Selective Catalytic Oxidation of CO: Effect of Chloride on Supported Au Catalysts

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Supported Au catalysts are generally prepared from chloride-containing Au precursors and their properties are highly sensitive to preparation procedures. To better understand and control the variables important in the preparation of these catalysts, the effect of chloride on the catalytic performances of highly active Au/Al$_2$O$_3$ catalysts in the selective catalytic oxidation of CO (SCO) was probed. The complex manner in which Cl$^-$ affected Au catalysis was deconvoluted in a series of complementary experiments where chloride was quantitatively removed and added. The residual chloride was found to affect the activities in two different ways. It facilitates the agglomeration of Au particles during heat treatment, and it inhibits the catalytic activity by poisoning the active site. Interestingly, chloride poisoning is not only observed at the steady state, it is in fact more pronounced in the transient toward steady state. In order to better assess the poisoning effect of Cl$^-$, phosphate was introduced to the support surface as a postsynthesis treatment before the addition of Cl$^-$ in some experiments. The results showed that activity suppression was observable at a Cl$^-$/Au molar ratio as low as 0.0006. Thus a very small fraction of Au is associated with the active site. This implies that the activity per active site is extremely high. © 2002 Elsevier Science (USA)

Key Words: chloride; gold; poisoning; selective CO oxidation.

I. INTRODUCTION AND BACKGROUND

Supported Au catalysts are active for CO oxidation at very low temperatures (1, 2). They are also active for a wide variety of reactions, including selective CO oxidation (3, 4), alkene epoxidation (5, 6), selective NO$_x$ reduction (7, 8), and water–gas shift (9). However, implementation of supported Au catalysts for practical application has been slow. This is in part due to a lack of thorough understanding of the relationship between preparation variables and catalytic performance. Recently, Wolf and Schuth (10) compared the CO oxidation activities of supported Au catalysts prepared using manual and automatic synthesis methods. They observed small differences between these two meth-

ods when the catalysts were synthesized on the same day. However, for catalysts prepared on different days, even with the automated method, sometimes large differences in activities were observed. Thus, the properties of a supported Au catalyst are highly sensitive to preparation conditions (11).

While the nature of the active site is being investigated intensively (1, 12–15), the issue is still not resolved. Highly active catalysts often contain small Au particles. Therefore, a critical issue in understanding the preparation of Au catalysts is to identify the parameters that affect Au particle size. In the preparation of supported Au catalysts, chloride-containing Au precursors are generally used (1, 2). Haruta (16) reported that the pH of the synthesis solution impacted strongly on the size of the Au particles, and catalysts with small Au particle sizes were prepared at higher pHs. He attributed this to the more facile hydrolysis of HAuCl$_4$ at a higher pH to yield precursors containing fewer Cl$^-$ ligands. In addition, he and his co-workers also (17) reported agglomeration of Au particles after they impregnated an Au/Ti–MCM-41 catalyst with CsCl. Thus the chloride content before calcination appeared to be related to the degree of agglomeration of Au particles. The work of Lin *et al.* (18) suggested that the low catalytic activities in catalysts with high chloride contents may also be due to an inhibitive effect. They prepared catalysts by introducing AuCl$_3$ onto TiO$_2$ using the incipient wetness method and observed that the CO oxidation activities for catalysts reduced with H$_2$ at 500°C was 40-fold higher than those reduced at 200°C. The improvement in catalytic property was accompanied by a threefold decrease in the residual Cl$^-$ content of the catalyst but no significant change in the particle size of Au, as determined by XRD. However, the XRD results gave only an average Au particle size, and redispersion of a small fraction of the Au particles would not be detected. Since small Au particles could be orders of magnitude more active than large particles, the difference in the activities between the samples reduced at different temperatures may still be related to particle size. Their comparative study of catalysts prepared from chloride-free and

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chloride-containing precursors introduced further ambiguity to the role of chloride as a poison. Their chloride-free catalyst had only one-sixth the activity of their chloride-containing catalyst, despite a smaller average particle size (19).

In general, the literature results to date suggest that the average Au particle size is large for catalysts with high residual Cl^- contents, but there are few details available on how Cl^- influences the evolution of the Au particle morphology. It is also not clear whether Cl^- also inhibits the catalytic activities. Therefore, the goal of this research is to provide a clearer understanding of the impact of Cl^- in order to permit a better evaluation of other factors important in the preparation of Au catalysts. Specifically, one objective of this work is to confirm the agglomeration of Au particles by Cl^- and to determine how the growth of Au particles depends on the Cl^- content. The second objective is to establish whether Cl^- has any direct effect on the catalytic activity. These are accomplished by examining the changes in Au particle size and catalytic activity when Cl^- is removed or quantitatively added to a catalyst.

The selective oxidation of CO in a H_2-rich stream (SCO) was used as the primary probe reaction in this study. Some CO oxidation study was also undertaken to compare our catalysts with those in the literature. Au/Al_2O_3 is the catalyst of choice because we have prepared samples that are as active as the well-studied Au/TiO_2 catalyst for CO oxidation (12, 15, 20) and they are stable in the very reducing atmosphere of the reformate stream (4).

SCO is a reaction important for fuel cell application (3, 4). Unlike CO oxidation, there is no deactivation with time on stream. A good SCO catalyst should selectively oxidize CO without oxidizing H_2 at temperatures close to that of the reformate stream. Au/Al_2O_3 has been shown to exhibit high selectivity for this reaction (4, 15).

Various synthesis procedures were used in the preparation of the catalysts. Some of the adopted procedures, such as deposition–precipitation at neutral pH, are known to produce small Au particles (16). The inclusion of Mg citrate in the synthesis procedure was explored in some detail, as Tsubota *et al.* observed that addition of Mg citrate in the synthesis solution appears to favor the formation of small Au particles (21).

II. EXPERIMENTAL

II.A. Preparation of Catalysts

Unless specified, the Al_2O_3 used was synthesized by hydrolysis of aluminum isopropoxide (Aldrich, 99.99+%) in the presence of the chelating agent 2-methyl-2, 4-pentanediol, as detailed previously (22).

II.A.1. Catalysts prepared with $HAuCl_4$ precursor at $0°C$ and with addition of Mg citrate. Figure 1 details the synthesis of such catalysts. Some 50 ml of an 8.4 mM $HAuCl_4$
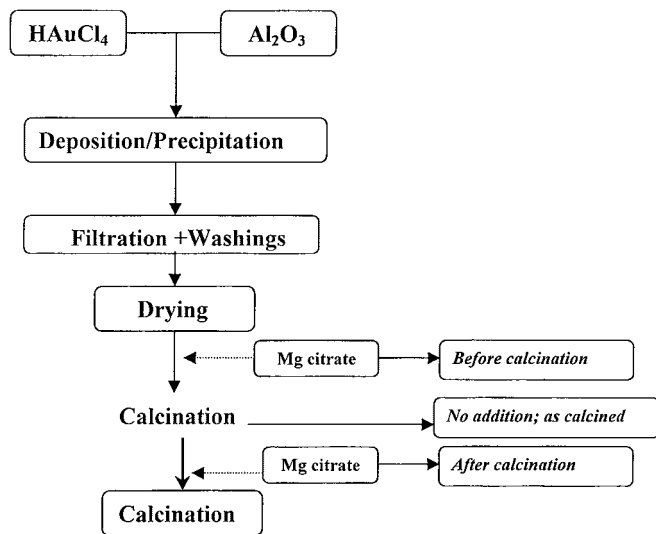

FIG. 1. Steps in the preparation of catalysts with $HAuCl_4$ precursor and with the addition of Mg citrate.

(Aldrich, 99.999%) solution was added with vigorous stirring to 2.5 g of Al_2O_3 suspended in 50 ml of doubly distilled H_2O at 0°C. In order to minimize possible light-sensitive reactions of the Au precursor, the synthesis was carried out with minimal exposure to light. The sample was then suction filtered, resuspended in 50 ml of room temperature deionized water, and suction filtered. This procedure was repeated again with 50 ml of room temperature water followed by 50 ml of warm (~50°C) water. The catalyst was dried at room temperature overnight and then calcined in a very shallow ceramic dish at 350°C.

Some of the catalysts were treated with magnesium citrate either before or after calcination. The treatment consisted of resuspending the dried or calcined catalyst in a Mg citrate solution (Mg citrate/Au = 1.6). The suspension was stirred for 1 h and then suction filtered. It was then washed with doubly distilled water twice, followed by drying and calcination at 350°C for 4 h.

II.A.2. Catalysts prepared with $HAuCl_4$ precursor at pH 7 (no Mg citrate added) and 70°C. These catalysts were prepared similarly to those in II.A.1, except that the pH of the solution was 7, the temperature at 70°C, and no Mg citrate was added. The pH was adjusted with NaOH. To avoid contamination by impurities on the electrode, the pH of the synthesis solution was monitored by removing a drop of the liquid and testing its pH with 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.

II.A.3. Catalysts prepared with Au acetate (Alfa Aesar, 99.9%) precursor. An aqueous suspension of Au acetate, containing the appropriate weight of Au, was introduced onto Al_2O_3 via incipient wetness.

II.B. Chloride Analysis

Analysis of the chloride in solution for the NaCl adsorption on Al_2O_3 experiment (Fig. 12) was usually performed using Quantab Chloride Low Range Titrators (Fisher Scientic). The accuracy of the Quantab titrator was verified using NaCl standards. The Quantab titrator is a good indicator of free chloride but its accuracy is compromised when $AuCl_xOH_{4-x}$ is also present in solution. A few of the chloride tests were conducted using both an ion electrode and a Quantab titrator, and when the pH was not extreme (chloride electrode measurement is affected by pH), the two results agreed well.

Analysis of chloride in the solid was done using H_2 temperature-programmed reduction (TPR) coupled with Fourier transform infrared spectroscopy (FTIR). For calibration, a known weight of $CuCl_2$ was placed in a reactor and reduced by heating in H_2 with a heating ramp of $10°C/min$ to $800°C$. The effluent gaseous HCl was passed into a gas cell and its concentration was monitored as a function of time using time-resolved FTIR. The sum total of the areas under the HCl IR band was plotted against the chloride content of $CuCl_2$ in the reactor to generate the calibration curve shown in Fig. 2. The chloride contents of Au/Al_2O_3 catalysts were then determined using the same procedure and the calibration curve. The technique is very sensitive and can detect chloride levels as low as 0.01 wt% using 1 g of sample. Except for a few experiments where chloride was added deliberately as HCl, the chloride in the samples was residual chloride from the Au precursor.

II.C. Catalyst Tests

For selective CO oxidation, 20–80 mg of catalyst was mixed with 0.5 g of SiC and placed in a quartz microreactor. SiC was used b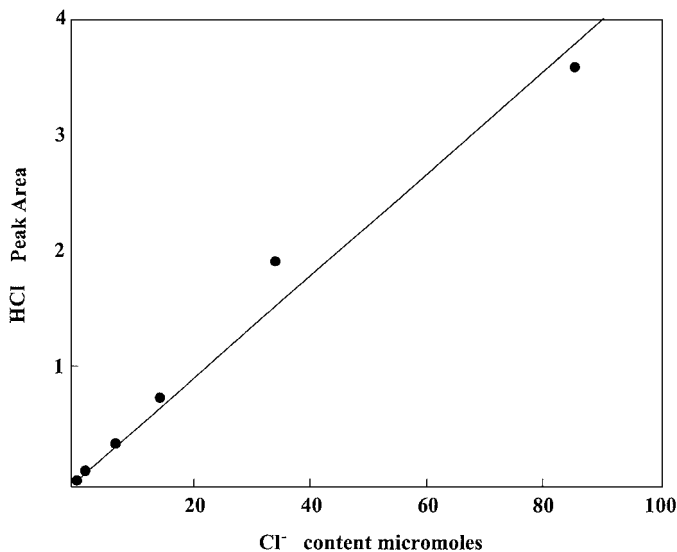ecause it is an excellent heat conductor and not reactive under these conditions. The feed was 1% CO, 0.5% O_2, 48% H_2, and balance He. A trap filled with high-surface-area oxide and kept at dry ice temperature was used to remove water in the feed. Unless specified, the feed flow rate was 90 cm^3/min and the reaction temperature was $100°C$. The products were analyzed with gas chromatography using two columns: a molecular sieve 13X column for H_2, CO, and O_2, and a Haysep Q column for H_2O and CO_2. The reported selectivity of the reaction was calculated as

$$\text{Selectivity} = \text{Rate(CO oxidation)}/2^*\text{(Rate of } O_2 \text{ consumption)}. \quad [1]$$

Selectivity could also be calculated as

$$\text{Selectivity} = \text{Rate(CO oxidation)}/\text{Rate(CO} + H_2 \text{ oxidation)}, \quad [2]$$

and usually the results of the two methods of calculation agree well.

CO oxidation was carried out in a feed stream of 1% CO, 0.5% O_2, and balance He. The water in the feed was removed by a trap containing high-surface-area oxide particles immersed in dry ice and placed close to the entrance of the reactor.

Reproducibility from run to run was reflected by the uncertainties in the activities shown in the tables. The variation of activities of the catalysts from one preparation to another was determined with a few samples to be $\pm 25\%$, where such comparisons could be made meaningfully.

II.D. Catalyst Characterization

Unless stated, all the Au loadings were determined with a Thermo Jarrell Ash Atom Scan 25 spectrometer equipped with an inductively coupled argon plasma emission source. The Au catalyst (40–80 mg) was dissolved in a mixture of 0.38 ml of 49% HF, 0.125 ml of HNO_3, and approximately 0.4 ml of HCl. It was then diluted to volume with deionized water. Aluminum AA/ICP solution and gold atomic absorption standard (Aldrich) were used for calibration.

Hitachi H-8100 was used for low-resolution imaging (60 and 300 K) analysis (Fig. 3). Hitachi HF-2000 TEM with field emission gun (FEG) at 200 kV was used for high-resolution imaging (600 K) at a point-to-point resolution better than 2.3 Å. Lattice resolution of 1 Å was used for Figs. 5 and 7.

III. RESULTS

III.A. Effect of Chloride on Au Morphology

III.A.1. Mg citrate treatment on catalysts prepared from chloride containing Au precursor. Figure 3 shows the TEM pictures of catalysts prepared from $HAuCl_4$ with no pH adjustment (pH of $HAuCl_4$ and Al_2O_3 suspension was about 4) and after they were treated with Mg citrate either before

FIG. 2. Calibration curve for residue chloride analysis.

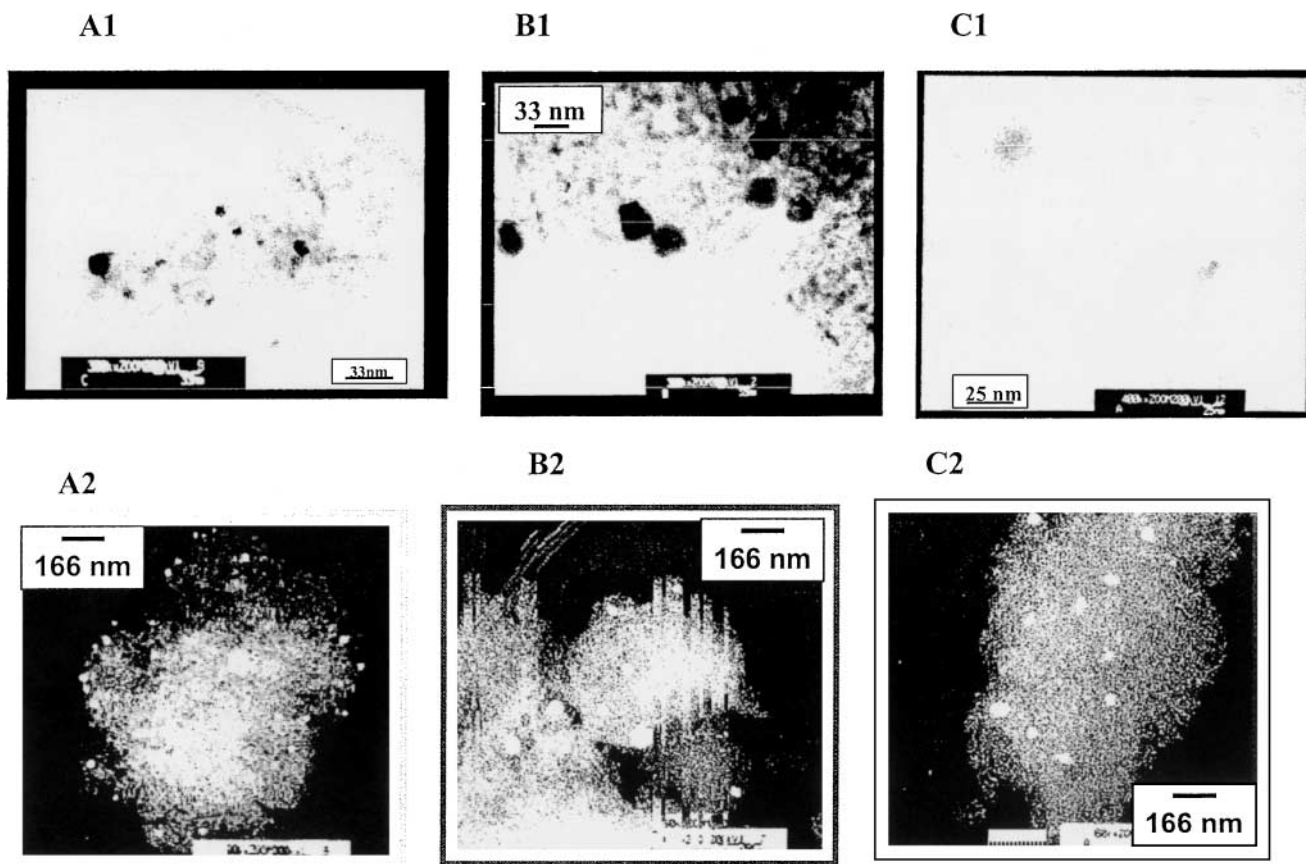**A1**

B1

C1

A2

B2

C2

FIG. 3. TEM images of catalysts prepared as detailed in Fig. 1, with the addition of Mg citrate (A) before calcination and (B) after calcination, and (C) with no Mg citrate addition.

or after calcination. Addition of Mg citrate after drying and before calcination (Fig. 3A) resulted in much smaller Au particles than when it was added after calcination (Fig. 3B) or when it was not used (Fig. 3C). Figure 4 compares the distribution of Au particle sizes of these catalysts as determined from 537, 828, and 236 Au particles for samples corresponding to Figs. 3A–C, respectively. It appears that citrate treatment before calcination resulted not only in
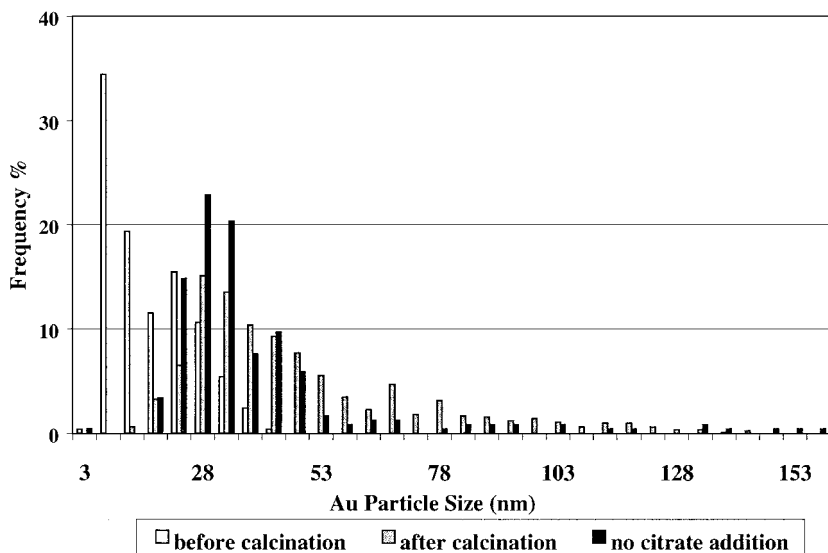
FIG. 4. Size distribution of Au particles in catalysts prepared as detailed in Fig. 1. For samples with no Mg citrate addition or addition after calcination, the few particles in the size range between 150 and 200 nm were not plotted, for the sake of clarity.

TABLE 1

Physical Characteristics and SCO Activities of Au/Al$_2$O$_3$

Mg citrate treatment	Au loading (wt%)	Average Au particle size by TEM (nm)	Residual Cl$^-$ molar ratio of Cl$^-$/Au (wt% cat.)	W/F (g-min/L)	% CO conversion	% O$_2$ conversion	CO activity[a]	O$_2$ activity[b]	Selectivity to CO$_2$
Before calcination	1.8	16.7	0.03 (0.01)	0.858	22 ± 2	79 ± 1	1.2 ± 0.1	1.7 ± 0.02	$29.8 \pm 1.4\%$
After calcination	2.0	49.6	<0.03 (<0.01)	0.858	19 ± 2.4	40 ± 1.8	0.96 ± 0.1	0.79 ± 0.04	$55.2 \pm 1.4\%$
Not treated	2.2[c]	44.6	0.98 (0.37)	0.858	1.2 ± 0.7	—	0.05 ± 0.03	—	—

Note. Catalysts prepared from HAuCl$_4$ with no pH adjustment.

[a] As derived from integral rates of reaction. Moles of CO/(moles of Au · min).

[b] As derived from integral rates of reaction. Moles of O$_2$/(moles of Au · min).

[c] Nominal value.

smaller Au particles but also narrower size distribution. There were minor differences between the sample not treated with Mg citrate and that treated with Mg citrate after calcination. The latter sample had a somewhat larger average Au particle size and broader size distribution. This was probably due to the fact that this sample was heated an additional 4 h at 350°C after the citrate treatment. There was also no redispersion of the larger Au particles to generate a new population of small Au particles when the sample was treated with citrate after calcination.

A possible role of Mg citrate is to displace the residual chloride from a dried or calcined catalyst. To test this hypothesis, 1 g of Al$_2$O$_3$ was suspended in a pH 4.5 solution containing 0.1436 mmol of Cl$^-$. The Cl$^-$ ions were readily adsorbed by the Al$_2$O$_3$, and the Cl$^-$ level in solution fell below the detectability limit. When 0.495 mmol of Mg citrate was added to the suspension, the Cl$^-$ level rose to the level before the addition of Al$_2$O$_3$ within 5 min.

Table 1 summarizes the physical characteristics of the catalysts, which include the average Au particle size as determined by TEM, Au loading, and the residual chloride level as determined by H$_2$-TPR. The residual chloride level, equivalent to one chloride per Au, was the highest in the sample without Mg citrate treatment. Mg citrate was very effective in removing chloride from the catalysts, as the Cl$^-$/Au ratio was 0.03 for the sample treated with citrate before calcination and less than this amount (below the limit of quantitative determination) for the sample treated after calcination. Since all the catalysts had similar Au loadings and differed only significantly in their chloride content, it appears that elevated temperature induced the agglomeration of Au in the presence of high residual chloride.

III.A.2. Chloride addition to calcined catalysts with little or no chloride. To further examine the effect of chloride on Au particle size, chloride was added as a postsynthe-

sis treatment to calcined catalysts. Two types of catalysts were examined. In the first series of experiments, chloride was added to catalysts prepared with a chloride-free precursor and, in the second, to catalysts prepared under conditions where residual chloride content should be low.

Figure 5A shows the TEM photographs of Au/Al$_2$O$_3$ prepared using an Au acetate precursor. The Au particles shown in these pictures were representative of the majority of the particles present. They were small and generally well separated from one another. However, occasionally, there were a few scattered clusters of larger Au particles, as shown in Fig. 5B. The presence of clusters of larger Au particles was probably due to the fact that Au acetate is only sparingly soluble in water. Thus, some solid particles of Au acetate were introduced onto Al$_2$O$_3$ during impregnation. While some of the Au particles looked distinctly nonspherical (e.g., Fig. 5A, c2), the quality of the pictures did not permit us to determine their shapes with certainty. The average particle size (Table 2) of the as-calcined, further heat treated, and chloride-treated samples were 4.8, 5.8, and 7.9 nm, respectively, and the particles counted to obtain these values ranged from 148 to 223 particles. Figure 6 shows the size distribution of these catalysts. The clusters of larger Au particles were not plotted in this graph, for clarity, and also because they were very scarce and far between. The average Au particle size of the chloride-treated sample had almost doubled and the population distribution broadened relative to the parent catalyst. Although this sample was heated for 4 h at 350°C after the addition of chloride, the agglomeration was primarily the effect of chloride because the increase in Au particle size of the sample subjected to an identical heat treatment of the calcined catalyst was significantly less.

Similar increases in average Au particle size by Cl$^-$ addition (Figs. 7 and 8) were observed for catalysts prepared with HAuCl$_4$ precursor at pH 7 and 70°C. These synthesis
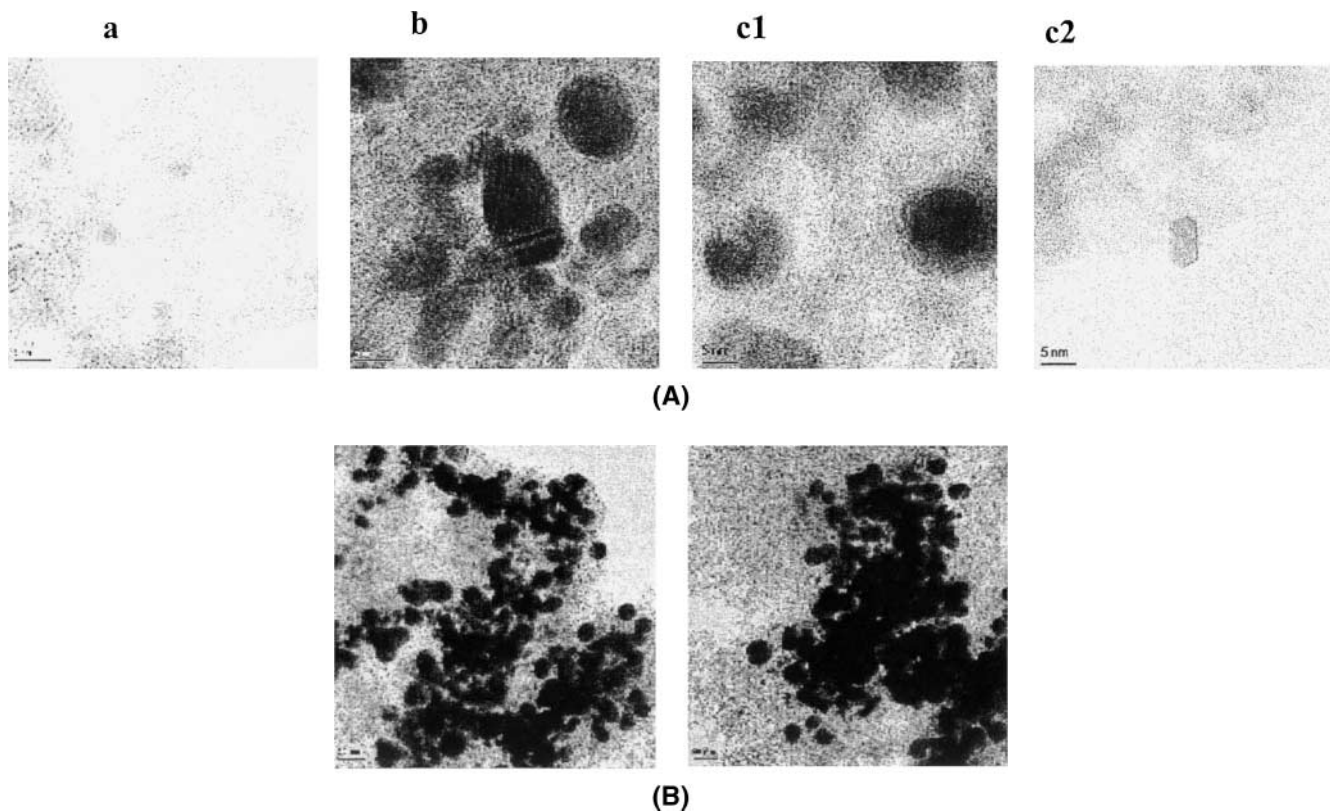
FIG. 5. (A) TEM images of Au/Al₂O₃ prepared from Au acetate precursor: (a) as calcined, (b) additional 4 h calcinations at 350°C, and (c1 and c2) catalyst with 0.3 wt% Cl added (Cl/Au = 0.15) and then calcined at 350°C for 4 h. The scale bar is 5 nm. (B) TEM images of Au/Al₂O₃ prepared from Au acetate precursor from two observed clusters. The scale bar is 50 nm.

conditions minimized the residual chloride on the catalysts due to replacement of chloride ligands with hydroxide ligands (23) and suppression of Cl^- adsorption on Al_2O_3. It is interesting that most of the agglomeration of Au induced by the presence of chloride took place at the low temperature of 100°C (Table 3).

The location of the added chloride in the sample prepared with Au acetate precursor was examined by Cl K-edge absorption in XANES, which is due to the s–p transition at 2.833 keV. For Cl^- bonded to a transition metal atom, there is mixing of the metal d orbital with the Cl 3p orbital, giving rise to the pre-edge absorption at 2.828 keV and this was clearly seen for the $HAuCl_4$ standard (Fig. 9A, curve a). For an Au/Al₂O₃ sample prepared with $HAuCl_4$ at low pH such that the residual $Cl^- = 0.4$ wt% (Cl^-/Au of unity), the pre-edge absorption was distinctly observable (Fig. 9A, curve b). The pre-edge absorption was absent in the catalyst prepared with the acetate precursor (Fig. 9B, curve c). For the sample with added chloride (Cl/Au = 0.15) there was again no clearly detectable pre-edge absorption, although there was K-edge absorption, indicating the presence of chloride in the sample (Fig. 9B, curve b).

TABLE 2

Physical Characteristics and SCO Activities of Au/Al₂O₃ (1.1 wt% Au Loading) Prepared with Au Acetate Precursor

Catalysts prepared with acetate precursor	Average Au particle size[a] (nm)	Molar ratio Cl^-/Au (wt% cat.)	W/F (g-min/L)	% CO conversion	% O_2 conversion	CO activity[c]	O_2 activity[d]	Selectivity to CO_2
Calcined	4.8	5.3×10^{-4b}	0.075	28 ± 1	66 ± 2	28 ± 0.2	33 ± 1	42 ± 1
+350°C (4 h)	5.8	5.3×10^{-4b}	0.233	26 ± 1	60 ± 3	8.2 ± 0.3	9.6 ± 0.5	43 ± 1
+Cl + 350°C (4 h)	7.9	0.15	0.911	28 ± 1	69 ± 1.5	2.3 ± 0.1	2.8 ± 0.05	39 ± 1
		(0.03)	0.229	13 ± 0.5	28 ± 1	4.1 ± 0.2	4.6 ± 0.2	43 ± 1

[a] Determined from TEM.
[b] Manufacturer's specification.
[c] As derived from integral rates of reaction. Moles of CO/(moles of Au · min).
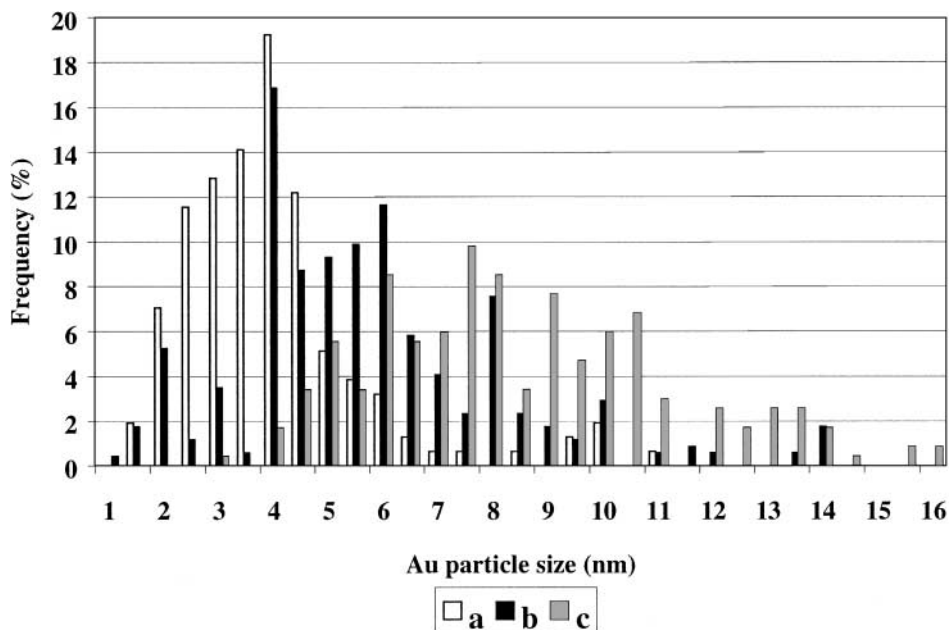[d] As derived from integral rates of reaction. Moles of O_2/(moles of Au · min).

FIG. 6. Size distribution of Au particles on Au/Al$_2$O$_3$ prepared from Au acetate precursor. Sample labeled as in Fig. 5.

III.B. Catalytic Properties

The effect of chloride on the SCO activity was examined for the catalysts listed in Tables 1–3. The catalysts in Table 1 were designed to see the changes in the catalytic property upon removal of residual chloride. It was observed that the oxidation activities of the catalyst that contained high residual chloride were very poor, but improved greatly after chloride removal with Mg citrate treatment. The CO oxidation activities in SCO of catalysts treated with Mg citrate were more than an order of magnitude higher than the parent catalyst. Furthermore, Mg citrate treatment before calcination resulted in catalysts with the highest oxidation activities.

The other sets of experiments were designed to see the effect of chloride addition. The impact of chloride addition to catalysts prepared with Au acetate is shown in Table 2. The CO oxidation activity of the parent acetate catalyst was nearly 30 times better than the active catalysts in Table 1. Additional heating of the parent catalyst decreased the activity by over three times compared under similar O$_2$ conversions. Addition of chloride decreased the activity by more than 10 times.
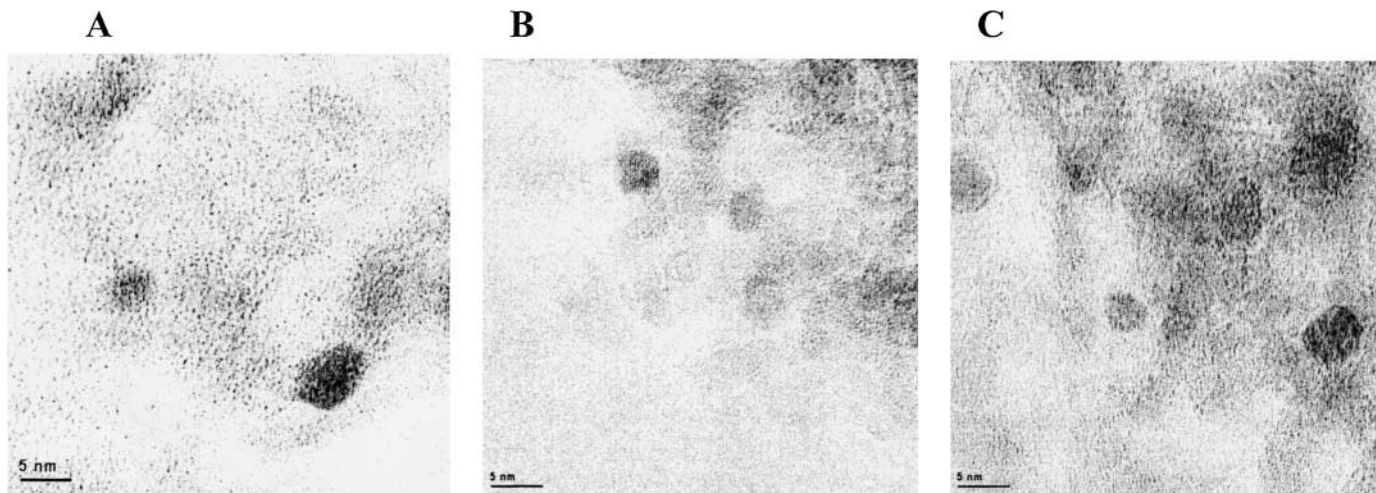

FIG. 7. TEM images of Au/Al$_2$O$_3$ prepared by hydrolyzing HAuCl$_4$ at pH 7 and 70°C. (A) as calcined; (B) catalyst with 0.3 wt% Cl added (Cl/Au = 0.15) and then heated at 100°C for 1 h; and (C) catalyst with 0.03 wt% Cl added (Cl/Au = 0.15) and then heated at 350°C for 4 h. The scale bar is 5 nm.

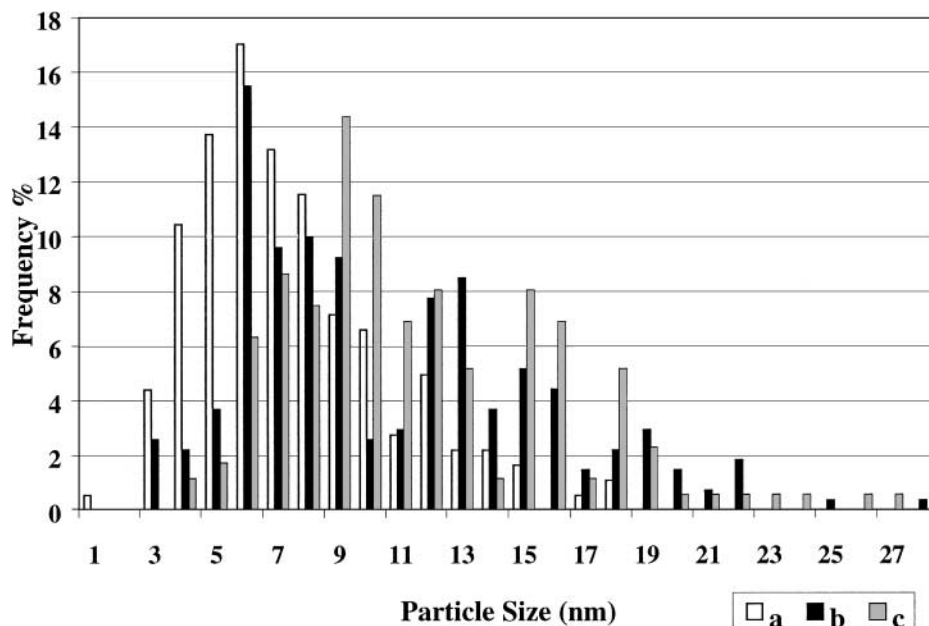**FIG. 8.** Size distribution of Au particles on Au/Al$_2$O$_3$ prepared from HAuCl$_4$ at pH 7 and 70°C. Sample labeled as in Fig. 7.

Similarly, addition of chloride to the catalyst prepared with HAuCl$_4$ at high pH and a higher temperature (Table 3) resulted in a decrease in activity. The decrease was less when the sample was heated to only 100°C after the chloride addition than when the sample was heated to 350°C. The CO oxidation activity, in the absence of H$_2$, of the as-calcined catalyst was also examined to better compare it with literature results. The steady-state CO oxidation activity at room temperature was 0.046 mol of CO mol^{-1} of Au-s, and compared favorably with the best catalysts reported in the literature for Au/TiO$_2$, Au/Al$_2$O$_3$, and Au/SiO$_2$ (20, 24).

The selectivity to CO$_2$ formation, which is a measure of the relative rates of oxidation of CO to oxidation of H$_2$, generally ranged from 40 to 55%. The selectivities depended only weakly on conversions, as can be seen from Fig. 10.

The effect of chloride on the activity was actually more pronounced than can be seen from the steady-state data reported in Tables 2 and 3. Catalysts without addition of chloride generally reached a steady state rather rapidly after introduction of the feed (Fig. 11, curve a). On the other hand, a sample with added chloride (0.15 Cl/Au) showed very little activity initially. The activity gradually increased over the next 150 min until it reached a steady state (Fig. 11, curve b). At a higher Cl/Au ratio of 0.3, a Au/Al$_2$O$_3$ prepared by the deposition–precipitation method at pH 7 and 70°C did not reach a steady state after 800 min on stream. Thus the time needed to reach a steady state appeared to be related to the amount of chloride added. This gradual increase in activity after the introduction of the feed may be related to the redistribution of chloride anions between the Au and Al$_2$O$_3$ surface sites under reaction conditions. To examine this aspect of chloride migration, a chloride-free sample was tested in a physical mixture with Al$_2$O$_3$ (Fig. 11, curve c) and the presence of Al$_2$O$_3$ did not have much effect on the activity of the Au sample. However, if the Al$_2$O$_3$ was first impregnated with 0.72 wt% Cl$^-$, a significant

TABLE 3

Chloride Effect on Au/Al$_2$O$_3$ (Au Loading $=$ 1.0 wt%) Prepared by Deposition–Precipitation at pH 7 and 70°C

Catalysts	Average Au particle size (nm)[a]	Molar ratio of added Cl$^-$/Au (wt% cat.)	W/F (g-min/L)	% CO conversion	% O$_2$ conversion	CO activity[b]	O$_2$ activity[b]	% CO$_2$ selectivity
Calcined	8	—	0.06	32 ± 1	61 ± 2	42 ± 1	40 ± 1	54 ± 1
			0.04	26 ± 1	48 ± 1.5	51 ± 2	48 ± 1.5	54 ± 1
Chloride added and then 100°C 1 h	11.2	0.15 (0.03)	0.11	24 ± 1	51 ± 1.5	24 ± 1	19 ± 0.5	47 ± 1
Chloride treated and heated 350°C 1 h	12.3	0.15 (0.03)	0.24	18 ± 0.7	44 ± 1	6 ± 0.2	7.5 ± 0.2	41 ± 1

[a] Number of particles counted were 267, 166, and 173 for calcined, for chloride treated and heated to 100°C, and for chloride treated and heated to 350°C.
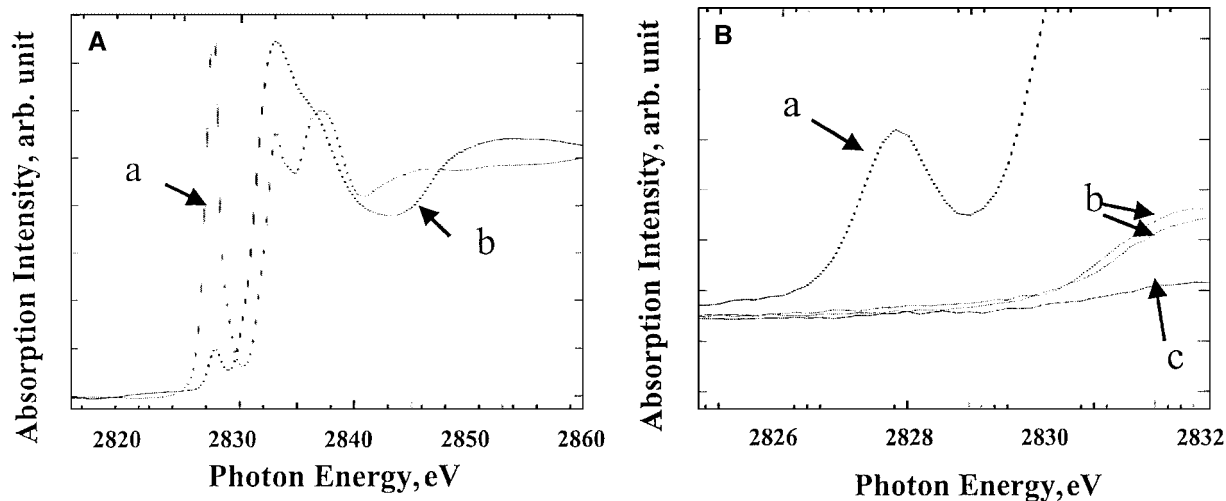
[b] As defined in Table 1.

FIG. 9. (A) Cl K-edge absorption. (a) $HAuCl_4$; (b) Au/Al_2O_3 containing 0.4 wt% Cl prepared by deposition–precipitation method with $HAuCl_4$ at low pH. (B) Cl K-edge absorption. (a) Au/Al_2O_3 containing 0.4 wt% Cl prepared by deposition–precipitation method with $HAuCl_4$ at low pH; (b) duplicate runs of catalyst with 0.03 wt% Cl added (Cl/Au $= 0.15$); and (c) Au/Al_2O_3 prepared from Au acetate precursor.

effect was observed. Although a high catalytic activity was reached rapidly, it declined with time on stream (Fig. 11, curve d), indicating gradual poisoning of the active site.

III.C. Phosphate-Treated Catalysts

Since most of the added Cl^-, as indicated by the XANES result in Fig. 9, was associated with the alumina support, experiments were conducted to attempt to maximize the inter-

action of Cl^- with the Au active site in order to more clearly define the role of chloride. Figure 12 shows that the Cl^- uptake by the Al_2O_3 support could be significantly suppressed if the surface was first impregnated with phosphate anions (200 μmol per gram of Al_2O_3, using a mixture of KH_2PO_4 and H_3PO_4 at pH 4.5). In particular, beyond pH 6.5, chloride uptake by the alumina became insignificant. When a catalyst, prepared in a manner similar to that of the parent sample in Table 3, was impregnated with phosphate
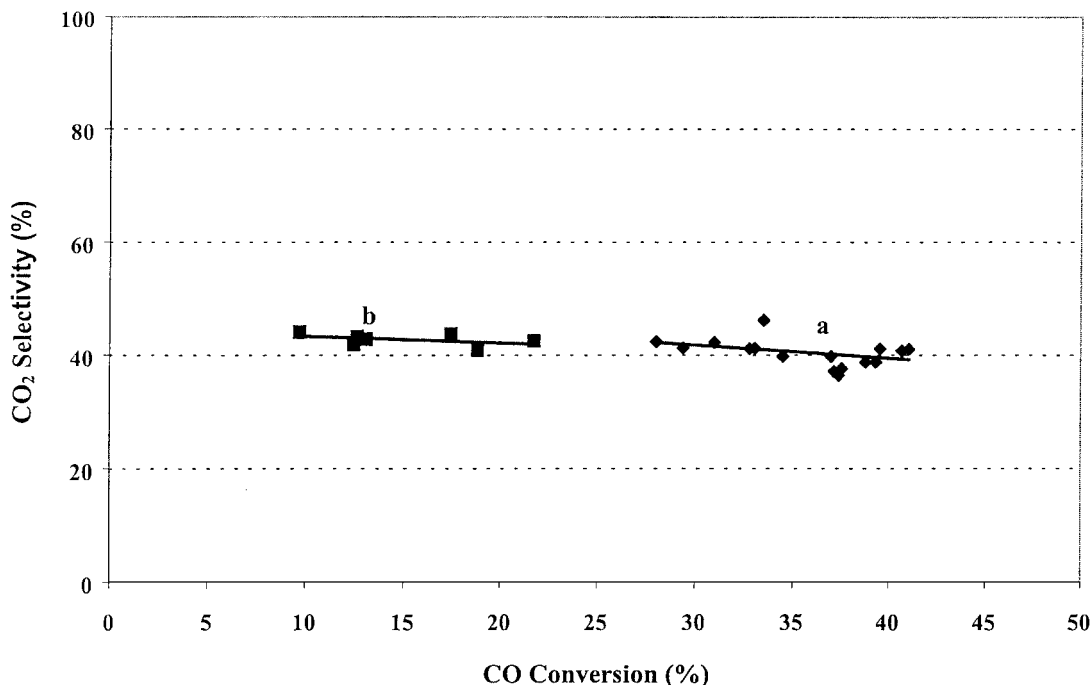

FIG. 10. Selectivity versus conversion for Au/Al_2O_3 catalyst prepared from acetate precursor (Table 2). (a) no Cl^- added and (b) chloride added (0.15 Cl/Au). Feed composition: 1% CO, 0.5% O_2, 49.3% H_2, balance He. Temperature, 100°C.
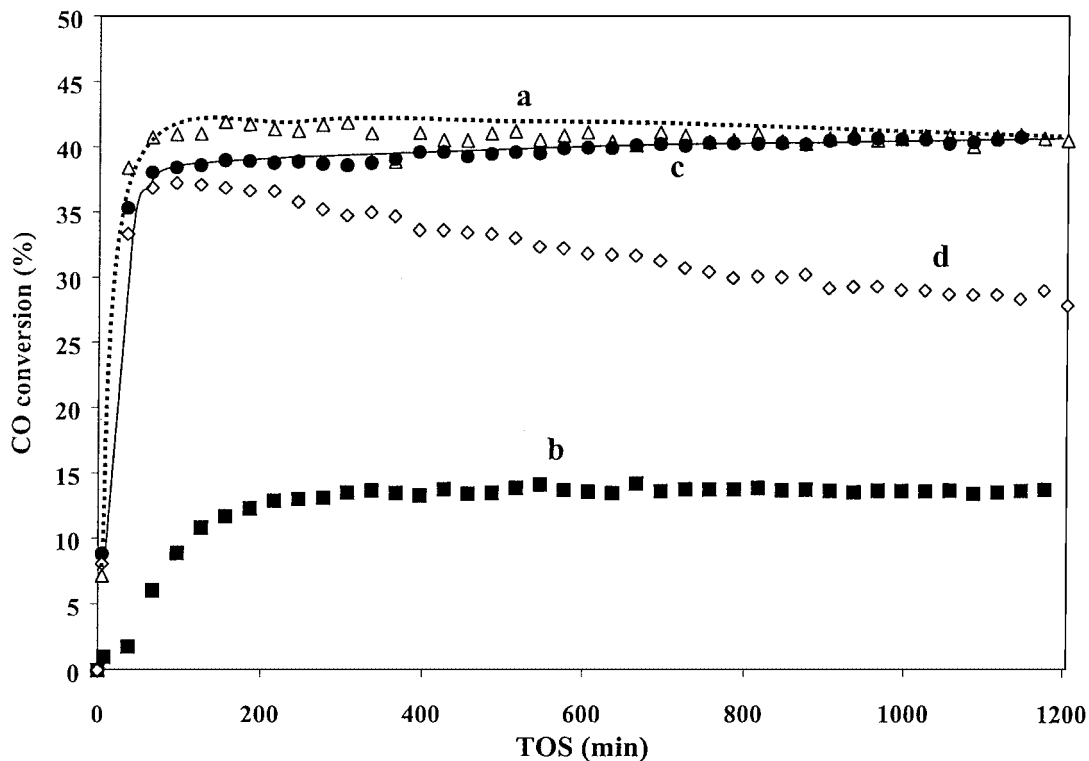
FIG. 11. Time-on-stream plot of CO conversion over 0.02 g of Au/Al$_2$O$_3$ prepared from Au acetate: (a) as calcined; (b) 0.03 wt% Cl$^-$ added as a mixture of NH$_4$OH and HCl at pH 5.5; (c) mixed with 0.02 g of Al$_2$O$_3$; and (d) mixed with 0.02 g of Al$_2$O$_3$ that contained 0.72 wt% Cl. Feed composition: 1% CO, 0.5% O$_2$, 49.3% H$_2$, balance He. Temperature, 100°C.
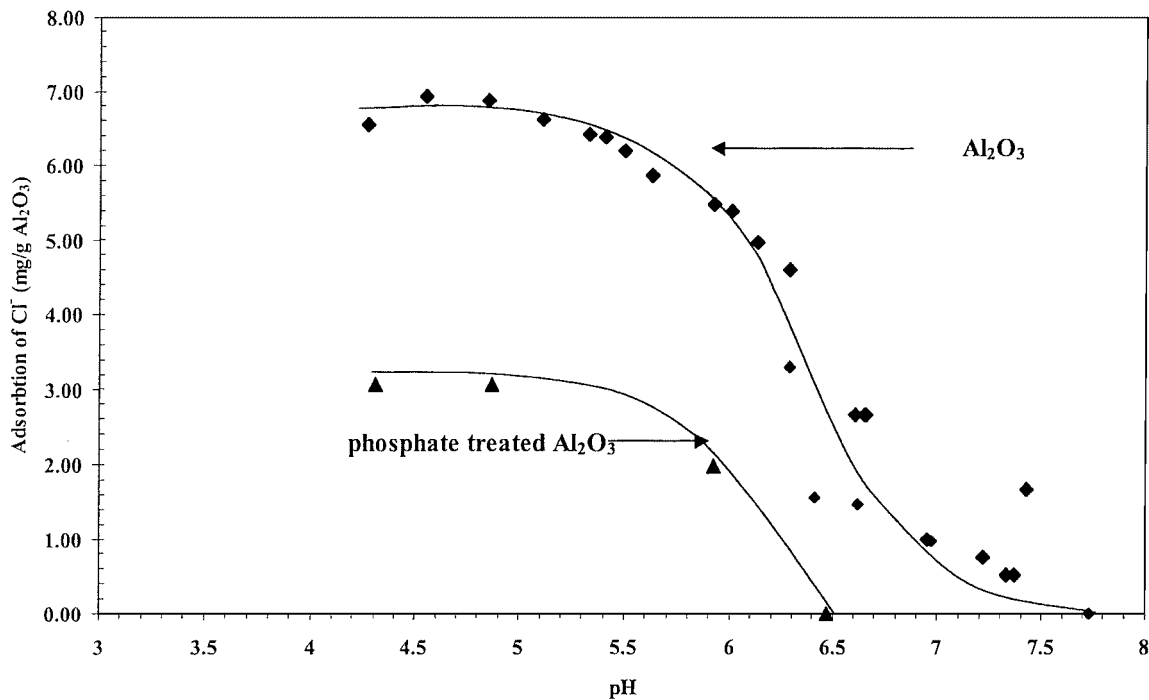

FIG. 12. Cl$^-$ uptake by Al$_2$O$_3$ and phosphate-treated Al$_2$O$_3$ (phosphate loading = 200 μmol/g of Al$_2$O$_3$); 0.5 g of Al$_2$O$_3$ or phosphate-treated Al$_2$O$_3$ in 20 ml of solution containing 291 ppm Cl$^-$. pH adjusted with NaOH.
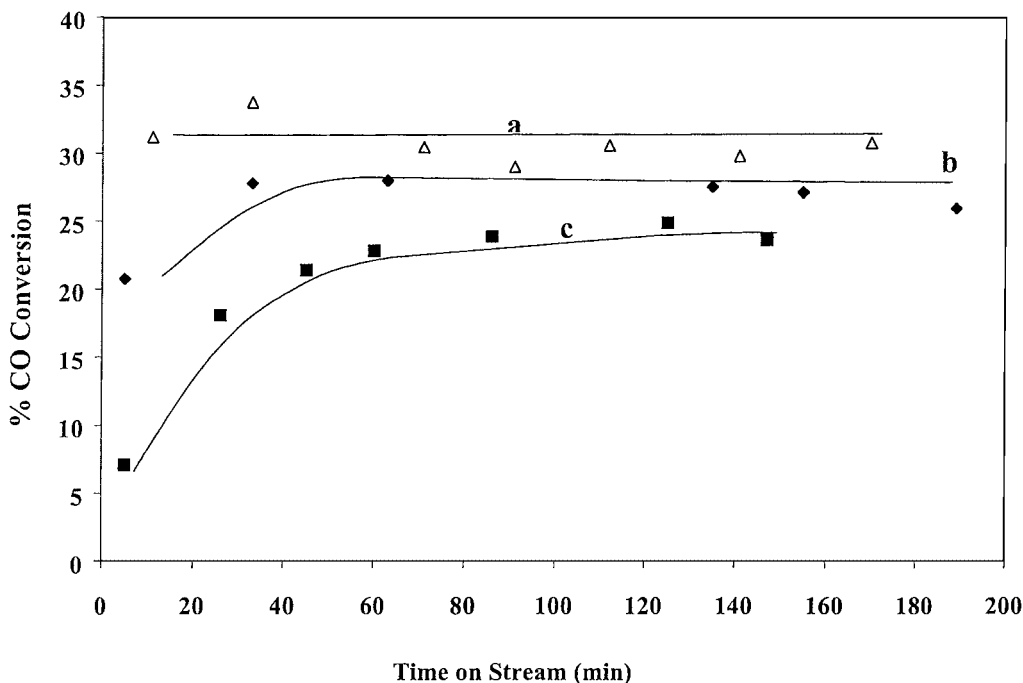
FIG. 13. Time-on-stream plot of CO conversion over 0.02 g of Au/Al$_2$O$_3$ prepared with HAuCl$_4$ at pH 7 and 70°C. (a) Catalyst with phosphate (4 phosphate/Au); (b) sample a with Cl$^-$ added (Cl/Au $= 0.0006$); and (c) sample a with Cl (Cl/Au $= 0.01$). Feed composition: 1% CO, 0.5% O$_2$, 49.3% H$_2$, balance He. Temperature, 100°C.

(phosphate to Au, ∼4), the CO conversion declined by one-third. The actual decline in activity would be higher since the conversions were high for the parent sample. When Cl$^-$ was added to the phosphate-treated Au/Al$_2$O$_3$ catalyst, a further decline in activity was seen, as shown in Fig. 13. An addition of Cl/Au $= 0.01$ suppressed the initial activity almost completely (curve c), although a significant portion of the loss was recovered with time. This recovery was similar to that observed for other Cl$^-$-treated samples. The suppression of activity was evident even when only a very small amount of chloride was added (curve b, Cl/Au $= 0.0006$). For these experiments, the chloride was added as NaCl at pH 7.

IV. DISCUSSION AND CONCLUSION

The results reported here clearly established the dual role of Cl$^-$ in suppressing the SCO activity of a Au/Al$_2$O$_3$ catalyst: accelerating the agglomeration of Au particles and poisoning the active sites. Au particles agglomerate faster at elevated temperatures in the presence of chloride. This can be seen from the data in Figs. 3 and 4, which show that the Au particle size of a catalyst washed with Mg citrate after drying is significantly smaller than if the washing is carried out after calcination. Furthermore, the agglomeration is less severe for a sample with less chloride (comparing sample with 0.15 Cl/Au in Tables 2 and 3 to that with Cl/Au $= 0.98$ in Table 1).

Chloride poisoning of the active sites is best illustrated by the experiments where chloride is removed from the catalyst by citrate. As shown in Table 1, starting with a parent sample, the activity of the catalyst can be increased by nearly 20-fold by removing the chloride, even though there is no detectable change in the average particle size of Au. The reverse experiment of adding chloride to an active catalyst provides additional support. As shown in Fig. 11, the initial activity of a sample containing added chloride is quite low, and the transient to reach a steady state is much slower than the sample without chloride. As discussed later, we believe that the transient is due to removal of the chloride from the active site by hydrolysis. Thus, the effect of chloride on the steady-state activity is less obvious.

Due to the high affinity of the alumina support for chloride, the overall chloride content in the sample may not be a definitive indicator of its catalytic activity. That is, how the chloride is introduced to the catalyst may influence its effect on the activity. The XANES results in Fig. 9 show that the chloride introduced by impregnation resides mostly on the support and is not associated with Au. Thus, a relatively high chloride content is needed for a significant effect on the activity. On the other hand, if the sample is first impregnated with phosphate to occupy the adsorption sites of alumina, the addition of a minute amount of chloride already has an effect (Fig. 13).

The evaluation of the effect of chloride on the activity is further complicated by the mobility of chloride in the

presence of moisture. The mobility is demonstrated in the experiment shown in Fig. 11. The activity of the physical mixture of a catalyst with chloride-containing alumina decreases with increasing time on stream. We postulate that the increase in activity of chloride-containing catalysts with time on stream is due to displacement of chloride at the active site by water, or more specifically hydroxyl. This follows from our postulate of the nature of the active site for CO oxidation, which is an ensemble consisting of Au^+–OH^- surrounded by Au atoms (12, 15). Poisoning by chloride is due to the formation of Au^+–Cl^-. Water can hydrolyze this bond, regenerating the Au^+–OH^- center. Although water was not added as part of the feed for the SCO reaction, it was formed as a product of oxidation of hydrogen.

The fact that residual Cl^- can impact the catalytic properties of supported Au catalyst in more than one way is a possible reason that the reported performances of Au catalysts are very among different research groups (11), and why apparently inconsequential changes in synthesis variables sometimes have deleterious effects. The pH of the synthesis solution is important not only in determining the speciation of $AuCl_x(OH)_{4-x}^-$ and the amount of Au adsorbed on the catalyst, it also influences the amount of chloride adsorbed on the support, as can be seen from Fig. 12. The amount of adsorbed chloride on a support depends on the isoelectric point of the support and its adsorption capacity. Thus, the required conditions for the synthesis of an active catalyst may be more stringent for some supports than others. Although Al_2O_3 has an IEP close to 8 and competitive adsorption of the anionic $Au(OH)_{4-x}Cl_x$ with Cl^- is inevitable, discrimination of the interaction of these two anions with Al_2O_3 is possible. Cl^- adsorption is by electrostatic attraction and has little temperature dependence. On the other hand, in the preparation method of deposition–precipitation, the interaction of Al_2O_3 with $Au(OH)_{4-x}Cl_x^-$ is also by ligand substitution (25), which is temperature dependent. This explains why preparation at a higher temperature is desirable.

Understanding the chloride effect generated here will permit a better control of variables important in catalyst preparation. The high affinity of Cl^- for the Au active site suggests that the active site is partly cationic in nature. The suppression observed at a Cl/Au molar ratio as low as 0.0006 also suggests that the number of active sites per mole of Au is very low. In view of the high catalytic activity of these catalysts, the activity per active site must be extremely high. Thus, increasing the density of the active sites is a challenge for this area of research.

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