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A Kinetic and Adsorption Study of CO Oxidation over Unsupported Fine Gold Powder and over Gold Supported on Titanium Dioxide

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The catalytic oxidation of CO with O_2 and adsorption of CO_2 and O_2 on Au deposited on TiO_2 (Au/TiO_2, mean diameter of gold particles 3.5 nm), TiO_2, and unsupported Au powder (mean diameter 76 nm) have been investigated by using a closed recirculation reaction system. The catalytic oxidation of CO with O_2 on Au/TiO_2 measured at 253–293 K proceeded very rapidly. In the same temperature range, fine gold powder was catalytically active, while TiO_2 alone was entirely inactive for the oxidation. The rate constant of CO oxidation per unit of surface area of gold was larger by two orders of magnitude for Au/TiO_2 than for Au powder. Adsorption of CO and CO_2 occurred almost instantaneously and reversibly on preoxidized Au/TiO_2, whereas a slow increase in the O_2 pressure was observed at 273 K in the absence of evacuation. A similar increase of O_2 pressure was observed from oxidized TiO_2, but Au powder did not show any increase. The increase was ascribed to the desorption of weakly adsorbed O_2 on the support surface of Au/TiO_2. The rate of the reduction of preoxidized Au/TiO_2 with CO almost corresponded to the increase in the O_2 pressure and was far smaller than the rate of the catalytic oxidation of CO with O_2 on the catalyst, indicating that molecular oxygen weakly adsorbed on the support surface of Au/TiO_2 contributes only partly to the catalytic oxidation of CO. During the oxidation, O_2 in the gas phase may be directly activated on the surface of deposited gold particles and/or on the very narrow perimeter interface between the gold and the support.
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Key Words: **Au/TiO_2; Au powder; CO oxidation; adsorption.**

INTRODUCTION

Gold has long been regarded as being catalytically far less active than platinum group metals. However, when gold is 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 (1–4). For example, gold catalysts supported on Fe, Co, and Ni oxides are able to oxidize CO even at 195 K (1). This finding has evoked growing attention to the novel properties of supported gold catalysts and the reasons for the activity enhancement (5–19). The oxidation has been found to be a notable structure-sensitive reaction, i.e., the activity markedly depends upon the size and the shape of gold particles attached on the support (5–19).

A number of studies have been carried out to clarify the reasons for the remarkable enhancement through efforts to elucidate the reaction mechanism for the low temperature CO oxidation with O_2 on a gold catalyst supported on TiO_2 by using a flow type reaction system (5–7, 9, 10, 16, 17). However, the mechanisms proposed differ from one another, which may partly be due to the different methods of preparation as well as to the pretreatment conditions of Au/TiO_2 catalysts. Accordingly, the reasons for the enhancement have not yet been well understood until now. Recently, Goodman and his co-workers (19) have reported that there is a critical thickness of gold layers which gives a maximum in catalytic activity of gold nanoparticles deposited on the single crystal surfaces of TiO_2.

We have started a fundamental study in an attempt to obtain some insight into the mechanism of the enhancement for the low temperature oxidation of CO on supported gold catalyst (20). The catalyst examined was gold supported on titanium dioxide (hereafter it will be referred to as Au/TiO_2). Catalytic activity measurements were carried out by using a closed recirculation reaction system with a liquid nitrogen cooled trap, by which adsorption of CO_2 and O_2 on the catalyst was also investigated. Furthermore, ultrafine gold powder not supported on a TiO_2 carrier and TiO_2 powder not loading gold particles were examined for comparison (20).

METHODS

Preparation of Catalysts and Reactant Gases

A highly dispersed Au/TiO_2 catalyst was prepared by a deposition–precipitation method in an $HAuCl_4$ solution at

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pH 7, followed by washing, drying, and calcination in air at 673 K. The TiO_2 powder used was Japan reference catalyst JRC-TIO-4. The catalyst has a specific surface area of 45 m^2 g^{-1}, which was measured by the BET method using N_2 as adsorbate at liquid nitrogen temperature. Titanium dioxide powder with no gold loading was prepared by treating the JRC-TIO-4 in the same manner as that used for Au/TiO_2, except that HCl was used instead of $HAuCl_4$. Fine gold powder not supported on TiO_2 was manufactured by evaporating high purity gold metal (>99.99%) in inert gas (Vacuum Metallurgical Co., Ltd.).

Both CO and O_2 from commercial cylinders were fractionally distilled by using liquid-nitrogen-cooled traps for purification, while CO_2 was purified by repeating the sublimation and condensation cycles several times using a trap cooled by liquid nitrogen or a dry-ice ethanol mixture.

Adsorption and Catalytic Activity Measurements

A glass closed recirculation reaction system (base pressure 1.3×10^{-3} Pa, dead volume 187 cc) was used for both catalytic activity and adsorption measurements. Prior to the measurements, the catalyst in the reactor was oxidized with O_2 of 1 atm for 3 h at 523 K for Au/TiO_2 and TiO_2 and at 423 K for Au (hereafter we refer to this as "oxidizing pretreatment"). After cooling to room temperature, the catalyst was still aged under O_2 for a further 2 h at a fixed temperature, after which the line was evacuated for 30 min before the measurements were started.

For a catalytic activity measurement, a reaction mixture of CO and O_2 with the stoichiometric composition was introduced into the circulatory line and the CO_2 produced was collected in the trap cooled by liquid nitrogen. Gas circulation was provided by a glass electromagnetic pump with four nonreturn flaps at gas pressures above 1.3 kPa. The reaction rate was determined from the decrease of the pressure of the reaction mixture in the circulatory line of known volume. The pressure measurements were made by a mercury manometer with an accuracy of ±1.3 Pa. When the reaction was carried out under a gas pressure of about 1.3 Pa, the circulation pump was separated from the reaction system, because the diffusion velocity of gas was thought to be fast enough. In this case, the pressure change in the system was recorded every 1–5 min by using a McLeod gauge.

When the system was used for the adsorption measurements, one of the adsorbate gases such as CO_2 and O_2 was introduced into the circulation line. The amount of gas adsorbed was determined volumetrically.

RESULTS

Characterization of Au/TiO_2, TiO_2, and Fine Au Powders

X-ray diffraction patterns of Au/TiO_2 catalyst taken after calcination in air at 673 K showed the diffraction lines predominantly due to the anatase phase of TiO_2. The most intense peak was attributed to that derived from the (101) anatase crystal plane. Weak diffraction lines due to rutile phase could also be observed. Those assigned to metallic gold could not be observed, indicating that Au is highly dispersed on the support surface. In fact, the TEM photograph of Au/TiO_2 presented in Fig. 1a shows that gold particles are homogeneously dispersed on the support surface, with uniform hemispherical shape and with a mean diameter of 3.5 nm.

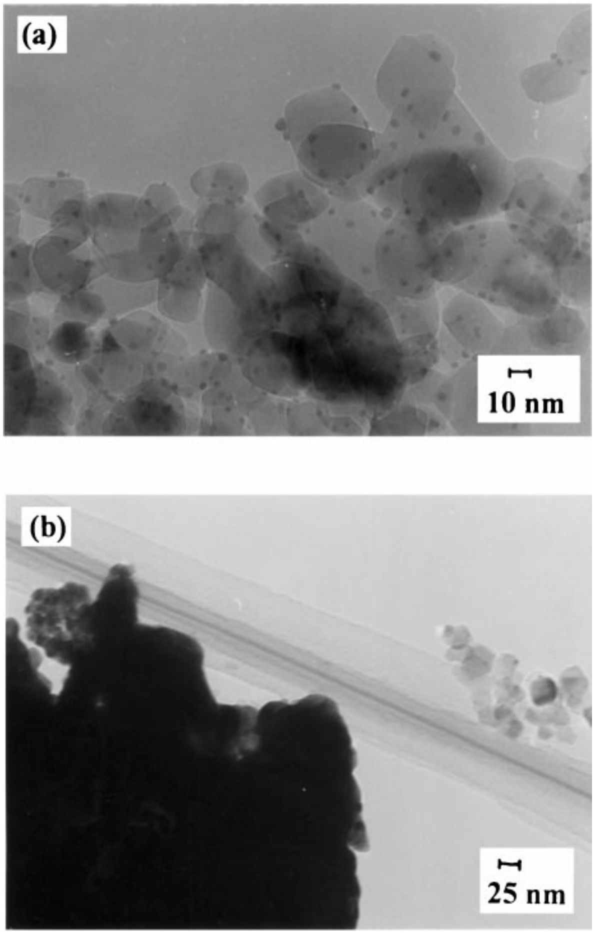

FIG. 1. The TEM photograph of (a) Au/TiO_2 (×400,000 magnification) taken after calcination at 673 K. Gold particles appear as small gray spots. (b) Au powder (×160,000 magnification) taken after a long period of use.

Assuming that such gold particles have a close-packed structure in the bulk as well as on the surface, the number of Au atoms contained in one deposited gold particle and that exposed on the surface could be calculated to be 660 and 270, respectively. In this case, nearly 40% of all Au atoms of the gold particle exist on the surface (20).

The gold loading of Au/TiO_2 was determined to be 3.3 wt% by X-ray fluorescence analysis. The number of Au particles deposited on the support was calculated to be

1.5×10^{17}/g-cat from the gold loading and the mean weight of a deposited gold particle (2.2×10^{-19} g). Furthermore, the mean distance between two adjacent gold particles and the coverage of TiO_2 surface by gold particles were calculated to be 17 nm and 3%, respectively. The number of Ti^{4+} ions exposed on the support surface, coverted to the volume of gas at STP, was calculated to be 10.3 ml(STP) g^{-1} on the assumption that TiO_2 preferentially exposes its (101) anatase crystal plane on the surface.

Figure 1b shows the TEM photograph of Au powder taken after a long period of use. Gold particles which appear in the right-hand side of the photograph have a sphere shape and diameters between 25 and 50 nm. However, a large part of the gold particles aggregate and seem to begin sintering, as observed in the left-hand side of Fig. 1b as the black shadow with a complicated form. In fact, the BET specific surface area of unsupported gold powder was determined to be 4.1 $m^2 g^{-1}$, and the mean particle diameter of gold powder calculated on the assumption of a spherical shape was 76 nm. It is worth mention that (1) the calculated mean particle size of unsupported gold powder is about 22 times larger than that of gold particles deposited in Au/TiO_2 in Fig. 1a and (2) 1.8% of all Au atoms contained in one unsupported gold particle exist on the surface.

The TiO_2 powder used as the reference had a BET surface area of 44 $m^2 g^{-1}$ and consisted mainly of anatase crystal form.

Catalytic Activity of Au/TiO_2

After the oxidizing pretreatment, Au/TiO_2 (51 mg) was kept at a definite temperature and evacuated for 30 min. Afterwards, a reaction mixture of CO and O_2 with the stoichiometric composition at an initial pressure of ca. 6.5 kPa was fed into the circulation line. The pressure decreased rapidly. Figure 2 shows the change of the percentage of the reaction mixture converted to CO_2 as a function of time. It can be seen that Au/TiO_2 is highly active even below room temperature. The activity does not appreciably depend upon the temperature. Noticeable deterioration in the activity was not observed during several repeated runs. In all runs, the amount of CO_2 produced and that calculated from the amount of the reaction mixture consumed agreed within the experimental error (±2%). One run was carried out at 273 K by using traps cooled by a dry-ice ethanol mixture. The product CO_2 in the reaction mixture was found to retard scarcely the rate of the oxidation at this temperature.

Kinetics of CO Oxidation over Au/TiO_2

To examine the effect of partial pressures of CO and O_2 on the reaction rate, a series of experiments were carried out using various reaction mixtures in which initial CO/O_2 ratios were varied between 4/1 and 1/1. Initial values of dP/dt were taken at various partial pressures of CO corresponding to constant O_2 partial pressure, or vice versa. In each experiment, the catalyst was confirmed to show a steady activity in the stoichiometric reaction mixture, then the reaction mixture having CO/O_2 ratios other than 2/1 was introduced into the system.

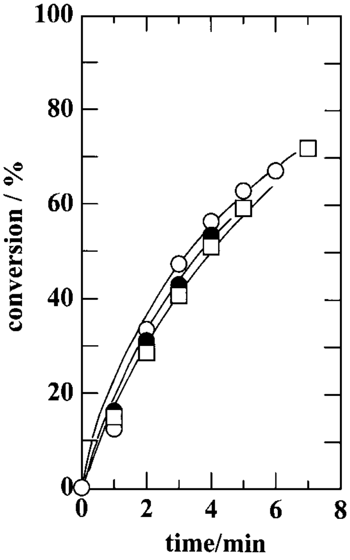

FIG. 2. The change of the percentage of the reaction mixture ($CO/O_2 = 2/1$) converted to CO_2 with time measured on Au/TiO_2 at: 293 K, ○; 273 K, ●; and 253 K, □.

The results are shown in Table 1. The rate of the oxidation is clearly independent of the O_2 pressure, suggesting that the adsorption of O_2 to active sites is fast during the catalysis. The rate is also independent of the CO pressure when the pressure of CO is higher than 1850 Pa. However, when the run was carried out at the CO pressure lower than 1850 Pa, the rate observed was small.

TABLE 1

Effect of Partial Pressures of CO and O_2 on the Rate of CO Oxidation on Au/TiO_2

No.	*T* (K)	Pressure (Pa) CO	Pressure (Pa) O_2	Rate (Pa min^{-1})
1	293	1940	970	290
2	293	3870	940	250
3	293	1860	930	255
4	293	2900	920	230
5	293	1850	930	260
6	293	900	960	110
7	273	1800	890	260
8	273	1850	6330	230
9	273	1760	880	250
10	273	1850	4060	240
11	273	1730	870	255
12	273	1800	1940	280

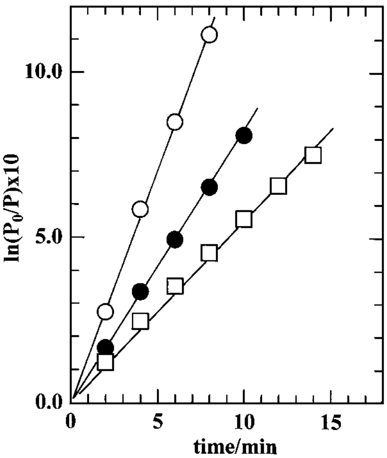

FIG. 3. The first-order plots of the pressure decrease of the reaction mixture ($CO/O_2 = 2/1$) with time measured on fine Au powder at: 294 K, ○; 273 K, ●; and 249 K, □.

Catalytic Oxidation of CO on Fine Au Powder and TiO_2 Powder

After the oxidizing pretreatment was conducted on Au powder (2.89 g), a stoichiometric reaction mixture of CO and O_2 at a initial pressure of ca. 6.5 kPa was introduced over the catalyst. Figure 3 shows the first-order plots of the pressure decrease of the reaction mixture with time measured at 249, 273, and 294 K. It is obvious that Au powder is active for the CO oxidation in the same temperature range in which Au/TiO_2 works as a highly active catalyst. On the other hand, TiO_2 powder (87 mg) which had undergone the oxidizing pretreatment was entirely inactive for CO oxidation at room temperature.

Adsorption of CO_2 on Au/TiO_2, Au, and TiO_2

Figure 4 shows the adsorption isotherms of CO_2 measured on Au/TiO_2, TiO_2, and Au at 273 K by circulating CO_2. The adsorption isotherm of CO_2 on Au/TiO_2 and that on TiO_2 almost overlap one another. Adsorption of CO_2 occurred instantaneously and reversibly both on Au/TiO_2 and on TiO_2. On the other hand, the amount of CO_2 adsorbed on Au powder was almost negligible.

The Langmuir isotherm plots of CO_2 adsorption on Au/TiO_2 and TiO_2 gave linear plots, indicating that CO_2 is chemically adsorbed on these catalysts as a monolayer at 273 K. The saturation volumes of CO_2 calculated from the slopes of Langmuir isotherm straight plots are summarized in Table 2 together with those of CO on these catalysts reported in the previous paper (20). Both the amounts of CO_2 adsorbed on Au/TiO_2 and those adsorbed on TiO_2 were almost twice as much as those of CO adsorbed on these two respective catalysts. The saturation volumes of CO_2 on Au/TiO_2 and TiO_2 almost corresponded to the amount of Ti^{4+} ions exposed on the surface of these two catalysts, i.e., 10.3 ml(STP) g^{-1}.

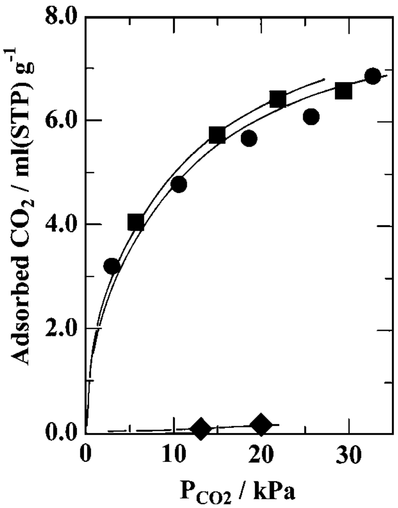

FIG. 4. Adsorption isotherms of CO_2 measured at 273 K in the closed recirculation system with a trap cooled with a dry-ice ethanol mixture for Au/TiO_2, ●; TiO_2, ■; and Au, ◆.

Desorption of O_2 from Au/TiO_2, TiO_2, and Au

After evacuating the preoxidized Au/TiO_2 at 273 K for 30 min, O_2 of ca. 6.5 kPa was introduced into the circulation line. However, the adsorption of O_2 could not be detected. Then, after evacuating the preoxidized Au/TiO_2 at 273 K for 30 min, the evacuation of the system was stopped. A slow increase in the O_2 pressure at a rate of approximately 0.13 Pa min^{-1} was observed. The pressure increase of O_2 with time is presented in Fig. 5. The pressure finally stabilized near at 50 Pa after about 15 h. On the other hand, the increase of O_2 pressure could not be observed from Au/TiO_2 evacuated for a prolonged period of time, for example, overnight.

A similar increase in the O_2 pressure was observed on TiO_2 powder which had equally undergone the oxidizing pretreatment and the subsequent evacuation at 273 K for 30 min. On the other hand, Au powder that had undergone the same oxidizing pretreatment and the subsequent evacuation did not show any increase in O_2 pressure at 273 K.

TABLE 2

The Saturation Volumes of CO and CO_2 on Au/TiO_2, TiO_2, and Au at 273 K per Unit Weight and per Unit Surface Area

	CO		CO_2	
Catalyst	ml(STP) g^{-1}	ml(STP) m^{-2}	ml(STP) g^{-1}	ml(STP) m^{-2}
Au/TiO_2	3.4	0.076	6.9	0.15
TiO_2	3.5	0.079	7.7	0.17
Au	0.25	0.061	—	—

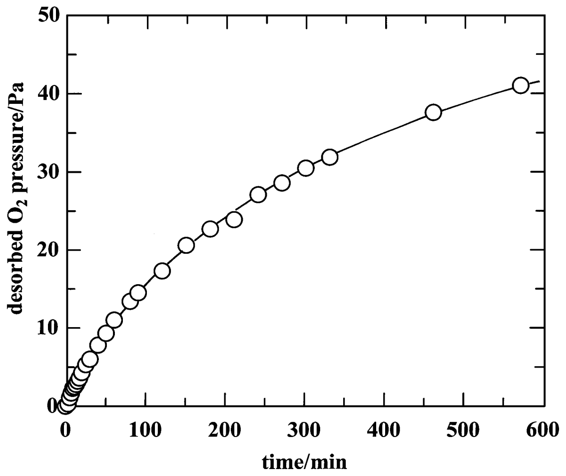

FIG. 5. The increase of the pressure of O_2 due to the desorption from the surface of oxidized Au/TiO_2 at 273 K. The measurement was started after the evacuation of the preoxidized catalyst was stopped at 273 K for 30 min.

Comparison of the Rate between the Reduction of Au/TiO_2 with CO and the Catalytic Oxidation of CO with O_2 on Au/TiO_2

The preoxidized Au/TiO_2 was evacuated for 30 min at 273 K. Then, the catalyst was exposed to CO at a pressure of ca. 16.7 Pa. The pressure of CO decreased slowly with time. The logarithmic plots of the CO pressure are shown in Fig. 6 as a function of time. The CO pressure at first decreased according to a linear line and then deviated at around 6 min, showing another slow rate of CO pressure decrease. After the reduction was continued for 29 min, the CO in the system was evacuated thoroughly. Then CO_2 produced and then condensed in the trap during the reduction was vaporized and determined volumetrically. The amount, i.e., 2.43 μmol, practically agreed with that of CO consumed in the reduction, i.e., 2.29 μmol.

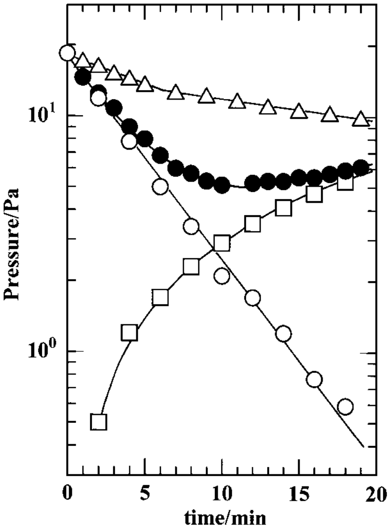

FIG. 6. Comparison of the rate of reduction of Au/TiO_2 with CO and that of the catalytic oxidation of CO with O_2 on Au/TiO_2 at 273 K: △, the change of the pressure of CO during the reduction of Au/TiO_2 with CO; ●, the change of the pressure in the system during the catalytic oxidation of CO with O_2; □, the estimated increase of the pressure of O_2 due to desorption; ○, the estimated decrease of the pressure of the reaction mixture ($CO/O_2 = 2/1$) due to catalytic oxidation.

After the preoxidized Au/TiO_2 was evacuated for 30 min at 273 K, the catalyst was exposed to a reaction mixture of CO and O_2 ($CO/O_2 = 2/1$) at an initial pressure of ca. 18.0 Pa in order to compare the rate of the catalytic oxidation with that of the reduction of Au/TiO_2 with CO in the same pressure range. The change of the pressure in the system during the oxidation is also presented in Fig. 6. The pressure at first decreased rapidly. However, the logarithmic plots of the pressure showed a minimum at near 13 min and then began to increase slowly. The oxidation was continued for 19 min, followed by evacuation. The amount of CO_2 produced and collected in the trap during the oxidation for 19 min, i.e., 2.98 μmol, agreed well with that calculated from the amount of the reaction mixture introduced at first into the reaction system, i.e., 2.96 μmol.

DISCUSSION

Catalytic Activity of Fine Gold Powder for the Oxidation of CO

Sault and Madix (21) reported that any dissociative adsorption of O_2 molecules does not occur on the clean Au (110) surface in the temperature range between 300 and 500 K up to the O_2 pressure of ca. 190 kPa. Outka and Madix (22) reported that the clean Au (110) surface does not adsorb CO above 125 K. Accordingly, the clean Au (110) surface should be inactive for the catalytic oxidation of CO with O_2 at least in the temperature range between 125 and 500 K, because neither CO nor O_2 adsorbs on the surface. In fact, Bollinger and Vannice (10) reported that ultrahigh purity Au powder does not show any measurable activity at temperatures up to 573 K.

In contrast to these results, as shown in Fig. 3, the present pure fine gold powder evidently exhibits catalytic activity for CO oxidation at temperatures between 249 and 294 K. There is no noticeable difference in the purity of Au powder used in Vannice's laboratory (99.994%) and that used in the present study (>99.99%) (10). However, Au powder obtained by his laboratory from Johnson Matthey had a calculated crystallite size of 10 μm based on its BET surface area of 0.025 $m^2\,g^{-1}$ (10). The size is ca. 130 times larger than that of the Au powder used in the present study.

It is likely that the catalytic activity of gold for CO oxidation observed in the present study is characteristic of gold powder with extremely small mean particle size, for example, 76 nm. Different from Au(110) single crystal, the present fine gold powder adsorbs some amount of CO at 273 K, as reported in the previous paper (20) (see Table 2). Dumas *et al.* (23) studied the adsorption of CO at low temperatures on evaporated films of gold by using infrared absorption spectroscopy and stated that gold films deposited at temperatures below 290 K contain chemically active sites at which CO chemisorbs, while films deposited at higher temperature do not show CO chemisorption. The film deposited at very low temperature could be so rough on an atomic scale that it contains a certain number of adsorption sites (23). The surface of the present fine gold particles presented in Fig. 1b might have much more coordinately unsaturated sites such as corners, edges, and steps than those of an Au(110) single crystal and large Au particles (10, 20, 21). Chemisorption of CO might occur at such sites and at defect sites at around room temperature. In fact, a linearly adsorbed CO species on gold has been observed on Au/TiO_2 at room temperature by infrared spectroscopy by Haruta *et al.* (3), Boccuzzi *et al.* (17, 24), and Bollinger *et al.* (10).

On the other hand, as reported previously (20), oxidized Au powder produced a considerable amount of CO_2 during CO adsorption performed at 273 K. The production of CO_2 indicates that (1) some surface Au atoms of the fine gold powder were oxidized by oxygen, probably during the oxidizing pretreatment performed at 423 K prior to the CO adsorption, and (2) at least a part of oxidized surface Au atoms are reducible with CO at 273 K. Again, different from the Au(110) single crystal (21, 22), the dissociative adsorption of O_2 should occur on the surface of the present fine gold particles at a temperature lower than 423 K. This means that the surface of the fine gold powder has much more affinity towards oxygen than that of the Au(110) single crystal (25). In fact, Ho (26) found that the oxidation of gold with O_2 began near 300 K by measuring the adsorption of O_2 (1.3×10^4 Pa) on unsupported microcrystalline gold (with a surface area ca. 3 $m^2\ g^{-1}$) gravimetrically. It may be worth mentioning here that Au powder which had not undergone the oxidizing pretreatment did show very little activity for the CO oxidation at room temperature.

Summarizing these results, the fine gold powder adsorbs CO at much higher temperatures and O_2 at much lower temperatures compared with the Au(110) single crystal (21, 22), which might result in the occurrence of the catalytic oxidation of CO with O_2 on fine Au powder as presented in Fig. 3.

Synergy Effect between Gold and the Support

The catalytic oxidation of CO with O_2 proceeds on Au powder (Fig. 3), but does not proceed at all on TiO_2 at 273 K. As reported in the previous paper (20), the amount of CO_2 produced during CO adsorption at 273 K per unit surface area of oxidized Au powder is 185 times larger than that produced on oxidized TiO_2 powder. Judiging from these two results, it is concluded that the gold surface is indispensable in the catalytic oxidation of CO with O_2 which occurs on Au/TiO_2 catalyst (Figs. 2 and 6). Hence, the rate constant of CO oxidation with O_2 per unit surface area of gold, i.e., k_{CO2}, was calculated for both Au/TiO_2 and Au powders. In this case, the surface area of gold particles dispersed on Au/TiO_2 powder was estimated from the mean surface area of one deposited hemispherical gold particle (1.9×10^{-17} m^2) and the mean number of gold particles per unit weight of the catalyst (1.5×10^{-17}).

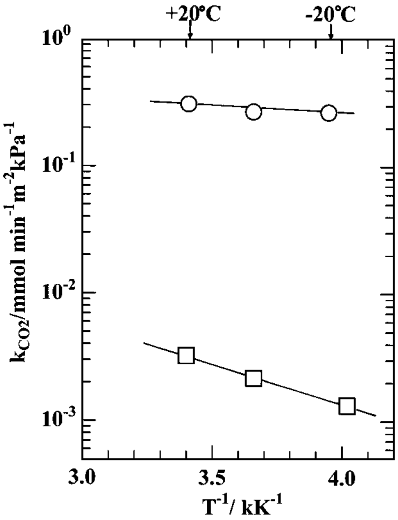

FIG. 7. The Arrhenius plots of the rate constants of CO oxidation with O_2 per unit surface area of gold, k_{CO2}, for Au/TiO_2 and Au powders: Au/TiO_2, ○; Au, □.

The Arrhenius plots of k_{CO2} are shown in Fig. 7. The values of k_{CO2} on Au/TiO_2 are larger than those on unsupported Au powder by about two orders of magnitude at temperatures between 253 and 293 K. It is clear that the TiO_2 support contributes to the remarkable enhancement of the catalytic activity per surface Au atom of deposited gold particles. Althogh other experiments must be done to elucidate definitely what enhances the activity of a supported gold catalyst, the possible cause for the enhancement is worth discussing here.

Physico-chemically, there are two distinct differences between supported and unsupported gold. The one is the particle size of gold and the other is the presence of the contact interface between gold and the support, as can be observed in Figs. 1a and 1b. Since the affinity of the gold surface towards CO and O_2 is assumed to increase with a decrease in particle size as discussed above, the fact that the mean particle size of gold deposited on Au/TiO_2 (3.5 nm) is ca. 1/20 times smaller than that of Au powder (76 nm) is important as a possible cause for the higher catalytic activity per surface Au atom in gold supported on TiO_2. The structure sensitivity of CO oxidation on gold clusters supported on TiO_2 was recently proposed by Valden and Goodman by using combined scanning tunneling microscopy/spectroscopy and elevated pressure reaction kinetics measurements (19, 29). The structure sensitivity is related to a quantum size effect with respect to the thickness of gold islands and a maximum in TOF of Au clusters for the oxidation occurs near 3.2 nm diameter (19, 29), which is very near the mean size of deposited gold particles in the present Au/TiO_2 catalyst, i.e., 3.5 nm (see Fig. 1a).

On the other hand, Fig. 1a also shows that almost all Au particles are attached to the surface of TiO_2 with hemisperical shape, suggesting that there exists a strong interaction between Au particles and the support. Tsubota *et al.* (8, 27) pointed out that the perimeter interface created by intimate contact between Au and TiO_2 is critical for the enhancement of the activity for CO oxidation. They prepared a mechanical mixture of TiO_2 powder and colloidal gold particles with spherical shape and with a mean diameter of 5.1 nm and then calcined it at different temperatures. The mixture calcined at temperatures up to 473 K was poorly active for CO oxidation. However, the activity appreciably increases with an increase in calcination temperature up to 873 K even though the gold particles grow larger (8, 27). The TEM photograph of the mixture of Au/TiO_2 calcined at 873 K shows that Au particles changed their shape from round to irregular facing and attached to the TiO_2 surface with a flat plane, suggesting the creation of strong interaction between Au and TiO_2 (8, 27). In this case, the specific crystalline orientation of TiO_2 powder, for example, the anatase(101) plane with the (111) plane of Au, may be important for the creation of the strong contact. Miyamoto *et al.* (28) reported that gold can be deposited on the (101) plane of anatase with epitaxial contact. In addition, Bollinger and Vannice reported that deposition of $TiOx$ overlayers onto an inactive Au powder with a crystallite size of 10 μm produced high activity for the CO oxidation. All of these findings strongly support the importance of perimeter interface between gold and TiO_2 as a possible cause for the enhancement of the supported gold catalysts, including the present one.

The apparent activation energy for the oxidation on Au/TiO_2 was calculated to be 2.1 kJ mol^{-1} (Fig. 7), which is very small compared with that reported by Haruta *et al.* (3) measured by using a flow-type reaction system, i.e., 34.4 kJ mol^{-1}. The reason for this discrepancy is not clear at the present stage; however, it is worth mentioning that Lin *et al.* (6, 7) measured the activity of Au/TiO_2 (HTR/C/LTR) for CO oxidation and reported that the data are not linear and the activation energy is around 38.6 kJ mol^{-1} at lower temperatures and drops down to 9.7 kJ mol^{-1} at above 350 K. The former value is near that of Haruta *et al.* (3), and the latter is rather close to the present value.

Adsorption of CO and CO_2 and Reaction Mechanism for CO Oxidation with O_2 on Au/TiO_2

The adsorption of CO on oxidized Au/TiO_2, Au, and TiO_2 was reported in the previous paper (20). Briefly, the adsorption equilibrium of CO was reached instantaneously on both Au/TiO_2 and TiO_2 at 273 K. The adsorption isotherms of CO on Au/TiO_2 and that on TiO_2 measured at 273 K almost overlapped one another. Almost 90% of adsorption proceeded reversibly on Au/TiO_2, while almost all did on TiO_2. On the other hand, the amount of CO adsorbed on Au is much small compared to the amounts adsorbed on Au/TiO_2 and TiO_2 (20). Judging from these results, a large part of the adsorption of CO on Au/TiO_2 would occur quickly on the support surface of Au/TiO_2 during the adsorption of CO.

On the other hand, the adsorption of CO on deposited gold particles on Au/TiO_2 during the catalytic oxidation is also considered to proceed rapidly, because the rate of oxidation does not depend upon the pressure of CO, as presented in Table 1. However, whether the adsorption of CO occurs directly on the surface of deposited gold or via the support surface is not clear.

The adsorption isotherm of CO_2 on Au/TiO_2 closely overlaps with that on TiO_2, as shown in Fig. 4. Adsorption of CO_2 proceeded reversibly on both Au/TiO_2 and TiO_2 at 273 K, and its equilibrium was also reached immediately after the introduction of CO_2. On the other hand, the amount of CO_2 adsorbed on Au powder is almost negligible. These results indicate that a large part of the adsorption of CO_2 occurs quickly on the support surface of Au/TiO_2 during the adsorption of CO_2.

On the other hand, the fact that the amount of CO_2 produced during the oxidation of CO on Au/TiO_2 agreed well with that calculated from the amount of the reaction mixture consumed indicates that the amounts of both CO and CO_2 which may be adsorbed on the surface of Au/TiO_2 during the oxidation are negligibly small. The presence of CO_2 in the gas phase does not affect the rate of CO oxidation on Au/TiO_2. Judging from these results, CO_2 produced on the surface of gold on Au/TiO_2 during the oxidation leaves the surface immediately and does not retard the oxidation.

Desorption of O_2 and Reaction Mechanism for CO Oxidation with O_2 on Au/TiO_2

In contrast to the adsorption of CO and CO_2 on Au/TiO_2, the adsorption of O_2 on Au/TiO_2 could not be detected. On the contrary, as shown in Fig. 5, the pressure of O_2 increased gradually and finally attained a plateau value at ca. 50 Pa. A similar increase of O_2 pressure was observed on the oxidized TiO_2, while oxidized Au powder did not show any increase of O_2 pressure. Accordingly, O_2 must come from the support surface of Au/TiO_2.

The fact that the increase of O_2 pressure could not be observed from Au/TiO_2 evacuated for a long period of time indicates that there exists a limited amount of O_2 which can desorb from the support surface of Au/TiO_2. Yanagisawa *et al.* studied thermal and photostimulated desorption of chemisorbed oxygen molecules from $^{18}O_2$

preadsorbed TiO_2 powder. They found $^{18}O_2$ thermal desorption peaks at 180 K (peak α) and attributed it to physisorbed O_2 molecules on the TiO_2 surface (30). Lu *et al.* (31) investigated the adsorption and photodesorption of molecular oxygen ($^{18}O_2$) on a $TiO_2(110)$ surface at 105 K and concluded that oxygen adsorbs on the $TiO_2(110)$ surface primarily in a molecular fashion at the oxygen vacancy sites to a saturation coverage of less than $\sim$0.12 monolayer ($\sim 2.5 \times 10^{14}$ O_2/cm^2).

Taking these results into consideration, we can conclud that O_2 must be present as a loosely bound molecular adsorbate on the support surface of Au/TiO_2 after the oxidizing pretreatment followed by evacuation at 273 K for 30 min, and the desorption of adsorbed O_2 occurred from the support surface of Au/TiO_2 at 273 K, as presented in Fig. 5.

Figure 5 also shows that the rate of increase of O_2 pressure, i.e., the rate of desorption of adsorbed O_2, decreased with increasing pressure of O_2 in the system, indicating that the desorption rate of O_2 depends upon the concentaration of adsorbed O_2 on the surface of Au/TiO_2. Then, assuming simply that the desorption rate of O_2 is proportional to the amount of adsorbed O_2 left behind on the support surface, we estimated from the initial rate of O_2 desorption and the one finally observed, as well as the amount of O_2 accumulated in the system by that time, the total amount of adsorbed O_2 which exists on the surface of Au/TiO_2 just after the oxidizing pretreatment followed by evacuation at 273 K for 30 min. The estimated amount was $\sim$2.42 ml(STP)/g-cat ($\sim 1.6 \times 10^{14}$ O_2/cm^2), which corresponds to ca. 30% of the total amount of exposed Ti^{4+} ions on the support surface and is near that reported by Lu *et al.* (31).

In the catalytic oxidation of CO under low pressure, the pressure in the system first decreases rapidly. Then the rate of the decrease diminishes with time and, after showing a minimum at near 13 min, the pressure begins to increase, as shown in Fig. 6. The good coincidence between the amount of CO_2 produced during the reaction and that calculated from the amount of the reaction mixture first introduced into the system indicates that the oxidation proceeded almost completely. In other words, the pressure of the reaction mixture in the system must have become negligibly small after 19 min. Judging from the results shown in Fig. 5, where the pressure of O_2 in the system increases gradually, we assume that the desorption of O_2 from the support surface of Au/TiO_2 would occur simultaneously with the oxidation and be responsible for the increase of the pressure in the system observed after 14 min. In this case, the minimum in the pressure should be reached through the dynamic balance between the decreasing rate of the pressure of the reaction mixture due to oxidation and the increasing rate of the oxygen pressure due to desorption. Hence, the rate of decrease of the reaction mixture as well as the rate of increase of oxygen pressure could be estimated.

Since the system was continuously evacuated before the reaction was started, the pressure of oxygen attributable to the desorption is negligible at the start of the oxidation. Thus, the specific rate of decrease of the reaction mixture can be obtained from the initial decrease of the pressure in the system (Fig. 6). Then, the rate of decrease of the reaction mixture at 13 min, where the pressure shows a minimum, was calculated from the specific rate and the initial pressure of the reaction mixture. This rate should be equal to the rate of increase of oxygen due to desorption. As the increase of the pressure of oxygen due to desorption is approximately proportional to time in a limited period of time (see Fig. 5), the time dependence of the pressure of oxygen could be calculated and plotted as presented in Fig. 6. The oxygen pressures thus estimated were then subtracted from the pressure in the system measured at intervals of 2 min. The results should express the change of the pressure of the reaction mixture with time and are plotted in Fig. 6. It can be seen that the plots lie well on a straight line. The amount of the reaction mixture remaining at 19 min was calculated to be smaller than 2% of that first dosed into the system. This result explains well the observed agreement between the amount of CO_2 produced and that calculated from the reaction mixture first introduced into the system and supports the calculated decrease of the pressure of the reaction mixture.

The rate of the catalytic oxidation thus obtained was then compared with that of the reduction of oxidized Au/TiO_2 by CO. The fact that the amount of CO_2 produced during the reduction agreed well with that of CO consumed indicates that CO reacts with some surface oxygen species adsorbed on Au/TiO_2 and CO_2 thus formed mostly leaves the catalyst surface. The first-order linear plots of the pressure of CO presented in Fig. 6 consist of two parts. The first part has a somewhat larger slope than the later part. However, the slope due to the reduction, i.e., the rate of reduction of Au/TiO_2 with CO, is far smaller than that of the decrease of the reaction mixture due to oxidation, i.e., the rate of catalytic oxidation. It is at most 30% of the rate of catalytic oxidation even in the initial part.

It is noticed in Fig. 6 that the pressure increase observed in the oxidation can not be observed during the reduction. The amount of CO consumed during the reduction continued for ca. 30 min (2.29 μmol) was found to approximately coincide with the calculated amount of oxygen (atoms) which can cause desorption (3.10 μmol) for 30 min (see Fig. 5), indicating that the decrease in the CO pressure is mainly caused by the reduction of O_2 which can desorb from the support surface. However, in this case, TiO_2 alone is entirely inactive for the CO oxidation at 273 K, and the reduction of preoxidized TiO_2 with CO at 273 K did hardly produce CO_2 (20). Therefore, O_2 molecules loosely bound on TiO_2 could not react with CO on the TiO_2 support surface. On the other hand, CO can readily react with O_2 on the surface of supported and unsupported gold at 273 K, as described above. Therefore, the production of CO_2 during the reduction of Au/TiO_2 by CO should occur on the surface of deposited gold and/or the perimeter interface between gold and TiO_2. This means that molecular O_2 loosely bound on TiO_2 must move to the gold surface via the gas phase and/or the migration on the support surface to cause the reaction with CO. However, the reduction rate is far smaller than the rate of catalytic oxidation of CO in the presence of O_2 in the gas phase, as shown in Fig. 6. The large difference suggests that during CO oxidation over Au/TiO_2, O_2 in the gas phase should be activated directly on the surface of deposited gold and/or its perimeter interface without landing on the surface of TiO_2 and may enhance the adsorption of CO (17).

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