

122d Molecular Organometallic Chemistry and Catalysis on Oxide and Zeolite Surfaces

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Oxide- and zeolite-supported metal complexes and clusters have found industrial applications, illustrated by "single-site" olefin polymerization catalysts. Such materials can be synthesized to be nearly uniform in structure and therefore susceptible to precise characterization, even in reactive atmospheres and when functioning as catalysts. We illustrate their characterization with methods including infrared, NMR, and X-ray absorption spectroscopies, even under catalytic reaction conditions, complemented by high-resolution TEM and density functional theory. The catalysts include complexes of Rh and of Re and clusters of Rh, Re, and Os, tested for reactions such as ethylene hydrogenation, CO oxidation, and acetylene cyclotrimerization. The results provide evidence of metal-support interactions as metal-ligand interactions and of ligands that are reaction intermediates; they also illustrate the importance of metal oxidation state in catalysis, even by supported clusters.