Catalysis Letters 56 (1998) 131–135

Effect of calcination temperature on the catalytic activity of Au colloids mechanically mixed with TiO_2 powder for CO oxidation

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Received 6 May 1997; accepted 26 October 1998

In order to elucidate the role of the contact structure between gold and metal oxide support in low-temperature CO oxidation, a mechanical mixture of colloidal gold with TiO_2 powder was prepared and calcined at different temperatures. The sample calcined at 473 K, which is composed of spherical gold particles with a mean diameter of 5.1 nm and TiO_2 powder, is poorly active for CO oxidation at temperatures up to 473 K. The catalytic activity appreciably increases with an increase in calcination temperature up to 873 K even though gold particles grow to larger ones, reaching a level with almost the same turnover frequency as that of Au/TiO_2 prepared by a deposition–precipitation method.

Keywords: CO oxidation, colloidal gold, titanium dioxide, mechanical mixing, calcination temperature

1. Introduction

We have already reported that gold turns out to be surprisingly active for low-temperature CO oxidation when it is deposited as nanoparticles on other metal oxides [1,2]. Coprecipitation [2–4], deposition–precipitation [1,5] and co-sputtering [6] can produce highly dispersed gold catalysts, which exhibit unique catalytic nature in many different reactions depending on the type of metal oxide supports [7,8]. In CO oxidation, the oxides of 3d transition metals, especially of group VIII, and hydroxides of alkaline earth metals [9,10] lead to high activities even at a temperature as low as 203 K. The requirements to the size of gold particles differ between the former and the latter supports. With TiO_2, Fe_2O_3 and Co_3O_4 supports, gold particles in the range of 2–10 nm in diameter, for example, exhibit high activity, but, by contrast, only gold clusters smaller than 1.5 nm [11] can exhibit high activity with $Be(OH)_2$ and $Mg(OH)_2$ supports.

Among the supported gold catalysts, Au/TiO_2 can be regarded as the most ideal catalytic system for investigating the origin of the evolution of the unique catalytic properties, because neither gold nor TiO_2 alone is active for CO oxidation. Titanium dioxide has also been extensively studied in connection with the so-called “strong metal–support interaction” [12].

The catalytic activity of Au/TiO_2 for CO oxidation markedly changes depending on preparation methods. Turnover frequency differs by four orders of magnitude between deposition–precipitation and photodeposition [13]. An impregnation method usually yields poorly active gold catalysts [13], however, Vannice and his coworkers have reported that a specific sequence of pretreatments (H_2 reduction at 773 K, calcination in 20% O_2 at 673 K, and H_2 reduction at 473 K) appreciably enhances the catalytic activity of Au/TiO_2 [14]. Moreover, they have recently reported that the deposition of titanium oxide onto the surface of gold powder markedly enhances the catalytic activity for CO oxidation [15].

Taking these results into account, we have been tempted to assume that the contact structure between Au particles and support is the most important factor for the genesis of high activity of Au catalysts. In order to verify this hypothesis, mechanical mixtures of TiO_2 powder and gold colloids with a mean particle diameter of 5 nm were prepared and tested for CO oxidation. Mechanically mixed samples should have much weaker Au–TiO_2 interaction than those prepared by the deposition–precipitation (DP) method.

2. Experimental

2.1. Preparation of Au/TiO_2 catalysts

Colloidal gold suspended in α-terpineol at a Au concentration of 10 wt% was supplied by Vacuum Metallurgical Co., Ltd., Japan. The mean diameter of Au particles, which were prepared by vacuum evaporation in inert gas atmosphere, was 5.1 nm with a standard deviation of 25%. For the support powder TiO_2, JRC-TIO4 (a reference catalyst of the Catalyst Society of Japan, Degussa P-25) was used. It was mainly composed of anatase with a specific surface area of about 50 m^2/g.

The colloidal solution of Au was diluted with isopropyl ether by 50 times and to this solution TiO_2 powder was added to make an organic suspension containing Au with 3 wt% of TiO_2. After stirring for 1 h, the organic solvent was vacuum evaporated at 373 K for 4 h, and the Au/TiO_2 mixture obtained was calcined in air at different temperatures in the range of 473–873 K for 4 h. These samples are denoted as Au/TiO_2(Mix). Other samples prepared by deposition–precipitation as a reference are denoted as Au/TiO_2(DP). The preparation procedures are described in our previous papers [5,13].

2.2. *Characterization of Au/TiO_2 catalysts*

The mean diameter of Au particles was determined through the observation of more than 100 particles by using Hitachi H-9000 TEM operated at 300 kV. The numbers of surface metal atoms were calculated for Au particles with face-centered-cubic structure by using mean particle diameters and metal loadings. Further detailed nanostructures were observed with a JEOL JEM-3000F field emission electron microscope operated at 300 kV. IR measurements were carried out with a Nicolet 20SXC to examine the presence of the organic solvents on the catalyst surfaces. Catalytic activity measurements were carried out in a fixed-bed reactor by passing a standard gas containing 1 vol% CO in air through the catalyst bed at a space velocity of $SV = 20{,}000\ h^{-1}$ ml/g-cat.

For the comparison of catalytic activity, two parameters are used: temperature for 50% conversion which is obtained from the conversion vs. catalyst temperature curves and reaction rate at 273 K which is obtained from the Arrhenius plots of the logarithm of rate vs. $1/T$. Turnover frequencies (TOFs) were calculated by dividing the rate with the number of surface metal atoms. The reaction rates were calculated under the conditions of an integral reactor in the presence of an excess of oxygen and on the assumption that the reaction rate was independent of the concentrations of CO and O_2, although it is slighly dependent on the concentration of O_2 [1].

3. Results

Figure 1 shows the Arrhenius plots for CO oxidation over Au/TiO_2(Mix) and Au/TiO_2(DP) catalysts. The Au/TiO_2(Mix) catalyst calcined at 473 K initially exhibited poor catalytic activity at temperatures below 473 K, however, the catalytic activity was, for example, at 325 K, gradually improved with time reaching a steady state within 5 h. The steady-state activities were used for the Arrhenius plots. The catalytic activity increases with increasing calcination temperature from 473 to 873 K. On the other hand, the Au/TiO_2(DP) sample calcined at 673 K, which exhibits catalytic activity even at temperatures below 273 K, reduces its activity with an increase in calcination temperature to 873 K.

Figures 2 and 3 show TEM photographs taken by a Hitachi H-9000 and their size distributions of gold particles, respectively, for Au/TiO_2(Mix) samples calcined in air at 473, 673 and 873 K. In the case of calcination at 473 K, gold particles are well dispersed on TiO_2 keeping the size and the spherical shape of original colloidal particles. On the other hand, in the case of calcination at 873 K, gold particles become larger and are accompanied by changes in their shape from round to irregular facing. The bimodal distribution indicates that coagulation amongst several gold particles may preferentially take place.

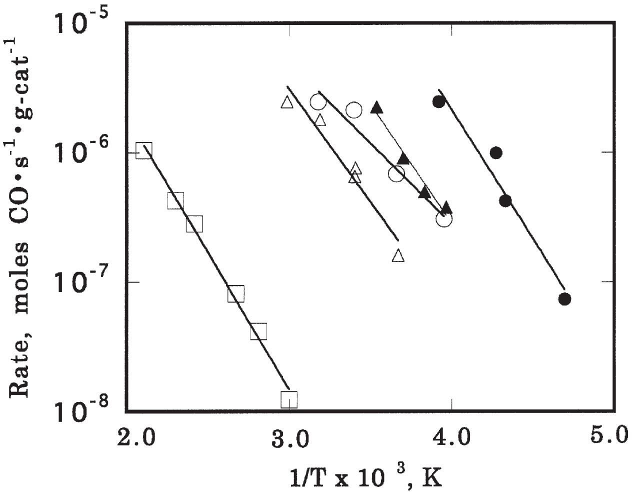

Figure 1. Arrhenius plots for CO oxidation over Au/TiO_2 catalysts as a function of reciprocal temperature. Au/TiO_2 prepared by mechanical mixing, Au 3.0 wt%, calcined at 473 K (□), 673 K (△) and 873 K (○). Au/TiO_2 prepared by deposition–precipitation, Au 3.3 wt%, calcined at 673 K (●) and 873 K (▲).

Figure 4 shows typical HRTEM photographs of Au/TiO_2 (Mix) calcined at 473 and 873 K. A photograph of the sample calcined at 873 K shows that a Au particle attaches to the TiO_2 surface with a flat plane. The atomic structure of the Au–TiO_2 interface could not be observed, because Au particles were too big to clarify the interface structure with an atomic resolution. On the other hand, Au particles seen in a photograph of the sample calcined at 473 K have round shape.

Through the extrapolations of the slopes of the linear Arrhenius plots, reaction rates at 273 K and apparent activation energies were obtained. Table 1 summarizes the mean diameters of the Au particles and the kinetic data for CO oxidation. In the case of Au/TiO_2(Mix), although an increase in calcination temperature causes the growth of Au particles, it lowers the temperatures for 50% conversion of CO to room temperature. Both reaction rates and TOFs differ by more than three and four orders of magnitude, respectively, between 473 and 873 K for calcination. On the other hand, among Au/TiO_2(DP) samples, an increase in calcination temperature causes the growth of gold particles and lowers catalytic activities in terms of TOFs at 273 K as well as the rates at 273 K and the temperatures for 50% conversion of CO. Both of apparent activation energies of Au/TiO_2(Mix) and Au/TiO_2(DP) are in the range of 10–18 kJ/mol, which are almost the same as the values reported previously for integral reactor condition [13] and are smaller than those for differential reactor conditions [1]. The discrepancy may arise from a slight dependency of the reaction rate on O_2 partial pressure.

Figure 5 shows IR spectra for Au/TiO_2(Mix) calcined at different temperatures. Organic solvents are not completely

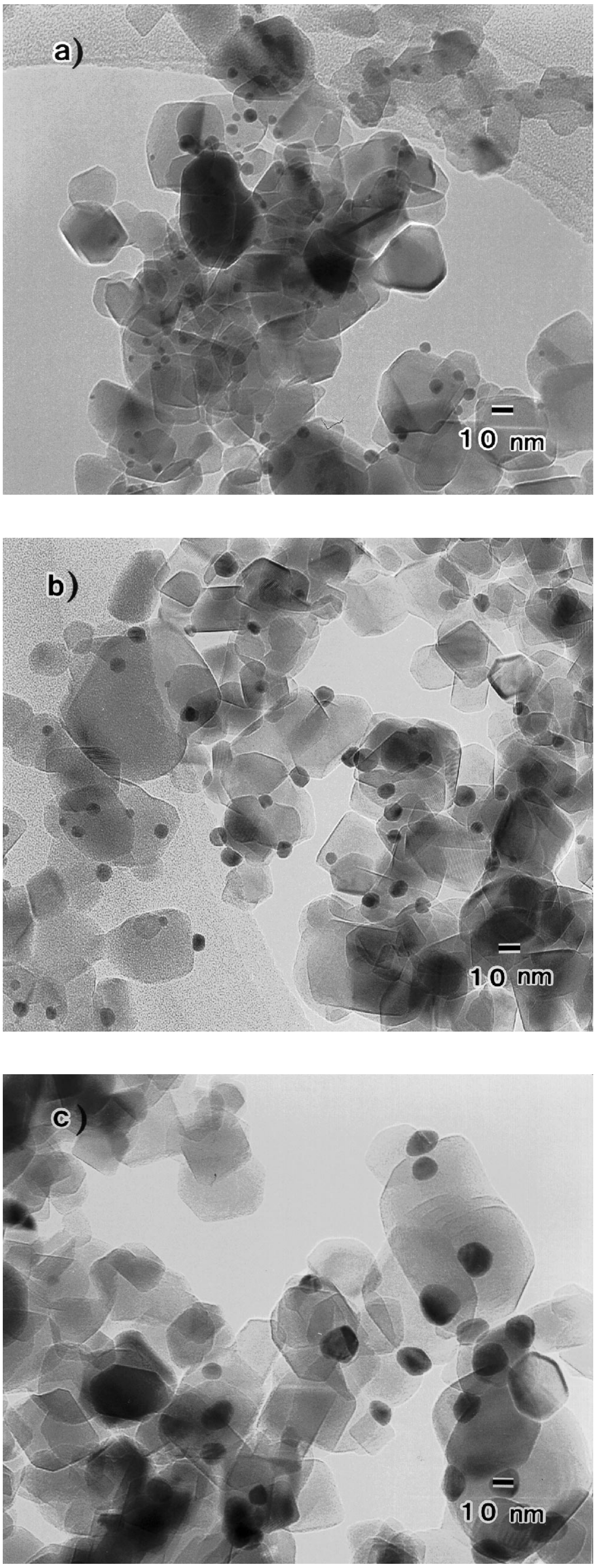

Figure 2. TEM photographs of a mechanical mixture of Au colloids with TiO_2 powder calcined in air at different temperatures. Au loading is 3.0 wt%; (a) 473 K, (b) 673 K, (c) 873 K.

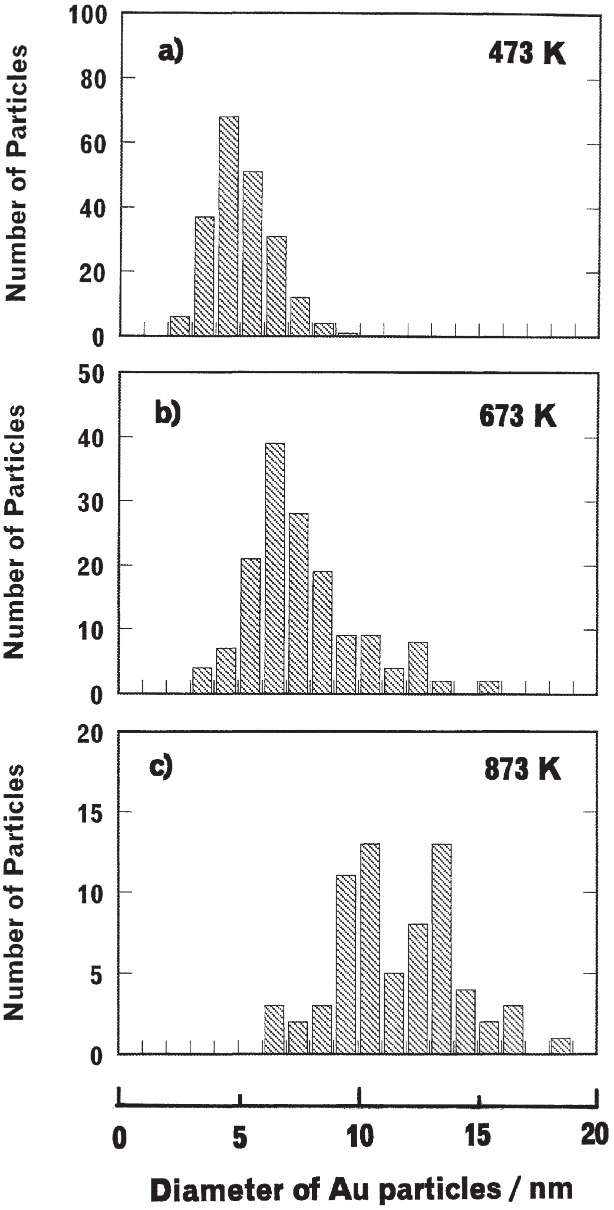

Figure 3. Size distribution of Au particles for a mechanical mixture of Au colloids with TiO_2 powder calcined in air at different temperatures. Au loading is 3.0 wt%; (a) 473 K, (b) 673 K, (c) 873 K.

removed from the sample calcined at 473 K (figure 5(a)), while no detectable amounts of solvents remain on the samples calcined at temperatures above 573 K.

4. Discussion

Although the presence of organic solvents on the Au/TiO_2 catalyst surface may partly depress the catalytic activity for CO oxidation, this effect is presumed to be marginal and the appreciably low activity of the simple mixture of gold particles and TiO_2 powder calcined at 473 K is more likely to be a result of the weak contact between them. The increase in catalytic activity with increasing calcination temperature can be ascribed to the formation of stronger

Table 1
Kinetic data for CO oxidation over Au–TiO_2 catalysts prepared by mechanical mixing and deposition–precipitation.

Catalyst[a]	Au diameter (nm)	$T_{1/2}$ (K)	Rate (273 K) ($\text{mol s}^{-1}\text{g}^{-1}$)	TOF (273 K) (s^{-1})	E_a (kJ/mol)
Mix473	5.1 ± 1.3	479	5.9×10^{-10}	1.6×10^{-6}	18
Mix673	7.5 ± 2.2	303	2.1×10^{-7}	8.7×10^{-3}	15
Mix873	12 ± 2.5	278	7.3×10^{-7}	4.6×10^{-2}	10
DP673	3.6 ± 0.7	236	1.0×10^{-5}	1.9×10^{-1}	17
DP873	6.7 ± 1.4	263	1.3×10^{-6}	4.6×10^{-2}	16

[a] Mix473, Mix673, and Mix873: Au–TiO_2 prepared by mechanical mixing of Au colloid with TiO_2 powder and by calcination in air for 4 h at 473, 673 and 873 K, respectively. Au loading is 3.0 wt%. DP673, DP873: Au–TiO_2 prepared by deposition–precipitation and calcined in air for 4 h at 673 and 873 K, respectively. Au loading is 3.3 wt%.

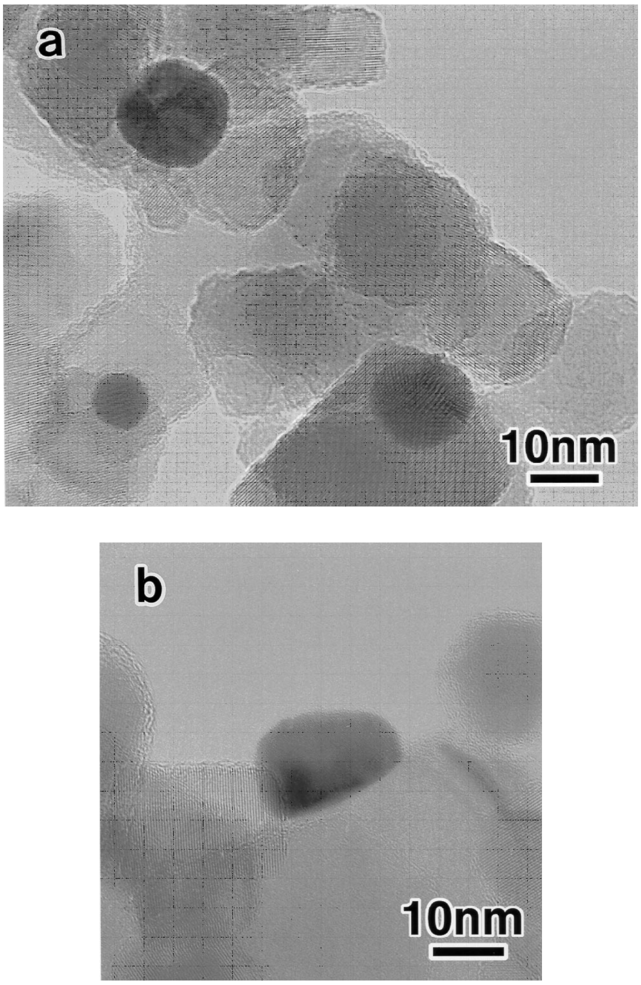

Figure 4. HRTEM photographs of a mechanical mixture of Au colloids with TiO_2 powder calcined in air at at different temperatures. Au loading is 3.0 wt%; (a) 473 K, (b) 873 K.

interaction between the two phases. This is supported by TEM and HRTEM observations of the particle shapes of Au and the Au–TiO_2 contact structure. The TOF for the sample calcined at 473 K is very low, $1.6 \times 10^{-6}\ s^{-1}$, close to those of the Au/TiO_2 samples prepared by impregnation and photodeposition [13].

It is worth noting that TOFs of Au/TiO_2(Mix) calcined at 873 K are almost the same as that of Au/TiO_2(DP) calcined at 873 K and that apparent activation energies are also similar to each other. These results indicate that the same type of catalytically active sites would be generated between Au/TiO_2(Mix) calcined at high temperatures and Au/TiO_2(DP).

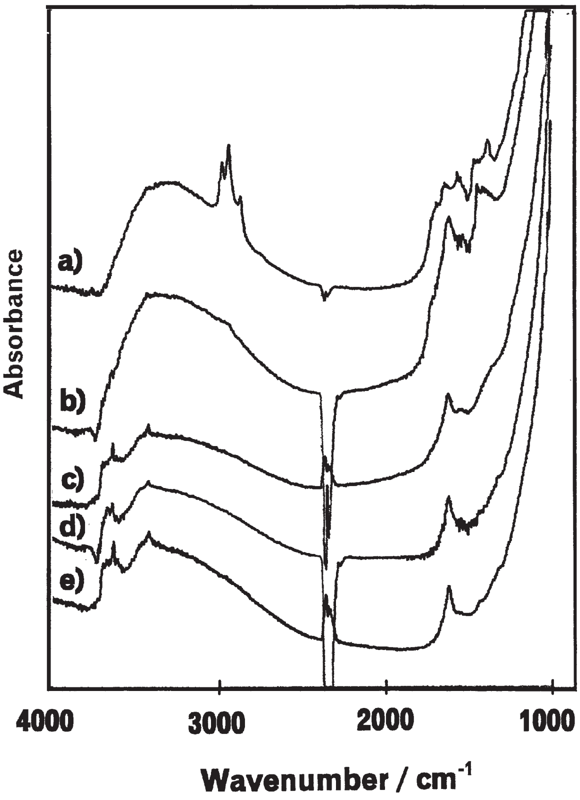

Figure 5. IR spectra of a mechanical mixture of Au colloids with TiO_2 powder calcined at different temperatures. Au loading is 3.0 wt%; (a) before calcination, (b) 473 K, (c) 573 K, (d) 673 K, (e) 873 K.

In the mechanical mixture of Au colloids and TiO_2 powder, as can be seen from figure 2, during calcination at higher temperatures, Au nanoparticles melted and coagulated, because their melting points are far below that of bulk gold, 1337 K [17]. Gold melts are considered to be strained and thermodynamically unstable. This would allow the gold to rearrange its atomic structure and perhaps to generate stronger interactions with the TiO_2 support. If we assume that the site for activating oxygen molecules is the perimeter interface between gold particles and the metal oxide support, a strong contact should be indispensable for the genesis of high catalytic activity for CO oxidation at low temperatures.

5. Conclusions

Based on the catalytic activity data of a mechanical mixture of Au particles and TiO_2 powder calcined at different temperatures, the following conclusions are obtained:

(1) A simple mechanical mixture of colloidal gold and TiO_2 powder is poorly active for CO oxidation.

(2) The Au/TiO_2 mixture becomes catalytically active when calcined at temperatures of 673 K and above, giving TOFs comparable to that of Au/TiO_2 prepared by deposition precipitation.

(3) The above results support our previous proposal that the distance of the perimeter interface around gold particles can be related to the high catalytic activity.

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