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A kinetic study on the low temperature oxidation of CO over Ag-contaminated Au fine powder

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ABSTRACT

The mechanism of CO oxidation with O_2 on Ag-contaminated Au fine powder (Ag/Au) was studied by kinetic measurements combined with the determination of the amount of CO_2 produced. The kinetic behavior of "Ag/Au having the steady state surfaces" indicated that the oxidation proceeds through co-adsorption of CO and O_2 to form (CO3)* succeeded by its decomposition enhanced by the interaction with CO and O_2 to produce CO_2 at the contact interface between surface silver and gold support. The kinetics measurements performed on "Ag/Au having the oxidized surfaces" indicated that only the reduction of reactive adsorbed oxygen with CO in the reaction mixture to produce CO_2 proceeds at first without incorporation of O_2 in the gas phase and that the participation of O_2 in the CO_2 production process as well as its incorporation into the catalyst surface starts gradually as the reduction of reactive adsorbed oxygen on Ag proceeds.

1. Introduction

It was reported in 1987 for the first time that gold nanoparticles highly dispersed on 3d metal oxides such as TiO_2, Fe_2O_3, and Co_3O_4 exhibited unexpectedly high catalytic activity for the oxidation of CO in the temperature range far below ambient temperature by Haruta et al. [1,2]. Since then continuously growing interests have been paid to the catalysis of gold from both practical and fundamental points of view [3,4]. In order to elucidate the mechanism for the genesis of unique catalysis of gold, the oxidation of CO with O_2 has most frequently been investigated because of its simplicity that it accompanies no side reaction and practical significance in applications to purification of air and H_2. Among several hypotheses proposed to explain the enormously high activity of supported gold catalysts, particle size effect and contact interface effect have long been discussed and investigated extensively [5]. However, so far as we investigate CO oxidation which proceeds on supported gold catalysts with high metal dispersion, it is difficult to discuss each of the two effects separately [6].

Recent studies on the interaction of gold clusters produced by laser ablation with a mixture of CO and O_2 have brought fundamental information about the genesis of gold catalysis [7–10]. Xu and Jiang have studied the reaction between laser-ablated Au atoms and mixture of CO and O_2 in solid Ar by using IR and reported that carbonyl metal oxides such as $OCAuO_2CO$, OAuCO and OOAuCO were confirmed to be produced, and that CO_2 was eliminated from $OCAuO_2CO$ and OOAuCO upon UV radiation [7]. The structure of $OCAuO_2CO$ optimized from DFT calculation is very similar to that early proposed by Huber et al. [7,11]. Wallace and Whetten have studied the co-adsorption of CO and O_2 on mass-selected anionic gold clusters by using pulsed-helium flow-reactor techniques and reported that CO and O_2 are not competing for bonding sites, but aid in the adsorption of one another and that the gas phase Au_6 anion (Au_6^-) is highly active for the oxidation of CO with O_2 [8].

In contrast to studies using gold clusters having no contact interface [7–11], Wang et al. reported recently that Au–Ag alloy catalyst supported on mesoporous aluminosilicate is highly active for the low temperature CO oxidation [12–14]. Since the Ag–Au bimetallic particles have a big size of ca. 30 nm and are supported on traditional inert support, they claimed that the size effect was no longer a critical factor but a synergistic effect between Ag and Au was more important. They indicated that silver plays a key role in oxygen activation and the Au site adsorbs CO [12–14]. Zielasek et al. demonstrated nanoporous gold with a sponge-like morphology, formed through the selective leaching of silver from a gold

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silver alloy, exhibits an unexpectedly high activity for CO oxidation at ambient pressures and temperatures down to 253 K [15,16]. The gold sponge consists of interconnecting ligaments with diameters of the order of tens of nanometers and contains 0.7% silver in the bulk and 4.4% silver at the surface [15]. Residual Ag on the surface of gold sponge was reported to be probably responsible for the high catalytic activity for CO oxidation [16].

We reported previously that XPS analysis of the Au fine powder with a mean particle size larger than 80 nm synthesized by evaporating high purity gold metal (>99.99%) in an inert gas detected Ag and that the activity of the powder for CO oxidation measured on several samples containing various amounts of surface Ag showed a strong correlation with the surface concentration of Ag [6]. We concluded from this result that the activity of the Au powder is due to the existence of Ag in the surface layer. The very faint activity detected on one sample of Au fine powder on which the concentration of Ag had been below the detection level by XPS, was also ascribed to the existence of Ag, because the results of ICP bulk analysis of the sample clearly indicated that slight amount of Ag still remained [6]. We concluded furthermore that the activity of Au powder ascribed to proper gold surface must be negligibly small, in other words, the activity of the Au fine powder attributable to so-called “particle size effect” is not recognized for unsupported “pure” Au powder and that the activity observed on the samples of Ag contaminated Au fine powder can be ascribed only to so-called “contact interface effect” due to Ag which is probably partly oxidized and inversely supported on the surface of the Au powder [6].

In order to investigate kinetics and mechanism of the oxidation ascribed to “contact interface effect” alone, the Au fine powder having known surface and bulk contents of Ag was used in the present study of CO oxidation. Since a strong relationship between the catalytic activity and the surface Ag concentration of the powders indicated that the oxidation proceeds on Ag surface and/or the interface between Ag and the Au support, a reaction mixture having a pressure corresponding to the half of the amount of surface Ag was introduced into the reaction system to measure the rate of catalytic oxidation. The rate of catalytic oxidation of CO with O_2 over the fine Au powder was then compared with that of reduction of the Au fine powder with CO and that of the oxidation with O_2 to elucidate the mechanism of the catalysis.

2. Experimental and methods

The Au fine powder which contains 0.110 wt% Ag in the bulk and 10.8 at% Ag on the surface, which was denoted “Au-b” in the previous paper, was used in the present work [6]. We refer the Au fine powder as “Ag/Au” hereafter. Table 1 summarizes the physicochemical properties of Ag/Au. The amount of Ag inversely supported per unit weight of Ag/Au, i.e., 4.72 μmol, was simply calculated from BET specific surface area and XPS surface atomic concentration of Ag assuming that Ag covers the surface of Ag/Au with a monolayer thickness. The surface area of Ag on “Ag/Au” was also calculated to be 0.204 m^2/g based on the same assumption. The saturation volume of CO adsorbed per unit weight of Ag/Au determined from the adsorption isotherm measurement at 273 K was almost half of the amount of surface Ag. Unsupported Ag powder manufactured by evaporating high purity Ag metal in inert gas and has a BET specific surface area of 1.03 m^2/g (Vacuum Metallurgical Co., Ltd.), was also used for comparison.

Table 1
Physico-chemical properties of Ag/Au.

BET specific surface area	1.89 $m^2\ g^{-1}$
Mean particle size[a]	166 nm
ICP bulk Ag content	0.110 wt%
XPS surface Ag content	10.8 at%
Amount of Ag contained per unit weight	10.2 μmol
Amount of surface Ag per unit weight[b]	4.72 μmol (=105 μl (STP))
Saturated amount of CO adsorbed per unit weight at 273 K	55 μl (STP)/g

[a] Calculated from BET specific surface area on the assumption that all particles of Au powder (Ag/Au) are non-porous and have uniform sphere shape.

[b] The amount of 4.72 μmol corresponds to 105 μl (STP) when converted to the volume of ideal gas.

Both CO and O_2 from commercial cylinders were purified by fractional distillation by using liquid nitrogen traps. A glass-made recirculation reaction system (base pressure 1.3×10^{-3} Pa) was the same as described previously and was used both for the pretreatments as well as for the catalytic activity measurements [17,18]. The weight of Ag/Au loaded in the reactor was 1.89 g, which contained 8.92 μmol of Ag on the surfaces. In order to prevent the Au powder from the contamination by mercury and grease vapor, the circulation loop was equipped with greaseless stop cocks and a trap connecting the circulation loop with a vacuum line was always cooled by liquid nitrogen. Since Ag/Au had exhibited the highest activity after oxidizing pretreatment at 423–453 K [6], Ag/Au in the reactor was pretreated in circulating oxygen of 1 atm at 423 K for 1 h prior to the activity measurements. After cooling the catalyst to room temperature still in O_2, the line was evacuated to a pressure around 1.3×10^{-3} Pa, and then the catalyst was heated to the reaction temperature (313 K). Subsequently, a reaction mixture of CO and O_2 with a stoichiometric composition of $CO/O_2 = 2/1$ at an initial pressure of ca. 6.5 kPa was introduced into the circulation line. Gas circulation was provided by a glass electromagnetic pump with 4 non-return flaps and CO_2 produced was condensed in the trap cooled by liquid nitrogen, so that reaction rate was derived from the decrease in total pressure. After finishing the reaction rate measurements typically for 60 min, the reaction mixture unreacted was removed thoroughly from the circulatory line. The amount of the reaction mixture consumed during the reaction was calculated from the pressure decrease. After that CO_2 collected in the trap during the reaction was evaporated at 195 K to determine the amount volumetrically.

Rate measurements under a pressure lower than 13 Pa were also performed by changing the reaction system from a circulatory one to a static one in order to investigate the catalytic behavior of Ag/Au for CO oxidation with O_2. The pressure change accompanied by the catalytic oxidation was followed by using a McLeod gauge. The rate of the catalytic oxidation of CO with O_2 carried out under such a low pressure range was then compared with that of the reduction of Ag/Au with CO and with that of the oxidation of Ag/Au with O_2, both of which were performed at similar low pressure range.

Prior to rate measurements under such a low pressure range, the catalyst was subjected to the following two kinds of pretreatments:

(1) Ag/Au was pretreated with a stoichiometric reaction mixture of CO and O_2 at an initial pressure of 5.3 kPa at 313 K for 1 h and then evacuated to around 1.3×10^{-3} Pa: hereafter denoted as “Ag/Au having the steady state surfaces”.
(2) “Ag/Au having the steady state surfaces” was oxidized in circulating O_2 of 13.3 kPa at 393 K for 2 h and then cooled to room temperature and subsequently evacuated to around 1.3×10^{-3} Pa at 313 K: hereafter denoted as “Ag/Au having the oxidized surfaces.”

3. Results

After the oxidizing pretreatment of Ag/Au in O_2 of 0.1 MPa at 423 K for 60 min, a stoichiometric mixture of CO and O_2 was introduced into the reactor. Fig. 1 shows the first-order plots of

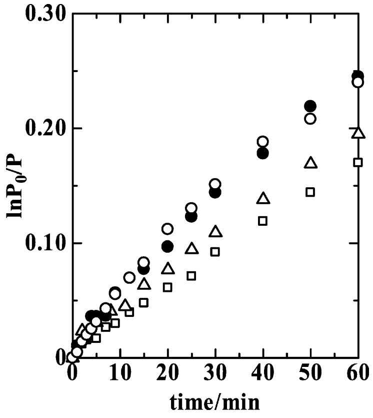

Fig. 1. The first-order plots of the pressure of CO and O_2 mixture measured on Ag/Au at (○) 311 K, (●) 299 K, (△) 275 K, (□) 253 K.

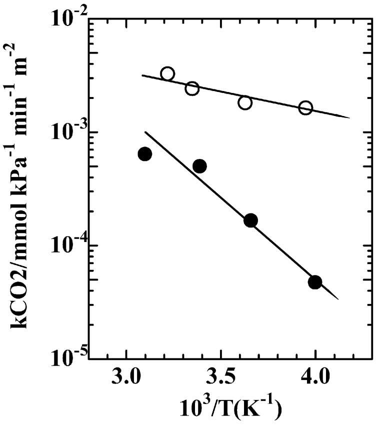

Fig. 2. Arrhenius plots of k_{CO_2} per unit area of Ag surface measured on (○) Ag/Au, (●) unsupported Ag powder.

the reactant pressure measured at 253, 275, 299 and 311 K. The amounts of CO_2 produced at 253, 275, 299, and 311 K were calculated to be 13, 16, 19 and 32 times as large as the number of surface Ag atoms, respectively. All of these amounts of CO_2 agreed well with 2/3 of the amounts of the reactant mixture consumed at each temperature, indicating that the oxidation proceeds catalytically. The first-order plots observed at 253 K and at 275 K showed good linearity, whereas the plots at 299 K and at 311 K deviated downward from the initial linear line with time, suggesting a gradual decrease in activity.

The rate constants for the catalytic oxidation of CO at each temperature were then calculated from the initial slope of the linear plots in Fig. 1. Since the oxidation can be assumed to proceed on Ag surface including the interface between Ag and the Au support [6], the rate constants of oxidation per unit surface area of Ag, i.e., k_{CO_2}, was calculated. Fig. 2 presents Arrhenius plots of k_{CO_2} measured on Ag/Au and those on unsupported Ag powder measured for comparison. The values of k_{CO_2} of Ag/Au are 30 times as high as those of unsupported Ag powder at 253 K and 4 times at room temperature. The apparent activation energies were 7 kJ/mol for Ag/Au, and 28 kJ/mol for unsupported Ag powder, respectively. The large difference in Ea indicates that the mechanism of the oxidation observed on Ag/Au differs from that on unsupported Ag powder owing to the contribution from Au support.

3.1. *The relation between the catalytic activity of Ag/Au and the amount of CO_2 desorbed assisted by O_2 treatment*

The gradual loss in the catalytic activity of Ag/Au with time is the most appreciable at 313 K in Fig. 1. However, the initial activity of Ag/Au as well as the time–course curve was well reproduced by treating Ag/Au in circulating O_2 of 13 kPa at 393 K for 1 h.

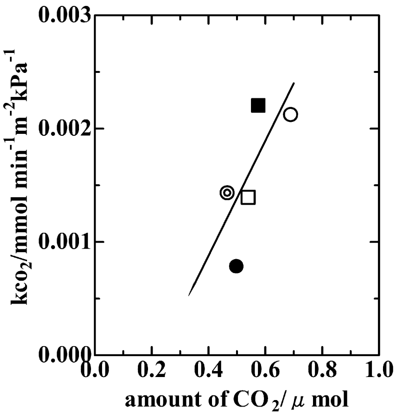

Fig. 3. The rate of CO oxidation over Ag/Au at 313 K measured just before starting the evacuation as a function of the amount of CO_2 desorbed during the treatment in circulating O_2 of 13 kPa at 393 K for 2 h. The initial pressures of the reaction mixture and the duration of the catalysis were (○) 5.3 kPa, 30 min; (◎) 5.3 kPa, 60 min; (●) 5.3 kPa, 120 min; (□) 2.7 kPa, 60 min; (■) 2.0 kPa, 60 min.

Accumulation of carbonate species on active sites has been proposed as a possible cause for deactivation during CO oxidation on Au/TiO_2 [19–22], Au/SiO_2 [20], Au/Al_2O_3 [20,23,24], Au/ZrO_2 [25], Au/MgO [26], Au/Y and Au/Fe/Y [27], and Au/Fe_2O_3 and Au/CeO_2 [22].

Therefore, the following experiments were performed to examine the relation between the catalyst deactivation and the formation of carbonate species. The CO oxidation experiments on Ag/Au were carried out at 313 K for 30, 60 and 120 min by introducing a stoichiometric reaction mixture at different initial pressures between 2.0 and 5.3 kPa, and then the reaction line was evacuated for 30 min at the same temperature to remove CO_2 physisorbed on Ag/Au. In each run, the rate of CO oxidation just before starting the evacuation was measured to evaluate the extent of deactivation. After CO_2 collected in a liquid N_2 trap during the catalytic oxidation was evaporated and removed thoroughly, Ag/Au was treated in circulating O_2 of 13 kPa at 393 K for 2 h with a trap again cooled by liquid N_2 in order to collect CO_2 produced by the decomposition of carbonate species accumulated on the catalyst surface.

Fig. 3 shows the rate of CO oxidation measured just before starting the evacuation as a function of the amount of CO_2 collected during the treatment in O_2 at 393 K. As opposed to our presumption, the rates were almost proportional to the amounts of CO_2 desorbed during the oxidizing treatment. The amounts of CO_2 were lower than 10% of the number of surface Ag atoms, i.e., 8.92 μmol.

3.2. *Kinetic measurements performed on "Ag/Au having the steady state surfaces"*

The reaction mixture at an initial pressure of 5.3 kPa was circulated over Ag/Au at 313 K for 60 min to establish the steady state surfaces and then evacuated thoroughly. After that, the reaction mixture at an initial pressure of 13 Pa was exposed at the same temperature for 60 min. Fig. 4 shows that the first-order plots of the pressure decrease observed in the two catalytic experiments performed at largely different pressures overlap with one another, indicating that the oxidation is first order with respect to the total pressure and the mechanism of the oxidation is independent of the pressure of the reaction mixture.

After again establishing the steady state surfaces, Ag/Au was exposed to CO and/or O_2 with an initial pressure of 11 Pa. In Fig. 4, the first-order plots of the pressure decrease observed during the

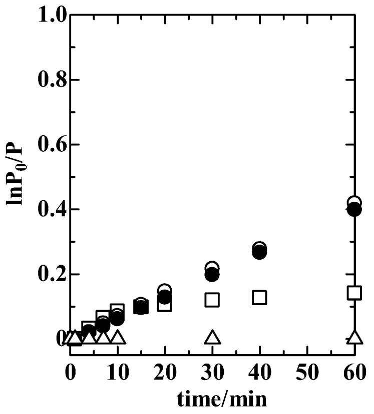

Fig. 4. The first-order plots of the pressure decrease observed at 313 K during (●) the catalytic oxidation of CO on Ag/Au performed to establish the steady state surfaces by using a stoichiometric reaction mixture ($CO/O_2 = 2/1$) under an initial pressure of 5.3 kPa, (○) the catalytic oxidation of CO performed on "Ag/Au on the steady state surfaces" by using the stoichiometric reaction mixture under an initial pressure of 11 Pa, (□) the reduction of "Ag/Au with the steady state surfaces" with CO under an initial pressure of 11 Pa, and (△) the oxidation of "Ag/Au with the steady state surfaces" with O_2 under an initial pressure of 11 Pa.

Table 2
The amount of CO or O_2 consumed and that of CO_2 produced during the exposure of "Ag/Au having the steady state surfaces" to CO or O_2 of 11 Pa at 313 K for 60 min.

Run	Amount of gas measured/10^{-6} mol	
Exposure to CO of an initial pressure of 11 Pa	CO consumed for 60 min	0.54
	(CO consumed during a period of initial 20 min)	(0.41)
	CO_2 produced after 60 min	0.79
Exposure to O_2 of an initial pressure of 11 Pa	O_2 consumed after 60 min	0.0
	CO_2 produced after 60 min	0.21

exposure to CO and/or O_2 are also compared with that observed during the catalytic CO oxidation with O_2. With respect to CO, the first-order plots overlap well with that observed during the catalytic oxidation for a period of initial 20 min. However, the pressure decrease of CO almost ceased after the break at 20 min. On the other hand, with respect to O_2, the pressure of O_2 did not decrease at all during the exposure for 60 min.

Table 2 summarizes the amount of CO consumed and that of CO_2 produced during the exposure of "Ag/Au having the steady state surfaces" to CO and/or O_2. The amount of CO consumed during a period of initial 20 min was 0.41 μmol and was found to correspond to 4.6% of surface Ag, suggesting that only a small part of surface Ag inversely supported on Ag/Au powder participates in the catalytic oxidation of CO with O_2. The total amount of CO consumed after the exposure for 60 min was 0.54 μmol, whereas the amount of CO_2 produced after finishing the exposure was found to be 0.79 μmol, which is larger by 46% compared to that of CO consumed from the gas phase. In spite of no consumption of O_2 during the exposure, 0.21 μmol of CO_2 was produced after finishing the exposure.

3.3. Kinetic measurements performed on "Ag/Au having the oxidized surfaces"

Fig. 5 shows time dependences of the pressure of O_2, CO, and a stoichiometric reaction mixture which were exposed to "Ag/Au having the oxidized surfaces" at 313 K for 60 min. All three gases had an initial pressure of 12 Pa. A slow increase in O_2 pressure was observed during the exposure. This can be ascribed to the desorption of O_2 which had been adsorbed on Ag/Au during oxidizing pretreatment performed in circulating O_2 of 13 kPa for 2 h at 393 K. On the other hand, the pressure of both CO and a reaction mixture at first decreased rapidly, and then turned to a slow increase after about 20 min.

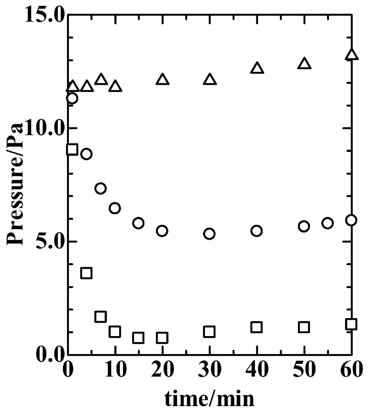

Fig. 5. The time dependencies of the pressure of (△) O_2, (□) CO, and (○) a stoichiometric reaction mixture of CO and O_2 exposed to "Ag/Au having the oxidized surfaces" at 313 K for 60 min. All the three gases exposed had an initial pressure of 12 Pa.

Table 3
The amount of CO exposed and that of CO_2 produced in the experiments where CO or a reaction mixture were exposed to "Ag/Au having the oxidized surfaces" at 313 K for 60 min.

Run	Amount of gas measured/10^{-6} mol	
Exposure to CO at an initial pressure of 12 Pa	CO exposed	3.7
	CO_2 produced	3.6
Exposure to a reaction mixture at an initial pressure of 12 Pa	CO contained in the reaction mixture	2.5
	CO_2 produced	2.6

Table 3 summarizes the amount of CO exposed and that of CO_2 produced in the experiments where "Ag/Au having the oxidized surfaces" was exposed to CO or a reaction mixture at 313 K for 60 min. In both the experiments, the amount of CO_2 produced agreed well with that of CO exposed and that of CO contained in the reaction mixture, indicating that CO admitted into gas phase was totally converted into CO_2 within 20 min by the contact with "Ag/Au having the oxidized surfaces" irrespective of the coexistence of O_2. It can be assumed from these results that there exists reactive adsorbed oxygen species on the surface of "Ag/Au having the oxidized surfaces." According to this assumption, the agreement between the amount of CO exposed and that of CO_2 produced means that the amount of reactive oxygen species exceeds that of CO exposed, i.e., 3.7 μmol. The slow increase of the pressure observed after 20 min in the CO exposure experiment in Fig. 5 may be due to the desorption of reactive adsorbed O_2 still remained on Ag/Au after CO exposure. Fig. 5 shows that the pressure of the reaction mixture did not decrease below 5 Pa, which is near 1/3 of the initial pressure. Taking into consideration of the agreement between the amount of CO contained in the reaction mixture exposed and that of CO_2 produced, incorporation of O_2 into the catalyst surface would not occur during the exposure to the reaction mixture. In other words, the catalytic oxidation of CO with O_2 did not occur on the oxidized surfaces of Ag/Au.

In order to determine the amount of reactive adsorbed oxygen species, CO of 17 Pa, which corresponds to 67% of the total amount of surface Ag, was exposed to "Ag/Au having the oxidized surfaces" at 313 K for 60 min. The decrease of the CO pressure is plotted against time in Fig. 6. The pressure decreased rapidly in the initial period of 7 min and then it gradually decreased after 10 min. The first-order plots of the CO pressure against time showed a break at around 7–10 min. However, in contrast with the case where CO of 12 Pa was exposed to "Ag/Au having the oxidized surfaces" as

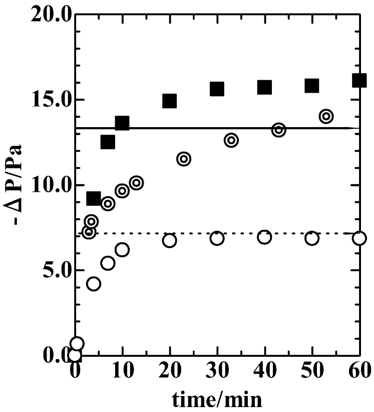

Fig. 6. The time dependencies of the pressure decrease of (■) CO exposed to "Ag/Au having the oxidized surfaces" at 313 K. An initial pressure of 17 Pa CO corresponds to 67% of the total number of surface Ag atoms. The time dependencies of the pressure decrease of (○) a reaction mixture of CO and O_2 exposed to "Ag/Au having the oxidized surfaces" at 313 K at first run and (◎) a stoichiometric reaction mixture of CO and O_2 exposed at second run. The reaction mixtures were introduced successively.

Table 4
The amounts of CO and CO_2 measured in the experiments where 17 Pa of CO was introduced to "Ag/Au having the oxidized surfaces" at 313 K for 60 min. The initial pressure of CO corresponds to 67% of the total number of surface Ag atoms.

	Amount of gas measured/10^{-6} mol
CO introduced	5.7
CO consumed	5.4
CO_2 produced	5.5

presented in Fig. 5, the pressure of CO continued to decrease even at 60 min.

Table 4 summarizes the amount of CO introduced, that of CO consumed as well as that of CO_2 produced for 60 min. The amount of CO consumed agreed well with that of CO_2 produced. The moles of CO_2 produced correspond to 62% of the total number of surface Ag atoms. The horizontal solid line drawn in Fig. 6 shows the decrease of gas pressure corresponding to one half of the total number of surface Ag atoms. The initial rapid decrease in CO pressure can be attributed to reduction of reactive oxygen species and it ceased when the pressure change reached to the amount corresponding to one half of the amount of surface Ag atoms. Judging from this fact, it can be assumed furthermore that oxygen species adsorbed on "surface Ag" represent the reactive oxygen species on the surface of "Ag/Au having the oxidized surfaces."

Fig. 6 also shows the pressure decrease with time observed in the experiment where a reaction mixture with an initial pressure of 11 Pa was successively introduced twice to "Ag/Au having the oxidized surfaces" at 313 K for 60 min. Table 5 summarizes the amount of the reaction mixture introduced, that of CO contained in the reaction mixture, that of the reaction mixture consumed and that of CO_2 produced. In the first exposure, the pressure of the reaction mixture decreased rapidly during the initial period for 10 min, as presented in Fig. 6. However, the decrease ceased at around 30 min. The amount of CO_2 produced during the first exposure was somewhat larger than that of CO initially contained in the reaction mixture supplied and that of the reaction mixture consumed. If the consumption of the reaction mixture during the first exposure was only due to the catalytic CO oxidation with O_2, the amount of CO_2 produced should be 1.49 µmol, i.e., 2/3 of the reaction mixture consumed. In addition, the amount of gas remained after exposure, i.e., 1.38 µmol was comparable to that of O_2 contained in the reaction mixture admitted, i.e., 1.19 µmol. All these results indicate that only the reduction of reactive adsorbed oxygen on "Ag/Au having the oxidized surfaces" with CO in the reaction mixture occurred during the first exposure without incorporation of O_2 in the gas phase into the surfaces of Ag/Au. In other words, almost half of the amount of reactive adsorbed oxygen on "Ag/Au having the oxidized surfaces" was removed in the first exposure. The horizontal dotted line drawn in Fig. 6 shows the extent of reduction estimated from the amount of CO admitted in the first exposure.

Table 5
The amounts of gas measured in the experiments where a reaction mixture was successively introduced twice to "Ag/Au having the oxidized surfaces" at 313 K for 60 min.

	Amount of gas measured/10^{-6} mol	
	First run	Second run
The stoichiometric reaction mixture introduced	3.61	3.57
CO contained in the reaction mixture	2.41	2.38
The reaction mixture consumed	2.23	2.44
CO_2 produced	2.56	2.19

The plots showing the pressure decrease recorded in the second exposure were shifted upward by the amount of CO admitted in the first exposure in order to examine at what extent of the reduction of the Ag/Au surfaces, the catalysis of CO oxidation with O_2 starts. In the second exposure, the pressure of the reaction mixture decreased more slowly compared to the first exposure, and ceased to decrease after 60 min. Table 5 shows that the amount of the pressure decrease in the second exposure again almost coincided with the amount of CO in the reaction mixture supplied. The amount of CO_2 produced in the second exposure, i.e., 2.19 µmol was much larger than 2/3 of the reaction mixture consumed, i.e., 1.63 µmol. These results again indicate that a large part of CO_2 production in the second exposure was still due to the reduction of reactive oxygen species adsorbed on the Ag/Au surfaces. However, the amount of CO_2 produced was somehow smaller than the amount of CO in the reaction mixture and the amount of reaction mixture consumed different from the case in the first exposure. This fact indicates that O_2 in the gas phase started to be incorporated in the second exposure.

Although a large part of CO_2 production in the second exposure can still be attributed to the reduction of reactive oxygen species with CO in the reaction mixture, Fig. 6 shows that the rate of the pressure decrease was much smaller than that observed in the reduction with pure CO when compared at the same extent of the reduction of the Ag/Au surfaces.

This tendency became conspicuous, as the reduction proceeded. Since O_2 is contained in the reaction mixture different from pure CO and that the incorporation of O_2 into the surface of Ag/Au is indicated to start in the second exposure, O_2 molecule from the gas phase should begin to take part in the CO_2 production process because the reactive oxygen species are mostly consumed by the reaction with CO at the Ag/Au surfaces.

4. Discussion

4.1. Mechanism of catalytic CO oxidation with O_2 on "Ag/Au"

Fig. 2 shows that the apparent activation energy for CO oxidation on Ag/Au is much smaller than that on unsupported Ag powder and that the catalytic activity of Ag/Au is appreciably higher than that of unsupported Ag powder, particularly in the low temperature range, indicating that the mechanism of catalytic CO oxidation on Ag supported on the fine Au powder differs from that on unsupported Ag powder. The ratio of the total amount of Ag contained per unit weight of Ag/Au (=10.2 µmol) to that of surface Ag calculated on the assumption of monolayer coverage (=4.72 µmol) is only 2.2, as can be seen in Table 1. This means that a large portion of Ag exists at surface and covers the surface of the Au fine powder as extremely thin layer. Valden et al. reported that gold catalyst supported on TiO_2 (110) exhibited the highest activity for CO oxidation when islands of gold had a thickness of two or three atomic layers [28]. It might also be interesting to examine whether the whole Ag surface takes part in the catalytic CO oxidation or not from the viewpoint of a mechanism involving the contact perimeter interface.

The rapid pressure decrease observed in the CO exposure experiment performed with "Ag/Au having the oxidized surfaces" was ascribed to the reduction of reactive oxygen species adsorbed on Ag with CO to produce CO_2 (Fig. 6). The fact that the amount of CO_2 produced corresponded almost half of the amount of surface Ag suggests that every 4 surface Ag atoms adsorb one molecule of O_2 during the oxidizing pretreatment carried out at 393 K. In other words, almost all surface Ag atoms practically participated in O_2 adsorption and in subsequent CO_2 production through the reduction with CO at 313 K. Similar results were reported by Keulks and Chang who studied interaction between CO and preadsorbed oxygen on Ag powder at 373 K and they reported that the coverage of preadsorbed oxygen was equivalent to 3.2×10^{14} O adatoms per cm^2 and 75% of which could be removed by CO [29,30].

However, the initial rate of the reduction of reactive adsorbed oxygen species with CO is 16 times larger than the rate of the catalytic oxidation of CO at the steady state (Fig. 4). Moreover, the incorporation of O_2 molecule did not occur until almost all reactive adsorbed oxygen species were removed as shown in the exposure experiments of the reaction mixture to "Ag/Au having the oxidized surface" (Fig. 6 and Table 5). Therefore, reactive adsorbed oxygen species would not take part in the catalytic oxidation with O_2 which proceeds on "Ag/Au having the steady state surfaces." It is probable that when the reaction mixture of CO and O_2 at an initial pressure of 5.3 kPa was started to circulate on the surface of Ag/Au undergone oxidizing pretreatment, the reactive oxygen species adsorbed on Ag surface would instantaneously be removed with CO before establishment of the steady state.

The result presented in Fig. 4 that the rate of the reduction of "Ag/Au having the steady state surfaces" with CO almost coincided with that of the catalytic oxidation of CO with O_2 during the period of initial 20 min indicates that the process of the reduction of "Ag/Au having the steady state surfaces" with CO must constitute one of the elementary steps of the mechanism of catalytic CO oxidation with O_2 on Ag/Au. The fact that the amount of CO consumed for initial 20 min, i.e., 0.41 μmol corresponds to 4.6% of total surface Ag suggests that only a small part of surface Ag participates in the catalytic CO oxidation on Ag/Au. The fact that the amount of CO_2 produced is larger by 46% than that of CO consumed during the CO exposure to "Ag/Au having the steady state surfaces" cannot be explained, if we consider the so-called redox mechanism where one CO molecule reacts with one active oxygen atom to produce one molecule of CO_2 and one vacancy of oxygen [31]. It is likely that a step where CO_3 intermediate reacts with CO to produce two molecules of CO_2 is involved in the mechanism of catalytic CO oxidation with O_2 on Ag/Au.

The absence of the decrease in O_2 pressure during the O_2 exposure to "Ag/Au having the steady state surfaces" indicates that adsorption of O_2 molecule does not occur on the steady state surfaces of Ag/Au and again excludes the redox mechanism where the rate of oxidation of the catalyst with O_2 is dynamically balanced with that of the reduction with CO at the steady state [31]. However, the O_2 exposure to "Ag/Au having the steady state surfaces" produced a small amount of CO_2, i.e., 0.21 μmol. This fact indicates that a process to produce CO_2 without accompanying the decrease of the O_2 pressure is involved in the mechanism of CO oxidation on Ag/Au. The experimental results presented in Fig. 3 also indicate the existence of the CO_2 production process due to the decomposition of some carbonate species formed on "Ag/Au having the steady state surfaces" with O_2 in the gas phase.

Although the decrease in O_2 pressure could not be observed during its exposure to "Ag/Au having the steady state surfaces," the pressure of reaction mixture of CO and O_2 decreased steadily during its exposure, as presented in Fig. 4. It can be assumed from this fact that O_2 molecule can be incorporated into active site only when it coexists with CO molecule to produce CO_2. Cooperative co-adsorption of CO and O_2 on gold clusters and subsequent production of CO_2 has recently been proposed by Xu and Jiang [7] and Wallace and Whetten [8].

Considering all the results and discussion stated above, we propose that the catalysis of CO oxidation with O_2 on "Ag/Au having the steady state surfaces" proceeds according to the following scheme:

$$O_2 + CO \rightarrow (CO3)^*, \tag{1}$$

$$(CO3)^* \xrightarrow{CO,\ O_2} CO_2 + O, \tag{2}$$

$$O + CO \rightarrow CO_2, \tag{3}$$

where (1) CO and O_2 adsorb cooperatively to form $(CO3)^*$, (2) subsequent decomposition of $(CO3)^*$ by the interaction with CO and/or O_2 produces one molecule of CO_2 and leaves one oxygen atom on active site, and (3) the oxygen atom is then scavenged by CO to produce CO_2. It is worth to mention that $(CO3)^*$ can also be (HCO3) in the presence of H_2O [20].

4.2. *Active sites of "Ag/Au having the steady state surfaces" for CO oxidation with O_2*

According to the pathways above, $(CO3)^*$, which acts as active intermediate in the catalysis, produces two molecules of CO_2 by the interaction with CO and/or one molecule of CO_2 with the interaction with O_2. From the other point of view, the amount of $(CO3)^*$ which exists on "Ag/Au having the steady state surfaces" may be estimated from both half of the amount of CO_2 produced during the CO exposure experiment and/or the amount CO_2 produced during the O_2 exposure experiment. The amount of CO_2 produced by the CO exposure was 0.79 μmol as shown in Table 2, indicating that the amount of $(CO3)^*$ intermediate is 0.40 μmol. The amount of $(CO3)^*$ intermediate which was estimated from the amount of CO_2 produced in the O_2 exposure was 0.21 μmol as also presented in Table 2. On the other hand, the amount of CO_2 produced in the experiment where "Ag/Au having the steady state surfaces" was treated in circulating O_2 of 5.3 kPa at 393 K for 60 min ranges from 0.4 to 0.7 μmol as presented in Fig. 3, indicating that the amount of $(CO3)^*$ changes according to the activity of Ag/Au for the CO oxidation. The amount of $(CO3)^*$ intermediate estimated from three kind of different experiments corresponds to 2.4–7.8% of the amount of surface Ag. Since the Au support is suggested to participate in the active sites for the CO oxidation which proceeds on Ag surface on Ag/Au from the large difference in Ea for the CO oxidation between Ag/Au and unsupported Ag powder (Fig. 2), the fact that at most lower than 8% of total surface Ag participates with the CO oxidation on Ag/Au implies that $(CO3)^*$ might be formed at the perimeter contact interface between surface Ag and the Au support.

At present the structure of partly oxidized Ag species supported on Au powder with extremely thin layer is quite unknown. However, it is worth to mention that the structure analysis of Ag species by using Ag K-edge EXAFS of Ag/Au catalyst is under progress.

5. Conclusions

A kinetic study has been made on the catalytic oxidation of CO with O_2 over Ag/Au (Ag-contaminated fine Au powder, ICP bulk

Ag content 0.110 wt%, XPS surface Ag content 10.8 at%) by the rate measurements combined with the measurements of CO_2 produced. Carbon monoxide, O_2, and a reaction mixture of CO and O_2, each of which had a pressure corresponding to about a half of the amount of surface Ag atoms, were introduced to “Ag/Au having the steady state surfaces” and to “Ag/Au having the oxidized surfaces.”

The oxidized surfaces of Ag/Au were covered with highly reactive oxygen adsorbed on Ag surface atoms, which was preferentially reduced with CO even in a reaction mixture of CO and O_2. On the other hand, in the experiments where CO was introduced to “Ag/Au having the steady state surfaces,” the pressure of CO decreased at the same rate as that of a reaction mixture of CO with O_2 until the pressure decrease reached a value corresponding to 4.6% of surface Ag atoms. The amount of CO_2 produced during CO introduction was larger by 46% than that of CO consumed. A mechanism has been proposed for CO oxidation with O_2 at the steady state surfaces of Ag/Au that the reaction proceeds at the perimeter interface between surface Ag and the Au support through co-adsorption of CO and O_2 to form CO_3, which are successively decomposed by the interaction with CO and/or O_2 to produce CO_2.

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