Theoretical Study of Gas-Adsorption to Metal-Organic-Framework (MOF)

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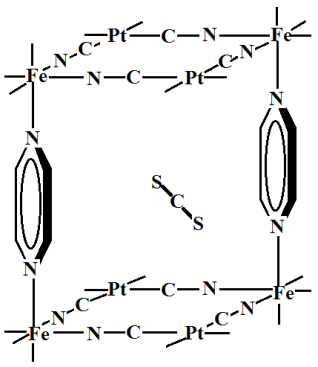
Metal-organic framework (MOF) attracts a lot of recent interests as separate absorption material, functional material, and catalyst. For instance, the Hoffmann type MOF induces the high spin (HS) to low spin transition (LS) by CS_2 adsorption.[1] Theoretical evaluation of interaction between gas molecule and MOF is necessary for well understanding of such functions of MOF and further development of the MOF chemistry. However, the evaluation of the interaction is not easy because of its very large size. Here, we wish to report highly reliable approximate method to evaluate binding energy of molecular cluster and its application to the interaction between gas molecule and MOF. Also, we wish to report the high-spin to low-spin transition of the Hoffmann type MOF by CS_2 adsorption.

In our new method, the binding energy of molecular cluster/complex is provided by eq 1,[2]

$$BE = BE(HF) + \Sigma\,[BE(Mi\text{-}Mj)^{MP2.5} - BE(Mi\text{-}Mj)^{HF}] \qquad (1)$$

where HF represents the Hartree-Fock method, and Mi etc. represents a molecule involved in the molecular complex. This equation can be derived based on the MP2 and MP3 energies.

We applied this method to evaluate the binding energy of CS_2 and CO_2 molecules with the Hoffmann type MOF $\{Fe(Pz)Pt(CN)_4\}_n$ (Pz = pyrazine); see Scheme 1.[1] In this MOF, CS_2 is sandwiched by two Pz molecules. The binding energy is not different very much between CS_2 and CO_2 when two Pz molecules are considered, but very different between them when total MOF framework is considered. Detailed discussion of the binding energy and the mechanism of the high-spin to low-spin transition will be presented in the talk.



Scheme 1

1) Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M.C.; Gaspar, A.B.; Real, J. A.; Yamasaki, M., Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. *Angew Chem Int Ed*, **2009**, 48, 4767.

2) Deshmukh, M.; Sakaki, S. to be published.

3) Ando, H.; Nakao, Y.; Sato, H.; Ohba, M.; Sakaki, S. to be published.