

Effect of oxygen treatment on the catalytic activity of Au/SiO₂ catalysts

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Abstract

In this paper we investigated the effect of oxygen treatment on the catalytic performance of Au/SiO₂ catalysts towards CO oxidation. The Au/SiO₂ catalysts were prepared via the deposition–precipitation method. The as-prepared Au/SiO₂ catalyst behaves a poor catalytic activity, which is attributed to the relatively large size of Au particles. Treatment of the catalyst in O₂ at temperatures higher than 800 °C greatly enhances the catalytic activity. However, XRD results demonstrate that the oxygen treatment at temperatures above 800 °C leads to the agglomeration of Au particles. Meanwhile, TEM results reveal the co-existence of well-dispersed ultrafine Au particles on the surface. XPS results reveal that the Au 4f binding energy shifts to higher binding energy after the oxygen pretreatment at temperatures above 800 °C. Interestingly, treatment of the Au/SiO₂ catalyst in He at 800 °C also shows the similar geometric and electronic structure changes of Au particles and thus the enhancement effect as that in O₂, indicating that the Au–O₂ interactions at high temperatures do not contribute much to the improvement of catalytic activity. We propose an evaporation–deposition mechanism of gold particles treated at high temperatures, accounting for the formation of ultrafine Au particles, which are responsible for the enhancement of the catalytic activity.

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Keywords: Structure–activity relation; Thermal treatment; Au nanoparticles; SiO₂; CO oxidation

1. Introduction

Since the first demonstration of its catalytic activity by Haruta et al. [1], highly dispersed Au has recently received considerable attention because of its extraordinary catalytic properties [2–8]. Of the various reactions known to be catalyzed by supported gold particles, the low temperature CO oxidation has been received the most extensive attention experimentally and theoretically [1–5,8–14]. Although it is generally accepted that the catalytic activity of Au depends to a large extent on the size of the Au particles, the nature of the active sites and the catalytic mechanism, which are purported to be of fundamental importance, still remain obscure because of the widely varying data reported in the literature. For example, for the highly active Au/TiO₂ catalyst, Haruta et al. emphasized the role of the perimeter interface between Au particles and the support as a unique reaction site for CO oxidation [11], whereas results of model catalyst study reported by Goodman's group demonstrated that Au particles with a bilayer structure can solely behave an extremely high

catalytic activity without the participation of the TiO₂ support into CO oxidation [13]. There are seldom experimental results directly correlating the geometric/electronic structure and the catalytic performance of Au particles for supported Au catalysts.

The nature of the support is important for the preparation of active supported Au catalyst. With the most common Au compound (HAuCl₄) as the precursor, using routine wet chemical catalyst preparation methods (deposition–precipitation and coprecipitation) can facilely prepare highly dispersed Au on reducible oxides, such as TiO₂, Fe₂O₃, and Co₃O₄, which thus behave very high catalytic activity towards CO oxidation [15–17]. However, with SiO₂ as the support, the same route usually form relatively large Au particles because of the acidity of SiO₂, and therefore, the as-prepared Au/SiO₂ catalyst behaves a poor activity [18–21]. Finely dispersed Au on SiO₂ have been prepared by means of chemical vapor deposition (CVD) [18], trapping Au nanoparticles in the ordered mesoporous silica [20,22], using micelle-derived Au nanoparticles [21] and cationic Au complex (Au(PPh₃)Cl, [Au(en)₂]³⁺) [23–25] as precursors.

Although the Au/SiO₂ catalyst is not a good catalyst for low temperature CO oxidation, it is a good candidate for the funda-

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mental study based on the following facts: (1) SiO_2 is so inert that the contributions of the support and of the metal–support interaction to the reaction can be minimized, therefore, the correlation between the geometric/electronic structures and the catalytic activity of Au particles can be unambiguously established in the Au/ SiO_2 catalytic system [26–29] and (2) the promotion effect of additives or other treatments on the catalytic activity can be pronouncedly reflected in the Au/ SiO_2 catalytic system because of its poor performance, which might shed insights on the fundamental understanding [19,30]. Dekkers et al. observed a pronounced promotion effect of metal oxide additives (CoO_x , LaO_x , and CeO_x) on the catalytic activity of the Au/ SiO_2 catalyst, which was attributed to the beneficial role of metal oxides related to the stabilization of active Au structures [19].

It is well known that many supported metal particles are subjected to the geometric/electronic changes when treated in oxidizing atmosphere at high temperatures [31,32]. Recently, Qu et al. reported that pretreatment in oxygen at 500 °C can markedly improve the activity of Ag/ SiO_2 catalysts for the low temperature CO oxidation; they found that the oxygen pretreatment at 500 °C redisperses and restructures the Ag particles on the surface, and more interestingly, that subsurface oxygen species formed during the pretreatment can not only stabilize the active Ag structures but also participate the CO oxidation [33,34]. Surface science studies have already established that, similar to silver [35], treatment of gold under atmospheric oxygen at high temperatures will restructure the gold surface [36]. It is thus our interest to investigate the effect of oxygen treatment on the supported Au particles and subsequent their catalytic activity towards the CO oxidation reaction. Based on the reasons described above, we chose the Au/ SiO_2 catalyst and studied the structures–activity relation of supported Au particles pretreated in oxygen at high temperatures. Our results reveal an oxygen treatment effect on the catalytic activity of the Au/ SiO_2 catalyst completely different from that on the Ag/ SiO_2 catalyst. Treatment of the catalyst in O_2 at temperatures higher than 800 °C greatly enhances the catalytic activity, and we proposed an evaporation–deposition mechanism.

2. Experimental

1% Au/ SiO_2 catalysts (weight ratio) were prepared via the deposition–precipitation method. Typically, 0.1046 g $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ dissolved in 20 ml deionized water and the ammonia water were slowly co-added into a three-neck bottle containing 5 g SiO_2 (40–120 mesh, Qingdao Haiyang Chemicals Co.). The pH was controlled to be between 9 and 10. The system was kept at 60 °C and stirred for 1 h, and was furthermore dispersed by ultrasonic at room temperature for 10 min. Then the solid was filtered and washed several times. The resulted yellow powder was dried at 60 °C for 6 h, followed by calcinations at 120 °C for 2 h and finally at 400 °C for 4 h. The as-prepared catalyst was red powder.

The catalytic activity of the Au/ SiO_2 catalyst was evaluated with a fixed-bed flow reactor. 0.05 g catalyst was used and the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 20 ml/min. The composition of the effluent gas was detected with an online GC-14C gas chromatograph equipped with a TDX-01 column ($T = 80$ °C, H_2 as the carrier gas at 30 ml/min). The conversion of CO was calculated from the change in CO concentrations in the inlet and outlet gases. Prior to the catalytic reaction, the Au/ SiO_2 catalyst was treated in oxygen at various temperatures (500, 650, 800, and 900 °C) for 1 h and then cooled down to room temperature in oxygen and finally swept by He for 1 h. These catalysts were denoted as Au/ SiO_2 -as prepared, Au/ SiO_2 - O_2 -500, Au/ SiO_2 - O_2 -650, Au/ SiO_2 - O_2 -800, Au/ SiO_2 - O_2 -900, respectively. The catalyst was also pretreated in Helium at 800 °C for a comparison, which was denoted as Au/ SiO_2 -He-800.

XRD measurements were performed on a Philips Xpert PRO SUPER X-ray diffractometer with a Ni-filtered $\text{Cu K}\alpha$ X-ray source operating at 40 kV and 50 mA. Diffuse reflectance UV–vis spectra were acquired on a DUV-3700 DUV–VIS–NIR Recording Spectrophotometer. XPS measurements were performed on an ESCALAB 250 high performance electron spectrometer using nonmonochromatized $\text{Mg K}\alpha$ excitation source ($h\nu = 1253.6$ eV). The binding energy of Si 2p in SiO_2 , which

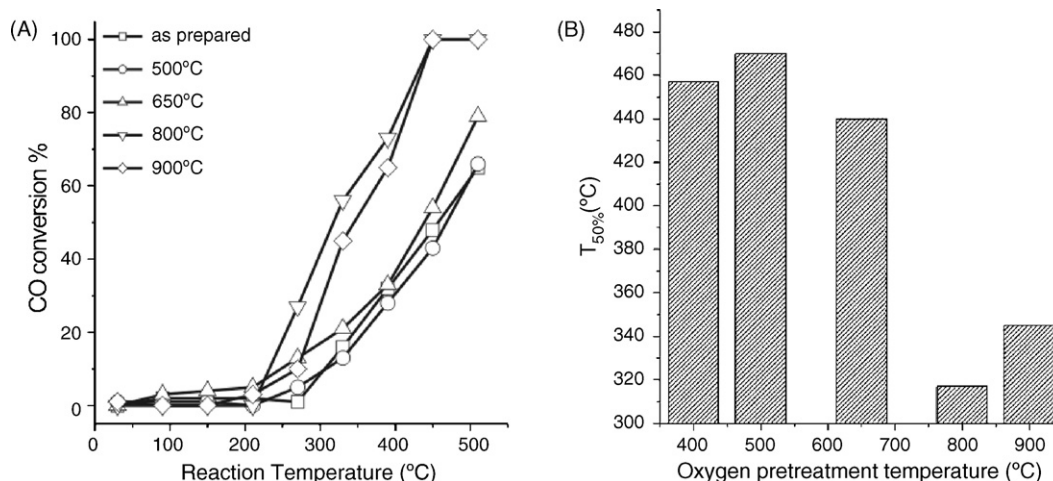


Fig. 1. The CO conversion (A) and the $T_{50\%}$ (the temperature corresponding to the 50% conversion) (B) of Au/ SiO_2 -as prepared, Au/ SiO_2 - O_2 -500, Au/ SiO_2 - O_2 -650, Au/ SiO_2 - O_2 -800, and Au/ SiO_2 - O_2 -900 catalysts.

was assumed to be 103.3 eV [37], was employed as the reference to correct the likely charging effect during the XPS measurements. BET surface area measurements were performed using N_2 adsorption at 77 K on a Micromeritics ASAP 2000. The TEM experiments were performed on an H-800 transmission electron microscopy.

3. Results and discussion

Fig. 1A shows the catalytic activity of Au/SiO₂ catalysts pretreated in O₂ at various temperatures towards CO oxidation. The catalytic activity of Au/SiO₂-as prepared is very poor, showing an initial activity at about 300 °C. Pretreating the catalysts in O₂ at 500 or 650 °C does not result any change in the catalytic activity. However, increasing the pretreating temperature to 800 and 900 °C greatly enhances the catalytic activity. Under the experimental conditions, the 100% CO conversion is not achieved over Au/SiO₂-as prepared, Au/SiO₂-O₂-500, and Au/SiO₂-O₂-650 whereas Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900 show the 100% CO conversion at 450 °C. The effect of oxygen pretreatment can be demonstrated more obviously by the $T_{50\%}$ (the temperature corresponding to the 50% conversion), as shown in Fig. 1B. The $T_{50\%}$ of Au/SiO₂-as prepared, Au/SiO₂-O₂-500, and Au/SiO₂-O₂-650 is as high as ca. 450 °C, however, decrease to ca. 320 °C for Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900.

Fig. 2 shows the XRD patterns of various catalysts. Au/SiO₂-as prepared shows the Au(111) and Au(200) diffraction peaks at 38.2° and 44.5°, respectively. According to the Scherrer equation, the average crystalline size of Au particles is estimated from the half-peak width of the (111) diffraction peak to be 15 nm. This result agrees with previous results that the deposition–precipitation method fails to prepare highly dispersed ultrafine Au nanoparticles on SiO₂ mainly because the point of zero charge (PZC) of SiO₂ is around pH 2 and then SiO₂ exhibits a large negative surface charge under the deposition–precipitation condition (pH between 9 and 10), com-

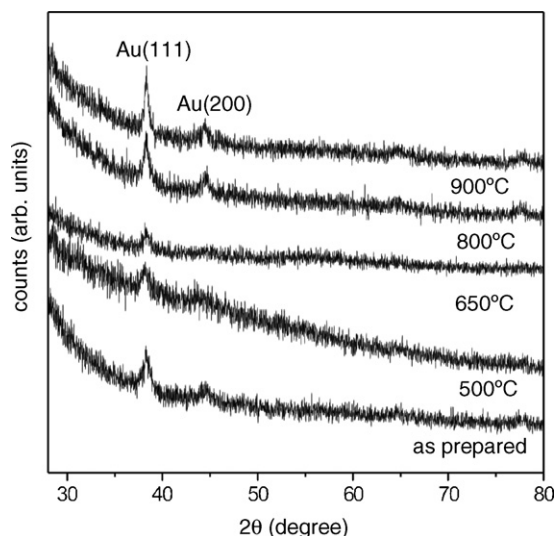


Fig. 2. XRD patterns of Au/SiO₂-as prepared, Au/SiO₂-O₂-500, Au/SiO₂-O₂-650, Au/SiO₂-O₂-800, and Au/SiO₂-O₂-900 catalysts.

plicating the deposition process of anionic gold species such as $[AuCl_4]^-$ [18,19]. Choosing appropriate cationic Au species as precursors can effectively overcome this difficulty and prepare highly dispersed ultrafine Au nanoparticles on SiO₂ via wet chemical preparation methods [23–25]. Similar results were also reported to prepare highly dispersed Au/TiO₂ catalysts via the impregnation method [38–40]. It has been established that ultrafine Au nanoparticles less than 5 nm diameter are active for low temperature CO oxidation [1]. Therefore, the poor activity of Au/SiO₂-as prepared can be attributed to the relatively large size of Au nanoparticles. Inferred from the XRD results, treating the catalyst in oxygen at 500 and 650 °C does not change the size of Au nanoparticles much. However, much sharper diffraction peaks appear for Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900, whose average crystalline sizes of Au nanoparticles were calculated to be 22 and 25 nm, respectively. These results demonstrate that the agglomeration of Au nanoparticles occurs on SiO₂ when treated in O₂ above 800 °C.

Above activity test results and XRD results seem to contradict the well-established fact that Au particles with small size are active for the CO oxidation. However, direct observations by TEM give comprehensive information on the geometric structure of Au particles on Au/SiO₂ treated in O₂ at various temperatures (Fig. 3). Au particles on Au/SiO₂-O₂-500 (Fig. 3a) and Au/SiO₂-O₂-650 (Fig. 3b) are mostly around 14 nm in size. But a broad size distribution of Au nanoparticles on Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900 were observed. Large Au aggregates exist on Au/SiO₂-O₂-800 (Fig. 3d) and (Fig. 3f), in consistent with XRD results; meanwhile, highly dispersed Au nanoparticles (Fig. 3c and e) are also clearly visible; moreover, some ultrafine Au nanoparticles also appear. These highly dispersed Au nanoparticles were not detected by XRD, implying that average crystalline sizes of these Au nanoparticles are smaller than those in Au/SiO₂-O₂-500 and Au/SiO₂-O₂-650. Therefore, TEM results demonstrate that, comparing Au nanoparticles on Au/SiO₂-O₂-500 and Au/SiO₂-O₂-650, larger and smaller Au nanoparticles coexist on Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900, the latter of which is responsible for the enhancement of the catalytic activity. The BET measurements also support the existence of highly dispersed Au nanoparticles on Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900. The surface areas of SiO₂, Au/SiO₂-as prepared, Au/SiO₂-O₂-650, Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900 are 446, 458, 466, 445, and 392 m²/g, respectively. Calcining SiO₂ at temperatures above 700 °C dramatically decreases its surface area [41]. The result that Au/SiO₂-O₂-800 still possesses a comparable surface area as Au/SiO₂-as prepared and Au/SiO₂-O₂-650 indicates the formation of smaller Au particles on Au/SiO₂-O₂-800, which can compensate the surface area loss induced by SiO₂.

Fig. 4 shows the diffuse reflectance UV–vis spectra of various samples. Au/SiO₂-as prepared and Au/SiO₂-O₂-650 exhibit a band at 522 nm, a characteristic of the plasmon resonance of metallic metal particles. The plasmon resonance of Au particles on Au/SiO₂-O₂-800 and Au/SiO₂-O₂-900 slightly blue-shifts to 518 nm, which could be taken as an indicative of the existence of smaller Au particles. All samples exhibit an additional band in the region of 245–290 nm. The band with

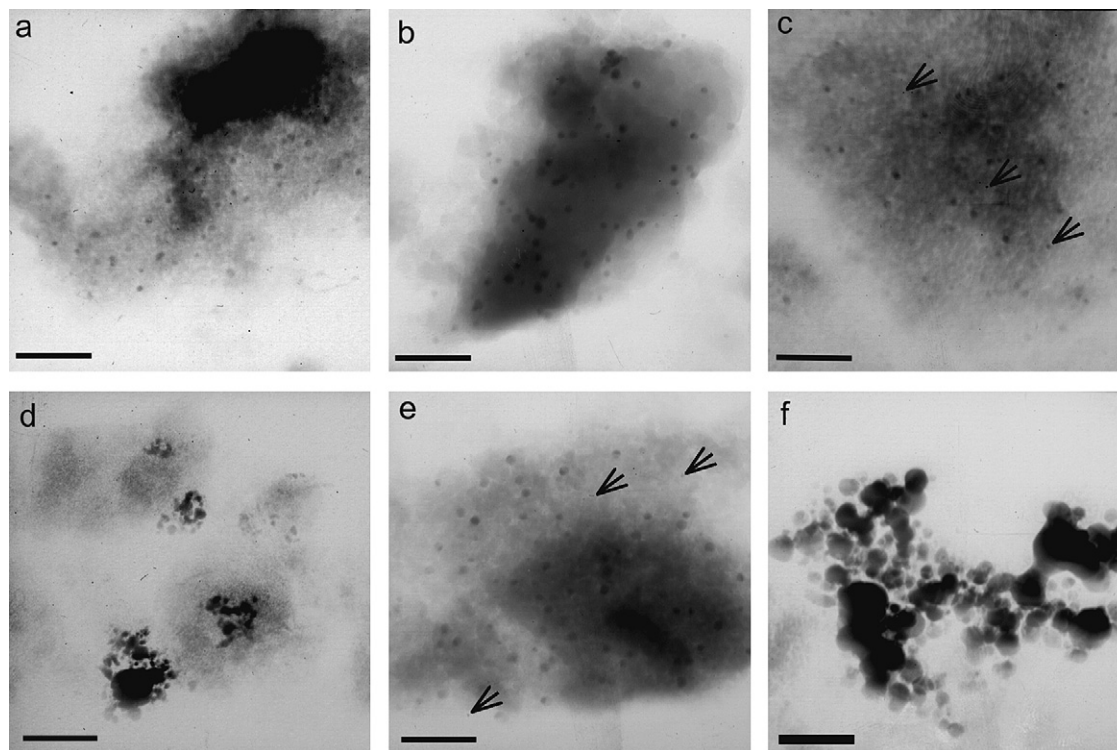


Fig. 3. TEM images of Au/SiO₂-O₂-500 (a), Au/SiO₂-O₂-650 (b), Au/SiO₂-O₂-800 (c and d), and Au/SiO₂-O₂-900 (e and f) catalysts. The bars are 100 nm in (a–e), 250 nm in (d), and 125 nm in (f), respectively. The arrows in (c and e) indicate the ultrafine Au nanoparticles.

maxima in the region of 240–320 nm was attributed to charge-transfer transitions in Au(I), Au(III), and gold charged clusters Au^{nδ+} [42–44]. It is thus assumed that both metallic and positively charged Au species are present on these samples.

We further investigated the oxidation state of Au particles on various catalysts by means of XPS. XPS detected no Cl on all catalysts, ruling out its adverse influence on the catalytic activity [15]. Fig. 5 shows the Au 4f XPS spectra for various catalysts.

Although the S/N ratio is not satisfying because of the low content of Au, the Au 4f_{7/2} binding energy can be well identified to locate at 83.5 eV for Au particles on Au/SiO₂-as prepared. Treating Au/SiO₂-as prepared in O₂ at 500 and 650 °C does not induce detectable change in the Au 4f_{7/2} binding energy. Increasing the treating temperature in O₂ to 800 and 900 °C up-shifts the Au 4f_{7/2} binding energy as much as 0.4 eV. The Au 4f_{7/2} binding energy of Au particles on Au/SiO₂-O₂-800

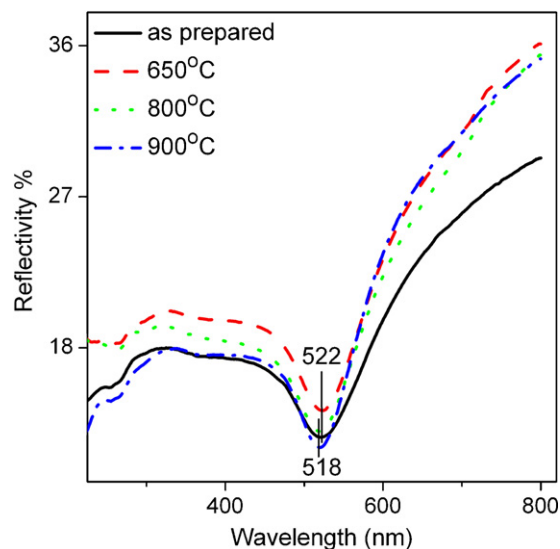


Fig. 4. The diffuse reflectance UV–vis spectra of Au/SiO₂-as prepared, Au/SiO₂-O₂-650, Au/SiO₂-O₂-800, and Au/SiO₂-O₂-900 catalysts.

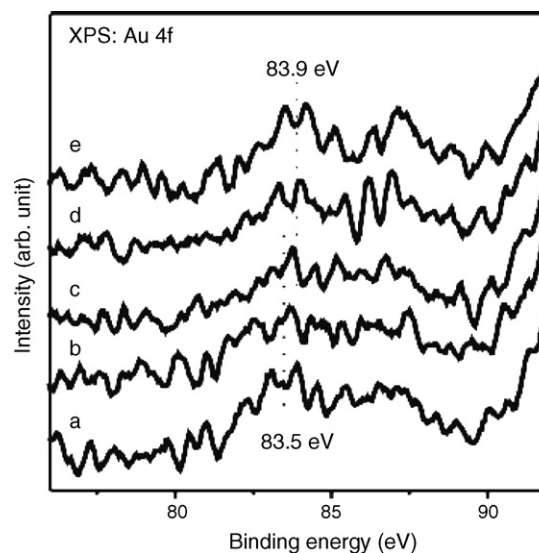


Fig. 5. Au 4f XPS spectra of Au/SiO₂-as prepared (a), Au/SiO₂-O₂-500 (b), Au/SiO₂-O₂-650 (c), Au/SiO₂-O₂-800 (d), and Au/SiO₂-O₂-900 (e) catalysts. *hν* = 1253.6 eV.

and Au/SiO₂-O₂-900 is 83.9 eV. Both values are in the range for metallic Au [37]. The XPS results and activity test results clearly demonstrate that Au particles on Au/SiO₂ being more cationic exhibit a higher catalytic activity towards CO oxidation. Model catalyst studies have shown that chemisorbed or dissolved oxygen on Au surface does not change the Au 4f binding energy and that only the oxide formation will result in significant Au 4f shifts [27,45]. Meanwhile, model catalyst studies have established the size-dependent positive binding energy shifts in Au 4f of Au particles supported on SiO₂ [27,46–49]. Dalacu et al. examined gold particles of various sizes on SiO₂ supports with XPS and observed positive binding energy shifts for the Au 4f peak of up to 0.5 eV; the shift increases to even higher binding energies (up to 1.3 eV) after annealing [48]. Lim et al. employed STM and XPS to study the Au particles on SiO₂ and observed the gradual shifts of the Au 4f states to higher binding energy up to 0.8 eV with the decreasing Au particle size [27]. The positive shift observed by XPS dominantly arises from final state effects with only minor contribution from initial state effects [47]. The interactions of Au particles with the supports (reduced surfaces or oxygen vacancies) were also proposed to be responsible for the observed shift in the core level of Au particles [50,51]. Therefore, the observed positive shift (0.4 eV) in Au 4f of Au/SiO₂ pretreated in O₂ at 800 and 900 °C can be reasonably attributed to the formation of smaller Au particles, consistent with TEM observations.

Above results demonstrate that treating Au/SiO₂ in O₂ at 500 and 650 °C essentially does not change the geometric and electronic structures of Au particles, and thus the catalytic performance. However, the structure of Au particles in Au/SiO₂ experience great changes after treating in O₂ at 800 and 900 °C. Geometrically, Au particles with larger and smaller sizes coexist; electronically, Au particles exhibit a higher binding energy in the Au 4f core level; the catalytic performance is also greatly improved, which can be attributed to the formation of Au particles with smaller size and higher binding energy. In order to clarify the role of oxygen in the observed changes of Au parti-

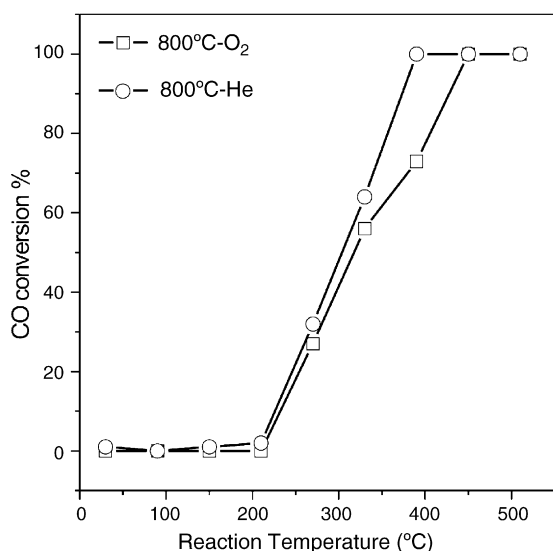


Fig. 6. The CO conversion of Au/SiO₂-O₂-800 and Au/SiO₂-He-800 catalysts.

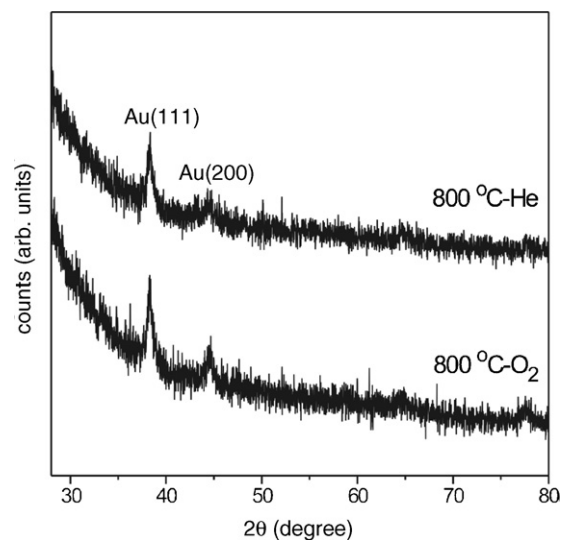


Fig. 7. XRD patterns of Au/SiO₂-O₂-800 and Au/SiO₂-He-800 catalysts.

cles, we pretreated Au/SiO₂ in He at 800 °C as a comparison. Fig. 6 compares the catalytic activity of Au/SiO₂ pretreated at 800 °C in O₂ and He, respectively. These two catalysts behave similar catalytic performances. The geometric structures of Au particles in these two catalysts as revealed by XRD (Fig. 7) and TEM (results not shown) are similar: co-existence of large and small Au particles. More importantly, Fig. 8 illustrates that the electronic structures of Au particles are nearly same in these two catalysts: both showing an Au 4f_{7/2} binding energy at 83.9 eV. These results clearly show that the pretreatment temperature, instead of the pretreatment atmosphere, play the key role in the observed structural changes and activity enhancement of Au/SiO₂. Although O 1s XPS spectra fail to provide any information on the Au–O₂ interactions because of the huge background intensity from the support, it can be inferred from the reaction results that Au particles in Au/SiO₂ will interact with

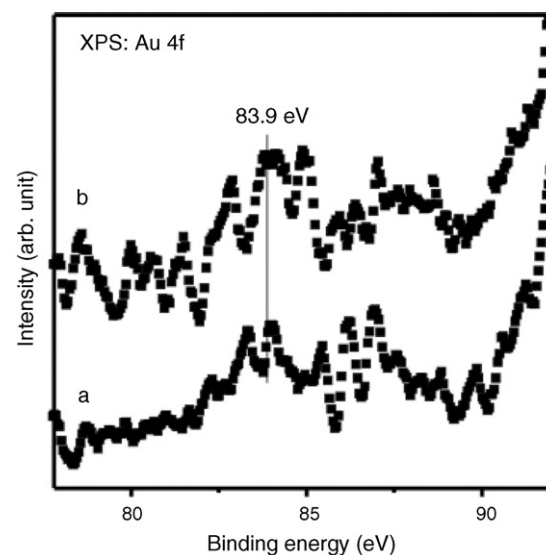


Fig. 8. Au 4f XPS spectra of Au/SiO₂-O₂-800 (a) and Au/SiO₂-He-800 (b) catalysts. $h\nu = 1253.6$ eV.

O₂ when treated in O₂ at high temperatures because Au/SiO₂ can catalyze the CO oxidation reaction. But it turns out that the interaction does not exert any influence on the catalytic activity of Au particles. The observed oxygen pretreatment effect on Au/SiO₂ is quite different from that on Ag/SiO₂. Ag/SiO₂ pretreated at high temperatures in oxygen behaves a much higher catalytic towards CO oxidation than that pretreated in He [33]. The difference could be attributed to the different activities of oxygen species on Ag and Au particles towards CO oxidation. The chemisorbed or dissolved oxygen species resulted from Ag particles–O₂ interactions at high temperatures can react with CO at RT [33]. However, a recent study shows that chemisorbed or dissolved oxygen species resulted from Au particles–atomic oxygen interaction are inert for CO oxidation at RT whereas the formed Au₂O₃ can react with CO at RT [27].

We propose an evaporation–deposition mechanism to account for the observed experimental results. The melting point of Au is 1064 °C. When Au/SiO₂ are treated at high temperatures (800 and 900 °C), Au particles will evaporate into the gas phase, which then deposit onto the support again. The deposition is actually the nucleation of Au atoms in gas phase on the support, followed by agglomeration of the Au clusters, leading to the formation of highly dispersed Au nanoparticles, which are responsible to the great improvement of the catalytic activity. Meanwhile, high temperature treatment will cause the direct agglomeration of Au particles originally existing on the support, thus forming large Au particles. The evaporation–deposition mechanism is mainly dependent on the treating temperature and not on the treating atmosphere, consistent with our experimental results. This evaporation–deposition process is similar to the chemical vapor deposition (CVD) process. In CVD process, the support is at RT whereas the support is at high temperatures in our case. It is quite surprising that the highly dispersed ultrafine Au nanoparticles can be stabilized on the inert SiO₂ support at 800 °C or even higher temperatures. It has been found that dehydroxylation reaction occurs on SiO₂ at such high temperatures, which might create oxygen vacancies. These oxygen vacancies can interact and stabilize the highly dispersed ultrafine Au nanoparticles that exhibit high catalytic activity towards CO oxidation.

It is noteworthy that highly active silica-supported Au catalysts for CO oxidation at low temperatures have been prepared by chemical vapor deposition [18] and a wet chemical process employing [Au(en)2]³⁺ (en = ethylenediamine) [25], in which the average size of Au particles is about 5 nm. The catalytic performance of Au/SiO₂ catalysts in our study is poor due to the relatively large size of Au particles. But because SiO₂ does not participate into the CO oxidation reaction, our study establishes a relation among the geometric structure, the electronic structure, and the catalytic activity of Au particles: the smaller the Au particle size, the higher the Au 4f binding energy of the Au particle, the more active the Au particles.

4. Conclusions

The effect of oxygen treatment on the catalytic performance of Au/SiO₂ catalysts prepared via deposition–precipitation

method towards CO oxidation was investigated in detail. Treatment of the catalyst in O₂ at temperatures higher than 800 °C greatly enhances the catalytic activity. XRD and TEM results demonstrate the co-existence of large Au particles and highly dispersed ultrafine Au nanoparticles on the surface after the oxygen treatment at temperatures above 800 °C. XPS results reveal that the Au 4f binding energy shifts to higher binding energy after the oxygen pretreatment at temperatures above 800 °C. Treatment of the Au/SiO₂ catalyst in He at 800 °C also shows the similar geometric and electronic structure changes of Au particles and thus the enhancement effect as that in O₂, indicating that the Au–O₂ interactions at high temperatures do not contribute much to the improvement of catalytic activity. We propose an evaporation–deposition mechanism of Au particles treated at high temperatures, accounting for the formation of highly dispersed ultrafine Au nanoparticles, which are responsible for the enhancement of the catalytic activity. Our results clearly demonstrate the geometric structure–electronic structure–catalytic activity relation of Au particles.

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