

# Anomalous Valence Change of Zinc Ion Exchanged in MFI-Type Zeolite Being Efficient for Dissociative Adsorption of Dihydrogen

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## 1 Introduction

Zinc ion-exchanged zeolites have been well-known to exhibit high levels of catalytic activity for dehydrogenation and aromatization of light alkanes [1,2]. In addition, the dissociative adsorption of dihydrogen ( $H_2$ ) molecule has so far been recognized to occur on the zinc ion-exchanged samples at relatively low temperature [3]. Therefore, it is important to clarify the state of active centers in the samples for these phenomena from the viewpoint of the development of efficient activation catalysts for alkanes and  $H_2$ . However, the kind of exchangeable sites for zinc ions in zeolites and the state of zinc ions exchanged are not completely elucidated, although some reports have so far been made on the subject [4,5]. In this contribution, the state of zinc ions exchanged in MFI-type zeolite and/or the change in the state of zinc ions exchanged by heat-treatment in vacuo and/or heat-treatment under an atmosphere of  $H_2$  were studied by means of X-ray absorption fine structure (XAFS) method. Through this work, we found the unprecedented redox behavior of zinc ions in MFI which work as the real activation sites for  $H_2$  [6].

## 2 Experiment

Zinc ion-exchanged MFI zeolite (ZnMFI) (Si/Al ratio of 11.9; zinc ion-exchange level = 95%) was prepared at room temperature in a  $Zn(NO_3)_2$  solution. The XAFS spectra were collected in transmission mode at the beamlines PF-7C and 9C equipped with a double crystal monochromator of Si(111). The self-supporting disk was placed into an in situ sample cell which is capable of pre-treatment of sample and gas introduction in situ.

## 3 Results and Discussion

Fig. 1 shows the Fourier transform of the extended X-ray absorption fine structure (EXAFS) oscillations at the K-edge of the zinc-ion exchanged for ZnMFI evacuated at 873 K. The analysis of the EXAFS data clarified that the zinc ion situated at the neighbourhood of three zeolite-lattice oxygen atoms with bond distance of about 2.05 Å. Taking accounts of the results of the density functional theory (DFT) calculations and other experiments, the EXAFS data indicated that the zinc ion is present at the M7 site in MFI with a certain environment and acts as the active center for  $H_2$  dissociation: the formation of  $-ZnH$  and  $-OH$  species.

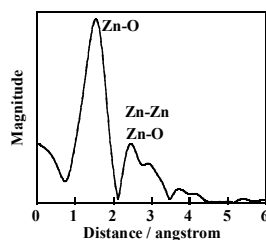


Fig. 1. EXAFS spectrum for ZnMFI.

In next, we chased the change of the state of zinc ions in ZnMFI by heat-treatment under an atmosphere of  $H_2$ . Fig. 2 represents the first derivative spectra of the X-ray absorption near edge structure (XANES) spectra (DXANES) for ZnMFI treated at various conditions. In this study, we look more closely at the

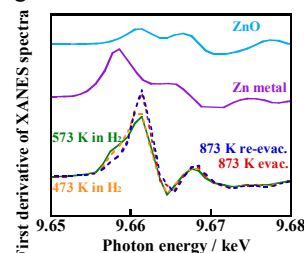


Fig. 2. DXANES spectra for ZnMFI and reference materials.

change of the state of zinc ion in ZnMFI from the DXANES spectra since the distinct difference was hardly confirmed from the XANES spectra. The DXANES spectra exhibited clear difference in the changes in the respective XANES spectra; the characteristic shoulder band appears at around 9.658 keV in the DXANES spectrum for the  $H_2$ -treated sample at 573 K, together with the 9.660 keV- and 9.668 keV-bands observed for every sample. The latter two bands are assigned to the  $1s-4p$  electronic transitions of  $Zn^{2+}$ . The Zn metal ( $Zn^0$ ), which was measured as the reference material, also shows the band at 9.659 keV in the DXANES spectrum. Therefore, we can consider that the 9.658 keV-band observed for the  $H_2$ -treated sample at 573 K (in DXANES) is due to the  $Zn^0$  formed in ZnMFI, which is well supported by DFT calculations. It is interesting that a stable  $Zn^0$  species is nevertheless formed in MFI by the reaction of  $Zn^{2+}$  with  $H_2$ , also the order in the ionization tendency series is situated in the position between  $Zn^{2+}$  ( $E^0 = -0.762$  V) and  $H^+$ . The  $Zn^0$  species formed were completely converted into the  $Zn^{2+}$  by re-evacuation at 873 K, which is accompanied by the disappearance of the characteristic band at 9.658 keV. From these results, we found the reversible redox cycle of zinc ions in ZnMFI being efficient for the dissociative adsorption of  $H_2$ :  $Zn^{2+} \rightarrow ZnH \rightarrow Zn^0 \rightarrow Zn^{2+}$ .

## References

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