DFT investigation on H_2 and O_2 activation by bio-inspired NiFe complexes

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Molecular hydrogen is a promising candidate for the next generation of clean energy resource alternative to fossil fuel which is finite and emits undesirable chemical compounds, CO_2, NO_x, and SO_x into the environment. The development of the catalyst which can efficiently and selectively activate and generate the hydrogen molecule is highly demanded. For the industrial application, it is crucial to use non-precious metals such as Ni, Fe, and Mn as the central metal and to design ligand so as to work in the non-toxic solvent. It is known that the biological enzyme hydrogenase found in cyanobacteria can catalyze the activation/generation of H_2.[1] Therefore, a great effort has been devoted to synthesizing complexes mimicking the function and structure of the catalytic center in hydrogenase.

Recently, Ogo and co-workers,[2,3] developed model complexes of NiFe hydrogenase which catalyze H_2 and O_2 activation. The catalyst of H_2 activation is the first reported catalyst which accomplished electron, hydride, and proton transfer. In order to develop the further highly efficient catalyst, the clarification of the mechanistic details is crucial. The density-functional calculation is useful for this purpose. In this seminar, our recent DFT studies on the bio-inspired NiFe complexes for H_2 and O_2 activation[4] are presented. The mechanistic insight revealed in this study helps to interpret the catalytic cycle of NiFe hydrogenase and to develop the efficient bio-inspired catalyst for H_2 and O_2 activation.

(1) Lubitz, W.; Ogata, H.; Rudiger, O.; Reijerse, E., Hydrogenases. *Chem. Rev.* **2014,** *114*, 4081-4148.
(2) Ogo, S.; Ichikawa, K.; Kishima, T.; Matsumoto, T.; Nakai, H.; Kusaka, K.; Ohhara, T., A Functional [NiFe]Hydrogenase Mimic That Catalyzes Electron and Hydride Transfer from H_2. *Science* **2013,** *339*, 682-684.
(3) Kishima, T.; Matsumoto, T.; Nakai, H.; Hayami, S.; Ohta, T.; Ogo, S., A High-Valent Iron(IV) Peroxo Core Derived from O_2. *Angew. Chem. Int. Ed.* **2016,** *55*, 724-727.
(4) Isegawa, M.; Sharma, A. K.; Ogo, S.; Morokuma, K., DFT Study on Fe(IV)-Peroxo Formation and H-Atom Transfer Triggered O_2 Activation by NiFe Complex. *Organometallics* **2018,** *37*, 1534-1545.