Ammonia Hydrothermal Treatment on Mesoporous Silica Structure Synthesized from Acidic Route

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We report a post-synthesis procedure-ammonia hydrothermal treatment- to improve the structural features of surfactant-templated mesoporous silica synthesized from acidic route. The mesoporous products after this treatment become highly ordered and hydrothermally stable and the original hierarchical morphology are preserved.

Mesoporous silica can be synthesized in either the alkaline route[1,2] or the acidic route.[3,4] In the acidic route, the typical silica source is silicon alkoxides, which were hydrated to a more fuzzy and soft network.[5] The corresponding interaction between surfactant and silica framework ($S^+X^-I^+$) is weaker than the S^+I^- interaction in the alkaline route; and thus it can usually lead to many interesting topological constructions.[6-9] However, the mesoporous silica materials from acidic route are usually less stable, while in alkaline route, surfactant and silicates organize by the strong S^+I^- electrostatic interactions and form highly condensed and compact structure, especially after hydrothermal treatment.[10,11] But for acidic route, the nanostructure normally collapses during hydrothermal treatment. Thus, it would be desirable to find a single-step way for improving structure order and stability of the mesoporous silica from acidic route.

Here we report a novel two-step procedure to manufacture mesoporous silica that is highly ordered and stable. In the first step, the mesoporous materials with gyroidal spheres and silica ropes from the quaternary ammonium halides (C_nTMAX; n = 16 or 18, X = Cl or Br)-tetraethyl orthosilicate (TEOS)-nitric acid (HNO_3) system, where the pH < 1, at room temperature under a shear flow.[7] The resultant white silica product was recovered by filtration, washed with water to remove the HNO_3 and dried at 100 °C. In the second step, 1.0 g dried acid-made sample was added into a 50.0 g 1.0 M NH_4OH aqueous solution, sealed in an autoclave, and heated at 100 or 150 °C for 2 days(pH about 11.0). The surfactants were then removed by calcination at 560 °C for 6 h in air.

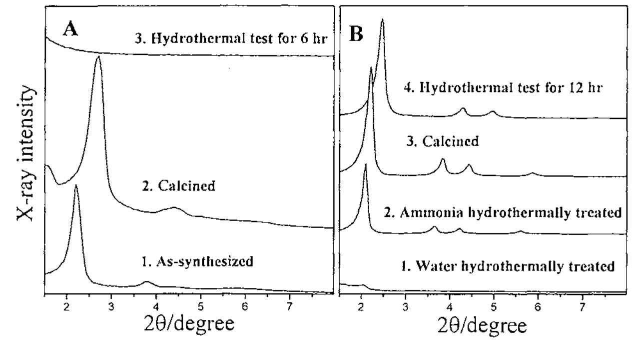


Figure1. XRD patterns of the as-synthesized, calcined and hydrothermal test mesoporous materials prepared from $C_{16}TMAB$-HNO_3-TEOS-H_2O systems with and without ammonia hydrothermal treatment at 100 °C. A. without ammonia hydrothermal treatment, B. with ammonia hydrothermal treatment.

The X-ray diffraction spectra for a series of samples are shown in Figure 1. The samples without ammonia hydrothermal treatment are shown in Figure 1A. Figure 1A1 shows only two broad peaks for the as-synthesized sample; which is typical for acid route. After calcination, the structure becomes even worse as shown in Figure 1A2. And a hydrothermal test of the calcined Figure 1A2 sample in boiling water for 6 h leads to a complete collapse of the structure (Figure 1A3).

The XRD spectra for samples with ammonia hydrothermal treatment are in Figure 1B. When we just perform a direct hydrothermal treatment in the mother solution or water, the meso-structure collapses as shown in Figure 1B1. The surfactants would be extracted out to hot water and thus results in the collapse of the nanochannels. Only with the ammonia hydrothermal treatment could one obtain a much-improved structure (Figure 1B2) showing 4-5 sharp XRD peaks. After calcination, the structure becomes even better as shown in

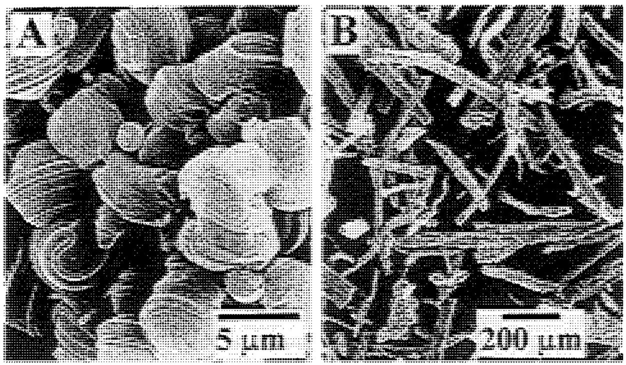


Figure2. The SEM micrographs of different hierarchical structure after ammonia treatment at 100 °C. A. Gyroidal spheres, B. Silica ropes.

Table 1. The physical properties of the mesoporous materials synthesized from $C_{18}TMACl$, $C_{16}TMAB$-TEOS-HNO_3-H_2O systems with and without ammonia hydrothermal treatment

Samples[a]	XRD d_{100} /nm	Wall thickness[b] /nm	Pore size[c] /nm	Q_3/Q_4	N/C ratio[d]
C16-UH	3.69	1.48	2.78 (1.20)	0.80	0.119
C16-100	3.95	1.93	2.63 (0.10)	0.58	0.062
C16-150	4.82	2.44	3.36 (0.18)	0.39	0.061
C18-UH	4.10	1.23	3.50 (1.50)	1.02	0.10
C18-100	4.20	1.88	2.96 (0.12)	0.62	0.052
C18-150	5.60	2.41	4.06 (0.18)	0.38	0.051

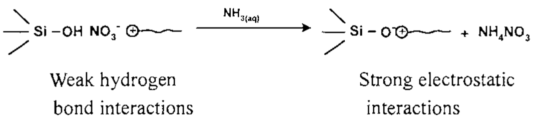
[a] UH: without the ammonia hydrothermal treatment; 100, 150 indicates the ammonia hydrothermal treatment at 100 or 150 °C. [b] Wall thickness = $2/\sqrt{3}*d_{100}$ - pore size [c] The values in parenthesis are full width at half maximum (FWHM) of the pore size distribution. [d] The N/C ratio of $C_{16}TMAB$ and $C_{18}TMACl$ is 0.061 and 0.055.

Figure 1B3 with a d-spacing shrinkage of only about 0.1 nm. Furthermore a hydrothermal test of the calcined 1A2 sample in boiling water for 12 h preserves the structure almost intact. (Figure 1B4). The SEM micrographs of the mesoporous materials after the ammonia hydrothermal treatment at 100 °C show that the hierarchical morphologies, gyroidal spheres[5] and silica ropes,[7] are largely preserved.(Figure 2)

Comparison of the physical properties (d_{100} value, pore size, wall thickness) of these materials of C_{16}TMAB and C_{18}TMACl with and without ammonia hydrothermal treatment are listed in Table 1. All these mesoporous materials possess high surface area of about 1000-800 m^2/g and decreases with the increase of hydrothermal temperature. Without the ammonia hydrothermal treatment, the pore size distribution is rather broad (FWHM about 1.2 ~ 1.5 nm) due to some structural collapses during calcination. But the ammonia hydrothermal treatment leads to the mesoporous materials with sharp distribution with FWHM of only 0.10-0.18 nm, which is as narrow as the ones obtained from alkaline route.[11] Table 1 also shows that the d-spacing, pore size and wall thickness of the mesoporous materials increase with the hydrothermal temperature.

To check the silica condensation taking place during the hydrothermal treatment, we measured the ^{29}Si-MAS NMR of the as-synthesized materials. By deconvoluting the solid state ^{29}Si MAS NMR spectra, the Q_3/Q_4 ratios are listed in Table 1. For both C_{16}TMAB and C_{18}TMAB samples, the Q_3/Q_4 ratio clearly decreases upon the ammonia hydrothermal treatment and the higher temperature the lower the ratio. This indicates that hydrothermal treatment causes the less-condensed silica species to rearrange into an well-ordered structure with a thicker wall, which leads to higher thermal and hydrothermal stability.

For estimating the interaction strength between the silica framework and templates, we immersed the as-synthesized samples into ethanol at 50 °C for 5 h to examine the extraction of surfactants. Figure 3A shows the TGA traces of the sample without ammonia hydrothermal treatment. The weight loss in the temperature range from 200 to 450 °C is due to surfactant removal. About 85 % surfactant of the sample obtained from acidic condition can be easily extracted by hot ethanol. This means the interaction between surfactant and silica is indeed weak for the acid-made sample. Figure 3B shows the samples with ammonia hydrothermal treatment, the surfactant is resistant to solvent extraction. Thus we assume the interactions between the surfactant and silicate after ammonia hydrothermal treatment would be transformed as:



$$\equiv Si-OH\ NO_3^-\ \oplus\!\sim\!\sim \xrightarrow{NH_{3(aq)}} \equiv Si-O^{-}\oplus\!\sim\!\sim + NH_4NO_3 \qquad (1)$$

The stronger electrostatic interactions between the negative charge silicate and the surfactant cationic headgroup make the organic surfactant resist elimination upon solvent extraction and by hot water during hydrothermal reaction.

To further provide the quantitative evidence for the removal of the counterion (NO_3^-), the elemental analysis was performed to examine the N/C elemental ratio of the as-synthesized mesoporous materials before and after ammonia hydrothermal treatment. In Table 1, the N/C molar ratio of the mesoporous materials before ammonia hydrothermal treatment is twice of the sample after ammonia treatment. And the N/C ratio of the sample after ammonia treatment is the same with that of surfactant template. These results indicate that a nitrate counterion, existing between surfactant molecules and framework silica under acid condition is completely removed and the surfactant structure is still intact after ammonia hydrothermal treatment at 100 and 150 °C.

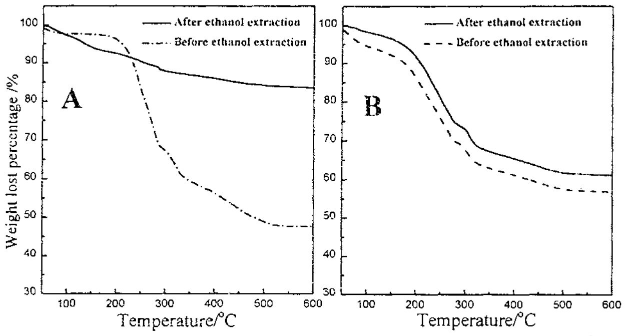


Figure3. The TGA plots of the as-synthesized mesoporous materials from C_{16}TMAB before and after ethanol extraction process at 50 °C for 5 h. A. Without ammonia hydrothermal treatment, B. With ammonia hydrothermal treatment.

This ammonia hydrothermal treatment can also be successfully used to refine the mesoporous materials synthesized from different acid sources (such as, HCl, HBr or H_2SO_4). While using either water or NaOH solution in the post-synthesis treatment, the structure of the materials collapses or the pH is difficult to control. Therefore, the fine pH tuning is important for restructuring the mesoporous materials,[12,13] and a buffered ammonia solution provides the right pH value.

This two step process combines the advantages of the acid route and the basic hydrothermal route. We believe that many desired morphologies of mesoporous materials with high order and stability can be successfully synthesized by this process. We also note that the large expansion of nanochannels also sometimes leads to further morphological construction.[14] These rich morphological transformation could lead to versatile applications in low dielectric film, optical, and electronic materials where the morphology matters.[15]

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