Molecular Metal Catalysts on Supports: Organometallic Chemistry Meets Surface Science

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Industrial catalysts range from the simple—molecules in solution—to the complex—surfaces of robust solids, and these are represented respectively by the fields of organometallic chemistry and surface science. These fields are now rapidly merging, benefiting from synthetic chemistry showing the way to essentially molecular metal-containing species anchored on solid supports. The best understood of these catalysts are highly uniform, being isolated on crystalline supports such as zeolites and metal organic frameworks. Less uniform supports such as crystalline MgO are helping to move this field a step closer toward the complexity of technological catalysts incorporating metal oxide supports. The catalyst syntheses involve reactions of organometallic compounds (e.g., $Ir(C_2H_4)_2$(acetylacetonate)) with OH groups on support surfaces—to give structures such as $Ir(C_2H_4)_2$, with the Ir atom bonded to two support oxygen atoms. Spectra, atomic-resolution electron microscopy images, and calculations at the level of density functional theory characterize the surface structures and demonstrate their high degrees of uniformity. Catalyst performance data representing families of isostructural catalyst precursors, such as $M(C_2H_4)_2$, $M(CO)(C_2H_4)$, and $M(CO)_2$ (M = Rh, Ir), show how the metals and ligands affect catalytic properties—just as in molecular homogeneous catalysis. New catalysts provide potentially valuable properties, such as high selectivity for hydrogenation of 1,4-butadiene to give butenes catalyzed by selectively poisoned dirhodium species on MgO. The new results are helping to unravel the effects of the design variables of site-isolated catalysts: the metal, the number of metal atoms in a catalytic site, the support, and other groups (ligands) bonded to the metal—thereby laying a foundation for a role of theory in catalyst design.