# Methane Partial Oxidation over $[Cu_2(\mu\text{-}O)]^{2+}$ Active Species in Small-, Medium-, and Large-Pore Zeolites

**Muhammad Haris Mahyuddin,**[a] **Aleksandar Staykov,**[b] **Yoshihito Shiota,**[a] **and Kazunari Yoshizawa**[a,*]

[a]*Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, 819-0395, Japan*
[b]*International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, 819-0395, Japan*

**kazunari@ms.ifoc.kyushu-u.ac.jp, TEL: 092-802-2529, FAX: 092-802-2528*

**Abstract:** The direct conversion of methane to methanol over $[Cu_2(\mu\text{-}O)]^{2+}$ species hosted in SSZ-13 (CHA), ZSM-5 (MFI), and mordenite (MOR) zeolites is evaluated by using density functional theory (DFT) calculations. We found C–H bond activation energies that excellently agree with the experimental values. Strong candidates for the actual active sites are proposed and main factors influencing the reactivity of $[Cu_2(\mu\text{-}O)]^{2+}$ toward $CH_4$ are elucidated comprehensively.

**Keywords:** Methane hydroxylation, Methanol, Zeolites, Dicopper.

## 1. Introduction

The depletion of fossil energy sources, primarily oil and coal, has driven the utilization of abundant natural gas as a transitional solution toward sustainable energy sources although gas is difficult to transport. To overcome this difficulty, methane, the major component of natural gas, should be converted to liquid forms such as methanol. While the existing technology for such a gas-to-liquid process involves an expensive process, methane can actually be converted in a one-step catalytic reaction called partial oxidation. However, this direct conversion strategy requires a highly reactive catalyst that can easily cleave the strong C–H bonds of methane at low temperatures.

Among all solid catalysts suitable for methane hydroxylation, metal-exchanged zeolites are the ones that can achieve activity and selectivity as high as those of the enzyme catalysts. The $[Cu_2(\mu\text{-}O)]^{2+}$ core has been proposed to be the active species in Cu-exchanged zeolites.[1,2] The small-pore Cu-CHA and large-pore Cu-MOR zeolites were reported to produce more amount of methanol (42.4 and 48.3 mmol/mol-Cu, respectively) than the medium-pore Cu-MFI does (14.3 mmol/mol-Cu).[3] Herein, we calculate the reaction energy diagrams for methane partial oxidation over $[Cu_2(\mu\text{-}O)]^{2+}$-CHA, -MFI, and -MOR to elucidate the discrepancy in their catalytic activities.[4–6]

## 2. Theoretical

DFT calculations were performed by using Vienna Ab-initio Simulation Package (VASP). The electron exchange-correlation was treated by GGA-PBE functional. The plane wave basis sets with cutoff energy of 550 eV and $\Gamma$ point-only Brillouin zone were used. The Grimme's D2 method was used to account for van der Waals interactions. Climbing-image Nudged Elastic Band (cNEB) method was used to locate transition states. One unit cell of CHA and MFI frameworks and two unit cells of MOR framework were used to construct their periodic structures. Two Si atoms of each zeolite framework were replaced by two Al atoms, resulting in a negative charge of –2, which is then compensated by $[Cu_2(\mu\text{-}O)]^{2+}$ to form neutral systems. Both the high-spin state (triplet) and the low-spin state (open- and closed-shell singlet) are considered.

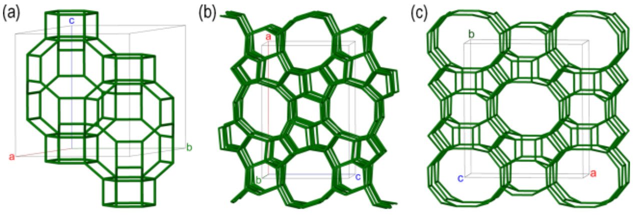

**Figure 1.** (a) CHA, (b) MFI, and (c) MOR zeolite frameworks.

## 3. Results and discussion

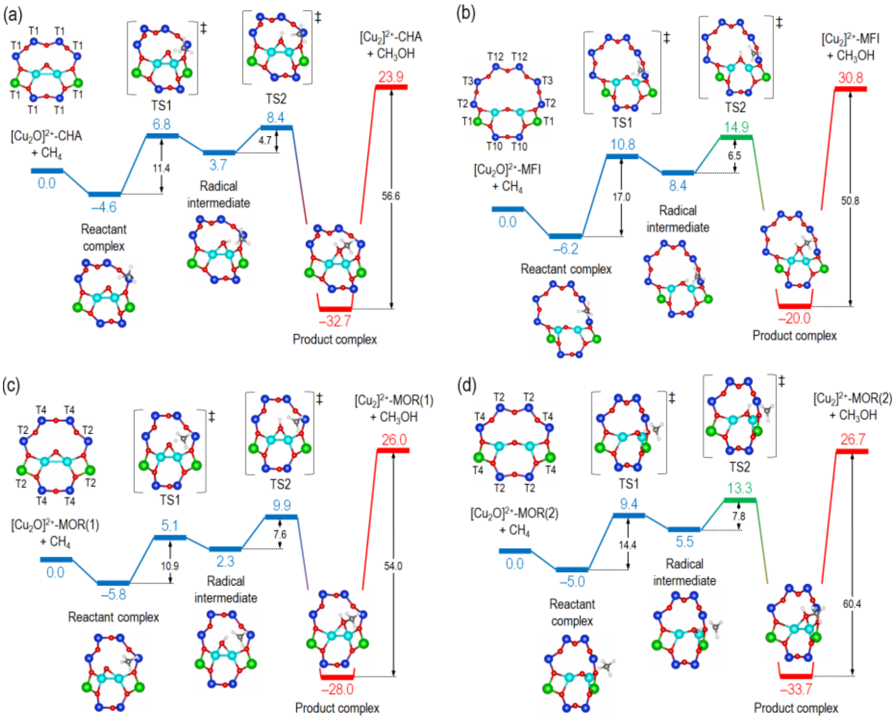

**Figure 2.** Energy diagrams for the reaction over $[Cu_2(\mu\text{-}O)]^{2+}$ on (a) CHA(T1/T1), (b) MFI(T1/T1), (c) MOR(T2/T2), and (d) MOR(T4/T4) in the ground state.

As shown in Figure 2, the C–H bond activation energies for $[Cu_2(\mu\text{-}O)]^{2+}$-CHA, -MFI, -MOR(1), and -MOR(2) are respectively calculated to be 11.4, 17.0, 10.9, and 14.4 kcal/mol. Surprisingly, the last three values perfectly match the experimental values of 15.7, 11.1, and 14.7 ± 0.5 kcal/mol, respectively.[1,2] The calculated ∠CuOCu angles for **TS1** of $[Cu_2(\mu\text{-}O)]^{2+}$-CHA, -MFI, -MOR(1), and -MOR(2) are 86.0°, 134.2°, 82°, and 126.3°, respectively, which seem to be related to the activation energy.

To understand the reasons for such a reactivity difference, we investigate the role of zeolite confinement and ∠CuOCu angle. Small cluster models of each reactant complex and **TS1** are calculated and their relative energies are compared with those for the periodic models. We found that $CH_4$ activation energies calculated for the cluster models of $[Cu_2(\mu\text{-}O)]^{2+}$-CHA, -MFI, and MOR(1) are similarly (about 4~5 kcal/mol) higher than the corresponding periodic models. This suggests that CHA, MFI, and MOR zeolites exhibit similar confinement effects on methane partial oxidation. Thus, zeolite confinement effects are not responsible for the reactivity difference toward methane. We then calculate a Walsh diagram of $[Cu_2(\mu\text{-}O)]^{2+}$-zeolite cluster in the triplet state for different ∠CuOCu angles. The Walsh diagram shows that the energy of the HOMO −1, which is one of the singly-occupied orbitals and the acceptor orbital of the active species, is decreased when the ∠CuOCu angle becomes smaller. Such an energy decrease in HOMO −1 strengthens its interactions with the donor orbital (HOMO) of $CH_4$ and thus reduces the activation energy. Since **TS1** of $[Cu_2(\mu\text{-}O)]^{2+}$-CHA and -MOR(1) has smaller ∠CuOCu angles than **TS1** of $[Cu_2(\mu\text{-}O)]^{2+}$-MFI does, it is thus apparent that ∠CuOCu plays an important role in the H-atom abstraction of methane.

## 4. Conclusions

We have successfully calculated activation energies ($E_a$) for C–H bond cleavage over $[Cu_2(\mu\text{-}O)]^{2+}$-CHA, -MFI, -MOR zeolites. Based on an agreement with the experimental $E_a$, we suggest T2/T2 and T4/T4 sites of MOR as strong candidates for the actual Al-pair sites. Confinement of methane by the zeolite cage and CuOCu angle of the active species are found to contribute significant energy reduction to the $E_a$.

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