Vol 10 No 5, May 2001
1009-1963/2001/10(05)/0429-04

Chinese Physics

© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

STUDY OF MESOPOROUS SILICA MATERIALS BY SMALL ANGLE X-RAY SCATTERING*

Li Zhi-hong(李志宏)[a], Gong Yan-jun(巩雁军)[a], Zhang Ye(张 晔)[a], Wu Dong(吴 东)[a], Sun Yu-han(孙予罕)[a]†, Wang Jun(王 俊)[b], Liu Yi(柳 义)[b], and Dong Bao-zhong(董宝中)[b]

[a] *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan* 030001, *China*

[b] *National Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100039, *China*

(Received 1 November 2000; revised manuscript received 15 January 2001)

Small angle X-ray scattering experiments have been performed to study the microstructure of mesoporous silica materials prepared by condensation of tetraethylorthosilicate using non-ionic alkylpolyethyleneoxide (AEO_9) and ionic cetyltrimethylammonium bromide (CTAB) surfactant as templates. It is the pores within the nanometre range that produce the main scattering. The scattering of the pure silica systems obey Porod's law. The scattering of the systems with templates remaining in the pores show positive deviations from Porod's law. This may be because the templates produce some additional scattering background and then make the scattering of pores distorted. The results show that the full removal of templates from the pores of the materials by Soxhlet extraction is very easy for AEO_9, but it is difficult for CTAB. The positive deviation correction is also performed.

Keywords: mesoporous silica, templates, small angle X-ray scattering
PACC: 6110, 6140

I. INTRODUCTION

Mesoporous silica materials formed by the condensation of silica oligomers around self-assembled surfactant micelle templates have recently attracted much interest owing to their potential for use in catalytic or adsorbent applications.[1−3] Structural characterization of these materials is therefore of fundamental importance. Commonly, the pore structure of porous silica is measured by gas adsorption and transmission electron microscopy (TEM), but these techniques cannot 'see' the closed pores and the pores filled with a certain medium such as templates. Small angle X-ray scattering (SAXS) does not suffer from this restriction, since it arises from spatial fluctuations of the electronic density within the material. Thus, SAXS has been used in the study of porous silica materials.[3,4] Unfortunately, no information concerning the scattering by templates within the materials has been found. In fact, templates might exert some influence on the physical and chemical properties of the materials, though the influence and the acting mechanism remain equivocal until now. Therefore, this paper mainly aims at an understanding of the scattering phenomena caused by the templates in porous materials and the corresponding structural characteristics of mesoporous silica materials with or without templates, respectively.

II. EXPERIMENTAL DETAILS

Mesoporous silica were prepared by an improved synthesis strategy using tetraethoxysilane (TEOS) as precursor and non-ionic alkylpolyethyleneoxide $CH_3(CH_2)_n(OCH_2CH_2)_9OH$ (AEO_9) or cetyltrimethylammonium bromide $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) surfactant as templates.[5] The surfactant extractions were performed by Soxhlet extraction with ethanol for 24h, and then the final solids were filtered, washed with distilled water and dried at 100°C in air. Some samples were calcined at 550°C at heating rate of 1°C/min. The resultants are listed in Table 1, where the template/silica molar ratios for all samples are the same.

*Project supported by the National Natural Science Foundation of China (Grant Nos.29625307 and 29973057), and the National Key Basic Research Special Foundation of China (G20000480).

†Corresponding author, Fax:(0351)4041153; E-mail:yhsun@sxicc.ac.cn

Table 1. SAXS results of the mesoporous silica.

Sample	Template	Extraction	Calcination temperature/°C	Slope of $\ln[q^3J(q)]$ vs. q^2 in high angle range	Average pore radius of gyration/nm
GZ1	AEO_9	No		+0.257	1.79
GZ2	AEO_9	Yes		0	1.65
GZ3	AEO_9	No	550	0	1.64
GZ4	CTAB	No		+1.872	2.01
GZ5	CTAB	Yes		+0.805	1.50
GZ6	CTAB	No	550	0	1.32

SAXS experiments were performed using synchrotron radiation as an X-ray source with a long-slit collimation system at the Beijing Synchrotron Radiation Facility. The incident X-ray wavelength λ was 0.154nm, and the scattering angle 2θ was approximately 0°–3°, the scattering vector was denoted as q, $q=4\pi\sin\theta/\lambda$. The scattered X-ray intensities were recorded using imaging plate technology. The air scattering and the absorption of the sample were corrected.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) measurements have indicated that all samples in Table 1 are in the amorphous state. N_2 adsorption at 77K with ASAP2000 and high-resolution TEM (HRTEM) measurements have illustrated that all the samples are of mesoporous structure.

SAXS data analysis was directly based on slit-smeared intensities $J(q)$. A Porod plot (see Fig.1), i.e. $\ln[q^3J(q)]$-q^2 curve,[6–8] is used to determine whether the scattering system is ideal or not. The results are given in Table 1. The average pore radii of gyration obtained with SAXS (after correction of deviations from Porod's law) also show that the pores are nanometre-sized (see Table 1), which give rise to the SAXS.

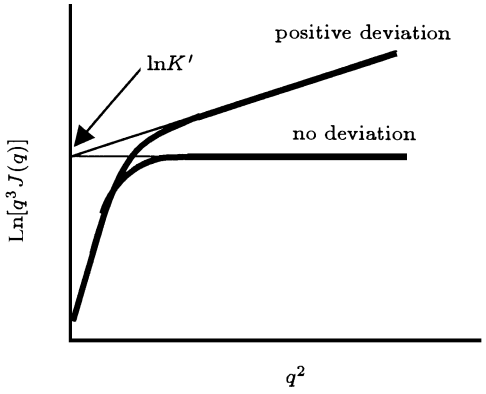


Fig.1. Porod plots and deviation correction.

It is very interesting that two types of Porod curves appear, i.e. no deviation and positive deviation from Porod's law (see Fig.2). This suggests that structural differences exist between these materials.

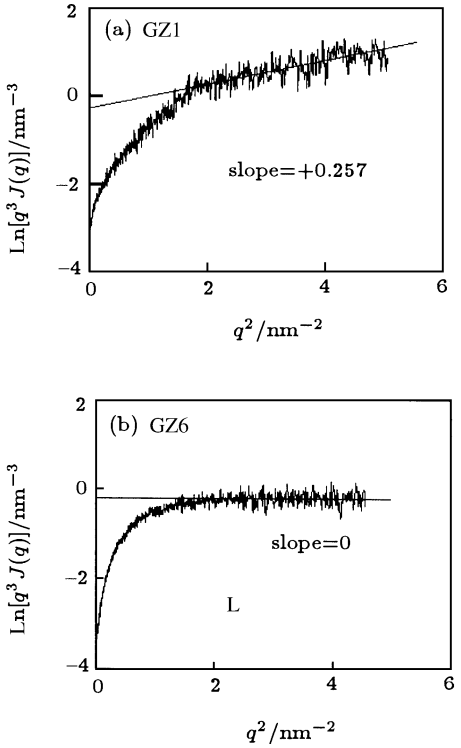


Fig.2. Porod plots of mesoporous silica.

According to Porod's law, for an ideal two-phase structure having sharply defined phase boundaries, the asymptotic behaviour of the intensity curve was found to be[9]

$$\lim J(q) = K'/q^3, \tag{1}$$

where K' is a Porod constant. Formula (1) means that the slope of the $\ln[q^3J(q)]$-q^2 curve in the high q range is close to zero. The slopes of $\ln[q^3J(q)]$-q^2 curves in the high-angle range of samples GZ2, GZ3 and GZ6 are equal to 0 (see Table 1) and agree with Porod's law, indicating that they are of ideal two-phase structures, i.e. the respective electron density in the silicate

skeletons and the pores is homogeneous. This may be attributed to the full removal of the templates. Fourier-transform infrared ray (FT-IR) experiments have not found the information of the templates.

In contrast, GZ1, GZ4 and GZ5 show positive deviations from Porod's law. This suggests that nonideal two-phase structures are presented, as the templates are located in the pores or channels and then produce a kind of electron density micro-fluctuations within the pores, which gives rise to some additional scattering. The $\ln[q^3J(q)]$-q^2 curve showing a positive deviation might be fitted by using the following formula[10]

$$\ln[q^3J(q)] = \ln K' + \sigma^2 q^2, \qquad (2)$$

where σ is a parameter in relation to the size of the electron density micro-inhomogeneity within any phase in the system. GZ4 shows a higher slope than GZ1, implying that the electron density micro-fluctuation by CTAB is stronger than that by AEO_9. This is reasonable if the difference of two templates is considered. AEO_9 is a kind of non-ionic template, and CTAB is an ionic-type template. The chemical bonds between CTAB and the matrix are, of course, stronger than the molecular forces between AEO_9 and the matrix.

Both GZ2 and GZ3 obey Porod's law, and this suggests that AEO_9 could be fully removed by both Soxhlet extraction with ethanol and calcination at a certain temperature. In contrast, GZ5 shows a positive deviation from Porod's law, but its slope is smaller than that of GZ4. This indicates that CTAB can only be partially removed by Soxhlet extraction with ethanol. This agrees with that from their FT-IR spectra.[5] The result also comes from the stronger chemical force between CTAB and the silica matrix. However, CTAB could be fully removed by calcination at a certain temperature, and then GZ6 obeys Porod's law. Thus, SAXS is capable of determining whether the templates are fully removed.

On the other hand, the existence of template results in the scattering from the distorted pore (i.e. negative or positive deviation). It is, therefore, necessary to correct the deviation first before the study of the pore structure. From Fig.1 and formulae (1) and (2), the following relation can be derived for the positive deviation correction:

$$J(q) = q^{-3}\exp\{\ln[q^3J_{\rm obs}(q)] + \sigma^2 q^2\}, \qquad (3)$$

where the original scattering intensity is labelled as $J_{\rm obs}(q)$. Then, a positive deviation could be easily corrected, regardless of the causes leading to the deviation, and the structure of the main scattering matter (such as the pores in a porous material) can be analysed after the deviation is corrected. The deviation correction method does not need the SAXS measurement up to a very high angle. It can be completed in one SAXS experiment. By using this method, Porod's law is satisfied and the structural parameters of pores can be obtained. Table 2 shows the average pore sizes (i.e. average diameters of pores if they are supposed to be spherical) of two typical samples derived from SAXS and N_2 adsorption. For the ideal two-phase structure of GZ2, the result from SAXS is close to that from N_2 adsorption. For positive-deviated structure of GZ1, the result from SAXS, in which the positive deviation has been corrected, is larger than that from N_2 adsorption. This might be due to the effect that the residual template CTAB in the pores could, to some extent, prevent the N_2 molecules from coming into the pores.

Table 2. Average pore sizes obtained from SAXS and N_2 adsorption.

Sample	Average pore size obtained from SAXS/nm	Average pore size obtained from N_2 adsorption/nm
GZ1	4.63	2.39
GZ2	4.07	3.89

IV. CONCLUSION

SAXS is a powerful tool for studying the microstructure of mesoporous silica materials prepared by one-pot template-directed synthesis methodology. The pores of a nanometre size can induce small angle X-ray scattering. The scattering data of pure silica system obey Porod's law. Full removal by Soxhlet extraction is easy for non-ionic template AEO_9, but it is difficult for ionic template CTAB. The templates remaining in the channels of the materials produce the additional scattering background and then lead to a positive deviation from Porod's law. The structural characteristics of the pores can be deduced from the data in which the deviation from Porod's law has been corrected.

References

[1] Sayari A 1996 *Chem. Mater.* **8** 161
[2] Corma A 1997 *Chem. Rev.* **97** 2373
[3] Edler K J and White J W 1999 *J. Mater. Chem.* **9** 2611
[4] Pauly T R *et al* 1999 *J. Am. Chem. Soc.* **121** 8835
[5] Gong Y J, Li Y, Wang S G, Wu D and Sun Y H 2000 *Chem. J. Chin. Universities* **21** 1916
[6] Koberstein J T, Morra B and Stein R S 1980 *J. Appl. Cryst.* **13** 34
[7] Hashimoto T, Fujimura M and Kawai H 1980 *Macromolecules* **13** 1660
[8] Li Z H *et al* 2000 *Acta Phys. Sin.* **49** 775 (in Chinese)
[9] Porod G 1951 *Kolloidn. Zh.* **124** 83
[10] Li Z H *et al* 2000 *Acta Phys. Sin.* **49** 1312 (in Chinese)