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Characterization of CuO-ZnO Catalyst Prepared by Decomposition of Carbonates Using Dielectric-Barrier Discharge Plasma

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Abstract In this work, we confirmed that dielectric barrier discharge (DBD) plasma is excellent for the decomposition of carbonates to prepare CuO-ZnO catalysts in a rapid and energy efficient way. According to the characterization using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Field Emission Scanning Electron Microscope (FE-SEM), the DBD plasma generated CuO-ZnO catalyst was smaller in particle size with higher copper-zinc surface ratio, compared to the catalyst prepared thermally. Diffuse reflectance infrared Fourier transform (DRIFT) analysis and the activity test showed that the DBD plasma prepared catalysts had higher activities towards synthesis of methyl formate (MF) directly from syngas.

Keywords Cu catalyst · Methyl formate · Plasma · Decomposition

1 Introduction

Catalyst is of great importance in the production of almost all major chemicals. Because of the depleting petroleum resources, more catalysts will be needed for the conversion of feedstock based on natural gas, coal, and renewable resources. Exactly, use of catalyst has been considered to be one of principles of green chemistry [1]. The novel catalyst preparation has become a hot topic and, in some cases, a challenge to chemists worldwide. Recently, using various plasmas for catalyst preparation has attracted a lot of attentions [2–10]. Plasma is a substance in which part of the atoms or molecules are effectively ionized. If sufficient energy is added into gas or a gas mixture, plasma can be generated. Depending on the energy level, plasmas are usually classified as high temperature plasmas and low temperature plasmas. Low temperature plasmas include thermal plasmas and cold plasmas. High temperature plasmas are normally for nuclear applications. Low temperature plasmas are important for the syntheses and processing of matters for catalysis. Thermal plasmas are plasmas with which almost all its components are at thermal equilibrium. However, cold plasmas are different. The electrons in cold plasmas can reach temperatures of 10,000–100,000 K [11], while the gas temperature can remain as low as room temperature. It is the high electron temperature that determines the unusual chemistry of cold plasmas. Based upon the mechanism how plasma generated, the pressure applied and the electrode geometry, cold plasmas can have several very different types including glow discharge, silent discharge (or dielectric barrier discharge) and radio frequency (RF) discharge [11, 12].

Both thermal and cold plasmas have been exploited for the catalyst preparation. The major progresses have been summarized in the previous review article [12]. The recent researches confirmed that plasmas can be efficiently and effectively applied for the size and shape control of metal or metal oxide nano-particles for catalytic uses [3, 4, 7]. Especially, argon or air plasma can be directly applied for the reduction of noble metal ions at room temperature [13]. The use of hazardous reducing chemicals becomes unnecessary.

Previous investigations on cold plasmas for catalyst preparation used mostly glow discharge, microwave discharge, and RF discharge. Few works has been conducted

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using dielectric-barrier discharge (DBD) [9]. The DBD plasma is one of cold plasma phenomena, initiated at ambient conditions. It is different from other plasma phenomena, because one or both of the electrodes are covered by a dielectric-barrier material, like quartz or a ceramic material. A typical advantage of the DBD plasma is that it can be operated at atmospheric pressure. In this work, we attempt to use the DBD plasma for the preparation of CuO-ZnO catalysts. The performance of such DBD prepared catalysts was tested with synthesis of methyl formate (MF) from hydrogen and carbon monoxide.

2 Experimental and Setup

2.1 The Catalyst Preparation

To prepare the CuO-ZnO catalysts, the conventional co-precipitation method was used to prepare copper and zinc carbonate precipitation. A 500 ml aqueous solution of copper and zinc nitrates which contained 0.25 mol of copper and 0.25 mol (or 0.5 mol) of zinc was added to aqueous solution of sodium carbonate with constant stirring. After aged at pH = 7.5 and room temperature for 2 h, the obtained precipitate was washed and filtrated with distilled water. The sample was then dried at 383 K over night. After that, the obtained carbonate powder was placed on the quartz plate in the gap of the DBD reactor. The carbonate mixture was decomposed under the influence of DBD plasmas. The catalyst prepared this way was referred to as CuO-ZnO-dbd (with bulk Cu/Zn ratio of 1:1 or 1:2) and was directly applied for synthesis of MF. For the purpose of comparison, the catalyst was also prepared using the conventionally thermal decomposition, which was conducted at 623 K for 3 h. The catalyst prepared thermally was referred to as CuO-ZnO-c (with bulk Cu/Zn ratio of 1:1 or 1:2). The DBD decomposition is quicker than the thermal decomposition. The average DBD plasma decomposition rate was more than two times higher than the thermal decomposition rate. Further kinetic analysis will be reported in our future works.

The setup applied for the DBD plasma has been described previously in detail [14, 15]. Figure 1 is a schematically representative of the DBD reactor. Briefly, a steel plate high voltage electrode is attached to the inner surface of a quartz plate with a thickness of 2 mm. Another steel plate is performed as the grounded electrode, which is also covered by a quartz plate with the same thickness. The diameter of the quartz plate was 60 mm, whereas it was 50 mm for the steel plate. The width of the discharge gap was 14 mm. The DBD decomposition operation was performed for 9 min in stationary air under atmospheric pressure. A high voltage generator (CTP-2,000 K; Corona Laboratory, Nanjing, China) was applied to supply a voltage from 0 to 30 kV with a sinusoidal waveform at a frequency of about 25 kHz. The voltage and current were measured using a digital oscilloscope (Agilent DSO6052A) with a high voltage probe and a current transformer built into the high voltage generator. The maximum applied voltage measured was 20 kV, whereas the input power was 150 W.

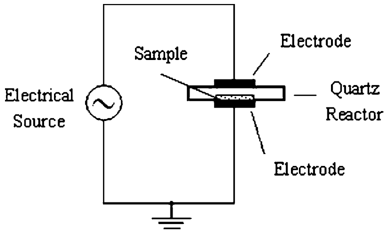

Fig. 1 Schematically representative of DBD plasma setup

The infrared (IR) imaging was used to measure the temperature of the DBD reactor. The IR image was taken with an IR camera (Ircon, USA). Figure 2 shows the IR image of the quartz plate attached with the high voltage electrode, taken immediately after the DBD decomposition. From this image, the highest temperature of the plate was 103 °C. The thermal effect is not significant with the DBD decomposition.

2.2 Catalyst Characterization

X-ray diffraction (XRD) analyses were carried out with a Panalytical X'Pert pro diffractometer with Co Kα radiation. The X-ray was operated at 30 mA and 30 kV. Field Emission Scanning Electron Microscope (FE-SEM) observations were performed on a JEOL JSM-6700F system. X-ray photoelectron spectroscopy (XPS) analyses were conducted using a Perkin Elmer PHI-1600 system employing Mg Kα radiation. DRIFT (diffuse reflectance infrared Fourier transform) spectra were collected on a BRUKE Tensor-27 FTIR spectrometer with a Harrick diffuse reflectance attachment. During the DRIFT study,

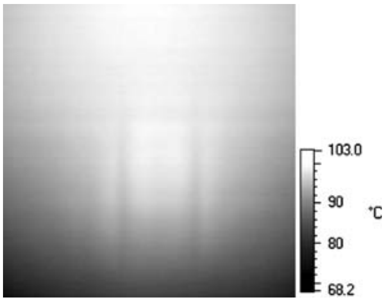

Fig. 2 IR image of the quartz plate taken immediately after DBD plasma decomposition

the catalyst powder was hold in a diffuse reflectance IR cell with CaF_2 windows. The catalyst was completely reduced in hydrogen (20 ml min^{-1}) at 573 K for 1 h. Then the sample was swept by flowing helium (20 ml min^{-1}) at 573 K for 30 min. After cooled down to 363 K in flowing helium, the sample was exposed to flowing syngas (20 ml min^{-1}, 1:1.1 molar ratio of CO/H_2) for 30 min to get the information of in situ reaction on Cu-ZnO catalyst surface. Then the catalyst was purged with flowing helium for 30 min to study the stability of absorbed CO and formate. At last the catalyst was exposed to hydrogen (20 ml min^{-1}) for 30 min to study the catalyst activity in formate hydrogenation.

2.3 Catalytic Tests

The synthesis of methyl formate from syngas was carried out in an autoclave reactor equipped with a stirrer. The inner volume of the reactor is 250 ml. The CuO-ZnO catalyst (5 g, un-reduced), methyl sodium (8 g), dimethylbenzene (85 ml), and methanol (15 ml) were mixed in the reactor. After purged the air by helium, the reactor was loaded to 2 MPa with syngas and was heated electrically. The temperature of the reactor was kept at 363 K. The pressure was then raised to 5 MPa. The stirring speed was set to 200 rpm. Fresh syngas was added every 10 min to maintain the pressure constant at 5 MPa. After 2 h reaction, the reactor was cooled to 278 K, and the liquid was collected. The liquid products were analysed by an Agilent 4890D gas chromatogram with a Porapark Q column.

3 Results and Discussion

The catalyst characterization using XRD, XPS, and CO adsorbed DRIFT shows the DBD plasma decomposition of carbonates generates CuO-ZnO particles with significant differences in the size, phase structure and surface composition, compared to the particles prepared thermally. These differences induce a further difference in the catalytic activity as discussed below.

Figure 3 shows the XRD patterns of CuO-ZnO-c and CuO-ZnO-dbd with bulk Cu/Zn ratio 1:1. From the XRD patterns, the full widths at half maximum (FWHM) of CuO of CuO-ZnO-dbd ($2\theta = 41.51°$, $45.07°$, $57.22°$, $69.16°$) were larger than those of CuO-ZnO-c. The particle size of CuO calculated by Scherrer formula using the FWHM of the CuO (200) peak ($2\theta = 45.07°$) is 16 nm for CuO-ZnO-c and 11 nm for CuO-ZnO-dbd. This indicates that smaller CuO particles were formed through DBD decomposition. The SEM images confirm too that the DBD plasma decomposition generates smaller particles, as shown in Fig. 4.

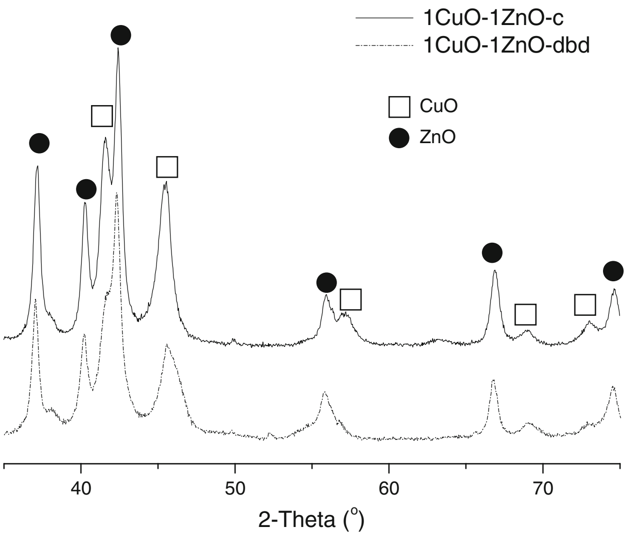

Fig. 3 XRD patterns of CuO-ZnO-c and CuO-ZnO-dbd with the bulk Cu/Zn ratio of 1:1

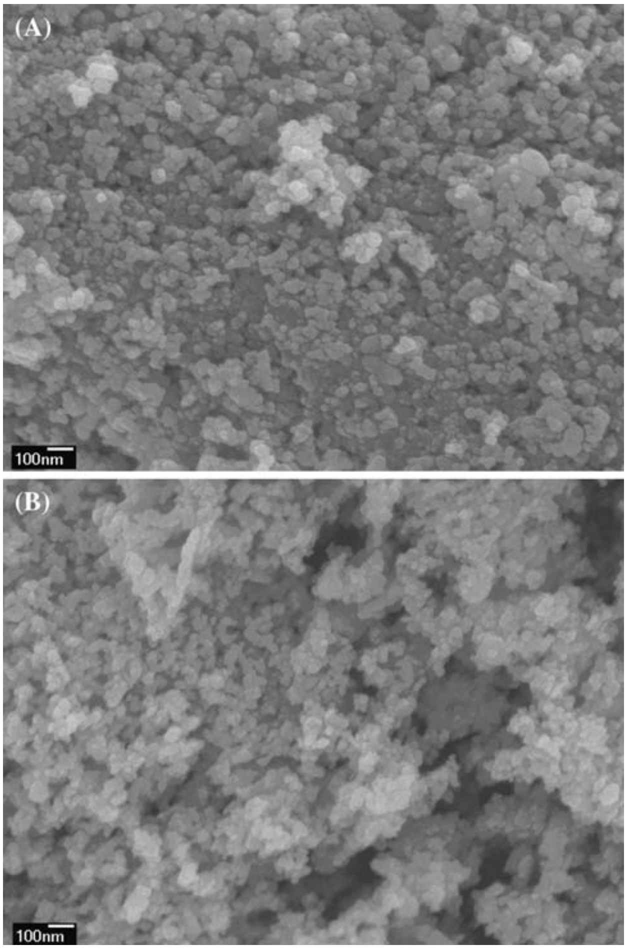

Fig. 4 SEM images of **a** CuO-ZnO-c and **b** CuO-ZnO-dbd with the bulk Cu/Zn ratio of 1:1

In addition to the difference in the particle size, the XPS analyses showed a significant difference in the surface Cu/Zn molar ratio of CuO-ZnO-c and CuO-ZnO-dbd, as demonstrated in Table 1. The surface Cu/Zn molar ratio was obviously less than that of the bulk phase. It can be concluded that zinc tends to present easily on the surface. For the samples with the bulk Cu/Zn ratio of 1:1, the surface Cu/Zn ratio was 0.352 for CuO-ZnO-c and was 0.447 for CuO-ZnO-dbd, respectively. For the samples with the bulk Cu/Zn ratio of 1:2, the surface Cu/Zn ratio was 0.185 for CuO-ZnO-c, while it was 0.282 for CuO-ZnO-dbd. Obviously, the decomposition using DBD plasma increases the Cu/Zn ratio on the surface, which would be favored for the catalytic reactions with the Cu species as the active sites.

The CuO-ZnO-dbd catalyst shows better activities for synthesis of methyl formate from syngas, as shown in Table 1. At Cu/Zn ratio of 1/1, the time space yield of MF over CuO-ZnO-dbd is 7.47 g L^{-1} h^{-1}, 1.03 times higher than that obtained over CuO-ZnO-c. At Cu/Zn ratio of 1/2, it is 7.07 g L^{-1} h^{-1}, 1.35 times higher than that obtained over CuO-ZnO-c. In order to better understand the reaction mechanism, the used samples were analyzed using XRD. Figure 5 shows the XRD patterns of the used catalysts (with bulk Cu/Zn ratio of 1:1). No CuO peak is present on the patterns of the used CuO-ZnO-dbd, while the CuO peaks still exists for the used CuO-ZnO-c. This means that CuO in CuO-ZnO-dbd is easier to be reduced under reaction conditions. ZnO cannot be reduced during the reaction. The peaks at 50.76° and 59.32° belong to Cu (111) and Cu (200), indicating the formation of metallic Cu. The peaks at 42.65°, 49.66°, and 72.87° can be assigned to be Cu_2O (111), Cu_2O (200), and Cu_2O (220), indicating the formation of Cu_2O. Although Cu_2O can be found on both of used CuO-ZnO-dbd and CuO-ZnO-c, the intensity of Cu_2O peaks of used CuO-ZnO-dbd is much more intensive. It indicates more Cu_2O formed on the CuO-ZnO-dbd sample during the reaction. The formation of more Cu_2O helps the synthesis of methyl formate because Cu_2O was considered to be an active species for it. The DRIFT studies indicate the change in the structure is another reason for the differences in the catalytic activity between samples CuO-ZnO-c and CuO-ZnO-dbd.

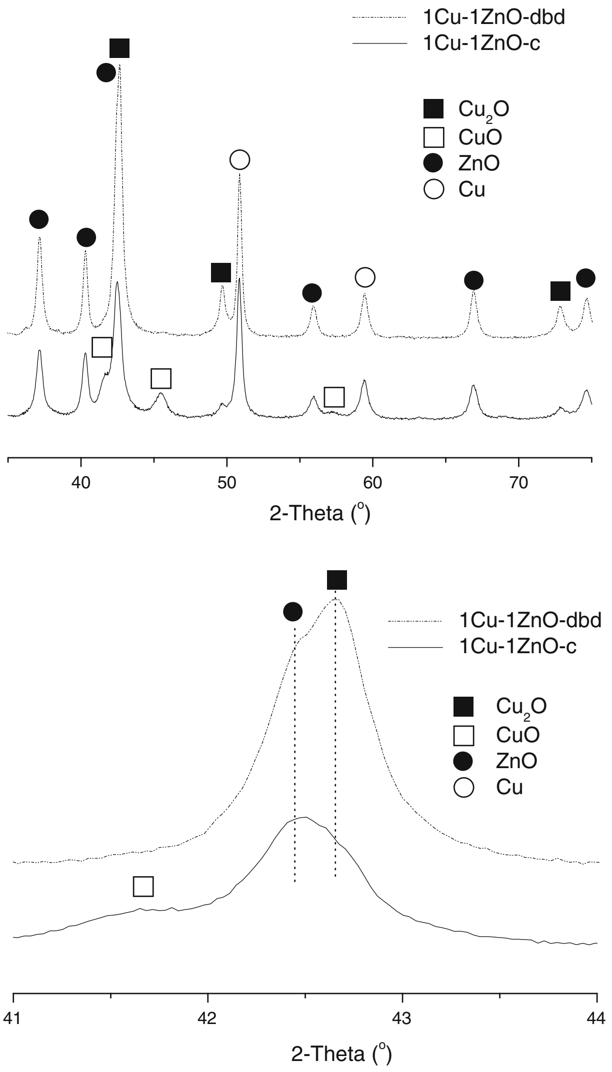

Fig. 5 XRD patterns of CuO_x-ZnO-c and CuO_x-ZnO-dbd (partly reduced in reaction) with the bulk Cu/Zn ratio of 1:1

Table 1 The activities for the synthesis of methyl formate from syngas

	Bulk Cu/Zn molar ratio	Surface Cu/Zn molar ratio	Time space yield of MF (g L^{-1} h^{-1})
CuO-ZnO-c	1:1	0.352	7.27
CuO-ZnO-dbd	1:1	0.447	7.47
CuO-ZnO-c	1:2	0.185	5.23
CuO-ZnO-dbd	1:2	0.282	7.07

CuO-ZnO catalyst: 5.0 g; 363 K; 5.0 MPa; 200 rpm; CO/H_2 = 1:1.1

Figure 6 shows the CO adsorbed DRIFT spectra of the CuO-ZnO-c and CuO-ZnO-dbd samples with the bulk Cu/Zn ratio of 1:2. The CO adsorbed DRIFT spectra were taken from the in situ DRIFT tests. Obviously, for Cu-ZnO-c, CO-Cu band shows the most intensive peaks at 2,102 cm^{-1}, while peak at 2,124 cm^{-1} is weaker and peak at 2,080 cm^{-1} is the weakest. However, for Cu-ZnO-dbd, CO-Cu has its most intensive peak at 2,080 cm^{-1} and the weakest peak is at 2,124 cm^{-1}. The bands at 2,124, 2,102, and 2,080 cm^{-1} can be assigned to CO adsorbed on step and/or defects sites, on atomically rough surfaces and on atomically smooth surfaces, respectively [16]. Therefore, Cu on the completely reduced Cu-ZnO-dbd has less step and defects sites and has more smooth surfaces such as Cu (111). This gives us

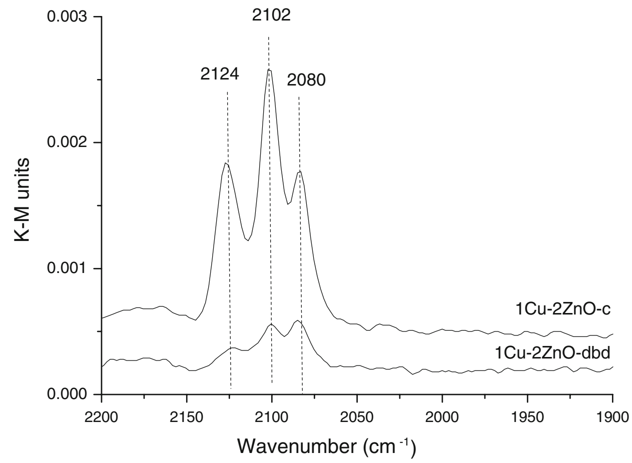

Fig. 6 Comparison of DRIFT spectra of CO absorbed on Cu-ZnO-c and Cu-ZnO-dbd with the bulk Cu/Zn ratio of 1:2 at 363 K

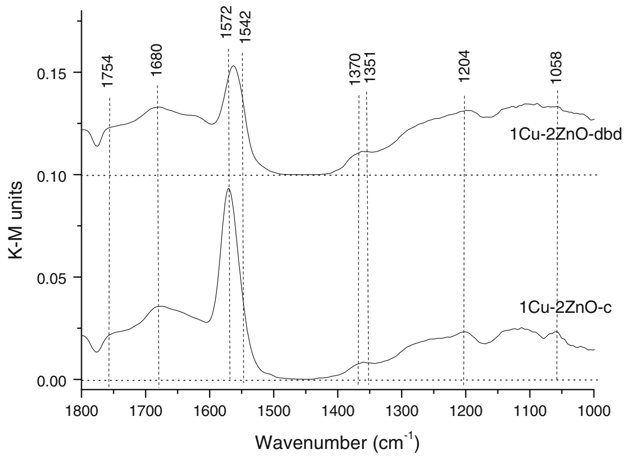

Fig. 7 Comparison of DRIFT spectra of syngas reaction on Cu-ZnO-c and Cu-ZnO-dbd with the bulk Cu/Zn ratio of 1:2 at 363 K

evidence that the DBD plasma decomposition induces a different structure in CuO-ZnO compared to the thermal decomposition.

Figure 7 shows the in situ DRIFT of the Cu-ZnO catalysts with the bulk Cu/Zn ratio of 1:2. The peaks at 1,572 and 1,370 cm^{-1} are typical of the bidentate formate species on ZnO. The peaks at 1,542 and 1,351 cm^{-1} belong to bidentate formate species on Cu. The peaks at 1,754 and 1,204 cm^{-1} are bands of gas-phase methyl formate [17, 18]. Further more, the peak at 1,680 cm^{-1} is the band of absorbed methyl formate [18, 19], and the peak at 1,058 cm^{-1} is zinc methoxide [20]. Therefore, formate, methyl formate and methoxy are formed on the catalysts. The H-COO-Cu/H-COO-Zn intensity ratio of Cu-ZnO-dbd is higher than Cu-ZnO-c, as a result of higher Cu/Zn surface ratio. The peak at 1,680 cm^{-1} is more intense on Cu-ZnO-c, inferring to that Cu-ZnO-c absorbed more methyl formate on its surface. The peak at 1,058 cm^{-1} of Cu-ZnO-dbd is more intense, inferring to that more methoxy was formed on Cu-ZnO-dbd.

Figure 8 shows the DRIFT spectra of the catalysts after purged with flowing helium for 30 min. Formate species on Cu and ZnO, absorbed methyl formate and methoxy can still be found after He purged. Although there was more formate species formed on Cu-ZnO-c, as shown in Fig. 7, the amount of formate remains on the Cu-ZnO-dbd sample was much higher than that on Cu-ZnO-c sample after He purged. Therefore, the formate species absorbed more stably on Cu-ZnO-dbd catalyst.

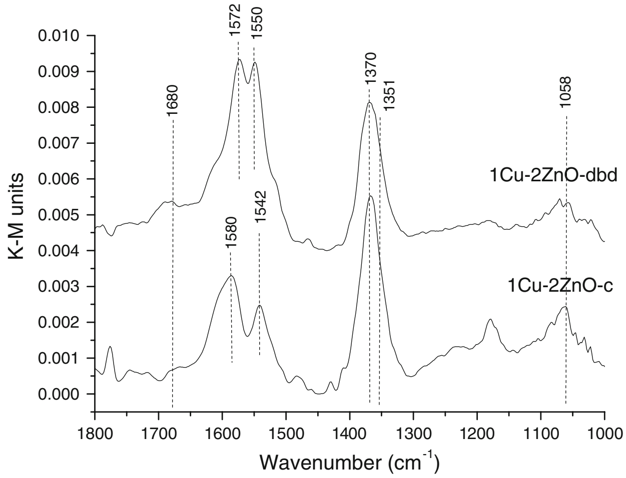

Fig. 8 Comparison of DRIFT spectra of formate remains on Cu-ZnO-c and Cu-ZnO-dbd with the bulk Cu/Zn ratio of 1:2 at 363 K

The samples applied for the tests in Fig. 8 were further exposed to pure hydrogen (20 ml min^{-1}) at 363 K in order to further investigate the catalytic activity of the hydrogenation of adsorbed formate. Figure 9 shows that the formate absorbed can react with hydrogen to form adsorbed methoxy species. The bands of H-COO-Cu and H-COO-Zn on Cu-ZnO-c and Cu-ZnO-dbd decreased, while the bands of CH_3O-Zn increased. This means that both of the catalysts have the activities towards the hydrogenation of adsorbed formate. The formate decreased more rapidly and more CH_3O-Zn was formed on Cu-ZnO-dbd. Therefore, Cu-ZnO-dbd has a higher activity on formate hydrogenation.

It was considered methanol formation by the hydrogenation of formate via methoxy as: $HCOO + H_2 \leftrightarrow CH_3O \leftrightarrow CH_3OH$ [21–23]. We concluded the main pathway of MF synthesized from syngas is as follows: (1) $CO + 2H_2 \leftrightarrow HCOO \leftrightarrow CH_3O \leftrightarrow CH_3OH$ (on Cu-ZnO catalyst); (2) $CO + CH_3OH \leftrightarrow HCOOCH_3$ (on methyl sodium). As the result of DRIFT study, although Cu-ZnO-c sample shows a higher activity in formate species formation step, Cu-ZnO-dbd catalyst shows a better performance in stabilizing formate species and has a much higher activity in formate hydrogenation step, which is a key step

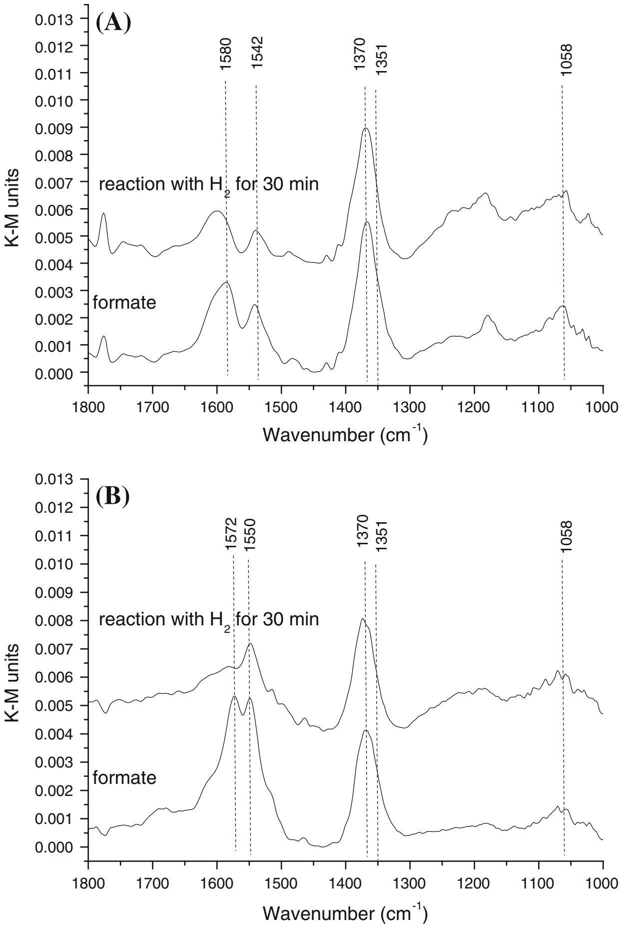

Fig. 9 DRIFT spectra of formate hydrogenation on **a** Cu-ZnO-c and **b** Cu-ZnO-dbd with the bulk Cu/Zn ratio of 1:2 at 363 K

in this reaction. As a result, more methoxy was formed on Cu-ZnO-dbd catalyst at reaction condition, as shown in Fig. 7. Therefore, Cu-ZnO-dbd has higher activity in methanol formation, which decides the higher activity of Cu-ZnO/methyl sodium catalyst system for synthesis of MF.

4 Conclusion

The present study confirms that dielectric barrier discharge (DBD) plasma can be effectively and efficiently applied for the decomposition of carbonates to prepare CuO-ZnO catalyst. The average DBD plasma decomposition rate was more than two times higher than the thermal decomposition rate. Compared to the catalyst prepared thermally, the DBD plasma generated catalyst shows smaller particle size and higher Cu content on the catalyst surface. DRIFT analysis and the activity test show that the DBD plasma prepared CuO-ZnO catalyst possesses higher activities towards the synthesis of methyl formate (MF) directly from syngas.

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