Oxide overcoat boosts nanoparticle catalysts

Cordelia Sealy

Researchers believe they have unraveled the intertwined effects of geometry and electronic structure on the catalytic properties of metal nanoparticles [Wang et al., *Science Advances* **5** (2019) eaat6413, https://doi.org/10.1126/sciadv.aat6413]. Because of their size, metal nanoparticles have found broad applications in biology and medicine, sensors, batteries, and, in particular, catalysis. Smaller particles make better catalysts because of the increased surface area but quantum size effects (QSEs) also alter internal energy levels, boosting catalytic activity.

"These two distinct effects make precise tailoring of the particle size, in addition to the composition, a valuable means of optimizing catalysts," explains Junling Lu at the University of Science and Technology of China, Hefei, who led the work.

However, size-related effects on the geometry and electronic structure of metal nanoparticles are difficult to distinguish. Smaller nanocrystals have more low-coordination sites (LCSs) than high-coordination sites (HCSs), which affect how chemical bonds are broken and formed during catalysis. QSEs, simultaneously, influence the energy levels in smaller particles, which in turn impact on charge transfer between the metal and reactants. To hone reaction kinetics as far as possible, it would be useful to understand exactly how the size and shape of nanocrystals, as well as their energy levels, affect catalysis.

"Disentangling these two effects and identifying when one or the other starts to dominate the reactivity could breakdown established structure-activity relationships," says Lu.

Together with collaborators from Wei-Xue Li's theoretical group at the University of Science and Technology of China, the researchers have developed a new strategy enabling them to manipulate the geometric structure of palladium (Pd) nanocrystals without affecting the electronic structure. Pd nanocrystals supported on Al_2O_3 are a valuable type of catalyst for the oxidation of alcohols to carbonyl compounds, which are important intermediates in industrial fine chemical synthesis. The oxidation of benzyl alcohols has two major pathways: the preferred dehydrogenation path to benzaldehyde or the undesirable hydrogenolysis route, which produces toluene as a by-product.

The researchers worked out that coating 4-nm Pd nanocrystals with either Al_2O_3 or FeO_x using atomic layer deposition (ALD) independently suppresses the catalytic effects of LCSs and HCSs, respectively. They found that blocking LCSs results in remarkable selectivity for benzaldehyde, while blocking HCSs had the opposite effect. The findings demonstrate that dehydrogenation occurs at HCSs and hydrogenolysis at LCSs, which indicates selectivity of Pd nanocrystals can be tuned via the HCS: LCS ratio without changing the particle size.

However, when a similar exploration was undertaken with nanoparticles smaller than 4.2 nm, the trend was reversed. This, the researchers believe, indicates that at these scales electronic QSEs start to dominate the process. In other words, geometric effects dominate catalysis in nanocrystals larger than 4 nm, while electronic effects dominate at smaller scales (Fig. 1).

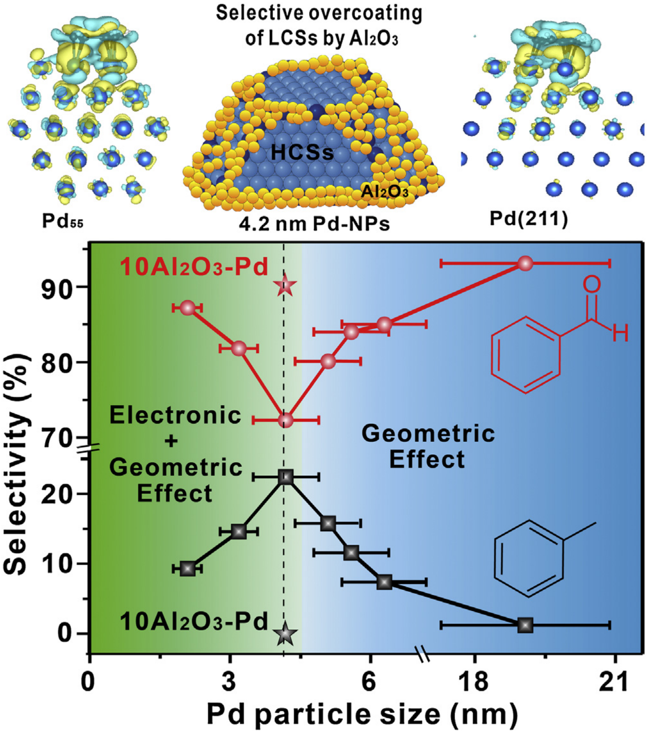

Fig. 1. (Bottom) Benzaldehyde and toluene selectivity of Pd/Al_2O_3 catalysts as a function of Pd particle size during aerobic oxidation of benzyl alcohol. The selectivity and TOF of 4.2 nm Pd/Al_2O_3 catalyst with ALD alumina overcoat ($10Al_2O_3$-Pd) under the same reaction conditions are presented for comparison (star). (Top) The electronic effect is highlighted by the charge density difference upon adsorption of benzyl on Pd55 and Pd(211) (Pd atoms shown in blue), while the areas of depletion and accumulation of electrons are shown in cyan and yellow, respectively. The geometric effect is addressed by selective blocking of LCSs by Al_2O_3. Credit: Junling Lu's and Wei-Xue Li's research groups at the University of Science and Technology of China.

"Given the essential roles of geometric and electronic effects in metal nanoparticles, disentangling these two factors opens a new dimension for rational design of metal nanoparticles for broad applications," says Lu. "Selectively blocking sites on size-optimized Pd nanoparticles for undesirable reaction paths achieves high activity, high selectivity, and high stability, showing great potential for practical applications."

The researchers are confident that their oxide overcoat approach could work just as well with different reactions, such as the dehydrogenation of ethane, and gold nanoparticle catalysts.

"We believe this strategy is universal," Lu told Nano Today, "and can be extended to other reactions and metal catalysts. This methodology opens up new understanding of the distinct size-dependent functionalities of the geometric and electronic structures of metal nanoparticles, as well as for the rational design of catalysts."

Richard Catlow FLSW FRS, professor of catalytic and computational chemistry at the Cardiff Catalysis Institute in Wales, believes the advance is significant.

"Nanoparticle-based systems have a very wide range of applications not only in catalysis and sensors but also in biosciences and medicine," he points out. "These applications are to a large extent dependent on both the electronic and geometric properties of nanostructures. The importance of this work is that through a combined experimental-theoretical approach based on

ALD and density functional theory Lu et al. are able to deconvolute the two effects."

As the researchers suggest, Catlow thinks that the approach may advance the ability to design nanostructured catalysts in the future.

Cordelia Sealy has many years' experience as a scientific journalist and editor in areas spanning nanotechnology, materials science and engineering, physics and chemistry. She has served as Editor of *Materials Today* and *Nano Today*, and more latterly as Managing Editor of both titles. She has also worked in academic publishing as a books acquisitions editor and in business-to-business publishing as a journalist on *European Semiconductor*. She has a First in Physical Sciences (BSc) from University College London and a DPhil in materials science from the University of Oxford, and is a Member of the Institute of Physics. Cordelia is currently a freelance science writer for her own company, Oxford Science Writing, and News and Opinions Editor for *Nano Today*.

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1748-0132/$ — see front matter
https://doi.org/10.1016/j.nantod.2019.02.004