

CHEMICAL SCIENCES

A Closer Look at Dynamic Restructuring in Catalysts



Three-dimensional artists' rendering of the silver and gold alloy under study. Image credit: Ryan W. Chen, Lawrence Livermore National Laboratory, © Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC) Energy Frontier Research Center (EFRC), Harvard University.

Gold-based alloys have emerged as promising catalysts with high product selectivity: that is, they can be "tuned" to yield specific chemicals of interest. Yet, little is known about the physical tuning mechanism-the dynamic restructuring these alloys undergo as their catalytic properties are activated. To better understand these transformations, researchers have structurally and chemically "visualized" the surface of a silver-gold alloy as it reorganizes itself during the process of catalytic activation. The methodology, which includes ambient-pressure x-ray photoelectron spectroscopy (APXPS) at the ALS, provides insights that can lead to improved catalysts for energy-intensive industrial applications, thereby increasing efficiency and reducing waste.

Nanoporous gold (npAu) is a dilute alloy of 3% silver and 97% gold. Nanoscale pores and ligaments (connecting strips) provide ample surface area for catalytic reactions. As a highly crystalline alloy requiring no underlying support material, it is not complicated by lattice mismatches, intermetallic bonding, or metal-support interactions. Thus, npAu presents a straightfoward platform for investigating the step-by-step transformation of a bimetallic alloy into a working catalyst. Activation is achieved by first preconditioning the npAu surface by flowing ozone gas (O_3) over it, followed by the reactive mixture of methanol (CH₃OH) and oxygen (O_2) at a working temperature of 150 °C. The activated npAu is an extremely robust and selective catalyst



A Silver Lining

Pure gold is a noble metal, chemically unreactive and thus resistant to corrosion and rust. This makes gold useful in coins and jewelry, but not so useful as a catalyst. Catalysts don't just participate in chemical reactions, they initiate and speed them up. Interestingly, adding a pinch of silver (another noble metal) to gold makes the resulting alloy a very good catalyst that can be preconditioned to selectively initiate certain reactions. Important chemicals such as esters, used as precursors for polymers and as fragrances and flavorings, are among the products of such reactions.

Here, researchers sponsored by the Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC) **Energy Frontier Research Center** (EFRC) at Harvard University report on what happens during the catalytic activation of a silver-gold alloy. A silver-rich oxide layer forms at the surface and a key reactive form of oxygen is uncovered. The methods pioneered in this work should catalyze the discovery of new and better materials and processes. Given that nearly one-third of the world's energy is devoted to the chemical industry, finding ways to make those processes more efficient could have a significant economic and environmental impact.

for oxygen-assisted "coupling reactions" that join simple hydrocarbon fragments into more complex end products (e.g., alcohols, esters).

To explore the physical origins of npAu activation and selectivity, the researchers used three techniques:

APXPS, transmission electron microscopy (TEM), and temporal analysis of products (TAP). In the TAP experiments, the researchers exposed ozone-preconditioned npAu to repeated short pulses of reactant gases (CO and CH₃OH) and tracked the product outflow over time. They observed an abrupt transition between the production of CO₂ (during an initial combustion phase) and the selective oxidation of CH₃OH to produce methyl formate (HCOOCH₃-the simplest form of alcohol) and formaldehyde (HCHO-the simplest form of ester). The results indicated that there are two chemically distinct oxygen species on the surface: one responsible for the initial combustion and the other for the selective oxidation of CH₂OH. TEM experiments on ozone-preconditioned npAu revealed a thin layer of amorphous oxide on the surface. Environmental TEM experiments (TEM in the presence of gases) showed that exposure to CO and then CH₃OH resulted in the removal of the amorphous oxide layer and the growth of highly crystalline metallic nanoparticles.

The researchers then performed APXPS studies at ALS Beamline 11.0.2. According to the data, ozone preconditioning concentrates silver near the surface as silver oxide (AgO). Thin films of gold oxide are also formed. These metallic oxides are identified as the oxygen species responsible for the initial combustion phase. A second form of oxygen (O_{sel}), with a binding energy of 531.5 eV, is identified as the species that leads to selective oxidation of CH₂OH. It appears in conjunction with the CO reduction step and persists until reduction by CH₃OH, after which only a small amount of residual (subsurface) oxygen remains (O_{res}). In addition, a steady increase in undercoordinated gold sites $(Au_{u/c})$ is attributed to the formation and growth of small crystalline particles on the npAu surface, as was observed in the TEM results.

In summary, a series of complementary studies has demonstrated that preconditioning with ozone creates a silver-rich oxide layer on the npAu surface. Removal of this reactive oxygen species by CO



APXPS data for gold, silver, and oxygen, showing the dynamic evolution of the npAu surface. (a) After ozone preconditioning, thin layers of silver oxide (AgO) and gold oxide (Au_{oxide}) form at the surface. (b) After reduction by CO, a new O 1s contribution is observed (O_{sel}), which is responsible for selective CH₃OH oxidation. (c) Further reduction by CH₃OH shows that the remaining silver oxide is reduced, and only a small amount of residual (subsurface) oxygen remains (O_{res}). Au_{u/c} = undercoordinated gold sites associated with the outgrowth of irregularly shaped crystalline nanoparticles on the surface.

leads to a restructuring that reveals the distinct oxygen species that reacts with CH_3OH to form selective oxidation products. The work clearly demonstrates that the behavior of alloy catalysts can be tuned using carefully constructed

preconditioning methods, and that a fuller understanding of the dynamic changes that occur during preconditioning is necessary to unlock the full potential of bimetallic catalytic materials.

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