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Tin dioxide supported nanometric gold: synthesis, characterization, and lowtemperature catalytic oxidation of CO

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The Au/SnO_2 catalysts were prepared by a co-precipitation method. The structure of the sample treated at different temperatures was investigated by means of HRTEM and XPS. The structure of the samples after various treatments and their activity in the CO oxidation were compared. The results showed that the catalytic behavior was related to the particle size of gold and surface oxygen species on the support. Highly dispersed gold particles and adsorbed surface oxygens and hydroxyl groups on the support were responsible for the high catalytic activity of the Au/SnO_2 catalyst.

KEY WORDS: Au/SnO_2 catalyst; synthesis; characterization; CO oxidation.

1. Introduction

Since Haruta's [1] report of the remarkably high activity of supported gold catalysts for low-temperature CO oxidation, interest in the potential applications of supported gold catalysts has increased dramatically, along with research efforts to understand the origin of this surprising activity [2–4]. Gold finely dispersed on metal oxides has been demonstrated to be a promising catalyst in a number of catalytic reactions including complete oxidation of hydrocarbons, hydrogenation, water–gas shift reaction, and NO reduction [5–14]. Moreover, supported Au catalysts are also promising catalysts in various practical areas such as CO removal in CO_2 lasers, CO gas sensors, air-purification devices for respiratory protection, and pollution control devices for removing trace quantities of CO from ambient air in submarines and space crafts on long missions [6, 7]. There has already been a general consensus that the preparation method, the synthesis parameters, pretreatment conditions and the choice of the support all exert a significant influence on the ultimate catalytic performance. Haruta *et al.* [15–17] found when co-precipitation of gold with various metal oxides, the gold catalysts possessed a dramatic activity for low-temperature CO oxidation. They discovered when gold was highly dispersed on semiconductor metal oxides such as TiO_2, α-Fe_2O_3, and Co_3O_4 with diameters smaller than 5 nm, it turns out to be surprisingly active for the low temperature catalytic oxidation of CO [18]. The property of support, the size of gold particles and the properties of the gold–support interface were considered to affect the activity of gold catalysts for CO oxidation significantly [5, 19]. Many investigations showed that the pretreatment conditions exert decisive effects on the chemical state of gold, and consequently on the ultimate catalytic activity [20–21].

Although the catalytic activity of gold catalysts in the low temperature CO oxidation has been intensively studied during the last decade, the catalytic activity of gold supported on SnO_2 has seldom been discussed [22]. In this work, we studied the low temperature CO oxidation over gold-loaded tin dioxides calcined at different temperatures. High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) were employed to characterize differently treated Au/SnO_2 samples. The main purpose of present investigation is to find the relationship between the catalytic activity and the microstructure catalysts and properties of the support. Some preliminary results have been achieved.

2. Experimental

2.1. Catalyst preparation

The Au/SnO_2 catalyst was prepared by a co-precipitation method using $HAuCl_4 \cdot 4H_2O$ and $SnCl_4 \cdot 5H_2O$. Under vigorous stirring, 1 mol/L NH_4OH aqueous solution was added drop-wise to a combined solution of 0.25 mol/L $SnCl_4$ and 0.004 mol/L $HAuCl_4$ freshly prepared until the pH of the solution was 7. The suspension formed was stirred for 3 h and then alternatively centrifuged and washed several times with deionized water and ethanol alternately until Cl^- could

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not be examined by 0.1 mol/L $AgNO_3$ aqueous solution, then the sample was overnight dried in air at 353 K. The gold loading of Au/SnO_2 was determined to be 2.94 wt.% by inductively coupled plasma atom emission spectroscopy (ICP-AES). The as-prepared material was then ground and calcined in air at 473, 523, 573, 623, 673 and 773 K for 3 h, respectively, and stored in a desiccator for subsequent use. Tin oxide was prepared by precipitation from $SnCl_4 \cdot 5H_2O$, and the preparation procedure was similar to that for the preparation of the Au/SnO_2 catalyst.

2.2. *Catalyst characterization*

High-resolution transmission electron microscopy (HRTEM) was carried out on a Philips-T20ST electron microscope, operating at 200 kV. The sample powder was ultrasonically dispersed in ethane. The particle-size distribution was obtained from TEM pictures. At least 100 particles were chosen to determine the mean diameter of gold particles.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Perkin-Elmer PHI 5600 spectrophotometer with the MgKα radiation. The operating conditions were kept constant at 187.85 eV and 250.0 W. In order to subtract the surface charging effect, the C1s peak has been fixed, in agreement with the literature, at a binding energy of 284.6 eV.

2.3. *Measurement of catalytic activity*

Catalytic activity tests were performed in a continuous-flow fixed-bed microreactor, using 100 mg catalyst powder. A stainless steel tube with an inner diameter of 8 mm was chosen as the reactor tube. The reaction gas mixture consisting of 1 vol.% CO balanced with air was passed through the catalyst bed at a total flow rate of 33.4 ml/min. A typical weight hourly space velocity (WHSV) was 20,040 mL/h/g. The temperature dependence of the sample catalytic activity was recorded in the range 293–393 K. After 30 min under reaction conditions, the effluent gases were analyzed online by GC-508A gas chromatography. The activity was expressed by the degree of conversion of CO.

3. Results and discussion

3.1. *Catalytic performance*

Figure 1 showed the influences of reaction temperature on the CO oxidation reaction over the Au/SnO_2 catalysts calcined at different temperatures. It could be seen that the samples calcined at 523–623 K exhibited the highest catalytic activity in all samples. There was a markedly decrease in the activity when the calcination temperature above 673 K. The samples uncalcined and calcined at 773 K displayed no activity below 393 K. The sample calcined at 473 K reached a maximum at 333 K, but declined to a lower value with the further increasing test temperature. In order to study catalyst stability with time, the samples were reinvestigated at 323 K under the same reaction conditions. Clearly, the samples calcined at 523–623 K also demonstrated better stability than the other samples. This indicated that it was effective to gain high activity catalyst for low-temperature CO oxidation by selecting the proper calcination temperature. Although neither SnO_2 powders nor Au particles are active in low temperature CO oxidation [22], the SnO_2 supported fine Au particles exhibit high activity in low temperature CO oxidation. Thereafter, some structure characterizations were carried out in order to explore the essence of the catalytic behavior induced by treating catalysts at different calcination temperatures.

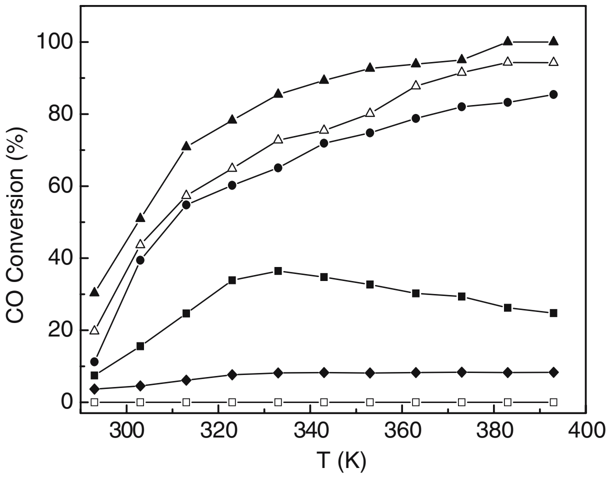

Figure 1. Temperature effects on CO oxidation over the Au/SnO_2 catalysts calcined at different temperatures: (■) 473 K, (●) 523 K, (▲) 573 K, (△) 623 K, (◆) 673 K, and (□) 773 K.

3.2. *Catalyst characterization*

Figures 2 and 3 presented the bright-field images and the Au size distributions of the Au/SnO_2 catalysts calcined at different temperatures in static air. In the sample calcined at 473 K, the particle size of Au was too small to be observed clearly, but the large agglomerates of gold clusters were occasionally found in the transmission electron micrograph (figure 2a), which can be related to the lower activity of the sample calcined at 473 K. The sample calcined at 573 K presented in figure 2b showed highly dispersed gold particles with the particle sizes between 2 and 5 nm. The TEM results in figure 2c showed gold particles in Au/SnO_2 sintered after calcined at 673 K, almost no gold particles with particle size < 4 nm existed and the particle size lied between 5 and 10 nm. From the TEM results, we suggested that the increasing size of the gold particles was responsible for the decreasing catalytic activity at higher calcination temperature.

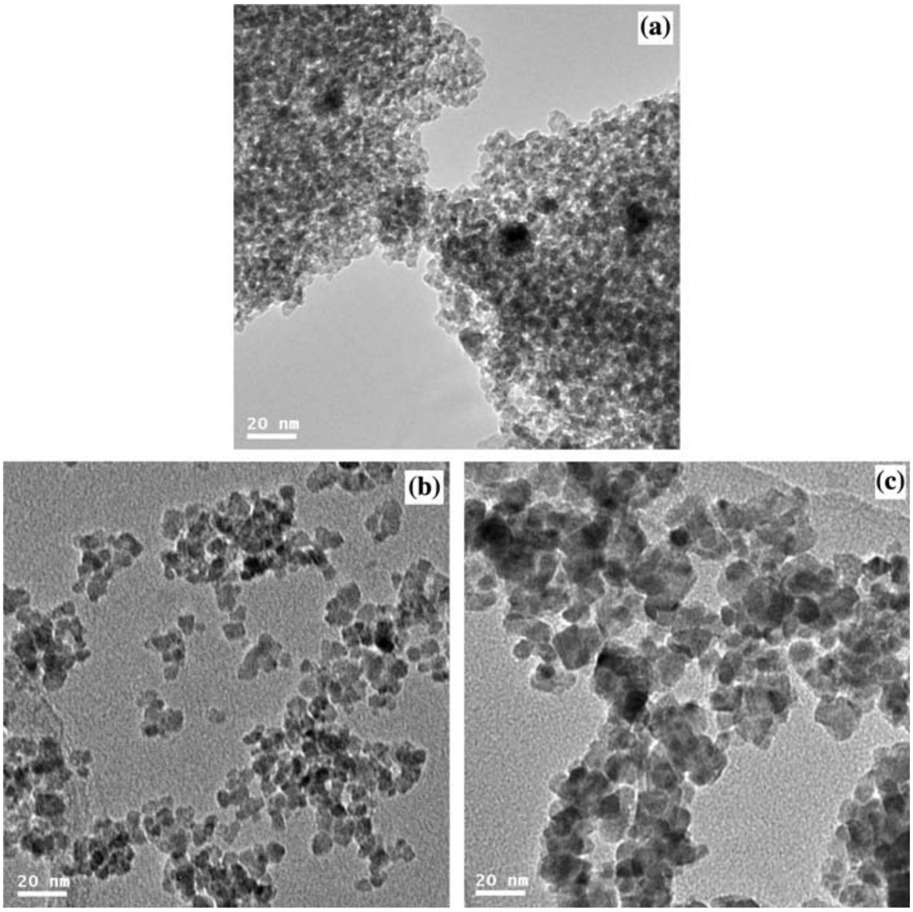

Figure 2. HRTEM images of the Au/SnO_2 catalysts prepared at different calcination temperatures: 473 K (a), 573 K (b), and 673 K (c).

From the full-range XPS spectra of the Au/SnO_2 samples calcined at different temperatures, it could be found that the Au4f signal was relatively weak in all the samples. The Au concentration estimated from ICP-AES was 2.94 wt.% in the Au/SnO_2 catalyst, the nominal Au/Sn atom ratio was 0.023. However the surface Au/Sn atom ratio of all samples in XPS was lower than 0.005. The Au/Sn atom ratio in XPS is tentatively used to represent the Au dispersion, however, the low Au/Sn atom ratio could be complicated by phenomena other than Au agglomeration. The activity of pure SnO_2 in the CO oxidation reaction becomes significant only at temperature above 573 K [22]. After being modified by gold, the tin dioxide showed high catalytic activity at low temperature, suggesting the incorporation of gold during co-precipitation might affect the structure and environment of tin dioxide crystallites during the calcination step [23]. The low Au/Sn atom ratio could be due to the strong mutual interaction between Au and SnO_2, that resulted in the Au/Sn cluster formation and simultaneous buried inside the SnO_2 lattice [24]. Or the transport of Au species deeper into the pore to result in an Au-depleted skin is also possible [25–27]. This could also be an important reason that catalytic activity of the Au/SnO_2 catalysts was relatively lower than that of the Au/TiO_2 or Au/Fe_2O_3 catalysts reported by Haruta et al. [15–18].

The estimated atomic ratios O/Sn of these samples were listed in table 1. Compared to other samples, the sample calcined at 573 K showed higher oxygen contents. With the increasing calcination temperature, the O/Sn atomic ratio reached approximately 2. This implied the decrease of the structural defects and the increase of the degree of crystallinity of tin dioxide support, leading to the serious decrease of the catalytic activity.

The O1s XPS spectra of the Au/SnO_2 catalysts calcined at different temperature were given in figure 4. By means of computer simulation, the experimental curve in the O1s spectrum was presented as a sum of two components for all the samples. We assigned the signal at lower binding energy (530.3 eV) to surface lattice oxygen and the signal at higher binding energy (531.5 eV) to adsorbed oxygen species such as O^-, O_2^- and OH^- [28–31]. The intensity of O1s signal at 531.5 eV over the sample calcined at 573 K was much higher than other samples. It implied that in this sample, the amount of adsorbed oxygen increased as more

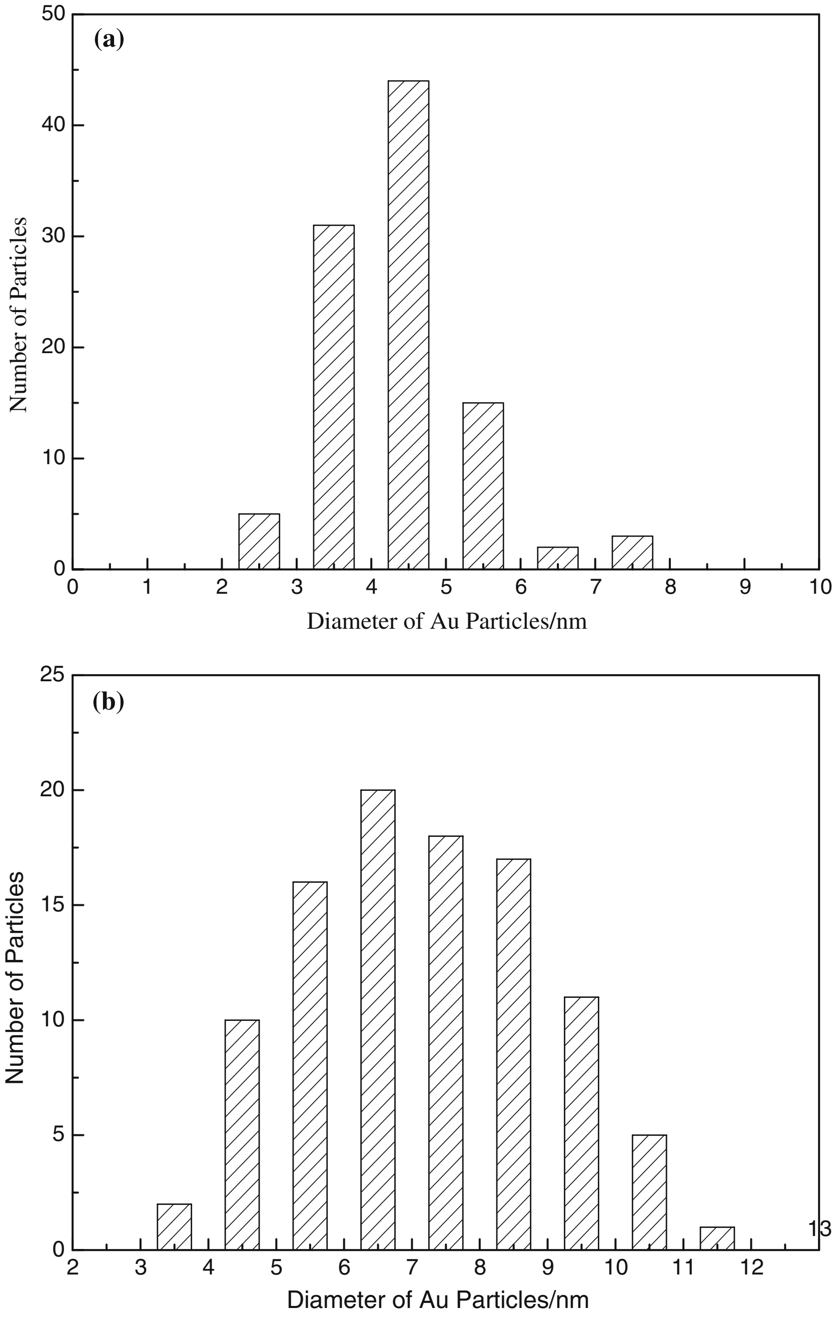

Figure 3. Size distribution of Au particles for the Au/SnO_2 catalysts calcined at different temperatures: 573 K (a) and 673 K (b).

Table 1

The O/Sn atomic ratios and the peak area ratios of different O1s binding energy in the Au/SnO_2 samples calcined at different temperatures measured by XPS

T (K)	O/Sn	Area (%)	
		530.3 eV	531.5 eV
473	2.25	67.01	30.99
573	2.49	62.86	37.14
673	2.13	72.04	27.96
773	2.08	72.94	27.06

oxygen vacancies were created [23]. As the treatment temperature increased from 573 to 773 K, the component at 531.5 eV decreased in intensity and, whereas the intensity of the component at 530.3 eV increased. It implied that in this sample, the amount of adsorbed surface oxygen and hydroxyl groups decreased. It was suggested that the amount of the higher activity of surface oxygen and hydroxyl groups could play a crucial role in the CO oxidation [23]. In the CO oxidation the sample calcined at 523–623 K showed the higher activity and it might be related to the more adsorbed surface oxygen and hydroxyl groups than the other samples.

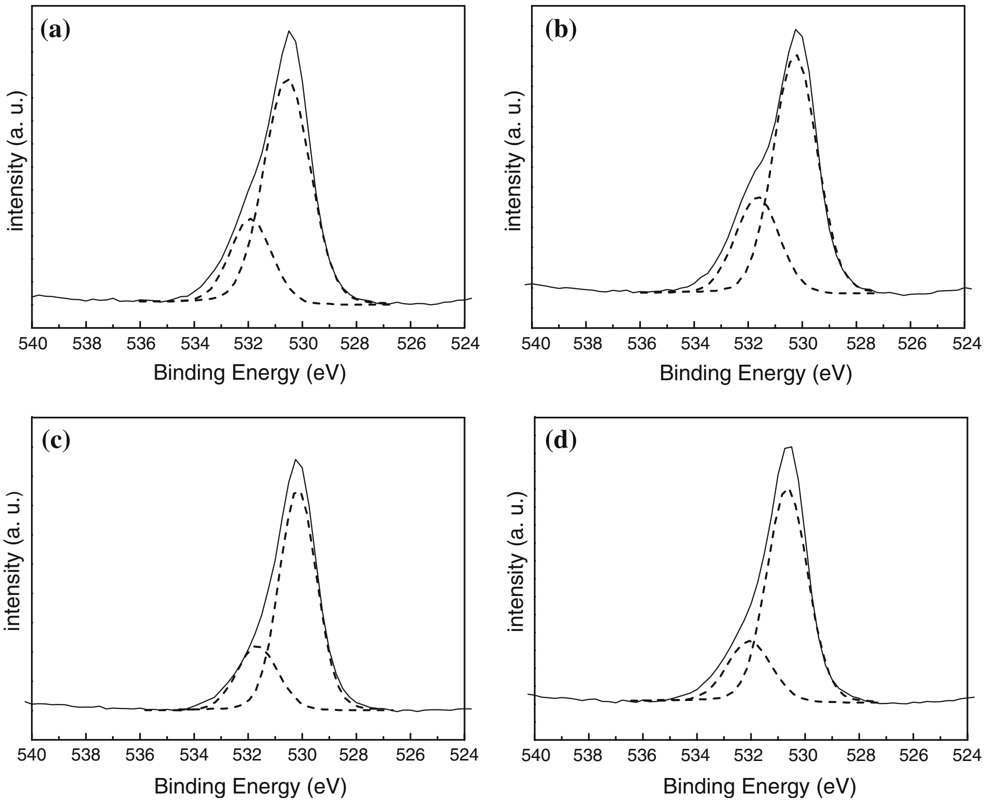

Figure 4. O1s spectra of the Au/SnO_2 catalysts calcined at different temperatures: 473 K (a), 573 K (b), 673 K (c), and 773 K (d).

4. Conclusions

The Au/SnO_2 catalysts were prepared by co-precipitation method. The as-prepared material was calcined in air at 473, 523, 573, 623 and 673 K for 3 h, respectively. The samples calcined at 523–623 K exhibited the higher catalytic activity and better stability in CO oxidation than the other samples. This indicted that the proper selective of calcination temperature was effective to gain high activity catalyst for low-temperature CO oxidation. According to the above TEM and XPS results, we suggested that the catalytic activity of gold/tin dioxide catalysts calcined at different temperatures depended strongly not only on the dispersion of gold species, but also on surface oxygen species on the support. Firstly, the decrease in the activity observed with lower calcination temperature (below 473 K) of the investigated samples could be related to the agglomerate of gold species. Secondly, the Au/SnO_2 samples calcined at 523–623 K exhibited higher catalytic activity than other samples, due to highly dispersed gold particles and the more adsorbed surface oxygen and hydroxyl groups on the support than other samples. Thirdly, an increasing size of the gold particles and the decreasing amount of adsorbed surface oxygen and hydroxyl groups were found with the further increasing pretreatment temperature (above 673 K), leading to the serious decrease of the catalytic activity.

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References

[1] M. Haruta, T. Kobayashi, H. Sano and N. Yamada, Chem. Lett. (1987) 405.
[2] A. Knell, P. Barnickel, A. Baiker and A. Wokaun, J. Catal. 137 (1992) 306.
[3] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.
[4] M.C. Kung, J.-H. Lee, A. Chu-Kung and H.H. Kung, Stud. Surf. Sci. Catal. 101 (1996) 701.
[5] M. Haruta, Catal. Today 36 (1997) 153.
[6] G.J. Hutchings, M.R.H. Siddigui, A. Burrows, C.J. Kiely and R. Whyman, J. Chem. Soc. Faraday Trans. 93 (1997) 187.
[7] G.B. Hoflund, S.D. Gardner, D.R. Chryer, B.T. Upchurch and E. Jielin, Appl. Catal. B 6 (1995) 117.
[8] A. Baiker, M. Maciejewski and S. Tagliaferri, J. Catal. 151 (1995) 407.
[9] M.A. Bollinger and M.A. Vannice, Appl. Catal. B 8 (1996) 417.
[10] F.E. Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano and S. Calogero, J. Chem. Soc. Faraday Trans. 93 (1997) 3403.

[11] Y. Yuan, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, Chem. Lett. (1996) 755.

[12] Y. Yuan, A.P. Kozlova, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, J. Catal. 170 (1997) 191.

[13] A.P. Kozlova, S. Sugiyama, A.I. Kozlov, K. Asakura and Y. Iwasawa, J. Catal. 176 (1998) 426.

[14] A.I. Kozlov, A.P. Kozlova, H.C. Liu and Y. Iwasawa, Appl. Catal. A 182 (1999) 9.

[15] M. Haruta, T. Kobayashi, H. Sano and N. Yamada, Chem. Lett. (1987) 405.

[16] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal. 115 (1989) 301.

[17] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, J. Catal. 144 (1993) 175.

[18] Y. Iizuka, T. Tode, T. Takao, K. Yatsu, T. Takeuchi, S. Tsubota and M. Haruta, J. Catal. 187 (1999) 50.

[19] H. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, K. Asakura and Y. Iwasawa, J. Catal. 185 (1999) 252.

[20] Z.P. Hao, L.D. An, H.L. Wang and T.D. Hu, React. Kinet. Catal. Lett. 70 (2000) 153.

[21] D. Horvath, L. Toth and L. Guczi, Catal. Lett. 67 (2000) 117.

[22] S.R. Wang, S.H. Wu, J. Shi, X.C. Zheng and W.P. Huang, Acta. Phys.-Chim. Sin. (Wuli Huaxue Xuebao) 20(4) (2004) 428.

[23] M. Haruta, T. Kobayashi, S. Iijima, F. Delannay, in M.J. Phillips, M. Ternan eds. *Proceedings of the Ninth International Congress on Catal. Calgary*, vol. 2, (The Chemical Institute of Canada, Ottawa, 1998), p. 1206.

[24] H. He, H.X. Dai and C.T. Au, Appl. Catal. B 33 (2001) 65.

[25] S.D. Lin, M. Bollinger and M.A. Vannice, Catal. Lett. 17 (1993) 245.

[26] M.A. Bollinger and M.A. Vannice, Appl. Catal. B 8 (1996) 417.

[27] Y.-S. Su, M.-Y. Lee and S.D. Lin, Catal. Lett. 57 (1999) 49.

[28] W.S. Epling, G.B. Hoflund and J.F. Weaver, J. Phys. Chem. 100 (1996) 9929.

[29] N. Yamazoe, Y. Teraoka and T. Seiyama, Chem. Lett. (1981) 1767.

[30] K. Tabata, Y. Hirano and E. Suzuki, Appl. Catal. A 170 (1998) 245.

[31] D. Andreeva, T. Tabakova, V. Idakiev, P. Christov and R. Giovanoli, Appl. Catal. A 169 (1998) 9.