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ABSTRACT

We have studied the temperature stability of M41S class siliceous mesoporous materials loaded with carbonaceous material by temperature programmed small-angle X-ray scattering (TPSAXS) techniques. Results show the thermal structural instability of large pore pure silica sieve material with carbonaceous material (such as coal extracts) occluded within the pores of mesoporous 31 Å M41S materials. Unfilled pore M41S materials do not show thermal-related structural instability.

INTRODUCTION

Mesoporous silicates are attractive candidates for separations and applications in catalysis due to their high surface areas and highly ordered mesoporous (20-100Å) 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. True molecular sieving on the size range of molecular and cluster types found in aggregating solutions should be possible with M41S materials by tuning the pore size.

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 m²/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.

EXPERIMENTAL

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

Monochromatic X-rays (8.5–23.0 keV) are scattered off the sample and collected on a 19 x 19 cm² position sensitive two-dimensional gas detector. More recent data are taken using a 9-element mosaic CCD detector (15 x 15 cm) with maximum resolution of 3000 x 3000 pixels. An advantage of this new detector is that unlike the wire detector, the full beam for the undulator can be used, which gives a factor of 1000 increase in intensity. 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 $0.03 < q < 0.7 \text{ Å}^{-1}$.

A quartz capillary heating apparatus was constructed to obtain a controlled heating rate under an inert atmosphere of nitrogen for in situ SAXS 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°/minut.

Synthesis of MCM-41 was an approach combining the advantages of several literature works.^{2,3,5} Different chain length of surfactants, ranging from dodecyltrimethylammonium to octadecyltrimethylammonium bromide, were used as a template to construct a periodic mesophase. 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.

X-ray diffraction (XRD) analyses were carried out on a Rigaku Miniflex+ instrument using $\text{CuK}\alpha$ radiation, a NaI detector, a 0.05° step size, and a $0.50^\circ/2\text{ min}$ scan rate. XRD and SAXS showed pore sizes of 25 Å and 31 Å for the two M41S-class zeolites.

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.

TGA-DTA (thermal gravimetric analysis and differential thermal analysis) measurements were obtained on a SDT 2960 from TA Instruments. These samples were measured against an alumina standard in a 100 mL/min O_2 flow with a temperature ramp of $10^\circ\text{C}/\text{min}$ to 800°C . The TGA data is also represented in its first-derivative or differential thermal gravimetry (DTG) format. Total organic loss were calculated by measuring the weight loss over the approximate temperature range of 200-600 °C.

RESULTS AND DISCUSSION

Small angle X-ray scattering

A typical plot of the scattering data for the two pore sizes of M41S material is shown in Figure 1. At low q ($< 0.04 \text{ \AA}^{-1}$), 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 25 Å and 31 Å for the two materials synthesized. The relatively narrow diffraction peaks indicate good crystalline structure. The acquisition time for each data set was 0.1 sec.

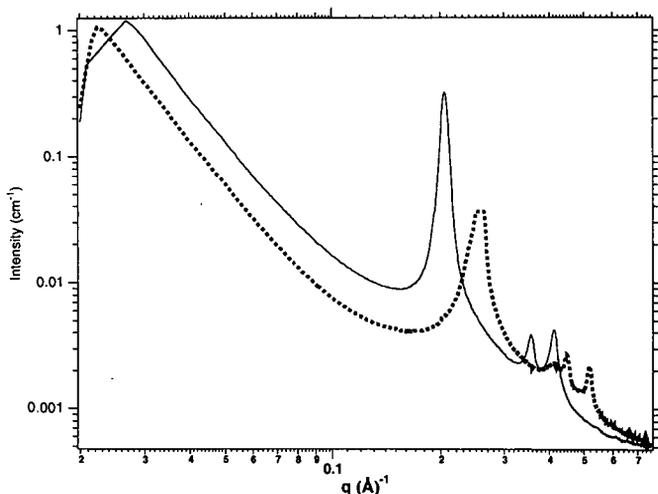


Figure 1. The small-angle X-ray scattering from 25 Å (dotted line) and 31 Å (solid line) M41S mesoporous silicate materials.

In the TPSAXS experiments, the M41S materials retain their structure even at temperatures as high as 650 °C.

When the void spaces in the M41S materials were filled with pyridine extracts from coal, the scattering is quite similar to the unfilled materials. This can be seen in comparing Figure 1 with the room temperature scattering of Figures 2 and 3. The extracts are expected to contain clusters of organic molecules which fill the pores of the M41S materials.

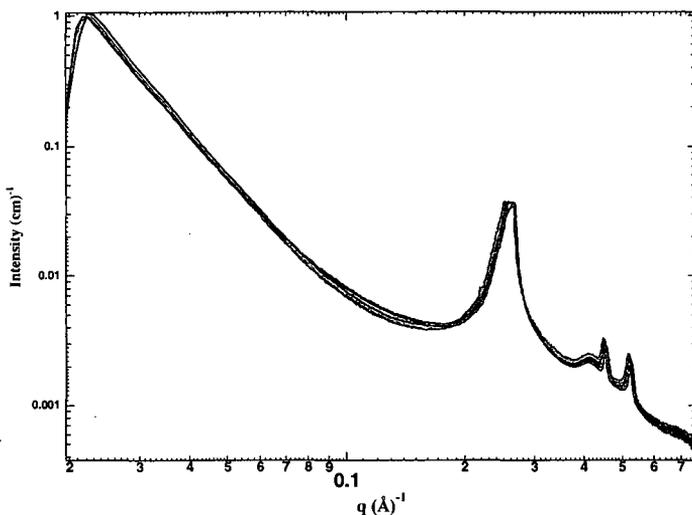


Figure 2. The temperature programmed small-angle X-ray scattering of coal extract imbibed in 25 Å M41S mesoporous material. The temperature range is from 25 °C to 600 °C.

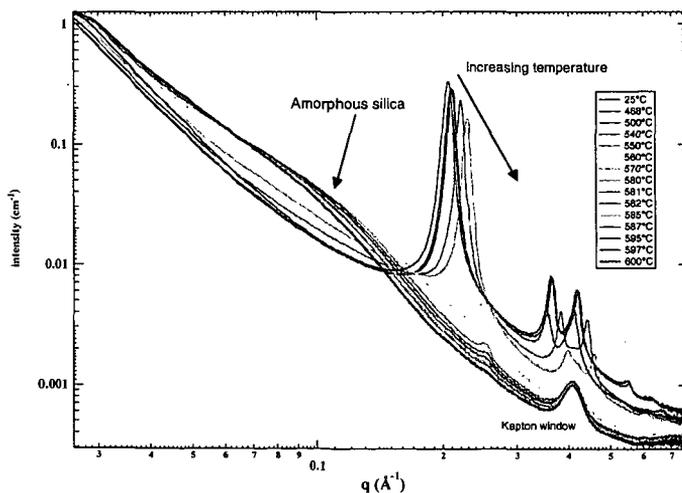


Figure 3. The temperature programmed small-angle X-ray scattering of coal extract imbibed in 31 Å M41S mesoporous material. The temperature range is from 25 °C to 600 °C.

Figure 2 shows that the mesoporous structure for the 25 Å material is maintained throughout the temperature range of 25-600 °C. The scattering is dominated by the mesoporous material and remains essentially unchanged over the entire temperature range. We used TGA to determine the weight loss as a function of temperature. From this data we can determine the total amount of organic material in the mesoporous zeolite. The TGA data shows a weight loss per cent of the total sample weight of 15.6% for the 25 Å material. The TGA indicates that very low molecular weight material is evolved at about 60 °C, which we assign to occluded pyridine. The major part of the organic material begins to come off at roughly 300 °C and peaks at 500 for the 25 Å material. In addition, there is a distinct shoulder at 520 in the 25 Å which may indicate different organic compounds or clusters of compounds.

The TPSAXS data for the 31 Å material is shown in Figure 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. The 31 Å pore size material contains a larger amount of coal extract from the pyridine solution 22.6% for the 31 Å material versus 15.6 % for the 25 Å M41S mesoporous material. In the TGA analysis the major part of the organic material begins to come off at roughly 300 °C and peaks at 440 °C for the 31 Å material. In addition, there is a distinct shoulder at 460 in the 31 Å that may correspond to different organic compounds or clusters of compounds. A peak at 675 in the 31 Å material is only 1.5% of the total weight, but may be related to very tightly bound (very polar) organic material on the silica.

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 suggests 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 using TPSAXS is planned.

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