Methanol Synthesis from CO_2 and H_2 over a ZnO Catalyst. Effect of the Pretreatment with CO–H_2 upon the Reaction

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Synopsis. Methanol Synthesis from CO_2–H_2 was carried out over a ZnO catalyst. Pretreatments with a CO–H_2 mixture caused a transient increase of the methanol formation as Bowker et al. found.[12] It was shown that methoxide species was formed in the course of the pretreatments, being readily hydrolyzed to methanol by water formed via the reverse water gas shift reaction.

Zinc oxide is a major component of Cu/ZnO based catalysts which are highly effective for the methanol synthesis from CO_2–H_2 and CO–H_2. However, there is still a controversy about the role of ZnO in the methanol synthesis.[1,2] A number of papers concerning the CO–H_2 reaction over ZnO and the adsorptive properties of ZnO have been opened in the literature.[1,3—10] Only a limited number of papers have been published on the CO_2–H_2 reaction over ZnO.[11,12] Bowker et al. previously found that the methanol synthesis from CO_2–H_2 was markedly enhanced by pretreatments with CO–H_2 over ZnO.[12] They concluded that anion vacancies were produced on ZnO by the pretreatments and were responsible for the enhancement of the methanol formation from CO_2–H_2. However, no surface species were analyzed for the catalyst pretreated with CO–H_2. We previously showed[13] that a considerable amount of zinc methoxide species was formed from CO–H_2 over a Cu/ZnO catalyst, and this species was rapidly hydrolyzed to methanol in a mixture of CO_2–H_2. Hence, there is a possibility that this hydrolysis process occurred over ZnO pretreated with CO–H_2.

In the present work, methanol synthesis from CO_2–H_2 were carried out at atmospheric pressure over a ZnO catalyst, and the effect of the pretreatment with CO–H_2 upon the CO_2–H_2 reaction was elucidated by the use of diffuse reflectance FT-IR spectroscopy and temperature programmed desorption (TPD) method.

Experimental

A ZnO catalyst was prepared by precipitation from a solution of zinc nitrate with sodium carbonate in a similar way to that adopted by Herman et al.[14] The resulting precipitate was dried at 383 K overnight, and calcined in air at 623 K for 4 h. The catalyst thus prepared was reduced in a reactor or in an IR cell in a H_2 stream at 523 K for 2 h. The BET surface area of the catalyst was 39.8 $m^2 g^{-1}$. Detail of the catalyst preparation was described in elsewhere.[13]

Methanol synthesis from CO_2–H_2 and TPD runs were carried out in a flow reactor at atmospheric pressure. The weight of the catalyst used was 1.0 g. Temperature was ramped at a rate of 5 K min^{-1} in TPD runs. Experimental procedures in the TPD runs were similar to those adopted in the previous study.[13] The effluent from the reactor was analyzed by gas chromatography.

FT-IR spectra of adsorbed species were recorded in He at room temperature with a JASCO FT-IR-5M infrared spectrophotometer to which a diffuse reflectance equipment DR-500/H was attached. A spectrum of the catalyst reduced was used as the background.[13]

Results and Discussion

When a CO_2–H_2 mixture ($CO_2/H_2=1/9$) was fed over the catalyst at 523 K, CH_3OH was produced together with CO and H_2O. Methanol synthesis ($CO_2+3H_2 \rightarrow CH_3OH+H_2O$) occurred along with the reverse water gas shift reaction ($CO_2+H_2 \rightarrow CO+H_2O$). At the steady state of the reactions, selectivity to methanol was 15% at 0.27% of the CO_2 conversion. The outlet partial pressure of CH_3OH and CO increased with increasing residence time, suggesting that CH_3OH and CO were produced through a parallel pathway.

Figure 1 shows how the outlet partial pressure of CH_3OH and CO varies with time over the catalyst pretreated with flowing H_2 at 523 K for 2 h or with a mixture of CO–H_2 ($CO/H_2=1/9$) at 523 K for various periods of time. Over the catalyst pretreated with H_2, the outlet partial pressure of CH_3OH increases slowly to a steady state value in a monotonic manner. However, over the catalyst pretreated with the CO–H_2 mixture, methanol is rapidly formed in the initial period of the CO_2–H_2 reaction and then decreases with time to the steady state value. The methanol formation is greatly enhanced by the pretreatment with CO–H_2 at the initial period of the CO_2–H_2 reaction. The enhancement of the methanol formation increases with increasing time for the CO–H_2 pretreatment. On the other hand, the formation of CO is unaffected by the pretreatments (Fig. 1). The results obtained over the catalyst pretreated with CO–H_2 were quite the same as those obtained by Bowker et al.[12]

For elucidation of the enhancement of the methanol formation, the surface species formed in the CO–H_2 mixtures were analyzed with the aid of TPD and FT-IR spectroscopy. Figure 2A illustrates the TPD profiles of CO_2 and CO for the catalyst subjected to the pretreatments with CO–H_2 at 523 K. Desorption peaks of CO_2 and CO are seen at 553 and 590 K, respectively. The amount of CO desorbed increased rapidly with increasing time for the pretreatment in the initial 30 min, and thereafter increased slowly, reaching to 2.3 $\mu mol\, m^{-2}$ for the catalyst pretreated with CO–H_2 for

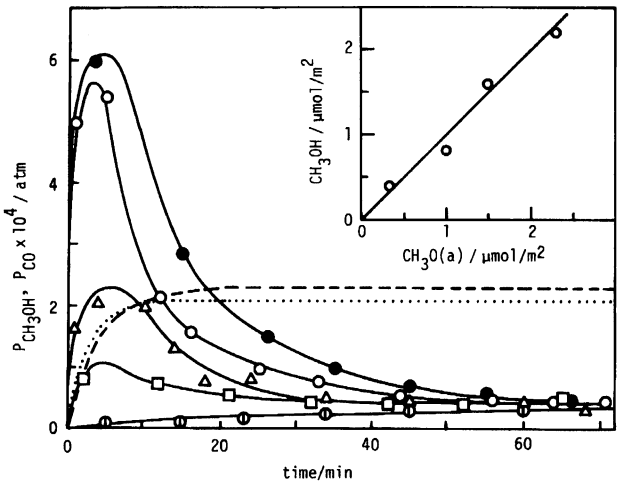

Fig. 1. Variation of the outlet partial pressure of CH_3OH with time over the catalyst (Φ) pretreated with H_2 at 523 K for 2 h, and pretreated with CO–H_2 at 523 K (□) for 2 min, (△) for 5 min, (○) for 30 min and (●) for 4 h. Bloken and dotted lines show outlet partial pressure of CO formed over the catalyst pretreated with H_2 for 2 h and with CO–H_2 for 30 min, respectively. The inset shows the relationship between the total amount of increased methanol and that of zinc methoxide preadsorbed.

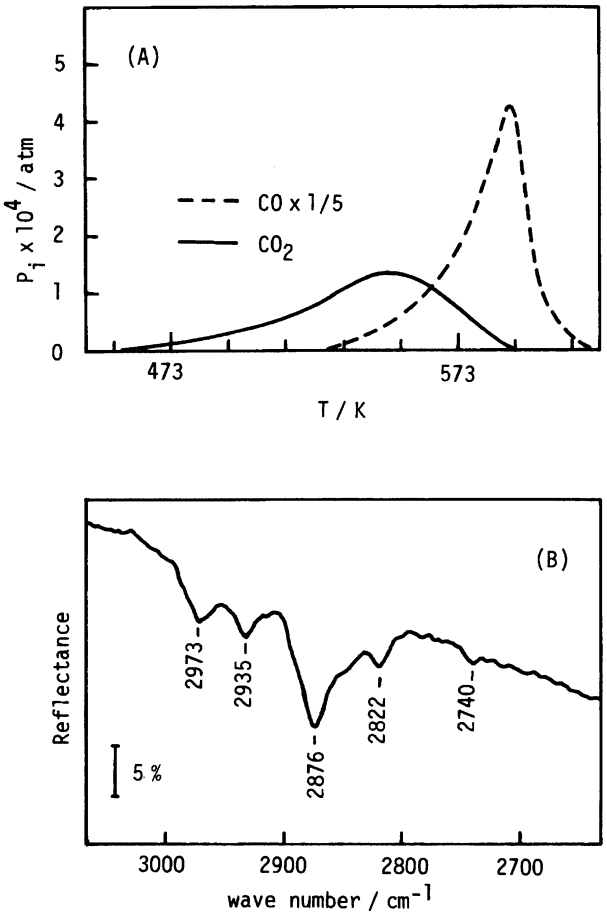

Fig. 2. TPD spectra of CO and CO_2 (A), and diffuse reflectance IR spectra of the catalyst (B). The TPD and the IR spectra were obtained after the pretreatment with CO–H_2 was carried out at 523 K for 4 h.

4 h. The amount of CO_2 desorbed rapidly attained a constant value of 0.3 μmol m^{-2} within 10 min. For the catalyst preadsorbed with CH_3OH, an intense peak of CO was observed at 588 K in TPD runs, suggesting that the CO peak for the catalyst pretreated with CO–H_2 was originated from methoxide species.

Figure 2B shows IR spectra of the catalyst previously treated with CO–H_2 at 523 K for 4 h. Absorptions at 2935 and 2822 cm^{-1} occurs along with those at 2973, 2876, and 2740 cm^{-1}. When the catalyst was heated in flowing He at 573 K, the absorptions at 2973, 2876, and 2740 cm^{-1} disappeared while those at 2935 and 2822 cm^{-1} still remained. The absorptions at 2973, 2876, and 2740 cm^{-1} were ascribable to the CH stretching of surface bidentate formate species.[8,15—18] When methanol was adsorbed on the catalyst, strong absorptions ascribed to CH stretching of methoxide species[8,16,19,20] occurred at 2930 and 2830 cm^{-1}. Hence the absorptions at 2935 and 2822 cm^{-1} were assigned to methoxide species. Based upon these findings we concluded that methoxide and bidentate formate species were formed by the pretreatments with CO–H_2 at 523 K.

It is widely accepted that both of the forward and the reverse water gas shift reaction $CO+H_2O \rightleftharpoons CO_2+H_2$, proceed through the decomposition of formate species over zinc oxide.[15,18] The formate species decomposed, giving CO and CO_2 as carbon-containing products. Therefore, it is highly probable that bidentate formate species formed in the CO–H_2 mixture decompose to CO and CO_2. When the catalyst was exposed to the CO–H_2 mixture at 440 K, the absorptions ascribed to bidentate formate species occurred at 2973, 2876, and 2740 cm^{-1}. No absorptions ascribed to methoxide species appeared. Upon heating, the formate species decomposed, giving CO and CO_2 peaks at 563 K in TPD runs. On the basis of the intensities of the CO_2 and the CO peaks, CO and CO_2 desorbed in 1 to 7 molar ratio for the decomposition of bidentate formate. For the catalyst pretreated at 523 K, the TPD peak of CO arisen from the decomposition of bidentate formate was probably indistinguishable from that arisen from methoxide species in TPD runs because of the intense peak of CO arisen from the later species.

The amounts of methoxide and bidentate species formed by the CO–H_2 pretreatment were determined on the basis of intensities of the respective TPD peaks of CO and CO_2 for the decomposition of methoxide and bidentate formate species and the CO/CO_2 ratio ($CO/CO_2=1/7$) for gases evolved in the TPD runs for bidentate formate species. In the inset of Fig. 1 the total amount of methanol increased by the pretreatment is plotted against to that of methoxide species formed

by the pretreatment. The total amount of the increased methanol is practically the same as that of methoxide species.

When CO_2 alone was fed over the catalyst having methoxide species, no formation of methanol occurred. Upon feeding H_2, a slight amount of methanol was detected in the effluent (Fig. 3A). However, no rapid formation of methanol was observed. In contrast, upon feeding of H_2O (8×10^{-3} atm), CH_3OH was produced even at lower temperature, 383 K, (Fig. 3A). The amount of CH_3OH formed was in fair agreement with that of methoxide previously formed by the treatment with CO–H_2. TPD runs and IR measurements showed that methoxide decreased upon feeding the CO_2–H_2 mixture or H_2O. These findings suggested that methoxide was formed on ZnO by the pretreatment with the CO–H_2 mixture at 523 K, and rapidly hydrolized by water formed via the reverse water gas shift reaction in the CO_2–H_2 reaction.

In further confirmation of the involvement of this process, 2.3 μmol m^{-2} of d_3-methoxide species, CD_3O-(a), was previously formed by CD_3OH adsorption on ZnO at room temperature followed by a He treatment at 523 K and then the CO_2–H_2 reaction was carried out. In confirmation with the proposed mechanism of the hydrolysis of methoxide, CD_3OH was found to be preferentially produced at the initial period of the reaction (Fig. 3B).

Based upon these findings, we concluded that on the pretreatment with CO–H_2 a considerable amount of methoxide species were produced on ZnO and the methoxide species reacted rapidly with water formed via the reverse water gas shift reaction, converting to methanol. This caused a rapid transient increase in the methanol formation in the reaction with CO_2–H_2.

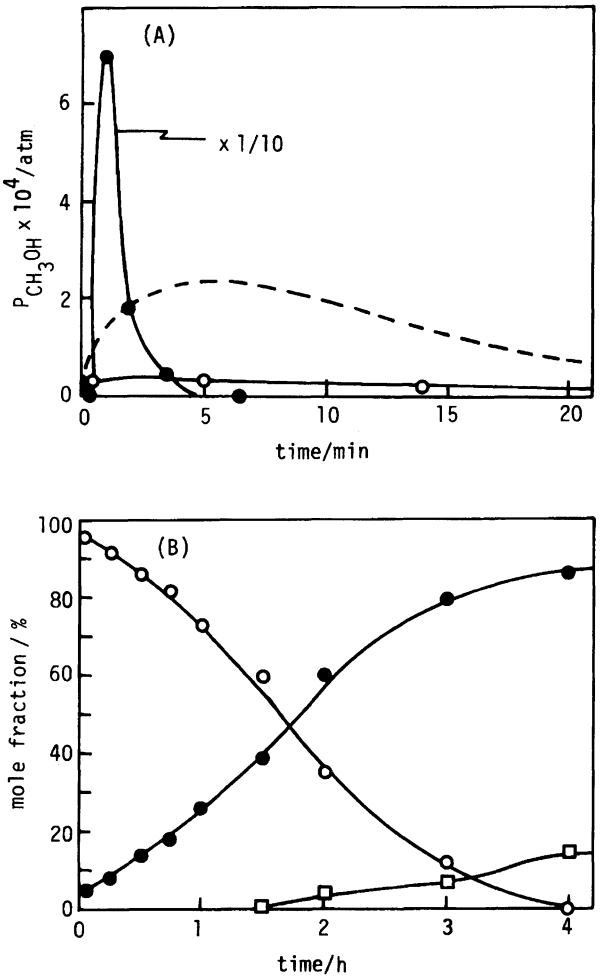

Fig. 3. (A) Methanol formation in streams of (●) H_2O at 383 K, (---) CO_2–H_2 at 523 K and (○) H_2 at 523 K over the catalyst preadsorbed with 1.6 μmol m^{-2} of methoxide species. (B) Variation of the isotopic distribution of methanol with time. ○, CD_3OH; ●, CH_3OH; □, CH_2DOH. The CO_2–H_2 reaction was carried out at 523 K over the catalyst preadsorbed with deuterated zinc methoxide, CD_3O(a).

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