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Methanol synthesis from carbon dioxide at atmospheric pressure over Cu/ZnO catalyst. Role of methoxide species formed on ZnO support

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Methanol synthesis from CO_2 and H_2 was carried out over a Cu/ZnO catalyst (Cu/Zn = 3/7) at atmospheric pressure, and the surface species formed were analyzed by diffuse reflectance FT-IR spectroscopy and temperature programmed desorption method. Two types of formate species and zinc methoxide were formed in the course of the reaction. Zinc methoxide was readily hydrolyzed to methanol. H_2O formed through the reverse water gas shift reaction was suggested to be involved in the hydrolysis of zinc methoxide.

Keywords: Methanol synthesis; CO_2 hydrogenation; Cu/ZnO catalyst

1. Introduction

The methanol synthesis from CO_2 and H_2 has received considerable attention in recent years [1–14]. It has been shown that Cu/ZnO-based catalysts are highly effective for this reaction [5,9,11,12,14]. However, the details of the reaction mechanism and the role of ZnO support are still controversial [15,16]. In the present study, the methanol synthesis from CO_2 was carried out at atmospheric pressure over a Cu/ZnO catalyst, and the adsorbed species formed were investigated by diffuse reflectance FT-IR spectroscopy and temperature programmed desorption method. We show that methanol is produced via hydrolysis of methoxide species, $CH_3O–Zn$, over Cu/ZnO catalyst.

2. Experimental

2.1. CATALYST PREPARATION

Cu/ZnO catalyst (Cu/Zn = 3/7 mole ratio) was prepared by a coprecipitation method similar to that adopted by Herman et al. [17] and Okamoto et al.

[18]. An aqueous solution of Na_2CO_3 (1.5 M) was added dropwise to a mixed solution of copper and zinc nitrates (total metal concentration 1 M) at 353 K until the pH reached to 8.0. Precipitates formed were aged in the mixed solution at 353 K for 1 h. During the course of the aging, the pH of the solution was adjusted to 8.0–8.2 by adding a small amount of Na_2CO_3 solution. Thereafter the precipitate was filtered out, washed with distilled water, dried in air at 363 K overnight, and calcined in air at 623 K for 3 h. The catalyst thus prepared was first reduced in a reactor or in an IR cell 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 a pure H_2.

2.2. METHANOL SYNTHESIS

The methanol synthesis was carried out with a CO_2–H_2 mixture in a flow reactor at atmospheric pressure. The total flow rate was kept at 100 cm^3/min. The weight of the catalyst used was 1.88 g. The gaseous composition in the effluent was followed in time by a gas chromatograph equipped with a thermal conductivity and a flame ionization detector.

2.3. TEMPERATURE PROGRAMMED DESORPTION (TPD)

TPD runs were carried out over 0.94 g of the catalyst in a He or in a N_2 stream at a flow rate of 200 cm^3/min. After exposure to a stream of a CO_2–H_2 mixture for a given period of time, the catalyst was rapidly cooled to 353 K. Gases in the reactor were then flushed with a helium or a N_2 stream and the catalyst was subsequently cooled to room temperature. Thereafter the temperature was ramped at a rate of 5 K/min. The effluent from the reactor was analyzed by gas chromatography.

2.4. DIFFUSE REFLECTANCE FT-IR SPECTROSCOPY

FT-IR spectra of adsorbed species were recorded in He at room temperature with an infrared spectrophotometer (Japan Spectroscopy Co., FT-IR-5M) to which a diffuse reflectance instrument (Japan Spectroscopy Co., DR-500/H) was attached. The structure of the infrared cell was similar to one developed previously by one of the present authors [19,20]. The catalyst was packed in the cell and subjected to exposure to streams of gaseous mixtures of various compositions at elevated temparatures. A spectrum of the catalyst, which was reduced at 523 K and treated in flowing He at 583 K, was used as the background.

3. Results and discussion

When a CO_2–H_2 mixture was fed over the catalyst, CH_3OH was produced together with CO and H_2O. Methanol synthesis, $CO_2 + H_2 \rightarrow CH_3OH + H_2O$, occurred along with the reverse water gas shift reaction, $CO_2 + H_2 \rightarrow CO + H_2O$. Fig. 1 illustrates the outlet partial pressure of CH_3OH and CO against time. The outlet partial pressure of CH_3OH and CO varies with time differently. CO is rapidly formed and then decreases to a steady state value within a few minutes. By contrast, CH_3OH increases slowly in a monotonic manner. A steady state value is obtained after 2–3 h. These findings suggest that CH_3OH and CO are produced through a parallel pathway.

XPS spectra of the catalyst revealed that metallic copper and zinc oxide were present before and after the reaction [21]. No other species were detected. This suggested that the slow increase of the partial pressure of CH_3OH under the transient state is not resulted from a creation of new active sites such as monovalent copper Cu(I). The length of the induction period seems to be governed by the kinetics of the CH_3OH formation.

Fig. 2 illustrates the TPD profiles of CO and CO_2 obtained after the reaction attained to a steady state. Two CO_2 peaks are seen at 448 K (α-CO_2) and at 563 K (β-CO_2), and one CO peak is seen at 553 K (α-CO). These three peaks were always accompanied by H_2 peaks at the same temperatures. No H_2O desorption was observed. When the catalyst was preadsorbed with formic acid at room temperature, strong peaks ascribed to α- and β-CO_2 appeared in the TPD

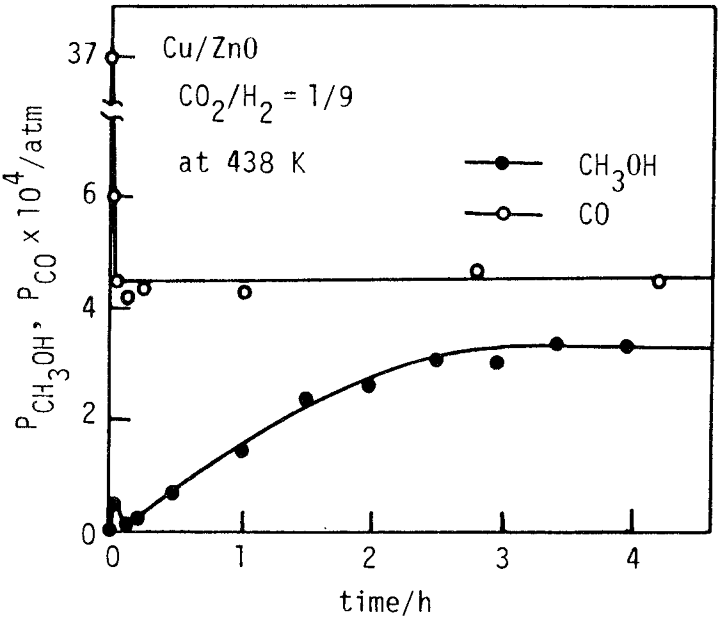

Fig. 1. Variation of the outlet partial pressure of CH_3OH and CO with time.

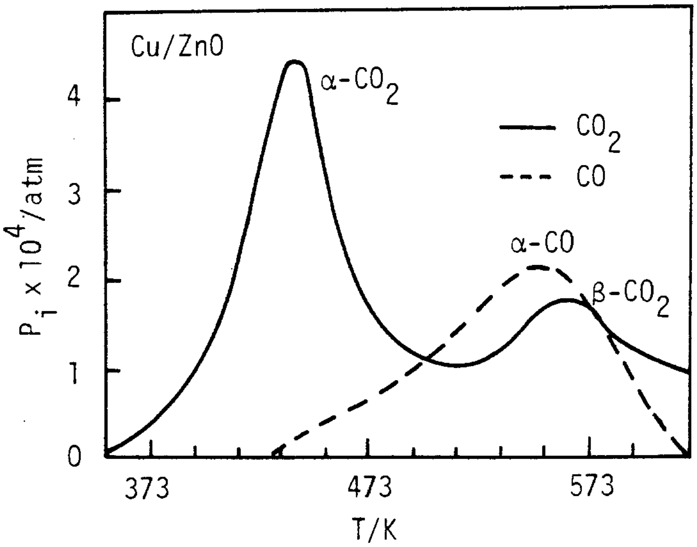

Fig. 2. TPD spectra of CO_2 and CO obtained after the CO_2–H_2 reaction was carried out at 438 K for 4h.

spectra. The amount of CO desorbed was negligible. For the catalyst preadsorbed with CH_3OH, an intense peak of CO was observed at 550 K together with that of H_2 in the TPD spectra. These findings suggest that α- and β-CO_2 are originated from formate species whereas α-CO is originated from methoxide species.

Fig. 3 shows the IR spectra of the catalyst previously subjected to the reaction. Spectrum A was recorded after the CO_2–H_2 reaction was carried out at 438 K for 4 h. The absorptions appear at 2970, 2930, 2880, 2850, 2825, and 2740 cm^{-1} in a higher wave number region. In a lower wave number region the absorptions appear at 1620 (shoulder), 1580, 1383, 1365, 1350 (shoulder), and 1060 cm^{-1}. After spectrum A was recorded, the catalyst was exposed to flowing He for 10 min at 438 K, at which the desorption of α-CO_2 was completed, and then spectrum B was obtained. On completion of the desorption of α-CO_2, the absorption at 2850 cm^{-1} disappears and that at 2930 cm^{-1} decreases. The absorptions around 1580 and 1365 cm^{-1} sharpen to some extent. Spectrum C shows the ratio spectrum of A/B. It is evident that the absorptions at 2930, 2850, 1620 and 1350 cm^{-1} decrease appreciably by the He treatment at 438 K. The intensities of other absorptions remained unchanged. They vanished in a He stream at 573 K at which the desorption of β-CO_2 and α-CO were completed.

Sexton [22] previously showed that the peaks appeared at 2910, 2840, 1640 and 1330 cm^{-1} in the EELS spectrum of formate on Cu(100). Hence, we assigned the absorptions at 2930, 2850, 1620 and 1350 cm^{-1} to copper formate (HCOO–Cu). On the other hand, the absorptions at 2970, 2880, 2740, 1580,

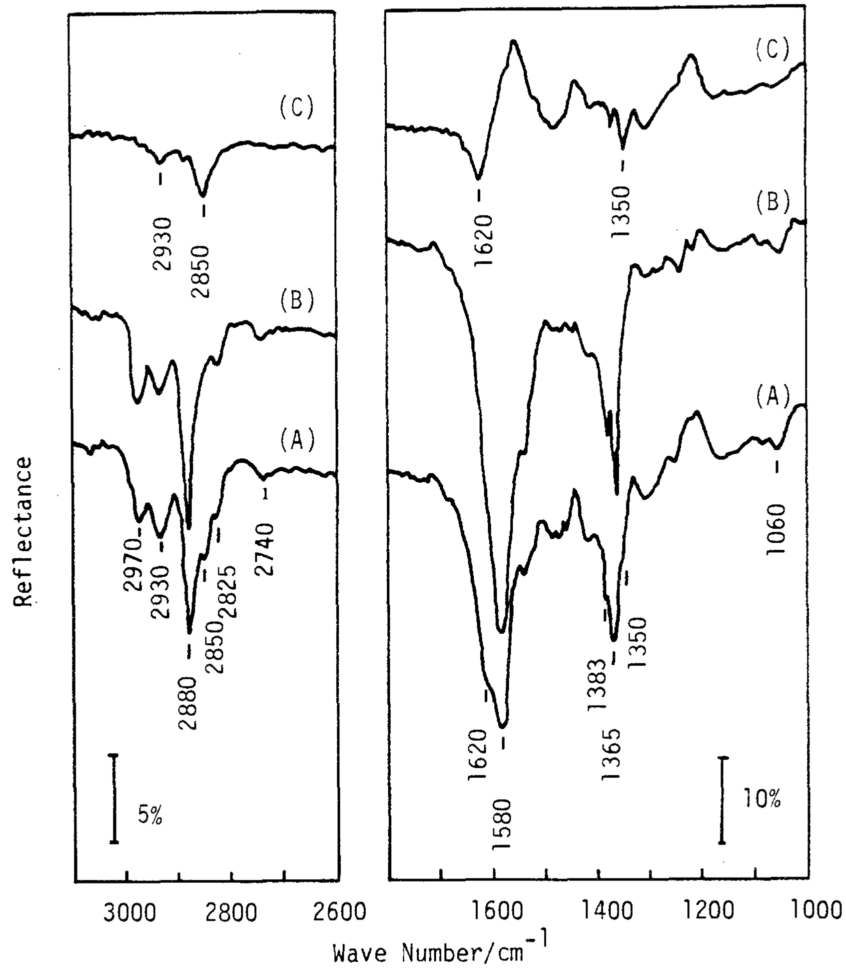

Fig. 3. Diffuse reflectance IR spectra of the catalyst (A) after the CO_2–H_2 reaction at 438 K for 4 h, (B) after He treatment at 438 K for 10 min following the CO_2–H_2 reaction at the same conditions as A, and (C) ratio spectrum of A/B.

1383 and 1365 cm^{-1} were assignable to bidentate zinc formate (HCOO–Zn), since absorptions for this species occurred at 2966, 2875, 2739, 1575, 1380 and 1365 cm^{-1} [23–25]. When methanol was adsorbed on Cu/ZnO or ZnO at room temperature, the strong absorptions appeared at 2930, 2830 and 1050 cm^{-1}. Therefore the absorptions occurring at 2930, 2825 and 1060 cm^{-1} in the CO_2–H_2 mixture were ascribable to zinc methoxide (CH_3O–Zn) [24,26–28]. The collected data are listed in table 1 with their assignments. On the basis of these results, we concluded that HCOO–Cu, HCOO–Zn and CH_3O–Zn were present in the methanol synthesis. HCOO–Cu, HCOO–Zn and CH_3O–Zn were decomposed, giving α-CO_2, β-CO_2 and α-CO in TPD runs, respectively.

In contrast to the present observations, Bowker et al. recently reported that no HCOO–Zn was formed in the course of CO_2–H_2 reaction over

Table 1
Absorptions of the surface species formed over Cu/ZnO catalyst

	Wave number (cm^{-1})	Assignment
HCOO–Cu	2850	CH stretching
	1620	asym OCO stretching
	1350	sym OCO stretching
	2930	CH bending + asym OCO stretching
HCOO–Zn	2880	CH stretching
	1580	asym OCO stretching
	1383	CH bending
	1365	sym OCO stretching
	2970	CH bending + asym OCO stretching
	2740	CH bending + sym OCO stretching or 2 × CH bending
CH_3O–Zn	2930	asym CH_3 stretching
	2825	sym CH_3 stretching
	1060	CO stretching

$Cu/ZnO/Al_2O_3$ catalyst (Cu/Zn/Al = 6/3/1) [29]. This discrepancy seems to be caused by the difference in the ratio of Cu/Zn of the catalyst. In fact, when TPD runs were performed after the CO_2–H_2 reaction was carried out over Cu/ZnO catalysts with high Cu/Zn ratios of 7/3 and 9/1, the CO_2 peak assigned to HCOO–Zn was much broader and weaker than that observed over the catalyst with Cu/Zn ratio of 3/7.

The amounts of HCOO–Cu, HCOO–Zn and CH_3O–Zn formed under the transient state of the reaction were determined by TPD method. Fig. 4 illustrates how the amounts of these species vary in the course of the reaction. The amounts of HCOO–Cu and HCOO–Zn increase rapidly and reach to steady state values within 2–3 min. By contrast, the amount of CH_3O–Zn increases slowly with time and attains to a constant value after 2 h. Consistent with these observations, only the IR absorptions of CH_3O–Zn increased in intensity with time and reached to their steady state value, while those of HCOO–Cu and HCOO–Zn were held at constant intensities. It is to be noted that the amount of CH_3O–Zn was unaffected by the total flow rate, i.e. by the partial pressure of CH_3OH, even under the transient state. This suggested that the readsorption of CH_3OH from gas phase was practically negligible for the formation of CH_3O–Zn.

Since the partial pressure of CH_3OH in the gas phase varies with time in a similar manner to the amount of CH_3O–Zn present on the surface, CH_3O–Zn was suggested to be involved in the title reaction. A CO_2–H_2 mixture was fed over the catalyst on which various amounts of CH_3O–Zn were previously formed by the reaction with CO_2–H_2 or CH_3OH adsorption at room tempera-

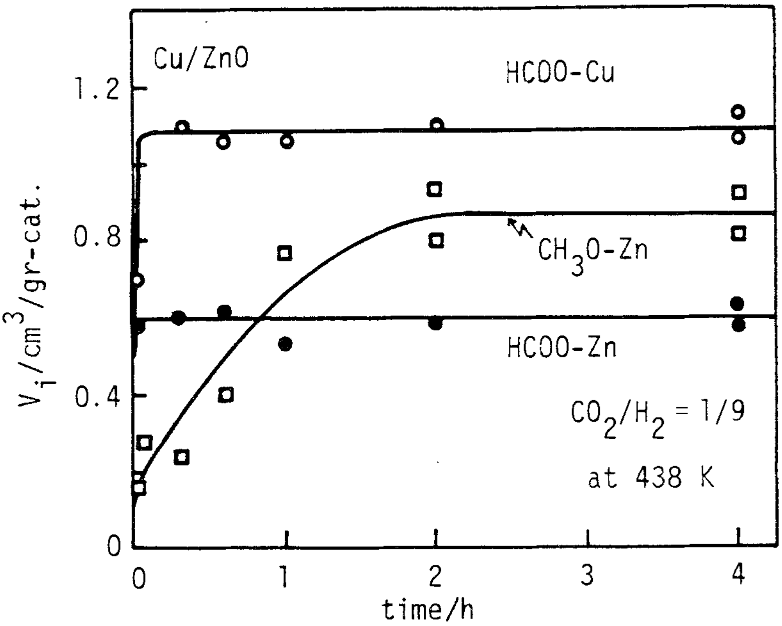

Fig. 4. Variation of the amount of the surface species formed in the course of the CO_2–H_2 reaction with time.

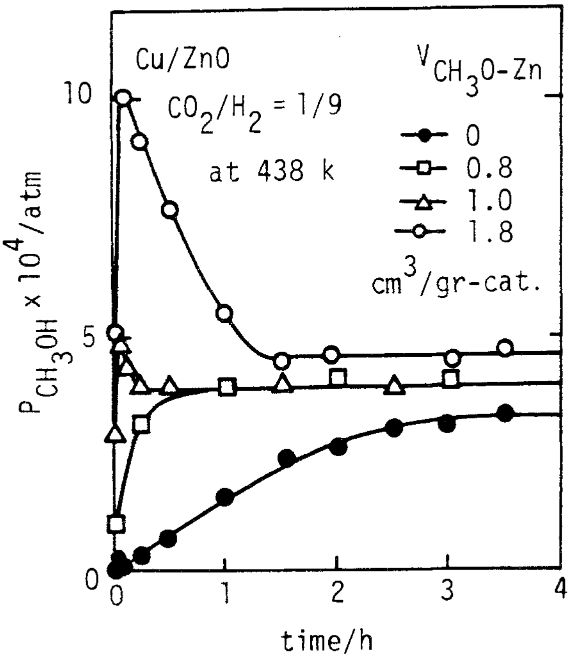

Fig. 5. CH_3OH formation from the CO_2–H_2 mixture over the catalyst which were preadsorbed with various amounts of CH_3O–Zn.

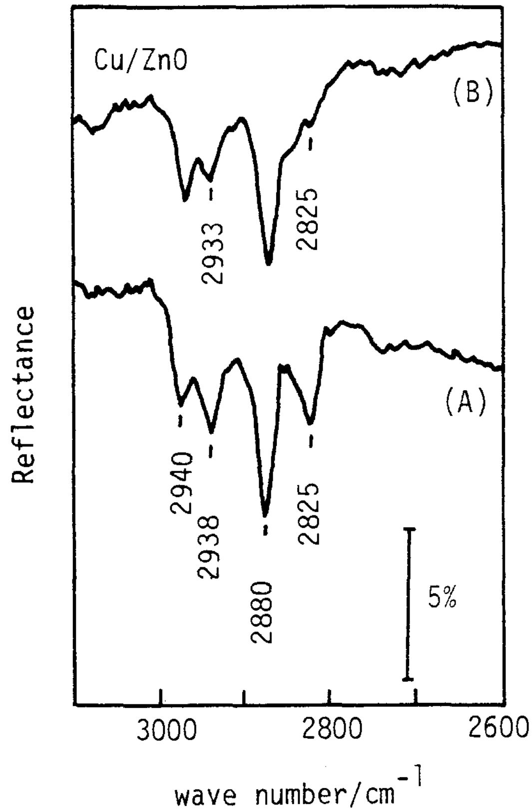

Fig. 6. Decrease of the IR absorptions of CH_3O–Zn by feeding of H_2O. Spectra were taken (A) before feeding and (B) after feeding. A helium stream containing 1.24×10^{-3} atm of H_2O was fed over the catalyst at 383 K for 20 min.

ture followed by a He treatment at 438 K. As fig. 5 shows, with increasing the amount of preadsorbed CH_3O–Zn, CH_3OH in the effluent is rapidly built up and reaches to a steady state value. When the amount of the preadsorbed CH_3O–Zn is in excess of that at the steady state, the outlet partial pressure of methanol overshoots and decreases to a steady state value. In contrast, when H_2 or CO_2 alone was fed over the catalyst preadsorbed with CH_3O–Zn, no CH_3OH was produced However, on feeding of H_2O, CH_3OH was detected in the effluent even at lower temperature, 383 K. When H_2O was fed over the catalyst preadsorbed with HCOO–Cu and HCOO–Zn, CH_3OH was undetected. Fig. 6 illustrates IR spectra in the CH stretching region before and after the H_2O feeding. It shows that the absorptions ascribed to CH_3O–Zn decrease on addition of H_2O, suggesting that CH_3OH is produced via hydrolysis of CH_3O–Zn. Consistent with these findings, when a stream of a CO_2–H_2 mixture was switched to that of the mixture containing water at a steady state of reaction, the outlet partial pressure of methanol increased rapidly and decreased to a new steady state value. Hence, we concluded that H_2O formed by the reverse water gas shift reaction was effectively involved in the hydrolysis when the CO_2–H_2 mixture was fed over the catalyst preadsorbed with CH_3O–Zn.

Experiments were attempted with a CO–H_2 mixture over the catalyst at 438 K. Methanol was undetected in the gas phase. However, an appreciable amount of CH_3O–Zn was formed. The amount of this species increased with time in a monotonic manner and was unaffected by the total flow rate. During the first 15 h, the amount of CH_3O–Zn reached to about five times that present at the steady state of the CO_2–H_2 reaction. When H_2O was fed over the catalyst after the CO–H_2 reaction, the amount of CH_3O–Zn decreased and CH_3OH was detected in the effluent at 383 K as observed in the system of CO_2–H_2. These findings indicated that even when the large amount of CH_3O–Zn was present on the surface, no methanol was formed in the absence of H_2O, strongly suggesting that the hydrolysis of CH_3O–Zn was involved in the formation of methanol.

Based on these results, we concluded that CH_3OH is produced by hydrolysis of CH_3O–Zn in the course of the methanol synthesis, CH_3O–Zn being attacked by H_2O formed via the reverse water gas shift reaction.

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