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Synergism in methanol synthesis from carbon dioxide over gold catalysts supported on metal oxides

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Abstract

Gold deposited on various oxides with high dispersion was found to be active for the hydrogenation of CO_2 at temperatures between 150 and 400°C. Product selectivities greatly depended on the nature of support oxide. Acidic oxides like TiO_2 gave higher CO_2 conversions but low methanol yields. Zinc oxide component was indispensable for selective methanol synthesis. Significantly, large particle size effect of gold was observed and smaller gold particles gave higher methanol productivity per exposed surface area of gold. This can be explained by an increase in the perimeter area of gold particles with a decrease in particle size. Methanol yield was greatly enhanced in a $Au/ZnO-TiO_2$ catalyst probably due to an increase in gold–zinc oxide interface.

Keywords: Au catalysts; Metal oxide support; CO_2 hydrogenation

1. Introduction

Methanol is one of the essential chemicals which have applications as wide as ethylene. Industrially methanol has been synthesized from CO and hydrogen with a small amount of CO_2 and recently methanol synthesis from pure CO_2 tends to redraw interest in connection with the discussion about the role of CO_2 in the industrial methanol synthesis conditions and with the attention to the green house effect of CO_2 [1–5]. We have already reported that gold catalysts supported on metal oxides are active for CO_2 hydrogenation [6], in accordance with the report of Frost [7] and Baiker et al. [8]. In this report, methanol synthesis activity and the synergistic effect between gold and oxides is reported.

2. Experimental

Highly dispersed gold catalysts were prepared either by coprecipitation or deposition–precipitation method according to the procedure described elsewhere [6]. Chloroauric acid and metal nitrate were used for coprecipitation method. Only for the preparation of Ti-containing catalysts, titanium sulfate was used instead of nitrate, and Mg–citrate solution was added in some case. Gold loading, expressed by atom.-% (= 100 Au/(Au + Metal)), was 5 atom.-% or 33 atom.-%. The catalyst precursors were finally calcined in air at 400°C for 4 h.

The mean diameter of Au particles was calculated from the results of TEM and XRD observation. Crystallite sizes of Au were calculated from the peak halfwidth of Au(111) by using Scherrer's equation. Catalytic activity was

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measured by using a fixed-bed continuous flow reactor under a total pressure of 50 atm and at a space velocity of 3000 h^{-1} ml/g cat. The composition of reactant gases used are $CO_2/H_2/Ar = 23/67/10$.

3. Results and discussion

3.1. Gold supported on simple oxide (Au/MO_x)

To clarify the basic nature of supported gold as methanol synthesis catalysts, gold with small loading (< 5 atom.-%, unless otherwise noted) was highly dispersed on simple oxides and the catalytic nature was investigated.

3.1.1. Deposition method of gold

Table 1 shows the physical properties and catalytic activities of Au/ZnO and Au/TiO_2 catalysts prepared by various method. In the case of low gold loading less than 5 atom.-%, coprecipitation and deposition–precipitation method gave very fine gold particles with diameter smaller than 5 nm, while the impregnation method gave much larger gold particles. When the gold loading increased above a level of 33 atom.-%, gold particles became larger even when using the coprecipitation method. As we reported earlier [9], the addition of Mg-citrate was effective to reduce the particle size of gold for the preparation of Au/TiO_2.

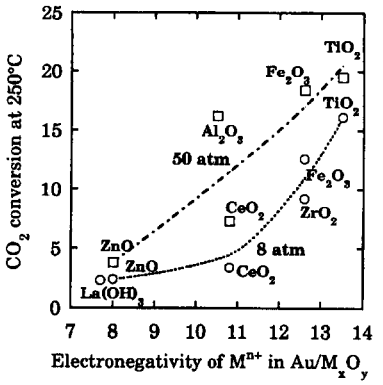

Fig. 1. Effect of the acidity of support oxides in CO_2 hydrogenation.

Both Au/ZnO and Au/TiO_2 were active for CO_2 hydrogenation except for Au/ZnO prepared by impregnation method. Catalysts with smaller gold particles showed higher CO_2 conversion and Au/ZnO gave methanol much more selectively than Au/TiO_2.

3.1.2. Effect of electronegativity of oxides

Surface acidity of oxides affected the reactivity of CO_2. Fig. 1 shows the relationship between the electronegativity of the oxides, and CO_2 conversion at 250°C. The mean particle size of gold in these catalysts was smaller than 5 nm except the case of Au/CeO_2 (10.5 nm).

Table 1
Effect of preparation method

Catalysts	Deposition method [a]	Au loading [b] (atom.-%)	d_{Au} [c] (nm)	BET S.A. ($m^2\ g^{-1}$)	CO_2 conversion at 250°C (%)	MeOH selecitvity at 250°C (%)
Au/ZnO	cop.	5	3.5	41.0	8.2	48.8
Au/ZnO	imp.	5	33.9	6.2	0.0	–
Au/ZnO	cop.	33	19.5	14.0	4.0	67.9
Au/TiO_2	d.p.	2	3–4 [d]	41.0	18.6	6.5
Au/TiO_2	cop.	33	7.9	109	19.0	10.0
Au/TiO_2	cop. [e]	33	2.8	139	20.5	3.9

[a] cop.: coprecipitation, imp: impregnation, d.p.:deposition–precipitation.
[b] Au loading in solution for catalyst preparation.
[c] Crystallite size of gold calculated by using Scherrer's equation from XRD data.
[d] Particle diameter of gold obtained from TEM photograph.
[e] Addition of Mg–citrate solution during preparation.

The relatively acidic support, TiO_2, showed the highest CO_2 conversion and the basic support, ZnO, the lowest. This implies that the initial activation of CO_2 may occur on the oxide surface and too much strong adsorption of CO_2 over basic support leads to low reactivity. The most basic ZnO support showed the highest methanol selectivity.

3.1.3. Product selectivity

Fig. 2 shows the product distribution over some typical gold catalysts. As has been described before, Au/TiO_2 gave the highest CO_2 conversion especially at low temperatures (ca. 150–200°C). The main product at this temperature range was CO, which was formed by reverse water gas shift reaction, and the yields obtained were very close to equilibrium ones. At temperatures above 350°C, a large amount of methane was produced over Au/TiO_2 with selectivities exceeding 50%. Gold on Al_2O_3 showed selectivity similar to Au/TiO_2, though the CO_2 conversion at 150°C was lower than with Au/TiO_2.

Over Au/ZnO and Au/Fe_2O_3, methanol was produced with a relatively high selectivities in the temperature range of ca. 200–350°C. At higher temperatures, methane was formed in addition to CO.

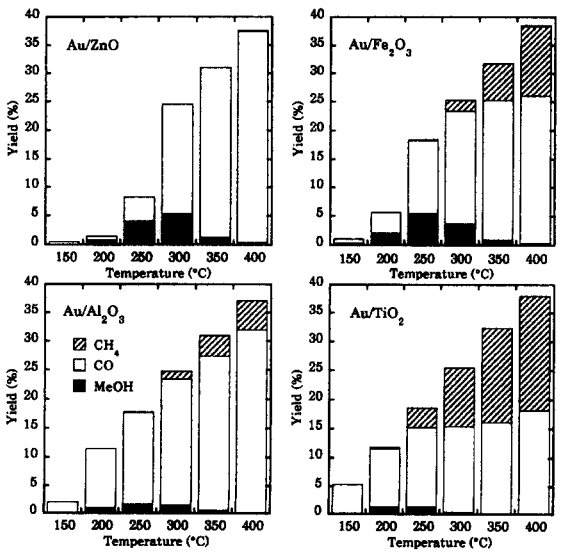

Fig. 2. Product distribution in CO_2 hydrogenation over supported gold catalysts.

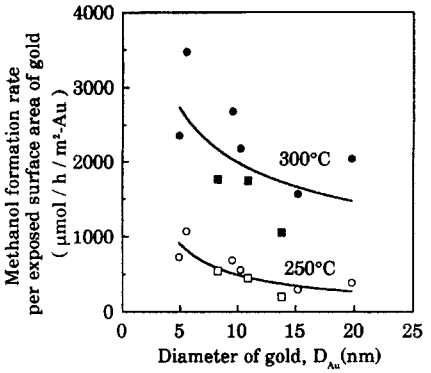

Fig. 3. Effect of particle diameter of gold in methanol synthesis from CO_2. ●○ d_{Au} determined by TEM observation, ■□ crystallite size of gold determined by XRD.

3.1.4. Effect of gold particle size

In order to investigate the particle size effect, a series of Au/ZnO catalysts which have different gold diameters were prepared. The gold diameter was controlled by changing the calcination temperature (ca. 400–750°C) after the deposition–precipitation of Au over ZnO support which was precalcined at 800°C.

Fig. 3 clearly shows that the methanol production rate per exposed Au surface area increased with decreasing the Au diameter. This tendency roughly corresponds to the increase of the peripheral sites of gold–oxide interface, the number of which is inversely proportional to the square of gold particle diameter.

3.2. Gold supported on mixed oxides (Au/MO_x–$M'O_y$)

The commercial methanol synthesis catalysts have very high Cu loading, e.g., 50 atom.-%, and have oxide components such as Al_2O_3 or Cr_2O_3 in addition to Cu/ZnO. To examine the catalytic performance of gold in more practical form, the gold loading was increased to more

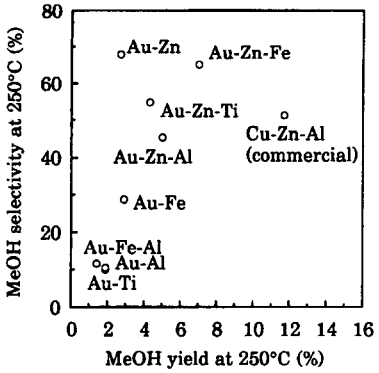

Fig. 4. Relationship between methanol yield and selectivity over $Au/MO_x/M'O_y$ (Au:M = 1:2 or Au:M:M' = 1:1:1 in atomic ratio).

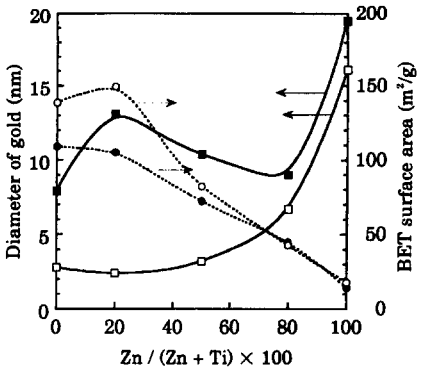

Fig. 5. Diameter of gold and BET surface area as a function of Zn content in Au/ZnO–TiO_2. ○□ Prepared with Mg–citrate addition, ●■ prepared without Mg–citrate addition.

than 30 atom.-% and supported on mixed oxides.

3.2.1. Combination of oxides

Fig. 4 shows the relationship between methanol yield and selectivity at 250°C over various gold catalysts with a metal loading of 33 atom.-%. High methanol selectivities were observed over zinc oxide containing gold catalysts. By the addition of oxides like Fe_2O_3 and TiO_2 to Au/ZnO, methanol yield can be enhanced, maintaining high selectivity exceeding that for commercial $Cu/ZnO–Al_2O_3$ catalyst. Although the $Au/ZnO–Fe_2O_3$ catalyst showed the highest methanol yield and selectivity, the stability of the methanol yield during reaction changed depending on the prereduction conditions.

3.2.2. Au / ZnO–TiO_2 catalyst

The combination of ZnO and TiO_2 as oxide component was investigated in more detail, because this catalyst gives methanol stably and selectively. Fig. 5 shows the BET surface area and gold diameter as a function of Zn content in oxide phase. BET surface area decreased with increasing Zn content. By adding Mg–citrate, BET surface area increased and the diameter of gold obtained from XRD dramatically became smaller when Ti was rich in oxide component. XRD analysis further showed that the ZnO phase was more dispersed in Mg–citrate added catalysts than in the catalysts without Mg–citrate addition. These XRD data suggests the amount of gold–zinc oxide interface can be increased by the addition of TiO_2 with Mg–citrate. Fig. 6 shows the change of the methanol yield with Zn content. Methanol yields were definitely enhanced by the use of mixed oxides and by the addition of Mg–citrate. The similarity of the shape of curves between the methanol yield and the reverse of the gold particle diameter may also suggest the importance gold–oxide interface in methanol formation.

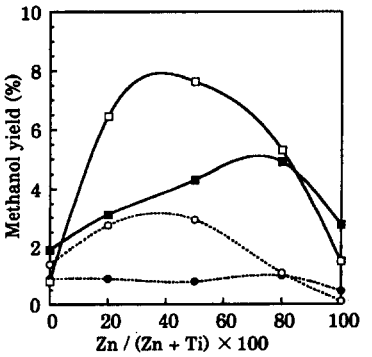

Fig. 6. MeOH yield as a function of Zn content in Au/ZnO–TiO_2. ○● MeOH yield at 200°C, □■ at 250°C, ○□ prepared with Mg–citrate addition, ●■ prepared without Mg–citrate addition.

4. Conclusions

The results in this study show the methanol synthesis activity over supported gold catalysts strongly depends on the nature of support oxides and requires high dispersion of gold. Such a synergistic effect is ascribed to the gold–oxide interface sites, which should play some important role for methanol production as we already reported in CO oxidation mechanism over supported Au catalysts [10]. The combination of Au and zinc oxide is essential for selective methanol synthesis, while the role of ZnO has not been clarified. The addition of TiO_2 component together with Mg–citrate is an effective method for making smaller gold particles and increase the amount of such interfacial sites.

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