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Effect of crystal structure of copper species on the rate and selectivity in oxidative carbonylation of ethanol for diethyl carbonate synthesis

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Abstract

The oxidative carbonylation of ethanol for diethyl carbonate synthesis offers prospects for a "green chemistry" replacement of phosgene used for polymer production and other processes. Effects of a potassium promoter on the $CuCl_2$–$PdCl_2$–$NaOH/AC$ catalyst for diethyl carbonate synthesis were evaluated. The catalytic activity was improved significantly when KCl was added to the catalyst while other promoters only had little influence on the catalytic performance. Further investigations on the KCl promoter indicated that the conversion of ethanol reaches over 30% while the selectivity is around 95%. The optimal molar ratio of the reactant ($CO:O_2:C_2H_5OH$) is around 10:1:4. Analysis by X-ray diffraction and XPS showed that copper chloride hydroxides ($Cu(OH)Cl$) is formed when KCl is added to the catalyst and is beneficial for the catalytic activity for the oxidative carbonylation of ethanol. The great improvement on the catalytic performance of the catalyst $CuCl_2$–$PdCl_2$–KCl–$NaOH/AC$ is attributed to the efficient electronic transfer between $PdCl_2$ and $Cu(OH)Cl$.
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1. Introduction

Diethyl carbonate (DEC) has been attracting wide attention as an environmentally benign chemical raw material [1]. It is widely used for organic synthesis, because it has versatile chemical properties as a nontoxic carbonylating and ethylating agent, because of the presence of a carbonyl group and ethoxy groups in its molecule. Besides these applications as a chemical intermediate, DEC is also drawing attention as a safe solvent and an additive in lithium cell electrolyte [2–5]. In recent years, diethyl carbonate is found to be a substitute for methyl *tert*-butyl ether (MTBE), which is used as an oxygen-containing fuel additive. It has more favorable gasoline/water distribution coefficient and lower volatility than other promising substitutes for MTBE such as dimethyl carbonate and ethanol [6].

There are several synthetic methods for producing DEC, such as the phosgene process, oxidative carbonylation of ethanol [7–11], carbonylation of ethyl nitrite [12,13] and ester exchange [14]. The synthesis of DEC by oxidative carbonylation of ethanol can be carried out in both liquid- and gas-phases. The DEC production process based on a liquid phase oxidative carbonylation of ethanol is performed in the presence of copper(I) chloride as a catalyst [7]. This process, however, have some difficulties such as separation of products from the catalyst, corrosion of equipment and rapid deactivation of the catalyst due to the accumulation of water in the liquid phase. To overcome these problems vapor phase oxidative carbonylation processes have been proposed. The overall reaction is

$$2C_2H_5OH + CO + \tfrac{1}{2}O_2 \rightarrow C_2H_5OCOOC_2H_5 + H_2O \quad (1)$$
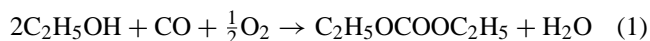
Eyring and co-workers [8] reported a process for producing DEC by a vapor phase oxidative carbonylation in the presence of a catalyst comprising copper(II) chloride/palladium chloride loaded on active carbon (AC) treated with potassium

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hydroxide. A pulse-quench-flow reactor was used to investigate the influence of the amounts of reactant and the reaction conditions on continuous production of DEC [9,10]. According to the batch reactor experiments, this catalyst has proven to be more active than those prepared without PdCl$_2$, with other copper salts Cu(NO$_3$)$_2$, Cu(CH$_3$COO)$_2$, etc. [10]. The selectivity to DEC reached over 99% but the conversion of ethanol was not satisfactory, only 18%. Seehra and co-workers [11] put emphasis on the characteristics of catalysts and concluded that paratacamite (γ-Cu$_2$(OH)$_3$Cl) was more active than CuCl$_2$ in the synthesis of DEC.

This work focused on the evaluation of catalytic activity and the detailed characterization of KCl promoted CuCl$_2$–PdCl$_2$–NaOH/AC catalysts. Four different potassium promoters were added to the CuCl$_2$–PdCl$_2$–NaOH/AC catalyst in order to enhance the conversion of ethanol. Morphological analysis by XRD and XPS was conducted in order to characterize the employed catalysts. The reaction mechanism was also discussed.

2. Experimental

The catalyst was prepared by impregnating activated carbon with methanol solution of CuCl$_2$, PdCl$_2$ and a potassium salt (potassium acetate (KAc), potassium citrate tribasic monohydrate (KCTM), potassium sorbate (KSor) or potassium chloride). Then the mixture was refluxed with vigorous stirring for 4 h at 333 K, and the methanol was removed by vacuum distillation and the catalyst was dried at 353 K for 4 h in a vacuum oven. The Cu and Pd contents in the catalyst are 3 wt.% Cu and 0.25 wt.% Pd, both measured as metals.

The molar ratio of K/Cu was 1. The catalyst sample was then impregnated with methanol solution of sodium hydroxide (Cu/OH = 1, molar ratio), and again treated by the above method. The BET specific surface area of the activated carbon employed here was 900 m^2/g.

Catalytic activity was measured by a computer-controlled continuous micro reactor system (MRCS-8004B) with a stainless steel tubular reactor of 8 mm inner diameter. The reaction products passed through a cooling trap and uncondensed gas products were analyzed by gas chromatographs (GC-8A, Shimadzu) with a TCD detector, which employed a column packed with TDX-01 and Propak-Q. The liquid products collected in the cooling trap were taken out every hour, and were analyzed by a gas chromatograph (4890D, Agilent) with an FID detector. The reaction conditions were as follows: 2 g catalyst, 0.1 ml/min ethanol (as liquid), 4 sccm O$_2$, 40 sccm CO, 20 sccm N$_2$, reaction temperature 423 K and reaction pressure 0.64 MPa. The structures of catalysts were determined by XRD using a Rigaku C/max-2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) in the 2θ ranges from 10 to 80°. XPS analysis was carried out on a Perkin-Elmer PHI 1600 ESCA system using Al Kα radiation (1486.6 eV).

3. Results and discussion

Conversion and selectivity were calculated according to the following equations: conversion of C$_2$H$_5$OH (C_{EtOH}, %) = (1 − C$_2$H$_5$OH unreacted/C$_2$H$_5$OH fed) × 100. Selectivity for DEC from C$_2$H$_5$OH or CO (S_{EtOH} or S_{CO}, %) = (DEC produced/(C$_2$H$_5$OH or CO reacted/2)) × 100.
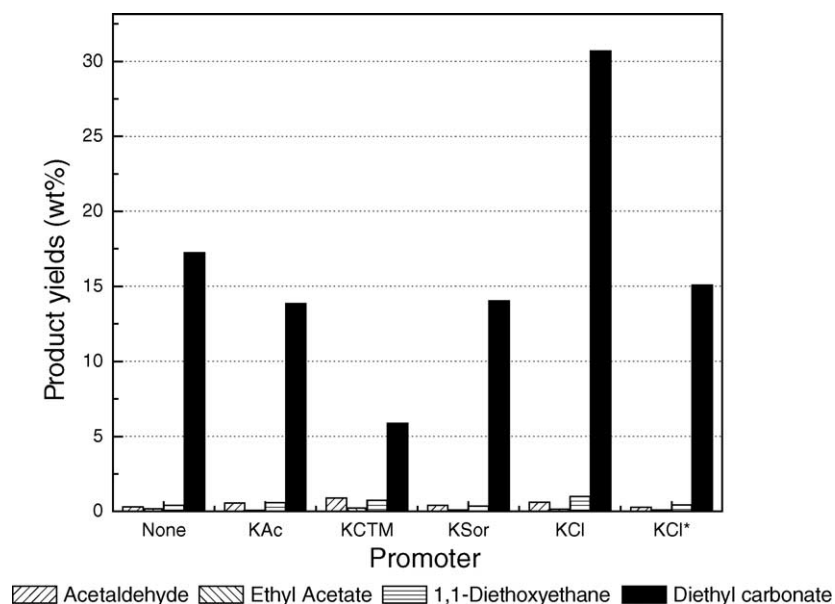

Fig. 1. Influence of treating an activated carbon-supported CuCl$_2$–PdCl$_2$–NaOH catalyst with various potassium salts on the product yields. Reaction conditions: 2 g catalyst; 0.1 ml/min ethanol (as liquid); 10 sccm O$_2$; 40 sccm CO; 14 sccm N$_2$; temperature 413 K; pressure 0.64 MPa (KCl*: 4 sccm O$_2$, 40 sccm CO, 20 sccm N$_2$). KAc, potassium acetate; KCTM, potassium citrate tribasic monohydrate; KSor, potassium sorbate.
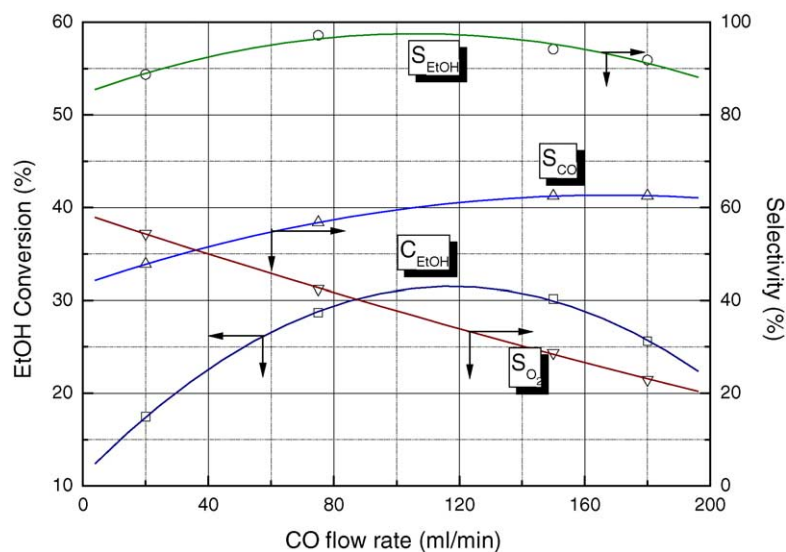
Fig. 2. Effect of the flow rate of CO. Reaction conditions: catalyst $CuCl_2$–$PdCl_2$–KCl–NaOH/AC; temperature 413 K; pressure 0.64 MPa; 2 g catalyst; 0.1 ml/min ethanol (as liquid); 10 sccm O_2.

3.1. Catalytic activity

As shown in Fig. 1, for the catalyst of $CuCl_2$–$PdCl_2$–KCl–NaOH/AC, the conversion of ethanol and the yield of diethyl carbonate increased remarkably without any decrease in the selectivity at the same space velocity, when the oxygen/ethanol molar ratio was increased from 1:8 to 1:4. The conversion of ethanol reached over 30%, about 50% higher than the hitherto reported level. However, those catalysts with other potassium promoters showed a slight change in its catalytic performance at the same space velocity when the oxygen/ethanol molar ratio increased. There are some vital differences between KCl and non-KCl promoted catalysts from the results mentioned above.

According to Eq. (1), the stoichiometric ratio of reactants is 2:1:0.5 for C_2H_5OH, CO and O_2. The reactant feed ratio, which have significant effects on C_{EtOH} (conversion of ethanol), S_{EtOH} (selectivity of ethanol to DEC), S_{CO} (selectivity of CO to DEC) and S_{O_2} (selectivity of oxygen to DEC), were examined on a $CuCl_2$–$PdCl_2$–KCl–NaOH/AC catalyst.

First, the flow rate of CO was changed from 20 to 180 ml/min at a constant feed rate of C_2H_5OH and O_2. As shown in Fig. 2, C_{EtOH} and S_{EtOH} increased with the increase in the flow rate of CO in the range of 20–100 ml CO/min, beyond which the C_{EtOH} and S_{EtOH} decreased together. S_{CO} increased linearly in the flow rate range of 20–150 ml CO/min, and then levelled off. S_{O_2}, however, deceased linearly with the increase in the flow rate of CO. The amount of by-products,
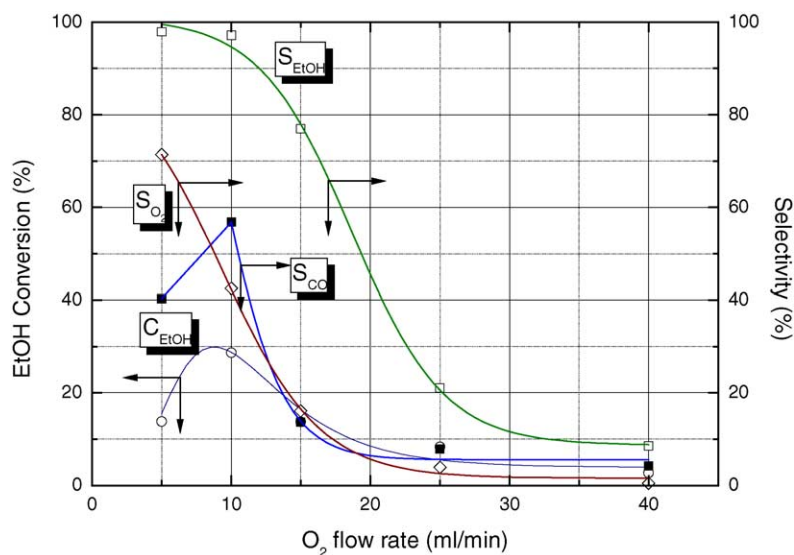

Fig. 3. Effect of the flow rate of O_2. Reaction conditions: catalyst $CuCl_2$–$PdCl_2$–KCl–NaOH/AC; temperature 413 K; pressure 0.64 MPa; 2 g catalyst; 0.1 ml/min ethanol (as liquid); 75 sccm CO.
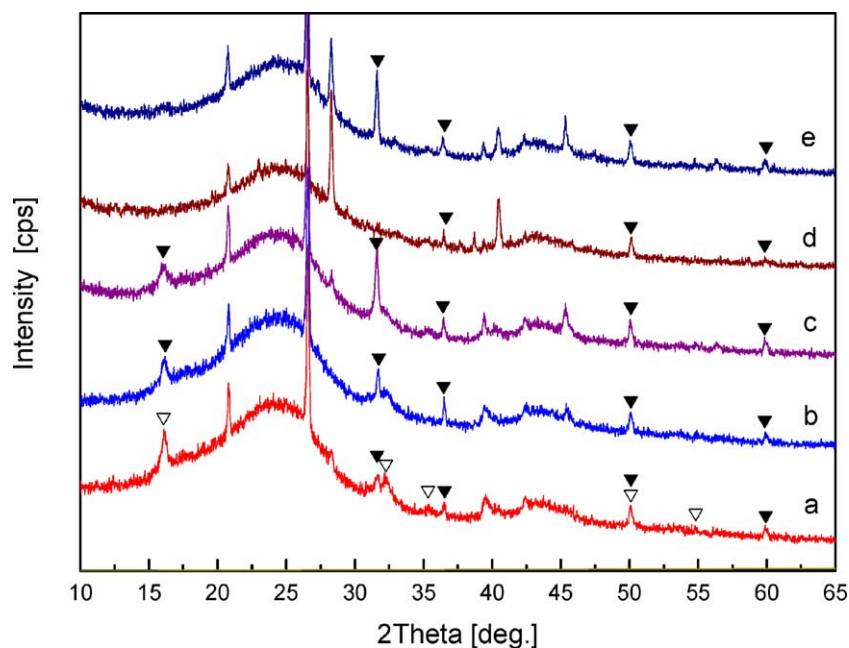
Fig. 4. XRD patterns for (a) CuCl₂–PdCl₂–KCl–NaOH/AC, (b) CuCl₂–PdCl₂–NaOH/AC, (c) CuCl₂–PdCl₂–KAc–NaOH/AC, (d) CuCl₂–PdCl₂–KCTM–NaOH/AC and (e) CuCl₂–PdCl₂–KSor–NaOH/AC; Cu:K = 1:1, Cu:OH = 1:1; (▲) γ-Cu₂(OH)₃Cl, (△) Cu(OH)Cl.

such as carbon dioxide, acetaldehyde, ethyl acetate and 1,1-diethoxyethane, increased with the increase in the CO flow rate. The optimal flow rate of carbon monoxide is considered to be around 100 ml CO/min.

Next, the effect of the oxygen flow rate was examined in the same way as above for CO. The results were plotted in Fig. 3. C_{EtOH} and S_{CO} increased significantly in the range of 4–10 ml O₂/min. In the same range, S_{O_2} decreased from more than 65% to 40% but S_{EtOH} was still maintained around 95%. Above this range, the conversion of ethanol, the selectivity of carbon monoxide and ethanol decreased significantly. It is

obvious that the flow rate of oxygen has great influence on the performance of the CuCl₂–PdCl₂–KCl–NaOH/AC catalyst. The conversion of ethanol reached maximum when the flow rate of oxygen increased to the stoichiometric ratio (based on ethanol). When the flow rate of oxygen increased beyond the stoichiometric ratio, carbon monoxide is more easily oxidized to carbon dioxide. At the same time, ethanol is more easily oxidized to the other by-products. The optimal molar ratio of O₂/C₂H₅OH is considered to be around 0.25.

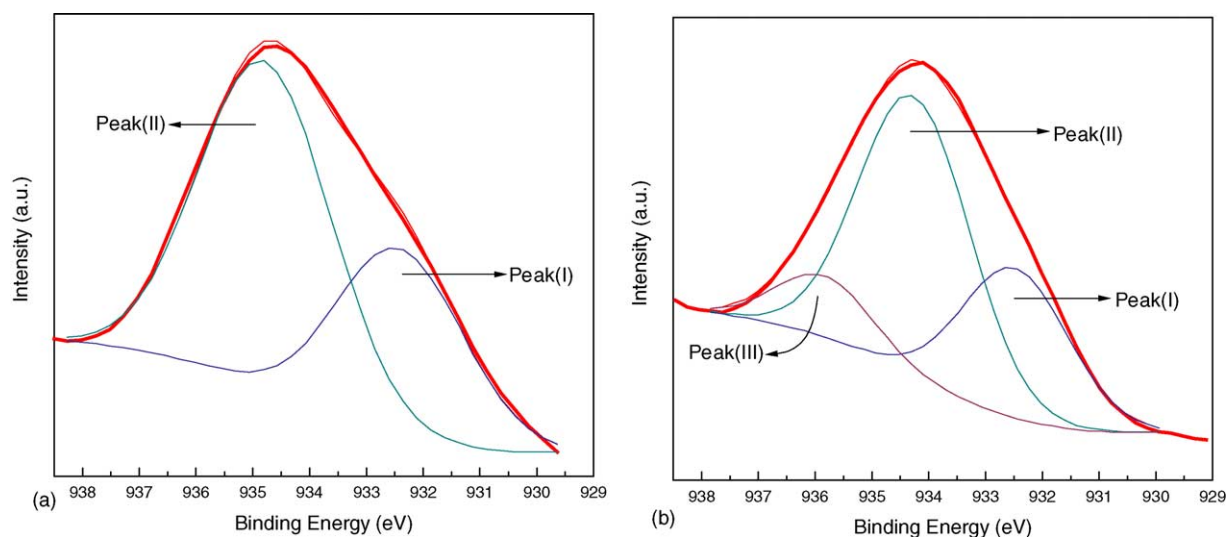From the results above, the best molar ratio of CO, O₂ and C₂H₅OH as reactants should be 10:1:4.

Fig. 5. XP spectra of Cu 2p₃/₂ for CuCl₂–PdCl₂–NaOH/AC and CuCl₂–PdCl₂–KCl–NaOH/AC catalysts.

3.2. XRD analysis

As described above, there must be some vital differences between KCl and non-KCl promoted catalysts. X-ray diffraction (XRD) was employed to determine the structural properties of five fresh samples (with and without adding KCl). Fig. 4 compares the X-ray diffraction patterns of $CuCl_2$–$PdCl_2$–NaOH/AC catalysts with different potassium promoters added. A prominent copper chloride hydroxides peaks were detected in the cases of (a), (b), and (c), but little for (d) and (e). As a result of perusal of copper chloride hydroxide peaks in XRD patterns, the existence of two different crystal habits of copper chloride hydroxide peaks was observed. According to the JCPDS reference files, one is γ-$Cu_2(OH)_3Cl$ (paratacamite, JCPDS #25-1427), which is rhombohedral, while the other is Cu(OH)Cl (JCPDS #23-1063), which is also rhombohedral. It can be concluded that the catalyst phase was γ-$Cu_2(OH)_3Cl$ dominant in $CuCl_2$–$PdCl_2$–NaOH/AC and the catalyst with KAc, KCTM or KSor promoter, while some of γ-$Cu_2(OH)_3Cl$ converted to Cu(OH)Cl when KCl as a promoter was added to the catalyst as evidenced by matching XRD patterns of the catalysts with JCPDS reference files. For the catalysts of (b), (c), (d) and (e), with the amount of γ-$Cu_2(OH)_3Cl$ increasing, the catalytic performance for DEC synthesis improved. But, due to the presence of Cu(OH)Cl in the case of (a), the production of DEC was increased to a distinctly higher level.

The XRD peak intensity of Cu(OH)Cl is not very strong, because of the low loading of copper so that we cannot be sure about the change in the crystal structure. According to the reaction activity test, there must be some essential changes in the active species of the catalyst before and after KCl was added. XP spectra were employed for the analysis of the catalysts to obtain further information of the surface-active species.

3.3. XPS analysis

Fig. 5 illustrates XP spectra of Cu $2p_{3/2}$ of the $CuCl_2$–$PdCl_2$–NaOH/AC and $CuCl_2$–$PdCl_2$–KCl–NaOH

Table 1
Results of XPS analysis for $CuCl_2$–$PdCl_2$–NaOH/AC catalyst

Sample	Binding energy (eV)	Atom (%)
A	932.2	30.3
	934.6	58.6
	936.5	11.1
B	932.2	35.7
	934.6	64.3

(A) With KCl promoter added; (B) without any promoter added.

/AC catalysts. The XPS peaks of the two catalysts were different in shape as well as in intensity. This indicates that the bonding type and energy of Cu in catalysts might be different.

According to Fleet's work [15], paratacamite (γ-$Cu_2(OH)_3Cl$) consists of $Cu(OH)_4Cl_2$ and $Cu(OH)_6$. The ratio of $Cu(OH)_4Cl_2$ and $Cu(OH)_6$ in paratacamite is known to be 3:1. Meanwhile according to Iitaka [16], Cu(OH)Cl consists of $Cu(OH)_3Cl_3$. The structures of $Cu(OH)_4Cl_2$, $Cu(OH)_6$ and $Cu(OH)_3Cl_3$ are single edge-sharing octahedral. Cl–Cu–Cl and OH–Cu–OH are characteristic bonds in paratacamite.

As a result of curve fitting, the $CuCl_2$–$PdCl_2$–NaOH/AC catalyst was found to have two peaks as shown in Fig. 5(a). The first peak (I) was found at 932.2 eV and the second peak (II) at 934.6 eV. Peak I at 932.2 eV was revealed to be attributed to OH–Cu–OH bond, while peak II at 934.6 eV to Cl–Cu–Cl bond. That is, the $CuCl_2$–$PdCl_2$–NaOH/AC catalyst showed the exactly same characteristics of γ-$Cu_2(OH)_3Cl$. However, the relatively stronger intensity of peak I to II imply that the ratio of Cl–Cu–Cl bond to OH–Cu–OH could be 2:1, which is not exactly equal to the characteristics of γ-$Cu_2(OH)_3Cl$. This dissimilarity may be derived from the difference in the content of active species between the surface and bulk phases. On the other hand, the $CuCl_2$–$PdCl_2$–KCl–NaOH/AC catalyst was found to have three peaks at 932.2, 934.6 and 936.5 eV. A new peak (III) at 936.5 eV was attributed to the copper bond in $Cu(OH)_3Cl_3$ octahedra, which compose the Cu(OH)Cl crystals. It is clear that when KCl was added to the catalyst, some of the active species of γ-$Cu_2(OH)_3Cl$ was converted to Cu(OH)Cl.
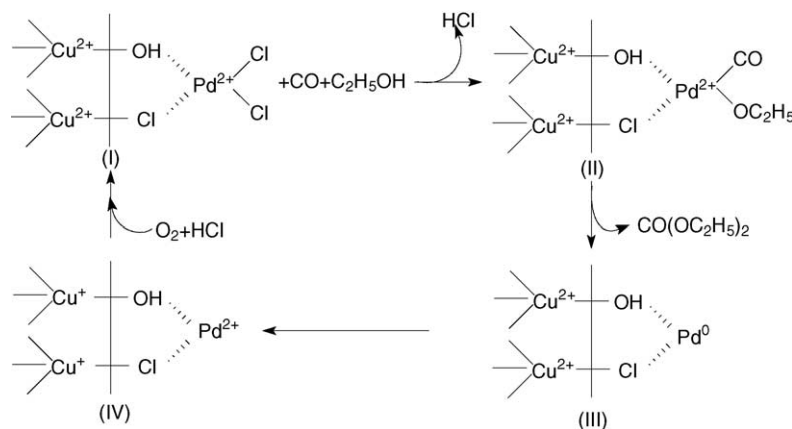

Fig. 6. Schematic reaction scheme for ethanol oxidative carbonylation over the $CuCl_2$–$PdCl_2$–KCl–NaOH/AC catalyst.

Table 1 compared the percentage of different copper species on the catalysts with and without KCl added. Based on these observations, it can be concluded that these XPS analysis results are in a very good accordance with XRD analysis results.

3.4. Reaction mechanism

A general reaction scheme for this supported Wacker-type catalyst is presented in Fig. 6. The Pd(II) species coordinated with the chlorine ligands is assumed to interact weakly with the active copper phase, Cu(OH)Cl, through chlorine and hydroxyl ligands (I). It is attacked by carbon monoxide and ethanol. The coordinated chlorine might be substituted by carbon monoxide and ethoxy group (II). Choi and Vannice [17,18] conducted an infrared study for alumina-supported $PdCl_2$–$CuCl_2$ catalysts and proposed PdClCO as a reaction intermediate. For the same catalyst system, Lee et al. [19] also suggested that carbonyl ligand might be incorporated into palladium on the basis of EXAFS analysis. The production of diethyl carbonate from carbonyl and oxyethyl ligands coordinated to palladium induces the reduction of the Pd(II) species to Pd(0) (III). The cupper atoms of the intermediates (III) and (IV) have different valences of +1 and +2 without any change in the structure. We consider the electron transfer mechanism between Cu(II) and Pd(0) as an "outer-sphere" mechanism. It is an electron rearrangement process. This process follows the Franck–Condon principle [20] that in fast reactions such as electron transfer reactions, there is no time for geometry to change [21,22]. The reduced palladium can be reoxidized by Cu(OH)Cl easily. The last step in this cycle is the reoxidation of the Cu(I) compound into Cu(OH)Cl by O_2 (IV).

A similar mechanism may be valid in the DEC conversion compared with Wacker-type catalysts that Cu(OH)Cl is more efficient than paratacamite in regenerating Pd^0 to Pd^{2+} and reducing Cu^{2+} to Cu^+. Cu(OH)Cl was more active due to the structure of crystals [23–25]. The polyhedron $Cu(OH)_3Cl_3$ present in Cu(OH)Cl has two chloride atoms, which are located in *trans*-positions at a long distance from copper and one atom placed at a very short distance in the very distorted square-plane surrounding copper [26]. This short distance for Cu–Cl bonds, which is due to the important John–Teller effect, make it easy for the electron transfer between the Cu and Pd species. The reduced Pd species can be reoxidized more easily by Cu(OH)Cl to become a more active site for CO oxidation in the synthesis of DEC.

4. Conclusion

The effect of potassium promoters on the activity of $CuCl_2$–$PdCl_2$–NaOH/AC catalyst in the oxidative carbonylation of ethanol to diethyl carbonate was investigated. There were some vital differences in the catalytic activity between KCl and non-KCl promoted catalysts. The conversion of ethanol reached over 30% and the selectivity of ethanol for DEC synthesis was maintained around 95%. The best molar ratio of CO, O_2 and C_2H_5OH as reactants should be 10:1:4.

The analysis by X-ray diffraction and XPS indicated that the improved performance of $CuCl_2$–$PdCl_2$–KCl–NaOH/AC catalysts was closely related to the existence of copper chloride hydroxides (Cu(OH)Cl). It was revealed that γ-$Cu_2(OH)_3Cl$ was changed to Cu(OH)Cl by adding KCl promoter. Cu(OH)Cl is more efficient than γ-$Cu_2(OH)_3Cl$ in regenerating Pd^0 to Pd^{2+} and reducing Cu^{2+} to Cu^+. The improvement in the catalytic performance of the catalyst $CuCl_2$–$PdCl_2$–KCl–NaOH/AC was attributed to the efficient electronic transfer between $PdCl_2$ and Cu(OH)Cl.

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