Optimum Accelerating Voltage for HRTEM Imaging of the Zeolites

Kaname Yoshida and Yukichi Sasaki

Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

Zeolites which are composed of alumino-silicate frameworks have potentials for use as ion exchangers, catalysts and molecular sieves. Their frameworks are built from TO_4-tetrahedra (T: Si or Al) to produce nano-channels or nano-cavities inside the crystals. The most of synthesized zeolites are obtained as a fine powder. The local nanostructures such as a surface and some kinds of defects of zeolite crystals are important elements which affect their properties [1,2]. High-resolution transmission electron microscopy (HRTEM) has been proven as a powerful technique for nanostructural analyses in material science. However, the application of this method to zeolites is severely restricted owing to radiation damage of the specimen with the high energy electron beam. Electron irradiation damage has been a serious problem from the time of the development of electron microscope. While reducing the total electron dose is most important step for HRTEM imaging of electron sensitive materials, it is necessary to optimize various parameters of TEM operation. Accelerating voltage of incident electron beam is a one of such parameters. Electron irradiation damage is progressed by two mechanisms. One is a radiolysis of specimen and the other is knock-on sputtering caused fast electron bombardment. Both of these mechanisms strongly depend on an accelerating voltage. Taking electron sensitivity of electron detector into consideration, influence of accelerating voltage on HRTEM imaging is more complicated.

In this study, we observed damaging process of MFI-type zeolite with HRTEM under various accelerating voltages to find out optimum condition for nanoscale observations of zeolites. The MFI zeolite has an orthorhombic unit (a = 2.01 nm, b = 1.97 nm and c = 1.31 nm) and forms straight channels along the b axis as shown in Fig.1a. Each channel is resolved clearly as a bright dot in HRTEM images taken under Scherzer defocus conditions (ex. Fig. 1b). Damaging process was explored by successive capturing such images with CCD camera. Electron doses on the specimen were estimated from a magnification of the microscope and beam current on a fluorescent viewing screen. Fig. 2 shows four HRTEM images of MFI irradiated under various dose of 300 keV electron beam. Increasing the electron dose, crystal structure was collapsed gradually. Crystal structure was turned into amorphous finally by electron irradiation. Degradation levels of the crystal structure in HRTEM images were estimate by fast Fourie transform (FFT) pattern calculated from the experimental images. To resolve all nano-channels in HRTEM image, maximum information frequency contributing the image need to be > ~0.3 nm^{-1}. Then maintenance of the 6 0 0 spot whose frequency is 0.33 nm^{-1} was made into the tolerance range for each accelerating voltage. Figure 3 shows critical electron dose estimated from the 6 0 0 FFT spot. Tolerance range of MFI zeolite for 100 keV electron beam was very low compared with another voltages. Although minimum detection limit of CCD camera decreased with lower accelerating voltage, 100 keV beam could not fill up the above-mentioned disadvantage. Taking the sensitivity of camera into account, the 200 keV beam was more advantageous to HRTEM observations of the MFI zeolite than to 300 keV beam.

This work is supported by NEDO's "Development of fundamental technologies for Green and Sustainable chemical processes, Green and sustainable chemistry/ fundamental development of ordered nanoporous membranes for highly refined separation technology" (FY2009–FY2011).

References

[1] Neena S. John et al., Chem. Eur. J. 16 (2010) 2220.
[2] T. Osuna et al., Chem. Eur. J. 10 (2004) 5031.
[3] O. Terasaki et al., Catalysis Today 23 (1995) 201.

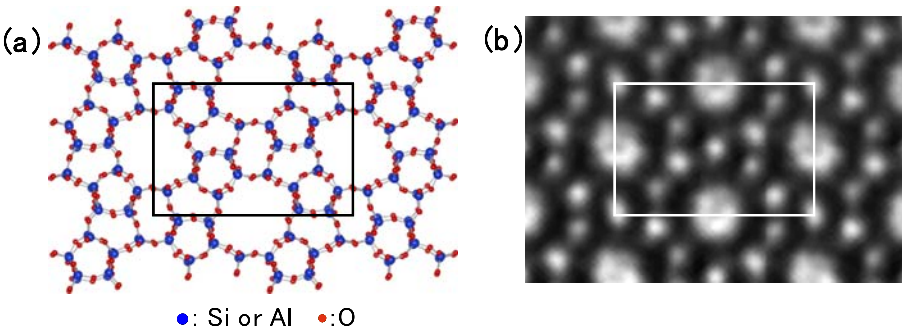

FIG. 1. (a) Crystal structure of MFI zeolite and (b) a corresponding HRTEM image observed with 300keV electron beam. A quadrilateral in the image indicates a crystallographic unit cell (1.31 nm × 2.01nm).

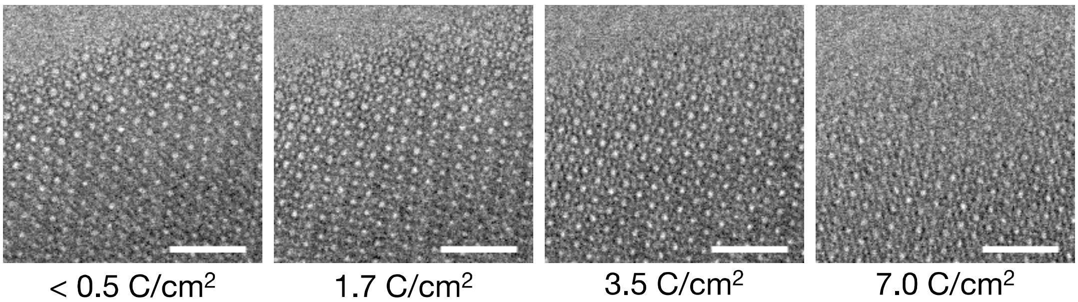

FIG. 2. Damaging process of MFI zeolite under 300keV beam irradiation. Each number bellow the image indicates electron dose.

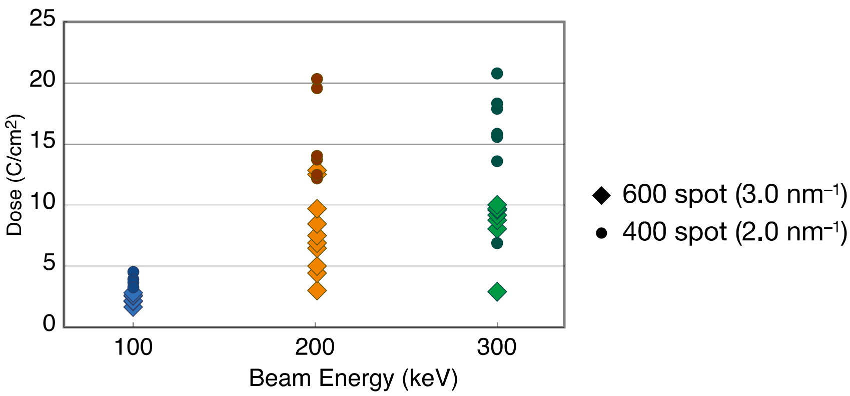

FIG. 3. Tolerance limits estimated from two kinds of FFT spots.