

XAFS Study on the Local Structure Change around Silver in Zeolite.

I. Performance Test of BL01B1 toward Ag K-edge Spectrum

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Various kinds of silver microclusters are created in the cages of zeolites when they are heated. Besides the structural interests, some calcined Ag⁺-exchanged zeolites adsorb more N₂ than O₂. Ag edge XAFS is a suitable technique to reveal this adsorption character from the structural information of Ag. Since very small difference is expected for Ag among their environments, a high signal/noise ratio is required in the absorption measurement. This report confirms the performance of BL01B1 for Ag K-edge absorption spectrum and finds the optimum conditions.

The monochromator was operated in Si(111), Si(311), and Si(511) diffraction plane modes. Si(111) mode measurements were performed as a part of the proposal of No. 1997B0118. X-ray beam cross section was ca. 6.5 mm × 0.15 mm at sample position. Total reflection mirrors were used to remove higher harmonics. 5A-type zeolite was purchased from TOSO and exchanged Na⁺ for Ag⁺ up to 20% to the exchange capacity. After dried at 60°C in the air, the exchanged zeolite was calcined at 400°C in vacuo.

Figure 1 shows Ag K-edge absorption spectra for silver metal foil just above the edge. The spectrum with Si(111) reveals poor energy resolution. Si(511) at BL01B1 is quite similar but has higher resolution than Si(311) at Photon Factory BL-10B. Fourier transforms for silver metal are shown in Fig. 2. The effect of energy resolution is small enough, except for Si(111), to ignore within usual experimental errors of the amplitude of EXAFS. The lower resolution of Si(311) at BL01B1 than that at PF may come from the imperfection of the mirror surfaces. Figure 3 shows EXAFS χk^3 for Ag₂O with Si(311). Above 7 Å⁻¹ the random noise level is clearly less for BL01B1 than for PF

BL-10B. Large steps in the BL01B1 spectrum, however, appear when the monochromator crystals were tuned to be parallel with each other, and increase their height with increasing k . They may due to the change of the ratio of harmonics intensities in the X-ray, because there was no step in the spectra of silver foil. To avoid this step, we should tune the degree of parallel much more frequently to minimize the change of harmonics ratios at the tuning. EXAFS in Fig. 3 were transformed as shown in Fig. 2. Though the first peak for BL01B1 is slightly lower than that for PF BL-10B, peaks at 3.7 Å show no such difference. Si(511) mode was expected to reveal the difference in the XANES of Ag-exchanged zeolites with treatment conditions. Figure 4 shows XANES for Ag⁺-exchanged zeolite. Probably because of the natural band width of transition, there is no difference on the spectra. Thus, Si(311) at BL01B1 has enough resolution for the silver cluster study in zeolite.

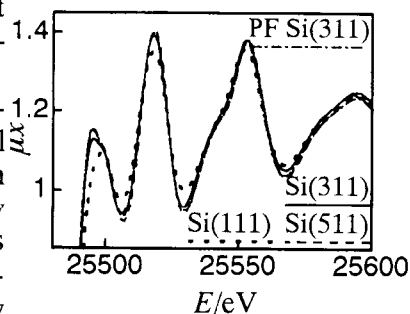


Fig. 1. X-Ray absorption spectra of silver foil.

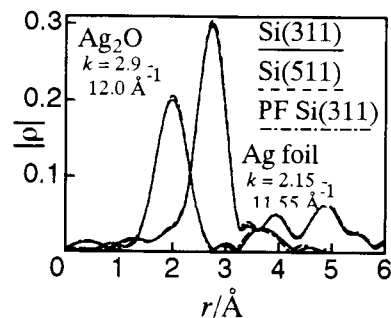


Fig. 2. EXAFS Fourier transforms.

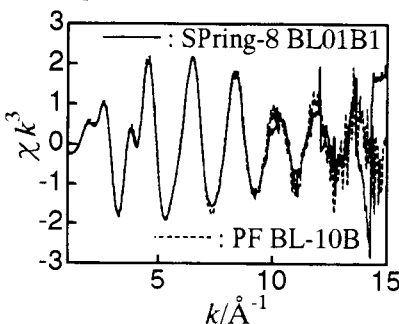


Fig. 3. EXAFS χk^3 for Ag₂O with Si(311)

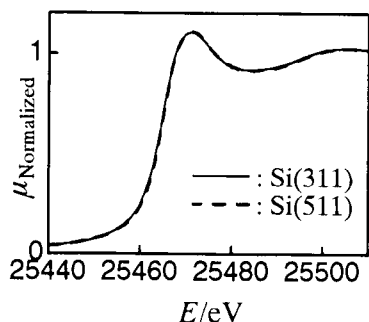


Fig. 4. Ag K-edge XANES of 20% Ag⁺-exchanged zeolite.