## Electronic Metal-Support Communication in Surface Organometallic Catalysis

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Chemisorption of organometallic complexes on inorganic support materials offers a convenient route to catalytically-active materials at the interface between homogeneous and heterogeneous catalysis, however, the surface as an inner sphere ligand is underutilized as a tool to modulate catalyst reactivity. In this talk, a series of supported organometallic complexes will be examined with an eye toward understanding how the electronic interaction between the surface and the metal center can be leveraged to control catalytic reactivity. The stoichiometric and catalytic chemistry of organoiridium complexes chemisorbed on a series of traditional and modified metal oxides will be discussed as a multifaceted probe for stereoelectronic communication between the support and organometallic center. Electrophilic bond activation in these systems was explored in the context of stoichiometric hydrogenolysis and dehydrogenation as well as catalytic hydrogenation, and H/D exchange.<sup>1,2</sup> Concepts from this comparative study were then applied toward the rational design of a highly active organoiridium pincer catalyst supported on sulfated zirconia, exhibiting high activity and stability.<sup>3</sup> The observation of an unexpected redox interaction between an organometallic precursor and the sulfated oxide surface prompted new directions for the study of redox active surfaces as a mechanism for catalyst control and activation.



<sup>[1]</sup> Klet, R. C.; Kaphan, D. M.; Liu, C.; Yang, C.; Kropf, A. J.; Perras, F. A.; Pruski, M.; Hock, A. S.; Delferro, M. J. Am. Chem. Soc. 2018, 140, 6308-6316.

<sup>[2]</sup> Kaphan, D. M.; Klet. R. C.; Perras, F. A.; Pruski, M.; Yang, C.; Kropf, A. J.; Delferro, M. ACS Catal. 2018, 8, 5363-5373.

<sup>[3]</sup> Syed, Z. H.; Kaphan, D. M.; Perras, F. A.; Pruski, M.; Ferrandon, M. S.; Wegener, E. C.; Celik, G.; Wen, J.; Liu, C.; Dogan, F.; Goldberg, K. I.; Delferro, M. J. Am. Chem. Soc. **2019**, *141*, 6325-6337.