In-Situ DRIFT Study of a New Low-Temperature Methanol Synthesis Mechanism

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In-situ DRIFTS was used to clarify the reaction mechanism of a new methanol synthesis method on a Cu/ZnO catalyst at low temperature from syngas containing CO_2 using an ethanol promoter. The formate species was formed by exposing Cu/ZnO catalyst to syngas, and it reacted easily with ethanol to form an ethyl formate species at low temperature. Ethyl formate was easily reduced to form methanol.

Methanol is industrially produced under high temperature and high pressure, using a copper–zinc-based oxide catalyst. However, the efficiency of methanol synthesis is severely limited by thermodynamics, because methanol synthesis is an extremely exothermic reaction.[1–3] Therefore, developing a low-temperature process for methanol synthesis will greatly reduce the production cost, and high CO conversion will become available at low temperature. The present authors have proposed a new method of low-temperature synthesis of methanol from syngas containing CO_2 on Cu/ZnO catalyst using ethanol as a promoter, by which methanol can be produced at 443 K and 3.0 MPa.[4] This new process not only lowers the reaction temperature of methanol synthesis, but can also use low-grade syngas containing carbon dioxide and water without purification, because CO_2 and H_2O are involved in the reaction steps mentioned above. As expected, a low reaction temperature realized a high CO conversion of 50–80%.[3–5]

Until now, although many studies have focused on reaction mechanism of high-temperature methanol synthesis on Cu based catalysts,[6–8] the methanol synthesis at low temperature from $CO/CO_2/H_2$ on Cu/ZnO using a catalytically-active ethanol promoter is a new process, and its mechanism has not been clear until now. In the present work, the reaction mechanism of the low-temperature methanol synthesis mentioned above was investigated by in-situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS).

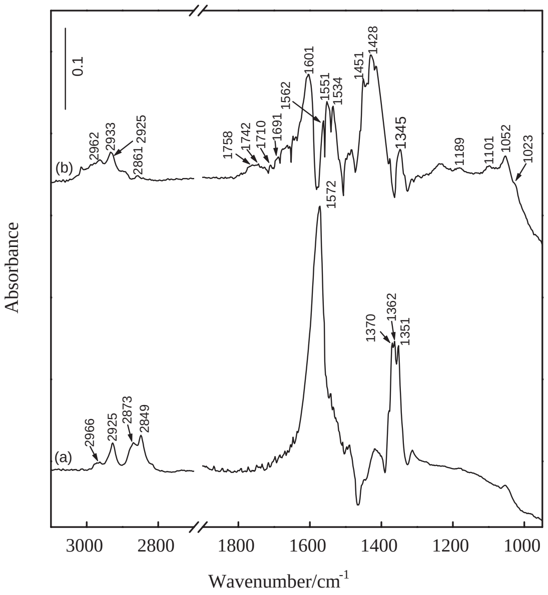

Fig. 1. In-situ DRIFT spectra of the reaction for adsorbed formate with ethanol at 443 K at atmospheric pressure in He. (a) formate adsorption species, (b) after reaction of formate with ethanol for 30 min.

Figure 1 shows the spectra of an in situ reaction for adsorbed formate with ethanol at 443 K and atmospheric pressure. The Cu/ZnO catalyst was exposed to $CO/CO_2/H_2$ at 443 K for 30 min, and then swept in helium for 20 min; the temperature of cell was decreased to 298 K in flowing helium. The saturated ethanol vapor (298 K, 7.9 kPa) was carried by helium into an IR cell at 298 K for 2 min after the formation of a formate species on Cu/ZnO; the IR cell was then closed with the vapor inside, and increasing the temperature to 443 K. The DRIFT spectra were obtained after reacting for 30 min at 443 K. The bands at 2966, 2873, 1572, 1370, 1362 cm^{-1} can be attributed to the bidentate formate species on ZnO; 2925, 2849, 1351 cm^{-1} can be attributed to the bidentate formate species on Cu, which are the stretching vibrations of the carbon–hydrogen bond (2966, 2873, 2925, and 2849 cm^{-1}), and the antisymmetric and symmetric stretching vibrations of the carbon–oxygen bond (1572 and 1370, 1362, 1351 cm^{-1}) in spectra (a) of $CO/CO_2/H_2$ adsorption, respectively.[6–12] This indicates that the formate adsorption species can be formed with exposing syngas containing CO_2 to Cu/ZnO catalyst, but it is difficult for the reaction of formate species to occur with hydrogen in $CO/CO_2/H_2$ to form methanol at 443 K and atmospheric pressure. Therefore, methanol can hardly be synthesized from syngas containing CO_2 on Cu/ZnO at a temperature as low as 443 K.[1,2] However, the bands of the formate adsorption species at 2873, 2849, 1572, 1370, 1362, 1351 cm^{-1}, which are not interfered by the bands of the adsorbed ethoxy and other species, can hardly be observed after introducing ethanol into the reacting system at 443 K for 30 min. We could not clearly observe any change in the formate adsorption bands at 2966, 2925 cm^{-1}, which were interfered by other adsorption species, although these bands also disappeared after the reaction. The bands of the gas-phase ethyl formate (1758, 1742, 1189 cm^{-1}) and physisorbed ethyl formate (1710, 1691 cm^{-1}) could be detected after the reaction. The assignments of the ethyl formate bands were made by analogy with the spectra of known compounds ($HCOOC_2H_5$, see Fig. 2). This means that the reaction of the adsorbed formate species with ethanol proceeds easily to produce ethyl formate

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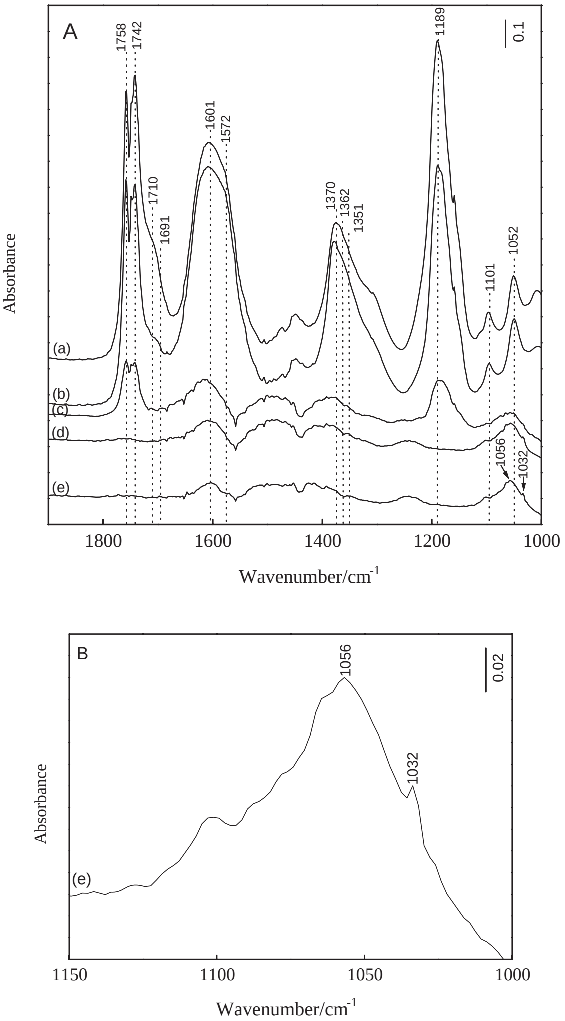

Fig. 2. In-situ DRIFT spectra of the hydrogenation reaction of ethyl formate on Cu/ZnO at (a) 298 K, (b) 343 K, (c) 393 K, (d) 423 K, (e) 443 K.

at a temperature as low as 443 K.

The acetate adsorption species (2933, 1562, 1451, 1023 cm^{-1}) and the carbonate adsorption species (1551, 1534, 1428, 1345 cm^{-1}) were formed by the dehydrogenation of the ethoxy adsorption species (2962, 2925, 2861, 1101, and 1052 cm^{-1}) on Cu/ZnO after reactions at 443 K for 30 min in Fig. 1.[13] The band at 1601 cm^{-1} is for H_2O on Cu (H_2O–Cu).[8]

In order to prove the hydrogenation reaction of ethyl formate to produce methanol on Cu/ZnO, the catalyst Cu/ZnO was exposed to a saturated ethyl formate vapor (273 K, 8.3 kPa) carried by a hydrogen stream at 298 K for 5 min, and then closing the IR cell with the vapor inside. The spectra were collected after a reaction for 30 min at every temperature between 298 K and 443 K in Fig. 2. The bands at 1758, 1742, 1189 cm^{-1} are attributed to the carbonyl (C=O) stretching vibration of the gas-phase ethyl formate, and the bands at 1710, 1691 cm^{-1} can be ascribed to physisorbed ethyl formate on Cu/ZnO. Furthermore, the bands of bidentate formate on ZnO (1572, 1370, 1362 cm^{-1}), bidentate formate on Cu (1351 cm^{-1}), the ethoxy adsorption species (1101, 1052 cm^{-1}) and H_2O on Cu (1601 cm^{-1}) were also observed. We could not observe the ethyl formate molecular species being chemisorbed, because it may be rapidly transformed into the formate species and the ethoxy species on Cu/ZnO.[14] The bands of the gas phase and physisorbed ethyl formate disappeared, and the bands of the gas phase methanol species were produced (1056, 1032 cm^{-1} in Fig. 2) when the temperature was higher than 393 K in Fig. 2A. In order to clearly observe the gas-phase methanol bands, the absorption band (e) in Fig. 2A was enlarged in size from wavenumbers of 1150 to 1000 cm^{-1}, as shown in Fig. 2B. This indicates that ethyl formate is easily reduced by hydrogen atoms on Cu to form methanol at low temperature. The decrease in the formate band intensity in Fig. 2A is due to the reaction of formate with alcohol formed by hydrogenation of ethyl formate with increasing temperature, and then the produced alkyl formate is reduced again, leading to the formation of methanol.

The study results mentioned above mean that ethyl formate is not only formed easily by the reaction of the formate species with ethanol, but is also easily reduced by hydrogen atoms on Cu to form methanol. Therefore, the formation of ethyl formate is a key step to decrease the reaction temperature in low-temperature methanol synthesis. According to the observation above, it is possible to determine the reaction mechanism as shown below:

$$\begin{array}{lrl}
\text{Route A:} & CO + H_2O + ROH \rightarrow HCOOR + H_2O & (1) \\
 & \underline{HCOOR + 2H_2 \rightarrow CH_3OH + ROH} & (2) \\
 & CO + 2H_2 \rightarrow CH_3OH & (3) \\
\text{Route B:} & CO_2 + H_2 + ROH \rightarrow HCOOR + H_2O & (4) \\
 & \underline{HCOOR + 2H_2 \rightarrow CH_3OH + ROH} & (5) \\
 & CO_2 + 3H_2 \rightarrow CH_3OH + H_2O. & (6)
\end{array}$$

The water in Eq. 1 offers hydroxyl, which reacts with CO to form the formate adsorption species ($HCOO_{ads}$); then, $HCOO_{ads}$ reacts with ROH to form HCOOR, while water is produced again. Route A and Route B are connected by a water-gas shift reaction on a Cu/ZnO catalyst, since $CO/CO_2/H_2$ is used as the reactant gas, and water is contained in the used alcohol.

In conclusion, the reaction mechanism of a new low-temperature methanol synthesis method from syngas containing CO_2 using an ethanol promoter was studied by using DRIFTS. The results show that the formate adsorption species are formed by exposing the Cu/ZnO catalyst to $CO/CO_2/H_2$, and the reactive intermediate ethyl formate is formed by the reaction of the adsorbed formate with ethanol. Finally, ethyl formate is reduced by hydrogen to form methanol. The formation of ethyl formate is a key step in the low-temperature methanol synthesis reaction. The reaction temperature is significantly decreased due to promoting, catalytically-active action of ethanol and a new reaction route.

Experimental

The Cu/ZnO catalyst was prepared by the conventional co-precipitation method.[3] In situ DRIFT spectra were collected on a Nicolet Nexus 470 FT-IR spectrometer supplied with a diffuse reflectance attachment and with an MCT detector. The catalyst powder, weighing approximately 14 mg, was contained in a diffuse reflectance infrared cell with a ZnSe window, which could work at high temperature and high pressure. In situ absorbance spectra were obtained by collecting 32 scans at 2 cm^{-1} resolution. Before the adsorption of the reactant, the catalyst sample was treated in situ in a He stream at 298 K for 20 min, and then 493 K for 20 min. The catalyst sample was reduced in a H_2 stream flowing at 20 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ 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.

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