silanol groups in the meso-framework. Third, disorder in a certain degree of the meso-structure is another favorable factor. The high hydrothermal stability of KIT-1 was attributed to its disordered structure

originally, although it is attributed to the salt effect later.<sup>12</sup> One type of mesoporous silica that is prepared from Na-kanemite shows distorted channels and better hydrothermal stability than MCM-41.<sup>14</sup> Fourth, small amount of Al substitution in the framework of Si-MCM-41 gives great improvement of the hydrothermal stability.<sup>15,16</sup> It is proposed that the aluminum-rich layer on the inner surface of Al-MCM-41 might function as a protective layer for the meso-framework under hydrothermal treatment conditions.<sup>15</sup>

Recently, a novel method to prepare mesoporous materials was reported that used preformed zeolite nanoclusters (or zeolite seed solution) as precursors to assembly with surfactant templates.<sup>7–10</sup> Through this method, mesoporous aluminum silicates (MAS-7,<sup>9b</sup> MAS-9,<sup>9a</sup>) and titanium silicate (MTS-9<sup>9b</sup>) have been synthesized in strong acidic media, using zeolite Beta, ZSM-5, and TS-1 nanoclusters, respectively, as a precursor to assembly with a triblock copolymer surfactant. MSU-S<sup>7</sup> and MAS-5<sup>8</sup> have been prepared in the past using this strategy in basic media. All the mesoporous samples prepared this way show high hydrothermal stability,<sup>7–10</sup> which was attributed by the authors to the presence of zeolite-like connectivity in the framework that is introduced by preformed zeolite nanoclusters precursors. It is thought that, compared to conventional mesoporous silica with an amorphous nature, this type of material has a better local order (zeolite-like connectivity), which is important for high hydrothermal stability. However, this view has not been confirmed further.

In this study, a new mesoporous pure silica—denoted as MPS-9—is prepared using preformed Silicalite-I nanoclusters as the precursor to assemble with a copolymer surfactant under strong acidic conditions. By comparing MPS-9 with other mesoporous

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**TABLE 1: Properties of Calcined Samples and Their BET Surface Areas before and after Treatments in Boiling Water for 60 or 120 h<sup>a</sup>**

sample	pore size (Å)	wall thickness (Å)	Si/M (M = Al, Ti)		BET surface area (m <sup>2</sup> /g)		
			in gel	in product	synthesized	treated, 60 h <sup>b</sup>	treated, 120 h <sup>c</sup>
SBA-15	76	34			910	308 (33%)	98 (11%)
MPS-9	85	46			936	559 (60%)	171 (18%)
MAS-9	80	50	40	89	947		918 (97%)
MAS-9			60	256	1087		904 (83%)
MAS-7	78	52	30	58	856		749 (88%)
MTS-9	80	48	20	75	980		720 (73%)
MTS-9			40	110	1155		638 (55%)
Al-SBA-15 <sup>d</sup>	84	35	30	35	905		789 (87%)
Al-SBA-15 <sup>e</sup>	92	32	50	56	886		695 (78%)
Al-SBA-15 <sup>f</sup>	74	31	40	825	1024		442 (43%)

<sup>a</sup> Pore size distributions were determined from N<sub>2</sub> adsorption isotherms, and the wall thickness was calculated as  $a_0 - \text{pore size}$  (where  $a_0 = 2 \times d \times (100/3)^{1/2}$ ). Values in parentheses are percentages of the residual surface areas of the treated samples, relative to their original surface areas.

<sup>b</sup> Treated in boiling water for 60 h. <sup>c</sup> Treated in boiling water for 120 h. <sup>d</sup> Prepared from the “post-synthesis” route, according to ref 19. <sup>e</sup> Prepared from the “pH-adjusting” route. <sup>f</sup> Prepared from the “direct synthesis” route, according to ref 18.

materials, the hydrothermal stability of mesoporous materials prepared from preformed zeolite nanoclusters is further investigated.

## Experimental Section

**Synthesis.** A typical synthesis procedure for MPS-9 is given as follows:

(1) The preformed precursor solution with Silicalite-I primary and secondary building units (Silicalite-I nanoclusters solution) was prepared by mixing 6 mL of tetrapropylammonium hydroxide (TPAOH) aqueous solution (20%–25%) and 5.6 mL of tetraethyl orthosilicate (TEOS) with 12 mL of H<sub>2</sub>O under stirring (SiO<sub>2</sub>/(TPA)<sub>2</sub>O/H<sub>2</sub>O molar ratios of 1/0.14/36). The mixture was then aged at 100 °C for 2–3 h and the final product is a clear solution.

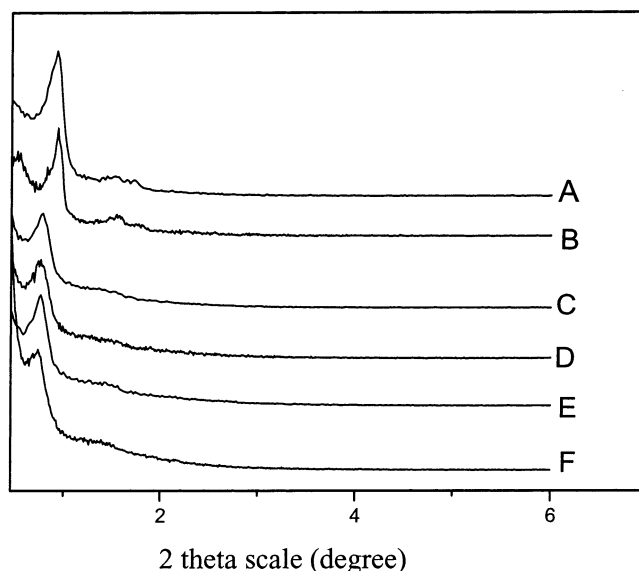
(2) A quantity (0.8 g) of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (Pluronic P123) was dissolved in 20 mL of H<sub>2</sub>O with 5 mL of HCl (10 M/L), followed by 7.0 mL of the preformed precursor solution obtained in step (1). The mixture was stirred at 40 °C for 20 h and then transferred into autoclaves 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.

MAS-7, MAS-9, and MTS-9 were prepared under similar conditions, in which zeolite Beta, ZSM-5, and TS-1 nanocluster solutions, respectively, were used instead of the Silicalite-I precursor. The detailed procedures have been reported in previous work.<sup>9,10</sup> In the preparation of MAS-9, aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) was chosen as the aluminum source instead of NaAlO<sub>2</sub>, which was used in our previous paper, because it was found that more Al species could be introduced into MAS-9 using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as the aluminum source in later investigations.

The samples of MAS-9 and MTS-9 with various aluminum and titanium contents were prepared by adjusting the amount of aluminum or titanium source in the initial gel mixture (Table 1). Two MAS-9 samples (with Si/Al ratios of 89 and 256) and two MTS-9 samples (with Si/Ti ratios of 75 and 110) were prepared. The MAS-9 sample with a Si/Al ratio of 89 and the MTS-9 sample with a Si/Ti ratio of 75 were used for discussion in this study, unless special reference is mentioned. Pure silica SBA-15 was prepared under conditions that were completely the same as those for the MPS-9 sample, except that the preformed precursor solution was replaced by a corresponding amount of TEOS.

Three Al-SBA-15 samples were prepared by various routes: “direct synthesis”,<sup>18</sup> “post-synthesis”,<sup>19</sup> and “pH-adjusting” that



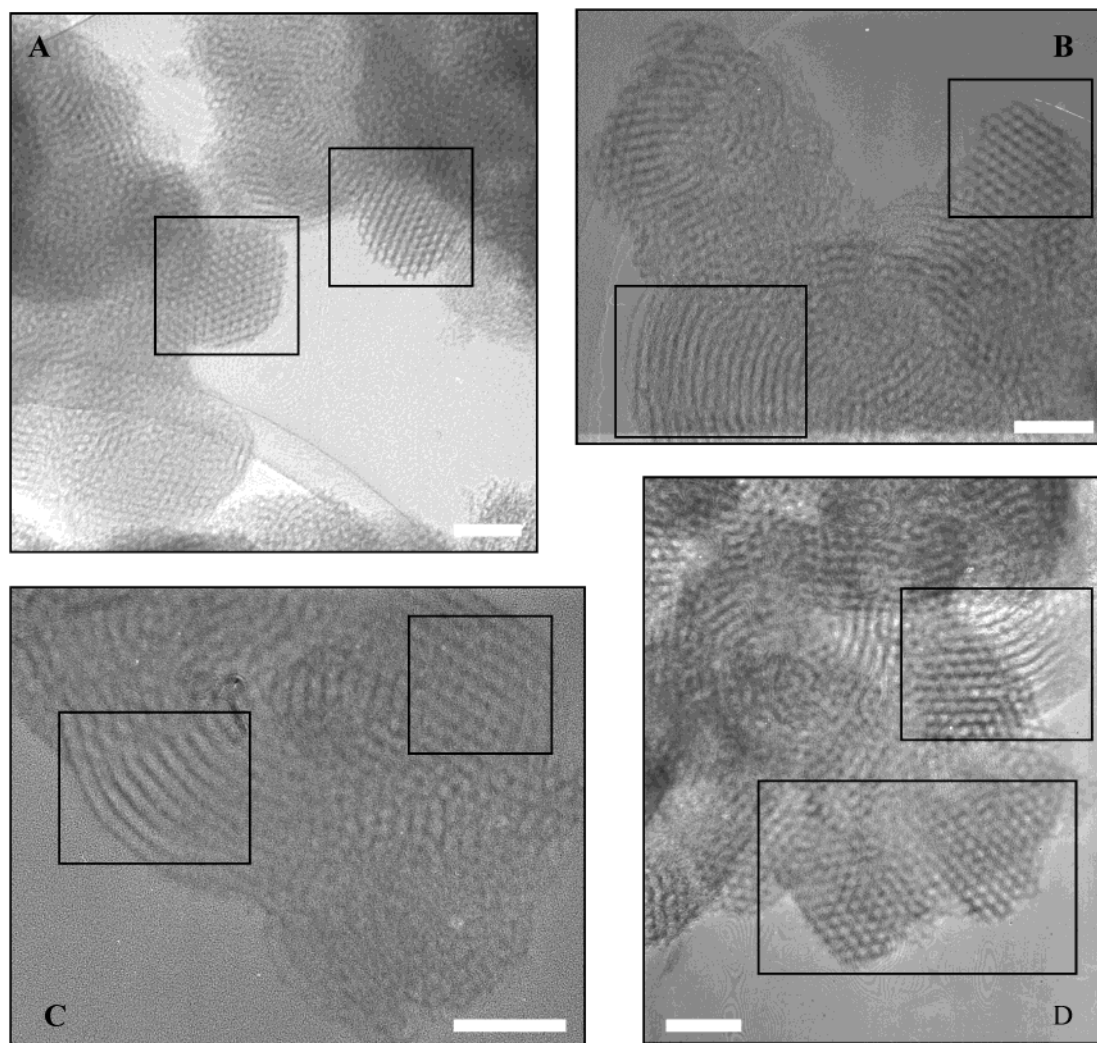
**Figure 1.** Powder XRD patterns of (A) SBA-15, (B) Al-SBA-15 prepared from the “direct synthesis” route, (C) MAS-9 with a Si/Al ratio of 89, (D) MTS-9 with a Si/Ti ratio of 75, (E) MPS-9, and (F) MAS-7 with a Si/Al ratio of 58.

was invented by our group and will be separately discussed in detail elsewhere.

**Characterization.** X-ray diffraction (XRD) patterns were obtained with a Siemens model D5005 diffractometer using Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) experiments were performed on a model JEM-2010F electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The sample isotherms for nitrogen at the temperature of liquid nitrogen were measured using a Micromeritics model ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model.<sup>27</sup> Al NMR spectra were recorded on a Bruker model MSL-300WB spectrometer, and the chemical shifts were referenced to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. The Si/Al and Si/Ti ratios of the samples were determined by the results of inductively coupled plasma (Perkin–Elmer model 3300 DV) and chemical analysis.

## Results and Discussion

XRD patterns and TEM images of various samples are shown in Figures 1 and 2, respectively. MAS-7, MAS-9, and MTS-9 have been reported<sup>9,10</sup> with a two-dimensional hexagonal



**Figure 2.** TEM images of (A) MAS-9 with a Si/Al ratio of 89, (B) MTS-9 with a Si/Ti ratio of 75, (C) MAS-7 with a Si/Al ratio of 58, and (D) MPS-9. Scale bars indicate 100 nm.

structure ( $P6mm$ ). MPS-9 shows a similar symmetry (see Figures 1E and 2D). It is found that all the mesoporous materials prepared from preformed zeolite nanocluster precursors, including MAS-9, MPS-9, MTS-9, and MAS-7, have some common characteristics that are different from SBA-15 or Al-SBA-15 that has been prepared from conventional precursors. One common trait is that the mesoporous materials prepared from preformed zeolite nanoclusters possess thicker mesoporous walls than SBA-15 (or Al-SBA-15) that has been synthesized under similar conditions. The thicknesses of the mesopore walls are calculated from the results of XRD and  $N_2$  adsorption experiments and are summarized in Table 1. On the other hand, the mesoporous materials prepared from zeolite nanoclusters are not as highly ordered as SBA-15 or Al-SBA-15. XRD results reveal that, compared to SBA-15 (Figure 1A, B), the samples prepared from zeolite nanoclusters have weaker intensities of the (100) peaks and the peaks that are associated with higher indices are not well-resolved (Figure 1C, F). Correspondingly, the TEM images (Figure 2) show that these materials do not have structures that are as well-ordered as SBA-15. For these samples, it is difficult to find large areas with a highly ordered structure, although hexagonal or striped arrays in small areas can be found sporadically (see rectangular areas in Figure 2).

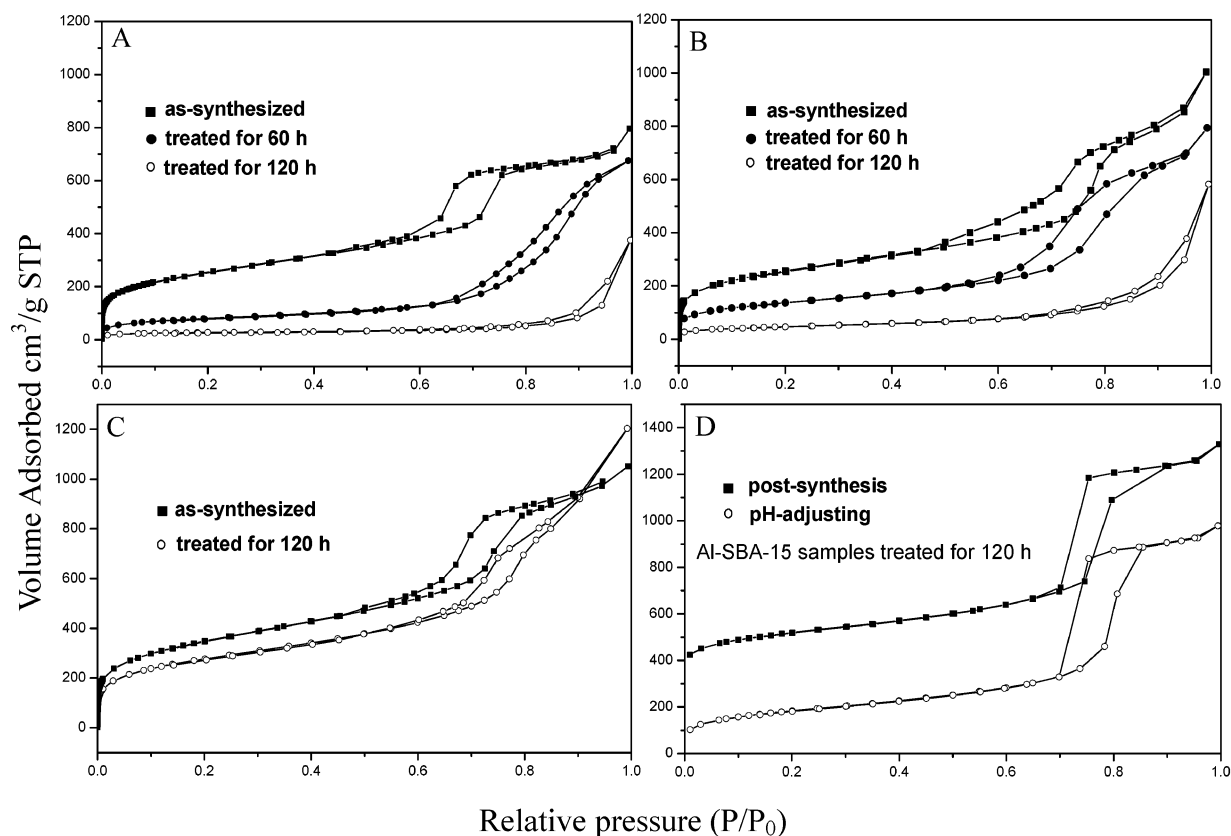
As discussed in the previous papers, these phenomena are attributed to the nanoclustered silicon species that have stronger rigidity and larger volumes than those nonstructured silicon

species used in the conventional synthesis of SBA-15 or Al-SBA-15. The assembly of these zeolite nanoclusters is relatively difficult and needs more space to connect to each other, which results in a thicker wall and some disorder in the products.<sup>9</sup>

MAS-9<sup>9a</sup> and MTS-9<sup>10</sup> have been reported with high hydrothermal stability. It was proposed that “zeolite-like connectivity” introduced by preformed nanoclusters possibly have a crucial role, and their thicker walls and distorted structures may be cooperative reasons. Because a large amount of tetra-alkylammonium ions ( $TPA^+$ ) is added into the synthesis system of MAS-9 and MTS-9, the salt effect is also a possible reason for their improved hydrothermal stability. Further unpublished investigation indicates that MAS-7 prepared from zeolite Beta nanoclusters also possesses high hydrothermal stability, similar to that of MAS-9.

Here, MPS-9 is prepared using a pure silica Silicalite-I nanocluster solution as the precursor. The solution has been characterized by de Moor et al. using small-angle X-ray scattering (SAXS) in detail, and two types of nanoparticles were observed: 2.8-nm-sized primary units and their aggregates ( $\sim 10$  nm).<sup>20</sup> A small amount of this solution can effectively induce the nucleation and crystallization of Silicalite-I in a template-free system. That is to say, the solution used here can be seen as a seed solution for Silicalite-I. Moreover, previous investigations show that “zeolite-like connectivity” can be introduced





**Figure 3.**  $N_2$  adsorption/desorption isotherms of calcined (A) SBA-15, (B) MPS-9, (C) MAS-9 with a Si/Al ratio of 89, and (D) Al-SBA-15 samples after various treatments in boiling water. For clarity, the isotherm of “post-synthesis” Al-SBA-15 is offset by 400 along the y-axis.

into the framework of mesoporous materials using such zeolite seed solution as a precursor.<sup>7–10</sup>

If factors such as zeolite-like connectivity, the salt effect, thicker walls, and a disordered structure are indeed the source of the super hydrothermal stability of MAS-7, MAS-9, and MTS-9, MPS-9 should be expected to be similarly hydrothermally stable, because it has all of the aforementioned characteristics.

XRD and  $N_2$  adsorption experiments are the most-common methods for the assessment of the hydrothermal stability of mesoporous materials. Comparatively, the results of  $N_2$  adsorption are more reasonable and sensitive. Therefore, the hydrothermal stability of various samples are evaluated in this study by observing their  $N_2$  adsorption behaviors before and after they are treated in boiling water for certain periods of time.

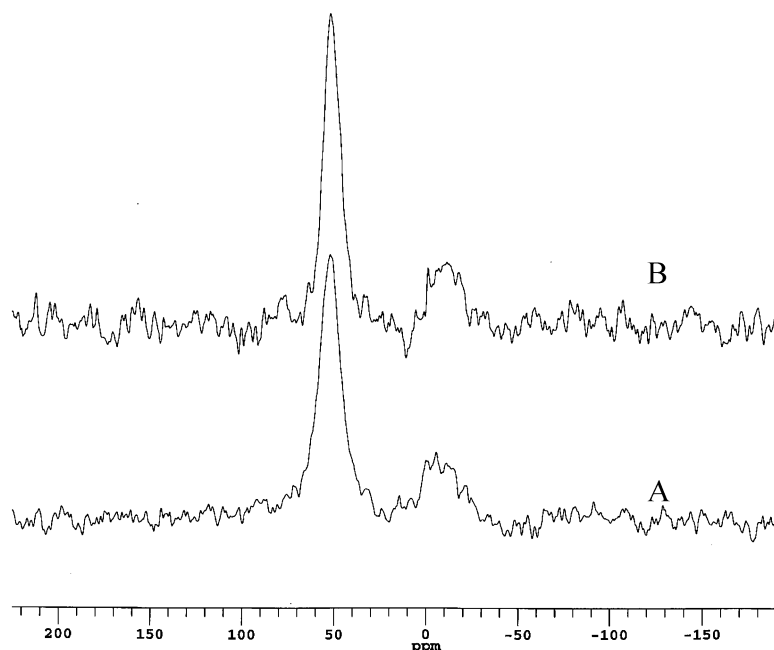
Figure 3 shows the  $N_2$  adsorption isotherms of various samples treated in boiling water for different periods. SBA-15 loses most of its large surface area (from 910  $m^2/g$  to 308  $m^2/g$ ; see Table 1), together with the high order in pore size distribution (Figure 3A) during the first 60 h in boiling water. Under the same treatment, MPS-9 retains ~60% of its original surface area (from 936  $m^2/g$  to 559  $m^2/g$ ; see Table 1) and the well-defined pore size distribution (Figure 3B). This result clearly indicates a better hydrothermal stability of MPS-9 than that of SBA-15. When the treatment is prolonged to 120 h, the mesostructures of both MPS-9 and SBA-15 are destroyed completely (Figure 3) with surface areas of <200  $m^2/g$  (Table 1).

Notably, in the cases of MAS-9, MTS-9, and MAS-7, much higher hydrothermal stability is observed. For example, MAS-9 (with a Si/Al ratio of 89) with a Brunauer–Emmett–Teller (BET) surface area of 947  $m^2/g$  shows an almost unchanged large surface area of 918  $m^2/g$  after the treatment in boiling

water for 120 h. The treated MAS-9 still exhibits a type IV isotherm, indicating the presence of uniform mesopores that become somewhat larger during the hydrothermal treatment (Figure 3C). MAS-7 has a high hydrothermal stability, similar to that of MAS-9 (Table 1). MTS-9 is also very hydrothermally stable, although not as stable as MAS-9. As shown in Table 1, MTS-9 (with a Si/Ti ratio of 75) maintains a majority of its surface area (from 980  $m^2/g$  to 720  $m^2/g$ ) during the treatment but its pore size distribution become much broader and more disordered.

From the result that MPS-9 is more hydrothermally stable than SBA-15 prepared under the same conditions, it is concluded that those well-known factors—including thicker walls, a disordered structure, the salt effect, and zeolite-like connectivity—are indeed helpful to improve the hydrothermal stability of mesoporous silica. It is unclear yet which one has the most important role among these factors or if maybe they act together. However, MPS-9 exhibits obviously weaker hydrothermal stability than MAS-9 (or MAS-7, MTS-9). This result suggests that there must be some other reasons contributing to the higher hydrothermal stability in the cases of MAS-9, MAS-7, and MTS-9. Otherwise, MPS-9 should exhibit a hydrothermal stability that is similar to that of these three samples, because they are all prepared from preformed zeolite nanoclusters with the aforementioned favorable factors.

The difference between MPS-9 and MAS-9 (or MTS-9) lies in that MPS-9 is pure silica whereas MAS-9 and MTS-9 are aluminum- and titanium-containing silica materials, respectively. It is noticed that, up to now, almost all the mesoporous materials with good hydrothermal stability (including Al-MCM-41,<sup>15</sup> the MSU-S family,<sup>7</sup> and the MAS family<sup>8–10</sup>) are aluminosilicates instead of pure silica. Therefore, the presence of heteroatoms (Al or Ti) could possibly be a factor that is crucial for higher



**Figure 4.**  $^{27}\text{Al}$  NMR spectra of MAS-9 with a Si/Al ratio of 89 (A) before and (B) after treatment in boiling water for 120 h.

hydrothermal stability. Lutz et al.<sup>17</sup> reported that the hydrothermal stability of zeolite Y could be enhanced by an external introduction of a nonstructural aluminum species on the surface of the inner pores of zeolite Y. Lutz proposed that the surface layer of aluminum-rich aluminosilicate could function as a protective layer in two ways. On one hand, it protects the zeolite framework from the attack of water molecules by blocking the terminal OH group and Si—O—Si bonds on the surface of zeolite. On the other hand, the negative charge of the aluminosilicate layer repels the access of  $\text{OH}^-$  ions, which catalyze the hydrolysis procedure of the zeolite framework. Shen and Kawi also employed this mechanism to explain the remarkable improvement of the hydrothermal stability of Al-MCM-41, compared to pure silica MCM-41.<sup>15</sup>

The  $^{27}\text{Al}$  NMR spectrum of MAS-9 (Figure 5A) shows that most Al species are four-coordinated in the framework and a small amount of Al species are six-coordinated on the non-framework sites. As proposed by previous works,<sup>15,17</sup> the remarkable hydrothermal stability of MAS-9 may be due, in part, to the Al species on the framework and, in part, to the Al species on the nonframework sites. After treatment in boiling water for 120 h, the  $^{27}\text{Al}$  NMR spectrum (Figure 5B) of MAS-9 does not show visible change, indicating that the Al species in the framework are stable and dealumination does not occur.

To give further evidence to prove that the higher hydrothermal stability of MAS-9 is directly related to the presence of aluminum, MAS-9 samples with various amounts of aluminum are prepared. As shown in Table 1, MAS-9 with a Si/Al ratio of 89 maintains 97% of its surface area after the treatment in boiling water for 120 h, whereas MAS-9 with a Si/Al ratio of 256 maintains ~83% of the surface area (from 1087  $\text{m}^2/\text{g}$  to 904  $\text{m}^2/\text{g}$ ) under the same treatment.

In addition, three Al-SBA-15 samples are prepared from various routes to prove that the doping of an Al species can effectively enhance the hydrothermal stability of mesoporous silica. It is very interesting to note that both Al-SBA-15 samples prepared from “post-synthesis”<sup>19</sup> and “pH-adjusting” routes (with Si/Al ratios of 35 and 56, respectively) are very stable in the hydrothermal condition. They retain >75% of their surface area and well-defined mesopore size distributions after the

hydrothermal treatment for 120 h (Figure 3D, Table 1). Although the “direct synthesis”<sup>18</sup> Al-SBA-15 sample contains a trace of aluminum (with an Al/Si ratio of only  $1/825$ ), it retains a surface area of 442  $\text{m}^2/\text{g}$  under the same conditions, which is also much more stable than pure silica SBA-15 (Figure 3A, Table 1).

In our previous paper,<sup>9a</sup> it was reported that SBA-15 and Al-SBA-15 have similar hydrothermal stability. However, later investigations show that the Al-SBA-15 sample used in that paper had very little aluminum content. Here, it should be claimed that Al-SBA-15 is indeed more hydrothermally stable than pure silica SBA-15, as long as there is enough aluminum in the sample, and the ability to retain mesostructure is directly associated with the amount of aluminum present. In the scale of the Si/Al ratio discussed in this study (Si/Al > 30), the greater the aluminum content, the higher the hydrothermal stability.

Compared to Al-SBA-15 with a similar aluminum content, MAS-9 shows a slightly stronger ability to keep the large surface area (Table 1), and this may be due to the additional favorable factors (thicker wall, salt effect, disordered structure, and zeolite-like connectivity) in the case of MAS-9 besides the presence of an Al species.

Notably, it is not easy to synthesize Al-SBA-15 with high aluminum contents by the “direct synthesis” method. For example, the Si/Al ratio in the gel mixture for the synthesis of the Al-SBA-15 sample used in this study is 40, whereas the Si/Al ratio in the product is 825. This is because of the acidic synthesis conditions, in which Al species exist in the cationic form, rather than as their corresponding oxo species, and cannot enter the framework of SBA-15. In contrast, Al species can be introduced into the mesostructure easily in our case, using preformed zeolite nanoclusters solution as precursors, and MAS-9 with relatively high aluminum contents can be obtained.<sup>9</sup> When the Si/Al ratio in the initial gel for MAS-9 is 40, the Si/Al ratio is 89 in the product. The post-synthesis reported by Ryoo<sup>19</sup> and the pH-adjusting referenced here are more effective ways for the preparation of aluminum-rich mesoporous silica that is synthesized from an acidic medium.

As for MTS-9, it shows a moderately high hydrothermal stability, which is somewhat weaker than that of MAS-9 and stronger than that of MPS-9 (Table 1). It is attributed to the

neutral framework of MTS-9, in contrast to the negatively charged framework in the case of MAS-9. As proposed by Lutz,<sup>17</sup> the negatively charged aluminosilicate species contribute to the high stability by repelling the attack of OH<sup>-</sup>. However, this mechanism does not work in the case of MTS-9, because of its neutral framework. On the other hand, a small amount of extra-framework Ti species, which are likely produced during the calcination process, can protect the framework from the attack of water molecules by blocking the terminal OH group and Si—O—Si bonds on the surface. Thus, MTS-9 shows a moderate hydrothermal stability. MTS-9 samples with various amounts of titanium show different hydrothermal stabilities (Table 1), just as in the case of MAS-9 and Al-SBA-15, confirming that the hydrothermal stability of MTS-9 is related to the presence of a Ti species.

## Conclusions

Ordered mesoporous pure silica, designated as MPS-9, is successfully synthesized from the assembly of preformed Silicalite-I nanoclusters with a triblock copolymer surfactant. By comparing MPS-9 with other mesoporous materials, it is proved that the high hydrothermal stability of mesoporous aluminum silicates (MAS-9, MAS-7) and titanium silicates (MTS-9) is mainly due to the presence of heteroatoms (Al or Ti), although previously proposed reasons, such as “thicker walls”, a “disordered structure”, the “salt effect”, and “zeolite-like connectivity”, also have important roles. MAS-9 is also found to be more hydrothermally stable than MTS-9, because of the different types of heteroatoms that are incorporated. In addition, the amount of heteroatom substitution is another factor that can influence the hydrothermal stability.

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