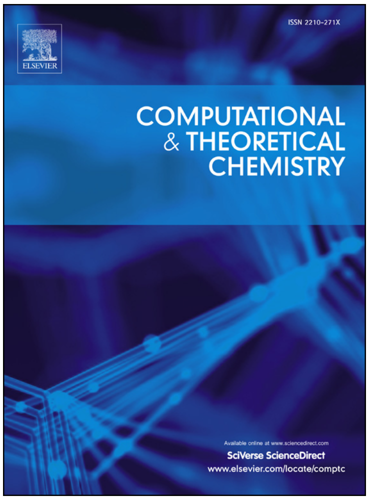

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Molecular Models of Site-Isolated Cobalt, Rhodium, and Iridium Catalysts Supported on Zeolites: Ligand Bond Dissociation Energies

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Abstract

The chemistry of zeolite-supported site-isolated cobalt, rhodium, and iridium complexes that are essentially molecular was investigated with density functional theory (DFT) and the results compared with experimentally determined spectra characterizing rhodium and iridium species formed by the reactions of $Rh(C_2H_4)_2(acac)$ and $Ir(C_2H_4)_2(acac)$ (acac = acetylacetonate) with acidic zeolites such as dealuminated HY zeolite. The experimental results characterize ligand exchange reactions and catalytic reactions of adsorbed ligands, including olefin hydrogenation and dimerization. Two molecular models were used to characterize various binding sites of the metal complexes in the zeolites, and the agreement between experimental and calculated infrared frequencies and metal–ligand distances determined by extended X-ray absorption fine structure spectroscopy was generally very good. The calculated structures and energies indicate a metal–support-oxygen (M(I)–O) coordination number of two for most of the supported complexes and a value of three when the ligands include the radicals C_2H_5 or H. The results characterizing various isomers of the supported metal complexes incorporating hydrocarbon ligands indicate that some carbene and carbyne ligands could form. Ligand bond dissociation energies (LDEs) are reported to explain the observed reactivity trends. The experimental observations of a stronger M–CO bond than M–(C_2H_4) bond for both Ir and Rh match the calculated LDEs, which show that the single-ligand LDEs of the mono and dual-ligand complexes for CO are ~12 and ~15 kcal/mol higher in energy (when the metal is Rh) and ~17 and ~20 kcal/mol higher (when the metal is Ir) than the single-ligand LDEs of the mono and dual ligand complexes for C_2H_4, respectively. The results provide a foundation for the prediction of the catalytic properties of numerous supported metal complexes, as summarized in detail here.

Key words zeolite supported catalysts; Group 9 transition metals; density functional theory; ONIOM; olefin hydrogenation

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