ABSTRACT

Lanthanide Scandate Supported Noble Metal Nanoparticle Catalysts

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The complex structure of typical heterogeneous catalysts, where nanoparticles of active material are dispersed onto the surface of a thermally stable support with a high surface area, complicates the understanding of how the support can affect the resulting catalyst structure and properties. Using well-faceted and shape-controlled oxides as supports would allow for further control of the catalyst shape and orientation, which would produce model catalytic systems in determining structure-property relationships. In this thesis, lanthanide scandate supports were used with different noble metal nanoparticle catalysts, as they have similar lattice parameters so well-understood concepts related to epitaxy may be used to control the catalyst shape, size, and orientation.

Lanthanide scandate supports were prepared with high surface area and a consistent surface termination using a new water vapor-assisted sol-gel reaction. Reactions that occurred under dry conditions only resulted in an amorphous product, whereas reactions that had a high chemical potential of water led to rare-earth hydroxides as the primary phase. As a consequence, hydrothermal synthesis was unable to produce the desired

perovskite phase, necessitating the need for another synthetic approach. When a balance of water vapor was achieved, the perovskite phase was formed in a high yield. The water vapor assisted in the crystallization process, which we speculate is because the gel was imbibed by the water vapor to preserve the open solid matrix of the gel and allow for greater diffusion at lower temperatures. Further, the supports could be made as beveled cubes, primarily terminated with pseudocubic-{100} surfaces by exploiting a two-step heat treatment. The first step was performed at higher temperatures, where the reaction had a strong driving force, which nucleated many small particles of the perovskite particle phase. The second step was then performed at a lower temperature, which lessened the driving force and promoted particle smoothing. This process successfully produced well-faceted particles across the lanthanide scandates explored.

The lanthanide scandate particles were used as supports for gold and platinum catalysts. Gold catalysts deposited using deposition-precipitation were monodisperse in size across any given support. The orientation of the gold nanoparticles was a function of their size and the support used, as both were critical in determining the relative lattice matching and interfacial energy. When the lattice parameter of the gold was well-matched with that of the support, the interfacial energy pushed the system to adopt gold particles where the {110} sat atop the support. When the lattice parameters of the gold and support differed, the gold particles instead oriented with the {111} surface on the support because of the low energy of the close-packed gold {111} surface. During preliminary investigations of these systems for CO oxidation, well lattice-matched catalysts were found to be less active, deactivate quicker, and sinter more significantly.

Utilizing the different lattice parameters of the lanthanide scandates led to varying degrees of tensile strain in platinum nanoparticles. With increasing tensile strain in the platinum, the percentage of CO bound between several metal atoms rather than atop a single platinum atom increased, and a greater percentage of the CO was bound more weakly. The role of basic supports in CO oxidation and the reverse water-gas shift reactions was investigated by using the lanthanide scandates as model supports with platinum catalysts. A greater binding strength of carbon dioxide on the lanthanide scandate support correlated with the bond valence sum of the scandium in the support. The binding strength was a controlling variable in both the rate of CO oxidation and the degree of reverse water-gas shift. A support that bound carbon dioxide more strongly had a stronger driving force for producing carbon dioxide and correspondingly had a greater CO oxidation rate. Similarly, such a system had a smaller driving force for losing carbon dioxide and experienced a lesser degree of reverse water-gas shift.