In Situ XANES of Au/γ-Al_2O_3 Catalysts

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Introduction

Gold has historically been regarded as being too chemically inert to be of any catalytic interest. However, since Haruta first reported that supported gold nanoparticles showed excellent catalytic properties [1], there has been increasing interest in the field of gold catalysis. Supported gold catalysts have been intensely investigated for low-temperature CO oxidation because of their exceptionally high activity. Despite intense research efforts, the importance of metallic versus ionic gold is still an unresolved issue, and the nature of the active site for CO oxidation is still unclear.

It is generally accepted that the activity of supported gold catalysts depends strongly on the pretreatment conditions. Recent studies have begun to focus on the effects of calcination temperature in the preparation of active supported gold catalysts by the deposition-precipitation method, and several of them have found that milder calcination temperatures (100-200°C) result in more active catalysts for CO oxidation [2]. These observations may be the result of differing degrees of reduction of gold (Au). However, the characterization of the catalysts used in most of these studies was carried out only on fresh catalyst samples. It is possible that the oxidation state of Au changes during the CO oxidation reaction. Therefore, it is important not only to study the fresh catalyst but also to gather information about the working catalyst. This report describes the study of the activation of as-prepared Au/γ-Al_2O_3 and includes characterization by *in situ* x-ray absorption near-edge structure (XANES) studies of the working catalyst, in order to determine the Au oxidation state requirement for CO oxidation.

Methods and Materials

The γ-Al_2O_3 used was synthesized by hydrolysis of aluminum isopropoxide (Aldrich, 99.99+%) in the presence of 2-methyl-2,4-pentanediol. The Au/γ-Al_2O_3 catalysts were prepared by deposition-precipitation at pH 7 and 70°C with an $HAuCl_4$ precursor (Aldrich, 99.999%), as described previously [3]. The samples were washed twice with room-temperature water, then once with 50°C water followed by suction filtering, and they were dried at room temperature. The resulting sample was the uncalcined or as-prepared sample. The Au content of the Au/γ-Al_2O_3 samples was determined by ICP to be 1.3 wt% Au.

The Au/γ-Al_2O_3 powder sample is supported at the end of a stainless steel tube between two layers of quartz wool and two aluminum wire grids. Aluminum windows are attached to the cell on both ends by stainless steel flanges. Gases can flow through the sample with little bypass. In each of the XANES experiments, 0.1 g of catalyst was used, and all CO oxidation reactions were conducted at room temperature in 1% CO and 2.5% O2 with the balance being He, at a total flow rate of 500 mL/min. All the CO activity measurements were duplicated in a quartz microreactor by using 0.04 g of catalyst at a total flow rate of 200 mL/min. The CO concentration in the effluent was monitored by a gas chromatograph with a molecular sieve column. Water vapor, when used, was added by passing the feed stream through a water saturator at room temperature. The estimated water content was between 1% and 1.5%. For the activation procedures involving H_2, a flow rate of 250 mL/min was used.

The XANES experiments were preformed at DND-CAT beamline station 5-BM-D at the APS. All spectra were collected at the L_{III} edge of Au, which occurs at an energy of 11.919 keV. The monochromator was used to vary the energy between 11.779 keV and, typically, 12.9 keV. The background was typically collected from –140 eV below the edge to –40 eV below the edge in 5-eV increments, at which point the pre-edge region was reached and data were collected at energy increments of 0.25 eV. In the EXAFS region (K = 2-16), data were collected at K ($Å^{-1}$) increments of 0.05. All the spectra were analyzed by WinXAS software.

Results

The Au/γ-Al_2O_3 samples were examined with *in situ* XANES to determine whether the changes in activity corresponded to changes in the oxidation state of Au. Changes in the oxidation state of Au correlate with a change in the intensity of the white line, which occurs around 11.922 keV. This feature corresponds to a 2p3/2 $\rightarrow$ 5d transition, so its intensity is proportional to the density of unoccupied d states, which is largest for Au^{III} and decreases as the Au in the sample is reduced to metallic Au [4]. This phenomenon is illustrated in Fig. 1, which shows several Au standards. The white line has the highest intensity for the Au^{III} compounds, such as Au acetate, and is absent in the metallic Au foil. $Au^{I}Cl$ gave an intermediate white line intensity. The metallic

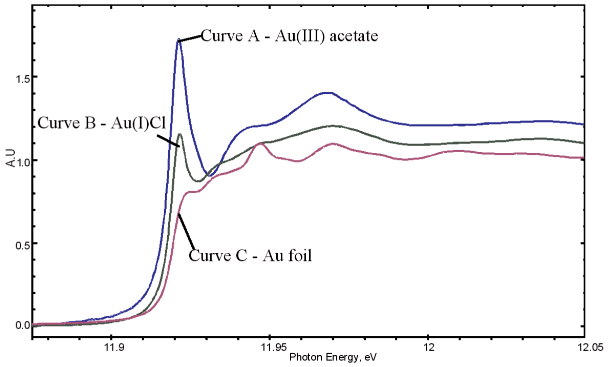

FIG. 1. XANES characterizing Au standards. A = Au (III) acetate, B = Au(I)Cl, and C = Au foil.

samples also have a more well-defined peak at 11.947 keV, whereas this peak is obscured by the broad peak at 11.971 keV in the samples containing ionic Au. The XANES spectra of three standards — Au acetate, AuCl, and Au foil — were used to estimate qualitatively the oxidation states of Au present in the Au/γ-Al_2O_3 samples under various pretreatment conditions and during reaction.

The as-prepared Au/γ-Al_2O_3 catalyst was inactive for CO oxidation. Its XANES spectra are shown in Fig. 2 (curve A). All the Au in this sample was predominately ionic. Curve B shows the same sample after treatment at 100°C in H_2 for 30 minutes. Some reduction of the Au in this sample had occurred, as indicated by the decrease in the white line intensity. This sample was still inactive for CO oxidation. Treatment in H_2 alone at 100°C resulted in only about 1% initial CO conversion. XANES spectra of the highly active sample are presented in curves C and D, which were collected after treatment at 100°C in H_2 for 30 minutes followed by H_2 saturated with H_2O for 30 and 60 minutes, respectively. The majority of the Au in this sample was metallic, and it exhibited a pseudo-steady-state CO conversion of 17% and 19% after 30 and 60 minutes of treatment, respectively. This suggests that once the catalyst is activated by reducing Au species to a certain point, further reduction does not significantly improve its activity.

It had been previously demonstrated that a calcined Au/γ-Al_2O_3 sample could be deactivated for CO oxidation by treatment in dry He at 100°C and fully regenerated by treatment in He saturated with H_2O at room temperature [5]. An uncalcined sample that has been activated by the procedure mentioned above exhibits similar behavior. The CO conversions were determined by using a laboratory-scale quartz microreactor with 0.04 g of catalyst and a flow rate of 200 mL/minute (Fig. 3). Curve A shows the uncalcined sample after treatment in H_2 at 100°C for 30 minutes followed by H_2 saturated with H_2O at 100°C for 30 minutes. The sample was cooled to room temperature in H_2 and H_2O, then purged with He before beginning the reaction test. The resulting sample was highly active, with an initial CO conversion of 70% at 1-minute time-on-stream (TOS), and it was deactivated to a pseudo-steady-state with about 20% CO conversion after 20-minute TOS. The behavior of a thermally deactivated sample is shown by curve B. A fresh uncalcined sample was activated by the same procedure as that shown in curve A, then heated to 100°C in He for 1 hour, and cooled to room temperature before the reaction test. This sample was much less active, with an initial CO conversion of only 13% at 1-minute TOS. The activity of a thermally deactivated sample could be regenerated by flowing ~1.5% H_2O in He at room temperature over it, as illustrated by curve C. The resulting sample was highly active for CO oxidation, with an initial CO conversion of 82% that deactivated to a pseudo-steady-state conversion of approximately 20%.

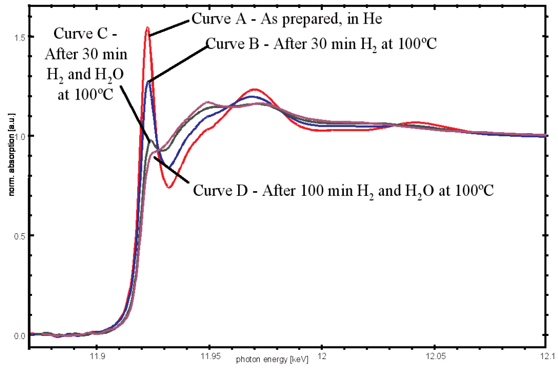

FIG. 2. XANES characterizing 1.3 wt% Au/Al_2O_3. A = as-prepared uncalcined, B = after 30 min in H_2 at 100°C, C = after subsequent treatment in H_2O and H_2 at 100°C for 30 min, and D = after an additional 30 min in H_2 and H_2O at 100°C.

XANES results of the thermal deactivation and regeneration with H_2O over the uncalcined Au/γ-Al_2O_3 sample are presented in Fig. 4. Curve A shows the sample after activation in H_2 at 100°C for 30 minutes followed by H_2 and H_2O at 100°C, at which point it was highly active for CO oxidation at room temperature. This sample was then treated in He at 100°C for 1 hour. It was then cooled to room temperature, at which point curve B was obtained and the sample was tested for CO oxidation. The corresponding initial (2-minute TOS) CO conversion was 16.7%. Finally, the sample was treated at room temperature in a flow of ~1.5% H_2O in He for 30 minutes, then purged with He at room temperature, after which the spectrum designated as curve C was collected and the sample was tested for CO oxidation. This sample had an initial CO conversion of 44% at 2-minute TOS. There was no discernable difference between the XANES spectra of these samples shown in curves A, B, and C.

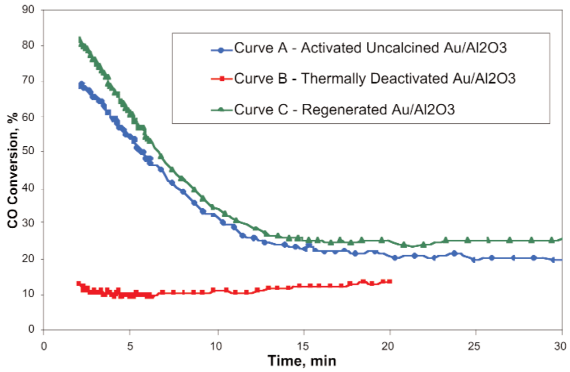

FIG. 3. CO conversion of 1.3 wt% Au/γ-Al_2O_3 at 22°C. A = uncalcined, activated sample; B = uncalcined, activated sample followed by thermal deactivation; and C = uncalcined, activated, thermally deactivated, then H_2O-regenerated sample

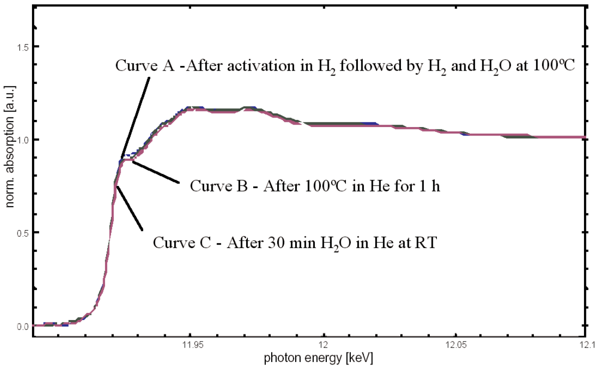

FIG. 4. XANES characterizing 1.3 wt% Au/γ-Al_2O_3. A = after activation by H_2 followed by H_2 and H_2O at 100°C, B = after 1 hour in He at 100°C, and C = after subsequent treatment in H_2O at room temperate for 30 min.

Discussion

Uncalcined Au/γ-Al_2O_3 catalyst can be activated by treating it with H_2 at 100°C followed by H_2 saturated with H_2O at 100°C for 30 minutes. The *in situ* XANES results demonstrate that this activation procedure will partially reduce an uncalcined Au/γ-Al_2O_3 catalyst and result in an active, predominantly reduced Au sample. This suggests that the presence of metallic Au is required for CO oxidation at room temperature. However, it is interesting to note that the activity does not correlate directly with the degree of reduction. This suggests that, although metallic Au is a necessary requirement, it is not the only requirement for high CO oxidation activity. This is supported by the XANES experiments performed on the thermally deactivated and H_2O-regenerated Au/γ-Al_2O_3 samples, which indicate that the majority of the Au is in the metallic state. After deactivation by treatment in He at 100°C, the Au is still mostly metallic. In fact, there is no discernable difference between the activated and thermally deactivated samples. Although regeneration with ~1.5% H_2O in He regenerates the thermally deactivated samples, there is no change in the XANES spectra. The presence of metallic Au does not correlate with the presence or absence of activity. This supports the proposal that metallic Au is not the only necessary requirement for activity and suggests that some form of H_2O must be present for high CO oxidation activity. It is possible that water is present in the form of Au-hydroxyl, as proposed in the model of the active site consisting of metallic Au atoms and Au-OH [5].

Acknowledgments

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