Preparation of Supported Gold Catalysts by Liquid-Phase Grafting of Gold Acethylacetonate for Low-Temperature Oxidation of CO and of H_2

Mitsutaka Okumura* and Masatake Haruta
Osaka National Research Institute, AIST, 1-8-31 Midorigaoka, Ikeda 563-8577

(Received December 24, 1999; CL-991092)

Gold nanoparticles can be deposited on several metal oxides by liquid phase grafting (LG) of dimethyl gold acetylacetonate. They exhibit high catalytic activities for the oxidation of CO and of H_2 at low temperatures, below and above 273 K, respectively.

Gold was previously recognized as a really noble metal in catalysis. But, it was found that gold could exhibit high catalytic activities for many reactions, when it was dispersed as nanoparticles onto the support surface. Because of the low melting point of Au (1335 K), a major problem to prepare active gold catalysts is the difficulty to achieve the high dispersion of gold particles on the supports. Several methods have already been developed, for example, deposition precipitation,[1,2] coprecipitation methods,[3,4] and impregnation methods followed by reduction and oxidation pretreatments.[5,6] Recently, the group of Asakura and Iwasawa developed an impregnation method using $[Au(PPh_3)](NO_3)$ in acetone solution.[7] The limitation of this method is that it is applicable only to freshly prepared hydroxides of metal and it is not applicable to acidic metal oxides as in the case of deposition precipitation. On the other hand, we have later reported[8-11] that vapor phase grafting method using a volatile organogold complex is applicable to a variety of metal oxide supports including acidic support like SiO_2.

In this work, liquid phase grafting (LG) method is used for depositing gold on several metal oxide supports by using $(CH_3)_2Au(CH_3COCHCOCH_3)$, abbreviated to $Me_2Au(acac)$, as a gold precursor. It was used without further purification of the reagent available from Tri Chemical Laboratory Inc.. Its vapor pressure at room temperature was about 8.5×10^{-3} torr. For the support of gold catalysts, TiO_2 (ST-01 with a specific surface areas of 286 m^2/g : Ishihara Sangyo Kaisha, Ltd.), Al_2O_3 (JRC-ALO-7 with 117 m^2/g), and SiO_2 (Merck extra pure grade with 270 m^2/g) were used. Instead of the aqueous solution of $HAuCl_4$, $Me_2Au(acac)$ was dissolved in acetone. Then, a weighed quantity of metal oxide support was introduced into this solvent and was kept in a refrigerator overnight. Finally, this solvent and metal oxide were separated by filtration and the metal oxide with the gold absorbed precursor was calcined in air at 673 K.

Figures 1a, 1b, and 1c show TEM photographs for Au deposited on TiO_2, Al_2O_3 and SiO_2 by LG method (LG-Au/TiO_2, LG-Au/Al_2O_3 and LG-Au/SiO_2), respectively. The images of gold particles are seen as dark spots. The mean diameters of Au particles on TiO_2, Al_2O_3 and SiO_2 are estimated by TEM images to be 2.9 nm, 6.6 nm and 16 nm, respectively. The mean diameter of Au deposited on SiO_2 was 2 times larger than that of Au/SiO_2 prepared by gas phase grafting (GG-Au/SiO_2) and similar to that of Au/SiO_2 prepared by impregnation method (IMP-Au/SiO_2).

In order to examine the actual amount of gold loading, ICP (Induced Coupled Plasma) measurements were carried out for LG-Au/TiO_2, LG-Au/Al_2O_3, and LG-Au/SiO_2. The results are shown in Table 1. As the amount of Au precursor dissolved in acetone was fixed at 3 wt% with respect to the support, the actual Au loadings were 76% and 95% of the initial Au content of the Au precursor in the case of LG-Au/TiO_2 and LG-Au/Al_2O_3, respectively. On the other hand, the actual Au loading of LG-Au/SiO_2 was only 0.18 wt%, suggesting that it was difficult to graft the gold precursor onto the support surface which had the low pH of the zero point of charge (Z.P.C.). This feature was completely different from that of GG method, and similar to that of deposition-precipitation method in aqueous solution. The limitation to the support in LG method may come from the strong interaction between the support surface and the solvent. In other words, the solvent adsorbed may inhibit the tight interaction between Au precursor and the support surface.

The catalytic activities of Au catalysts were examined for the oxidation of H_2 and of CO (SV=20000 mL/h g-cat., reactant

Table 1. Mean diameters of Au particles and kinetic parameters of CO and H_2 oxidation for Au supported on TiO_2, Al_2O_3 and SiO_2

Catalyst[a]	Preparation method	Au[b] wt%	D_{Au}[c] nm	CO oxidation $T_{1/2}$ K	CO oxidation E_0 kJ/mol	H_2 oxidation $T_{1/2}$ K
LG-Au/TiO_2	Liquid phase grafting	2.28	2.9±0.7	236	36	313
LG-Au/Al_2O_3	Liquid phase grafting	2.84	6.6±5.2	299	39	369
LG-Au/SiO_2	Liquid phase grafting	0.18	16±9.1	-	-	669
GG-Au/TiO_2[d]	Gas phase grafting	4.70	3.8±2.7	239	41	321
GG-Au/Al_2O_3[d]	Gas phase grafting	5.30	3.5±2.7	261	36	331
GG-Au/SiO_2[d]	Gas phase grafting	6.60	6.6±3.8	227	17	329
IMP-Au/SiO_2[d]	Impregnation	14.7	20[e]	477	-	357

[a]Calcined in air at 673 K for 4 h. [b]ICP analysis. [c]TEM. [d]Ref. 9. [e]XRD.

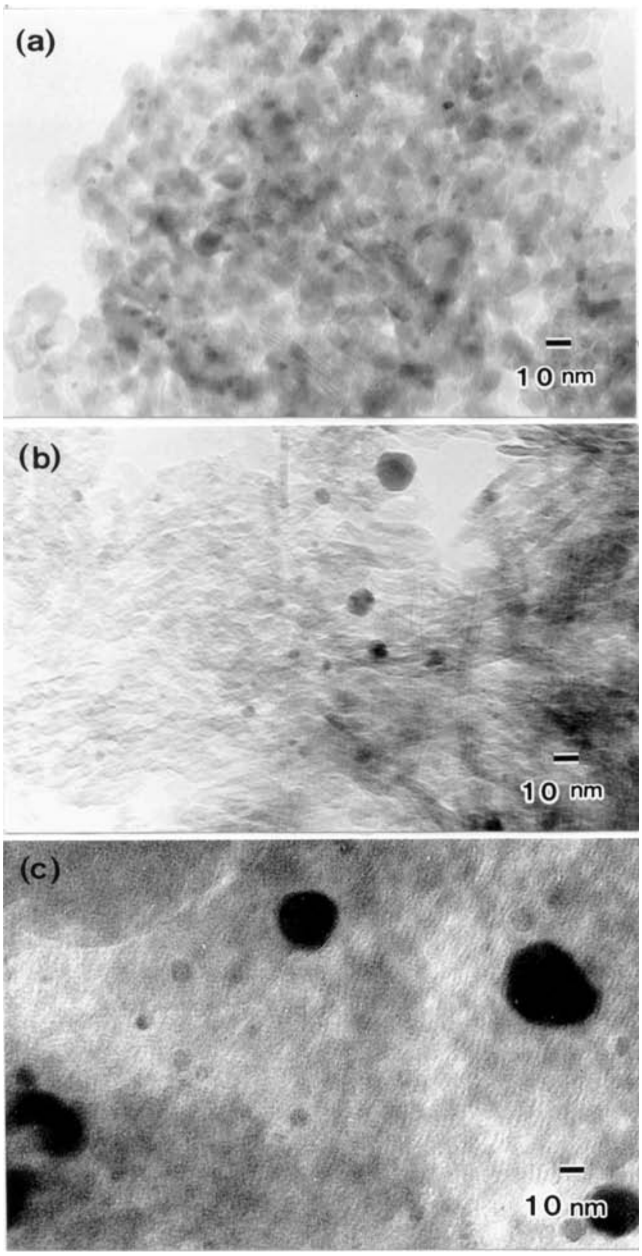

Figure 1. TEM images of (a) Au/TiO_2, (b) Au/Al_2O_3 and (c) Au/SiO_2 prepared by LG and calcined in air at 673K for 4 hours.

gas : 1 vol% H_2 or CO in air, fix-bed flow reactor). The results were summarized in Table 1. Gold catalysts prepared by LG and calcined in air at 673 K for 4 hours exhibit high catalytic activities for H_2 oxidation. The catalytic activity of H_2 oxidation over Au/TiO_2 and Au/Al_2O_3 are thought to be almost independent of the type of metal oxide supports and therefore to be primarily proportional to the exposed Au surface area.[11] As the conversion curves of H_2 oxidation over Au catalysts had almost same shapes, the catalytic activities were compared with the temperature for 50% conversion of H_2 ($T_{1/2}$). The fact that $T_{1/2}$ of H_2 oxidation is below 320 K supports the results of TEM observations that ultrafine Au particles are highly dispersed on TiO_2 and Al_2O_3. LG-Au/TiO_2 and LG-Au/Al_2O_3 catalysts exhibit higher catalytic activities in CO oxidation than in H_2 oxidation. CO oxidation took place at temperatures below 273 K. On the other hand, the catalytic activity of CO and H_2 oxidation over LG-Au/SiO_2 are extremely low, mainly because of a low loading and a poor dispersion of gold particles.

The apparent activation energies of CO oxidation over LG-Au/TiO_2 and LG-Au/Al_2O_3 catalysts were obtained by measuring reaction rates at different temperatures while keeping conversion of CO below 15%. The values obtained are 36 kJ/mol for LG-Au/TiO_2 and 39 kJ/mol for LG-Au/Al_2O_3. They are similar to those of the Au catalysts prepared by other methods like gas phase grafting and deposition precipitation methods. Therefore, it is confirmed that LG method can prepare Au catalysts having the same features like those prepared by representative methods.

In conclusion, this communication reports that LG method of organogold complex, typically, gold acetylacetonate, is an effective and simple technique to deposit Au nanoparticles on select metal oxide supports except for SiO_2 and that catalysts thus obtained are active for the oxidation of CO and of H_2 at low temperatures. Though the present LG method is similar to the method reported by the group of Iwasawa, this method is advantageous in the points that it can be applied to the metal oxide support commercially available instead of freshly prepared metal hydroxide support and the planer organo gold complex have the strong interaction with a support surface. Additionally, this method may give a good catalyst sample which are free from the contamination by alkaline metals and chloride ions, which often poisons or promotes the catalysis, though the standard deviations of D_{Au} for LG-Au catalysts are larger than those of Au catalysts prepared by other methods.

References and Notes

1 S. Tsubota, D. A. H. Cunningham, Y. Bando, and M. Haruta, in "Preparation of Catalysts VI," ed by G. Poncelet, J. Martens, B. Delmon, P. A. Jacobs, and P. Grange, Elsevier, Amsterdam (1995),Vol.11, p.227.

2 M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, and B. Delmon, *J. Catal*, **144**, 175 (1992).

3 M. Haruta, N. Yamada, T. Kobayashi, and S. Iijima, *J. Catal.*, **115**, 301 (1989).

4 T. Kobayashi, M. Haruta, S. Tsubota, and H. Sano, *Sensors and Actuators*, **B1**, 222 (1990).

5 S. D. Lin, M. Bollinger and M. A. Vannice, *Catal. Lett.*, **17**, 245 (1993).

6 Z. M. Liu and M. A. Vannice, *Catal. Lett*., **43**, 51 (1997).

7 Y. Yuan, K. Asakura, H. Wan, K. Tsai, and Y. Iwasawa, *Chem. Lett*., **1996**, 755.

8 M. Okumura, K. Tanaka, A. Ueda, and M. Haruta, *Solid State Ionics*, **95**, 143 (1997).

9 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma, and M. Haruta, *Catal. Lett*., **51**, 53 (1998).

10 M. Okumura, S. Tsubota, M. Iwamoto, and M. Haruta, *Chem. Lett.*, **1998**, 315.

11 M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Haruta, in "Preparation of Catalysts VII," ed by G. Poncelet, J. Martens, B. Delmon, P. A. Jacobs, and P. Grange, Elsevier, Amsterdam (1998), Vol. 188, p.277.

12 S. Inagaki, K. Fukumoto, and Y. Fukushima, *Shokubai (Catalysis & Catalysts)*, **37(2)**, 191 (1995).