

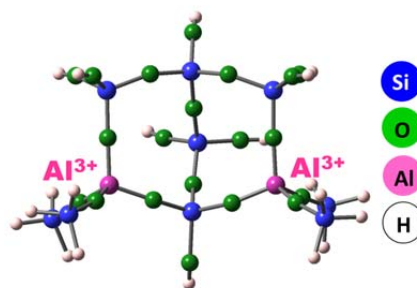
# Unprecedented electronic states of exchanged ions endowed by zeolite lattice – From where does such specificity come? -

Yasushige Kuroda

Department of Chemistry, Okayama University, Okayama, Japan

Email: kuroda@cc.okayama-u.ac.jp

Zeolites are crystalline aluminosilicates with subnano-sized pores. They are widely applied as catalysts in the modern petrochemical industry. Well-defined structures of zeolite comprise of the orderly inter-connected  $TO_4$  units (generally,  $T = Si^{4+}$  or  $Al^{3+}$ ). The negative charges that originate from the substitution of  $Al^{3+}$  for  $Si^{4+}$  are neutralized by the exchanged cations: protons or various kinds of metal ions. In this regard, it is well known that the properties of the exchanged cations significantly depend on the position and concentration of the Al atoms in the lattice, as well as their mutual array. Hence, understanding the relationship between the Al distribution and properties of the exchanged cations is essential for obtaining new insight into ways to improve the catalytic performance of the general zeolite-based catalysts or design new catalysts with higher functionalities. However, only few attempts have so far been made on the researches regarding the Al-array in zeolites. This is because nobody has found any phenomena which give useful information on the Al-array in zeolites utilizing the adequate real reaction system. In this work, we will propose a new, reliable, and significant idea; the important roles of **the Al array** in the reactivity observed on the metal-ion exchanged in zeolites, as well as of **the space** emanating from the curvature of zeolites, are examined by utilizing the spontaneous heterolytic cleavage reaction of  $H_2$  (or  $CH_4$ ) as the model reaction,<sup>1,2</sup> which was observed experimentally by our group on  $Zn^{2+}$ -ion exchanged in MFI-type zeolite ( $Zn^{2+}$ -MFI), with the aid of the DFT calculation method. In this work, we adopted two types of models for considering the Al positions in the case of calculation on our zeolite system, predominantly utilizing the M7-S2 site in MFI-type zeolite (**Figure** shown below): **the first type**, the Al atoms with appropriate distances are aligned in the circumferential direction of the straight channel (the **circumferentially arrayed Al-Al site**) and **the second type**, the nearest neighboring Al atoms with appropriate distances are directed toward the straight channel axis (the **channel directionally arrayed Al-Al site**). As the results, it is distinctly indicated that the Al-array direction governs the reactivity of  $Zn^{2+}$ -MFI; **the former type of array** well explains the experimental fact that the spontaneous and irreversible heterolysis of  $H_2$  takes place on  $Zn^{2+}$ -MFI even at room temperature, whereas **the latter type of array** is less reactive.



## References

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- (2) A. Oda, H. Torigoe, A. Itadani, T. Ohkubo, T. Yumura, H. Kobayashi, Y. Kuroda, *J. Phys. Chem. C* **2013**, 117, 19525–19534.