

Activation and Deactivation of Oxide-Supported Gold Catalysts for CO Oxidation prepared from an Organometallic Precursor: Characterization by Infrared and X-Ray Absorption Spectroscopies

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Introduction

Highly dispersed supported gold catalysts have attracted wide interest because of their high activities and selectivities for reactions including low-temperature oxidation of CO, even in the presence of H₂. Notwithstanding extensive research on supported gold catalysts, fundamental questions remain, such as what are the catalytically active sites and reaction mechanisms. By using Au(CH₃)₂(acac) (acac is acetylacetonate) as a precursor and controlling the degree of aggregation of the gold on the support (MgO or CeO₂), we have been able to investigate the genesis of a CO oxidation catalyst containing extremely small gold clusters resulting from activation by removal of methyl ligands from the supported gold complex.

Methods

The catalysts were tested in a flow reactor at atmospheric pressure. By using IR, XANES, and EXAFS spectroscopies to characterize the catalysts (some in the working state), we have determined the nature of the species formed on the catalysts and changes in the nuclearity of the gold species and evidence of the oxidation state of the gold.

Results and Discussion

The MgO-supported and CeO₂-supported catalysts were found initially by IR and EXAFS spectroscopies to incorporate dimethyl gold complexes that were bonded to the support; they lacked measurable catalytic activity for CO oxidation at room temperature. As the temperature was increased with each of the samples in flowing CO + O₂ at atmospheric pressure, removal of methyl ligands from the gold was observed by IR and EXAFS spectroscopies. The samples then became active for CO oxidation catalysis. EXAFS characterization of the MgO-supported sample right after the activation indicated that the gold had aggregated into clusters consisting of approximately 4–6 Au atoms each, on average. These are among the smallest supported gold clusters yet reported, and they are inferred to be the catalytically active species. The XANES data suggest that the gold in the activated catalyst had not been reduced to the metallic state.

During CO oxidation catalysis in a batch reactor, at least some of the gold on MgO was oxidized, as evidenced by the appearance of an Au^{δ+}–CO band at 2151 cm⁻¹ in the IR spectrum; these species may play a role in the catalysis. During operation in a flow reactor, the catalyst underwent deactivation, accumulating species such as carbonate and bicarbonate on its surface, as indicated by IR spectra. The accumulation of such anionic species on the gold

provides further evidence of cationic gold. Accumulation of species such as carbonates also took place on the MgO support, but only during the initial period of operation of the catalyst, whereas the accumulation of such species on the gold continued throughout the operation, consistent with the blocking of the catalytically active sites on the gold. The catalyst was reactivated by decomposition of the latter species by treatment in helium at 473 K. After three activation-deactivation cycles, the average diameter of the supported gold clusters had increased to about 30 Å, and the activity increased. Thus, the results provide a resolution of the separate effects on the catalytic activity of gold aggregation and accumulation of species such as carbonates and bicarbonates.

The CeO₂-supported mononuclear gold species catalyzed CO oxidation at 353 K, with a turnover frequency of 6.3×10^{-3} molecules of CO (Au atom s)⁻¹ at CO and O₂ partial pressures of 1.0 kPa and 0.5 kPa, respectively. As the catalyst functioned in a flow reactor, the activity increased markedly, so that within about 10 h the conversion of CO had increased from about 1% to almost 100%. Activated catalyst samples were characterized by X-ray absorption spectroscopy and found to incorporate clusters of gold, which increased in size, undergoing reduction, with increasing time of operation (Figure 1). The XANES spectrum of the CeO₂-supported catalyst used for the longest period was indistinguishable from that characterizing gold foil. EXAFS data characterizing this catalyst after the longest period of operation indicated the presence of clusters of approximately 30 Au atoms each, on average. Further details of the catalyst performance are reported [1].

Significance

The data demonstrate that mononuclear gold complexes on CeO₂ are active for CO oxidation catalysis and that extremely small gold clusters formed from them are much more active. Carbonate-like species on the gold supported on MgO cause catalyst deactivation (whereas these species on the support do not play this role), but they can be removed by treatment in He; in contrast. The data point to the possible role of cationic gold species in the catalysis.

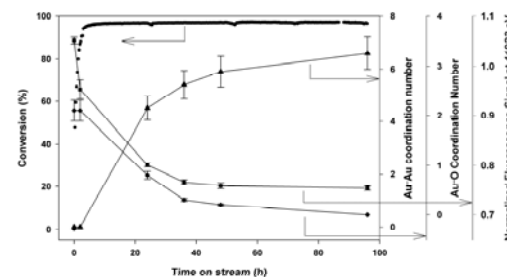


Figure 1. Changes in parameters determined by X-ray absorption spectroscopy correlated with CO conversion in CO oxidation catalyzed by CeO₂-supported gold during operation in flow reactors at 353 K.

Reference

1. Aguilar-Guerrero, V.; Gates, B. C. *J. Catal.* **2008**, 260, 351.