Quantum chemical studies on methane hydroxylation by various transition-metal–oxo species

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Abstract: We have discussed the mechanisms of methane hydroxylation by simple metal–oxo species, metalloenzymes, their synthetic models, and metal-exchanged zeolites on the basis of DFT calculations. Special attention is paid to the reactivity of metal-exchanged zeolites in this talk. The influence of different metals on this reaction is investigated by using DFT calculations on a periodic system of MO^+-ZSM-5 zeolite (M = Fe, Co, Ni, and Cu).

Keywords: DFT calculation, Metalloenzyme, Methane hydroxylation, Zeolite

The bond dissociation energy and bond length of a parent molecule producing a radical are useful measures in considering the stability of a free radical. We have discussed a non-radical mechanism for methane hydroxylation by the bare MO^+ complex and methane monooxygenases (sMMO and pMMO) using DFT calculations.[1,2] This mechanism is applicable when metal–oxo species are coordinatively unsaturated. A radical mechanism that involves carbon radical as an intermediate can take place when the active species are coordinatively saturated as in compound I of cytochrome P450, which is believed to be iron(IV)-oxo porphyrin π-cation radical. Direct interaction between methane and a metal active center can form a weakly bound methane complex in the initial stages of the reaction. Subsequent C–H bond cleavage to form an intermediate with an HO–M–CH_3 moiety in a non-radical manner and recombination

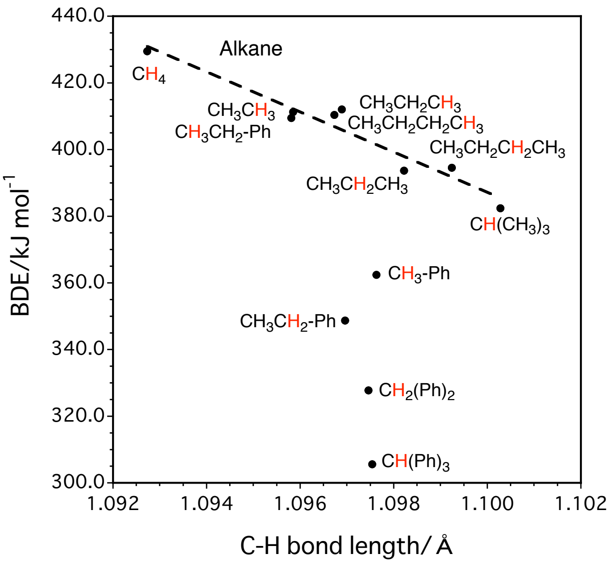

Fig. 1. Correlation between C–H bond dissociation energies and bond lengths calculated at the B3LYP/6-311++G** level of theory.

of the resultant OH and CH_3 ligands take place at a metal active center to form a final methanol complex. Thus, this is a non-radical, two-step reaction. The fact that methyl radical is 10–20 kcal/mol less stable than secondary and tertiary carbon radicals and benzyl radicals leads us to reasonably propose this non-radical mechanism. This mechanism is widely applicable to enzymatic and metal-exchanged zeolite systems.[2,3] Metal-exchanged zeolites are known to exhibit catalytic activity in the direct conversion of methane to methanol. The influence of different metals on this reaction is theoretically investigated by using DFT calculations on a periodic system of MO^+-ZSM-5 zeolite (M = Fe, Co, Ni, and Cu).[3] The results indicate a high dependency of the reaction on the metals, where the reactivity towards C–H bond dissociation is predicted to increase in the order of CoO^+-ZSM-5 < NiO^+-ZSM-5 < FeO^+-ZSM-5 < CuO^+-ZSM-5 and the selectivity of methanol is predicted to increase in the order of FeO^+-ZSM-5 < CoO^+-ZSM-5 < NiO^+-ZSM-5 < CuO^+-ZSM-5. The role of ZSM-5 zeolite in the catalytic activity is also investigated by comparing our calculation results with those reported for the reaction by the bare MO^+ species in the gas phase.[4] We found that the nanopores of ZSM-5 zeolite exert a confinement effect, which destabilizes the adsorption of methane and can lower the activation energy for the C–H bond dissociation. In addition to the conversion of methane, we investigated the direct conversion of ethane to ethanol by FeO^+-ZSM-5 and found that this reaction proceeds with a lower C–H bond activation energy and a higher product selectivity compared to the conversion of methane to methanol by the same catalyst.

References

1. Yoshizawa, K. *Acc. Chem. Res.* **2006**, *39*, 375; *Bull. Chem. Soc. Jpn.* **2013**, *86*, 1083.

2. Yoshizawa, K.; Shiota, Y. *J. Am. Chem. Soc.* **2006**, *128*, 9873; Shiota, Y.; Juhasz, G.; Yoshizawa, K. *Inorg. Chem.* **2013**, *52*, 7907.

3. Mahyuddin, M. H.; Staykov, A.; Shiota, Y.; Yoshizawa, K. *ACS Catal.* **2016**, *6*, 8321; Mahyuddin, M. H.; Staykov, A.; Shiota, Y.; Miyanishi, M.; Yoshizawa, K. *ACS Catal.* **2017**, *7*, 3741.

4. Schröder, D.; Schwarz, H. *Angew. Chem. Int. Ed.* **1995**, *34*, 1973.