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Authors: Hieu A. Doan, Zhanyong Li, Omar K. Farha, Joseph T. Hupp, Randall Q. Snurr

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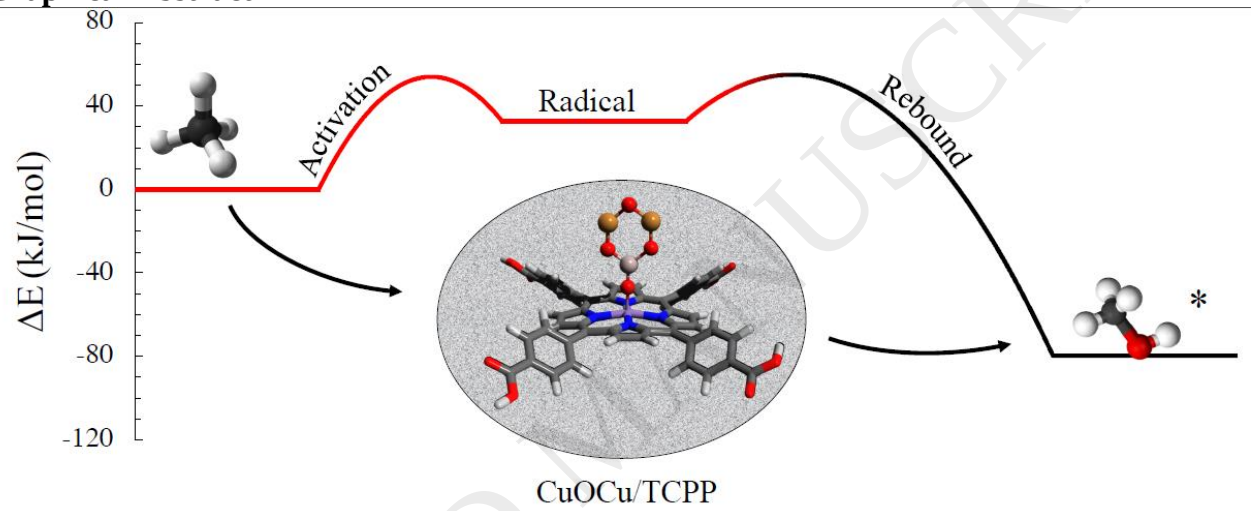
Theoretical Insights into Direct Methane to Methanol Conversion over Supported Dicopper Oxo Nanoclusters

Hieu A. Doan[1], Zhanyong Li[2], Omar K. Farha[2], Joseph T. Hupp[2], and Randall Q. Snurr[1,*]

[1]Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA
[2]Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

[*]**Corresponding author**. E-mail address: snurr@northwestern.edu

Graphical Abstract



Highlights

- Copper nanoclusters on porphyrin supports via atomic layer deposition
- Thermal treatment leads to the formation of a dicopper oxo active site
- Favorable methane activation is attributed to the radical-like active oxygen
- Water predicted to enhance methanol extraction

ABSTRACT

The prospect of using copper oxide nanoclusters grown by atomic layer deposition on a porphyrin support for selective oxidation of methane to methanol was examined by means of density functional theory (DFT) calculations. Ab initio thermodynamic analysis indicates that an active site in the form of Cu(μ-O)Cu can be stabilized by activation in O_2 at 465 K. Furthermore, a moderate methane activation energy barrier (E_a = 54 kJ/mol) is predicted, and the hydrogen abstraction activity of the active site could be attributed to the radical character of the bridging oxygen. Methanol extraction in this system is limited by a thermodynamic barrier to desorption of ΔG = 57 kJ/mol at 473 K; however, desorption can be facilitated by the addition of water in a "stepped conversion" process. Overall, our results indicate similar activity between porphyrin-supported copper oxide nanoclusters and existing Cu-exchanged zeolites and provide a