Chinese Chemical Letters Vol. 12, No. 8, pp 741 – 744, 2001

Determination of Average Wall Thickness of Mesoporous Silica

Zhi Hong LI[1], Yan Jun GONG[1], Dong WU[1], Yu Han SUN[1]*, Jun WANG[2], Yi LIU[2], Bao Zhong DONG[2]

[1]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O.Box 165,Taiyuan 030001

[2]Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, P.O.Box 918, Beijing 100039

Abstract: Small Angle X-ray Scattering (SAXS) experiment using Synchrotron Radiation as X-ray source was used to determine the average wall thickness of mesoporous silica prepared by condensation of tetraethylorthosilicate (TEOS) using non-ionic alkylpolyethyleneoxide (AEO_9) surfactant as templates. The results agreed with that of high-resolution TEM (HRTEM) measurement.

Keywords: Small Angle X-ray Scattering (SAXS), mesoporous silica, average wall thickness.

Mesoporous silica formed by the condensation of silica oligomers around self-assembled surfactant micelle templates has recently attracted much interest owing to its potential for use in catalytic or adsorbent applications[1]. Much attention has been focused on characterization of its pore structure by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), N_2 adsorption, small angle X-ray scattering (SAXS) *et al.*, but seldom concerning its average wall thickness[2-7]. This short communication introduced a flexible method to evaluate the average wall thickness of mesoporous silica under examination by SAXS.

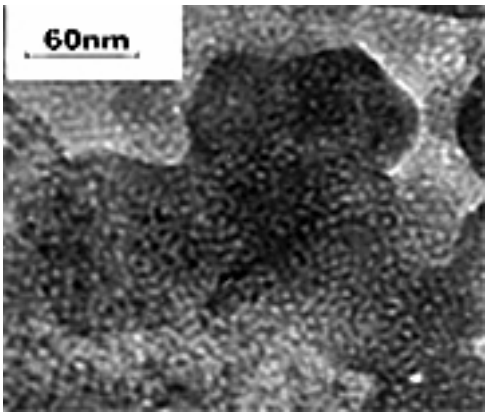
Mesoporous silica was prepared using tetraethylorthosilicate (TEOS) as precursor and non-ionic alkylpolyethyleneoxide $CH_3(CH_2)_n(OCH_2CH_2)_9OH$ (AEO_9) surfactant as templates[8]. The surfactant extraction was performed by Soxhlet extraction with ethanol for 24h, and then the final solid was filtered, washed with distilled water and dried at 100°C in air.

XRD measurement indicated that the resultant silica was in amorphous state. N_2 adsorption at −196°C with ASAP2000 and HRTEM measurement (see **Figure 1**) with HITACHI-9000 illustrated that the sample was of mesoporous structure.

SAXS experiment was performed using Synchrotron Radiation as X-ray source with a long-slit collimation system at Beijing Synchrotron Radiation Laboratory. Incident X-ray wavelength λ was 0.154nm, and the scattering angle 2θ was approximately 0~3°, the scattering vector was denoted as q, where $q=4\pi\sin\theta/\lambda$. The scattered X-ray intensity was recorded using imaging plate technology. The

background scattering and the absorption of the sample were corrected. Data analysis was directly based on slit-smeared intensity $J(q)$.

Figure 1 HRTEM image of a representative region of mesoporous silica



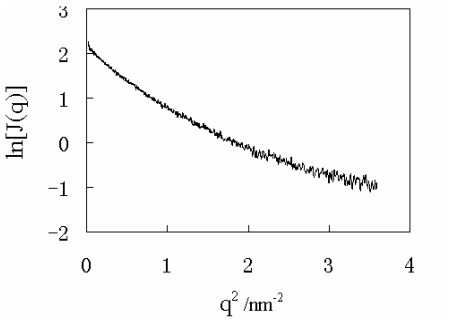
In the small angle X-ray scattering of ideal two-phase system of mesoporous material, there is the following relation between the average pore size l_p, the average wall thickness of the solid matrix l_s and the correlation distance a_c that is a measure of phase size[9]:

$$\frac{1}{a_c} = \frac{1}{l_p} + \frac{1}{l_s} \tag{1}$$

Thus, once a_c and l_p have been determined, l_s could then be deduced from the formula (1). In this paper, a_c and l_p were determined from Debye plot and Guinier plot, respectively.

Guinier plot of the sample (see **Figure 2**) is continuous and strongly concave shows that the pores, which give the small angle X-ray scattering[10], in the sample are polydispersive[10]. The relation between the scattering intensity $J(q)$ and the pore size distribution $V_i(D) \sim D_i$ is as following[11]:

Figure 2 ln[J (q)] *versus* q^2 plot of mesoporous silica



$$J(q) = \sum_{i=1}^{n} CV_i D_i^{\ 3} \exp(-\frac{3}{20} D_i^{\ 2} q^2) \tag{2}$$

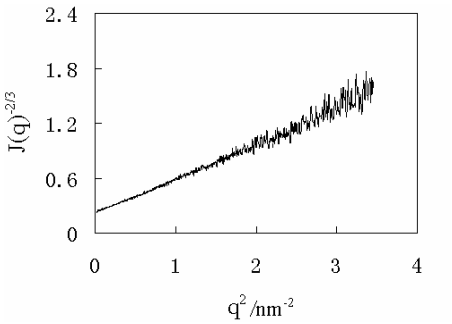
where C is a constant, $V_i(D)$ is the fraction of the volume of the pores with diameter D_i to the total volume of all pores in the sample. By using the Shull-Roess method[12], the pore size distribution $V_i(D) \sim D_i$ is deduced from equation (2) and **Figure 2**[13]**.** The average pore diameter l_p can then be determined as:

$$l_p = \sum_{i=1}^{n} D_i V_i \tag{3}$$

The result is that l_p equals to 2.86nm.

Figure 3 is Debye plot of the sample. The well linear relation in **Figure 3** indicates that the sample is a completely random two-phase system, *i.e*. the uniform electron density of certain value in the silicon matrix and the zero electron density in pores. According to Debye's theory[14], for slit-smeared intensities[15]:

Figure 3 J $(q)^{-2/3}$ *versus* q^2 plot of mesoporous silica



$$J(q) = \frac{A}{(1 + a_c^{\ 2} q^2)^{3/2}} \tag{4}$$

where A is a constant. Thence a_c may be evaluated from **Figure 3**, where

$$a_c = \left(\frac{Slope}{Intercept} \right)^{1/2} \tag{5}$$

The result is that a_c equals to 1.18nm.

Having obtained a_c and l_p, the average wall thickness l_s in the sample could then be determined with formula (1), and the result is that l_s equals to 2.01nm. This lies within the range of 1.50nm to 3.50nm obtained from HRTEM experiment in **Figure 1**.

Unlike other characterizing techniques such as gas adsorption, TEM and HRTEM, SAXS can be used to the study of the microstructure of both wet and dry porous materials whether the pores are open or closed. So, comparatively speaking, measurement of the average wall thickness of mesoporous material by SAXS represents probably the value close to the absolute limit.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No.29625307 and No.29973057) and the National Key Basic Research Special Foundation (G20000480).

References

1. J. Edler, J W. White, *J. Mater. Chem.*, **1999,** *9*, 2611.
2. Z. H. Li, J. H. Sun, J. P. Zhao, D. Wu, Y. H. Sun Yuhan, *Acta Physica Sinica*, **2000**, *4*9 (7), 1312 (in Chinese).
3. P. W. J. G. Wijnen, T. P. M. Beelen, K. P. J. Rummens, H. C. P. L. Saeijs, R. A. V. Santen, J. *Appl. Cryst.*, **1991**, *24*, 759.
4. N. A. Clark, T. Bellini, R. M. Malzbender, B. N. Thomas, *et. al.*, *J. Appl. Cryst.*, **1993**, *71*, 3505.
5. P. Fratzl, G. Vogl,. S. Klaumunzer, J. Appl. Cryst., **1991,** *24*, 588.
6. P. W. Schmidt, J. Appl. Cryst., **1991,** *24*, 414.
7. T. R. Pauly, Y. Liu, T. J. Pinnavaia, S. J. L. Billinege, T. P. Rieker, *J. Am. Chem. Soc.*, **1999**, *124*, 8835.
8. Y. J. Gong, Y. Li, S. G. Wang, D. Wu, Y. H. Sun, *Chemical Journal of Chinese Universities*, **2000**, *21*, 1916.
9. G. W. Pei, W. L. Zhong, S. B. Yue, *X-ray Diffraction of Monocrystal, Polycrystal and Noncrystal Matter*, Shangdong University Press, Jinan, **1989**, pp.386-445 (in Chinese).
10. M. Setek, H. K. Wagenfeld, W. O. Stacy, L. T. Kiss, *Fuel*, **1983**, *62*, 480.
11. C. L. Guo, Y. H. Huang, *J. Inorganic Mater.*, 1991, *6* (3), 336 (in Chinese).
12. Z. F. Meng, *Theory and Application of Small Angle X-ray Scattering*, Jinlin Science and Technology Press, Changchun, **1996**, pp.29-30 (in Chinese).
13. S. T. Huang, *Structure and Structural Analysis of Noncrystal Material*, Science and Technology Press, Beijing, **1987**, p.142 (in Chinese).
14. P. Debye, A. M. Bueche, *J. Appl. Phys.*, **1949**, *20*, 518.
15. D. S. Brown, F. P. Warner, R. E. Wetton, *Polymer*, **1972**, *13* (12), 575.

Received 31 January, 2001