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Spectroscopic and kinetic analysis of a new low-temperature methanol synthesis reaction

Ruiqin Yang[a,b], Yi Zhang[a], and Noritatsu Tsubaki[a,]*

[a]*Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, 930-8555 Toyama, Japan*
[b]*Department of Applied Chemistry, Shenyang Institute of Chemical Technology, 110142 Shenyang, P. R. China*

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The spectroscopy and kinetics of a new low-temperature methanol synthesis method were studied by using *in situ* DRIFTS on Cu/ZnO catalysts from syngas ($CO/CO_2/H_2$) using alcohol promoters. The adsorbed formate species easily reacted with ethanol or 2-propanol at 443 K and atmospheric pressure, and the reaction rate with 2-propanol was faster than that with ethanol. Alkyl formate was easily reduced to form methanol at 443 K and 1.0 MPa, and the hydrogenation rate of 2-propyl formate was found to be faster than that of ethyl formate. 2-Propanol used as promoter exhibited a higher activity than ethanol in the reaction of the low-temperature methanol synthesis.

KEY WORDS: *in situ* DRIFT; methanol; ethanol; 2-propanol; Cu/ZnO; syngas($CO/CO_2/H_2$).

1. Introduction

Methanol is industrially produced under high temperature and high pressure, using copper–zinc-based oxide catalyst. However, as methanol synthesis is an exothermic process, the equilibrium yield declines with increasing temperature [1, 2]. Therefore, developing a low-temperature process for methanol synthesis will increase CO conversion, and greatly reduce the production cost [3]. Wender *et al.* realized this synthesis in liquid phase using a mixed catalyst comprised of Cu compound/alkali alkoxide system and Ni compound/alkali alkoxide system under the mild conditions of 373–453 K and 5.0–6.5 MPa, and gave high methanol synthesis rates and high one-pass CO conversions [4–7]. However, 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 [4, 5], making commercialization of low-temperature methanol synthesis impossible now.

Tsubaki *et al.* reported that catalytically active alcohol solvent remarkably lowered the reaction temperature of methanol synthesis from syngas containing carbon dioxide by using Cu/ZnO catalyst, by which methanol was produced at 443 K and 3.0 MPa [8–10]. Furthermore, as the alcohol 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 are involved in the reaction steps above. As expected, low reaction temperature enabled a CO conversion high as 50–80% [10–12].

Until now, many different findings have been provided regarding the nature of the adsorbed intermediate species on catalysts for the high-temperature methanol synthesis reaction [13–16]. Most of the experimental data supporting these findings were based on FTIR spectroscopy of the adsorbed species formed during the hydrogenation of CO and/or CO_2. Many studies showed that the nature of the adsorbed intermediates for the methanol synthesis reaction depended on the catalyst components and the catalyst preparation conditions [17–21]. Tsubaki *et al.* have proposed the reaction mechanism of the methanol synthesis at low temperature from $CO/CO_2/H_2$ on Cu/ZnO using an ethanol or 2-propanol promoter by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and indicated that the formate and alkyl formate species were the intermediate species of the low-temperature methanol synthesis reaction [22, 23]. In the present work, the reaction kinetics of the low-temperature methanol synthesis described above is investigated by *in situ* DRIFTS. The promoting action of different alcohols involved in the reaction is quantitatively discussed.

2. Experimental

The catalyst was prepared by the co-precipitation method [22]. *In situ* DRIFT spectra were collected on a Nicolet Nexus 470 FT-IR spectrometer with a diffuse reflectance attachment and an MCT detector. The scheme was shown in figure 1. The catalyst powder, approximately 14 mg, was contained in a diffuse-reflectance infrared cell with a ZnSe window, which can work at high temperature and high pressure. *In situ*

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* To whom correspondence should be addressed.
E-mail: tsubaki@eng.toyama-u.ac.jp

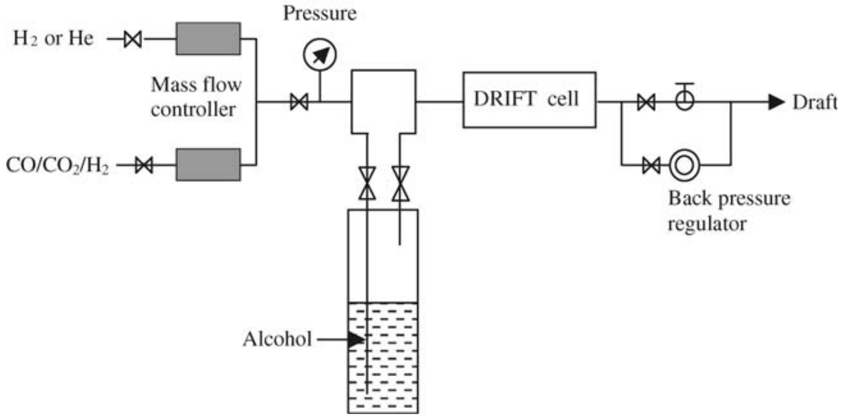


Figure 1. The scheme of *in situ* DRIFT apparatus for adsorption and reaction.

absorbance spectra were obtained by collecting 32 scans at 2 cm^{-1} resolution. Each spectrum was referenced to the spectrum of the catalyst collected at the same temperature under He flow as appropriate. The syngas used in the experiments was $CO/CO_2/H_2/Ar$ with a ratio of 32/5/61/2, the same composition as used in the catalyst development [9–12]. Before the adsorption of the reactant, the catalyst sample was treated *in situ* in a 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 a 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 (443 K).

In order to carry out the kinetic analysis for the reaction of the formate species with ethanol or 2-propanol, the peak areas of the HCOOCu species at 1351 cm^{-1} and HCOOZn species at 1362 cm^{-1} were calculated by the method of the Gaussian multi-peaks separating. The hydrogenation reaction kinetic analysis of ethyl formate or 2-propyl formate was carried out, using the peak areas of the gas-phase ethyl formate or 2-propyl formate, which were calculated by the integration for the gas-phase peaks.

HCOOH was adsorbed onto ZnO, Cu, CuO or Cu_2O solid to determine the peaks of formate species on Cu and ZnO, along with the published literature. A detailed summary of IR peaks assignments was given in our previous study [22].

In the present work, reaction kinetics was investigated by a diffuse-reflectance IR cell with two ZnSe windows in, which could work at high pressure. The solid catalyst powder was loaded at a sample holder which could be heated. IR beam entered from inlet ZnSe window to reach solid surface before getting information from solid surface, and reflected from solid surface to outlet ZnSe window. The peaks of the gases inside IR cell were included in the final signals of IR beam arriving at MCT detector. A shown IR spectrum here was difference spectrum between real spectrum at a reaction condition and background spectrum, where background spectrum was obtained using helium to fill in IR cell with solid itself only in. By this difference method, signals of the IR-active gases, such as those of CO, alkyl formate, could be collected, along with the peaks from adsorbed species on the solid surface. In our experiments on hydrogenation of alkyl formate, due to the quick decomposition of the adsorbed alkyl formate on the surface of the catalyst, monitoring of gaseous alkyl formate peaks was utilized alternatively to conduct kinetics analysis.

3. Results and discussion

The results of our previous studies showed that the adsorbed bidentate formate species could be formed with exposing syngas containing CO_2 to a Cu/ZnO catalyst, and that the adsorbed formate species easily reacted with ethanol or 2-propanol to form gas-phase and physisorbed ethyl formate or 2-propyl formate on the Cu/ZnO catalyst at 443 K and atmospheric pressure. The alkyl formate was easily reduced by hydrogen atoms on Cu to form methanol at 443 K and 1.0 MPa. The reaction mechanism of the new low-temperature methanol synthesis is expressed as follows [22, 23]:

$$CO + OH_{(ads)} \rightarrow HCOO_{(ads)} \qquad (1)$$

$$CO_2 + OH_{(ads)} \rightarrow HCOOO_{(ads)}H_{(ads)}HCOO_{(ads)} + H_2O_{(ads)} \qquad (2)$$

$$CO_2 + H_{(ads)} \rightarrow HCOO_{(ads)} \qquad (3)$$

$$HCOO_{(ads)} + ROH \rightarrow HCOOR + OH_{(ads)} \qquad (4)$$

$$HCOOC_2H_5 + H_{(ads)} \rightarrow CH_3OH + C_2H_5OH \qquad (5)$$

The formation of alkyl formate was a key step in the low-temperature methanol synthesis reaction. It changed the normal reaction path of classical, high-temperature methanol synthesis, which was from formate via methoxy to methanol. The low-temperature methanol synthesis reaction proceeded through a new route, which was from formate via alkyl formate to methanol. To study the effects of different alcohol on the reaction of the new low-temperature methanol synthesis, the kinetic analysis is conducted for the reactions of the equations (4) and (5).

3.1. *Kinetic analysis for the reaction of adsorbed formate with alcohol at atmospheric pressure*

In order to compare the reaction activity of the different alcohols with adsorbed formate species, the reaction kinetic analysis was conducted by *in situ* DRIFTS. Saturated ethanol vapour (7.9 kPa) was carried by helium, with the flow rate of 20 $cm^3\ min^{-1}$, into the IR cell at 443 K and atmospheric pressure after formation of formate species by syngas containing CO_2 on Cu/ZnO, and spectra were obtained after reaction at 443 K for 0.5, 1, 2, and 3 min (figure 2). In another experiment, saturated 2-propanol vapour (7.9 kPa) was carried by helium, with the flow rate of 20 $cm^3\ min^{-1}$, into the IR cell at 443 K and atmospheric pressure after formation of formate species on Cu/ZnO, the spectra were obtained after reaction at 443 K for 0.5, 1, 1.5, and 2 min (figure 3). The results in figures 2 and 3 show that the band intensities of the formate species (1572, 1370, 1362, 1351 cm^{-1}) decrease with increasing reaction time. There are two types of formate species in the reaction system, HCOOCu (1351 cm^{-1}) and HCOOZn (1572, 1370, 1362 cm^{-1}) [22]. The reaction kinetic analysis of the formate species was represented by the reaction of HCOOCu or HCOOZn with alcohol. The reactions of the formate species should obey first-order reaction kinetics because the dosage of alcohol was constant in the flowing reaction system. Also, the amount of alcohol was much more than the limited amount of formate at the surface of the catalyst sample. Therefore, the reaction rate of formate species with alcohol should be expressed as:

$$r_{(\mathrm{HCOOCu})} = k_1 C_{(\mathrm{HCOOCu})}$$

$$r_{(\mathrm{HCOOZn})} = k_2 C_{(\mathrm{HCOOZn})}$$

where k_1 and k_2 are the rate constants, and $C_{(\mathrm{HCOOCu})}$ and $C_{(\mathrm{HCOOZn})}$ are the concentrations of the HCOOCu and HCOOZn species on catalyst surface, respectively, which are in direct proportion to the peak areas of HCOOCu and HCOOZn species, respectively. Figures 4 and 5 show the variation of $\ln(C_0/C)$ as a function of reaction time t, where C_0/C corresponds to A_0/A, A_0 is the initial peak area of the HCOOCu or HCOOZn species, and A is the peak area at time t. The peak areas of the HCOOCu species at 1351 cm^{-1} and HCOOZn species at 1362 cm^{-1} were calculated with reaction proceeding in figures 2 and 3. Figure 4 indicates that the rate constant of the reaction of the HCOOCu species with ethanol is 0.44 min^{-1}, and with 2-propanol is 0.95 min^{-1}, and figure 5 indicates that the reaction rate constant of HCOOZn species with ethanol is 0.38 min^{-1}, and with 2-propanol is 0.94 min^{-1}. The reaction rate constants of the HCOOCu and HCOOZn species with 2-propanol are larger than those with ethanol. Therefore, it can be concluded that the reaction activity of the adsorbed formate species with 2-propanol is higher than that of them with ethanol.

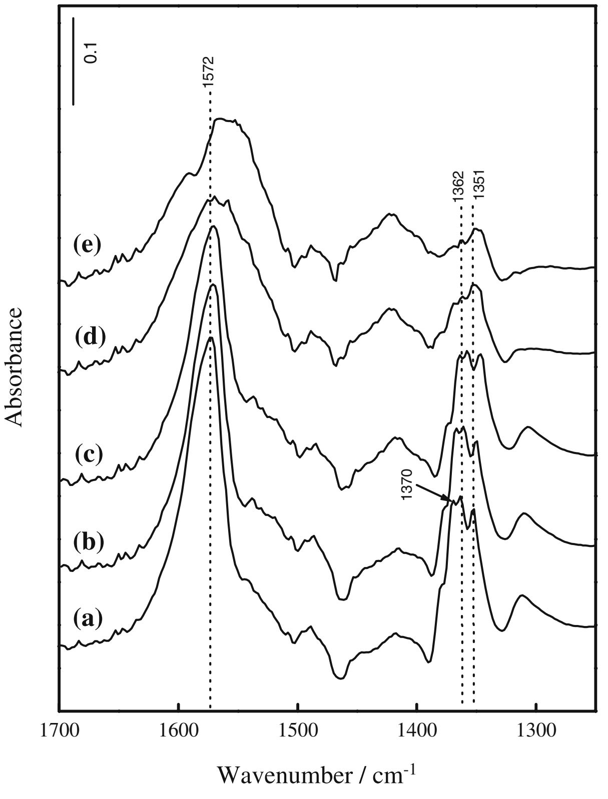
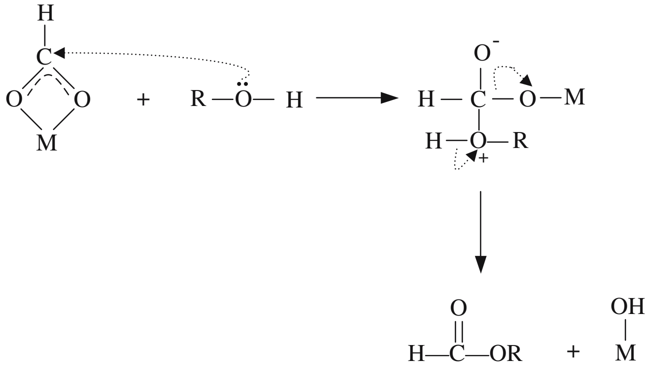


Figure 2. *In situ* DRIFT spectra of the reaction of adsorbed formate with ethanol at 443 K and atmospheric pressure in He ((a) adsorbed formate species, subsequent reaction with ethanol after, (b) 0.5 min, (c) 1 min, (d) 2 min, and (e) 3 min).

This reaction is a nucleophilic addition-elimination reaction, and alcohol is the nucleophilic reagent of the reaction. The reaction route is represented as follows:



(6)

[M is Cu or ZnO, R is C_2H_5 or $(CH_3)_2CH$]

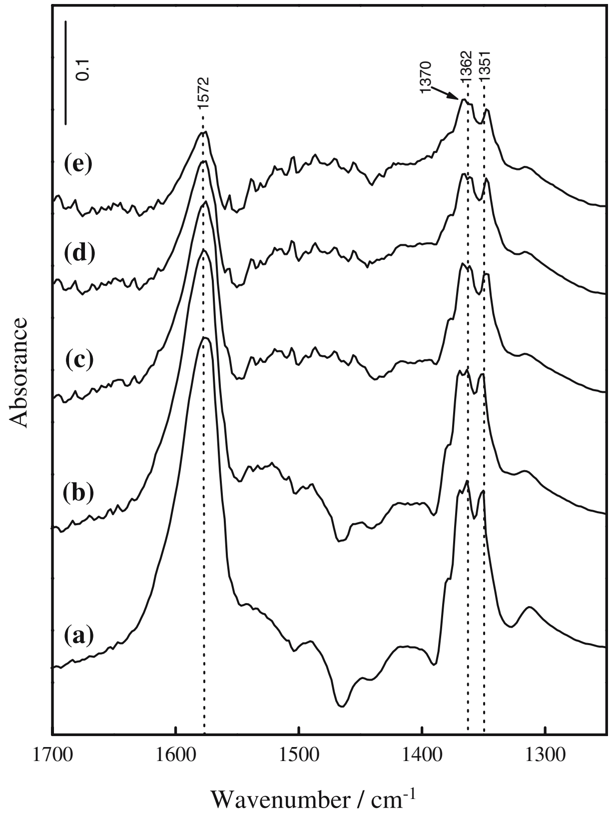


Figure 3. *In situ* DRIFT spectra of the reaction of adsorbed formate with 2-propanol at 443 K and atmospheric pressure in He ((a) adsorbed formate species, subsequent reaction with 2-propanol after, (b) 0.5 min, (c) 1 min, (d) 1.5 min, and (e) 2 min).

2-Propanol has a higher electronic density on its oxygen atom than ethanol due to the larger electron-releasing inductive effect from the two neighbouring methyl groups, but steric hindrance of 2-propanol is slightly larger in the nucleophilic attack.

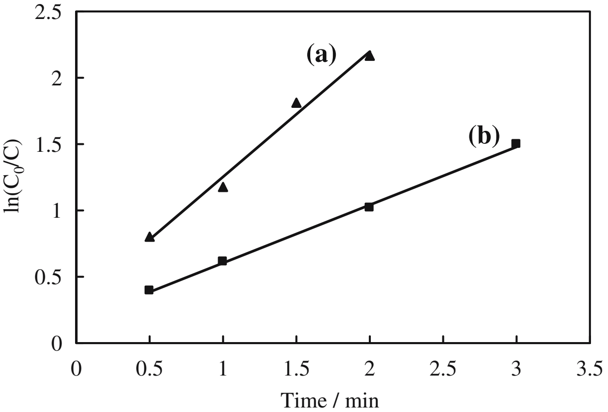


Figure 4. The variation of $\ln(C_0/C)$ as a function of time t in the reaction of HCOOCu with alcohol ((a) 2-propanol and (b) ethanol).

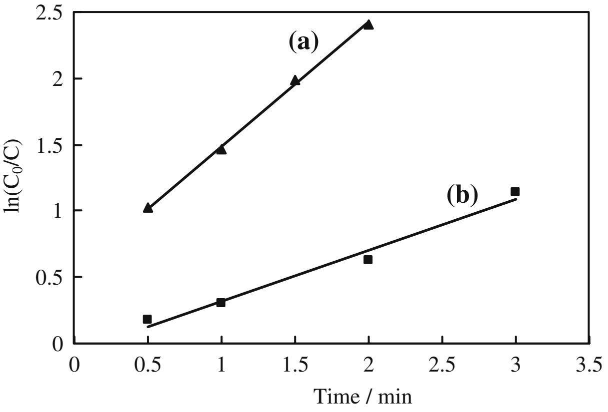


Figure 5. The variation of $\ln(C_0/C)$ as a function of time t in the reaction of HCOOZn with alcohol ((a) 2-propanol and (b) ethanol).

Tsubaki *et al.* have indicated that among the alcohols with the same carbon number but different structure, the second alcohol had highest activity in actual reaction of the low-temperature methanol synthesis, such as the activity sequence: 2-butanol > 1-butanol > iso-butanol > *t*-butanol. For 1-butanol, because the electronic density of oxygen atom is lower, it is more difficult to attacks the carbon atom of the formate. But the steric hindrance of 1-butanol is the smallest among all butanols, and this is favorable to the nucleophilic attack in the esterification reaction. On the other hand, iso-butanol or *t*-butanol has high electronic density in its oxygen atom and this should accelerate the reaction. But their large molecular volume becomes a severe steric hindrance in the nucleophilic attack. Therefore, the esterification rate of iso-butanol or *t*-butanol was low. As a balanced effect between electronic factor and spatial factor, 2-butanol exhibited highest activity among 4 butanols in the esterification reaction [11].

Similar to these findings, the compromise result of higher electronic density and slight steric hindrance leads to the fact that 2-propanol exhibited a higher activity than ethanol.

3.2. *Kinetics analysis for the hydrogenation of alkyl formate at 1.0 MPa*

The Cu/ZnO catalyst was exposed to an inlet partial pressure of 28.5 kPa ethyl formate or 2-propyl formate using hydrogen to balance the total pressure of 1.0 MPa at 298 K. After closing the IR cell with 1.0 MPa reactants inside, the temperature was rapidly increased to 443 K. The hydrogenation spectra of ethyl formate and 2-propyl formate were collected within 1 h at regular intervals. In order to observe the adsorption peak change of the gas-phase ethyl formate or 2-propyl formate in their hydrogenation reactions, the hydrogenation spectra of gas-phase ethyl formate or 2-propyl formate have to be collected in the closed system. The results indicate that the band intensities of gas-phase ethyl formate at 1758, 1753, 1742, and 1189 cm^{-1} (figure 6) and the band intensities of gas-phase 2-propyl formate at 1753, 1743, 1739, and 1190 cm^{-1} (figure 7) decrease with increasing reaction time. At last these bands disappear, while the bands of gas-phase methanol species (1056, 1032, 1008 cm^{-1}) are clearly observed with increasing reaction time (figures 6 and 7). The bands of gas-phase ethanol (1065, 1056 cm^{-1}) and 2-propanol (1147 cm^{-1}) are also observed in figures 6 and 7. These results indicate that the gas-phase ethyl formate and 2-propyl formate are reduced easily by hydrogen atoms on Cu to form methanol at 443 K and 1.0 MPa. In fact, ethyl formate or 2-propyl formate is also easily reduced to methanol at lower temperature and atmospheric pressure (not shown here). However, in order to clearly observe the bands of gas-phase methanol and to conduct the kinetic analysis described below, hydrogenation reaction of alkyl formate is conducted under increased pressure of hydrogen, and the vapor pressure of alkyl formate. The hydrogenation reaction of physisorbed alkyl formate is very rapid even at 373 K and atmospheric pressure (not shown here), and this physisorbed species is not observed at 443 K, because its hydrogenation reaction is finished in the process of rapidly increasing temperature from 298 to 443 K at 1.0 MPa.

In order to compare the hydrogenation reaction activities of different alkyl formates, reaction kinetic analysis was conducted for the reactions shown in figures 6 and 7. The hydrogenation reactions for the alkyl formate obey a first-order model because the high pressure hydrogen is present in excess in the reaction process. Therefore, the hydrogenation reaction rate of alkyl formate can be expressed as:

$$r_{(\mathrm{HCOOR})} = k_3 P_{(\mathrm{HCOOR})} \qquad (7)$$

where k_3 is the rate constant and $P_{(\mathrm{HCOOR})}$ is the partial pressure of gas-phase alkyl formate, which is proportional to the peak area of the gas-phase alkyl formate. Figure 8 shows variation of $\ln(P_0/P)$ as a function of reaction time t, where P_0/P corresponds to A_0/A and A_0 is the initial peak area of gas-phase alkyl formate, while A is the peak area at time t. The peak areas of gas-phase alkyl formate (ethyl formate peaks at 1758, 1753, 1742 cm^{-1}, 2-propyl formate peaks at 1753, 1743, 1739 cm^{-1}) were calculated for the reactions proceeding in figures 6 and 7. Figure 8 indicates that the hydrogenation reaction rate constant of ethyl formate is 0.18 min^{-1}, and the reaction rate constant of 2-propyl formate is 0.21 min^{-1}. Therefore, the hydrogenation of 2-propyl formate is faster than that of ethyl formate.

Based on these observations, it is very easy for the adsorbed formate species to react with alcohol, such as

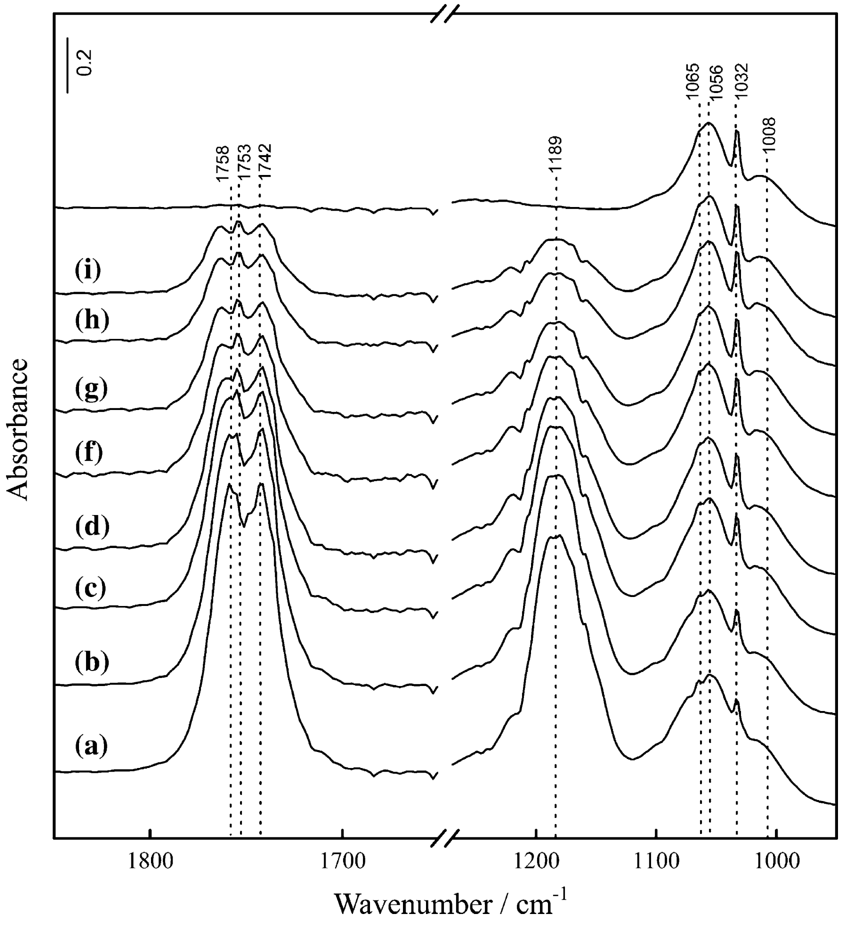


Figure 6. *In situ* DRIFT spectra of the hydrogenation reaction of ethyl formate on Cu/ZnO at 443 K and 1.0 MPa ((a) 0 min, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min, (f) 4 min, (g) 5.5 min, (h) 7 min, and (i) 1 h).

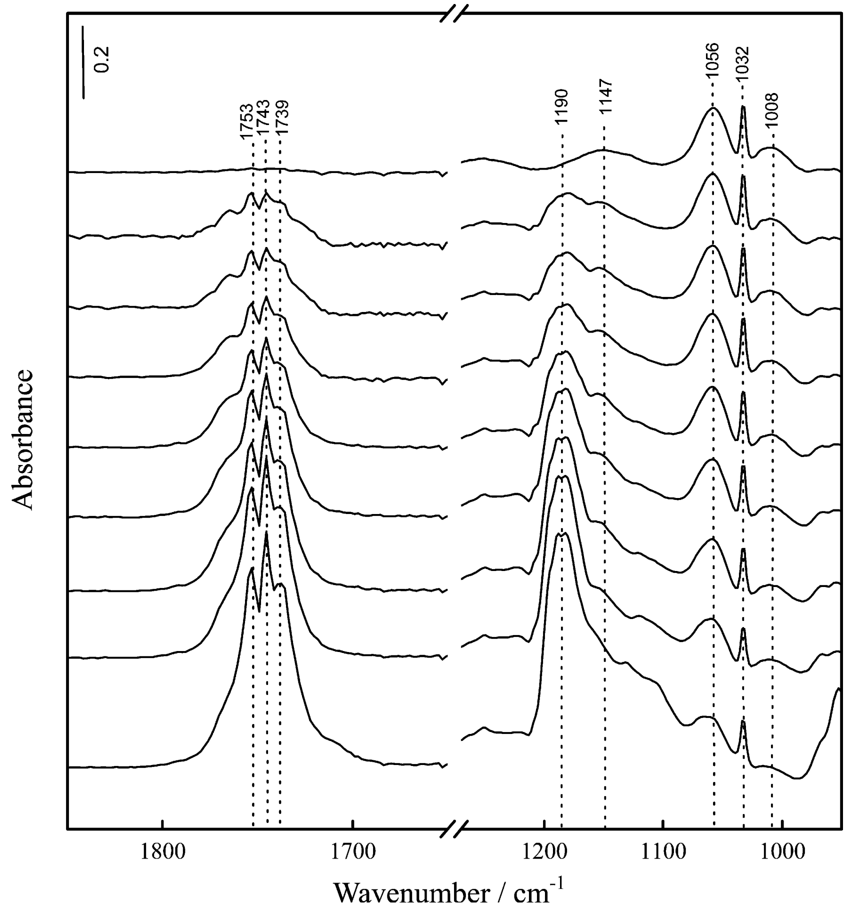


Figure 7. *In situ* DRIFT spectra of the hydrogenation reaction of 2-propyl formate on Cu/ZnO at 443 K and 1.0 MPa ((a) 0 min, (b) 0.5 min, (c) 1 min, (d) 2 min, (e) 3 min, (f) 4 min, (g) 5.5 min, (h) 7 min, and (i) 1 h).

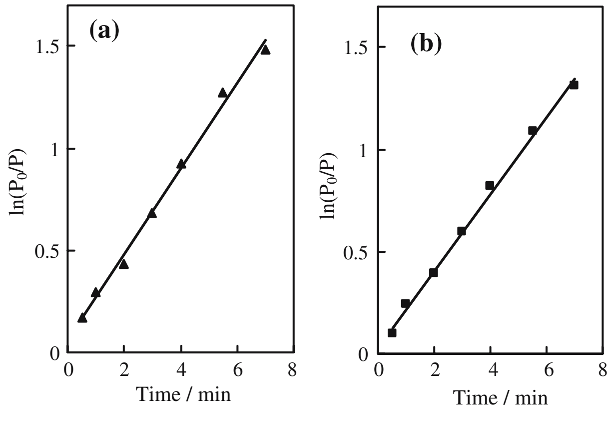


Figure 8. The variation of $\ln(P_0/P)$ as a function of time t in the hydrogenation reaction of alkyl formate species ((a) 2-propyl formate, and (b) ethyl formate).

ethanol or 2-propanol, but the reaction rate of 2-propanol with formate species is faster than that of ethanol. Alkyl formate is easily reduced to form methanol at 443 K and 1.0 MPa, and the hydrogenation reaction rate of 2-propyl formate is faster than that of ethyl formate. Therefore, although the reaction of methanol synthesis is promoted by ethanol as well as 2-propanol, the promoting effects of 2-propanol are larger than those of ethanol.

In the actual low-temperature methanol synthesis, it was a three-phase reaction where reactant gas and vapors of solvents were gaseous, Cu/ZnO was solid, and the alcoholic solvent was liquid. From our previous study where ethanol acted as the solvent [22], only gaseous ethanol molecules attacked the surface formate species, while the IR peak strength of the adsorbed ethoxy kept unchanged. These findings indicated that three-phase reaction could be simplified to two-phase reaction as liquid phase ethanol did not interact with formate species directly. We will report detailed results on the kinetics of this solvent-involved gas–solid surface reaction in the near future. The real reaction rate constant is independent of ethanol pressure or concentration from vapor or liquid ethanol.

For hydrogenation of alkyl formate, as alkyl formate was only an intermediate and could be converted to methanol quickly, its accumulated amount was not enough to form a vapor–liquid coexisting alkyl formate system. The two-phase reaction regime, vapor–solid interface, in the IR cell was in accordance to actual catalysis process related to this step.

4. Conclusions

In situ DRIFTS was employed to study the spectroscopy and kinetics of a new low-temperature methanol synthesis method on Cu/ZnO catalyst from $CO/CO_2/H_2$ using different alcohols as a promoter. The results showed that two types of reaction, the nucleophilic addition-elimination reaction of adsorbed formate species with alcohol and the hydrogenation of alkyl formate, happened consecutively after the formation of the formate species in Cu/ZnO catalyst in this synthesis process. The adsorbed formate species easily reacted with ethanol or 2-propanol, and the reaction rate with 2-propanol was faster than that with ethanol. The alkyl formate was easily reduced by hydrogen atoms on Cu to form methanol at 443 K and 1.0 MPa, while the hydrogenation reaction rate of 2-propyl formate was also faster than that of ethyl formate. Therefore, the synthesis reaction of low-temperature methanol was easier by using 2-propanol as promoter than ethanol on Cu/ZnO catalyst at 443 K, in good accordance to the catalytic reaction results.

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