In-situ XAFS study of Ag clusters in zeolite 4A

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Introduction

In the fully Ag^+-exchanged zeolite 4A (Ag-4A) the 12 Ag^+ ions are present inside of the zeolite cages, as needed to balance the anionic charge of the zeolite framework. The white color of the hydrated Ag-4A changes through yellow to brown by heating under vacuum. These changes in color are related to the formation of silver clusters by dehydration [1]. In this report, we study the structural change of Ag-4A by in-situ XAFS measurements.

Experimental

Ag-4A powder samples were prepared by immersing Na-4A ($Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]27.5H_2O$) zeolite in an aqueous $AgNO_3$ solution at 25°C[2,3]. The air-dried Ag-4A was set into the in-situ XAFS measurement cell in which the sample can be heated under vacuum. Ag *K*-edge EXAFS spectra were measured at BL-10B. A Si(311) channel-cut monochrometer was used, and energy and current of the storage ring were 3.0 GeV and 250~300 mA, respectively. The analyses were performed by XANADU code [4] and FEFF6 code [5].

Results and Discussion

Figure 1 shows the change of $k\chi(k)$ EXAFS spectra measured for 2 minutes (2 minutes scan EXAFS) for Ag-4A by keeping the evacuation of the sample at room temperature. After 12 minutes evacuation, any more changes cannot be observed in the spectra.

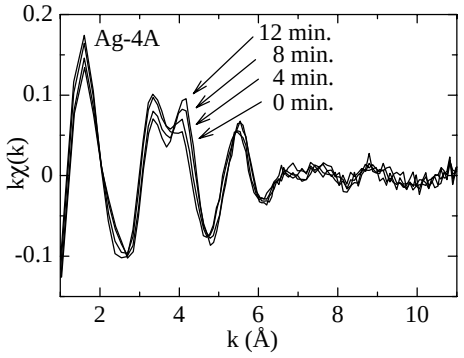

Fig. 1 The change of $k\chi(k)$ of 2 minutes scan EXAFS for Ag-4A by keeping the evacuation. Time interval for each spectrum is 4 minutes.

The corresponding change of Fourier transforms is shown in Fig. 2. First peak is assigned to short Ag-O distance and second peak to long Ag-O and Ag-Ag [3]. It is observed that the intensity of the second peak increases continuously during the evacuation.

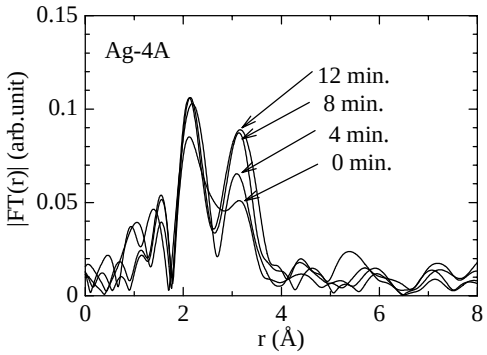

Fig. 2 Fourier transforms of 2 minutes scan EXAFS for Ag-4A shown in Fig. 1.

We have additionally measured 20 minutes scan (not 2 minutes) EXAFS for the sample at 1 atm and for the sample fully evacuated. The structural parameters obtained from these EXAFS are summarized in Table 1. The interatomic distance of the short Ag-O decreases due to the evacuation, which means that the water molecules are removed from the vicinity of Ag ions. The distance of the Ag-Ag decreases and the coordination number (*N*) increases by evacuation. It is expected that the Ag ions are reduced by the removal of the water molecules. More detailed analyses are now in progress.

Table 1 Structural parameters obtained from 20 minutes scan EXAFS.

	short Ag-O		long Ag-O		Ag-Ag	
	r (Å)	*N*	*r* (Å)	*N*	*r* (Å)	*N*
1 atm	2.38	5.7	2.87	2.0	2.88	2.5
Vac.	2.28	3.3	2.86	2.3	2.83	3.7

References

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