

Understanding preparation variables in the synthesis of Au/Al₂O₃ using EXAFS and electron microscopy

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Abstract

The catalytic performance of Au/Al₂O₃ catalyst is highly sensitive to preparation procedure. EXAFS and TEM characterization of key steps in the preparation in conjunction with activity measurements result in deeper insights into precautions needed and the complex manner residual chloride impacts catalytic activity. Chloride affects the morphological (Au particle size), chemical (reducibility) as well as the catalytic (poisoning) properties of Au. Alternate preparation procedures to the conventional calcination of a catalyst prepared with deposition–precipitation at neutral pH were explored to increase Au loadings. It was found that low temperature H₂ reduction of a catalyst prepared at low pH but washed with NaOH is an effective preparation method.

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1. Introduction

Recent research has shown that highly-dispersed Au particles on supports have unusual catalytic properties. Some of the reactions catalyzed by supported Au particles include CO oxidation at temperature as low as –78 °C [1] and propylene epoxidation [2]. For the extensively studied CO oxidation reaction, the nature of the Au active site has not been resolved, but researchers generally agree that there is an apparent correlation between metal particle size and activity [3]. However, it has also been shown that the catalytic activity of Au catalysts is highly sensitive to the

preparation procedure. There are large variations in the reported catalytic activity over catalysts of similar compositions and containing small Au particles [4–6]. Among the different supported Au catalysts, Au/Al₂O₃ shows one of the largest variations in activity, ranging from being very inactive [5,7] to being comparable with the performance of Au/TiO₂ catalyst [8]. Thus, it appears that additional factors besides Au particle size impact on the performance of these catalysts. Some of these factors such as residual chloride [9,10] and moisture content [11,12] have been identified.

There are reports relating catalytic activities to preparation variables [13,14]. However, the emphasis of these studies is on the characterization and catalytic performance of the calcined catalysts. The purpose of this paper is to follow the evolution of the Au species throughout preparation in order to better understand the parameters critical in influencing catalyst activity. Different stages in the

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preparation and activation processes were monitored using X-ray absorption spectroscopy (XAS). Additional characterization by electron microscopy was included when needed to better understand the changes in Au particle size during synthesis. Residual chloride was also analyzed as it has been shown to cause agglomeration of Au and suppress catalytic activity [9].

Perhaps the most common way to prepare supported Au catalyst is the deposition–precipitation method of Haruta et al. [15]. In this procedure, after adjusting the pH of the Au solution, the support oxide is added and the resultant suspension is aged at 70 °C, followed by filtration and washing. There are minor variations to this method including different temperatures [14,16] adjusting the pH after mixing the Au solution and the support [17] or adding the Au solution to the support [14]. The impact of these variations on the catalytic activity is minor compared to the need to adjust the pH of the synthesis solution to 7 or higher. It has been shown that at lower pH, Au loading is higher [9,13,14], the residual chloride is also higher [16], but the activity of the catalyst is dramatically lowered [9,13,14,16]. This is in part related to the degree of hydrolysis of Au–Cl bond of the Au complex at different pHs [18]. While higher pH generates much more active catalysts, the Au loading is generally less than 1%. It would be interesting for practical purposes to obtain higher Au loading catalyst with proportionally higher activity. In order to do so, it would be helpful to understand the transformation of the Au species on the support during preparation. This paper is a stepwise examination of the catalyst structure and activity after each key stage of catalyst preparation and lifetime; these include deposition of Au complex onto the support at different pHs, washing, activation and storage. The study is focused on Au/Al₂O₃, since this catalyst has the largest variation in reported activity.

2. Experimental

2.1. Sample designation

Notations for catalysts will be as follows: the first number in the notation denotes the pH of the alumina oxide–Au precursor suspension. It is followed by a letter **a** or **b** if more than one batch was made using the same synthesis conditions. All catalysts were washed with de-ionized (DI) water after the filtration step. When an additional washing step was introduced; it will be denoted by—**W** followed by the type of washing solution and the pH of the wash in brackets. The types of alumina used will be next in the notation. The commercial Catapal γ -alumina (surface area = 220 m²/g and pore volume = 0.52 ml/g) is designated as **Cat**. In the case when Catapal alumina was pre-washed with a pH 9 NaOH solution and then rinsed twice with de-ionized water before use, the **Cat** designation has **PW** preceding it. **SCCa** (Sasol-chemie GmbH) alumina is

denoted as **SCC** and is primarily of θ phase and has a surface area of 90 m²/g. Sol–gel alumina synthesized by hydrolysis of aluminum isopropoxide (Aldrich 99.99+%) in the presence of chelating agent 2-methyl-2,4 pentanediol at Northwestern University has a surface area of approximately 250 m²/g and is identified as **sol-gel**.

Catalysts **4a-Cat** and **4b-Cat**: 200 ml of 22.5 mM HAuCl₄ solution was added to 50.0 g of Catapal γ -alumina in 500 ml H₂O. The solution pH was approximately 4. The solution was stirred for 1 h, filtered and washed with 500 ml room temperature H₂O, filtered and dried at 100 °C.

Catalyst **4a-CatW(NaOH-9)**: 35 g of **4a-Cat** was slurried in 200 ml H₂O and heated to about 70 °C. A solution of NaOH (pH 13) was added dropwise to maintain a pH between 7 and 9 until eventually the pH remained at 9. The solid was filtered, and washed with 100 ml H₂O, filtered and dried at 100 °C.

Catalysts **7-Cat**, **7-PWCat**, **7-sol-gel**: The pH of a 50 ml solution of 7.60 mM HAuCl₄ (Aldrich 99.999%) solution was adjusted to 7 at 70 °C with NaOH. To minimize contamination by the pH electrode, the pH was monitored by placing a drop of the synthesis solution on Hydrion short-range (pH 6–8) pH test paper (Fisher Scientific). The color of the pH paper was compared to another pH paper where a drop of certified pH 7 buffer had been added. In order to minimize possible light sensitive reaction of Au precursors, the synthesis was carried out with minimal exposure to light. After half an hour, the solution was added with vigorous stirring to 2.5 g of Al₂O₃ suspended in 50 ml of doubly distilled H₂O at 70 °C and the adsorption process was allowed to proceed for 1 h at pH 7. The sample was then suction filtered, re-suspended in 50 ml room temperature de-ionized water and suction filtered again. This procedure was repeated with 50 ml of room temperature water followed by 50 ml of warm (~50 °C) water. The catalyst was dried at room temperature overnight.

Catalyst **4-SCC** was prepared by adding 0.8 g of a HAuCl₄ solution containing 25 wt.% Au to 100 ml slurry containing 20 g of alumina in de-ionized water. After 1 h of stirring, the slurry was steam evaporated to dryness. The nominal Au loading is 1%.

Catalysts **4-SCCW(formic acid-6.5)**, **4-SCCW(Acetic acid-7)**, **4-SCCW(NH₄HCO₃-8)**, **4a-SCCW(NH₄OH-9)**, **4b-SCCW(NH₄OH-9)** were prepared using a modified procedure of catalyst **4-SCC**. After stirring, instead of evaporation, the slurry was filtered using a vacuum filtration setup. The filtercake was washed at least twice, using 100 ml of de-ionized water for each wash, and then placed in 100 ml of DI water. The wash solution was added dropwise to the slurry until the desired pH was reached and then the slurry was stirred for 1 h, filtered, washed with DI water, and dried. In the acetic acid and formic acid washes, tetramethylammonium hydroxide (TMAOH) was also added in order to achieve the desired pH. **4a-SCCW(NH₄OH-9)** was prepared where the 1 h stirring time was increased to 24 h before filtration.

2.2. Activation of catalysts

Catalysts prepared using Catapal or sol–gel alumina were activated either by calcination at 350 °C or by reduction in H₂. Calcination was carried out in an oven in static air and all calcined catalysts were cooled down in ambient air and, therefore, were hydrated.

In the H₂ activation procedure, the catalyst was reduced at 250 °C in a flow of H₂ for 30 min (100% when catalyst was prepared for catalytic test and 4% for EXAFS structural study). The sample was cooled to room temp in flowing H₂. For re-oxidation studies, the reduced catalyst was exposed to 20% O₂ either at room temperature or at 175 °C.

Catalysts prepared with SCCa alumina were calcined to 600 °C for 6 h.

2.3. Catalyst testing

The catalysts were tested using two different methods. Catalysts prepared with Catapal or sol–gel alumina were tested in a U-shaped fused-silica microreactor using 40 mg of catalyst and 200 ml/min flow of a feed containing 1% CO, 2.5% O₂, balance He. The testing was conducted either in a dry feed where the reaction stream was purified by passing through a silica gel trap at dry ice-acetone temperature, or in a wet feed (1.5% water) that was passed through a water saturator at room temperature. The reaction was conducted at room temperature and the products were analyzed by FTIR for CO and CO₂ using a gas cell of about 74 ml. They were also analyzed but at a much longer time intervals by gas chromatography using a molecular sieve 13X columns for CO and O₂, and a Haysep Q column for CO₂ and H₂O.

Catalysts prepared with SCCa alumina were tested using a 1/4 in. OD stainless steel U-shaped microreactor. About 50 mg of catalyst sample was retained between glass wool layers, and a thermocouple was inserted into the microreactor to record the temperature. The feed was nearly stoichiometric with a slight excess of O₂. The flow rates were 5.9 sccm of O₂, 11.4 sccm of CO and 40 sccm of He (10.3% O₂, 9.9% CO). CO oxidation activity was determined from 25 to 400 °C by increasing the temperature, after which the temperature was lowered from 400 to 25 °C, completing one cycle. At least two more cycles were then performed on these catalysts. The reaction mixture leaving the reactor was analyzed with an on-line gas chromatograph equipped with a TCD detector.

2.4. Elemental analysis

The Au content of the catalysts was determined by inductive coupled plasma (ICP) or X-ray fluorescence (XRF). The Cl content was also determined by XRF and calibrated using Al₂O₃ impregnated with dilute solutions of NaCl.

2.5. EXAFS and XANES data collection and analysis

X-ray absorption 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. A cryogenically cooled double-crystal Si (1 1 1) monochromator was used in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.07 s per data point. Measurements were made in transmission mode with the ionization chambers optimized for the maximum current with linear response (<10¹¹ photons detected/sec) using a mixture of nitrogen and helium in the incident X-ray detector and a mixture of ca. 20% argon in nitrogen in the transmission X-ray detector. A gold foil spectrum was acquired simultaneously with each measurement for energy calibration.

Catalyst samples were pressed into a cylindrical holder with a thickness chosen to give a total absorbance (μx) at the Au L_{III} edge of about 3, corresponding to approximately 100 mg of catalyst, which resulted in a gold edge step ($\Delta\mu x$) of ca. 0.5 for 2% Au on alumina. EXAFS and XANES spectra of the calcined catalysts were obtained at room temperature in air. Reduced catalysts were pre-treated in a continuous-flow EXAFS reactor cell (18 in. long, 0.75 in diameter) fitted at both ends with polyimide windows and valves to isolate the reactor from the atmosphere. The catalysts were heated to 250 °C for 1 h in 4% H₂/He, then cooled to room temperature, and sealed. The spectra were obtained in the presence of H₂. The reduced catalysts were oxidized by treatment in flowing air at room temperature or at 175 °C, and the XAFS spectra were obtained at room temperature in air.

Phase shifts, backscattering amplitudes and XANES references were obtained from reference compounds: HAuCl₄ for Au⁺³–Cl, Au₂O₃ for Au⁺³–O, and Au foil for Au⁰ and Au–Au. The XANES fits of the normalized spectra were made by linear combination of experimental standards. Standard procedures based on WINXAS97 software were used to extract the EXAFS data. The coordination parameters were obtained by a least square fit in *k*- and *r*-space of the isolated multiple-shell, *k*²-weighted Fourier transform data.

2.6. TEM characterization

High-resolution scanning transmission electron microscopy (STEM) in high angle annular dark field (HAADF) mode was performed using a JEOL 2010F microscope operating at 200 kV. A catalyst sample was lightly ground in ethanol (200 proof) using a mortar and pestle, and a holey Cu carbon grid was dipped just beneath the surface of the ethanol to collect the particles.

3. Results

3.1. Au speciation and adsorption on Al_2O_3

In the deposition–precipitation method, $AuCl_4^-$ complexes were hydrolyzed and adsorbed onto Al_2O_3 surface at $pH \geq 7$. The speciation of $AuCl_4^-$ as a function of pH had been studied using UV visible spectroscopy [19], laser Raman spectroscopy [19,20] and in this study EXAFS Fig. 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 decreased approximately linearly. At a pH of 7, in a 200 or 500 ppm solution (solid square and solid circle, respectively) Au exists as $Au(OH)_4^-$. The presence of a 50-fold molar excess of Cl^- has little influence on the solution species (\diamond). There was no precipitate at any pH for fresh Au solutions. 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 [21] leading to more extensively hydrolyzed Au species and more Au–O bonds (open triangle). At pH's above about 6, there were few Au–Cl bonds in the adsorbed Au^{3+} . The adsorption capacity for anionic Au^{3+} complexes at a given pH depends on the IEP of the support. Fig. 1b shows the saturation surface density ($\mu\text{mol}/\text{m}^2$) of Au^{3+} on catapal γ -alumina, with the

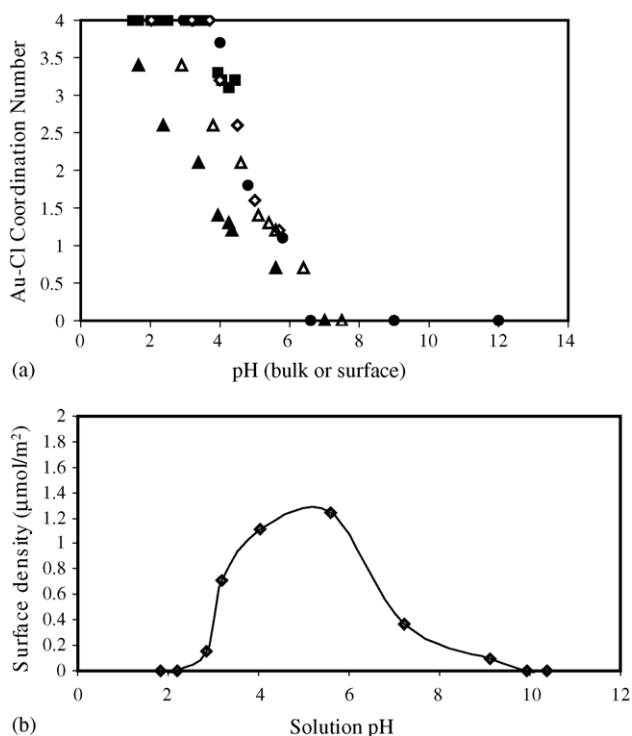


Fig. 1. (a) Au–Cl coordination of Au species in solution and adsorbed on Al_2O_3 as a function of pH. $H AuCl_4$ concentration: (■) 200 ppm, (●) 500 ppm, and (\diamond) 200 ppm + 10,000 ppm chloride ions. (\blacktriangle) Adsorbed Au at bulk pH and (\triangle) adsorbed Au at surface pH. (b) Density of adsorbed Au on alumina at different pH's as determined by ICP. $H AuCl_4$ is 500 ppm.

greatest amount adsorbed between pH 5 and 6 and the density decreased steeply at pH's greater than about 6.

3.2. Deposition at pH4

Catalyst **4a-Cat**, prepared by deposition at pH 4, contained 1.4 wt.% Au (78% of the Au originally present in the preparation solution) and 0.9 wt.% residual Cl^- (Table 1). Table 2a shows 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, and the Au–Cl bond still accounted for $\sim 25\%$ of the total bonds of cationic Au. Such a calcined catalyst was inactive under our testing condition. The average first shell Au–Au coordination number ($1NN_{Au-Au}$) can be used to estimate the metal particle size [22]. For bulk Au, $1NN_{Au-Au} = 12$. For sample **4a-Cat**, the Au–Au coordination was 11.4 ($=5.7/0.5$) after adjustment for oxidation state (calculated by assuming that the reduced Au exists as separate particles from oxidic clusters), implying that the Au particle size was relatively large.

Complete reduction of the catalyst was achieved after H_2 treatment at 250°C . The particle size of this reduced catalyst was much smaller ($1NN_{Au-Au} = 7.1$), between 1.5 and 2 nm [23]. Exposure of the catalyst to air at room temperature and 175°C did not result in detectable reoxidation of Au, but agglomeration of the Au particles occurred as evidenced by the small increase in the Au–Au coordination number. Despite the small metal particle size, the catalyst was inactive even after treatment in a flow of He containing H_2O vapor, which is known to be beneficial to catalyst that has been dehydrated thermally [8]. Including water in the testing feed, however, did result in low but detectable CO oxidation activity.

The activity of the sample prepared by adsorption at pH 4 as seen in Table 2(b) was improved significantly by washing with NaOH solution at pH 9 (catalyst **4a-CatW(NaOH-9)**). Elemental analysis showed that the Au content was reduced to 1.02% after washing and the chloride content was less than 0.01%. As seen in Table 2(b), the sample was now somewhat more reducible; 60% of total Au, as determined by XANES, was metallic after calcination at 350°C . The metallic Au particle size of the calcined sample was between 1.5 and 2 nm as suggested by $1NN_{Au-Au}$ of 6.9 (adjusted for unreduced Au) [23]. Increasing the calcination temperature to 400°C resulted in further reduction and more agglomeration with an increase of $1NN_{Au-Au}$ to 9. H_2 at 250°C completely reduced the gold to particles less than 1 nm as suggested by $1NN_{Au-Au}$ of 5. The Au–Au distance of these small particles was noticeably shorter than the calcined sample. This observed lattice parameter contraction is consistent with the presence of small metal particles [23–

Table 1
Au loading and residual chloride analysis of catalysts

Catalyst	pH of adsorption of Au complex	pH of wash ^a	Au (wt.%)	Cl (wt.%)
4a-Cat	4	–	1.38	0.9
4b-Cat	4	–	0.94	1.7
4a-CatW(NaOH-9)	4	9	1.02	<0.01%
7-Cat	7	–	1.87	0.08
7-PWCat	7	–	0.67	0.03
7-sol-gel	7	–	1.42	0.036
4-SCC^b	4	–	1 ^c	0.72
4-SCCW(formic acid-6.5)	4	6.5	0.91 ^d	0.19
4-SCCW(acetic acid-7)	4	7	0.62 ^d	0.091
4-SCCW(NH₄HCO₃-8)	4	8	0.72 ^d	0.092
4a-SCCW(NH₄OH-9)	4	9	0.76 ^d	0.019
4b-SCCW(NH₄OH-9)	4	9	0.77 ^d	0.014

^a Wash solution used in addition to the basic washes with de-ionized water.

^b Not washed with de-ionized water.

^c Nominal gold loading.

^d Calculated using the Au leached into solution and a nominal Au loading of 1 wt.%.

Table 2
Physical and catalytic properties of catalyst: (a) **4a-Cat** and (b) **4a-CatW(NaOH-9)**

Treatment	<i>T</i> (°C)	XANES			EXAFS					Activity
		Fraction Au ⁺³ -O	Fraction Au ⁺³ -Cl	Fraction Au ⁰	Scatterer	1NN ^b	<i>R</i> (Å)	DWF (×10 ⁻³)	<i>E</i> _o	
(a) 4a-Cat										
Air (static)	100	0.80	0.20	0	Au-O	3.0	2.04	-2.4	2.0	–
					Au-Cl	1.0	2.28	-2.4	2.6	
Air (static)	350	0.5	0	0.5	Au-O	2.0	2.03	0.5	-0.7	0 ^c
					Au-Cl	0.6	2.28	0.5	2.0	
					Au-Au	5.7	2.88	1.0	-1.5	
H ₂	250	0	0	1.0	Au-Au	7.1	2.84	1.0	-3.9	–
H ₂ , air	250, 25	0	0	1.0	Au-Au	7.5	2.86	1.0	-3.2	–
H ₂ , 20% O ₂	250, 175	0	0	1.0	Au-Au	8.0	2.86	1.0	-3.9	–
H ₂ , 20% O ₂ , H ₂ O ^d	250, 175, 25	–	–	–	–	–	–	–	–	0 ^e , 1.2 ^e
(b) 4a-CatW(NaOH-9)										
Air (static)	25	1.0	0	0	Au-O	4.0	2.03	-1.0	1.1	–
Air (static)	350	0.40	0	0.60	Au-O	2.0	2.04	-1.0	2.0	2 ^{c,f}
					Au-Au	4.1	2.85	1.0	-2.7	
Air (static)	400	0.20	0	0.80	Au-O	0.7	2.05	-1.0	2.0	–
					Au-Au	7.0	2.85	1.0	-3.0	
H ₂	250	0	0	1.0	Au-Au	5.0	2.71	3.0	-7.2	2 ^c
H ₂ , air	250	0.1	0	0.90	Au-O	0.4	2.03	-1.0	2.0	–
	25				Au-Au	4.6	2.72	3.0	-6.5	
H ₂ , 20% O ₂	250	0.15	0	0.85	Au-O	0.6	2.04	-1.0	2.0	0.44 ^c
	175				Au-Au	3.9	2.72	3.0	-7.6	
H ₂ , 20% O ₂ , H ₂ O ^g	250, 175, 25	–	–	–	–	–	–	–	–	3.5 ^c , 39.1 ^c

^a Unless specified, flow mode.

^b First shell coordination number.

^c Mol CO (mol Au s)⁻¹ × 100; tested in a feed of 1% CO, 2.5% O₂ at room temperature, pseudo steady state result taken after 30 min.

^d He containing 1.5% H₂O for 40 min and then purged in dry He for 30 min.

^e Mol CO (mol Au s)⁻¹ × 100; tested in a wet feed of 1% CO, 2.5% O₂, 1.5% H₂O at room temperature.

^f Exposed to ambient air before reaction test.

^g 1.5% H₂O for 40 min.

Table 3

Comparison of catalysts prepared by adsorption on Catapal γ -alumina at different pH's and washed with different procedures

Catalyst	T ($^{\circ}\text{C}$) calcined	XANES		EXAF					Activity
		Fraction $\text{Au}^{+3}\text{-O}$	Fraction Au^0	Scatterer	INN	R (\AA)	DWF ($\times 10^{-3}$)	E_o	
4a-CatW(NaOH-9)	100	1.0	0	Au–O	4.0	2.03	–1.0	1.1	–
4a-CatW(NaOH-9)	350	0.40	0.60	Au–O	2.0	2.04	–1.0	2.0	2 ^a
				Au–Au	4.1	2.85	1.0	–2.7	
7-Cat	25	1.0	0	Au–O	4.0	2.03	–0.5	–0.5	
7-Cat	350	0.55	0.45	Au–O	2.3	2.02	0.5	–1.3	0 ^a
				Au–Au	5.9	2.86	1.0	–2.0	
7-PWCAT	100	1.0	0	Au–O	4.0	2.02	–0.6	–0.5	–
7-PWCAT	350	0.40	0.60	Au–O	1.8	2.02	0.5	–1.8	5.3 ^a
				Au–Au	3.9	2.85	1.0	–2.8	

^a Mol CO (mol Au s)^{–1} \times 100; tested in a feed of 1% CO, 2.5% O₂ at room temperature; pseudo steady state result taken after 30 min; sample had been exposed to ambient air after treatment.

25]. When the reduced sample was exposed to air, 10 and 15% of the Au was re-oxidized at room temperature and 175 $^{\circ}\text{C}$, respectively. Also different from the chloride-containing sample, no agglomeration took place upon exposing the reduced sample to oxygen. The activity of the reduced sample was the same as the calcined one but higher than after it had been re-oxidized at 175 $^{\circ}\text{C}$ in flowing 20% O₂. When the latter sample was exposed to water vapor at room temperature, the activity increased seven fold. The highest activity was observed when the catalyst was tested in a feed containing 1.5% water.

3.3. Deposition at pH 7

Table 3 shows the structural and catalytic properties of catalysts prepared by adsorption of the Au complex at pH 7 onto Catapal γ -alumina. Sample **7-Cat** was prepared with unwashed alumina. The Au loading was 1.87% (63% of the Au in the synthesis solution). The % of Au in solution adsorbed onto alumina was less than **4-Cat** but substantially higher than that predicted in the adsorption studies with low concentration of HAuCl₄ solution (Fig. 1b). The residual chloride was significantly lower (800 ppm), which is consistent with no detectable Au–Cl bond in the EXAFS spectra. Slightly more than half of the sample remained oxidized after calcination at 350 $^{\circ}\text{C}$ and the Au–Au coordination number was similar to that of bulk Au (after adjustment for the presence of oxidized Au). The catalyst was inactive under our testing condition. If the same procedure was used to prepare a catalyst (**7-PWCat**) with a washed Catapal γ -alumina, significant structural and catalytic property differences were observed. Only 21% of the Au in the synthesis solution was adsorbed (Au loading = 0.7%) which is more in line with the adsorption data using dilute HAuCl₄ solution. The chloride content was only 330 ppm. The degree of reduction of Au after calcination was increased and the resultant Au particles were between 1.5 and 2 nm (adjusted $1\text{NN}_{\text{Au-Au}} = 6.5$). The catalyst was very active.

Extensive analysis of the washed and unwashed alumina was done and the result is tabulated in Table 4. After normalization using the weight of Al, within the accuracy of the analysis, there was no significant difference between the washed and unwashed alumina.

The activity of the Au catalyst supported on sol–gel alumina (catalyst **7-sol–gel**) was similar to the sample prepared using the washed Catapal γ -alumina (Table 5). The calcined sol–gel sample was somewhat lower in activity, but given the susceptibility of Au alumina to contaminants, a factor of 2 may not be too significant, especially when the sample reduced in H₂ and exposed to O₂ gave the same activity as the one prepared on the washed commercial alumina.

Table 4

Elemental analysis of washed and unwashed Catapal γ -alumina

Element	Washed Al ₂ O ₃	Unwashed Al ₂ O ₃	Unit
Li	<5	<5	ppm
Na	65	70	ppm
Mg	<5	<5	ppm
Al	36.3	47.3	wt. %
Si	<25	170	ppm
P	430	435	ppm
S	310	400	ppm
K	<5	<5	ppm
Ca	42	45	ppm
Ti	785	1020	ppm
V	10	10	ppm
Cr	<5	<5	ppm
Mn	<5	<5	ppm
Fe	20	7	ppm
Co	<5	<5	ppm
Ni	<5	<5	ppm
Cu	<5	<5	ppm
Zn	<5	<5	ppm
Sr	<5	<5	ppm
Zr	<5	<5	ppm
Mo	150	180	ppm
Pb	280	295	ppm
Cl	<5	12	ppm

Table 5
Comparison of structural and catalytic properties of calcined Au catalyst prepared on washed Catapal γ -alumina and sol-gel alumina

Catalyst	Treatment		XANES		EXAF					Activity
	Gas ^a	T (°C)	Fraction Au ⁺³ -O	Fraction Au ⁰	Scatterer	1NN	R (Å)	DWF ($\times 10^{-3}$)	E _o	
7-PWCat	Air (static)	350	0.40	0.60	Au-O	1.8	2.02	0.5	-1.8	5.3 ^c
					Au-Au	3.9	2.85	1.0	-2.8	
7-PWCat	H ₂ , 20% O ₂ H ₂ O ^b	300, 175, 25	0.1	0.9	Au-Au	4.1	2.74	3.0	-8.0	4.3 ^c
7-Sol-gel	Air (static)	350	0.20	0.80	Au-O	0.9	2.03	1.0	-1.3	2.4 ^c
					Au-Au	7.9	2.86	1.0	-3.2	
7-Sol-gel	H ₂ , 20% O ₂ H ₂ O ^b	250, 175, 25	0.10	0.90	Au-Au	3.6	2.75	3.0	-8.6	4.6 ^c

^a Unless specified, flow mode.

^b He containing 1.5% H₂O for 40 min, then purged in dry He for 30 min.

^c Mol CO (mol Au s)⁻¹ $\times 100$; tested in a feed of 1% CO, 2.5% O₂ at room temperature; pseudo steady state result taken after 90 min.

Transmission electron micrographs of the three calcined samples prepared at pH 7 are shown in Fig. 2. Qualitatively, the trend seen in the micrographs agreed with the EXAFS results. Catalyst **7-Cat** had large particles around 8–10 nm. In addition, some large particles around 30–50 nm (not shown) were also present. The average size of the easily detectable particles for the fresh **7-PWCat** and **7-sol-gel** catalysts were around 2–4 and 4–5 nm,

respectively; although some particles less than 2 nm were discernible.

3.4. Alternate washing methods

In addition to washing with NaOH at pH 9, other washing procedures were also explored to determine the most successful means of removing chloride from the material

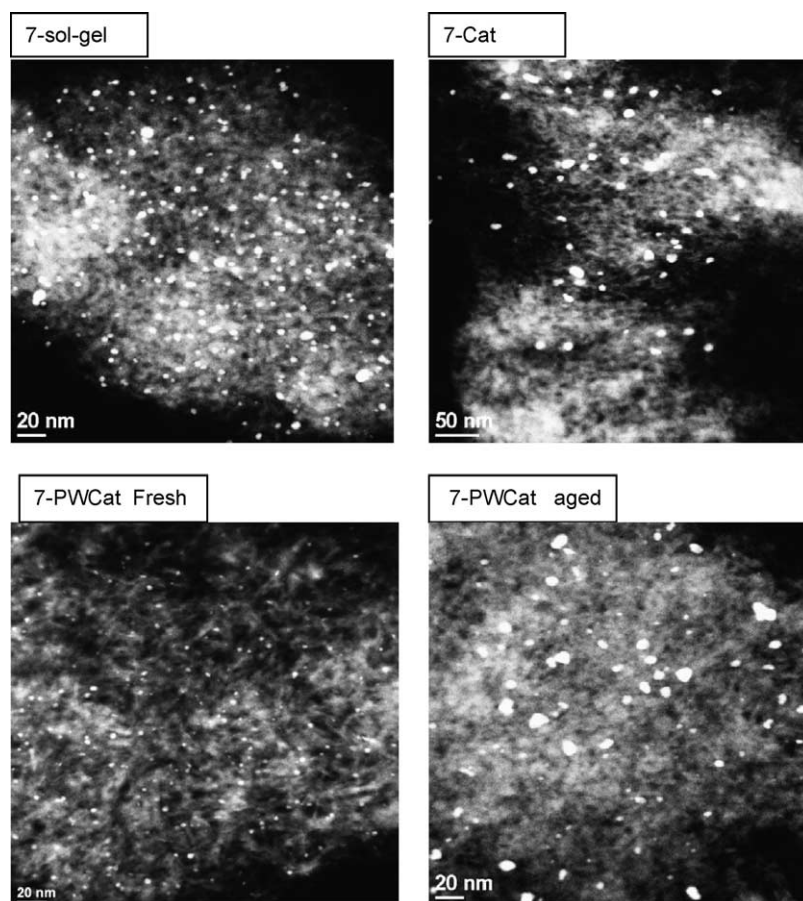


Fig. 2. STEM HAADF (high angle annular dark field) images of catalysts **7-sol-gel**, fresh and aged **7-PWCat**, and **7-Cat**. The scale bars for the first three catalysts are 20 nm and that of the last catalyst is 50 nm.

Table 6

Physical and catalytic properties of Au/Al₂O₃ catalyst prepared with different washing procedures and calcined at 600 °C

Catalyst	% Au loss due to leaching	Average Au size (nm)	Catalytic properties	
			Onset <i>T</i> (°C)	Activity at 100 °C ^a
4-SCC	N/A	90	400	0
4-SCCW(formic acid-6.5)	9.3	71	200	0
4-SCCW(acetic acid-7)	38.2	–	150	2.1
4-SCCW(NH₄HCO₃-8)	28.4	–	150	4.5
4a-SCCW(NH₄OH-9)	24.4	–	25	22
4b-SCCW(NH₄OH-9)	23.4	6	50	29

^a Mol CO (mol Au s)⁻¹ × 100.

without removing gold in the process. For this series of experiments, the alumina was SCCa. Tables 1 and 6 shows the physical and catalytic properties of this series of catalysts treated with different wash solutions, and calcined at 600 °C. The **4-SCCW(formic acid-6.5)** retained the most Au as well as chloride. This catalyst was inactive at 100 °C for CO oxidation. Washing with acetic acid/TMAOH (**4-SCCW(Acetic acid-7)**) resulted in the highest degree of gold leaching. On the other hand, washing with NH₄OH was the most effective way in removing chloride. There was some leaching of gold using this procedure, but the differences in the amount of Au and

chloride removed were minor when the stirring time in the wash solution was increased from 1 to 24 h (**4a-SCCW(NH₄OH-9)** and **4b-SCCW(NH₄OH-9)**). These catalysts were the most active at 100 °C for CO oxidation but the catalyst that was stirred for 24 h instead of 1 h was more active both with respect to the onset temperature of CO oxidation and the CO conversion at 100 °C. STEM images in Fig. 3 show that of **4b-SCCW(NH₄OH-9)** had nano-particles of Au, whereas **4-SCCW(formic acid-6.5)** and **4-SCC** had large Au particles. The size of the Au particles strongly depends on the chloride content. Increasing the wt.% chloride from 0.014 to 0.19 significantly

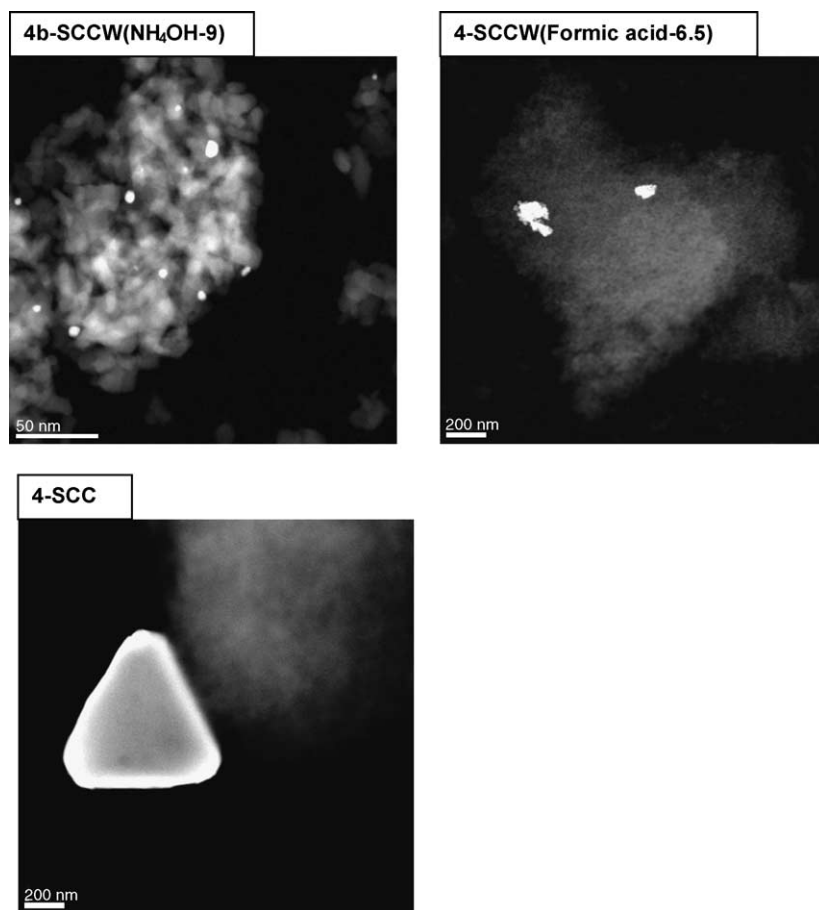


Fig. 3. STEM HAADF images of catalysts **4b-SCCW(NH₄OH-9)**, **4-SCCW(formic acid-6.5)**, and **4-SCC**. The scale bar for the image of the first catalyst is 50 nm while those for the latter two catalysts were 200 nm.

Table 7
Effect of aging for 1.5 years on pH 4 deposited catalysts

Sample	Age/further treatment	XANES			EXAF				
		Fraction Au ⁺³ -O	Fraction Au ⁺³ -Cl	Fraction Au ⁰	Scatterer	1NN	R (Å)	DWF (×10 ⁻³)	E _o
Catalyst 4-CatW(NaOH-9)									
Dried 100 °C	Fresh	1.0	0	0	Au-O	4.0	2.03	-1.0	1.1
Dried 100 °C	Aged 1.5 years	0.75	0	0.25	Au-O	3.1	2.02	0.5	0.3
					Au-Au	3.6	2.86	1.0	-4.2
H ₂ 250 °C	Fresh	-	-	1.0	Au-Au	4.2	2.71	1.0	-8.0
Dried 100 °C	Aged 1.5 years; H ₂ 250 °C	-	-	1.0	Au-Au	2.7	2.70	1.0	-8.6
					Au-Au	3.6	2.86	1.0	-4.2
Catalyst 4b-Cat									
Dried 100 °C	Fresh	0.65	0.35	0	Au-O	2.6	2.04	-2.2	-0.1
					Au-Cl	1.4	2.28	-2.2	1.4
Dried 100 °C	Aged 1.5 years	0.70	0.30	0	Au-O	2.8	2.03	-1.1	0.8
					Au-Cl	1.2	2.27	-1.1	-1.0
H ₂ 250 °C; air, 25 °C	Fresh	0	0	1.0	Au-Cl	0.4	2.28	-2.0	2.0
					Au-Au	8.0	2.86	1.0	-4.1
H ₂ 250 °C; air, 25 °C	Aged 1.5 years	0	0	1.0	Au-Au	12.0	2.88	1.0	-2.4

increased the average Au particle size from 6 to 71 nm, thus rendering the catalyst inactive for low-temperature CO oxidation. Therefore, complete removal of chloride with minimal loss of Au in the wash process is important in order to obtain a catalytically active catalyst for low-temperature CO oxidation.

3.5. Aging

The structural stability of the catalysts synthesized at pH 4 was examined one and a half years after the initial preparation and the results are shown in Table 7. For the washed sample (**4a-CatW(NaOH-9)**) that was dried at 100 °C, about 25% of the sample had been reduced to large metallic Au particles (Table 7). The unreduced fraction, upon H₂ treatment resulted in small Au particles similar to the fresh sample after the same treatment. Thus, the EXAFS data were best fitted with two populations of Au particles of different sizes. The unwashed, dried (100 °C) sample (**4b-Cat**), with 1.7% residue Cl, remained oxidic after aging and was completely reduced after 250 °C H₂ treatment as characterized by XANES although some Au-Cl species were still detected by EXAF. When reduced **4b-Cat** was aged in ambient air, the Au-Cl bond was no longer detected and the Au particles were very large as the 1NN_{Au-Au} became 12.

Catalyst prepared with sol-gel alumina aged well. In contrast, calcined **4-PWCat** was inactive after 6 months storage. However, when an uncalcined portion of aged **4-PWCat** was calcined at 350 °C, the freshly calcined catalyst was active for CO oxidation. Electron micrographs of the freshly calcined **4-PWCat** shows Au particle size averaged between 2 and 4 nm (Fig. 2) while an aged sample contained

two population of particles, those between 3 and 7 nm and those around 9–11 nm.

4. Discussion

Decreasing the density of positively charged sites on alumina by increasing pH can effectively reduce the concentration of adsorbed chloride ions on alumina surface. It does not matter whether the pH adjustment is performed during deposition-precipitation or after Au deposition as long as it is done before thermal treatment, the resulting physical and catalytic properties are similar (compare catalysts **4a-CatW(NaOH-9)** and **7-PWCat**). Residual chloride on Au/Al₂O₃ catalyst affects the reducibility of Au cation, the particle size, and the catalytic activity. All catalysts are partially oxidized after calcination at 350 °C as the XANES fits of the calcined samples are consistent with the presence of a mixture of Au³⁺ and Au⁰. The 1NN of Au-O (or Au-Cl) from the EXAFS data is near 4 in all cases, suggesting that the oxidized species are Au³⁺ instead of Au¹⁺. The presence of chloride appears to decrease the reducibility of oxidized Au as the population of Au³⁺ is higher in samples containing higher chloride.

Consistent with the literature results [9,10], high residual chloride is observed to cause the agglomeration of Au upon high temperature calcination to form large particles as attested by the large Au-Au coordination number and the electron micrograph images. The degree of agglomeration is very sensitive to the residual chloride level: the Au particle size grew from 6 to 71 nm when the chloride

level increased from 0.014 (**4b-SCCW(NH₄OH-9)**) to 0.19% (**4-SCCW(formic acid-6.5)**). Chloride can even cause agglomeration of metallic Au at room temperature. Samples with high chloride content activated in H₂ reduction still contain small Au particles. The size of these particles increases slightly upon exposure of the pre-reduced sample to room temperature air.

Heating in H₂ to 250 °C can effectively deter this agglomeration and also result in complete reduction of Au. Although the particle size of the H₂ reduced sample (**4a-Cat**) is less than 2 nm, the catalyst is inactive at room temperature using a dry feed and W/F = 0.012 g s cc⁻¹. Upon addition of 1.5% water to the reaction feed, there is a very slight increase in oxidation activity, but the catalyst is nearly 40 times less active than the washed sample (**4a-CatW(NaOH-9)**) activated and tested under identical conditions. Thus, chloride is a very potent inhibitor of the CO oxidation activity. A possible mechanism for the poisonous effect of chloride may be deduced from the EXAFS of the oxidized, pre-reduced catalyst. These features, however, are very small and overlap the much larger Au–Au peaks in the Fourier transform. These small features, however, can be reliably resolved by analysis of the difference file [26], i.e., subtraction of the oxidized spectrum from the reduced spectrum. In the difference file, unchanged Au species, 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. Fig. 4 shows the Fourier transform of the difference file for catalyst **4b-Cat**, 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 bond (Table 7). In a catalyst with somewhat lower residual chloride (**4a-Cat**), exposure of the pre-reduced catalyst did not result in either detectable

Au–O or Au–Cl bond. In contrast, Au–O bond formation is detected upon exposure of the pre-reduced washed catalyst (**4-CatW(NaOH-9)**) to air at room temperature and the number of Au–O bonds increases when the re-oxidation takes place at higher temperatures. It is reasonable to postulate that the active site may involve Au species that can undergo facile redox reaction and chloride hinders formation of Au–O bond.

The Au particle size of **4-CatW(NaOH-9)** after 350 °C calcination is small, between 1.5 and 2 nm, and is even smaller if H₂ reduction at 250 °C is used for activation. Although the calcined and H₂ reduced samples appear to have the same activity, the observed activity of the latter sample is actually compromised by dehydration of the catalyst in the gas flow at elevated temperature. The moisture content of the sample before H₂ reduction is high, and the short duration in the reduction stream did not fully dehydrate the catalyst. However, additional treatment at elevated temperature such as reoxidation at 175 °C increased the severity of the dehydration and this is manifested in a four-fold decrease in the activity without accompanying changes in the Au particle size (Table 2b). The activity of this re-oxidized catalyst can be improved to about twice that of the H₂ reduced or calcined sample by simply rehydrating in a flow of He containing 1.5% H₂O at room temperature for 40 min. This loss of activity in flowing O₂ at 175 °C and re-activation upon hydration at room temperature is consistent with our previous observation [8]. The catalytic activity of Au/Al₂O₃ catalyst is quite sensitive to the moisture content [12]. When the reaction is performed with 1.5% H₂O in the feed stream, the activity increases by more than an order of magnitude. Furthermore, unlike reaction tests in a dry feed where the rates decline with time-on-stream, rates in the wet feed remain steady.

The H₂ reduced sample has unusually short Au–Au bond length. A similar lattice contraction is also observed for Au/TiO₂ catalysts with low Au–Au coordination numbers [27]. Thus it appears that very small Au particles have unusually short Au–Au bond length. The short bond length may have consequences on the catalytic activity of the catalysts but its effect is convoluted with the effect due to different concentrations of exposed Au or Au at the perimeter for different Au particle sizes.

The catalysts prepared at pH 7 on sol–gel alumina (**7-sol-gel**) and washed Catapal γ -alumina (**7-PWCat**) are active after activation without additional washing procedures. Unexpectedly, the calcined Au catalyst prepared with unwashed Catapal γ -alumina (**7-Cat**) has large Au particles and poor activity similar to the unwashed catalyst prepared at pH 4 (**4a-Cat**). Since catalyst (**7-Cat**) was prepared at pH 7, a condition where there is extensive hydrolysis of the anionic AuCl₄⁻ we had expected a highly active catalyst. The difference between Au catalysts prepared on the washed and unwashed Catapal γ -alumina was reproducible. This need to pre-wash the alumina suggests possible contaminants in the support. Extensive elemental analysis (Table 4)

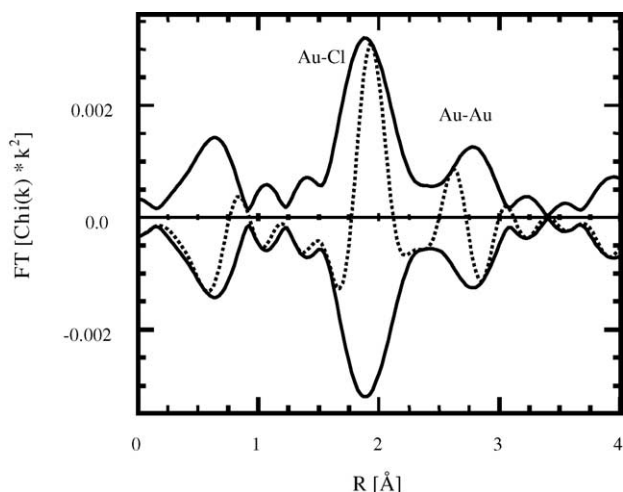


Fig. 4. Fourier transform of the difference files of **4b-Cat** (1.7% Cl) reduced at 250 °C and exposed to air at RT following reduction (k^2 : $\Delta k = 3.05\text{--}12.8 \text{ \AA}^{-1}$, Au–Cl is 180° out of phase). (—) Fourier transform-magnitude and (···) imaginary part of Fourier transform.

of the washed and unwashed alumina by ICP failed to identify a difference in the contaminant level that can account for the dramatic differences between catalysts **7-Cat** and **7-PWCat**. The impact of low levels of contaminants is underscored by the fact that sol–gel alumina prepared with ultra pure aluminum isopropoxide needs no washing to produce an active catalyst. This strong dependence on the different sources of alumina is also manifested by the low activity of the catalysts prepared using SCCa alumina which is of θ instead of γ phase. This low activity is in part due to the fact that chloride adsorption appears to be stronger on this alumina—after the pH 9 wash the residual chloride content was between 0.014 and 0.019% in contrast to less than 0.01% for the Catapal alumina.

Upon aging, a fraction of the Au was reduced to large metallic Au particles in the washed uncalcined sample (**4-CatW(NaOH-9)-Cat**). This did not occur in the unwashed sample (**4b-Cat**). This is consistent with the observation that chloride appears to lower the reducibility of Au. The remaining oxidized Au in the washed, aged sample is reduced by H_2 at 250 °C to form small Au particles similar to the fresh sample. Thus this sample has a bimodal distribution in the Au particles. It is interesting that upon aging, Au on calcined **7-PWCat** agglomerated to render the catalyst inactive whereas the calcined **7-sol–gel** is stable with storage. Thus trace impurities also impact highly on the long term stability of supported Au catalysts.

5. Conclusions

It is generally acknowledged that the synthesis of supported Au catalysts is more sensitive to preparation variables than other supported catalysts. In this paper, extensive characterization techniques, applied at critical stages in the preparation and storage of Au/Al₂O₃ catalysts, permits insight into the underlying reasons for the sensitivity of the catalytic performance to some preparative parameters.

The catalytic performance of Au/Al₂O₃ catalyst strongly depends on the amount of residual chloride. Chloride impacts the catalytic performance in complex ways. It suppresses the reducibility of Au, causing a significant population of Au to remain oxidized after calcination. It also causes the agglomeration of Au particles upon calcination to high temperature. To decouple the factors that cause low activities due to morphological reasons, methods to activate high chloride containing catalysts without Au particle sintering were explored. A mild activation condition, H_2 reduction at 250 °C, was found to result in small Au particle size in samples with high residual chloride. The catalytic activity of such a sample was still poor, thus definitively proving the poisoning effect of chloride. A possible mode of inhibition is the prevention of oxidation of reduced Au upon exposure of such catalysts to O₂ as no Au–O bond formation was detected. The amount of residual chloride can be minimized by either adsorption of Au at high pH or washing

a catalyst prepared at low pH with alkaline solution. The effectiveness of the wash, the extent of chloride removal, and Au retention depend not only on the pH of the wash solution but also on the alumina used. The latter may be due to trace impurities found on commercial alumina. Upon aging, uncalcined samples, with low chloride content and prepared on commercial alumina, become partially reduced. Such uncontrolled reduction results in large Au particles and contributes to decrease in performance upon storage.

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