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Activation of Au/γ-Al_2O_3 Catalysts for CO Oxidation: Characterization by X-ray Absorption Near Edge Structure and Temperature Programmed Reduction

C. K. Costello,[‡] J. Guzman,[†,#] J. H. Yang,[‡] Y. M. Wang,[‡] M. C. Kung,*[,‡] B. C. Gates,*[,#] and H. H. Kung*[,‡]

Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL, 60208-3120 and Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616

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Gold catalysts supported on γ-Al_2O_3 (Au/γ-Al_2O_3) were prepared by deposition-precipitation of aqueous $HAuCl_4$ and, alternatively, by deposition of $Au(CH_3)_2(acac)$ from pentane solution. The samples were characterized by in situ XANES and temperature-programmed reduction and by their performance as CO oxidation catalysts at room temperature. The Au was found to be present as Au(III) in both as-prepared catalysts, and the Au(III) was stable upon exposure to reducing gases at room temperature. Reduction of Au(III) occurred at elevated temperatures, and the rate and extent of reduction were found to depend strongly on the reducing conditions. Water vapor facilitated reduction, but only after the sample had been reduced to some extent by CO or H_2. Exposure of an as-prepared catalyst to a catalytically reacting mixture of CO + O_2 at 100 °C was effective in activating it, though to a lesser extent. The data indicate that zerovalent Au is necessary for catalytic activity, but there is no correlation between the activity and the extent of reduction, implying that cationic Au may play a role in the catalytic sites. Water or surface species derived from water also appears to play a significant role.

Introduction

Since Haruta's[1] initial report of the remarkably high activity of supported gold catalysts for low-temperature CO oxidation, interest in the potential applications of supported gold catalysts has increased dramatically, along with research efforts to understand the origin of this surprising activity. However, notwithstanding the intensive study, the nature of the active sites and the mechanism of the CO oxidation reaction remain unknown. Nonetheless, it is well established that the activity of supported gold prepared by deposition-precipitation or coprecipitation methods depends strongly on the pretreatment conditions and, more generally, on the history of the sample.

A focus of recent investigations of the effects of pretreatment has been the calcination temperature and atmosphere. Schumacher et al.[2] reported that Au/TiO_2 treated in H_2 at 200 °C is more active than that calcined in O_2 at 400 °C, and a sample treated only by drying was the least active. The authors attributed the results to the need for small metallic Au particles for high activity. On the other hand, Hutchings and co-workers[3,4] reported that Au/Fe_2O_3, used as prepared without additional calcinations, is more active than Au/Fe_2O_3 calcined at 400 °C. A similar observation was reported for Au/zeolite Y by Wan et al.,[5] and Minicò et al.[6] reported that the activity for hydrocarbon oxidation catalyzed by Au/Fe_2O_3 decreased with increasing calcination temperature. On the basis of Mössbauer and electron microscopy investigations, Hutchings's group attributed the high activity of samples dried at 120 °C to the presence of $AuOOH\cdot xH_2O$ and its interaction with Fe in the samples. Catalysts calcined at higher temperatures contained mostly metallic gold and exhibited low activity for CO oxidation.[3,4]

Other groups have reported similar conflicting findings. Park and Lee[7] observed that the activities of Au/TiO_2 and Au/Fe_2O_3 decreased as the calcination temperature was increased from 100 to 400 °C. Results of X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) indicated reduction from oxidic to metallic Au with increasing temperature, suggesting that cationic Au species are responsible for the higher catalytic activity. For Au/γ-Al_2O_3, they reported that the activity of a sample calcined below 300 °C increased with time on stream, suggesting a change in the oxidic species to acquire activity. For samples calcined above 300 °C, the activity decreased with increasing calcination temperature.

Wolf and Schüth[8] found that Au/TiO_2 samples prepared by deposition-precipitation and calcined at 200 °C had much higher activities than those calcined at higher temperatures (300, 400, and 500 °C) or dried at 90 °C. Although they did not exclude the presence of cationic Au as the reason for the higher activity at the lower calcination temperatures, they noted that, after calcination at 400 °C, the samples should contain entirely metallic gold, yet they still exhibited respectable activity for CO oxidation. The authors concluded, therefore, that metallic gold provides the active sites, and the decrease in catalytic activity with increasing temperature is associated with the corresponding increase in gold particle size and decreasing surface area. Boccuzzi et al.[9] also suggested a similar interpretation of the role of Au particle size. In experiments with a series of Au/TiO_2 samples prepared by deposition-precipitation and calcined at 200, 300, 400, and 600 °C, the highest activity was observed for the sample calcined at 300 °C, followed by 200, 400, and then 600 °C. The authors attributed the activity to steps, edges, and corners of metallic Au particles, the numbers of which increased with decreasing particle size and calcination

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* E-mail: m-kung@northwestern.edu, hkung@northwestern.edu, bcgates@ucdavis.edu.

[‡] Northwestern University.

[#] University of California, Davis.

[†] Institute of Chemical Technology, UPV-CSIC, Valencia 46022, Spain.

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temperature. The lower activity of the sample calcined at 200 °C may be because the oxidic gold precursor was not completely decomposed into metallic Au, although this sample had the smallest Au particle size. However, although the Au particle sizes in the samples calcined at 300 and 400 °C were approximately the same, the former showed higher CO oxidation activity.

We emphasize that in some of these investigations, the researchers noted that the activity of some of the catalysts increased with time on stream before reaching a pseudo-steady state. This behavior was reported, for example, for uncalcined Au/Fe_2O_3[3,4] and Au/Al_2O_3 calcined at low temperature.[7] The evolution in activity signified changes in the catalyst, which could have been changes to the ligands coordinated to Au(III), reduction of the Au(III) in the precursor to Au(I) and/or Au(0), development of desirable surface structures on metallic Au particles, or of perimeter sites between gold and the support. Lee et al.[10] reported a similar observation of increasing activity with time-on-stream for uncalcined Au/MnO catalysts prepared by coprecipitation. In this case, the Au in the uncalcined sample was already in the metallic state; with time-on-stream, the size of the Au particles increased.

In many of these investigations, characterization was carried out with fresh catalyst or one that had been deactivated during operation for CO oxidation. Only few examinations of active catalysts in the working state have been reported. Such characterizations could be particularly useful for supported Au, because it is known that these catalysts may change upon storage, which suggests that the state of Au could respond readily to its environment. Previously, we employed transient in situ XANES measurements to follow changes of the oxidation state of V in VPO catalysts during reduction by butane;[11] transformation of CuO during methanol reforming;[12] and changes in Au/MgO prepared from the precursor $Au(CH_3)_2$(acac) (acac is $C_5H_7O_2$) during treatment in reactants and during CO oxidation catalysis.[13] In the latter case, the experiments also yielded EXAFS data, which complemented the XANES data in showing that the catalyst calcined at 100 °C contained very small clusters of Au (approximated as Au_6 octahedra), whereas the sample calcined at 300 °C had much larger Au particles (about 3 nm in average diameter). Furthermore, the former sample contained predominantly cationic gold, whereas the latter contained mostly metallic Au. A correlation of the activity with the fraction of gold present as Au(I) led to the conclusion that the catalytic sites incorporate cationic gold.[14]

In view of the insights that can be obtained from in situ X-ray absorption measurements, we have now extended the observations to follow changes in the oxidation state of Au during pretreatment of Au/Al_2O_3 catalysts, with the intent to elucidate the role of Au(0) in the catalytic activity. Our preliminary results had already shown that activation at 100 °C of an uncalcined sample prepared by deposition-precipitation depended significantly on the conditions, such as atmosphere and time.[15] The XANES measurements were complemented by temperature-programmed reduction (TPR) measurements to provide quantitative information about the Au oxidation states. Two types of samples were examined, one prepared from aqueous $HAuCl_4$ by deposition-precipitation and one from an organic solution of $Au(CH_3)_2$(acac).

Experimental Methods

Catalyst Preparation. The samples referred to as $Au/\gamma\text{-}Al_2O_3$(DP) were prepared by deposition-precipitation from aqueous solution at pH 7 and 70 °C with $HAuCl_4$ (Aldrich, 99.999%) as the precursor, as described previously.[16] The $\gamma\text{-}Al_2O_3$ support was synthesized by hydrolysis of aluminum isopropoxide (Aldrich, 99.99+%) in the presence of 2-methyl-2,4-pentanediol;[17] its BET surface area was about 250 $m^2\ g^{-1}$. Each supported Au sample was washed twice with room-temperature water, then once with water at 50 °C followed by suction filtration and drying at room temperature. The resultant sample is referred to as the as-prepared sample. Calcined samples were calcined at 350 °C in air for 4 h. The Au content was determined by ICP to be in the range of 1−1.5 wt %. The chloride contents of the samples were not determined, but based on experience they are expected to be below the detection limit of 0.01 wt % Cl (corresponding to Cl/Au atomic ratios < 0.03).

The samples referred to as $Au/\gamma\text{-}Al_2O_3$(AC) were synthesized from $\gamma\text{-}Al_2O_3$ powder (Aluminum Oxide C, Degussa) that was made into a paste by addition of deionized water, followed by overnight drying at 393 K. It was then ground and calcined at 673 K, evacuated, and stored in a drybox (Vacuum Atmospheres HE−63-P) until subsequent use. The BET surface area was approximately 100 $m^2\ g^{-1}$. The precursor Au $(CH_3)_2(C_5H_7O_2)$, or $Au(CH_3)_2$(acac) (dimethylauric acetylacetonate; Strem, 98%) was brought in contact with the partially dehydroxylated $\gamma\text{-}Al_2O_3$ powder in a slurry with dried and deoxygenated *n*-pentane. The slurry was stirred for 1 day and the solvent removed by evacuation (pressure < 10^{-3} torr) for 1 day. The syntheses and transfers were carried out as before under anaerobic and anhydrous conditions.[18] The resultant $\gamma\text{-}Al_2O_3$-supported gold sample, containing 1 wt % Au, was treated in flowing He or H_2 at atmospheric pressure as the temperature was ramped at a rate of 3 °C min^{-1} from room temperature to a temperature in the range of 323−573 K to remove the ligands bonded to the gold.[19]

Catalyst Characterization by Transmission Electron Microscopy (TEM). TEM examination of $Au/\gamma\text{-}Al_2O_3$(DP) samples was performed with a Hitachi HF-2000 TEM with field emission gun at 200 keV.

Catalytic Activity for CO Oxidation. Catalytic reactions were conducted in a flow microreactor and also in X-ray absorption cells that served as flow reactors at the synchrotrons where XANES experiments were carried out. The microreactor experiments at Northwestern University were conducted with $Au/\gamma\text{-}Al_2O_3$(DP) with a flow system incorporating a fused silica reactor operated at room temperature, using a feed of 1% CO, 2.5% O_2, and the balance He, with a total flow rate of 200 mL min^{-1} unless otherwise specified. The feed was purified by passage through a trap containing particles of silica at dry ice temperature immediately upstream of the reactor. Typically, 0.040 g of catalyst was used. After pretreatment of the catalyst, the reactor was purged with He for 30 min, and then a premixed feed was allowed to flow into the reactor; the CO concentration in the effluent was determined by IR spectroscopy with a gas-phase cell in the product line and by gas chromatography.[16]

When a dry feed was used, the catalyst deactivated rapidly in 5−10 min time on stream (TOS),[16,20] and the initial activity was defined as that observed at 1 min TOS. Water vapor, when included in the feed stream, was added by passing the feed gas through a water saturator at room temperature. The estimated water content was between 1 and 1.5%. In a wet feed, the catalyst gave a stable activity.

Experiments were carried out similarly at the University of California with $Au/\gamma\text{-}Al_2O_3$(AC) samples. The catalyst (typically, 0.05 g) was loaded into the reactor in a N_2-filled glovebox and transferred to the flow system without contacting air. Total feed flow rate to the flow system was 100 mL (NTP) min^{-1}

with a composition of 1.45% CO and 1.45% O_2, with the remainder being He. Each reactant, CO and O_2 (Matheson, 99.999%), each in a 10% mixture in He, was purified by passage through a trap containing activated γ-Al_2O_3 particles and zeolite 4A to remove any traces of metal carbonyls (from the high-pressure gas cylinder) and moisture, respectively. The conversions of CO and O_2 were determined by gas chromatographic analysis (Hewlett-Packard, HP-589 Series II) of the product stream, to determine the removal of CO and the formation of CO_2; the conversions were determined with an accuracy of about ±5%.

In Situ XANES Measurements. A flow-through sample cell was used for the XANES measurements carried out with Au/γ-Al_2O_3(DP). About 0.1 g of loose powder sample was supported at the end of a stainless steel tube between two layers of quartz wool and two aluminum wire grids. The cell itself was quartz and could be heated to 400 °C. Aluminum windows were attached to the cell on both ends by stainless steel flanges. Gases flowed through the sample with little bypass. CO oxidation reactions were conducted at room temperature with a feed of 1% CO, 2.5% O_2, and the balance He with a flow rate of 500 mL min^{-1}, so that the space velocity was the same as in the microreactor. After pretreatment of the catalyst, the sample cell was purged with He for 30 min before flow of a premixed gas was started through the reactor/cell. The CO concentration in the effluent was monitored by a gas chromatograph with a molecular sieve column. Water vapor, when present in the feed stream, was added by passing the feed through a water saturator at room temperature. The estimated water content was between 1 and 1.5%. In activation procedures with 1% CO in He, a flow rate of 500 mL min^{-1} was used, but the activation procedures involving H_2 were carried out with a flow rate of 250 mL min^{-1}.

These XANES experiments with Au/γ-Al_2O_3(DP) were carried out at Beamline 5-BMD of the DuPont Northwestern Dow Collaborative Access team at the Advanced Photon Source at Argonne National Laboratory in Argonne, IL. The storage ring electron energy was 7.0 GeV, and the ring current was in the top-off mode at 100 mA. All spectra were collected in transmission mode at the Au L_{III} edge (11.919 keV) with the sample in flowing He at atmospheric pressure after at least 30 min of He purge after any pretreatment, unless otherwise specified. Higer harmonics in the X-ray beam were minimized by detuning the Si(111) monochromator by 15−20% at the Au L_{III} edge.

XANES spectroscopy experiments characterizing the catalyst Au/γ-Al_2O_3(AC) were performed similarly at Beamline 4−1 of the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center, Stanford, CA. The storage ring electron energy was 3 GeV, and the ring current varied within the range of 50−100 mA. Data were collected at the Au L_{III} edge (11.919 keV) in transmission mode with the catalysts in flowing He at atmospheric pressure and room temperature and after subsequent treatment in He or H_2 at increasing temperatures. Higher harmonics in the X-ray beam were minimized by detuning the Si(220) monochromator by 20−25% at the Au L_{III} edge.

Temperature-programmed Reduction (TPR). TPR experiments characterizing Au/γ-Al_2O_3(AC) were performed at the University of California with an RXM-100 multifunctional catalyst testing and characterization system (Advanced Scientific Designs, Inc.) with a vacuum capability of 10^{-9} torr; it was equipped with a thermal conductivity detector (TCD). In an N_2-filled glovebox, the sample for TPR (typically 0.3 g) was weighed, loaded into a quartz tube, sealed, and transferred to the characterization system without exposure to air or moisture.[21] Prior to each experiment, the sample was pretreated at room temperature in flowing Ar (10 mL (NTP) min^{-1}) for 20 min. The sample powder was treated by heating from 25 to 800 °C at a rate of 10 °C min^{-1} in a flow of 5 vol % H_2 in Ar. The total gas flow rate was 10 mL (NTP) min^{-1}. The experimental parameters were chosen so that the “K number” (defined as the ratio of reducible substance (mol) divided by the H_2 flow rate (mol s^{-1})[22]) had a value in the range of 55−140 s. The TCD signal was calibrated to determine H_2 consumption by using the complete reduction of CuO powder as a standard (Aldrich, 99.995%) and by measuring the area under the TCD signal for known H_2 concentrations. The H_2 uptakes were determined with an accuracy of about ±10%.

TPR experiments were performed similarly at Northwestern University with 0.2 g of Au/γ-Al_2O_3(DP) in a quartz reactor. The sample was loaded into the reactor, subjected to the pretreatment, and then purged with Ar prior to each experiment. Subsequently, the sample was heated from 20 to 520 °C at a rate of 10 °C min^{-1} in a flow of 5 vol % H_2 in Ar. The total gas flow rate was 60 mL min^{-1}. The rate of H_2 consumption was monitored by a thermal conductivity detector and calibrated against pulses of known amounts of H_2.

Results

Activation of Au/Al_2O_3(DP). As reported previously,[15] an uncalcined Au/Al_2O_3 sample was found to be inactive for CO oxidation at room temperature, even with a wet feed or if H_2 was present. The sample became active at 100 °C under these conditions. In fact, the activity of an activated sample was over twice of that calcined at 350 °C for 4 h. One possible mechanism of activation was reduction of Au. To investigate this possibility, various pretreatments were performed to test their effectiveness in activating the catalyst, and the corresponding extents of reduction of the samples were monitored. The activation procedures that were investigated and the corresponding CO oxidation activities in a dry feed are summarized in Table 1. Exposing the catalyst at 100 °C to a feed of CO, O_2, and water (Exp. 3), or CO, O_2, and H_2 (Exp. 4), or H_2 and O_2 (Exp. 5) was highly effective. However, treatment in H_2 followed by treatment in O_2 was insufficient for catalyst activation (Exp. 6), suggesting that these two gases need to be present simultaneously. Treatment in a reducing gas (1% CO in He or pure H_2) alone, either with or without water present (Exps. 7 to 9), was less effective, as was treatment in 1.5% H_2O in He (Exp. 10). On the other hand, treating the sample first in a dry reducing gas followed by a wet gas (1% CO, H_2, or He) improved the resulting activity (Exps. 11 to 13). Therefore, to activate these samples, it is necessary to treat the catalysts in a reducing gas and H_2O. If O_2 is present in the treatment mixture, the reducing gas and H_2O can be present simultaneously; if O_2 is not present, then the sample must be treated in the reducing gas alone first, following by H_2O in He or H_2O in a reducing gas.

XANES of Uncalcined Au/Al_2O_3(DP). Figure 1 shows the X-ray absorption of Au at the 11.919 keV edge for a number of reference compounds. The intensity of the white line, which occurs at about 11.922 keV and corresponds to a $2p_{3/2} \rightarrow 5d$ transition, is proportional to the density of unoccupied d states, which is greatest for Au(III) in gold acetate and $Au(OH)_3$ and decreases as the Au in the sample is reduced to Au(I) and further to metallic Au.[13,23] Au(III) is also characterized by a shoulder at 11.939 keV and an intense broad peak at 11.968 keV. Au(0) is characterized by a shoulder at 11.923 keV and peaks at

TABLE 1: Initial CO Conversion (TOS = 1 min) for CO Oxidation at Room Temperature Catalyzed by Activated Uncalcined Au/Al$_2$O$_3$(DP) in a Flow Microreactor

exp. no.	pretreatment condition[a]	initial CO conversion, %	initial CO oxidn rate, mol CO (mol Au-s)$^{-1}$
1	30 min CO Ox[b]+ H_2O at room temperature	0	0
2	Calcined 350 °C for 4 h in air	25	0.12
3	30 min CO Ox[b]+ H_2O at 100 °C	49.4	0.25
4	30 min SCO[c] at 100 °C	61.9	0.31
5	30 min H_2 Ox[d] at 100 °C	62.3	0.31
6	30 min H_2 at 100 °C then 20 min He at 100 °C then 15 min O_2 at 100 °C	1.5	0.007
7	2 h H_2 at 100 °C	1.5	0.007
8	1 h H_2 + 1.5% H_2O at 100 °C	1.5	0.007
9	1 h 1% CO + 1.5% H_2O at 100 °C	23.1	0.12
10	1 h 1.5% H_2O in He at 100 °C	1	0.005
11	30 min H_2 at 100 °C then 30 min H_2 + H_2O at 100 °C	71	0.35
12	2 h H_2 at 100 °C then 30 min 1.5% H_2O/He at room temperature	59.6	0.30
13	30 min 1%CO at 100 °C then 30 min 1%CO + H_2O at 100 °C	56.9	0.28

[a] The reactor was purged with 200 mL min^{-1} He after each pretreatment for 30 min and before the catalytic reaction test. In treatments at elevated temperatures, the sample was cooled to room temperature in the pretreatment feed stream before purging with He. In each experiment, 0.04 g of Au/γ-Al$_2$O$_3$(DP), containing 1.4 wt % Au, was used. [b] CO ox feed consisted of 1% CO, 2.5% O_2, balance He. [c] SCO feed consisted of 200 mL min^{-1} 1% CO, 0.5% O_2, 40.5% H_2, balance He. [d] H_2 Ox feed consisted of 200 mL min^{-1} 0.5%O_2, 40.5% H_2, balance He.

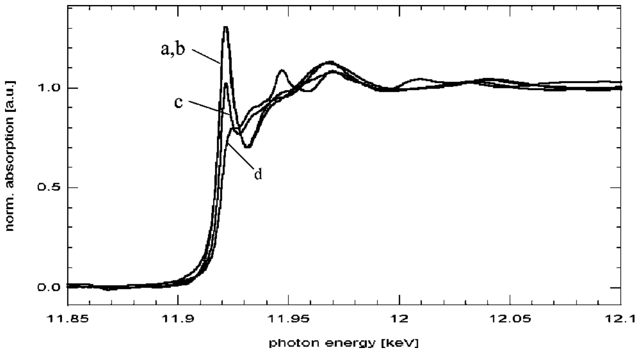

Figure 1. XANES spectra of Au standards: (a) Au (III) acetate, (b) Au(III)(OH)$_3$, (c) Au(I)Cl, (d) Au foil. The spectra were collected at room temperature in air. Note that curve a and b fall directly on top of one another.

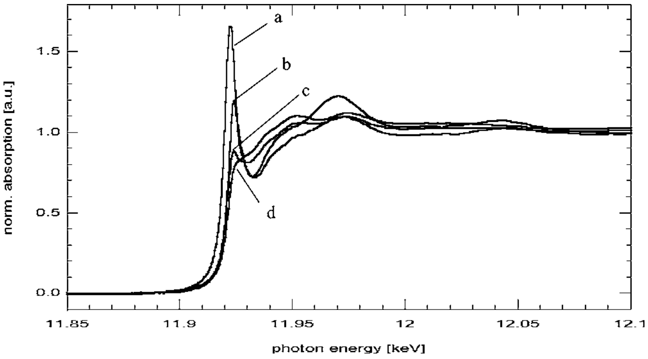

Figure 2. XANES characterizing 1.3 wt % Au/γ-Al$_2$O$_3$(DP): (a) as-prepared uncalcined, (b) after 30 min in H_2 at 100 °C, (c) after subsequent treatment in H_2O and H_2 at 100 °C for 30 min, (d) after an additional 30 min in H_2 and H_2O at 100 °C. After each treatment, the sample was cooled to room temperature in the treatment gas mixture. The XANES cell was purged with He while the spectra were collected.

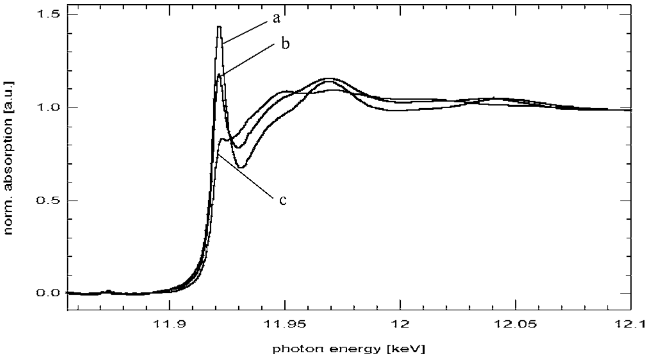

Figure 3. XANES characterizing 1.3 wt % Au/γ-Al$_2$O$_3$(DP): (a) as-prepared uncalcined, (b) after 30 min in 1% CO in He at 100 °C, (c) after subsequent treatment in ~1.5% water and 1% CO in He at 100 °C for 30 min. After each treatment, the sample was cooled to room temperature in the treatment gas mixture. Then, the XANES cell was purged with He while the spectra were collected.

11.934, 11.947, and 11.971 keV. The Au(I) spectrum is similar to that of Au(III), but with an intermediate white line intensity. These spectra did not change from one scan to another, indicating the absence of beam damage of the sample.

The spectrum of an inactive, as-prepared sample is shown in Figure 2(a). The intense absorption at 11.922 keV suggests that all the Au in this sample was Au(III), presumably as Au(OH)$_{4-x}$Cl$_x^-$, which is consistent with the TPR results. Curve (b) shows the spectrum of the same sample after treatment at 100 °C in H_2 for 30 min. Based on the decrease in the white line intensity and the broad peak at 11.986 keV, it is apparent that reduction of some of the Au in this sample had occurred. By fitting the XANES spectrum to the standards, it was estimated that 15 (±5)% of the Au was reduced. This sample was only barely active for CO oxidation when tested in the microreactor with 0.04 g of catalyst under the standard conditions; the initial CO conversion was about 1%, declining with TOS.

XANES spectra of the highly active samples are shown in curves (c) and (d) of Figure 2, which were collected after treatment at 100 °C in H_2 for 30 min followed by H_2 saturated with water for 30 and 60 min, respectively. Compared to curve (b), these samples were much more severely reduced, and sample (d) was more reduced than sample (c). The majority of the Au in these samples was metallic, and the pseudo steady state (TOS = 20 min) CO oxidation conversion of 17% was observed for the sample (c), and 19% for sample (d) when tested in the XANES cell. When tested in the microreactor, the same pretreatment corresponding to (c) and (d) gave the same initial CO conversion of about 70%, which decreased to 14% after 20 min TOS. Thus, once the catalyst had been reduced to a certain point, further reduction did not improve its activity significantly.

Similar results were obtained when the catalyst was treated with CO instead of H_2 as the reducing gas (Figure 3). Curve (a) shows the as-prepared sample, and curve (b) shows the sample after treatment in 1% CO in He at 100 °C for 30 min.

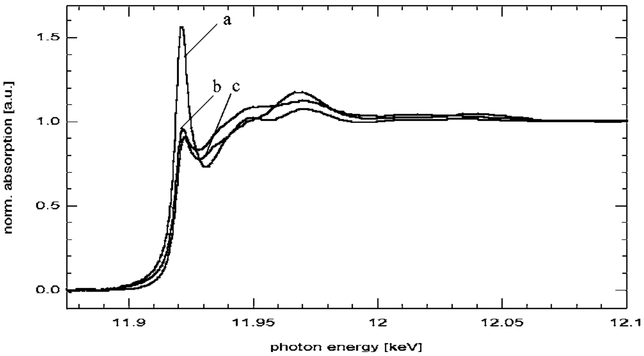

Figure 4. XANES characterizing 1.3 wt % Au/γ-Al_2O_3(DP): (a) uncalcined, (b) after 1 h in 1% CO in He saturated with water at 100 °C. The sample was cooled to room temperature in the treatment gas mixture. The XANES cell was purged with He while the spectra were collected. (c) Calcined sample (350 °C for 4 h). This spectrum was collected in air at room temperature.

A small amount of reduction had occurred, approximately matching that observed after treatment of the sample in H_2 for 30 min at 100 °C. However, the sample remained essentially inactive for CO oxidation catalysis. After a subsequent treatment in 1% CO saturated with water at 100 °C for 30 min, however, the sample was found to contain gold predominantly as metallic Au (curve c), and it was highly active for CO oxidation, with a CO conversion of 55% after 2 min TOS.

Other treatments, such as that in H_2 alone for 2 h at 100 °C or He saturated with water for 1 h at 100 °C, resulted in little or no reduction of Au. Such samples were also barely active for CO oxidation, showing an initial CO conversion of less than 1%. Treatment solely in H_2 and water at 100 °C for 1 h was not sufficient to reduce the Au/Al_2O_3 samples significantly. Such samples were also characterized by initial CO conversions of only about 1%. In contrast, when the sample was treated in 1% CO in He saturated with water at 100 °C for 1 h, it did undergo reduction (Figure 4), giving an initial CO conversion of 29% at 2 min TOS in the XANES cell and 23% at 1 min TOS in the microreactor.

Calcination at 350 °C for 4 h in air also gave a sample consisting mainly of metallic Au, as shown in Figure 4, spectrum c. This sample was less than half as active for CO oxidation as those activated at 100 °C, and it appeared to contain roughly the same amount of metallic Au as these samples. However, this sample also contained larger Au particles, as indicated by transmission electron micrographs, which show that the Au particles in the calcined sample ranged from 5 to 20 nm in diameter,[24] whereas they were in the 3−5 nm diameter range for the 100-°C activated samples (Figure 5).

Changes resulting from other pretreatment procedures were also examined. Figure 6, curve (b), shows data representing a sample that had been heated to 100 °C for 1 h in H_2, then cooled to room temperature and purged with He. Only about 15 (±5)% of the Au in this sample was reduced. When the sample was subsequently treated with water in He at 100 °C for 30 min and then cooled to room temperature in this feed and purged with He, curve (c) was recorded. Slightly over half of the Au in this sample had been reduced. When tested for CO oxidation with a wet feed, this catalyst gave a CO conversion at 2 min TOS of 56.8%. Over the course of 1 h in this feed, the conversion increased to 86%, and more Au in the sample was reduced, until the sample appeared to contain almost exclusively metallic Au.

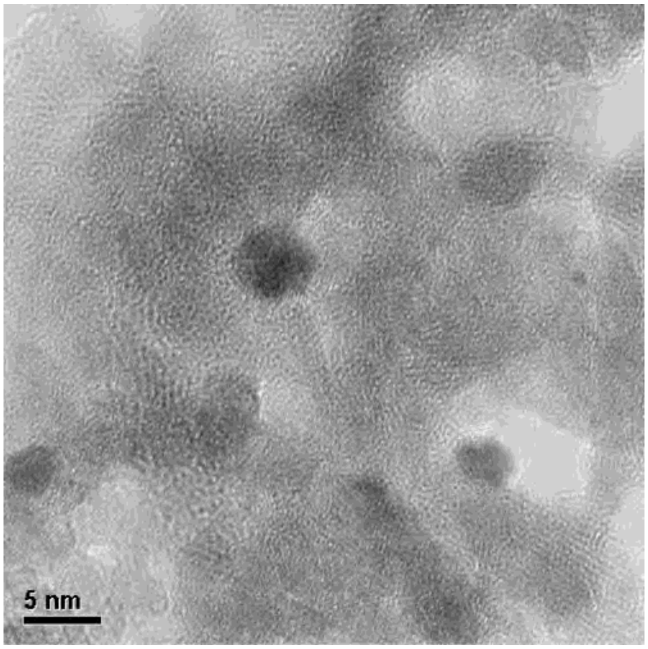

Figure 5. TEM micrograph of Au/γ-Al_2O_3(DP) pretreated at 100 °C with H_2 for 30 min and then wet H_2 for 30 min.

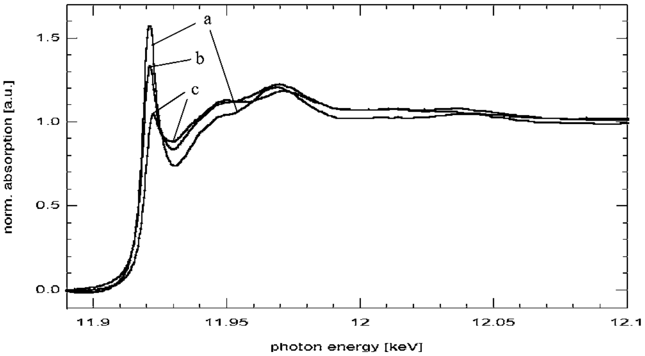

Figure 6. XANES characterizing 1.4 wt % Au/γ-Al_2O_3(DP): (a) uncalcined, (b) after 1 h in H_2 at 100 °C, (c) after subsequent 30 min in water/He at 100 °C. After thermal treatments, the sample was cooled to room temperature in the treatment gas mixtures. The XANES cell was purged with He while the spectra were collected.

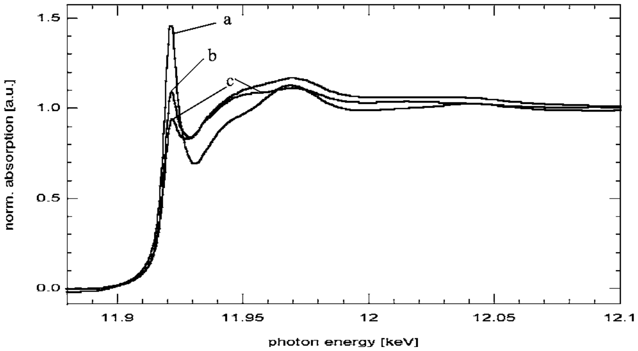

Figure 7. XANES characterizing 1.3 wt % Au/γ-Al_2O_3(DP): (a) uncalcined, (b) after 1 h in 1% CO in He at 100 °C, (c) after subsequent 30 min in He saturated with water at 100 °C. After thermal treatments, the sample was cooled to room temperature in the treatment gas mixtures. The XANES cell was purged with He while the spectra were collected.

A similar procedure was carried out with a feed containing 1% CO in He instead of H_2; the results are presented in Figure 7. The treatment in 1% CO at 100 °C (curve b) was much more effective in reducing the catalyst than the treatment in H_2 at 100 °C (Figure 6, curve b). Further treatment in He saturated with water at 100 °C for 30 min did not produce a marked

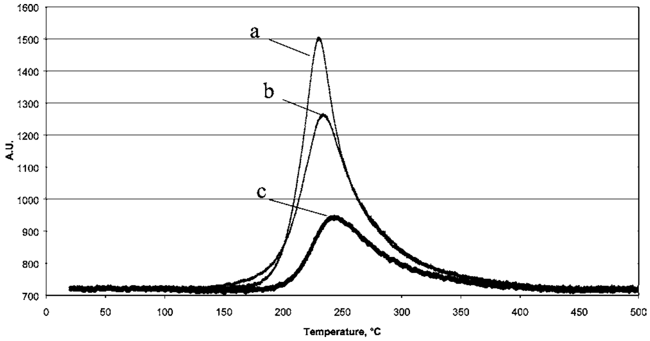

Figure 8. TPR curves for uncalcined 1.39 wt % Au/γ-Al_2O_3(DP): (a) no treatment, (b) after 30 min at 100 °C in H_2, (c) after activation by 30 min H_2 and 100 °C followed by 30 min H_2 saturated with water at 100 °C.

TABLE 2: TPR Results Characterizing Au/Al_2O_3(DP) Shown in Figure 8

Sample	H_2 consumption (mol of H_2 (mol of Au)$^{-1}$)	Avg Au Oxidation State
a (as-prepared)	1.52	3
b (after H_2 at 100 °C)	1.35	2.7
c (as for b, plus additional H_2/H_2O treatment at 100 °C)	0.62	1.2

TABLE 3: Initial CO Conversion (TOS = 1 min) for CO Oxidation Catalyzed by Au/γ-Al_2O_3(AC) Prepared from $Au(CH_3)_2(acac)$

pretreatment		
gas	temperature (°C)	CO conversion (%)
none	none	2
He	50	2
He	100	3
He	200	0
He	300	0
H_2	100	0
H_2	300	0

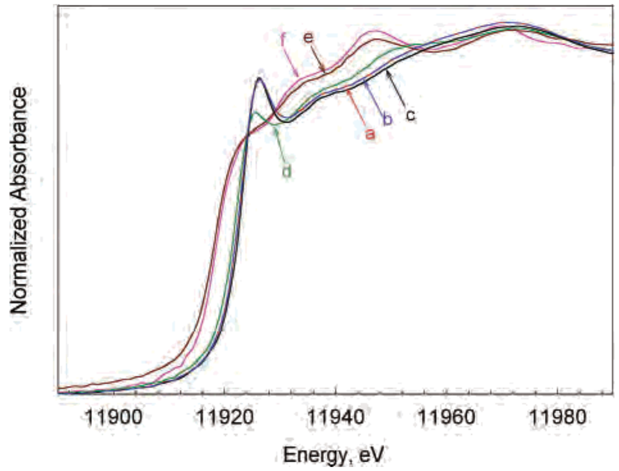

Figure 9. XANES data characterizing Au/γ-Al_2O_3(AC) samples obtained after (a) absorption of $Au(CH_3)_2(acac)$ and after subsequent exposure to He for 1 h at the following temperatures (°C): (b) 25, (c) 50, (d) 100, (e) 200, and (f) 300.

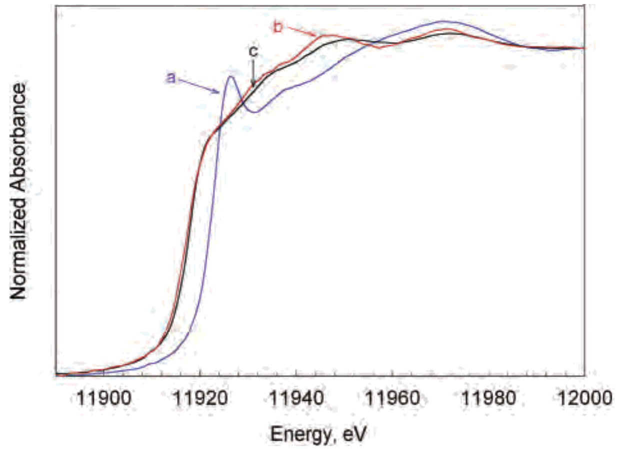

Figure 10. XANES data characterizing Au/γ-Al_2O_3(AC) samples obtained after (a) absorption of $Au(CH_3)_2(acac)$ and after subsequent exposure to H_2 for 1 h at the following temperatures (°C): (b) 100 and (c) 300.

increase in the amount of reduced Au in this sample, in contrast to the result observed with H_2. The sample also had a lower initial activity, with a CO conversion of 22% at 2 min TOS. When tested in the microreactor, the catalyst subjected to this treatment gave a CO conversion of 25% at 1 min TOS. This sample was characterized by less reduction of the Au than one treated in 1% CO in He at 100 °C followed by 1% CO in He saturated with water at 100 °C.

TPR of Au/Al_2O_3(DP). TPR was conducted to complement the XANES measurements. The results are shown in Figure 8, and the H_2 consumption for each sample is presented in Table 2. Curve (a) shows the TPR of the as-prepared sample, in which the gold was present entirely as Au(III). After treatment in H_2 at 100 °C for 30 min, curve (b) was obtained. The H_2 consumption corresponds to about 12% reduction of the Au. After treatment in H_2 at 100 °C for 30 min followed by H_2 and H_2O at 100 °C for 30 min, the sample was much more reduced, as shown in curve (c). These results correlate well with the XANES observations.

Activation of Au/Al_2O_3(AC). *CO Oxidation Activity.* The as-prepared γ-Al_2O_3-supported gold sample, consisting mainly of Au(III) complexes, as well as the samples treated for 1 h in He at 50, 100, 200, and 300 °C or in H_2 at 200 and 300 °C were tested for room-temperature CO oxidation catalysis. The initial conversions, reported at a TOS of 1 min, are shown in Table 3. The samples treated in He or H_2 at the higher temperatures were completely inactive for CO oxidation at room temperature. Only the initially prepared sample and those treated in He at low temperatures were active, but the CO conversions were low, less than 3%.

XANES. The XANES spectrum of the sample prepared from $Au(CH_3)_2(acac)$ deposited on γ-Al_2O_3 showed features that matched those characterizing Au(III) in $Au(CH_3)_2(acac)$, $HAuCl_4$, and Au_2O_3.[13,25] Treatments of the samples in flowing He at increasing temperatures decreased the area under the white line (Figure 9), indicating increasing reduction of Au. Exposure of the initially prepared sample to He at 100 °C for 1 h resulted in a decrease in intensity of the peak at 4 eV and the appearance of an intense peak at 25 eV above the Au L_{III} edge (curve d). The data demonstrate reduction of the gold to an intermediate oxidation state; a comparison with the spectra of AuCl, (PPh_3)-AuCl (Ph is phenyl), and metallic Au suggest the presence of a mixture of Au(I) and Au(0). The samples treated in He at higher temperatures, 200 and 300 °C for 1 h (curves e and f), are characterized by two broad peaks, at energies 25 and 50 eV, respectively, higher than that of the edge, and the disappearance of the peak at 4 eV, corresponding to the formation of Au(0).

Exposure of the initially prepared sample to H_2 at 100 and 300 °C (Figure 10) led to the complete disappearance of the peak at 4 eV and to the appearance of an intense peak at 25 eV

TABLE 4: Results of TPR Experiments Characterizing γ-Al_2O_3-supported Gold Samples Prepared from $Au(CH_3)_2(acac)$

sample	pretreatment conditions		H_2 consumption (mol of H_2 (mol of Au)$^{-1}$)	reduction temperature (°C)	avg Au oxidation state
	gas	temperature (°C)			
γ-Al_2O_3	none	none	0	not reduced	-
$Au(CH_3)_2(acac)$	none	none	1.53	150	3
Au/γ-Al_2O_3	none	none	1.51	107	3
Au/γ-Al_2O_3	He	100	0.34	107	0.7
Au/γ-Al_2O_3	He	300	0	none	0
Au/γ-Al_2O_3	H_2	100	0	none	0
Au/γ-Al_2O_3	H_2	300	0	none	0

above the Au L_{III} edge, and the peak at 50 eV above the edge became narrower; these features correspond to the formation of metallic gold.

TPR. The TPR results characterizing the gold precursor and the catalyst initially prepared from Au $(CH_3)_2(acac)$ indicate peaks at 150 and 107 °C, respectively (Table 4), with measured H_2 uptakes of 1.53 ± 0.15 mol of H_2 (mol of Au)$^{-1}$ and 1.51 ± 0.15 mol of H_2 (mol of Au)$^{-1}$, respectively, consistent with a complete reduction of Au(III) to Au(0). These features were absent in the data representing a blank sample consisting of the support without the Au; thus, the $Au(CH_3)_2(acac)$ complex is inferred to have remained as Au(III) after adsorption on γ-Al_2O_3, consistent with the XANES results. After the sample had been treated in flowing H_2 at 100 or 300 °C, no reduction peak was observed, indicating that complete reduction to Au(0) had occurred during the treatment in H_2. In contrast, when the sample was treated in flowing He at 100 °C, a small reduction peak was observed at 107 °C with a measured H_2 uptake of 0.34 ± 0.05 mol of H_2 (mol of Au)$^{-1}$, suggesting the presence of a mixture of Au(0) and Au(I).

Discussion

The as-prepared, uncalcined Au/γ-Al_2O_3 samples, whether prepared by the aqueous deposition-precipitation method or by deposition of $Au(CH_3)_2(acac)$ from pentane, have no measurable activity for CO oxidation catalysis. Both XANES and TPR indicate that these samples contain gold entirely as Au(III). This result suggests that the ionic Au(III) precursor on γ-Al_2O_3 does not catalyze CO oxidation. The data also show that Au(III) on this support is stable at room temperature, even when it is exposed to a reducing atmosphere.

The samples could be activated at increasing temperatures. For the sample Au/γ-Al_2O_3(AC), heating in He at 50 °C was sufficient to generate some activity (Table 3). Further heating to 100 °C resulted in a further increase in activity (Table 3). The XANES results did not indicate much reduction after heating to 50 °C, but there was significant reduction after heating to 100 °C. We emphasize that both the XANES and TPR results indicate that the Au in the most active sample was not completely reduced.

Complementary information was obtained with the sample Au/γ-Al_2O_3(DP). The reduction of Au(III) and the onset of catalytic activity were found to depend sensitively on the time and atmosphere of treatment. Treatment in H_2 alone at 100 °C for 30 min did not significantly reduce the Au, resulting in a mix of ionic and metallic Au that was inactive for CO oxidation. Longer treatment times (1 or 2 h) did not result in any discernible additional reduction of the Au or activity. However, when water was added to the H_2 stream at 100 °C, the reduction of Au was significantly enhanced. The XANES and TPR spectra (Figure 2 and Figure 8, respectively) for Au/Al_2O_3 after 30 min of treatment in H_2 at 100 °C followed by 30 min in H_2 and H_2O at 100 °C indicate that the Au in this sample was predominantly metallic. These samples were also highly active for CO oxidation, suggesting that metallic Au is a necessary catalyst component for this reaction. However, it is important to note that, as in the sample Au/γ-Al_2O_3(AC), the Au in this highly active catalyst was not completely reduced.

Similar results were observed in the attempts to activate the uncalcined Au/Al_2O_3(DP) sample with CO. Treating the sample with 1% CO in He at 100 °C for 30 min did not result in marked reduction or CO oxidation activity. A sample treated in 1% CO in He at 100 °C for 30 min followed by 1% CO in He saturated with water at 100 °C for 30 min exhibited significant reduction, resulting in a sample that contained gold predominantly as metallic Au (Figure 3). This sample was highly active for CO oxidation, reinforcing the earlier observation that metallic Au is a necessary component of the active site.

Most significant is the reduction observed after treatment in H_2 at 100 °C for 1 h followed by treatment in He saturated with water at 100 °C for 30 min (Figure 6). Significant reduction did not occur after the treatment in H_2, but treatment in H_2O in He reduced the majority of the Au in the sample, rendering it active for CO oxidation. The chemistry underlying this reduction is unclear at present. It could be due to decomposition of a surface Au complex that is promoted by moisture.

Calcination at 350 °C in air was also highly effective in generating Au(0), although the resulting catalyst was not as active as those of the samples generated by the other effective activation procedures; the activity of this sample was less than half the activity of the other active Au/Al_2O_3 samples (Table 1). At least part of the difference is attributed to different Au particle sizes. According to the TEM results, the calcined samples incorporated slightly larger particles than the samples activated at 100 °C, likely, we infer, because there was more sintering of the Au at the higher calcination temperature.

For each of these different procedures that resulted in an active catalyst, metallic Au was present in the sample, consistent with the inference that it is essential for activity, and no specific combination of pretreatment gases is needed. However, the activity does not correlate directly with the degree of reduction of the Au. This result suggests that, although metallic Au is a necessary component, it is not the only requirement for high CO oxidation activity.

This conclusion is consistent with the observation reported by Date and Haruta that water has a strong effect on the catalytic activity.[26,27] We have shown previously that an active Au/γ-Al_2O_3(DP) catalyst can be deactivated by mild thermal treatment in He at 100 °C, and the activity can be completely recovered by exposing the deactivated sample to water vapor at room temperature.[16,20] The XANES and TPR experiments performed with the thermally deactivated and water-regenerated Au/Al_2O_3 samples indicated no discernible difference (to be published). Thus, the presence of metallic Au does not correlate with the presence or absence of activity. This inference further supports the conclusion that metallic Au is not the only necessary requirement for catalytic activity of γ-Al_2O_3-supported Au. It is possible that water or surface species formed from it must be present as well for high CO oxidation activity.[27−29]

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