

Synthesis of Highly Ordered Mesoporous Silicon Oxynitride with High Nitrogen Content

Keshu Wan, Qian Liu,* and Cunman Zhang

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, P. R. China

(Received January 6, 2003; CL-030010)

Mesoporous silicon oxynitride materials, which were highly ordered and had high nitrogen content, were prepared by heat treatment of fresh SBA15 precursors in flowing ammonium at high temperatures.

Base catalysts have attracted great attentions in recent years because they play an important role in the production of fine chemicals.¹⁻³ Compared to the vast number of known solid acid catalysts, reports of new solid base materials are rare, so new base solid catalysts are highly desirable. In the 1990s, it was found that the nitrogen incorporation is an effective way to increase the surface basicity. Thorough treating amorphous silicate,^{4,5} aluminum orthophosphate,⁶ zirconium phosphohate,⁷ and aluminum vanadate⁸ using ammonia at temperatures of 1000-1100 °C, a series of base catalysts were made. Although the nature of the base site is still under discussion, it was found that the basicity enhancement was directly connected to the nitrogen content.⁷

Considering the high surface area and the ordered pore structure, crystalline microporous zeolites⁹ and ordered mesoporous silica^{10,11} were treated in ammonium or nitrogen either, but because of the crystallization of zeolites and the instability of ordered mesoporous silica, the nitridation of them was quite difficult and the nitrogen content was low. Recently, porous silicon nitride as a superbase catalyst was made using silicon tetrachloride and ammonium, but their pores were not ordered.^{12,13} In the present paper, considering the good structural stability of SBA15, an ordered mesoporous silica reported by Stucky et al.,¹⁴ we synthesized a new mesoporous silicon oxynitride from SBA15, which was highly ordered and had high nitrogen content.

The SBA15 precursors were synthesized by a sol-gel modified method according to the following procedure; in a typical preparation route, 4 g of P123 [(EO)₂₀(PO)₇₀(EO)₂₀] was dissolved into the solution of 30 mL deionized water and 120 mL of 2 M HCl, followed by slowly adding of 9.15 mL of tetraethylorthosilicate (TEOS, >98%). The mixture had been maintained at 40 °C for 24 h under a stirred condition, then it was loaded into an autoclave and heated at 100 °C under autogenous pressure for

48 h. The solid product was recovered by filtration, washed with deionized water and dried at 80 °C for 24 h in a vacuum dryer, and the product was defined as fresh SBA15 precursors. SBA15 was made from calcining the fresh SBA15 precursors at 550 °C for 24 h.

Mesoporous silicon oxynitride (MSON) was accomplished by heating fresh SBA15 precursors in ammonia in a flow-through quartz tube furnace. The flow rate of ammonia was 500 mL/min, and the volume of the tube was 4.5 L. The precursors were heated at 5 °C/min to the final temperatures (1000, 1050, 1100 °C) and then held for 18 h. According to the treated temperatures, we defined the synthesized samples as MSON1, MSON2, and MSON3. The quartz tube was evacuated several times and flushed with N₂ to remove air before the run was started.

Table 1 listed the physical properties of SBA15 and three treated samples. As expected, the nitrogen content¹⁵ in MSON materials increases with nitridation temperature. The sample MSON3 treated at 1100 °C had the highest nitrogen content, 24.3 wt%, which could be formally written as SiO_{0.67}N_{0.89}. The high nitrogen content and evolution of the nitrogen content could be seen from infrared spectra (Figure 1). In SBA15 precursor, the -1080 cm⁻¹ and -800 cm⁻¹ peaks corresponds to a Si-O-Si stretching vibration in a fully connected three-dimensional framework. With increasing treated temperature and nitrogen content, the peak at 1080 cm⁻¹ gradually lowers and the band at

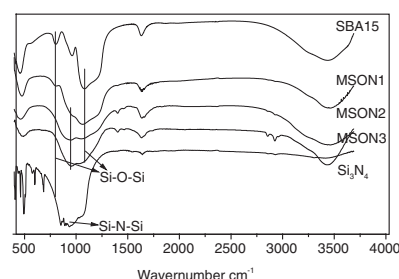


Figure 1. Infrared spectra (in KBr) of some samples tested.

Table 1. Physical property of four typical samples

Sample	N wt%	Composition	S_{BET} /m ² g ⁻¹	V_{BJH} /cm ³ g ⁻¹	$D_{\text{BJH}}^{\text{a}}$ /Å	d_{100} /Å	a_0^{b} /Å	$D_{\text{Wall}}^{\text{c}}$ /Å
SBA15	—	—	685	1.07	65	92.3	106.7	41.7
MSON1	14.3	SiO _{1.16} N _{0.56}	454	0.87	65	83.2	96.2	31.0
MSON2	20.6	SiO _{0.84} N _{0.78}	390	0.79	64	80.1	92.6	28.6
MSON3	24.3	SiO _{0.67} N _{0.89}	350	0.67	62	77.8	89.9	28.0

^aThe pore diameter calculated from the desorption isotherm. ^bThe lattice parameter, from the XRD data using the formula. $a = 2d_{(100)}/\sqrt{3}$. ^cWall thickness = $a_0 - D_{\text{BJH}}$.

-800 cm^{-1} gradually disappears, while at the same time, a band around -935 cm^{-1} develops, which should be a transition between Si-O-Si and Si-N-Si, such as O_3SiN , O_2SiN_2 , OSiN_3 , and SiN_4 . All this information reflect the formation of SiN_xO_y tetrahedron at the expense of SiO_4 tetrahedron.

Not only did the MSON materials have high nitrogen content, they also kept the highly ordered mesoporous structure. We found that the structure of MSON was not significantly collapsed. Although the surface area, pore volume were decreased with the increase of temperature, the MSON still retained the mesoporous structure, large BET surface area, large pore volume, and narrow pore distribution (Table 1 and Figure 2). Figure 2b shows the LAXRD diffraction patterns of two samples. The MSON3 has good diffraction patterns with three reflections, which are typical in ordered mesoporous silicas. After nitridation, the broader and less intense main peak (100) represents lower crystallinity, and the 2-theta position shift to a higher value indicating a contraction of the lattice caused by the higher temperature treatment that coincides with the results shown in Figure 2a, decreasing in both surface area and pore volume. Although the (110) and (200) peaks, which indicates the long range ordering of the mesoporous structure, were less intense, they still could be clearly seen. HRTEM images (Figure 3) fully correlate with the LAXRD results, even MSON3 show highly regular hexagonal arrays of uniform pores and channels, and the selected area diffraction was strong either.

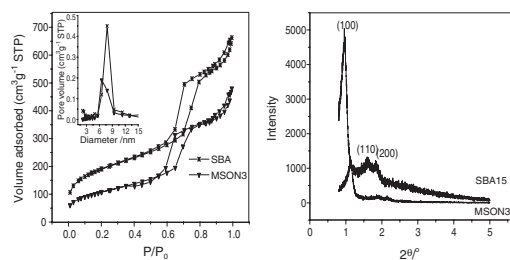


Figure 2. (a) Nitrogen adsorption-desorption isotherms and BJH pore size distribution of SBA15 and the treated sample MSON3. (b) Low-angle XRD patterns of SBA15 and the treated sample MSON3.

Although the BET surface area of MSON3 is just a half of the SBA15, why does it still have such ordered structure (Figure 2 and Figure 3)? The reason could be explained by the high temperature structure rearrangement of SBA15. A main character of SBA15 is its bimodal structure: there are many micropores due to the partial occlusion of PEO chains into the silica walls which form some connections between the mesopores.^{16,17} When heated in high

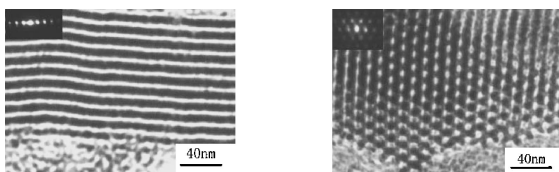


Figure 3. HRTEM images of SON3.

temperatures, the micropores in the walls collapsed first, and the collapse strengthened the wall in return, while the mesopore kept uncollapsed. The diminishment of micropore decreased the surface area greatly, but it could not disrupt the ordered mesoporous structure. The phenomenon could be further confirmed by the shrinkage of the lattice and wall thickness. Although the lattice of the MSON shrunked greatly, the pore size was almost not changed. The fresh SBA15 precursor has the wall thickness of 4.2 nm, while the wall thickness of MSON3 is just 2.8 nm (Table 1), and such a great shrinkage of the wall would be inconceivable if the collapse of micropore in the wall of SBA15 did not occur.

In conclusion, a new class of highly ordered, and high nitrogen content mesoporous silicon oxynitride (MSON) materials, on the basis of heat-treatment of fresh SBA15 precursors in flowing ammonium at high temperature was introduced, and the high temperature structure arrangement was explained. Considering the high nitrogen content and the ordered mesopore structure, this class of materials may be an effective base catalyst in future. Besides, transition metal oxynitride can be implanted in the pore of these materials and expand the catalytic properties, which were undergone in our group now.

References and Notes

- H. Hattori, *Chem. Rev.*, **95**, 537 (1995).
- Y. Ono and T. Baba, *Catal. Today*, **38**, 321 (1997).
- H. Hattori, *Stud. Surf. Sci. Catal.*, **78**, 35 (1993).
- P. W. Lednor and R. de Ruiter, *J. Chem. Soc., Chem. Commun.*, **1991**, 1625.
- P. W. Lednor, *Catal. Today*, **15**, 201 (1992).
- J. J. Benftze, J. A. Odriozola, R. Marchand, Y. Laurent, and P. Grange, *J. Chem. Soc., Faraday Trans.*, **91**, 4477 (1995).
- N. Fripiat, V. Parvulescu, V. I. Parvulescu, and P. Grange, *Appl. Catal. A*, **181**, 331 (1999).
- H. M. Wiame, C. M. Cellier, and P. Grange, *J. Phys. Chem. B*, **104**, 591 (2000).
- S. Ernst, M. Harmann, S. Sauerbeck, and T. Bongers, *Appl. Catal., A*, **200**, 117 (2000).
- J. E. Haskouri, S. Cabrera, F. F. Sapina, J. Latorre, C. Guillem, A. B. Porter, M. D. Marcos, and P. Amomos, *Adv. Mater.*, **13**, 192 (2001).
- M. P. Kaor and S. Inagaki, *Chem. Lett.*, **32**, 94 (2003).
- S. Kaskel, D. Farrusseng, and K. Schlichte, *Chem. Commun.*, **2000**, 2481.
- S. Kaskel and K. Schlichte, *J. Catal.*, **201**, 270 (2001).
- D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.*, **120**, 6024 (1998).
- Nitrogen content was analyzed by CNH elemental analysis. CNH analysis (Model 2400 CNH Elemental Analyzer, Perkin-Elmer, Norwalk, CT) was performed at a temperature of 1000 °C, with oxygen and high temperature oxidant ($\text{Ag}_2\text{WO}_4 + \text{MgO}$) as additives.
- I. Clerc, M. Davidson, and P. Davidson, *J. Am. Chem. Soc.*, **122**, 11925 (2000).
- A. Galarneau, H. Cambon, F. D. Renzo, and F. Fajula, *Langmuir*, **17**, 8328 (2001).