JOURNAL OF Materials CHEMISTRY

Supported gold catalysts prepared by using nano-sized gold particles dispersed in nylon-11 oligomer

Koichi Sayo,[a] Shigehito Deki*[a] and Shigehiko Hayashi[b]

[a]*Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, 1–1, Rokkodai-cho, Nada-ku, Kobe 657–8501, Japan. E-mail: deki@kobe-u.ac.jp*
[b]*Mitsuboshi Belting Ltd., 4-1-21, Hamazoe-dori, Nagata-ku, Kobe 653–0024, Japan*

Received 13th November 1998, Accepted 26th January 1999

Gold catalysts supported on titanium oxide (TiO_2) have been prepared by using nano-sized gold particle/nylon-11 oligomer composites. The composite was prepared through vapor-deposition of gold onto a nylon-11 oligomer film followed by heat treatment. The gold particles/nylon-11 oligomer composite in solution was adsorbed rapidly on the surface of TiO_2. When the gold particles/nylon-11 oligomer composite adsorbed on TiO_2 was calcined at various temperatures in air, nano-sized gold particles were supported directly on the surface of TiO_2 without coagulation. The catalytic activity of the gold particles for oxidation of CO was measured in a flow type reactor. The catalytic activity of gold supported on TiO_2 prepared by a one-stage calcination was not so high as that of gold catalysts reported previously. This result was considered to be due to growth of the size of the gold particles during calcination. When the calcination was carried out in two stages (the first at 500 °C in vacuum, and the second at 400 °C in air), the growth of the size of the gold particles was suppressed considerably. The supported gold catalyst thus obtained showed very high activity for the oxidation of CO, with a temperature of −10 °C for 50% conversion of CO.

Introduction

Nano-sized metal particles supported on oxides have attracted a great deal of interest owing to their novel properties as catalysts.[1] Supported gold catalysts are one of such systems, and show a good catalytic activity in the low-temperature oxidation of CO.[2–4] Many applications to gas sensors and the removal of CO from air have been developed.[5,6]

The catalytic activity of a supported metal catalyst is affected by the size of metal particles[7] and the interaction between metal particles and supports.[8] In general, supported metal catalysts prepared by impregnation in conventional oxides show poor catalytic activity. For supported gold catalysts, an interaction between the gold and the support is a prerequisite for high catalytic activity because gold itself shows only poor catalytic activity.[9] Therefore, specific methods such as precipitation–deposition are required to prepare desirable supported metal catalysts.[2,10]

Here, we propose a novel process to modify a surface of titanium oxide (TiO_2) with nano-sized gold particles. We have already reported a novel preparation method for nano-sized particles using a thermal relaxation technique.[11,12] Through this technique, a composite of nano-sized gold particles dispersed in nylon-11 oligomer has been prepared.[13]

The composite dissolves into various organic solvents, and produces a stable colloidal solution. We found that the nano-sized gold particles/nylon-11 oligomer composite was adsorbed rapidly onto the surface of TiO_2 when TiO_2 was immersed into a colloidal solution of the gold composite. The adsorbed gold particles were supported directly on TiO_2 by a two-stage calcination without particle size growth. The supported gold catalyst thus obtained showed very high activity for oxidation of CO.

Experimental

A composite containing nano-sized gold particles was prepared according to the previous paper.[13] Nylon-11 oligomer was prepared by thermal degradation of commercial nylon-11 (Rilsan BMN0, Toray Industries). The molecular weight of the oligomer was *ca.* 652. Gold (99.99%, Tanaka Kikinzoku, 3.6×10^{18} atoms cm^{-2}) was vapor-deposited onto a film of the nylon-11 oligomer to a thickness of 75 μm. Samples were heat-treated at 120 °C in air to complete dispersion of the gold particles. A TEM image of the gold particles/nylon-11 oligomer composite prepared is shown in Fig. 1(a) and the gold content in the composite was *ca.* 15 wt%. The mean size of the gold particles measured by counting more than 1000 particles in transmission electron micrographs was 5.0 ± 1.3 nm [Fig. 1(b)]. The gold particles/nylon-11 oligomer composite was dissolved in CH_2Cl_2 (guaranteed reagent, Nacalai Tesque), which yielded a stable colloidal solution of gold.

Commercial P25-TiO_2 powder (Nippon Aerosil) was used as a support after it was heated at 200 °C for 1 h in air. TiO_2 powder (2 g) was suspended in CH_2Cl_2 (100 ml) by stirring. A colloidal solution (150 ml) with a gold concentration of 0.46, 2.0 or 4.6 mmol l^{-1} was poured into the suspension, and after the mixture was stirred for several hours, the modified TiO_2 was collected by filtration through a PTFE membrane (0.8 μm, Advantec Toyo). The modified TiO_2 was washed several times with CH_2Cl_2 and dried at 40 °C in an oven. The modified TiO_2 was then calcined at temperatures from 400 to 700 °C for 1 h in air to remove the nylon-11 oligomer. A two-stage calcination was also used to improve the characteristics of the catalyst; the first calcination was carried out at 500 °C for 1 h in nitrogen or in vacuum (1 mmHg), and the second at 400 °C for 1 h in air.

Characterization of the samples was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM) and IR spectroscopy. XRD patterns were measured by the 2θ method using Cu-Kα radiation on a Rigaku RINT-1000 instrument with a thin film attachment. The incidence angle of X-rays onto the sample was set to 1°. TEM images of the samples were observed using a JEOL JEM-2010 electron microscope operated at 200 kV. The samples were dispersed in methanol, and drops of suspensions were placed on carbon coated Cu grids and dried. IR spectra were measured with a JEOL FT-IR JIR-6000 spectrometer using the diffuse reflection method.

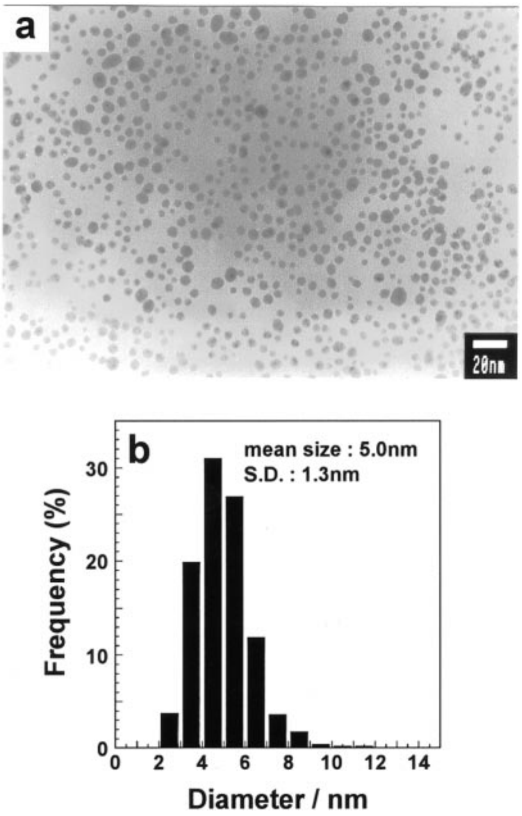


Fig. 1 (a) TEM image and (b) particle size distribution of the gold particles/nylon-11 oligomer composite.

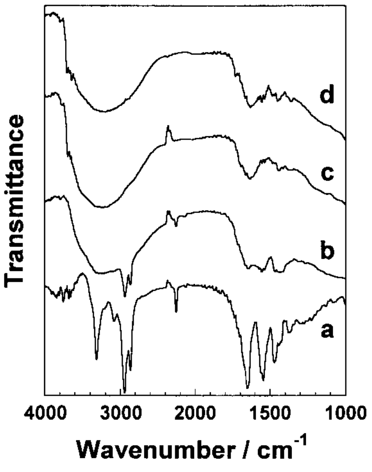
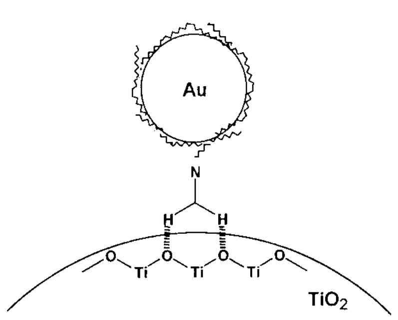


Fig. 2 IR spectra of (a) the gold particles/nylon-11 oligomer composite, (b) TiO_2 modified by using 4.6 mmol l^{-1} colloidal solution of gold, (c) the modified TiO_2 after one-stage calcination at 400 °C for 1 h in air, and (d) the intact P25-TiO_2.



Scheme 1

Table 1 Content of gold adsorbed and supported on TiO_2

Concentration of gold in the colloidal solution/mmol l^{-1}	Content[a] of gold adsorbed on TiO_2 (wt%)	Content[a] of gold supported on TiO_2 (wt%)[b]
0.46	0.8	0.8
2.0	3.8	3.8
4.6	6.6	6.6

[a]Obtained by energy dispersive fluorescent X-ray spectroscopy. [b]Calcined at 500 °C for 1 h in air.

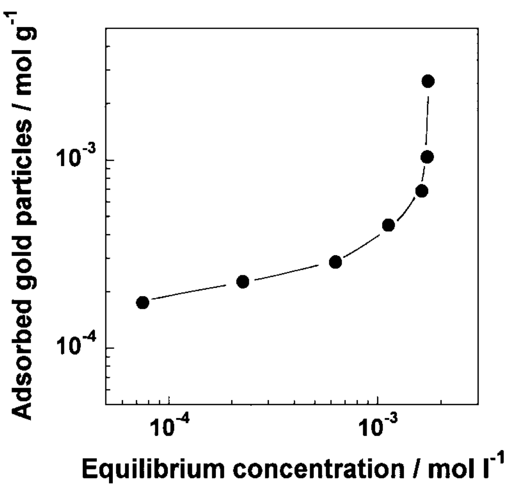


Fig. 3 Adsorption isotherm of the gold particles/nylon-11 oligomer composite on TiO_2.

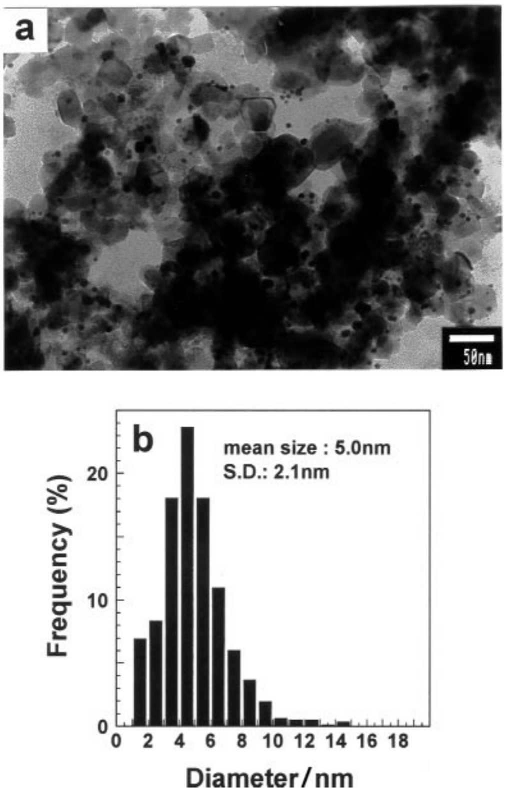


Fig. 4 (a) TEM image and (b) particle size distribution of the gold particles adsorbed on TiO_2. Content of gold was 6.6 wt%.

Energy dispersive fluorescent X-ray analysis was carried out to obtain the gold concentration in TiO_2 using a Seiko Instruments SEA-2010 with Rh-Kα radiation.

Adsorption of the gold particles/nylon-11 oligomer composite onto TiO_2 was examined by measurements of

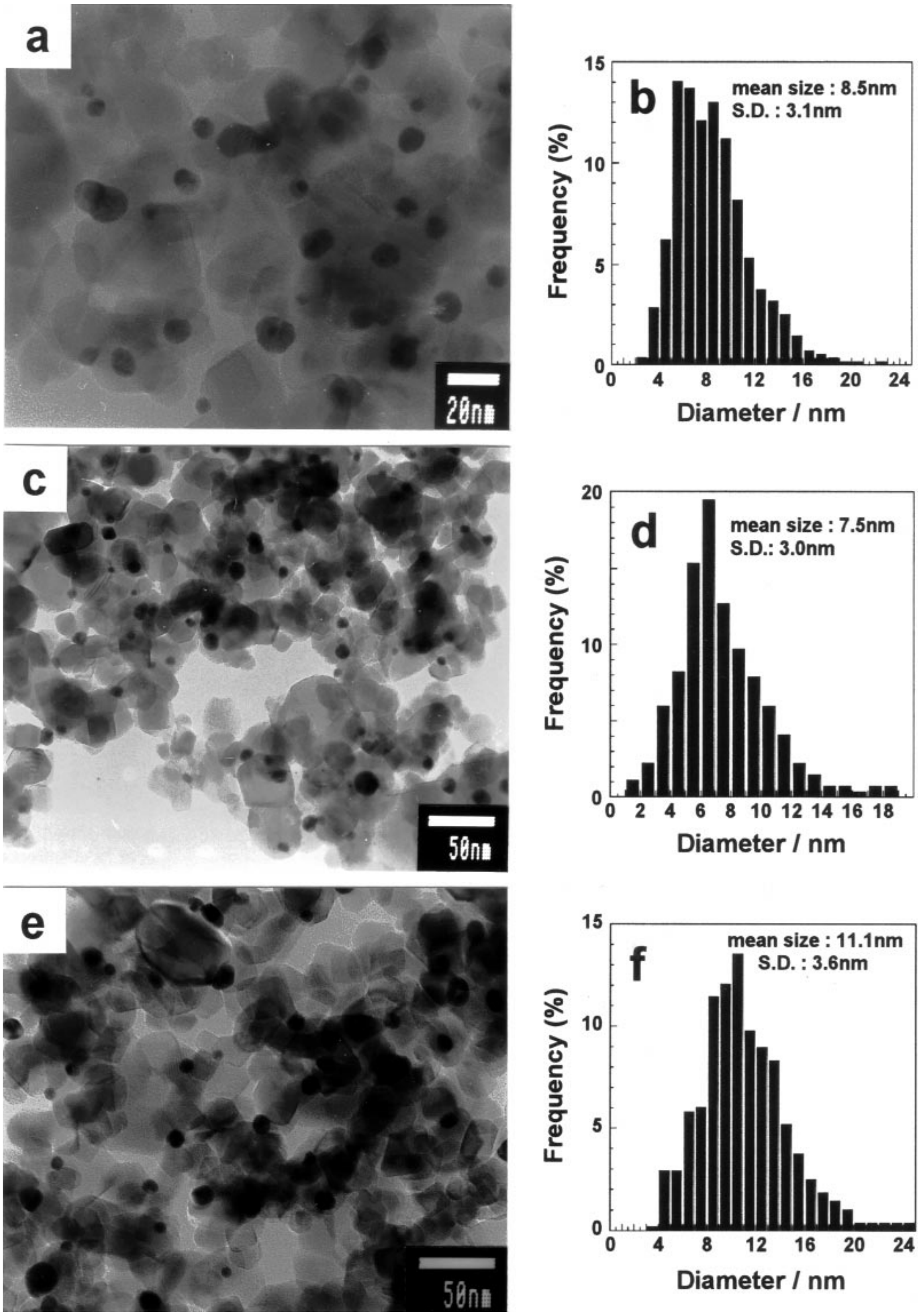


Fig. 5 TEM images and particle size distributions of the gold particles supported on TiO_2 by one-stage calcination at 400 °C (a, b), 500 °C (c, d), and 700 °C (e, f) for 1 h in air. Content of gold in each sample was 6.6 wt%.

adsorption isotherms. 1,2,3-Trichloropropane (guaranteed reagent, Wako Pure Chemical Industries) was used as a solvent. Various amounts of TiO_2 powder dried at 200 °C for 1 h in air were added to colloidal gold solutions. The mixtures were kept at 20 °C for 72 h with shaking. After filtration of TiO_2 through a 0.8 μm PTFE membrane, concentrations of the gold particles in the filtrate were calculated from the absorbance of the plasmon absorption of the gold particles at 524 nm in the visible spectrum.

The catalytic properties of the supported gold particles on TiO_2 were examined for oxidation of CO. A flow type reactor connected to an auto-sampling unit was used. The reaction gas (O_2 and N_2 containing 1.0 vol% CO) was purified through a molecular sieve column, and then passed through the sample (100 mg) bed at a flow rate of 33 ml min^{-1} (space velocity = *ca.* 20 000 ml h^{-1} g^{-1}). The concentration of CO was measured at various catalyst temperatures by a gas chromatograph equipped with a 5 Å molecular sieve column.

Results and discussion

1 Supported gold catalysts prepared by one-stage calcination of the gold particles/nylon-11 oligomer composite adsorbed on TiO_2

Adsorption of the gold particles/nylon-11 oligomer composite onto TiO_2 proceeded rapidly, and the gold particles were

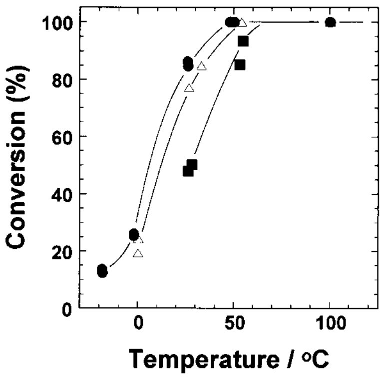


Fig. 6 Relationship between conversion ratio and reaction temperature for oxidation of CO by using the supported gold catalysts produced by one-stage calcination at 400 °C (●), 500 °C (△), and 700 °C (■) for 1 h in air. Content of gold in each sample was 6.6 wt%.

tightly adsorbed on the surface of TiO_2. When the transparent ruby-red colloidal solution of gold was added to the suspension of TiO_2, the ruby-red color immediately faded and reddish-purple precipitates were formed. When the precipitates were washed repeatedly with CH_2Cl_2, the color of the precipitate did not change.

Fig. 2 shows FTIR spectra of the gold particles/nylon-11 oligomer composite and the modified TiO_2. The composite showed bands assigned to N–H (3311 cm^{-1}), C–H (3078, 2937 and 2858 cm^{-1}), C≡N (2247 cm^{-1}) and C=O (1649 cm^{-1}), which are characteristic of the nylon-11 oligomer. These bands, except for the N–H band, were also observed in the spectrum of the modified TiO_2 [Fig. 2(b)]. The absence of the N–H band suggested that the gold particles/nylon-11 oligomer composite was adsorbed on TiO_2 through a reaction between the nylon-11 oligomer and TiO_2 as shown in Scheme 1.

Gold contents in the modified TiO_2 samples were measured by fluorescent X-ray analysis. The contents varied according to the variation of concentration of gold in the colloidal solutions (Table 1). Fig. 3 shows an adsorption isotherm of the gold particles/nylon-11 oligomer composite on TiO_2. The gold particles/nylon-11 oligomer composite showed multilayered adsorption characteristics at higher equilibrium concentrations of gold. When a 4.6 mmol l^{-1} colloidal solution of gold was used, the adsorption was saturated, and a maximum content of 6.6 wt% was obtained. This value was larger than that reported previously (*ca.* 3 wt%).[14]

Fig. 4 shows a TEM image and the size distribution of the adsorbed gold particles. The gold particles were observed clearly at a higher contrast because the electron density of gold is higher than that of TiO_2. The mean size of 5.0 nm indicated that the gold particles were adsorbed onto TiO_2 in the same state as in the composite. The gold particles were homogeneously dispersed on TiO_2 without coagulation owing to protection by the nylon-11 oligomer. In this state, however, gold particles adsorbed on TiO_2 were not active for the oxidation of CO.

For the appearance of catalytic activity for the oxidation of CO, removal of the nylon-11 oligomer from the modified TiO_2 was essential. Fig. 5 shows TEM images and size distributions of the gold particles on TiO_2 after one-stage calcination of the modified TiO_2 at various temperatures in air. The contents of gold did not vary after the one-stage calcination (Table 1), but the mean size of the gold particles supported on TiO_2 increased with increasing calcination temperature and the growth of the particle size indicates that adjacent gold particles coalesce. However, the mean size of 7.5 nm for the gold particles calcined at 500 °C was still relatively small compared to supported gold particles prepared by chemical methods such as impregnation.[10] XRD results showed that the structure of TiO_2 did not change after calcination at temperatures up to 500 °C.

The removal of the nylon-11 oligomer was monitored by IR spectroscopy. Fig. 2(c) shows the IR spectrum after one-stage calcination of the modified TiO_2 at 400 °C in air. The bands attributed to the nylon-11 oligomer disappeared, and the spectrum was almost the same as that of intact P25-TiO_2 [Fig. 2(d)].

For supported metal catalysts, the particle size is an important factor to acquire high catalytic activity. Supported gold particles in this study were of nanometer size, and were expected to show high catalytic activity for the oxidation of CO. The catalytic activity was improved by lowering the calcination temperature as shown in Fig. 6. As the content of gold was increased, the curves showing the conversion of CO, shifted toward lower temperatures. For the catalyst calcined at 400 °C, which contained 6.6 wt% of gold particles, the temperature for 50% conversion of CO ($T_{50\%}$) was *ca.* 10 °C.

The catalytic activity measured here was higher than that of supported gold particles prepared by using gold complexes and titanium hydroxides ($T_{50\%} = 31$ °C, $T_{100\%} = 163$ °C).[10] However, the activities of our catalysts were lower than those reported by Haruta *et al.*[9] They reported that gold particles with diameters below 1.0 nm were most effective for oxidation of CO.[15] Our supported gold particles were larger in size (8.5 mm for the catalyst calcined at 400 °C), and hence the catalytic activity was considered to be low.

2 Supported gold catalysts prepared by two-stage calcination of the gold particles/nylon-11 oligomer composite adsorbed on TiO_2

The catalytic activity was improved by lowering the calcination temperature to 400 °C, but the $T_{50\%}$ value of *ca.* 10 °C for the oxidation of CO on the supported gold catalyst was still relatively high. One-stage calcination leads to a growth of the particle size owing to violent decomposition of the nylon-11 oligomer. In order to suppress the growth of particles, therefore, two-stage calcination, which leads to a moderate removal of the nylon-11 oligomer, was adopted.

Fig. 7 shows TEM images and size distributions of gold particles supported on TiO_2 produced by two-stage calcination (the first calcination in vacuum at 500 °C for 1 h and the second in air at 400 °C for 1 h). The gold particles were isolated and distributed homogeneously. The mean size (5.7 nm) of the gold particles supported on TiO_2 calcined at 500 °C in vacuum was almost the same as that on the modified TiO_2 before calcination (5.8 nm) and the mean size (5.5 nm) was maintained after the second calcination at 400 °C in air. It was noteworthy that the nylon-11 oligomer is removed without any growth of the gold particles. In vacuum, it is considered that the nylon-11 oligomer decomposes moderately with volatile components being smoothly removed. On the other hand, the catalysts obtained by a different two-stage calcination (first calcination in N_2 at 500 °C for 1 h, the second in air at 400 °C for 1 h) showed size growth from 5.8 to 6.5 nm.

Fig. 8 shows the catalytic properties of the supported gold catalyst prepared by the two-stage calcination. After the first calcination in vacuum at 500 °C, the supported gold particles showed little catalytic activity for the oxidation of CO. However, after the second calcination in air at 400 °C, the supported gold catalyst showed excellent catalytic activity. A value of $T_{50\%}$ of *ca.* -10 °C was much lower than that of the catalyst prepared by the one-stage calcination and was comparable to the best $T_{50\%}$ value of a supported gold catalyst prepared by precipitation–deposition,[9] even though the mean

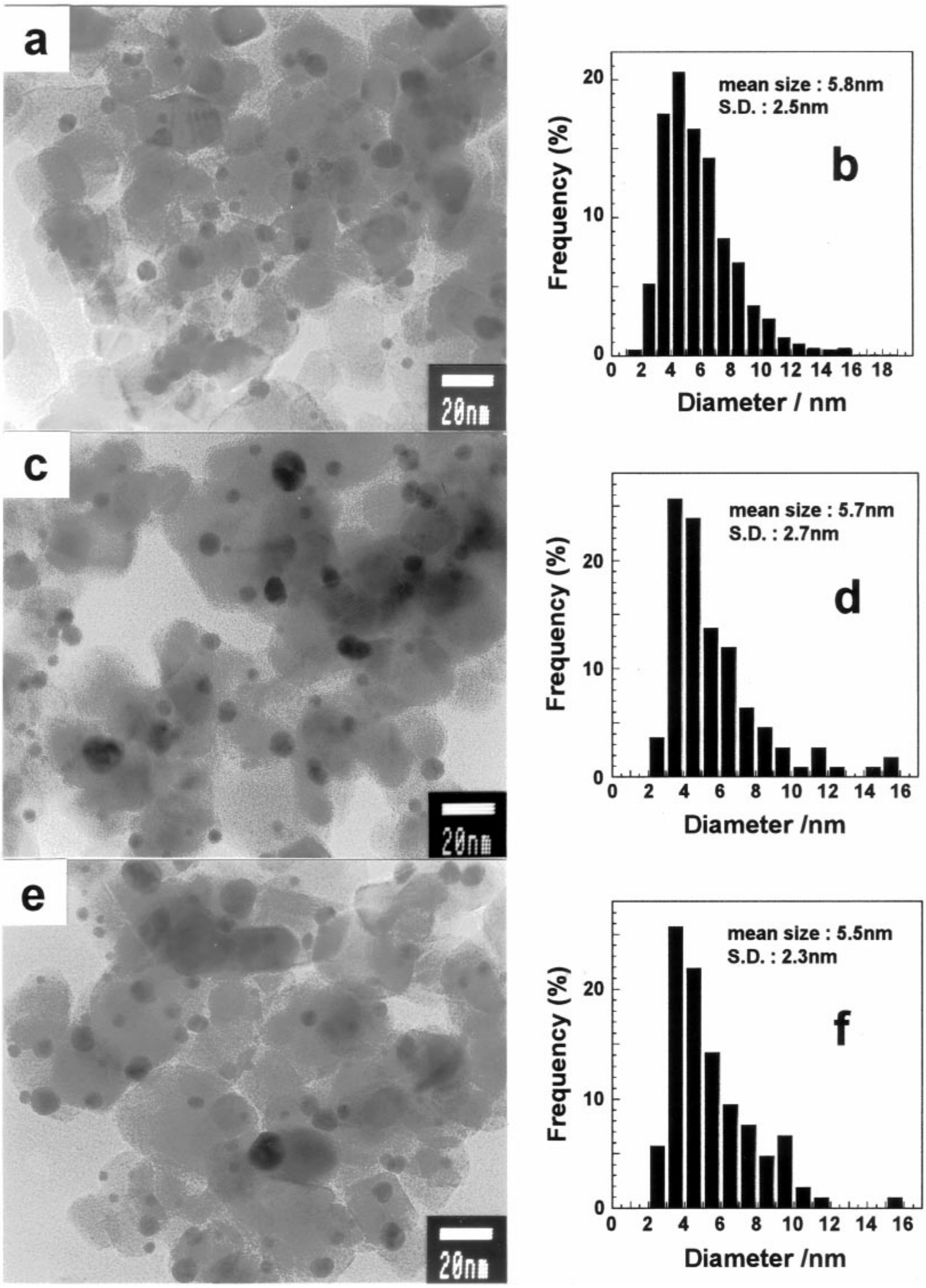


Fig. 7 TEM images and particle size distributions of the gold particles adsorbed on the modified TiO_2 (a, b), the supported gold particles on TiO_2 by the first calcination at 500 °C for 1 h in vacuum (c, d), and the supported gold catalyst produced by two-stage calcination (the first calcination at 500 °C for 1 h in vacuum, the second at 400 °C for 1 h in air) (e, f). Content of gold in each sample was 6.6 wt%.

size of the gold particles in our catalyst was larger. If the first calcination of the modified TiO_2 was carried out in N_2 at 500 °C for 1 h, the catalyst, which was obtained after the second calcination in air at 400 °C for 1 h, showed lower catalytic activity for the oxidation of CO ($T_{50\%}$ *ca.* 0 °C).

Conclusion

Nano-sized gold particles dispersed in nylon-11 oligomer were adsorbed rapidly on the surface of TiO_2. Two-stage calcination of the gold particles/nylon-11 oligomer composite adsorbed on TiO_2 gave gold particles supported directly on the surface of TiO_2. The supported gold catalyst thus obtained showed very high activity for oxidation of CO, since the size growth of the gold particles was suppressed by two-stage calcination.

Acknowledgments

The authors thank Dr Tetsuhiko Kobayashi and Dr Atsushi Ueda, Osaka National Research Institute, for helping us to measure catalytic properties.

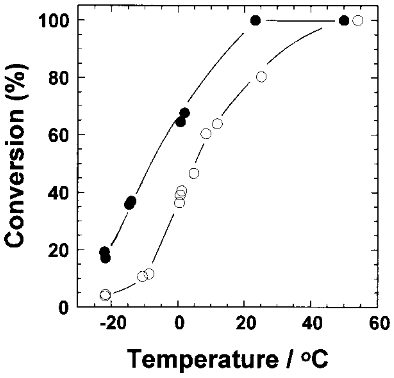


Fig. 8 Relationship between conversion ratio and reaction temperature for oxidation of CO by using the supported gold catalysts produced by two-stage calcination: ●, the first calcination at 500 °C for 1 h in vacuum and the second at 400 °C for 1 h in air; ○, the first calcination at 500 °C for 1 h in N_2 and the second at 400 °C for 1 h in air. Content of gold in each sample was 6.6 wt%.

References

1 J. van de Loosdrecht, A. M. van der Kraan, A. J. van Dillen and J. W. Geus, *Catal. Lett.*, 1996, **41**, 27.

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

3 S. D. Gardner, G. B. Hoflund, B. T. Upchurch, D. R. Schryer, E. J. Kielin and J. Schryer, *J. Catal.*, 1991, **129**, 114.

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

5 N. Funazaki, Y. Asano, S. Yamashita, T. Kobayashi and M. Haruta, *Proc. 4th Int. Meeting on Chemical Sensors, Tokyo, September 13–17, 1992*, Elsevier Sequoia, Lausanne, 1993, p. 536.

6 M. Haruta, T. Takase, T. Kobayashi and S. Tsubota, in *Catalytic Science and Technology*, Kodansha, Tokyo, 1991, vol. 1, p. 331.

7 Y. Takasu, X. G. Zhang, S. Minoura and Y. Murakami, *Appl. Surf. Sci.*, 1997, **121/122**, 596.

8 S. J. Tauster, S. C. Fung and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.

9 M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet and B. Delmon, *J. Catal.*, 1993, **144**, 175.

10 Y. Yuan, A. P. Kozlova, K. Asakura, H. Wan, K. Tsai and Y. Iwasawa, *J. Catal.*, 1997, **170**, 191.

11 T. Noguchi, K. Gotoh, Y. Yamaguchi and S. Deki, *J. Mater. Sci. Lett.*, 1991, **10**, 477.

12 K. Akamatsu and S. Deki, *J. Mater. Chem.*, 1997, **7**, 1773.

13 K. Sayo, S. Deki and S. Hayashi, *Int. J. Adhes. Adhes.*, in the press.

14 G. R. Bamwenda, S. Tsubota, T. Kobayashi and M. Haruta, *J. Photochem. Photobiol. A*, 1994, **77**, 59.

15 D. A. H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota and M. Haruta, *J. Catal.*, 1998, **177**, 1.

Paper 8/07931E