

## Formation of Stable Monomeric Zn<sup>0</sup> and Zn<sup>+</sup> Species in MFI-Type Zeolite: Insight from *in-situ* XAFS Spectroscopy and DFT Calculation

In this work, we examined the H<sub>2</sub>-activation in ZnMFI and found a new and fascinating phenomenon that a stable Zn<sup>0</sup> species is formed through the reaction with H<sub>2</sub> at 423 K, followed by evacuation at 573 K, on the M7 site with S2 configuration of aluminum atoms in ZnMFI. The DFT calculation, combined with XAFS, IR, and UV-Vis-DR spectra, provided evidence that the formed species is composed of an atomic Zn<sup>0</sup> which is stabilized in the confined space. In addition, we also obtained a surprising finding that this stable Zn<sup>0</sup> species responds to UV-light, resulting in the formation of a novel Zn<sup>+</sup> species which exhibits an unusual reactivity with O<sub>2</sub> at 300 K.

In the ZnMFI-H<sub>2</sub> system, IR spectra show the behavior characteristic of heterolytic dissociation of H<sub>2</sub> below the temperature of 423 K; the dissociation of H<sub>2</sub> takes place heterolytically and with simultaneous formation of zinc hydride ( $\nu = 1933\text{ cm}^{-1}$ ) and Brønsted acidic site ( $\nu = 3615\text{ cm}^{-1}$ ). The changing processes of these species are also examined by the UV-Vis DR spectral method, as shown in Fig. 1. First, the sample evacuated at 873 K shows a weak band at around 39,000 cm<sup>-1</sup> which may be assignable to the band resulting from the 3d-4s transition of Zn<sup>2+</sup> (spectrum 1). On this surface, the H<sub>2</sub> molecules are introduced; a small change in the spectrum took place after the treatment temperature was raised to 423 K (spectrum 2). Subsequent evacuation at 473 K brought about the appearance of distinct bands at 42,000 and 47,000 cm<sup>-1</sup> (spectrum 3). These bands increase in their intensities with increasing evacuation temperature, and reached a maximum intensity by treatment at 523 or 573 K (spectra 4 and 5). The changes of IR spectra in these processes are also given in this figure as the difference spectra with the spectrum of the H<sub>2</sub>-treated sample (at 423 K). It is clearly found that the amount of formed -ZnH species decreases through evacuation at temperatures higher than 473 K, whereas the amount of -OH increases. Taking account of the IR data, these behaviors can be reasonably interpreted by

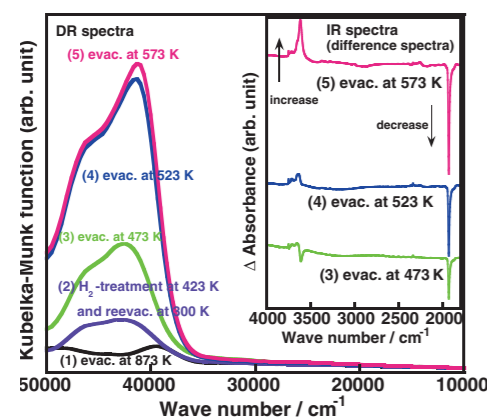
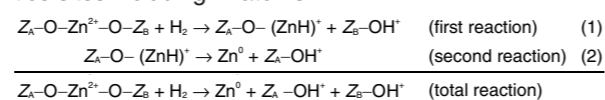


Figure 1: UV-Vis diffuse reflectance and IR spectra.

assuming the formation of the zinc metal species (reaction 2), where Z<sub>A</sub> and Z<sub>B</sub> mean the MFI-type zeolite lattice sites including Al atoms:



To verify the formation of metal species after H<sub>2</sub> treatment of ZnMFI at 423 K and subsequent evacuation at 573 K, we measured the XANES spectra for the sample treated with H<sub>2</sub> at 423 K, followed by evacuation at 573 K, as shown in Fig. 2. In connection with ZnMFI treated with H<sub>2</sub> at various temperatures, the change in the XANES spectra was very small. If the spectra are examined in detail, a shoulder band can be seen at the lower energy side in the first main band for the sample treated with H<sub>2</sub> at 423 K, followed by evacuation at 573 K. The XANES spectrum of atomic zinc vapor was reported by Mihelič *et al.* [1]; their datum is also depicted in this figure, clearly indicating the appearance of the highest band at around 9.66 keV. This fact strongly supports the presence of metal species in our sample: atomic zinc species. This band decreased in intensity after evacuation at 873 K and finally reverted to its original intensity. These facts give clear evidence that the reversible redox cycle is completely repeated: Zn<sup>2+</sup> → ZnH → Zn<sup>0</sup> → Zn<sup>2+</sup>.

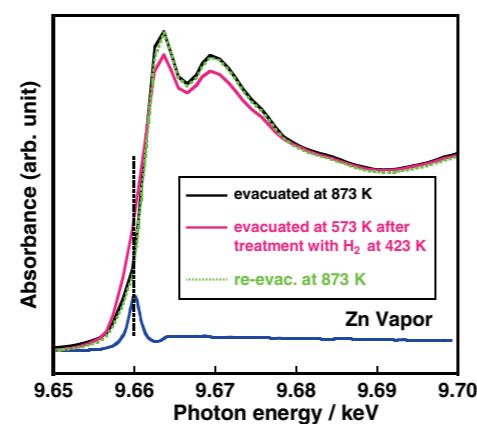


Figure 2: XANES spectra.

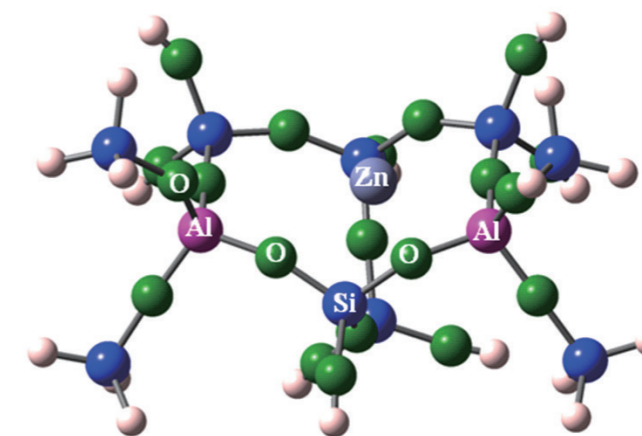


Figure 3: The M7-S2 model: ZnAl<sub>2</sub>Si<sub>9</sub>O<sub>20</sub>H<sub>20</sub>.

The heterolytic dissociation process of H<sub>2</sub> was followed with the aid of the DFT calculation method adopting the M7-S2 model (Fig. 3) that includes two aluminum atoms inserted into the skeleton of the MFI lattice in the six-membered ring, 6-MR, of the M7 site instead of two silicon atoms. First, we examined the possibility of simultaneous compensation of charges emanating from two alternative aluminum atoms to silicon atoms with a single Zn<sup>2+</sup> ion. Furthermore, the formation of -ZnH species, together with -OH, as well as the formation process of an atomic Zn<sup>0</sup> species, is completely explained by utilizing this model with the aid of the DFT calculation method [2].

In the next stage, the paramagnetic Zn<sup>+</sup> species was, for the first time, successfully prepared by excitation with UV light in the region being ascribable to the absorption band due to the 4s-4p transition of an atomic Zn<sup>0</sup> species encapsulated in the MFI-type zeolite. The formed species gives a specific ESR band at  $g = 1.998$  and also peculiar absorption bands at around 38,000 and 32,500 cm<sup>-1</sup>, which are clearly indicating the formation of the Zn<sup>+</sup> species in MFI. The transformation process (Zn<sup>0</sup> → Zn<sup>+</sup>) was explained by considering the mechanism via the excited triplet state (<sup>3</sup>P) caused by

the intersystem crossing from the excited singlet state (<sup>1</sup>P) of an atomic Zn<sup>0</sup> species grafted in MFI; the transformation process was well reproduced with the aid of the DFT calculation method. The thus-formed Zn<sup>+</sup> species exhibits a characteristic reactivity at room temperature with an O<sub>2</sub> molecule, forming a  $\eta^1$ -type of Zn<sup>2+</sup>-O<sub>2</sub><sup>-</sup> species [3].

### REFERENCES

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### BEAMLINES

AR-NW10A and BL-9C

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