The influence of the preparation methods on the catalytic activity of platinum and gold supported on TiO_2 for CO oxidation

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The influence of the preparation methods on the catalytic activity for CO oxidation was markedly large for Au–TiO_2 and negligible for Pt–TiO_2 catalysts. Platinum and gold were deposited on TiO_2 by deposition–precipitation (DP), photodeposition (FD) and impregnation (IMP). The DP method gave the most active catalysts for both Pt and Au. Gold catalysts prepared by DP were active at temperatures below 273 K and showed a much greater activity than Pt catalysts.

Keywords: CO oxidation, platinum, gold, titania support, preparation methods

1. Introduction

The reaction of CO with O_2 over supported noble metal catalysts is an important reaction for both industrial and automotive pollution control [1–4]. Recent studies have shown that palladium [5–8], platinum [9–15] and gold [16–28] particles, when dispersed on a specific group of reducible metal oxide supports, become active for the low temperature oxidation of carbon monoxide, even at room temperature.

Since the above enhanced catalytic activities for the low-temperature oxidation of CO can be ascribed to a significant metal–support interaction, it seems very probable that the degree of the interaction and thus the catalytic performance differ depending on the preparation methods. Therefore, in this paper, we have attempted to compare under identical conditions the CO oxidation performance of several Pt catalysts with those of Au catalysts prepared by different methods.

2. Experimental

2.1. Materials and catalyst preparation

Powdered TiO_2 (purity > 99.5%, P-25 produced by Japan Aerosil Co.) was one of the reference catalysts of the Catalysis Society of Japan (JRC-TIO-4). Its phase was primarily anatase with a surface area of ca. 50 m^2 g^{-1}. The $HAuCl_4{\cdot}4H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ were both of 99.5% purity. The impurity levels of other noble metals in chloroauric acid were approximately 2, 7, and 11 ppm for Pt, Ir, and Pd, respectively, as determined by atomic emission spectroscopy.

Deposition–precipitation samples (hereafter denoted by DP) were prepared by mixing TiO_2 powder(1–2.2 g) with appropriate amounts of aqueous solutions of chloroplatinic or chloroauric acid at a fixed pH from 7 to 10 [18]. The selection of the amount, pH and concentration led to different metal loadings. The slurry was then aged for 1 h, after which it was washed in 2 dm^3 of distilled water, decanted and the procedure was repeated six times. The resulting material was vacuum dried at 0.4 Pa for 15 h and calcined in air at 673 K for 4 h. The calcined samples were then flushed with pure argon (80 cm^3 min^{-1}) while raising the temperature to 723 K and reduced in flowing H_2 (1 vol% in N_2, 80 cm^3 min^{-1}) for 10 h after which it was finally cooled to room temperature under a flow of pure argon. Although the reduction treatment after calcination in air was not necessary for Au/TiO_2 and markedly lowered the catalytic activity for CO oxidation as was observed after vacuum calcination [17], the pretreatment in a hydrogen stream was carried out for both Au/TiO_2 and Pt/TiO_2 in order to compare both the catalysts prepared under similar conditions. The content of Cl^- remained in the samples was between 30 and 50 ppm for Pt–TiO_2 and was between 20 and 50 ppm for Au–TiO_2. A similar procedure was used for the unloaded TiO_2 sample, except that HCl was used instead of $HAuCl_4$ or H_2PtCl_6.

For obtaining catalysts prepared by impregnation (hereafter denoted by IMP), TiO_2 (1–2 g) was suspended in 20 cm^3 of desired amounts of aqueous $H_2PtCl_6{\cdot}6H_2O$ or $HAuCl_4{\cdot}4H_2O$, followed by evaporation to dryness in a rotary evaporator at 313 K under reduced pressure. The remaining paste was dried, calcined in air at 673 K for 4 h, and subsequently reduced in flowing H_2 according to the procedure described above.

The photochemical deposition (hereafter denoted by FD) of Au and Pt onto TiO_2 was carried out as follows [29]. Following a 1 h ultrasonic agitation in 4 cm^3 distilled water, the TiO_2 (100 mg) slurry was transferred to

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a cylindrical quartz photoreactor (120 cm^3) and solutions containing 1 : 1 (v/v) water–methanol and desired amounts of aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ or $HAuCl_4 \cdot 4H_2O$ were added. The pH of the suspension was adjusted to 4 for the $H_2PtCl_6 \cdot 6H_2O$ and about 7 for the $HAuCl_4 \cdot 4H_2O$ suspensions. The mixture was then deaerated with pure argon (75–80 cm^{3}min^{-1}) for 30 min, under magnetic stirring. After deaeration, the suspension was irradiated with a 125 W high-pressure Hg lamp (Ushio) operated at 25 mW cm^{-2} and 313 K for 0.5–1 h. After irradiation, the metal–TiO_2 was filtered, washed four times in hot distilled water to remove Cl^- and the resulting paste was vacuum dried for 15 h. The obtained catalysts were used without further treatment.

The amount of metal deposited on TiO_2 was determined both by X-ray fluorescence (Rigaku 3370 analyzer) and inductively coupled plasma spectrometry ICP-AES (Seiko SPS 1200 VR). Transmission electron micrographs (TEM) of the catalysts were obtained with a Hitachi H-9000 microscope. The sizes of the metal particles were obtained by using a computerized image analyzer (Excel, Nippon Avionics Co. Ltd.). The size distribution of the gold and platinum crystallites was determined by measuring 100–600 crystallites for each sample.

2.2. Apparatus and procedure

The catalyst (50 mg, 44–125 μm fraction) was placed between two glass wool plugs in a quartz reactor (6 mm, i.d.) with a bed length of about 5 mm for Pt and Au catalysts and 11 mm for unloaded TiO_2. Other experimental apparatus and procedures used in this study are identical to those described previously [16]. Prior to each experiment the catalysts were treated in air at 200°C for 30 min. This pretreatment could recover the catalytic activity of Au/TiO_2 samples which were reduced in a hydrogen stream after calcination in air. Activity measurements were performed as a function of temperature using a feed stream of 1 vol% CO in air (balance) at a flow rate of 17 ml min^{-1}. The feed stream was dried with silica gel at 273 K. The reaction gases were analyzed with a Yanaco G2800 gas chromatograph ($T = 313$ K, helium as a carrier gas at 40 cm^3 min^{-1}) equipped with a TCD and a stainless steel column (2 m) packed with 13X molecular sieves.

For the comparison of catalytic activity, three parameters are used: temperature for 50% conversion of CO ($T_{1/2}$) obtained from the reaction curves of %conversion of CO vs. catalyst temperature, reaction rate at 300 K which was obtained from the Arrhenius-type plots of logarithm of rate vs. $1/T$, and turnover frequency based on surface metal atoms. The reaction rates were calculated based on a differential reactor from the data corresponding to %conversion of CO below 15%. The numbers of surface metal atoms were calculated for particles with face-centered cubic structure using the mean particle diameter and metal loading.

3. Results

Fig. 1 shows the Pt and Au particle size distribution of some of the catalyst samples determined from TEM examinations. Platinum particles were distributed in a narrow range and had diameters between 1 and 5 nm. The majority of Au particles in the Au–TiO_2 samples were appreciably larger than those of Pt and lay in a broad range from 1 to 10 nm. In the case of Au-IMP, although X-ray fluorescence analysis confirmed the presence of Au, only a small number of metallic Au particles could be observed with TEM so that we could not obtain reliable data for size distribution.

Fig. 2 shows logarithmic plots of the reaction rate against $1/T$ for various Pt–TiO_2 and Au–TiO_2 catalysts. Most of the Pt–TiO_2 catalysts oxidized 100% of CO at temperatures between 333 and 373 K under the experimental conditions described previously and were less sensitive to the preparation method. The catalytic activity of Pt–TiO_2 samples decreases in the order $DP \approx IMP > FD$. Unloaded TiO_2 showed a poor activity at temperatures below 673 K to yield conversions of CO smaller than 10%. The reaction rate over anatase at 673 K was reported to be about 6.3×10^{-11} mol s^{-1} m^2 cmHg, which corresponded to 4.1×10^{-9} mol s^{-1} g-cat under the conditions of this work [31].

The activity of Au–TiO_2 samples strongly depended on the method of preparation and decreased in the order $DP \gg IMP \approx FD$. The activity of DP samples was extraordinarily high and clearly superior to Pt catalysts. DP samples with Au content higher than 2 wt% exhibited a very high activity, oxidizing 100% of CO at temperatures below 253 K. In contrast, IMP and FD samples showed smaller activity than Pt catalysts.

Table 1 summarizes catalyst parameters and some kinetic parameters for CO oxidation. These results show that the method of preparation and metal loading have a great influence on the mean particle diameter and on the catalytic activity. The mean particle diameter of Pt is always smaller, by ca. two times, than that of Au. DP and IMP gave almost the same particle size for Pt and DP tended to give a little smaller particles. FD yielded Pt particles larger by about two times than DP and IMP, although the sample was neither calcined nor reduced. For Au, only DP produced small gold particles. Impregnation yielded much larger particles and with a poor dispersion.

As shown in fig. 2 and in table 1, the catalytic activity for CO oxidation in terms of $T_{1/2}$ and rate at 300 K decreases in the order Au-DP $\gg$ Pt-DP $\approx$ Pt-IMP $>$ Pt-FD $\gg$ Au-IMP $\approx$ Au-FD $\gg$ TiO_2. It is very striking that the turnover frequency for Au-DP is larger by about four orders of magnitude than for Au-IMP and Au-FD, and

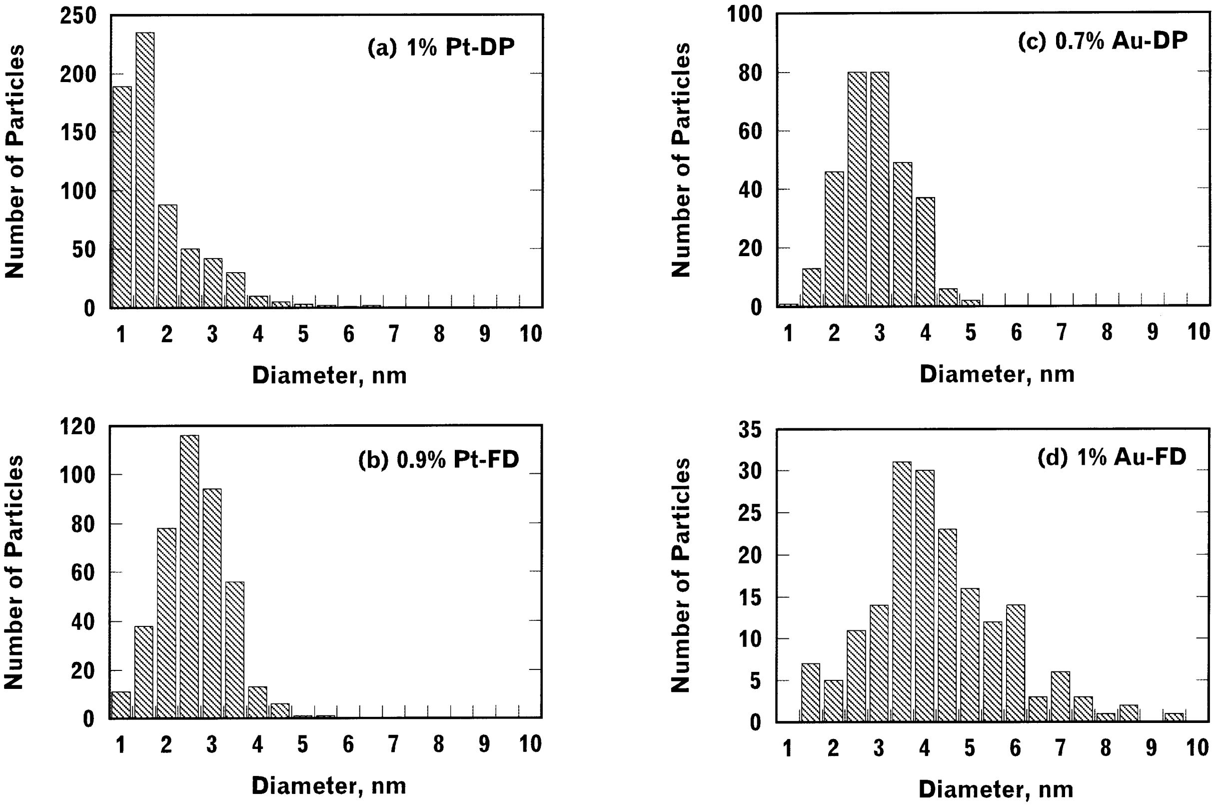

Fig. 1. Size distribution of Pt and Au particles deposited on TiO_2.

is larger by one to two orders of magnitude than for Pt catalysts. The apparent activation energies also show an interesting contrast: for all Pt catalysts and Au catalysts prepared by IMP and FD it is in the range of 50–60 kJ/mol and for Au catalysts prepared by DP around 20 kJ/mol.

4. Discussion

The differences in catalytic behavior between Pt–TiO_2 and Au–TiO_2 catalysts can be summarized in three points. (1) In terms of metal dispersion, both Pt and Au are sensitive to preparation methods: DP and IMP gave higher dispersion than FD for Pt, and only DP can give high dispersion of Au. (2) In terms of TOF, Pt is almost insensitive to the preparation methods and Au is remarkably sensitive: Au-DP exhibited TOF larger by four times than Au-IMP and Au-FD. (3) The apparent activation energy for Au-DP is two times smaller than those of Au-FD, Au-IMP and Pt catalysts.

The difference in metal dispersion, especially for impregnation, between Pt and Au can be explained by a large difference in the melting point, 2042 K for Pt and 1336 K for Au. The marked difference in structure sensitivity can be ascribed to the fundamental differences in the oxidation mechanism of CO over these catalysts. It is now established that for Pt supported on metal oxides,

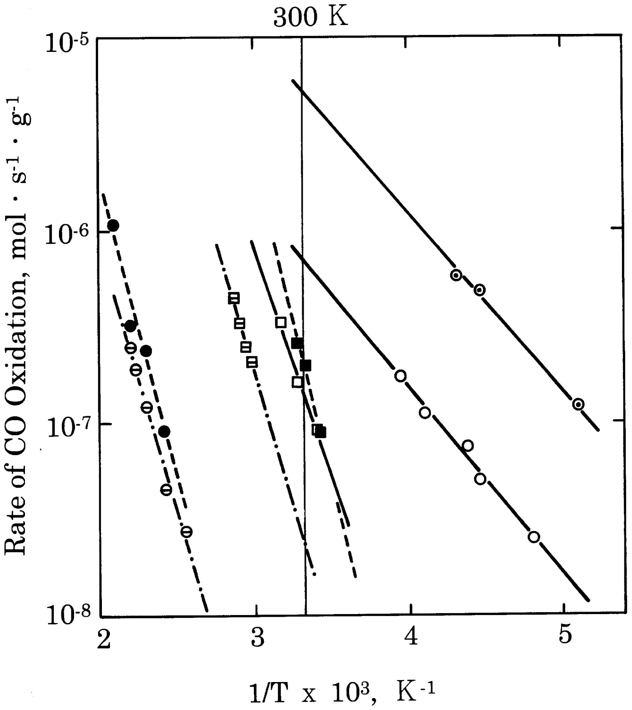

Fig. 2. Logarithmic reaction rate of CO oxidation over Pt–TiO_2 and Au–TiO_2 catalysts as a function of reciprocal temperature. (□) 1.0% Pt-DP; (■) 1.0% Pt-IMP; (⊟) 0.9% Pt-FD; (⊙) 1.8% Au-DP; (○) 0.7% Au-DP; (●) 1.0% Au-IMP; (⊖) 1.0% Au-FD.

Table 1
Mean diameters of metal particles and kinetic parameters of CO oxidation for Pt–TiO_2 and Au–TiO_2 prepared by different methods

Catalyst	D_{metal} (nm)	$T_{1/2}$ [a] (K)	Rate at 300 K (mol s^{-1} g-cat^{-1})	TOF at 300 K (s^{-1})	E_a (kJ/mol)
TiO_2	–	673 < [b]	–	–	–
1.0% Pt-DP	1.3±0.3	334	1.4×10^{-7}	2.7×10^{-3}	49
1.0% Pt-IMP	1.4±0.3	339	1.9×10^{-7}	3.8×10^{-3}	60
0.5% Pt-FD	2.6±0.9	375	1.2×10^{-8}	9.0×10^{-3}	51
0.9% Pt-FD	2.4±0.6	363	2.4×10^{-8}	9.2×10^{-3}	53
3.0% Pt-FD	–	358	4.3×10^{-8}	–	49
0.5% Au-DP	3.5±1.1	320	3.8×10^{-7}	3.7×10^{-2}	27
0.7% Au-DP	3.1±0.7	282	6.9×10^{-7}	3.4×10^{-2}	19
1.8% Au-DP	2.7±0.6	253	5.5×10^{-6}	1.2×10^{-1}	18
2.3% Au-DP	2.5±0.6	235	4.5×10^{-6}	6.8×10^{-2}	20
3.1% Au-DP	2.9±0.5	235	2.0×10^{-5}	2.6×10^{-1}	27
1.0% Au-FD	4.6±1.5	477	1.5×10^{-10}	9.6×10^{-6}	56
3.6% Au-FD	6.0±2.5	443	3.6×10^{-10}	8.3×10^{-6}	57
1.0% Au-IMP	–	481	1.7×10^{-10}	–	58

[a] Temperature for 50% conversion of 1 vol% CO contained in air under a space velocity of 2×10^4 h^{-1} ml/g-cat.
[b] The conversion of CO at 673 K was smaller than 10%.

the reaction CO + O_2 takes place on the platinum surface [2–4,30]. On the other hand, our recent studies indicate that CO adsorbed on gold particles react with oxygen species which are probably transported from the perimeter interface between Au and the metal oxide support [32]. This may explain the reason why the performance of Pt–TiO_2 samples is less sensitive to the method of preparation and/or the nature of the contact between Pt and the support. On the other hand, the activity of Au–TiO_2 for CO oxidation is affected by the preparation and pretreatment procedures and is strongly dependent on the nature of the Au–titania interaction and the distance of the Au/TiO_2 perimeter interface [16–18,20]. Deposition–precipitation can produce hemispherical Au particles which have their flat planes in good contact with TiO_2, yielding the longest perimeter interface, whereas impregnation and photodeposition give spherical particles which are simply loaded on the metal oxide support [33].

5. Summary

The above results can be summarized as follows:

(1) The activity for CO oxidation is strongly dependent on the preparation method in the case of Au–TiO_2 and insensitive in the case of Pt–TiO_2 catalysts.

(2) The Au-DP exhibit the highest activity and are certainly more active than Pt-DP, whereas platinum catalysts prepared by IMP and FD show a better activity than corresponding Au catalysts.

(3) The turnover frequency of Au-DP is larger by more than 10 times than those of Pt catalysts.

(4) The remarkable structure sensitivity in Au/TiO_2 catalysts can be explained by the contribution from the perimeter interface between Au particles and TiO_2 support.

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References

[1] F.G. Dwyer, Catal. Rev. 6 (1972) 261.

[2] A. Bielanski and J. Haber, in: *Oxygen in Catalysis* (Dekker, New York, 1991) p. 211.

[3] G.I. Golodets and J.R.H. Ross, in: *Heterogenous Catalytic Reactions Involving Molecular Oxygen*, Studies in Surface Science and Catalysis, Vol. 15 (Elservier, Amsterdam, 1983) p. 280.

[4] D. Bocker and R.D. Gonzalez, in: *Closed-Cycle, Frequency-Stable CO_2 Laser Technology*, NASA Conf. Publ. 2456, eds. G.E. Batter, I.M. Miller, G.M. Wood Jr. and D.V. Willets (NASA Sci. Techn. Inf. Branch, 1987) p. 85.

[5] M. Sheintuch, J. Schmidt, Y. Lectham and G. Yahav, Appl. Catal. 49 (1989).

[6] D.S. Stark and M.R. Harris, J. Phys. E 16 (1983) 492.

[7] G. Croft and M.J. Fuller, Nature 269 (1977) 585.

[8] G.C. Bond, L.R. Molloy and M.J. Fuller, J. Chem. Soc. Chem. Commun. (1975) 796.

[9] S.D. Gardner, G.B. Hoflund, D.R. Schryer and B.T. Upchurch, J. Phys. Chem. 95 (1991) 835.

[10] D.R. Schryer, B.T. Upchurch, B.D. Sidney, K.G. Brown, G.B. Hoflund and R.K. Herz, J. Catal. 130 (1991) 314.

[11] D.R. Schryer, B.T. Upchurch, J.D.V. Norman, K.G. Brown and J. Schryer, J. Catal. 122 (1990) 193.

[12] J.E. Drawdy, G.B. Hoflund, S.D. Gardner and E. Yngvadottir, Surf. Interf. Anal. 16 (1990) 369.

[13] P.A. Sermon, V.A. Self and E.P.S. Barrett, J. Chem. Soc. Chem. Commun. (1990) 1572.

[14] H.G. Lintz, C.F. Sampson and N. Gudde, in: *Proc. 2nd Int. Conf. Spillover*, Leipzig, 12 June 1989.

[15] T. Dawood, J.R. Richmond and B.W. Riley, in: *Low-Temperature CO-Oxidation Catalysts for Long-Life CO_2 Lasers*, NASA Conf. Publ. 3076 (NASA Sci. Tech. Inf., 1990) p. 157.

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

[17] D. Cunningham, S. Tsubota, N. Kamijo and M. Haruta, Res. Chem. Interm. 19 (1993) 1.

[18] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, in: *Preparation of Catalysts*, Vol. V, eds. G. Poncelet, P.A. Jacobs, P. Grange and B. Delmon (Elsevier, Amsterdam, 1991) p. 695.

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

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

[21] C. Sze, E. Gulari and B.G. Demczyk, in: *Materials Research Society Proceedings*, Vol. 286, eds. S. Komarneni, J.C. Parker and G.J. Thomas (Boston, 1993) p. 143.

[22] S. Takamatsu, M. Ishii, M. Kinbara, T. Kikuta and T. Fukushima, Shokubai (Catalysis) 34 (1992) 126.

[23] A.K. Tripathi, N.M. Gupta, U.K. Catterji and R.M. Iyer, Ind. J. Technol. 30 (1992) 107.

[24] A. Knell, P. Barnickel, A. Baiker and A. Wokaun, J. Catal. 137 (1992) 306.

[25] S.K. Tanielyan and R.L. Augustine, Appl. Catal. 85 (1992) 73.

[26] T. Aida, H.G. Ahn and H. Niiyama, in: *Catalytic Science and Technology*, Vol. 1, eds. S. Yoshida, N. Takezawa and T. Ono (Kodansha, Tokyo, 1991) p. 297.

[27] S.D. Gardner and G.B. Hoflund, Langmuir (1991) 74.

[28] S.D. Gardner, G.B. Hoflund, B.T. Upchurch, D.R. Schryer, E.J. Kieln and J. Schryer, J. Catal. 129 (1991) 114.

[29] B. Kraeutler and A.J. Bard, J. Am. Chem. Soc. 100 (1978) 5985.

[30] T. Matsushima, Surf. Sci. 127 (1983) 403; Hyomen (Surface) 23 (1985) 259.

[31] Y. Onishi, Bull. Chem. Soc. Jpn. 44 (1971) 1460.

[32] F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, J. Phys. Chem. 100 (1996) 3625.

[33] G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, J. Photochem. Photobiol. A 89 (1995) 177.