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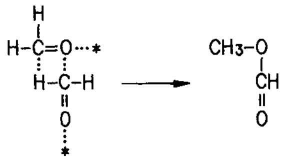
Mechanism of Methyl Formate Formation on Cu/ZnO Catalysts

Methyl formate can be formed from methanol and/or formaldehyde on copper-based catalysts. The mechanism of methyl formate formation is still controversial. Miyazaki and Yasumori (*1*) proposed that methyl formate is formed by the bimolecular reaction of formaldehydes, as shown in Scheme I, and Cant *et al.* (*2*) supported this Tischenko type reaction mechanism with a deuterium labeling study. On the other hand, Takahashi *et al.* (*3*) proposed that methyl formate is formed by the reaction between methanol and formaldehyde, via the hemiacetal-like species, as shown in Scheme II, and Mueller and Griffin (*4*) supported it by kinetic study of formaldehyde hydrogenation on Cu/ZnO catalysts.

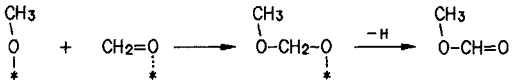
In this work, the reaction mechanism on Cu/ZnO catalysts was investigated through ^{13}C labeling study, and the reaction between surface methoxy species and formaldehyde (methanol–formaldehyde reaction) was suggested as the major reaction route to methyl formate from methanol and/or formaldehyde.

The catalysts were prepared by the coprecipitation method at 60°C. The mixture of 1 *M* nitrate precursor solution was added to 1 *M* sodium carbonate solution as described elsewhere (*5*). 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 (*6*). The catalyst of 0.2 g was loaded in the fixed-bed continuous-flow reactor, which was heated by the temperature-controlled electric furnace. Prior to the reaction, the catalyst was pretreated with 5% H_2/N_2 at 250°C for 2 h. Formaldehyde was sublimed from paraformaldehyde, methanol was vaporized in the temperature-controlled saturator, and both were supplied to the reactor with carrier gas. [^{13}C]methanol (99 at.%) (Sigma Aldrich Co.) was used for the labeling study. The product gas was analyzed by on-line GC (Gow-Mac 580, FID/TCD) with Hayasep R packed column ($\frac{1}{8}$ in. o.d. × 2 m) and the ^{13}C-labeled products were analyzed by GC/MS (HP 5890/HP 5971) with HP-1 capillary column (0.2 mm i.d. × 50 m).

To investigate the role of Cu and ZnO in the methyl formate formation, the catalytic activities for the methyl formate formation from methanol were studied on the catalysts of different composition. It was found that Cu is active for methyl formate formation from methanol, while ZnO is not so active. As shown in Fig. 1, conversion of methanol to methyl formate reached 0.28 over Cu catalyst, while it was no more than 0.04 over ZnO catalyst. The catalyst with a Cu/ZnO ratio of 80/20 showed higher activity still. CO was produced with methyl formate and



Scheme I. Methyl formate formation from the bimolecular reaction of formaldehyde.



Scheme II. Methyl formate formation from the reaction between methoxy species and formaldehyde (methanol–formaldehyde reaction).

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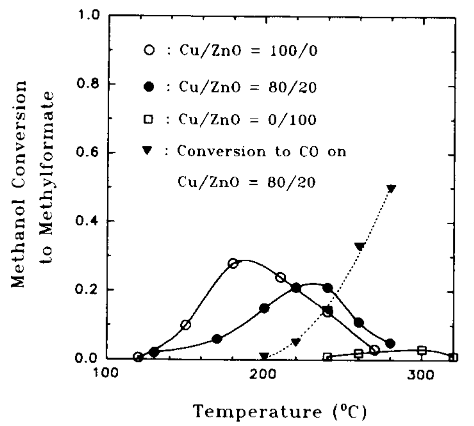

FIG. 1. Methyl formate formation from methanol over different catalysts (P_{methanol} = 22 kPa, space velocity = 1500/h).

increased with temperature up to 350°C as shown in Fig. 1, and CO_2 was produced as a minor product. Formaldehyde was detected in the reaction product even though it was less than 1%.

It is shown in Table 1 that the activity for the methyl formate formation is independent of the Cu or ZnO surface area. Although it was proposed that the irreversible chemisorption of CO is associated with defect site, the correlation between the activity and the surface area does not seem to be clear, and further investigation is needed. The surface areas of the present catalysts were comparable to those of a previous investigation (*6*).

When formaldehyde was supplied to the catalyst bed most of the formaldehyde was converted to methyl formate, methanol, CO, and CO_2, as shown in Fig. 2. Below 60°C, the reaction rate was unstable and showed fluctuation, and no reaction products were detected at room temperature.

TABLE 1

Surface Area and Activity of the Catalysts of Different Composition

Catalyst composition (Cu/ZnO)	Cu surface area (m^2/g catalyst)	ZnO surface area (m^2/g catalyst)	Productivity of methyl formate (g/g catalyst/h)
0/100	—	21.6	0.03
30/70	13.8	27.2	0.09
80/20	12.6	3.5	0.16
100/0	4.4	—	0.22

Investigation of the effect of hydrogen on the methyl formate formation might be a method with which to distinguish the reaction mechanisms, since the schemes stated above have different hydrogenation/dehydrogenation steps from each other. When hydrogen was introduced together with methanol or formaldehyde, methyl formate formation was suppressed markedly with the increase in the partial pressure of hydrogen as shown in Fig. 3. It was also found that the production of CO and CO_2 was almost independent of the partial pressure of hydrogen. There seems to exist a dehydrogenation step to methyl formate in the reaction route, which must be different from the dehydrogenation step in the route to the decomposition of methanol or formaldehyde toward CO or CO_2. These results could support the methanol–formaldehyde reaction. On the other hand, the hydrogenolysis of methyl formate to methanol increases with the partial pressure of hydrogen (*7*), and thermodynamic equilibrium between methanol and methylformate might explain the hydrogen effect.

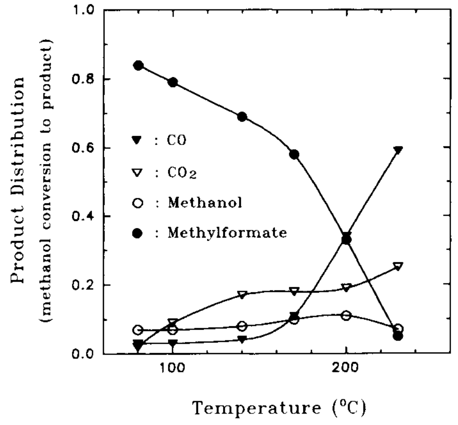

FIG. 2. Product distribution from formaldehyde over Cu/ZnO catalyst (Cu/ZnO = 80/20, $P_{\mathrm{formaldehyde}}$ = 11 kPa, space velocity = 1500/h).

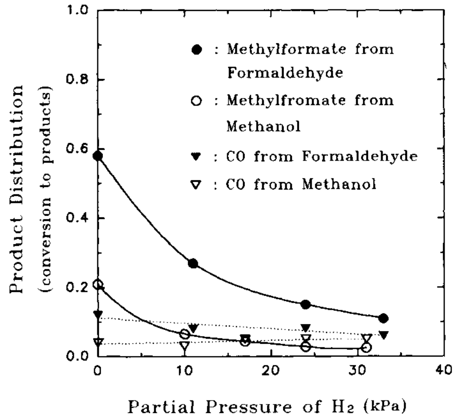

FIG. 3. Effect of hydrogen pressure on the product distribution from methanol and formaldehyde, respectively, over Cu/ZnO catalyst. (Cu/ZnO = 80/20, reaction temperature = 175°C, P_{methanol} = 22 kPa, $P_{\text{formaldehyde}}$ = 11 kPa, space velocity = 1500/h).

Detailed mechanistic interpretation has yet to be made concerning the effect of hydrogen.

When methanol was delivered together with formaldehyde, methyl formate was produced even at room temperature, which could be evidence for the methanol–formaldehyde reaction being the major reaction route to methyl formate (*3*). The origin of the carbons in methyl formate might be traced by the reaction of [^{13}C]methanol with unlabeled formaldehyde. Unlabeled methyl formate shows two distinct peaks at mass number 60 and 31 in the mass spectrum. The former corresponds to the molecular ion peak and the latter to the fragment ion peak of the methoxy group. These peaks are found at 62 and 32 for $^{13}CH_3O^{13}CHO$, at 61 and 32 for $^{13}CH_3OCHO$, and at 61 and 31 for $CH_3O^{13}CHO$. The fraction of each isotopic methyl formate was estimated by comparing the relative intensity of each peak. At a low temperature below 60°C, methyl formate was mainly composed of $^{13}CH_3OCHO$, produced most probably through the reaction between methanol and formaldehyde. This result is consistent with the deuterium labeling study by Takahashi *et al.* (*3*). At a higher temperature above 80°C, the formation of unlabeled methyl formate, which originated from formaldehyde, was increased. However, the fraction of labeled methanol and labeled methyl formate varied in a similar manner over the wide temperature range as shown in Fig. 4. This is possible either when the unlabeled methyl formate is formed by the reaction between formaldehyde and unlabled methanol produced from formaldehyde or when the labeled methyl formate is formed by the transesterification between the labeled methanol and unlabeled methyl formate produced from formaldehyde by the Tischenko reaction.

One of the basic differences between the methanol–formaldehyde reaction and the Tischenko reaction is the chemical and electronic structure of the nucleophilic species, which attacks the carbonyl carbon in formaldehyde. The nucleophilic species is a methoxy one for the former and a formaldehydic one for the latter. It was reported that rapid transesterification equilibrium exists between methyl formate and methanol (*8*, *9*), and the transesterification was explained as a reaction between methoxy oxygen and carbonyl carbon (*2*). To attain the rapid equilibrium, the reaction between me-

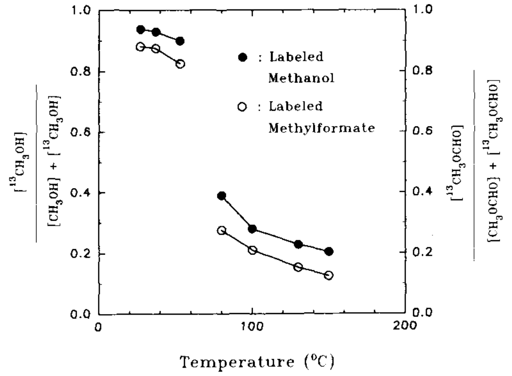

FIG. 4. Fraction of the labeled methanol and fraction of the labeled methyl formate in the reaction between [^{13}C]methanol and unlabeled formaldehyde over Cu/ZnO catalyst (Cu/ZnO = 80/20, partial pressure of [^{13}C]methanol = 8 ~ 22 kPa, $P_{\text{formaldehyde}}$ = 11 kPa, space velocity = 1500/h).

thoxy species and carbonyl carbon should take place rapidly, and it might imply that the methanol–formaldehyde reaction is an active route.

The fact that methyl formate formation was suppressed markedly with the increase in hydrogen partial pressure can also be interpreted by the equilibrium between methyl formate and methanol. It was suggested that the hydrogenolysis of methyl formate proceeds by C–O bond cleavage producing surface methoxy species and formaldehyde (*8*). The existence of equilibrium implies that the reaction between surface methoxy species and formaldehyde takes place as fast as the hydrogenolysis.

In the Tischenko reaction, a hydrogen transfer to attacking species takes place during a new carbon–oxygen bond-forming process (*1, 2*), as shown in Scheme I. Formaldehyde has a trigonal configuration utilizing sp^2 orbitals, and if any nucleophile approaches to the carbonyl carbon, it changes to tetrahedral configuration as hydrogens move away from the attacking nucleophile. Therefore the direct hydrogen transfer to the attacking species in the carbon–oxygen bond-forming process would not be an easy step.

The aforementioned arguments suggests that the probable reaction route to methyl formate is the methanol–formaldehyde reaction rather than Tischenko type reaction. Accordingly, it is proposed in the present work that the reaction between the surface methoxy species and formaldehyde is the major reaction route to methyl formate from methanol and/or formaldehyde over Cu/ZnO catalysts.

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