JOURNAL OF CATALYSIS 157, 259–261 (1995)

NOTE

Synergistic Effects between Cu and ZnO in the Hydrogenation of Their Formates

The chemistry of formate on Cu/ZnO catalysts has been an active area of interest because of the controversy regarding the synergistic effects between Cu and ZnO. Surface formate has been suggested as an intermediate for the $CO/CO_2/H_2$ hydrogenation reaction to form methanol on copper-based catalysts (1-5). Bowker *et al.* proposed that formate could be easily formed on the surface of polycrystalline copper metal at 305 K from codosing of CO_2/H_2, and the rate-determining step of the CO_2 hydrogenation reaction was the hydrogenation and hydrogenolysis of the formate (6). Klingler and Rathke observed that formate of alkali metal converted into methanol and methyl formate in the presence of PbO (7). Methanol was also produced from carbon monoxide and water via *in situ* generation of formate. Herein, we have investigated the hydrogenation of copper formate/ZnO mixture, copper formate and zinc formate, focusing on the synergistic effects between copper and ZnO in the CO_2 hydrogenation to methanol. It was found that the hydrogenation of zinc formate produced methanol and methyl formate. However, the hydrogenation of copper formate yielded formic acid as a unique organic product. In particular, mixing of ZnO into copper formate was found to increase the yields of methyl formate and methanol in its hydrogenation reaction.

Formates of copper and zinc were prepared by the addition of corresponding metal carbonates into formic acid solutions (8, 9). The precipitates were filtered and washed with ether four times to remove excess formic acid and dried in vacuum for 3 days. Temperature-programmed hydrogenation (TPH) experiments on copper formate/ZnO mixture, copper formate and zinc formate, were conducted in hydrogen atmosphere with programmed heating up to 570 K at a rate of 10 K/min. The hydrogen flow was regulated by a mass flow controller at 50 ml/min. The reaction products were analyzed by a quadrupole mass detector (Balzers, MS-Cube 200). The products were also condensed at liquid nitrogen temperature and analyzed by gas chromatography (Gow-Mac, Thermal Conductivity Detector, porapak Q column, 1/8 × 4 m). Metal formates (10 mg) and copper formate/ZnO mixture (15 mg, 2:1 in weight ratio) were charged in a quartz reactor (6 mm O.D. and 45 cm length). The peaks at $m/e = 30, 31, 46$, and 60 were monitored to detect H_2CO, CH_3OH, HCOOH, and $HCOOCH_3$, respectively (10) (HCOOH, 29(100), 46(62), 45(48); H_2CO, 29(100), 30(88), 28(30); CH_3OH, 31(100), 32(67), 29(65); HCOOCH, 31(100), 29(78), 32(34), 60(32)). Since the parent peak of methanol overlapped with the fragment peak of $HCOOCH_3$ at $m/e = 31$, the yields of methanol and methyl formate were confirmed by GC analysis as well.

In TPH experiments on copper formate, formic acid was formed as the only organic product in addition to CO_2 and CO at 458 K (Table 1, A). Meanwhile, in TPH experiments on zinc formate, further hydrogenated products such as methyl formate (21.4%), methanol (0.8%), and formaldehyde (0.3%) were produced. Formic acid, however, was not detected from zinc formate. It is noteworthy that TPH of copper formate mixed with ZnO produced a significant amount of methyl formate, while TPH of copper formate did not produce any methyl formate. In addition to methyl formate, trace amounts of methanol and formaldehyde were also identified.

During TPH of metal formates, products were also monitored by a mass detector, and the peak intensities of organic products versus temperature are shown in Fig. 1. Copper formate showed the maximum hydrogenation temperature (T_{max}) at 458 K with the characteristic peak of formic acid, a major organic product from the GC analysis, at $m/e = 46$ (Fig. 1A). On the other hand, the T_{max}(515 K) of the hydrogenation of zinc formate appeared at a higher temperature than that of copper formate. The hydrogenation of zinc formate showed the mass spectrum peaks at $m/e = 31, 30$, and 60, assigned to methyl formate + methanol, formaldehyde, and methyl formate, respectively (Fig. 1C). The major organic product in the TPH experiment of zinc formate was methyl formate, as shown in Table 1C. The mass spectrum of TPH of zinc formate also indicated product distribution identical to that in the GC analysis.

The T_{max} of copper formate mixed with ZnO was shifted to 488 K, 30 K higher than that of copper formate. Figure 1B shows a major peak of $m/e = 31$ corresponding to the

0021-9517/95 $12.00

TABLE 1

Product Distribution from the Hydrogenation of Metal Formates with Programmed Heating at a Rate of 10 K/min

	ZnO (μmol)	Cu formate (μmol)	Zn formate (μmol)	Product yield (mole%)					
				CO_2	CO^a	H_2CO	CH_3OH	$HCOOCH_3$	HCOOH
A		65.1		66.1	21.0	—	—	—	12.4
B	61.4	65.1		69.8	16.3	0.2	Trace	5.5	3.1
C			64.4	47.6	25.2	0.3	0.8	21.4	—
D	61.4	65.1		69.5	18.4	—	—	1.5	6.1

(A) copper formate, (B) copper formate/ZnO (physical mixing), (C) zinc formate, (D) copper formate/ZnO (series packing).

[a] Calculated by the intensity ratio of CO_2 and CO in a mass detector.

fragments of methanol and methyl formate at T_{max} of 488 K. The formaldehyde peak at $m/e = 30$ appeared between 450 and 490 K. The formic acid peak at $m/e = 46$, the only organic product in the TPH of copper formate, was reduced in intensity.

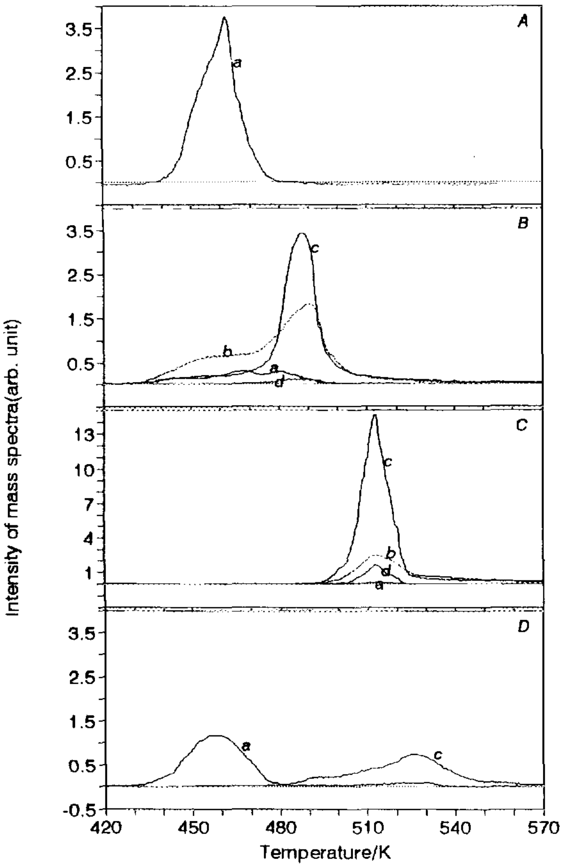

FIG. 1. The spectra of organic products from the hydrogenation of metal formates with programmed heating at a rate of 10 K/min. (A) copper formate, (B) copper formate/ZnO (physical mixing), (C) zinc formate, (D) copper formate/ZnO (series packing); (a) $m/e = 46$ (HCOOH), (b) $m/e = 30$ (H_2CO), (c) $m/e = 31$ (CH_3OH and $HCOOCH_3$), (d) $m/e = 60$ ($HCOOCH_3$).

The experimental results described above have demonstrated the active participation of ZnO for the hydrogenation of formate to methanol and methyl formate. There are three possible mechanistic routes for the hydrogenation of formate in the presence of ZnO: (1) the formation of zinc formate from the reaction of ZnO with formic acid formed in copper formate hydrogenation and the hydrogenation of the formate on ZnO; (2) the migration of formate onto ZnO from copper and subsequent hydrogenation of the formate on ZnO; and (3) the hydrogenation of formate at the interface of copper and ZnO. Since the reaction of formic acid with ZnO to form zinc formate is well known (11), the TPH experiment was performed in a reactor packed with copper formate and ZnO in consecutive layers (Table 1D and Fig. 1D). The mass spectrum of this reaction showed two T_{max} at 458 and 515 K, assigned to the T_{max} of the hydrogenation of copper and zinc formates, respectively. The methyl formate yield was only 1.5% (Table 1D), however, smaller than the yield (5.5%) from the copper formate/ZnO physical mixture. Furthermore, T_{max} of the separate layer reaction was different from T_{max} of mixture reaction. If zinc formate were formed from formic acid, the mass spectrum of the separate layer experiment would have been similar to the mass spectrum of the copper formate/ZnO mixture. But, the T_{max} and the product distribution of the separate layer experiment were different from those of the mixture experiment. These results could exclude the possibility of the first mechanistic route. The second hypothesis was supported by the similar product distributions of the TPH experiments with zinc formate and the copper formate/ZnO mixture, which produced methyl formate and methanol. The third hypothesis, however, was supported by the T_{max} shift of the TPH of copper formate/ZnO mixture. The T_{max} was 488 K, between T_{max} values of copper formate and zinc formate. Kiennemann *et al.* (12) and Bussche and Froment (13) reported the interfacial formate from a peak appearing between T_{max}'s of copper formate and that of zinc formate in TPD experiments on $Cu/ZnO/Al_2O_3$ catalyst. Our results support the second and the third mechanistic routes rather than the first one.

The formate hydrogenation has been suggested as a rate-determining step in the methanol synthesis reaction from the hydrogenation of carbon oxides. In the industrial catalysts of methanol synthesis, ZnO is an essential component along with copper, but its role in the catalytic reaction has not been clearly understood. The addition effect of ZnO in the hydrogenation of copper formate has suggested a synergistic effect between copper and ZnO in methanol synthesis catalysts. The formation of methanol and methyl formate in the TPH of zinc formate and the copper formate/ZnO mixture suggested that the hydrogenation of formate might take place at a ZnO site. Since the formate was known to form easily on copper, the synergistic effects of adding ZnO may be attributed to the hydrogenation capability of ZnO.

The mechanism of ZnO participation in the hydrogenation of formate is under investigation and will be published in a full paper. Whatever the reasons for the promoting effects of ZnO, these findings provide important insight into the synergistic effect between copper and ZnO.

ACKNOWLEDGMENTS

This research was supported by the Korea Institute of Science and Technology and the Korea Ministry of Science and Technology. We thank Dr. J. H. Baeck for helpful discussion.

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Received July 20, 1994