

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

Authors : Chun-Wei Yeh, Santhanamoorthi Nachimuthu, Jyh-Chiang Jiang

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 (Cu₂O_x, Cu₃O_x) 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

Conference Title : ICACE 2023 : International Conference on Applications of Catalysis Engineering

Conference Location : Tokyo, Japan

Conference Dates : May 22-23, 2023