

Mechanism of C-H Bond Activation by High-Spin Iron in a MOF

Alkanes are a major component of natural gas, and their conversion into functionalized chemicals is a challenging task. Enzymes that support high-valent iron(IV)–oxo intermediates are known to activate the strong C–H bond present in alkanes, converting them into more useful chemicals, but duplicating this reactivity in synthetic materials is difficult. A collaborative work between the University of Minnesota-Twin Cities and the University of California, Berkeley has shown that a synthetic metal–organic framework (MOF) presents similar reactivity. Specifically, an iron containing MOF can catalyze the activation of one of the strongest known C–H bonds, that of ethane, via the formation of an iron(IV)–oxo species with an unusual spin ($S = 2$).

The unusual high spin state of iron in the MOF is made possible by the constrained environment of five weak-field ligands held in place by the MOF; this demonstrates the power of MOFs to contain metal ions in coordination environments that do not exist in liquid solvent environments. A detailed mechanism of the catalytic conversion in the MOF has been investigated by employing both Kohn-Sham density functional theory and multi-configuration wave function theory. It has been found that a high-spin iron(IV)–oxo is the catalytically active species and that it can lower the activation barrier from 67 kcal/mol for the uncatalyzed reaction to 20 kcal/mol for the slowest step in the iron(IV)–oxo catalyzed reaction.

The quantum mechanical characterization of the structures of the species involved in the reaction was performed by graduate student Pragya Verma in Professor Truhlar's group and three members of Professor Gagliardi's group, namely postdoctoral research associates Konstantinos Vogiatzis and Nora Planas and graduate student Joshua Borycz. This project is sponsored by the US Department of Energy funded Nanoporous Materials Genome Center based at the university of Minnesota: <http://www.chem.umn.edu/nmgc/>

Full details of the study are available at “Mechanism of Oxidation of Ethane to Ethanol at Iron(IV)–Oxo Sites in Magnesium-Diluted $\text{Fe}_2(\text{dobdc})$,” P. Verma, K. D. Vogiatzis, N. Planas, J. Borycz, D. J. Xiao, J. R. Long, L. Gagliardi, and D. G. Truhlar, *Journal of the American Chemical Society*, Article ASAP. dx.doi.org/10.1021/jacs.5b00382

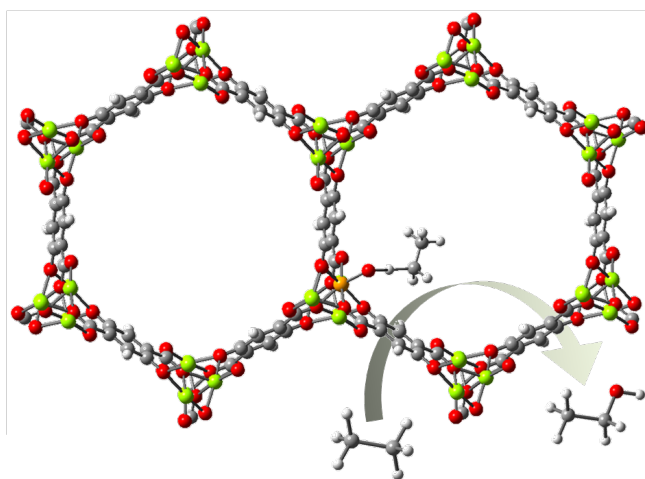


Figure 1. The transformation of ethane to ethanol facilitated by high-spin ($S = 2$) Fe(IV)=O intermediate formed in magnesium-diluted metal–organic framework, $\text{Fe}_{0.1}\text{Mg}_{1.9}(\text{dobdc})$. [Color code: orange = Fe, green = Mg, red = O, gray = C, white = H]