

Effect of aging time and calcination on the preferential oxidation of CO over Au supported on doped ceria

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Au/CeLaO_x mixed oxide catalysts containing 0.6–1.0 wt% Au were prepared by co-precipitation with Na₂CO₃. BET surface areas ranged from 15 to 45 m²/g depending on aging time (precipitation time) and calcination conditions. The differences in the activity of the catalysts for preferential oxidation (PROX) of CO are ascribed to the differences in the metal loading, Ce/La ratio and support crystallinity, chloride content, and the resultant effect on the reduction properties of the catalysts. The catalysts did not require activation in H₂ prior to reaction. The temperature at which the catalysts exhibit significant activity correlates with the temperature of reduction, indicating that reduction of the metal and support is important for high activity.

KEY WORDS: PROX of CO; gold catalyst; La doped Ceria; aging; calcination.

1. Introduction

PROX of CO in hydrogen-rich mixtures is an important reaction in fuel cell technology. The hydrogen used as fuel in a polymer electrolyte membrane fuel cell (PEMFC) should be essentially free of CO to avoid poisoning of the Pt anode catalyst [1] which substantially decreases the fuel cell performance. Pure hydrogen is an ideal fuel for PEMFC with the advantage of simple system integration, high efficiency, and zero emissions; however the poor storage capacity, safety problems, and lack of hydrogen infrastructure are major disadvantages. To overcome the difficulties with hydrogen distribution and storage, research into the onboard production of H₂ in a fuel-processing unit has increased. H₂ would be generated through reforming or partial oxidizing liquid fuels, such as LPG, gasoline, and methanol and then further processed by a water-gas shift catalyst to maximize the yield of H₂. However, the CO concentration from a reformer/water-gas shift unit is typically about 1 mol%, which is set by the thermodynamic equilibrium of the water-gas shift reaction and must be removed or converted to a compound inert for the anode reaction before being fed into the fuel cell. Even with advances in the anode materials for a PEM fuel cell, the CO levels must be below 100 ppm to maintain efficiency. Thus, CO removal plays a significant role in the feasibility of mobile or small scale (gas station), local hydrogen generation. Among various methods for removing CO from the H₂ rich feed gas, the selective CO oxidation has been recognized as one of the most straightforward

and cost-effective ones to reduce CO concentration down to acceptable levels [2–4].

The catalytic performance of gold has received significant attention since supported Au catalysts were found to exhibit exceptional CO oxidation activity at low temperatures [5]. More recently, their use as selective materials has been explored for selective oxidation of CO in H₂ rich fuels for fuel cells. Several studies have indicated that the rate of CO oxidation over supported Au catalysts exceeds that of H₂ oxidation [5,6], making Au based catalysts attractive for the selective oxidation of CO. A wide range of oxide supported gold catalysts have been investigated for PROX of CO. In comparative studies, it has been shown that the support material employed can have a significant effect on the activity of Au/MeO_x catalysts for the selective CO oxidation reaction [7–11]. The activity difference among the various catalysts is ascribed to the difference in the sizes of the gold clusters and the varying ability of the supports to supply oxygen to facilitate the CO oxidation reaction in presence of H₂.

Previous studies have shown that Au/CeLaO_x is very active for the low temperature water-gas shift reaction [12–14] and more recently is active and has good selectivity for selective CO oxidation [15–16]. In this paper, we report on the activity and selectivity of Au/CeLaO_x for the PROX of CO. Specifically, we have investigated the effect of aging (precipitation time) and calcination on the catalyst morphology and the activity and selectivity of the catalysts in the temperature range of 95–150 °C. The results of this work demonstrate that even preparation steps which may appear trivial can have a significant impact catalytic performance.

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2. Experimental

2.1. Catalyst Synthesis

The Au/CeLaO_x catalysts used in this study were prepared by conventional co-precipitation using Na₂CO₃ [17]. A 20 mL solution of 0.01M chloroauric acid (HAuCl₄·4H₂O) and a 40mL solution of the desired amount of ammonium cerium (IV) nitrate (99.99% Sigma-Aldrich) and lanthanum (III) nitrate (99.9% Alfa Aesar) were mixed. The resulting solution was added dropwise to 60 mL amount of 0.1 M sodium carbonate (Na₂CO₃) at room temperature with vigorous stirring. The fine suspension formed was aged for different time periods at room temperature to study the effect of aging time on the catalyst performance. The precipitate was then washed with warm deionized water and filtered. The filtered precipitate was dried overnight at 110 °C, followed by crushing and calcination in air at either 200, 400, or 600 °C (heating rate of 2 °C/min) for 2 h.

2.2. Catalyst Characterization

Specific surface areas of the samples were determined by BET adsorption analysis using a Gemini II 2370 apparatus (Micromeritics). Prior to the analysis, the samples (0.1 g) were degassed at 150 °C for 4 h. X-ray diffraction (XRD) was performed at the University of Kansas Crystallography Laboratory using a Bruker-AXS D8 Advance powder diffractometer with Cu K α radiation. Scans were taken with an increment size of 0.05 ° over a range of 2-theta from 10° to 70°. Inductively coupled plasma (ICP) was performed by Galbraith Laboratories to determine the elemental composition of the catalysts.

Temperature programmed reduction (TPR) of the catalyst was carried out using either 5% hydrogen or 5% CO in Ar at 20 sccm. 50 mg of catalyst was loaded into a quartz tube reactor and heated from room temperature to 800 °C at 8 °C/min. The effluent gases were analyzed using a mass spectrometer. Calibration of the hydrogen consumption was performed using 1 mL injections of an H₂ or CO standard.

2.3. Catalytic Performance

Selective catalytic oxidation of carbon monoxide was carried in a fixed bed quartz tube reactor under atmospheric pressure and at temperatures ranging from 95 to 150 °C. Between 20 and 50 mg of catalyst was used for each experiment. The reactant gas mixture consisted of 1% CO, 1% O₂, 50% H₂, and the balance Ar. The total flow rate through the reactor was 110 mL/min. Exit gases were analyzed using an SRI 8610C gas chromatograph equipped Supelco Carboxen 1010 Plot capillary column (30 m, 0.53 mm ID) and a thermal conductivity detector, methanizer, and a flame ioniza-

tion detector in series. CO, H₂, and O₂ conversions were calculated by comparing the signal of the respective gas during the reaction to calibration injections of the reaction mixture through a bypass line taken before each experiment.

3. Results and Discussion

3.1. Effect of Aging

The amount of time the catalyst precursor is allowed to age in the precipitating solution before washing, drying, and calcination can be an important step in catalyst preparation. Aging can influence the final catalyst properties, such as surface area, porosity, and catalyst composition. Table 1 compares the effect of the aging time (15 min and 3 h) on the surface area and the composition of the AuCeLaO_x catalysts after calcination at 400 °C for 2 h. The BET surface areas of the 15 min aged catalyst (ACL-15m-c) and the 3 h aged (ACL-3h-c) catalyst were similar at 31 and 32 m²/g, respectively. Higher surface areas have been reported in the literature [13–15]; however those catalysts were prepared by urea co-precipitation which has been shown to result in higher surface areas and smaller support crystallite sizes.

The results of the elemental analysis performed by Galbraith Laboratories for the ACL-15m-c and ACL-3h-c catalysts are also shown in Table 1. The data indicates that, under the conditions employed, neither of the aging times resulted in complete precipitation of the Au since the targeted weight percentage of Au was 1.5 wt%. The ACL-3h-c catalyst showed higher loading of Au compared to ACL-15m-c catalyst which suggests that increasing the aging time even further could result in complete precipitation of the Au. Although the amount of Au was almost 50% higher in the catalyst aged for 3 h the Ce/La atomic ratio in both catalysts were similar, at 9.6 and 10.4 for the ACL-3h-c and the ACL-15m-c catalysts, respectively.

It has been suggested that the amount of residual chloride can have a significant negative impact on catalyst performance [18]. In a recent study, Kung and coworkers [18] have shown that Cl[−] can play a dual role in suppressing the selective CO oxidation activity by accelerating the agglomeration of Au particles and by

Table 1
BET surface area and elemental analysis of the AuCeLaO_x catalyst aged for 3 h (ACL-3h-c) and aged for 15 min (ACL-15m-c) after calcination at 400 °C for 2 h

Catalyst	BET surface area (m ² /g)	wt% Au	Ce/La Atomic ratio	Cl [−] content
ACL-3h-c	32	0.94	9.6	29 ppm
ACL-15m-c	31	0.67	10.4	626 ppm

poisoning the active site. Table 1 shows the effect of aging on the residual chloride content after calcination at 400 °C for 2 h. While the catalyst aged for 3 h had low residual chloride content (29 ppm), the chloride content on the catalyst aged for 15 min was greater than 600 ppm. The difference in the amount of chloride remaining after calcination could have a significant impact on the activity of the catalyst for the selective CO oxidation reaction.

Figure 1 shows the XRD spectra for the ACL-3h-c and the ACL-15m-c catalysts after calcination at 400 °C for 2 h. The main peaks for both catalysts are similar and consistent with the cubic CeO₂ structure. A slight shift to smaller 2θ's is observed for the ACL-3h-c catalyst compared to the ACL-15m-c catalyst. It has been suggested [19] that the addition of Au and promoters

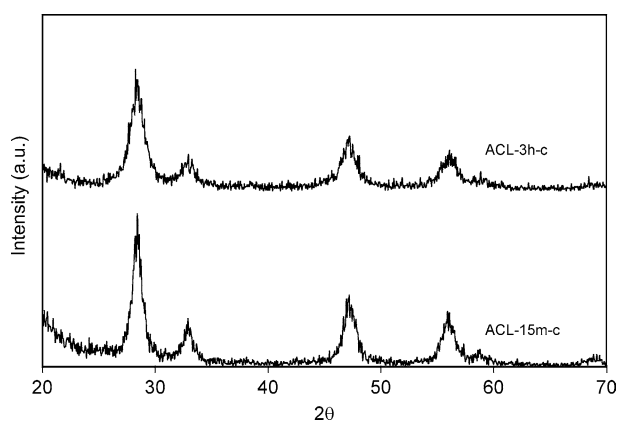


Figure 1. X-ray diffraction pattern for the AuCeLaO_x catalyst aged for 3 h (ACL-3h-c) and aged for 15 min (ACL-15m-c) after calcination at 400 °C for 2 h.

such as La or Zr to CeO₂ can result in an increase in the lattice spacing of the CeO₂ due to the incorporation of the promoter or metal into the CeO₂ lattice. The amount of Au deposited in our cases is very small and we do not anticipate any structural changes in the CeO₂ lattice due to the presence of Au. However, it cannot be ruled out that the increase in the amount of La, indicated by a small decrease in the Ce/La ratio for the catalyst aged for 3 h, results in an increase in the lattice spacing and a resultant shift in the XRD peak to lower 2θ's.

Hydrogen TPR studies were performed on both the catalysts to observe the effect of aging time on the temperature of reduction for the metal and the support. Figure 2 shows that increasing the aging time resulted in a decrease in the temperature required for reduction. The ACL-3h-c catalyst had a reduction peak that started near 100 °C with a maximum near 145 °C, while reduction on the ACL-15m-c catalyst was not observed until 150 °C with a maximum closer to 185 °C. In a study on Au/CeO₂, Andreeva and coworkers [20] reported that the H₂ TPR peak is centered at 135 °C for a 1 wt% Au/CeO₂ and at 110 °C for 5 wt% Au/CeO₂ catalyst. In the previous studies done in our laboratory, we have observed similar shifts to higher temperatures with lower metal content on Pt/Ce_xZr_{1-x}O₂ catalysts. Based on the loading determined by elemental analysis, the ACL-3h-c catalyst has a higher Au content than the ACL-15m-c catalysts and would thus be expected to have a lower reduction temperature. Furthermore, the loading on our catalysts is slightly lower than that reported by Andreeva and coworkers [20] and thus the higher temperature of the TPR peaks in this study is in good agreement with the literature.

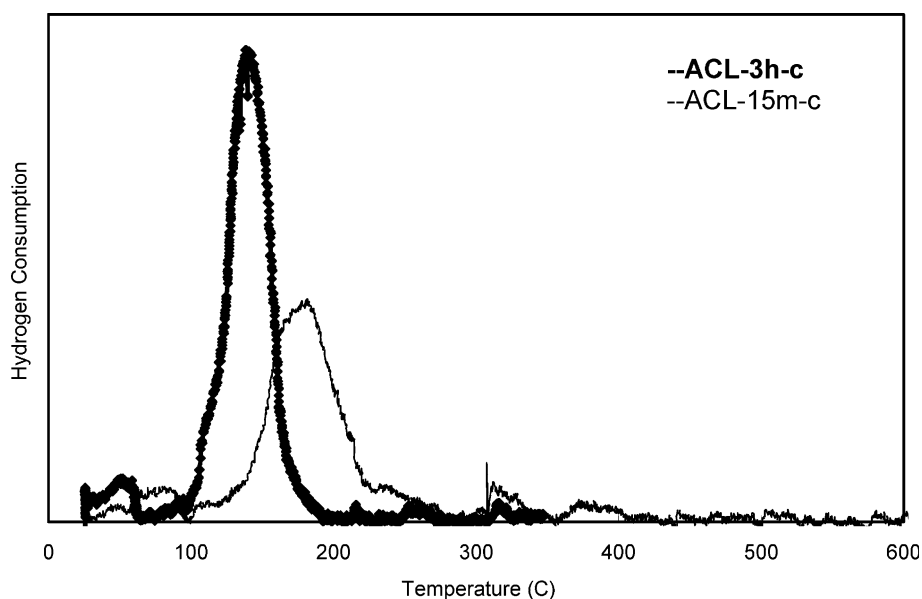


Figure 2. Hydrogen consumption during a temperature programmed reduction for the AuCeLaO_x catalyst aged for 3 h (ACL-3h-c) and aged for 15 min (ACL-15m-c) after calcination at 400 °C for 2 h.

The hydrogen consumption is most likely associated with two processes. The first is the reduction of the oxygen species associated with the gold particles and the second is the reduction of ceria in the CeLaO_x support. Typically, the low temperature part of the peak is connected with oxygen species associated with the gold particles and the high temperature part is due to the reduction of support surface on the border with gold [20]. The higher gold loading would facilitate the reduction of surface oxygen of the support by increasing the metal support interaction. The elemental analysis of the catalyst indicated that the chloride content of the catalyst aged for 15 min was much higher than the chloride content on the catalyst aged for 3 h. The higher chloride content can also affect the ability of the Au to facilitate surface reduction of support by decreasing the degree of metal-support interaction. Thus, it is possible that in addition to the decrease in the gold content, the higher chloride content on the catalysts aged for 15 min is also contributing to the decrease in the surface reduction of the support.

The activity and selectivity of the catalysts were tested at reaction temperatures of 95, 120, and 150 °C. Table 2 shows the comparison of the activity data for 50 mg of the ACL-3h-c and ACL-15m-c catalysts after 12 h. When the reaction was performed at 95 °C, no appreciable activity was observed on the ACL-15m-c catalyst. In contrast, the catalyst aged for 3 hours exhibited 68% CO conversion and a selectivity near 55%. It should be noted that neither of the catalysts were reduced prior to reaction.

As the temperature of reaction was increased from 95 to 120 °C, an increase in the CO conversion on the ACL-3h-c catalyst to 74% was observed with a decrease in the selectivity to 42%. The conversion of O_2 for this experiment was 100%, so the activity observed is not representative of the intrinsic activity of the catalyst because the reaction was limited by the amount of O_2 . Increasing the temperature of reaction to 120 °C did result in an increase in the activity of the ACL-15m-c catalyst, but the CO conversion observed was still low at 26%. The selectivities for the two catalysts were very similar.

Finally, when the reaction temperature was increased to 150 °C for the ACL-15m-c, the CO conversion increased to 66%. The reaction was not performed on the ACL-3h-c catalyst at 150 °C because the increase in

temperature was only expected to lead to a decrease in the selectivity due to the complete depletion of O_2 at 120 °C. The activity observed for the 15 min aged catalyst at 150 °C is still lower than the activity of the catalyst aged for 3 h at 95 °C.

It is interesting to note that the temperature at which the catalysts exhibited significant conversion is slightly lower than the temperature at which they exhibited a maximum in the consumption of H_2 during the H_2 TPR studies. Temperature programmed reduction studies have also been performed using CO, and the results showed that the temperature of reduction decreased by approximately 40 °C compared to the maximum temperature observed for the H_2 TPR. Thus, based on the reduction temperatures observed in figure 2, the high activity at 95 °C for the ACL-3h-c catalyst and the high activity at 150 °C for the ACL-15m-c catalyst are consistent with the temperature at which the catalysts are reduced by CO.

Previous studies have suggested [21] that the particles size of Au must be less than 5 nm in order to obtain an active species. Thus, for the Au based catalysts it is not the average particle size that is important, but the fraction of particles that are less than 5 nm. TEM studies have been performed in order to investigate the particle size of the Au on the various catalysts. Figure 3 shows a particle size distribution for the ACL-3h-c and the ACL-15m-c catalysts. For these studies, more than 100 particles were counted on each sample. The results show that the fraction of particles smaller than 5 nm was higher in the ACL-3h-c catalyst compared to the ACL-15m-c catalyst.

Based on the characterization of the catalysts, the effect of aging time on the catalytic performance can be summarized as follows. Increasing the aging time from 15 min to 3 h was shown to result in (1) an increase in the loading of Au and an increase in the fraction of Au particles smaller than 5 nm, (2) a slight increase in the incorporation of La into the support lattice, and (3) a

Table 2
CO conversion after 12 h of reaction with 1% CO, 1% O_2 , 50% H_2 , and the balance Ar at different temperatures for the AuCeLaO_x catalyst aged for 3 h (ACL-3h-c) and aged for 15 min (ACL-15m-c)

Catalyst	95 °C	120 °C	150 °C
ACL-3h-c	68%	74%	—
ACL-15m-c	Inactive	26%	66%

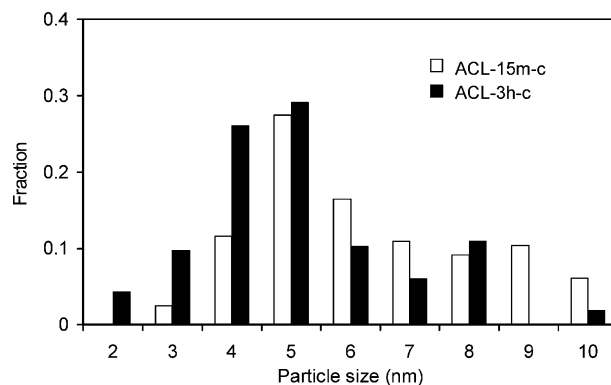


Figure 3. Effect of aging time on the particle size distribution, as determined by transmission electron microscopy, for the AuCeLaO_x catalyst aged for 3 h (ACL-3h-c) and aged for 15 min (ACL-15m-c) after calcination at 400 °C for 2 h.

decrease in the residual chloride content. All of the above effects lead to an increase in the degree of metal-support interaction and a resultant decrease in the temperature at which the metal and the support are reduced by CO. This lowering of the reduction temperature leads to an increase in the low temperature activity of the catalyst for the selective oxidation of CO and allows for the catalyst to be active without pre-treatment. The correlation of the temperatures of reduction and activity supports the theory that a reduced Au species is important for catalytic activity.

3.2. Effect of Calcination

Based on the results presented above, the catalyst aged for 3 h was selected for studying the effect of calcination. Calcination was found to have a significant impact on the surface area. The catalyst calcined at 200 °C had a surface area near 45 m²/g, almost 3 times larger than the uncalcined catalyst (16 m²/g). Increasing the calcination temperature to 400 °C and further to 600 °C resulted in a decrease in the surface area to 32 and 15 m²/g, respectively. Since both the uncalcined and calcined catalysts belong to the same preparation batch, no difference in the gold content or Ce/La atomic ratio was observed. Elemental analysis was also performed to determine the residual chloride content on the catalyst before and after calcination. In contrast to the differences observed with the different aging times, the Cl⁻ content before calcination is only slightly higher than the Cl⁻ content after calcination at 400 °C, at 29 ppm and 49 ppm, respectively. This suggests that it is the time spent in the nitrate solution, not the calcination step, which reduces the chloride content significantly in these AuCeLaO_x catalysts.

XRD studies were performed to determine the effect of calcination on the support structure. Figure 4 compares the XRD pattern for the catalysts aged for 3 h before and after calcination. The uncalcined catalyst showed some minor peaks in the cubic ceria region, but in general demonstrated no significant long range order. These results show that calcination, even at 200 °C, is an important step in obtaining the cubic CeO₂ structure. Increasing the calcination temperature further resulted in an increase in the degree of crystallinity of the support.

To further study the effects of calcination, H₂ TPR studies were performed on the uncalcined catalyst and the catalyst calcined at 400 °C. Figure 5 shows the hydrogen consumption for the two catalysts. The hydrogen consumption for the ACL-3h-c catalyst is the same as shown in figure 2 and discussed above. While the ACL-3h-c catalyst only had one reduction peak at low temperatures, the ACL-3h-uc catalyst showed one intermediate temperature reduction peak and one broad low temperature peak. The peak at 470 °C has been ascribed to the reduction of the support surface oxide

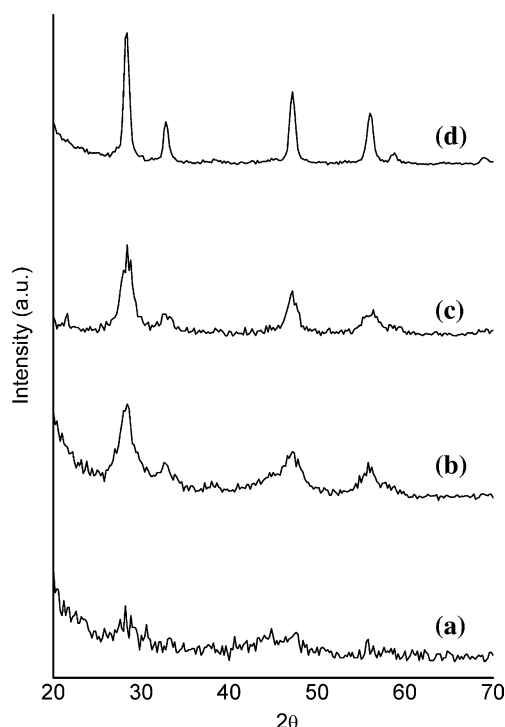


Figure 4. X-ray diffraction pattern for the AuCeLaO_x catalyst aged for 3 h (a) before calcination and after calcination for 2 h at (b) 200 °C, (c) 400 °C, and (d) 600 °C.

species [20] not associated with Au. The low temperature peak observed for the uncalcined catalyst is significantly smaller and very broad compared to the peak observed for the calcined catalyst. The decrease in hydrogen consumption and the increase in the width of the peak suggest that the uncalcined catalyst has decreased Au-support interaction and a decrease in the extent of surface reduction of the support. These results indicate that calcination is a necessary step in developing strong Au-support interaction for the AuCeLaO_x catalyst.

To study the effect of calcination on the particle size of AuCeLaO_x catalyst TEM studies were performed. Figure 6 shows that the particle size distribution for the uncalcined and calcined catalysts. The fraction of Au particles smaller than 5 nm is significantly higher on the calcined catalysts compared to the uncalcined catalysts. Increasing the calcination did result in the appearance of some large particles of Au, but did not significantly impact the total fraction of particles in the region between 3 and 5 nm.

Based on the particle size distributions shown in figure 6, the calcined catalysts having similar particle sizes should show similar activity. However, the rate of CO conversion measured at 95 °C for the calcined catalysts shown in Table 3 clearly shows that the rate increases with increasing calcination temperature. The results of the XRD studies show an increase in the degree of crystallinity of the support as the calcination temperature increased. The increase in the crystallinity

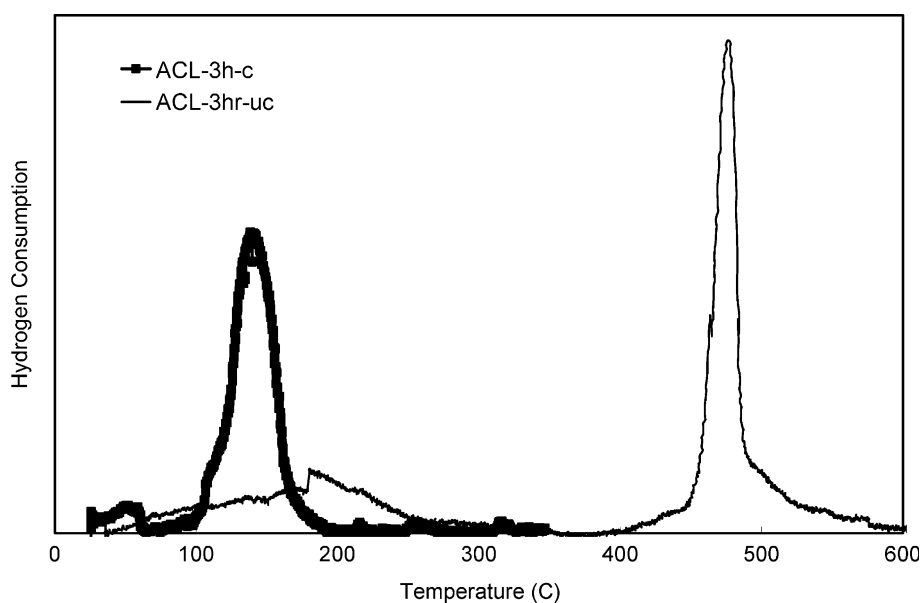


Figure 5. Hydrogen consumption during a temperature programmed reduction for the AuCeLaO_x catalyst aged for 3 h before (ACL-3h-uc) and after calcination (ACL-3h-c) at 400 °C for 2 h.

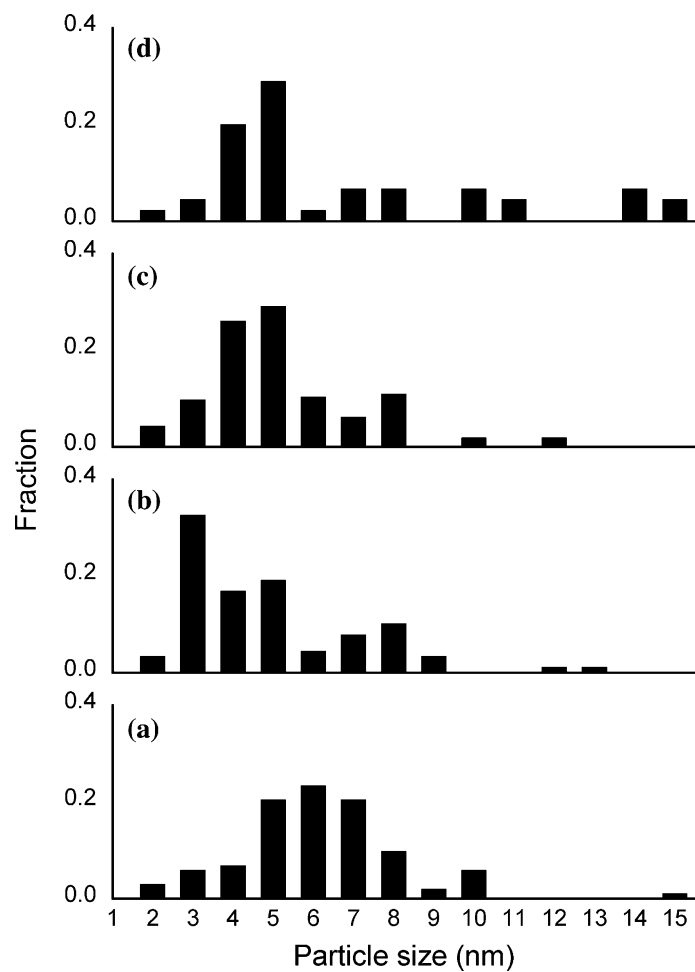


Figure 6. Effect of calcination on the particle size distribution, as determined by transmission electron microscopy, for the AuCeLaO_x catalyst aged for 3 h (a) before calcination and after calcination for 2 h at (b) 200 °C, (c) 400 °C, and (d) 600 °C.

Table 3

Rate of CO conversion ($\text{mol}_{\text{CO}}/\text{g}_{\text{Au}} \cdot \text{s}$) after 12 h of reaction at 95 °C for the AuCeLaO_x catalyst aged for 3 h after different calcination pretreatments. Gas flow 110 cc/min of 1% CO, 1% O_2 , 50% H_2 , and the balance Ar; 20 mg of catalyst

Calcination temperature (°C)	Rate ($\text{mol}_{\text{CO}}/\text{g}_{\text{Au}} \cdot \text{s}$)
Uncalcined	0.9
200 °C	2
400 °C	4
600 °C	13

would result in an increase in the support reduction properties and the degree of metal-support interaction, improving the catalytic activity. This point is further demonstrated by the very low activity observed on the uncalcined catalyst at 95 °C. Although the activity of the uncalcined catalysts was always lower than the calcined catalysts, a significant increase in activity was observed when the uncalcined catalyst was exposed to reaction at 150 °C. This temperature is consistent with the temperature of the broad low temperature reduction peak observed during the TPR studies.

The correlation between the temperature of reduction and the temperature at which activity is observed for both the aging and the calcination studies indicates that the reduction of the metal and the reduction of the support are both important in determining the activity of the catalyst. Similar results have been obtained with a 0.6 wt% AuCeLaO_x catalyst with a lower Ce/La ratio. TPR studies on the catalyst with lower Au loading showed that the temperature of reduction was near 200 °C which can be ascribed to the lower Au loading and the decreased level of dopant. When activity studies were performed on the calcined catalyst, no activity was observed at temperatures between 95 and 150 °C. However, when the catalyst was reduced at 200 °C prior to reaction, the catalyst was active even at 95 °C. While it cannot be ruled out that an ionic Au species is also present, these results suggest that the formation of a reduced Au species is necessary for PROX activity.

4. Conclusions

Increasing the aging time resulted in an increase in the fraction of Au particles less than 5 nm. In addition, increasing the aging time led to a decrease in chloride content and an increase in the Au content. All of these factors lowered the reduction temperature of the AuCeLaO_x catalyst which improved its activity for low temperature selective CO oxidation. Calcination of the AuCeLaO_x catalyst significantly improved the crystallinity of the CeLaO_x support. Furthermore, calcination resulted in smaller Au particle sizes, which significantly lowered the reduction temperature and improved the activity. The catalysts did not require activation in H_2 prior to reaction when the reaction temperature was

near the temperature at which Au reduction was observed. The correlation of the temperature at which the catalysts exhibit significant activity and the temperature of reduction indicates that reduction of the metal and support is important for high activity. Finally, the results of this work have shown that many factors in the preparation process can have a significant impact on performance and even seemingly trivial steps should be reported if accurate comparisons between catalysts are to be made.

Acknowledgements

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