

Investigation of Metal Sites within Metal-Organic Frameworks for Oxidation Catalysis

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Metal-organic frameworks, or MOFs, are a new class of nanoporous crystalline materials. They self-assemble in solution to form networks with metal corners and organic linkers. Variation of the linker or corner allows great flexibility to tailor the local pore environment for desired applications. MOFs have received much attention for hydrogen storage, separations, and more recently catalysis. Metal cations coordinated within MOFs have become attractive active sites for reactions of interest. Recently, Corma and coworkers (Xamena et al., *J. Catal.*, 2008, 255, 220) showed that cobalt and copper sites in two particular MOFs were active for peroxide decomposition during tetralin autooxidation. During this process, tetralin in the presence of dioxygen reacts to form tetralin-hydroperoxide, whose subsequent decomposition leads to the desired oxidized products, tetralone and tetralol. Corma and coworkers suggest that the intermediate hydroperoxide molecules decompose into peroxy and hydroperoxy radicals through a Haber-Weiss cycle, where the metal switches between two different oxidation states. Using density functional theory (DFT), we have investigated these Haber-Weiss decomposition reactions over different metal sites. As a starting point, we mapped the reaction coordinate of the decomposition reactions over bare cations and estimated enthalpies of reaction for each decomposition reaction. Our results indicate that overcoming significant activation barriers is required to break both oxygen-oxygen and oxygen-hydrogen bonds of the intermediate hydroperoxide. Additionally, we find that the complete Haber-Weiss cycle involving the decomposition of two intermediate hydroperoxides into water and peroxy and alkoxy radicals is endothermic by approximately 7 kcal/mol. Currently we are mapping these reactions over representative clusters from within each MOF to determine the electronic and steric effects of coordinating ligands around the metal on the energetics of these reactions.