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## EXAFS study of silver clusters in zeolites

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The EXAFS measurements on Ag *K*-edge have been carried out at 298K on completely Ag<sup>+</sup>-exchanged zeolite 4A(Ag-4A) with different dehydration treatments. In the Fourier transforms  $F(r)$  of EXAFS spectra there appear two distinct peaks. By two-shell curve-fitting analysis it is found that the Ag ion-framework oxygen and Ag-Ag contact distances decrease as the color of Ag-4A changes from white (fully hydrated) to brown (fully dehydrated). The coordination number of Ag atom (Ag<sup>0</sup>) around a central Ag<sup>0</sup>,  $9.0 \pm 0.5$ , for brown Ag-4A suggests a formation of a silver cluster with Ag<sup>0</sup>-Ag<sup>0</sup> contact distance of 2.81 Å.

**Keywords:** EXAFS, Ag cluster, zeolite.

### 1. Introduction

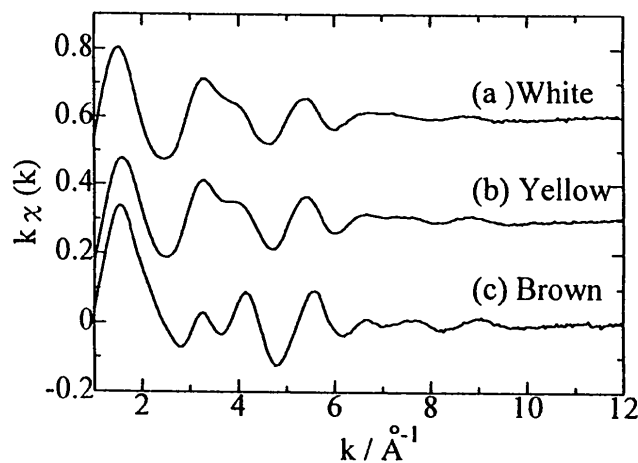
The silver zeolite 4A (Ag-4A) contains Ag<sup>+</sup> ions inside wall of their channels and cavities, as needed to balance the anionic charge of their framework. The white color of the hydrated silver zeolite changes to brown by heating under vacuum up to 500°C. This color change with dehydration is related to the formation of silver clusters due to the interaction of the silver atoms produced by autoreduction and the other silver atoms or Ag<sup>+</sup> ions (Sun & Seff, 1994). The X-ray diffraction experiments of the clusters has only been made on the single crystal of silver zeolite (Kim & Seff, 1987, Gellens et al., 1981) and revealed the presence of a silver cluster. EXAFS technique provides an important structural information on the changes in the local environment around a central atom in the disorder system. It is interesting to study the local structure around Ag in the silver cluster located in zeolite cage by means of EXAFS.

In this paper, we report the results of the EXAFS measurements on Ag *K*-edge for a silver cluster in the cavity of powdered zeolite.

### 2. Experimental

The fully Ag<sup>+</sup>-exchanged 4A (Ag-4A) powder samples were prepared by immersing Na-4A ( $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]27.5\text{H}_2\text{O}$ ) zeolite in an aqueous AgNO<sub>3</sub> solution at 25°C. The white Ag-4A powder (hydrated, white (a)) was dried for 5 days in air at room temperature. During heating the white powder at 150°C and 500°C, respectively, for 10 h under vacuum of 10<sup>-3</sup> Torr, the colors of the Ag-4A changed to brown at 500°C (fully dehydrated, brown(c)) from yellow at 150°C (about 70% dehydrated, yellow(b)). The details of the sample preparation are described elsewhere (Hoshino, 1996).

For the X-ray absorption measurement the samples were treated in the glove box filled by He gas. The sample powder was pasted on an adhesive tape. The tape was mounted on a copper holder which was set in a chamber where evacuation up to 10<sup>-5</sup> Torr was possible. Ag *K*-edge X-ray absorption spectra were obtained at BL-10B of the Photon Factory in KEK (Tsukuba). Si(311) channel-cut monochromator was used. Energy and current of the storage ring are 3.0GeV and 250 ~ 400mA, respectively. X-ray absorption spectra were recorded in transmission mode using the ionization chamber detector. The EXAFS interference function extracted from the absorption spectra was Fourier transformed by the program of XANADU code described elsewhere (Sakane *et al.*, 1993). In order to obtain the structural parameters, the EXAFS function was fitted by non-linear least squares method. In the fitting process, theoretical parameters calculated by FEFF code (Rehr *et al.*, 1991) was used. The energy correction was made by fitting our results on Ag foil and AgNO<sub>3</sub> as standard samples. The *k*-range for the curve-fitting method was around 3.5 ~ 11.3 Å<sup>-1</sup>.



**Fig. 1** Ag *K*-edge EXAFS,  $k\chi(k)$ , function for three different Ag-4A zeolites at 298K: white(a), yellow (b) and brown(c).

### 3. Results and Discussion

Figure 1 shows the EXAFS spectra,  $k\chi(k)$ , of Ag  $K$ -edge measured at 298 K for three different Ag-4A; white(a), yellow(b) and brown(c). The oscillations are detectable in the  $k$ -region up to  $11 \text{ \AA}^{-1}$ . The spectrum for white(a) is similar to that for yellow (b), while the spectrum for brown(c) is considerably different from that for yellow(b) in the  $k$ -region between 3 and  $5 \text{ \AA}^{-1}$ .

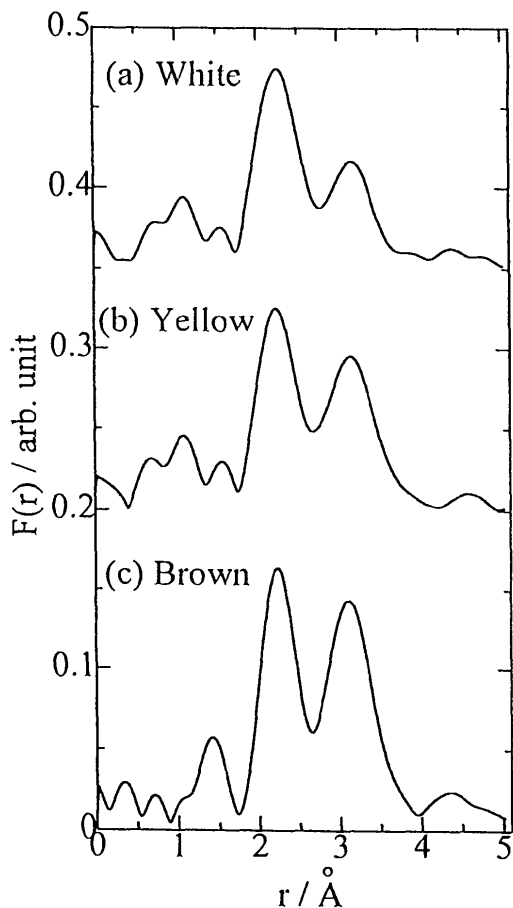


Fig. 2 Fourier transforms of EXAFS,  $F(r)$ , for three different Ag-4A zeolites at 298K: white (a), yellow (b) and brown (c).

Figure 2 shows the Fourier transforms  $F(r)$  of EXAFS spectra measured at 298 K for three different Ag-4A samples. There appear two peaks in  $F(r)$ . As the vacuum-dehydration of Ag-4A zeolite proceeds from (a) to (c), the second peaks around  $3 \text{ \AA}$  become prominent. The two-shell curve-fitting analysis which is enough to derive the structural parameters has been carried out. The structural parameters are compiled in Table 1. Figure 3 shows the comparison for the brown(c) sample between the experimental curve  $k\chi(k)$  and the calculated curve by using the

structural parameters. The agreement is fairly good.

The peak positions of the first peak are in the range between  $2.28$  and  $2.37 \text{ \AA}$ . Since the  $\text{Ag}^+$ -oxygen (O) distance is found to be around  $2.4 \text{ \AA}$  from the present EXAFS spectra for  $\text{AgNO}_3$  powder, the first peak of  $F(r)$  for Ag-4A zeolites is assigned to bonds between  $\text{Ag}^+$  and oxygen. It has been reported by the X-ray diffraction experiment that there is a  $\text{Ag}^+$ -framework oxygen contact in  $\text{Ag}^+$ -exchanged 4A zeolite (Gellens *et al.*, 1981). In the hydrated Ag-4A zeolite a contact between  $\text{Ag}^+$  and water oxygen is considered to be present. The peak positions of the second peak of  $F(r)$  are in the range between  $2.81$  and  $2.87 \text{ \AA}$ . Since the Ag atom ( $\text{Ag}^n$ ) and  $\text{Ag}^n$  distance is found to be around  $2.8 \text{ \AA}$  from the present EXAFS spectra for Ag foil, the second peak of  $F(r)$  for Ag-4A zeolites is assigned to bonds between Ag and Ag.

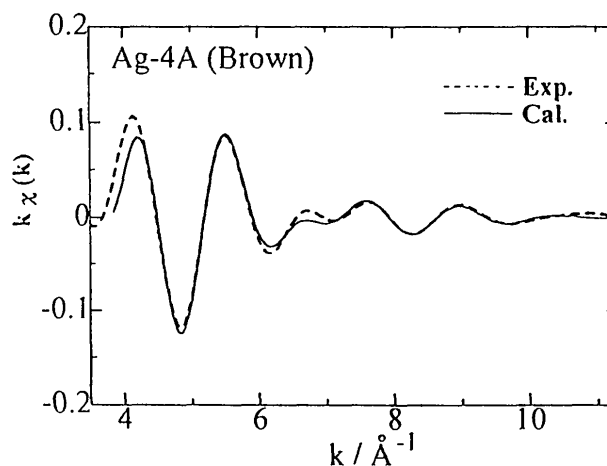


Fig. 3 Comparison for the brown(c) sample between the experimental curve  $k\chi(k)$  and the calculated curve by using the structural parameters.

Table 1 Structural parameters ( $r$ : contact distance,  $N$ : coordination number and  $\sigma^2$ : mean square displacement) for Ag-4A zeolites at 298K.

	Ag-O			Ag-Ag		
	$r/\text{\AA}$	$N$	$\sigma^2/\text{\AA}^2$	$r/\text{\AA}$	$N$	$\sigma^2/\text{\AA}^2$
white(a)	2.37	5.1	0.018	2.87	5.4	0.029
yellow(b)	2.36	4.7	0.017	2.85	6.2	0.024
brown (c)	2.28	3.9	0.012	2.81	9.0	0.025

The  $\text{Ag}^+$ -O distance in white(a),  $2.37 \text{ \AA}$  is longer than the  $\text{Ag}^+$ -framework oxygen contact distance,  $2.15 \sim 2.19 \text{ \AA}$  (Gellens *et al.*, 1981)). The coordination number of oxygen around a central  $\text{Ag}^+$ ,  $5.1 \pm 0.5$  is higher than that for  $\text{Ag}^+$ -framework oxygen contact,  $3.3$  (Kim and Seif, 1987). The presence of the  $\text{Ag}^+$ -

water oxygen contact with distances between 2.4 and 2.5 Å (Herdman and Neilson, 1990) is associated with the differences. Since there are only  $\text{Ag}^+$  in white(a), the contact distance, 2.87 Å, corresponds to  $\text{Ag}^+-\text{Ag}^+$ . This is longer than the sum of the ionic radii of  $\text{Ag}^+$ , 2.54 Å, which is because that the distance between Ag and Ag in the zeolite 4A cage containing two  $\text{Ag}^+$  is dominated by their Coulomb repulsion (Brandle and Calzaferri, 1994). The coordination number  $N$  of  $\text{Ag}^+$  around a central  $\text{Ag}^+$  is  $5.4 \pm 0.5$  which is nearly the same as previous results, 6.6 (Kim and Seff, 1987). When the color of Ag-4A zeolite changes from white(a) to yellow(b), the  $\text{Ag}^+-\text{O}$  and  $\text{Ag}-\text{Ag}$  contact distances decrease. The coordination numbers of oxygen around a central  $\text{Ag}^+$  decrease, but those of  $\text{Ag}^+$  around a central  $\text{Ag}^+$  increase. As the vacuum-dehydration proceeds,  $\text{Ag}^+$  ions are reduced to Ag atoms by oxide ion of residual water molecules or of the zeolite framework (Sun and Seff, 1994), which results in a brown Ag-4A. By reduction of  $\text{Ag}^+$  ions bonding interactions between Ag-Ag occur and hence the Ag-Ag contact distance becomes small (Brandle and Calzaferri, 1994).

At the complete removal of water molecules the  $\text{Ag}^+-\text{O}$  contact distance changes into 2.28 Å for brown(c) and the coordination number of oxygen around  $\text{Ag}^+$  is  $4.1 \pm 0.5$ , which suggests that the contribution of  $\text{Ag}^+$ -framework oxygen contact is dominant in brown(c). The mean square displacements,  $\sigma^2$ , of oxygen around a central  $\text{Ag}^+$  is small because of strengthening the bond between  $\text{Ag}^+$  and framework oxygen. Since there are Ag atoms in brown(c), the contact distance, 2.81 Å, corresponds to  $\text{Ag}^0-\text{Ag}^0$ . The fact that the coordination number of  $\text{Ag}^0$  around a central  $\text{Ag}^0$  is  $9.0 \pm 0.5$  for brown(c) suggests a formation of a silver cluster. The relatively large mean square displacement,  $\sigma^2$ , of  $\text{Ag}^0$  around a central  $\text{Ag}^0$  may be related to large density fluctuations of Ag atoms consisting of the cluster in the zeolite cage. A contribution of  $\text{Ag}^+$  ions may not always be negligible. It is noticed that the presence of the  $\text{Ag}^+-\text{Ag}^0$  contacts in addition to the  $\text{Ag}^0-\text{Ag}^0$  contacts has been reported for a silver cluster located in the cages of the fully dehydrated Ag-4A zeolite (Kim and Seff, 1978).

#### 4. Conclusion

EXAFS measurements of Ag  $K$ -edge have been carried out on the vacuum-dehydrated powdered Ag-4A zeolite. The EXAFS data have been analyzed by the two-shell curve fitting method. The

contact distances, coordination numbers and mean square displacements are derived. The coordination number of  $\text{Ag}^0$  around a central  $\text{Ag}^0$ ,  $9.0 \pm 0.5$ , in the fully dehydrated Ag-4A zeolite suggests a formation of a silver cluster with  $\text{Ag}^0-\text{Ag}^0$  contact distance of 2.81 Å.

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