

Effective Au-Au⁺-Cl_x/Fe(OH)_y catalysts containing Cl⁻ for selective CO oxidations at lower temperatures

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Abstract

Supported Au catalysts Au-Au⁺-Cl_x/Fe(OH)_y ($x < 4$, $y \leq 3$) and Au-Cl_x/Fe₂O₃ prepared with co-precipitation without any washing to remove Cl⁻ and without calcining or calcined at 400 °C were studied. It was found that the presence of Cl⁻ had little impact on the activity over the unwashed and uncalcined catalysts; however, the activity for CO oxidation would be greatly reduced only after Au-Au⁺-Cl_x/Fe(OH)_y was further calcined at elevated temperatures, such as 400 °C. XPS investigation showed that Au in catalyst without calcining was composed of Au and Au⁺, while after calcined at 400 °C it reduced to Au⁰ completely. It also showed that catalysts precipitated at 70 °C could form more Au⁺ species than that precipitated at room temperatures. Results of XRD and TEM characterizations indicated that without calcining not only the Au nano-particles but also the supports were highly dispersed, while calcined at 400 °C, the Au nano-particles aggregated and the supports changed to lump sinter. Results of UV-vis observation showed that the Fe(NO₃)₃ and HAuCl₄ hydrolyzed partially to form Fe(OH)₃ and [AuCl_x(OH)_{4-x}]⁻ ($x = 1-3$), respectively, at 70 °C, and such pre-partially hydrolyzed iron and gold species and the possible interaction between them during the hydrolysis may be favorable for the formation of more active precursor and to avoid the formation of Au-Cl bonds. Results of computer simulation showed that the reaction molecular of CO or O₂ were more easily adsorbed on Au⁺ and Au⁰, but was very difficultly absorbed on Au⁻. It also indicated that when Cl⁻ was adsorbed on Au⁰, the Au atom would mostly take a negative electric charge, which would restrain the adsorption of the reaction molecular severely and restrain the subsequent reactions while when Cl⁻ was adsorbed on Au⁺ there only a little of the Au atom take negative electric charge, which resulting a little impact on the activity.

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1. Introduction

Supported Au catalysts have been studied extensively for many years since it was reported that these catalysts were exceptionally active for CO oxidation at low temperatures [1–14]. Co-precipitation methods have been particularly utilized to obtain an active metal oxide supported Au catalyst, in which chloroauric acid has been almost the only precursor available in large quantities at a reasonable cost since precursors based on organic complexes of Au tend to be costly and unstable. However, Cl⁻ in these catalysts has been considered to have strongly deleterious effect on the activity in oxidation of CO, although, up to present, the detailed interaction mechanism between Au species and Cl⁻ is still not

clear. The fact that residual Cl⁻ can impact the catalytic properties of supported Au catalysts in more than one way has been a possible reason that the reported performance of Au catalysts were varied among different research groups. Since Cl⁻ has been considered to act as a catalyst poison, it has led to an indispensable, troublesome and water-consuming washing procedure. Due to the reason as mentioned above, a large amount of distilled water (e.g. ca. 1000 kg water would be consumed for washing 1 kg gold catalyst precursor) are generally needed to wash the chloride away from the resulted precipitates during the gold catalyst preparation so as to obtain a active gold catalysts for CO oxidation. In view of sustainable chemistry, such method of catalyst preparation is totally unacceptable.

On the other hand, metal oxide as support obtained by being calcined at elevated temperature was regarded as another important factor for the high catalyst activity [5]. Au nano-particles dispersed on metal oxide have the highest activity and

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the metal oxide support could participate in the reaction and/or stabilize the active Au species [15]. However, calcining at elevated temperatures to form oxide are processes of time and energy consuming and releasing polluted gases, such as NO_x , HCl, etc. Several papers have reported that Au catalysts prepared with co-precipitation and then calcined at relatively mild temperature were more active than those calcined at elevated temperatures [16–21]. Hutchings's and Gavrilidis' groups had, respectively, found that ferric oxides and manganese oxides supported gold catalysts prepared with co-precipitated without being calcined and only dried at about 100 °C could also have higher activity [22,23]. Our previous investigation showed that ferric hydroxide supported Au catalysts prepared without any heat treatment could be highly effective catalysts for CO oxidation in air and for selective CO oxidation in the presence of H_2 [24]. But none of the above works have been correlative to the effect of Cl^- on the catalytic performance.

In this work, an attempt was made to prepared ferric hydroxide supported Au catalysts containing relatively large amount of Cl^- through a modified co-precipitation method, in which traditional water-washing and calcinations were omitted. These catalysts exhibited enough high activity for CO oxidation in air and selective oxidation in the presence of H_2 in comparison with the standard supported Au catalysts prepared by the World Gold Council.

2. Experiment

2.1. Preparation procedure of supported Au catalysts

All chemicals used in the experiments were analytical grade, and were used without further purification. Catalysts were prepared by co-precipitation of aqueous solutions of HAuCl_4 and $\text{Fe}(\text{NO}_3)_3$ with an aqueous solution of Na_2CO_3 . At 70 °C, aqueous of 10% Na_2CO_3 (mass) was added slowly to the mixture of aqueous solutions of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (0.24 M) and $\text{Fe}(\text{NO}_3)_3$ (1.0 M) with vigorous stirring until pH to ca. 10. The resulted precipitates were filtrated and dried at ambient temperature and atmospheric pressure for 24 h without any water-washing. The resulted solids without further heat treatment and used as catalysts directly were denoted as Au/Fe-UW-UC. For comparison purpose, the catalysts Au/Fe-UW-UC were further calcined in air at 200 °C (denoted as Au/Fe-UW-C2) and 400 °C (Au/Fe-UW-C4), respectively. Catalysts of Au/Fe-W-C4 and Au/Fe-W-UC were also prepared as this procedure except that the precipitates were washed with distilled water before dried and calcined at 400 °C or without calcined. It was found that the temperatures of aqueous solutions of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3$ during precipitation had some impact on the catalytic performance, therefore the co-precipitation processes for the preparation of catalysts Au/Fe-UW-UC and Au/Fe-UW-C4 were also proceeded at room temperature (about 20 °C). It should be noted that, in spite of the same amount of gold precursor was used, the different calcination temperature and with or without washing result to a little differences in gold loadings.

2.2. Characterization techniques

Au loadings in the catalyst samples were measured using a 3520 ICP AES instrument of ARL Co., USA. Due to water losing and support transforming from hydroxide to oxide, it should be noted that different Au loadings were resulted between uncalcined and calcined, washed and unwashed samples, although the same quantity of gold precursors were initially charged.

BET surface areas were obtained by physisorption of N_2 at 77 K using a Micromeritics ASAP 2010. The catalyst samples prepared without any further calcination were outgassed to 0.1 Pa at 50 °C so as to insure no changes in the support structure.

The surface compositions of the catalysts were examined with XPS (VG ESCALAB 210 instrument). Mg $\text{K}\alpha$ radiation at a pass energy of 150 eV at an energy scale calibrated versus C 1s at 284.4 eV were used. The surface compositions of the samples were determined from the peak areas of the corresponding lines using a Shirley-type background and empirical cross section factors for XPS.

X-ray diffraction was performed on a Siemens D/max-RB powder X-ray Diffractometer. Diffraction patterns were recorded with Cu $\text{K}\alpha$ radiation (40 mA, 40 kV) over a 2θ range of 15–70°. Transmission electron microscopic investigations were carried out using a JEOL JEM-1200EX electron microscope. The powder of Au catalysts was suspended in toluene with an ultrasonic dispersion for 5–10 min and then the resulted solution was dropped on a carbon film of copper grid.

UV–vis observation of the HAuCl_4 and $\text{Fe}(\text{NO}_3)_3$ solution before and after being heated at 70 °C were record with a Agilent 8453 UV–vis spectrophotometer. UV–vis absorption spectra were taken using 1 cm path length quartz cuvette. 1×10^{-3} M HAuCl_4 solutions heated at 70 °C for 30 s, 1 and 2 min and without heat treatment were investigated, respectively. 0.1 M $\text{Fe}(\text{NO}_3)_3$ solutions heated at 70 °C for 2 min, without heated at 20 °C and adjusted with 0.1 M NaCO_3 at 20 °C were also investigated, respectively.

2.3. Measurements of catalytic activities

Catalytic activity measurements were carried out in a micro fixed-bed reactor with 100 mg of catalyst sieved to 60 and 80 mesh. Before measurements, catalysts were treated with feed gas of 1% CO in air at 70 °C for 30 min. The feed gas for the oxidation was 1 vol% CO or 1 vol% H_2 balanced with air. For selective oxidation, the feed gas was 1 vol% CO and 1 vol% H_2 and 4 vol% O_2 balanced with argon. The flow rate was 20 ml/min (space velocity was $12,000 \text{ ml h}^{-1} \text{ g}^{-1}$ cat, a typical space velocity adopted generally for CO oxidation over the supported Au catalysts in the previously reported literatures [25,26]). The concentrations of CO and H_2 and O_2 in the effluent gas were on-line analyzed by a gas chromatograph (Agilent 1790T, molecular sieve 5A plot column) using Argon as the carrier gas. To benchmark the activity measurements system, 4.4 wt% Au/ Fe_2O_3 catalysts prepared by World Gold Council (denoted as TYPE C Au/ Fe_2O_3) were also tested under same reaction conditions.

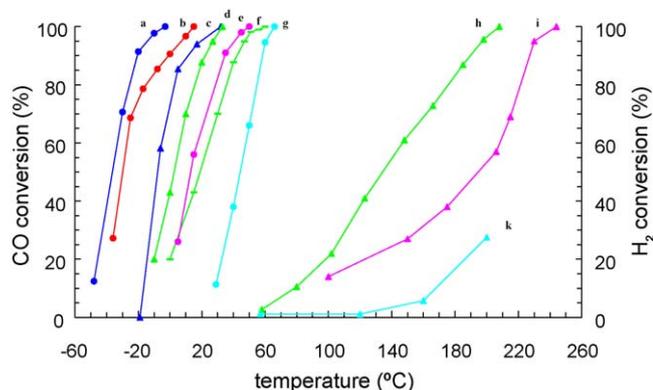


Fig. 1. Oxidations of CO in air. (a and c) 4.1 wt% Au/Fe-W-UC 4.6 wt% Au/Fe-W-C4; (b) 4.4 wt% TYPE C Au/Fe₂O₃; (d, f and h) 4.6 wt% Au/Fe-UW-UC, 5.1 wt% Au/Fe-UW-C2 and 5.6 wt% Au/Fe-UW-C4; (e and i) 2.2 wt% Au/Fe-UW-UC and 2.6 wt% Au/Fe-UW-C4; (g and k) 2.2 wt% Au/Fe-UW-UC and 2.6 wt% Au/Fe-UW-C4 precipitated at 20 °C.

3. Results

3.1. Measurements of catalytic activities for oxidations of CO and H₂

Over TYPE C Au/Fe₂O₃ catalyst, temperature at 50% conversion for CO oxidation in air was -30 °C, temperature at 50% conversion for H₂ oxidation was 55 °C and temperatures at total oxidations for CO or H₂ in air were 10 and 123 °C, respectively (curves b in Fig. 1 and curves a in Fig. 2), which were almost same with that given from the World Au Council, indicating that the reaction test system used in this work was reliable. Complete CO oxidations in air at ca. 33, 60 and 208 °C were observed over 4.6 wt% Au/Fe-UW-UC (curve d), 5.1 wt% Au/Fe-UW-C2 (curve f) and 5.6 wt% Au/Fe-UW-C4 (curve h) while ca. -3 and 32 °C over 4.1 wt% Au/Fe-W-UC (curve a) and 4.6 wt% Au/Fe-W-C4 (curve c), respectively, Fig. 1, indicating that the catalytic activities for CO oxidation were more sensitive to existence of Cl⁻ only after the catalysts were calcined at elevated temperatures, e.g. at 400 °C, although better activities were obtained if the Cl⁻ in the catalyst was

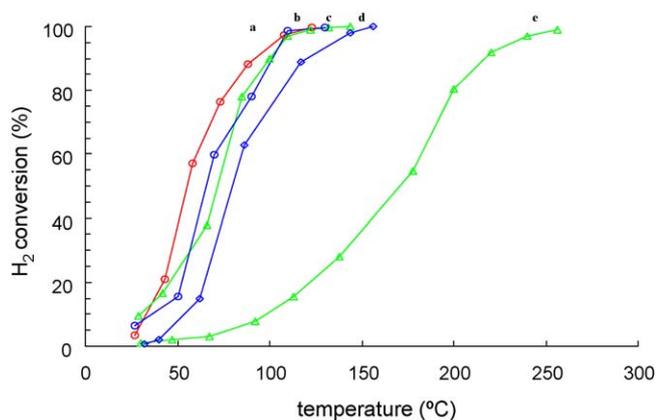


Fig. 2. Oxidations of H₂ in air. (a) 4.4 wt% TYPE C Au/Fe₂O₃; (b and d) 4.1 wt% Au/Fe-W-UC and 4.6 wt% Au/Fe-W-C4; (c and e) 4.6 wt% Au/Fe-UW-UC and 5.6 wt% Au/Fe-UW-C4.

washed away. Catalysts with lower Au loading were also tested and the same trend, i.e. complete CO oxidation at 50 and 244 °C (curves e and i) were, respectively, observed over 2.2 wt% Au/Fe-UW-UC and 2.6 wt% Au/Fe-UW-C4, which was resulted from 2.2 wt% Au/Fe-UW-UC. Also, it can be seen that catalyst precipitated at ca. 20 °C were less active than that precipitated at 70 °C that the temperatures of CO total conversion over either 2.2 wt% Au/Fe-UW-UC or 2.6 wt% Au/Fe-UW-C4 precipitated at ca. 20 °C were slightly higher than that precipitated at 70 °C (curves g and k). Previously reported work [19] indicated that small amount of water in the feed gas might be favorable for the CO total oxidation at lower temperatures. Since calcinations at elevated temperature were omitted, Au/Fe-UW-UC catalysts should contain relatively higher content of water. However, it was found that the catalytic activity of Au/Fe-UW-UC catalysts would not almost decrease when they were dried at 110 °C for several hours to remove the water completely, indicating that higher activity of Au/Fe-UW-UC catalysts may less related to the relatively higher content of water in the catalysts.

Catalytic performance for H₂ in air over these catalysts were also tested, Fig. 2, and H₂ could be removed completely at 130, 144 and 156 °C over 4.1 wt% Au/Fe-W-UC (curve b), 4.6 wt% Au/Fe-UW-UC (curve c) and 4.6 wt% Au/Fe-W-C4 (curve d), suggesting the activity of these catalysts for H₂ oxidations could also be comparable to that of TYPE C Au/Fe₂O₃ catalyst. For the 5.6 wt% Au/Fe-UW-C4, the catalytic activities decreased remarkably and the conversion of H₂ could not achieve 100% even at 256 °C, curve f, suggesting that, according to our previous work [24], the decrease of activity may be less related to the changes of chemical states and structures of Au species and support due to the calcinations at elevated temperatures, but much related to the Cl⁻ in the catalyst, i.e. Cl⁻ became a catalyst poison after the catalyst was calcined at elevated temperatures.

When these catalysts as mentioned above were exposed to the mixture gas of 1.0 vol% H₂, 1.0 vol% CO and 4.0 vol% O₂ balanced with argon, different oxidation behaviors of CO and H₂ were exhibited, Fig. 3, CO oxidation was strongly inhibited

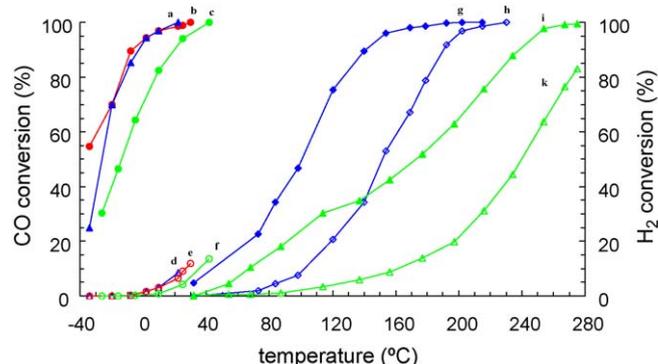


Fig. 3. Oxidations of CO and H₂ in mixture gas. (a and d) 4.1 wt% Au/Fe-W-UC for oxidations of CO and H₂; (b and e) 4.4 wt% TYPE C Au/Fe₂O₃ for oxidations of CO and H₂; (c and f) 4.6 wt% Au/Fe-UW-UC for oxidations of CO and H₂; (g and h) 4.6 wt% Au/Fe-UW-C4 for oxidations of CO and H₂; (i and k) 5.6 wt% Au/Fe-UW-C4 for oxidations of CO and H₂.

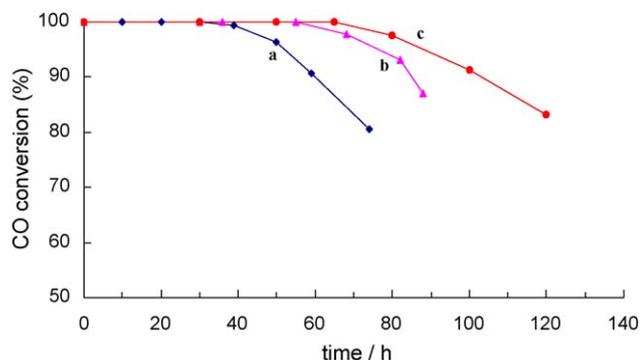


Fig. 4. Stability test of catalytic activity with CO oxidation in air over supported Au catalyst at 40 °C. (a) 4.6 wt% Au/Fe-UW-UC, (b) 4.4 wt% TYPE C Au/Fe₂O₃ and (c) 4.1 wt% Au/Fe-W-UC.

due to the presence of H₂, which resulted in temperatures of complete CO oxidation raised from 32 to 215 °C over 4.6 wt% Au/Fe-W-C4 (curve g) and from 208 to 275 °C over the calcined 5.6 wt% Au/Fe-UW-C4 (curve i), respectively. H₂ oxidations in the presence of CO, on the other hand, were less affected, and occurred and developed almost simultaneously with CO oxidation (curves h and k), therefore, selective CO oxidation in the presence of H₂ over the calcined catalysts were impossible. As to the uncalcined 4.1 wt% Au/Fe-W-UC and 4.6 wt% Au/Fe-UW-UC catalysts, CO oxidations in the presence of H₂ were less affected although the temperatures of complete CO oxidation raised from –3 to ca. 22 °C (curve a) and from 33 to 42 °C (curve c), respectively. At these temperatures, a detectable oxidation of H₂ occurred (curves d and f) and result in a decrease of selectivity, even so, they were the most effective selective oxidation catalysts at lower temperatures compared with other gold catalysis system [27–31], over 4.1 wt% Au/Fe-W-UC and 4.6 wt% Au/Fe-UW-UC the selectivity still reached to about 93% and 88%, respectively. Also it was worth to note that the catalytic performance for the co-oxidation of CO and H₂ were less sensitive to the Cl[–] content in the catalysts. TYPE C Au/Fe₂O₃ was also tested in this mixture gas, and CO oxidation was slightly inhibited by the existence of H₂ that temperatures of complete CO oxidation raised from 10 to 30 °C, curve b, however, H₂ oxidations were hardly affected in the existence of CO at lower temperatures, curve e. These results suggested that the catalytic activity of 4.6 wt% Au/Fe-UW-UC, which was prepared without any

water-washing and heating treatment, could be comparable to that of TYPE C Au/Fe₂O₃ catalyst.

Also, the stability of catalytic activities of the 4.4 wt% TYPE C Au/Fe₂O₃ and 4.6 wt% Au/Fe-UW-UC and 4.1 wt% Au/Fe-W-UC for CO oxidation in air were tested at 40 °C, Fig. 4, the total conversion of CO to CO₂ over 4.4 wt% TYPE C Au/Fe₂O₃ could be maintained for about 55 h, and 90% of CO conversion could be further maintained for about 20 h. Over 4.6 wt% Au/Fe-UW-UC, the total conversion of CO to CO₂ could be maintained for about 40 h (a 99.6% conversion at 39 h), shorter than over 4.4 wt% TYPE C Au/Fe₂O₃ while 90% of CO conversion could also be further maintained for about 20 h. Such activity stability, though not too long, is reasonably comparable with those previously reported results [22,32]. The washed catalyst was more stable than the unwashed catalyst and the total conversion of CO to CO₂ could be maintained for 65 h and 90% of CO conversion could be further maintained for 35 h. This fact indicated that removing residual chlorides could promote the catalysts stability. It should be noted that the washed catalyst with intrinsically higher activity was probably another reason that the washed catalysts were more stable.

3.2. Catalysts characterization

Results of Au loadings, BET surface areas and XPS of the prepared catalysts are listed in Table 1. Au loadings, as mentioned above, were increased after being calcined at elevated temperature and this should be related to the losing adsorbed water and the transformation of ferric hydroxide into metal oxide. Au loadings of the washed catalysts were lower than the unwashed, indicating that gold losing occurred inevitably during the washing process, which was remarkably unfavorable for such catalysts preparation in large scale. BET adsorption measurement showed that the surface areas decreased greatly with increasing calcining temperatures. XPS analysis indicated that the surface chemical states of Au were mixture of metal (B.E. 4f_{7/2} = 84.1 eV) and Au⁺ (B.E. 4f_{7/2} = 86.4 eV) over the uncalcined and unwashed catalysts, while after calcinations at 400 °C the Au species changed to metal completely (B.E. 4f_{7/2} = 83.8 eV). It was worth to note that catalysts precipitated at 70 °C could form more Au⁺ species than that precipitated at room temperature since the area ratio of Au⁺/Au⁰ in catalysts prepared at 70 °C was larger than that in the catalysts precipitated at room temperature (Table 1; Figs. 5 and 6). As expected, more Cl[–] and

Table 1
Some physicochemical properties of the supported Au catalysts

	Au loading (wt%)	BET surface area (m ² /g ^{–1})	Average pore diameter (Å)	B.E. of Au4f _{7/2} (eV)	Area ratio of Au ⁺ /Au ⁰	Atom ration of Cl [–] /Au	LT ^b for CO total conversion
Au/Fe-W-UC	4.1	243.3	46.7	86.5, 84.2	0.33	0.56	–3
Au/Fe-W-C4	4.6	83.6	131.5	83.7	0	0.29	32
Au/Fe-UW-UC	2.2	260.7	32.9	86.5, 84.1	0.88	2.4	50
Au/Fe-UW-UC	4.6	265.8	32.7	86.4, 84.1	0.93	2.6	33
Au/Fe-UW-C4	5.6	47.4	151.9	83.8	0	1.9	208
Au/Fe-UW-UC ^a	4.6	262.5	34.7	86.8, 84.4	0.85	2.2	–

^a Precipitated at 20 °C.

^b Lowest temperatures.

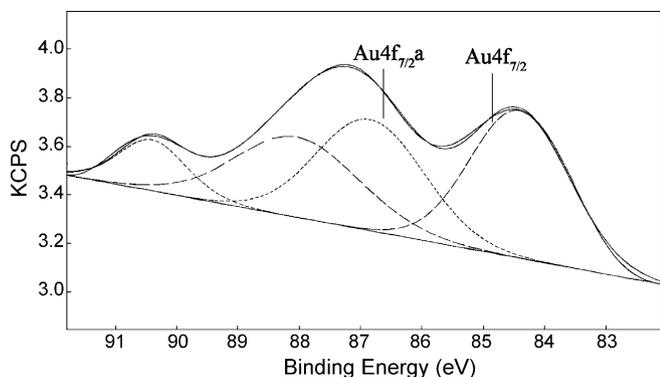


Fig. 5. XPS spectra for catalyst precipitated at 20 °C.

some nitrate species could be observed on the unwashed catalyst surface, and the contents of Cl^- and nitrate species could be reduced and removed, respectively, after the catalyst was calcined at 400 °C.

XRD analyses showed that there was no detectable crystallite formation of ferric oxide or hydroxide over the 4.6 wt% Au/Fe-UW-UC catalyst, Fig. 7, which indicated that the supports were amorphous and that there was no detectable crystallite formation of Au species since Au species should be

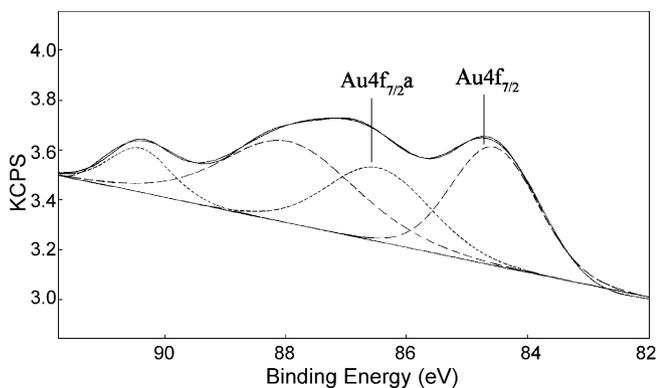


Fig. 6. XPS spectra for catalyst precipitated at 70 °C.

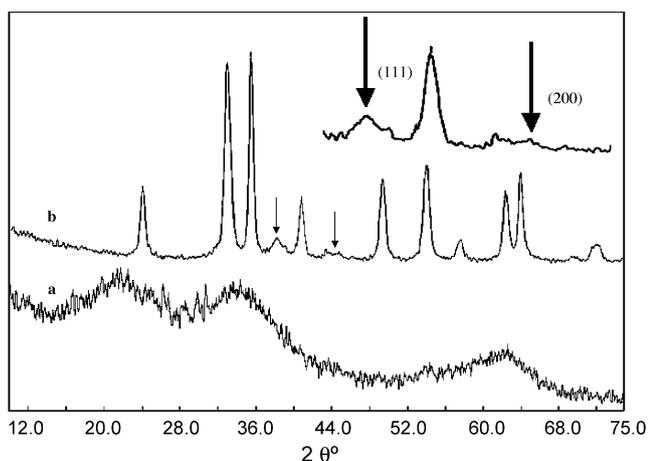


Fig. 7. XRD patterns of Au catalysts uncalcined and calcined at 400 °C. (a) 4.6 wt% Au/Fe-UW-UC and (b) 5.6 wt% Au/Fe-UW-C4.

highly dispersed without calcining [22]. When 4.6 wt% Au/Fe-UW-UC catalyst was calcined at 400 °C, crystallite formation of $\alpha\text{-Fe}_2\text{O}_3$ and metallic Au could be observed, indicating that the supports had transformed from amorphous ferric hydroxide into Fe_2O_3 and the Au species had aggregated to form some metallic Au crystallite.

TEM observations of the 4.6 wt% Au/Fe-UW-UC catalyst and 5.6 wt% Au/Fe-UW-C4 catalyst (resulted from 4.6 wt% Au/Fe-UW-UC with being calcined at 400 °C), Fig. 8, showed that Au was highly dispersed that almost no Au nano-particles could be observed and the support seemed more uniform and amorphous over the 4.6 wt% Au/Fe-UW-UC, which was considered to be important to have the uniformly distributed nano-sized Au metal [33]. After being calcined at 400 °C, aggregated Au particles could be observed with 5–20 nm in diameters and the support changed to lump sinter.

Since higher catalytic activity could be observed when the precipitation was conducted at 70 °C in comparison with that at room temperature (ca. 20 °C), UV–vis absorption was employed to investigate the possible changes of AuCl_4^- complex and possible interaction between $\text{Fe}(\text{NO}_3)_3$ and HAuCl_4 before precipitation (Figs. 9 and 10). It was shown that, when 1×10^{-3} M AuCl_4^- solution was heated at 70 °C for 30 s and further to 1 min, the maximum absorption of AuCl_4^- shifted from 306.9 to 303.4 nm and further to 302.4 nm, which indicated that the AuCl_4^- complex were hydrolyzed partially to form $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ ($x = 1-3$) species [34]. If the heating time was lasted for over 2 min, the maximum absorption was almost unchanged in comparison with that heated for 1 min, suggesting that the hydrolyzation could be accomplished in 1 min. When being heated from room temperature (ca. 20 °C) to 70 °C, 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution also hydrolyzed, and the maximum absorption peak shift to high wavelength, i.e. from about 375 to 400 nm (Fig. 10), which was consistent with the results that adjusted with Na_2CO_3 at 20 °C, indicating the hydrolyzation of $\text{Fe}(\text{NO}_3)_3$ occurred markedly at 70 °C even without adding Na_2CO_3 . Based on these results, it can be conjectured that the $\text{Fe}(\text{NO}_3)_3$ and HAuCl_4 hydrolyzed partially to form $\text{Fe}(\text{OH})_3$ and $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ ($x = 1-3$), respectively, if the solutions were heated at 70 °C, and such prepartially hydrolyzed iron and gold species and the possible interaction between them during the hydrolysis may be favorable for the formation of more active precursor.

In order to get more insight into the possible interaction between Au species and Cl^- , computer modeling of Cl^- adsorbed on Au (1 1 1) surface was performed with Casetp/Materials Studio (Accelrys). The results, Fig. 11, showed that if Cl^- was adsorbed on a Au^0 species, the Cl atom would take 0.05 positive electric charge while the conjoint gold atom would take -0.190 negative electric charge, and the others surface gold atom would take negative electric charge from -0.05 to -0.08 . But if Cl^- was adsorbed on a Au^+ surface, the Cl atom would take 0.09 positive electric charge and the conjoint gold atom would still take -0.190 negative electric charge, while the others surface gold atom would partially take positive electric charge from 0.01 to 0.05 and partially take negative electric charge from -0.01 to -0.03 , lower than that

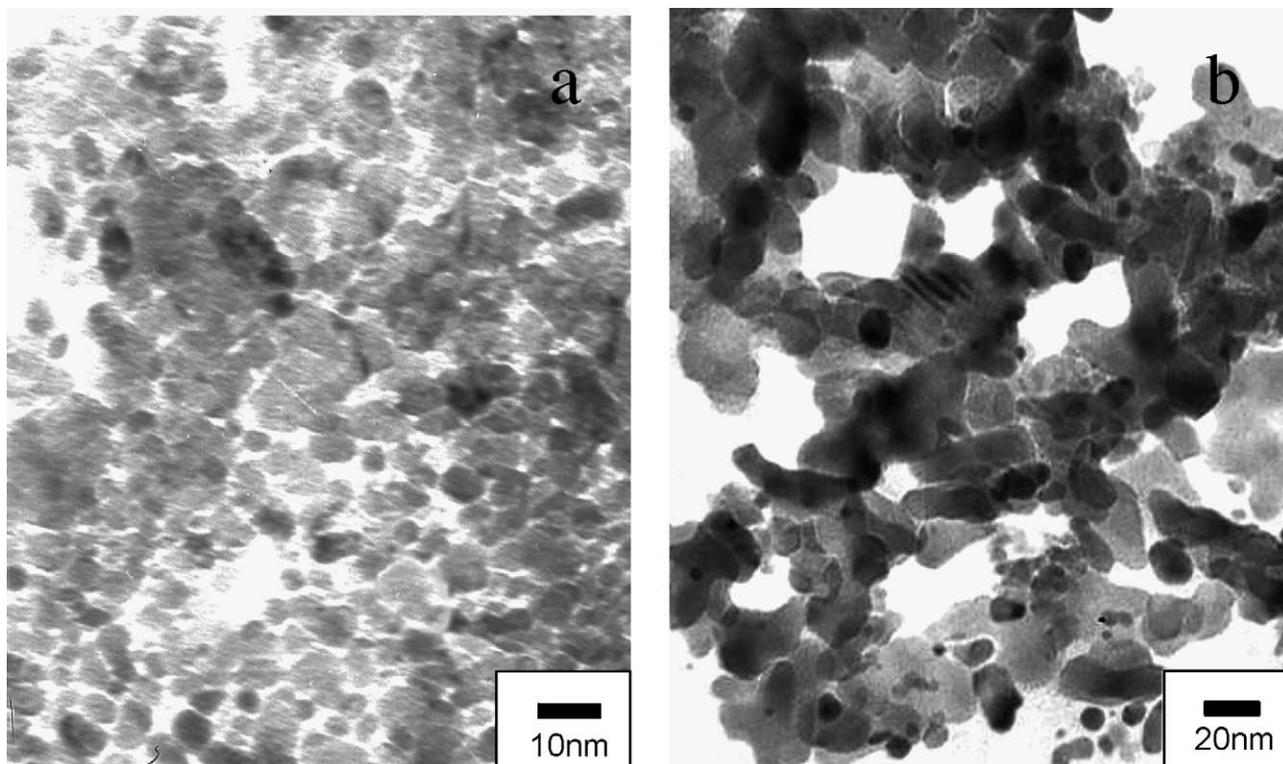


Fig. 8. TEM pictures of Au catalysts uncalcined and calcined at 400 °C. (a) 4.6 wt% Au/Fe-UW-UC and (b) 5.6 wt% Au/Fe-UW-C4.

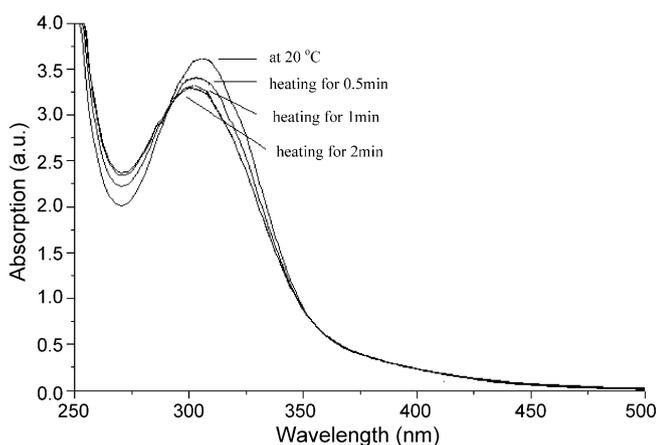


Fig. 9. UV-vis spectra of 1×10^{-3} M HAuCl_4 solution at 20 °C and heating at 70 °C for 0.5, 1 and 2 min.

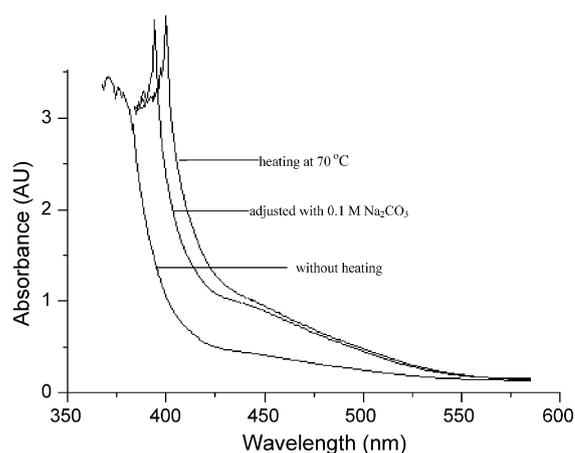


Fig. 10. UV-vis spectra of 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution without heating at 20 °C and heating at 70 °C for 2 min and adjusted with 0.1 M Na_2CO_3 .

of -0.05 to -0.08 . And the results also showed that either O_2 or CO easily adsorbed on Au^+ or Au^0 (more easier on Au^+), but adsorbed on Au^- very difficultly, which had the decisive influence on the subsequent oxidation reactions. So, over the uncalcined catalysts, Cl^- less affect the activity due to the presence of Au^+ , but Cl^- would inhibit the activity greatly over the calcined catalysts due to the absence of Au^+ .

4. Discussion and conclusion

Based on the results of characterization and reaction and the previously reported literatures, it can be conjectured that the

presence of Cl^- on the catalyst was not the most important factor for decreasing the catalytic activity of supported Au catalysts for CO oxidation, although Cl^- could promote the agglomeration of Au particles, thus resulting in a less active catalyst for CO oxidation. In fact, even without Cl^- , Au nano-particles would agglomerate when they were calcined at elevated temperatures. Moreover, Kung and co-workers had pointed that the activity of supported Au catalyst could be increased by nearly 20-fold by removing the chloride, even though there was no detectable change in the average particles size of Au [35]. Also, it can be seen from Table 1 that the activity was not directly related to the amount of the residual Cl^- .

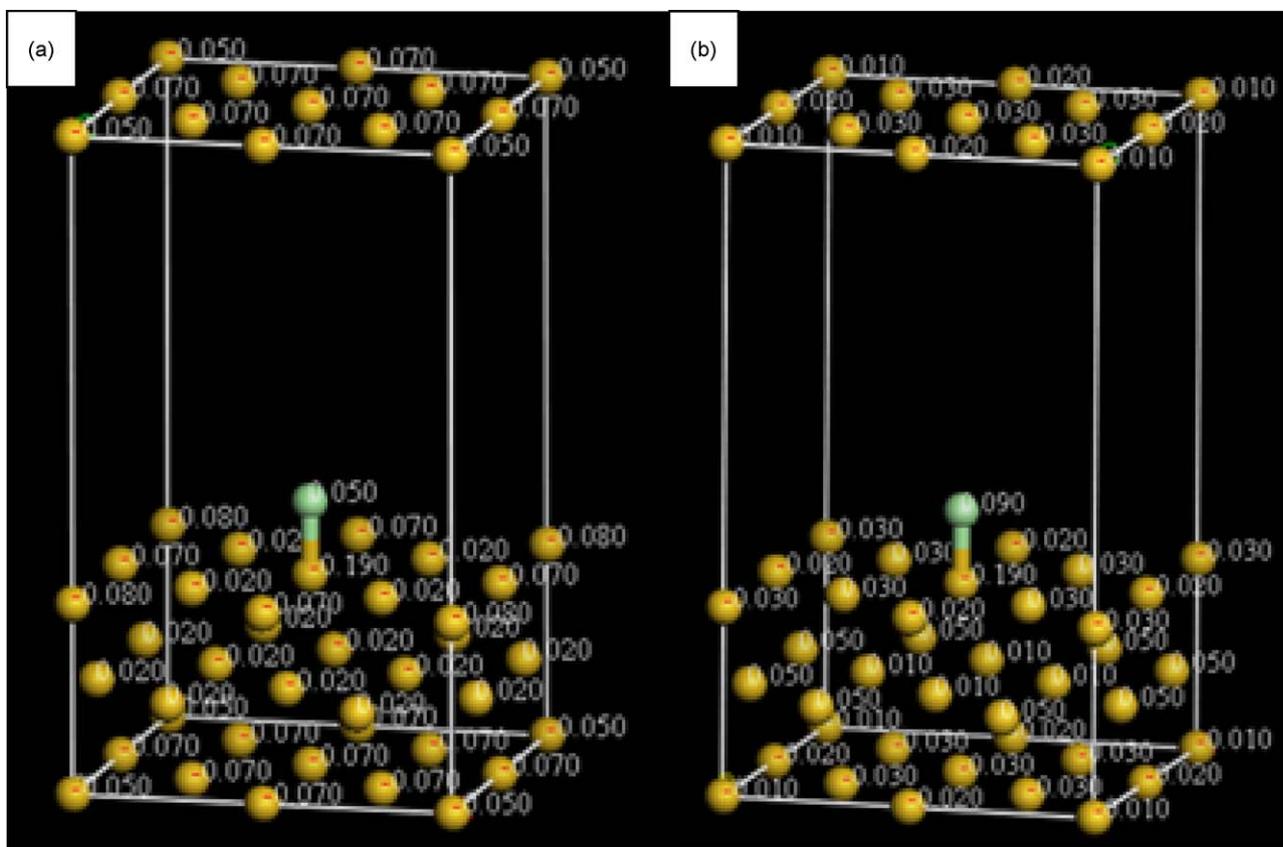


Fig. 11. Computer model of Cl^- adsorbed on Au(1 0 0) surface. (a) Cl^- adsorbed on Au crystal cell without electric charge and (b) Cl^- adsorbed on Au crystal cell take one positive electric charge.

This work clearly showed that the most important role of Cl^- was to poison the active site by the formation of Au–Cl bond. Lin et al. reported that Cl^- residue in the alumina supported Au sample may be located near the Au deposit, but not directly bonded to Au. When being treated at elevated temperatures, reduced density of hydroxyl groups occurred, causing Cl^- to bond to Au again [36]. Such case may also occur in the ferric hydroxide supported Au catalysts containing relatively large amount of Cl^- and the hydroxyl species on the $\text{Au-Au}^+\text{-Cl}_x/\text{Fe}(\text{OH})_y$ may weaken the interactions between Au species and Cl^- , thus resulting in enough high activity for CO oxidation. Results of UV–vis observation showed that precursor solution, if being heated at 70°C would lead AuCl_4^- and $\text{Fe}(\text{NO}_3)_3$ to hydrolyzing to form $[\text{AuCl}_x(\text{OH})_{4-x}]^-$ ($x = 1\text{--}3$) species and $\text{Fe}(\text{OH})_3$, respectively, and the following interaction between them may be favorable to avoid the formation of Au–Cl bond.

No calcination was the key factor to obtain highly active supported Au catalysts containing Cl^- for CO oxidations. Calcination converted the support from hydroxide ferric to oxide ferric and resulted in great decrease of the amount of hydroxyl groups, causing Cl^- to bond to Au again. Calcinations would also results in the reduction of Au^+ to Au^0 and all of the uncalcined catalysts have a high ratio of Au^+/Au^0 while over calcined catalysts there were no Au^+ . Our computer simulation results suggested that the Au^+ could weaken the negative effect of residual Cl^- .

It should be noted that, with either higher or lower Au loadings, the catalysts without calcinations could possess higher activity even containing relatively large amount of Cl^- , while when being calcined at elevated temperatures, such as 400°C the activity would decrease markedly. Furthermore, removing the residual Cl^- from the catalysts could, though very limited, improve the activity stability of these catalysts containing Cl^- .

In conclusion, ferric hydroxide supported Au catalyst containing Cl^- was prepared with co-precipitation without being washing and calcined and this catalyst could still be highly effective for CO oxidation in air at lower temperatures. The presence of Cl^- might have little impact on the activity over the unwashed and uncalcined catalysts; however, CO oxidation would be much sensitive to existence of Cl^- only after they were calcined. Although the detailed interaction mechanism between Au species and Cl^- is still not clear at this stage, it can be conjectured that hydroxyl species on the $\text{Au-Au}^+\text{-Cl}_x/\text{Fe}(\text{OH})_y$ may weaken the interactions between Au species and Cl^- , thus resulting in enough high activity for CO oxidation in the presence of relatively large amount of Cl^- in catalysts. To our best knowledge, it should be the first time to report a supported Au catalyst prepared without washing and containing relatively large amount of Cl^- could also possessed high catalytic activity for CO oxidations and it also should be the first time to show that the conception that supported gold must be chloride-free may not be correct.

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