Controlling the formation of silver cluster in silver-ion-exchanged MFI-type zeolites by different treatment methods

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Introduction
Very recently, we have found that a copper-ion-exchanged MFI-type zeolite (CuMFI) strongly interacts with a xenon (Xe) gas, even at temperatures around room temperature[1]. The Xe gas has been well-known to have a nonreactive nature since Xe belongs to the category of inert gases. The effective sites in CuMFI for Xe have been suggested to be the monovalent copper ions (Cu(I)) formed in the sample through the heat treatment at high temperatures in vacuo[1]. Interestingly, a silver-ion-exchanged MFI zeolite (Ag(I)MFI), which takes the same electronic structure as Cu(I) in the CuMFI sample pretreated at high temperatures, has also been found to exhibit a specific adsorption property for Xe gas at room temperature. We have so far examined the state of the active sites formed in Ag(I)MFI during the evacuation at high temperatures in vacuo[1]. In the present study, we examined the change of the state of the silver ions in Ag(I)MFI zeolite during the evacuation at temperatures from 300 K to 873 K by the measurement of the X-ray absorption fine structure (XAFS) spectra. Regarding the treatment of the sample, two different methods were adopted.

Results and discussion
Prior to the measurements of the XAFS spectra, the Ag(I)MFI sample (Si/Al = 11.9; silver-ion-exchange level: 80%) was treated by two different manners as follows: (i) the sample was treated at a definite temperature for 2 h under a reduced pressure of 1.3 mPa (denoted as evac. at X K; X: evacuation temperature); (ii) the sample was maintained at a definite temperature for 1 h under an O2 pressure of about 13.3 kPa and then cooled to 300 K, followed by evacuation at 300 K for 1 h (denoted as O2 treat. at Y K; Y: O2 treatment temperature). In the latter case, the desorbed gases or the reaction products were removed using a liquid N2 trap during the O2 treatment. Figure 1 shows the Fourier transform of the extended X-ray absorption fine structure (EXAFS) oscillations at the K-edge of the silver-ion exchanged in the Ag(I)MFI sample. For the Ag(I)MFI sample treated in both manners, the bands observed at around 1.6 Å are responsible for the back-scattering from the nearest neighboring oxygen atoms, i.e., zeolite-lattice oxygen atoms (no phase-shift correction)[2]. With increase in the treatment temperature, the additional bands start to appear at around 2.7 Å (no phase-shift correction). Such the peaks can be due to the Ag–Ag species since the 2.7 Å-peaks are also observed in the case of the metallic silver. Here, it is noteworthy that the intensity of the band observed at around 2.7 Å is clearly different, depending on the treatment methods of the sample. In the case of the Ag(I)MFI sample evacuated at 473–873 K, it is clearly evidenced from the measurement of the DR-UV-Vis spectra that a large amount of the silver cluster in the sample has been formed. The results obtained here were in good agreement with the ones evaluated from the DR-UV-Vis spectra. The present result suggests that the state of the silver ions in Ag(I)MFI is capable of being controlled by the pre-treatment method of the sample. The detailed analysis of the change in the state of silver ions and the investigation relating to the correlation between the treatment method and the formation of the silver cluster are now in progress.

References

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