Supported Gold Catalysts Derived from Gold Complexes and As-Precipitated Metal Hydroxides, Highly Active for Low-Temperature CO Oxidation

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Supported gold catalysts were prepared by attaching phosphine-stabilized gold complex and cluster on as-precipitated metal hydroxides $M(OH)^*_X$ ($M=Mn^{2+}$, Co^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Mg^{2+},and Cu^{2+}), followed by thermal decomposition and calcination. The obtained catalysts were remarkably active for CO oxidation at low temperatures below 273 K.

It is established that "ultra-dispersed metal particles" can be obtained by decomposition of molecular metal complexes including metal cluster compounds on inorganic oxide supports.[1-5] In these systems metal-support interface is more efficiently interacted to sometimes generate unique catalysis. However, it is scarcely known that supported small gold particles are obtained by decomposition of gold complexes or gold clusters, though catalysis of gold has accepted increasing interests.[6-11] Highly dispersed gold particles on metal oxides which show high catalytic activities for the oxidation of CO and H_2 at low temperatures have been reported by Haruta and his coworkers[6] who obtained dispersed gold catalysts by coprecipitation, deposition-precipitation,[10,11] Co-sputtering[12] and CVD method.[13] Our earlier works[14,15] on oxide-supported heteronuclear and homonuclear gold clusters stabilized by phosphine ligands showed that the gold compounds on oxide surfaces were readily decomposed to form metallic particles, but their catalytic activities for CO oxidation were lower than those of the catalysts prepared by coprecipitation of $HAuCl_4$ and $Fe(NO_3)_3$ due to the larger size of gold particles in the former systems. Here we report a new approach to prepare supported gold catalysts which show tremendously high activity for CO oxidation at low temperatures. Gold catalysts were obtained by supporting phosphine-stabilized gold complex $[Au(PPh_3)](NO_3)$ (**1**)[16] and cluster $[Au_9(PPh_3)_8](NO_3)_3$(**2**)[17] on wet as-precipitated metal hydroxides ($(MOH)_x^*$) originated from $Mn(NO_3)_2$, $Co(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Ti(i\text{-}OC_3H_7)_4$, VCl_3, $Al(NO_3)_3$ and $Cr(NO_3)_3$.

Metal hydroxides were prepared by precipitation of metal nitrates (99.9% purity) with an aqueous 5.0 wt% solution of Na_2CO_3 (99.9% purity). Titanium hydroxide and vanadium hydroxide were obtained by hydrolysis of titanium-tetra-*iso*-propoxide (99.999%) and vanadium trichloride (99.9%) with an aqueous 5.0 wt% solution of Na_2CO_3, respectively. The precipitates were washed repeatedly with distilled water till the pH reached 7.0 and filtered. The obtained as-precipitated metal hydroxides without drying were impregnated with an acetone solution of **1** and a methanol solution of **2**, while vigorously stirring for 12 h, followed by evacuation for 5 h to remove the solvents. The gold content on each oxide was controlled to be 3.0 wt%. Decomposition and calcination of the Au complexes on the metal hydroxides were performed by heating to 673 K at a heating rate of 4 K/min at which temperature the samples were held for 4 h under a flow of air at 30 ml/min. The obtained samples are denoted as $1/M(OH)_x^*$ (x=2 or 3), where asterisk stands for the as-precipitated metal hydroxides. For comparison, conventional samples were also prepared by impregnation of **1** on calcined metal oxides, followed by decomposition and calcination in the similar way to $1/M(OH)_x^*$, which are denoted as **1**/oxide. Catalytic CO oxidation was carried out in a fixed-bed flow reactor equipped with a computer-controlled auto-sampling system by using 200 mg of catalyst powder. The reaction gas containing 1.0% CO balanced with air purified by a molecular sieve column was passed through the catalyst bed at a flow rate of 67 ml/min ($SV=20000\ h^{-1}$). The reaction products were analyzed by a gas chromatgraph using a column of Unibeads C for CO_2 and a column of 5A molecular sieve for CO and O_2.

Table 1. Catalytic activities for CO oxdiation of various gold catalysts derived from $1/M(OH)_x^*$

Catalyst	T_S / K	$T_{50\%}$ / K	$T_{100\%}$ / K
$1/Mg(OH)_2^*$	203	250	>373
$1/Ti(OH)_4^*$	<273	304	433
$1/V(OH)_3^*$	~383	649	>773
$1/Cr(OH)_3^*$	473	735	>773
$1/Mn(OH)_2^*$	<203	<203	273
$1/Fe(OH)_3^*$	<203	231	273
$1/Co(OH)_2^*$	<203	<203	273
$1/Ni(OH)_2^*$	<203	230	273
$1/Cu(OH)_2^*$	<273	334	443
$1/Zn(OH)_2^*$	<203	248	273
$1/Al(OH)_3^*$	373	606	>633

T_S: temperature for CO oxdiation start; $T_{50\%}$: temperature for 50% conversion; $T_{100\%}$: temeprature for 100% converion.

Table 1 shows CO conversion to CO_2 measured on the catalysts obtained from **1** supported on a variety of as-precipitated metal hydroxides. Among all catalysts the catalysts prepared by using the supports prepared from $Mn(NO_3)_2$, $Co(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, and Ti(i-

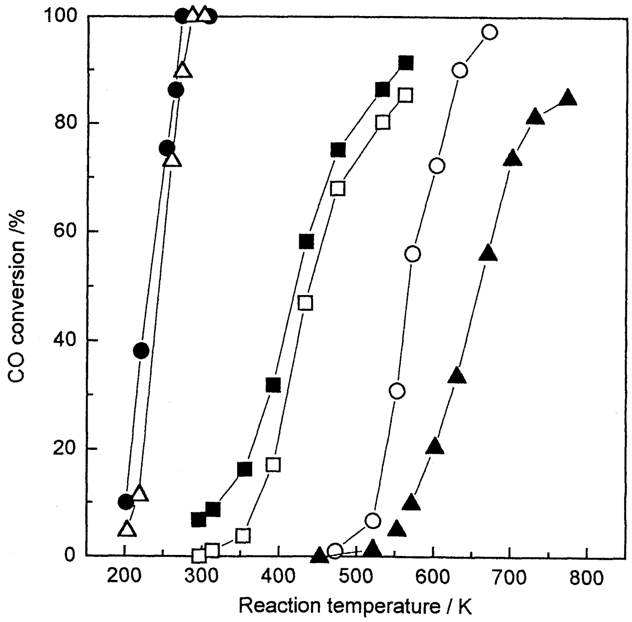

Figure 1. Temperature dependence of CO oxidation activity of supported gold catalysts.

—●— 1/$Fe(OH)_3$*; —△— 2/$Fe(OH)_3$*; —■— 1/Fe_2O_3; —□— $Fe(OH)_3$*; —○— $HAuCl_4$/$Fe(OH)_3$*; —▲— $Au(PPh_3)Cl$/$Fe(OH)_3$*.

$OC_3H_7)_4$ were highly active for CO oxidation below 273 K. Especially Au/$Mn(OH)_2$ showed quite higher activity than Au/MoOx catalysts ones previously reported. As typical examples, Figure 1 compares the catalytic activities for the CO oxidation of various iron-oxide-supported gold catalysts such as **1**/$Fe(OH)_3$*, **2**/$Fe(OH)_3$*, **1**/Fe_2O_3, $HAuCl_4$/ $Fe(OH)_3$*, $Au(PPh_3)Cl$/ $Fe(OH)_3$* and $Fe(OH)_3$* alone. It was found that the catalytic activity of **1**/$Fe(OH)_3$* was remarkably high as compared with that of **1**/Fe_2O_3. The catalyst **1**/Fe_2O_3 was only active above 400 K, while the catalyst **1**/$Fe(OH)_3$* catalyzed CO oxidation even at 203 K. The **1**/$Fe(OH)_3$* showed better catalysis than **2**/$Fe(OH)_3$* for the CO oxidation in Figure 1.

TEM photographs showed that the gold particles in **1**/$Fe(OH)_3$* were nearly 4 times smaller on average than those in **1**/Fe_2O_3. The gold complexes **1** on oxides were decomposed to metallic gold particles at 573 K, while at this temperature the hydrated as-precipitated metal hydroxides ($M(OH)_x$*) were dehydrated to form metal hydroxide anhydrides and partially converted to metal oxide. These transformations of the as-precipitated hydroxide supports may facilitate the gold-support interaction during the thermal decomposition, stabilizing the gold precursor on the surface of the metal hydroxides, and prevent the gold species aggregating on the support. On the other hand, there may exist weak interaction between the crystalline metal oxide and the gold particles in case of **1**/oxide, leading to the aggregation of gold particles during the calcination.

We have also tried to use $HAuCl_4$ and $Au(PPh_3)Cl$ as precursors which were impregnated on $Fe(OH)_3$* in the similar way. The catalysts obtained from $HAuCl_4$/$Fe(OH)_3$* and $Au(PPh_3)Cl$/$Fe(OH)_3$* showed much lower catalytic activities as compared to **1**/$Fe(OH)_3$* and **2**/$Fe(OH)_3$*, and also $Fe(OH)_3$* alone as shown in Figure 1. The samples derived from $HAuCl_4$/$Fe(OH)_3$* and $Au(PPh_3)Cl$/$Fe(OH)_3$* gave a sharp XRD pattern at $2\theta=38.2$ ° for Au(111) growth, contrasting to a broad weak diffraction line observed with **1**/$Fe(OH)_3$*.

The high activity for CO oxidation did not appear when **1** and **2** were supported on Fe_2O_3 treated with water vapor or water, and on $Fe(OH)_3$ commercially available. It is to be noted that the tremendous catalysis of the new supported gold catalysts for the low-temperature CO oxidation was achieved by choosing the suitable gold complexes as precursors and the as-precipitated metal hydroxides as supports.

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