Chinese Chemical Letters Vol. 12, No. 8, pp 737 – 740, 2001 737

Synthesis of Mesoporous Silica and Ti-containing Molecular Sieves *via* A Novel Assembly

Jing XIN, Ji Shuan SUO*, Xiao Ming ZHANG

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000

Abstract: Thermally stable mesoporous silica and Ti-containing molecular sieves have been synthesized at mild temperature using low-cost and biodegradable---amphoteric tetradecyl betaine as template. The physicochemical characterizations proved that Ti(Ⅳ) could be incorporated in the mesoporous struture.

Keywords: Synthesis, meosoporous silica and Ti-containing molecular sieves, amphoteric tetradecyl betaine, novel assembly.

Although titanium silicate-1 (denoted TS-1) is an effective catalyst for the selective oxidation of organic substrates[1,2], the substrates that can be oxidized by TS-1 are limited to species having kinetic diameters < 6 Å. However, the recently discovered silica-based mesoporous molecular sieve offers new opportunities for the preparation of large-pore TS-1 analogs capable of transforming larger organic molecules. The Ti-containing mesoporous molecular sieve catalysts thus obtained, are promising in the heterogeneous catalysis[3-7]. As a result, there has been a growing interest in synthesis of mesoporous materials and analogs in recent years[3-11].

So far, ionic and neutral surfactant including neutral alkylamine[8], polyethylene oxide[9], gemini[10], and amphiphilic triblock copolymer[11] have been most commonly used as templates for directing the formation of mesoporous. Here, we report a low-cost and biodegradable amphoteric templating route to mesoporous materials. Using low-cost and biodegradable amphoteric tetradecyl betaine ($C_{14}H_{29}N^{+}(CH_3)_2CH_2COO^{-}$) as template, we successfully synthesized the mesoporous silica and Ti-containg molecular sieves under acidic conditions at mild temperature.

In a typical synthesis, the appropriate amount of tetradecyl betaine (TB) was dissolved in water, when the turbid mixture became clear, aqueous HCl was added to adjust the pH to 2.2. With magnetic stirring, the designed amount of tetraethylorthosilicate (TEOS) was introduced dropwise into the above mixture. The final composition of the reaction mixture was 1 TEOS : 0.35 TB : 0.000173 HCl:40.5 H_2O. After allowing the resulting gel to age at 323 K under gentle stirring for 24 h, the resulting solid product was recovered by filtration, washed with diluted ethanol. The product was finally air-dried and calcined in air at 973 K for 6 h. If designed amounts of tetrabutyl orthotitanate (TBOT) were dropped into the reaction system mentioned above following the TEOS, the Ti-containing mesoporous molecular sieves (denoted Ti-STO) with different titanium contents could be obtained.

Figure 1 The XRD patterns of calcined Si-STO (A) and Ti-STO (B) samples

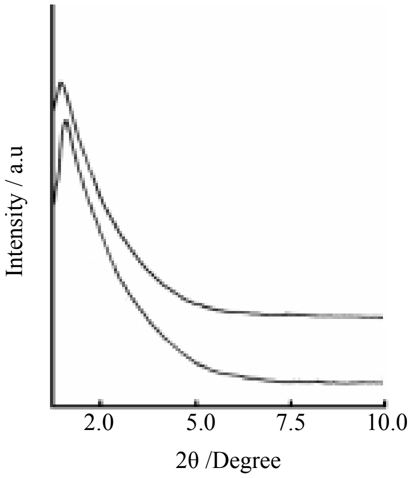


Figure 2 TEM image of calcined STO Si-STO (A) and Ti-STO (B) samples

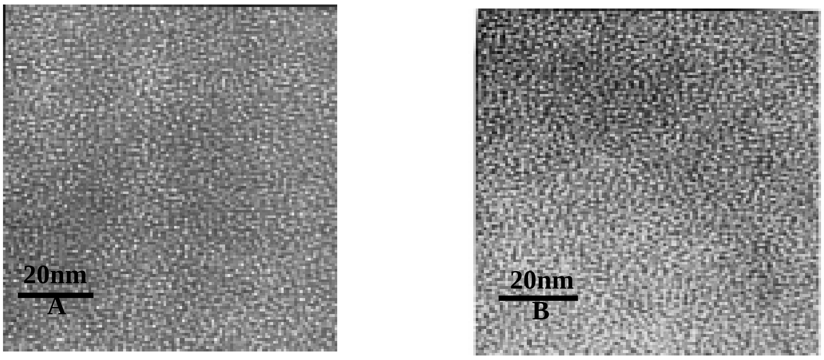


Figure 1 shows the powder X-ray diffraction patterns (XRD, Rigaku, D/Max-2400, with Cu-Ka radiation; λ=0.15418 nm) of the calcined Si-STO and Ti-STO-4 samples, both of them clearly exhibits an intense reflection at low angle, while higher order Bragg reflections are not resolved. The absence of higher order reflections is attributed to the lack of long-range order or finite size effects[10]. Furthermore, the XRD pattern of the sample obtained showed the typical of MSU wormhole structures assembled from polyethylene oxide as template[9]; this result was supported by the transmission electron microscopy (Philips CM-120) in **Figure 2**. In addition, upon introducing of transition-metal atoms, the d_{100} spacing shifted to the higher value, this may be the

reason that the introducing of Ti can cause an improvement of the silica structures.

Table 1 lists the chemical compositions and some structure properties of the calcined STO mesoporous molecular sieves. For calcined Ti-STO mesoporous materials, the Si/Ti rations were close to those used in the precursor gels, indicating that the efficient incorporation Ti in the silica STO mesophase.

Table 1 Synthesis parameters and characterization results

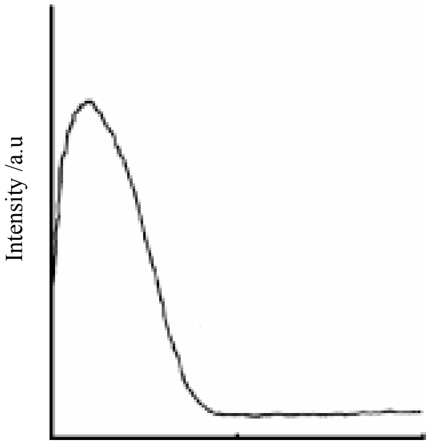
Sample	SiO_2/TiO_2		d_{100}/nm	BJH pore size/nm	$S_{BET}/m^2/g$
	Gel	Product			
Si-STO	∞	∞	5.31	3.60	1013
Ti-STO-1	100	103	5.58	3.62	985
Ti-STO-2	75	77	5.56	3.62	994
Ti-STO-3	50	53	5.56	3.64	992
Ti-STO-4	25	26	5.61	3.65	997

Figure 3 shows the diffuse reflectance (DR) spectrum (Shimadzu, UV-360) of Ti-STO-4 in the ultraviolet-visible region. It is can be clearly seen that the absorption band at *ca.* 330 nm (corresponding to anatase TiO_2) is absent, indicating that titanium ions contained in Ti-STO-4 are highly disprsed in the silica-based framework. This result was also supported by the FT-IR spectra (Bruker, IFS 120) and the Raman spectra (Nicolet, Raman 910).

In this study, the BET surface areas was calculated on the basis of the nitrogen adsorption/desorption (Micromertics ASAP 2010 sorptometer), the titanium content in the framework of the mesoporous molecular sieves were carried out on an ARL 3520 ICP atomic emission spectrometer.

As mentioned above, the mesoporous silica and Ti-containing molecular sieves were synthesized by a novel templating scheme. The physicochemical characterization confirmed that in the Ti-STO samples obtained, Ti was found in the framework positions.

Figure 3 The UV-Vis DR spectrum of Ti-STO



Systematic investigations for the mechanisms in the synthesis and catalytic properties of the titled materials are still in progress and will be reported in the full paper following this letter.

References

1. D. R. C.Huybrechts, L.De Bruycker, P. A. Jacobs, *Nature*, **1990**, *345*, 240.
2. M. G. Clerici, U. Romano, *US Patent* 4,410,216, **1990**.
3. A. K. Keiko, T. Takashi, *J. Chem. Soc. Chem. Commun.*, **1996**, 145.
4. W. Zhang, M. Froba, J. Wang, P. T. Tanev, J. Wong, T. J. Pinnavaia, *J. AM. Chem. Soc.*, **1996,** *118*, 9164.
5. A. Sayari, *Chem. Mater.,* **1996**, *8*, 1840.
6. P. T. Tanaev, M. Chibwe, T. J. Pinnavaia, *Nature*, **1994**, *368*, 321.
7. T. R. Pauly, Y. Liu, T. J. Pinnavaia, S. J. L. Billinge, T. P. Rieker, *J. AM. Chem. Soc.*, **1999,** *121*, 8835.
8. P. T. Tanev, T. J. Pinnavaia, *Science,* **1995,** *267,* 865.
9. S. A. Bagshaw, E. Prouzet, T. J. Pinnavaia, *Science,* **1995**, *269*, 1242.
10. Q. S. Huo, R.Leon, P. M. Petroff, G. D. Stucky, *Science*, **1995**, *268*, 1324.
11. D. Y. Zhao, J.L. Feng, Q. S. Huo, N. Melosh, G. H. Fredri Ckson, B. F. Chmelka, G. D. Stucky, *Science,* **1998,** *279,* 548.

Received 14 August, 2000
Revised 8 May, 2001