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Physica B 350 (2004) 224-226



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# Determination of size and ordering of pores in mesoporous silica using small angle neutron scattering

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#### Abstract

Small angle neutron scattering (SANS) has been used to study the size and ordering of the pore structure of mesoporous silica. Mesoporous silica was synthesised in the presence of a 16 carbon chain surfactant, cetyl-trimethyl ammonium bromide (CTAB) using the sol-gel method. The SANS patterns of the mesoporous silica were measured on samples before and after calcination. Calcination at  $600^{\circ}$ C for 2 h results in removal of the surfactant template. The SANS study revealed the presence of an ordered pore structure with pore spacing of approximately 3.5 nm. After calcination the pore spacing decreased. Using the SANS technique it was possible to quantify the pore sizes and pore spacing and then determine the wall thickness.

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PACS: 61.12.Bt; 81.20.Fw

Keywords: Mesoporous silica; Small angle neutron scattering; MCM-41; Pore size; Pore spacing

## 1. Introduction

Synthesis of mesoporous silica exhibiting nanoscale periodicity resulting from pore ordering has been a major technological advance in the last decade [1]. The evolution of a nanoscale ordering in these materials occurs through the formation of a surfactant/inorganic mesophase during hydrolysis and cross-linking of inorganic precursors at

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surfaces of supramolecular surfactant assemblies [2,3]. The most well known of this class of materials is a hexagonal silica MCM-41 prepared by using a cetyl-trimethyl ammonium bromide (CTAB) surfactant as the template. On removal of the template by calcination, a crystalline product is obtained with hexagonal or cubic arrays [4,5].

This paper focuses on the use of small angle neutron scattering (SANS) as a technique to study the pore characteristics of mesoporous silica produced using different drying methods. Small angle scattering studies have been used to find the interplanar spacing between the cylindrical pores. The size of the pores should also contribute to the

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<sup>0921-4526/\$ -</sup> see front matter  $\odot$  2004 Elsevier B.V. All rights reserved. doi:10.1016/j.physb.2004.04.033

scattering pattern in the small angle limit. The contribution to the scattering intensity from the size and shape of the pores can be modelled numerically using known models. The size, shape and ordering of the pores are important parameters in the design of mesoporous materials and the use of the SANS technique to investigate these factors is discussed.

## 2. Materials and methods

### 2.1. Production of silica

Mesoporous silica was prepared by the sol-gel route. An aqueous solution of quaternary ammonium surfactant cetyl-trimethyl ammonium bromide (CTAB) was added dropwise to a mixture of tetraethyl orthosilicate (TEOS) and ethanol at a pH in the range of 1-2 (HCl), with vigorous stirring at room temperature ( $20^{\circ}$ C). The molar ratios of TEOS:CTAB:H2O:ethanol were 1.0:0.27:10.0:9.09, respectively. Hydrolysis of TEOS gave a clear sol of silica. The resulting sol was aged at  $40^{\circ}$ C for 12 h and then fired at  $600^{\circ}$ C for 2h to remove the surfactant and to achieve final sintering.

An overview of pore sizes and spacings of silica powders studied is given in Table 1. Pore formation occurs after calcination. The micelles that are present before calcination are not true pores but will be referred to as pores in this paper.

## 2.2. Small angle neutron scattering

SANS experiments were performed at the Australian Small Angle Neutron Scattering

Table 1

Diameters and spacing of pores in mesoporous silica powders as obtained from modelling of SANS data

Sample	Surfactant	Drying temperature (°C)	Pore diameter (Å)	Pore spacing (Å)
0C	_	600	_	
0D		40		
2C	CTAB	600	$15.0 \pm 0.3$	$34\pm1$
2D	CTAB	40	$14.4 \pm 0.2$	$39\pm1$

Facility (AUSANS). The q range of this instrument is 0.013–0.23 Å<sup>-1</sup> with the detector in an offset position. The data was reduced and radially averaged using standard methods. The data was converted to an absolute scale by calibration with a standard silica sample of known differential cross-section.

## 2.3. Modelling of data

The data was modelled with the addition of a power-law model and a cylindrical form factor with a hard sphere interaction structure factor. The scattering intensity then become:

$$I = P(q, r, L)S(q, r_{\rm hs}, \eta_{\rm hs}) + Aq^{-m} + b.$$
(1)

Here,  $Aq^{-m}$  is the power-law scattering, b is the background scattering,  $S(q, r_{hs}, \eta_{hs})$  is the hard sphere structure factor for spheres of radius  $r_{hs}$  and volume fraction,  $\eta_{hs}$ .  $P(q, r, L) = \eta F^2(q, r, L)\Delta\rho^2 V_p^2$  where F(q, r, L) is the form factor for scattering from a cylinder,  $\Delta\rho$  is the scattering length density difference between the pore and the silica,  $V_p$  is the pore volume and  $\eta$  is the volume fraction of pores. The modelling was performed with the Igor Pro software package with model macros provided by NIST [6]. The macros were modified to allow  $r_{hs}$  to be linearly related to the cylinder radius.

A cylindrical form factor was chosen as previous electron microscopy studies have shown that the pores formed in MCM-41 silica are cylindrical and ordered [7]. This is believed to be due to the surfactant micelle forming a hexagonal array of micellar rods in solution [8]. The hard sphere structure factor is used to describe the spacing between the pores. The radius,  $r_{\rm hs}$ , is the distance of closest approach of the pores. In this model,  $r_{\rm hs}$  is a multiple of the pore radius to account for the presence of a regular silica wall between the pores.

#### 3. Results

A broad peak was observed at approximately  $q=0.2 \text{ Å}^{-1}$  for the silica produced in the presence of a surfactant molecule (Fig. 1). At  $q<0.5 \text{ Å}^{-1}$ 



Fig. 1. Radially averaged SANS data from calcined (X) and uncalcined  $(\blacksquare)$  mesoporous silica powders. The lines through the data are the modelled fit to the data.

the SANS patterns of all the silica powders displayed power law behaviour.

## 3.1. Effect of calcination of pore ordering

Calcining the silica at 600°C for 2 h is expected to completely remove any organic material from the silica. The pore spacing decreases after the heat treatment (Table 1). There also appears to be an increase in pore size after calcination. From the results of the modelling of the SANS data, as shown in Table 1, the pore wall thickness was calculated to decrease from 24.6 to 19 Å after calcination.

#### 4. Discussion

The power-law scattering in the low q region is interpreted as being due to scattering from particle sizes outside the range probed by the neutron scattering instrument. The peak in the scattering pattern is due to the ordered nature of the pore space in that the pores have a regular pore size and spacing. Calcination of the powders to remove the organic matter appears to decrease the silica wall thickness between the pores. This is most likely due to densification and sintering of silica. In addition, the hard sphere interaction factor may not fully describe interaction potential between pore volumes. As it neglects the length of the pore completely, it can only be an approximation to the true interaction between the pores. This may have an effect on the pore spacing calculated using the model.

## 5. Conclusions

The diameter of the pore and the pore spacing can be determined using modelling of SANS data. Pore wall thickness can be calculated from these values. However, the technique needs to be further developed to be a reliable method for accurately finding the pore characteristics.

#### Acknowledgements

The authors are grateful to the Australian Institute of Nuclear Science and Engineering for access to the AUSANS facility.

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