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In situ DRIFT study of low-temperature methanol synthesis mechanism on Cu/ZnO catalysts from CO_2-containing syngas using ethanol promoter

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Abstract

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to study the reaction mechanism of a new methanol synthesis method on Cu/ZnO at low temperatures from syngas ($CO/CO_2/H_2$) using ethanol promoter. The adsorbed formate species were formed by exposing Cu/ZnO catalysts to syngas ($CO/CO_2/H_2$), and it reacted easily with ethanol in the gas phase to form ethyl formate in two states of species, gas phase and physisorbed, at low temperatures. Ethyl formate was the reactive intermediate, and it was reduced easily by hydrogen atoms on Cu to form gas-phase methanol. The reaction temperature was significantly decreased due to the catalytic action of ethanol and a new reaction route. In order to accelerate this reaction, a large amount of ethanol must be introduced into the reaction system. When there was no ethanol or little ethanol in the reaction system, this reaction was difficult to complete at a temperature as low as 443 K.

Keywords: In situ DRIFT; Methanol; Ethanol; Cu/ZnO; Syngas($CO/CO_2/H_2$); Promoter; Formate; Ethyl formate

1. Introduction

Methanol, which is a fundamental chemical and fuel for fuel cells or vehicles, is being produced by 30 million tons per year around the world from $CO/CO_2/H_2$. Methanol is industrially produced under high temperature and high pressure, using copper–zinc-based oxide catalysts. However, the efficiency of methanol synthesis is severely limited by thermodynamics because methanol synthesis is an extremely exothermic reaction [1,2]. For example, at 573 K and 5.0 MPa, the theoretical maximum of one-pass CO conversion is around 20% [3]. Therefore, developing a low-temperature process for methanol synthesis will greatly reduce the production cost and high CO conversion becomes available at low temperatures.

Brookhaven National Laboratory in the USA (BNL) realized this synthesis in the liquid phase at 373–403 K and 1.0–5.0 MPa, using a very strong base catalyst (mixture of NaH, alcohol, and acetate) and pure syngas ($CO + H_2$). However, a remarkable drawback of this process is that trace amounts of carbon dioxide and water in the feed gas ($CO + H_2$) or reaction system will deactivate the strongly basic catalyst soon [4,5], which implies high cost coming from the complete purification of the syngas from the methane reformer or the gasification plant, as well as the reactivation process of the deactivated catalyst.

Methanol synthesis from pure CO and H_2 via the formation of methyl formate has been widely studied, where carbonylation of methanol and hydrogenation of methyl formate were considered as two main steps of the reaction [6–9]. Wender realized this synthesis in the liquid phase using a mixed catalyst comprised of potassium methoxide and copper chromite under mild conditions of 373–453 K and 5.0–6.5 MPa, and gave high methanol synthesis rates and high one-pass CO conversions [7,8].

$$CO + CH_3OH \overset{RONa}{=} HCOOCH_3 \tag{1}$$

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$$HCOOCH_3 + 2H_2 \overset{\text{Solid Cat.}}{=} 2CH_3OH \qquad (2)$$

$$CO + 2H_2 = CH_3OH \qquad (3)$$

Similar to the BNL method, in this liquid-phase reaction process, CO_2 and H_2O act as poisons to the alkoxide catalyst (RONa) and must be completely removed from syngas, making commercialization of low-temperature methanol synthesis impossible now.

The present authors proposed a new method of low-temperature synthesis of methanol from CO_2/H_2 on a Cu-based oxide catalyst using ethanol as a promoter, by which methanol was produced at 443 K and 3.0 MPa [10]. This new process consisted of three steps: (1) formic acid synthesis from CO_2 and H_2; (2) esterification of formic acid by ethanol to ethyl formate; and (3) hydrogenation of ethyl formate to methanol and ethanol. Considering the fact that water–gas shift reaction is easily conducted on Cu/ZnO catalysts [11,12], a new route of methanol synthesis from CO/H_2 containing CO_2 is proposed, as a more practical way of methanol synthesis. It consists of the following fundamental steps:

$$CO + H_2O = CO_2 + H_2 \qquad (4)$$

$$CO_2 + H_2 + ROH = HCOOR + H_2O \qquad (5)$$

$$HCOOR + 2H_2 = CH_3OH + ROH \qquad (6)$$

$$CO + 2H_2 = CH_3OH \qquad (3)$$

As formic acid was not detected in the products, the present authors suggested the reaction path as steps (5) and (6) above. The present authors reported that ethanol solvent, as well as Cu/ZnO catalyst, remarkably lowered the reaction temperature of methanol synthesis from syngas containing carbon dioxide [13]. Furthermore, as ethanol solvent contained a small amount of water, it is considered that this new process can use low-grade syngas containing carbon dioxide and water without purification as CO_2 and H_2O were involved in the reaction steps above. As expected, low reaction temperature realized high CO conversion as 50–80% [14–16].

Until now, many different views have been proposed regarding the reaction mechanism and the nature of the surface active sites of Cu-based catalysts for methanol synthesis reactions [17–21]. Especially, for the important Cu/ZnO-based catalysts, different types of interaction between Cu and ZnO have been proposed [22–27,29]. Many studies showed that the reaction mechanism and the nature of the surface active sites of Cu/ZnO for methanol synthesis reaction depended on the component of catalyst system and the preparation conditions of the catalysts [28–30].

Although many studies showed a reaction mechanism of methanol synthesis on Cu/ZnO catalysts, the methanol synthesis at low temperatures from syngas ($CO/CO_2/H_2$) on Cu/ZnO using ethanol promoter is a new process, and study of its mechanism has not been done until now. In the present work, the reaction mechanism of low-temperature methanol synthesis above is investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We find that low-temperature methanol synthesis from syngas ($CO/CO_2/H_2$) using ethanol promoter is proceeded via reactive intermediates of ethyl formate, which is produced by the reaction of formate with ethanol on Cu/ZnO, and the formation of ethyl formate is a key step of this reaction.

2. Experimental

The catalyst was prepared by the conventional coprecipitation method. An aqueous solution containing copper and zinc nitrates (Cu/Zn in molar ratio = 1) and an aqueous solution of sodium carbonate were added simultaneously to 300 of ml water with constant stirring. The precipitation temperature and pH value were maintained at 333 K and 8.5, respectively. The obtained precipitate was filtrated and washed with distilled water, followed by drying at 393 K for 6 h and calcination in air at 623 K for 1 h. This precursor was then reduced by a flow of 5% hydrogen in nitrogen at 493 K for 10 h and successively passivated by 1% oxygen diluted by nitrogen.

In situ DRIFT spectra were collected on a Nicolet Nexus 470 FTIR spectrometer supplied with a diffuse reflectance attachment and with a MCT detector. The catalyst powder weighing approximately 14 mg was contained in a diffuse reflectance infrared cell with a ZnSe window which can work at high temperatures and high pressures. In situ absorbance spectra were obtained by collecting 32 scans at $2\ cm^{-1}$ resolution. The scheme is shown in Fig. 1. The syngas used in this experiment was $CO/CO_2/H_2/Ar$ at a ratio of 32/5/61/2, the same composition as that used in catalyst development [14–16], and the degree of purity of H_2 and He is 99.99%, respectively.

Before the adsorption of reactant, the catalyst sample was treated in situ in He stream flowing at $20\ cm^3\ min^{-1}$ at 298 K for 20 min, and then at 493 K for 20 min. The catalyst sample was reduced in H_2 stream flowing at $20\ cm^3\ min^{-1}$ at 493 K for 1 h, and then in He at 493 K for 1 h. Subsequently the catalyst sample was cooled down in He to the adsorption temperature.

The spectra of formate adsorption species were obtained according to the following procedure after the catalyst pretreatment: the Cu/ZnO catalyst was exposed to syngas/He at a ratio of 10/10 flowing at a total rate of $20\ cm^3\ min^{-1}$ at 443 K for 30 min, followed by sweeping in helium for 20 min to yield the formate species. The saturated vapor of ethanol (vapor pressure 7.9 kPa at 298 K) was carried into IR cell by a stream of helium or syngas flowing at $20\ cm^3\ min^{-1}$ for certain time after formate species formation, and then sweeping in helium. The in situ DRIFT spectra of methanol synthesis reaction at low temperature were recorded respectively in the course of the different experiments. Each spectrum was then referenced to a spectrum

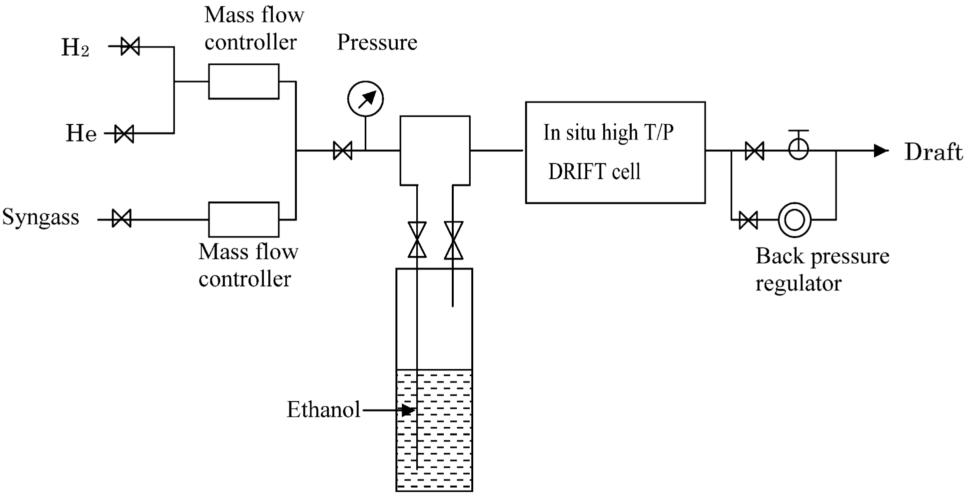


Fig. 1. The scheme of in situ DRIFT apparatus for adsorption and reaction.

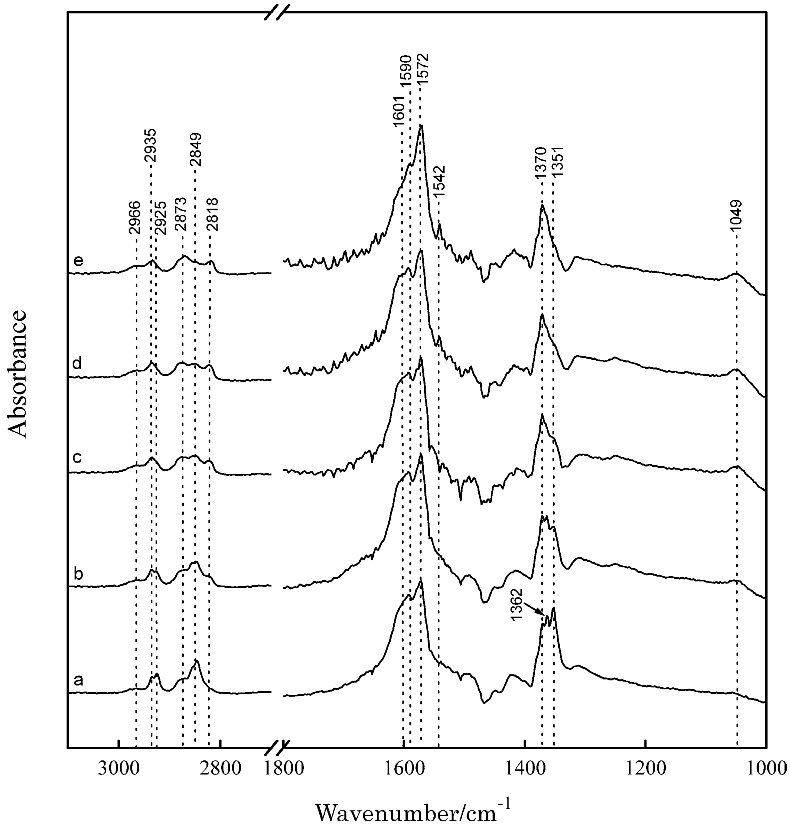


Fig. 2. In situ DRIFT spectra obtained during exposure of Cu/ZnO to syngas flowing at a total rate of 20 $cm^3\ min^{-1}$ at 443 K and atmospheric pressure ((a) 10 min, (b) 40 min, (c) 2 h, (d) 3 h, (e) after d in He 20 min).

of the catalyst collected at the same temperature under He or H_2 flow as appropriate.

3. Results

3.1. Adsorption of syngas on Cu/ZnO

The catalyst was exposed to syngas ($CO/CO_2/H_2/Ar$) at 443 K and atmospheric pressure for 3 h, and then swept in helium for 20 min. The DRIFT spectra were recorded for different adsorption times in Fig. 2. Assignment of the bands for adsorption species was made by analogy with the spectra of known compounds and by comparison with published literature. A summary of assignments is given in Table 1. The bands of the bidentate formate species on ZnO (H–COO–Zn), the bidentate formate species on Cu (H–COO–Cu) [21, 31–40], methoxy species on ZnO (CH_3O–Zn) [21,35,40, 41], and H_2O on Cu (H_2O–Cu) are observed in Fig. 2 [33]. Because the formate bands at 2966, 1590, and 1542 cm^{-1}

Table 1
Infrared bands assignment of the surface species for $CO/CO_2/H_2$ adsorbed on Cu/ZnO at 443 K and atmospheric pressure

Frequency (cm^{-1})	Assignment	Species
2966(sh) 2873	$\nu(CH)$	
1590(sh) 1572	$\nu_{as}(OCO)$	
1370 1362	$\nu_s(OCO)$	b-HCOO–Zn
2925 2849	$\nu(CH)$	
1542(sh)	$\nu_{as}(OCO)$	
1351	$\nu_s(OCO)$	b-HCOO–Cu
2935 2818	$\nu(CH)$	
1049	$\nu(C\text{–}O)$	CH_3O–Zn
1601	$\delta(OH)$	H_2O–Cu

are weak shoulder peaks and interfered by other absorption bands, sometimes we cannot observe clearly these bands or the change of these bands in the spectra of in situ reaction for methanol synthesis using the ethanol promoter below. The intensity of bands for adsorbed formate on Cu is decreased slightly with increasing adsorption time, and the intensity of bands for adsorbed formate on ZnO does not change. The band intensity of methoxy species is very weak in the adsorption process, and the band intensity increases slightly with increasing adsorption time.

3.2. Hydrogenation of formate species on Cu/ZnO

The hydrogenation spectra of the adsorbed formate on Cu/ZnO between 443 and 573 K are shown in Fig. 3. The catalyst was exposed to syngas/He at 443 K for 30 min followed by hydrogen flowing at a total rate of 20 $cm^3\,min^{-1}$ between 443 and 573 K and atmospheric pressure. The spectra of formate hydrogenation were obtained after 30 min at every temperature. The experimental results indicate that the band intensities of b-HCOO–Zn species (2966(sh), 2873, 1590(sh), 1572, 1370, 1362 cm^{-1}) and b-HCOO–Cu species (2925, 2849, 1542(sh), 1351 cm^{-1}) do not change clearly when the temperature is lower than 493 K, but those band intensities are decreased rapidly with increasing temperature from 523 to 573 K, and the formate adsorption species almost cannot be detected when the temperature rises to 573 K in H_2. A little adsorbed methoxy species (2935, 2818,

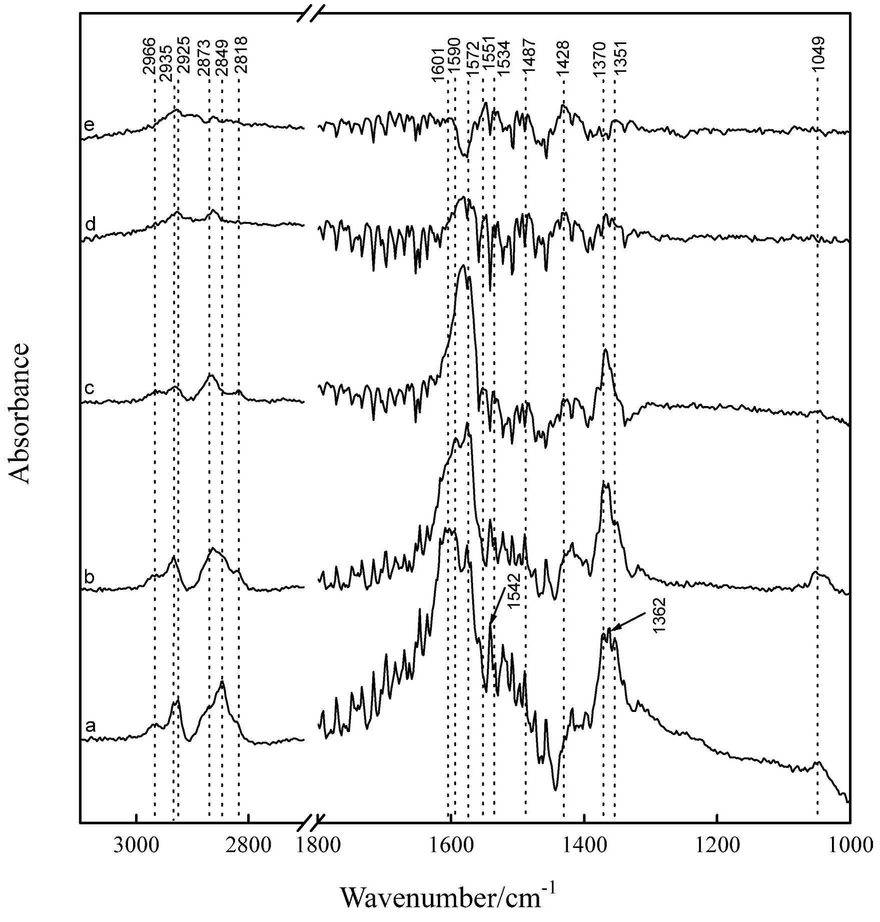


Fig. 3. In situ DRIFT spectra of hydrogenation of formate species on Cu/ZnO at atmospheric pressure ((a) formate adsorption species, subsequent reacting with H_2 at (b) 443 K, (c) 493 K, (d) 523 K, and (e) 573 K, respectively).

1049 cm^{-1}) are observed with temperature increase, and it is hardly detected when the temperature is higher than 493 K. This is due to hydrogenation of methoxy to gas-phase methanol, which is carried out in IR cells by flowing H_2. The weak bands at 1551, 1534, 1487, and 1428 cm^{-1} are attributed to carbonate species [33,34], and the band at 1601 cm^{-1} is H_2O on Cu (H_2O–Cu).

3.3. *Reaction of the adsorbed formate with ethanol between 298 and 443 K at atmospheric pressure on Cu/ZnO*

Fig. 4 shows the spectra of reaction for adsorbed formate with ethanol between 298 and 443 K at atmospheric pressure. The saturating ethanol vapor (298 K) was carried by helium into an IR cell at 298 K for 2 min after formation of formate species on Cu/ZnO, then closing the IR cell with the vapor in. Spectra of the reaction were obtained after 30 min at each temperature and at last swept in helium at 443 K for 20 min. The assignment of formate species here is the same as that in Table 1. The band intensities of formate adsorption species are decreased with temperature increase, and these bands disappear when the temperature is higher than 393 K. The disappearance of formate absorption bands at 2849, 1370, 1362, and 1351 cm^{-1}, which are not interfered by the bands of adsorbed ethoxy and other species, can be observed clearly, but we cannot observe the change of other formate absorption bands due to interfering action of ethoxy and other by-product absorption bands. The bands of gas-phase ethyl formate (1758, 1742, 1189 cm^{-1}) and physisorbed ethyl formate (1710, 1691 cm^{-1}) can be detected when the temperature rises to 373 K. The bands at wavenumbers of 2962, 2925, 2861, 1380, 1101, and 1052 cm^{-1} can be attributed to the ethoxy adsorbed on Cu/ZnO, those at 2933, 1562, 1451, 1049, and 1023 cm^{-1} to acetate species adsorbed, and those at 1551, 1534, 1345, and 1428 cm^{-1} to carbonate species [33,34,42,43]. The band intensity of ethoxy adsorption species decreases with temperature increase. This may be due to the carbonate adsorption species and acetate adsorption species to be formed by dehydrogenation of the ethoxy group. To confirm the assignment of ethoxy species and its transforming action, experiments of ethanol or acetic acid adsorption were conducted on Cu/ZnO between 298 and 443 K. The bands assignment of ethoxy, acetate, and carbonate adsorption species is given in Table 2. The acetate and carbonate species are derived from ethoxy dehydrogenation with temperature increase [42,43]. The band assignment of the ethoxy, acetate, and carbonate species in Fig. 4 is consistent with that of known compounds in Table 2.

3.4. *In situ DRIFT spectra of low-temperature methanol synthesis using ethanol promoter on Cu/ZnO*

3.4.1. *Reaction at 443 K and atmospheric pressure*

Fig. 5 shows the spectra of in situ reaction for methanol synthesis using ethanol promoter at 443 K and atmospheric pressure. The saturating ethanol vapor (298 K) was carried by syngas into an IR cell at 443 K for 1 h after formate species formation on Cu/ZnO, then sweeping in helium for 20 min. The spectra were detected after the in situ reaction. The results indicate that the formate adsorption species disappear after the reaction because the bands of formate adsorption species (2849, 1370, 1362, 1351 cm^{-1}) not interfered by other neighboring peaks can hardly be detected. The bands of ethoxy (2962, 2925, 2861, 1101, and 1052 cm^{-1}), acetate (2933, 1451, and 1023 cm^{-1}), and carbonate species

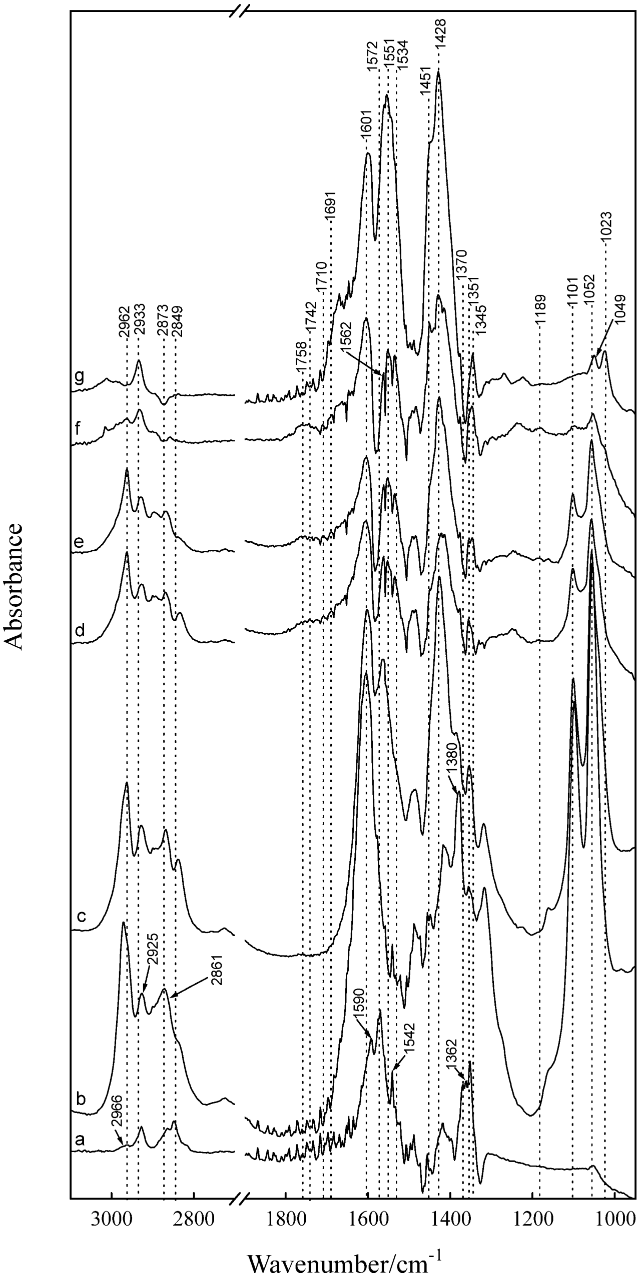


Fig. 4. In situ DRIFT spectra of the reaction for adsorbed formate with ethanol between 298 and 443 K at atmospheric pressure in He ((a) formate adsorption species, reacting with ethanol at (b) 298 K, (c) 343 K, (d) 373 K, (e) 393 K, and (f) 443 K, respectively, (g) sweeping in He for 20 min at 443 K).

Table 2
Infrared bands assignment of the surface species for ethanol and acetic acid adsorbed on Cu/ZnO between 298 and 443 K and atmospheric pressure

Ethoxy bands (cm^{-1})		Acetate bands (cm^{-1})		Carbonate bands (cm^{-1})	
2961 2925 2889(sh) 2861	ν(CH)	2933	ν(CH)		
1380 1440	δ(CH)	1562 1451	ν(OCO)	1551 1534 1428 1345	ν(COOO)
1101 1052	ν(C–O)	1049 1023	$\rho(CH_3)$		

(1551, 1534, 1345, and 1428 cm^{-1}) are also observed after the reaction. Furthermore, the bands of gas-phase and physisorbed ethyl formate on Cu/ZnO are not observed after introducing ethanol vapor into an IR cell due to the flowing reaction system and reduction atmosphere. The band at 1601 cm^{-1} is H_2O on Cu (H_2O–Cu).

3.4.2. *Reaction at 443 K and higher pressure*

Fig. 6 shows the spectra of in situ reaction for methanol synthesis using ethanol promoter at 443 K and 0.3 MPa. The saturating ethanol vapor (298 K) was carried by syngas into an IR cell at 443 K and 0.3 MPa for 1 h after formate species formation on Cu/ZnO, and the spectra were detected after sweeping in helium for 20 min at 443 K and atmospheric pressure. The formate absorption bands (2849, 1370, 1362, 1351 cm^{-1}) which are not interfered by other neighboring peaks can hardly be observed after the reaction. Furthermore, the bands of ethoxy (2962, 2925, 2861, 1101, 1052 cm^{-1}), acetate (2933, 1451, 1023 cm^{-1}), and carbonate species (1551, 1534, 1345, 1428 cm^{-1}) are also observed.

Fig. 7 shows the spectra of in situ reaction for methanol synthesis using ethanol promoter at 443 K and 1.0 MPa. The conditions of reaction and detection are the same as those in Fig. 6 except reaction pressure. The results show that the bands of formate species (2966, 2925, 2873, 2849, 1572, 1370, 1362, and 1351 cm^{-1}) are not changed after reaction. The bands of acetate and carbonate species cannot be detected. It is notable that there are a great deal of ethoxy adsorption species (2962, 2925, 2861, 1101, 1052 cm^{-1}) after reaction. It implies that the formate species do not react with adsorbed ethoxy; it should react with ethanol in gas phase directly. The gas-phase and physisorbed ethyl formate cannot be observed due to the flowing reaction system and reduc-

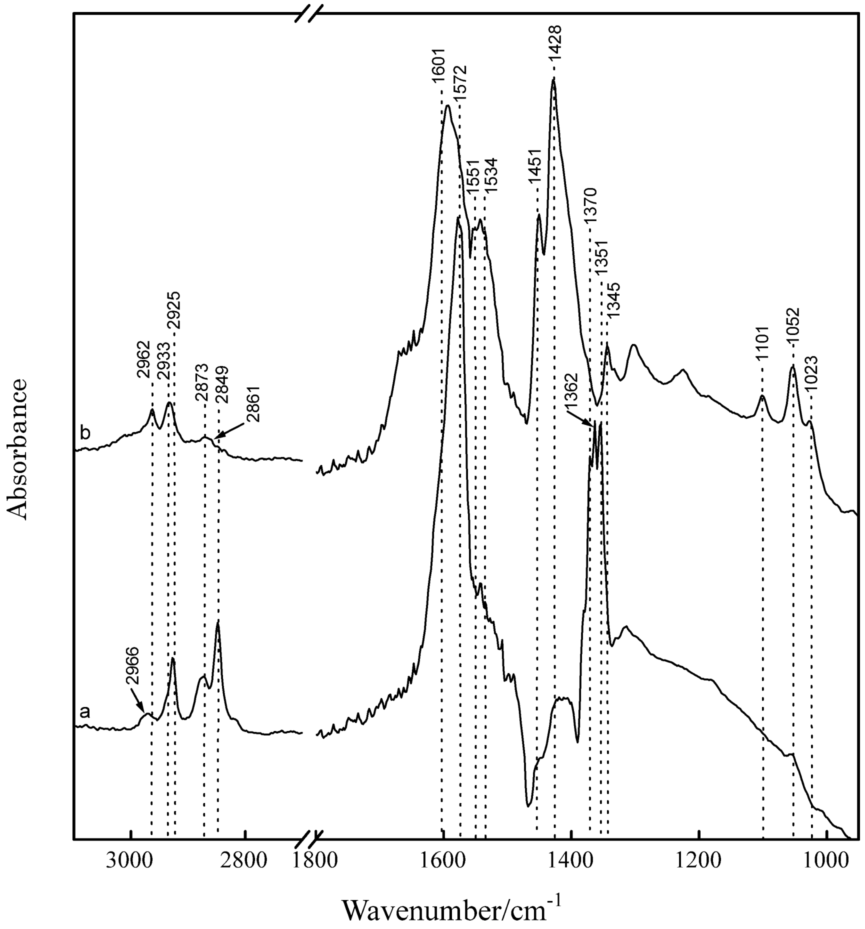


Fig. 5. In situ DRIFT spectra of methanol synthesis reaction on Cu/ZnO from syngas using ethanol promoter at 443 K and atmospheric pressure ((a) formate adsorption species, (b) sweeping in He for 20 min after introducing ethanol by syngas for 1 h).

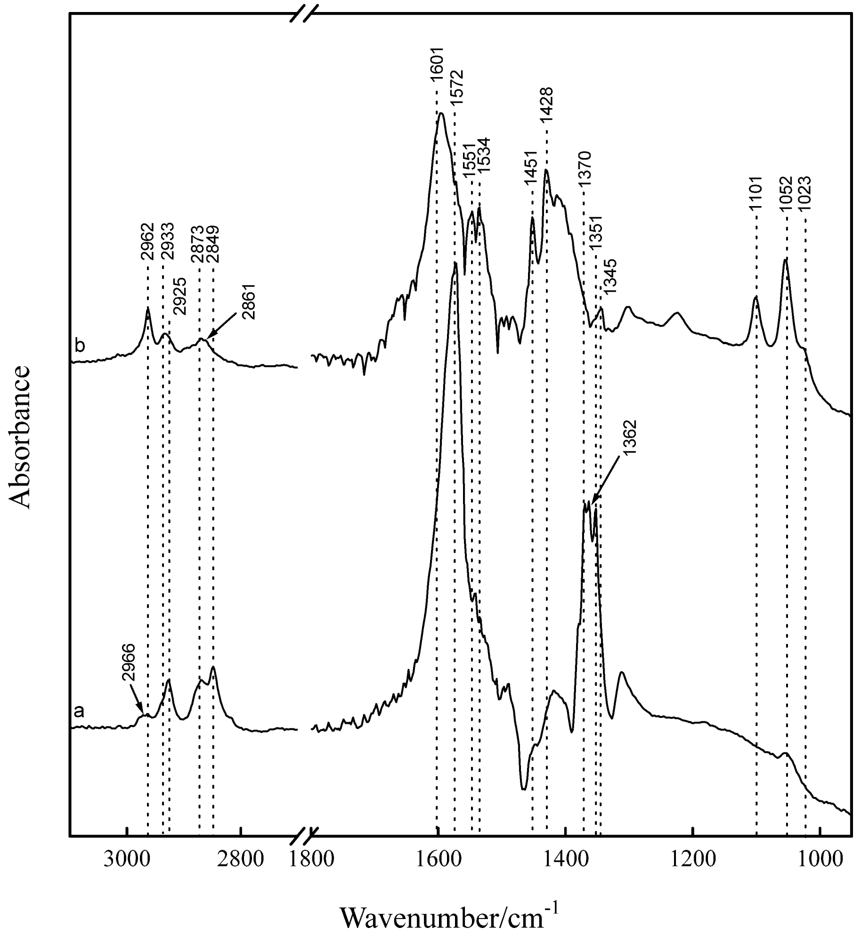


Fig. 6. In situ DRIFT spectra of methanol synthesis reaction on Cu/ZnO from syngas using ethanol promoter at 443 K and 0.3 MPa ((a) formate adsorption species, (b) sweeping in He for 20 min after introducing ethanol by syngas for 1 h).

tion atmosphere in Figs. 6 and 7. The band at 1601 cm^{-1} is H_2O on Cu (H_2O–Cu).

3.5. *In situ DRIFT spectra of hydrogenation of ethyl formate*

In order to prove the hydrogenation reaction of ethyl formate on Cu/ZnO, the catalyst Cu/ZnO or quartz sands were exposed to the saturated ethyl formate vapor (vapor pressure 8.3 kPa at 273 K) carried by hydrogen stream between 298 and 443 K and atmospheric pressure, respectively. As a blank measurement, solid-state but inert quartz sands with very low surface areas are necessary to observe gas phase by DRIFTS. The spectra were collected after closing hydrogen stream under every temperature for 30 min. Fig. 8 is the spectra of ethyl formate exposed to quartz sands. The bands of gas-phase ethyl formate (2998, 2984, 2929, 1758, 1742, 1189 cm^{-1}) are observed, and the bands are not more changed except that the intensity of the bands decreases a little with increasing temperature. It may originate from the reduction of local gas density with increasing temperature.

Fig. 9 is the spectra of ethyl formate exposed to Cu/ZnO catalyst. The bands of gas-phase ethyl formate (2998, 2984, 2929, 1758, 1742, 1189 cm^{-1}), physisorbed ethyl formate (1710(sh), 1691(sh) cm^{-1}), ethoxy species (2962, 2925(sh), 2861, 1380, 1101, 1052 cm^{-1}), and H_2O (1601 cm^{-1}) are observed on Cu/ZnO, and the band intensity of gas-phase and physisorbed ethyl formate is rapidly decreased when the temperature is higher than 343 K in Fig. 9. The bands of gas-phase and physisorbed ethyl formate disappear, and the bands of gas-phase methanol species at 1032 and 2838 cm^{-1} are observed when the temperature is higher than 393 K in Fig. 9 (gas-phase methanol spectra are not shown in this paper).

3.6. *Adsorption of $HCOOC_2H_5$ on Cu/ZnO*

In order to confirm the assignment of gas-phase and physisorbed ethyl formate species above, the experiment of ethyl formate adsorption on Cu/ZnO was done. Fig. 10 shows spectra taken after exposure of the Cu/ZnO catalyst to ethyl formate in a helium stream at 298 K. The spectra were collected after introducing ethyl formate for 1 min and after sweeping by helium for 1, 2, and 15 min, respectively. The bands at 2998, 2984, 2929, 1758, 1742, and 1189, which rapidly disappeared during subsequent sweep-

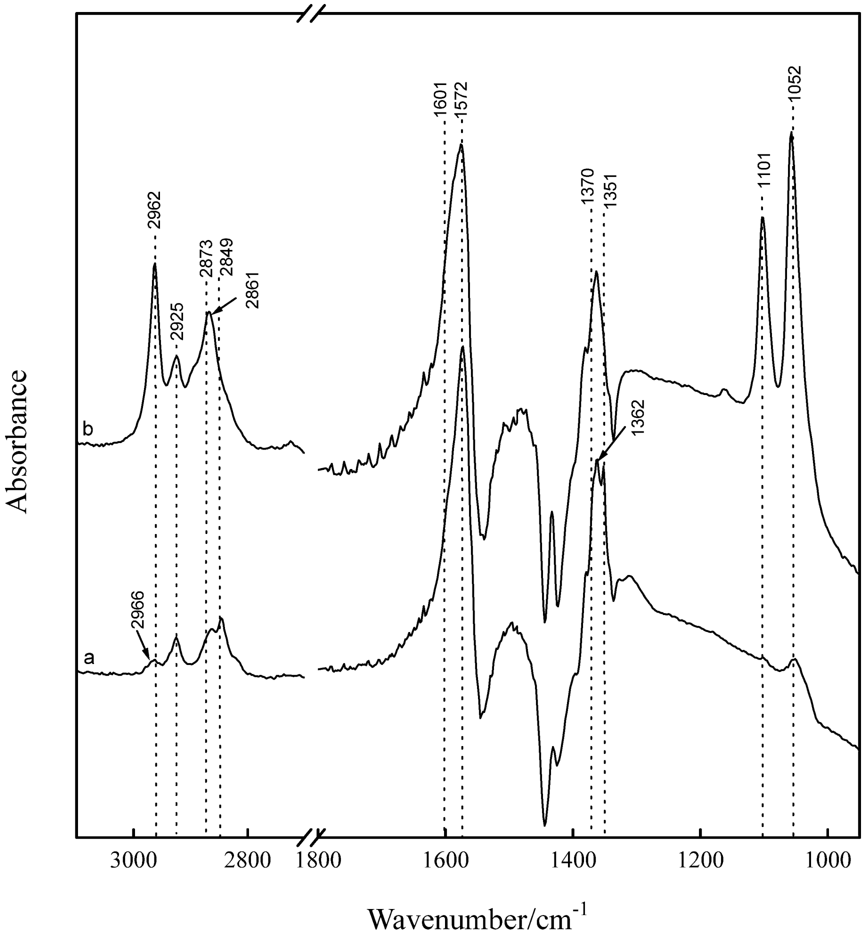


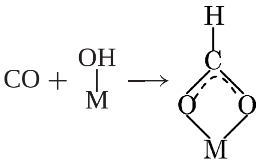
Fig. 7. In situ DRIFT spectra of methanol synthesis reaction on Cu/ZnO from syngas using ethanol promoter at 443 K and 1.0 MPa ((a) formate adsorption species, and (b) sweeping in He 20 min after introducing ethanol by syngas for 1 h).

ing, are attributed to the carbonyl (C=O) stretching vibration of gas-phase ethyl formate, and the bands at 1710, 1691, and 1208 cm^{-1}, which diminished at a slow rate, can be ascribed to physisorbed ethyl formate on Cu/ZnO. Furthermore, the bands of bidentate formate (2966, 2873, 2925, 2849, 1572, 1370, 1351 cm^{-1}) and ethoxy adsorption species (2962, 2925, 2889, 2861, 1380, 1101, 1052 cm^{-1}) are also observed. The band at 1601 cm^{-1} is H_2O on Cu (H_2O–Cu).

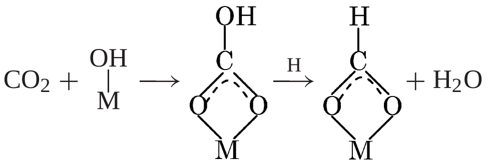
4. Discussion

4.1. *Formation and reactivity of formate adsorption species on Cu/ZnO*

The studies of Fisher and co-workers [31], Fujita et al. [21], and Waugh [17] show that the formate and carbonate species were formed when Cu-based catalyst was exposed to CO_2/H_2 or $CO/CO_2/H_2$ at low temperatures, and carbonate species were transformed to stable formate species by hydrogenation reaction with temperature increase. In the study, when Cu/ZnO catalyst was exposed to $CO/CO_2/H_2$, the reactions proceeded according to Eqs. (7) and (8). The carbonate and formate species were formed by the reaction of CO_2 or CO with hydroxyl on metal at low temperatures, but a large amount of carbonate species was hydrogenated to more stable formate species with temperature increase. Therefore, the band intensity of carbonate species is weaker than that of the formate species when $CO/CO_2/H_2$ was exposed to Cu/ZnO catalyst at 443 K.



(7)



(8)

(M is Cu or ZnO)

Formate adsorption species can react with hydrogen atoms on Cu to form methoxy adsorption species, and then to form methanol. This reaction must proceed at higher

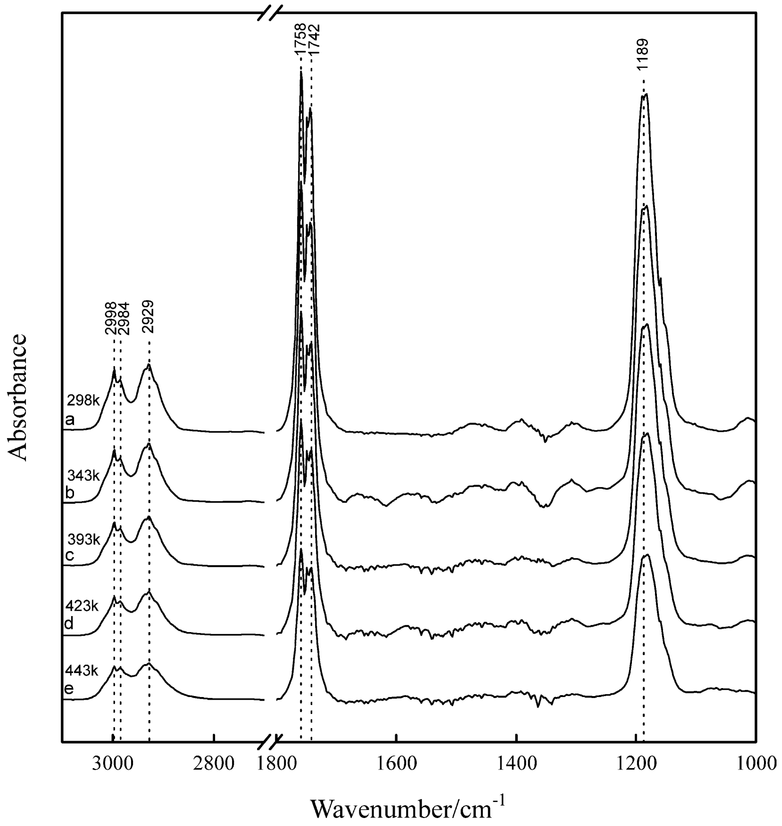


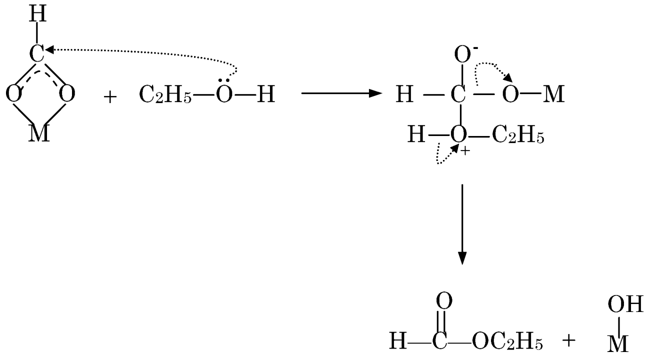
Fig. 8. In situ DRIFT spectra of the reaction of ethyl formate and hydrogen on quartz sands at atmospheric pressure ((a) 298 K, (b) 343 K, (c) 393 K, (d) 423 K, and (e) 443 K).

temperatures and pressures, leading to a high-temperature, conventional methanol synthesis process. It was demonstrated by many investigators and our experiments. Fig. 3 indicates that a little adsorbed methoxy is formed, and the band intensity of formate adsorption species is not changed obviously at 443 K except that formate on Cu (HCOO–Cu) is decreased a little. The band intensity of formate species is decreased rapidly with increasing reaction temperature from 523 to 573 K, and the bands are difficult to be observed when the reaction temperature rises to 573 K. Fig. 2 shows also that a little adsorbed methoxy is formed, and the band intensity of formate on ZnO is not changed at 443 K for 3 h, and the band intensity of formate on Cu is decreased slightly with increasing reaction time at 443 K. Figs. 2 and 3 indicate that the formate adsorption species are difficult to react with hydrogen at 443 K and atmospheric pressure, and a little methoxy is formed due to hydrogenation of HCOO–Cu [21]. It also implies that the hydrogenation reaction activity of HCOO–Cu is higher than HCOO–Zn. These experiments demonstrate that the hydrogenation reaction of adsorbed formate is available only at temperature as high as 523–573 K.

Although the hydrogenation reaction of formate adsorption species is difficult at 443 K and atmospheric pressure, the experimental results in Fig. 4 show that the band intensity of the formate adsorption species decreases progressively, and at last these species disappear with temperature increased from 298 to 443 K when ethanol is introduced into the reaction system at atmospheric pressure. This indicates that the formate adsorption species can react easily with ethanol at low temperatures and atmospheric pressure. It implies that the reaction of formate species can be accelerated by ethanol introduced into reaction system.

4.2. Formation and hydrogenation action of ethyl formate

The band intensity of ethyl formate species increases with the band intensity decrease of formate adsorption species from 373 to 443 K in Fig. 4. This means that the ethyl formate is formed by the reaction of adsorbed formate species with ethanol at low temperatures, and reaction process can be illustrated as follows:



(M is Cu or ZnO)

(9)

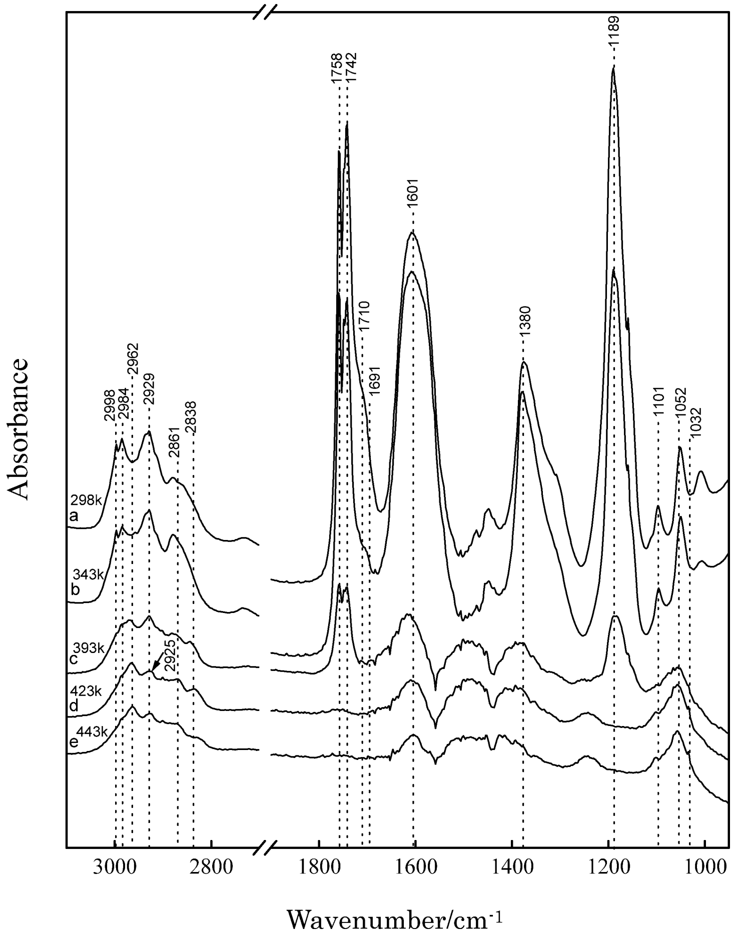


Fig. 9. In situ DRIFT spectra of the reaction of ethyl formate and hydrogen on Cu/ZnO at atmospheric pressure ((a) 298 K, (b) 343 K, (c) 393 K, (d) 423 K, and (e) 443 K).

The reaction is a nucleophilic addition–elimination reaction; ethanol is the nucleophilic reagent of the reaction. Gas-phase ethanol more easily reacts with formate species than adsorbed ethoxy because the electronic cloud density on oxygen of gas-phase ethanol is bigger than that of adsorbed ethoxy. This has been proven by the high-pressure experiment of Fig. 7. Although there is a great deal of adsorbed ethoxy in Fig. 7, the band intensity of formate adsorption species is not changed with the reaction process. It implies that the species reacted with adsorbed formate are gas-phase ethanol rather than ethoxy adsorption species. The produced ethyl formate exists in two states of gas-phase and physisorbed species, and they can transform each other. Monti et al. have proven that gas-phase and physisorbed ethyl formate can transform each other under similar experiment conditions to those in our experiment [44].

The ethyl formate is a reactive intermediate in a low-temperature methanol synthesis reaction, and it is very easy to be reduced by active hydrogen atoms on Cu to form methanol by its gas-phase and physisorbed species. The reaction of hydrogenation for gas-phase and physisorbed ethyl formate species on Cu/ZnO has been proven by this work (Figs. 8 and 9) and the reaction is expressed by Eq. (10).

The band intensity of gas-phase ethyl formate decreases a little due to local gas density decreasing with temperature increasing in Fig. 8. Moreover, we do not observe any change of the spectra in Fig. 8. This shows that the hydrogenation reaction of gas-phase ethyl formate with hydrogen molecules cannot proceed on quartz sands, which cannot adsorb the compound molecule and has no reaction activation, due to its inert surface and low BET value. The bands of gas-phase and physisorbed ethyl formate disappear, and the bands of gas-phase methanol appear in Fig. 9. This indicates that the ethyl formate exposed to Cu/ZnO is different from that to quartz sands, and the hydrogenation reaction of ethyl formate occurs on Cu/ZnO catalysts rather than on quartz sands. Therefore, we think that the hydrogenation reaction of ethyl formate is not the result of the reaction between ethyl formate and hydrogen molecules, and its hydrogenation reaction may be due to hydrogen atoms on Cu, which provide the source of hydrogen to hydrogenate ethyl formate species in the experiment of Fig. 9. In particular, gas-phase ethyl formate may also be reduced by the atomic hydrogen spillover species on Cu when it contacts the Cu/ZnO catalyst. In fact, Tsubaki and co-workers have proved that ethyl formate species exist in actual reactions of low-temperature methanol synthesis,

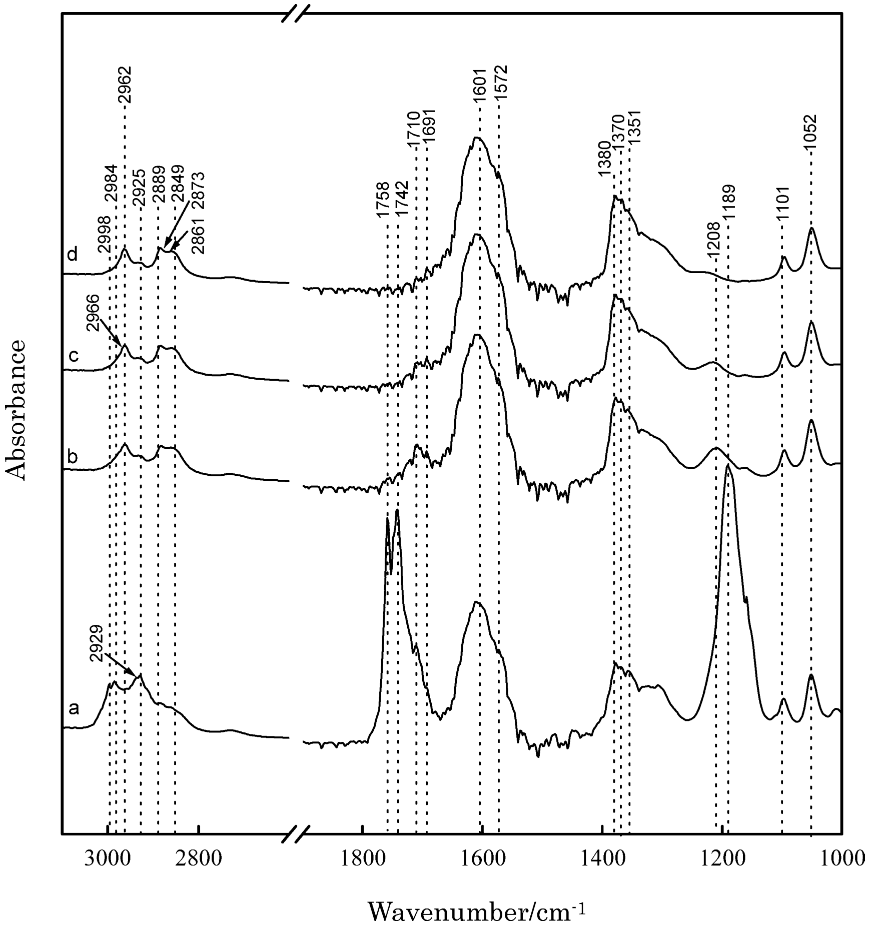
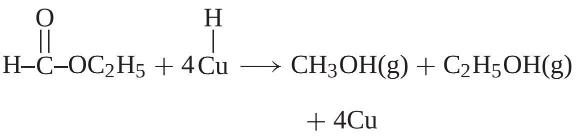


Fig. 10. In situ DRIFT spectra of ethyl formate adsorption on Cu/ZnO at 298 K ((a) adsorbing ethyl formate for 1 min, subsequent sweeping in He for (b) 1 min, (c) 2 min, and (d) 15 min).

and it can be easily transformed to methanol and ethanol by hydrogenation reactions at lower temperatures and pressures on Cu/ZnO [13–16]. Evans et al. also proved that the hydrogenation of ethyl formate can be completed easily at lower temperatures and pressures on Cu-based catalysts [45].



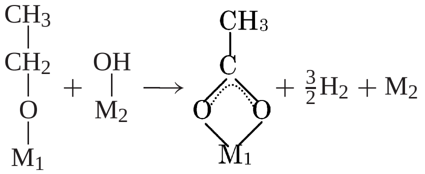
$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5} + 4\,\overset{\overset{\displaystyle H}{|}}{\mathrm{Cu}} \longrightarrow \mathrm{CH_3OH(g)} + \mathrm{C_2H_5OH(g)} + 4\mathrm{Cu} \qquad (10)$$

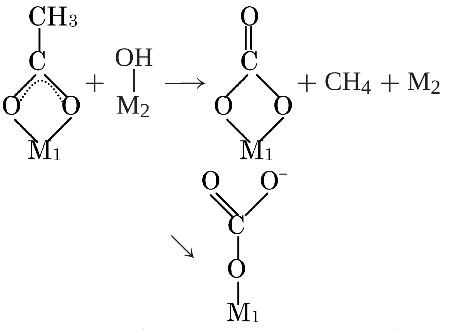
4.3. *Study of in situ reaction for low-temperature methanol synthesis*

The bands of formate species cannot be observed after in situ reaction at 443 K and atmospheric pressure in Fig. 5, and these species bands also cannot be observed after in situ reaction at 443 K and 0.3 MPa in Fig. 6. This shows that the reaction rate of formate species with ethanol is faster than the rate of formate formation under the above reaction conditions. Therefore, we cannot observe the bands of formate species after in situ reaction due to the reaction of formate species with ethanol proceeding rapidly in the experiments of Figs. 5 and 6. However, the bands of formate species are not changed almost after in situ reaction at 443 K and 1.0 MPa in Fig. 7. Although the amount of syngas increases 10 times relative to the amount of ethanol when reaction pressure is increased from atmospheric pressure to 1.0 MPa here, ethanol dosage is the same in experiment of Fig. 7 as that in experiment of Fig. 5 because saturated vapor pressure of ethanol is hardly influenced by environmental pressure. As a result, although the formation and consumption rate of formate species is increased in the experiment of Fig. 7 relative to the experiments of Figs. 5 and 6, the rate of formate formation, from syngas of 1.0 MPa, is faster than the rate of its consumption; thus, a large amount of formate species is accumulated in the reaction process. Therefore, we cannot observe the formate species changing in the experimental process of Fig. 7. It implies that if ethanol dosage is increased, the rate of in situ reaction will be increased; i.e., one-pass CO conversion will be increased at high-pressure reactions of low-temperature methanol synthesis. Therefore, we think that a large mount of ethanol must be introduced into the reaction system so as to increase the yield of methanol in low-temperature methanol synthesis from $CO/CO_2/H_2$ on Cu/ZnO. The reaction of methanol synthesis is difficult to be completed by reaction and regeneration of a little ethanol at low temperatures. In fact, a large amount of ethanol has been used in the actual reaction of low-temperature methanol synthesis [13–16].

It is notable that methoxy adsorption species are not observed after in situ reaction in the experiments of Figs. 5–7. This shows that the reaction does not pass through methoxy species, which are intermediates of ICI high-temperature methanol synthesis, and gas-phase methanol is produced directly by the hydrogenation reaction of ethyl formate intermediate in the methanol synthesis reaction process. The gas-phase methanol cannot be observed due to the flowing reaction system in the experiments of Figs. 5–7.

The other surface species produced on Cu/ZnO are acetate and carbonate species formed by the dehydrogenation of ethoxy adsorption species. The formation process of acetate and carbonate species may be represented by Eqs. (11) and (12).


(11)


(12)

(M_1 or M_2 is Cu or ZnO)

The amount of these species is affected by reaction atmosphere. For example, the band intensity of acetate and carbonate species is weaker in experiment of Fig. 5 than that in Fig. 4. If Fig. 7 is compared with Figs. 5 and 6, we found that the acetate and carbonate are hardly detected in Fig. 7. This may be from the fact that the pressure of syngas is increased greatly in the experiment of Fig. 7 than those in the experiments of Figs. 5 and 6, and that there is no syngas in the reaction system of formate species with ethanol in Fig. 4. Because hydrogen is formed in Eq. (11) where acetate is formed, followed by the carbonate formation in Eq. (12), with the increased syngas pressure including hydrogen pressure, the reaction of the Eqs. (11) and (12) will be difficult due to the equilibrium. Therefore, we think that the main reactions of forming methanol are accelerated in the competing reactions of the catalyst surface, that the secondary reactions of ethoxy species transforming into acetate and carbonate species are restrained with increasing syngas pressure. Furthermore, we did not detect methane gas in the DRIFT experiments of Figs. 5 and 6 because of the flowing reaction system. Because the stretching and bending vibration bands of the carbon–hydrogen bond of methane are interfered by the bands of ethoxy, acetate, and carbonate species, we cannot observe characteristic methane bands in Fig. 4. Therefore, the methane in Eq. (12) was not detected experimentally by FTIR, but we detected experimentally very little methane in the actual reaction of low-temperature methanol synthesis.

Based on the observation above, a possible mechanism is offered as a scheme of Fig. 11 for methanol synthesis at low temperature from syngas ($CO/CO_2/H_2$) using an ethanol promoter on Cu/ZnO. In this scheme, at first formate adsorption species are formed by adsorbing syngas on Cu/ZnO catalysts, then gas-phase and physisorbed ethyl formate, the reactive intermediate, is formed by the reaction of adsorbed formate and gas-phase ethanol, and at last ethyl formate is reduced by hydrogen atoms on Cu/ZnO to form gas-phase methanol directly.

The results above mean that ethyl formate is not only formed easily by the reaction of formate species with ethanol, but also reduced quickly by hydrogen atoms on Cu to form methanol. Therefore, the formation of ethyl formate is a key step in low-temperature methanol synthesis. Ethanol used in this reaction not only significantly decreases the reaction temperature due to its promotional action, but also is not consumed due to its regeneration by hydrogenation of ethyl formate, acting like a catalytic solvent.

5. Conclusions

The reaction mechanism of a new low-temperature methanol synthesis method from syngas (CO/CO_2H_2) using ethanol promoter was studied by using DRIFTS. The results show that formate adsorption species are formed by exposing Cu/ZnO catalyst to syngas ($CO/CO_2/H_2$), and the reactive intermediate ethyl formate is formed by the reaction of adsorbed formate with ethanol in the gas phase. Finally, gas-phase and physisorbed ethyl formate are reduced by hydrogen atoms on Cu to form gas-phase methanol.

The reaction temperature is significantly decreased due to the promoting action of ethanol. In order to accelerate this reaction, a large amount of ethanol must be introduced into the reaction system. When there is no ethanol or little ethanol in the reaction system, this reaction was difficult to complete at temperatures as low as 443 K.

It is a key step for the reaction of formate adsorption species with ethanol in gas phase to form ethyl formate at low temperatures. It changes the normal reaction path of conventional, high-temperature methanol synthesis, which is from formate via methoxy to methanol, and no longer passes through the step of methoxy formation.

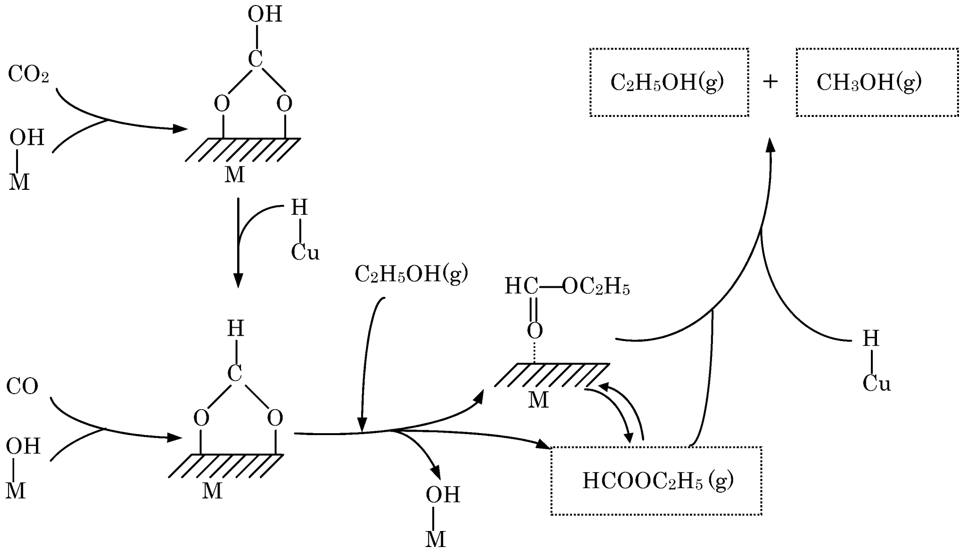


Fig. 11. Proposed mechanism for the synthesis reaction of low-temperature methanol from syngas ($CO/CO_2/H_2$) using ethanol promoter (M is Cu/ZnO).

Acknowledgment

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