Heterogeneous Catalysis

Vital Role of Moisture in the Catalytic Activity of Supported Gold Nanoparticles**

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Why can inert gold become catalytically active only when dispersed in the form of nanoparticles?—This simple question has attracted growing interest in the field of not only catalytic and industrial chemistry,[1–4] but also cluster and theoretical science.[5–7] To answer this question, CO oxidation has been intensively studied as a model reaction.[8–14] The reaction is known to be greatly influenced by moisture in the reactant gas.[10,15] However, only a few recent studies discuss the reaction mechanisms taking water into account.[16,18] Even in these studies on the effect of moisture, for practical reasons, the addition of water vapor has been examined only at high concentrations.

It was first reported in 1989 that gold nanoparticles deposited on metal-oxide supports form active catalysts.[8] Supported Au catalysts exhibit significant activity not only at low temperatures,[8] but also in the presence of moisture.[15] These two features make the catalysts advantageous for applications at ambient conditions, that is, moderate temperatures and humid atmospheres, and have led to their commercialization for odor removal in restrooms in Japan in 1992. On the other hand, fundamental studies are usually carried out under relatively dry conditions.[5,11,13,14] Therefore, it is important to elucidate the effect of moisture to understand the unique catalysis of gold. The effect of moisture in gold catalysts has been investigated mainly for CO oxidation,[10,16] because of the extremely low reaction temperature ($(<273\,\mathrm{K})$) and because of the remarkable effect of moisture. In most cases to date, however, the effect has been studied only qualitatively, that is, to determine whether the addition of a few mole percent of water vapor enhances or suppresses the reaction. In this study, we employ a special apparatus that allows the control of water vapor to extremely low levels,[19] and show that such low levels can still influence the catalytic reaction.

The effect of moisture on the catalytic activity for CO oxidation was examined on three gold catalysts prepared by using TiO_2, Al_2O_3, and SiO_2 supports (Figure 1). Gold nanoparticles were deposited onto these supports by originally developed methods,[20,21] so that high catalytic activities could be achieved. Experimental details, including the sample characterizations and activity measurements, are described in the Experimental Section.

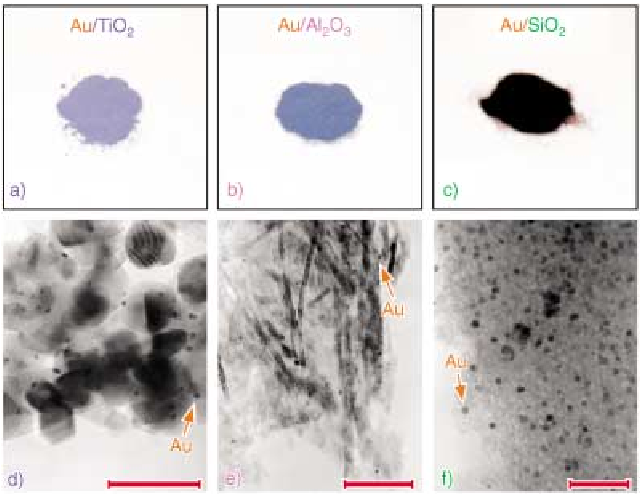

Figure 1. Photographs of a) Au/TiO_2 (violet in appearance), b) Au/Al_2O_3 (grayish blue) and c) Au/SiO_2 (dark red) catalyst samples along with TEM micrographs of d) Au/TiO_2, e) Au/Al_2O_3 and f) Au/SiO_2. Scales in the micrographs indicate 50 nm.

The degree of rate enhancement depends on the type of support used: high for insulating Al_2O_3 and SiO_2; moderate for semiconducting TiO_2 (Figure 2). The effect of moisture becomes significant only above about 200 ppm H_2O for Au/Al_2O_3, while the activity for Au/SiO_2 diminishes considerably with a decrease in moisture to about 0.3 ppm. The activity of

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[**] The authors would like to acknowledge Dr. Satoshi Ichikawa for his TEM observations, as well as Mr. Takeshi Yamashita and Mr. Akihiko Yamaguchi for their assistance in catalyst preparation and activity measurements. The authors would also express their deep thanks to Prof. Ted S. Oyama for his critical comments and valuable discussion.

DOI: 10.1002/ange.200453796

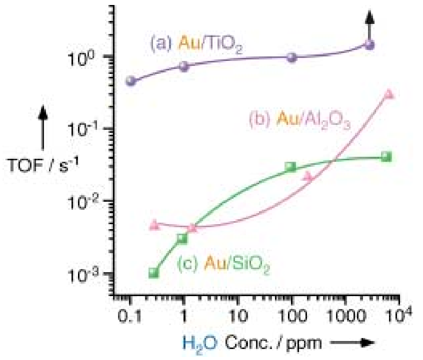

Figure 2. Turnover frequencies per surface gold atom at 273 K for CO oxidation over a) Au/TiO$_2$, b) Au/Al$_2$O$_3$ and c) Au/SiO$_2$ as a function of moisture concentration. Upright arrow indicates the saturation of CO conversion.

Au/TiO$_2$ at about 3000 ppm H$_2$O is so high that it reaches full conversion of CO (100 %). The arrow in Figure 2 a means that the actual value of the reaction rate at about 3000 ppm H$_2$O is much higher than that shown by the solid circle. In the case of Au/TiO$_2$, several samples were prepared under different conditions, for example, by changing pH of the starting HAuCl$_4$ solution. Representative data for such catalysts are shown in Figure 2 a. A few Au/TiO$_2$ catalyst samples with lower initial activities, for example, with smaller Au loadings or larger particle sizes, tend to show somewhat different behavior, as previously reported.[19] It should be noted that the activity for the Au/Al$_2$O$_3$ is slightly higher at about 0.1 ppm H$_2$O than at about 2 ppm H$_2$O. It was experimentally confirmed that Al$_2$O$_3$, as well as TiO$_2$, without deposited gold shows trace activity (a few percent of conversion at 600 K) only after being dried at 623 K in a stream containing about 0.1 ppm H$_2$O. The reaction over the support surface could then contribute to the slight increase in activity of Au/Al$_2$O$_3$ at about 0.3 ppm H$_2$O, whereas a decrease in the activity of gold by the elimination of moisture seems to be predominant over TiO$_2$ and SiO$_2$ at <0.3 ppm H$_2$O.

Despite the large effect of moisture, the apparent activation energies for Au/TiO$_2$ and Au/Al$_2$O$_3$ are almost independent of moisture concentration (Figure 3), thus indicating that moisture does not significantly change the reaction mechanisms for CO oxidation over these two catalysts, for example, by adding a new reaction path. In other words, moisture should be involved in the reaction at any concentration >0.1 ppm H$_2$O. On the contrary, the conversion curves for Au/SiO$_2$ are unusual and are drastically altered by the moisture concentration (Figure 4). A peak was observed at about 320 K, which decreased in intensity as moisture was eliminated. The activity for about 150 and about 1 ppm H$_2$O at around 400 K was much lower than that at approximately 300 K. This inversion can be attributed to the desorption of moisture at higher temperatures. It is clear that moisture in the reactant gas is a prerequisite for the activity of Au/SiO$_2$ at lower temperatures. Since the particle size of Au over SiO$_2$ is relatively large, its lower turnover frequencies (TOFs) can be partly attributed to the size effect.[1]

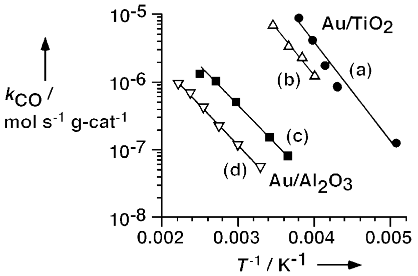

Figure 3. Arrhenius plots for CO oxidation over (a),(b) Au/TiO$_2$ and (c),(d) Au/Al$_2$O$_3$. Moisture concentration and apparent activation energy are a) ≈ 40 ppm and 26 kJ mol^{-1}, b) ≈ 0.1 ppm and 25 kJ mol^{-1}, c) ≈ 200 ppm and 22 kJ mol^{-1}, d) ≈ 2 ppm and 22 kJ mol^{-1}, respectively.

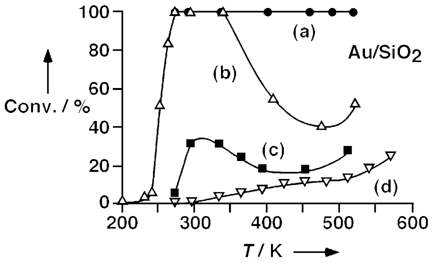

Figure 4. CO conversion over Au/SiO$_2$ as a function of reaction temperature. Moisture concentration is a) ≈ 6000 ppm, b) ≈ 150 ppm, c) ≈ 1 ppm and d) ≈ 0.3 ppm.

As depicted in Figures 2–4, the effect of moisture on CO oxidation over the three catalyst samples are different. This suggests that the reaction mechanisms depend strongly on the nature of support and in a more complex manner than expected from the simple comparison of activities measured at a certain concentration of moisture (usually ca. 3 ppm).[16,21] Since the abrupt switching in H$_2$O concentration is always followed by a gradual change in activity,[19] the amount of H$_2$O adsorbed on the catalyst surface mainly determines the catalytic activity. The effect of moisture is basically reversible and no significant change in the particle size of the gold was observed by TEM before and after the reaction.[19]

As for the origin of the moisture effect, the possibility of the water-gas shift (WGS) reaction can be ruled out (Equation 1 in Scheme 1). Although this reaction takes place over Au/TiO$_2$,[22] the reaction temperature (ca. 573 K) is much higher than in the present study. Actually, formation of H$_2$ was not detected by gas chromatography. Moreover, the concentration of H$_2$O (0.1–6000 ppm) is far less than that required by stoichiometry for reaction with CO (10 000 ppm).

Based on the above experimental results together with those reported previously, we consider that moisture plays two roles in the reaction: one is the activation of oxygen and the other is the decomposition of carbonate. The possibility of the former is suggested in a spectroscopic study.[17] Oxygen may be activated by moisture according to Equations (2a) and (2b). The perimeter interfaces appear to function as major active sites,[1,10,23] whereas the support surface serves as a moisture reservoir. The activated oxygen will rapidly react

$$CO + H_2O \nrightarrow CO_2 + H_2 \qquad (1)$$

$$O_2(p) + H_2O(s) \longrightarrow O^*(p) + 2OH(p) \qquad (2a)$$

$$2OH(p) \longrightarrow O^*(p) + H_2O(s) \qquad (2b)$$

$$CO(Au) + O^*(p) \rightarrow COO(p) \rightarrow CO_2(g) \qquad (3)$$

$$CO_3(p) + H_2O(s) \longrightarrow CO_3H(p) + OH(p) \qquad (4a)$$

$$CO_3H(p) \longrightarrow CO_2(g) + OH(p) \qquad (4b)$$

$$CO(Au) + O_2(p) \longrightarrow CO_3(p) \qquad (5a)$$

$$COO(p) + O^*(p) \longrightarrow CO_3(p) \qquad (5b)$$

Scheme 1. Possible reaction steps at around the perimeter interfaces between gold and oxide support. (p), (s) and (Au) represent the adsorption at the perimeter interfaces, support surfaces, and Au surfaces, respectively, while (g) denotes the gas phase. O* indicates the activated oxygen species.

with CO adsorbed on the gold particles to form an intermediate,[17] which is immediately transformed into CO_2 [Eq. (3)]. Formation of the O–Au–CO species was observed by FTIR.[17] Under ambient pressure, the active interface sites are gradually covered with an inert carbonate species accumulated during the reaction,[24] so that the activity steadily decreases. The deactivated catalyst can be regenerated by the addition of moisture in the reactant gas.[15] A model for the decomposition mechanism of carbonate was recently proposed by Costello et al.,[25] as shown in Equations (4a) and (4b). Carbonate species are formed by the reverse reaction of Equation (4a) under dry conditions, as well as by Equations (5a) and (5b). It should be noted that neither H_2O nor OH is substantially consumed to produce CO_2 in Equations (2)–(4), but they contribute to increase the reaction rate. This is consistent with the experimental results, although there are still other possibilities, for example, involvement of OH groups in the reaction intermediate in the form of hydroxy carbonyl (CO–Au–OH) and/or bicarbonate (Au–CO_3H) species,[10,25] or modification of the electronic states at the perimeter interface.

The influence of the type of support on the catalytic activity of gold requires explanation. For "inert" (irreducible or insulating) oxide supports, the reaction steps are restricted to gold surfaces, thus resulting in lower activities than in the case of "active" (reducible or semiconducting) oxide supports.[26,27] The dependence of the effect of moisture on the support oxides may thus reflect the difference in the mobility of surface oxygen species. In the case of Au/TiO_2, CO adsorbed on the gold nanoparticles is ready to react with oxygen coming from the support surface even under dry conditions with a trace amount of moisture,[17] as evidenced by the observation that the reaction rate is almost independent of the partial pressure of CO or O_2.[9] The reaction can be further enhanced by the addition of moisture, according to Equations (2) and (4). In fact, no substantial contribution of support oxygen is expected for Au/SiO_2. Since the reaction takes place only with a considerable amount of moisture, the presence of moisture might be indispensable for the adsorption of oxygen on Au/SiO_2. Although the mobility of oxygen on Al_2O_3 is much less than that on the semiconducting oxides, oxygen is still mobile to some extent.[28] This may explain why the intrinsic activity of Au/Al_2O_3 is lower than that of Au/TiO_2, despite the fact that they exhibit a similar effect with moisture. A probable reaction model that summarizes the discussion is shown in Figure 5.

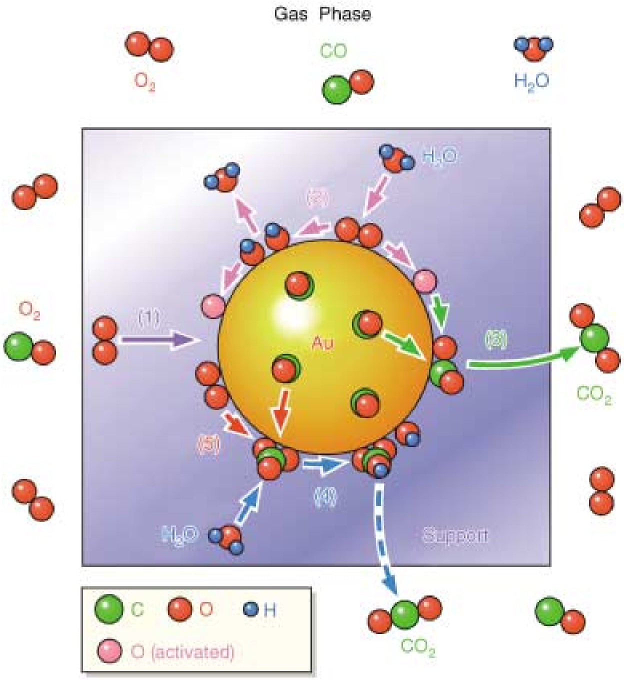

Figure 5. Schematic model (top view) for CO oxidation under the coexistence of moisture. Arrows indicate the processes on the catalyst surface: (1) oxygen diffusion from the support surface, (2) activation of oxygen, (3) production of CO_2, (4) decomposition of carbonate and (5) formation of carbonate. The numbers except for (1) correspond to Equations (2)–(5) in Scheme 1.

In summary, the effect of moisture in the reactant gas has been investigated for the low-temperature oxidation of CO by Au/TiO_2, Au/Al_2O_3, and Au/SiO_2 over a wide range of concentrations, from about 0.1 to 6000 ppm H_2O, which includes ultralow levels, <1 ppm. Moisture enhances the catalytic activities for no less than two orders of magnitude and the effect of moisture depends on the type of metal oxides. We consider that moisture plays two roles in the reaction: one is the activation of oxygen and the other is the decomposition of carbonate. A mechanism model for its action is proposed.

Experimental Section

Au/TiO_2 and Au/Al_2O_3 catalyst samples were prepared by the deposition-precipitation (DP) method.[20] Because the DP method is not applicable to acidic supports with isoelectric points (IEP) less than 5, Au nanoparticles were deposited on SiO_2 (IEP = 2) by the gas-phase grafting method.[21] All the samples were calcined in air at 673 K for 4 h. The loading amounts of gold over TiO_2 (P-25, provided by a courtesy of Nippon Aerosil, Co., Ltd.), Al_2O_3 (reference catalyst JRC-ALO-7, The Catalysis Society of Japan) and SiO_2 (type G, Fuji Silicia), determined by ICP analysis, were 0.9, 0.4, and 10 wt%, respectively, and the mean diameter of the Au nanoparticles calculated from TEM micrographs were 3.0, 3.9 and 8.2 nm, respectively.

The catalytic activities were measured by using an "ultraclean" fixed-bed flow reactor specially designed for the measurements under extremely dry conditions (0.1–3 ppm H_2O),[19] as well as by using a conventional reactor for the measurements at moisture concentrations higher than 3 ppm. The former consists of stainless-steel tubes with inner walls coated with chromium oxide to suppress the accumulation of moisture. The reactant gas, 1 vol% CO in air, was fed with a space velocity of 20000–80000 $mL\,h^{-1}\,g^{-1}$ of catalyst. The gas supplied from a commercial gas cylinder, which contained about 3 ppm H_2O, was dried with a gas purifier and moistened with wet molecular sieves, as well as a water bubbler. Moisture concentration was monitored with two cryoptical dew-point meters before and after passing through the catalyst bed and an electrostatic capacitance dew-point meter after the catalyst bed. The effluent gas was analyzed with a gas chromatograph equipped with a thermal conductivity detector, in which N_2, O_2, CO, CO_2, and H_2 were monitored. Prior to the measurements, the catalyst samples were heated at 523 K for 0.5 h in an air stream as a standard pretreatment. For the measurements at about 0.1 ppm H_2O, the samples were thoroughly heated at 673 K over 3 days by using an air purifier for the semiconductor process. Reaction rates were calculated from the steady-state CO conversions by assuming the zero-order kinetics.[9]

Received: January 19, 2004 [Z53796]

Keywords: gold · heterogeneous catalysis · nanotechnology · oxidation

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