Low-temperature water–gas shift reaction over gold deposited on TiO_2

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Gold exhibits very high catalytic activities, comparable with that of a conventional $Cu/ZnO/Al_2O_3$ catalyst, for forward and reverse water–gas shift reactions when supported on titanium oxide by the deposition–precipitation method.

The water–gas shift reaction is used as one of the important industrial processes to adjust the CO/H_2 ratio for methanol synthesis and to produce H_2 for ammonia synthesis. For this reaction, two kinds of catalysts are commercially used.[1] One is a high-temperature shift catalyst, which is based on iron oxide structurally promoted with chromium oxide and is used in the temperature range 583–723 K and at 2.5–3.5 MPa. Another is a low-temperature shift catalyst composed of copper, zinc oxide and alumina, and is used between 483 and 513 K. Recently, Andreeva *et al.* reported that Au deposition enhances the catalytic activity of iron oxide for the water–gas shift reaction.[2,3] The activity is comparable with that of a conventional copper catalyst. Here, we report a novel and more active catalyst, Au deposited on TiO_2, which contains neither copper nor iron oxide, but exhibits low-temperature activities both for the forward and reverse water–gas shift reactions.

The catalysts were prepared by deposition–precipitation (DP) of gold hydroxide from $HAuCl_4$ on titanium dioxide powder (P25, Japan Aerosil Co.).[4] To obtain fine gold particles, magnesium citrate solution was added during preparation.[5,6] The catalyst was finally calcined in air at 673 K. Gold loading in the starting solutions is expressed as atom% [100Au/(Au+M) for Au/M_xO_y]. For comparison, other gold and copper catalysts were prepared by coprecipitation (Cop) and impregnation (Imp) methods.

Table 1 shows the catalyst parameters and some kinetic data under forward water–gas shift conditions. Other than Au catalysts, a commercial $Cu/ZnO/Al_2O_3$ catalyst (Catalysts and Chemicals Inc., Far East) was examined for comparison. The reactant gas containing CO (1%), H_2O (2%) and He (balance) was fed at a space velocity of 12 600 h^{-1} ml (g cat)$^{-1}$ and under a pressure of 0.1 MPa, and the introduction of H_2O was carried out using a micro-feeder or by bubbling. At 373 K, CO conversion was $< 20\%$ and much lower than the equilibrium conversion (99.97%), therefore, the reaction rate, TOF, and activation energy were calculated around this temperature. The catalysts tested were stable during catalytic activity measurements and the change of CO conversion during 2.5 h was less than $< 0.5\%$. In the calculation of TOF for supported metal catalysts, generally, the number of exposed metal atoms is determined by titration using CO and H_2. In the case of supported gold, the titration method is not applicable because of the lack of irreversible stoichiometric adsorption of these molecules on the surface of gold. The number of gold atoms exposed to the surface was thus simply calculated from the mean diameter of the gold particle. The shape of the gold particles deposited on the TiO_2 surface was well defined and hemispherical by TEM observation.[4]

Table 1 Catalytic activity of supported gold catalysts for the water–gas shift reaction[a]

Catalyst[b]	D_{metal}[c] /nm	Rate at 373 K/mol s^{-1} (g cat)$^{-1}$	TOF at 373 K/s^{-1}	E_a/kJ mol^{-1}
Au/TiO_2(DP, 3.4%)[d]	4.4	1.0×10^{-7}	7.9×10^{-4}	46
Au/TiO_2(DP, 5%)[d]	—	1.4×10^{-7}	—	45
Au/TiO_2(DP, 10%)[d]	4.4	3.0×10^{-7}	9.2×10^{-4}	31
Au/TiO_2(Cop, 33%)[d]	2.8	6.4×10^{-8}	5.6×10^{-5}	47
Au/Fe_2O_3(Cop, 5%)	3.3	2.2×10^{-8}	9.1×10^{-5}	52
Au/Al_2O_3(Cop, 5%)	3.7	3.4×10^{-8}	1.1×10^{-4}	24
Au/ZnO(Cop, 5%)	4.9	9.0×10^{-9}	5.7×10^{-5}	34
$Cu/ZnO/Al_2O_3$[e]	13.4	1.2×10^{-7}	2.0×10^{-4}	53

[a] Reactant gas CO(1%)–H_2O(2%)–He(balance); SV = 12 600 h^{-1} ml (g cat)$^{-1}$; pressure 0.1 MPa. [b] DP, deposition–precipitation; Cop, coprecipitation, Au loading in atom%. [c] Calculated from XRD by using Scherrer's equation. [d] Addition of magnesium citrate during preparation. [e] Commercial catalyst, with Cu content of 42 atom% by XRF analysis.

Particle sizes of Au and Cu given in Table 1 were calculated from the XRD data. The titania powder P25 is composed of both anatase and rutile. Because the broad diffraction peaks for gold overlapped with these diffraction lines, the diffraction profile of TiO_2 itself was mathematically subtracted from the profile of Au/TiO_2, and then the Au particle size was calculated by using Scherrer′s equation. It was found that Au was deposited on the oxide surface with diameters < 5 nm.

Among gold catalysts (Table 1), Au/TiO_2 showed the highest reaction rates. While the reaction rate at 373 K increased with increasing Au loading for a series of Au/TiO_2 catalysts prepared by the deposition–precipitation method, Au/TiO_2 prepared by coprecipitation showed a lower rate despite the higher metal loading and the smallest gold particle sizes. This may be attributed to differences in exposure of gold particles on the surface and the crystalline nature of TiO_2 depending on the preparation method. The activation energies listed in Table 1, except for Au/Al_2O_3 and Au/ZnO, are close to the reported values for Cu/Al_2O_3 (55.6 kJ mol^{-1}) and Au/Al_2O_3 (48.8 kJ mol^{-1}), both prepared by incipient wetness impregnation.[7] However, the reaction rate and turnover frequency were very different depending on the preparation method. The TOF reported for Au/Al_2O_3(Imp) was only 1/342 that of the value for Cu/Al_2O_3(Imp).[7] On the other hand, Au/Al_2O_3(Cop) was more active and had half of the TOF of the $Cu/ZnO/Al_2O_3$ catalyst. The activities of Au/TiO_2 (DP) were much more striking. The rates of reaction at 373 K were comparable and the TOF was more than 4 times higher than that of $Cu/ZnO/Al_2O_3$. Although this comparison is not made under industrial reaction conditions and the lifetime (the commercial Cu catalyst has a lifetime of *ca.* 2–4 years by adding the alumina component[1]) has not yet been examined, the results clearly show that gold is potentially as active as copper, when highly dispersed on suitable support oxide.

Fig. 1 shows the activities of gold catalysts under the reverse water–gas shift conditions. The reactant gas mixture CO_2(23%)– H_2(67%)–Ar(balance) was passed through the catalyst bed at a space velocity of 3000 h^{-1} ml (g cat)$^{-1}$ and under a pressure of 0.1 or 5 MPa. Catalytic activities are expressed by k defined as $[CO][H_2O]/[CO_2][H_2]$. The concentration of each component was calculated from analytical data and the material balance equations.[8] Au on TiO_2 and Al_2O_3 showed higher activities than Au/Fe_2O_3, and the most active Au/TiO_2 reached thermodynamic equilibrium at a temperature as low as 423 K at 5 MPa. However, Au/TiO_2 and Cu/TiO_2

prepared by impregnation methods were only poorly active, and did not reach equilibrium even at 673 K.

As reported previously, these gold catalysts produce methanol, methane and other hydrocarbons under such high- pressure conditions, and the product selectivity greatly differs depending on the nature of the oxide supports.[8–10] When the total pressure was decreased from 5 to 0.1 MPa, the activity decreased as shown in Fig. 1, however, CO selectivities were very much improved. For example, Au/TiO_2 produced methanol, methane and CO with selectivities of 4, 10 and 86%, respectively, at 523 K and 5 MPa, CO selectivity reached values $>99\%$ at 0.1 MPa.

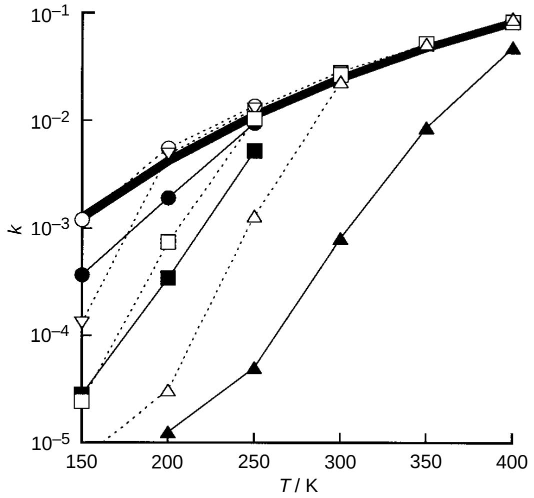

Fig. 1 Catalytic activities of supported gold catalysts for the reverse water–gas shift reaction. Reactant gas mixture CO_2(23%)–H_2(67%)–Ar(balance); SV = 3000 h^{-1} ml (g cat).$^{-1}$ Activities are expressed in terms of k at a total pressure of 5 MPa over (○) Au/TiO_2 (DP, 2 atom%), (▽) Au/Al_2O_3 (Cop, 5 atom%), (□) Au/Fe_2O_3 (Cop, 5 atom%), (△) Au/ZnO (Cop, 5 atom%) and 0.1 MPa over (●) Au/TiO_2 (DP, 2 atom%), (■) Au/Fe_2O_3 (Cop, 5 atom%), (▲) Au/ZnO (Cop, 5%). The thick continuous line shows the thermodynamic equilibrium limit.

Gold deposited on TiO_2 is known to exhibit very high activity for CO oxidation to CO_2 even below 273 K.[4,5] CO_2 formation is further enhanced when moisture is added to the reactant mixture of CO and air.[11] This enhancement is not due to the shift reaction of CO and water because the shift activity is almost zero at 273 K under the conditions used here.

Footnote

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References

1 C. Rhodes, G. J. Huchings and A. M. Ward, *Catal. Today*, 1995, **23**, 43.
2 D. Andreeva, V. Idakiev, T.Tabakova and A. Andreev, *J. Catal.*, 1996, **158**, 354.
3 D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev and R. Giovanoli, *Appl. Catal.*, 1996, **134**, 275.
4 S. Tsubota, D. A. H. Cunningham, Y. Bando and M. Haruta, *Preparation of Catalysts VI*, ed. G. Poncelet *et al.*, Elsevier, Amsterdam, 1995, p. 227.
5 S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, *Preparation of Catalysts*, ed. V. G. Poncelet *et al.*, Elsevier, Amsterdam, 1991, p. 695.
6 H. Sakurai and M. Haruta, *Catal. Today*, 1996, **29**, 361.
7 D. C. Grenoble, M. M. Estadt and D. F. Ollis, *J. Catal.*, 1981, **67**, 90.
8 H. Sakurai and M. Haruta, *Appl. Catal. A*, 1995, **127**, 93.
9 H. Sakurai, S. Tsubota and M. Haruta, *Appl. Catal. A*, 1993, **102**, 125.
10 H. Sakurai, S. Tsubota and M. Haruta, *Science and Technology in Catalysis*, ed. Y. Izumi *et al.*, Kodansha, Tokyo, 1995, p. 111.
11 S. Tsubota, A. Ueda, H. Sakurai, T. Kobayashi, and M. Haruta, *Environmental Catalysis*, ed. J. N. Armor, American Chemical Society, Washington DC, 1994, p. 420.

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