

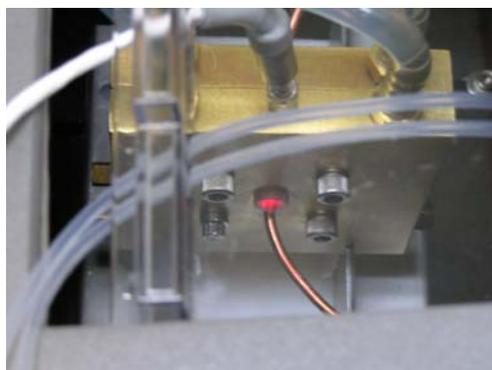
Characteristics of CO Oxidation Reactions Over Au catalysts Revealed By Transient Reactor Studies

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Catalysis by Au has been of high interest since it was discovered that nanosized Au particles have exceedingly high activity for CO oxidation at low temperature and activity for other catalytic reactions. In spite of growing interest in Au catalysts, kinetic studies have been unable to clarify important mechanistic details of the CO oxidation reaction. Researchers at ORNL have now for the first time used a dynamically operated reactor to probe the reaction mechanism. Using this *in operando* approach, it has been possible to probe the elementary steps in the CO oxidation reaction for a Au catalyst. The experiments clearly demonstrate that CO and O₂ both adsorb rapidly and non-competitively and that their reaction on the catalyst surface is also very rapid. Unexpectedly, reaction rate is limited by desorption of the surface CO₂ intermediate, a result that is hinted at previously by conventional kinetic studies but never fully appreciated prior to these results. Such results promise to shed new light on the size effect and causes of support dependence.

The measurements were performed in a variable temperature reactor designed to have essentially zero dead-volume and therefore rapid response to step changes in gas flow. Infra red absorption spectroscopy permits monitoring of surface species while a down stream continuously recording gas analyzer permits time correlated gas product data. Variation in gas flow protocols by transient switching of reactants results in time dependent changes in surface and gas composition on a sub-second time scale which can be analyzed to obtain kinetic information. Using this approach a series of measurements were conducted on active Au catalysts supported on titanium dioxide. Controlled switching between the reactants alone or mixed permitted analysis of adsorption and desorption rates and the competition between reactants for surface sites. Two types of carbonates (bidentate, monodentate) and carboxylates were observed and their formation on the TiO₂



support was shown to be catalyzed by Au particles. These species were not associated with rapid formation of CO₂. Instead a surface species of CO₂ was demonstrated to have a relatively long residence time and to desorb slowly with respect to its rapid formation by surface oxidation of CO. Gas switching experiments (see figure) show that pre-adsorption of O₂ does not interfere with subsequent CO uptake nor does CO pre-adsorption interfere with O₂ uptake. Surface CO oxidation during flow of reactant mixture (CO/O₂) is so fast that adsorbed CO is not observed, although adsorbed CO₂ is evident. Further experiments are planned to determine how mechanistic details vary between different catalyst formulations and under different reaction conditions. Such results will help clarify observed support effects, the impact of Au particle size variation and the role of water in the mechanism. The techniques are general and will be applied to other catalytic reactions to explore catalytic pathways on Au catalysts.

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