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SYNERGY BETWEEN Cu AND ZnO FOR METHANOL CONVERSIONS OVER Cu-ZnO CATALYSTS

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It was found that Cu-ZnO catalysts showed maximum specific activities at the composition of 70 wt% CuO for the CH_3OH conversions both in the absence and presence of H_2O. Taking into considerations the kinetic isotope effects and the electronic state and particle size of the Cu metal, it is proposed that the synergistic promotion is bifunctional in nature.

Copper-zinc oxide phases are active ingredients in industrial catalysts for the methanol synthesis from CO and H_2 at low pressures. It is also well known that strong synergies between Cu and ZnO operate in the synthesis. However, the origin of the synergies and the catalytically active species in Cu-ZnO catalysts are open to question.1) In our previous study on Cu-ZnO catalysts,2) it has been proposed that strong interactions between Cu and ZnO result in an electron transfer from ZnO to Cu metal and in the formations of two types of Cu metal species as well as stabilized Cu^{1+} species. The correlations between catalytic properties and these interaction modes have not been explored yet. In this study, the bimolecular dehydrogenation and steam reforming reactions of CH_3OH were carried out over Cu-ZnO catalysts to obtain informations as to whether the catalysts show synergies for these reactions and to establish the relations, if present, between the catalytic properties and interaction modes in these catalyst systems.

Cu-ZnO catalysts having various compositions were prepared by a coprecipitation with Na_2CO_3 using copper and zinc nitrates.2) The precipitates were washed thoroughly with distilled water, followed by drying at 110 °C and calcining at 350 °C for 4 h. The resultant CuO-ZnO catalysts were reduced in a stream of H_2 at 250 °C for 2 h prior to use. The physicochemical properties of the activated Cu-ZnO catalysts have shown elsewhere.2) Two types of methanol conversions were examined by using a fixed bed flow reactor at an atmospheric pressure; $2CH_3OH = 2H_2 + HCOOCH_3$ and $CH_3OH + H_2O = 3H_2 + CO_2$. The reactant pressures were 0.18 atm (1 atm = 0.10 MPa) of CH_3OH for the former reaction and 0.11 atm of each CH_3OH and H_2O for the latter in an Ar stream (total flow rate; 57 and 65 ml STP/min, respectively). The reaction gases were gas-chromatographycally analyzed.

In the decomposition of CH_3OH over the Cu-ZnO catalysts in the absence of H_2O, $HCOOCH_3$ was selectively formed at < 200 °C, whereas CO was a major product at ca. 350 °C and HCHO was predominantly formed at > 450 °C. Small amounts of CO_2 and CH_4 were also detected at > ca. 300 °C. The selective $HCOOCH_3$ formation was investigated here between 140 and 180 °C. The selectivities were better than 99% below 160 °C and 97% at 180 °C on the Cu-containing catalysts. With the steam reforming of CH_3OH, no products other than CO_2 and CO were formed even at 500 °C except a small amount of CH_4. The fraction of CO increased gradually with the reaction temperature at the expense of CO_2. When the reaction temperature was lower than 200 °C, $CO_2/(CO_2 + CO) = 1.0$ and $H_2/CO_2 = 3.0 \pm 0.1$. The selective CO_2 and H_2 formations were studied further below 200 °C.

It is considered that metallic Cu is a major species active for these reactions, since the ZnO catalyst alone showed only negligible activities at < 200 °C whereas Raney-Cu and borided-Cu metal catalysts that contained no oxidized Cu species (XPS) showed relatively high activities. Similar conclusions are deduced by Kobayashi et al.[3] for Cu/SiO_2 catalysts. Accordingly, the specific activities of the catalysts for both reactions are represented by the amount of CH_3OH converted per unit surface area of Cu metal. The specific activity of the catalyst for the $HCOOCH_3$ formation at 160 °C is depicted in Fig. 1 against the CuO content. The activation energy is also shown there. Apparently, the 70 wt% CuO catalyst shows the highest specific activity. On the other hand, the activation energy decreased with decreasing the CuO content. As for the steam reforming reaction of CH_3OH, the specific activity (Fig. 1) and activation energy behaved similarly to those for the dehydrogenation. It is evident that synergistic effects are observed for the conversions of CH_3OH. In the low Cu content catalysts, only the low specific activities were observed. Taking into account the previous findings[2,4] that the fraction of Cu^{1+} species in the catalyst surface increases with decreasing the Cu content, it is concluded that the Cu^{1+} species shows no special activities for the CH_3OH conversions. The activity maxima at the 70 wt% CuO catalyst are, accordingly, considered to be due to 1) the change in the reaction mechanism, 2) the changes in the properties of the Cu metal such as an electron density and particle size, and 3) bifunctional promotion for the reactions.

In order to assess the first point, kinetic isotope effects were examined by using CD_3OD, CH_3OD, and D_2O. The results are summarized in Table 1. It is demonstrated that the cleavages of both C-H and O-H bonds are involved in the rate-controlling steps. Assuming that there are no isotope effects in the physical adsorptions of CH_3OH and H_2O, the k_H/k_D ratios were estimated on the basis of the following transition states; Models 1 and 2. The C-H (2987 cm^{-1}) and O-H (3400 cm^{-1}) stretching frequencies[5] of liquid CH_3OH were used for the physi-

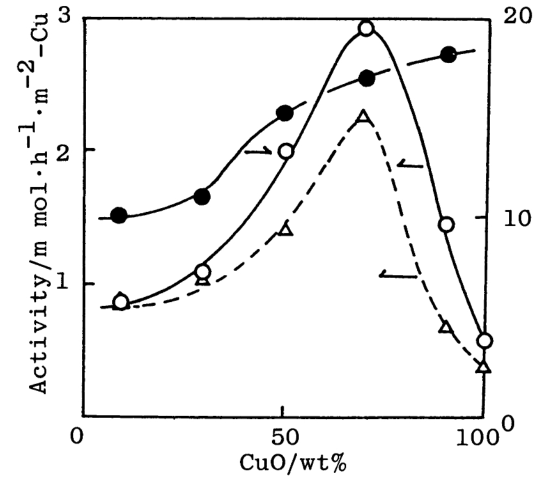
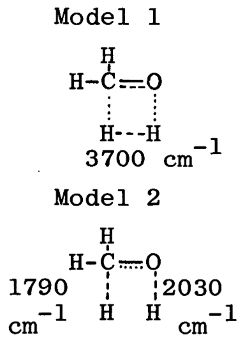


Fig. 1. Specific activity at 160 °C (○) and activation energy (●) for the $HCOOCH_3$ formation and specific activity at 200 °C (△) for steam reforming of CH_3OH as a function of the CuO content in the Cu-ZnO catalyst.

Table 1. Kinetic isotope effects in the bimolecular dehydrogenation to $HCOOCH_3$ and steam reforming reactions of CH_3OH over Cu-ZnO catalysts

CuO/ZnO	Reactant	Reaction tempera-ture/°C	Isotope effect; k_H/k_D		
			Observed	Calculated	
				Model 1	Model 2
30/70	CD_3OD	161	3.0	2.81	3.00
	CH_3OD	161	2.0	2.02	1.80
	CD_3OD/D_2O	200	2.6	2.56	2.74
	CD_3OD/H_2O	201	2.1	1.85*	1.92*
70/30	CD_3OD	172	2.5	2.70	2.91
	CH_3OD	172	1.8	1.97	1.77

*) A complete mixing between D in -OD and H in H_2O is assumed.



sorbed CH_3OH. In Model 1, which has been proposed by Miyamoto and Ogino,[6)] the C-H and O-H bonds are extremely weakened and H-H is just formed. In Model 2, both C-H and O-H bonds are simultaneously weakened and the reaction coordinates are taken along the C-H and O-H bonds. It is also assumed that the differences in the zero point energies are predominating in the isotope effects. Although it is not clear which model is more appropriate, the experimental k_H/k_D ratios can be excellently simulated in both models by using the same parameters regardless of the reaction mode and the catalyst composition. This means that the simultaneous bond scissions of C-H and O-H groups in CH_3OH are rate-determining in both the $HCOOCH_3$ formation and steam reforming of CH_3OH and that the rate-determining step and, presumably, the reaction mechanisms are independent of the catalyst composition. Consequently, the synergy is not caused by the change in the reaction mechanism.

The electron density of the Cu metal was estimated from the XPS chemical shift ΔE of the Cu $2p_{3/2}$ band due to Cu metal.[2)] The ΔE values are corrected for relaxation energy shifts. It is revealed that the electron density of the Cu metal is not significantly modified in the catalysts with high Cu contents as shown in Fig. 2. In addition, the Cu-content dependencies of the specific activities differ considerably from that of the ΔE. Thus, the electronic effects seem less important for the synergy. However, a comparison between Figs. 1 and 2 suggests that the decrease in the activation energy is induced by the increase in the electron density of the Cu metal. As for the effects of the particle size of the Cu metal, Kobayashi et al.[3)] reported

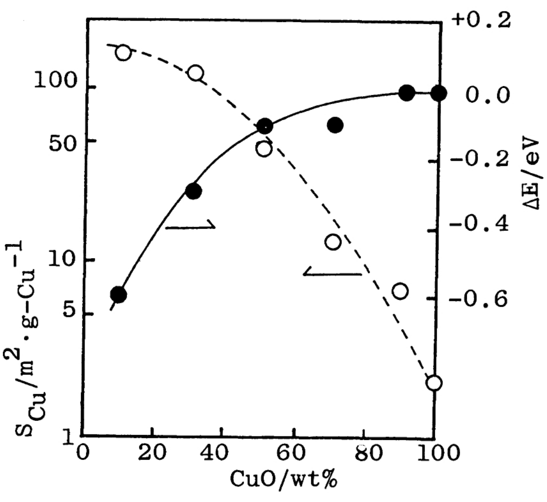
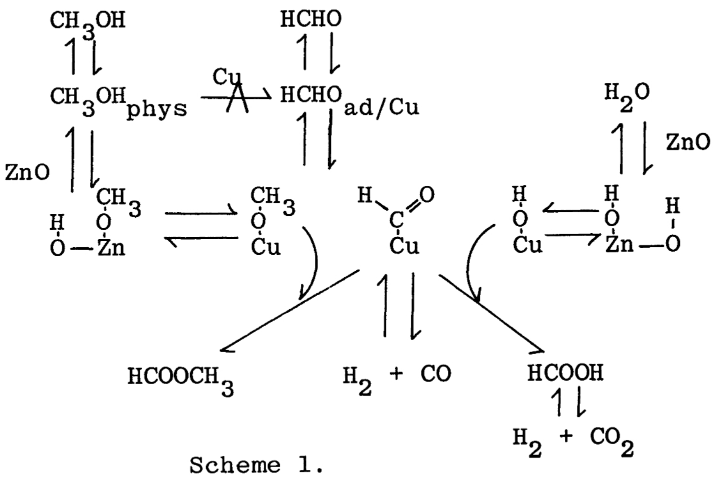


Fig. 2. Surface area of Cu metal and Cu $2p_{3/2}$ chemical shift (ΔE) corrected by relaxation energy shifts vs. CuO content in Cu-ZnO catalyst

that the turnover frequency decreases for the steam reforming of CH_3OH when the specific surface area is lower than ca. 30 $m^2 \cdot g\text{-}Cu^{-1}$ for Cu/SiO_2 catalysts. This may explain partially the decreased specific activities at the low Cu content catalysts. However, the low activity in the high Cu content catalysts cannot be interpreted in terms of the particle size alone. Accordingly, it seems unlikely that the electronic and structural effects constitute a major part of the strong synergy. It is also revealed that the zero-valent Cu species with a two-dimensional structure and/or in the ZnO lattice, which are observed mainly in the low Cu content catalysts,$^{2)}$ show no special activities for these reactions.



Scheme 1.

It is concluded that the synergistic promotion of the specific activity over Cu-ZnO catalysts is bifunctional in nature. A plausible reaction mechanism is proposed in Scheme 1. Methanol is activated by Cu metal to form adsorbed HCHO, this step being rate-determining in both reactions. The synergistic effects of ZnO are considered to be due to the increased surface concentration of physisorbed CH_3OH over Cu metal by providing a CH_3OH_{phys} reservoir.$^{7)}$ ZnO is considered also to activate CH_3OH and H_2O to form CH_3O- and HO- species, respectively. These species equilibrate with the corresponding species on Cu which react with a common intermediate formyl species HCO. A similar reaction path is suggested by Takezawa and Kobayashi.$^{8)}$ Surface HCO is also conjectured to be important in the methanol synthesis from H_2 and CO over Cu-ZnO catalysts.$^{9)}$

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