

Selective CO Oxidation over Au Supported On Mixed Oxides: Effect of Preparation on Activity and Selectivity

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Au/CeLaO_x mixed oxide catalysts containing 0.5 to 1.0 wt% Au were prepared via co-precipitation with HAuCl₄, the appropriate nitrate precursors, and either urea or Na₂CO₃ as the precipitant. BET surface area measurements for the Au/CeLaO_x catalysts varied in the range of 16-107 m²/g depending on the precipitant, aging time, and calcination conditions. The catalysts were tested for the selective oxidation of 1% CO in a stream containing 50% H₂, at temperatures between 95°C and 150°C. Although the selectivities of the Au/CeLaO_x catalysts were similar, the activity of the catalyst prepared with Na₂CO₃ was higher than the catalyst prepared with urea at low temperatures. The differences in the activity are ascribed to the differences in the metal loading and the Ce/La ratio in the catalysts, and the resultant effect on the reduction properties of the catalysts. When Na₂CO₃ was used as a precipitant, the catalysts did not require activation in H₂, but did exhibit an induction period during the first 1.5 hours of reaction. Lower activity was observed for both the Na₂CO₃ and urea prepared catalysts without calcination.

Introduction

Considerable progress has been made in the development of proton exchange membrane (PEM) fuel cells, advancing the commercial possibilities for generating clean and efficient power for stationary and mobile source applications [1,2]. The fuel cell promises to deliver electricity with virtually no emission of harmful pollutants and with increased efficiency because it directly converts chemical energy to electricity. The electrochemical system operates at about 70-80⁰ C using H₂ as the anode fuel and O₂ (air) at the cathode.

Hydrogen can be obtained from reforming of hydrocarbon feedstocks such as natural gas, methanol, or gasoline. The main products formed from hydrocarbon reforming are H₂, CO₂, CO, H₂O, and CH₄. Among these gases, CO₂ and CH₄ are inert, i.e. these gases only dilute the hydrogen concentration. In contrast, CO acts as a severe poison by strongly adsorbing on to the Pt anode of the PEM fuel cell, resulting in a significant performance drop in terms of power output and efficiency [3]. 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. 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.

The oxidation of CO to CO₂ is a viable reaction for reduction of CO to acceptable levels. However, many of the catalysts that are capable of performing the CO oxidation reaction are also very good at oxidizing hydrogen. Therefore, having a catalyst with high selectivity and activity for selective oxidation of CO in presence of large amounts of hydrogen is critical.

The catalytic performance of gold has received significant attention since supported Au catalysts were found to exhibit exceptional CO oxidation activity at low temperatures [4-6]. More recently their use as selective materials has been explored for preferential oxidation (PROX) 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, 7-8], 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. [9-12]. The activity difference among the various catalysts is ascribed to the varying ability of the supports to supply oxygen to facilitate the CO oxidation reaction in presence of H₂. Thus, combining supports with high oxygen storage capacities and metals that are selective to CO should result in catalysts with increased activity and selectivity for the CO oxidation reaction.

Previous studies have shown that Au/CeLaO_x is very active for the low temperature water gas shift reaction [13] and more recently is active and has good selectivity for selective CO oxidation [14]. When prepared using urea co-precipitation, the catalyst was found to have very high surface area and a small support crystallite size. The Au loading investigated was near 5 wt%, and it has been found that through leaching that the majority of the Au is not responsible for the activity. Other studies have shown that the type of active precursor, precursor concentrations, pH, and precipitating agent can have a significant impact on the catalyst activity and selectivity. Wang and coworkers [15] reported that the precipitant has a strong influence on the initial activity and stability of Au/ZnO catalysts. Na₂CO₃ was reportedly the best precipitant. In addition, they reported that catalysts containing more Na⁺ ions such as Au/ZnO/Na₂CO₃ and Au/ZnO/NaOH exhibit better stability than Au/ZnO/(NH₄)₂CO₃. The specific surface area of Au/ZnO catalysts was strongly dependent on the type of precipitant, changing in a range of 7-70 m²/g with the catalyst prepared using Na₂CO₃ having the highest surface area.

In this paper, we report on the activity and selectivity of Au supported on La-doped CeO₂ for the low temperature selective CO oxidation reaction. Specifically we have investigated the effect of using different precipitants and pre-treatments on the surface area of the supports and the activity and selectivity in the temperature range of 95°C to 150°C.

Experimental

Catalyst Preparation

The Au/CeLaO_x catalysts used in this study were prepared by urea co-precipitation and co-precipitation using Na₂CO₃. Cerium ammonium nitrate ((NH₃)₂Ce(NO₃)₆ (99.99%)), lanthanum nitrate (La(NO₃)₃·6H₂O (99.9%)), and HAuCl₄·4H₂O were used as precursors for Ce, La, and Au respectively. For the urea co-precipitation, the 0.1M metal salts solutions were mixed with 0.4M urea solution at a 2 to 1 volumetric ratio. The resulting solution was heated to 100°C and continuously stirred using a magnetic stirrer. Upon reaching 100°C the resulting solution was refluxed for 8 hours. The precipitate was then filtered, washed and dried (90-110°C) overnight. The dried samples were crushed and calcined in flowing air at 400°C (heating rate of 2°C/min) for 2 hours.

Co-precipitation with Na_2CO_3 was performed by mixing a 20ml solution of 0.01M chloroauric acid ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) and 40ml of nitrate salt solutions of the required metals. The resulting solution was added dropwise to 60ml of 0.1M sodium carbonate (Na_2CO_3) 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 on the performance of the catalyst. The precipitate was then washed and filtered with warm deionized water. The filtered precipitate was dried overnight at 110 °C, followed by crushing and calcination in air at 400°C (heating rate of 2°C/min) for 2 hours.

Characterization and activity study of catalysts

Specific surface areas of the samples were determined by BET adsorption analysis. Prior to the analysis, the samples were degassed at 150°C for 4 h. The crystal structure of the supports was verified by X-ray diffraction (XRD) on a BrukerAXS X-ray Diffractometer system using Cu K α radiation operated at a power of 40kV \times 30mA and at a scanning rate of 0.2° (2 θ) s⁻¹ in a range of 10-70°. Temperature programmed reduction (TPR) of the catalyst was carried out using either 5% hydrogen or 5% CO in argon. 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.

Selective catalytic oxidation of carbon monoxide was carried in a fixed bed quartz tube (10.5 mm ID) reactor under atmospheric pressure and at temperatures ranging from 95°C to 150°C. 50 mg of catalyst was loaded into the reactor. The reactant gas mixture consisted of 1% CO, 1% O₂, 50% H₂, and the balance Ar. The total flow rate through the reactor was maintained at 100 ml/min. Exit gases were analyzed using an SRI 8610C gas chromatograph equipped with a thermal conductivity detector, methanizer, and a flame ionization detector in series.

Results and discussion

Elemental Analysis, BET, and X-ray diffraction

An elemental analysis of the Au, Ce, and La contained in the urea precipitated catalyst after calcination at 400°C was performed by Galbraith Laboratory. The results of the analysis show that when urea was used as a precipitant and the solution was refluxed at 100°C for 8 hours, complete precipitation of the Au, Ce, and La was not achieved. The weight percent of Au in the final calcined catalyst was 0.55 wt% with a Ce/La atomic ratio of 4.4. The use of La as a structure stabilizer has been previously reported in the literature, and atomic ratios of Ce/La near 10 have been shown to result in increased surface area in the calcined catalyst [13]. Even though the Ce/La ratio was lower in our catalysts than those reported in the literature, the BET surface area of the catalyst calcined at 400°C for 2 hours was still high at 107 m²/g. X-ray diffraction studies performed on a CeLaO_x support prepared using urea as a precipitant show peaks at 2 θ 's of 28.5, 33.0, 47.4, and 56.2. The position of the peaks is consistent with the cubic CeO₂ structure. When Au was co-precipitated with the support, no significant change in position of the peaks in the XRD pattern was observed. Due to the low loading of Au on this catalyst, it is unlikely that any shifts in the lattice parameters would be detected even if the Au were incorporated into the lattice.

In contrast to the high surface area of the catalyst prepared by urea, the catalyst prepared using Na_2CO_3 as a precipitant and 3 hours of aging had a surface area after calcination of only $32 \text{ m}^2/\text{g}$. The elemental analysis for this material showed that, in spite of the lower surface area, more Au and La was incorporated into the material with the final wt% of Au being 0.94 and the Ce/La ratio close to 9.5. The XRD pattern for the Au/CeLaO_x catalyst prepared with Na_2CO_3 again matched that of the cubic structure of CeO_2 . However, the peaks were narrower than those observed for the catalyst prepared with urea. The narrowing of the diffraction peaks can be due to an increase in the crystallite size of the material which would be consistent with the results of the BET surface area measurements for the two catalysts.

The effect of aging in the Na_2CO_3 solution was investigated by changing the aging time at room temperature from 3 hours to 15 minutes. The remaining drying and calcination steps of the preparation procedure were the same as described above. BET surface area analysis showed that the aging time had no effect on the surface area of the catalysts. The surface areas for the calcined catalysts after 3 hours and 15 minutes of aging were $32 \text{ m}^2/\text{g}$ and $31 \text{ m}^2/\text{g}$, respectively. These results are consistent with the XRD patterns obtained for the two samples which show no changes in the peak positions, intensity, or peak width with aging time. The surface area of the uncalcined Au/CeLaO_x catalyst prepared using Na_2CO_3 was the lowest of all of the catalysts studied at $16 \text{ m}^2/\text{g}$.

Temperature Programmed Reduction Studies

Figure 1 compares the temperature programmed reduction profiles for the Na_2CO_3 precipitated Au/CeLaO_x catalysts aged for 3 hours and 15 minutes. Both of the catalysts were calcined for 2 hours at 400°C prior to the TPR. On the sample aged for 3 hours the main H_2 consumption is centered at approximately 140°C compared to the 183°C on the sample aged for 15 minutes. Andreeva and co-workers [16] observed that an H_2 TPR peak, ascribed to the reduction of Au oxide, is centered at 135°C for a 1 wt% Au/ CeO_2 sample and at 110°C for a 5 wt% Au/ CeO_2 catalyst. We have observed similar shifts

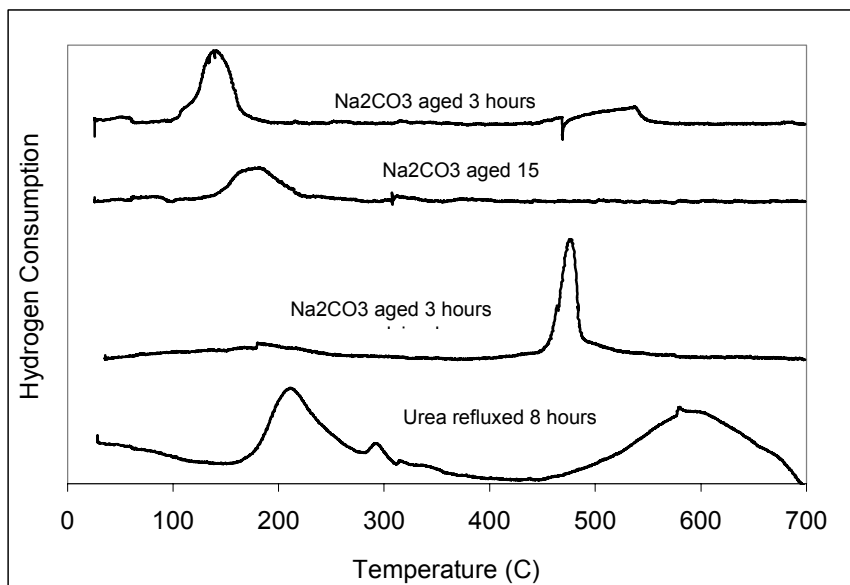


Figure 1 - Effect of aging time, calcination, and precipitant on the TPR profile of Au/CeLaO_x

to higher temperatures with lower metal content on Pt/Ce_xZr_{1-x}O₂ catalysts. Based on the Au loading determined by elemental analysis for the calcined catalyst aged for 3 hours (0.94 wt % Au), the 140°C H_2 TPR peak observed is in good agreement with the studies reported in the literature.

In addition to a 40°C increase in the reduction temperature, the catalyst aged for 15 minutes also exhibits a significant decrease in the amount of hydrogen consumed. The increase in the reduction temperature and the decrease in the hydrogen consumption are most likely due to a decrease in the Au content in the catalyst due to the short aging time. It has been suggested [16] that although Au has no effect on the bulk reduction of CeO₂, surface reduction of CeO₂ occurs near the same temperature as the reduction of the Au oxide and is enhanced by the presence of Au. Therefore, it can not be ruled out that part of the reduction in the hydrogen consumption is also due to a decrease in the surface reduction of the support.

Figure 1 also shows the TPR profile for the Au/CeLaO_x catalyst aged for 3 hours, prior to calcination at 400°C. In addition to a small broad peak centered near 200°C, a large peak appears centered at 475°C. The large reduction peak is most likely due to the presence of the preparation precursors which are removed during the calcination at 400°C. The presence of Cl⁻ has been shown to have a significant negative effect on the activity of an Au/Al₂O₃ catalyst for the selective CO oxidation reaction [17]. Residual chloride can lead to Au agglomeration and poisoning of the active site, even in low concentrations. Thus, it is expected that the uncalcined catalyst would exhibit lower activity than the calcined catalyst.

The last profile shown in Figure 1 is for the Au/CeLaO_x catalyst prepared with urea. For this catalyst, the low temperature reduction peak is shifted to higher temperatures with the peak maximum appearing near 210°C. As discussed previously, a decrease in the loading of Au results in an increase in the TPR peaks. Based on the elemental analysis results, the temperature of the reduction is consistent with the 0.55 wt% loading of Au on the urea precipitated catalyst.

Selective CO Oxidation Activity

Figure 2 compares the CO conversion after 14 hours of reaction at 95°C, 120°C, and 150°C (100 cc/min of 1% CO, 1% O₂, 50% H₂ and balance Ar) for the Au/CeLaO_x catalysts prepared using Na₂CO₃ (3 hours) and urea as the precipitant. Both catalysts had been calcined at 400°C for 2 hours prior to reaction. The most interesting comparison between the two catalysts is that the catalyst prepared using Na₂CO₃ was not reduced prior to reaction. In contrast, significant CO conversion was only observed on the urea co-precipitated catalyst when the catalyst was exposed to a reduction pretreatment prior to reaction. The data shown in Figure 2 corresponds to a reduction of

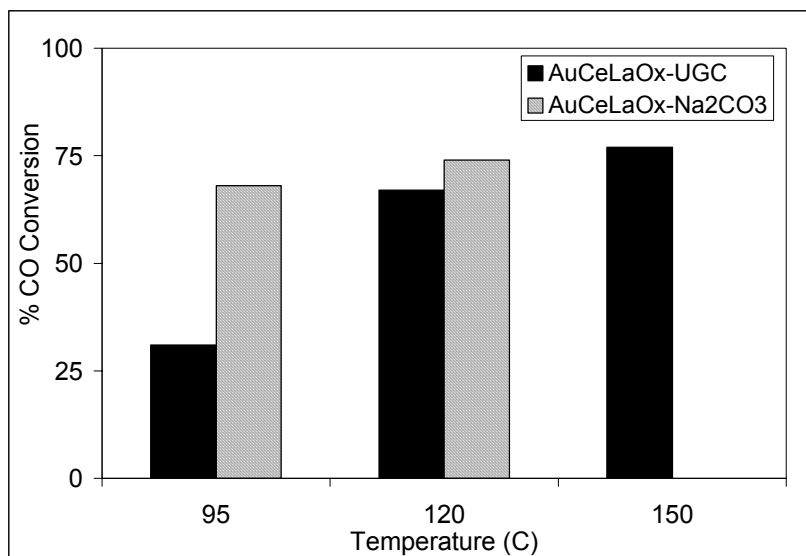


Figure 2 - Comparison of % CO conversion for the Au/CeLaO_x catalysts prepared using urea and Na₂CO₃ during reaction with 1% CO, 1% O₂, 50% H₂, and the balance Ar.

210°C. If the conversion of the catalysts are compared on a per metal loading basis, the differences in the activity at 120°C is very small compared to the 1.7 times greater loading of Au on the Na₂CO₃ prepared catalyst. However, at 95°C the difference in activity is much more pronounced, and the Na₂CO₃ prepared catalyst exhibits higher activity, even when the higher Au loading is accounted for.

A debate in the literature still exists over the active Au species for the PROX reaction. One belief is that the metallic gold is not necessary for the CO oxidation reaction and that the active site is ionic gold highly dispersed on the catalyst [14]. Others believe that the active site involves an ensemble of Au⁺-OH sites surrounded by Au atoms [17]. This work shows that catalysts which exhibit low temperature reduction also exhibit low temperature activity. Catalysts which exhibit higher temperature reduction profiles need to be pretreated first in order to be active. Since reduction of the Au and the support can occur at the reaction temperature, it is unlikely that Au is an oxide form. Because of the correlation with reduction temperature, we believe that the active species involves Au atoms and partially reduced Au species as well as the hydroxyls formed during the reduction step.

The effect of the aging time for the Na₂CO₃ precipitated catalyst was also studied. Figure 3 compares the CO conversion during reaction at 120°C (100 cc/min of 1% CO, 1% O₂, 50% H₂ and balance Ar) for the Au/CeLaO_x catalysts aged for 3 hours and 15 minutes. Again, the catalysts were not reduced prior to reaction, only heated to the reaction temperature in Ar. The activity of the sample aged for 15 minutes was very low with an initial CO conversion of only 34%. Complete conversion of O₂ was not achieved at 120°C. Furthermore, the deactivation observed on the catalyst with the shorter aging time is greater, with a CO conversion after 12.5 hours of 26%. Increasing the reaction temperature to 150°C resulted in an increase in the CO conversion to 72% but did not change the deactivation profile. Minimal activity was observed on the catalyst aged for 15 minutes at 95°C.

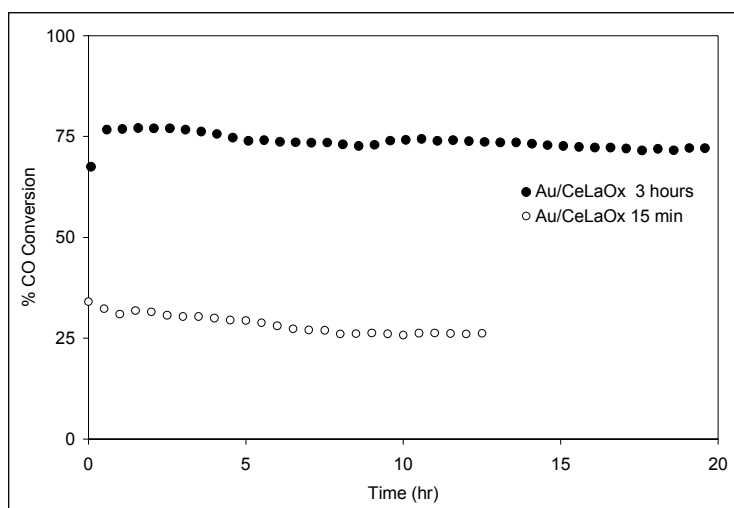


Figure 3 – Effect of aging time on CO conversion during reaction at 120°C.

In contrast to the catalyst aged for 15 minutes, aging for 3 hours resulted in complete O₂ conversion at 120°C. The CO conversion for the catalyst aged for 3 hours begins near 67% and exhibits an initial increase in activity for the first 30 minutes of reaction. After reaching a maximum conversion of 76%, slight deactivation is observed during the 20 hour reaction with a final conversion near 72%. When the reaction was performed at 95°C, the initial increase in activity was more pronounced with the conversion beginning near 30% and reaching 67% after 1 hour.

We believe that the increase in activity and stability with increased aging time can be explained by differences in Au and chloride content on the catalysts. The TPR studies indicate that the Au species and the surface of the support are more easily reduced when the aging time is increased. As previously discussed, the ability to increase the reduction capability of the oxides support at lower temperatures has been shown to correlate with increased selective CO oxidation activity at lower temperatures. We postulate that the deactivation of the catalyst is due to more chloride species being present after calcination on the catalyst that is aged for 15 minutes compared to the catalyst aged for 3 hours. It has been reported that the ease of hydrolysis of HAuCl_4 can determine the amount of Cl^- ligands present in the precursors remaining after preparation [18]. It is possible that the 15 minute aging time at room temperature is not sufficient, and ligands with high Cl^- content remain on the surface after the preparation and calcination. The migration of the chloride species under reaction conditions could lead to a gradual poisoning of the active site. It is interesting to note that the selectivity was not significantly affected by the aging time or the reaction temperature, remaining between 45-50% in all cases.

The increase in the initial activity observed on the catalyst prepared with Na_2CO_3 and aged for 3 hours, has been previously observed in $\text{Au}/\text{Al}_2\text{O}_3$ catalysts and have been ascribed to the redistribution of residual chloride anions from Au to the support under reaction conditions [17]. These studies showed that catalysts with lower chloride content reached steady state more rapidly and the steady state conversion was much higher than the conversion observed on the high chloride content samples.

To study if the initial increase in activity observed on the Au/CeLaO_x catalyst precipitated with Na_2CO_3 was due to the presence of precursors left from the pretreatment, an experiment was performed on the catalyst aged for 3 hours without any calcination. In the absence of calcination, it is expected that the chloride content of the sample would be much higher and result in an increase in the induction observed. The uncalcined catalyst was exposed to reaction at 100°C for 2 hours, followed by reaction at 120°C for 2.5 hours and finally reaction at 150°C . The initial conversion at 100°C was only near 7%, and the maximum conversion at 150°C (31%) was much lower than the conversion achieved at 120°C for the calcined catalyst. Furthermore, the maximum activity on the uncalcined catalyst was achieved after 7 hours of reaction at 150°C compared to 30 minutes for the calcined sample. Thus, the increase in the initial activity during reaction does appear to be consistent with the level of chloride species on the catalyst. The fact that the calcined sample reached steady state within 30 minutes indicates that the residual chloride content is probably small. The lower steady state conversion on the uncalcined catalyst could be due to either Au agglomeration [19] or chloride poisoning of the active species during the low temperature reactions [17].

Conclusions

The results of this work show that Au/CeLaO_x catalysts can be prepared with low Au loadings and show high activity and good selectivity for the selective CO oxidation reaction between 95°C and 150°C . The precipitant and the preparation time can have a significant effect on the loading of Au and the Ce/La ratio in the final catalyst. Catalyst prepared using Na_2CO_3 exhibited higher activity at low temperatures and did not require pretreatment before reaction. In contrast, co-precipitation with urea resulted in a material which exhibited significant activity above 120°C but required activation in H_2 at 210°C prior to reaction. An induction period,

ascribed to redistribution of residual chloride species, was observed on the Au/CeLaO_x catalyst prepared with Na₂CO₃. The induction period was much more pronounced and the final CO conversion achieved was much lower when the catalysts were not calcined prior to reaction. These changes are ascribed to a higher chloride content due to precursors remaining on the surface after precipitation.

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