

Framework Stability and Framework Structure of Disordered Microporous Silicas

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Introduction

Microporous materials with a very high surface area/volume ratio are very important in the field of catalysis and molecular sieving. Recently, new approaches have been developed for making microporous materials with 10-100 nm diameter pores by templating surfactant vesicles in solution using silica.¹ When charged surfactants are used, the vesicles order into hexagonal arrays. An alternative synthesis route, pioneered at Michigan State University, uses neutral surfactants and results in disordered wormhole-like structures.²

Of critical importance for applications is the stability of the framework to pressure, temperature, and chemical environments. Different synthesis routes produced material with remarkably different framework stabilities. It is obviously important to characterize these different samples to try and understand what factors are important for the framework stability. The silica framework surrounding the pores is amorphous in structure and therefore its structure cannot be studied using conventional crystallography.

We recently showed that, using high-energy x-rays from beamline ID-1 at the APS, very high real-space resolution, high-quality, atomic pair distribution functions (PDFs) can be determined from aluminosilicate glasses.³ We would like to leverage this expertise and use the MU-CAT ID-6 beamline to study the microporous silicate materials.

Results and Discussion

Two samples studied were made with different synthesis routes and having markedly different framework stabilities. The experiments are very difficult because of the weak scattering of the silicates and the low packing density of these microporous materials. Nonetheless, with the high flux of ID-6 we successfully obtained good-quality total scattering data and PDFs, as is evident in Fig. 1.

The data were collected at room temperature in flat-plate transmission geometry on the MU-CAT ID-6 beamline at room temperature using 40-keV x-rays. The data are corrected for detector deadtime, absorption multiple scattering, backgrounds are moved, and the data are normalized to obtain the sample-dependent total scattering intensity.

Surprisingly, we found that the framework in the microporous silicas is significantly different from that in bulk silica glass with a longer Si-O bond length and lower density. Also, there are significant framework-breaking defects in the microporous silicas in the form of OH terminated Si bonds. These could be quantified in the current measurement. However, we found very little difference between the structures of the stable and unstable frameworks.

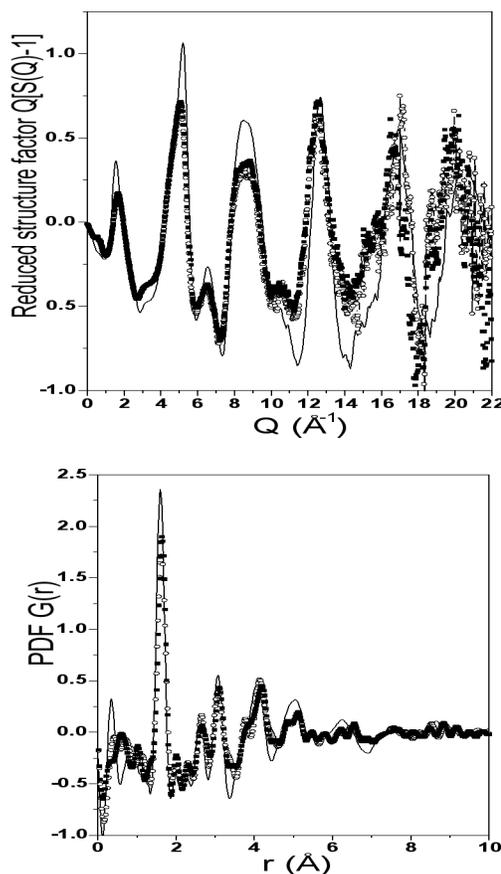


FIG. 1. (a) Reduced, normalized total scattering intensity from microporous SiO_2 powder (open circles) measured at room temperature using 40-keV x-rays and bulk SiO_2 glass (solid line). (b) The PDFs obtained by Fourier transforming the data in (a).

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