Improved Catalyst Performance through Strong Metal Support Epitaxy

Robert M. Kennedy,1,2 James A. Enterkin,2 Laurence D. Marks,1 Christopher L. Marshall,2 Peter C. Stair,1,2 and Kenneth R. Poeppelmeier1,*
1Northwestern University, Evanston, Illinois 60201 (USA)
2Chemical Science and Engineering, Argonne National Laboratory, Argonne, Illinois 60439 (USA)
*krp@northwestern.edu

Introduction

Selective, active, and robust catalysts are necessary for the efficient utilization of new feedstocks. Face-selective catalysts can precisely modify catalytic properties, but are often unstable under reaction conditions, changing shape and losing selectivity. Herein we report a method for synthesizing stable heterogeneous catalysts in which the morphology and selectivity can be tuned precisely and predictably. Using nanocrystal supports, we epitaxially stabilize specific active phase morphologies. This exposes active sites of different coordination with correspondingly different catalytic properties. Specifically, we utilize the variable strength of interaction between different perovskite titanate nanocube supports and a platinum active phase. By substituting different sized cations into the support, we change the epitaxy and stabilize the active phase in different morphologies in a predictable manner. We correlate these changes in active phase atomic coordination with changes in catalytic performance (activity and selectivity), using the hydrogenation of acrolein as a test reaction [1]. The method is general and can be applied to many nanocrystal supports and active phase combinations.

Materials and Methods

Nanocrystalline perovskite supports with cubic shape (nanocubes) were synthesized by a microwave hydrothermal synthesis. Barium cations were substituted into the a-site position in SrTiO$_3$, creating a range of supports, Sr$_x$Ba$_{1-x}$TiO$_3$. Platinum nanoparticles were grown on the surface of the perovskite nanocubes via atomic layer deposition (ALD). Nanoparticles were characterized by aberration corrected transmission electron microscopy (TEM). The platinum nanoparticles were tested for the selective hydrogenation of acrolein in a gas-photocatalysis reactor; the flow rate of acrolein was varied at 100°C. Quantities of gas-phase compounds were measured via gas chromatography – mass spectroscopy (GC-MS).

Results and Discussion

Single-phase nanocube supports through the Sr$_{1-x}$Ba$_x$TiO$_3$ range were synthesized via microwave hydrothermal synthesis, with average sizes in the range of 20-30 nm. Platinum particles grown by ALD were epitaxially grown on the (100) surfaces of the support (the majority facet in the nanocube shape), with an average diameter of 1.5 nm and a shape that can be modeled by the Winterbottom construction [2]. High-resolution aberration-corrected TEM demonstrated that the epitaxy of the platinum particles was determined by the lattice-mismatch between the (100) lattice dimensions of the support and the platinum particles. The platinum particles grown on SrTiO$_3$ nanocubes, which have the smallest lattice-mismatch, are stabilized the most, and have the smallest ratio of edge and corner surface area of platinum particles grown on nanocubes in the Sr$_{1-x}$Ba$_x$TiO$_3$ range, as predicted by the calculated Winterbottom construction for Pt (Figure 1).

The Pt/Sr$_{1-x}$Ba$_x$TiO$_3$ nanoparticles were tested for their selectivity for the hydrogenation of acrolein. Pt/SrTiO$_3$ had the highest selectivity for the minority product, the unsaturated allyl alcohol. It has previously been demonstrated that the (111) facet of Pt has a slightly higher selectivity for allyl alcohol than the (100) facet or edge or corner atoms [1]. The decrease in selectivity for the allyl alcohol as barium is substituted for strontium matches the observed changes in the shape of the platinum particles, with the stabilized platinum particles on SrTiO$_3$ having the highest ratio of (111) surface area to (100) or edge or corner Pt.

Significance

It is demonstrated here that the selectivity of small (1.5 nm) metal nanoparticle catalysts can be improved by carefully choosing support materials that stabilize the shape of the metal nanoparticles. This principle may be used to design low-loading nanoparticle catalysts that have comparable performance to higher loading catalysts with larger metal particles.

![Figure 1. HRTEM images of Pt on (100) facets of SrTiO$_3$ (top) and Sr$_0$Ba$_0$TiO$_3$ (bottom) nanocubes. Winterbottom construction for Pt overlaid in green, revealing that wetting on SrTiO$_3$ is ~61%, and wetting on Ba$_0$Sr$_0$TiO$_3$ is ~44%.](image)

Acknowledgement

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

References