Lawrence Berkeley National Laboratory

Recent Work

Title

Microtomy of Large Particle Zeolites for TEM

Permalink

<https://escholarship.org/uc/item/3hw9x0ct>

Authors

Ulan, J.G.
Schooley, C.
Gronsky, R.

Publication Date

1990-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

National Center for Electron Microscopy

Presented at the Spring Materials Research Society Meeting,
San Francisco, CA, April 16-20, 1990, and
to be published in the Proceedings

Microtomy of Large Particle Zeolites for TEM

J.G. Ulan, C. Schooley, and R. Gronsky

April 1990

For Reference

Not to be taken from this room

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

MICROTOMY OF LARGE PARTICLE ZEOLITES FOR TEM

J.G. Ulan*, C. Schooley†, and R. Gronsky*

*National Center for Electron Microscopy, Lawrence Berkeley Laboratory
University of California, Berkeley, CA. 94720

†University of California, Electron Microscope Laboratory
26 Giannini Hall, Berkeley, CA. 94720

Proc. Spring MRS, San Francisco, CA. 4/16-4/20/90

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

MICROTOMY OF LARGE PARTICLE ZEOLITES FOR TEM

J. G. ULAN*, C. SCHOOLEY** AND R. GRONSKY*

*National Center for Electron Microscopy, Materials and Chemical Science Division, Lawrence Berkeley Laboratory, 1 Cyclotron Rd. Berkeley California 94720

**University of California, Berkeley, Electron Microscope Laboratory, 26 Giannini Hall, Berkeley, California 94720

ABSTRACT

Uniformly thin specimens of powders, suitable for electron microscopy, can be prepared by ultramicrotomy. There is a size limit to the particles that can be studied since larger particles tend to be dislodged from the available resins when microtomed. A method is described to strengthen the binding of the organic resin to the inorganic zeolite, allowing large particles to be sectioned. The particle size limit increased from 3 μm to greater than 20 μm in diameter for FeZSM-5 aggregates. This method can be applied to a variety of oxide powder samples, extending the utility of microtomy as a materials science tool.

INTRODUCTION

A common technique of preparing TEM samples of particulates is to crush the material and disperse it on a grid. With this method only very small particles and a few areas at the edges of the larger particles are thin enough for the electron beam to penetrate and very often it is not possible to obtain a desired orientation. In microtomy, particulate samples are first embedded in resins and then electron transparent thin sections are sliced. With this method the entire particle can be examined by TEM for compositional and structural information and there may be the option to "orient" the particle before slicing.

There is a limit to the size of particles that can be microtomed since larger particles tend to dislodge from the embedding resin when sectioned. In our particular case we were studying the effect of preparing Fe-zeolites in the presence of various alkali cations. These zeolites grow as aggregates of crystalites as shown in Figure 1. The samples that do not have added alkali cation have an average aggregate diameter of 2 μm . When treated with Li^+ , Na^+ or K^+ the size of the aggregates increased to 3, 10 and 8 μm in diameter, respectively. The Na^+ and K^+ aggregates were extensively fused resulting in an effective aggregate size that was often much greater than 100 μm . A previously successful procedure for preparing microtomed zeolite samples for TEM [1] failed for all but the smallest aggregates. This paper reports the methods used to overcome this limit and successfully prepare microtomed sections of all specimens.

Figure 1: SEM of FeZSM-5 aggregates. a) standard treatment, b) Li^+ c) Na^+ d) K^+ .

XBB 897-5671

Figure 2: TEM micrograph of aggregates of FeZSM-5 synthesized with Li^+ . The Si/Fe ratio of each aggregate is indicated.

By increasing the LR White infiltration time it was possible to section aggregates up to 5 μm in diameter. Figure 2 shows samples of aggregates of FeZSM-5 treated with Li^+ embedded using this procedure. The Si/Fe ratios of the different aggregates are indicated, illustrating how compositional information can be obtained from microtomed samples. We would suggest trying this simple modification first because the procedure is still relatively fast and LR White acrylic is easy to handle and less hazardous than the multicomponent, viscous epoxy resin.

By using a coupling reagent and Aradite 6005 it was possible to section aggregates larger than 20 μm in diameter. Figure 3 shows samples of aggregates of FeZSM-5 treated with K^+ embedded using the Z-6040-Aradite 6005 procedure, notice that the total particle is greater than 20 μm across.

EXPERIMENTAL

Acrylic Embedding for Small Aggregates

The aggregates were embedded in LR White and microtomed as described previously.[1]

Acrylic Embedding for Intermediate Sized Samples

The samples were crushed with a mortar and pestle. A few mg of crushed iron zeolite was placed in the tip of a 00 gelatin capsule; (LR White penetrates most polyethylene molds) the capsule was filled with the acrylic resin LR White (hard grade) and left for 24 hours at room temperature under house vacuum. Vacuum was used to remove trapped gases; oxygen impedes polymerization and decreases block hardness. The blocks were heat cured rapidly, 94 - 100 °C for 1.5 to 2 hrs, to further reduce the exposure to oxygen. After cooling to room temperature the gelatin capsules were removed by soaking in water.

The block faces were trimmed with a razor blade to form a small trapezoid. Using a microtome with a pivoting stage and a glass knife, the block face was reduced to a smaller trapezoid with 0.1 mm sides. TEM sections were cut on a RMC MT-6000 microtome with a 55° diamond knife. A slow cutting speed of 0.1-0.3 mm/sec was used and silver to silver grey (< 80 nm) sections were collected on 400 mesh formvar coated grids. The sections were stabilized with a 20 nm carbon film.

Epoxy Embedding for Large Particles

A coupling reagent was used to strengthen the interface between the zeolite aggregates and resin so that the interface could withstand the force of cutting during microtomy. 3-glycidioxy-propyltrimethylsilane (trade name DOW Z-6040) has a trimethyl silane end which, after hydrolysis to form silanolhydroxy groups, can react with zeolite surface SiOH groups to form silano bonds and has an epoxy end which can react with the amine groups in epoxy resins [2] The use of this coupling reagent to prevent pullout during microtomy was reported by Swab and Klinger for TEM specimen preparation of optical multilayer devices.[3]

An epoxy resin must be used with the zeolites after they are treated with Z-6040 to provide the amine groups which react with the coupling reagent. The commonly used epoxy resin, Araldite 6005 was chosen because it has good cutting qualities. The proportions of resin components were modified from standard proportions reported in the literature.[4] BDMA was used as an accelerator to improve the viscosity of the resin and achieve better polymerization.[5]

Samples were crushing in a liquid nitrogen cooled mortar because cooling the material increased its brittleness and produced smaller fragments.

A 0.3 wt. % (g/g) aqueous solution of DOW Z-6040 was prepared, the pH adjusted to 3-4 with acetic acid and the solution was stirred for 45 minutes. A 120 mg sample of crushed iron zeolite was added to 30 ml of the 0.3 wt % solution of Z-6040 and again stirred for 45 minutes. The mixture was filtered and the solid iron zeolite dried at 100°C for 4 hrs.

A 20 mg sample of the iron zeolite was dehydrated with two washes of 100% methanol (3 ml, for 10 minutes each) and then two washes of propylene oxide (3 ml, for 10 minutes each) and stored under propylene oxide to avoid rehydration.

The resin components were mixed in the following proportions and order; 13.5 ml of Araldite 6005, 11.5 ml of dodecylsuccinic anhydride (DDSA) and 0.5 ml of benzyldimethylamine (BDMA). This quantity was enough for ten blocks. The resin mixture can be stored up to four days in a refrigerator. To avoid water condensation the container was tightly capped and brought to room temperature before uncapping. (Resin components are hazardous and should be handled with appropriate safety precautions). Air bubbles, which can form during mixing, prevent polymerization so the mixture was degassed using a house vacuum.

The iron zeolite was infiltrated with a 1 part propylene oxide (3.5 ml) and 1 part resin mixture (3.5 ml) for 24 hours at room temperature. Then the propylene oxide/resin mixture was pipetted off and the iron zeolite was infiltrated with 100% Araldite resin mixture for 24 hours at room temperature. The Araldite 6005 resin mixture was pipetted off and small amounts of iron zeolite were transferred to the tips of an embedding molds after which the molds were filled with resin mixture. The molds were degassed under house vacuum before curing at 60 °C for 24-48 hours.

The blocks were microtomed as described previously.

Figure 3: TEM micrograph of microtomed aggregates of FeZSM-5 synthesized with K⁺.

With microtomed samples the morphology and crystallinity of the center and surface of the aggregates can be compared, and the composition at various places in an aggregate can be measured. This information is unattainable with crushed and dispersed samples because the centers of the aggregates are too thick to study. The use of a coupling reagent to extend the size range of particles that can be sectioned should be useful for other oxide powder samples, extending the utility of microtomy as a materials science tool.

ACKNOWLEDGEMENTS

JGU wishes to thank the Natural Sciences and Energy Research Council of Canada (NSERC) for a postdoctoral fellowship. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Material Sciences, U. S. Department of Energy, under contract number DE-AC03-76SF00098.

REFERENCES:

1. R. Csencsits, C. Schooley, and R. Gronsky, *J. Electron. Microsc. Tech.*, **2**, 643 (1985).
2. Dow Corning Product Bulletin 23-012B (1985).
3. P. Swab, and R. E. Klinger, in Specimen Preparation for Transmission Electron Microscopy of Materials, edited by J. C. Bravman, R. M. Anderson, and M. L. McDonald (Mat. Res. Soc. Proc. **115**, Pittsburgh, PA 1988) pp. 229-234.
4. A. M. Glauert, Practical Methods in Electron Microscopy Vol. 3 edited by A. M. Glauert (American Elsevier, New York, N.Y. 1974) pp. 130-147.
5. A. M. Glauert, *Proc. Royal Microsc. Soc.* **22**, 264, (1987).

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720