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Structural change of Cu/ZnO by reduction of ZnO in Cu/ZnO with methanol

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The reducibility of ZnO was investigated in the temperature range of 523–623 K in a stream of a reducing agent such as H_2, CO, and methanol. ZnO was reduced only in the presence of copper in the vicinity of ZnO with CO and methanol, but it was not reduced with H_2. Methanol was a stronger reducing agent in the reduction of ZnO than CO, while CO was stronger in the reduction of CuO than methanol. Two types of brass were observed resulting from the reduction of ZnO in the Cu/ZnO sample by XRD. Zanghengite brass started to be formed at 573 K in addition to α-brass which was observed at the temperature above 523 K in the temperature range of 523–623 K during the ZnO reduction with methanol. The carbon monoxide chemisorption showed that the copper surface areas decreased during the reduction of ZnO with methanol.

Keywords: Cu/ZnO, reduction of ZnO, temperature-programmed reduction, α-brass, zanghengite brass, methanol

1. Introduction

Cu/ZnO systems have been used as catalysts for methanol dehydrogenation to form methyl formate, the water–gas shift reaction and the methanol synthesis [1]. The synergistic effects of Cu and ZnO have been studied for several decades in the aspects of electronic properties of copper or zinc oxide [2], stabilizations of special morphologies [3,4], mechanisms featuring spillover [5–8] and specific interaction at the Cu/ZnO interface [9]. The stability of Cu/ZnO depending on the composition of reactants has been discussed in view of the stability of Cu^+ [10], the sintering of copper [11], and the alloy formation [12]. Recently, it was proposed that the reduction of ZnO could be a main reason in the deactivation of the Cu/ZnO catalyst during methanol dehydrogenation [13]. In this study, the reducibility of ZnO in Cu/ZnO samples was studied with H_2, CO, and methanol, and the structural change resulting from the reduction of ZnO was investigated.

2. Experimental

Cu/ZnO catalysts were prepared by coprecipitation. Copper acetate (Aldrich Co.) and zinc acetate (Aldrich Co.) were dissolved in 500 ml of distilled water, and 400 ml of 2.5 M ammonium carbonate (Aldrich Co.) aqueous solution was added dropwise into the acetate solution. A final pH of 7 was observed. The resulting precipitate was filtered, washed with distilled water and dried in a vacuum drying oven overnight, followed by calcination at 623 K for 16 h.

BET surface areas of the prepared Cu/ZnO catalysts were determined by a surface area analyzer (Micromeritics Co., ASAP 2000). The standard deviations of BET surface area measurements were within ±4%. The copper surface areas of the fresh catalysts were obtained by N_2O titration, following the procedure described by Evans et al. [19]. Duplicate experiments showed the copper surface areas had standard deviations of ±4%.

Copper oxide and ZnO reduction was monitored by the weight change of the samples by a microbalance (Cahn Co., Cahn 2000) which was connected to a gas handling apparatus. H_2, CO, and methanol were introduced into a probe tube of the balance with He carrier gas (9.2 mol% methanol or carbon monoxide in He, or 18.4 mol% H_2 in He, total flow rate of 120 ml/min). In the experimental conditions, the deviation of the weight measurements was within $100\ \text{mg} \pm 10\ \mu\text{g}$.

XRD data were obtained by a Rint 2000 wide angle goniometer (Rigaku Co.) after the reduction of catalyst samples with methanol for 3 h. Samples for XRD were prepared in a glove box to prevent oxidation from air after the 3 h reduction with methanol at GHSV of $1500\ \text{h}^{-1}$.

CO chemisorption was conducted at 298 K and N_2O titration was conducted at 363 K after the reduction with methanol. The samples were evacuated at the reduction temperature for 10 h before CO chemisorption. The duplications of CO chemisorptions thus obtained had deviations of ±5%.

The X-ray photoelectron spectra of the samples reduced in a stream of methanol were obtained using Al Kα radiation (Surface Science, 2803-S spectroscope). The reduced samples were pelletized and mounted on a sample holder in a glove box before the XPS investigation. Charging effects

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present during the analysis of the samples were corrected using the C(1s) peak due to adventitious carbon fixed at the binding energy of 289.1 eV. The reproducibility of the peak positions thus obtained was ±1 eV.

3. Results

The composition, BET surface areas and copper surface areas of the prepared samples are listed in table 1. The Cu/ZnO (5/5) sample was found to have largest surface area among the prepared samples, while BET surface areas were little dependent on the composition of the samples.

The coprecipitated CuO/ZnO (5/5) sample (60 mg) in a hangdown probe tube of a microbalance was reduced with H_2, CO, and methanol. Figure 1 shows the weight changes of the samples during the temperature-programmed reduction (TPR) in the range of 323–623 K.

The TPR studies with CO and methanol show two distinctive reduction steps while the one with H_2 shows one reduction step. The weight change in the temperature range from 373 to 523 K can be assigned to copper oxide reduction, while at temperatures above 523 K it can be attributed to ZnO reduction. The reduction temperature of the copper oxide component with CO is lower than those of methanol or H_2. H_2 reduces the copper oxide component over a rather broad temperature range from 443 to 523 K while methanol reduces the copper oxide within a narrow range of the similar temperature to CO. It is observed that H_2 cannot reduce the ZnO component up to 623 K under the same reduction conditions, while CO and methanol start to reduce the ZnO component from about 523 K in the presence of the reduced copper. It is interesting to note that ZnO reduction with methanol is faster than with carbon monoxide.

Table 1
The composition, BET surface areas and copper surface areas of the prepared samples.

Catalyst	Mol ratio of Cu to Zn	BET surface area (m^2/g_{cat})	Copper surface area (m^2/g_{cat})
CuO/ZnO (1/9)	1 : 1	20.5	0.9
CuO/ZnO (3/7)	3 : 7	21.0	1.6
CuO/ZnO (5/5)	5 : 5	26.9	5.0
CuO/ZnO (7/3)	7 : 3	22.2	4.2
CuO/ZnO (9/1)	9 : 1	16.3	2.7
CuO	10 : 0	–	0.7
ZnO	0 : 10	20.1	–

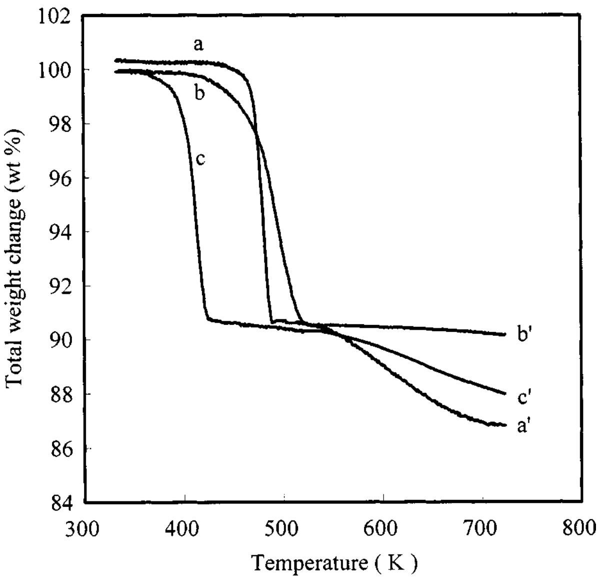

Figure 1. Temperature-programmed reduction of CuO/ZnO (5/5) in a stream of (a–a′) methanol, (b–b′) H_2, and (c–c′) CO.

For the investigation of the role of copper in the ZnO reduction with methanol, isothermal reduction experiments were conducted with 30 mg of ZnO, 60 mg of the physical mixture of CuO and ZnO at the mole ratio of 1/1, and 60 mg of the coprecipitated CuO/ZnO (5/5) sample. Each sample was pre-reduced at 623 K for 3 h in 5% H_2/Ar to obtain copper in its metallic state. Then, the sample was reduced in a methanol stream at 623 K and the resulting weight change was monitored.

Figure 2 shows that ZnO in the coprecipitated Cu/ZnO among three samples is easily reduced using methanol at 623 K. The slight weight increase in the initial reduction time is attributed to the adsorption of organic species derived from methanol.

Figure 2 indicates that the proximity of copper and ZnO is important to reduce ZnO with methanol. For the confirmation of the importance of the proximity of copper and ZnO, the isothermal reduction experiments were conducted at 623 K in a stream of methanol over the coprecipitated samples with the copper/zinc molar ratio of 1/9, 3/7, 5/5, and 7/3. Figure 3 shows the isothermal reduction at 623 K with methanol. Each sample was pre-reduced at 623 K for

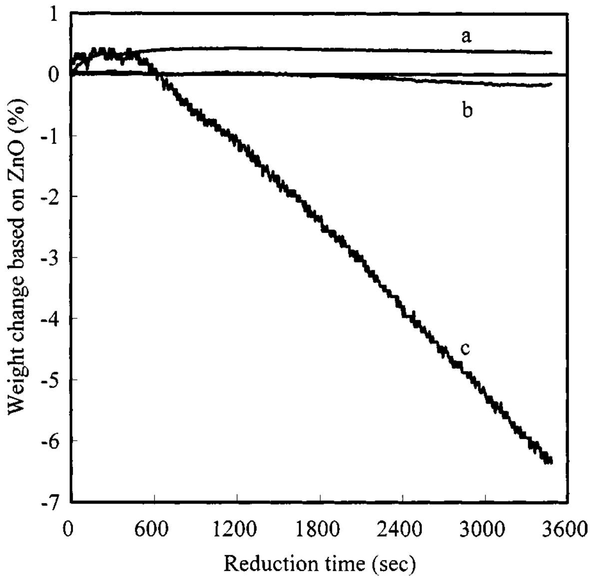

Figure 2. Weight loss of ZnO in (a) ZnO only, (b) physically mixed CuO/ZnO (5/5), and (c) coprecipitated CuO/ZnO (5/5) during the reduction with methanol at 623 K after reducing the copper component to metallic copper at 623 K for 1 h with 5% H_2/Ar.

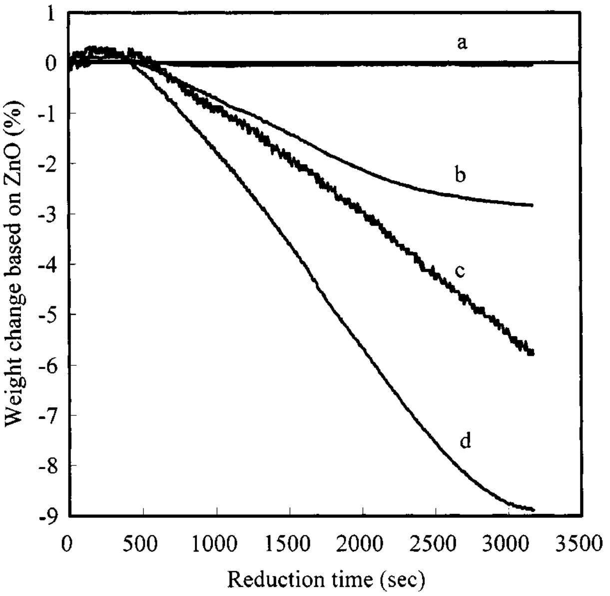

Figure 3. Weight loss of ZnO in Cu/ZnO catalysts at the molar ratio of Cu to Zn of (a) 1/9, (b) 3/7, (c) 5/5, and (d) 7/3 with methanol at 623 K after reducing the copper component to metallic copper at 623 K for 1 h with 5% H_2/Ar.

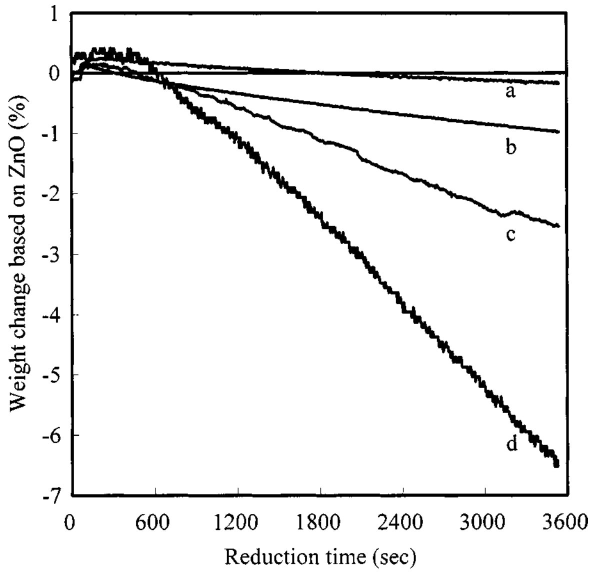

Figure 4. Weight loss of ZnO in Cu/ZnO (5/5) with methanol at (a) 523, (b) 553, (c) 573, and (d) 623 K after reducing the copper component to metallic copper at 623 K for 1 h with 5% H_2/Ar.

3 h in 5% H_2/Ar to obtain copper in its metallic state. Figure 3 indicates that ZnO in a Cu/ZnO sample with high ratio of copper to ZnO is more easily reduced. After ZnO reduction for 1 h at 623 K with methanol, the weight changes of ZnO based on ZnO were −0.1, −1.9, −6.1, and −9.0% with samples with the copper/zinc molar ratio of 1/9, 3/7, 5/5, and 7/3, respectively.

Figure 4 shows the isothermal reduction of ZnO in the Cu/ZnO (5/5) catalyst at 523, 553, 573, and 623 K in a methanol stream. The sample was pre-reduced at 623 K for 3 h in 5% H_2/Ar to obtain copper in its metallic state.

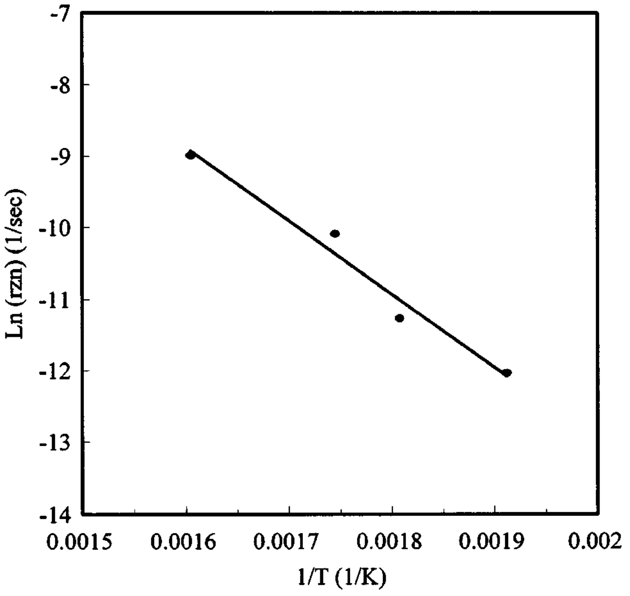

Figure 5. The Arrehenius plot for the reduction of ZnO in Cu/ZnO (5/5) with methanol.

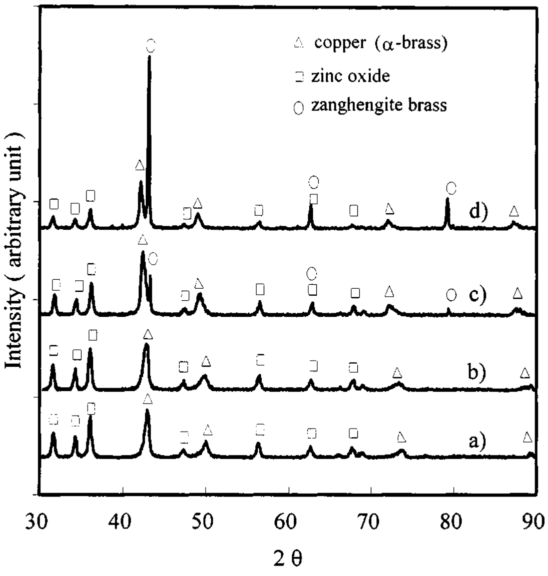

Figure 6. XRD spectrum of the Cu/ZnO (5/5) catalyst after 3 h reduction with methanol at (a) 523, (b) 553, (c) 573, and (d) 623 K after reducing the copper component to metallic copper at 623 K for 1 h with 5% H_2/Ar.

In figure 4, 1 wt% decrease based on ZnO is equivalent to 5.1 mol% reduction of ZnO. The apparent activation energy was calculated to be 20.4 kcal/mol from the Arrhenius plot shown in figure 5, assuming that the reduction rate was zero order with respect to reactants. It is interesting to note that the activation energy of the ZnO reduction with methanol was similar to or slightly higher than that of copper oxide reduction with H_2 (16.0–20.0 kcal/mol) [25].

XRD studies were conducted to observe the structural changes of the reduced Cu/ZnO (5/5) sample after reduction with methanol at 523, 553, 573, and 623 K for 3 h, as shown in figure 6. The sample was pre-reduced at 623 K for 3 h in 5% H_2/Ar to obtain copper in its metallic state. It

Table 2
Experimental zinc concentration in α-brass after the reduction of ZnO in Cu/ZnO (5/5) sample in a stream of methanol.

Treatment	Lattice parameter (Å)	Zinc concentration in α-brass (at%)
No reduction with methanol	3.6130	0.00
Reduction with methanol at 523 K for 3 h	3.6362	0.11
Reduction with methanol at 553 K for 3 h	3.6464	0.15
Reduction with methanol at 573 K for 3 h	3.6942	0.34
Reduction with methanol at 623 K for 3 h	3.7030	0.37

is interesting to note that the characteristic peaks of copper metal at 43.3°, 50.4°, and 74.1° shifted to 42.2°, 49.1°, and 72.1° after methanol reduction at 623 K, while those of ZnO did not. The shifts of the characteristic peaks of copper metal to the lower angles are attributed to the diffusion of the reduced zinc metal ± 4% into copper forming α-brass, which results in the increase of the lattice parameter of copper. Rao and Anantharaman [14] gave the quantitative relation of the copper lattice parameter to the zinc concentration in α-brass. From their relationship, the concentration of zinc metal in the brass could be calculated after the reduction of ZnO in Cu/ZnO (5/5) with methanol at 493, 523, 553, 573, and 673 K for 3 h as shown in table 2. The lattice parameters were calculated by the Nelson and Riley method [15]. Reproducibility was ±0.0004 Å. Table 2 indicates that zinc concentrations in α-brass increase with the reduction temperature.

In addition to α-brass, new peaks at 43.2°, 63.2°, and 79.1° are observed on the samples reduced at 573 and 623 K with methanol, suggesting that a brass with zanghengite structure was formed [16].

XPS experiments were conducted to measure the binding energy of copper at the surface of the Cu/ZnO (5/5) sample. Figure 7 shows the spectra of Cu($2p_{2/3}$) in three samples: (a) reduction at 623 K for 3 h in 5% H_2/Ar, (b) reduction with methanol at 493 K for 3 h after the H_2 reduction, and (c) reduction with methanol at 523 K for 3 h after the H_2 reduction.

The Cu($2p_{2/3}$) peak of the reduced sample with H_2 appeared at the binding energy of 932.5 eV. The Cu($2p_{2/3}$) binding energy of the reduced sample with methanol was 0.3 eV higher than that with H_2. Steiner et al. [17] calculated that the core-level binding energy of copper could be shifted upto 0.65 eV higher in the alloy of dilute copper in zinc matrix.

XPS investigations indicate that ZnO on the surface of the Cu/ZnO sample can be reduced with methanol, but cannot with H_2, although the reduction temperature with methanol was 100 K lower than the one with hydrogen. The brass formation following the reduction of ZnO in Cu/ZnO can induce the change of the copper surface area on the Cu/ZnO sample. CO chemisorptions [18] and N_2O titrations [19] were conducted to measure the change in copper surface area in Cu/ZnO (5/5) at 298 and 363 K, respectively, after the reduction at 523 K for 15, 30, 60, and

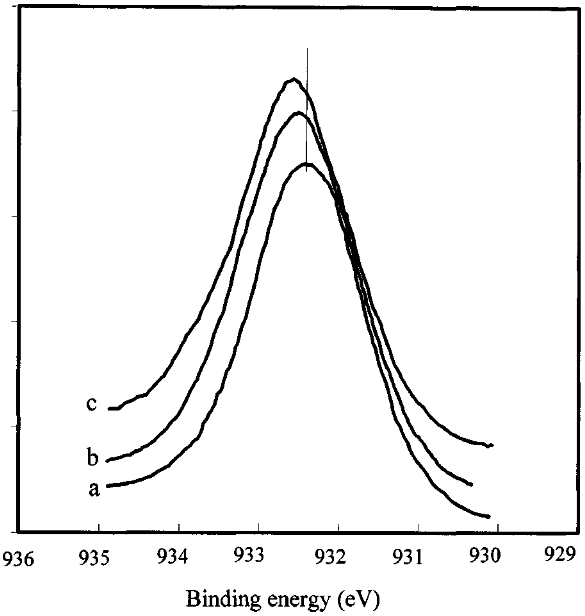

Figure 7. XPS spectra of Cu($2p_{3/2}$) of the Cu/ZnO (5/5) catalyst: (a) reduced at 623 K for 1 h with 5% H_2/Ar, (b) reduced at 493 K for 3 h with methanol after the reduction with 5% H_2/Ar, and (c) reduced at 523 K for 1 h with methanol after the reduction with 5% H_2/Ar.

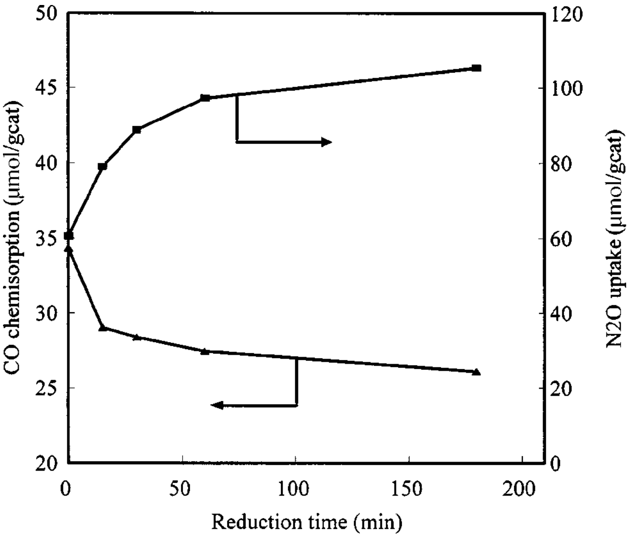

Figure 8. CO chemisorption at 298 K (▲) and N_2O uptake at 363 K (■) on the Cu/ZnO (5/5) catalyst after the reduction at 523 K with methanol. The samples were evacuated at the reduction temperature for 10 h before the CO chemisorption or the N_2O titration.

180 min with methanol, as shown in figure 8. The sample was pre-reduced at 623 K for 3 h in 5% H_2/Ar to obtain copper in its metallic state. The amount of N_2O uptake of the fresh sample is about twice as high as that of CO chemisorption, as previously reported [18]. The amount of N_2O uptake increased from 60.5 μmol/g for a fresh catalyst to 105.4 μmol/g for the sample after the 3 h reduction with methanol, while the amount of CO chemisorption decreased from 34.3 μmol/g for a fresh catalyst to 26.1 μmol/g for the sample after that. It can be deduced that the large amount of increase of N_2O uptake of the sample after the reduction with methanol resulted from the oxygen deficient ZnO as well as from the reduced zinc metal in α-brass. However, since CO cannot adsorb on zinc metal [20], the amount of CO chemisorption indicates the surface area of copper. Therefore, it can be concluded that the reduction of zinc oxide induced the decrease of the copper surface area (figure 8).

4. Discussion

The weight changes below 523 K in figure 1 are ascribed to the reductions of CuO in the CuO/ZnO (5/5) sample. It indicates that the CuO reduction is more difficult with H_2 than with CO, as previously reported [21]. The CuO reduction with methanol occurs at the similar temperature to the one with H_2, but in the broad temperature range. The weight changes above 523 K in figure 1 show that the ZnO is reduced with CO and methanol, but not with H_2. The ZnO is more reduced with methanol than with CO. However, the ZnO only cannot be reduced even with methanol. The proximity of copper and ZnO is an important factor for reducing ZnO with methanol (figure 2). It was observed that the reduced ZnO forms brass with copper (figure 6).

The reactions to reduce zinc oxide with H_2, CO and methanol can be written as

$$\mathrm{ZnO} + \mathrm{H_2} \rightleftharpoons \mathrm{Zn} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{ZnO} + \mathrm{CO} \rightleftharpoons \mathrm{Zn} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{ZnO} + \tfrac{1}{3}\mathrm{CH_3OH} \rightleftharpoons \mathrm{Zn} + \tfrac{1}{3}\mathrm{CO_2} + \tfrac{2}{3}\mathrm{H_2O} \tag{3}$$

Gibbs energy equations for reactions (1)–(3) were obtained using the data in the literature [22,23]:

$$\Delta G = 27761.2 + 11.333T\log T - 1.36\times10^{-3}T^2 - 67250/T - 46.3405T, \tag{4}$$

$$\Delta G = 16440.9 + 4.4256T\log T - 1.08\times10^{-3}T^2 + 24250/T - 15.2327T, \tag{5}$$

$$\Delta G = 29981.4 - 2.8168T\log T + 2.35\times10^{-3}T^2 - 38917/T - 21.0719T - 3.81\times10^{-7}T. \tag{6}$$

Zn/ZnO ratio without copper can be calculated as follows:

$$x_{\mathrm{Zn}} = KR.$$

The zinc concentration in brass can be calculated as follows [24]:

$$x_{\mathrm{Zn\ in\ brass}} = \frac{K}{\gamma_{\mathrm{Zn}}}R,$$

where

$$R = \frac{P_{\mathrm{H_2}}}{P_{\mathrm{H_2O}}}, \frac{P_{\mathrm{CO}}}{P_{\mathrm{CO_2}}}, \text{ or } \frac{P^{1/3}_{\mathrm{CH_3OH}}}{P^{1/3}_{\mathrm{CO_2}}P^{2/3}_{\mathrm{H_2O}}},$$

$$\gamma_{\mathrm{Zn}} = \exp\left(-0.7360 - \frac{2977}{T}\right),$$

$$K = \exp\left(-\frac{\Delta G}{RT}\right).$$

Table 3 shows the Gibbs energies, the reduced zinc fraction to ZnO at the R value of 1 and the zinc fraction in brass at the R value of 1. Table 3 indicates that the reduction of ZnO without copper is not allowed below 623 K thermodynamically.

The thermodynamic barrier for the reduction of zinc oxide can be lowered by forming brass with copper. For the formation of brass, the reduced zinc metal should migrate from the ZnO surface to copper. Therefore, no reduction of ZnO in the physically mixed Cu/ZnO sample with methanol can be attributed to the inability of the diffusion of zinc metal to copper. The R value in H_2 reduction can be assumed to be above 1000 (H_2 purity is 99.999%).

The thermodynamic zinc concentration in brass at $R = 1$ can be calculated to be 12 mol% at 623 K with H_2, but figure 1 shows that H_2 cannot reduce the ZnO in the Cu/ZnO sample (5/5). It indicates that no reduction of ZnO in Cu/ZnO with H_2 is kinetically suppressed in the reduction step of ZnO.

The reduction of ZnO in Cu/ZnO with methanol is shown to be proportional to the mole ratio of Cu to ZnO

Table 3

The reduced zinc fraction at $R = 1$ in a stream of H_2, CO, and methanol by thermodynamic calculation.

Temp. (K)	H_2 reduction		CO reduction		Methanol reduction	
	x_{Zn}	$x_{\mathrm{Zn\ in\ brass}}$	x_{Zn}	$x_{\mathrm{Zn\ in\ brass}}$	x_{Zn}	$x_{\mathrm{Zn\ in\ brass}}$
423	3.1×10^{-11}	7.3×10^{-8}	2.3×10^{-8}	5.5×10^{-5}	3.8×10^{-10}	9.0×10^{-7}
493	2.3×10^{-9}	2.0×10^{-6}	3.4×10^{-7}	3.0×10^{-4}	5.9×10^{-8}	5.2×10^{-5}
523	1.0×10^{-8}	6.2×10^{-6}	8.6×10^{-7}	5.3×10^{-4}	3.4×10^{-7}	2.1×10^{-4}
553	3.8×10^{-8}	1.7×10^{-5}	2.0×10^{-6}	8.9×10^{-4}	1.6×10^{-6}	7.4×10^{-4}
573	8.4×10^{-8}	3.2×10^{-5}	3.2×10^{-6}	1.2×10^{-3}	4.2×10^{-6}	1.6×10^{-3}
623	4.9×10^{-7}	1.2×10^{-4}	9.8×10^{-6}	2.4×10^{-3}	3.5×10^{-5}	8.6×10^{-3}

(figure 3). Assuming that Cu particles are half spheres, the ratio of the interfacial grain boundary between Cu and ZnO can be calculated to be 1 : 1.1 : 6.2 : 3.1 for Cu/ZnO (1/9) : Cu/ZnO (3/7) : Cu/ZnO (5/5) : Cu/ZnO (7/3) from the measured copper surface area. The length of interfacial grain boundary of Cu/ZnO (7/3) is shorter than that of Cu/ZnO (5/5). It indicates that the reduction of ZnO with methanol can be interpreted with the bulk reaction to form brass between the reduced zinc metal and the copper.

The reduction of ZnO resulted in the decrease of copper surface area in Cu/ZnO (figure 8). It has been suggested that the reduction of ZnO can be responsible for the reason of deactivation during methanol dehydrogenation. This study shows that the decrease of copper surface area, a clear cause of deactivation, is induced by the disintegration of the support, the reduction of ZnO.

5. Conclusion

Experimental data show that methanol and CO reduce ZnO in Cu/ZnO, while H_2 does not below 723 K. Thermodynamic calculations show that ZnO can be reduced only in the presence of copper with CO and methanol by forming brass. It is demonstrated that the proximity of copper metal and ZnO is essential for the reduction of ZnO. The reduction of ZnO in Cu/ZnO induces a decrease in the copper surface area, which can be the direct cause of deactivation in the catalytic reactions on Cu/ZnO-containing catalysts such as methanol dehydrogenation, methanol synthesis by CO hydrogenation, and higher alcohol synthesis conducted under reductive conditions.

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