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Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide

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Novel gold catalysts were prepared by coprecipitation from an aqueous solution of $HAuCl_4$ and the nitrates of various transition metals. Calcination of the coprecipitates in air at 400°C produced ultrafine gold particles smaller than 10 nm which were uniformly dispersed on the transition metal oxides. Among them, Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO were highly active for H_2 and CO oxidation, showing markedly enhanced catalytic activities due to the combined effect of gold and the transition metal oxides. For the oxidation of CO they were active even at a temperature as low as −70°C. © 1989 Academic Press, Inc.

INTRODUCTION

During the course of an investigation into new oxide catalysts useful for the low-temperature catalytic combustion of hydrogen (*1–4*), it became evident that the catalytic activities of transition metal oxides for hydrogen oxidation had a volcano-like relation with the heat of formation of oxides per gram-atom of oxygen (*5*). The volcano relation indicates that the formation of metal–oxygen (*M*–O) bonds is rate determining for the oxides of Ag and Au, which are located on the left side, while the breaking of *M*–O bonds is the slow step for the other metal oxides located on the right side. Therefore, an attempt was made to develop composite oxides of Ag with the 3*d* transition metals, for which an enhancement in both catalytic activity and thermal stability was expected.

Our earlier paper (*5*) reported that an appreciable enhancement in catalytic activity was, in fact, achieved in some composite oxides of silver with 3*d* transition metals which were prepared by coprecipitation. Specifically, a mixed oxide composed of Co, Mn, and Ag (20 : 4 : 1 in atom ratio) was both thermally stable and highly active for the oxidation of H_2 and CO. The successful results obtained for these composite oxides of silver led us to expect that a significant enhancement in catalytic activity might also be exhibited by composites of gold and the other metal oxides. The present investigation into gold-based oxide catalysts was undertaken to test this hypothesis.

Previous work on gold catalysts has been reviewed by several authors (*6–10*). All the gold catalysts investigated so far are gold supported on inactive ceramic oxides, such as SiO_2 (*11–17*), Al_2O_3 (*14–16, 18*), MgO (*15–17, 19*), and TiO_2 (*20*), or unsupported gold filaments (*21*), powder (*22, 23*), sponges (*24*), filings (*25*), and gauze (*26*).

The chemical reactivity of gold catalysts has been studied for the oxidation by oxygen or nitrogen oxides of CO (*11, 22, 24, 26*) and H_2 (*12, 15, 17, 21–23*), selective oxidation of organic compounds by nitrogen dioxide (*13*), hydrogenation of alkenes (*7*), and so on. However, the conventional gold catalysts prepared by impregnation have been reported to be usually far less active than platinum-group metal catalysts, although they are superior in selectivity for only a few reactions such as the oxidation

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of 1-pentanol to 1-pentaldehyde by NO_2 (*13*) and the hydrogenation of 1-pentene to *n*-pentane (*7*). The present paper deals with a new type of gold catalyst prepared by coprecipitation instead of impregnation. In a previous short communication (*27*), we reported that combination with the oxides of Group VIII 3*d* transition metals makes gold so active that it catalyzes the oxidation of CO, even at −70°C.

EXPERIMENTAL

The gold catalysts were prepared by coprecipitation. An aqueous solution of chloroauric acid and a transition metal nitrate was poured into an aqueous solution of sodium carbonate under stirring. The precipitate was washed, vacuum dried, and calcined in air at 400°C for 4 h. Gold powder and the simple oxides of Fe, Co, and Ni were also prepared in this manner. Conventional gold catalysts were prepared by immersing support oxides in an aqueous solution of $HAuCl_4$ with a small excess volume. After drying, the impregnated samples were reduced with hydrogen at 200 or 300°C. They were then washed in hot water several times and dried in air at 200°C. The support oxides used were α-Fe_2O_3 calcined at 400°C (SA = 42 m^2/g) and γ-Al_2O_3 (anhydrous extra pure, Merck, SA = 97 m^2/g). Another type of gold catalyst was prepared by the reduction of $HAuCl_4$ with diammonium citrate in an aqueous dispersion of colloidal SiO_2 (STO, Nissan Chemicals Ind., Ltd.). This catalyst was finally calcined in air at 300°C after washing and drying.

All the starting materials used were reagent grade (Kishida Chemicals Co., Ltd.). Elemental analysis of chloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was conducted by means of atomic emission spectroscopy using an inductively coupled argon plasma source (Hitachi, Ltd., ICP Emission Analysis System 306) to determine the impurity levels of Pd, Pt, and Ir, because trace amounts of these Pt-group metals may sometimes account for part or almost all the catalytic activity of the gold sample under study (*10*). The impurity levels were approximately 11, 2, and 7 ppm, for Pd, Pt, and Ir, respectively.

Catalytic activity measurements were carried out in a small fixed-bed reactor, with 0.20 g of catalyst that had passed through 70- and 120-mesh sieves. After the pretreatment of catalysts in a dried air stream at 200°C for 30 min, a standard gas consisting of 1.0 vol% H_2 or CO balanced with air to 1 atm was passed through the catalyst bed at a flow rate of 66 ml/min. This reaction gas was dried by passing through columns of silica gel and P_2O_5 granules. In the experiments at temperatures below 0°C, the reaction gas was further passed through a silica gel column cooled to −77°C to prevent the accumulation of moisture in the catalyst bed. In order to investigate the influence of moisture on the catalytic activity, the reaction gas was passed into a constant moisture device (*28*) which contained saturated NH_4Cl aqueous solution. The relative humidity of the reaction gas was kept constant at 76%, as confirmed by humidity measurements using a Humidector (Shinyei Co., Ltd.).

Activated carbon and molecular sieve 13X were used as column packing agents to analyze CO_2 and CO, respectively, in the effluent gas by a gas chromatograph. The conversion efficiencies, determined from the changes in concentrations of CO_2 and CO, were in good agreement with each other under all the conditions tested.

The activity of a given catalyst is usually expressed in terms of the temperature corresponding to 50% conversion ($T_{1/2}$), which can be obtained from the conversion vs temperature curves. A lower temperature for $T_{1/2}$ indicates correspondingly greater catalytic activity.

Specific surface areas were determined by the single-point method using a Quantasorb surface area analyzer. A mixture of 30 vol% N_2 in He gas was used, with N_2 as adsorbate at a temperature of −195.8°C. The reproducibility of the data was within

±5%. X-ray diffraction experiments were performed after each thermal treatment in a Rigaku X-ray powder diffractometer with Ni-filtered Cu$K\alpha$ radiation. Crystallite sizes of Au were calculated from peak half-widths by using the Scherrer equation with corrections for instrumental line broadening.

The fine structure of the gold catalysts was observed using an Akashi EM-002A electron microscope operated at 120 kV. X-ray photoelectron spectroscopic analyses were made using a Shimazu ESCA 750 under vacuum below 5×10^{-6} Torr. The surface composition was determined by using a sensitivity factor for each element (*29*). The bulk composition was determined by X-ray fluorescence analysis.

RESULTS

Oxidation of Hydrogen

A variety of mixtures of metallic gold with single and binary oxides was prepared to seek appreciable enhancement in the catalytic oxidation of H_2. The results are summarized in Table 1. Among the 3*d* transition metal oxides investigated, the oxides of cobalt, iron, and nickel, the Group VIII metal oxides, were found to exhibit appreciably enhanced catalytic activity in the presence of gold.

Figure 1 shows the catalytic activities expressed by $T_{1/2}$ and specific surface areas as a function of gold content. Maximum activities were obtained at 5 at.% of gold for the Fe–Au and Co–Au systems and at 10 at.% for Ni–Au. As the $T_{1/2}$ values for gold powder and the host metal oxides individually were above 130°C, it was clear that their combination resulted in noticeably enhanced catalytic activities.

TABLE 1

Catalytic Activities for H_2 Oxidation and Specific Surface Areas of Various Metal Oxides and Gold Catalysts

Catalysts	Au (at.%)	$T_{1/2}$ (°C)	Surface area (m^2/g)
Au/MnO_x	10	152	69
Au/MnO_x	50	134	115
Au/α-Fe_2O_3	10	73	73
Au/Co_3O_4	10	66	69
Au/NiO	10	73	116
Au/CuO	10	143	20
MnO_2	0	244	32
α-Fe_2O_3	0	225	43
Co_3O_4	0	128	47
NiO	0	221	55
CuO	0	>300	6
Ag_2O	0	89 ~ 103	—
PdO	0	1	—
PtO_2	0	38	—
Au_2O_3	100	131	1

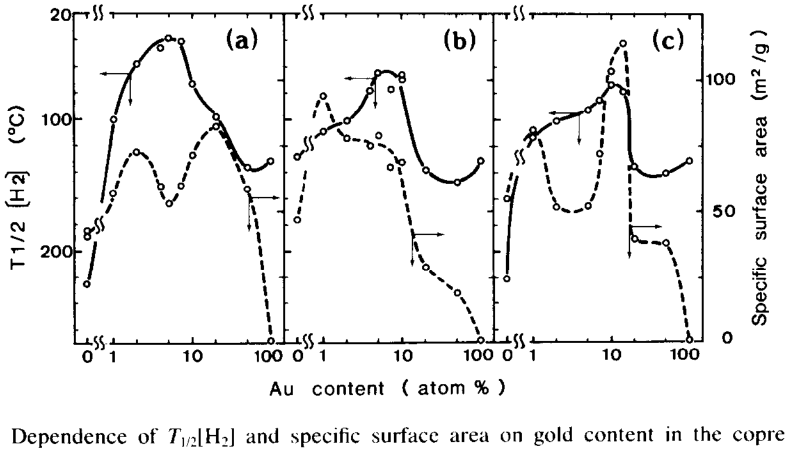

FIG. 1. Dependence of $T_{1/2}[H_2]$ and specific surface area on gold content in the coprecipitates calcined at 400°C. (a) Au/α-Fe_2O_3; (b) Au/Co_3O_4; (c) Au/NiO.

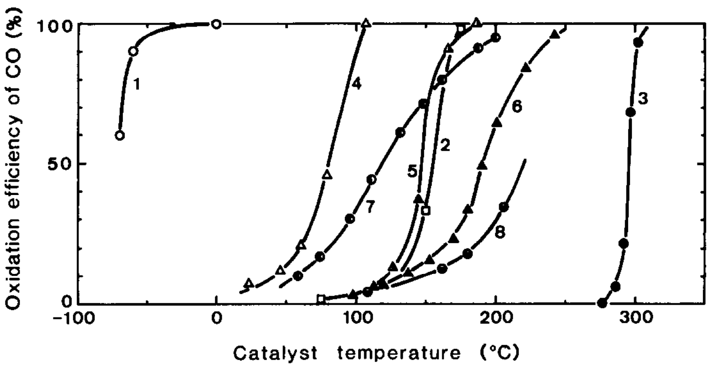

FIG. 2. Oxidation efficiencies of CO over various catalysts as a function of temperature. 1, Au/α-Fe_2O_3 (Au/Fe = 1/19, coprecipitation, 400°C); 2, 0.5 wt% Pd/γ-Al_2O_3 (impregnation, 300°C); 3, Au fine powder; 4, Co_3O_4 (carbonate, 400°C); 5, NiO (hydrate, 200°C); 6, α-Fe_2O_3 (hydrate, 400°C); 7, 5 wt% Au/α-Fe_2O_3 (impregnation, 200°C); 8, 5 wt% Au/γ-Al_2O_3 (impregnation, 200°C).

The changes of specific surface area with composition appeared to be bimodal for all three systems. The maximum catalytic activity was obtained at the minimum in specific surface area in the Fe–Au system, while it was observed at the second peak in the Co–Au and Ni–Au systems.

Oxidation of CO

The coprecipitated gold catalysts were much more active for the oxidation of CO than for the oxidation of H_2. The three typical gold catalysts, hereinafter denoted Au/α-Fe_2O_3 (Au/Fe = 1/19), Au/Co_3O_4 (Au/Co = 1/19), and Au/NiO (Au/Ni = 1/9) (see characterization), were able to oxidize CO even at −70°C (*27*). They were also able to oxidize the CO completely at 30°C even under a relative humidity of 76%. While a Hopcalite catalyst (mixed oxides mainly composed of Mn and Cu) commercially used for CO safety gas masks had lost its activity after 20 min, the Au/α-Fe_2O_3 and Au/Co_3O_4 catalysts maintained their activity for at least 7 days.

Comparison of Catalytic Activity for CO Oxidation with That for H_2 Oxidation

It is useful to compare the new gold catalysts with the support metal oxides, gold powder, impregnated gold catalysts, and a supported Pd catalyst, for the oxidation of CO and H_2. Figures 2 and 3 show such a comparison. The impregnated gold catalysts, Au/γ-Al_2O_3 and Au/α-Fe_2O_3, were active only at temperatures above 100°C, although they were calcined at 200°C, which was lower by 200°C than the calcination temperature for the coprecipitated catalysts. The support oxides, namely Co_3O_4, NiO, and α-Fe_2O_3, and gold powder are active only at temperatures in the range 60 to 300°C under the same experimental conditions. These comparisons clarify that it is only the gold catalysts prepared by coprecipitation that exhibit marked enhancement in catalytic activity.

Figure 4 shows $T_{1/2}$ values for CO oxidation and H_2 oxidation as a function of mean diameter of Au crystallites determined from TEM and/or XRD. The coprecipitated gold catalysts exhibited the highest activities when they were calcinced at 300–400°C, while the impregnated and reduction-deposited catalysts exhibited lower catalytic activities with an increase in calcination or reduction temperature. For example, the gold catalyst supported on α-Fe_2O_3 by impregnation (No. 5 in Fig. 4) had higher catalytic activity, although much lower than those of coprecipitated catalysts, when calcined at 70°C than at 200 and 300°C.

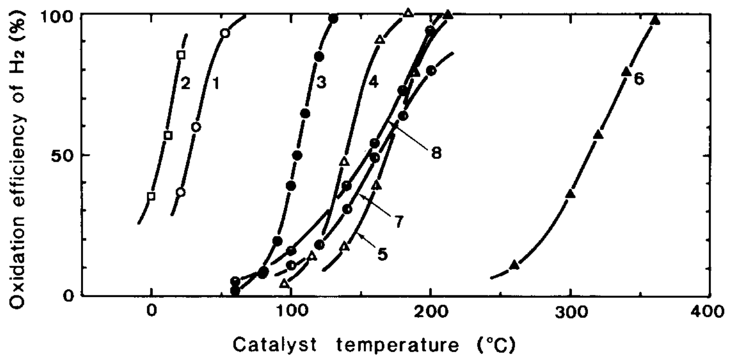

FIG. 3. Oxidation efficiencies of H_2 over various catalysts as a function of temperature. 1, Au/α-Fe_2O_3 (Au/Fe = 1/19, coprecipitation, 400°C); 2, 0.5 wt% Pd/γ-Al_2O_3 (impregnation, 300°C); 3, Au fine powder; 4, Co_3O_4 (carbonate, 400°C); 5, NiO (hydrate, 200°C); 6, α-Fe_2O_3 (hydrate, 400°C); 7, 5 wt% Au/α-Fe_2O_3 (impregnation, 200°C); 8, 5 wt% Au/γ-Al_2O_3 (impregnation, 200°C).

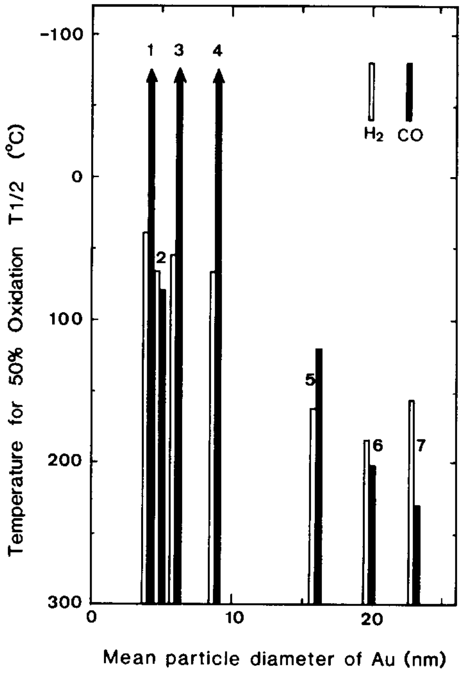

FIG. 4. Catalytic activities for H_2 and CO oxidation as a function of mean particle diameter of Au. 1–4, coprecipitates calcined at 400°C; 1, Au/α-Fe_2O_3 (Au/Fe = 1/19); 2, Au/Al_2O_3 (Au/Al = 1/19); 3, Au/Co_3O_4 (Au/Co = 1/19); 4, Au/NiO (Au/Ni = 1/9); 5, Au/α-Fe_2O_3 (5 wt%, impregnation, reduction at 200°C); 6, Au/SiO_2 (17 wt%, reduction, calcination at 300°C); 7, Au/γ-Al_2O_3 (5 wt%, impregnation, reduction at 200°C).

A general trend is that catalytic activity increases with the decreasing diameter of Au crystallites in the oxidation of both CO and H_2. However, small crystallites of Au do not necessarily lead to catalytic activity at such an extremely low temperature as −70°C. In the Au/Al_2O_3 catalysts prepared by coprecipitation, the $T_{1/2}$ value for CO oxidation is much higher than those for Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO even though the crystallite size of Au is similar in all cases. On the other hand, the $T_{1/2}$ value for H_2 oxidation is comparable for all four catalysts. Accordingly, the oxidation of CO at low temperatures seems to require both the control of Au crystallite size and the selection of appropriate support oxides.

Characterization

The X-ray diffraction patterns showed that the coprecipitates calcined at 400°C in air were composed of metallic crystallites of Au and the oxides, namely α-Fe_2O_3, Co_3O_4, and NiO. The crystallite sizes of Au were estimated to be 3.6 nm for Au/α-Fe_2O_3 from the peak half-width of Au(111) at 2θ = 38.2°, ca. 6.0 nm for Au/Co_3O_4 from Au(200) at 2θ = 44.4°, and ca. 8.0 nm for Au/NiO from Au(220) at 2θ = 64.6°. The crystallite sizes of Au in the impregnated catalysts were estimated to be 16, 20, and

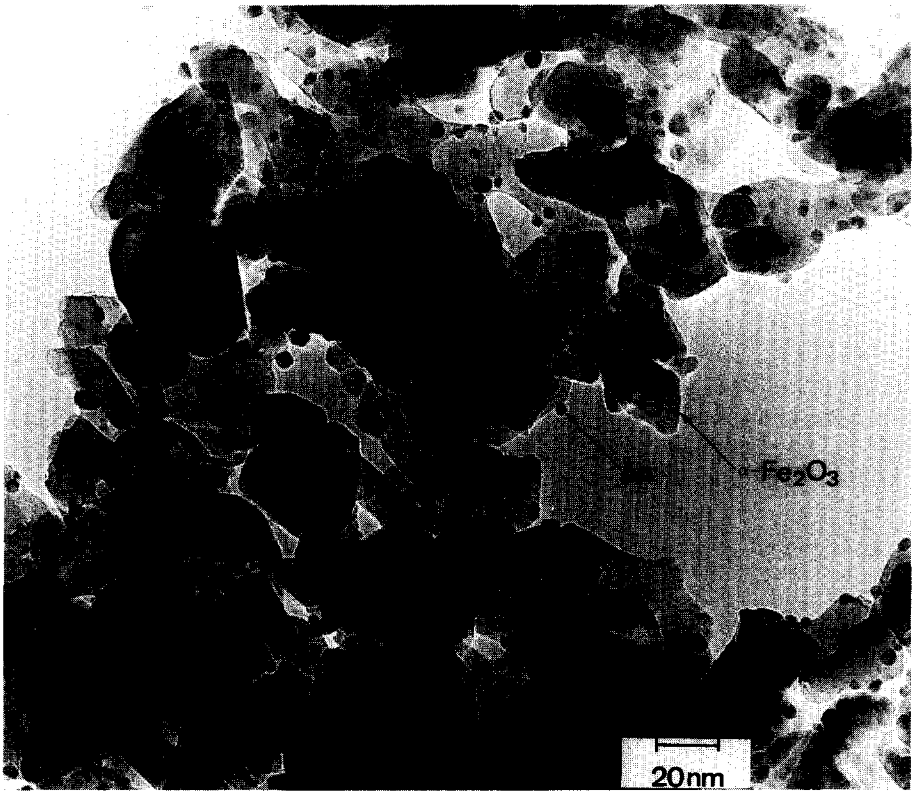

FIG. 5. TEM of Au/α-Fe_2O_3 (Au/Fe = 1/19) prepared by coprecipitation and calcination at 400°C.

23 nm for α-Fe_2O_3-, SiO_2-, and γ-Al_2O_3-supported catalysts, respectively.

Figure 5 shows a high-resolution TEM photograph of Au/α-Fe_2O_3 (Au/Fe = 1/19). Gold particles are uniformly dispersed on the hematite particles of size around 20–50 nm. The histogram in Fig. 6 shows that gold particles exist with a rather sharp size distribution. The mean diameter of 2131 particles of Au is 4.1 nm with a standard deviation of 1.4 nm (34%). This diameter agreed well with the value estimated from XRD data.

In the XPS spectra of coprecipitated Au/α-Fe_2O_3 (Au/Fe = 1/19), the binding energy of Au $4f_{5/2}$ was 83.9 eV, a little larger but very close to that of metallic gold evaporated onto α-Fe_2O_3 and appreciably different from that of Au_2O_3, 86.3 eV. No detectable differences in the Fe $2p_{3/2}$ and O 1*s*

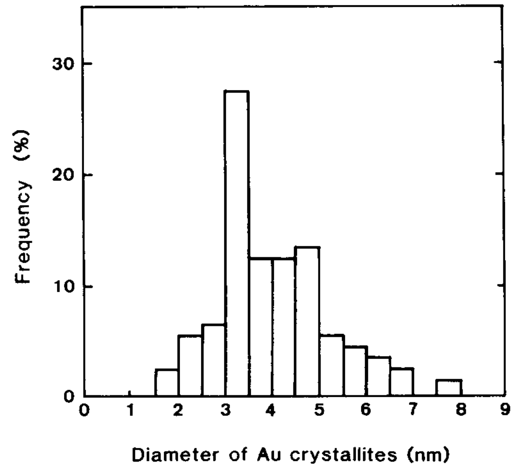

FIG. 6. Histogram of gold crystallites in Au/α-Fe_2O_3 (Au/Fe = 1/19) prepared by coprecipitation and calcination at 400°C.

TABLE 2

Composition of Au/α-Fe_2O_3 Catalysts Prepared by Coprecipitation

Oxides	Fe	Au
Prepared (at.%)	95	5
Elem. anal. (at.%)	94.6	5.4
XPS (at.%)	93.4	6.6
XRD	Au particles and α-Fe_2O_3	

spectra between Au/α-Fe_2O_3 (Au/Fe = 1/19) and α-Fe_2O_3 were observed.

Table 2 summarizes the results of analyses for the surface composition calculated from the peak area of Au $4f_{5/2}$ and Fe $2p_{3/2}$ in XPS and the bulk composition obtained from X-ray fluorescence measurements. The compositions of the starting solution, surface layer, and bulk were nearly identical. This result shows that gold particles are deposited mainly on the surface of hematite particles with little, if any, being incorporated into the bulk of the hematite.

DISCUSSION

It has been demonstrated in the present study that gold becomes a very active catalyst for the oxidation of CO when small gold particles are prepared in the presence of 3*d* transition metal oxides. In the impregnation and reduction methods, which were used for the preparation of almost all the conventional gold catalysts, gold was obtained only as large particles, usually above 10 nm in diameter. This is because gold has a very low melting temperature, low sublimation energy, and very low Tammann temperature (*10*). These properties, in addition to the intrinsically poor reactivity of gold metal, make gold markedly different from Pt-group metals in catalytic behavior.

An attempt has recently been made by Zhang (*10*) to prepare small gold particles supported on MgO and Y-zeolite by incipient wetness impregnation of chloroauric acid and by ion exchange with gold diethylenediamine trichloride, respectively. Although gold particles smaller than 2 nm were obtained by calcining at temperatures below 200°C, the reported catalytic activity for H_2 oxidation was not appreciably high. It could be assumed that chloride ions remained in the MgO carrier because the catalysts were not washed by hot water after reduction. In fact, the catalytic activity of Au/Al_2O_3 prepared in our laboratory by impregnation was appreciably improved by washing with hot water. In the coprecipitated gold catalysts, the coprecipitates were thoroughly washed before calcination and therefore were considered to be almost free from chloride ions. It could also be expected that Pt-group metal impurities contained in $HAuCl_4$ might be mostly excluded during the coprecipitation of gold and 3*d* transition metals because of the extremely low concentrations of those impurities in the starting solution. The small gold particles held inside the supercages of zeolite Y containing Na^+ grew at temperatures above 100°C, indicating that they were not thermally stable when used as an oxidation catalyst.

From a comparison with Zhang's work, it is evident that coprecipitation is an effective method to prepare small gold particles with good thermal stability and possibly to avoid contamination from chloride ions and Pt group metals which are usually contained in the starting materials. During calcination, gold components were decomposed to form metallic gold crystallites which move out from the inner part of the coprecipitate particles toward the surface. This process might cause the gold particles to be strongly held by the support oxides thereby preventing their coagulation.

The parabolic changes in catalytic activity for H_2 oxidation shown in Fig. 1 may be closely related to the dispersion and exposed surface area of Au metal. The total surface area of exposed Au metal increases with an initial increase in Au content and may then decline with a further increase in Au content due to the coagulation of Au particles. This compensating effect of Au content gives rise to the maximum in the exposed surface area of Au and, accordingly, to the maximum catalytic activities at 5–10 at.% of Au. It seems to be a coincidence that a catalyst supporting smaller gold particles requires a smaller content of Au to reach the maximum catalytic activities: Au/α-Fe_2O_3 (4.1 nm, 5–7 at.%) < Au/Co_3O_4 (ca. 6 nm, 5–10 at.%) < Au/NiO (ca. 8 nm, 10–14 at.%).

The bimodal change of the specific surface area appears to be complex in comparison with the simple parabolic change observed for the composite oxides of Ag with Co and Mn (*5*). The initial increase in the specific surface area up to 2 at.% of Au might be due to the incorporation of gold into the precipitates of Fe, Co, and Ni, as in the case of Ag–Co and Ag–Mn oxides. Since the ionic radius of Au^{3+} is 1.37 Å, larger than 0.65–0.78 Å for divalent or trivalent ions of Fe, Co, and Ni, gold may retard the crystal growth of the coprecipitates leading to a larger specific surface area than that of the pure oxides of Fe, Co, and Ni.

In a sodium carbonate solution of pH around 8.5, gold tetrachloride anions were progressively transformed, before coprecipitation, to gold hydroxide anions thereby releasing free chloride ions. This reaction is not as fast as the precipitation of hydroxides of Fe, Co, and Ni. With an increase in Au content, the amount of chloride ions released appreciably increases during coprecipitation to change the precipitation conditions. Au at 5 at.% causes release of chloride ions of more than one-tenth the concentration of nitrate ions. The coexistence of the chloride ions in a concentration comparable to that of nitrate ions might possibly result in a change in the size of primary solid coprecipitates and their coagulation phenomena. The above phenomena can be considered to be closely related to the occurrence of the bimodal change in specific surface area.

The final decline toward the small surface area of gold powder for a gold content above 20 at.% could be ascribed to the sintering of gold and the decreased proportion of metal oxides. In fact, the catalyst with 20 at.% Au had the same appearance as that of metallic gold powder. It should be noted that the maximum catalytic activity was obtained at the minimum in specific surface area for Au/α-Fe_2O_3, but at the second peak or plateau in Au/NiO or Au/Co_3O_4.

It is noteworthy that the catalytic activity of Au/Al_2O_3 was comparable to those of Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO for H_2 oxidation but remarkably inferior for CO oxidation. As shown in Fig. 4, the catalytic activity for H_2 oxidation seems to be solely dependent on the particle diameter, namely the exposed surface area of gold metal. On the other hand, the support oxides may also play an important role in the oxidation of CO. Even though gold was supported in the form of small particles of 5 nm in diameter, the catalytic activity is not as high with inactive Al_2O_3 as that obtained for Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO. These results indicate that either a kind of metal–support interaction occurs or oxidation may proceed through a bifunctional mechanism in which both gold particles and support oxides activate different steps of the CO oxidation.

Hydrogen is considered not to chemisorb on the gold surface while CO chemisorbs weakly on the gold surface (*10*). Therefore, it is probable that the contribution of support oxides may differ in H_2 oxidation from that in CO oxidation. The interaction of gold crystallites with the support oxides, α-Fe_2O_3, Co_3O_4, and NiO, which are all semiconductors, might alter the surface properties of gold crystallites so as to favor CO adsorption. According to simple calculations, outer surface atoms compose about 40% of the total atom content for hemispherical gold particles of diameter 4.0 nm. This suggests that the electronic states of the outer surface gold atoms can be readily modified by the interaction with the support oxides.

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