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The effect of ZnO in methanol synthesis catalysts on Cu dispersion and the specific activity

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The effect of ZnO in Cu/ZnO catalysts prepared by the coprecipitation method has been studied using measurements of the surface area of Cu, the specific activity for the methanol synthesis by hydrogenation of CO_2, and XRD. Although the Cu surface area increases with increasing ZnO content (0–50 wt%) as is generally known, the specific activity of the Cu/ZnO catalysts with various weight ratios of Cu : ZnO is greater than that of a ZnO-free Cu catalyst. These facts clearly indicate that the role of ZnO in Cu/ZnO catalysts can be ascribed to both increases in the Cu dispersion and the specific activity. The XRD results indicate the formation of a Cu–Zn alloy in the Cu particles of the Cu/ZnO catalysts, leading to the increase in specific activity. It is thus considered that the Cu–Zn surface alloy or a Cu–Zn site is the active site for methanol synthesis in addition to metallic copper atoms that catalyze several hydrogenation steps during the methanol synthesis. Furthermore, the advantage of the coprecipitation method through a precursor of aurichalcite is ascribed to both improvements in the Cu surface area and the specific activity.

Keywords: methanol synthesis, Cu/ZnO catalyst, hydrogenation of CO_2, role of Zn

1. Introduction

The synthesis of methanol from $CO/CO_2/H_2$ using Cu/ZnO-based catalysts is an important industrial process. Although mechanistic research has been extensively carried out by the classical methods of catalyst studies as well as surface science techniques, debate is still continuing concerning the role of ZnO and the active sites [1–5]. One of the most important points to solve is to clarify whether or not an additional effect of ZnO exists, except for the role of dispersing Cu particles. Here, one should be careful concerning the difference in the role of ZnO between the hydrogenation of CO and hydrogenation of CO_2, because both CO and CO_2 can be hydrogenated to methanol so that the active sites may be different.

Even for the hydrogenation of CO_2, completely different mechanisms have been proposed for the additional role of ZnO in Cu/ZnO catalysts. A recent model for the promotional effect of ZnO on the catalytic activity for methanol synthesis is concerned with the morphology of the Cu particles on the ZnO surfaces, which has been independently proposed by Campbell et al. [3,4], Ovesen et al. [5], and Waugh et al. [2]. They agree that the ZnO support changes the morphology of the Cu particles depending on the reaction atmosphere, and during the methanol synthesis reaction, the surface of the Cu particles mainly consists of catalytically active planes such as (110). They do not admit any active component except for the copper atoms. On the other hand, our group has insisted on an “active site creation model” in that ZnO provides Zn atoms on the Cu surface as active sites for the methanol synthesis from CO_2 and H_2 [6–15]. Strong evidence for the promotion of methanol synthesis activity by a small amount of Zn was given in the experiments using a physical mixture of Cu/SiO_2 and ZnO/SiO_2 reduced with H_2 at different temperatures, where the catalytic activity increased upon migration of ZnO_x species from the ZnO particles onto the surface of the Cu particles. That is, the promotion by the tiny amount of Zn was clearly seen without using ZnO as a support or a spacer material [6,8,13]. The model has been further proved by surface science studies, in which the methanol synthesis activity of Zn-deposited Cu(111) measured at a high pressure of 18 atm was found to be greater than that of a clean Cu(111) surface by a factor of 13 [11,12]. In our project on the mechanism of the Cu–ZnO-catalyzed methanol synthesis since 1993, we initially proposed that the role of ZnO was to create the active sites such as Cu^+ species, and that the Cu^+ and Cu^0 cooperate to catalyze the methanol synthesis [16]. The mechanism was then modified to a model such that the Cu–Zn site and Cu^0 are both active components of the Cu/ZnO catalysts, because the state of Zn was found not to be ZnO but a Cu–Zn alloy during the reaction [11,12,14].

The results of the model studies using the $Cu/SiO_2 + ZnO/SiO_2$ mixture as well as Zn/Cu(111) suggested that the role of ZnO for industrial Cu/ZnO-based catalysts prepared by the coprecipitation method can be separately discussed from the viewpoints of the dispersion effect and the creation of the Cu–Zn active sites. In the chemistry of the coprecipitation method, the kind of catalyst precursors, such as malachite, aurichalcite, or hydrozincite, significantly affects the catalytic performance of the methanol synthesis [17,20].

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It is thus interesting to examine the effect of the catalyst precursors on both the Cu dispersion and the specific activity of the Cu/ZnO catalysts.

We now discuss the following topics: (i) Can the role of ZnO be separated into two factors, the dispersion effect and the creation of active sites? What is the important role for industrial Cu/ZnO-based catalysts? (ii) Is the Cu/ZnO catalyst prepared by the coprecipitation method identical with the previous model catalysts of the Cu/SiO_2 + ZnO/SiO_2 physical mixture and the Zn/Cu(111) surface with regard to Zn promotion and Cu–Zn alloy formation? (iii) How does the kind of catalyst precursors affect the dispersion of Cu, the specific activity of methanol synthesis, and the Cu–Zn alloy formation?

2. Experimental

2.1. Catalyst preparation

The precursors of the Cu/ZnO catalysts with the final composition of Cu/ZnO weight ratios ranging from 100 : 0 to 0 : 100 were prepared by the coprecipitation method. 200 cm^3 of a mixed aqueous solution of copper and zinc nitrate at a total concentration of 1.0 mol/l and 200 cm^3 of an aqueous solution of sodium carbonate (1.0 mol/l) were simultaneously added dropwise to 400 cm^3 of distilled water over a period of 40 min with vigorous stirring at room temperature. The dropping rates of both solutions were carefully controlled at 0.5 cm^3/min using microfeeders, which kept the pH of the suspension at 6.8–7.0. The suspension was further aged for 48 h with stirring at room temperature to form precipitates. The precipitates were then washed, filtered, and dried at 393 K for 24 h, which was repeated five times to remove Na ions contained in the precipitates. This washing process is known to reduce the Na contamination below 20 ppm [21]. As the final stage, the calcination of precursors was carried out at 623 K for 3 h in air.

2.2. Catalytic activity test

The catalytic activity for methanol synthesis was evaluated in a high-pressure fixed-bed flow reactor at 50 atm, 523 K, with a specific velocity of 18000 cm^3/g-cat h. The composition of the gas feed was $CO_2/H_2 = 25/75$. Before the activity measurements, the catalyst was reduced with 10 vol% hydrogen in helium at 50 atm, 523 K, with a specific velocity of 30000 cm^3/g-cat h. The flow rate was controlled by a mass flow controller. The effluent gases were analyzed using an on-line gas chromatograph with thermal conductivity and flame ionization detectors.

2.3. Catalyst characterization

The surface area of metallic copper was evaluated by monitoring the reaction of N_2O with copper atoms, which is called reactive frontal chromatography (RFC) [1]. After the methanol synthesis reaction, CO_2 and H_2 were depressurized and swept out of the reactor, and then the catalyst was rereduced with 10 vol% hydrogen in helium at 523 K for 1 h under atmospheric pressure. The rereduced post-reaction catalyst was cooled to ambient temperature with flowing helium, and then 2.5 vol% of N_2O in the helium gas stream was fed over the catalyst to estimate the total copper surface area of each catalyst. The amount of N_2 formed by the reaction between Cu and N_2O was measured with a thermal conductivity detector at 333 K.

The X-ray diffraction (XRD) pattern of the catalyst precursor was recorded using an X-ray powder diffractometer with a nickel-filtered Cu Kα radiation source at 40 kV and 30 mA. The lattice constant and the particle size of the Cu in the rereduced post-reaction catalysts were also estimated from the Cu(111) reflection in the XRD using the Bragg and Scherrer equation. Furthermore, the surface area of Cu was calculated from the particle size of Cu, assuming that each Cu particle was a perfect sphere.

3. Results and discussion

3.1. The role of ZnO-dispersion or specific activity?

The methanol synthesis by hydrogenation of CO_2 was carried out at 50 atm and 523 K using Cu/ZnO catalysts by varying the weight ratio of Cu and ZnO at a total weight of 1 g. Figure 1 shows the yield of methanol as a function of ZnO content in the Cu/ZnO catalysts. No production of methanol was detected when using the ZnO (100 wt%) catalyst. For the Cu (100 wt%) catalyst, the methanol yield was only 6 g-CH_3OH/kg-cat h, while the maximum yield was 522 g-CH_3OH/kg-cat h for the Cu/ZnO catalyst with a ZnO content of 50 wt%. This is the well known promotional effect of ZnO for copper-catalyzed methanol synthesis, and the optimal content of ZnO is close to that re-

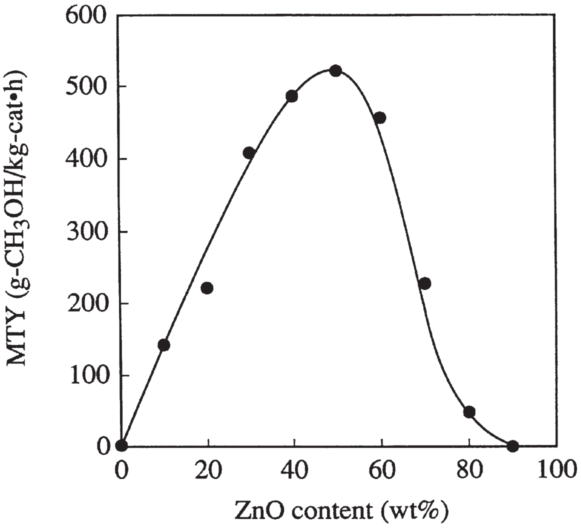

Figure 1. Yield of methanol as a function of ZnO content in the Cu/ZnO catalysts.

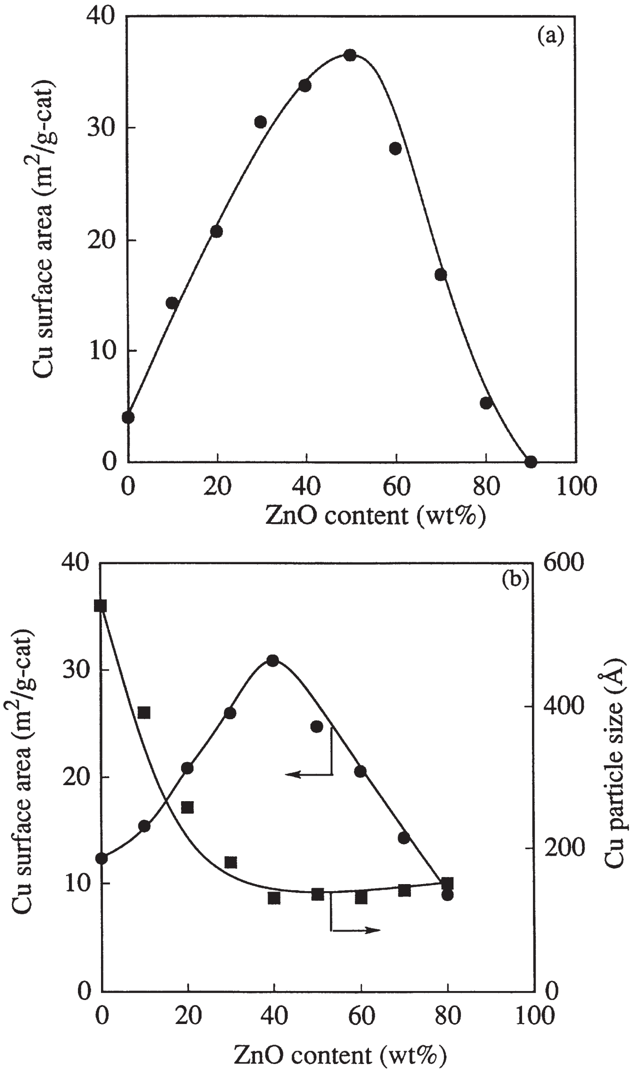

Figure 2. Cu surface area measured by RFC (a), and both Cu surface area and Cu particle size measured by XRD (b), as a function of ZnO content in the Cu/ZnO catalysts.

ported for Cu/ZnO/Al_2O_3 (60/30/10 wt%) [22] and Cu/ZnO (40/60 wt%) [23] catalysts.

To examine the role of ZnO in the Cu/ZnO catalysts, the Cu surface area and the Cu particle size were measured by the RFC method and XRD. Figure 2 shows the Cu surface area measured by RFC (a), and both the Cu surface area and the Cu particle size measured by XRD (b), as a function of ZnO content. It is clearly shown that the Cu surface area significantly increased with the addition of ZnO at 0–50 wt%. In the RFC method, which is a more direct measurement than XRD, the maximum area (36 m^2/g-cat) is nine-fold larger than that for the Cu surface area of Cu alone (4 m^2/g-cat). The decrease in the Cu surface area above ZnO contents of 40–50 wt% was just explained by a decrease in Cu content, because the particle size of Cu shown in figure 2(b) is constant above a ZnO content of 40 wt%.

The results of the Cu surface area measurements indicate that the addition of ZnO (10–40 wt%) makes the Cu particles disperse, leading to an increase in the methanol synthesis yield. The relationship between the methanol yield and the Cu surface area measured by RFC is shown in figure 3. This result is very similar to the literature data of Chinchen et al. [1] and Pan et al. [23]. These authors concluded that the active component was metallic copper and the role of ZnO was to increase the Cu dispersion. However, we cannot agree with their conclusion because the specific activity, i.e., the methanol yield divided by the Cu surface area, was very different between the Cu alone (ZnO content of 0 wt%) and Cu/ZnO (above 10 wt%) catalysts, as shown in figure 4. This clearly indicates the additional effect of ZnO, that is, a significant promotion in the catalytic quality of the Cu surface by a factor of 13–22. In other words, the Cu alone has little activity for methanol synthesis by

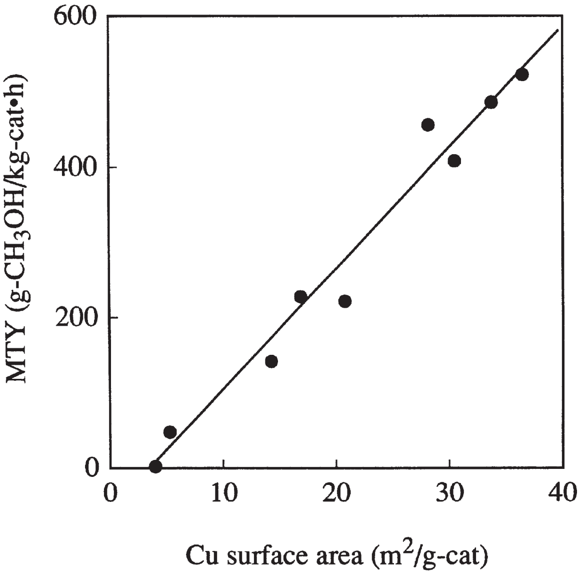

Figure 3. Yield of methanol as a function of Cu surface area.

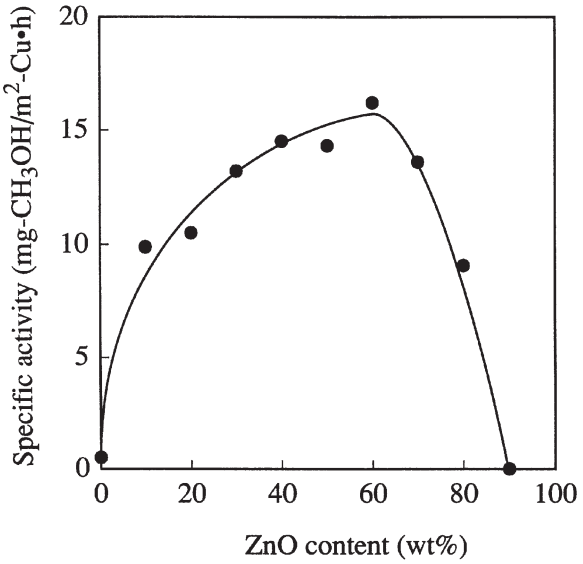

Figure 4. Specific activity for methanol synthesis as a function of ZnO content in the Cu/ZnO catalysts.

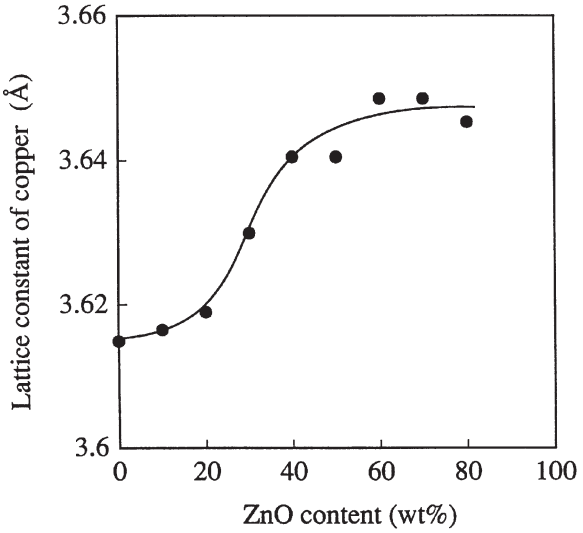

Figure 5. Lattice constant of metallic copper as a function of ZnO content in the Cu/ZnO catalysts.

hydrogenation of CO_2. Accordingly, we conclude that the role of ZnO in Cu/ZnO-based catalysts is ascribed to both increases in the Cu dispersion and the specific activity.

3.2. Cu–Zn alloy formation

As described in the introduction, previous studies [8,12, 13] have suggested that the increase in the specific activity by ZnO is ascribed to the presence of the Cu–Zn active sites on the surface of the Cu particles. The formation of a Cu–Zn alloy in the Cu/ZnO catalysts prepared by the coprecipitation method was thus examined by XRD in this study as previously carried out [6]. Figure 5 shows the lattice constant of Cu for Cu/ZnO catalysts including various contents of ZnO. For only Cu, the XRD peak appeared at $2\theta = 43.3^\circ$, corresponding to that for pure copper with a lattice constant of 3.615 Å. With increasing ZnO content, on the other hand, the lattice constant of Cu was found to increase, indicating the formation of a Cu–Zn alloy as previously observed for the $Cu/SiO_2 + ZnO/SiO_2$ physical mixture [8,13] and the Cu/ZnO catalyst [6]. Above 40 wt% of ZnO, the lattice constant was held constant at 3.64–3.65 Å, corresponding to a Zn content of 13–17% in Cu particles estimated by the literature [24].

The results obtained here are consistent with the previous results on the active site created by Zn addition on Cu surfaces. In surface science studies, the Zn-deposited Cu(111) surface with Zn coverage of $\Theta_{Zn} = 0.19$, where $\Theta = 1$ corresponds to the number of Cu surface atoms, was 13-fold more active for methanol synthesis than a clean Cu(111) surface [11,12]. In the post-reaction analysis by XPS, the active state of Zn on the Zn/Cu(111) surface was found to be metallic during the reaction. STM results of the Zn-deposited Cu(111) showed the formation of a Cu–Zn surface alloy [24] so that we have regarded the Zn atom in the Cu–Zn surface alloy as an active species, although metallic Cu atoms are also necessary for several hydrogenation steps in the methanol synthesis.

Also, in powder catalysts, we have admitted the importance of the Cu–Zn alloy formation. Based on the activity measurements of the Cu/SiO_2 and ZnO/SiO_2 physical mixture for the methanol synthesis from CO_2 and H_2, the specific activity increased with increasing reduction temperature of the mixture. The increase in the specific activity was then found to be due to the migration of Zn from the ZnO particles to the Cu particles upon reduction, leading to the formation of the Cu–Zn alloy [8,13]. Again, we made sure that special sites that catalyze methanol synthesis except for Cu atoms are related to the Cu–Zn alloy formation.

Based on the consistency with previous results on the promotional effect of the Cu–Zn alloy formation, the results in this study indicate that the increase in the specific activity shown in figure 4 is due to the Cu–Zn surface alloy formation. The significant increase in the specific activity (figure 4) for a ZnO content of 10 wt%, where the lattice constant is not very different from that for Cu alone (figure 5), is consistent with the fact that the surface of the Cu–Zn alloy is more stable than the bulk Cu–Zn alloy as observed in the Zn/Cu(111) experiment [15]. Currently, we consider that the promotional effect of Zn is ascribed to promoting the hydrogenation of bridging bidentate formate on the Cu–Zn site to methoxy species, which is evidenced by the *in situ* IRAS experiments [14].

The Cu–Zn alloy formation has been reported by several groups in powder catalyst studies [18,25–27]. Van Herwijnen et al. [25] have reported that ZnO is partly reduced at 473–573 K, resulting in the formation of an α-brass, which cause deactivation for the water–gas shift reaction. Spencer [27] has reported the thermodynamics of α-brass formation in Cu/ZnO catalysts, in which he suggested that the high specific activity of Cu/ZnO catalysts, compared with, e.g., Cu/SiO_2 catalysts, could be a consequence of brass formation. These reports are consistent with the present and previous papers concerning the promotion for methanol synthesis as well as the deactivation for the reverse water–gas shift reaction by the formation of the Cu–Zn alloy [11,12]. On the other hand, the surface chemistry of Cu–Zn alloy drastically changes at high Zn concentration. That is, the activity of the Zn/Cu(111) model catalyst toward methanol synthesis decreases with increasing Zn coverage at $\Theta_{Zn} > 0.19$, which corresponds to the decrease in RWGS activity at high Zn coverage [11,12]. Both decreases in the catalytic activity are probably due to deactivation of H_2 dissociation required for the several hydrogenation processes during methanol synthesis, where the Zn has been found to be oxidized to ZnO. Thus, the decrease in the specific activity above ZnO content of 60 wt%, shown in figures 4 and 5, can be ascribed to the decrease in the number of surface copper atoms used for the H_2 dissociation. In this sense, metallic copper and the Cu–Zn site work cooperatively to catalyze the methanol synthesis reaction.

It should be emphasized that the active species involved in Cu/ZnO for methanol synthesis seems to be different between the hydrogenation of CO_2 and the hydrogenation of CO. Previously, we found that upon formation of the Cu–Zn alloy, the specific activity of methanol synthesis by the hydrogenation of CO_2 increased, while the specific activity decreased for the hydrogenation of CO [6]. We currently consider that the Cu–Zn site is the active species only for the methanol synthesis by hydrogenation of CO_2.

3.3. Advantage of the coprecipitation method

The industrial Cu/ZnO-based catalysts for methanol synthesis are generally prepared by a coprecipitation method, in which an aqueous solution of carbonates such as Na_2CO_3 or $NaHCO_3$ is mixed with solutions of Cu and Zn salts such as nitrate, resulting in the formation of precipitates, such as malachite, $Cu_2(OH)_2CO_3$, aurichalcite, $(Cu,Zn)_5(CO_3)_2(OH)_6$, or hydrozincite, $Zn_5(CO_3)_2(OH)_6$ as a catalyst precursor. It is known that Cu/ZnO or Cu/ZnO/Al_2O_3 catalysts prepared by coprecipitation are far more active than those prepared by kneading or impregnation methods [28]. Furthermore, the kind of catalyst precursor used in the coprecipitation significantly affects the catalytic activity for methanol synthesis, as has been reported so far [17–20]. Here, we examined the advantage of the coprecipitation method from the viewpoints of both the surface area of Cu and the specific activity for methanol synthesis.

Figure 6 shows the composition of Cu- or Zn-containing catalyst precursors, malachite, aurichalcite, and hydrozincite, determined by the intensity of the XRD peaks [29] as a function of the ZnO content in the Cu/ZnO catalysts. The kind of major precursor is found to sequentially vary as malachite, aurichalcite, and hydrozincite with increasing ZnO content. At a ZnO content of 40 wt%, the catalyst precursor includes only aurichalcite, at which the yield of methanol shows a maximum as seen in figure 1. That is, the catalyst prepared from aurichalcite is excellent for the catalytic performance, as Fujita et al. have already reported [19]. In order to further prove the excellence of aurichalcite, the methanol yields were measured for various catalysts prepared using the physical mixtures of the catalyst precursors, as shown in table 1. The methanol yields of the catalysts prepared from malachite, aurichalcite, and hydrozincite corresponding to the ZnO contents of 0, 40, and 100 wt%, respectively, have been already shown in figure 1. The catalyst #4 prepared from malachite and hydrozincite showed little activity although the catalyst included Cu and ZnO adequately (50 : 50). On the other hand, the catalysts prepared from aurichalcite (0.5 g) + malachite (0.5 g), #5, and aurichalcite (0.5 g) + hydrozincite (0.5 g), #6, are both active, and the methanol yields are about half the yield of the catalyst #2 prepared from the pure aurichalcite precursor (1 g). This clearly indicates the methanol production activity depends not on the Cu/ZnO weight ratio but on the aurichalcite precursor. That is, methanol is mainly produced over the catalyst prepared from aurichalcite.

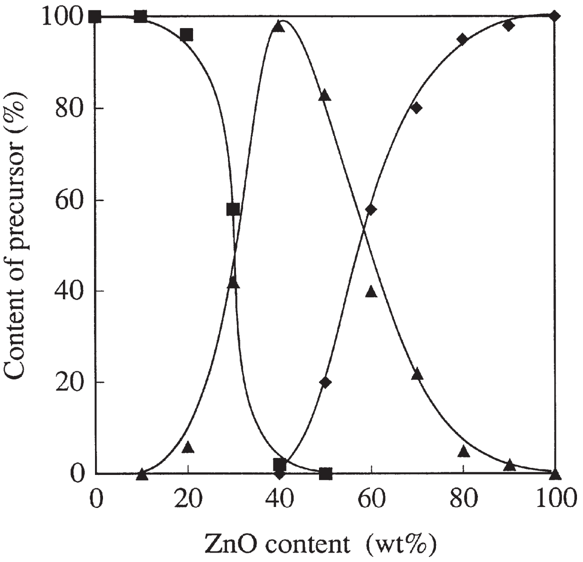

Figure 6. Composition of Cu- or Zn-containing catalyst precursors determined by the XRD peaks as a function of ZnO content in the Cu/ZnO catalysts. (■) Malachite ($Cu_2CO_3(OH)_2$), (▲) aurichalcite ($(Cu,Zn)_5(CO_3)_2(OH)_6$), (◆) hydrozincite ($Zn_5(CO_3)_2(OH)_6$).

We can discuss the advantage of the preparation from aurichalcite, based on the results of the Cu surface area (figure 2) and the specific activity for methanol synthesis (figure 4). First of all, it is clear from the results of figures 2(b) and 6 that the use of aurichalcite precursor renders Cu particles smaller and more dispersive, leading to an increase in the Cu surface area. On the other hand, it is worth noting that the specific activity of methanol synthesis at ZnO contents of 30–70 wt% (figure 4) remains high for the catalysts that were prepared from the aurichalcite pre-

Table 1

Methanol yields of various catalysts prepared using the physical mixtures of the catalyst precursors.[a]

Catalyst	Catalyst precursor	Catalyst weight (g)	Cu : ZnO weight ratio (wt%)	Yield of CH_3OH (%)
#1	Malachite	1	100 : 0	0.03
#2	Aurichalcite	1	60 : 40	7.56
#3	Hydrozincite	1	0 : 100	0
#4	Malachite + hydrozincite	0.5 + 0.5	50 : 50	0.12
#5	Malachite + aurichalcite	0.5 + 0.5	80 : 20	3.31
#6	Aurichalcite + hydrozincite	0.5 + 0.5	20 : 80	3.19

[a] Reaction conditions: temperature = 523 K, total pressure = 50 atm, H_2/CO_2 = 4, feed gas rate 300 cm^3/min.

cursor (figure 6). The excellent specific activity is probably due to the character of aurichalcite, $(Cu,Zn)_5(CO_3)_2(OH)_6$, such that copper is atomically mixed with zinc, leading to Cu–Zn alloy formation upon calcination and reduction. The advantage of the preparation from aurichalcite is thus ascribed to both improvements in the Cu surface area and the specific activity.

4. Conclusions

(1) The role of ZnO in Cu/ZnO catalysts prepared by the coprecipitation method was separated into two factors, Cu dispersion and the specific activity for methanol synthesis from CO_2 and H_2, and was found to play a key role by increasing both the Cu dispersion and the specific activity.

(2) The formation of Cu–Zn alloy in the Cu particles was shown by an increase in the lattice constant of Cu with increasing ZnO content in the Cu/ZnO catalysts, leading to an increase in the specific activity for methanol synthesis. This is consistent with the results of the previous model studies using Zn/Cu(111) and a physical mixture of $Cu/SiO_2 + ZnO/SiO_2$ such that the Cu–Zn active site is created upon Zn addition.

(3) The precursor of the Cu/ZnO catalysts in the coprecipitation method successively changed to malachite, aurichalcite, and hydrozincite with increasing ZnO content. The advantage of using the aurichalcite precursor is to improve Cu dispersion as well as the specific activity, thus resulting in a high methanol yield.

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