ABSTRACT

Synthesis, Shape, and Surfaces of Strontium and Barium Titanate Nanocrystals

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The atomic surfaces structures of shape-controlled oxide supports prepared hydrothermally result in nanocrystals for use as model catalysts to bridge the "materials gap" from studies on single crystals. $SrTiO_3$ (001), (110), and $BaTiO_3$ (001) surfaces are investigated using several techniques, and synthetic approaches to obtain these materials are discussed in detail.

The Wulff shape of $SrTiO_3$ was determined to be an octadecahedron with six {100} facets and twelve {110} facets. TEM measurements of the faceting ratios $h_{110} : h_{100}$ were found to agree well with surface energy ratios $\gamma_{110} : \gamma_{100}$ derived from first-principles calculations.

Using aberration-corrected HREM, the surface structure of {110}-faceted $SrTiO_3$ nanoparticles synthesized solvothermally using glycerol as the surfactant yielded (n $\times$ 1) reconstructions with n=3 or 4. These structures are titania-rich and contain tetrahedrally coordinated TiO_4 units, similar to prior observations for $SrTiO_3$ (110) single crystal surfaces.

Aberration-corrected HREM investigation of $SrTiO_3$ nanocuboids made using caprylic acid, ethanol, and also $BaTiO_3$ nanocuboids revealed that the (001) surfaces for all these nanoparticles are terminated with a TiO_2 double layer. These results are similar to prior

observations of TiO_2-rich surface reconstructions on $SrTiO_3$ nanocuboids made hydrothermally and single crystals prepared via wet chemical etching.

Pt and Pt deposited onto $SrTiO_3$ nanopolyhedra were investigated by HREM to determine the stable Winterbottom construction. The supported Pd particles were found to be predominantly multiply twinned particles while Pt particles were predominantly single crystals.

The effects of sub-nanometer atomic layer deposition of films of titania and alumina are compared for the acrolein hydrogenation selectivity of Pt catalysts supported on $SrTiO_3$. The titania-overcoated catalyst is similar to strong metal-support interaction catalysts formed by high temperature reduction, with a thin titania film on top of the supported Pt nanoparticles and an increase in allyl alcohol selectivity, neither of which are observed for the alumina-overcoated catalyst.

Pt-$SrTiO_3$ (110) catalyst samples prepared by ALD onto $SrTiO_3$ dodecahedra are compared with Pt-TiO_2 catalysts prepared by ALD onto commercially purchased anatase TiO_2. Catalytic testing of the CO oxidation reaction indicate that the turnover frequency for $SrTiO_3$ dodecahedra is significantly higher than anatase TiO_2.

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