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Effect of impurity and pretreatment conditions on the catalytic activity of Au powder for CO oxidation

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Recent X-ray photoelectron spectrometer(XPS) analysis of Au powder synthesized by evaporating high purity gold metal (> 99.99%) in an inert gas detected impurity metals such as Ag and In at levels which far exceed those expected from the impurity levels of raw gold metal. Several samples of Au powder containing different amount of impurity metals were prepared to examine whether the activity of the Au powder for CO oxidation depends upon the impurity or not. The activity of the powder showed a strong correlation with the surface concentration of Ag.

KEY WORDS: unsupported Au powder; CO oxidation; surface impurity; contact interface effect; particle size effect.

1. Introduction

There have been proposed two theories regarding the reason why gold catalysts highly dispersed on reducible metal oxides such as TiO_2, Fe_2O_3, and Co_3O_4 show enormously high activity for the low temperature oxidation of CO, i.e., particle size effect and contact interface effect [1]. However, when we investigate the CO oxidation which proceeds on such a supported gold catalyst, we cannot discuss about each of two effects separately. Hence, we have studied CO oxidation by using unsupported Au powder (mean particle size, ca. 100 nm) which had been manufactured by evaporating ultra high purity gold metal (> 99.99%) in inert gas expecting that the Au powder has no contact interface with metal oxide. We have hitherto reported two results in the papers already published that (1) Au powder which had undergone the oxidizing pretreatment in circulating O_2 of 1 atom at temperatures 423–453 K turned out to be catalytically active for CO oxidation below room temperature where Au/TiO_2 exhibits high catalytic activity and (2) the amount of CO_2 produced on such oxidized Au powder during CO adsorption at 273 K was 187 times as large as that produced on TiO_2 powder undergone the same oxidizing pretreatment [2,3]. We attributed the catalytic activity for CO oxidation as well as the production of CO_2 during CO adsorption to probable existence of active oxygen species bound to coordinatively unsaturated Au sites such as corners, edges, and steps, where chemisorption of CO might also occur at around room temperature. We considered that these might be a sort of particle size effect of gold particles of Au powder with no contact interface with metal-oxide [2,3].

However, recent X-ray photoelectron spectrometer (XPS) analysis of Au powder revealed that it contains much amount of impurity metals such as Ag and In at levels which far exceed those expected from the impurity levels of raw gold metal. Delgass and his collaborators also reported recently that XPS analysis of Au powder which they manufactured by evaporating ultra high purity gold metal (Engelhard, 99.9999%) detected about a 6% Ag in the surface layer [4]. This finding impelled us to investigate whether the activity as well as the production of CO_2 exhibited by oxidized Au powder depend upon the existence of surface impurities or not, because we could not rule out the possibility that Ag and In might be oxidized on gold surface during the pretreatment to form some oxidized species of which interface with gold might cause the CO oxidation at around room temperature as well as the production of CO_2 during CO adsorption.

Several samples of Au powder with different levels of impurities were produced with earnest cooperation of Vacuum Metallurgical Company and were examined to investigate the effect of surface impurity and pretreatment conditions on the emergence of the catalytic activity of Au powder for CO oxidation.

2. Experimental

In addition to the four samples previously studied, 11 samples of Au powder containing gradually decreasing amount of impurity metals were newly prepared by

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repeating the evaporation of raw Au metal in the chamber whose wall had been coated by Ag and/or In powders. The bulk analysis of Au powder was conducted by means of inductively coupled plasma (ICP). The surface composition of Au powder was analyzed by using XPS (JEOL JPS-9010 MC). MgKα line (1365 eV) was used as X-ray source. Binding energy in the obtained spectra was calibrated by referring to the C1s peak at 284 eV.

The specific surface area of Au powder was measured in a glass made static adsorption equipment by BET method using N_2 as adsorbate at liquid nitrogen temperature. The mean particle size of gold was calculated from the BET surface area of Au powder assuming that all of the gold particles of Au powder have uniformly sphere shape. A glass made recirculation reaction system (base pressure $< 1.3 \times 10^{-3}$ Pa) was used for both the pretreatment and the measurement of the catalytic activity of Au powder for CO oxidation. In order to prevent Au powder from the contamination by mercury and grease vapor, the circulation loop was equipped with greaseless stop cocks and the trap connecting the circulation loop to the vacuum line was always cooled by liquid nitrogen. Prior to the activity measurement, Au powder in the reactor was pretreated under various conditions. Subsequently, the mixture of CO and O_2 with a stoichiometric composition of CO/O_2 = 2/1 was introduced into the loop at 273 K. The product CO_2 was condensed in the trap cooled by liquid nitrogen. The pressure change during the reaction was monitored at least for 1 h.

3. Results and discussion

3.1. ICP bulk and XPS surface analyses of Au powder

Table 1 summarizes the result of a series of ICP bulk analysis conducted on raw Au metal and 14 samples of Au powder. Samples Au-a to Au-c are unsupported Au powder used in the previous studies and samples Au-1 to Au-11 are those newly manufactured by monitoring the change in the level of impurities, (the suffix denotes the number of evaporation repeated). The raw Au metal (> 99.99% purity) contains at most 0.01% impurity. However, after evaporation, all samples of Au powder were more or less contaminated with trace amount of Ag, In and other metals (Sn, Pb, Zn, Fe, Ni, Al, and Cu). The major contaminants were Ag and In. As for the sample Au-1 to Au-11, the concentrations of contaminant metals except Ag lowered rapidly with the number of evaporation. After repeating evaporation four times, most part of contamination was Ag. The lowering of Ag content was slow compared to the other metals including In. The abrupt decrease in the Ag concentration seen in the seventh evaporation was owing to the fact that particularly a large amount of Au raw metal was evaporated at this time. However, a trace amount of Ag persistently remained even after the evaporation of 11 times as compared to Au raw metal.

Table 2 summarizes the surface chemical composition of 15 samples of Au powder, including sample Au-d also used in the previous studies, determined by XPS. Whereas Ag and/or In were detected for some Au

Table 1
ICP Bulk Analysis of Au raw metal and Au Powder

Samples	Bulk composition (wt %)									Sum of impurities	Au
	Ag	In	Sn	Pb	Zn	Fe	Ni	Al	Cu		
Au raw metal	< 0.001	0.001	0.002	0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.011	> 99.989
Au-a	10.400										88.5
Au-b	0.110	0.023	0.009	0.003	0.002	0.015	0.005	0.004	0.019	0.190	99.810
Au-c	0.038	0.400	0.008	0.013	0.008	0.008	0.001	0.007	0.004	0.487	99.513
Au-1	0.540	0.013	0.005	0.010	0.024	0.039	0.004	0.007	0.004	0.646	99.354
Au-2	0.420	0.013	0.002	0.008	0.015	0.028	0.003	0.003	0.002	0.494	99.506
Au-3	0.280	0.003	0.002	0.008	0.010	0.024	0.003	0.003	0.001	0.337	99.663
Au-4	0.350	0.001	0.003	0.002	0.002	0.006	0.001	0.002	0.001	0.368	99.632
Au-5	0.190	0.001	0.003	0.001	0.001	0.004	< 0.001	0.002	0.001	< 0.204	> 99.796
Au-6	0.240	0.001	0.002	0.001	0.002	0.003	< 0.001	0.002	0.001	< 0.253	> 99.747
Au-7	0.032	0.001	0.001	0.001	< 0.001	0.001	< 0.001	0.002	< 0.001	< 0.041	> 99.959
Au-8	0.010	0.001	0.001	< 0.001	< 0.001	0.001	< 0.001	0.002	0.001	< 0.019	> 99.981
Au-9	0.020	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	0.003	< 0.001	< 0.030	> 99.970
Au-10	0.016	0.001	0.001	< 0.001	< 0.001	0.002	< 0.001	0.003	< 0.001	< 0.027	> 99.973
Au-11	0.016	0.001	0.001	< 0.001	< 0.001	0.002	< 0.001	0.002	< 0.001	< 0.026	> 99.974

Table 2
XPS Surface Analysis of Au powder

Samples	Surface composition/wt%		
	Au4f	Ag3d	In3d
Au-a	57.0	40.9	2.1
Au-b	89.2	10.8	Not detected
Au-c	78.4	4.9	16.7
Au-d	92.8	4.0	3.3
Au-1	81.3	18.7	Not detected
Au-2	90.2	9.8	Not detected
Au-3	93.5	6.5	Not detected
Au-4	96.1	3.9	Not detected
Au-5	98.6	1.4	Not detected
Au-6	98.8	1.2	Not detected
Au-7	98.9	1.1	Not detected
Au-8	<100	<1	Not detected
Au-9	<100	<1	Not detected
Au-10	<100	<1	Not detected
Au-11	<100	<1	Not detected

samples, the other seven sorts of metals listed in Table 1 were below the detection limit. Regarding the 11 samples newly prepared, the peaks due to Ag5/2 and Ag3/2 decreased gradually with the number of evaporation and almost disappeared at sixth time evaporation.

3.2. The change of the BET surface area of Au powder due to sintering during the pretreatment

In order to check the extent of the decrease in the surface area of Au powder due to sintering which would occur during the pretreatment at elevated temperatures, the change of specific surface area of Au powder was examined by gradually increasing the temperature. Two samples which differ in the concentration level of surface impurities, i.e., Au-b and Au-7, were selected and were heated in O_2 of 1 atom for 1 h. The results are presented in figure 1. As for Au-7, for which the peaks due to Ag3d were not detected by XPS, the decrease in the surface area started slowly near at 423 K and proceeded rapidly at 493 K. On the other hand, Au-b, for which the distinct XPS peaks due to Ag was detected, did not show the significant decrease in the surface area even at 493 K. Consequently, the upper limit of the pretreatment temperature for newly prepared Au powder was determined to be 453 K. It should be noted that the impurities play a role to prevent Au powder from sintering.

3.3. Effect of pretreatment condition on the catalytic activity of Au powder for CO oxidation

All the samples of Au powder did not show any activity without the oxidizing pretreatment in circulating oxygen at temperatures between 423 and 453 K performed in the reactor. Five samples of Au powder with various levels of impurities, i.e., (1)Au-b, (2)Au-d, (3) Au-3, (4) Au-7, and (5) Au-11, were selected to examine the effect of pretreatment condition, as well as surface impurities, on the activity of Au powder. All of the five samples were undergone five steps of pretreatment conducted in the following order; (1) oxidation in circulating O_2 of 1 atom at 453 K for 1 h (for Au-b, at 483 K in addition), (2) degassing at 423 K for 1 h, (3) re-oxidation in circulating O_2 of 1 atom at 423 K for 1 h, (4) reduction in H_2 of 33 kPa at 423 K for 1 h (except Au-b), and finally again (5) re-oxidation in circulating O_2 of 1 atom at 423 K for 1 h. After each pretreatment step, the sample was cooled down to 273 K to measure the activity.

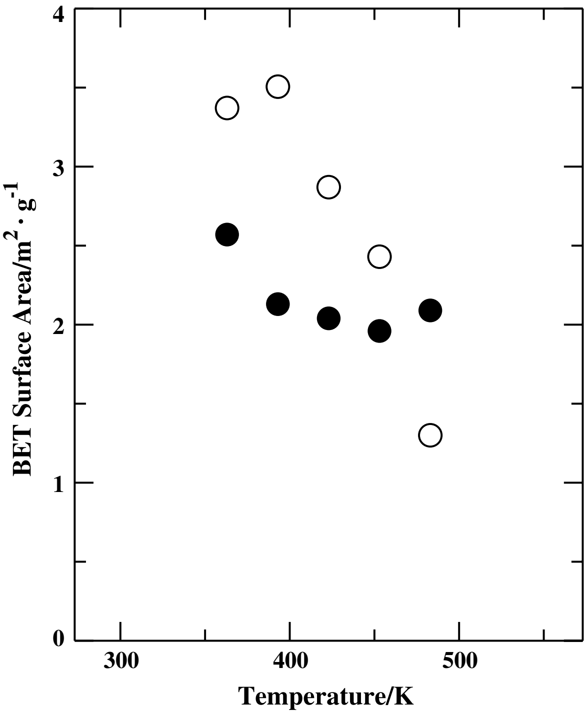

Figure 1. Effect of temperature on the specific surface area of Au powder. Samples Au-b(filled circles) and Au-7(open circles), which differ in the level of surface contamination, were heated in O_2 of 1 atom for 1 h at temperatures gradually elevated. ●,Au-b; ○,Au-7.

Figure 2 presents the results observed on Au-b and Au-d, which contains 10.8% Ag and 4.0% Ag + 3.3% In in the surface layer, respectively. Although the total contents of surface impurities of Au-b and Au-d are almost the same level, the activities of Au-b determined after any pretreatment step were much larger than those of Au-d, suggesting that the activity depends upon the concentration as well as kinds of surface impurities. It is also seen in figure 2 that the response of the activity to the pretreatment condition for Au-b somewhat differs from that for Au-d. The degassing of oxidized Au powder in the second pretreatment step increased the activity of both Au-b and Au-d. However, in the subsequent oxidizing step, the activity of Au-b further increased, while that of Au-d lowered. It is noted that Au-d showed the highest activity after undergoing the fourth step of reduction by H_2, though, the subsequent oxidation reduced the activity to the same level just before the reduction.

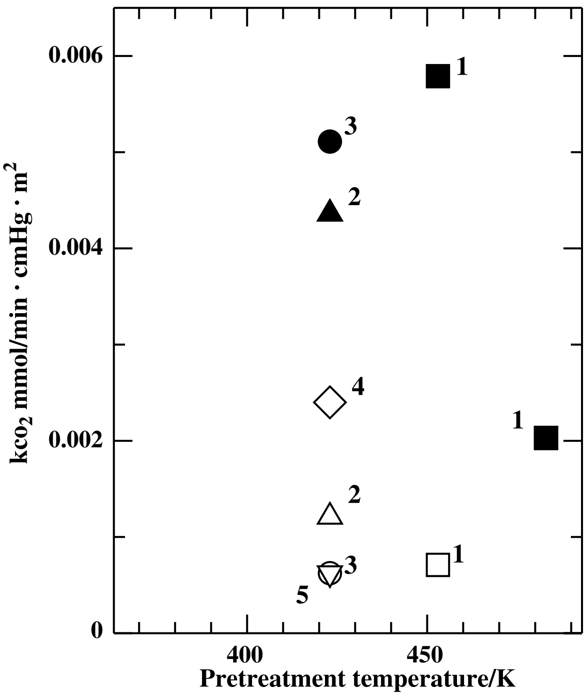

Figure 2. Effect of pretreatment condition on the activity of Au-b (filled marks) and Au-d (open marks). The activities expressed by kCO$_2$ (= the rate constant of CO oxidation per unit surface area of Au calculated on the assumption that the oxidation obeys the first order kinetics) are plotted against the pretreatment temperature. Five sorts of pretreatments conducted on both Au samples were:(1) □,■; oxidation in circulating O$_2$ of 1 atom at 453 K for 1 h(for Au-b, at 483 K in addition), (2) △,▲; degassing at 423 K for 1 h, (3) ○,●; re-oxidation in circulating O$_2$ of 1 atom at 423 K for 1 h, (4) ◇; reduction in H$_2$ of 33 kPa at 423 K for 1 h, and finally again (5) ▽; re-oxidation in circulating O$_2$ of 1 atom at 423 K for 1 h.

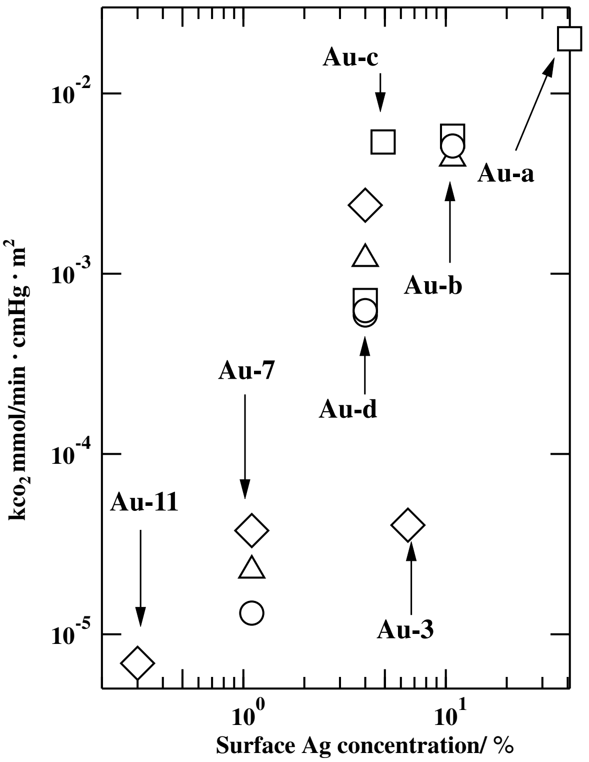

Figure 3. Logarithmic plots of the activity of Au powder, versus surface concentration of Ag(except for Au-11, see text) pre-treated under various conditions; (1) □, oxidation in circulating O$_2$ at 453 K for 1 h, (2) △, degassing at 423 K for 1 h, (3) ○, re-oxidation in O$_2$ at 423 K for 1 h, (4) ◇, reduction in H$_2$ of 33 kPa at 423 K for 1 h.

The activity of Au-7 with little impurity was much weaker than those of Au-d. However, the response of the activity to the pretreatment conditions for Au-7 was entirely the same as that observed for Au-d. Au-3 and Au-11 showed the very faint activity only after the reduction by H$_2$ in the fourth pretreatment step.

3.4. Effect of Ag and In on the activity of Au powder

Since Ag and In were the only metallic impurities detected by XPS, we assumed that the other metallic impurities tabulated in Table 1 do not participate the enhancement of the activity. In order to examine the effect of Ag and In on the activity of Au powder, all the data for the activity measurements including those previously obtained for Au-a and Au-c were plotted against the surface concentration of Ag and In in figures 3 and 4, respectively. It is noted that the activity exhibits a strong correlation with the surface concentration of Ag (Figure 3), though the activity of each Au powder varies to some extent according to the pretreatment condition. On the other hand, such dependence of the activity upon the surface concentration of In is not found in figure 4. We conclude from these results that 1) the activity of Au powder is mainly due to the existence of Ag in the surface layer and 2) the surface In does not substantially contribute to the activity. The very faint activity detected on Au-11 exhibited only when it was reduced by H$_2$ would also be due to the existence of Ag below the detection level, because the results of ICP bulk analysis in Table 1 clearly indicate that slight amount of Ag still remains in Au-11. The plot of Au-11 in figure 3 is just our estimation for the surface concentration of Ag of Au-11 from the activity shown by Au-11. From the other point of view, these results indicate that the activity of Au powder ascribed to the proper gold surface must be negligibly small, if it exists.

Keulks *et al.* studied the oxidation of CO with O$_2$ as well as the adsorption of CO and O$_2$ on Ag powder in a recirculation reactor [5,6]. They reported that oxygen is chemisorbed at 373 K rapidly and irreversibly to form O$^-$ and atoms which serve as irreversible adsorption sites for CO in the initial CO doses. Successive doses of CO, however, resulted in the production of CO$_2$ to remove 75% of the preadsorbed oxygen. Whereas, the adsorption of CO does not occur on Ag surface without preadsorbed oxygen [5]. The kinetics of the CO oxidation on Ag powder are first order in CO, zero order in O$_2$ at 373 K and the activation energy at 353–403 K is 57.3 kJ/mol [6]. Considering the results reported by

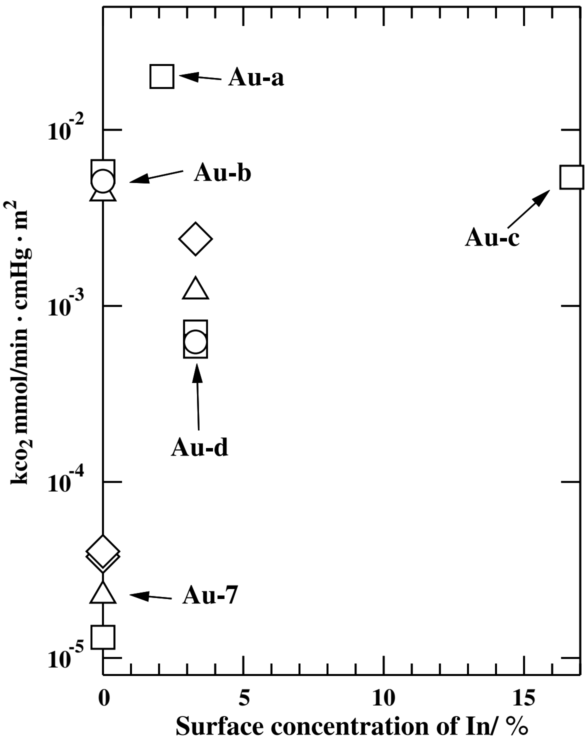

Figure 4. Logarithmic plots of the activity of Au powder, versus surface concentration of In, pre-treated under various conditions: (1) □, oxidation in circulating O_2 at 456 K for 1 h, (2) △, degassing at 423 K for 1 h, (3) ○, re-oxidation in O_2 at 423 K for 1 h, (4) ◇, reduction in H_2 of 33 kPa at 423 K for 1 h.

Keulks *et al.* and the experimental facts in the present study that (1) the surface of Au powder is partly covered with Ag as shown in Table 2 and (2) any Au powder did not exhibit the activity without undergoing the oxidizing pretreatment at temperatures between 423 and 453 K, it is presumed that oxidized Ag supported on the surface of Au powder and/or the interface produced between the oxidized Ag and the Au surface operate as catalytically active sites for CO oxidation.

It is noted that the activity of Au-3 which contains 6.5% Ag is exceptionally low in figure 3, i.e., Au-3 is less active by about one order magnitude than both Au-c and Au-d, which contain about 4.9 and 4.0% Ag (Table 2), indicating that the activity of Au powder does not simply depend upon the surface concentration of Ag. As shown in Table 2, both Au-c and Au-d contain In in the surface layer, whereas Au-3 does not. Therefore, though the surface In alone is hard to create catalytically active sites, we cannot rule out the possibility that the coexistence of In with Ag enhance the activity for CO oxidation.

3.5. *"Particle size effect" and "contact interface effect" in the activity of Au powder for CO oxidation*

Particle size effect is a theory frequently used to explain the origin of the activity of the gold catalyst for the low temperature oxidation of CO. Since the present samples of Au powder have various mean particle sizes, it is worth to examine the size effect on the activity of Au powder. The activity data measured after various pretreatment conditions were plotted as a function of the mean particle size of gold in figure 5. It is found that Au-b, Au-c, and Au-7, which have almost the same mean particle size, exhibited largely different activities due to different levels in the concentration of impurity metals in the surface layer. In other words, prior to examine the particle size effect of gold on the activity of Au powder, the effect of surface impurities must be separated.

It is noticed in figure 5 that the activity of Au-3, Au-7, and Au-11 decreases with the mean particle size. However, the concentration of surface Ag also decreases in accord with this order (Table 2), to which the decrease of the activity was ascribed as presented in figure 3. The very faint activity exhibited by Au-11 which has a mean particle size of ca. 80 nm was assumed to be due to a trace content of Ag remained at some undetectable level. This means that as to Au powder with a mean particle size larger than 80 nm, the activity attributable to proper gold surface must be negligible.

Figure 5 shows that Au-a having the smallest gold particle size of 23 nm showed the highest activity. However, this sample contains quite a large amount of Ag both in the bulk and the surface layer (Tables 1 and 2),

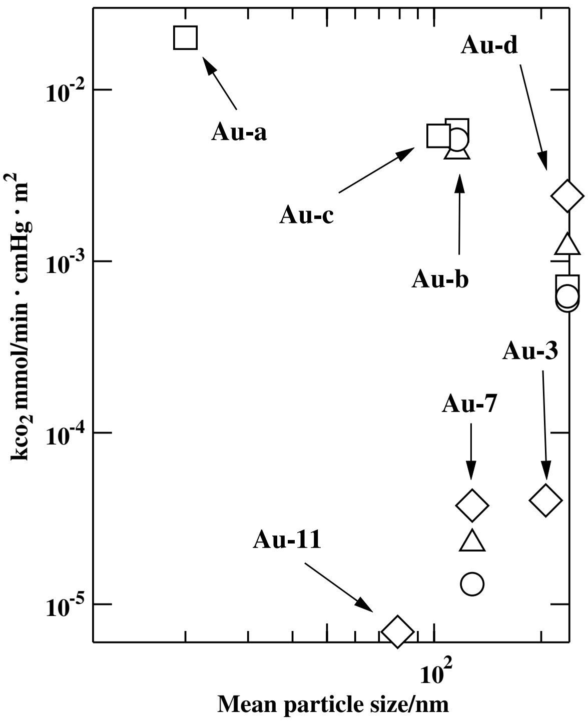

Figure 5. Logarithmic plots of the activity of Au powder, versus mean particle size, pre-treated under various conditions: (1) □, oxidation in circulating O_2 at 453 K for 1 h, (2) △, degassing at 423 K for 1 hr, (3) ○, re-oxidation in O_2 at 423 K for 1 h, (4) ◇, reduction in H_2 of 33 kPa at 423 K for 1 h.

which should be the main attribution to the catalytic activity as presented in figure 3.

It can be concluded from our experimental results that the activity of Au powder attributable to so-called "particle size effect" is not recognized for unsupported Au powder with a mean particle size larger than 80 nm. This provides a contrast to the supported gold particles smaller than ~10 nm, for which the significant size effect is observed (1). Conversely, the activity of Au powder observed in the present work can be ascribed only to so-called "contact interface effect" due to the existence of Ag which is probably partly oxidized and inversely supported on the surface of Au powder. Contrast experiments of the kinetics of CO oxidation using pure Ag powder, Au-b and Au-7 which would contribute to clarify the mechanism of the reaction enhanced only by "contact interface effect" are in progress.†

†The material appeared in the proceedings of the Gold 2003:New Industrial Applications for Gold Conference held in Vancouver, Canada.

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