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Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far Below 0 °C

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A variety of gold catalysts can be used to catalyze the oxidation of carbon monoxide at temperatures as low as -70 °C and are stable in a moistened gas atmosphere. The novel catalysts, prepared by coprecipitation, are composed of ultra-fine gold particles and one of the oxides of 3d transition metals of group VIII, namely, Fe, Co, and Ni.

Oxidation of CO is an important matter in industrial, environmental, and domestic sectors of society. Stationary emissions of CO are continuing problems in many industrial processes involving combustion and partial oxidation of hydrocarbons. In mining and the coal industry, CO safety gas masks are indispensable and have long been used. Quite recently, catalytic oxidation of CO to reproduce CO_2 has found its application to sealed CO_2 laser.1,2) In the environmental, emission of CO from gasoline and diesel engines of vehicles is one of the major causes of air pollution. Since ventless petroleum heaters have widespread domestic use in Japan, the control of CO emission from these household appliances is also becoming of great concern.

In most of the above cases, the oxidation of CO should be carried out at relatively low temperatures. In practice, Hopcalite catalysts (mixed oxides mainly composed of Mn and Cu) have been most frequently used. However, they are not water tolerant and are not sufficiently active at ambient temperatures.3) Palladium and platinum are active catalysts, but only for dilute concentrations of CO, i.e., hundreds of ppm near ambient temperatures4) and are generally used at temperatures above 100 °C.2,5,6) It has been demonstrated that heterogenized Wacker catalyst ($PdCl_2$-$CuCl_2$) has high activity for CO oxidation at temperatures around 60 °C, but it works only in the presence of water vapor.7) Mochida et al. have recently reported that cobalt tetraphenylporphyrin supported on TiO_2 exhibits significantly high catalytic activity below room temperature.8) However, the catalyst tends to gradually lose its activity after 15 min. Taking into account the above consideration, it is clear that there is still a strong need for low temperature oxidation catalysts that are durable in an ambient atmosphere over a long period of time.

Our novel gold catalysts were prepared by coprecipitation from an aqueous solution of chloroauric acid and the nitrate of transition metals. The precipitates were washed, vacuum dried and calcined in air at 400 °C for 4 h.9) Several tens of gold catalysts were prepared and investigated, including combinations with MnO_2, α-Fe_2O_3, Co_3O_4, NiO, CuO, and Co-Mn composite oxides. Catalytic activity measurements were carried out in a small fixed-bed reactor, with 0.20 g of catalysts that had passed through 70 and 120 mesh sieves. A standard gas consisting of 1.0 vol% CO balanced with air to 1 atm. was passed through the catalyst bed at a flow rate of 66 ml/min. The 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 layer. 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 highest oxidation activity was achieved using gold combined with α-Fe_2O_3, Co_3O_4, or NiO. The optimum content of gold was found to be 5 atom% (=100Au/(Au+Metal)) with α-Fe_2O_3 and Co_3O_4, while it was 10 atom% with NiO. Figure 1 shows the conversion efficiency of CO as a function of duration time at various catalyst temperatures. These gold catalysts are able to oxidize completely CO even at -70 °C, and exhibit remarkably enhanced activity in comparison with those of gold powder and the host metal oxides. When such single compounds are used, the oxidation of CO needs much higher temperatures, ranging from 100 °C for Co_3O_4 to 300 °C for gold powder under the same experimental conditions (Fig.2).

The new gold catalysts are not only much more active but also are much more stable than the conventional Hopcalite catalysts. In particular, the catalyst composed of Au and α-Fe_2O_3 (Au 5 : Fe 95 in atom%) was sufficiently stable that it could maintain the initial activity observed at -70 °C even after a subsequent continuous run with dried reaction gas at 0 °C for 7 d. The Hopcalite catalyst shown in Fig. 1 is the most active one among the commercially available catalysts used for CO gas masks. It was not stable and became appreciably deactivated, even during experiments in dried gas.

Figure 1-c shows that the conversion efficiency declined in a similar manner for all the Au-containing catalysts at -70 °C. However, this deactivation was not irreversible but only temporary. The initial activity could be recovered by heating the catalysts in a flow of dry air at 200 °C for 30 min. The temporary deactivation could not be attributed to the adsorption of carbon dioxide and water. Because, the time variation curve of CO oxidation efficiency for Au/α-Fe_2O_3 at -70 °C was almost the same as the one shown in Fig. 1-c even after the catalyst was previously exposed to air containing CO_2 or trace water at -70 °C for 80 min.

In order to investigate the influence of moisture on the catalytic activity, the reaction gas was passed into a constant moisture device10) which contained saturated NH_4Cl aqueous solution. The relative humidity of the reaction gas was

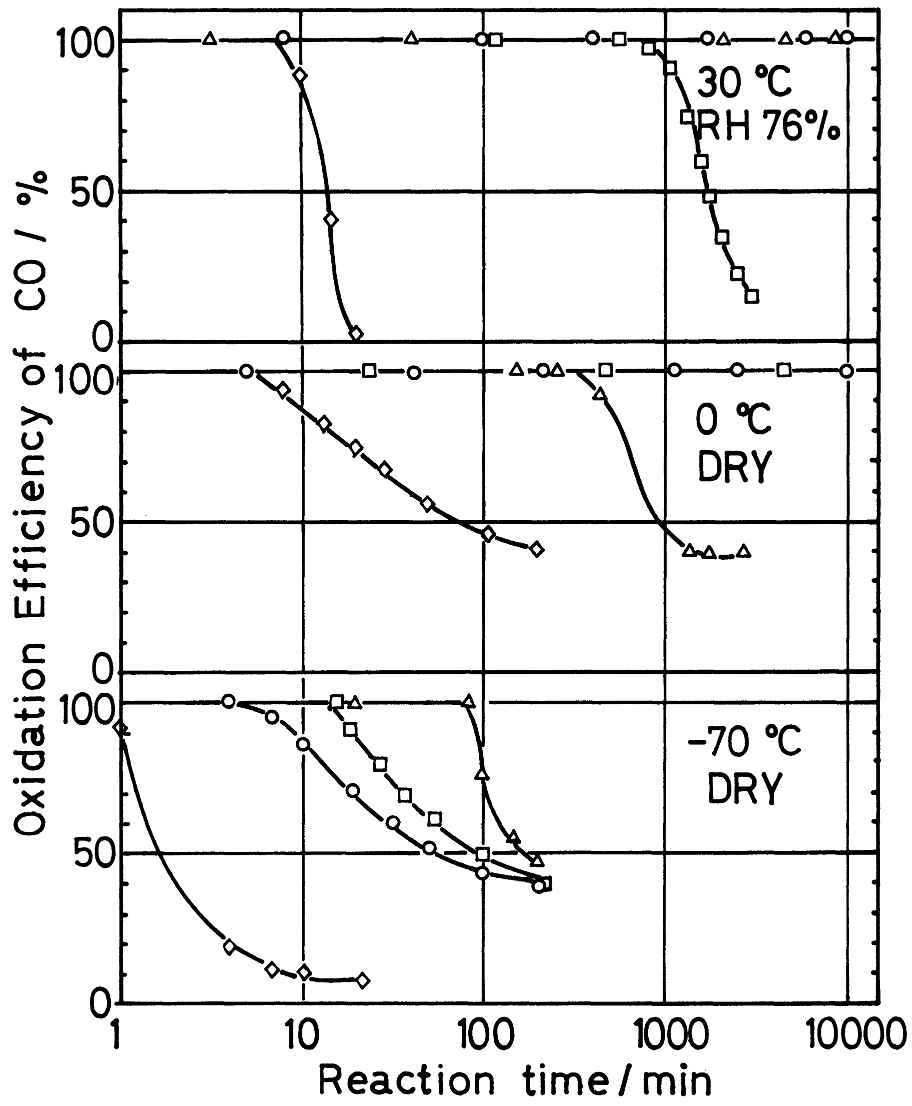

Fig.1. Oxidation efficiency of CO as a function of duration time.
○, 5 atom% Au/α-Fe_2O_3; △, 5 atom% Au/Co_3O_4; □, 10 atom% Au/NiO,
◇, Hopcalite catalyst; Catalysts 0.20 g, CO 1 vol% air 66 ml/min.

kept constant at 76%, as confirmed by humidity measurements using a Humidector (Shinyei Co. Ltd.). Figure 1-a shows the results of the activity measurements performed at 30 °C. The Au/α-Fe_2O_3 and Au/Co_3O_4 catalyst were able to completely oxidize all the CO during experiments conducted for 7 d, while the Hopcalite catalyst had lost its activity after 20 min.

In the X-ray diffraction patterns of the gold catalysts prepared by coprecipitation, the presence of metallic gold crystallites together with the corresponding oxides, namely, α-Fe_2O_3, Co_3O_4, or NiO can be seen. The mean diameter of the gold crystallites in Au/α-Fe_2O_3, estimated from peak half-widths using Sherrer's equation, is around 50 Å.

It is useful to compare the new catalysts with those obtained by an impregnation method. In the conventional gold catalysts supported on γ-Al_2O_3 or α-Fe_2O_3 by impregnation, even when they were calcined at 200 °C, the gold crystallites were much larger, c.a. 200 A. Results for these impregnated catalysts are given in Fig. 2 and show that such catalysts are active only at temperatures above 100 °C. Therefore, it is clear that coprecipitation led to much higher dispersion of gold than impregnation and that the high dispersion of gold brought about the extremely high activity for CO oxidation at temperatures below 0 °C. Since the selection of the host oxides is another important factor, the specific interaction of gold particles with the semiconductive oxides of Fe, Co, Ni might also be responsible for the remarkable enhancement of oxidation activity.

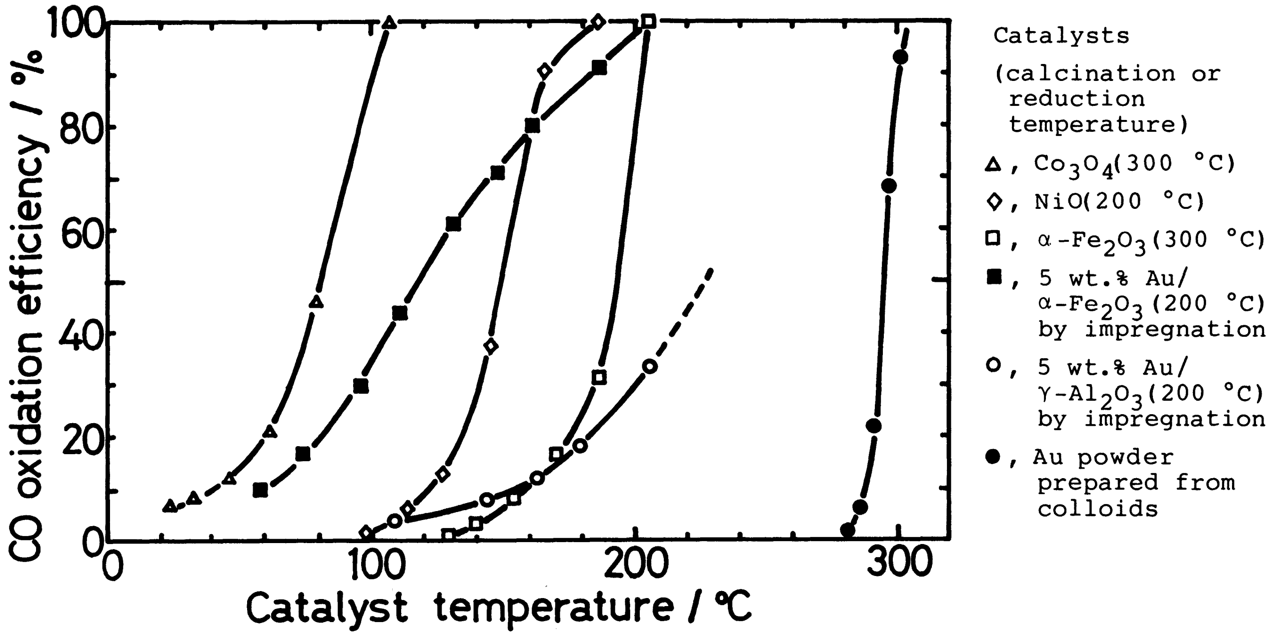

Fig. 2. Oxidation efficiencies of CO as a function of catalyst temperature. Catalysts 0.20 g, CO 1 vol% air 66ml/min.

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