

Quantum Chemical Studies of Methane Oxidation to Methanol on a Biomimetic Tricopper Complex: A Mechanistic View

Chen-Hao Yeh and Jyh-Chiang Jiang*

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

**Corresponding author E-mail address: jcjiang@mail.ntust.edu.tw*

Abstract:

In this work, we have investigated methane oxidation to methanol on the biomimetic tricopper complex $[\text{Cu}_3(7\text{-N-Etppz})]^{1+}$ using DFT calculations. Both the concerted mechanism and the radical rebound mechanism of methane oxidation to methanol have been considered. Regarding the adsorption of methane on the tricopper complex, we found that there is a C-H \cdots O hydrogen bond between CH₄ and the oxygen atom, resulting in a small activation barrier of C-H bond cleavage. The small reaction barriers of methane to methanol indicates that the biomimetic complex $[\text{Cu}_3(7\text{-N-Etppz})]^{1+}$ can be a good oxidizer for methane monooxygenase chemistry due to the low reaction barriers.

Keywords: Methane Conversion, PMMO, Tricopper catalyst.

1. Introduction (11-point boldface)

Particulate methane monooxygenase (pMMO) was found to be the most efficient oxidizer for the conversion of methane to methanol at room temperature. In this work, DFT calculation was applied to investigate the possible mechanism of methane conversion to methanol on the $[\text{Cu}_3(7\text{-N-Etppz})]^{1+}$ complex, which is the real complex synthesized by Chan laboratory.^{1,2} Since the mechanism of selective oxidation of methane to methanol by the $[\text{Cu}_3(7\text{-N-Etppz})]^{1+}$ complex is still unclear, both possible mechanisms of methane conversion (concerted and radical rebound) are calculated and discussed in this work.

2. Experimental (or Theoretical)

All calculations were performed using the Gaussian 09 package. The long range corrected functional of unrestricted B3LYP with the Coulomb-attenuating method (CAM-B3LYP) was carried out during structure optimization. The Los Alamos double- ξ (LANL2DZ) effective core potential basis set was implemented for the copper atom and the 6-31+G* basis set for carbon, nitrogen, hydrogen and oxygen elements was used in this study. The broken-symmetry approach was also adopted to describe the low-spin state energies from the unrestricted calculation.

3. Results and discussion

There are two possible mechanisms of methane conversion to methanol on copper-containing catalysts: (1) the concerted mechanism and (2) the radical rebound mechanism. In the concerted mechanism, the C-H bond cleavage of methane occurs through the nonlinear C--O--H transition state and is accompanied by oxygen insertion to form methanol. The calculated reaction barrier of concerted methane oxidation to methanol on the $[\text{Cu}_3(\mu\text{-O})_2(\text{L}_1)]^{1+}$ complex is 0.70 eV. In addition, the radical rebound mechanism takes place by hydrogen abstraction to produce methyl and hydroxyl groups, which are then recombined to form methanol. The reaction barriers of C-H bond cleavage and C-O recombination are 0.33 eV and 0.38 eV respectively.

4. Conclusions

To find the reaction barrier of methane conversion to methanol on the tricopper complex, both the concerted and radical rebound mechanisms were investigated. The rate-determining barrier through the radical rebound mechanism is smaller than that via the concerted mechanism. The calculated KIE values of the concerted and the radical rebound mechanisms at 30 °C are 4.91 and 0.88, respectively. Since there are no experimental KIE observations for methane conversion to methanol at the $[\text{Cu}_3(7\text{-N-Etppz})]^{1+}$ complex to date, our calculated KIE values can serve as a reference in future experimental studies.

References

1. Chan, S. I.; Lu, Y.-J.; Nagababu, P.; Maji, S.; Hung, M.-C.; Lee, M. M.; Hsu, I.-J.; Minh, P. D.; Lai, J. C.-H.; Ng, K. Y.; Ramalingam, S.; Yu, S. S.-F.; Chan, M. K. *Angew. Chem. Int. Ed.* 52 (2013) 3731.
2. Wang, V. C.-C.; Maji, S.; Chen, P. P.-Y.; Lee, H. K. Yu, S. S.-F.; Chan, S. I. *Chem. Rev.* 117 (2017) 8574.