Specific interaction observed at 300 K of Xe with silver clusters formed in silver-ion-exchanged zeolites

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Introduction

A xenon (Xe) gas has been well-known to have a nonreactive nature since Xe belongs to the category of inert gases. Therefore, as far as we know, there are little materials being capable of interacting with Xe easily and rapidly at ordinary temperatures. We have so far found that the monovalent copper ions (Cu(I)) in the copper-ionexchanged MFI-type zeolites (CuMFI), which had been formed in the samples through the heat treatment in vacuo, strongly adsorb a xenon (Xe) gas, even at room temperature[1]. Furthermore, for the stable Cu(I)-Xe compounds formed in CuMFI, the Cu(I)-Xe bond length has been, for the first time, clarified to be 2.45 Å from the X-ray absorption fine structure (XAFS) measurements using a BL-9C of KEK-PF[1]. Very recently, we have examined the adsorption feature of Xe onto the silver-ionexchanged MFI (Ag(I)MFI) zeolites at room temperature since the silver (I) ions in Ag(I)MFI take the same electronic structure as Cu(I) in CuMFI. It was consequently found that Ag(I)MFI exhibits more efficient adsorption property for Xe, in comparison that for with CuMFI. In addition, among the various types of the zeolite frameworks, the use of the ferrierite-type (FER) zeolites as the mother zeolite seems to be effective for the Xe adsorption. However, the state of the active centers in the silver-ion-exchanged zeolites for Xe has not been elucidated yet.

In the present work, we investigated the specific interaction of the silver-ion-exchanged FER (Ag(I)FER) zeolites with Xe at room temperature by the XAFS measurements.

Results and discussion

Figure 1 shows the fourier transform of the extended X-ray absorption fine structure (EXAFS) oscillations at the K-edge of the silver ion in Ag(I)FER (Si/Al = 9.1; silver-ion-exchange level: 75%) treated under various conditions. Each spectrum was measured at room temperature. For the Ag(I)FER sample evacuated at 300 K, the band at around 1.7 Å is observed, which is responsible for the back-scattering from the nearest neighboring zeolite-lattice oxygen atoms (no phase-shift correction)[2]. With increase in the evacuation temperature, the additional band starts to appear at around 2.6 Å (no phase-shift correction). Such a band can be ascribable to the formed silver cluster in the Ag(I)FER sample since the band centered at 2.6 Å is also observed in the case of the metallic silver. Here, for the sample

evacuated at 873 K, the coordination number and the distance between silver metals were evaluated to be 1.9 and 2.77 Å, respectively. Taking account of the DR-UV-Vis spectra of AgFER(I) treated in various conditions, it was suggested that the silver ions in Ag(I)FER are forming the Ag_3^{m+} cluster (m < 3). The formation of the silver clusters was also confirmed in the case of Ag(I)MFI[3]. The intensity of the band at around 2.6 Å clearly decreases after the Xe adsorption at room temperature on AgFER (Fig.1). Such a phenomenon is well explained by considering that the overlapping of EXAFS waves for silver and Xe causes the interference, resulting in the apparent decrease of the intensity of the band at around 2.6 Å. By applying the three-shell fitting for this band based on the assumption that the similar clusters are survived after the adsorption of Xe, the coordination number and the bond length between Ag and Xe were estimated to be 0.5 and 2.63 Å, respectively. The value of the bond length estimated (2.63 Å) is smaller than the value of the sum of an ionic radius of Ag^+ (0.81 Å) and the van der Waals radius of Xe (2.16 Å). From

these results, it has become that there is the strong interaction at 300 K between silver clusters formed in Ag(I)FER and Xe: the structural information about the Xe compounds formed in zeolites was, for the first time, obtained as the $Ag_3^{m+} - Xe$ complex.

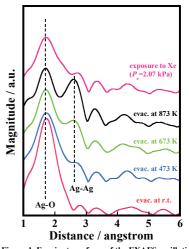


Figure 1. Fourier transform of the EXAFS oscillations at the K-edge of the silver-ion exchanged in Ag(I)FFR.

References

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