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In situ IR studies on the mechanism of methanol synthesis from CO/H_2 and CO_2/H_2 over Cu-ZnO-Al$_2$O$_3$ catalyst

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Abstract−Methanol synthesis from CO/H_2 and CO_2/H_2 was carried out at atmospheric pressure over Cu/ZnO/Al$_2$O$_3$ catalyst. The formation and variation of surface species were recorded by in situ FT-IR spectroscopy. The result revealed that both CO and CO_2 can serve as the primary carbon source for methanol synthesis. For CO/H_2 feed gas, only HCOO-Zn was detected; however, for CO_2/H_2, both HCOO-Zn and HCOO-Cu were observed, and without CH$_3$O-Cu. HCOO-Zn was the key intermediate. A scheme of methanol synthesis and reverse water-gas shift (RGWS) reaction was proposed.

Key words: Methanol Synthesis, Mechanism, In Situ, FT-IR

INTRODUCTION

Dimethyl ether (DME) is an important chemical and a chemical intermediate for the production of gasoline, ethylene, aromatics and other chemicals. Its applications as fuel and fuel additive have received growing attention in recent years. Using synthesis gas as a starting material, dimethyl ether can be prepared in a single-step process, which is more economically favorable than two-step method [1-3]. One-step synthesis of DME includes methanol formation, methanol dehydration and water-gas-shift reactions. Methanol formation is the premise of DME synthesis. To understand the mechanism of one-step synthesis of DME, the mechanism of the methanol synthesis should be studied first.

Effective synthesis of methanol has been investigated during the past decades since methanol is considered to be one of the materials that can overcome the forthcoming shortage of petroleum [4]. Methanol synthesis from CO/H_2 and CO_2/H_2 mixtures using Cu-based catalysts has received considerable attention and various reaction mechanisms have been proposed. However, there is still controversy over some important issues, particularly the dispute over the role of each carbon oxide in relation with the detected reaction intermediates. Boomer and Morris considered carbon monoxide to be the direct source for methanol synthesis [5]. But this viewpoint cannot explain the fact that the rate of methanol synthesis can be promoted remarkably with the addition of a small amount of CO_2 to the mixture of CO and H_2. After the isotopic tracer and in-situ IR methods were applied in the investigation of the mechanism, Bommer's viewpoint was questioned gradually. In the 1970s, Kagan [6] proposed that methanol was formed predominantly from CO_2 by using ^{14}C isotopic tracer to study the mechanism of methanol synthesis. Both Saussey [7] and Fujita [8] considered that methanol synthesis from CO/H_2 and CO_2/H_2 followed different mechanisms.

By the use of FT-IR spectroscopy, temperature-programmed-des-

orption (TPD) and chemical trapping methods, various surface species such as formaldehydel [9], formate [7,8,10,13], dioxymethylene [11], and methoxide [9,11-13] were detected on Cu based catalysts in the course of methanol synthesis. Fujita [8] considered that for CO+H_2 feed gas, zinc formate was formed first, followed by hydrogenated to zinc methoxy and then reacted with surface hydroxyl species to form methanol; while for CO_2+H_2 feed gas, both zinc formate and copper formate were observed, then copper formate and zinc formate hydrogenated to methoxide, and hydrolyzed to methanol. Qi Sun [13] proposed that methanol was formed directly from CO_2 hydrogenation both for CO_2 and for CO/CO_2 hydrogenation. b-HCOO$_s^-$ species was the key intermediate, the rate-limiting step was hydrogenation of b-HCOO$_s^-$ for methanol synthesis.

In this paper, methanol synthesis from CO/H_2 and CO_2/H_2 was investigated over Cu/ZnO/Al$_2$O$_3$ catalyst at atmospheric pressure by using in situ IR technique. A mechanism of methanol synthesis was proposed. The catalyst for methanol synthesis also functions for water-gas-shift reaction, based on the mechanism of methanol synthesis; a scheme of reverse water-gas shift (RGWS) was derived.

EXPERIMENTAL

A commercial methanol synthesis catalyst, Cu/ZnO/Al$_2$O$_3$, supplied by Si Chuan Tian Yi company (XNC-98) was chosen as the methanol synthesis catalyst. A total of 10 mg catalyst mixed with 90 wt% KBr was pressed into self-supporting wafer and mounted into the in situ IR cell, where the reaction took place. Infrared spectra were recorded with a Nicolet Nexus 460 FT-IR spectrometer equipped with a liquid nitrogen cooled MCT (Mercury-Cadmium-Telluride) detector. A resolution of 4.0 cm^{-1} was used throughout the investigation and 64 scans taken over a 10 s interval were averaged to achieve a satisfactory signal-to-noise ratio. The ultrahigh purity (>99.999%) gases of H_2, CO, N_2 and chemical purity CO_2 (>99.9%) were used.

Reduction was carried out in H_2 flowing (50 ml/min), The temperature was raised at 2 °C/min from ambient to 220 °C, after which the catalyst was further reduced at 220 °C for about 2 h in pure H_2

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flowing at 50 ml/min. Subsequently, the catalyst was cooled in an N_2-flow to room temperature.

The reduced samples were studied in situ during exposure to methanol synthesis gas (CO/H_2=1, CO_2/H_2=1). The reaction temperature was raised from ambient to 220 °C at 2 °C/min, and the reaction intermediates and products were monitored on-line by FT-IR spectrometer.

RESULTS AND DISCUSSION

1. Characterization of the Adsorbed Species

Assignment of the bands for adsorption species was made by analogy with the spectra of known compounds from literatures. The IR spectra of the catalysts under CO/H_2 and CO_2/H_2 flowing show the characteristic bands of the following species:

(i) carbonate species have been identified by bands appearing at 1,557, 1,539, 1,488 and 1,418 cm^{-1} [14]

(ii) formate species on ZnO (HCOO-Zn) (2,967, 2,873, 1,592, 1,575, 1,375, 1,362 cm^{-1}) [14,15]

(iii) formate species on Cu (HCOO-Cu) (2,925, 2,845 cm^{-1}) [8,14, 16]

(iv) methoxy species adsorbed on the support (CH$_3$O-Zn) have been identified by bands at 2,837 and 1,100 cm^{-1} [12,14,17]; the intensity of the 1,085 cm^{-1} band was chosen to follow the surface methoxy concentration; methoxy species adsorbed on copper (CH$_3$O-Cu), generally identified by a set of IR bands at 2,907, 2,861, 2,787 and 990 cm^{-1} [18].

(v) The broad band arising at 3,000-3,500 cm^{-1} is assigned to hydroxyl species. (hydroxyl species on Cu(Cu-OH) (3,200 cm^{-1}), hydroxyl species on ZnO(Zn-OH) (3,400 cm^{-1}) [19].

(vi) The band at 1,600-1,800 cm^{-1} is due to H_2O [13].

2. In Situ IR Study of Methanol Synthesis from CO

The reduced catalyst was exposed to CO/H_2 reaction gas at atmospheric pressure, and the reaction temperature was raised from ambient to 220 °C at 2 °C/min. The IR spectra of the reaction intermediates and products are shown in Fig. 1 and Fig. 2. It is found that the bands at 2,000-2,100 cm^{-1} are due to CO absorbed on Cu [13,18], the peaks at 2,171 and 2,116 cm^{-1} are characteristic of gaseous CO. A small amount of CO_2 (2,340, 2,360 cm^{-1}) can be observed, indicating that CO_2 species is formed from CO reacting with absorbed oxygen (Os) which exists on the catalyst after the catalyst is reduced. Meanwhile, the bands of formate species on ZnO (HCOO-Zn), carbonate species, methoxy species on ZnO (CH$_3$O-Zn), H_2O are observed in Fig. 1 and hydroxyl species is observed in Fig. 2. The band intensity of CO decreases gradually with the increasing temperature. When the temperature is lower than 60 °C, the band intensities of both formate species and carbonate species increase gradually, and the intensity of broad band at 3,000-3,500 cm^{-1} as-
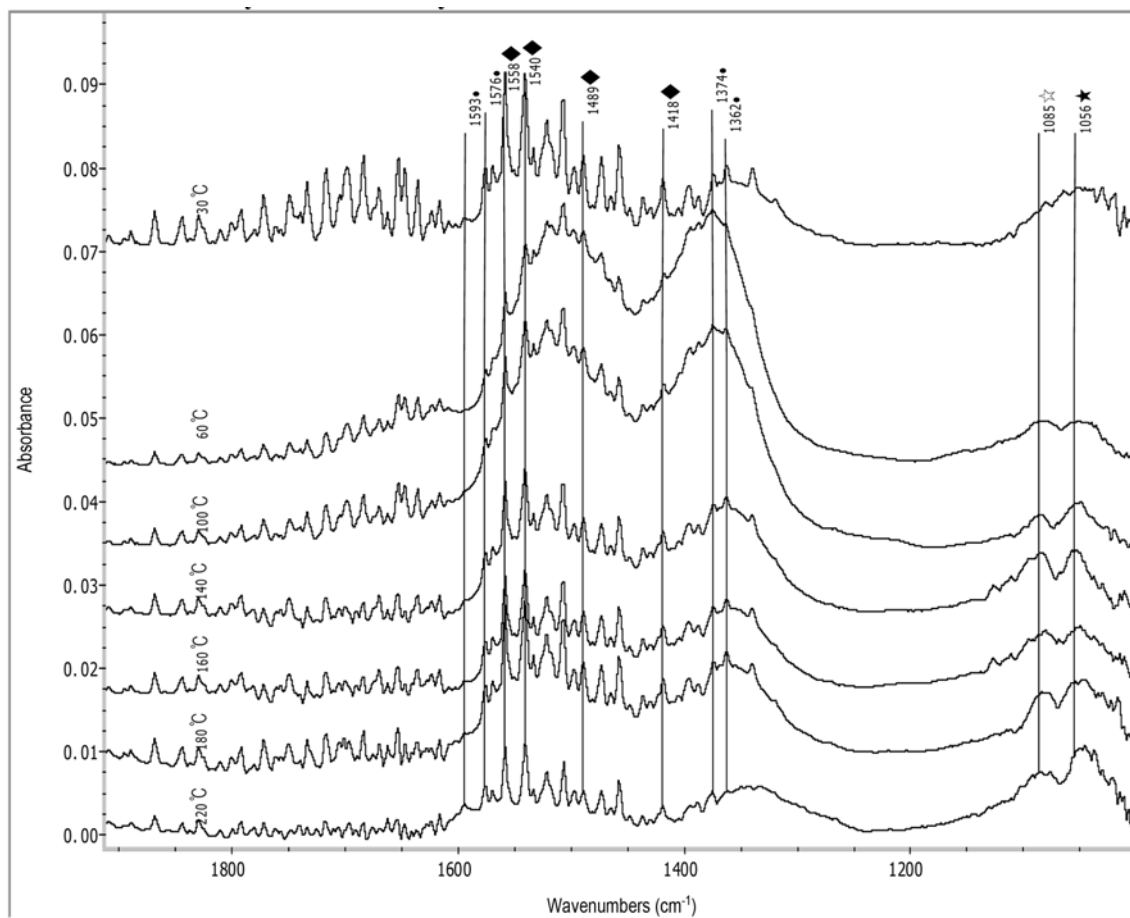

Fig. 1. In situ IR spectra for methanol synthesis from CO/H_2 recorded during temperature-programmed-reaction at low wave number area. HCOO-Zn (●), carbonate (◆), CH$_3$O-Zn (☆), CH$_3$OH (★).
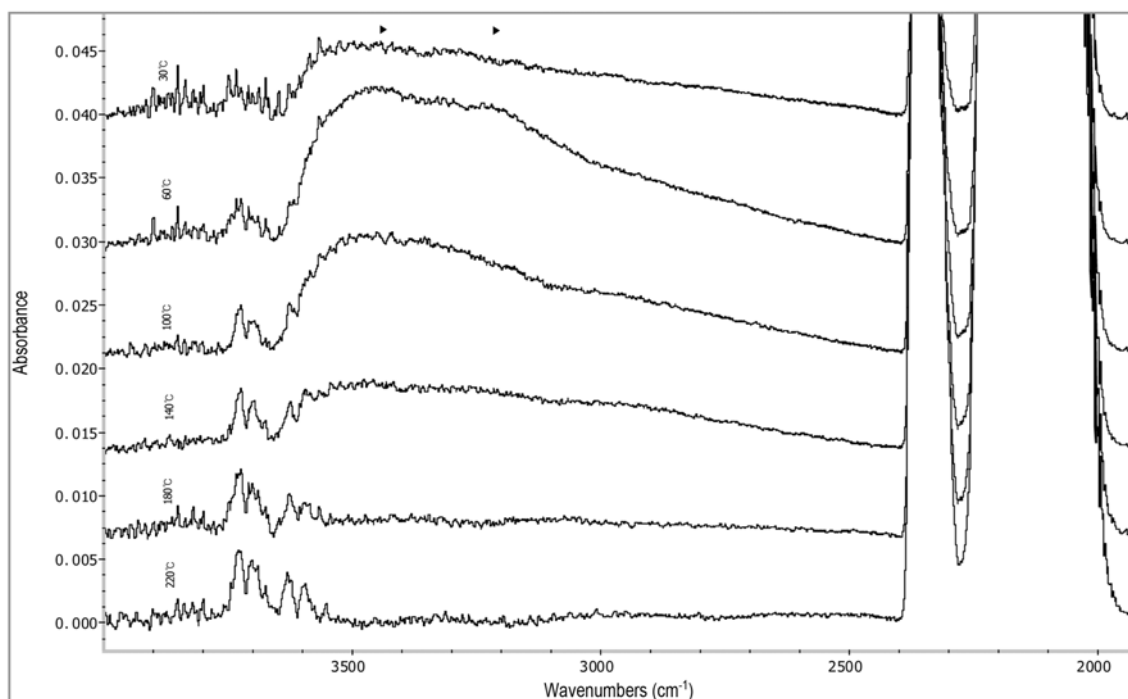
Fig. 2. Variation of hydroxyl species during temperature programmed reaction process for methanol synthesis from CO/H$_2$.

signed to hydroxyl species increases rapidly with the temperature rising. However, the intensity of those bands decreases gradually with the temperature rising from 60 °C to 140 °C. When the temperature is higher than 140 °C, the hydroxyl species nearly cannot be detected, and the peaks of formate species and carbonate species weaken slower than before. The band intensity of CO$_2$ decreases first, and then increases gradually when the temperature rises from 60 °C to 220 °C. The peaks at 1,085 cm^{-1} and 1,056, assigned to methoxy and CH$_3$OH species, respectively, are observed and amplify

gradually as the temperature increases until the temperature is above 140 °C, then no longer increase clearly.

Such a result reveals that IR absorption bands for methoxy grow at the expense of the absorption bands for formate and carbonate species. The variation of CH$_3$OH has something to do with hydroxyl species and methoxy species.

3. In Situ IR Study of Methanol Synthesis from CO$_2$

The IR spectra obtained in CO$_2$/H$_2$ reaction gas are shown in Fig. 3, Fig. 4 and Fig. 5. The reaction temperature was raised at 2 °C/min
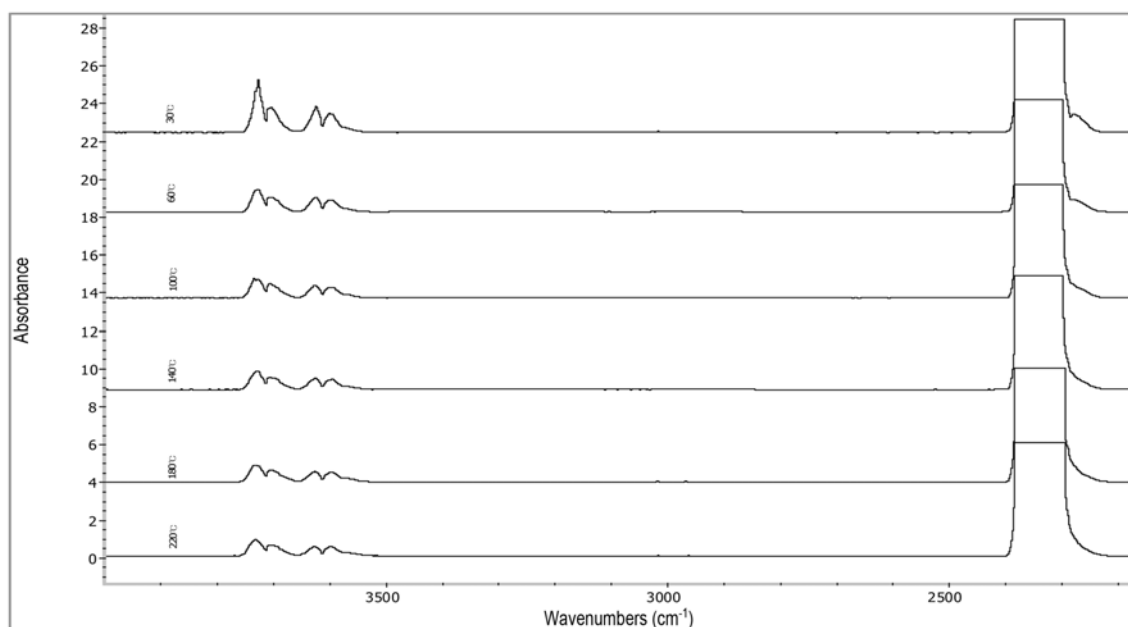

Fig. 3. Variation of CO$_2$ species during temperature programmed reaction process for methanol synthesis from CO$_2$/H$_2$.
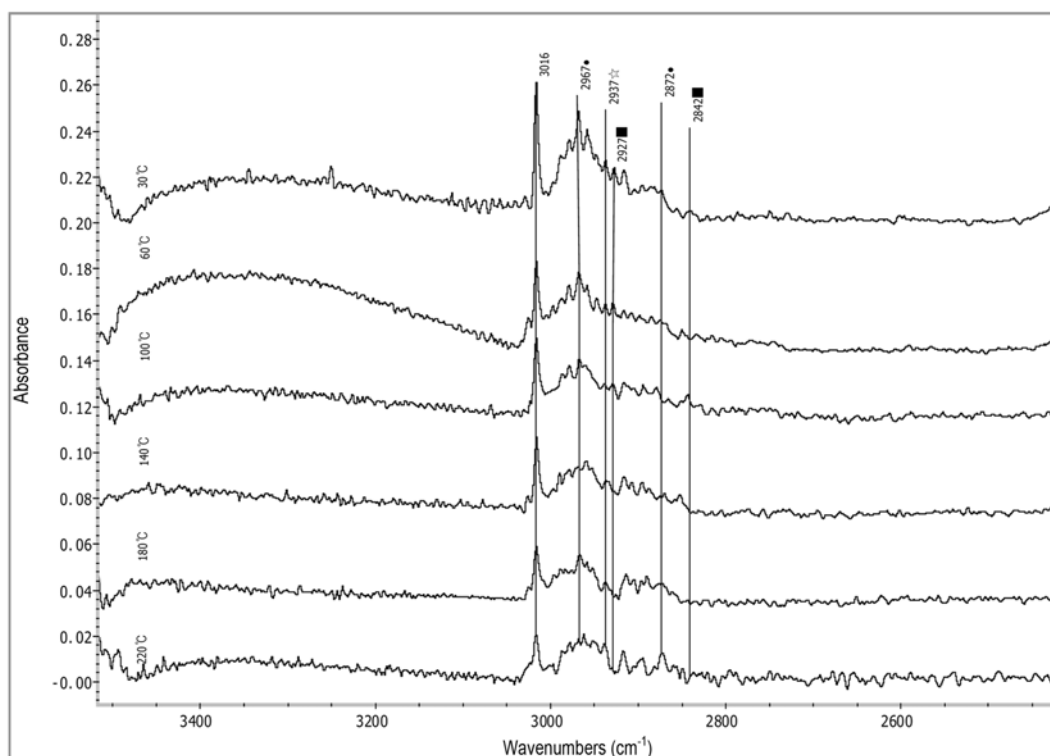
Fig. 4. In situ IR spectra for methanol synthesis from CO₂/H₂ recorded during temperature-programmed-reaction at high wave number area. HCOO-Zn (●), CH₃O-Zn (☆), HCOO-Cu (■).
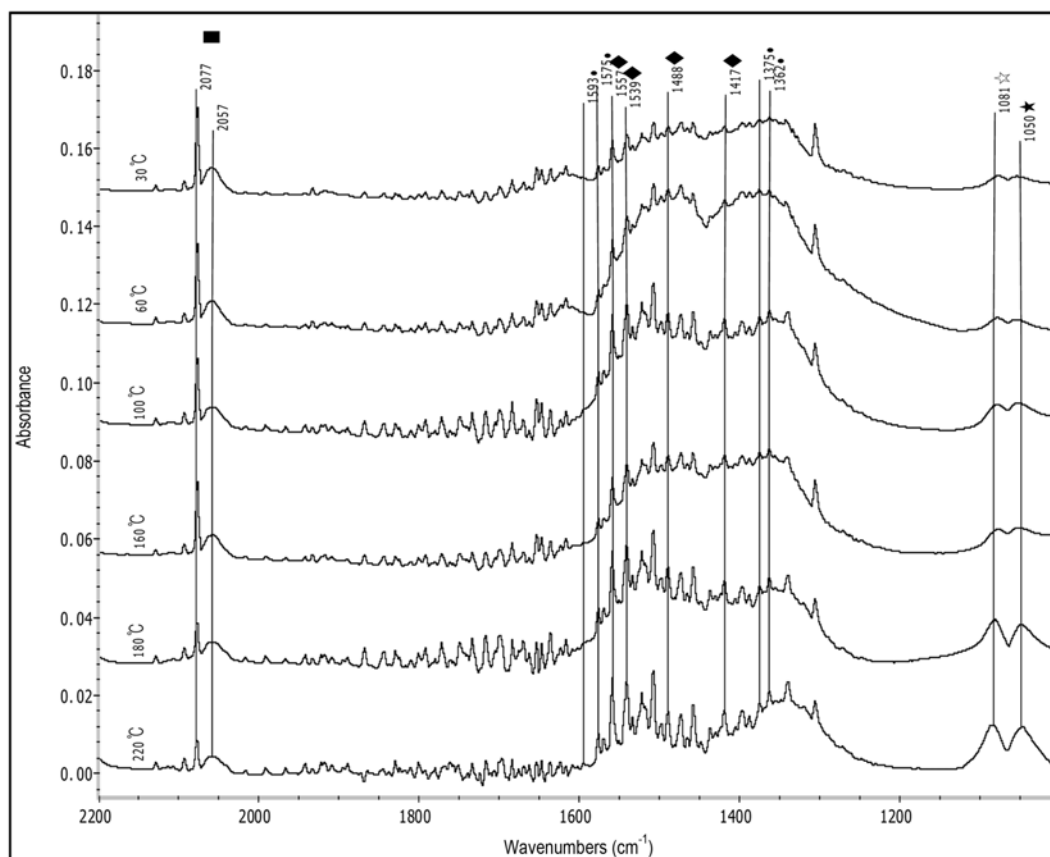

Fig. 5. In situ IR spectra for methanol synthesis from CO₂/H₂ recorded during temperature-programmed-reaction at low wave number area. HCOO-Zn (●), carbonate (◆), CH₃O-Zn (☆), CH₃OH (★).

from ambient to 220 °C at atmospheric pressure. It is found that CO can be formed easily at room temperature, the peaks at 2,077 and 2,057 cm^{-1} can be observed clearly, which are due to CO absorbed on Cu [13,20]. The bands at both sides of 3,715, 3,613 and 2,350 cm^{-1} are assigned to CO$_2$. As shown in Fig. 2, it is found that CO$_2$ has large adsorption capacity on Cu. This phenomenon indicates that CO species is formed from dissociative adsorption of CO$_2$ over the catalyst surface. With the temperature rising (lower than 60 °C), the band intensities of HCOO-Zn (2,966, 2,873, 1,592, 1,575, 1,375, 1,362 cm^{-1}) and carbonate species (1,557, 1,539, 1,488 and 1,418 cm^{-1}) increase rapidly; the intensity of the band at 3,000-3,500 cm^{-1} attributed to hydroxyl species also increases gradually. But as the temperature increases further (from 60 to 140 °C), the intensities of those bands decrease gradually. When the temperature is raised above 140 °C, the hydroxyl species nearly disappear, and the peaks of formate species and carbonate species weaken slower than before, similar to what happens in the CO/H$_2$ system. The bands of CO$_2$ and CO decrease in intensities gradually with temperature rising. The difference from CO/H$_2$ system is that a small amount of HCOO-Cu (2,827, 2,845 cm^{-1}) is observed in the CO$_2$/H$_2$ system. The peak of HCOO-Cu disappears at about 140 °C, and no CH$_3$O-Cu is detected. Considering the decomposition temperature of HCOO-Cu is 160 °C, it is concluded that formate species on Cu migrated from Cu to ZnO and formed HCOO-Zn species; this conclusion is consistent with the viewpoint of Joo [21]. The band intensities of CH$_3$O-Zn (1,081 cm^{-1}) and CH$_3$OH (1,050 cm^{-1}) increase gradually with the increase in temperature; however, when the hydroxyl species cannot be observed (above 140 °C), the peaks of the two species almost stop increasing. So we can conclude that methanol can also be formed from hydrogenation of CO$_2$.

According to the above analysis, some suggestions for methanol synthesis from CO/H$_2$ and CO$_2$/H$_2$ could be proposed:

1. The procedure of dissociative adsorption of CO$_2$ is reversible. So CO can be observed in the CO$_2$/H$_2$ system, while CO$_2$ appears in the CO/H$_2$ system. CO along with adsorbed Os are formed by dissociative adsorption of CO$_2$, these adsorbed oxygen species (Os) combine with nascent hydrogen (Hs) to form H$_2$O. So the band at 1,600-1,800 cm^{-1} is observed.

2. CO reacting with hydroxyl species on ZnO (Zn-OH) to form HCOO-Zn and CO$_2$ combining with adsorbed oxygen species (Os) to form carbonate species, respectively, are prior processes at low temperature. As temperature increases, the hydrogenation of HCOO-Zn and carbonate species to form methoxy species speeds up. As a result, the intensities of bands at 1,592, 1,575, 1,375, 1,362 cm^{-1} and 1,557, 1,539, 1,488, 1,418 cm^{-1} attributed to HCOO-Zn and carbonate species, respectively, shift from weak to intense when the temperature rises from ambient to 60 °C and then to weak again. The band intensity of methoxy species increases gradually with the increase of temperature. This result indicates that carbonate species hydrogenates to form formate species first, and then hydrogenates to methoxy species. In the CO/H$_2$ system, only HCOO-Zn is detected, while in the CO$_2$/H$_2$ system, both HCOO-Zn and HCOO-Cu are observed and without CH$_3$O-Cu. Therefore, it is concluded that HCOO-Zn is the key intermediate for methanol synthesis.

3. As is well known, the addition of a small amount of CO$_2$ into CO/H$_2$ feed gas promotes the formation rate of methanol significantly, whereas excessive CO$_2$ can suppress methanol synthesis.
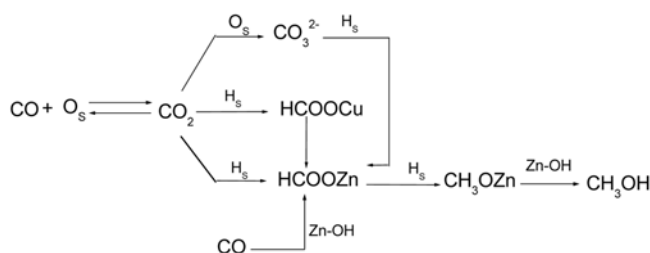

Fig. 6. Scheme for the mechanisms of methanol synthesis from CO/ H$_2$ and CO$_2$/H$_2$ over Cu/ZnO/Al$_2$O$_3$ catalyst.
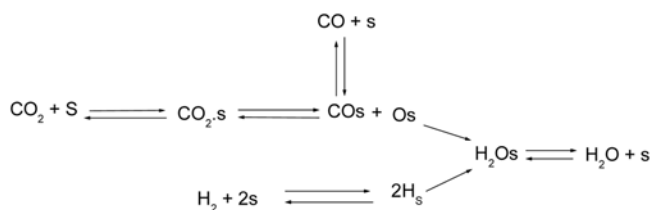

Fig. 7. Scheme for the mechanism of RGWS reaction.

The effects of addition of a small amount of CO$_2$ to CO/H$_2$ feed gas are ascribed to the fact that hydrogenation of CO$_2$ can also form methanol. According to the Klier's [22] point, we can conclude that when CO$_2$ is excessive, CO$_2$ and H$_2$ are competitive adsorption on Cu; the strong adsorbability of CO$_2$ on Cu suppresses the dissociation of H$_2$ on Cu, and as a result, the formation rate of methanol slows-down.

4. The hydroxyl species is important for methanol synthesis. When the bands of hydroxyl species diminish gradually, the band intensity of the methanol increases slightly with the temperature increase. When the bands of hydroxyl species almost disappear, the amount of methanol does not change clearly. From the result, it is concluded that the rate-limiting step for methanol synthesis is the process of the hydroxylation of CH$_3$O-Zn.

Based on these findings above, we propose the following mechanisms for methanol synthesis from CO/H$_2$, CO$_2$/H$_2$ over Cu/ZnO/ Al$_2$O$_3$ catalyst:

From the mechanisms of methanol synthesis, we can deduce the mechanism of the RGWS reaction:

CONCLUSION

The reaction mechanism of methanol synthesis from CO/H$_2$ and CO$_2$/H$_2$ was studied by using in situ IR technique. The experimental results show that methanol can be formed from CO hydrogenation as well as CO$_2$ hydrogenation. The strong adsorbability of CO$_2$ on Cu suppresses the dissociation of H$_2$ on Cu, and then the formation rate of methanol slows down. A scheme of methanol synthesis and RGWS reaction was proposed. HCOO-Zn is the key intermediate and the rate-limiting step is the hydroxylation of CH$_3$O-Zn for methanol synthesis.

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