Catalysis by Supported Gold: Correlation between Catalytic Activity for CO Oxidation and Oxidation States of Gold

Javier Guzman and Bruce C. Gates*

Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616

Received November 4, 2003; E-mail: bcgates@ucdavis.edu

Although bulk gold is barely reactive,[1] highly dispersed gold on metal oxide supports is catalytically active for a variety of reactions,[2] including CO oxidation at low temperatures.[3] Recent investigations directed toward elucidation of catalytically active species have led to hypotheses about the effects of gold nanocluster size related to the electronic structure[4] and roles of low-coordinated gold atoms in clusters with nonbulk geometries,[5] of cationic gold at the peripheries of supported clusters,[6,7] and of anionic gold clusters.[8] The influences of gold oxidation state and cluster size on CO oxidation catalysis remain unresolved.[9]

We reported spectroscopic evidence of cationic gold present with zerovalent gold clusters in working CO oxidation catalysts,[10] confirming suggestions of their simultaneous presence.[11] We now report quantitative results for MgO-supported gold catalysts, which offer the advantages of sufficiently simple structures to allow correlation of the catalytic activity with the amounts of cationic and zerovalent gold, but they are about 2 orders of magnitude less active than the most active supported gold catalysts.

We used extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopies, respectively, to characterize the average cluster size and identify the oxidation states of gold in the functioning catalysts, combined with temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) to characterize the catalysts as they had been working at steady state in a flow reactor to provide quantitative characterization of the gold oxidation states.

The synthesis and sample handling were done under anaerobic and anhydrous conditions.[12] The samples, containing 1 wt % Au (with a surface concentration of about 0.5 Au atom/nm^2), were prepared from Au(CH$_3$)$_2$(acac) (Strem) and MgO (EM Science, calcined at 673 K; surface area approximately 60 m^2/g), as described elsewhere.[12] X-ray absorption experiments were performed on beamline X-18B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Data were recorded at the Au L$_{III}$ edge during CO oxidation catalysis. Samples were tested with flowing mixtures of CO and O$_2$ (CO partial pressure, P_{CO}, 11–220 Torr; P_{O_2}, 11–220 Torr; the remainder He) at atmospheric pressure and 373 K. TPR and TPO experiments were performed[13] with a multifunctional catalyst testing and characterization system (RXM-100, Advanced Scientific Designs, Inc.) with a vacuum capability of 10^{-9} Torr.

EXAFS results characterizing the supported gold working as a CO oxidation catalyst after attainment of steady state at 373 K during exposure to a range of flowing mixtures of CO and O$_2$ demonstrate the presence in each of the catalysts of gold clusters with essentially the same average diameter of about 30 Å[14] (consisting of about 400 Au atoms/cluster), as indicated by the first-shell Au–Au coordination number of 10 ± 1 (with a bond distance of 2.86 ± 0.02 Å) and a second-shell Au–Au coordination number of 4.5 ± 0.5 (at a distance of 4.05 ± 0.04 Å)—regardless of the reactant composition (Supporting Information Tables 1 and 2).
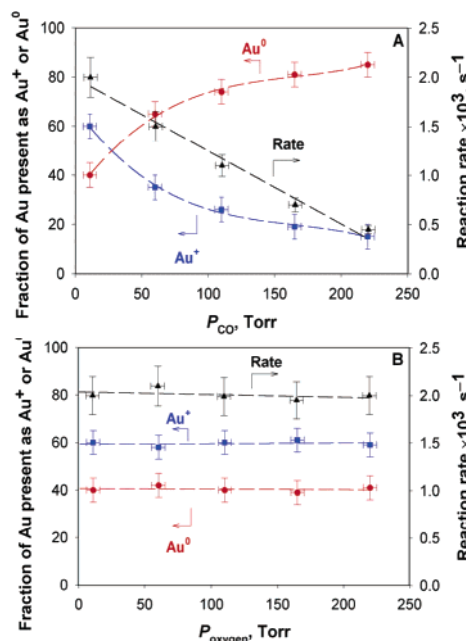

Figure 1. Effects of reactant composition on the oxidation states of gold and their influence on catalytic activity. (A) Effect of CO partial pressure on the surface concentrations of Au(I) and Au(0) at P_{O_2} = 11 Torr. (B) Effect of O$_2$ partial pressure on the surface concentrations of Au(I) and Au(0) at P_{CO} = 11 Torr. Rate of reaction per total gold atom.

Although the average cluster size was independent of the reactant composition, we cannot rule out the possibility of structural changes and rearrangement of the cluster–support interface.

Conversions of CO + O$_2$ in a once-through plug-flow reactor were determined by gas chromatographic analysis of products after a break-in period of about 60 min when the catalyst underwent deactivation;[10] data obtained after attainment of steady state were used to estimate rates of the catalytic reaction from differential conversion data (Supporting Information) with various compositions of the reacting gas. The catalytic activity was found to be dependent on the CO partial pressure but almost independent of O$_2$ partial pressure (Figure 1). Thus, combining these data with the EXAFS data referred to above, we have no evidence to determine whether cluster size affects the catalytic activity.

Expecting that the reactant composition might affect the oxidation states of gold, we characterized the functioning catalysts with XANES in a flow reactor during CO oxidation.[10]

Au(III) is known to be readily reduced (forming Au(I) and subsequently Au(0)) in reducing atmospheres, even at room temperature,[13,15] for example during reductive carbonylation of anhydrous AuCl$_3$ to form Au(CO)Cl.[16] XANES peak locations and intensities characterizing reference materials with gold in various oxidation states were used to provide a basis for interpreting the
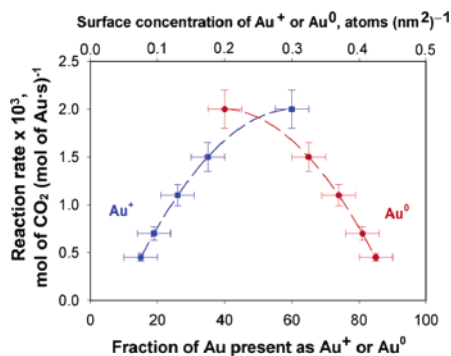
Figure 2. Correlation of the catalytic activity with the percentage and surface concentration of cationic and zerovalent gold (the concentrations of gold were calculated on the basis of the approximate surface area of MgO).

XANES features of our supported gold samples,[10,12,17] allowing us to distinguish Au(0), Au(I), and Au(III).

The XANES results show that exposure of the supported Au-(III) complex prepared from $Au(CH_3)_2(acac)$ to a mixture of CO and O_2 ($P_{CO} = P_{O_2} = 11$ Torr) at 373 K led to the formation of Au(I) and Au(0) and the disappearance of Au(III).[10] This conclusion is drawn on the basis of the XANES measured during steady-state catalysis (Supporting Information Figure 1): (i) the appearance of peaks at 15 and 25 eV above the Au L_{III} edge that demonstrate the formation of Au(0) (as confirmed by EXAFS spectra indicating gold clusters); (ii) the reduction in intensity (without disappearance) of the peak at 4 eV higher than the Au L_{III} edge, confirming reduction of Au(III), consistent with the formation of Au(I);[18] and (iii) the shift in energy of the absorption edge at $11\,923 \pm 0.5$ eV, characteristic of Au(III), to $11\,921 \pm 0.5$ eV, characteristic of Au-(I) complexes. Thus, we identify the cationic gold as Au(I) and infer the presence of a mixture of Au(I) and Au(0) in the functioning catalysts.[19] To determine quantitatively the amounts of Au(I) and Au(0) in an operating catalyst by TPR or TPO, the gas flowing through a bed of catalyst particles operating at steady state was switched from a stream of CO + O_2 to a stream of H_2 or O_2 at atmospheric pressure, whereupon a linear temperature ramp was started, with the H_2 or O_2 uptake being measured by a calibrated thermal conductivity detector (Supporting Information). Knowing which oxidation states of gold were present from the XANES data, we were able to calculate from the H_2 or O_2 uptake the amount of gold in each of the two oxidation states in the sample, Au(0) and Au(I).[13]

Specifically, for example, a catalyst that had been working at steady state at 373 K with $P_{CO} = P_{O_2} = 35$ Torr was found by XANES to incorporate Au(I) and Au(0), and the TPR data show that $40 \pm 5\%$ of the Au was Au(I) and $60 \pm 5\%$ was Au(0). TPO data gave a corresponding result, $42 \pm 5\%$ Au(I) and $58 \pm 5\%$ Au(0).[13] Similar data were obtained for catalysts working under other conditions, leading to the plots of Figure 1. The data demonstrate increasing reduction of cationic gold upon exposure of the catalyst to higher CO partial pressures at a given O_2 partial pressure and show that the percentage of cationic gold was unchanged upon exposure to higher O_2 partial pressures at a given CO partial pressure, demonstrating a resistance to oxidation of the supported gold even at high P_{O_2} in the presence of CO.[20]

Results demonstrating the relationship between the activity of the catalyst and the amounts of cationic and zerovalent gold in it are shown in Figure 2. Because the EXAFS data show that the average size of the gold clusters in each of these catalysts was essentially the same, any effect of this cluster size on the observed catalytic reaction rates was negligible, and the changes in catalytic activity were the result of changes in the oxidation state of gold. The data show that higher concentrations of cationic gold corresponding to lower partial pressures of CO in the reacting mixture lead to higher catalytic activity. Because CO must be adsorbed to react on the catalyst, increasing CO partial pressures would be expected to give higher CO surface coverages and thus higher rates of CO oxidation—but the effect is evidently more than offset by reduction of the gold by CO and removal of catalytic sites.

In summary, the data show that both Au(I) and Au(0) are present in the working catalysts, that their relative amounts depend on the composition of the reacting atmosphere, and that the catalytic sites incorporate Au(I). CO plays a dual role as a reactant and a reducing agent that converts Au(I) into Au(0), thereby diminishing the catalytic activity.

Supporting Information Available: X-ray absorption spectra and parameter values characterizing supported gold working as a CO oxidation catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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