Gold Catalysts for CO Oxidation

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Catalysis by gold is an increasingly popular field, as evidence by a substantial increase in catalysis by gold related papers. Many successful heterogeneous gold catalysts employ nanoparticles supported on metal oxides. These supported gold catalysts catalyze a wide variety of reactions under mild conditions including oxidative dehydrogenation, hydrogenation and oxidation.

Bulk gold is very un-reactive, but nanoparticle gold behave much differently from its metallic form and are therefore useful for catalysis. Supported gold nanoparticles are quite active towards the conversion of carbon monoxide to carbon dioxide, even below ambient temperatures. Metal nanoparticles have a band gap that causes the particles to behave more like a semiconductor than the bulk metal. Also, reduction in size leads to a reduction in coordination number on the surface of the gold atom which relates directly to chemical activity. Low coordination number particles have their d orbitals closer to the Fermi level, thus creating strong interactions with substrates.

Researchers agree on certain principal factors responsible for the high activity of supported nanoparticle gold in low temperature CO oxidation, but the importance of these factors remain disputed. Haruta and co-workers compared the catalytic activity of Pt and Au supported on TiO₂ for low temperature CO oxidation based on different preparation methods. Haruta observed that the dispersion of metal on the support for both Pt and Au depends on preparation methods. The deposition-precipitation (DP) method forms hemispherical metal particles that lie flat and adhere to the support, while impregnation (IMP) and photochemical deposition (FD) methods form spherical particles that have little interaction with the support. This affects the rate and turnover frequency (TOF) for Au/TiO₂, but had little effect on the rate and TOF for Pt/TiO₂, indicating that the reaction occurs strictly on the Pt surface. Thus, the reaction mechanism for CO oxidation on Au/TiO₂ must involve the interaction between gold and the support.

Goodman and co-workers performed studies to determine the sensitivity of CO oxidation with respect to the size of the gold nanoparticles. One observes the Ostwald ripening process when the Au/TiO₂ is exposed to CO₂ gas under ultra high vacuum (UHV). The cluster diameter increases continuously with Au coverage on the surface. The cluster density reaches a maximum at 2.0 monolayers of Au, then decreases with further increase in Au coverage. This phenomenon suggests that the cluster migrates along the surface and agglomerates with other clusters. Goodman discovered that a maximum activity is evident for Au/TiO₂ catalysts, either prepared by precipitation or prepared by vapor-deposition, when the cluster is ~3.0 nm (Figure 1). Haruta found the same size dependency on catalytic activity with gold on different types of supports.
Figure 1: CO oxidation turnover frequencies as a function of the Au cluster size supported on TiO₂ (A) prepared by precipitation method (B) prepared by vapor-deposition.

Grzybowska and co-workers analyzed the nature and properties of support oxide and catalytic performance with main group element oxides (Si, Mg, Sn), transition metal oxides (Fe, Ti, Ce) and mixed SiTiO gels. The activity of the catalysts for CO oxidation depends on the type of oxide support. The transition metal oxide supports containing gold nanoparticles (1 wt%) are more active for CO oxidation than the main group element oxides.

Several proposed mechanisms for the reaction exist. Despite these small difference these mechanisms fall into two categorizes: a mechanism involving solely the Au particle and a mechanism requiring an interaction with the support. Many factors such as kinetics, temperature studies, and the kinetic isotope effect help disprove or reinforce certain proposed mechanisms in the literature. Kinetic studies show a reaction rate $k [\text{CO}]^{0.05} [\text{O}_2]^{0.24}$, indicating that the CO and O₂ are absorbed on the surface until saturation and the reaction of the adsorbed CO and O₂ is the rate determining step. Arrhenius plots, in a wide range of temperatures from 90K to 400K, show three temperature regions where different rates and activation energies suggest three possible pathways for CO oxidation. Finally, the lack of a deuterium isotope effects show that water is not involved in the reaction mechanism.

Unfortunately there is no convergence by researchers as to what the mechanism is for low temperature CO oxidation. The difficulty lies in the quantity of variables involved in studying this reaction including preparation methods, particle size, types of supports, and oxidation state of gold. However, the high activity for low temperature CO oxidation with supported gold nanoparticles shows promise in future industrial applications like fuel cells.
References


