Investigation of the Electron Beam Damage Mechanisms on Zeolites

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Zeolites lose their crystallinity and become amorphous during electron beam irradiation. The damage of zeolites under electron beam has been well studied [1, 2]. The transformation from crystalline to amorphous structure takes place in such a short time that it makes it almost impossible to do high-resolution microscopy to study the local atomic structure. The goal of this work is to quantitatively investigate the damage mechanism on zeolites to find the optimum parameters to minimize the e-beam damage, which will eventually allow us to do high-resolution analytical work on zeolites.

In this study, we investigated electron beam damage mechanisms on zeolites using quantitative methods. Fast Fourier Transformation (FFT) of High Resolution Transmission Electron Microscope (HRTEM) images of zeolites have been used to measure the rate of the damage as a function of time (Fig. 1). The intensity of the spots in FFT has been measured and plotted as a function of time for each accelerating voltage. The slope of the fitted curves (Fig 1-d) has been used to measure damage rate at different accelerating voltages (Fig. 2). As a more quantitative measurement, ratio of oxygen-to-silicon in zeolites has been measured with Electron Energy Loss Spectroscopy (EELS) (Fig. 3) and plotted as a function of electron beam exposure time (Fig 4).

The electron beam damage mechanisms can be classified under two categories: knock-on damage and ionization damage [3]. In knock-on damage incident electron interacts with nucleus of an atom and the atom gets removed from the specimen. However, in ionization damage incident electron transfers energy to the valance electrons in the specimen and alters the structure by breaking the bonds instead of removing atoms. Figure 2 shows that both damage mechanisms play a role in electron beam induced damage of zeolites as a function of accelerating voltage. EELS analysis showed that at 300kV oxygen-to-silicon ratio decreases with time (Fig 4). This indicates a decrease in the number oxygen atoms due to knock-on damage. As the acceleration voltage decreases the effect of knock-on damage decreases and the irradiation damage starts to become the major damage mechanism.

We have also investigated the effect of temperature on the damage rate. The zeolite specimens have been heated for 30 minutes inside a TEM (*in vacuo*) with a heating holder. Specimens were imaged after they were cooled down to room temperature in the TEM (Fig 5). For 30 minutes of heating, increasing temperature showed a negative effect on the damage rate.

References

[1] L.A. Bursill, et al. Nature, 1980. **286**(5769): p. 111-13.
[2] Y. Yokota, et al. Ultramicroscopy, 1994. **54**(2-4): p. 207-214.
[3] R. Csencsits, et al. Zeolites, 1988. **8**(2): p. 122-126.

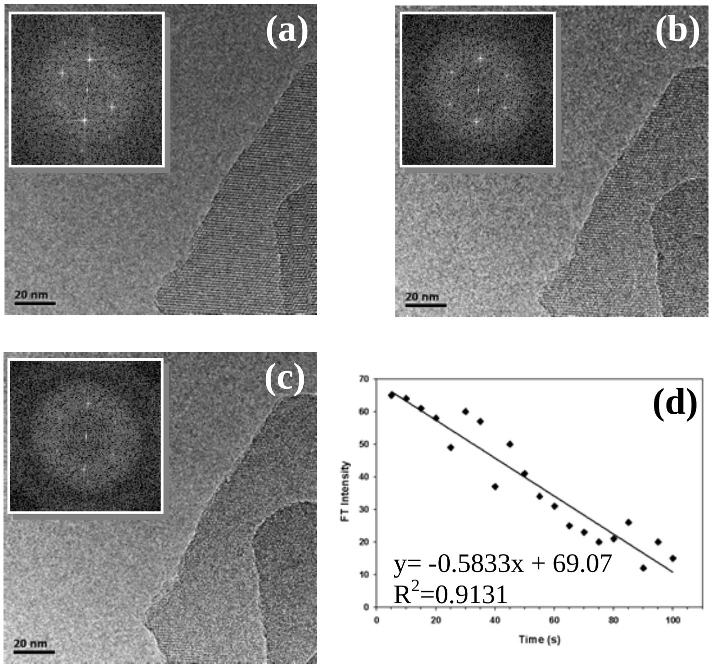

FIG. 1. (a,b and c) HRTEM images of zeolites and their FFTs, (a) 5 secs, (b) 50 secs and (c) 100 secs. (d) Degradation of the FFT spot intensity as a function of time at 200kV.

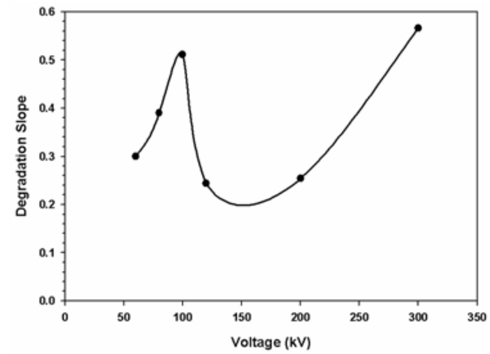

FIG. 2. The slopes of the degradation curves as a function of electron beam accelerating voltage.

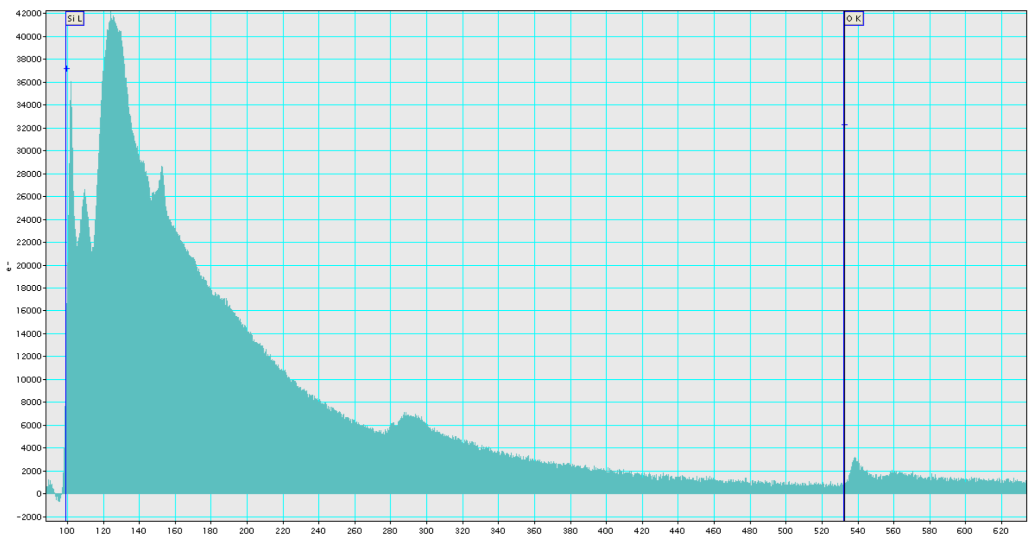

FIG. 3.
EELS spectrum of a typical fresh zeolite.

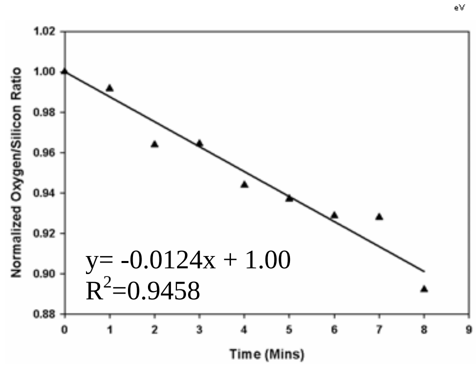

FIG. 4. Change in Oxygen-to-Silicon ratio over time (Measured with EELS).

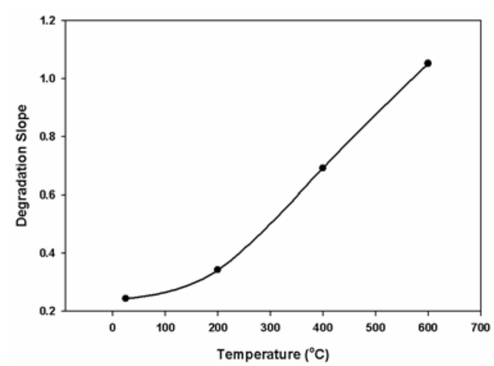

FIG. 5. Damage rate change as a function of temperature