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Low-temperature catalytic combustion of methanol and its decomposed derivatives over supported gold catalysts

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Abstract

Gold can be compared favorably with Pd and Pt in the catalytic combustion of CH_3OH, HCHO and HCOOH when it is deposited on some reducible metal oxides (α-Fe_2O_3, TiO_2, etc.). While the supported gold catalysts are less active in H_2 oxidation, they exhibit much higher activities in CO oxidation. For Au/TiO_2, the effect of catalyst preparation was further investigated. Since the activity for CO oxidation of the gold catalysts is not depressed but enhanced by moisture, they are practically applicable to CO removal from air at room temperature. Gold supported on manganese oxide is especially effective in the selective CO removal from hydrogen, indicating its potential applicability to polymer electrolyte fuel cells using the reformed gas of methanol.

Keywords: Au catalysts; Pd catalysts; Pt catalysts; CO oxidation; Methanol oxidation

1. Introduction

Gold has long been recognized to be poorly active as a catalyst, however, we have recently found that when it is highly dispersed on reducible metal oxides such as α-Fe_2O_3 and on the hydroxides of alkaline earth metals it can exhibit surprisingly high activity for CO oxidation at low temperatures [1,2]. Taking into consideration the low melting point and weak nature of chemisorption of gold, low-temperature catalytic combustion appears to be one of the most prosperous fields of applications for the supported gold catalysts. In fact, commercial application has already been started in Japan for the removal of odor in toilet.

Since methanol is readily combusted with noble metal catalysts and convertible into CO and H_2 by decomposition or reforming, it is expected that methanol will expand its usage as a clean fuel and a new energy carrier for hydrogen. The present paper deals with the catalytic combustion of CH_3OH and its decomposed derivatives over supported gold. An attempt has also been made to compare Au with Pd and Pt in catalytic behavior and to find optimum preparation conditions for Au/TiO_2 as a typical example.

2. Experimental

Catalyst samples of Au, Pd and Pt were prepared by coprecipitation [1], deposition–pre-

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cipitation [2–4] and impregnation methods. The precursors were calcined in air at 400°C or 300°C to decompose gold hydroxide into metallic particles. For Pd and Pt, the calcined samples were finally treated in a stream of 1 vol.-% H_2 (N_2 balanced) at 450°C.

Standard catalytic activity measurements were carried out in a small fixed bed reactor, with 0.10 g of catalysts that had been sieved between 70 and 120 mesh. A thermocouple was located at the inlet side of the catalyst bed to detect temperature increase accompanied by combustion. Five standard gases consisting of CH_3OH (0.5 vol.-%), HCHO (0.5 vol.-%), HCOOH (0.5 vol.-%), H_2 (1 vol.-%) or CO (1 vol.-%) balanced with air to 1 atm, were passed through the catalyst bed at a flow rate of 33 ml/min. The effluent gases were monitored by gas chromatography to analyze CH_3OH, H_2, CO and CO_2. For CO oxidation in H_2, CO (1 vol.-%) balanced with H_2 to 1 atm was passed through the catalyst bed of 0.20 g sample at a flow rate of 33 ml/min.

The sizes of Au particles were determined by a high-resolution TEM (Hitachi H-9000). At least 200 particles were chosen to determine the mean diameter by using computerized imaged analyzer (EXCEL, Nippon Avionics Co. Ltd.).

3. Results and discussion

3.1. *Catalytic oxidation of CH_3OH and its decomposed derivatives*

Fig. 1 shows that methanol and its decomposed derivatives, namely HCHO, HCOOH, H_2 and CO, can be oxidized at temperatures below 100°C over Au, Pd and Pt catalysts. Gold supported on α-Fe_2O_3 is much more active for CO oxidation than Pd and Pt supported on Al_2O_3, while for H_2 oxidation the other two are more active. For the oxidation of CH_3OH, HCHO and HCOOH, the activity differs much less and decreases in the order: $Pd/Al_2O_3 > Au/\alpha$-$Fe_2O_3 > Pt/Al_2O_3$. As the material balance of carbon in the effluent gases was almost perfect between CO_2 and CH_3OH, it can be assumed that the catalytic combustion of CH_3OH gives few intermediates like HCHO and HCOOH, if any.

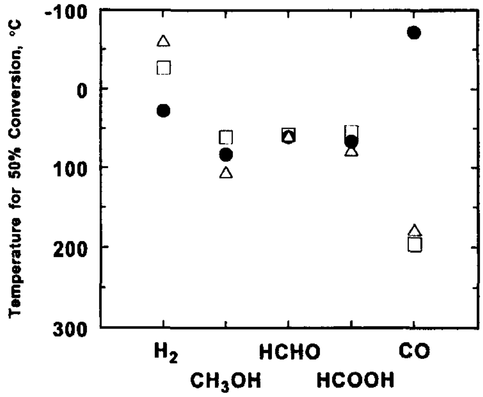

Fig. 1. Temperature for 50% conversion in the oxidation of CH_3OH and its decomposed derivatives over supported Au, Pd and Pt catalysts. ●: Au/α-Fe_2O_3, Au loadings 1 wt.-% for CH_3OH, HCHO and HCOOH, 13 wt.-% for H_2 and CO, □: Pd/γ-Al_2O_3, Pd loading 1 wt.-%, △: Pt/γ-Al_2O_3, Pt loading 1 wt.-%, Reaction gases: see the Experimental section, SV = 2×10^4 h^{-1} ml/g cat.

In the case of supported gold catalysts, catalytic activity is markedly dependent on both metal oxide supports and the particle size of Au. When gold is supported on SiO_2 or Al_2O_3, it is not more active than Pd and Pt catalysts. The turnover frequency for CO oxidation increases with a decrease in the diameter of gold particles, especially in the region below 4 nm [2].

It is one of the advantageous features of supported gold catalysts in low temperature applications that their activities are not depressed but enhanced by moisture. Fig. 2 shows that a commercial Al_2O_3-pellet (diameter 2 mm) catalyst coated with Au/α-Fe_2O_3 exhibits much enhanced activity for CO oxidation in a moistened gas. The reason for the moisture enhancement has not been clarified, however, the adsorption of FT–IR measurements indicate that CO adsorption on the surface of gold particles is enhanced by moisture [5].

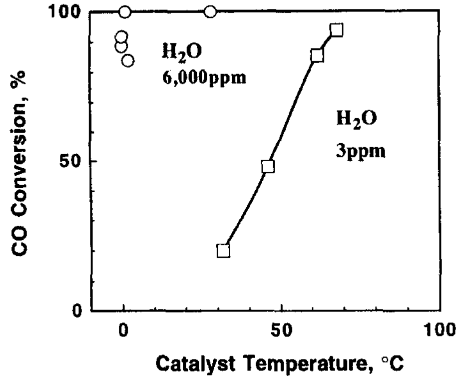

Fig. 2. The effect of water on CO conversion over a commercial Au/$\alpha-Fe_2O_3/Al_2O_3$ catalyst. Reaction gas: CO 1 vol.-% in air (□) dried at 0°C with SiO_2 gel column and (○) bubbled into water at 0°C, SV = 2×10^4 h^{-1}.

3.2. *CO removal from air: effect of catalyst preparation*

Gold and Pt catalysts with a metal loading of 1 wt.-% were prepared by different methods using TiO_2 as a support. The activity of Au for CO oxidation was markedly dependent on the preparation methods while that of Pt was almost independent [6]. Deposition–precipitation could produce Au catalysts far more active than Pt catalysts, however, impregnation resulted in much lower activity for Au than Pt. TEM observation showed that the diameter of Pt particles was 1.4–1.5 nm and smaller than that of Au at least by 2 nm in all preparation methods. It was also revealed that deposition–precipitation yielded smaller Au particles than impregnation and formed hemispherical metal particles with their flat planes in contact with TiO_2. This structure of contact led to increased distance of perimeter around Au particles and could be related to the genesis of the extraordinarily high catalytic activity.

In the case of deposition–precipitation, the appropriate control of experimental conditions was indispensable [3,4]. Specifically important are the types of TiO_2 support materials, pH of starting $HAuCl_4$ solution, Au metal loading, additives to the starting solution, temperature for precipitation and aging, and calcination atmosphere. Commercially available crystallized TiO_2 with low specific surface area could not give rise to active catalysts. Fine powder with a specific surface area larger than 40 m^2/g was favorable irrespective of the crystal structure, either anatase or rutile. The pH of an aqueous solution dramatically affects the particle size of Au. As shown in Fig. 3, at pH 6 the mean diameter of Au drastically changes. Above pH 6 where main species of Au in solution is transformed from $AuCl_4^-$ to $Au(OH)_nCl_{4-n}^-$ ($n = 1$–3), the mean particle diameter becomes smaller than 4 nm.

The highest catalytic activity for CO oxidation was usually obtained at a metal loading around 1.5 wt.-%. The addition of magnesium citrate to a starting solution, was effective to prepare active catalysts in the following three cases. The first case was observed, as shown in Fig. 4, when Au loading was higher than 1.5 wt.-%. The optimum metal loading was increased up to 8 wt.-% leading to an appreciably high catalytic activity to give 100% conversion even at a temperature as low as −70°C. The second case was observed when amorphous Ti hydroxide with a specific surface area above 100 m^2/g was used as a starting support material. The last case was when Au/TiO_2 catalysts were prepared by a coprecipitation method. Since IR transmission spectroscopy showed that

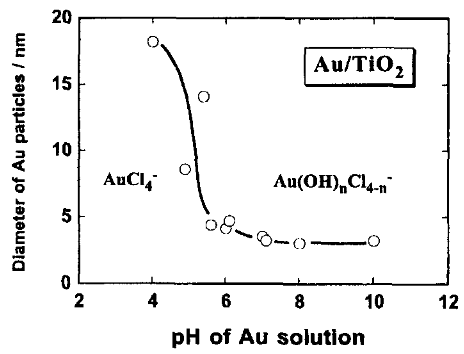

Fig. 3. The mean particle diameter of Au as a function of pH of $HAuCl_4$ solution. Calcination at 400°C in air for 4 h. Initial Au concentration corresponds to Au/TiO_2 = 13 wt.-%.

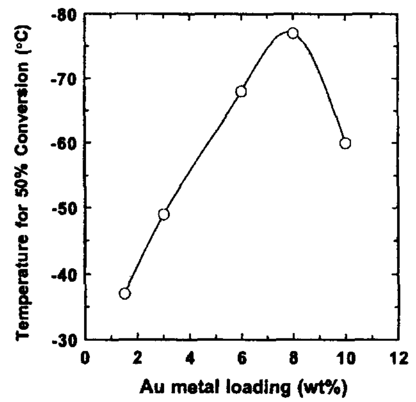

Fig. 4. Temperature for 50% conversion in CO oxidation as a function of Au metal loading. Mg citrate was added to an aqueous solution of $HAuCl_4$ containing TiO_2 at pH 9. Calcination at 300°C in air for 4 h. SV $= 2 \times 10^4$ h^{-1} ml/g cat.

citrate ions still remained on the catalyst surface up to 300°C, the unique role of Mg citrate might be, firstly, to prevent coagulation of gold particles during calcination due to the blockage by citrate anions sticking on TiO_2 surface (1st case). The second role can be assumed to suppress 'earthquake' effect caused by crystallization of $Ti(OH)_4$ to TiO_2 (2nd and 3rd case), because Mg^{2+} ion was found to retard the crystallization of amorphous titanium oxide.

As Table 1 shows, the effect of temperature and atmosphere for calcination is also significantly large. Calcination at temperatures above 300°C accelerates the coagulation of Au particles. When the precursors are calcined at 250°C in air, N_2, 10% CO + He or 10% H_2 + He, the mean particle diameter of gold is smallest in a H_2 + He mixture. This result might suggest that under hydrogen atmosphere the decomposition and reduction of $Au(OH)_3$ took place much faster yielding more number of nucleus for metallic gold particles, which finally resulted in smaller gold particles for a constant metal loading.

3.3. CO removal from H_2

The marked preference of supported gold catalysts for CO oxidation rather than to H_2 oxidation, shown in Fig. 1, has motivated us to apply them to the selective removal of CO from H_2, which is strongly needed for polymer electrolyte fuel cells [7]. For this reaction, Au supported on manganese oxide (probably Mn_2O_3) seemed to exhibit the best performance, because the gold catalyst with an atomic ratio of Au/Mn = 1/19 prepared by coprecipitation followed by calcination at 300°C was very ac-

Table 1
Mean diameters and standard deviations of Au for Au/TiO_2 prepared by deposition–precipitation followed by calcination under different conditions

Calcination conditions		Diameter of Au particles /nm	Standard deviation/nm
Temperature /°C	Atmosphere		
200	air	3.0	±1.0
300	air	3.1	±0.8
400	air	3.6	±0.7
500	air	4.3	±1.0
600	air	6.7	±1.3
250	air [a]	3.3	±0.6
250	N_2 [a]	2.7	±0.6
250	10% CO/He [a]	2.6	±0.5
250	10% H_2/He [a]	2.1	±0.5

Deposition at pH 7; calcined for 4 h; Au loading = 3.5 wt.-%.
[a] Under a stream of gas with a flow rate of 20 ml/m.

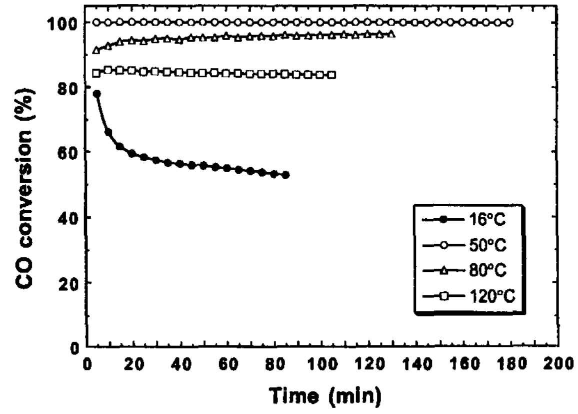

Fig. 5. CO conversions at different catalyst temperatures as a function of time-on-stream in the selective oxidation of CO in H_2 over Au/MnO_x. Catalyst: prepared by coprecipitation, Au/Mn = 1/19, calcined in air at 300°C for 4 h., Reaction gas: CO 1 vol.-%, O_2 vol.-%, N_2 balance, SV $= 1 \times 10^4$ h^{-1} ml/g cat.

tive for CO oxidation ($T_{1/2} = -40$°C) and much less active for H_2 oxidation ($T_{1/2} = 170$°C). The large temperature gap for the two reactions indicates the potential advantage of the Au/MnO_x catalysts.

In the experiments using a standard test gas of CO 1.0 vol.-%, O_2 1 vol.-% and H_2 98%, CO can be selectively removed with high conversion at relatively low temperatures. Fig. 5 shows that CO conversion reaches 100% at 50°C, below and above which the conversion decreases. Since the supported gold catalysts become less active after evacuation at 400°C and recover its activity during CO oxidation in air [8], the catalytic activity for CO oxidation in H_2 must be depressed compared with that in air. This nature may result in a low conversion and gradual decrease at 16°C. The conversions of oxygen at this temperature, ca. 37%–64%, show that about one third of oxygen is consumed by hydrogen oxidation. At 50°C and above this temperature, CO oxidation is accompanied by a nearly complete consumption of O_2, which implies that about 1 vol.-% of hydrogen is also oxidized. These results indicate that hydrogen oxidation is accelerated by the presence of CO and the competitive consumption of O_2 may decrease CO conversion. Accordingly, the temperature range for the selective oxidation of CO in H_2 is narrowed to the range of 50 to 80°C.

The stability of the catalyst during operation was satisfactory and no deactivation was observed within 50 h operation. The above performance of Au/MnO_x is more superior, especially in CO conversion and CO selectivity against H_2, to the data reported for Pt supported on A-type zeolite at 250°C [9], Ru/Al_2O_3 at 180°C [7] and a composite oxide of Ag at 90°C [10].

4. Summary

The present work on supported gold catalysts for the low-temperature catalytic combustion of CH_3OH and its decomposed derivatives can be summarized as follows.

1. Gold supported on α-Fe_2O_3 is as active as Al_2O_3-supported Pd and Pt catalysts in the oxidation of CH_3OH, HCHO and HCOOH. While the gold catalysts are less active in H_2 oxidation, they are markedly more active in CO oxidation at low temperatures.
2. The above large difference in the activity between CO and H_2 oxidation can lead to a very high performance of Au/MnO_x in the selective CO oxidation in H_2.
3. The catalytic activity of the supported gold catalysts, especially Au/TiO_2, strongly depend on the pH of a starting solution, metal loading, the addition of magnesium citrate and calcination atmosphere.

References

[1] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal., 115 (1989) 301.
[2] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, J. Catal, 144 (1993) 175 and references therein.
[3] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, Stud. Surf. Sci. Catal., 63 (1991) 695.
[4] S. Tsubota, D.A.H. Cunningham, Y. Bando and M. Haruta, Stud. Surf. Sci. Catal., 91 (1995) 227.
[5] F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, J. Phys. Chem., submitted for publication.
[6] M. Haruta, A. Ueda and G.R. Bamwenda, Proc. Workshop Catal. Comb., (1994) 1.
[7] S.H. Oh and R.M. Sinkevitch, J. Catal., 142 (1993) 254.
[8] D.A.H. Cunningham, S. Tsubota, N. Kamijo and M. Haruta, Res. Chem. Intermed. 19 (1993) 1.
[9] M. Watanabe, H. Uchida, H. Igarashi and M. Suzuki, Chem. Lett., (1995) 21.
[10] S.K. Chatterjee and P.N. Mukhfrjee, Indian J. Technol. 15 (1977) 403.