

# Effect of treatment temperature on the crystal structure of activated carbon supported $\text{CuCl}_2$ – $\text{PdCl}_2$ catalysts in the oxidative carbonylation of ethanol to diethyl carbonate

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## Abstract

Diethyl carbonate (DEC) was prepared via oxidative carbonylation of ethanol over a heterogeneous Wacker-type catalyst supported by activated carbon (AC). The active species of copper chloride hydroxide crystals has a great effect on the catalytic performance and chemical adsorption capacities.  $\text{Cu}(\text{OH})\text{Cl}$  crystal is the most active catalyst for the diethyl carbonate synthesis. *In situ* XRD technique was used to analyze the effect of treatment temperature on the crystal structures of catalyst in the oxidative carbonylation of ethanol to diethyl carbonate.  $\text{Cu}(\text{OH})\text{Cl}$  was easily formed at 523 K, which showed the best catalytic activities.  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  was formed at 573 K, which showed lower catalytic activities in the synthesis of DEC.  $\text{CuO}$  was formed at the treatment temperature of 673 K, which increased the yield of by-products—acetaldehyde and ethyl acetate. The catalytic performance of three catalysts of  $\text{CuCl}_2$ – $\text{PdCl}_2$ – $\text{KCl}$ – $\text{NaOH}/\text{AC}$  prepared at the different treatment temperatures above indicated the same trend which could be ascribed to the *in situ* effects on the catalysts under the reaction conditions.

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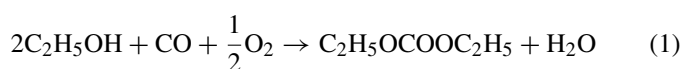
**Keywords:** Diethyl carbonate; Oxidative carbonylation; Copper chloride hydroxide; *In situ* XRD; Catalyst

## 1. Introduction

Diethyl carbonate (DEC) has attracted an increased attention as an environmentally friendly chemical raw material [1]. It is widely used for organic synthesis due to its versatile chemical properties as a non-toxic carbonylating and ethylating agent because of carbonyl and ethoxy groups in its molecule. In recent years, diethyl carbonate is found to be a substitute for methyl *tert*-butyl ether (MTBE), which is largely used as an oxygen-containing fuel additive. DEC features the more favorable gasoline/water distribution coefficient and lower volatility than other promising substitutes for MTBE—dimethyl carbonate (DME) and ethanol [2].

There are several methods for the DEC synthesis, such as a phosgene process, oxidative carbonylation of ethanol [3–8], carbonylation of ethyl nitrite [9–11], and an ester exchange process [12]. Among them, the vapor phase oxidative carbonylation of ethanol represents one of the proposed favorable processes. The

overall reaction is



Eyring and co-workers [4] reported a process for DEC production by vapor phase oxidative carbonylation in the presence of a catalyst, consisting of copper (II) chloride/palladium chloride loaded on the activated carbon (AC), which was treated with potassium hydroxide. The selectivity of DEC formation reached above 99% but the ethanol conversion was dissatisfactory, *ca.* 18%. Seehra and co-workers [7] stressed the importance of catalyst characteristics and concluded that paratacamite ( $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ ) was more active than  $\text{CuCl}_2$  for the DEC synthesis. Liu et al. [8] reported a  $\text{CuCl}$ – $\text{PdCl}_2/\text{C}$  catalyst for DEC production by vapor phase oxidative carbonylation of ethanol. The rate-limiting step in the carbonylation is the insertion of carbon monoxide to the ethoxy species,  $\text{C}_2\text{H}_5\text{O}-\text{CuCl}$ , and the catalyst is easily deactivated during on stream because of the sintering of cuprous chloride and the decomposition of the palladium chloride on the catalyst.

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In our previous work, KCl was proved to be a promoter for the  $\text{CuCl}_2\text{-PdCl}_2\text{-NaOH/AC}$  catalyst, which contributed to a conversion increase of 30% [13], and the conversion of ethanol increased beyond 30%. KCl also favored the  $\text{Cu(OH)Cl}$  crystal formation, increasing the efficiency for DEC synthesis. Further, we showed that temperature of catalyst treatment had an important effect on the crystal structure of catalytically active species. In this study we present results of the influence of treatment temperature on the crystal structure of catalyst and its activities in oxidative carbonylation of ethanol to diethyl carbonate. *In situ* XRD technique was employed to analyze the transformation of crystal structures of the  $\text{CuCl}_2\text{-PdCl}_2\text{-KCl-NaOH/AC}$  catalyst.

## 2. Experimental

### 2.1. Catalyst preparation

The catalyst was prepared by impregnating of activated carbon with methanol solution of  $\text{CuCl}_2$ ,  $\text{PdCl}_2$ , and potassium chloride. The resultant mixtures were refluxed with vigorous stir for 4 h at 333 K, the methanol was removed by the vacuum distillation, and catalyst was dried at 353 K for 4 h in a vacuum oven. Cu and Pd contents expressed by metal weight of catalyst were 3 and 0.25 wt.%, respectively, both measured as metals. And the molar ratio of K to Cu was 1. The catalyst sample was then impregnated in a sodium hydroxide methanol solution ( $\text{Cu/OH} = 1$ , molar ratio), and treated by the same procedure as described above. The BET specific surface area of the activated carbon employed here was  $900 \text{ m}^2/\text{g}$ .

### 2.2. Production and analysis of diethyl carbonate

Catalytic activities were measured by a computer-controlled continuous microreactor system (MRCs-8004B, HuaYang) with a stainless steel tubular reactor with an inner diameter of 8 mm. The reaction products passed through a cooling trap and uncondensed gas products were analyzed by a gas chromatograph (GC-8A, Shimadzu) supplied with a TCD detector with columns packed with TDX-01 and Porapak-Q. The liquid products collected in the cooling trap were sampled every 1 h and analyzed by a GC (4890D, Agilent) equipped a FID detector. The reaction conditions were as follows: 2 g catalyst, 0.1 ml/min ethanol (as liquid), 4 sccm  $\text{O}_2$ , 40 sccm CO, 20 sccm  $\text{N}_2$ , reaction temperature of 423 K and reaction pressure of 0.64 MPa.

### 2.3. Catalyst characterization

The catalyst structures were determined by the XRD method, using a Rigaku C/max-2500 diffractometer with  $\text{Co K}\alpha$  radiation ( $\lambda = 1.7890 \text{ \AA}$ ) in the  $2\theta$  ranges from 10 to  $90^\circ$  (D/Max-2500, Rigaku) and a scanning electron microscope (XL30ESEM, Philips). CO temperature-programmed desorption (TPD) analysis for catalysts was carried out by a Micromeritics 2910 instrument. The catalyst sample was (i) loaded in the tube reactor at room temperature, and (ii) processed at a constant heating rate of  $20 \text{ K min}^{-1}$  under nitrogen atmosphere up to 573 K for 30 min. Nitrogen gas was replaced by helium to cool the sample tube to 323 K. The sample was exposed to CO ( $20 \text{ ml min}^{-1}$ ) for 120 min. TPD measurements were carried out at a heating rate of  $5 \text{ K min}^{-1}$  with a helium flow of  $30 \text{ ml min}^{-1}$ .

## 3. Results and discussion

### 3.1. KCl promoted catalysts

$\text{CuCl}_2\text{-PdCl}_2/\text{AC}$ , a Wacker-type catalyst, has been the main catalytic system for the diethyl carbonate synthesis via oxidative carbonylation of ethanol. Wacker-type catalysts were mostly used as a catalyst of the low-temperature CO oxidation [14–19]. The main catalytic mechanism of this system was regarded as a redox cycle between copper and palladium. It has been recognized that paratacamite ( $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ ) is more active in the oxidative carbonylation process than atacamite ( $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ ) because  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  is more efficient than  $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$  for both regenerating  $\text{Pd}^0$  to  $\text{Pd}^{2+}$  and reducing  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  [20]. The Cu/OH mole ratio can control the crystal structure of the copper chloride hydroxide. When the mole Cu/OH ratio kept up to 2,  $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$  crystal was formed, while  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  was formed at Cu/OH ratio decreased to 1. In this regard, as shown in Table 1,  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  is very effective for the DEC synthesis, but not the best one.

As shown in Table 1, selectivity of diethyl carbonate was about 95%, while the ethanol conversion and space time yield (STY) of diethyl carbonate were quite different. At the lower oxygen feed concentration when KCl was added to the catalyst as a promoter, the ethanol conversion only slightly increased. However, when the feed mole ratio of  $\text{O}_2/\text{C}_2\text{H}_5\text{OH}$  increased from 1:8 to 1:4, the ethanol conversion dramatically increased by

Table 1  
Activity of various  $\text{CuCl}_2\text{-PdCl}_2\text{-NaOH/AC}$  catalysts for the ethanol<sup>a</sup> oxidative carbonylation

Catalyst	Promoter	Conversion <sup>b</sup> (%)	Selectivity (%)				STY (g DEC/l cat h)
			Acetaldehyde	Ethyl acetate	1,1-Diethoxy ethane	Diethyl carbonate	
1	None	15.2	2.0	0.7	2.0	95.3	181.2
2	KCl	32.4	1.9	0.3	3.0	94.8	317.4
3	None <sup>c</sup>	14.1	2.1	0.8	2.8	94.3	169.5
4	KCl <sup>c</sup>	15.9	1.9	0.6	2.5	95.0	208.3

<sup>a</sup> Reaction conditions: 2 g catalyst, 0.1 ml/min ethanol (as liquid), 10 sccm  $\text{O}_2$ , 40 sccm CO, 20 sccm  $\text{N}_2$ , reaction temperature 413 K, reaction pressure 0.64 MPa.

<sup>b</sup> Based on ethanol converted.

<sup>c</sup> 4 sccm  $\text{O}_2$ , 40 sccm CO, 14 sccm  $\text{N}_2$ .

about 2 times, with the same promoter, KCl. The STY of diethyl carbonate also increased from 208.3 to 317.4 (g DEC/l Cat h).

In our previous work, it has been shown that the part of  $\gamma$ - $\text{Cu}_2(\text{OH})_3\text{Cl}$  has converted to  $\text{Cu}(\text{OH})\text{Cl}$  when KCl was used as a promoter for the  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$  catalyst. Because of its insolubility, it is really difficult to synthesize pure  $\text{Cu}(\text{OH})\text{Cl}$  while to load it on the support, and further determine the relationship between the quantity of  $\text{Cu}(\text{OH})\text{Cl}$  crystal and its catalytic activity. However, this issue is still under intensive investigation in our lab and may be reported elsewhere. To address the reactivities of Cu with different valence states, understanding of the properties is necessary. As well known, copper is a quite variable material, which has the Ar electronic configuration  $3d^{10}4s^1$ . That means that the 4p orbital is completely vacant. It provides an opportunity for other molecules or ions to share their pairs of electrons with the empty Cu orbitals. Furthermore, copper has low electronegativity, leading to the much greater degree of covalence in the copper compounds. These features make copper chloride hydroxide many different crystal structures. The redox process between different copper species and palladium has a great influence on the oxidative ethanol carbonylation to diethyl carbonate by the variations of copper chloride hydroxide crystal structures. Not only does the crystal structure play an important role in the redox process, but puts certain affects on the chemical adsorption capacity of the catalytic active species. Thus, as follows, we mainly focus on the chemical adsorption of CO on the catalysts.

### 3.2. CO temperature-programmed desorption

The chemical adsorption capacity of the catalytically active species is very significant for the gas–solid phase catalytic reactions. Since the catalytic activities increases by the addition of KCl as a promoter, the catalyst performance was again compared by using CO temperature-programmed desorption (TPD). The CO chemical adsorption capacity has been considered as a very important factor for the catalytic performances in the vapor phase diethyl carbonate synthesis. Fig. 1 shows CO temperature-programmed desorption profiles for  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$  and  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{KCl}$ - $\text{NaOH}/\text{AC}$  ( $\text{Cu}/\text{K} = 1:1$ , molar ratio) catalysts.

As shown in Fig. 1, it was found that the activated carbon as a support possesses a certain capacity of CO chemical adsorption, which, however, does not agree with the results reported by Han et al. at some points [20]. They have studied the same catalytic system for dimethyl carbonate production, using an activated carbon as a support but did not find any response during CO adsorption, while other catalysts exhibited the characteristic TPD behavior. This difference could be caused by the different qualities of activated carbon supports. It has been known that the surface of activated carbon is enriched by oxygen containing groups, such as hydroxyl, carboxyl, and carbonyl groups. These oxygen containing groups could be ascribed to the chemical adsorption of carbon monoxide. As also shown in Fig. 1, the intensity of CO desorption began to increase at ca. 322 K and reached a maximum at about 370 K. The intensity of CO desorption increased with

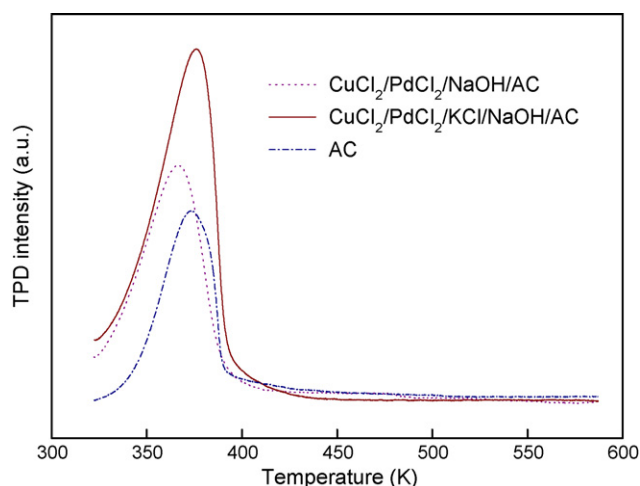


Fig. 1. CO temperature-programmed desorption (TPD) profiles of  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$ ,  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{KCl}$ - $\text{NaOH}/\text{AC}$  ( $\text{Cu}/\text{K} = 1:1$ ), and AC catalysts.

the further temperature increase. Therefore, at this point, it can be concluded that  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{KCl}$ - $\text{NaOH}/\text{AC}$  is the best candidate in terms of CO adsorption capacity (23.8 ml/g). Comparably the catalyst with no KCl promoter added had the CO adsorption capacity of 19.2 ml/g. Obviously, the KCl promoter made  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$  catalyst giving increases in both adsorption capacity and desorption temperature, which agrees with the catalytic reactivities presented in Table 1. In other words, the KCl promoter changed the active structural species of catalyst and enhanced its chemical adsorption capacity, which turns out to promote the DEC synthesis. Though the catalyst of  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$  with the KCl promoter is more favorable for the DEC synthesis via an ethanol oxidative carbonylation, our attention was focused on the transformation of copper chloride hydroxide crystal structure.

### 3.3. In situ temperature-programmed XRD analysis

Previous study of mechanism of catalytic ethanol oxidative carbonylation to diethyl carbonate indicated that the electron exchange between Pd and Cu species played an important role in the catalytic performance [13]. In order to promote the transformation of copper chloride hydroxide from  $\gamma$ - $\text{Cu}_2(\text{OH})_3\text{Cl}$  to  $\text{Cu}(\text{OH})\text{Cl}$ , the preliminary thermal treatment was considered as a basic approach. *In situ* XRD analysis was carried out at the temperature varied from 373 to 1073 K. Fig. 2 shows the *in situ* XRD patterns for the prepared  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{KCl}$ - $\text{NaOH}$  catalyst. There were significant changes in the crystal structures of copper hydroxide chloride at temperatures of 303, 523, 573 and 673 K. The comparison of obtained XRD patterns for the sample of  $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{KCl}$ - $\text{NaOH}$  catalyst with the reference ones (JCPDS files) gave evidence that at the room temperature the main part of copper crystal is  $\gamma$ - $\text{Cu}_2(\text{OH})_3\text{Cl}$  (paratacamite, JCPDS #25-1427) and that the smaller one is  $\text{Cu}(\text{OH})\text{Cl}$  (JCPDS #23-1063). A similar catalytic system ( $\text{CuCl}_2$ - $\text{PdCl}_2$ - $\text{NaOH}/\text{AC}$  catalyst with  $\text{Cu}/\text{OH} = 1:1$ , containing solely  $\gamma$ - $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) crystals) has been used for DMC

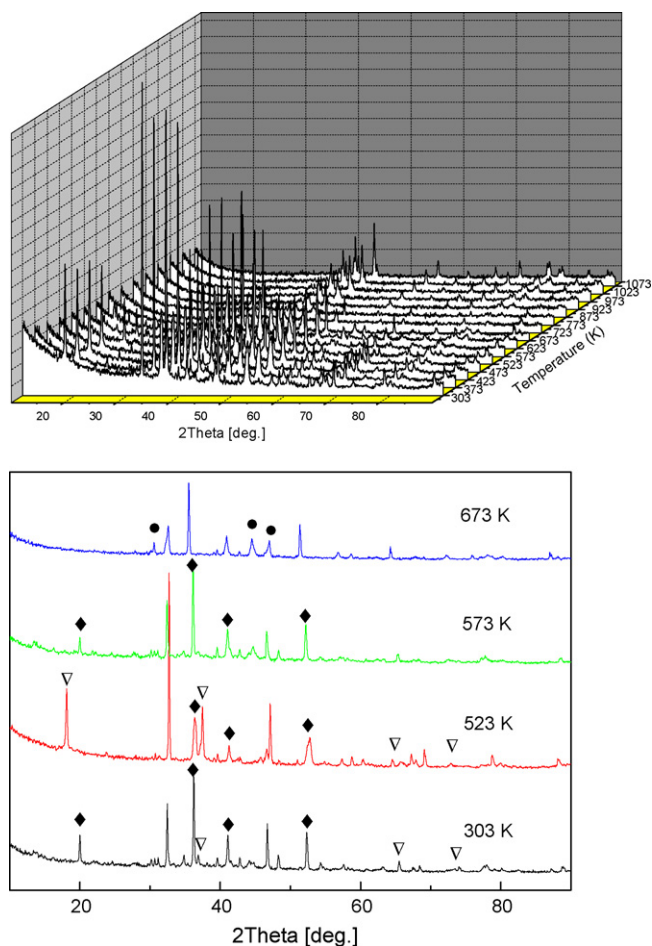


Fig. 2. *In situ* XRD patterns for  $\text{CuCl}_2\text{-PdCl}_2\text{-KCl-NaOH}$  catalyst. (●)  $\text{CuO}$ , (◆)  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ , (▽)  $\text{Cu}(\text{OH})\text{Cl}$ .

synthesis by Han et al. [20]. We note that if the above catalyst was prepared without KCl addition,  $\text{Cu}(\text{OH})\text{Cl}$  was not formed, which, as expected, is in contrast with our previous results [13] where the KCl promoter was used and  $\text{Cu}(\text{OH})\text{Cl}$  was formed.

Another notable feature is that the greater part of  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  crystals were converted to  $\text{Cu}(\text{OH})\text{Cl}$  at temperature 523 K, which indicates that the preheating method can be used as an efficient approach for the copper chloride hydroxide crystal transformation. However, when the treatment temperature increased above 573 K,  $\text{Cu}(\text{OH})\text{Cl}$  is converted to  $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$  due to the low thermal stability of  $\text{Cu}(\text{OH})\text{Cl}$  at higher temperatures, while it is decomposed to copper oxide at a temperature of 673 K and above. Considering the structure of  $\text{Cu}(\text{OH})\text{Cl}$ , based on the study of Iitaka et al. [21], it consists of  $\text{Cu}(\text{OH})_3\text{Cl}_3$ , which has a single edge-sharing octahedral structure. The  $\text{Cu}(\text{OH})_3\text{Cl}_3$  in  $\text{Cu}(\text{OH})\text{Cl}$  possesses two chloride atoms, locating in the *trans*-positions on the long distance from copper atoms, and one chloride atom on the very short distance in the significantly distorted square-plane surrounding copper atoms [22]. This distortion appears due to the well-known Jahn-Teller effect, which makes the crystallographic structure of  $\text{Cu}(\text{OH})_3\text{Cl}_3$  unstable, resulting in its transformation to the other crystallographic structures.

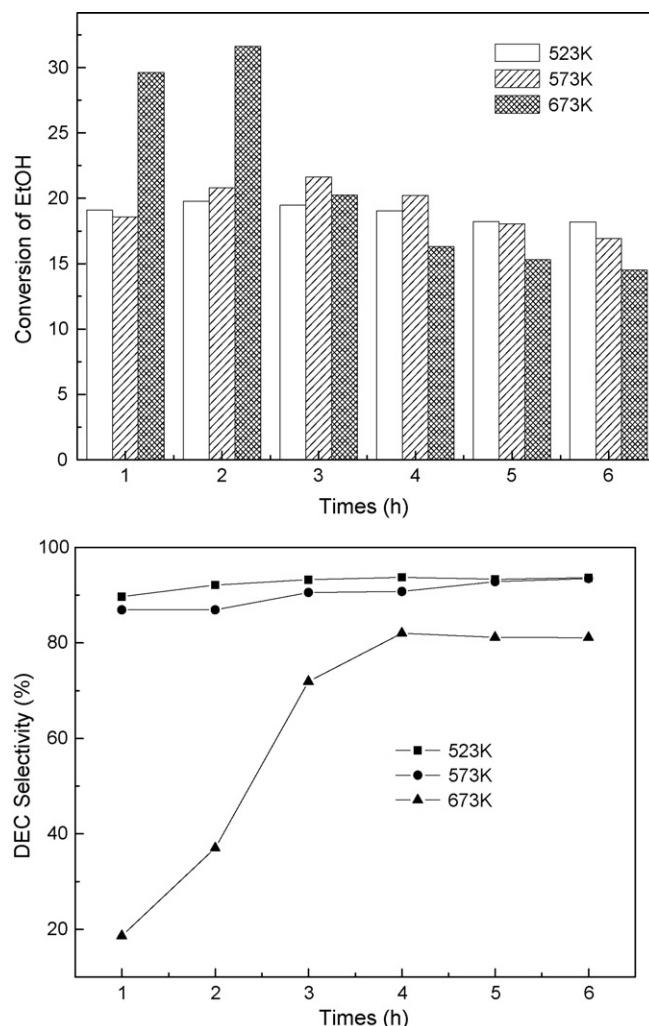


Fig. 3. Catalytic activities of  $\text{CuCl}_2\text{-PdCl}_2\text{-KCl-NaOH/AC}$  catalyst pretreated at different temperatures.

To further explore the chemistry of this Wacker-type catalyst, three fresh prepared samples of  $\text{CuCl}_2\text{-PdCl}_2\text{-KCl-NaOH/AC}$  catalyst were treated at the temperature of 523, 573 and 673 K, respectively, under the nitrogen atmosphere and their catalytic activities as a function of reaction time are shown in Fig. 3.

The ethanol conversion reached above 30% when the catalyst was pretreated at 673 K. However, the selectivity of DEC was somewhat low, about 20%, because ethanol was mostly converted to acetaldehyde and ethyl acetate. XRD patterns showed that the active component of the catalyst sample pretreated at 673 K was copper oxide, which implies that copper oxide can be used as a catalyst for acetaldehyde synthesis since it dramatically decreases the DEC selectivity. During the reaction time, DEC selectivity quickly increased probably due to the transformation of copper oxide to copper hydroxide chloride under the reaction conditions. On the other hand, the catalyst pretreated at 523 K demonstrates both better ethanol conversion and DEC selectivity because of a significant amount of  $\text{Cu}(\text{OH})\text{Cl}$  in the catalyst.

As it is also shown in Fig. 3, the conversion of ethanol decreased quickly with the time on stream of about 3 h. Then, the decrease in the rate of the ethanol conversion becomes moderate. Liu et al. [8] attributed the causes of the deactivation to the sintering of cuprous chloride and the decomposition of the palladium chloride on the catalyst. Our previous work [23] indicated that the deactivation could be caused by the volatilization of the Cl atom and the change of the crystal structure of cuprous species.

According to the proposed catalytic mechanism [13], Cu(OH)Cl is more effective for increasing ethanol conversion and DEC selectivity than paratacamite due to its highly redoxable properties for oxidation of Pd<sup>0</sup> to Pd<sup>2+</sup> and reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>. The outer-sphere mechanism in the oxidation–reduction of Pd/Cu and the Jahn-Teller effect, peculiar to Cu(OH)Cl crystals, make the reduced Pd atoms easily reoxidized by Cu(OH)Cl, which turns out to increase catalytic activity for CO oxidation in the DEC synthesis.

#### 4. Conclusion

The crystal structure of copper chloride hydroxide has an important effect on the synthesis of diethyl carbonate. Cu(OH)Cl is more active than  $\gamma$ -Cu<sub>2</sub>(OH)<sub>3</sub>Cl. CO-TPD analysis indicates that the capacity of CO adsorption increases and desorption temperature shifts to a lower value when Cu(OH)Cl is formed, which could directly account for catalytic promotions. The thermal pretreatment of catalyst significantly modifies the catalyst crystal structure; the crystal structure of copper chloride hydroxides was changed at temperatures 523, 573, and 673 K, respectively. Combinations of *in situ* XRD analysis and catalytic test indicated that Cu(OH)Cl was easily formed at pretreated temperature of 523 K while the corresponding sample demonstrated the best catalytic activities. CuO was formed at pretreated temperature of 673 K, leading to an increase in the yield of by-products such as acetaldehyde and ethyl acetate.

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