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DOI 10.1007/s11244-013-0118-y

ORIGINAL PAPER

Epitaxial Stabilization of Face Selective Catalysts

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Abstract 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 changes the distribution of active sites of different coordination, which have correspondingly different catalytic properties. Specifically, we utilize the different interfacial free-energies between perovskite titanate nanocube supports with different crystal lattice dimensions and

a platinum active phase. By substituting different sized cations into the support, we change the lattice mismatch between the support and the active phase, thereby changing the interfacial free-energy, and stabilizing 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. The method is general and can be applied to many nanocrystal supports and active phase combinations.

Keywords Epitaxy · Perovskite · Platinum · Heterogeneous catalysis · Hydrogenation · Acrolein

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Controlling the morphology of catalytic metal nanoparticles has incredible potential for improving selectivity and yield. This is because catalytic properties often depend upon the coordination of active site atoms [1]. In homogeneous catalysis, this can often be controlled by modifying the ligands surrounding the active metal center. One strategy for controlling active site atomic coordination in heterogeneous catalysis is to engineer catalysts with a specific active phase morphology, thereby exposing specific combinations of facets, edges, or corners. Often, however, the desired morphology is not stable under catalytic conditions.

We have recently observed that oriented oxide nanocrystal supports can epitaxially stabilize a specific orientation and morphology of the active phase [2]. Such supports can also stabilize a specific chemical state of the active material, leading to enhanced catalytic performance [3]. Here we demonstrate that modifying the oxide nanocrystal support structure leads to differences in the lattice mismatch, which changes the interfacial free-energy

between the support and the active phase, thereby changing the morphology of the active phase in a predictable and stable manner. This exposes different active phase facets, corners, and edges, leading to active sites of different atomic coordination and corresponding changes in catalytic properties. Most importantly, because the changes to the active phase morphology are predictable, the changes to the catalytic properties can be predicted as well. Our results demonstrate a remarkable new method of creating stable catalysts with precisely controlled catalytic properties. We anticipate that this method can be applied to a wide range of catalytic systems for a broad range of reactions where improving selectivity is of critical importance. For example, the processing of renewable fuel sources would benefit greatly from a method by which the selectivity can be predictably improved [4].

Many catalytic reactions are known to be structure sensitive: the reaction occurs differently on different faces, edges, or corners of the same catalytic material [1]. Most experiments detailing structure sensitivity at the level of coordination of individual active phase atoms have been conducted on large single crystals cut to expose a specific facet [5]. In addition to studying low index crystal facets in this manner, the effects of edges and corners can be investigated by cutting a crystal to a vicinal surface which exposes primarily steps or kinks [6]. Such studies have been conducted for a limited combination of reactions and active phase materials. Many more reactions are known to be structure sensitive, and more still likely have as yet unobserved structure sensitivity. It is possible, perhaps even likely, that differences in active phase atom coordination may account for many unexplained structural sensitivities. Creating catalysts with exposed active phase atoms of specific coordination geometries could lead to significantly improved selectivity and activity for a host of important reactions.

There are difficulties involved in exploiting known structure sensitivities. The single crystals used in controlled studies have surface areas too low for practical catalysts. Furthermore, the high surface area materials used to increase the number of active sites have poorly defined surfaces. One strategy to overcome this gap has been to create oriented nanocrystals [7]. Such nanocrystals have moderate to high surface area, and can be terminated by the same facets as the well-studied single crystals.

Catalytically active phases engineered to expose specific facets often lack stability. Under reaction conditions the atoms, in particular the surface atoms but also the overall morphology, may rearrange, yielding a structure with atoms of different coordination exposed. This is especially likely since the most desirable coordination for catalysis is often the least stable. It is desirable, therefore, not only to

create but also to stabilize a specific active phase morphology. Ideally, this would be done in a way where precise changes to the stabilized morphology were also possible.

With this in mind, we engineered the catalytic support to stabilize the active phase in a specific morphology. By choosing a combination of support and active phase between which there is a strong epitaxy, the orientation of the active nanoparticle phase can be stabilized. Epitaxy is well known to stabilize thin films in specific orientations. Model catalysts have been created by epitaxially stabilizing metal nanoparticles on oriented single crystals [8], but these systems have negligible surface area or catalytic relevance. Unfortunately, specific-orientation epitaxy cannot be transferred to typical high surface area catalytic supports because they are irregular in shape and therefore there is no synthetic control over the surfaces exposed. Owing to the synthetic methods commonly used for irregular high surface area oxide supports, the particle shapes can be ascribed to having a kinetic distribution of exposed surfaces, which do not approach the equilibrium Wulff shapes. Cuboid SrTiO_3 nanocrystals [9] make an ideal support for stabilizing active phases of specific morphologies. They have moderate to high surface area and are preferentially terminated by the thoroughly studied (100) facet [10, 11].

The thermodynamics governing nanoparticle shape are well understood [12, 13]. The morphology of a free metal particle follows the Wulff construction [12]. When such a particle is supported on a substrate, it will wet the surface to varying degrees. Just as water droplets will wet a hydrophilic surface and bead up on a hydrophobic surface, the degree to which a metal particle wets a surface varies with the interfacial free-energy. The degree of wetting and the exposure of various facets, edges, and corners can be quantified through the Winterbottom construction [13]. By controlling the difference in lattice mismatch between the support and active phase, we create an active phase with a specific morphology and exposed surface facets which is also thermodynamically stable.

Platinum is active for many types of catalytic reactions and has a lattice parameter very similar to SrTiO_3 . A strong cube-on-cube epitaxy is expected for platinum deposited on the SrTiO_3 (100) surface, and has been previously observed on SrTiO_3 single crystals [14] and more recently on nanocubes [2, 15]. Here Pt was deposited on SrTiO_3 nanocubes via a single cycle of atomic layer deposition (ALD) [16]. Analysis of the Pt particle shape revealed that it followed the Winterbottom construction [2]. The Winterbottom construction is the thermodynamically stable configuration [13], so the morphology should be maintained unless the conditions are altered drastically enough

to enter a different thermodynamic regime. Under sufficiently oxidizing conditions, for example, platinum oxides will begin to form and the morphology will be altered. However, we have demonstrated previously that controlling the Pt-support epitaxy can be used to stabilize metallic Pt even in oxidizing conditions. Under similar conditions, Pt nanoparticles on SrTiO₃ nanocubes maintain a metallic core, while Pt nanoparticles on other supports are completely oxidized [17]. The stabilization of the metallic core under such conditions stems from the similarity of the lattice parameter [3, 17]. This favorable epitaxy was used to extend the stability range of the Pt/SrTiO₃ particles, preventing the sintering-based loss in activity over time that was observed in the Pt/Al₂O₃ particles [3]. The Winterbottom construction also allows us to predict how the morphology will change as the interface is changed.

A straightforward method to change the interfacial free-energy is to change the degree of lattice mismatch, i.e. change the misfit.¹ This was accomplished by synthesizing Ba_{0.5}Sr_{0.5}TiO₃ nanocubes, which are similar to the SrTiO₃ nanocubes, but the larger Ba²⁺ cation replaces Sr²⁺ on half of the perovskite A-sites. This substitution causes the lattice, as measured by powder X-ray diffraction, to expand from 3.921 to 3.956 Å, thereby increasing the lattice mismatch with Pt (lattice parameter of 3.9231 Å [18]) from 0.05 to 0.84 %. While the lattice mismatch is small enough that epitaxy is maintained at the sizes of interest here, the interfacial free-energy will increase with increasing lattice mismatch due to the higher strain in the Pt nanoparticles. For particles of constant volume, a larger portion of a smaller Wulff shape will be exposed, and therefore more corner and edge platinum atoms as compared to surface facet platinum atoms.

High resolution transmission electron microscopy (HRTEM), using the Argonne chromatic aberration-corrected TEM with both Cs and Cc correction, allowed for detailed examination of the Pt particle morphology and the relative epitaxy and adhesion between Pt and support

¹ For completeness, changing the lattice mismatch is not the only way to change the interfacial free-energy and therefore the degree of wetting. Changing the bonding interactions or the composition of the interface will also change the interfacial free-energy. For example, changing to a more oxophilic active phase metal would increase the bond strength and lower the interfacial free-energy. By maintaining the same active phase and substituting one chemically similar cation in the support we minimize such effects in order to isolate the effect of the change in lattice mismatch. Preliminary catalytic results on a sample of Pt on commercial SrTiO₃ (non-nanocrystal) showed a lower selectivity than either the SrTiO₃ or Ba_{0.5}Sr_{0.5}TiO₃ support. These should have the same bonding effects as nanocrystal SrTiO₃, and support our hypothesis that the structural effect is paramount. However, at this time we cannot completely rule out the possibility that bonding effects make some contribution in addition to the structural effects.

(Fig. 1). The SrTiO₃ nanocube support had both a higher proportion of the platinum particles exhibiting the expected epitaxy, and a greater degree of wetting for those epitaxial particles. Examination of lattice fringes and fast Fourier transforms revealed that while many Pt particles grew in the (001) direction (cube-on-cube), some had a 45° rotation around the (001) axis (cube-on-cube R45). Additionally, some particles grew in a non-epitaxial direction. A total of 74 distinct Pt particles were counted to allow for statistical analysis (Table 1). Statistical analysis of the HRTEM images confirmed that the epitaxy was more likely on the SrTiO₃ support than on the Ba_{0.5}Sr_{0.5}TiO₃ support. The statistical significance for the differences in growth direction between supports was calculated using the Student's *t* test, a measure of the statistical significance of the difference between two populations of data. The *p* value, a measure of the likelihood that the difference between two populations is a coincidence, was found to be smaller than 0.01, signifying that there is >99 % confidence that the difference is real and statistically significant. The degree of wetting was calculated from the ratios of particle height to maximum particle width. (Overlay of the Wulff construction was not used so as not to bias results by manual fitting of the Wulff shape.) As expected, the degree of wetting was higher on the SrTiO₃ support than on the Ba_{0.5}Sr_{0.5}TiO₃ support. The statistical significance for the differences in degree of wetting was likewise calculated via the Student's *t* test, with *p* values found to be smaller than 0.01.

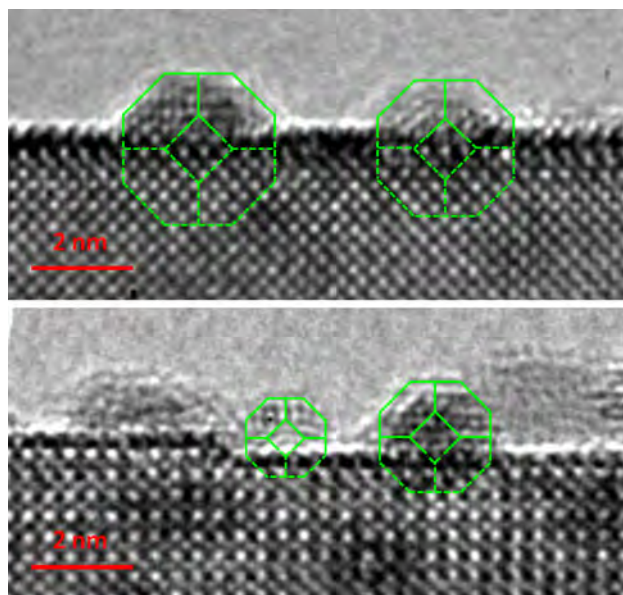


Fig. 1 HRTEM images of Pt on (100) facets of SrTiO₃ (top) and Ba_{0.5}Sr_{0.5}TiO₃ (bottom) nanocubes. Wulff construction for Pt overlaid in green (color online), revealing that wetting on SrTiO₃ is ~61 %, and wetting on Ba_{0.5}Sr_{0.5}TiO₃ is ~44 %

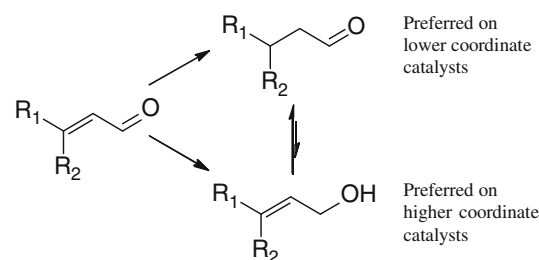
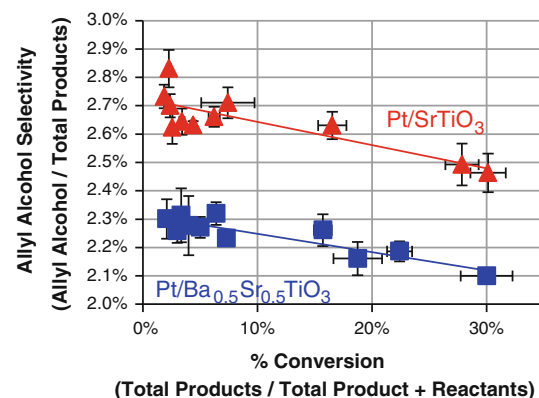
Table 1 Statistics for Pt particle growth direction and degree of wetting on SrTiO₃ and Ba_{0.5}Sr_{0.5}TiO₃ nanocube supports

Pt growth type	SrTiO ₃ nanocube supports		Ba _{0.5} Sr _{0.5} TiO ₃ nanocube supports	
	Percent of population (%)	Average wetting (%)	Percent of population (%)	Average wetting (%)
Cube-on-cube	61	61	41	44
Cube-on-cube R45	14	53	6	38
Non-epitaxial	25	34	53	32

Since the degree of wetting is higher for epitaxial Pt particles on SrTiO₃ nanocube supports, there are more facets exposed as compared to corners and edges. (For an 8 nm³ Pt particle with cube-on-cube epitaxy, a wetting of 61 % would result in 22 % of the surface atoms being corners or edges, while a wetting of 44 % would result in 41 % of the surface atoms being corners or edges.) Further, the Ba_{0.5}Sr_{0.5}TiO₃ support has more non-epitaxial Pt particles, which are similar in shape to a free Pt particle and have a higher proportion of corners and edges exposed (43 % of surface atoms are corners or edges for a free 8 nm³ Pt particle) than a cube-on-cube Pt/STO particle of the same volume. Thus, the Pt on Ba_{0.5}Sr_{0.5}TiO₃ nanocubes has a greater proportion of lower coordinated corner and edge Pt atoms than Pt on SrTiO₃ nanocubes. It should therefore exhibit different catalytic properties for structure sensitive reactions.

The selective hydrogenation of α,β -unsaturated aldehydes (Fig. 2) is particularly well-suited for testing the structure selective properties of platinum based catalysts. These hydrogenation reactions have been well-studied on platinum single crystals. Depending on which double bond is hydrogenated (olefin or aldehyde), the reaction results in either a saturated aldehyde or an unsaturated alcohol. Absent any steric effects from large *R* groups, the selectivity towards alcohol formation is greater on Pt (111) than on Pt (100) [19]. One key difference between these facets is that atoms on the (111) facet are nine coordinate, while those on the (100) facet are eight coordinate. Further, smaller particles, with more corners (six coordinate atoms) and edges (seven coordinate atoms) relative to either facet, have even lower selectivity for alcohols. This implies that the coordination of exposed Pt atoms is proportional to the selectivity towards alcohols. The selectivity to alcohols follows the trend (111) > (100) > edge > corner. Taken together with our understanding of the Pt morphology on perovskite titanate nanocubes, we can predict that the SrTiO₃ nanocube support will result in higher selectivity towards alcohols and lower overall activity than will the Ba_{0.5}Sr_{0.5}TiO₃ nanocube support.

To confirm this prediction, these catalysts were tested for the hydrogenation of acrolein, H₂C=CH-CH=O, the

**Fig. 2** Hydrogenation of α,β -unsaturated aldehydes**Fig. 3** Selectivity as a function of conversion for Pt/SrTiO₃ (red triangles) and Pt/Ba_{0.5}Sr_{0.5}TiO₃ (blue squares) catalysts for the hydrogenation of acrolein

simplest α,β -unsaturated aldehyde. Catalytic testing was carried out in the gas phase in a plug flow reactor at atmospheric pressure and 100 °C, with an excess of hydrogen while varying the space velocity of the feed (up to 500 mol acrolein/mol Pt/min). Results (Fig. 3) confirmed that across a wide range of acrolein feed rates, the SrTiO₃ nanocube support yielded a higher selectivity for allyl alcohol. Following an initial activation period, the selectivity towards allyl alcohol extrapolated to 0 % conversion were steady at 2.7 and 2.3 % for Pt/SrTiO₃ and Pt/Ba_{0.5}Sr_{0.5}TiO₃, respectively. While these selectivities are low, they exceed results typically reported for unpromoted platinum active phases of similar size under similar conditions, which have selectivities for allyl alcohol <1 % [20–22].

We have demonstrated a new method for precisely and predictably modifying catalytic properties. This is accomplished by controlling the active phase morphology which controls the coordination of the active site atoms. By our method, these factors can all be modified in a precise and predictable manner. Based on our previous study of propane oxidation over Pt/SrTiO₃ nanocubes and the difference in hydrogenation selectivity between Pt/SrTiO₃ and Pt/Ba_{0.5}Sr_{0.5}TiO₃, we conclude that the support stabilizes the active phase in a specific morphology through a wide range of conditions (e.g. temperature, pressure, and reacting gasses) [3]. Even more drastic modifications are possible by this technique. For example, active phases could be stabilized in different directions by employing nanocrystals with differently oriented terminations, as has been demonstrated for Pt on SrTiO₃ single crystal substrates [23]. The concepts of varying the lattice mismatch, wetting, and epitaxy are general and applicable to a wide range of systems. Because they are well understood, the changes in morphology can be modeled and predicted and can therefore be used to target selective pathways for a variety of reactions. Our methods should allow the creation, stabilization, and modification of a host of different catalysts, with applications in an equally wide variety of reactions and processes. This study proves the viability of this powerful concept. There is the potential to apply this concept any time there exists an oriented nanocrystal of a support material and an active phase material with a potential epitaxy. Because of the continuing progress in nanocrystal synthesis, it is difficult to define a limit for the potential catalytic systems. We anticipate the rapid expansion to include other support nanocrystals, capable of supporting an array of active phase materials in an even larger range of morphologies, and therefore of precisely modifying the selectivity of a multitude of reactions.

Acknowledgments The authors thank Mihai Anitescu for assistance with the statistical analysis. This work was funded in part by Institute for Atom-efficient Chemical Transformations, an Energy Frontier Research Center, funded through the U.S. Department of Energy, Office of Basic Energy Sciences; and in part by the Northwestern University Institute for Catalysis in Energy Processing, funded through the US Department of Energy, Office of Basic Energy Science (award number DE-FG02-03-ER15457). The electron microscopy was accomplished at the Electron Microscopy Center for Materials Research at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.

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