Intermediate-range Order in Mesoporous Silicas Investigated by a High-energy X-ray Diffraction Technique

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We perform a high-energy X-ray diffraction study comparing bulk amorphous silica with MCM-41 and SBA-15 that are representative mesoporous silicas prepared in basic and acidic conditions, respectively. It is revealed that mesoporous silicas, especially SBA-15, have less ordered structures and contain larger fractions of three- and four-membered rings than does bulk amorphous silica.

Mesoporous silica materials[1] have attracted great attention because of their potential applications in fields such as catalysis and adsorption. It is well known that mesoporous silica is constructed by an amorphous pore wall and so it is not easy to characterize the wall structure. NMR[2] and extended X-ray absorption spectroscopic (EXAFS) techniques[3] are not able to determine the nature of the ring-structures of amorphous materials, which are in an intermediate-range order (IRO); thus the IRO of bulk amorphous silica has been studied using both neutron and X-ray diffraction techniques. The IRO is characterized using reverse Monte Carlo modeling[4] based on neutron and X-ray diffraction data.[5] The important feature of the IRO of amorphous silica is that the six-membered ring (6R) produced by the connection of SiO_4 tetrahedra is dominant, as shown in Figure 1.[6]

The short-range structure of MCM-41 has been studied using X-ray diffraction technique, e.g., by Ookawa et al.,[7] Pophal and Fuess,[8] and Pauly et al.[9] These studies suggest that the IRO of mesoporous silica is less ordered than that of bulk amorphous silica. However, we are not aware of any details of the IRO because it is not easy to obtain high-quality diffraction data of mesoporous silica. It is important to accurately understand the structure of mesoporous silica to better assess various possible applications; this provided the motivation for our present study. To analyze the complicated structure of disordered material, it is necessary to obtain the structure factor $S(Q)$ in a wide scattering vector Q ($Q = 4\pi/\lambda \sin\theta$, θ: scattering angle, λ: wavelength of photons or neutrons) because the resolution in a real space function depends on the $Q_{\max}$ of the Fourier transformation of $S(Q)$. It is essential, therefore, to conduct measurements at high energies (a short wavelength of ca. 0.2 Å, which can now be realized using the third-generation synchrotron radiation sources). In this study, a high-energy X-ray diffraction investigation of MCM-41 and SBA-15, the representative mesoporous silicas prepared in basic and acidic conditions, respectively, was carried out, and the results were compared with data of bulk amorphous silica[10] and analyzed.

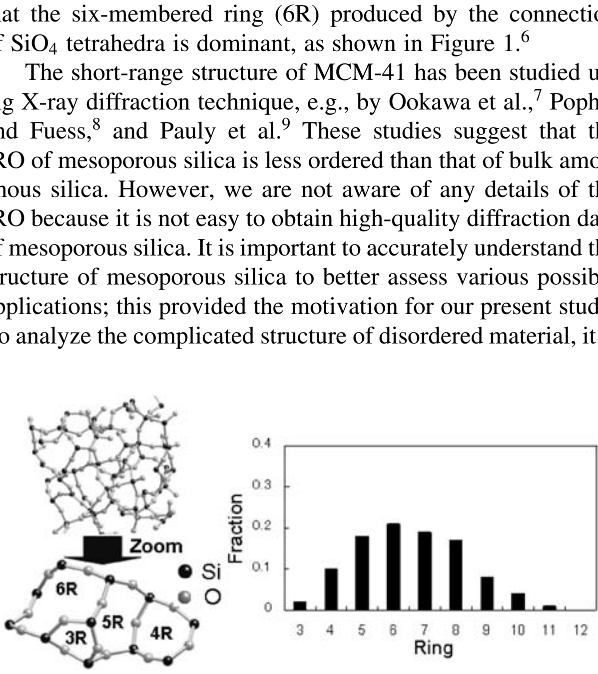

Figure 1. At the left, the structure of bulk amorphous silica with a magnified image is shown. The bar chart at the right shows the relative fractions of the various ring structures present in bulk amorphous silica. The fraction was calculated from a Reverse Monte Carlo snapshot for bulk amorphous silica.

Preparation methods of MCM-41 and SBA-15 and the details for high-energy X-ray diffraction measurement are shown in Supporting Information.[14] Total structure factors, $S(Q)$s, of bulk amorphous silica, MCM-41 and SBA-15 are shown in Figure 2. A comparison of $S(Q)$s reveals that the positions of the first sharp diffraction peaks (FSDPs) of MCM-41 and SBA-15 at $Q \approx 1.60$ and 1.68 Å^{-1}, respectively, are much higher than that of bulk amorphous silica at $Q \approx 1.52$ Å^{-1}. The magnitude of the FSDP decreases in the following order: bulk amorphous silica > MCM-41 > SBA-15, suggesting that SBA-15 has most disordered structure. SBA-15 is well known to have micropores as well as mesopores in its structure.[11] These might be the origin of its disordered structure. It has also been shown that the FSDP is sensitive to the ring size[12] present in amorphous materials, and the present results imply that mesoporous materials, in particular SBA-15, contain a large fraction of smaller rings[13] compared to bulk amorphous silica.

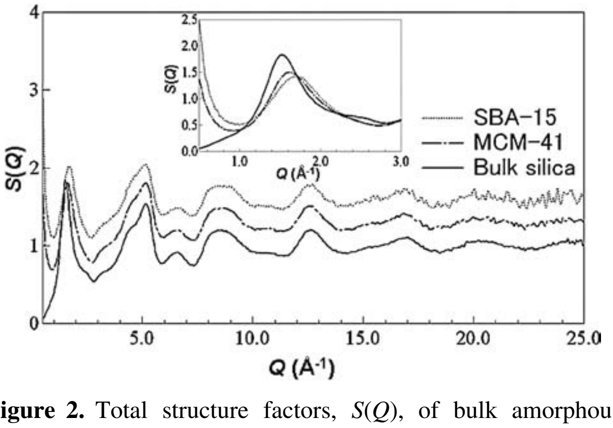

Figure 2. Total structure factors, $S(Q)$, of bulk amorphous silica, MCM-41, and SBA-15. The functions of MCM-41 and SBA-15 are offset vertically by 0.3 and 0.6, respectively, for clarity. The FSDP is highlighted in the inset, which clearly shows that there is a shift in the peak position and peak intensity. (The functions are not offset.)

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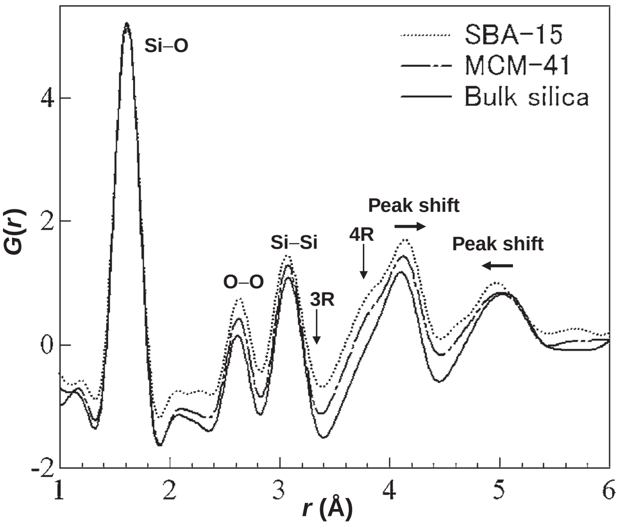

Figure 3. Pair distribution functions, $G(r)$, of bulk amorphous silica, MCM-41, and SBA-15.

Figure 3 shows the pair distribution functions, $G(r)$, of bulk amorphous silica, MCM-41, and SBA-15. From the $G(r)$ curves, it is possible to identify the various distances associated with several features. The first peak at ca. 1.61 Å in the $G(r)$ is related to Si–O distance. Distinct peaks are seen at around 2.6 and 3.1 Å, which are the O–O and Si–Si correlations, respectively. All these distances are closely similar to all possible ring structures and, hence, cannot provide any specific information required to identify the type of ring structures present in the samples. The peaks in the $G(r)$ indeed show differences in the distances appearing above 3.5 Å. Comparison of the $G(r)$ of MCM-41 and SBA-15 with that of bulk amorphous silica between 3.3 and 6 Å in Figure 3 clearly reveals the presence of different intermediate-range orders in these systems. It is found that the broad trail at 3.3 Å and the shoulder peak at 3.7 Å are more pronounced (SBA-15 > MCM-41 = bulk amorphous silica at 3.3 Å and SBA-15 > MCM-41 > bulk amorphous silica at 3.7 Å). The peaks at 3.3 and 3.7 Å are assigned to the second Si–O correlations in 3R and 4R, respectively, of SiO_4 tetrahedra on the basis of the characterization of fumed silica by high-energy X-ray diffraction and the result of molecular orbital calculations.[10] Mesoporous silica is known to be formed via a moderate hydrophilic/hydrophobic interaction between silicate species and surfactants; therefore, it has a high surface area (in the present study, the surface areas of MCM-41 and SBA-15 are 890 and 630 m^2/g, respectively). A previous report on fumed silica, where it was concluded that the fraction of smaller rings (3R and 4R) is larger on the surface of fumed silica ($390 \pm 40\,m^2/g$),[10] suggests that smaller rings such as 3R and 4R might be formed at the interface between mesoporous silica and surfactant.

There is a shift in the peak position at ca. 4.1 Å of mesoporous silicas to a higher value (SBA-15 > MCM-41 > bulk amorphous silica). Since this peak is assigned to mainly the second Si–O correlations (See Supporting Information[14]) except for 3R (3.3 Å) and 4R (3.7 Å) of the SiO_4 tetrahedra, it appears that the fraction of large rings in mesoporous silicas is also large; that is, mesoporous silicas have a broader ring distribution than that found in bulk amorphous silica. Furthermore, a shift in the peak position at ca. 5.0 Å of mesoporous silicas to a lower value (SBA-15 < MCM-41 < bulk amorphous silica) was confirmed. This peak is mainly due to the second Si–Si and O–O correlations in SiO_4 tetrahedra (See Supporting Information[14]). This peak shift, which is shown for the first time, also indicates that mesoporous materials, in particular SBA-15, contain a larger fraction of smaller rings than does bulk amorphous silica.

In this study, we clearly showed that MCM-41 and SBA-15 have less-ordered structures and contain larger fractions of 3R and 4R than does bulk amorphous silica from high quality diffraction data. In particular, SBA-15 has most disordered structure. Further work on the visualization of mesoporous amorphous network structure using Reverse Monte Carlo (RMC) modelling is now on going.

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References and Notes

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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