Understanding the Preparation Variables of the Synthesis of Au/Al$_2$O$_3$ Oxidation Catalysts [*]

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Introduction

Recent research has shown that Au particles of less than about 30 Å and supported on high surface area oxides have unusual catalytic properties. Some of the reactions catalyzed by supported Au particles include low temperature CO oxidation [1] and propylene epoxidation [2]. For CO oxidation, the nature of the Au active site has not been resolved, but researchers generally agree that there appears to be a correlation between metal particle size and activity [3]. However, it has also been shown that the catalytic activity of Au catalysts is very sensitive to the preparation method [4-6]. Among the different supported Au catalysts, Au/Al$_2$O$_3$ shows one of the largest variations in activity, [5,7]. Most studies have not characterized the state of Au during the various stages of preparation, thus the reasons for the large difference in performance for catalysts of nominally identical composition is unknown. We wished to follow the evolution of the Au species throughout preparation in order to better understand the parameters critical to development of catalystic activity.

Methods and Materials

Catalyst testing

The catalysts were tested in a microreactor using 40 mg of catalyst and 200 mL/min flow of a feed containing 1% CO, 2.5% O$_2$, balance He. The testing was conducted either under dry conditions where the reacting gases were purified by passing through a silica gel trap at dry ice-acetone temperature, or under wet conditions (1.5% water) where the reacting gases passed through a water saturator at room temperature.

EXAFS and XANES data collection and analysis

Transmission X-ray absorption spectrosocpy measurements were made on the insertion-device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. EXAFS and XANES spectra of the calcined catalysts were obtained at room temperature in air. Reduced catalysts were pretreated in a continuous-flow EXAFS reactor cell. The catalysts were heated to 250°C for 1 hour in 4% H$_2$/He and cooled to room temperature. The reduced catalysts were oxidized by treatment in flowing air at room temperature or at 175°C. Phase shifts, backscattering amplitudes and XANES references were obtained from reference compounds: HAuCl$_4$ for Au^{+3}-Cl, Au$_2$O$_3$ for Au^{+3}-O, and Au foil for Au^0 and Au-Au.

Results

Au speciation in aqueous solution and adsorbed on Al$_2$O$_3$

Figure 1a shows that the Au^{3+} ions contained 4 Au-Cl bonds in a solution at pH's less than about 4. As the pH increased, the number of Au-Cl bonds decreased approximately linearly. At a pH of 7, (solid square and solid circle) Au exists as Au(OH)$_4^-$. At all pH's, the Au species adsorbed on alumina (solid triangle) had fewer Au-Cl bonds than in solution at the same pH.

Modeling of the pH at alumina surface indicates that the adsorption plane of the double layer was more basic than the bulk solution [8] leading to more extensively hydrolyzed Au species with more Au-O bonds (open triangle). At pH's above about 6, there were few Au-Cl bonds in the adsorbed Au^{3+}.

Figure 1. Au-Cl coordination of Au species in solution and adsorbed on Al$_2$O$_3$ as a function of pH. HAuCl$_4$ concentration: ■ 200 ppm, ● 500ppm, ▲ adsorbed Au at bulk pH and △ adsorbed Au at surface pH (calculation).

Au/Alumina (Cl)

Adsorption of HAuCl$_4$ at pH 4 yielded a Au catalyst with significant residual Cl, ca. 0.9 wt.%. Table 1 shows the fits of the XANES, EXAFS and catalytic data of this catalyst after various treatments. After drying at 100°C, the XANES spectrum showed that Au existed as Au^{3+} with 20 % of the ligands being chloride and the remainder oxygen. EXAFS analysis showed that the bond lengths were similar to those for the respective Au reference compounds. Calcination in air at 350 °C, resulted in a reduction of 50% of Au to metal, but Au-Cl bonds still accounted for ~25% of the total bonding of cationic Au. Using the fraction of metallic Au from the XANES, the Au-Au coordination number of the metallic fraction can be estimated. For calcined Au/Al$_2$O$_3$, the Au-Au coordination was 11.4 (=5.7/0.5) implying large metallic particles. The calcined catalyst was inactive for CO oxidation.

Hydrogen reduction at 250°C gave smaller Au particles. Based on a correlation between the Pt-Pt CN and hydrogen chemisorption for metallic platinum, the reduced particles are estimated to be less than 20 Å. Exposure of this catalyst to air at room temperature or 175 °C did not result in detectable reoxidation of the metallic Au, although there was a small increase in the Au-Au co-ordination number. Despite the small metal particle size, the reduced catalyst had very low CO oxidation activity.

Table 2. XANES, EXAFS fits and catalytic activity for Au/Al$_2$O$_3$.

Treatment	Fraction Au^{+3}-O	Fraction Au^{+3}-Cl	Fraction Au^0	Scatterer	CN	R, Å	Act[1]
Air (100°C)	0.80	0.20	0	Au-O	3.0	2.04	-
				Au-Cl	1.0	2.28	
Air (350°C)	0.5	0	0.5	Au-O	2.0	2.03	0
				Au-Cl	0.6	2.28	-
				Au-Au	5.7	2.88	-
H$_2$ (250°C)	0	0	1.0	Au-Au	7.1	2.84	-
H$_2$ (250°C), air (175°C)	0	0	1.0	Au-Au	8.0	2.86	0
				Au-Au	3.9	2.72	(1.2[2])

[1] mol CO(mol Au.s)$^{-1}$ *100; feed of 1% CO, 2.5% O$_2$ at RT.
[2] With 1.5% H$_2$O.

Au/Alumina (no Cl)

The residual Cl was removed in Au/Al$_2$O$_3$ (Cl) by washing with NaOH. Elemental analysis showed that a portion of the Au was also reduced (1.02%). After reduction of the Cl the Au particles are significantly smaller. For example, after calcination at 350°C, the Au particle size was less than about 2 nm as suggested by Au-Au CN of 6.9 (adjusted for unreduced Au). Hydrogen reduction at 250°C produced even smaller gold particles of less than 1 nm as suggested by CN of 5. The Au-Au distance of these small particles was noticeably shorter (2.71 Å) than the calcined catalyst (2.85 Å). When the reduced Au/Al$_2$O$_3$ (no Cl) was exposed to air, 10% and 15% of the Au was re-oxidized to Au^{+3} at RT and 175°C, respectively.

The activities of the reduced and calcined catalysts were low and very similar. The activity of the oxidized catalyst was also low, however, when the tested for CO oxidation with water vapor in the reactant stream, there was a large increase in activity. This conversion would be considered high activity for Au supported on alumina.

Table 2. XANES, EXAFS fits and catalytic activity for Au/Al$_2$O$_3$ (no Cl).

Treatment	Fraction Au^{+3}-O	Fraction Au^{+3}-Cl	Fraction Au^0	Scatterer	CN	R, Å	Act[1]
Air (25°C)	1.0	0	0	Au-O	4.0	2.03	-
Air (350°C)	0.40	0	0.60	Au-O	2.0	2.04	2
				Au-Au	4.1	2.85	-
Air (400°C)	0.20	0	0.80	Au-O	0.7	2.05	-
				Au-Au	7.0	2.85	
H$_2$ (250°C)	0	0	1.0	Au-Au	5.0	2.71	2
H$_2$ (250°C), air (175°C)	0.15	0	0.85	Au-O	0.6	2.04	0.4
				Au-Au	3.9	2.72	(39[2])

[1] mol CO(mol Au.s)$^{-1}$ *100; feed of 1% CO, 2.5% O$_2$ at RT.
[2] With 1.5% H$_2$O.

Discussion

Increasing the pH during or after adsorption of HAuCl$_4$ can effectively remove chloride ions from the catalyst. Residual chloride on Au catalyst affects the reducibility of Au^{+3} cation, the particle size, and the catalytic activity. All catalysts are partially oxidized after calcination at 350°C. The XANES fits are consistent with the presence of a mixture of Au^{3+} and Au^0. The Au-O CN (or Au-Cl) from the EXAFS data is near 4 in all cases, suggesting that the oxidized species are Au^{3+} instead of Au^{1+}, which has coordination number of 2.

Reduction in H$_2$ at 250°C can minimize this agglomeration and also results in complete reduction. Although the particle size of the H$_2$ reduced Au/Al$_2$O$_3$ (Cl) is less than 2 nm, the catalyst is inactive. Even upon addition of 1.5% water to the

reaction feed, the activity is very low. Thus, chloride is a very potent inhibitor of the CO oxidation activity.

A possible explanation for this poisoning effect may be deduced from the EXAFS of the oxidized, pre-reduced catalyst. Air oxidation at RT results in small changes in the spectra, which overlap with the much larger Au-Au peaks in the Fourier transform. While direct fitting of the spectra did not give reliable results, these small features could be resolved by analysis of the difference spectrum, i.e., subtraction of the oxidized spectrum from the reduced spectrum. In the difference file, Au species that are unchanged are subtracted and are not present in the difference spectrum. Peaks that are present in the oxidized spectrum, but not in the reduced spectrum are 180° out of phase, e.g., Au-Cl. Figure 2 shows the Fourier Transform of the difference file for Au/Al$_2$O$_3$ (Cl), which was reduced and subsequently oxidized at 25°C. Oxidation of the reduced catalyst at 25°C leads to the formation of a small number of Au-Cl bonds, but no Au-O bonds. It is reasonable to postulate that the active site may involve Au species that can undergo facile redox reaction and that chloride hinders the formation of Au-O bond.
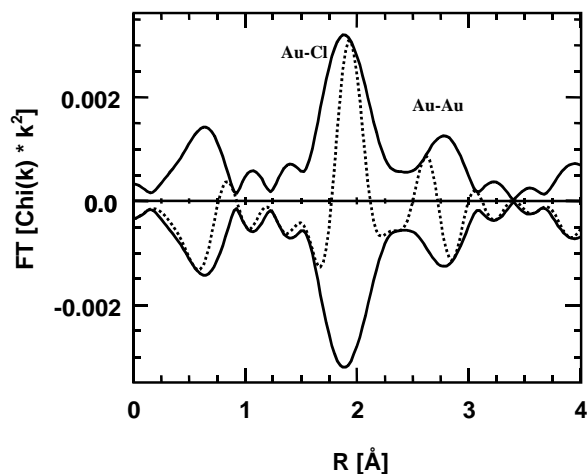

Figure 2. Fourier transform of the difference file of Au/Al$_2$O$_3$ H$_2$ at 250°C and exposed to air at RT following reduction. (k^2: Δk = 3.05 – 12.8 Å^{-1}, Au-Cl is 180° out of phase); solid line: Fourier Transform magnitude, and dotted line: imaginary part of Fourier Transform.

After 350°C calcination of Au/Al$_2$O$_3$ (no Cl), a portion of the Au is reduced to small articles of less than about 2 nm. Even smaller particles are formed by reduction in H$_2$ at 250°C. The small reduced Au particles are reactive to air at room temperature showing an increase in the white line or about 10% and an Au-O coordination in the EXAFS. Because of the shorter bond distance of Au-O (2.03 Å) compared to that of Au-Cl (2.28 Å), there is less overlap in the EXAFS spectrum allowing for a fit of the small Au-O coordination, with about 10% of the atoms being oxidized.

Despite their small size these metallic particles have low CO oxidation activity at RT. Dehydration of Au/alumina catalysts has been previously been shown to give low activity [4]. The activity of this oxidized catalyst improved significantly when the feed stream contained 1.5% H$_2$O.

The H_2 reduced sample has unusually short Au-Au bond length. The short bond length may have consequences for the catalytic activity. Whle these small particles did react with air to partially oxidize the metallic surface, in the absence of H_2O, their catalytic activity was low. Only in the presence of small particles (with short bond distances), without Cl and with H_2O was the catalytic activity high. EXAFS analysis of the catalysts in oxidized catalyst in the presence of H_2O showed no difference from those without H_2O.

Conclusions

The catalytic performance of Au/Al_2O_3 catalyst strongly depends on the Au particle size and the amount of residual chloride. Chloride causes agglomeration of Au particles upon calcination to high temperature. Even under mild activation conditions, such as H_2 reduction at 250°C, when the Au particles remain small, the catalytic activity is poor as chloride severely poisons catalytic activity. A possible mode of inhibition is the prevention of oxidation of reduced Au as no Au-O bond formation is detected upon exposure of such catalysts to O_2. The amount of residual chloride can be minimized by either adsorption of Au at high pH or washing of a catalyst prepared at low pH with alkaline solution.

It is unclear why small particles that react with air do not oxidize CO in the absence of H_2O, but have high activity when reacted with H_2O. EXAFS indicates no change in the catalyst structure due to H_2O.

References

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