Influence of the calcination temperature on the Au/FeO_x/Al₂O₃ catalyst

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Abstract: The effect of calcination temperature on the electronic structure of gold catalyst was investigated in this paper. CO oxidation was employed as a test reaction to correlate the phase changes to the catalytic activity. The TPR, XPS and XRD characterization showed that the highly active Au/FeO_x/Al₂O₃ catalyst contained both gold atoms and ions. The catalytic performance of gold catalyst may depend on the Au⁰/Au³⁺ ratio. The best activity in the present work was obtained when the Au⁰/Au³⁺ ratio was about 0.89.

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Keywords: gold catalyst; calcination; activity mechanism; CO oxidation

INTRODUCTION

The low reactivity of gold is attributed to the completely filled 5d atomic orbital and the relatively high value of its first ionization potential.¹ Since Haruta *et al.*² reported that CO oxidation could be achieved at room temperature over gold catalysts when very small gold nanoparticles were dispersed on suitable oxide supports, the last decade has witnessed a rapid growth of interest in catalysis by gold. Bond and Thompson³ have reviewed the advancement of gold catalyst in depth.

The choice of preparation method is very critical for gold catalyst performance. In fact, small variations in the method of preparation can make the difference between a good and a poor catalyst. On the preparation of the supported gold catalysts, contradicting results have been reported on the effect of calcination treatment. Haruta *et al.*^{2,4} found that co-precipitated gold on iron oxide is active only after calcination at 673 K. This causes the gold to form small metallic particles, which are the active species. Tanielyan *et al.*,⁵ however, prepared co-precipitated Au on iron oxide catalysts that were already active after drying at 368 K, whereas calcination at high temperature (653 K) led to a significant decrease in activity. Kozlova *et al.*⁶ studied a series of samples prepared by impregnation of several iron oxide supports prepared from the same precursors but with different contents of water or hydroxyls by appropriate drying and calcination procedures. The activity of the catalytic system, even after calcination, has been found to decrease on decreasing the amount of water and hydroxyls before impregnation with gold precursors. The catalytic activity of Au/Fe₂O₃ samples towards volatile organic compound oxidation over gold/iron oxide to CO₂ has been found to be strongly dependent on the catalyst pretreatment, decreasing on increasing

the calcination temperature.⁷ The same conclusions were drawn from the water-gas shift reaction by Hua *et al.*⁸

Since the discovery of the high catalytic activity of gold nanoparticles, several studies have been performed to elucidate the mechanism of the catalytic properties of gold. There are two different views on the relationship between the electron structure and the catalytic activity. One correlates the high activity of gold catalyst to the form of nano size metallic gold; the other attributes the activity to the oxidized gold.

Yuan *et al.*⁹ prepared highly dispersed gold catalyst from Au phosphine complexes and as-precipitated metal hydroxides. After calcination the catalyst showed extremely high activity, which was ascribed to the stabilization of [Au(PPh₃)]⁺ species leading to small metallic gold particles. Fourier transform infrared data¹⁰ showed that on a fresh sample CO is adsorbed on regular gold metallic sites, while on the used sample the adsorption sites are two-dimensional gold clusters made positive by interaction with the support. High-resolution transmission electron microscopy also indicated the disappearance of the gold metallic particles in the used catalyst. The study of Valden and Goodman¹¹ showed that the structure sensitivity of Au/TiO₂ catalyst is related to a quantum size effect with respect to the thickness of the gold clusters. Clusters that are only one atom thick have band gaps significantly larger, whereas with thickness of three atoms or greater they exhibit metallic properties. The population of two-atom-thick clusters clearly peaks at diameters ranging from 2.5 to 3.0 nm, which coincides with the maximum specific activity of Au/TiO₂ catalysts.

Salama *et al.*¹² prepared positively charged gold particles encapsulated in NaY zeolite and observed that they were more active than metallic gold

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Contract/grant sponsor: China Postdoctoral Science Foundation; contract/grant number: 2004035284

(Received 16 July 2005; revised version received 25 August 2005; accepted 29 November 2005)

DOI: 10.1002/jctb.1533

particles. On the highly active Au/Mg(OH)₂ samples, Au^{δ+} species were also observed by Mössbauer spectroscopy.¹³ Wagner *et al.*¹⁴ also suggested the importance of Au⁺ and Au³⁺ species in the case of Au/Fe₂O₃ catalyst. Au⁺ species showed more activity than Au⁰ species in the other literature.¹⁵ Hao *et al.*¹⁶ arrived at a similar conclusion. The 5d atomic orbital of oxidized gold is not filled completely, which is very similar to the electron structure of the Pt atom. Pt is one of the most active metals as a catalyst material. Au^{δ+} species can therefore be more active than Au⁰ species in catalysis.

The influences of gold oxidation state and cluster size on CO oxidation catalysis remain unresolved.¹⁷ Guzman reported spectroscopic evidence of cationic gold present with zerovalent gold clusters in working CO oxidation catalysts,^{18,19} confirming suggestions of their simultaneous presence by Fu *et al.*²⁰ The SIMS spectrum of the supported gold catalysts presented AuO⁺, AuO₂⁺, and AuOH ion clusters, which show direct evidence for oxidized gold on supported gold catalysts. In addition, Hodgea *et al.*²¹ suggest that the Au is uniformly dispersed in the form of a mixture AuOOH · xH₂O and Au⁰, and the precise Au³⁺/Au⁰ ratio in the material may have an important effect on the level of catalytic activity displayed. The most active material, containing 2.1 at.% Au (40% Au⁰ : 60% Au³⁺), exhibited 100% CO conversion for 10 h. These observations are consistent with the Bond and Thompson model²² in that those catalysts displaying good CO conversion definitely contained mixtures of Au^{x+} and Au⁰ species.

Notwithstanding the widening research on gold catalysts, there are still numerous conflicting pieces of evidence concerning the effect of calcination. Catalytic activity has been found to be strongly dependent on the catalyst pretreatment temperature according to our previous study.²³ In the present paper, we used H₂-TPR, XPS and XRD techniques to investigate the effect of calcination temperature. CO oxidation as test reaction was employed to correlate the phase changes to the catalytic activity.

EXPERIMENTAL

Catalyst preparation

γ-Al₂O₃ (surface area = 169 m² g⁻¹, total pore volume = 0.41 mL g⁻¹, particle size = 1 mm) was used as support. Fe(NO₃)₃ · 9H₂O was the precursor of the second support. Composite FeO_x/Al₂O₃ support was prepared via impregnation. The sample was dried at 373 K overnight, heated to 673 K at a heating rate of 10 K min⁻¹ and held at this temperature for 2 h. An aqueous solution of HAuCl₄ · 3H₂O was used as Au precursor. Au was dispersed on support materials by homogeneous deposition precipitation (HDP) using urea as a precipitation reagent. The suspensions were kept at 350 K under vigorous stirring to ensure a slow and gradual increase of pH value. When the pH

reached 8.0, the suspensions were filtered and washed thoroughly to remove chloride ions. The samples were dried overnight at 373 K and subsequently calcined at different temperatures at a heating rate of 10 K min⁻¹.

Activity evaluation

The activity of the catalysts for CO oxidation was evaluated in a fixed bed reactor. The CO + O₂ + N₂ (CO: 0.5%; O₂: 21.1%; N₂: 78.4%) mixture passed through the catalyst bed with a space velocity (SV) of about 8000 h⁻¹. The T_{100%} (lowest complete conversion temperature) was gained by the single-pass reactor, and the reactants and products were analyzed using a gas chromatograph (Beifen SQ-206), equipped with a hydrogen flame ionization detector connected to a converter which can convert the CO and CO₂ to CH₄, and the latter can be detected by FID. The reaction rate of CO oxidation was gained by the closed circulated reactor, and CO concentration was measured by CO gas sensor (Interscan 4140).

Catalyst characterization

The Au content of the catalysts was analyzed with inductively coupled plasma-atom emission spectroscopy (ICP-AES) using an IRIS Advantage spectrometer. Temperature-programmed reduction (TPR) characterization was carried out in a conventional flow apparatus with a thermal conductive detector (TCD). A sample of 0.05 g was inserted into a reactor made from a quartz tubing of 6 mm i.d., then pursued in a reductive flow of 50 mL min⁻¹ 5% H₂ in nitrogen on raising the system temperature linearly from room temperature to a predetermined maximum temperature at a ramp rate of 10 K min⁻¹. Transmission electron microscopy measurements were performed using a Hitachi H-700 electron microscope equipped with an EDAX 9100 spectroscopy. Maximum resolution was 0.34 nm at 250 000× magnification.

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max-Rc X-ray diffractometer with Cu K_α radiation. A proportional counter and a 0.02° step size in 2θ from 10° to 90° were used. The assignment of the various crystalline phases was based on JPDS power diffraction file cards. The XRD profiles obtained were fitted using the software provided with the instrument. The particle sizes of different phases were calculated from the line broadening of the most intense reflections using the Scherrer equation.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a KROTOS XSAM 800 system, equipped with a dual Mg/Al anode. The spectra were excited with Al K_α radiation operated at 12 kV and 10 mA. The analyzer was operated in the FRR mode.

RESULTS AND DISCUSSION

Activity of catalysts calcined at different temperatures

The gold loading determined by ICP-AES measurement is 1.94 wt% and showed a relatively small variation from the nominal content of 2 wt%. The result manifested a very high loading of gold by deposition–precipitation with urea as precipitation reagent.

We investigated the influence of calcination temperature on catalytic activity by treating the as-made materials, which had been dried at 353 K, at different temperatures, namely 373, 473, 573, 673 and 773 K. With increasing temperature of calcination a significant increase in the catalytic activity could be observed before it reached 573 K. The catalytic performance expressed in terms of the temperature needed to reach 100% CO oxidation ($T_{100\%}$) and reaction rate at 273 K are summarized in Table 1. The catalyst calcined at 573 K showed the best catalytic performance with $T_{100\%}$ at 252 K. Samples calcined at 473 K and 673 K had almost the same $T_{100\%}$. However, the reaction rate of both samples appeared different. The sample calcined at 473 K showed a slightly higher rate than that calcined at 673 K. The possible reason is that parts of oxidized gold on the sample calcined at 473 K were reduced by CO during the course of the reaction, which resulted in more active sites on the sample calcined at 473 K than at 673 K.

Temperature-programmed reduction

Temperature-programmed reduction profiles carried out on the samples calcined at different temperatures are reported in Fig. 1. Samples (a)–(e) are the catalysts calcined at 373, 473, 573, 673 and 773 K, respectively. From Fig. 1 two peaks with maxima at about 693 K and 898 K can be detected on all these samples, which should be attributed to the reduction peak of Fe_2O_3 . Sample (f) is the reduction profile of support $\text{FeO}_x/\text{Al}_2\text{O}_3$. It is well known that the reduction of bulk iron oxide by hydrogen proceeds through the following steps $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. Therefore, one of the peaks with T_{max} at ~ 693 K is related to the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ reduction step, whereas the other peak is attributed to the transition $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$.²⁴ The TPR spectra of $\text{Au}/\text{FeO}_x/\text{Al}_2\text{O}_3$ catalyst (Fig. 1a–e) differ substantially from those of $\text{FeO}_x/\text{Al}_2\text{O}_3$ catalysts (Fig. 1f). T_{max} of the peak related to the reduction step $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ for $\text{Au}/\text{FeO}_x/\text{Al}_2\text{O}_3$ catalyst is lower by ~ 150 K than that for the same transition in the absence of gold. The second reduction step $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ starts after the reduction of hematite has been completed, which showed no

difference in comparison to $\text{FeO}_x/\text{Al}_2\text{O}_3$. All these suggested that a correlation seems to exist between the reduction temperature and the presence of gold on the catalysts. The presence of gold lowered the reduction temperature of Fe_2O_3 . Knock and Fortuin²⁵ have reported that the onset temperature of the iron oxide reduction to magnetite depends on the amount of lattice defects. It is well known that the presence of Au^{3+} ions influences the nature and growth of the iron oxide crystallites,²⁶ which in turn can influence the metal–support interaction. Therefore, the presence of Au particles weakens the Fe–O bond, thus increasing the reducibility of the support. The difference of the peak area of the hematite to magnetite between curve (f) and others may be made by experiment. For the support, Al_2O_3 was in pellet form with a diameter of 1 mm; some of the FeO_x on the surface of the Al_2O_3 was lost during stirring.

There was clear variation in the patterns of the first reduction peaks on all the samples in Fig. 1(a–e). The peak area is related to the amount of hydrogen consumed, which corresponds to the content of oxidized gold. The position of the peak is decided by the oxide phase and the micro-environment around it. A clear and sharp peak can be observed in Fig. 1(a) with the temperature of the maximum of the peak at 493 K. The peak is likely related to the chloride-contaminated gold species (mainly $\text{AuCl}_n(\text{OH})_{4-n}^-$). Among the gold species prepared by the deposition–precipitation method, $\text{Au}(\text{OH})_3$ of the deposited gold species is thermally unstable at temperatures higher than 373 K, and tends to decompose into Au_2O_3 and metallic gold.

Figure 1. The TPR spectra of $\text{Au}/\text{FeO}_x/\text{Al}_2\text{O}_3$ catalysts calcined at different temperatures: (a) 373 K; (b) 473 K; (c) 573 K; (d) 673 K; (e) 773 K; (f) $\text{FeO}_x/\text{Al}_2\text{O}_3$ (calcined at 673 K).

Table 1. The CO oxidation activity and reaction rate at 273 K of catalysts calcined at different temperatures

Calcination temperature	373 K	473 K	573 K	673 K	773 K
$T_{100\%}$	298 K	263 K	252 K	261 K	313 K
Rate ($\text{mol}_{\text{CO}}/\text{g}_{\text{Au}} \text{ h}^{-1}$)	9.5×10^{-3}	3.3×10^{-2}	4.4×10^{-2}	1.8×10^{-2}	8.6×10^{-4}

After treatment at 373 K, the dominant gold species remaining on the sample is the chloride-contaminated gold species, the decomposition of which requires a higher temperature.²³ However, the calcination temperature is so low that most of the adsorption water was not released from the bulk of the sample. As a result, the peak of desorbed water was superposed with the reduction peak of the chloride-contaminated gold species.

The much lower temperature can be detected on sample (b) in Fig. 1. The broad peak at 476 K should be attributed to three overlapped peaks. The first one is due to the reduction of AuCl_n(OH)_{4-n}⁻ just like sample (a), the second one to the desorbed water, and the last one to the reduction of oxidized gold to metallic gold. The area of reduction peak was observed to be smaller in Fig. 1(c), which can be attributed to the reduction of Au₂O₃. So do the corresponding peaks in Fig. 1(d–e). However, a slightly increase of *T*_{max} in samples (d) and (e) can be observed. The reasons will be discussed below.

X-ray diffraction

Figure 2 reports the XRD spectra of the samples calcined at different temperatures. For sample (a) dried at 373 K, no reflections of gold could be detected. For sample (b), a serious broadening peak of the gold reflection can be observed. This suggested that the uncalcined material has a homogeneous dispersion of gold particles of size below 2 nm. After calcining at 473 K, the major fraction of gold particles is still smaller than 2 nm in size; however, in some fractions agglomeration to larger gold particles of 3–10 nm in size can be observed.

The three most intense diffraction peaks of metallic gold can be monitored in Fig. 2(c–e). Provided that the particle sizes are between approximately 3 and 50 nm, using the simple Scherrer equation the average particle size can be estimated. However, the gold particle size could not be determined from line broadening of the gold reflections at about 38° and 45° because of the superposition of the reflections of the support. Nevertheless, the average particle size of gold could be calculated according

Figure 2. XRD spectra of Au/FeO_x/Al₂O₃ catalysts calcined at different temperatures.

to Au(113) ($2\theta = 77.5^\circ$). The calculation was made assuming that the gold particles are hemispherical in shape, with the flat side on the support. Additional TEM measurement was necessary to validate this assumption. In Fig. 3, gold particles are visible as black dots on the support and are rather homogeneously distributed over the support.

The average particle size of gold is listed in Table 2. After calcination at 573 K, the average particle size was 6.2 nm. No further agglomeration of gold particles can be detected on the sample calcined at higher temperature, which showed that the average particle size calcined at 673 K and 773 K was 6.3 nm and 6.9 nm, respectively.

The study of Zanella *et al.*²⁶ showed that sintering of gold particles could be prevented during calcination because of the strong interaction between gold and the support. Au/TiO₂ samples were prepared by impregnation followed by washing. Even after several washings, 0.9 wt% gold remains on TiO₂ whatever

Figure 3. TEM micrograph of Au/Fe₂O₃/Al₂O₃ catalyst calcined at 573 K.

Table 2. The average particle size and the binding energy of Au 4f and the Au⁰/Au³⁺ of gold catalysts calcined at different temperatures

Catalyst	Au 4f _{7/2}	Au 4f _{5/2}	Au ⁰ /Au ³⁺	Average size
Metallic Au	83.9	87.7	–	–
Au ₂ O ₃	86.3	89.6	–	–
Sample a	86.05	89.35	0.27	–
Sample b	85.2	88.7	0.33	–
Sample c	84.85	88.21	0.89	6.2 nm
Sample d	84.4	87.85	1.69	6.3 nm
Sample e	84.2	87.8	2.87	6.9 nm

the initial Au loading, and the average particle size was still between 3 and 5 nm after calcination at high temperature.

The peaks characteristic of oxidized gold could not be observed in any spectra in Fig. 2, which is not consistent with the result of TPR. The possible reason may be that the particle size of oxidized gold is so small that it is not seen by X-ray diffraction.

XPS

The technique of XPS was employed to obtain information on the state of gold in Au/FeO_x/Al₂O₃ catalyst. Fig. 4 compares XPS of Au 4f for these catalysts prepared at increasing calcination temperature. Sample (a) calcined at 373 K shows peaks at 86.1 and 89.4 eV for Au 4f_{7/2} and Au 4f_{5/2} lines, respectively. These binding energies are very close to Au 4f binding energies of Au₂O₃, which are 86.3 and 89.6 eV,

Figure 4. XPS spectra of Au 4f peak of Au catalysts calcined at different temperatures: (a) 373 K; (b) 473 K; (c) 573 K; (d) 673 K; (e) 773 K.

respectively. With increase of pretreatment temperature, the Au 4f binding energies appeared to be lower. After calcination at 773 K (sample e), two peaks appeared at 83.9 and 87.7 eV, which is very close to Au 4f binding energies of metallic Au. To determine the relative amount of Au₂O₃ and metallic Au quantitatively, deconvolution of Au 4f peaks was conducted, and the results are listed in Table 2. It should be noted here that the oxidic Au was regarded as Au³⁺; measurement of the oxidic Au species would be done next. It also shown that the gold phase was transformed progressively from Au₂O₃ to metallic Au as the calcination temperature increased. It is likely that metallic Au plays a very important role in the activity of the catalyst. However, pure metallic Au phase was not formed thoroughly even though the calcination temperature was as high as 773 K, which showed decreasing performance on the catalytic CO oxidation.²³

In fact, there is little agreement as to the principal factors responsible for the activity of gold catalysts evaluated for carbon monoxide oxidation. It has been accepted that gold particles with high dispersion and nano size seemed unstable when kept for a long time. However, the oxidized gold can be stable through interaction between the gold and the oxide support. Bond and Thompson²² suggested that the active catalysts contain both gold atoms and ions (which are taken to be Au³⁺), and the latter form the 'chemical glue' that binds the particles to the support through covalent bonds. Metallic gold is located on the surface of oxidized gold, which is needed to provide a locus for the adsorption of carbon monoxide. Therefore, it is necessary to contain both metallic gold and ions in active gold catalysts with good performance.

The ratio of Au⁰/Au^{δ+} increases with increasing calcination temperature (Table 2), which agrees with the result of TPR. The oxidized gold in the gold catalyst decreases as the calcination temperature increases. However, this ratio of Au⁰/Au³⁺ is not very similar to the value received from the TPR area (Table 3). The possible reason is that the result calculated from the XPS curves was related to the active gold on the surface of the sample; otherwise, the data estimated by TPR were related to the gold in the bulk of the sample.

The sample calcined at 573 K showed the best activity for low-temperature carbon monoxide oxidation. Therefore, the good catalyst contained both metallic and oxidized gold, and the catalytic performance depended on the ratio of Au⁰/Au³⁺. When the ratio is

Table 3. The ratio of Au⁰/Au³⁺ of gold catalysts calcined at different temperatures estimated from the TPR areas

Sample	Calcination temperature	H ₂ consumption	Amount of Au ³⁺	Au ⁰ /Au ³⁺
a	373 K	—	—	—
b	473 K	—	—	—
c	573 K	2.86 × 10 ⁻⁵ mol	1.9 × 10 ⁻⁵ mol	0.68
d	673 K	2.14 × 10 ⁻⁵ mol	1.43 × 10 ⁻⁵ mol	1.29
e	773 K	1.4 × 10 ⁻⁵ mol	9.3 × 10 ⁻⁶ mol	2.37

around 0.89 on the surface, the corresponding catalyst showed the best performance in this paper.

We can also explain the increased temperature involved in reducing Au₂O₃ to metallic Au, as shown in Fig. 1(d–e). According to this mechanism, there is more oxidized gold in the bulk of the sample. More Au₂O₃ could be reduced to metallic gold with an increase in calcination temperature. However, part of it could not be decomposed into metallic gold because of the strong interaction between metallic gold and the support.

CONCLUSION

On the basis of the results reported, it can be concluded that nano-size gold particles were synthesized on Au/FeO_x/Al₂O₃ catalyst by deposition precipitation. TPR, XPS and XRD characteristics showed that the highly active Au/FeO_x/Al₂O₃ catalyst contained both gold atoms and ions. The catalytic performance of gold catalyst may depend on the Au⁰/Au³⁺ ratio. In the present work the best activity was obtained when the Au⁰/Au^{δ+} ratio was about 0.89 on the surface of the support.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the China Postdoctoral Science Foundation (2004035284) for the support of this work.

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