Thermal Degradation of M41S-Class Mesoporous Sieves as Revealed by Small-Angle X-ray Scattering

J. E. Hunt, L. Xu, R. E. Winans, S. Seifert
Chemistry Division, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Mesoporous silicates are attractive candidates for separations and applications in catalysis due to their high surface areas and highly ordered mesoporous (20-100 Å) nature. MCM-41 is one member of a family of highly uniform mesoporous silicate materials introduced by Mobil, whose pore size can be accurately controlled in the range 1.5 Å-10 nm.[1,2] This recently discovered class of zeolites, more generally called, M41S, should be useful to effect size separation, act as hosts to nanoclusters, and as shape selective separation media, due to their large pore sizes. The thermal stability is of crucial importance to the practical application of these mesoporous materials. Few reports of the thermal stability of these mesoporous materials are in the literature. Pure silica M41S is stable when heated to 850°C in air or 800°C in air with low water-vapor pressure.[3] However, the mesoporous structure collapses when mechanically compressed or when exposed to water vapor for long periods at room temperature.[4] There are enormous efforts devoted to improving the stability of these materials.

In the present investigation, we have synthesized mesoporous silicate materials with a surface area of approximately 1100 m^2/g and pore sizes of approximately 25 Å and 31 Å. The subject of this paper is the study of the temperature stability of these pore-filled mesoporous materials as measured by small-angle x-ray scattering (SAXS).

Experiment

The SAXS instrument constructed at ANL was used on the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) CAT undulator beamline 12-ID at the Advanced Photon Source.

Monochromatic x-rays (8.5 –23.0 keV) are scattered off the sample and collected on a 9-element mosaic CCD detector (15 x 15 cm) with maximum resolution of 3000 x 3000 pixels. The scattering intensity has been corrected for absorption, the empty capillary scattering, and instrument background. The differential scattering cross section has been expressed as function of the scattering vector q, which is defined as $q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength of the x-rays and θ is the scattering half-angle. The value q is proportional to the inverse of the length scale ($Å^{-1}$). The instrument was operated with a sample-to-detector distance of 68.5 to obtain data at $0.03 < q < 0.7$ $Å^{-1}$.

A quartz capillary heating apparatus was constructed to obtain a controlled heating rate under an inert atmosphere of nitrogen for *in situ* temperature programmed SAXS (TPSAXS) measurements. Quartz capillaries (1 mm) were used to sample 1 mg of M41S material. Scattering patterns were obtained as the sample is heated from 25-600°C under a nitrogen flow system at a rate of approximately 25°/ minute.

Synthesis of MCM-41 was an approach combining the advantages of several literature works.[2,3,5] The silica source used was tetramethyl orthosilicate. The synthesis was carried out at room temperature in the solution of methanol and sodium hydroxide mixture. The materials were annealed at 600°C. Pure silica versions of these zeolites were prepared to alleviate irreversible absorption by aluminum sites.

A pyridine extract of mv bituminous Upper Freeport coal (APCS 1) of the Argonne Premium Coal Samples series was divided and stirred for one week in 31 Å and 25 Å M41S material. After filtering, the zeolite material containing the coal was extracted with methylene chloride. Approximately 25% of the coal material was recovered from each zeolite by methylene chloride extraction. Further extraction with chlorobenzene resulted in only a few additional percent of coal.

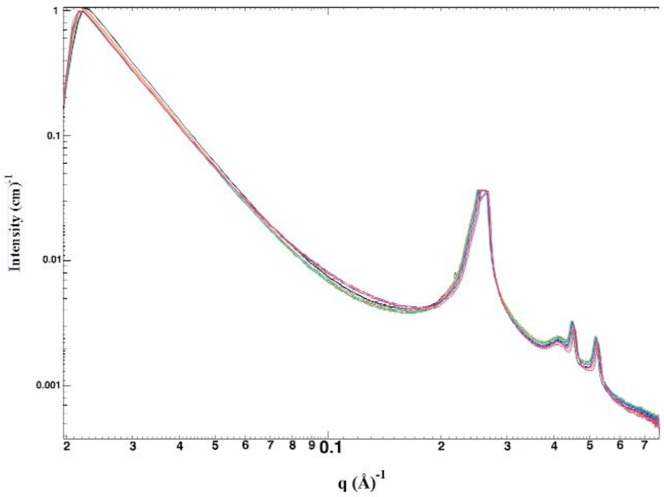

FIG. 1. The temperature-programmed small-angle x-ray scattering of coal extract imbibed in 25 Å M41S mesoporous material. The temperature range is from 25°C to 600°C.

Results and Discussion

A typical plot of the scattering data of M41S material filled with pyridine extracts from coal is shown in Fig. 1. The scattering is quite similar to the unfilled materials. At low q (< 0.04 $Å_{-1}$), scattering arises from the whole particle. This scattering can be related to information about the particle size, composition, and, ultimately, surface texture. The Bragg diffraction peaks give information about the internal structure of the particles, defining the nature and packing dimensions of the channel in the mesoporous materials. The curves clearly show relatively narrow Bragg diffraction peaks associated with the hexagonal lattice. The lattice spacing *d* is 31 Å. The relatively narrow diffraction peak indicates good crystalline structure. The acquisition time for each data set was 0.1 sec. In the TPSAXS experiments, the M41S materials retain their stucture even at temperatures as high as 650°C.

Figure 1 shows that the mesoporous structure for the 25 Å material is maintained throughout the temperature range of 25-

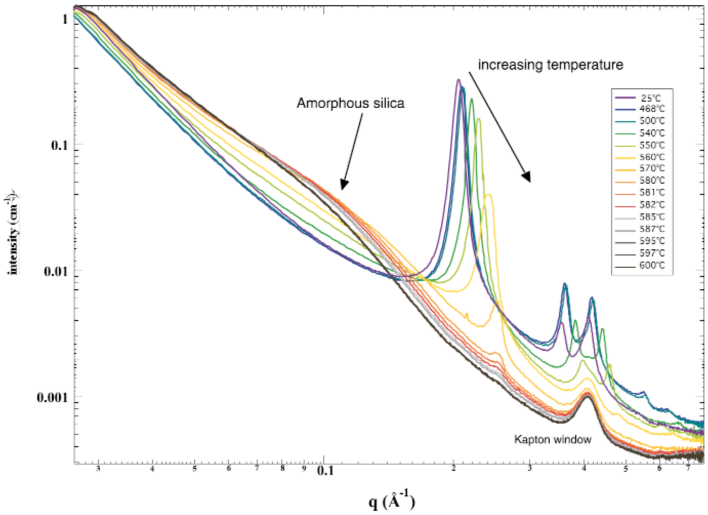

FIG. 2. The temperature-programmed small-angle x-ray scattering of coal extract imbibed in 31 Å M41S mesoporous material. The temperature range is from 25°C to 600°C.

600°C. The scattering is dominated by the mesoporous material and remains essentially unchanged over the entire temperature range.

The TPSAXS data for the 31 Å material is shown in Fig. 2. The most striking feature of this data is the clear structure collapse of the mesoporous material. The 31 Å material rapidly collapses beginning around 475°C as indicated by the decreasing Bragg diffraction peak. At the same time, a large hump appears around 0.08 Å^{-1}, which we assign to amorphous silica. The structure collapses completely at 600°C to what appears to be an amorphous silica phase. Certainly, very polar material from the coal extracts will bind to the silica. For both M41S mesoporous materials, only 25% can be removed from the zeolite by washing. The more nonpolar materials will be preferentially extracted in the washes of coal-infused M41S material leaving more tightly bound polar compounds. Mass spectrometry results show some differences in the nature of organic material in the two M41S materials. The 31 Å material has larger aromatic ring sizes than the 25 Å material.[6]

Clearly, the lower molecular weight materials (such as residual pyridine and other lower boiling point compounds) that are evolved from the M41S materials do not affect the ordered structure. However, at higher temperatures, the 31 Å material begins to decompose, while the 25 Å remains stable. There are two possibilities to consider. First, if the forces associated with thermal decomposition of the organic material are the same, then the larger pore material is less stable than the smaller. Alternatively, because data suggest that there are differences in the organic material structure, quantity, and the decomposition of the organic material, the 31 Å material may experience more stress on the structure than the 25 Å material, resulting in complete destruction of the larger mesoporous material. Further investigation of the surface structure of the mesoporous materials using TPSAXS is planned.

Acknowledgments

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, and use of the Advanced Photon Source was supported by BES-DOE, all under contract number W-31-109-ENG-38. The support of the BESSRC staff is appreciated, especially J. Linton, M. Beno, G. Jennings, and M. Engbretson.

References

[1] J.S. Beck, U.S. Pat., No. 5,057,296, 1991.

[2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, J.B. McCullen, J.B. Higgins, and J.L. Schlenker, J. Am. Chem. Soc. **114**, 10834-10843 (1992).

[3] C.Y. Chen, H.X. Li, and M.E. Davis, Microporous Mater. **2**, 17 (1993).

[4] For example, T. Tatsumi, K. A. Koyano, Y. Tanaka, S. Nakata, Chem. Lett. **5**, 469-470 (1997).

[5] T.J. Pinnavaia, M.F. Thorpe, *Access in Nanoporous Materials* (Plenum Press, New York, 1995).

[6] J.E. Hunt, R.E.; Winans, M. Ahrens, and L. Xu, Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem., 218th ACS National Meeting, New Orleans, Aug. 22-26, pp. 610-613 (1999).