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Methane Oxidation to Methanol Catalyzed by Copper Oxide Clusters Supported in MIL-53(Al): A Density Functional Theory Study

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Abstract : Reducing greenhouse gases or converting them into fuels and chemicals with added value is vital for the environment. Given the enhanced techniques for hydrocarbon extraction in this context, the catalytic conversion of methane to methanol is particularly intriguing for future applications as vehicle fuels and/or bulk chemicals. Metal-organic frameworks (MOFs) have received much attention recently for the oxidation of methane to methanol. In addition, biomimetic material, particulate methane monooxygenase (pMMO), has been reported to convert methane using copper oxide clusters as active sites. Inspired by these, in this study, we considered the well-known MIL-53(Al) MOF as support for copper oxide clusters (Cu2Ox, Cu3Ox) to investigate their reactivity towards methane oxidation using Density Functional Theory (DFT) calculations. The copper oxide clusters (Cu2O2, Cu3O2) are modeled by oxidizing copper clusters (Cu2, Cu3) with two oxidizers, O2 and N2O. The initial C-H bond activation barriers on Cu2O2/MIL-53(Al) and Cu3O2/MIL-53(Al) catalysts are 0.70 eV and 0.64 eV, respectively, and are the rate-determining steps in the overall methane conversion to methanol reactions. The desorption energy of the methanol over the Cu2O/MIL-53(Al) and Cu3O/MIL-53(Al) is 0.71eV and 0.75 eV, respectively. Furthermore, to explore the prospect of catalyst reusability, we considered the different oxidants and proposed the different reaction pathways for completing the reaction cycle and regenerating the active copper oxide clusters. To know the reason for the difference between bi-copper and tri-cooper systems, we also did an electronic analysis. Finally, we calculate the Microkinetic Simulation. The result shows that the reaction can happen at room temperature.

Keywords : DFT study, copper oxide cluster, MOFs, methane conversion
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