

## 571d Isotopic Transient Analysis of Co Oxidation over Alumina and Titania Supported Au Catalysts

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Bulk gold is typically regarded as the least reactive metal. However, supported gold nanoparticles are active catalysts in a variety of reactions, including the oxidation of CO at low temperature. Despite considerable investigation since the pioneering work of Haruta in 1989 [1], the underlying principles that govern the catalysis are still unresolved. The activity of gold nanoparticles has been attributed to several origins, namely an influence of the metal particle size, the chemical state of the gold, and a catalytic role of the gold-support interface.

The kinetics of CO oxidation on Au nanoparticles depend on the nature of the metal-oxide support. In this work, the oxidation of CO over alumina and titania-supported gold nanoparticles was explored. X-ray absorption spectroscopy at the Au LIII edge was used to determine the chemical state and atomic structure of the Au. Steady-state isotopic transient kinetic analysis during CO oxidation was used to determine the coverage and mean residence time of adsorbed reactive intermediates.

The catalysts used in this study were prepared by a deposition-precipitation method [2]. This procedure consists of adjusting an aqueous solution of H<sub>2</sub>AuCl<sub>4</sub> to pH = 7 with NaOH and contacting it with an aqueous slurry of the support at 343 K for 4 h. The samples were then rinsed with H<sub>2</sub>O and filtered four times followed by drying in air at 313 K for 24 h. Prior to kinetic studies, the samples were pretreated in flowing He at 623 K for 4 h.

The isotopic transient experiment was performed by making a switch from <sup>12</sup>CO to <sup>13</sup>CO during the steady-state reaction and monitoring the incorporation of <sup>13</sup>C label into the product by mass spectrometry. The area between the normalized responses of Ar tracer (used to determine the gas-phase hold up of the flow system) and <sup>12</sup>CO<sub>2</sub> is the mean residence time of reactive intermediates on the surface. The inverse of the mean residence time of reactive intermediates is denoted as the intrinsic turnover frequency since it is the characteristic rate at which the catalytic cycle turns over. The coverage of reactive intermediates is determined from the product of the measured global rate and the mean residence time of reactive intermediates, corrected for the Au dispersion. The influence of CO<sub>2</sub> readsorption was minimized by varying the total flowrate, as well as co-feeding additional CO<sub>2</sub> to introduce competitive adsorption.

X-ray absorption spectroscopy at the Au LIII edge showed the as-prepared materials contained cationic Au. However, the Au was autoreduced to metal particles following pretreatment in He at 623 K. The Au first-shell fit parameters derived from EXAFS analysis were consistent with Au in a highly dispersed state with an average Au particle diameter estimated to be approximately 1.3 nm on both metal-oxides. Electron microscopy confirmed the gold was highly dispersed. The kinetics of CO oxidation over gold particles supported on titania were different than those over Au/alumina. In particular, the apparent activation energy was found to be higher for Au/titania, 29 ± 3 kJ mol<sup>-1</sup> versus 12 ± 3 kJ mol<sup>-1</sup> for Au/alumina. Isotopic transient analysis of CO oxidation revealed the intrinsic turnover frequency to be independent of temperature, approximately 3 s<sup>-1</sup> and 1 s<sup>-1</sup> for Au/titania and Au/alumina, respectively, while the coverage of reactive surface intermediates actually increased with temperature. Therefore, the coverage of reactive intermediates is not a measure of the equilibrium surface coverage of CO. These results suggest the key step in CO oxidation over Au catalyst is activation of dioxygen.

1. Haruta, M., Yamada, N., Kobayashi, T., and Iijima, S. *J. Catal.* 115, 301 (1989). 2. Kung, H.H., Kung, M.C., and Costello, C.K. *J. Catal.* 216, 425 (2003).