X-ray Absorption Spectroscopy & Complementary Catalyst Characterization Techniques: Highly Uniform Supported Single-Site Metal Catalysts

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Solid catalysts work at their surfaces, and these surfaces are notoriously complex and nonuniform, with the catalytically active species often being a small minority. An approach to fundamental understanding of catalysts is to synthesize them precisely—to incorporate nearly uniform catalytic sites. But even these catalysts require multiple characterizations for deep fundamental understanding. In this work, we illustrate some precisely synthesized catalysts—single-site supported metals—and show how synchrotron radiation techniques, combined with complementary spectroscopic techniques, atomic-resolution electron microscopy, and theory, provides fundamental understanding that lays a foundation for catalyst design. We illustrate, for example, how high-resolution XANES (bolstered by theory), which offers higher sensitivity than the workhorse IR spectroscopy, identifies reactive ligands on metal sites; and how dynamic XAFS spectroscopy shows how single-atom iridium complexes in a zeolite are transformed into 4-atom clusters in one reactive atmosphere and then transformed back in another reactive atmosphere. XAS and electron microscopy demonstrate the first steps in metal cluster formation, and XAS and IR spectroscopy identify stable dimers of rhodium with unique catalytic properties. Keys to effective implementation of XAS in catalysis research include the effective integration with complementary methods and recording of changes taking place in samples in reactive atmospheres, often in flow systems, so that catalyst performance can be measured simultaneously with structure characterization data.