ABSTRACT

Synthesis and Catalysis Across a Series of Lanthanide Scandates

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Designing heterogeneous catalysts–those in which an active metal is supported on a high-surface area substrate–is a complex challenge owing to the many ways the metal and support can interact. Lanthanide scandates, a series of perovskites of the form $LnScO_3$, are suited to studies of catalyst-support interactions because they retain many structure and property similarities as the lanthanide (Ln) is changed. Thorough characterization of a series of $LnScO_3$ supports enables catalytic performance to be attributed to precise changes in properties of the support, thus eliminating the confounding variables that would otherwise obscure metal-support interactions. This dissertation demonstrates the effectiveness of a series of five $LnScO_3$ (Ln = La, Pr, Nd, Sm, and Gd) through their synthesis, characterization, and catalytic testing.

Synthesis of high-purity (> 96 mol%) $LnScO_3$ is achieved via a hydrosauna approach guided by density functional theory (DFT). Hydrosauna synthesis applies humidity in an open system at near atmospheric pressure, in contrast to a typical sealed hydrothermal autoclave. In the hydrosauna method, too low water-vapor partial pressures inhibit

$LnScO_3$ particle growth, while an excess of water vapor results in undesired hydroxide and oxyhydroxide phases. The optimal humidity is shown to vary with the lanthanide in a nonmonotonic manner: DFT is used to calculate the thermodynamics governing formation of undesired phases for each lanthanide, leading to precise prediction of the optimal water vapor pressure to synthesize faceted nanoparticles of each $LnScO_3$. Guided by these predictions, the partial pressures were observed to range from 1.0 torr (for synthesis of $LaScO_3$ and $GdScO_3$) to 8.5 torr (for $NdScO_3$ and $SmScO_3$)—much lower than the humidity of a typical lab.

DFT calculations for various $LnScO_3$, as well as established X-ray photoelectron spectroscopy measurements, indicate that their electronic structure gives rise to the nonmonotonic behavior across the support series. The proximity of Ln 4f states to the Fermi energy for each $LnScO_3$ does not trend monotonically with the atomic number of the lanthanide but does correlate strongly with the strength of CO_2 chemisorption to the $LnScO_3$ surface. Pt/$LnScO_3$ catalysts are tested using CO oxidation and reverse water-gas shift to observe that reaction rates across the $LnScO_3$ series follow this nonmonotonic trend in CO_2 binding strength. The Ln 4f electrons may cause an inductive effect which in turn allows neighboring oxygen atoms at the surface to better donate charge to species adsorbed on the metal. The binding of CO to $LnScO_3$-supported Pt metal is found to be governed by a combination of support effects, with contributions from both the electronic structure and the lattice parameter, which induces a strain at the Pt/$LnScO_3$ interface.

The consistent synthesis of well-faceted and highly phase pure $LnScO_3$ nanoparticles, combined with the understanding of how $LnScO_3$ electronic structure and properties change when varying the lanthanide ion, enables the use of the $LnScO_3$ series to identify that strain affects Pt/$LnScO_3$ monotonically while electronic effects do not. This library of materials can therefore be applied to other reactions as trends in catalytic performance across the $LnScO_3$ series can indicate the most important properties for which to design new catalysts.