Remarks on the assignments of temperature programmed desorption peaks for the surface species formed on Cu / ZnO and ZnO in the methanol synthesis from CO

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Temperature programmed desorption (TPD), IR spectroscopy and chemical trapping of the surface species with H_2O revealed that the TPD peak of CO frequently assigned to zinc formate species, which were formed in the course of the methanol synthesis from CO–H_2, arose from zinc methoxide species.

Keywords: Cu/ZnO catalyst; ZnO catalyst; methanol synthesis; surface formate species; methoxide species

1. Introduction

Cu / ZnO based catalysts are highly effective for methanol syntheses from CO_2–H_2 and from CO–H_2. A number of studies concerning the surface species formed in methanol synthesis have been performed over Cu/ZnO based and ZnO catalysts by using the temperature programmed desorption (TPD) method [1–15]. It has prevailingly been accepted that both peaks of CO and CO_2 desorbed at temperatures around 570 K or higher are assigned to the decomposition of formate species produced on ZnO [1–10,14,15], since these peaks were observed in TPD runs of formic acid adsorbed on single crystals of ZnO [1,2,6].

However, Chadwick and Zheng recently reported that methoxide on ZnO desorbed mainly as CO in TPD runs, whereas formate on ZnO decomposed to CO_2 [13]. The latter result was also reported by Millar et al. [11]. In previous studies [17,18], we conducted TPD runs and IR measurements over Cu / ZnO and ZnO catalysts subjected to methanol synthesis. By combining the results obtained by these methods, we concluded that zinc methoxide species decomposed to CO in the course of the TPD runs.

Hence, under these circumstances, there is still a controversy on the assignment of the CO peak.

In the present study, the CO–H_2 reaction was carried out over a Cu/ZnO and a ZnO catalyst. By TPD, IR spectroscopy and chemical trapping of the surface species with H_2O, we showed that the CO peak occurring around 570 K arose from the decomposition of zinc methoxide species.

2. Experimental

Cu/ZnO (30 mol% Cu) or ZnO were prepared by coprecipitation or precipitation of a mixed solution of copper and zinc nitrates or a solution of zinc nitrate with a solution of sodium carbonate in a similar way to that employed by Herman et al. [19]. The precipitates were dried at 383 K overnight, and calcined in air at 623 K for 4 h. 1 g of the catalyst thus prepared was first reduced in a reactor in a stream containing 3 vol% of H_2 at 483 K for 1 h. The temperature was then raised from 483 to 523 K stepwise by 10 K every hour and finally kept at 523 K for 1 h in 1 atm of H_2. Details of the catalyst preparation were described elsewhere [17].

The CO–H_2 reaction and TPD runs were carried out in a flow reactor over the reduced catalysts at atmospheric pressure. The total flow rate was kept at 200 cm^3-NTP/min. In the TPD runs, the temperature was ramped at a rate of 5 K/min in a helium flow or a nitrogen flow. Experimental procedures for the TPD runs were similar to those adopted in the previous study [17]. The effluent from the reactor was analyzed by gas chromatography.

Diffuse reflectance FT-IR spectra of adsorbed species were recorded in helium at room temperature with a JASCO FT-IR-5M infrared spectrophotometer to which a diffuse reflectance instrument DR-500H was attached. A spectrum of the catalyst, which was reduced in a flow of H_2 and then treated with a flow of helium, was used as the background.

Chemical trapping of methoxide with H_2O was carried out in the flow reactor. After the catalysts were subjected to the CO–H_2 reaction at a given temperature, the temperature of the reaction was lowered to 383 K and gases in the reactor were flushed with flowing helium. The helium flow was then switched to a helium stream containing 8×10^{-3} atm of H_2O. The gaseous composition of the effluent was followed in time by gas chromatography.

3. Results and discussion

Fig. 1 illustrates the TPD profiles of H_2, CO and CO_2 obtained over the Cu/ZnO catalyst previously exposed to a CO–H_2 mixture (CO/H_2 = 1/9) at 438 K for 4 h. Strong peaks of H_2 and CO are observed, respectively, at 533 and 548 K,

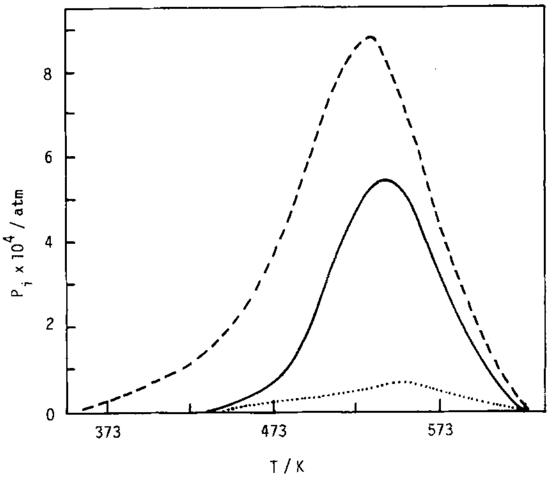

Fig. 1. TPD spectra of H_2 (- - -), CO (——) and CO_2 (· · ·) obtained after the CO–H_2 treatment was carried out at 438 K for 4 h over Cu/ZnO.

together with a weak one of CO_2 at 553 K. Other compounds such as water and formaldehyde were not detected in the TPD run.

Fig. 2 illustrates how the amounts of desorbed H_2, CO and CO_2 vary with time on stream of the CO–H_2 mixture. The amounts of desorbed H_2 and CO increase slowly with time, while that of desorbed CO_2 reaches the steady state value instantly. These findings strongly suggest that two kinds of surface species are produced in the course of the CO–H_2 treatment at different rates, respectively giving CO and CO_2 in the TPD runs as carbon-containing species. Fig. 3 plots the amount of desorbed H_2 against that of desorbed CO. It shows that the increased amount of H_2 is 1.5 times that of CO. This suggests that methoxide species were formed in the course of the treatment with CO–H_2, giving the TPD peaks of CO and H_2. In

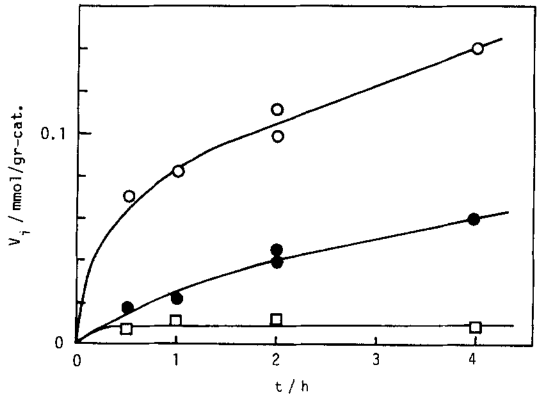

Fig. 2. Variation of the amounts of H_2 (○), CO (●) and CO_2 (■) peaks with time over Cu/ZnO.

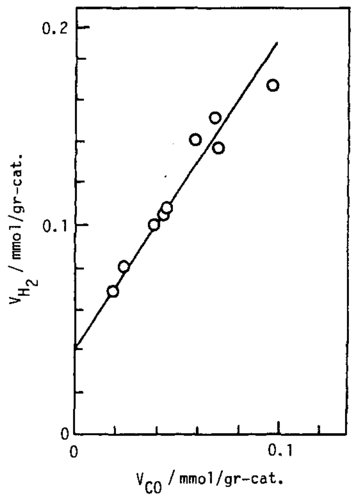

Fig. 3. Relationship between the amount of desorbed H_2 and that of desorbed CO over Cu/ZnO.

agreement with these observations, H_2 and CO desorbed in 1.5 to 1 molar ratio in TPD runs over the catalyst previously treated with methanol at room temperature. The CO_2 peak observed for the catalyst previously subjected to the CO–H_2 treatment arose from other surface species.

The line in fig. 3 crosses the ordinate at a value of 0.04 mol/g-cat. When a TPD run carried out over the Cu/ZnO catalyst after H_2 alone was fed at 438 K, a broad peak of H_2 was observed at 473 K. The amount of H_2 estimated on the basis of the peak intensity was 0.037 mol/g-cat. Therefore, the value at the intercept represents the amount of H_2 adsorbed in the course of the CO–H_2 treatment.

Fig. 4 shows the IR spectra in the CH stretching region for the catalyst previously treated with CO–H_2 at 438 K for various periods of time. Absorptions at 2940 and 2830 cm^{-1} occur along with those at 2970 and 2880 cm^{-1}. The intensities of the absorptions at 2940 and 2830 cm^{-1} increase with time, while those of the absorptions at 2970 and 2880 cm^{-1} are practically constant, irrespective of time. The variations of the former two and the latter two absorptions with time are quite similar to those of the CO and CO_2 peaks, respectively. All of these absorptions disappeared upon helium treatment at 573 K where the desorptions of H_2, CO and CO_2 were completed. On the basis of the IR spectra of methanol adsorbed on Cu/ZnO and ZnO [4,17,21,23,24], the absorptions at 2940 and 2830 cm^{-1} were assigned to zinc methoxide species (CH_3O–Zn), while the absorptions at 2970 and 2880 cm^{-1} were assigned to bidentate zinc formate (HCOO–Zn) [20–22]. Hence, it is highly probable that the CO and the CO_2 peaks originate from CH_3O–Zn from HCOO–Zn, respectively.

Similar experiments were carried out over ZnO. Fig. 5 shows TPD profiles of H_2, CO and CO_2 for the catalyst pretreated with the CO–H_2 mixture at 523 K for 30 min. Strong peaks of H_2 and CO are observed, respectively, at 573 and 588 K,

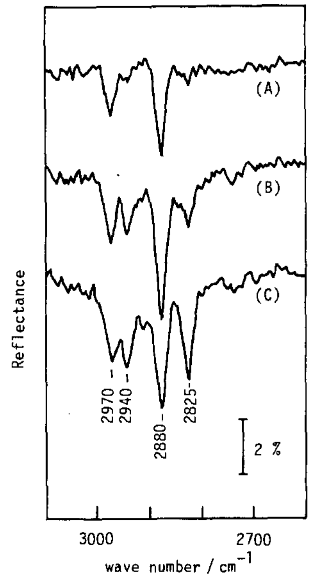

Fig. 4. Variation of IR spectra of Cu/ZnO with time in the course of the $CO-H_2$ treatment. The treatment was carried out at 438 K (A) for 30 min, (B) for 2 h and (C) for 8 h.

together with a weak one of CO_2 at 553 K. No other compounds were detected in the TPD run. When the catalyst was preadsorbed with methanol at room temperature, strong peaks of H_2 and CO were also observed at 568 and 583 K, respectively, in the TPD spectrum, confirming that the CO peak arose from CH_3O-Zn.

The amounts of desorbed H_2, CO and CO_2 were followed with time for the $CO-H_2$ treatment. It was found that the amounts of the H_2 and the CO increased slowly with time, while that of the CO_2 reached the steady state value instantly. Fig. 6 plots the amount of desorbed H_2 to that of the desorbed CO. It shows that

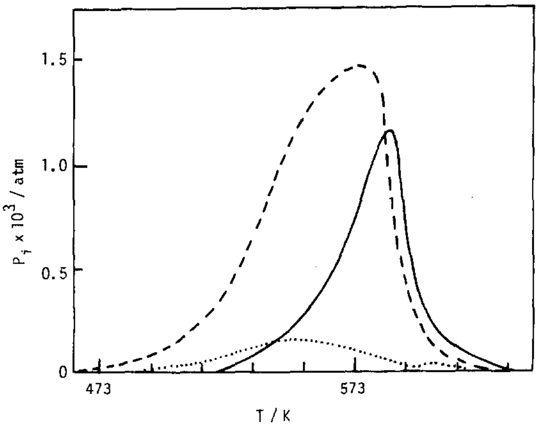

Fig. 5. TPD spectra of H_2 (- - -), CO (——) and CO_2 (···) obtained after the $CO-H_2$ treatment was carried out at 523 K for 30 min over ZnO.

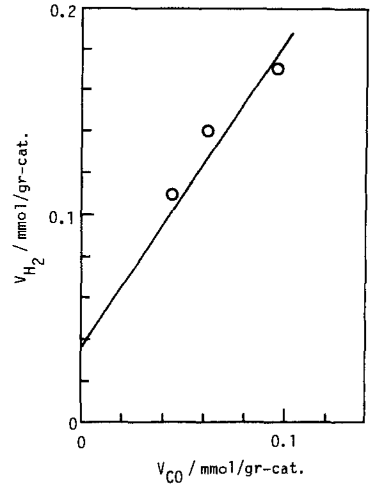

Fig. 6. Relationship between the amount of desorbed H_2 and that of desorbed CO over ZnO.

the amount of the H_2 increases with that of the CO by a factor of 1.5 as that on Cu/ZnO.

As discussed for Cu/ZnO, the value of the intercept of the line in the figure corresponds most likely to H_2 adsorbed in the course of the CO–H_2 treatment.

Surface species formed on ZnO was also inspected by IR spectroscopy. It was found that absorptions assigned to CH_3O–Zn occurred at 2935 and 2825 cm^{-1} along with those assigned to HCOO–Zn at 2970 and 2880 cm^{-1}.

Comparison of figs. 1 and 5 shows that the temperature of the CO peak on Cu/ZnO is lower than that of ZnO by 40 K, suggesting that the stability of CH_3O–Zn is markedly lowered in the presence of copper. When CH_3O–Zn species formed on Cu/ZnO decomposed to CO and H_2, the formed hydrogen probably spilt over to copper sites. This resulted in lowering of the peak temperatures of H_2 and CO in the TPD experiments.

In further confirmation of the present assignment of the CO peak, the chemical trapping of CH_3O–Zn was attempted with H_2O. Upon addition of H_2O in a helium flow over ZnO pretreated with CO–H_2, methanol was rapidly produced at 383 K [18]. IR spectra showed that the absorptions for CH_3O–Zn disappeared upon the feeding of H_2O. Fig. 7 plots the amount of formed methanol against that of CO determined on the basis of the integrated intensity of the TPD peak. It evidently shows that the amount of the methanol is in fair agreement with that of the CO.

Similar experiments were conducted over the Cu/ZnO catalyst previously subjected to the CO–H_2 treatment. Methanol was produced upon feeding H_2O [17]. When TPD runs were carried out after the feeding of H_2O, it was found that the CO peak vanished. However, the amount of methanol formed in the H_2O treatment was 60–80% that of CO desorbed in the TPD run. In the course of the feeding of H_2O, CO_2 and H_2 were also detected in the effluent. These results suggested that

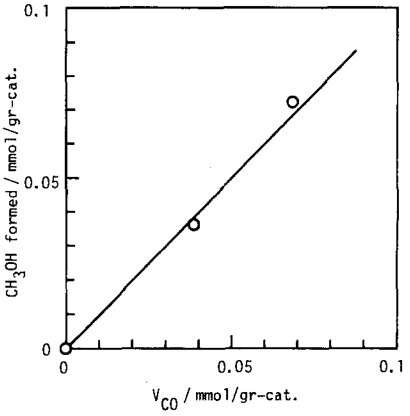

Fig. 7. The amount of methanol produced in the chemical trapping over ZnO versus that of CO peak in the TPD runs.

CH_3O–Zn was partly consumed through the reaction, $CH_3O\text{–}Zn + H_2O \rightarrow CO_2 + \frac{5}{2}H_2$, which proceeded probably through the steps involved in the steam reforming of methanol.

Based on the present findings, we concluded that the TPD peaks of CO and CO_2 could, respectively, be ascribed to CH_3O–Zn and HCOO–Zn formed in the course of the methanol synthesis over Cu/ZnO or ZnO. Hence, the CO peak frequently assigned to HCOO–Zn most probably originated from CH_3O–Zn.

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