

GUEST EDITORIAL

Gold Catalysis

Gold has long held the fascination of society because of its inertness making it useful for many applications including as jewelry and as interconnects in microelectronics. A revolution in thinking about gold chemistry has occurred more recently as gold has gained new prominence because of its demonstrated potential as a catalyst for driving efficient and selective chemical processes. Gold catalysis has proven both exciting and controversial because of initial skepticism and subsequently because of the competing views on how and why it is such an effective catalyst. Most interesting is that gold is capable of inducing highly selective reactions under mild conditions making it a candidate for selective and sustainable chemical production.

Catalysis is a cornerstone of chemistry, directing chemical reactions through kinetic control. Catalysts are used to produce massive amounts of commodity chemicals in energy-intensive processes and to synthesize smaller quantities of specialty chemicals. The common goal of all catalytic processes is to achieve the highest selectivity with the lowest cost. Remarkably, gold catalysts have great potential for both specialty synthesis and energy-efficient processing at a large scale.

In this special issue, leading work spanning both homogeneous and heterogeneous catalysis using gold is brought together for the first time. A common theme is the exquisite control of selectivity afforded by gold catalysts in a wide range of environments and under mild conditions. The studies of heterogeneous catalysis largely focus on how to reduce energy usage and waste in large scale, energy-intensive chemical processes. Homogeneous gold catalysts are used as a means of producing valuable chemicals at a smaller scale but with high selectivity.

Metallic gold has demonstrated potential for a range of heterogeneous selective oxidation and hydrogenation reactions of organic substrates. The key is to produce reactive species necessary for the selective reactions, surface-bound H atoms or O atoms for hydrogenation and oxidation, respectively. Mullins et al. used single crystal models to demonstrate highly selective hydrogenation of, for example, unsaturated metal carbonyls by ingeniously producing

H on the gold surface using a source of gas phase H atoms. Madix et al. studied analogous selective oxidation of alcohols on single crystals using ozone to deposit the active O atoms. These model studies clearly show that once highly active H or O are present on the surface, highly selective reactions occur at low temperature because the Au itself remains relatively inert limiting competing bond activation steps in the reactant substrate molecules. These studies also raise a key question regarding gold catalysis: How are these reactive species produced in a catalytic system as opposed to a model?

Several approaches to the production of active intermediates, such as adsorbed H or O atoms, using heterogeneous gold catalysts are described in this special issue. The most common approach to gold activation is the creation of active sites for production of reactive species using transition metal oxide supports for the gold. Using the prototypical CO oxidation reaction, both Yates et al. and Behm et al. discuss special sites for O₂ activation around the perimeter of supported Au particles on titania. Cao et al. extended this concept to more complex reactions, including amide synthesis and selective hydrogenation. Rodriguez et al. were able to tune activity for the water–gas shift reaction by tailoring the morphology and electronic properties of hybrid CeO₂ and TiO₂ supports that activate water so as to produce the critical formate intermediate, while Flytzani-Stephanopoulos demonstrated the utility of creating isolated gold sites embedded in metal oxide matrices.

An alternative approach to using the metal oxide support to create active species is the addition of a second more active metal to the catalyst. Hutchings et al. elegantly demonstrated the effect of a second metal by using Pd in the catalyst to facilitate the efficient production of hydrogen peroxide, a valuable intermediate for large-scale chemical production. Similarly, a small amount of Ag present in nanoporous gold catalysts activates O₂ to lead to partial oxidation activity that mirrors predictions on single crystal surfaces as described by Bauemer and Wittstock.

An ongoing discussion in heterogeneous gold catalysis is the charge state of gold nanoparticles and their effect on reactivity. Tsukuda asserts that negatively charged Au clusters promote oxidation in very small Au₂₅ clusters stabilized in a polymer matrix and supported on mesoporous silica. While there is still active discussion about Au clusters smaller than 2 nm, this control over size and morphology represents a transition from heterogeneous, metallic catalysts to the homogeneous, mononuclear Au complexes.

Homogeneous gold catalysis also enables remarkable syntheses but focuses on tailored synthesis of fine chemicals, including asymmetric catalysis yielding antiviral agents and also production of natural products instead of the commodity scale production in heterogeneous catalysis. For example, the activation and functionalization of carbon–carbon multiple bonds when Au acts as a π -acid is discussed by Fürstner. Toste et al. used mononuclear phosphite and phosphoramidite ligands to control enantioselective synthesis involving C=C activation by Au. In homogeneous gold catalysis, cyclization and skeletal rearrangement reactions are driven by Au(I) complexes. Gold catalysts have incredible potential for selective production of these high value added chemicals.

Alcaide applied gold catalysts in the modification of β -lactam derivatives and other strained four-membered rings. A high increase of molecular complexity can be achieved in gold-catalyzed conversion of different enynes, allenynes, and diynes. Both Zhang and Shin describe different perspectives on the easy oxidative access to α -ketocarbenoids via gold catalysis, which avoids the handling of dangerous diazocompounds.

Another nonoxidative way to carbenoids is described by Echavarren; a total synthesis of a natural product documents the versatility of this type of methodology.

Clearly there is a rich chemistry associated with gold-based catalysts, both homogeneous and heterogeneous. There is still as of yet unexplored reactivity, and we hope that the Accounts in this special issue will be an inspiration to further study the fascinating reactivity of gold.

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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