

## ABSTRACT

### Identifying Support Effects in Nanoparticle Catalysis

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This thesis focuses on identifying structure-property-performance relationships in supported nanoparticle catalysts, where an active catalyst material is supported on a high surface area substrate. Identifying these relationships in supported nanoparticle catalysts can be quite challenging, as the complex structure of these catalysts results in numerous potential sources for changes to the catalytic performance. This work surmounts that hurdle by minimizing the number of changing properties between different substrate materials and carefully studying and tabulating the properties that do change, allowing any variations to the performance of the catalyst system to be rationalized.

To reduce the potential sources of changes to material properties and performance, a series of structurally similar lanthanide scandate supports with well-defined facets were used. This allows changes in both behavior of the supported nanoparticles and in catalytic testing to be compared to the few changing material properties between the substrates, and structure-property-performance relationships to be identified. This is in contrast to comparing supports such as alumina and titania, where the vast number of differences

between the two complicate the identification of any particular one as the source of change in performance.

The lanthanide scandate nanoparticles are synthesized by collaborators as beveled cubes, and their surfaces are studied first using a combination of spectroscopy, electron microscopy, and density functional theory. A double layer, Sc-rich surface termination is identified on a majority of the exposed surface area, indicating that the surface structure and chemistry is unchanged across the series of support materials. The surfaces of the beveled edges are also identified, and theoretical Wulff shapes are calculated using the excess energies of each surface as a function of the chemical potential of the scandium species at the surface.

Following these studies, Au nanoparticles were deposited on the support surfaces and the structures, orientations, and interfacial energies of the supported nanoparticles were assessed and compared across the different supports. Many twinned particles of Au were identified, so a modified Winterbottom construction was derived to model the thermodynamics of these particles. Studying the populations of Au on the supports, the crystallinity and preferred orientation of the Au nanoparticles was found to be different on each support, and it is hypothesized that this is due to the different lattice parameter of the various lanthanide scandate materials. Additionally, the structure of the double layer reconstruction on the pseudocubic (100) surfaces of the lanthanide scandate nanoparticles forms a structurally matched interface with the (110) surface of FCC nanoparticles – an interface not frequently observed.

The Au/LnScO<sub>3</sub> materials were then used as catalysts for CO oxidation, and Au/NdScO<sub>3</sub> was found to have the highest activation energy barrier for the reaction. Furthermore,

desorption measurements identified  $\text{NdScO}_3$  as the support with the most basic surface. This behavior was found to be the result of chemically active 4f electrons in  $\text{NdScO}_3$ , identified by density functional theory and published spectroscopy of the different lanthanide scandates. While the activity of these electrons increased the energy barrier for CO oxidation using Au, preliminary work with Pt suggests that this effect can be leveraged to reduce energy barriers in other systems.