CONF-980713-1 RECEIVED

MAY 11 1998

O. S. T. H.

AN INVESTIGATION INTO BEAM DAMAGE OF MESOPOROUS MATERIALS

C. F. Blanford,* J. Bentley,[†] A. Stein,* C. B. Carter*

*Department of Chemistry, University of Minnesota, 207 Pleasant St. S.E., Minneapolis, MN 55455-0431

[†]Metals and Ceramics Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6376

*Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Ave. S.E., Minneapolis, MN 55455-0132

In 1992, researchers at Mobil Research and Development created a new class of porous silicates, most notably mesoporous¹ MCM-41.^{2,3} This material features a hexagonal arrangement of linear pores and surface areas in excess of 1000 m² g⁻¹. MCM-41 exhibits narrow pore size distributions in the nanometer range. The walls of MCM-41 are essentially amorphous silica, but its porous nature makes it about 3 kJ mol⁻¹ less stable than the collapsed form.⁴ Particles of MCM-41 are beam sensitive and it appears that they cannot withstand the large current densities required to obtain reliable analytical data at the nanometer scale in the transmission electron microscope (TEM). For example, low beam currents were used to preserve the structure but resulted in energy-filtered TEM elemental maps of oxygen K and Ti L_{2,3} edge intensities that were too noisy to reveal structure at 5 nm resolution. Similarly, EDS spectrum images (~0.5 nA for 0.5 s in 5 nm pixels) produced Si, S, and Ti (K) maps that were too noisy to reveal structure at 10 nm resolution. In order to improve the stability of MCM-41 and to extend applicability of TEM to these materials, it is necessary to understand the pathways by which the pore structure is damaged.

Preliminary studies of MCM-41 and Ti-grafted MCM-41 (Ti-MCM-41),⁵ have been undertaken. The organic template was removed prior to sample preparation. MCM-41 was treated with oxygen plasma overnight in an SPI Plasma-Prep II plasma etcher operating at full power; the Ti-MCM-41 was heated for 6 h in air at 550 °C. The removal of all hydrocarbons was confirmed by infrared spectroscopy. Samples were mixed with absolute ethanol and sonicated for 30 min. Five drops of the suspension were dripped on a "holey" carbon film on a copper grid. Samples were held at -140 °C while they were being examined by TEM. The particles were examined in a Philips CM30 transmission electron microscope operating at 300 kV. All images were captured digitally on the 1k x 1k slow-scan CCD camera of a Gatan imaging filter (GIF). Images were recorded at 2 μm underfocus with 4.8 mrad collection half-angle (objective aperture).

The initial effects of beam damage can be observed at higher energy locations near dislocations and at regions of curvature. Figs. 1 and 2 show images of MCM-41 taken perpendicular to the pore axis. Contrast from the lattice fringes disappeared first from the defect regions. Similarly, figs. 3a and 3b show the same region before and after two minutes under intense illumination. For comparison, figs. 4a and 4b show a defect-free region of MCM-41 looking down the pore axis before and after intense exposure, showing little beam damage to the structure. Similar patterns of electron irradiation damage have been reported in a study of natural quartz grains.⁶ It was concluded that dislocations in naturally deformed quartz widen due to vitrification at the dislocation core, caused by the large stresses at the core and subsequently at the crystalline/amorphous interface.

The stability of MCM-41 is affected by several variables in the synthesis such as the silicate source, pH, and the reaction temperature. By correlating the changes in synthesis to changes in the microstructure, it should be possible to fine-tune the material synthesis to produce a material on which high-resolution analytical electron microscopy can be performed.⁷

1. K. S. W. Sing et al., *Pure Appl. Chem.* 57 (1985) 603.
2. C. T. Kresge et al., *Nature* 359 (1992) 710.
3. J. S. Beck et al., *J. Am. Chem. Soc.* 114 (1992) 10834.
4. I. Petrovic et al., in J. Weitkamp et al., Eds., "Zeolites and Related Microporous Materials: State of the Art 1994," Elsevier (1994) 677.
5. B. J. Aronson, C. F. Blanford, A. Stein, *Chem. Mater.* 9 (1997) 2842.
6. C. B. Carter, D. L. Kohlstedt, *Phys. Chem. Miner.* 7 (1981) 110.
7. Research at ORNL SHaRE User Facility sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., and through the SHaRE Program under contract DE-AC05-76OR00033 with Oak Ridge Associated Universities. C.F.B. also acknowledges the Center for Interfacial Engineering (CIE), an NSF Engineering Research Center, for financial support.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DTIC QUALITY INSPECTED 1

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

MASTER

19980529 020

Figure 1. A particle of MCM-41 showing the beginning of beam damage concentrated in defect areas.

Figure 2. Another particle of MCM-41 showing the later stages of beam damage.

Figure 3. A particle of MCM-41 viewed perpendicular to the pore axis showing an edge dislocation and pore curvature. Images were acquired (a) before and (b) after intense electron bombardment.

Figure 4. A defect-free section of MCM-41 viewed along the pore axis (a) before and (b) after two minutes of intense beam exposure.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

M98004937

Report Number (14) ORNL/CP--96795
CONF-980713--

Publ. Date (11) 199802
Sponsor Code (18) DOE/ER, XF
UC Category (19) UC-404, DOE/ER

DOE