



# Au–Pd alloying-promoted thermal decomposition of PdO supported on SiO<sub>2</sub> and its effect on the catalytic performance in CO oxidation

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## ABSTRACT

We have prepared a series of Au–Pd/SiO<sub>2</sub> catalysts by the routine deposition–precipitation method followed by calcination at 200 °C in air for 4 h. The structures of these catalysts have been characterized with powder X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and H<sub>2</sub>-temperature-programmed reduction. Their catalytic activity in CO oxidation has also been studied. We found that the preparation procedure leads to the formation of highly dispersed PdO supported on SiO<sub>2</sub> in Pd/SiO<sub>2</sub>, but to the formation of both highly dispersed PdO and Au<sub>x</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub> catalysts. The fraction of metallic Pd in Pd species increases with the increase of Au:Pd molar ratio in Au–Pd/SiO<sub>2</sub> catalysts. We proposed that the alloying of Au and Pd can promote the thermal decomposition of PdO supported on SiO<sub>2</sub>. Because of the existence of metallic Pd, Au–Pd/SiO<sub>2</sub> catalysts are more active in CO oxidation than Pd/SiO<sub>2</sub>. Au–Pd/SiO<sub>2</sub>-0.5 exhibits the same activity as Pd/SiO<sub>2</sub>-H<sub>2</sub> in CO oxidation. Our results provide some novel information on the fabrication of supported Au<sub>x</sub>Pd alloy nanoparticles.

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## 1. Introduction

Bimetallic catalysts usually exhibit advantageous properties compared to those of their individual constituent metals [1]. Supported Au–Pd bimetallic catalysts have been reported to show very nice catalytic performance in acetoxylation of ethylene to vinyl acetate [2], direct synthesis of hydrogen peroxide from H<sub>2</sub> and O<sub>2</sub> [3], oxidation of benzyl alcohol, 1-butanol, 2-butanol, 2-buten-1-ol and 1,4-butanediol [4], hydrogenation reaction [5], CO oxidation [6], photocatalysis [7]. It is generally accepted that the synergistic effect exists in the bimetallic catalysts to modify the geometric and the electronic properties of the active site, increase the resistance to particle sintering, and eventually improve the catalytic performance. The structure and synergistic effect of supported Au–Pd bimetallic catalysts have also been much investigated. Hou et al. [4] found that bimetallic Au–Pd nanoparticles with a Au:Pd atomic ratio of 1:3 show a higher catalytic activity than bimetallic Au–Pd nanoparticles with other Au:Pd atomic ratios in oxidation of benzyl alcohol, 1-butanol, 2-butanol, 2-buten-1-ol and 1,4-butanediol. Edwards et al. [8] reported that acid pretreatment of a carbon support for Au–Pd alloy catalysts switches off the decomposition of H<sub>2</sub>O<sub>2</sub> by decreasing the size of alloy nanoparticles. Chen et al. [9]

revealed that the role of Au in Au–Pd alloy for acetoxylation of ethylene to vinyl acetate is to isolate single Pd sites to facilitate the formation of active sites consisting of two noncontiguous and suitably spaced Pd monomers. Gao et al. [10] proposed that contiguous Pd sites on the AuPd (1 0 0) alloy surface provide O<sub>ads</sub> and Au and Pd sites provide CO<sub>ads</sub> so that low-temperature CO oxidation can occur more facily on supported Au–Pd alloy nanoparticles than on supported Au or Pd nanoparticles. It is interesting that the support was reported to affect the synergistic effect in Au–Pd alloy nanoparticles. Gucci et al. observed a slight synergistic effect for Au–Pd alloy nanoparticles supported on TiO<sub>2</sub> in CO oxidation [6], but no synergistic effect for Au–Pd alloy nanoparticles supported on SiO<sub>2</sub> [11]. Therefore, the synergistic effect in supported Au–Pd alloy catalysts acts in different ways for different catalytic reactions and thus needs further investigation.

The preparation method of supported Au–Pd alloy catalysts is of great importance for the investigation of synergistic effect. Incipient wetness method, deposition–precipitation method, sol-immobilization method, and electroless deposition method that were all followed by H<sub>2</sub> reduction at high temperatures have been employed to synthesize supported Au–Pd alloy catalysts [2–8,11–17]. We consider that the deposition–precipitation method is very suitable for the preparation of supported Au–Pd bimetallic catalysts for the synergistic effect investigation because it does not introduce any other undesired ions and compounds in the catalysts. Meanwhile, our previous studies [18–20] demon-

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strate that  $\text{SiO}_2$  is an appropriate support for the investigation of structure–activity of supported nanoparticles because  $\text{SiO}_2$  does not participate in the catalytic reaction. Therefore, in our studies of synergistic effect of supported Au–Pd bimetallic catalysts, we chose  $\text{SiO}_2$  as the support and employ deposition–precipitation to prepare the catalysts. In this paper, we report the results of Au–Pd/ $\text{SiO}_2$  catalysts prepared by deposition–precipitation followed by calcination at  $200^\circ\text{C}$  in air for 4 h. Very interestingly, such a preparation procedure leads to the formation of highly dispersed PdO supported on  $\text{SiO}_2$  in Pd/ $\text{SiO}_2$ , but to the formation of both highly dispersed PdO and  $\text{Au}_x\text{Pd}$  alloy nanoparticles in Au–Pd/ $\text{SiO}_2$  catalysts. The fraction of metallic Pd in Pd species increases with the increase of Au:Pd molar ratio in Au–Pd/ $\text{SiO}_2$  catalysts. We proposed that the alloying of Au and Pd can promote the thermal decomposition of PdO supported on  $\text{SiO}_2$ . Because of the existence of metallic Pd, Au–Pd/ $\text{SiO}_2$  catalysts are more active in CO oxidation than Pd/ $\text{SiO}_2$ . Au–Pd/ $\text{SiO}_2$ -0.5 exhibits the same activity as Pd/ $\text{SiO}_2$ - $\text{H}_2$  in CO oxidation. Our results provide some novel information on the fabrication of supported  $\text{Au}_x\text{Pd}$  alloy nanoparticles.

## 2. Experimental

A series of supported Au–Pd catalysts with different Au:Pd molar ratios (denoted as Au–Pd/ $\text{SiO}_2$ - $x$ ,  $x$  is the Au:Pd molar ratio) were prepared by the traditional deposition–precipitation method employing  $\text{H}_2\text{AuCl}_4 \cdot 4\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co., Ltd, Au content  $\geq 47.8\%$ ) and  $\text{H}_2\text{PdCl}_4$  (Sinopharm Chemical Reagent Co., Ltd.,  $\text{PdCl}_2:\text{HCl}$  molar ratio: 1:2) as the precursors and inert  $\text{SiO}_2$  (40–120 mesh, Qingdao Haiyang Chemicals Co.) as the support. The loading of Pd in the catalysts was fixed with a Pd: $\text{SiO}_2$  weight ratio of 1% in all catalysts. Typically, calculated amounts of  $\text{H}_2\text{AuCl}_4$  and  $\text{H}_2\text{PdCl}_4$  aqueous solution were co-added into a three-neck bottle containing the support and adequately stirred, and then ammonia water was slowly added to adjust the pH between 9 and 10. The system was adequately stirred at  $60^\circ\text{C}$  for 24 h. Then the precipitate was filtered and washed several times, and the resulting powder was dried at  $60^\circ\text{C}$  for 12 h followed by calcination in air at  $200^\circ\text{C}$  for 4 h. For comparisons, Au/ $\text{SiO}_2$  catalyst with the same Au loading as that in Au–Pd/ $\text{SiO}_2$ -1 was prepared in a similar way; and Au–Pd/ $\text{SiO}_2$  catalysts (denoted as Au–Pd/ $\text{SiO}_2$ - $x$ - $\text{H}_2$ ) was prepared in a similar way but were finally reduced in  $\text{H}_2$  at  $200^\circ\text{C}$  for 4 h.

Powder X-ray diffraction (XRD) patterns were acquired on a Philips X'Pert Pro Super X-ray diffractometer with a Ni-filtered  $\text{Cu K}\alpha$  X-ray source operating at 40 kV and 50 mA. Transmission electron microscopy (TEM) measurements were carried out on a JEOL-2100F transmission electron microscope at an accelerating voltage of 200 kV. High resolution X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high performance electron spectrometer using monochromatized Al  $\text{K}\alpha$  excitation source ( $h\nu = 1486.6\text{ eV}$ ). The binding energies in the XPS spectra were referenced to the Si 2p binding energy in  $\text{SiO}_2$  at 103.3 eV. The reduction behavior of Au–Pd/ $\text{SiO}_2$  catalysts was measured by  $\text{H}_2$  temperature programmed reduction ( $\text{H}_2$ -TPR). 50 mg catalyst was placed in a quartz reactor and heated at a rate of  $10^\circ\text{C}/\text{min}$ . 5%  $\text{H}_2$  balanced with Ar was fed at a flow rate of 20 ml/min and the consumption of  $\text{H}_2$  was measured by a thermal conductivity detector (TCD).

The catalytic activity of catalysts towards CO oxidation was evaluated with a fixed-bed flow reactor. The catalyst experienced no pre-treatment prior to the catalytic reaction. The used catalyst weight was 100 mg and the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 20 ml/min. The steady-state composition of the effluent gas was analyzed with an online GC-14C gas chromatograph equipped with a TDX-01 column ( $T = 80^\circ\text{C}$ ,  $\text{H}_2$  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.

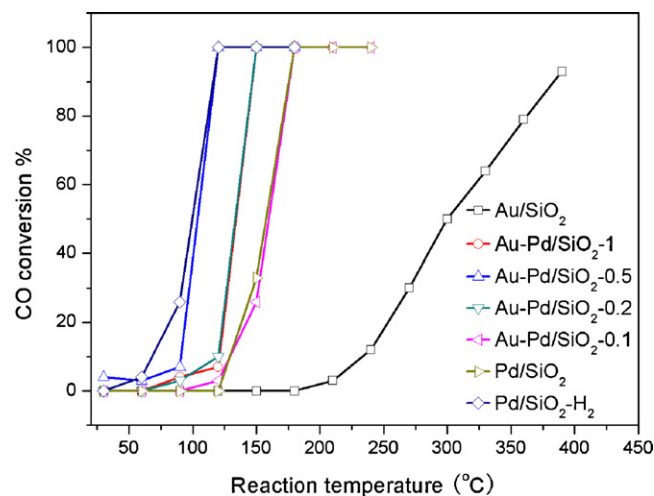


Fig. 1. Catalytic performance of Au–Pd/ $\text{SiO}_2$  catalysts in CO oxidation.

## 3. Results and discussion

Fig. 1 shows the catalytic performances of various Au–Pd/ $\text{SiO}_2$  catalysts in CO oxidation. Au/ $\text{SiO}_2$  prepared by deposition–precipitation exhibits a poor activity and becomes active at reaction temperatures above  $200^\circ\text{C}$ , in consistence with our previous results [21]. Pd/ $\text{SiO}_2$  becomes active at reaction temperatures above  $120^\circ\text{C}$  and acquires a 100% CO conversion at  $180^\circ\text{C}$ , and Pd/ $\text{SiO}_2$ - $\text{H}_2$  is more active, becoming active at reaction temperatures above  $60^\circ\text{C}$  and acquires a 100% CO conversion at  $120^\circ\text{C}$ . The addition of Au in Pd/ $\text{SiO}_2$  promotes its activity in CO oxidation, and the promotion effect depends on the Au:Pd molar ratio.  $T_{50}$  (temperature for a 50% CO conversion) was adopted to compare the activity of various Au–Pd/ $\text{SiO}_2$  and corresponding Au–Pd/ $\text{SiO}_2$ - $\text{H}_2$  catalysts, whose results are shown in Fig. 2. Au–Pd/ $\text{SiO}_2$ - $x$ - $\text{H}_2$  ( $x \leq 0.5$ ) exhibits a similar activity to Pd/ $\text{SiO}_2$ - $\text{H}_2$ , and Au–Pd/ $\text{SiO}_2$ -1- $\text{H}_2$  is less active. The activity of Au–Pd/ $\text{SiO}_2$ - $x$  exhibits a volcano-shape dependence on the  $x$  value. Au–Pd/ $\text{SiO}_2$ -0.5 shows the best catalytic activity and its  $T_{50}$  is  $105^\circ\text{C}$ . Interestingly, although Pd/ $\text{SiO}_2$ - $\text{H}_2$  is much more active than corresponding Pd/ $\text{SiO}_2$ , the difference in the  $T_{50}$  between Au–Pd/ $\text{SiO}_2$ - $x$  and corresponding Au–Pd/ $\text{SiO}_2$ - $x$ - $\text{H}_2$  decreases with

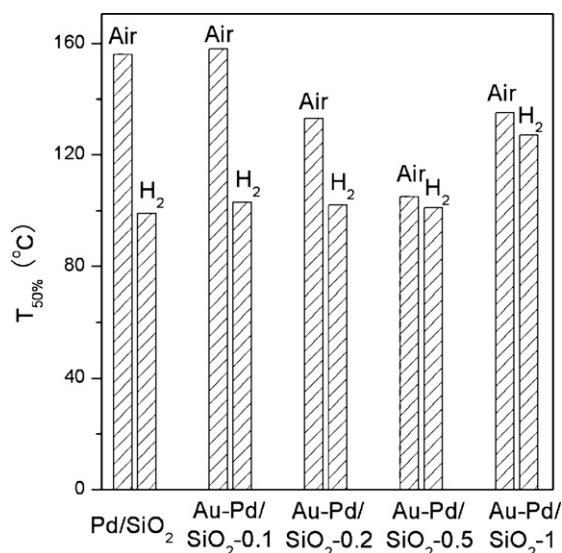


Fig. 2.  $T_{50}$  of Au–Pd/ $\text{SiO}_2$  and Au–Pd/ $\text{SiO}_2$ - $\text{H}_2$  catalysts in CO oxidation.

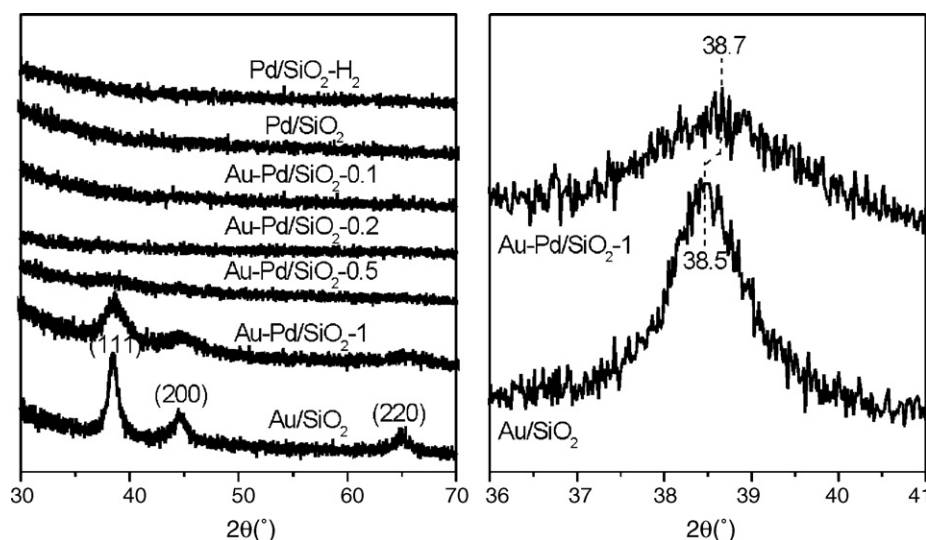


Fig. 3. XRD patterns of Au-Pd/SiO<sub>2</sub> catalysts (left) and the enlarged XRD patterns of Au/SiO<sub>2</sub> and Au-Pd/SiO<sub>2</sub>-1 between 36 and 41° (right).

the increase of  $x$  value. Au-Pd/SiO<sub>2</sub>- $x$  ( $x=0.5$  and  $1.0$ ) exhibits similar  $T_{50}$  to corresponding Au-Pd/SiO<sub>2</sub>- $x$ -H<sub>2</sub> although Au-Pd/SiO<sub>2</sub>- $x$  was prepared by calcination in air while Au-Pd/SiO<sub>2</sub>- $x$ -H<sub>2</sub> was prepared by reduction in H<sub>2</sub>.

Fig. 3 displays the XRD patterns of various catalysts. No obvious diffraction patterns appears in the XRD spectra of Pd/SiO<sub>2</sub>-H<sub>2</sub>, Pd/SiO<sub>2</sub>, and Au-Pd/SiO<sub>2</sub>- $x$  ( $x=0.1$ ,  $0.2$ , and  $0.5$ ), demonstrating that the Pd and Au species in these catalysts are highly dispersive. Au/SiO<sub>2</sub> shows a typical diffraction pattern arising from Au. The diffraction pattern of Au-Pd/SiO<sub>2</sub>-1 is similar to that of Au/SiO<sub>2</sub>, but the diffraction peaks of Au-Pd/SiO<sub>2</sub>-1 are much broader than those of Au/SiO<sub>2</sub>. A careful examination shows that the position of (1 1 1) diffraction peak of Au-Pd/SiO<sub>2</sub>-1 ( $2\theta=38.7^\circ$ ) is distinctly larger than that of Au/SiO<sub>2</sub> ( $2\theta=38.5^\circ$ ). The same trend also occurs for other diffraction peaks. The standard positions of Au (1 1 1) and Pd (1 1 1) diffraction peaks locate at  $38.2^\circ$  and  $39.9^\circ$ , respectively, therefore, the observed position of (1 1 1) diffraction peak in Au-Pd/SiO<sub>2</sub>-1.0 might indicate the formation of Au-Pd alloy, agreeing with previous reports [22,23]. According to the Scherrer equation, the average crystalline size of Au nanoparticles in Au/SiO<sub>2</sub> and Au-Pd alloy nanoparticles in Au-Pd/SiO<sub>2</sub>-1 was estimated to be  $\sim 10$  and  $\sim 4$  nm, respectively. Fig. 4 shows TEM images of Au/SiO<sub>2</sub>, Au-Pd/SiO<sub>2</sub>-1 and Pd/SiO<sub>2</sub>, in which Au nanoparticles between 7 and 12 nm are clearly visible in Au/SiO<sub>2</sub> whereas no obvious particles could be identified in Pd/SiO<sub>2</sub>. TEM results clearly demonstrate the existence of aggregates consisting of fine nanoparticles between 3 and 5 nm in Au-Pd/SiO<sub>2</sub>-1, and the HRTEM image reveals a lattice fringe of 0.230 nm for these fine nanoparticles that

could be assigned to the lattice fringe of (1 1 1) plane of Au-Pd alloy nanoparticles.

The Pd 3d and Au 4f XPS spectra are shown in Figs. 5 and 6, respectively. Since the Au 4d<sub>5/2</sub> binding energy is similar to the Pd 3d<sub>5/2</sub>, therefore we analyzed the Pd 3d XPS spectrum with the Pd 3d<sub>3/2</sub> peak. Pd/SiO<sub>2</sub> exhibits a single Pd 3d<sub>3/2</sub> component with the binding energy at 342.3 eV that can be attributed to PdO whereas Pd/SiO<sub>2</sub>-H<sub>2</sub> exhibits a single Pd 3d<sub>3/2</sub> component with the binding energy at 341.2 eV that can be attributed to metallic Pd [22,23]. Therefore, highly dispersive Pd nanoparticles in Pd/SiO<sub>2</sub>-H<sub>2</sub> is much more active than highly dispersive PdO nanoparticles in Pd/SiO<sub>2</sub> in CO oxidation reaction, agreeing with the results from surface science studies of model Pd surfaces [24]. Interestingly, although Au-Pd/SiO<sub>2</sub> catalysts were prepared with the same method as Pd/SiO<sub>2</sub>, the Pd 3d<sub>3/2</sub> peaks of Au-Pd/SiO<sub>2</sub> catalysts all exhibit two components with the binding energy at 341.2 and 342.3 eV, and the fraction of component at 341.2 eV gradually increases with the increase of Au:Pd molar ratio. These observations demonstrate that the Au additive promotes the thermal decomposition of PdO nanoparticles supported on SiO<sub>2</sub> to form metallic Pd, which is a very interesting result.

The same preparation procedure for Pd/SiO<sub>2</sub> leads to the preparation of metallic Au nanoparticles supported on SiO<sub>2</sub>, as demonstrated by the Au 4f<sub>7/2</sub> binding energy of Au/SiO<sub>2</sub> at 84.0 eV. The Au 4f XPS results also show that there is only metallic Au in Au-Pd/SiO<sub>2</sub>-1, Au-Pd/SiO<sub>2</sub>-0.5 and Au-Pd/SiO<sub>2</sub>-0.2. However, the Au 4f<sub>7/2</sub> binding energy shifts from 84.0 eV for Au-Pd/SiO<sub>2</sub>-1 to 83.9 eV for Au-Pd/SiO<sub>2</sub>-0.5 and 83.8 eV for Au-Pd/SiO<sub>2</sub>-0.2, sug-

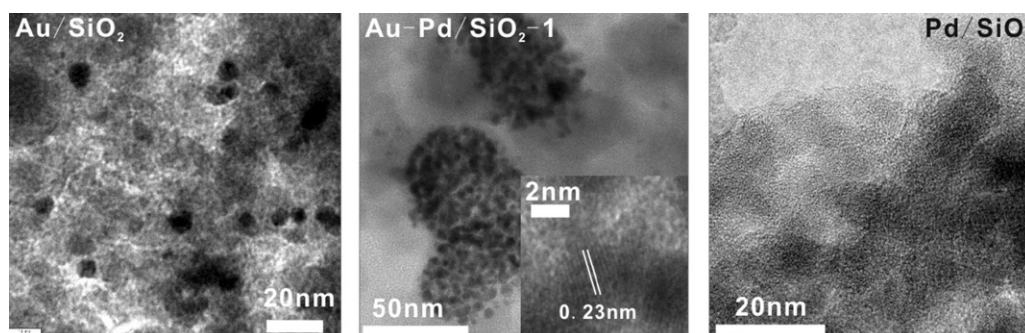
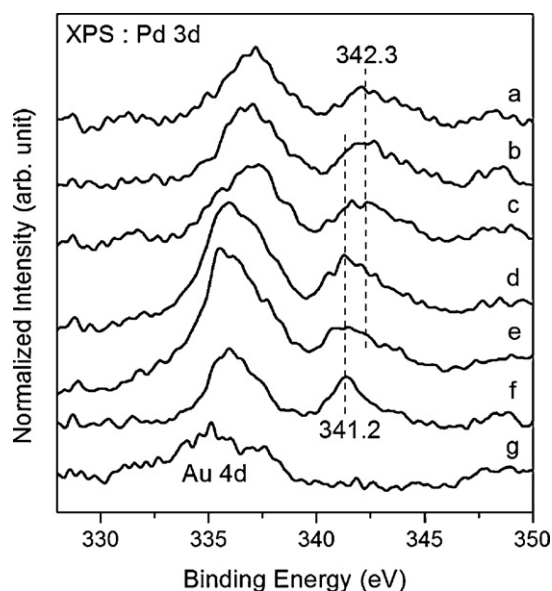


Fig. 4. TEM images of Au/SiO<sub>2</sub>, Au-Pd/SiO<sub>2</sub>-1 and Pd/SiO<sub>2</sub>. The inset shows the HRTEM of Au-Pd/SiO<sub>2</sub>-1.

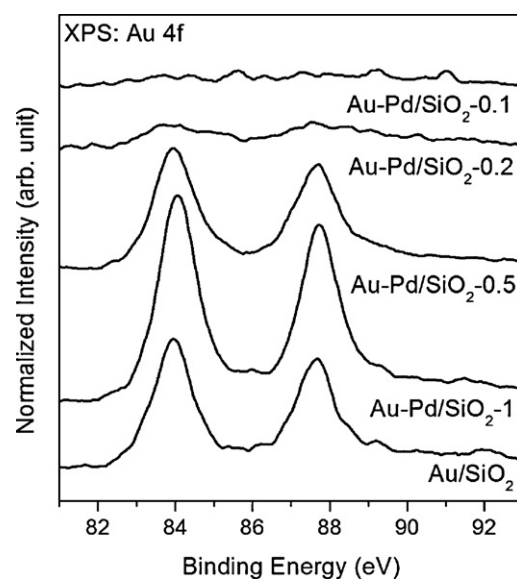




**Fig. 5.** Pd 3d and Au 4d<sub>5/2</sub> XPS spectra of Pd/SiO<sub>2</sub> (a), Au-Pd/SiO<sub>2</sub>-0.1 (b), Au-Pd/SiO<sub>2</sub>-0.2 (c), Au-Pd/SiO<sub>2</sub>-0.5 (d), Au-Pd/SiO<sub>2</sub>-1 (e), Pd/SiO<sub>2</sub>-H<sub>2</sub> (f), and Au/SiO<sub>2</sub> (g).

gesting that the charge transfer to metallic Au occurs in Au-Pd/SiO<sub>2</sub> catalysts and becomes more profound with the decrease of Au:Pd molar ratio. An interesting observation is the variation of Au 4f XPS peak intensity of Au-Pd/SiO<sub>2</sub> catalysts. Au-Pd/SiO<sub>2</sub>-0.1 actually shows no obvious Au 4f XPS peak and Au-Pd/SiO<sub>2</sub>-0.2 only displays a weak and diffuse Au 4f XPS peak, then Au-Pd/SiO<sub>2</sub>-0.5 shows a strong Au 4f XPS peak and the intensity of Au 4f peak for Au-Pd/SiO<sub>2</sub>-1 is nearly as twice as that of Au-Pd/SiO<sub>2</sub>-0.5. Since XPS is a surface-sensitive method, the intensity variation of Au 4f XPS peak might indicate that Au-Pd alloy nanoparticles in Au-Pd/SiO<sub>2</sub>-0.5 and Au-Pd/SiO<sub>2</sub>-1 are more surface-enriched with Au than those in Au-Pd/SiO<sub>2</sub>-0.1 and Au-Pd/SiO<sub>2</sub>-0.2. It could also be seen that the Au 4f XPS peak of Au-Pd/SiO<sub>2</sub>-1 is much more intense than that of Au/SiO<sub>2</sub> although both catalysts have the same Au loading. This agrees with the XRD results that nanoparticles in Au-Pd/SiO<sub>2</sub> are much more dispersive than those in Au/SiO<sub>2</sub>.

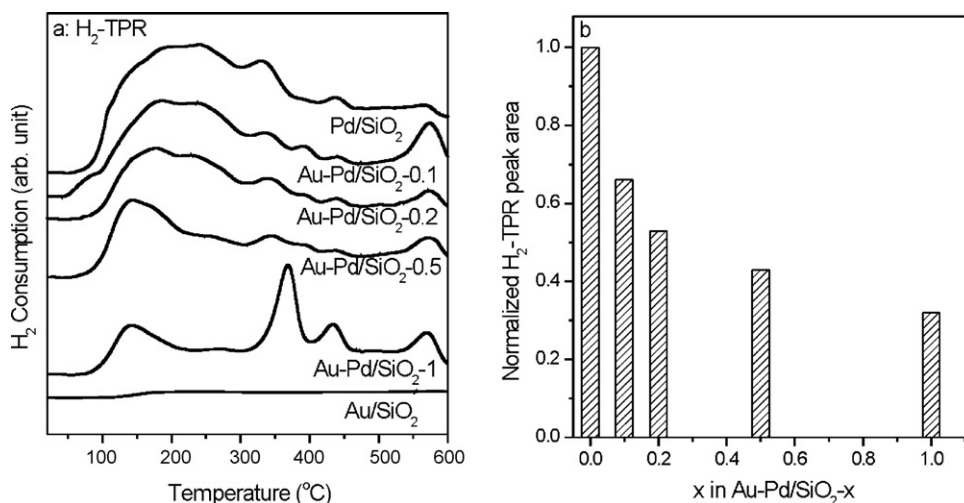
The thermal decomposition of PdO nanoparticles supported on SiO<sub>2</sub> promoted by Au additive is further by the H<sub>2</sub>-TPR experimental results (Fig. 7(a)). No reduction peak was observed for Au/SiO<sub>2</sub>



**Fig. 6.** Au 4f XPS spectra of Au-Pd/SiO<sub>2</sub> and Au/SiO<sub>2</sub> catalysts.

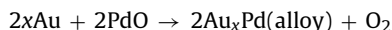
catalyst, in consistence with XRD and XPS results that only metallic Au nanoparticles exist in Au/SiO<sub>2</sub>. Pd/SiO<sub>2</sub> shows a broad reduction peak ranging from 100 to 600 °C, which could be assigned to the reduction of PdO nanoparticles interacting with SiO<sub>2</sub> with different interaction strengths [25]. PdO nanoparticles weakly interacting with SiO<sub>2</sub> are reduced at low temperatures. The reduction peak in the H<sub>2</sub>-TPR keep decreasing with the increase of Au:Pd molar ratio in Au-Pd/SiO<sub>2</sub> catalysts. It is noteworthy that Au-Pd/SiO<sub>2</sub>-1 exhibits two distinct reduction peaks at 370 and 430 °C although it shows the lowest H<sub>2</sub> consumption, suggesting the enhanced interaction of PdO with SiO<sub>2</sub>. Fig. 7(b) shows the H<sub>2</sub> reduction peak areas of Au-Pd/SiO<sub>2</sub> catalysts normalized with Pd/SiO<sub>2</sub>, clearly demonstrating the fraction of PdO species in Au-Pd/SiO<sub>2</sub> catalysts decreases with the increase of Au:Pd molar ratio. From the PdO fraction and Au:Pd molar ratio, the molar ratio of metallic Au:metallic Pd can be calculated to be 1.5, 0.9, 0.4 and 0.3 for Au-Pd/SiO<sub>2</sub>-1, Au-Pd/SiO<sub>2</sub>-0.5, Au-Pd/SiO<sub>2</sub>-0.2 and Au-Pd/SiO<sub>2</sub>-0.1, respectively.

The XPS and H<sub>2</sub>-TPR results clearly evidence that prepared with the same procedure, Pd/SiO<sub>2</sub> only contains PdO whereas Au-Pd/SiO<sub>2</sub> catalysts contain both metallic Pd and PdO and the fraction of Pd increases with the increase of Au:Pd molar ratio in



**Fig. 7.** H<sub>2</sub>-TPR profiles (a) and normalized H<sub>2</sub>-TPR peak areas (b) of Au-Pd/SiO<sub>2</sub> catalysts.

the catalysts. Au/SiO<sub>2</sub> containing only metallic Au nanoparticles can be prepared under the same condition; therefore, we propose the following reaction occurs during the course of calcination of Au–Pd/SiO<sub>2</sub> catalysts at 200 °C in air:



The alloying of Au and Pd is an exothermal reaction and thus can facilitate the thermal decomposition of PdO supported on SiO<sub>2</sub>. Without the alloying process, PdO supported on SiO<sub>2</sub> cannot decompose when calcined at 200 °C in air. The formation of Au<sub>x</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub> catalysts is also supported by the observed shift of Au 4f binding energy. The XRD results suggest that the Au<sub>x</sub>Pd alloy nanoparticles tend to be highly dispersed on SiO<sub>2</sub> with the decrease of Au: Pd molar ratio in the catalysts, which could be attributed to the strong interaction between Pd and SiO<sub>2</sub>.

The composition of various Au–Pd/SiO<sub>2</sub> catalysts could be estimated from the fraction of PdO (H<sub>2</sub>-TPR results) and the Au: Pd molar ratio in Au–Pd alloy nanoparticles. With the same preparation method, the acquired species supported on SiO<sub>2</sub> is highly dispersed PdO in Pd/SiO<sub>2</sub>, 66% highly dispersed PdO and 34% highly dispersed Au<sub>0.3</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-0.1, 53% highly dispersed PdO and 47% highly dispersed Au<sub>0.4</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-0.2, 43% highly dispersed PdO and 57% highly dispersed Au<sub>0.9</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-0.5, and 32% highly dispersed PdO and 68% Au<sub>1.5</sub>Pd alloy nanoparticles with an average crystalline size of 4 nm in Au–Pd/SiO<sub>2</sub>-1. On basis of the catalytic performance of Pd/SiO<sub>2</sub>-H<sub>2</sub>, Pd/SiO<sub>2</sub> and Au/SiO<sub>2</sub>, it could be concluded that highly dispersed Pd nanoparticles supported on SiO<sub>2</sub> are most active in CO oxidation, therefore, the composition and structure of Au–Pd/SiO<sub>2</sub> catalysts can well account for their catalytic performance in CO oxidation. Although the amount of metallic Pd in Au–Pd/SiO<sub>2</sub>-0.5 is 59% of that in Pd/SiO<sub>2</sub>-H<sub>2</sub>, Au–Pd/SiO<sub>2</sub>-0.5 exhibits nearly the same activity in CO oxidation as Pd/SiO<sub>2</sub>-H<sub>2</sub>. This indicates the existence of a synergistic effect between Au and Pd in Au<sub>0.9</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-0.5 for CO oxidation, as previously observed in CO oxidation over Au–Pd model catalysts [10,26,27]. Comparing Au<sub>0.9</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-0.5, the poor activity of Au<sub>1.5</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub>-1 could be attributed to both their poor dispersion and the likely Au-enriched surface of Au<sub>1.5</sub>Pd alloy nanoparticles. The detailed surface structures of Au–Pd alloy nanoparticles are needed for a comprehensive understanding of their catalytic performance in CO oxidation, which are still under investigation.

#### 4. Conclusion

Au–Pd/SiO<sub>2</sub> catalysts have been prepared by the routine deposition–precipitation method followed by calcination at 200 °C in air for 4 h. This preparation procedure leads to the formation of

highly dispersed PdO supported on SiO<sub>2</sub> in Pd/SiO<sub>2</sub>, but to the formation of both highly dispersed PdO and Au<sub>x</sub>Pd alloy nanoparticles in Au–Pd/SiO<sub>2</sub> catalysts. The fraction of metallic Pd in Pd species increases with the increase of Au: Pd molar ratio in Au–Pd/SiO<sub>2</sub> catalysts. We proposed that the alloying of Au and Pd can promote the thermal decomposition of PdO supported on SiO<sub>2</sub>. Because of the existence of metallic Pd, Au–Pd/SiO<sub>2</sub> catalysts are more active in CO oxidation than Pd/SiO<sub>2</sub>. Au–Pd/SiO<sub>2</sub>-0.5 exhibits the same activity as Pd/SiO<sub>2</sub>-H<sub>2</sub> in CO oxidation. Our results provide some novel information on the fabrication of supported Au<sub>x</sub>Pd alloy nanoparticles.

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#### References

- [1] J.H. Sinfelt, *Acc. Chem. Res.* 10 (1977) 15.
- [2] E.G. Allison, G.C. Bond, *Catal. Rev.* 7 (1972) 233.
- [3] J.K. Edwards, B.E. Solsona, P. Landon, A.F. Carley, A. Herzing, C.J. Kiely, G.J. Hutchings, *J. Catal.* 236 (2005) 69.
- [4] W.B. Hou, N.A. Dehm, R.W.J. Scott, *J. Catal.* 253 (2008) 22.
- [5] W. Juszczyk, Z. Karpinski, D. Lomot, J. Pielaszek, J.W. Sobczak, *J. Catal.* 151 (1995) 67.
- [6] L. Gucci, A. Beck, A. Horváth, Zs. Koppány, G. Stefler, K. Frey, I. Sajó, O. Geszti, D. Bazin, J. Lynch, *J. Mol. Catal. A: Chem.* 204–205 (2003) 545.
- [7] Y. Mizukoshi, K. Sato, T.J. Konno, N. Masahashi, *Appl. Catal. B* 94 (2010) 248.
- [8] J.K. Edwards, B. Solsona, E. Ntainjua, N. A.F. Carley, A.A. Herzing, C.J. Kiely, G.J. Hutchings, *Science* 323 (2009) 1037.
- [9] M.S. Chen, D. Kumar, C.W. Yi, D.W. Goodman, *Science* 310 (2005) 291.
- [10] F. Gao, Y.L. Wang, D.W. Goodman, *J. Am. Chem. Soc.* 131 (2009) 5734.
- [11] A.M. Venezia, L.F. Liotta, G. Pantaleo, G. Deganello, A. Beck, Zs. Koppány, K. Frey, D. Horváth, L. Gucci, *Appl. Catal. A* 251 (2003) 359.
- [12] N. Dimitratos, F. Porta, L. Prati, *Appl. Catal. A* 291 (2005) 210.
- [13] D. Wang, A. Villa, F. Porta, D. Su, L. Prati, *Chem. Commun.* (2006) 1956.
- [14] W.C. Ketchie, M. Murayama, R.J. Davis, *J. Catal.* 250 (2007) 264.
- [15] N. Dimitratos, J.A. Lopez-Sanchez, D. Morgan, A.F. Carley, R. Tiruvalam, C.J. Kiely, D. Bethell, G.J. Hutchings, *Phys. Chem. Chem. Phys.* 11 (2009) 5142.
- [16] J. Rebelli, M. Detwiler, S.G. Ma, C.T. Williams, J.R. Monnier, *J. Catal.* 270 (2010) 224.
- [17] F. Cárdenas-Lizana, S. Gómez-Quero, A. Hugon, L. Delannoy, C. Louis, M.A. Keane, *J. Catal.* 262 (2009) 235.
- [18] K. Qian, W.X. Huang, Z.Q. Jiang, H.X. Sun, *J. Catal.* 248 (2007) 137.
- [19] K. Qian, W.X. Huang, J. Fang, S.S. Lv, B. He, Z.Q. Jiang, S.Q. Wei, *J. Catal.* 255 (2008) 269.
- [20] K. Qian, H.X. Sun, W.X. Huang, J. Fang, S.S. Lv, B. He, Z.Q. Jiang, S.Q. Wei, *Chem. Eur. J.* 14 (2008) 10595.
- [21] K. Qian, Z.Q. Jiang, W.X. Huang, *J. Mol. Catal. A* 264 (2007) 26.
- [22] B. Pawelec, A.M. Venezia, V. La Parola, E. Cano-Serrano, J.M. Campos-Martin, J.L.G. Fierro, *Appl. Surf. Sci.* 242 (2005) 380.
- [23] Z.H. Suo, C.Y. Ma, M.S. Jin, T. He, L.D. An, *Catal. Commun.* 9 (2008) 2187.
- [24] F. Gao, Y. Wang, Y. Cai, D.W. Goodman, *J. Phys. Chem. C* 113 (2009) 174.
- [25] N.S. Babu, N. Lingaiah, R. Gopinath, P.S.S. Reddy, P.S.S. Prasad, *J. Phys. Chem. C* 111 (2007) 6447.
- [26] F. Gao, Y. Wang, D.W. Goodman, *J. Phys. Chem. C* 113 (2009) 14993.
- [27] F. Gao, Y. Wang, D.W. Goodman, *J. Phys. Chem. C* 114 (2010) 4036.