

Mechanistic Studies and Design of Supported Transition Metal Complexes

by

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Technical Summary

Supported transition metal (TM) complexes are an emerging class of materials with many potential applications in the chemical industry ranging from separations to catalysis. They offer increased tunability and often also improved performance over their bulk heterogeneous counterparts. Their study and rational design is, however, accompanied by several unique considerations and challenges that we address in this thesis.

The first part of the thesis broadly develops and applies computational screening strategies for supported TM complexes. First, we detail how weak C-H \cdots O hydrogen bonds can be exploited to increase selectivity of ferrocenium (Fc⁺)-based polymer electrode materials for formate adsorption over perchlorate adsorption while maintaining reasonable desorption rates in the reduced (ferrocene, Fc) state. Through a systematic characterization of formate and perchlorate interactions with a small (ca. 40) but diverse set of functionalized Fc⁺ complexes, we identify and rationalize design rules for functionalizations that simultaneously increase selectivity for formate in aqueous environments while permitting rapid release from Fc. Next, we screen a larger (ca. 500) set of model Fe(II) complexes for methane hydroxylation in order to assess if linear free energy relationships (LFERs), extensively developed to reduce the computational cost of computationally screening bulk heterogeneous catalysts, can also be applied to supported single-site TM catalysts. We demonstrate that structural distortions achievable in porous frameworks and chelating ligands break these LFERs by altering relative *d*-orbital splittings, thereby revealing a potential strategy for improving the activity of these catalysts. Finally, to address a particularly pervasive issue in density functional theory (DFT) studies of first-row open-shell TM complexes, we investigate how the fraction of exact exchange parameterized in the functional affects computed reaction and spin-splitting energies. We rationalize this sensitivity in terms of differences in metal-ligand electron delocalization and introduce the metal-ligand bond valence as a simple, yet robust, descriptor that unifies understanding of exchange sensitivity for catalytic properties and spin-state ordering in TM complexes.

The second part of the thesis investigates olefin metathesis catalyzed by well-dispersed tungsten oxide supported on silica, a system with industrial relevance as a promising technology for on-

purpose propylene production but particularly challenging to study because supported alkylidene complexes, the purported active sites, are highly unstable and only exist under reaction conditions. Through a combination of kinetic, spectroscopic and computational studies, we identify a hitherto unknown active site decay and renewal cycle, mediated by silanol groups proximal to the tungsten sites, operating in parallel with the classical Chauvin cycle for homogeneous metathesis catalysts that explains many puzzling features of heterogeneous olefin metathesis. We further show how this cycle can be manipulated using small quantities of promoter olefins to increase steady-state propylene metathesis rates by up to 30-fold at 250°C with negligible promoter consumption. The increase in activity and reduction of operating temperature requirements enabled by this strategy address major roadblocks associated with tungsten-based industrial metathesis processes.

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