

Combination of synthesis methods yield single atom metal catalysts

Catalytic materials were adopted for industrial applications at least as far back as 1750, when the insipient British chemical industry began using the lead chamber process to make sulfuric acid. Catalytic performance often depends on particle size and the nature of the support material underneath, and new catalytic properties using various combinations are still being discovered. This is especially true for catalysts at the extremely small scale, down to tens of atoms or even a single atom. At this scale, the surface structure, chemical properties, and reactivity of a catalyst tend to change dramatically.

To better explore these differences, there is great interest in creating methods to separately control particle size and the support materials. Now, a report published in a recent issue of the *Journal of Chemical Physics* (doi:10.1063/1.5128934) takes the field one step closer to gaining such control by describing a relatively simple and efficient way to synthesize single atom metal catalysts.

Many previous methods of synthesizing small clusters or single atom catalysts involved leeching with a cyanide treatment or a similar processing step. But this tends to remove most of the metal and is

not efficient. Justin Notestein, a professor of chemical and biological engineering at Northwestern University and senior author of the paper, and colleagues decided to take a different route. They built upon their prior work in overcoating oxide and catalyst surfaces with other oxides.

They started with a common aluminum oxide support. They deposited a 1-nm-thick layer of silica on the surface, selectively blocked in locally at several locations by an adsorbed molecular template. They did this under a pH of 4 because this falls between the isoelectric point—the pH at which a molecule carries no electric charge—of silica and alumina. This caused different surface charges to appear, leaving small patches of positive and negative charge. This was because, at a pH of 4, the silica surface exists at a negative charge and the underlying alumina surface should be positively charged. The researchers then introduced negatively charged Pt precursors, which bonded only to the small islands of positive charge and was helped along in its dispersal by the negative charges across the rest of the substrate's surface.

“In a very straightforward way, we drove the system to having a preponderance of single atom catalysts,” says Notestein. “We exploited the surface charges to get a nice distribution of Pt.”

As the researchers increased the amount of silica deposited on the support

material, they found that the percentage of single atom Pt increased, leading them to believe that their method would be well suited to creating highly dispersed supported Pt metal catalysts.

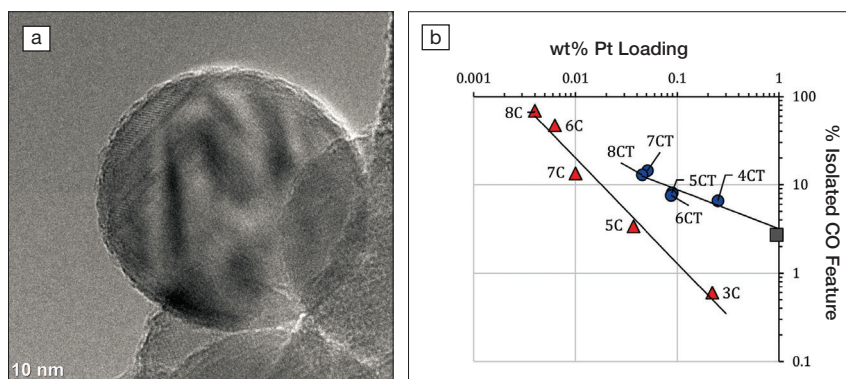
“Justin Notestein’s group has now demonstrated a powerful new way to produce uniform Pt nanoparticles below 1 nm in size attached to an alumina support material,” says Charles Campbell, the B. Seymour Rabinovitch Endowed Chair in Chemistry at the University of Washington, Seattle, who was not involved in the research. “This was achieved by a very creative combination of synthesis methods.”

“This is a really accessible way into creating these very small clusters of single atoms,” Notestein says. “This is a very simple way of spreading Pt atoms on a very normal support,” he added.

Single atom catalysts epitomize a classic tradeoff in catalysis, in which chemists struggle to find a sweet spot between a material being too reactive and not reactive enough. This concept is illustrated by the common “volcano plot” concept in catalysis, with the *x*-axis representative by strength of binding for one of the reactants. Reactants can be either too reactive, sticking to the surface and preventing another cycle of reaction, or not reactive enough, because of weak binding. Given this challenge, for now, Notestein and his colleagues do not know how the catalysts produced with their method would perform at larger scales. “There are a lot of practical questions, but our aim was fairly limited to saying, ‘Hey, this is a very straightforward way to make single atom catalysts,’” Notestein says.

Notestein especially sees these single atom catalysts as being useful for reactions related to carbon monoxide mitigation, including selectively removing CO from car tailpipes or industrial applications. Alternately, carbon monoxide could be converted into fuel or used as chemical feedstocks. Campbell says, “There is huge motivation to make better catalyst and electrocatalyst materials for environmentally clean and sustainable energy and chemical industries.”

Rachel Nuwer



(a) Transmission electron micrograph showing a thin silica shell over aluminum oxide spheres used as catalyst supports. Credit: Jie Wang. (b) Plot showing how increasing the cycles of silica addition decreases the amount of deposited Pt, but also increases the fraction of Pt present as isolated atoms. Blue points show that 5–8 cycles of silica addition with the use of a template strikes a good balance, with relatively high fractions of isolated atoms at reasonable Pt loadings. C is cycles; T is templated. Credit: Zhenyu Bo.