Evidence for the migration of ZnO_x in a Cu/ZnO methanol synthesis catalyst

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Received 16 February 1994; accepted 27 April 1994

The behavior and role of ZnO in Cu/ZnO catalysts for the hydrogenations of CO and CO_2 were studied using XRD, TEM coupled with EDX, TPD and FT-IR. As the reduction temperature increased, the specific activity for the hydrogenation of CO_2 increased, whereas the activity for the hydrogenation of CO decreased. The EDX and XRD results definitely showed that ZnO_x ($x = 0$–1) moieties migrate onto the Cu surface and dissolve into the Cu particle forming a Cu–Zn alloy when the Cu/ZnO catalysts were reduced at high temperatures above 600 K. The content of Zn dissolved in the Cu particles increased with reduction temperature and reached $\sim$ 18% at a reduction temperature of 723 K. The CO-TPD and FT-IR results suggested the presence of Cu^+ sites formed in the vicinity of ZnO_x on the Cu surface, where the Cu^+ species were regarded as an active catalytic component for methanol synthesis.

Keywords: methanol synthesis; Cu/ZnO catalyst; Cu–Zn alloy; effect of reduction temperature

1. Introduction

Methanol synthesis from syngas (CO–CO_2–H_2) over Cu/ZnO based catalysts is now a well established industrial chemical process, and has been studied for some decades. Despite a number of fundamental studies with respect to methanol synthesis, the active states of copper and the effects of ZnO are still subjects of considerable controversy [1–5]. Chinchen et al. [6–8] have reported that the methanol

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synthesis reaction occurs exclusively on the surface of metallic copper and ZnO acts as a carrier to prevent sintering of the copper particles; therefore, ZnO has no special role towards copper in the synthesis of methanol. On the contrary, there has been evidence that Cu^+ species are necessary for the synthesis of methanol from CO or CO_2 [9–12]. Sheffer and King [9,10] have studied the promotional effect of alkali ions such as potassium and cesium on methanol synthesis over unsupported copper catalysts using XPS and they observed that the catalytic activity increased with the amount of Cu^+ on the surface of the catalyst. They concluded that the active site for the reaction is Cu^+ and the alkali ions stabilize Cu^+ species against reduction to metallic Cu. Recently, Fujitani et al. [12] have studied the support effect for methanol synthesis from CO_2–H_2 over copper catalysts supported by various metal oxides [8], and found that the oxygen coverage (θ_o) of the copper surface after the hydrogenation of CO_2 well correlated with the specific activity for methanol formation. The activity increased linearly with the oxygen coverage below $\theta_o = 0.16$, while the activity decreased above $\theta_o = 0.18$. This strongly indicates that the active component is not only Cu^+ but also Cu^0, and the main role of supports such as ZnO is therefore to control the Cu^+/Cu^0 ratio which determines the catalytic activity.

Questions then arise as to how and where the Cu^+ sites are formed if Cu^+ is a pivotal species for methanol synthesis. It has been known that a Cu–Zn alloy phase is formed in a Cu/ZnO catalyst upon reduction at high temperatures above 600 K [13–17]. Also, ZnO in Cu/ZnO is known to migrate or sublimate upon reduction with H_2 [13,15,18,19]. It is therefore expected that ZnO partly migrates to the Cu particles and stabilizes Cu^+ as suggested by several authors [11,20]. The purpose of this study is to elucidate the behavior of ZnO in Cu/ZnO and the effect on the catalytic activity for methanol synthesis by characterizing the bulk and surface of Cu/ZnO using X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), temperature programmed desorption (TPD), and Fourier-transform infrared (FT-IR) spectroscopy.

2. Experimental

A series of Cu/ZnO catalysts were prepared by a coprecipitation method. Both an aqueous solution of Na_2CO_3 (1.1 M) and a mixed solution of copper and zinc nitrates (total metal concentration 1.0 M) were added dropwise to distilled water at 300 K. The precipitate was aged in the mixed solution at 343 K for 1 h, followed by washing thoroughly with distilled water. Subsequently, the precipitate was dried overnight in an oven at 383 K, and then calcined in air at 623 K for 3 h. Copper loadings for the prepared Cu/ZnO were 30, 50, and 70 wt%. Cu/SiO_2 catalysts were prepared by an alkoxide method by which the metal particle size can be controlled. The details of the preparation method have been reported elsewhere [24].

The hydrogenations of CO and CO_2 were carried out in a high-pressure

stainless-steel tubular reactor containing 3 cm^3 of a calcined catalyst placed between two plugs of quartz wool. The flow rate was controlled by a mass flow controller. Prior to the measurement of activity, catalysts were reduced in the reactor with hydrogen at the desired temperature. The reactant of CO–H_2 (H_2/CO = 2/1) or CO_2–H_2 (H_2/CO_2 = 3/1) was purified by passing it through active carbon. The reaction was performed at 523 K with a total pressure of 5 MPa and a space velocity of 6 000 h^{-1}. The effluent gases were analyzed by an on-line gas chromatograph equipped with a thermal conductivity and a flame ionization detector. Turnover frequencies (TOF) for methanol formation were calculated using the number of the surface Cu sites evaluated by N_2O chemisorption.

XRD patterns were measured with a Rigaku RINT 2000 using Cu Kα radiation. The lattice constant was estimated from the Cu [111] reflection by using Bragg's equation. TEM measurements were performed using a JEOL JEM-2010 microscope operated at 200 kV, and an EDX was used for elemental analysis of local sites (spot size 5–10 nm) in the Cu/ZnO catalysts. TPD experiments were performed using a multitask TPD spectrometer (BEL Japan), where the catalysts were reduced in situ at various temperatures before TPD measurements. CO and helium as an inert carrier gas were purified by passing them through molecular sieves 5A and active carbon. CO was admitted over 0.2 g of the sample cooled at about 90 K for 1 min, and then helium was passed through the sample at 90 K for at least 5 min. The sample was heated at a rate of 20 K/min in helium with a flow rate of 50 ml/min, while monitoring the flux of desorbed CO with a quadrupole mass spectrometer (ANELVA Q-MASS). Diffuse reflectance FT-IR spectra of CO adsorbed on Cu/ZnO catalysts were measured with a resolution of 4 cm^{-1} using a JEOL JIR-6000 spectrometer equipped with a temperature-controlled catalytic chamber (Spectra Tech). The adsorption of CO was carried out at room temperature by passing atmospheric CO continuously through the catalytic chamber for 1 min and subsequently changing CO to helium.

3. Results and discussion

The hydrogenations of CO_2 and CO were performed over Cu/ZnO catalysts reduced at various temperatures to examine the effect of reduction temperature on the catalytic activity. Main products of the hydrogenation of CO_2 were methanol, CO, and H_2O, whereas only methanol was produced in the hydrogenation of CO. Very small amounts of dimethyl ether and methane were also detected in both hydrogenations. Fig. 1 shows the turnover frequency (TOF) for methanol production over Cu/ZnO as a function of reduction temperature. As for the hydrogenation of CO_2, TOF increased with reduction temperature in the range of 523–723 K by a factor of two. In contrast, TOF for the hydrogenation of CO over Cu/ZnO decreased with reduction temperature. The significant effect of reduction tempera-

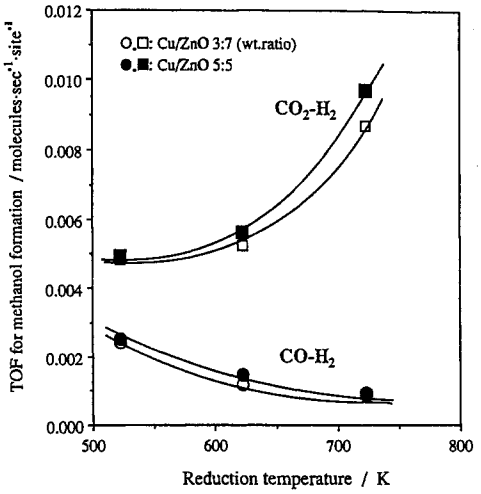

Fig. 1. Turnover frequencies (TOF) for methanol formation in the hydrogenations of CO_2 and CO over Cu/ZnO catalysts as a function of reduction temperature (●, ■) Cu/ZnO = 3/7, (○, □) Cu/ZnO = 5/5.

ture on TOF indicates that the chemical nature of the Cu/ZnO surface is considerably altered by reducing Cu/ZnO with H_2.

To elucidate the effect of reduction temperature, the Cu/ZnO catalysts reduced at different temperatures were characterized by XRD, TEM, and EDX. Fig. 2 shows the lattice constants of copper in Cu/ZnO measured by XRD for different ratios of Cu : ZnO as a function of reduction temperature. The XRD patterns were measured for the Cu/ZnO catalysts used for CO_2 hydrogenation at 523 K after reduction at various temperatures, where the composition of Cu/ZnO was varied

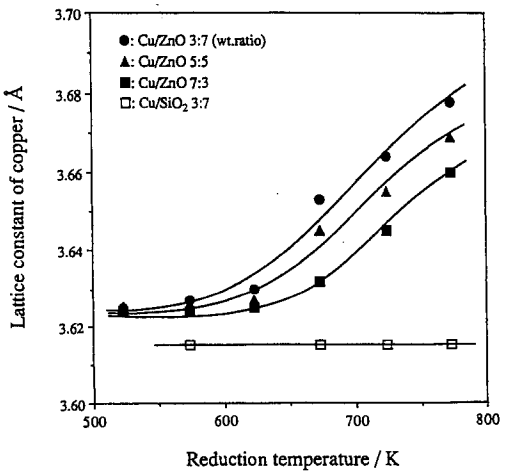

Fig. 2. The lattice constant of metallic copper in Cu/ZnO and Cu/SiO_2 catalysts determined from the position of the Cu [111] line after Kα-2 elimination as a function of reduction temperature.

as 3/7, 5/5, and 7/3 by weight. The lattice constant of Cu was determined from the peak position of the Cu [111] line after Kα-2 elimination using Bragg's equation. It is clear that the lattice constant increased from 3.625 to 3.670 Å with increasing reduction temperature. The increase in the lattice constant is more remarkable at high ZnO contents in Cu/ZnO. Since the lattice constant of Cu–Zn alloy is greater than that of Cu [25], the increase in the lattice constant upon the reduction at high temperatures is attributable to the formation of a Cu–Zn alloy. From the lattice constants of Cu, the average content of Zn in a Cu particle is estimated to be about 20 at% for the reduction temperature of 723 K using the literature value [26]. Note that the zinc content is 5 at% even at the low reduction temperatures of 523–623 K. For Cu/SiO_2, however, no change in the lattice constant was observed and the value was exactly the same as the standard Cu lattice constant of 3.615 Å.

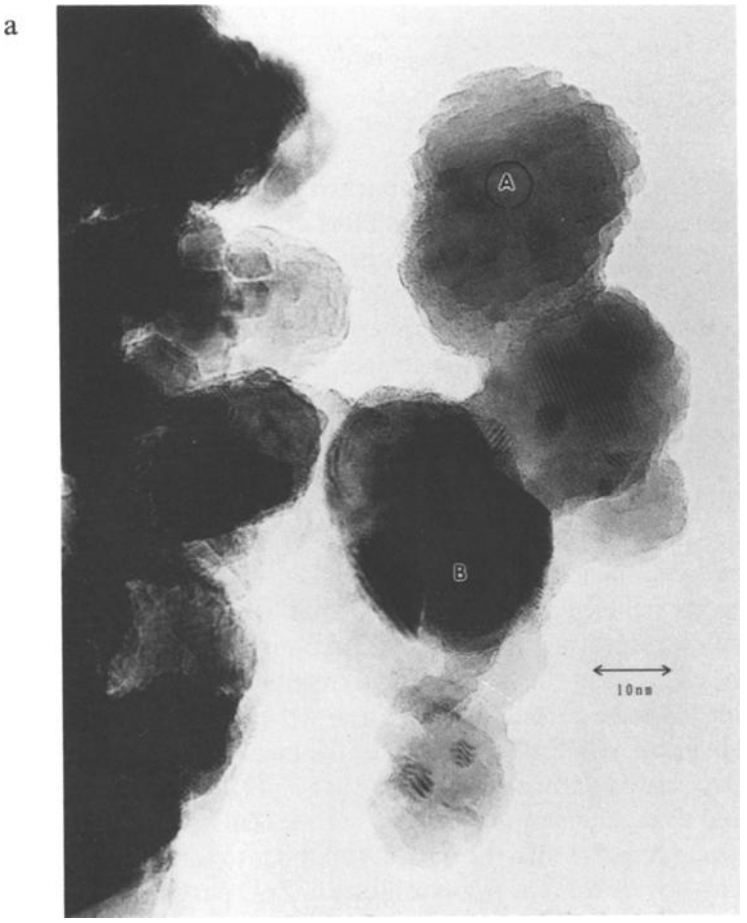

Fig. 3. TEM micrograph of a Cu/ZnO (3/7) catalyst reduced at 523 K for 2 h (a), and EDX spectra of local points A and B labeled on the picture (b).

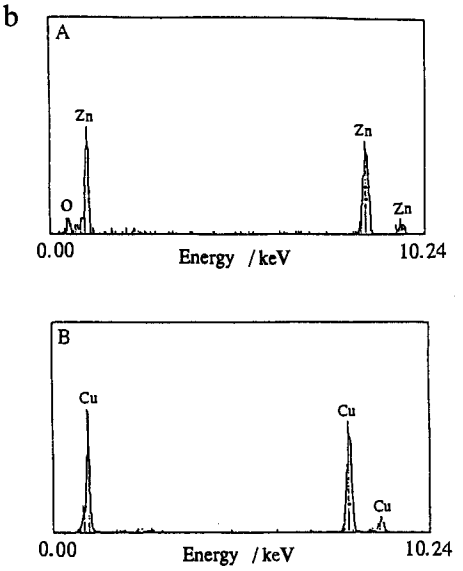

Fig. 3. (Continued).

To confirm the presence of Zn in Cu particles, elemental analysis of local sites on Cu/ZnO particles was performed by TEM coupled with EDX. Figs. 3 and 4 show the results of micrograph and elemental analysis of the local points on Cu/ZnO reduced at 523 and 723 K, respectively. The EDX analysis in fig. 3 shows that the spots labeled as A and B on the spherical particles in the Cu/ZnO catalyst reduced at 523 K correspond to the phases of zinc oxide and metallic copper, respectively. For the Cu/ZnO catalyst reduced at 723 K, on the other hand, the presence of Zn was observed in a copper particle as shown in fig. 4 (spots 2 and 3), which was confirmed by measuring more than ten sites with EDX. No Cu was observed in ZnO particles as manifested by the spectrum of spot 1. The content of Zn in a Cu particle estimated using elemental sensitivity was 16–18% which is in good agreement with the value obtained by XRD ($\sim$ 20%). The particle size for the Cu/ZnO catalysts reduced at 523 and 723 K are estimated as 200–300 and 300–500 Å in diameter, respectively, from the TEM photos. On the other hand, the spot size of incident electron in the EDX measurements is 30–40 Å in diameter which is much smaller than the particle size of Cu. Further, we selected the Cu particles which did not overlap with ZnO particles for the measurements of EDX. Thus, the XRD and EDX results definitely indicate that ZnO_x ($x = 0$–1) moieties formed by the reduction at high temperature migrate from ZnO particles onto the surface of Cu particles and dissolve into the bulk of te copper to form the Cu–Zn alloy. It is also clear that no observable Cu atoms migrate to ZnO particles [20].

To prove the surface states of the Cu/ZnO (3/7) catalysts reduced at 523 and 723 K, TPD measurements of CO were performed. Fig. 5 shows the TPD spectra of CO adsorbed on Cu powder, ZnO powder, and the Cu/ZnO catalyst. In the TPD

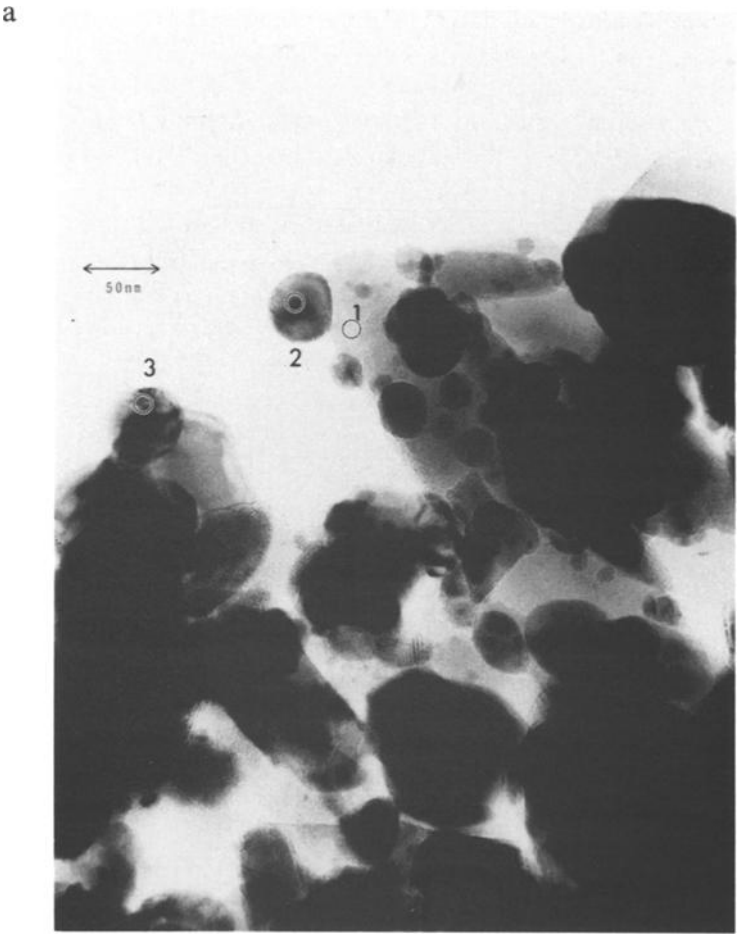

Fig. 4. TEM micrograph of a Cu/ZnO (3/7) catalyst reduced at 723 K for 2 h (a), and the EDX spectra of local points 1, 2, and 3 labeled on the picture (b).

spectra for the Cu powder reduced at 523 K, a peak for CO desorption was observed at 200 K with small peaks at 250–350 K. It has been reported that CO on Cu(110) and Cu(111) desorb at 210 and 165 K, respectively [27–29]; therefore, the peak at 200 K in this study is attributed to CO chemisorbed on metallic copper sites. Probably, the additional peaks at 250–350 K are due to the effect of surface impurities. The peaks disappear when the Cu powder was oxidized by exposing N_2O at 333 K after the reduction, suggesting no CO adsorption on Cu^+ sites [21]. On the pure ZnO surface, CO desorbed with a peak temperature at 115 K, which agrees with the data reported in the literature [22].

Shown in fig. 5 curves D and E are the TPD spectra for Cu/ZnO reduced at 523 K and for Cu/ZnO oxidized by N_2O after the reduction, respectively. For the reduced Cu/ZnO at 523 K, peaks were observed at 115, 200, and $\sim$ 300 K, where

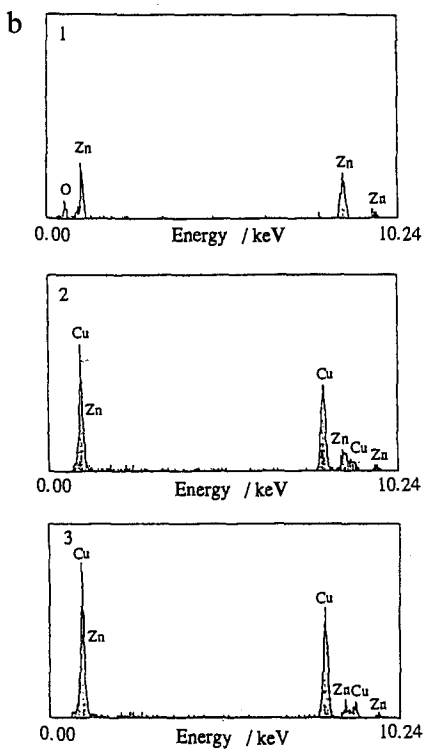

Fig. 4. (Continued).

the peaks at 115 and 200 K were assigned to the adsorption on ZnO and metallic copper, respectively. The broad peak at around 300 K was assigned to the adsorption on Cu sites affected by the presence of ZnO_x moieties on the surface, because such prominent peaks were not observed for Cu/SiO_2 catalysts and the Cu powder. It is considered that the ZnO_x migrating from ZnO particles partly covered the surface of Cu particles based on the results of XRD and EDX. The CO desorbed at $\sim$ 300 K may correspond to the "irreversible adsorption of CO" observed by Klier et al. [23] in the adsorption measurement over Cu/ZnO at room temperature, where they have concluded that the adsorption sites are Cu^+–O–Zn which are responsible for the activity of methanol synthesis from CO and H_2. The high temperature peaks, however, disappeared upon oxidation by N_2O as shown in spectrum E, indicating that the Cu^+–O–Zn sites are further oxidized thus resulting in no ability for CO adsorption.

For the reduced Cu/ZnO at 723 K as shown in spectrum E, the peaks from metallic Cu and ZnO are observed, but no peaks at $\sim$ 300 K are observed. The desorption of CO from the ZnO surface is quite small, which is explained by sublimation or migration of ZnO_x upon reduction with H_2 at the high temperature of 723 K, leading a significant decrease in the amount of ZnO. The ZnO_x partly migrates to Cu particles and partly sublimates and sticks to the reactor as usually

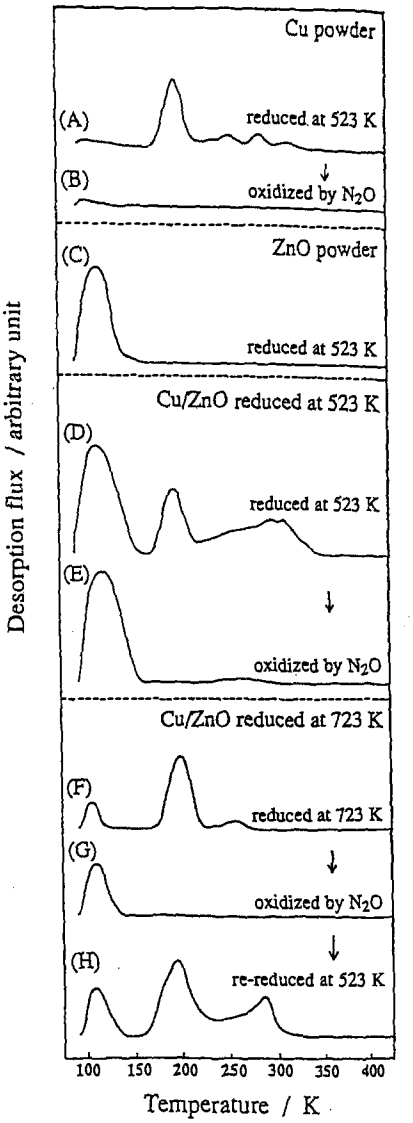

Fig. 5. TPD spectra for adsorbed CO at 90 K on Cu powder, ZnO powder, and Cu/ZnO catalysts. (A) Cu powder reduced at 523 K, (B) and subsequently oxidized by N_2O at 333 K, (C) ZnO powder reduced at 523 K, (D) Cu/ZnO reduced at 523 K, (E) and subsequently oxidized by N_2O at 333 K, (F) Cu/ZnO reduced at 723 K, (G) and subsequently oxidized by N_2O at 333 K, (H) and then re-reduced at 523 K. The intensity of the desorption flux is in logarithmic unit.

observed during the in situ FT-IR experiments in this study. It has been reported [18] that multilayer Zn atoms on Cu desorb at 600 K. Also, the Cu–Zn alloy formation is found to be accelerated at high reduction temperatures in this study. Accordingly, it is concluded that ZnO_x on the surface of Cu is reduced to Zn atoms at the high reduction temperature, leading to the desorption of Zn as well as the formation of a Cu–Zn alloy.

It is noted that the peaks at ~ 300 K appeared as shown in spectrum E when the Cu/ZnO catalyst reduced at 723 K was oxidized by N_2O and then re-reduced by H_2 at 523 K. This indicates that Zn atoms on the Cu surface or in the Cu particles are oxidized to form ZnO_x moieties which lead to Cu^+–O–Zn sites at the mild reduction condition. The formation of the sites is expected under methanol synthesis conditions from CO_2 and H_2 at 523 K since CO_2 can oxidize Zn atom to ZnO_x. On the other hand, the Zn atoms should not be oxidized during the hydrogenation of CO; therefore, the TOF decreases with reduction temperature as shown in fig. 1.

The results of the FT-IR measurements clearly show that the sites for the "irreversible adsorption of CO" are formed during the hydrogenation of CO_2 on Cu/ZnO reduced at the high temperature of 723 K. Fig. 6 shows the spectra for adsorbed CO at 300 K in helium, where the sites for the adsorbed CO are assigned to Cu^+–O–Zn species as described above. As shown in spectra A and D, no CO peak was observed for the Cu/ZnO catalyst reduced at 723 K, but the catalyst reacquires the ability of CO adsorption by exposing the Cu/ZnO catalyst to the reactant, CO_2–H_2, at 523 K, indicating the oxidation of Zn to form Cu^+–O–Zn by CO_2. This is also the case for a reduction temperature of 623 K in fig. 6 spectra B

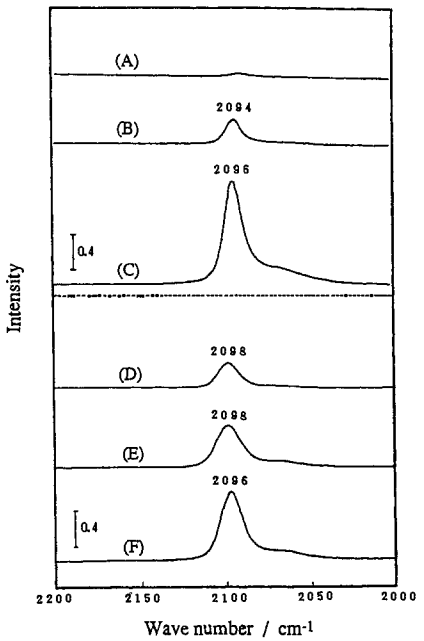

Fig. 6. Infrared spectra of adsorbed CO on Cu/ZnO (3/7) at 300 K with or without exposure to a 3 : 1 mixture of CO_2–H_2 at 523 K for 1 h after H_2 reduction at various temperatures. The reduction temperatures were (A), (D) 723 K, (B), (E) 623 K, and (C), (F) 523 K for 2 h. Prior to the CO dose, helium was admitted at 523 K for at least 20 min to remove residual gases adsorbed on Cu/ZnO as well as in the gas phase.

and E. However, no significant change upon exposure to CO_2 and H_2 was observed for Cu/ZnO reduced at 523 K.

In summary, the present results of EDX and XRD provided evidence for the migration of ZnO_x from ZnO particles to Cu particles to form a Cu–Zn alloy in a Cu particle by reducing a Cu/ZnO catalyst with H_2. The alloy formation upon the reduction was pronounced at high temperatures above 600 K. The TPD and FT-IR results strongly suggest that the ZnO_x migrating from ZnO particles partly cover the surface of Cu particles to form the sites for adsorption of CO which are more stable than those on metallic Cu. At high reduction temperatures above 600 K, ZnO_x on the Cu particles is reduced to Zn, but the Zn is re-oxidized by CO_2 under the reaction condition for the hydrogenation of CO_2. It is concluded that the ZnO_x on the surface of Cu particles stabilizes Cu^+ sites which is a pivotal catalytic species as we have already reported [12]. Recently, we have carried out the surface science experiments where Zn is deposited on the surface of a Cu polycrystalline plate and this model catalyst is used for the hydrogenation of CO_2 at 50 atm. It is clearly shown that the ZnO_x on the surface of Cu promotes methanol synthesis by a factor of ~ 9. Further, a mountain-shaped curve of the activity versus Zn coverage very similar to the one for the various supported catalysts [12] was obtained.

Acknowledgement

This work was partly supported by New Energy and Industrial Technology Development Organization.

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