

NOTE

## METHYLFORMATE FORMATION FROM METHANOL AND CO ON Cu/ZnO CATALYSTS

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**Abstract**—The reaction mechanism for the methylformate formation on Cu/ZnO catalysts from methanol and CO was investigated by the labeling study with  $^{13}\text{C}$  methanol. It was found that methylformate could be formed through two parallel reaction routes, i.e., methanol-formaldehyde reaction and carbonylation of methanol depending upon the catalyst composition as well as the reaction conditions. The major reaction route on the high ZnO-content catalyst (Cu/ZnO=30/70) was found to be the methanol-formaldehyde reaction, and changed to the carbonylation reaction with the increase of CO partial pressure. On the other hand, the major reaction route on the high Cu-content catalyst (Cu/ZnO=80/20) remained as methanol-formaldehyde reaction even under the high CO pressure.

### INTRODUCTION

Cu/ZnO-based catalysts have been developed for the synthesis of methanol, and modified for the synthesis of higher alcohols from syngas [1-3]. In the higher alcohol synthesis on Cu/ZnO-based catalysts, methylformate formation is related to the  $\text{C}_1 \rightarrow \text{C}_2$  step, which is one of the most important steps in the production of higher alcohols. Nunan et al. [4] proposed that carbonylation of methanol is the major reaction route of methylformate formation in the higher alcohol synthesis reaction on Cs doped Cu/ZnO catalyst. However, the reaction route might be more complex, because methylformate can be formed from methanol on Cu-based catalysts even in the absence of CO. In the methylformate formation from methanol on Cu-based catalyst, methanol-formaldehyde reaction was suggested as the most probable reaction route by the previous study [5] in accordance with Takahashi et al. [6], and bimolecular reaction of formaldehyde (Tischenko-type reaction) had also been suggested as the probable reaction route [7].

In this work, the reaction route to methylformate from methanol and CO on Cu/ZnO catalysts was investigated on the catalysts of different composition under the various partial pressures of CO.

### EXPERIMENTAL

Catalysts of different Cu/ZnO ratio (100/0, 80/20, 30/70, 0/100) were prepared by the coprecipitation method at 60°C as described elsewhere [8]. Mixture of 1 M-nitrate precursor solution was added to 1 M-sodium carbonate solution. The precipitation was completed at pH 7 and the precipitate was filtered, washed, dried at 120°C for 10 hours, crushed and calcinated at 400°C for 4 hours. The calcinated catalysts were crushed to fine powder and ion exchanged in 0.1% ammonium bicarbonate solution for 2 hours to exclude the effect of residual sodium. Extra pure (EP) grade chemical reagents were used in the catalyst preparation, and EP grade methanol and  $^{13}\text{C}$  methanol of 99 atom % from Sigma Aldrich Co. were used for the feed. Helium of 99.999%, CO of 99.99%, hydrogen of 99.99% and nitrogen of 99.99% were used.

The catalyst of 0.2 g was loaded in the fixed bed continuous flow reactor made of 316 stainless steel tube (ID 4.9 mm), which was heated by temperature controlled electric furnace. Prior to the reaction, the catalyst was pretreated with 5%  $\text{H}_2/\text{N}_2$  at 250°C for 2 hours. Methanol was vaporized from a saturator at room temperature, and delivered to the reactor with carrier or feed gases regulated by mass flow controller (Brooks 5850 E). The product gas was analyzed by on-line GC (Gow-Mac 580, FID/TCD) with Hayasep R packed column (1/8 inch O.D.  $\times$  2 m) and the  $^{13}\text{C}$  la-

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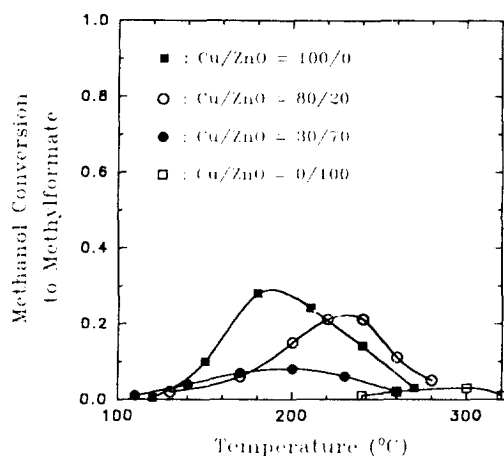


Fig. 1. Methylformate formation from methanol over Cu/ZnO catalysts of different composition ( $P_{\text{methanol}} = 22$  kPa, space velocity = 1500/h).

beled products were analyzed by GC/MS(HP 5890/HP 5971) with HP-1 capillary column (0.2 mm I.D.  $\times$  50 m). The surface area of metallic Cu was determined from the reversible CO chemisorption and the surface area of ZnO was determined from the difference between the Cu area and the total BET area measured with nitrogen, which has been proposed by Paris and Klier [9].

## RESULTS & DISCUSSION

When methanol was supplied to the catalyst bed with helium carrier, the formation of methylformate was dependent on the catalyst composition, and the catalyst of higher Cu content showed higher activity as shown in Fig. 1. It was suggested in the previous study [5] that the reaction between the surface methoxy species and formaldehyde was the major reaction route of methylformate formation from methanol over Cu/ZnO catalysts.

When methanol was supplied with CO to the catalyst bed, methylformate formation increased with the partial pressure of CO on high ZnO-content catalyst (Cu/ZnO = 30/70), but not on high Cu-content catalyst (Cu/ZnO = 80/20) as shown in Fig. 2. The carbonylation of methanol is most probably the major reaction route of methylformate formation on the high ZnO-content catalyst, but not on the high Cu-content catalyst. It could be considered that methylformate was formed through methanol-formaldehyde reaction [5] on the high Cu-content catalyst under the low CO pressure, and it might be valid even under the high CO pres-

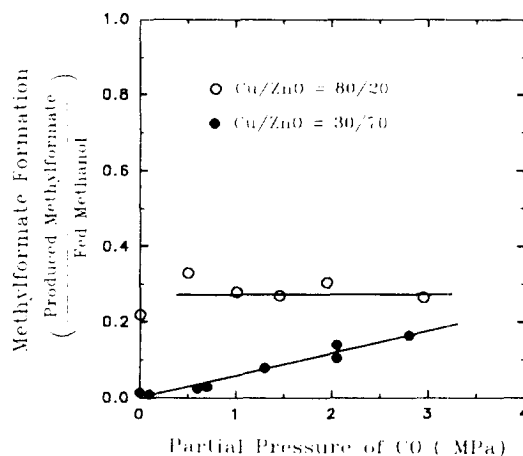


Fig. 2. Effect of CO pressure on the methylformate formation from methanol and CO over Cu/ZnO catalysts of different composition (reaction temp. = 200 °C,  $P_{\text{methanol}} = 22$  kPa, space velocity = 1500/h).

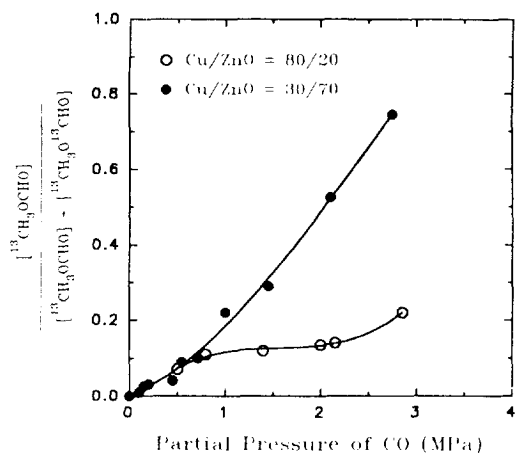


Fig. 3. Effect of CO partial pressure on the isotopic composition of methylformate produced from the reaction of the labeled methanol and unlabeled CO over Cu/ZnO catalysts of different composition (reaction temp. = 200 °C,  $P_{\text{methanol}} = 22$  kPa, space velocity = 1500/h).

sure.

More conclusive results could be obtained from the  $^{13}\text{C}$  labeling study.  $^{13}\text{C}$  labeled methanol was supplied to the catalyst bed with unlabeled CO, and the structure of the produced methylformate was analyzed by GC/MS. The mass spectrum of methylformate show two distinct peaks, the molecular ion peak and the fragment ion peak of methoxy group. Therefore, the

origin of the carbons in the methylformate can be traced by the analysis of the mass spectrum. When the partial pressure of CO was atmospheric, the product methylformate was mostly  $^{13}\text{CH}_3\text{O}^{13}\text{CHO}$  with MW 62, indicating that the incorporation of CO did not take place. When the partial pressure of CO increased, methylformate of MW 61 began to be formed as shown in Fig. 3. The structure of the methylformate of MW 61 was mostly  $^{13}\text{CH}_3\text{OCHO}$ , and unlabeled methanol was not formed under the reaction condition studied. Therefore, the methylformate of MW 61 must be formed through the reaction of the unlabeled CO with the labeled methanol. When the partial pressure of CO increased to 3 MPa, the production rate of methylformate on the high ZnO-content catalyst became comparable to that on the high Cu-content catalyst. However, the isotopic composition of the methylformate varied depending on the catalyst composition as shown in Fig. 3. The fraction of MW 61 reached to 0.8 on the high ZnO-content catalyst, while it was less than 0.3 on the high Cu-content catalyst. Those results could be explained by the rate of each probable reactions. The high ZnO-content catalyst is not so active for the methanol-formaldehyde reaction that methylformate formation is comparatively low under low CO pressure, and the increase of CO partial pressure causes the increase of methylformate formation through the carbonylation of methanol. The high Cu-content catalyst is so active for the methylformate formation through methanol-formaldehyde reaction, even in the absence of CO, that the conversion to methylformate reaches close to the equilibrium. Hence, the increase of CO pressure can not cause any significant increase in the production rate of methylformate, and the methanol-formaldehyde reaction remains as the major reaction route, although the fraction of methylformate formed through the carbonylation of methanol is increased with the partial pressure of CO.

## CONCLUSION

Methylformate can be formed from methanol and CO through two parallel reaction routes on Cu/ZnO catalysts. One route is the methanol-formaldehyde reaction and the other route is the carbonylation of methanol. The major route on the high ZnO-content catalyst changed from the methanol-formaldehyde reaction to the carbonylation reaction with the increase of the partial pressure of CO. On the other hand, the major route on the high Cu-content catalyst remained as methanol-formaldehyde reaction even under the high CO pressure.

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