

# Moisture Effect on CO Oxidation over Au/TiO<sub>2</sub> Catalyst

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The effect of moisture in the reactant gas on CO oxidation over Au/TiO<sub>2</sub> has been quantitatively investigated over a wide range of concentrations from 0.1 to 6,000 ppm. Moisture enhances the reaction by more than 10 times up to 200 ppm H<sub>2</sub>O, while further increase in the moisture content suppresses the reaction. The apparent activation energy is, however, independent of the amount of moisture. The amount of moisture adsorbed on the catalyst influences the activity rather than the moisture content in the gas phase, which suggests that the low-temperature CO oxidation over the gold catalyst involves water-derived species on the catalyst surface.

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**Key Words:** CO; oxidation; Au; TiO<sub>2</sub>; moisture.

The Au/TiO<sub>2</sub> system is not only of practical but also fundamental interest, because it is regarded to be the most suitable for a study of the metal–support interactions: neither the bulk gold nor titania is active for CO oxidation. Studies of this system have been carried out under various conditions—from ultrahigh vacuum (14, 15) to practical ambient (3, 4). If moisture has a significant effect on the catalytic activity, a difference in the moisture concentration should be taken into account, as well as that of pressure, when comparing and discussing the catalytic performances. In this paper, the effect of moisture is investigated in the range over four orders of magnitude.

## 1. INTRODUCTION

It is now well known that gold exhibits a high catalytic activity when it is deposited as nanoparticles on the metal–oxide supports (1–3). Among the various reactions catalyzed by the gold catalysts, a number of studies have focused on CO oxidation at low temperatures (4). It has been proved that the catalytic activity of gold strongly depends on the particle size: the smaller particles produce higher activities and the interface between the gold particles and the support surface plays an important role (1).

During the early stage of study on the gold catalyst, Haruta *et al.* were aware that moisture in the reactant gas influenced the catalytic activity of gold (5). To date, there have been several reports about the moisture effect on gold catalysts (6–12). The reported effect was positive (activity enhancement) for Au/Fe<sub>2</sub>O<sub>3</sub> (5, 6), Au/TiO<sub>2</sub> (6), Au/Al<sub>2</sub>O<sub>3</sub> (6), and Au/Mg(OH)<sub>2</sub> (7), while none or negative for Au/Fe(OH)<sub>3</sub> (8, 9), Au/Ti(OH)<sub>4</sub> (10), and Au/TiO<sub>2</sub> (11, 12). In most cases, the concentration of moisture was in the range of percent, water being one of the major coadsorbates on the catalyst surface under ambient conditions, but the effect of moisture was only qualitatively discussed. This situation is similar for that of other catalysts (13).

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## 2. EXPERIMENTAL

Gold was supported on TiO<sub>2</sub> (P-25, JRC-TIO-4) by the deposition–precipitation method (16) and the Au/TiO<sub>2</sub> sample was calcined at 670 K in air for 4 h. The actual loading of the gold in the catalyst sample analyzed by ICP (inductively coupled plasma) spectroscopy was 0.9 wt%. The average diameter of the gold nanoparticles calculated over 461 particles out of the TEM (transmission electron microscopy) photographs was 3.0 ± 0.9 nm. Reaction rates are normalized by the total surface area of gold particles, which has been estimated assuming all the particles have the same diameter of 3.0 nm.

The catalytic activities of the Au/TiO<sub>2</sub> samples were measured with fixed-bed flow reactors. One was specifically designed and constructed utilizing ultraclean technology developed by Ohmi *et al.* (17, 18) for measurements under an extremely dry condition (Fig. 1), while the other is an ordinary reactor at a H<sub>2</sub>O concentration above 3 ppm. A catalyst sample of 50 mg was used for the measurements and the reactant gas (1 vol% CO in air) was fed at the rate of 67 ml/min, which corresponds to the space velocity of 8 × 10<sup>4</sup> ml/h • g-cat. Moisture was added into the reactant gas using wet molecular sieves and a water bubbler. The H<sub>2</sub>O concentration was monitored using either cryoptical (HYCOSMO II, Osaka Sanso Kogyo) or electric capacitance dew-point hygrometers. The effluent gas was analyzed by TCD gas chromatographs (GC-8A, Shimadzu). CO conversion was calculated from the decrease of CO

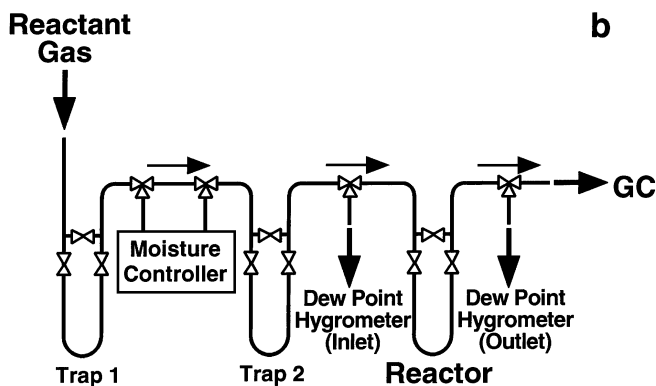
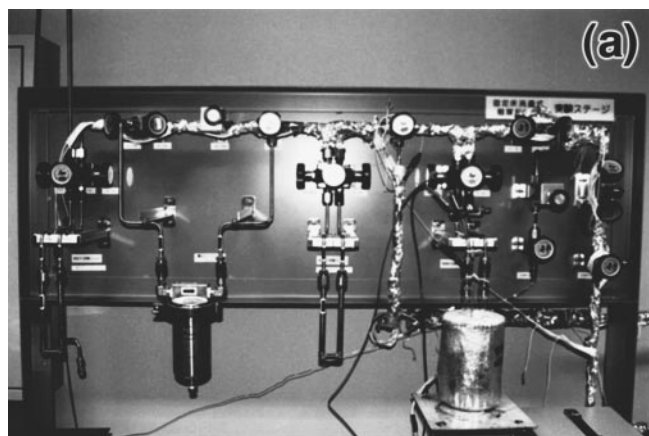


FIG. 1. (a) Photograph and (b) schematic diagram of the reaction line used for the measurement under an extremely dry condition.

detected by the chromatographs.  $N_2$ ,  $O_2$ , and  $H_2$  were simultaneously monitored for both the reaction lines, while  $CO_2$  was detectable only for the ultraclean line. Prior to the measurements, the catalyst sample was heated in an air stream at 520 K for 30 min, except for the thorough drying in the ultraclean condition (see below).

### 3. RESULTS AND DISCUSSION

Reaction rates measured at 270 K are shown in Fig. 2 as a function of the logarithmic moisture concentration in the reactant gas. It is noted that at  $\sim 0.1$  ppm  $H_2O$ , the catalytic activity is lower by about 10 times than under the usual reactant conditions (3–10 ppm  $H_2O$ ). With the addition of moisture, the activity increased and reached a maximum at  $\sim 200$  ppm  $H_2O$ , then dropped at  $\sim 6,000$  ppm  $H_2O$ . Suppression of the reaction by the excess amount of water can be explained by blocking of the active sites. The steady-state reaction rate at each  $H_2O$  concentration was obtained within several hours after the heating pretreatment at 520 K for 30 min except for the  $\sim 0.1$  ppm  $H_2O$  level.

Heat pretreatment for only 30 min at  $\sim 0.1$  ppm  $H_2O$  resulted in the activity comparable to that of  $\sim 3$  ppm  $H_2O$ .

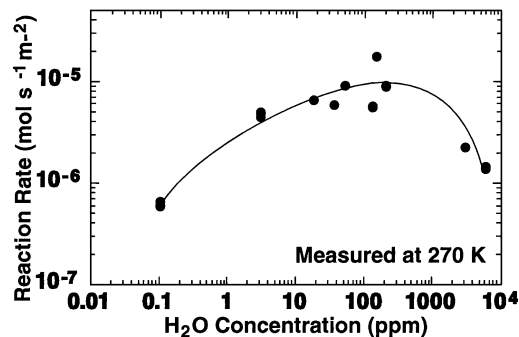


FIG. 2. Dependence of the CO oxidation reaction rate at 270 K over 50 mg of 1 wt% Au/TiO<sub>2</sub> on the moisture concentration in the reactant gas (measured at the inlet). Reaction was conducted in the ultraclean line for the  $H_2O$  concentration below  $\sim 3$  ppm, while the ordinary line was used for  $> 20$  ppm.

However, prolonged heat pretreatment at  $\sim 0.1$  ppm  $H_2O$  made the activity about half (Fig. 3). After the time-on-stream change in activity became smaller, the heating temperature was elevated at  $\sim 0.1$  ppm  $H_2O$ . As shown in Fig. 4, the lower activity was observed for the higher temperature. These results indicate that moisture adsorbed on the catalyst persistently remains in the airflow under the ambient pressure, which is a contrast to the condition of UHV. Since the catalyst sample was calcined at 670 K, the heat pretreatment was carried out at temperatures below 620 K. It was confirmed by TEM that no significant difference in the size distribution of gold particles was observed after the thorough drying. Therefore, the decrease in activity was not caused by the sintering of gold particles. The lowest reaction rate values in Fig. 4 were plotted in Fig. 2 for the  $\sim 0.1$  ppm  $H_2O$  level.

When the moisture concentration was switched from  $\sim 0.1$  to  $\sim 3$  ppm, the thoroughly dried catalyst gradually regained its activity (Fig. 5). The moisture concentration at the outlet of the reactor was simultaneously monitored, along with that at the inlet. While the latter was almost

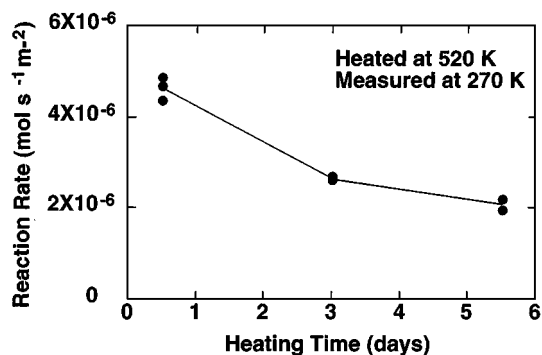


FIG. 3. Reaction rates at 270 K for 50 mg of the 1 wt% Au/TiO<sub>2</sub> catalyst pretreated by heating at 520 K for different times.

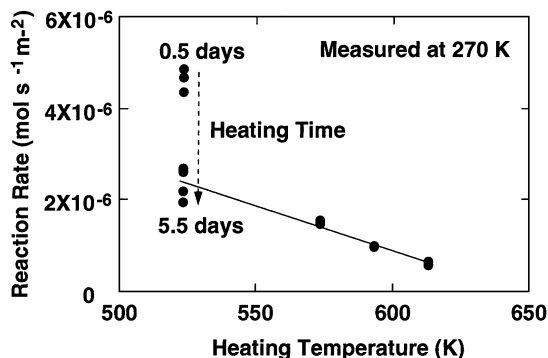


FIG. 4. Reaction rates at 270 K for 50 mg of the 1 wt% Au/TiO<sub>2</sub> catalyst pretreated by heating for more than 3 days as a function of heating temperature. The arrow shows the dependence on the heating time at 270 K also represented in Fig. 3.

constant at  $\sim 3$  ppm, the former remained at  $\sim 0.1$  ppm for more than 20 h and then abruptly increased to  $\sim 0.5$  ppm. A gradual but steady increase in the catalytic activity was observed without responding to the abrupt change in the moisture concentration at the outlet (The increase had not finished even after overnight and the outlet concentration of moisture was still lower than the inlet concentration. It is noted that moisture is adsorbed not only by the catalyst but also by the glass tube reactor). The above results indicate that the activity is mainly influenced by the amount of moisture adsorbed on the catalyst.

Arrhenius plots for the  $\sim 0.1$  and  $\sim 3$  ppm H<sub>2</sub>O levels are shown in Fig. 6. In spite of the large difference in activity, the apparent activation energies were almost the same. Little difference in the apparent activation energies was also observed for the higher concentrations of moisture. It is noted that the reaction orders and apparent activation energies at 200–330 K measured with a closed recycling system were quite similar to those measured with a fix-bed flow reactor (19). Since the reactant gas purified with liquid nitrogen is

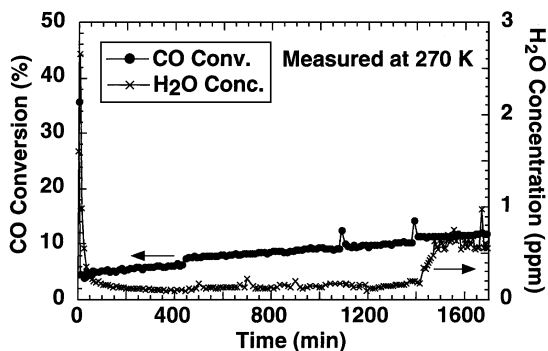


FIG. 5. Time-on-stream monitoring of CO conversion (filled circles) and H<sub>2</sub>O concentration at the reactor outlet (crosses). Measurement was started just after the H<sub>2</sub>O concentration at the reactor inlet switched from  $\sim 0.1$  to  $\sim 3$  ppm.

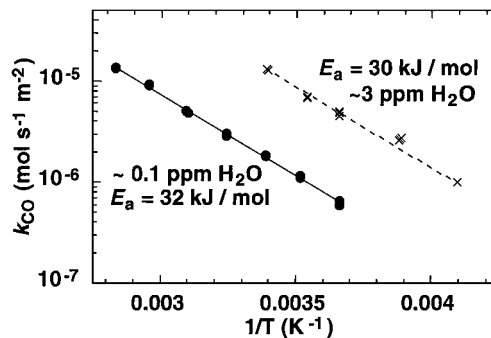


FIG. 6. Arrhenius plots for the catalytic activities measured for 50 mg of 1 wt% Au/TiO<sub>2</sub> at  $\sim 0.1$  and  $\sim 3$  ppm.

introduced into the evacuated system, the concentration of residual moisture in a closed recycling system is estimated to be less than 0.1 ppm (20), while that in a commercial gas cylinder is  $\sim 3$  ppm (2). These results indicate that moisture might not significantly affect the reaction mechanism but changes the preexponential factor of the rate law.

The moisture effect on CO oxidation over Au/TiO<sub>2</sub> forms a striking contrast to that over transition-metal oxides (without metal loading). The effect was studied for several oxides using the same ultraclean line (20). In the case of Co<sub>3</sub>O<sub>4</sub> and NiO, drying of the reactant gas to less than 1 ppm resulted in a drastic enhancement of the catalytic activity, while little effect was found for Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (20). However, the activity observed for Au/TiO<sub>2</sub> at  $\sim 0.1$  ppm H<sub>2</sub>O was much lower than that at  $\sim 3$  ppm. This indicates that it is not the bare support surface but the gold surface and/or perimeter interface between the gold and titania that is responsible for the moisture effect for Au/TiO<sub>2</sub>.

It was demonstrated that the amount of moisture adsorbed on the catalyst mainly determines the activity. Because the concentration of H<sub>2</sub>O below  $\sim 200$  ppm is much lower than those of the reactants, CO and O<sub>2</sub> (1 and 21 vol%, respectively), the possibility is excluded that the moisture effect originates from the direct reaction with H<sub>2</sub>O in the vapor phase to produce CO<sub>2</sub>. Although the water-gas shift reaction *does* proceed over Au/TiO<sub>2</sub> (21, 22), the reaction condition of this study is different from previous reports: higher reaction temperatures around 573 K for a flow-type reactor (21), while reduced pressures for FT-IR observation (22). Actually, hydrogen was not detected by the gas chromatograph in this study. The role of the water-derived species, such as -OH, on the catalyst surface should be considered instead. Since such species are considered to be present on the catalyst surface even at  $\sim 0.1$  ppm H<sub>2</sub>O, the moisture effect without any change in the reaction mechanism could be attributed to a change in the amount of the water-derived species, which may activate O<sub>2</sub> molecules or modify the electronic state of the gold atoms exposed at the

surface. Actually, Bond *et al.* proposed the reaction mechanism for CO oxidation that involves hydroxyl species (4). More recently, Boccuzzi *et al.* have found that the presence of moisture is crucial for the reaction over Au/TiO<sub>2</sub> at 90 K (23). Further spectroscopic studies will be required to elucidate the entire mechanism involving water molecule for CO oxidation catalyzed by gold.

When gold catalysts are heated as a pretreatment, their catalytic activities usually change with time on stream until a steady state is achieved (17, 24, 25). Such gradual changes in activity can be explained by the moisture effect to some extent, because the moisture content in a catalyst increased in a reactant stream after the pretreatment. The observed direction of the change (increasing or decreasing), however, was not always identical even for the Au/TiO<sub>2</sub> catalyst sample from the same rod. There must be another factor, e.g., desorption of oxygen from the catalyst surface, that controls the initial activity of the as-dried catalysts. Despite the direction of the activity change, the steady-state activities were basically reproducible.

Although the irreproducibility of the change in activity, as well as of apparent activation energy, made understanding of the moisture effect difficult, we have succeeded in a quantitative elucidation of the moisture effect over four orders of concentration. As far as we know, this is the first report on the moisture effect on a gold catalyst below ~1 ppm H<sub>2</sub>O. The observed difference in activity between ~0.1 and ~3 ppm H<sub>2</sub>O was of one order. A much more significant difference will be expected for the samples treated *in vacuo*. Therefore, the effect of moisture should be taken into account in discussing of the reaction rates measured under the various conditions including the ultrahigh vacuum (UHV) condition, the lowest limit of the moisture concentration.

#### 4. CONCLUSIONS

Moisture in the reactant gas has a significant effect on the activity of the Au/TiO<sub>2</sub> catalyst for CO oxidation. The activity is mainly affected by the amount of moisture adsorbed on the catalyst. The optimum concentration of moisture for the catalytic reaction is ~200 ppm. Enhancement of the reaction rate by moisture is no less than 10 times compared to that for ~0.1 ppm H<sub>2</sub>O. When the concentration of moisture is ~6,000 ppm, the catalytic activity is depressed probably due to the blocking of the active sites.

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