



## Research Note

## Preparation of highly effective ferric hydroxide supported noble metal catalysts for CO oxidations: From gold to palladium

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## ABSTRACT

Ferric hydroxide supported Pd catalyst prepared by a simple co-precipitation method without calcinations at elevated temperatures and only reduced at 50 °C possessed unexpectedly higher activity for CO oxidations even compared with that of supported Au catalysts. XRD and TEM results showed that the support was mixture of Fe(OH)<sub>x</sub> and Fe<sub>3</sub>O<sub>4</sub> and Pd was highly dispersed on it. XPS results showed that Pd existed as mixture of oxidation and metal state. The large amount of OH group on the supports may play an important role in O adsorption and activation.

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## 1. Introduction

Catalytic oxidation of CO has been studied extensively because of its great importance for both practical applications and fundamental research of catalysis sciences [1–4]. It is generally accepted now that supported gold catalysts were extraordinarily active for CO oxidations [2,3] and were an order of magnitude more active compared with a highly dispersed supported Pt catalysts [4]. Although much effort to improve the activity for CO oxidation has been made and remarkable progress has been achieved [5–8], the activities for CO oxidations over supported Pt and Pd catalysts were still relatively lower in comparison with that over supported Au catalysts. The question is that the catalytic activities of supported Pd or Pt for CO oxidation are intrinsically inferior to that of supported Au catalyst?

For CO oxidation over Au catalysts, O<sub>2</sub> adsorption and activation is regarded as a rate-limiting step since oxygen dissociation is inhibited on single gold crystals. While, over supported Pd/Pt catalysts, it is also a very important progress for O<sub>2</sub> adsorption and activation because the adsorption of CO on Pd/Pt active site is so strong that O<sub>2</sub> is hardly adsorbed and activated. Therefore, how to weaken the adsorption of CO on Pt/Pd at lower temperature and subsequently to promote adsorption and activation of O<sub>2</sub> become the crucial step for CO oxidation. Previous works mainly resolve this problem to promote the activity of CO oxidations by adding

different additives [9]. However, it was usually ignored to develop a suitable preparing method or to employ an appropriate “active supports” like that used in Au catalysts.

It is well known that preparation method and the synergism between active components and support play a key role in determining the catalytic performance. Various techniques and skills of preparation method of supported noble metal catalysts have been explored so as to achieve better catalytic performance. Impregnation and co-precipitation are the two traditional methods to prepare supported noble metal catalysts and the preparation process usually involves combining of the precursor of active components and support, then drying and calcining at elevated temperatures, and further reducing if necessary. Any modification or adjustment during preparation may result in unexpected catalytic behavior. There is still lot of space for further improvement of such preparation process and for further exploring traditional catalytic components of Pd or Pt to exhibit unexpected and new catalytic performance, although these supported noble metal catalysts are the one of the mostly investigated in catalyst family.

Recently, Hodge et al. [10] reported that Au catalysts prepared with co-precipitation and then dried at 100 °C were more active than those calcined at elevated temperatures. In our previous study [11,12], we had found that ferric hydroxide supported Au prepared by co-precipitation without calcining possessed better performance for CO selective oxidations in the presence of H<sub>2</sub> than that of the corresponding catalyst calcined at elevated temperatures. The results showed that the large amount of containing OH group played an important role in determining the catalytic performance. We had predicted that this simple method (and/or the unique sup-

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**Table 1**  
Some physicochemical properties of the supported Pd catalysts.

	Pd/Au loadings (wt%) (corresponding atom ratio of Pd/Fe)	BET surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	BE of Pd <sub>3d<sub>5/2</sub></sub> /Au <sub>4f<sub>7/2</sub></sub> (eV)	Area ratio of Pd/Pd <sup>2+</sup>	BE of Fe <sub>2p<sub>3/2</sub></sub> (eV)	Atom ratio of Pd or Au/Fe (from XPS)	Residual of Cl <sup>-</sup> (wt%)	Residual of Na <sup>+</sup> (wt%)
Fe(OH) <sub>x</sub>	–	276	2.2	–	–	–	–	–	–
Pd/Fe(OH) <sub>x</sub>	4.1 (0.04)	281	2.5	337.4	0	711.1	0.06	–	–
Pd/Fe(OH) <sub>x</sub> -R <sup>a</sup>	4.1 (0.04)	147	5.1	337.0, 335.4	1.0	711.0	0.07	0.1% <sup>c</sup>	0.13% <sup>d</sup>
Pd/Fe(OH) <sub>x</sub> -R <sup>b</sup>	4.1 (0.04)	–	–	337.2, 335.4	1.1	711.0	0.05	–	–
Au/Fe <sub>2</sub> O <sub>3</sub>	4.4 (0.02)	39	–	83.6	–	–	0.03	0.011%	–

<sup>a</sup> Pd/Fe(OH)<sub>x</sub> was reduced with 10 vol% H<sub>2</sub> at 50 °C for 30 min.

<sup>b</sup> After reaction for 290 h.

<sup>c</sup> Measured by Cl<sup>-</sup> ion selective electrode (Mettler Toledo).

<sup>d</sup> Measured by ICP.

ports) could be expand to other supported noble catalyst preparation, such as Pt and Pd. Herein, a supported Pd catalyst was prepared by this method simply improved with reduction of the catalyst at 50 °C and it exhibited unexpectedly high activities for CO oxidations.

## 2. Experiment

### 2.1. Preparation procedure of supported Pd catalysts

All catalysts were prepared by co-precipitation method. Under stirring, an aqueous mixture of H<sub>2</sub>PdCl<sub>4</sub> with ferric nitrate was added dropwise to Na<sub>2</sub>CO<sub>3</sub> solution and the pH of the finally resulted solution was controlled to ca. 8.5. After stirring and aging for 3 h, respectively, the resulted precipitate was filtrated and washed with distilled water for several times, then dried at 60 °C for 5 h without any further heat treatment hereafter. The resulted brown powder was denoted as Pd/Fe(OH)<sub>x</sub>. The brown powder was further reduced at 50 °C with 10 vol% H<sub>2</sub> (Argon balanced) for 30 min, denoted as Pd/Fe(OH)<sub>x</sub>-R. Au/Fe(OH)<sub>x</sub>, Pd/Co(OH)<sub>x</sub>, Pd/Al(OH)<sub>x</sub>, Pd/Co(OH)<sub>x</sub>-R, Pd/Al(OH)<sub>x</sub>-R were also prepared in this manner.

### 2.2. Measurements of catalytic activities

Catalytic activity measurements were carried out in a fixed-bed reactor with 80 mg of catalyst sieved to 60 and 80 mesh. The feed gas for the oxidation was about 1 vol% CO balanced with air. The gas flow rate was 20 ml/min which resulted in a space velocity of 15,000 ml/(h g<sub>cat</sub>). The concentrations of CO and O<sub>2</sub> in the effluent gas were on-line analyzed by a gas chromatograph using argon as the carrier gas. The catalytic activity was evaluated with the Lowest Temperatures at which CO was Totally oxidized (LTT), i.e. CO could not be detected by gas chromatograph.

### 2.3. Characterization techniques

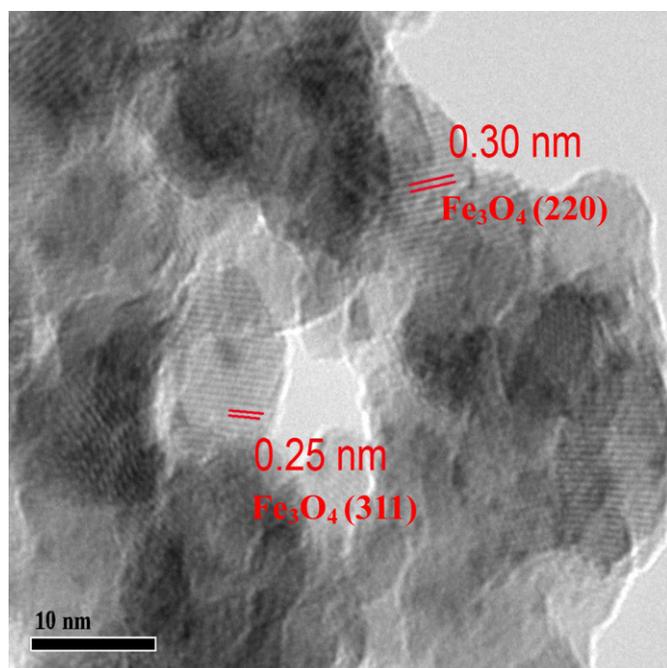
Pd loadings in the catalyst samples were measured using a 3520 ICP AES instrument of ARL Co. USA. BET surface areas were obtained by physisorption of N<sub>2</sub> using a Micromeritics ASAP 2010. The surface composition of the catalysts was examined by X-ray photoelectron spectra (XPS) (VG ESCALAB 210) with contaminated C as internal standard (C<sub>1s</sub> = 284.6 eV). X-ray diffraction (XRD) was performed with a Siemens D/max-RB powder X-ray diffractometer. Transmission electron microscopic (TEM) investigations were carried out using a JEM-2010F electron microscope (JEOL). More details of experimental information are presented in support information. TPR investigation were performed on a Auto Chem II 2920 automatic catalyst characterization system.

## 3. Results and discussion

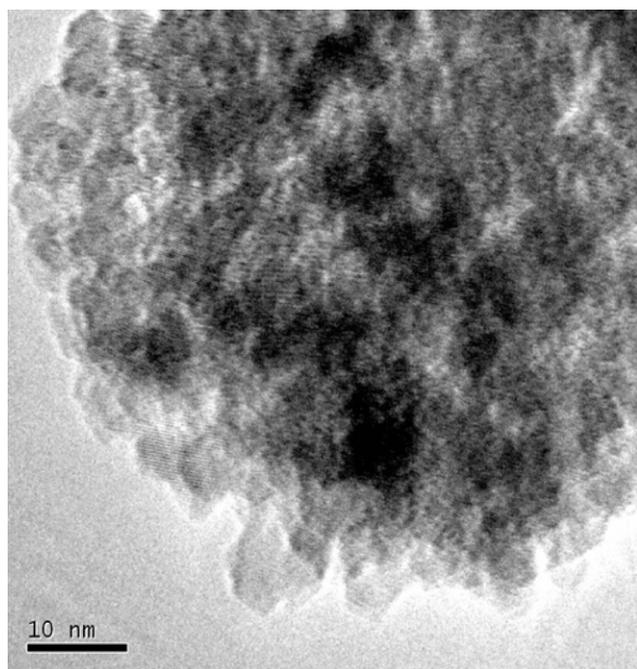
Typical data of metal loadings, BET surface areas in Table 1 showed that, although the reduction treatment even with mild conditions could result in a great decrease in the surface area, ferric hydroxide possessed relatively higher surface area. XPS results, in Table 1, showed that the chemical states of surface Pd species were the oxidized (BE3d<sub>5/2</sub> = 337.4 eV) and mixture of oxidized and reduced state (BE3d<sub>5/2</sub> = 337.4 eV and 335.5 eV) over the 4.1 wt% Pd/Fe(OH)<sub>x</sub> and 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R, respectively. The data of BE3d<sub>5/2</sub> = 337.4 eV indicates that the chemical state of the oxidized Pd species was > +2, which may be related to high dispersion of oxidized Pd species [13] and their strong interaction with Fe(OH)<sub>x</sub>. Slight increase in Pd/Fe atom ratio after being partially reduced suggested that Pd species were further concentrated onto the surface, which would be favorable to the catalytic activity. The concentration of Na<sup>+</sup> and Cl<sup>-</sup> were measured by ICP and Cl<sup>-</sup> ion selective electrode, respectively. The contents of Na<sup>+</sup> and Cl<sup>-</sup> in 4.1 wt% Pd/Fe(OH)<sub>x</sub> were 0.13 and 0.1 wt%, respectively, and such Cl<sup>-</sup> content is about 10 times of that of 4.4 wt% Au/Fe<sub>2</sub>O<sub>3</sub> bought from WGC, indicating that Pd/Fe(OH)<sub>x</sub> for CO oxidation may be less sensitive to Cl<sup>-</sup>, which was consistent with our previous work of Au/Fe(OH)<sub>x</sub> [12].

XRD results (Fig. S1) showed that the patterns of pure Fe(OH)<sub>x</sub> and 4.1 wt% Pd/Fe(OH)<sub>x</sub> were almost the same, indicating that the support and Pd in 4.1 wt% Pd/Fe(OH)<sub>x</sub> were amorphous and highly dispersed. Unexpectedly, when the catalyst was reduced with 10 vol% of H<sub>2</sub> at 50 °C, the crystallite of Fe<sub>3</sub>O<sub>4</sub>, though the diffractive peaks were weak, was observed, indicating the Pd species may be so active that some Fe(OH)<sub>x</sub> could be reduced partly and this would be helpful for the high activity for CO oxidations [14]. In addition, no obvious diffractive peaks of Pd or PdO particles were observed over 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R catalysts, indicating that, even after being reduced at 50 °C, the Pd or PdO particles were highly dispersed. TPR investigation of 4.1 wt% Pd/Fe(OH)<sub>x</sub> and pure Fe(OH)<sub>x</sub> were conducted and the results showed that the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> over pure Fe(OH)<sub>x</sub> occurred at 250–300 °C (Fig. S2, curve a). After incorporation of Pd, this peak disappeared and a strong reduction peak centered at about 50 °C appeared (Fig. S2, curve b) and the corresponding hydrogen consumption of 79.4 ml/g was greatly higher than the theory amount of PdO (ca. 10 ml/g), indicating that this peak was co-reductions of Pd<sup>2+</sup> and some Fe<sup>3+</sup> to Fe<sup>2+</sup>.

For TEM observation, no structural difference between pure Fe(OH)<sub>x</sub> and Pd/Fe(OH)<sub>x</sub> could be discriminated, and PdO or Pd particles were also invisible although Pd content in the catalyst was as high as 4.1 wt%, Figs. S3a, and S3b. While the HRTEM investigation showed that the supports of 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R were consist of amorphous Fe(OH)<sub>x</sub> and Fe<sub>3</sub>O<sub>4</sub> with crystal surface of (220) and (311), and that the diameter of Pd particles on Fe<sub>3</sub>O<sub>4</sub> crystal was mostly lower than 3 nm while Pd particles on amorphous Fe(OH)<sub>x</sub> were difficult to be distinguished, Fig. 1, Figs. S3c,



(a)

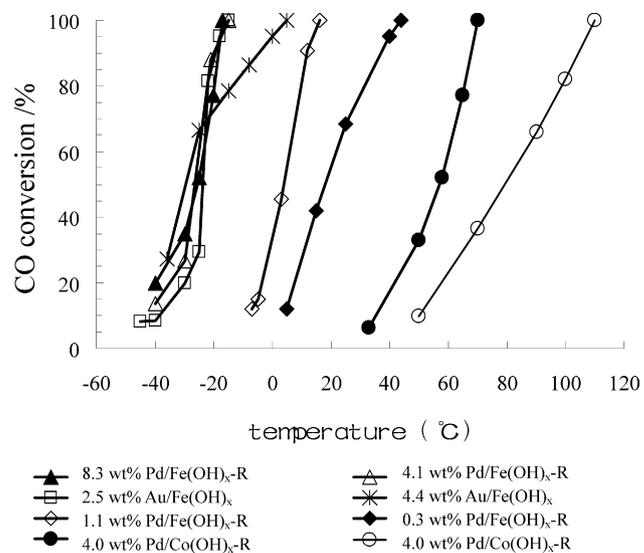


(b)

**Fig. 1.** HRTEM image of 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R. (a) Crystallized Fe<sub>3</sub>O<sub>4</sub> with few Pd particles <3 nm; (b) amorphous Fe(OH)<sub>x</sub> with highly dispersed Pd species.

and S3d. STEM results, Figs. S4 and S5, showed that Pd was uniformly dispersed on the support either in a larger range such as 108 nm or a smaller range of 38 nm.

For total oxidation of CO (Fig. 2 and Table S1), pure Fe(OH)<sub>x</sub> itself possessed lower activity. After incorporation of palladium, the activities for CO oxidation, as expected, were increased greatly, but unexpectedly, such activities increased so highly that it has never been observed or reported previously, i.e. the LTTs, as the Pd loading was increased from 0.3 to 8.3 wt%, were, respectively, decreased from ca. 90 to 10 °C and from 44 to −17 °C over Pd/Fe(OH)<sub>x</sub> and Pd/Fe(OH)<sub>x</sub>-R. For the purpose of comparison, 4.4 wt% Au/Fe<sub>2</sub>O<sub>3</sub> and 1.5 wt% Au/TiO<sub>2</sub> from WGC and 2.5 wt%



**Fig. 2.** Oxidations of CO over supported Pd and Au catalysts.

Au/Fe(OH)<sub>x</sub> prepared by the same method with 4.1 wt% Pd/Fe(OH)<sub>x</sub> were also tested, the resulted LTTs were 5 and −5 °C and −15 °C, respectively. These results showed that the activities of ferric hydroxide supported Pd catalysts for CO oxidation, though slightly inferior, may be comparable to supported Au catalysts, and reduction treatment at mild conditions, though not indispensable intrinsically, may further enhance the activity. To compare the intrinsic activity of supported Pd and Au catalysts, the specific reaction rate, the contact time, as well as the turnover frequencies (TOFs) were calculated, Table S3. It could be seen that, at −40 °C (233 K), 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R gave a specific reaction rate of 0.019 mol<sub>CO</sub>/(g<sub>Pd</sub> h) and TOFs of 0.33 s<sup>−1</sup>, slightly lower than that of 4.4 wt% Au/Fe<sub>2</sub>O<sub>3</sub> (0.091 mol<sub>CO</sub>/(g<sub>Au</sub> h) and 0.04 or 0.02 s<sup>−1</sup>), while, at 27 °C, it gave a specific reaction rate of 0.62 mol<sub>CO</sub>/(g<sub>Pd</sub> h) and TOFs of 0.33 s<sup>−1</sup>, which was about 6 and 8 times, respectively, of that of the 4.4 wt% Au/Fe<sub>2</sub>O<sub>3</sub> (0.091 mol<sub>CO</sub>/(g<sub>Au</sub> h) and 0.04 s<sup>−1</sup>). However, when compared with 2.5 wt% Au/Fe(OH)<sub>x</sub> (it gave a specific reaction rate of 2.1 mol<sub>CO</sub>/(g<sub>Au</sub> h) and TOFs of 3.02 s<sup>−1</sup>), the activity were only about one third and one ninth respectively, indicating that supported Pd catalysts, with a valid comparison, are still less active than supported Au catalyst. While the differences of the activity for CO oxidations between them were not too large as previously expected, i.e. supported Pd catalysts may also be intrinsically active for CO oxidation if proper preparation method and support are adopted. Cobaltic hydroxide and aluminum hydroxide supported Pd was also tested so as to estimate the contribution of the support to the activity (Table S1). The LTTs were 90 and 65 °C over 4.0 wt% Pd/Co(OH)<sub>x</sub> and Pd/Co(OH)<sub>x</sub>-R, and >>140 and 130 °C over 4.0 wt% Pd/Al(OH)<sub>x</sub> and 4.0 wt% Pd/Al(OH)<sub>x</sub>-R, respectively. These results showed that the activity of cobaltic hydroxide and aluminum hydroxide supported Pd for CO oxidation, though exhibited higher activity in comparison with conventional supported Pd catalysts [15], was much lower than that of ferric hydroxide supported Pd, indicating that the supports played a very important role in determining the activity.

The stabilities of catalytic activities for CO oxidation were examined at varied temperatures, Fig. S6. For 4.1 wt% Pd/Fe(OH)<sub>x</sub>-R, the total conversion of CO to CO<sub>2</sub> could be maintained for 10 h at 0 °C and for 210 h at 20 °C. While, total conversion of CO to CO<sub>2</sub> could be maintained for about 30 h at 20 °C over 4.4 wt% Au/Fe<sub>2</sub>O<sub>3</sub> or over 1.5 wt% Au/TiO<sub>2</sub> from the WGC. These results showed that the durability of Pd/Fe(OH)<sub>x</sub>-R could be superior to those oxides supported Au catalysts for the oxidation of CO although the deactivation mechanism is still not clear at this stage.

The XRD and TEM results showed that the supports consisted of crystal  $\text{Fe}_3\text{O}_4$  and amorphous  $\text{Fe}(\text{OH})_x$  which took large amount of OH group, and the Pd nanoparticles were highly dispersed on it with diameter of about or lower than 3 nm. It is well known that the size of metal particles is an important factor to determining the activity. Stara et al. [16] reported that the activation energy was much smaller on Pd particles with 2.5 nm diameters than that on the Pd(111) crystal face. Recently, Schalow et al. [17] reported a size-dependent oxidation mechanism of supported Pd nanoparticles, which showed that, only when lower than 3 nm, the Pd particles could be completely oxidized to form PdO and gave the best oxygen storage capability. However, small Pd particles with diameter of about or even lower than 3 nm have been prepared with impregnation and co-precipitation method in previous works, while the activities of these supported Pd catalysts were still unsatisfactory [7,18] compared with supported Au catalysts. Therefore, to prepare small Pd particles may be necessary but absolutely not sufficient to obtain high activity of supported Pd catalysts for CO oxidation.

It is well known now that support is another important factor affecting the activity of supported catalysts. It has been pointed out that the activity of supported catalysts critically depends on both the size of metal particles and the support itself [14] and high performance catalysts are now designed by taking into account the significant contribution of the supports [19]. In this work, the supports were proved to consist of ferric hydroxide and ferroferric oxide and contain large amount of OH group, which were important and favorable of the CO oxidation. Schalow et al. [14] proposed a oxygen storage and CO oxidation mechanism using Pd/ $\text{Fe}_3\text{O}_4$  as model catalyst, which proved that  $\text{Fe}_3\text{O}_4$  support was helpful to the O activation. As to OH group, it is well accepted that it plays a very important role in the CO oxidations. Recently, Smit et al. [20] reported that the amount of surface OH group played a crucial role in the activity of iron oxides without supporting any active metal, with which CO reacted forming very reactive adsorbed formats,  $\text{HCOO}_{(\text{ad})}$ . In addition, as to supported Pd catalysts, Golunski et al. [21] had found that the activity of ferric oxide supported Pd catalysts for CO oxidations could be dramatically enhanced by a short low-temperature exposure to hydrogen without any subsequent thermal treatment, which mainly related to the large amount of OH derived from the  $\text{H}_2$  treatment instead of the reduction of  $\text{Pd}^{2+}$  ions to metallic Pd. So, on the premise of Pd particles being small enough, the unique properties of the support may be the critical factor for the high activity of the catalysts in CO oxidation.

It was well accepted now that, for supported gold catalyst, the complex of  $\text{Au}^{\delta+}/\text{Au}$  active site was more active than the single site of Au [22]. Recently, Margitfalvi and Göbölös [23], etc., proposed a mechanism for CO oxidations with the involvement of “metal ion–metal nano-clusters” ensemble sites based on the results of Sn–Pt/ $\text{SiO}_2$  catalysts [5]. According to this mechanism, they prepared a Fe–MCM-41 catalyst, which possessed high activity for CO oxidations [24], indicating that the model of “metal ion–metal nano-clusters” were applicable to other metal. In this work, the XPS investigation showed that the surface Pd species were mixture of oxide and metal state, well according with the above model, which may be another reason for the high activity for CO oxidations.

## 4. Conclusion

In conclusion, it was the first time to successfully prepare a ferric hydroxide supported Pd catalyst with Pd loadings of about 4 wt% over which total oxidation of CO could be achieved at as low as  $-15^\circ\text{C}$ . Although supported Pd catalysts are still less active than supported Au catalysts prepared with the same method, the differences of the activity for CO oxidations between supported them were not too large as previously expected, i.e. supported Pd catalysts could also be intrinsically active for CO oxidation if proper preparation method and support are adopted. As a result, it would make people re-recognize or further understand the supported Pd catalysts, which may be more significant for this work.

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## Supported information

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## References

- [1] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* 115 (1989) 301.
- [2] M.S. Chen, D.W. Goodman, *Science* 306 (2004) 252.
- [3] C.T. Campbell, *Science* 306 (2004) 234.
- [4] M. Haruta, *Stud. Surf. Sci. Catal.* 110 (1997) 123.
- [5] J.L. Margitfalvi, I. Borbath, M. Hegedus, E. Tfirst, S. Göbölös, K. Lazary, *J. Catal.* 196 (2000) 200.
- [6] A. Fukuoka, J. Kimura, T. Oshio, Y. Sakamoto, M. Ichikawa, *J. Am. Chem. Soc.* 129 (2007) 10120.
- [7] S.N. Pavlova, V.I. Savchenko, V.A. Sadykov, V.I. Zaikovskii, A.V. Kalinkin, *React. Kinet. Catal. Lett.* 59 (1) (1996) 103.
- [8] H. Zhu, Z. Qin, W. Shan, J. Wang, *J. Catal.* 233 (2005) 41.
- [9] A.B. Hungria, A. Iglesias-Juez, A. Martínez-Arias, M. Fernández-García, J.A. Anderson, J.C. Conesa, J. Soria, *J. Catal.* 206 (2002) 281.
- [10] N.A. Hodge, C.J. Kiely, R. Whyman, M.R.H. Siddiqui, G.J. Hutchings, Q.A. Pankhurst, F.E. Wagner, R.R. Rajaram, S.E. Golunski, *Catal. Today* 72 (2002) 133.
- [11] B. Qiao, Y. Deng, *Chem. Commun.* (2003) 2192.
- [12] B. Qiao, Y. Deng, *Appl. Catal. B* 66 (2006) 241.
- [13] H.N. Aiyer, V. Vijaykrishnan, G.N. Subbanna, C.N.R. Rao, *Surf. Sci.* 313 (1994) 392.
- [14] T. Schalow, M. Laurin, B. Brandt, S. Schauer mann, S. Guimond, H. Kuhlenbeck, D.E. Starr, S.K. Shaikhutdinov, J. Libuda, H.J. Freund, *Angew. Chem. Int. Ed.* 45 (2006) 7601.
- [15] A.M. Venezia, L.F. Liotta, G. Pantaleo, V. La Parola, G. Deganello, A. Beck, Z. Koppány, K. Frey, D. Horváth, L. Guzzi, *Appl. Catal. A* 251 (2003) 359.
- [16] I. Stara, V. Nehasil, V. Matolin, *Surf. Sci.* 331–333 (1995) 173.
- [17] T. Schalow, B. Brandt, D.E. Starr, M. Laurin, S.K. Shaikhutdinov, S. Schauer mann, J. Libuda, H.J. Freund, *Angew. Chem. Int. Ed.* 45 (2006) 3693.
- [18] D.I. Kochubey, S.N. Pavlova, B.N. Novgorodov, G.N. Kryukova, V.A. Sadykov, *J. Catal.* 161 (1996) 500.
- [19] M. Haruta, *J. Nanopart. Res.* 5 (2003) 3.
- [20] G. Smit, S. Zrncvic, K. Lazar, *J. Mol. Catal. A* 252 (2006) 103.
- [21] S. Golunski, R. Rajaram, N. Hodge, G.J. Hutchings, J.C. Kiely, *Catal. Today* 72 (2002) 107.
- [22] J. Guzman, B.C. Gates, *J. Am. Chem. Soc.* 126 (2004) 2672.
- [23] J.L. Margitfalvi, S. Göbölös, in: J.J. Spivey (Ed.), *Catalysis*, in: Specialist Periodical Report, vol. 17, Royal Society of Chemistry, Cambridge, UK, 2004, p. 1.
- [24] A. Szegedi, M. Hegedus, J.L. Margitfalvi, I. Kiricsi, *Chem. Commun.* (2005) 1441.