(CEJ-D-15-05964, revised)

Structural and Kinetic Studies on the Supercritical CO₂ Dried Cu/ZnO Catalyst for Low-Temperature Methanol Synthesis

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Abstract

The Cu/ZnO catalyst prepared by supercritical phase CO₂ drying (denoted as CZS catalyst) and the conventional Cu/ZnO catalyst prepared by heating dry process (denoted as CZO catalyst) were comparatively investigated. The low-temperature methanol synthesis reaction from CO+CO₂+H₂ using 2-butanol as solvent was conducted over the CZS and CZO catalysts at 443 K and 5.0 MPa for continuous 20 h in a flow-type reactor. It was found that the total carbon conversion of the CZS catalyst was increased from 35.1 % to 46.4 % and the methanol yield of the CZS catalyst was enhanced from 33.8 % to 44.8 %, comparing with those of the CZO

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catalyst. The results of kinetic analysis by in situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) revealed that the reaction rate of the low-temperature methanol synthesis on CZS catalyst was faster than that on CZO catalyst at 443 K, in good accordance to the catalytic reaction performances. It was indicated that the supercritical fluid CO₂, which was used to dry the catalyst precursor, suppressed the sintering of the Cu and ZnO particles and increased both the BET surface area of the catalysts and metallic surface area of Cu⁰, which further improved the reaction activity of the catalyst for the low temperature methanol synthesis.

Keywords: Methanol; Syngas(CO/CO₂/H₂); Supercritical fluid drying; Cu/ZnO catalyst; In-situ DRIFTS

1. Introduction

Methanol, as a fundamental chemical feedstock and clean fuel, is being produced at 30-40 million ton per year around the world. At present, copper-zinc-based oxide catalyst developed by ICI Co. Ltd. is used under high temperature and high pressure (523-573 K, 10 MPa) for the commercial ICI high-temperature methanol synthesis. However, the maximum one-pass conversion of this high-temperature methanol synthesis is severely limited by thermodynamics because the reaction is an extremely exothermic reaction [1, 2]. In order to solve this problem, the present authors developed a new low-temperature process by using alcohol itself as both catalytically-active solvent and promoter over Cu/ZnO based catalyst at 423 - 443 K and 5.0 MPa from syngas containing CO₂ [3-7].

To furthermore increase the activity and selectivity of Cu/ZnO catalyst for the

low-temperature methanol synthesis, its preparation method should be improved. It is generally regarded that the particle size, surface area, metallic surface area and composition of the catalyst are important factors affecting the catalytic activity. A linear relationship between the high-temperature (ICI type) methanol synthesis catalytic activity and the metallic surface area of Cu/ZnO catalyst was proposed by Chinchin et al [8]. In recent years, various methods were developed to prepare Cu/ZnO based catalysts with large surface area and copper surface area, which was believed to have a high catalytic activity for methanol synthesis from CO (CO₂) hydrogenation [9-14].

Conventional procedure in the preparation of Cu/ZnO based catalyst is the co-precipitation of copper and zinc nitrates with different bases. The swelled precursor tends to be evident sintering during the drying in air at 393 K. The sintering of the precursor is caused by the large liquid-vapor interfacial forces as liquid vaporization increases volume to about 1000 times, which acts to disrupt the delicate surface structure during an evaporative drying procedure [15]. A new drying technique, supercritical drying, has recently been developed. Another solvent, which is above the critical point of the mixture of two solvents, is used to extract the solvent involved in the swelled catalyst for the supercritical drying [16]. Supercritical drying can maintain the skeletal structure of the swelled catalyst in theory [17, 18]. Supercritical drying media usually include alcohol and carbon dioxide [19, 20]. CO₂ has a relatively low critical temperature ($T_c = 304$ K) and is not flammable.

In the present work, the supercritical CO₂ dried Cu/ZnO catalyst is prepared, and

the low temperature methanol synthesis reactions are implemented using the supercritical CO₂ dried Cu/ZnO catalyst from the syngas containing CO₂. In order to compare the reaction activity of the methanol synthesis on the different catalysts in detail, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is employed to analyze the kinetics of the methanol synthesis reactions on the different catalysts.

2. Experimental

2.1. Supercritical fluid dried Cu/ZnO catalyst preparation

The supercritical fluid dried Cu/ZnO catalyst with Cu/Zn molar ratio of 1/1 (noted as CZS catalyst) was prepared by a co-precipitation method. An aqueous solution containing Cu(NO₃)₂ · 3H₂O (Kanto Chemical Co., Inc) and Zn(NO₃)₂ · 6H₂O (Kanto Chemical Co., Inc) with a molar ratio of 1:1, and an aqueous solution of Na₂CO₃ solution (Kanto Chemical Co., Inc) were added simultaneously into 300 ml deionized water with constant stirring. The precipitation temperature and pH value were maintained at 333 K and 8.5, respectively. The obtained precipitate was aged overnight, filtrated, and washed with adequate deionized water. The deposit was placed into an autoclave, and then the liquid CO₂ was fed by a high-pressure pump (JASCO Co. Ltd.) into the autoclave for 3 h at a rate of 20 ml/min at a temperature of 308 K to dry the precursor. The pressure was kept at 8.0 MPa during this operation. To compare with CZS catalyst, the catalyst which was dried by heating in air at 393 K for 12 h instead of the supercritical drying processing was also prepared (abbreviated as CZO catalyst). These precursors as mentioned above were then calcined in air at

623 K for 1 h, reduced by a flow of 5 % hydrogen diluted by nitrogen at 493 K for 10 h, and successively passivated by 1 % oxygen diluted by argon.

2.2. Catalyst characterization

The crystallographic structure of the samples was studied by X-ray diffraction using a Diffractometer (Rigaku RINT 2400 X-ray diffractometer) with Cu-K α radiation ($\lambda=0.154$ nm). The X-ray tube was operated at 40 kV and at 40 mA, and all the samples were scanned using Cu K α radiation in the range of $20^\circ < 2\theta < 80^\circ$ in the step mode (0.02 $^\circ$, 1.5 s).

The reduction behavior of the Cu catalysts was studied by temperature programmed reduction (TPR) method using a thermal conductivity detector (TCD). TPR experiments were performed in a quartz tube micro-reactor using about 0.2 g calcined catalyst. The temperature of micro-reactor was increased from 303 K to 700 K at a rate of 5 K/min. The reducing gas composed of 5% H₂ diluted by N₂ passed through the reactor at the flow rate of 50 ml/min. The 5 A molecular sieve in the outlet of the reactor absorbed the formed water during the reduction before entering the TCD.

The BET surface area of Cu/ZnO catalysts was measured by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics NOVA1000SP surface area and porosimetry analyzer. The surface areas were calculated according to the method of Brunauer, Emmett and Teller (BET), using 0.164 nm² as the cross-sectional area of the nitrogen molecule.

Specific metallic copper surface areas were determined by

reactive-decomposition method that N_2O reacts with surface Cu^0 .

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected on a Nicolet Nexus 470 FT-IR 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 could work at high temperature and high pressure. In situ absorbance spectra were obtained by collecting 32 scans at 2 cm^{-1} resolution. The syngas used in this experiment was $\text{CO}/\text{CO}_2/\text{Ar}/\text{H}_2$ at a ratio of 31.80/5.21/3.04/59.95, the same composition as that used in the activity measurements of the catalysts.

In order to compare the activity of CZS and CZO catalysts in the low temperature methanol synthesis, the kinetic analysis of the reaction on the catalysts was conducted by in-situ DRIFTS.

2.3. Catalytic activity measurements

The low temperature methanol synthesis was conducted in a flow-type semi-batch reactor. The reactor contained 3.0 g catalyst and 40 ml 2-butanol as solvent. The reaction was carried out with the feeding gas ($\text{CO}/\text{CO}_2/\text{Ar}/\text{H}_2 = 31.80/5.21/3.04/59.95$) of 20 ml/min at 443 K and 5.0 MPa under continuous stirring for 20 h. The products were collected after a 20-h semi-batch activity. The effluent gas component from the reactor through the ice-water-cooled trap was analyzed by an online Gas Chromatograph Thermal Conductivity Detector (GC-TCD) with an active carbon column. The liquid products in the cold trap and those remaining in the reactor were analyzed by another Gas Chromatograph Flame Ionization Detector (GC-FID).

with a combined Porapak N and Gasukuropack 54 column, attached by a methanator after the reaction for 20 h.

CO, CO₂ and the total carbon conversion were calculated by the equations as follows:

$$\text{CO conv.} = 100 \times [(\text{CO/Ar in feed} - \text{CO/Ar in effluent}) / (\text{CO/Ar in feed})]$$

$$\text{CO}_2 \text{ conv.} = 100 \times [(\text{CO}_2/\text{Ar in feed} - \text{CO}_2/\text{Ar in effluent}) / (\text{CO}_2/\text{Ar in feed})]$$

$$\text{Total carbon conv.} = \text{CO conv.} \times a / (a+b) + \text{CO}_2 \text{ conv.} \times b / (a+b)$$

(a, b were the contents of CO, CO₂ in the feed gas)

3. Results and discussion

3.1. Methanol synthesis on CZS or CZO catalyst using 2-butanol promoter

In order to examine the stability and activity of the catalyst, low-temperature methanol synthesis reaction was implemented at 443 K and 5.0 MPa for 20 h by using the CZS catalyst with Cu/Zn molar ratio of 1/1, whose precursor was dried in supercritical CO₂, and calcined in air at 623 K for 1 h and then reduced at 493 K for 10 h. The variations of CO, CO₂ and total carbon conversions with reaction time are shown in Fig. 1 for the continuous reaction of the low-temperature methanol synthesis during 20 h. It is clear in Fig. 1 that the CO conversion gradually increased with reaction time and was nearly stable at approximately 50 %, due to the dilution effect of the pressurized reactant gas at the initiation duration. The total carbon conversion gradually increased with time and become stable at about 40 %. CO₂ conversion stabled at about -4 %. Although the concentration of CO₂ in the feed gas was low, the negative CO₂ conversion meant that a part of CO was firstly converted to CO₂.

through the water-gas shift reaction. The CZS catalyst was very stable with the time on stream during 20 h.

To compare the activities of the CZS and CZO catalyst, low-temperature methanol synthesis reaction was also conducted at 443 K and 5.0 MPa for 20 h by using the CZO catalyst with Cu/Zn molar ratio of 1/1. Table 1 lists the results of the reaction over CZS and CZO catalysts. Table 1 indicates that the total carbon conversion, methanol selectivity, and methanol yield are higher on CZS catalyst than those on CZO catalyst. Both the BET surface area and Cu⁰ surface area (S_{Cu}) of the CZS catalyst are higher than those of CZO catalyst. These findings indicate that supercritical CO₂ drying conditions promoted the dispersion of the Cu/ZnO catalyst particles, prevented the Cu⁰ sintering and further increased the surface area of the catalyst and Cu⁰ surface area (S_{Cu}). Consequently, the activity of methanol synthesis reaction on CZS catalyst was significantly higher than that on CZO catalyst. As can be seen from Table 1, both the total carbon conversion and the methanol yield on the CZS catalyst are enhanced remarkably, compared with those on the CZO catalyst.

Besides, the different Cu/Zn molar ratios of the SC-CO₂ pretreated Cu/ZnO catalysts were investigated in the present work. The catalytic performances of methanol synthesis using SC-CO₂ pretreated Cu/ZnO catalyst with different Cu/Zn molar ratios were shown in Table 2. The CZS catalyst with Cu/Zn molar ratio of 1:1 obtained the largest BET surface area of 58.0 m²/g among all the tested catalysts. With the Cu/Zn molar ratio changed, the BET surface area showed a decreased tendency and stabled at about 56 m²/g. The Cu-specific surface area also exhibited the

same tendency at around 20 m²/g cat. With decrease of the BET surface area and Cu-specific surface area, the catalytic performance showed a decreased tendency. CO conversion decreased to 43.3% and the total conversion declined to 37.3 % when Cu/Zn molar ratio was 3:1.

3.2 Catalyst characterization

The crystalline forms identified by the XRD analysis of the Cu-based catalysts with bulk Cu/Zn molar ratio of 1:1 dried with and without SC-CO₂ fluid are shown in Fig. 2. By comparing the standard file, only the diffraction peaks of ZnO and Cu were predominant, and comparatively dispersive for the catalysts, indicating the good dispersion of ZnO and Cu in the catalysts as well as the strong interaction. Linked with the BET surface area and exposed metallic copper surface area, the CZS showed the smallest metallic copper crystallite size. Currently, it is generally accepted that copper metal (Cu⁰) is the main active component during hydrogenation of carbon oxides to methanol [21-24]. The present results obtained are in agreement with the findings reported in the literatures, and demonstrate that metallic copper is the main active site on the SC-CO₂ pretreated Cu-based catalyst.

Fig. 3 shows the TCD signal in terms of hydrogen consumption from H₂-TPR of the Cu-based catalysts. There were one broad peak and a small sharp peak in both of the samples. For the CZO catalyst, the broad peak was at about 456 K, and the shoulder peak was observed at about 474 K. The broad peak was corresponding to the reduction of CuO to metallic Cu. The shoulder peak was considered as Cu⁺ reduced to the metallic Cu. When the catalyst was dried by the SC-CO₂ fluid, the broad reduction

peak shifted to lower temperature of 445 K. Concurrently, the temperature of the shoulder peak also decreased. These findings suggested that the SC-CO₂ fluid drying extracted the water between the precursors and prevented the sintering. Consequently the catalytic activity could be improved.

For methanol synthesis from syngas using 2-butanol as solvent at low temperature, the Cu/ZnO catalyst prepared by SC-CO₂ drying method showed excellent catalytic performances. This might be due to the SC-CO₂ drying preventing the sintering of the Cu/ZnO catalyst particles. The Cu/ZnO catalyst prepared through SC-CO₂ drying achieved a large surface area and enhanced Cu-specific surface area. According to reaction results, the Cu-specific surface area of the catalysts was the key factor to determine the catalytic activity instead of the BET surface area. Our previous work also proved that the metallic Cu was the catalytic active center for methanol synthesis. As there was no liquid/gas phase boundary, there existed no surface tension and the supercritical fluid could be removed without distortion under supercritical conditions. SC-CO₂ drying could extract the water completely between the precursors without surface tension effects and prevented the sintering of the Cu and ZnO particles, resulting in enlarged BET surface area as well as the increased Cu-specific surface area. Therefore, the optimum SC-CO₂ drying conditions could obtain the high Cu-specific surface area and further increased the catalytic activity of Cu/ZnO catalyst.

3.3. Kinetic analysis by in-situ DRIFTS study on low-temperature methanol synthesis using CZS and CZO catalysts

The results of our previous studies showed that the adsorbed bidentate formate species (HCOO_{ads}) could be formed with exposing $\text{CO}/\text{CO}_2/\text{H}_2$ to a Cu/ZnO catalyst, and that the adsorbed formate species easily reacted with surrounding ethanol to form gas-phase and physisorbed ethyl formate (HCOOC_2H_5) on the Cu/ZnO catalyst at 443 K and atmospheric pressure. The ethyl 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 [25-28]:

The low-temperature methanol synthesis reaction proceeded through a new route as listed above, which was from formate via alkyl formate to methanol. To clarify quantitatively the effects of supercritical CO_2 drying process on the chemical property and reaction activity of the catalysts, the kinetic analysis was conducted for the reactions of the equations (4) and (5) on CZS and CZO catalyst, respectively. As reported by the present authors, the step (4) and step (5) are the rate-determining steps among the steps (1)-(5). It is clear that the difference of catalytic reaction rate constant of these two steps on CZS and CZO catalyst will determine the different overall reaction activity of the used catalysts.

3.3.1. Investigations on the kinetics of the reaction of adsorbed formate with ethanol

at 443 K and atmospheric pressure on CZS and CZO catalysts

In situ DRIFTS was used to investigate the reaction activity of the adsorbed formate species with ethanol on the two kinds of catalyst. After formation of formate species on the catalysts, the saturated ethanol vapour (7.9 kPa) was carried by helium into an IR cell with the flow rate of $20 \text{ cm}^3 \text{ min}^{-1}$ at 443 K and atmospheric pressure. Fig. 4 shows the infrared spectra of the reaction for adsorbed formate with ethanol at 443 K for 10 s, 15 s, 20 s, and 25 s on the CZS and CZO catalyst, respectively.

There are two types of formate species (HCOOCu , HCOOZn) in the reaction system, where 1351 cm^{-1} is the peak of the HCOOCu species, and 1370 and 1362 cm^{-1} are the peaks of the HCOOZn species [25]. The peaks at 1351 cm^{-1} and 1362 cm^{-1} were used to examine the reaction kinetics. The peak areas of HCOOCu species at 1351 cm^{-1} and HCOOZn species at 1362 cm^{-1} were calculated with reaction sequence in Fig. 4.

The reactions of formate species obey a first-order reaction kinetic model because the dosage of ethanol is constant and is of remarkably excessive amount in the flowing reaction system. Fig. 5 shows that the variation of $\ln(C_0/C)$ as a function of t in the reaction process, where C_0/C corresponds to A_0/A . A_0 is the initial peak area of the HCOOCu or HCOOZn species, A is the peak area at the time t . Fig. 5 indicates that the reaction rate constant of HCOOCu and HCOOZn species with ethanol on CZS catalyst is 0.1048 s^{-1} and 0.0953 s^{-1} , respectively, and the reaction rate constant of HCOOCu and HCOOZn species with ethanol on CZO catalyst is 0.0298 s^{-1} and 0.0405 s^{-1} , respectively.

The reaction rate constants of HCOOCu and HCOOZn species on the CZS catalyst are obviously higher than those on the CZO catalyst. Therefore, it is clear that the reaction activity of the adsorbed formate species with ethanol on CZS catalyst is higher than that of them on CZO catalyst.

3.3.2 Kinetic analysis for the hydrogenation of ethyl formate at 443 K and 1.0 MPa

Methanol could be produced by the hydrogenation reaction of the gas-phase ethyl formate at 443 K [25]. In order to demonstrate the kinetics of the hydrogenation reaction of ethyl formate, the CZS or CZO catalysts were exposed to an inlet partial pressure of 28.5 kPa ethyl 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 were collected at regular intervals on CZO or CZS catalysts in Fig. 6, respectively. The results in Fig. 6 show that the band intensity of the gas-phase ethyl formate ($1758, 1753, 1742 \text{ cm}^{-1}$) decreased with increasing the reaction time varied between 0-10 min at 443 K.

In order to compare the hydrogenation reaction activity of ethyl formate on the two kinds of catalyst, reaction kinetic analysis was conducted for the reactions in Fig. 6. The hydrogenation reactions for ethyl formate should obey a first-order reaction kinetic model, because the high pressure hydrogen is obviously excessive in the reaction process. Fig. 7 shows that the 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 ethyl formate, while A is the peak area at time t . The peak areas of gas-phase ethyl

formate (1758, 1753, 1742 cm^{-1}) were calculated with different reaction duration in Fig. 6. Fig. 7 indicates that the hydrogenation reaction rate constants of ethyl formate on the CZS and the CZO catalysts were 0.0953 s^{-1} and 0.0405 s^{-1} , respectively. Therefore, the hydrogenation reaction rate on the CZS catalyst was faster than that on the CZO catalyst.

In situ DRIFTS was used to investigate the reaction kinetics of the catalytic process for low-temperature methanol synthesis on supercritical dried Cu/ZnO catalyst from syngas ($\text{CO}/\text{CO}_2/\text{H}_2$) using 2-butanol as a promoter. It was demonstrated that the reaction rate of the formation of ethyl formate and its successive hydrogenation on CZS catalyst were faster than that on CZO catalyst at 443 K, consistent with the catalytic reaction results. Based on the experiment results above, the reaction activity on the CZS catalyst was higher than that on the CZO catalyst for the low-temperature methanol synthesis.

4. Conclusions

The supercritical dried CZS catalyst was obtained by a co-precipitation method, where the precursor was dried by supercritical CO_2 at 8.0 MPa. The results showed that the total carbon conversion on the CZS catalyst was relatively increased to 46.4 %, and the methanol yield on the CZS catalyst was increased to 44.8 % relatively if compared with the CZO catalyst. In situ DRIFTS demonstrated that the reaction rate of the formation of ethyl formate and its successive hydrogenation on CZS catalyst was faster than that on CZO catalyst at 443 K, in good accordance to the catalytic reaction results. Drying the catalyst precursor with supercritical fluid CO_2

suppressed the sintering of or between the Cu and ZnO particles and improved the specific metallic Cu surface area, resulting in the enhanced reaction rate constants of the CZS catalysts.

Acknowledgements

This work is supported by JST-CREST, JST-ACT-C of Japan Science and Technology Agency. The fund from National Science Foundation of China (NSFC) (No. 21528302) and Youth Innovation Promotion Association CAS (No. 2014155) is also greatly appreciated.

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Table 1 Catalyst activity comparison for CZS catalyst with CZO catalyst for low-temperature methanol synthesis

catalyst	Conversion(%)			Methanol yield(%)	Selectivity(%)		BET (m ² /g)	S _{cu} ^a (m ² /gcat)
	CO	CO ₂ ^b	Total		CH ₃ OH	HCOOR		
CZO	35.1	-1.2	35.1	33.8	96.3	3.7	55.0	18.9
CZS	51.9	12.4	46.4	44.8	96.6	3.4	58.0	23.7

Reaction conditions: T, 443 K; P, 5.0 MPa; time, 20 h; solvent, 2-butanol, 40 ml; W, 3.0 g; feeding gas,

$$\text{CO/CO}_2/\text{Ar/H}_2 = 31.80/5.21/3.04/59.95, 20 \text{ ml/min (STP); stirring speed, 2000 rpm.}$$

^a Based on N₂O pulse method.

^b CO₂ conversion at the 20th hour.

Table 2 The effects of SC-CO₂ fluid drying on the Cu/ZnO catalyst with different molar ratio ^a

Cu/Zn	BET	S_{cu}^b	Conversions (%)			Selectivity (%)	
(mol)	(m² / g)	(m² / g cat.)	CO	CO₂^c	Total	CH₃OH	HCOOR
1 : 1	58.0	23.7	51.9	12.4	46.4	96.6	3.4
1 : 2	56.1	19.9	43.1	-4.3	36.4	94.7	5.3
2 : 1	55.7	19.6	42.8	-1.6	36.5	95.0	5.0
3 : 1	56.3	20.1	43.3	1.4	37.3	94.9	5.1

Reaction conditions: T, 443 K; P, 5.0 MPa; time, 20 h; solvent, 2-butanol, 40 ml; W, 3.0 g; feeding gas,

CO/CO₂/Ar/H₂ = 31.80/5.21/3.04/59.95, 20 ml/min (STP); stirring speed, 2000 rpm.

^a The catalyst was dried by the SC-CO₂ fluid at 8.0 MPa, 308 K and for 3 h.

^b Based on N₂O pulse method.

^c CO₂ conversion at the 20th hour.

Figure captions

Fig. 1. Variations of CO, CO₂, and total carbon conversions with reaction time for the continuous reaction of low temperature methanol synthesis using CZS (1:1) catalyst. (reaction conditions: cat., 3 g; T, 443 K; P, 5.0 MPa; reaction time, 20 h; feed gas, CO/CO₂/Ar/H₂ = 31.80/5.21/3.04/59.95, 20 ml min⁻¹).

Fig. 2. XRD patterns of Cu/ZnO catalysts prepared by the conversional co-precipitation method: (CZO) dried at 393 K for 12 h; (CZS) dried by SC-CO₂ at 8.0 MPa 308 K for 3 h.

Fig. 3. TPR profiles of the Cu/ZnO catalyst: (CZO) dried at 393 K for 12 h; (CZS) dried by SC-CO₂ fluid at 8.0 MPa 308 K for 3 h.

Fig. 4. In-situ DRIFT spectra of the reactions of adsorbed formate with ethanol on CZS and CZO catalysts, respectively.

Fig. 5. The variation of $\ln(C_0/C)$ as a function of time t in the reaction of HCOOCu, HCOOZn with ethanol, respectively.

Fig. 6. In-situ DRIFT spectra of the hydrogenation reaction of ethyl formate on CZS and CZO, respectively, at 443 K and 1.0 MPa.

Fig. 7. The variation of $\ln(P_0/P)$ as a function of time t in the hydrogenation reaction of ethyl formate species.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.