

# Homogeneous Catalysis Meets Heterogeneous Catalysis: Alkanes and Alkenes Transformations

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Systematic study of the interactions between organometallic catalysts and metal oxide support materials is essential for the realization of rational design in heterogeneous catalysis. Herein we describe the stoichiometric and catalytic chemistry of a  $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{III})]$  complex chemisorbed on a variety of acidic metal oxides as a multifaceted probe for stereoelectronic communication between the support and organometallic center. Electrophilic bond activation was explored in the context of stoichiometric hydrogenolysis as well as catalytic H/D exchange. Further information was obtained from the observation of processes related to dynamic exchange between grafted organometallic species and those in solution. The supported organometallic species were characterized by a variety of spectroscopic techniques including DNP solid-state NMR spectroscopy, DRIFT, and XAS. Strongly acidic modified metal oxides such as sulfated zirconia engender high levels of activity toward electrophilic bond activation of both  $\text{sp}^2$  and  $\text{sp}^3$  C–H bonds, including the rapid deuteration of methane at room temperature; however, the global trend for the supports studied here does not suggest a direct correlation between activity and surface Brønsted acidity, and more complex metal surface interactions are at play. One such interaction was identified as an unexpected redox event between the organometallic species and the modified oxide surfaces.

Evidence of oxidative mechanism was provided by studying the analogous homogeneous reactivity of the organometallic precursors toward  $[\text{Ph}_3\text{C}]^+$ , a Lewis acid known to effect formal hydride abstraction by one electron oxidation followed

by hydrogen abstraction. Organometallic deuterium incorporation, a result of the surface redox process, was found to be correlated with surface sulfate concentration, as well as the extent of dehydration under thermal activation conditions of sulfated alumina and sulfated zirconia supports. Surface sulfate concentration dependence, in conjunction with a computational study of surface electron affinity, indicates an electron deficient pyrosulfate species as the redox active moiety. These results provide further evidence for the ability of sulfated metal oxides to participate in redox chemistry not only toward organometallic complexes, but also in the larger context of their application as catalysts for the transformation of light alkanes.

