SELECTIVE CATALYTIC OXIDATION OF CO IN H_2 OVER Au/γ-Al_2O_3

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Introduction

Gold has historically been considered one of the most inert elements, and, consequently, its potential catalytic properties have long been ignored. However, since Haruta's report[1] of the exceptionally high catalytic activity of supported gold for low temperature CO oxidation, these catalysts have been subject to intense investigation.

Supported gold catalysts have great potential for use in fuel cell applications. The H_2 feed to a proton exchange membrane fuel cell contains approximately 1–2% CO, which poisons the Pt anode, severely decreasing the fuel cell power output. For practical applications, the CO concentration must be reduced to less than 10 ppm[2]. One method to achieve this low CO concentration is to selectively oxidize the CO in the H_2 stream, and it is desirable to carry out this reaction at the fuel cell operating temperature (80-100°C) or at the methanol reformer unit temperature (250-300°C). The catalysts currently used include Pt, Ru, and Rh, which need temperatures of at least 150-200°C to operate efficiently, but experience a significant loss of selectivity at higher temperatures[3]. Supported gold catalysts can selectively oxidize CO at the fuel cell operating temperature, making them an attractive candidate for this application.

Despite the increasing number of published work on supported gold catalysts, the origin of their remarkable catalytic activity remains unknown. It is generally agreed that the activity is highly dependent upon the preparation procedure. These catalysts are typically prepared from chloride-containing precursors, and any residual chloride severely decreases catalyst activity. Highly active catalysts typically contain small (3-5 nm) Au particles, and it is well known that the presence of chloride facilitates Au particle agglomeration. However, chloride may also act to poison the catalytic active sites, which have been proposed to consist of an ensemble of Au^+–OH^- and metallic Au^0 atoms[4,5].

Supported gold catalysts may be affected by the addition of other ions, such as phosphate or cesium. The addition of phosphate anions to the catalysts significantly inhibits the activity for CO oxidation, while the addition of Cs has been observed to suppress H_2 oxidation[6]. This report examines the effects of chloride, phosphate, and cesium ions on Au/γ-Al_2O_3 for selective CO oxidation in H_2 (SCO) and discusses the results of further investigation into the nature of the active sites for this reaction.

Experimental

Catalyst Preparation. The γ-Al_2O_3 used as the support material was prepared by hydrolysis of aluminum isopropoxide in the presence of 2-methyl-2,4-pentanediol[7]. Three different procedures were used to prepare the catalysts described in this study. A preparation at low pH and low temperature was used to examine the effects of residual chloride on the catalysts. 50 ml of an 8.4 mM solution of $HAuCl_4$ (Aldrich 99.999%) was added to 2.5 g of Al_2O_3 suspended in 50 ml of de-ionized H_2O at 0°C. After 1 hr, the sample was suction filtered, re-suspended in 50 ml room temperature de-ionized water and then suction filtered again. This procedure was repeated with room temperature water, followed by 50°C water. The catalyst was dried at room temperature overnight and calcined at 350°C for 4 hr in air. A fraction of this catalyst was treated with magnesium citrate to remove chloride either before or after calcination. The dried or calcined catalyst was re-suspended in a Mg-citrate solution (Mg-citrate/Au=1.6), stirred for 1 hr, then suction filtered. It was washed twice with doubly distilled water, dried, and calcined at 350°C for 4 hr. Catalysts were prepared with Au acetate precursor to examine the effects of adding chloride to the catalysts. An aqueous solution of Au acetate containing the appropriate weight of Au was introduced to the Al_2O_3 support by incipient wetness. The catalysts used in the remainder of the studies were prepared from a $HAuCl_4$ precursor using a method similar to that described above, but the preparation was carried out at 70°C, and the pH of the $HAuCl_4$ solution was adjusted to 7 with NaOH.

Catalyst Characterization. The amount of Au in the catalysts was determined by ICP, and the particle size was found by averaging the diameters of over 200 particles using TEM. Analysis of the residual chloride in the catalysts was done using H_2 TPR coupled with FTIR spectroscopy.

Reaction Conditions. In the chloride experiments, 20-80 mg of catalyst was mixed with 0.5 g SiC and placed in a quartz microreactor. The feed was 1% CO, 0.5% O_2, 48% H_2, and balance He. The reactions were carried out at 100°C with a flow rate of 90 ml/min, and the reaction products were analyzed by gas chromatography using two columns: a molecular sieve 13X column for H_2, CO, and O_2 and a Hayesep Q column for H_2O and CO_2. The remainder of the SCO reactions were carried out at room temperature using 40 mg of catalyst with no diluent. The feed was 1% CO, 0.5% O_2, 40.55% H_2, and balance He at a flow rate of 200 ml/min. The products were analyzed with GC using the two columns described above and by FTIR for CO and CO_2 using a 75 ml gas phase cell.

Results and Discussion.

Effect of Chloride on Particle Size. When no attempt was made to remove residual Cl^- from the catalyst after the preparation with no pH adjustment (pH ~ 4), the catalyst had an average Au particle diameter of 44.6 nm and contained 0.37 wt% Cl^- after calcination. It had a SCO activity of 0.05±0.03 mol CO mol Au^{-1} min^{-1}. If Mg-citrate was added to this catalyst prior to calcination, the particle size was much smaller, 16.7 nm, with only 0.01 wt% Cl^- remaining after calcination, resulting in a catalyst with a much higher SCO activity of 1.2±0.1 mol CO mol Au^{-1} min^{-1}. If Mg-citrate was added to the catalyst after calcination, the amount of Cl^- in the catalyst was less than 0.01 wt%, but the average particle size was 49.6 nm. This catalyst had a SCO activity of 0.96±0.1 mol CO mol Au^{-1} min^{-1} despite its large particle size.

These data confirm that the presence of Cl^- causes Au particle agglomeration. The catalysts not treated with Mg-citrate prior to calcination, which had high residual amounts of Cl^-, had much larger Au particles than the catalyst calcined in the absence of Cl^-. The high activity of the catalyst treated with Mg-citrate after calcination is surprising, as the majority of published works suggest that very small Au particles are needed to affect CO oxidation. The difference in activity between this catalyst and the catalyst not treated with Mg-citrate suggests that small Au particle size cannot be the necessary requirement for high activity and that Cl^- has a direct inhibitive effect

on the catalyst. It is possible that Cl^- replaces the hydroxyl group in the active site to form $Au^+–Cl^-$, poisoning the sites active for CO oxidation.

Chloride Addition to Calcined Catalysts without Cl^-. In order to further examine the potential of Cl^- as a poison for the catalytic active site, Cl^- was added to a catalyst prepared with an Au acetate precursor. The catalyst was first impregnated with phosphate anions to a phosphate/Au ratio of approximately 4. The phosphate anions suppress uptake of Cl^- by the Al_2O_3 surface, so that the Cl^- can be added directly to the Au. The addition of phosphate decreased the catalyst activity for SCO by one-third, indicating that some phosphate is associated with the gold particles.

Cl^- was added to this catalyst with a Cl^-/Au ratio of 0.01. This suppressed the initial activity of the catalyst almost completely, though the activity did increase with time on stream before reaching a steady state (Figure 2). In fact, the activity could be suppressed at a Cl^-/Au ratio as low as 0.0006, indicating that only a small fraction of Au is associated with the active sites.

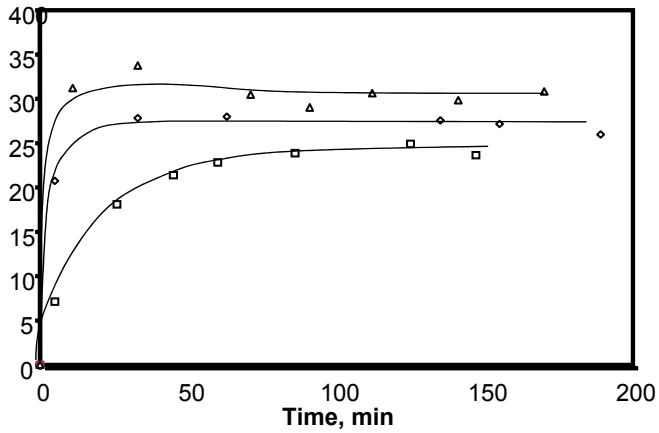

Figure 2. CO conversion (%) over 1.1 wt% Au/γ-Al_2O_3 during SCO at 100°C with 90 ml/min of 1% CO, 0.5% O_2, 48% H_2, and balance He. Δ: Cl^-/Au = 0, ◊: Cl^-/Au = 0.0006, : Cl^-/Au = 0.01.

The transient behavior of the catalysts to which Cl^- was added support the proposal that Cl^- acts to poison the active site by replacing the $Au^+–OH^-$ with $Au^+–Cl^-$. Initially, most of the active sites are poisoned, so the initial activity is very low. During the SCO reaction, the H_2O produced by H_2 oxidation hydrolyses the $Au^+–Cl^-$ and restores the $Au^+–OH^-$, gradually increasing the catalytic activity.

Effect of Phosphate Addition. Phosphate anions were added to the catalysts prepared at pH 7 to a phosphate/Au ratio of approximately 4 by impregnation followed by drying at room temperature. Prior to phosphate addition, the activity for SCO at room temperature was $4.12±0.26*10^{-4}$ mol CO g-cat^{-1} min^{-1}. After phosphate addition, this catalyst had no activity at room temperature. When the catalyst was heated to 100°C in the SCO feed, the activity increased to reach a steady state value of $5.06±0.44*10^{-4}$ mol CO g-cat^{-1} min^{-1}. Upon cooling back to room temperature, the activity dropped to the steady state value of $1.8±0.62*10^{-4}$ mol CO g-cat^{-1} min^{-1}. This behavior suggests that the phosphate anions initially block the active sites for CO oxidation, preventing the reaction from occurring, since it is unlikely that the Au particles would sinter at room temperature as a result of the presence of the phosphate anions. H_2O generated during the SCO reaction at 100°C can displace part of the phosphate from the gold, restoring some of the original activity. This behavior is similar to that of chloride poisoning.

Effect of Cesium Addition. Cesium was added to the catalysts prepared at pH 7 by impregnation with $CsNO_3$ followed by drying at 100°C. Preliminary results suggest that the addition of Cs does suppress H_2 oxidation, thereby increasing CO conversion in an O_2-limiting reaction (Figure 3). This implies that H_2 oxidation and CO oxidation occur at different active sites on the Au/γ-Al_2O_3 catalyst. The active sites for H_2 oxidation are blocked by the Cs ions, but those for CO oxidation are seemingly unaffected.

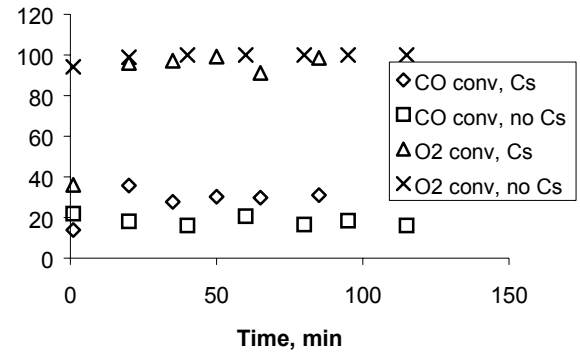

Figure 3. Effect of Cs addition on 1 wt% Au/γ-Al_2O_3 activity in SCO at room temperature, 200 ml/min of 1% CO, 0.5% O_2, 40.55% H_2, balance He.

Isotope Effects in SCO. A deuterium kinetic isotope effect (r_H/r_D) of 1.4±0.2 was observed when H_2 was replaced with D_2 in the SCO feed. The CO conversion during the reaction is 30% less in the presence of D_2, and the selectivity toward CO_2 formation relative to H_2O (D_2O) formation increased from 77% with H_2 to 87% with D_2 present in the feed.

Conclusions

The effect of Cl^- on Au/γ-Al_2O_3 catalysts is two-fold. Cl^- acts both to agglomerate Au particles and to poison the active sites by replacing the $Au^+–OH^-$ with $Au^+–Cl^-$. Phosphate anions also act to block the active sites for CO oxidation, while Cs ions appear to adversely affect H_2 oxidation. The suppression of activity by the addition of chloride, phosphate, and cesium ions and the suppression of activity that occurs in the presence of D_2 are phenomena that can be used to generate a better understanding of the active sites and mechanisms involved in selective CO oxidation.

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