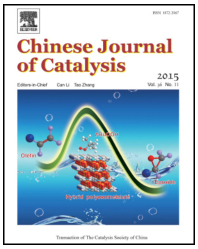
Chinese Journal of Catalysis 36 (2015) 2036–2043

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Article

Catalytic synthesis of diethyl carbonate with supported Pd-Cu bimetallic nanoparticle catalysts: Cu(I) as the active species

Pingbo Zhang, Yan Zhou, Mingming Fan*, Pingping Jiang

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu, China

A R T I C L E I N F O

Article history:
Received 29 August 2015
Accepted 16 September 2015
Published 20 November 2015

Keywords:
Cupric oxide
Copper-cuprous oxide
Diethyl carbonate
Sodium hydroxide concentration
Dosages of glucose
Active species

A B S T R A C T

Cupric oxide (CuO) and copper-cuprous oxide (Cu-Cu_2O) nanoparticles were prepared by a simple hydrothermal method for the synthesis of diethyl carbonate (DEC) from ethanol. During these syntheses, varying NaOH and glucose concentrations were applied to explore and pinpoint the active species. It was found that $PdCl_2$/CuO and $PdCl_2$/Cu-Cu_2O both catalysts exhibited good thermal stability and morphology. The results of catalytic tests showed that the catalysts prepared with 5 mol/L NaOH show superior catalytic performances because of their lower extent of agglomeration. It is noteworthy that the $PdCl_2$/Cu-Cu_2O catalysts were the most active, especially the $PdCl_2$/Cu-Cu_2O catalyst prepared with 10 mmol glucose and having a higher Cu_2O concentration. In Pd(II)-Cu(II) ($PdCl_2$/CuO) catalysts, there is an induction period, during which Pd(II) is reduced to Pd(0), that must occur prior to electron transfer between Pd and Cu, and this can slow the catalytic reaction. To further pinpoint the active species, $PdCl_2$/Cu-Cu_2O catalysts with different Cu_2O contents were prepared by controlling the dosages of glucose. The maximum DEC yield obtained with these catalysts was 151.9 $mg\cdot g^{-1}\cdot h^{-1}$, corresponding to an ethanol conversion of 7.2% and 97.9% DEC selectivity on an ethanol basis. Therefore, it was concluded that Cu^+ was the active species in this catalytic system, possibly because a higher proportion of Cu^+ reduces the Pd^{2+} concentration and limits the CO oxidation side reaction, thus increasing DEC selectivity. In addition, Cu^+ promotes electron transfer between Pd and Cu without an induction period, which could also promote the catalytic activity.

1. Introduction

Diethyl carbonate (DEC) is a fuel oxygenate additive with the potential to replace methyl *tert*-butyl ether (MTBE), and is currently thought to be superior to other alternative additives such as dimethyl carbonate (DMC) and ethanol (EtOH) [1]. DEC has also been considered for applications as a solvent [2] and as a component of a lithium cell electrolyte mixture because of its low toxicity [3,4]. Several commercial processes have been developed for the synthesis of DEC, including; (i) the reaction of highly toxic phosgene gas with EtOH [5], (ii) the oxidative carbonylation of EtOH in the liquid phase [6], (iii) the transesterification reaction of DMC and EtOH [7], (iv) the gas phase oxidative carbonylation of EtOH [1,8], (v) the reaction between carbon monoxide and ethyl nitrite (C_2H_5ONO) [9], (vi) the reaction of EtOH with urea over organotin catalysts [10] and (vii) the activation of carbon dioxide [11]. Among these, the oxidative carbonylation of EtOH in the gas phase is the most

---

* Corresponding author. Tel: +86-510-85917090; Fax: +86-510-85917763; E-mail: fanmm2000@126.com

This work was supported by the National Natural Science Foundation of China (21106054).

DOI: 10.1016/S1872-2067(15)60973-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 11, November 2015

attractive method because it is environmentally benign by nature [1,8,12].

There have been numerous reports concerning the application of chlorine-containing copper catalysts to the synthesis of DEC via the oxidative carbonylation of EtOH [13–18]. Various catalysts have been investigated for this purpose, all of which are prepared by dispersing $CuCl_2$ or $CuCl_2$ and $PdCl_2$ onto supports. Early studies showed that activated carbon (AC) [9,12,14], metal oxides [19] and zeolites [20] may all be used as the support. Subsequently, to reduce problems with equipment corrosion, chlorine-free catalysts were prepared by a solid-state ion exchange method for the synthesis of DEC [21,22]. However, uncertainties regarding the active species in these catalysts still remain. Thus, in early work with DMC catalytic systems, chlorine-free catalysts were prepared by solid-state ion exchange to explore the issues of equipment corrosion and the uncertainty of the active species [23,24]. Cu^+ ions were studied as the active species through experimental observations [23–25] as well as theoretical investigations [26,27]. Later, Cu_2O supported on carbon-based materials was also applied as a chlorine-free catalyst to address the above challenges [28,29]. More recently, nanoscale metal oxides have attracted much attention because of their unique size- and dimensionality-dependent physical and chemical properties [30,31]. Cupric oxide (CuO) and cuprous oxide (Cu_2O) nanostructures are of particular interest because of their interesting properties and promising applications, such as in lithium-ion batteries [32], catalysis [33,34] and CO oxidation [35]. Therefore, copper-based oxides with different valence states might be efficient supports to catalyze the synthesis of DEC in the gas phase, and studies using these material could also assist in elucidating the active species.

In the present work, the goal was to synthesize DEC from EtOH, CO and O_2 in the gas phase over $PdCl_2$-loaded CuO and Cu-Cu_2O prepared with different NaOH concentrations. Unfortunately, the initial results did not identify the active species for the synthesis of DEC. To further investigate such species, $PdCl_2$-loaded Cu-Cu_2O catalysts having a variety of Cu_2O contents were investigated by tuning the glucose concentration. By comparing the catalytic performances of catalysts incorporating different copper species, the active species involved in the gas phase synthesis of DEC were clearly identified.

2. Experimental

2.1. *Catalyst preparation*

Copper chloride (> 99%), sodium hydroxide (98%), hexadecyl trimethyl ammonium bromide (> 99%), ethanol (> 99%), $PdCl_2$ (> 99%) were obtained from Sinopharm Chemical Reagent Co, Ltd, China.

CuO and Cu-Cu_2O nanoparticles were prepared by hydrothermal synthesis based on literature methods [36,37]. In a typical synthesis, 20 mL of a 1 mol/L $CuCl_2\cdot 2H_2O$ solution was added dropwise into 80 mL NaOH and stirred vigorously at 50 °C. Subsequently, 40 mL CTAB (0.25 mol/L) was added and the mixture stirred vigorously at 50 °C for 1 h, after which the reaction mixture was sealed in a stainless steel pressure container and held at 140 °C for 24 h. The resulting product was collected, washed several times with distilled water followed by absolute EtOH and then dried under vacuum to obtain black CuO powder. Different NaOH concentrations (2.5, 5 and 10 mol/L) were used during the preparation. In addition, while employing the optimized NaOH concentration, different concentrations of glucose were added during the preparation process after adding the CTAB so as to prepare brick-red Cu-Cu_2O nanoparticles containing various Cu_2O species. In our previous work, the special roles of Pd and Cu in $PdCl_2$/Cu-HMS catalysts were investigated in detail [16,18]. Therefore, in the present work, catalysts were also prepared by impregnating the CuO or Cu-Cu_2O with a methanol solution of palladium chloride ($PdCl_2$). The total palladium concentration in the final products was 0.25 wt% based on the mass of CuO or Cu-Cu_2O.

2.2. *Catalyst characterization*

The composition and phase of each sample was identified by powder X-ray diffraction (XRD) with a D8 X-ray diffractometer (Bruker AXS, German) using Cu K_α radiation (λ = 1.5406 Å) at a scanning rate of 2°/min from 2θ = 10° to 80°. Thermogravimetric analysis (TGA) of the samples was performed using a Mettler TGA/SDTA 851E analyzer over the temperature range 25 to 800 °C at a heating rate of 10 °C/min under O_2. The morphologies of products were examined by scanning electron microscopy (SEM) with an S-4800 (Hitachi, Japan) scanning electron microscope at an accelerating voltage of 2.0 kV. Inductively couple plasma (ICP) spectrometry using a PE 5300DV was employed to determine the concentrations of metallic palladium in the catalysts. X-ray photoelectron spectroscopy (XPS) was performed with a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI) as a means of analyzing the various metallic species and their valence states.

2.3. *Catalytic performance measurements*

Catalytic activities were measured with a computer-controlled continuous micro-reactor system incorporating a stainless steel tubular reactor with an inner diameter of 8 mm. The reaction conditions were as follows: 3 mL catalyst, 0.1 mL/min liquid EtOH, 10 mL/min O_2, 80 mL/min CO, 50 mL/min N_2, reaction temperature of 150 °C and reaction pressure of 0.64 MPa. The analytical methods used during these trials have been previously reported in detail [16,18].

3. Results and discussion

The catalytic performances during the oxidative carbonylation of EtOH with CO and O_2 over $PdCl_2$/CuO and $PdCl_2$/Cu-Cu_2O catalysts prepared with different NaOH concentrations (2.5, 5 or 10 mol/L) are summarized in Table 1. From these data, it is evident that the product of the catalytic reaction was primarily DEC, together with lesser amounts of

Table 1
The catalytic performances of $PdCl_2/CuO$ and $PdCl_2/Cu\text{-}Cu_2O$ catalysts synthesized using various NaOH concentrations.

Catalyst	NaOH concentration (mol/L)	Conversion of EtOH (%)	STY of DEC (mg·g^{-1}·h^{-1})	Selectivity (%)		
				DEC	AH	EA
$PdCl_2/CuO$	2.5	3.0	63.2	90.8	6.2	3.0
	5	4.5	91.7	92.1	5.2	2.7
	10	2.7	53.8	91.4	6.5	2.1
$PdCl_2/Cu\text{-}Cu_2O$	2.5	4.5	93.7	94.2	3.8	2.0
	5	6.5	133.9	93.8	2.2	4.0
	10	3.2	65.1	91.9	6.1	2.0

Reaction conditions: 150 °C, 0.64 MPa, O_2 10 mL/min, CO 80 mL/min, N_2 50 mL/min.

acetaldehyde (AH) and ethyl acetate (EA). In comparison with other NaOH concentrations, the catalysts prepared with 5 mol/L NaOH showed better catalytic performances. Neupane et al. [36] pointed out that the use of a strong base in the precipitation reaction played a vital role during the catalyst of synthesis. Both low and high NaOH concentrations could lead to free electrons on the surfaces of the CuO and $Cu\text{-}Cu_2O$, possibly resulting in some powder agglomeration and partial coverage of the active sites. In addition, at the same NaOH concentration, the $PdCl_2/Cu\text{-}Cu_2O$ exhibits better catalytic performance than the $PdCl_2/CuO$. As previously reported [8], in the case of Pd(II)-Cu(II) ($PdCl_2/CuO$) catalysts, an induction period during which Pd(II) is reduced to Pd(0) is required prior to electron transfer between Pd and Cu, which might slow the catalytic reaction. Thus the presence of either Cu^0 or Cu^+ is beneficial with regard to improving the catalytic performance.

The phase compositions and structures of the catalysts were evaluated by XRD, with the results shown in Fig. 1. In Fig. 1(a), the diffraction peaks seen in the XRD patterns can be ascribed to pure CuO, and the principal peaks are indexed to the (11$\bar{1}$), (111) and (20$\bar{2}$) reflections, corresponding to the crystal structure of CuO (JCPDS 48-1548). In Fig. 1(b), prominent peaks appear at 43.30°, 50.43° and 74.13° corresponding, respectively, to the (111), (200) and (220) reflections of cubic Cu (JCPDS 04-0836). Weaker features are also seen at 36.42°, 42.30°, 61.34° and 73.53° and these are assigned to the (111), (200), (220) and (311) reflections of cubic Cu_2O (JCPDS 05-0667). Even when employing different NaOH concentrations, the $PdCl_2/CuO$ catalysts exhibit similar XRD patterns, as do the $PdCl_2/Cu\text{-}Cu_2O$ materials, suggesting that the same crystal structures are present, with major crystal planes diffracting at essentially the same 2θ angles.

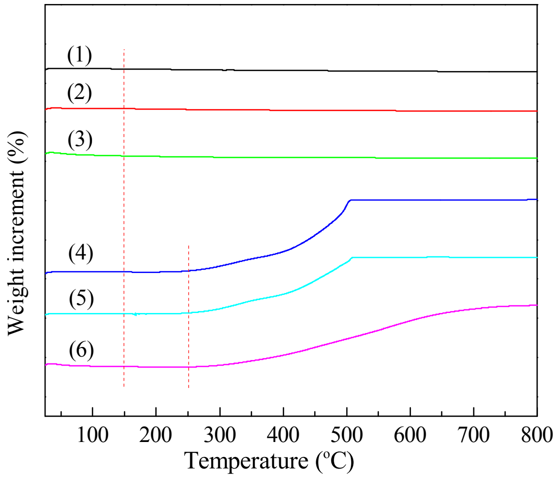


Fig. 2. TG patterns of $PdCl_2/CuO$ (1–3) and $PdCl_2/Cu\text{-}Cu_2O$ (4–6) catalysts synthesizing using different NaOH concentrations. (1, 4) 2.5 mol/L; (2, 5) 5 mol/L; (3, 6) 10 mol/L.

To assess the thermal stability of the catalysts throughout the reaction, TG analysis was performed under O_2 and the resulting data are summarized in Fig. 2. It is evident that there were no mass changes associated with any temperature for the $PdCl_2/CuO$ catalysts, while the $PdCl_2/Cu\text{-}Cu_2O$ catalysts exhibit obvious mass increases beginning at 500 °C. Combined with the XRD analysis, these results indicated that the former materials were composed of pure CuO while the latter were a combination of Cu and Cu_2O.

The morphologies of the catalysts were observed by means of SEM and EDS, and the results are shown in Fig. 3. These images demonstrated that CuO nanorods with rectangular

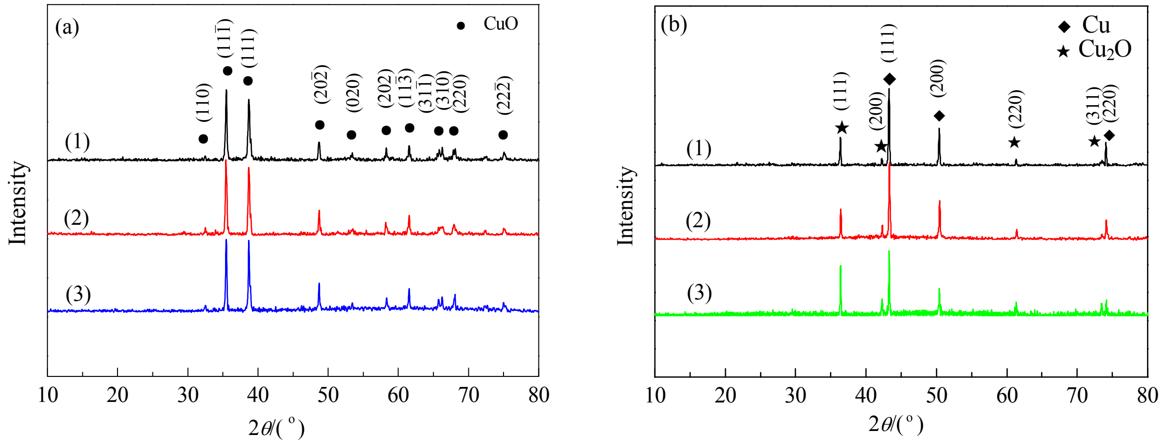


Fig. 1. XRD patterns of $PdCl_2/CuO$ (a) and $PdCl_2/Cu\text{-}Cu_2O$ (b) catalysts synthesized using various NaOH concentrations. (1) 2.5 mol/L; (2) 5 mol/L; (3) 10 mol/L.

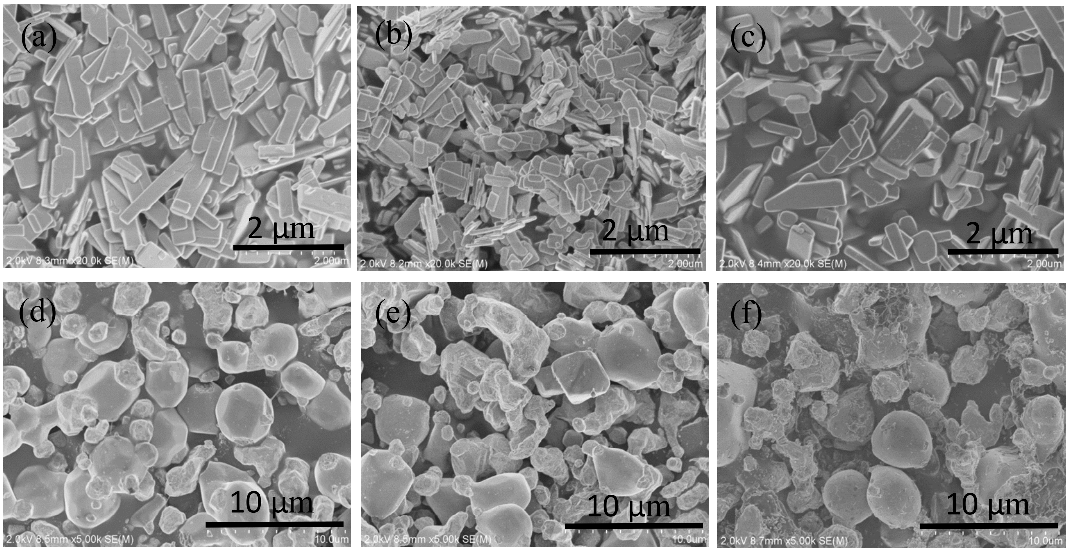


Fig. 3. SEM images of $PdCl_2/CuO$ (a–c) and $PdCl_2/Cu\text{-}Cu_2O$ (d–f) catalysts synthesized at various NaOH concentrations. (a, d) 2.5 mol/L; (b, e) 5 mol/L; (c, f) 10 mol/L.

sections (a–c) were present in the $PdCl_2/CuO$ catalysts, while the $PdCl_2/Cu\text{-}Cu_2O$ catalysts show sphere-like morphologies that might allow greater contact areas during the catalytic reaction. This result suggests one factor affecting the catalytic performance. In conclusion, the $PdCl_2/Cu\text{-}Cu_2O$ exhibited better catalytic performance than the $PdCl_2/CuO$ series of catalysts when the synthesis parameters were identical. It has been reported that copper atoms form the main active site during the synthesis of DEC by oxidative carbonylation of EtOH in the gas phase [38–40], although $PdCl_2$ also plays an important role such that its presence can improve the space time yield (STY) of DEC by a factor of three compared with catalysts without $PdCl_2$ [12]. For this reason, ICP analyses were performed to assess the $PdCl_2$-loadings. The resulting data showed that the $PdCl_2/CuO$ and $PdCl_2/Cu\text{-}Cu_2O$ catalysts both had similar $PdCl_2$ concentrations, at 0.15% and 0.16%, respectively.

Based on the above analysis, it was concluded that the $PdCl_2/Cu\text{-}Cu_2O$ catalyst exhibited better catalytic performance than the $PdCl_2/CuO$, although the main factors responsible for the differing catalytic performance between Cu^0 and Cu^+ remained unknown. Therefore, catalysts with different Cu^0 and Cu^+ contents were prepared for comparison purposes by varying the glucose concentration applied during synthesis. The catalytic performances over the $PdCl_2/Cu\text{-}Cu_2O$ catalysts are summarized in Table 2. From these data, it is evident that the $PdCl_2/Cu\text{-}Cu_2O$ prepared with 10 mmol glucose showed high catalytic performance. The STY for DEC obtained with this material was 151.9 $mg\cdot g^{-1}\cdot h^{-1}$, corresponding to an EtOH conversion of 7.2% and DEC selectivity of 97.9% on an EtOH basis. Additionally, it is worth noting that the selectivity for AH based on EtOH increased with the amount of glucose added. Cu^0 is the main active center during the synthesis of AH, and so these results could imply that the catalyst prepared with 10 mmol glucose had less Cu^0. Ding et al. [25] has reported that a higher ratio of Cu^+ can reduce the Pd^{2+} concentration and limit the CO oxidation side reaction, thus increased the DEC selectivity. This could explain the higher catalytic performance of the $PdCl_2/Cu\text{-}Cu_2O$ catalyst, which had a greater concentration of Cu^+ species. From the above results, it can be concluded that the active species in the synthesis of DEC is Cu^+.

Table 2
Catalytic performances of $PdCl_2/Cu\text{-}Cu_2O$ catalysts synthesized with varying concentrations of glucose (5 mol/L NaOH).

Dosage of glucose (mmol)	Conversion of EtOH (%)	STY of DEC ($mg\cdot g^{-1}\cdot h^{-1}$)	Selectivity (%)		
			DEC	AH	EA
10	7.2	151.9	97.9	0.7	1.4
15	6.8	140.8	96.5	1.2	2.3
20	6.5	133.9	93.8	2.2	4.0

Reaction conditions: 150 °C, 0.64 MPa, O_2 10 mL/min, CO 80 mL/min, N_2 50 mL/min.

Figure 4 displays the XRD patterns of the $PdCl_2/Cu\text{-}Cu_2O$ catalysts. It is well known that glucose is a strong reducing agent, and so Cu_2O can be expected to be further reduced to Cu in the presence of an excess of glucose, such that a two phase composition is produced. The diffraction peaks at 2θ values of 43.30°, 50.43° and 74.13° be assigned to Cu(111), (200) and

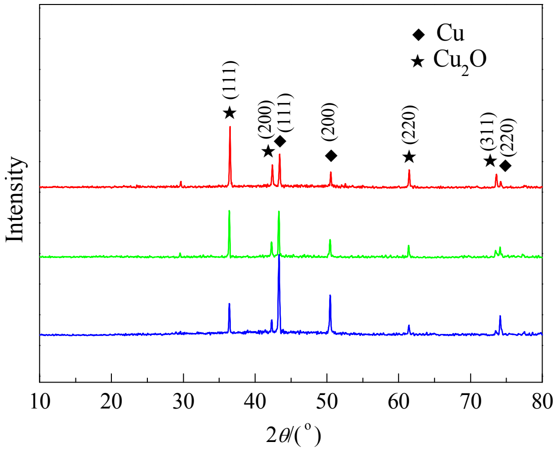


Fig. 4. XRD patterns of $PdCl_2/Cu\text{-}Cu_2O$ catalysts synthesized with varying amounts of glucose. (1) 10 mmol; (2) 15 mmol; (3) 20 mmol.

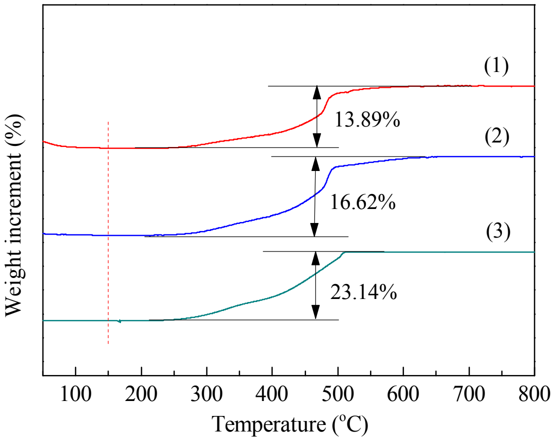


Fig. 5. TG data for $PdCl_2/Cu\text{-}Cu_2O$ catalysts synthesized with varying amounts of glucose. (1) 10 mmol; (2) 15 mmol; (3) 20 mmol.

(220) (JCPDS 04-0836). While the peaks at 36.42°, 42.30°, 61.34°, 73.53° and 77.32° are attributed to the (111), (200), (220), (311) and (222) reflections of Cu_2O (JCPDS 05-0667), respectively. The relative intensities of the Cu_2O diffraction peaks are seen to decrease with increasing glucose amounts, indicating that the $PdCl_2/Cu\text{-}Cu_2O$ catalyst prepared with 10 mmol glucose contained more of the Cu_2O, in accordance with its improved catalytic performance (Table 2). That is to say, the $PdCl_2/Cu\text{-}Cu_2O$ catalyst prepared with 10 mmol glucose had a higher Cu_2O content showed better catalytic performance. Accordingly, Cu^+ was the more active species in comparison with Cu^0.

The thermal stability of each $PdCl_2/Cu\text{-}Cu_2O$ catalyst was assessed by TG between 25 and 800 °C in under O_2, with the results shown in Fig. 5. These data allowed the comparison of experimental and theoretical mass gain rates, assuming that the theoretical mass gain rates were limited by the amounts of Cu and Cu_2O, respectively. That is to say, supposing that the catalyst was composed purely of Cu_2O, the theoretical mass gain rate can be calculated by the chemical equation $2Cu_2O + O_2 \rightarrow 4CuO$ with the same holding true for Cu, in which case the equation is $2Cu+O_2 \rightarrow 2CuO$. Theoretical weight gain rate of Cu is 25.11% and that of Cu_2O is 11.12%. If the theoretical mass gain rate based on Cu_2O is closer to the actual rate, this suggests that the catalyst contained a greater proportion of Cu_2O. The $PdCl_2/Cu\text{-}Cu_2O$ catalyst prepared with 10 mmol glucose had an experimental mass gain rate of 13.89% which was closer to the calculated rate based on Cu_2O of 11.12%, compared with the other catalysts. Thus, the $PdCl_2/Cu\text{-}Cu_2O$ catalyst prepared with 10 mmol glucose had more Cu_2O, which resulted in better catalytic performance, as further confirmed by the XRD analysis.

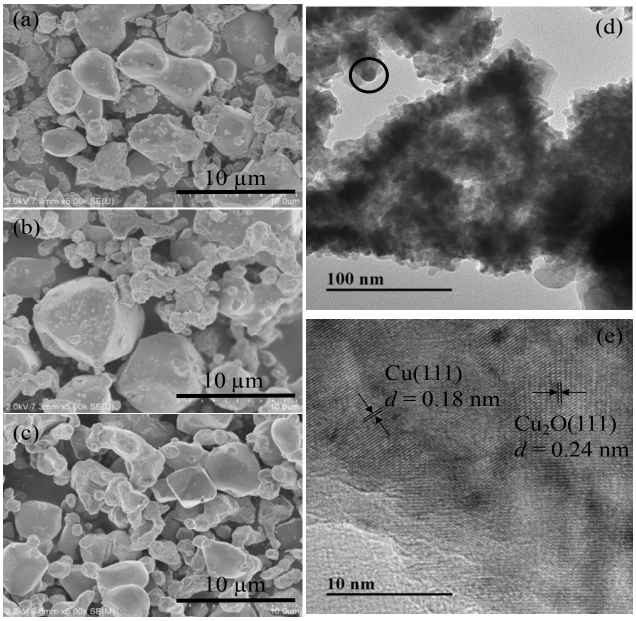


Fig. 6. SEM images of $PdCl_2/Cu\text{-}Cu_2O$ catalysts synthesized with varying amounts of glucose. (a) 10 mmol; (b) 15 mmol; (c) 20 mmol. TEM (d) and HRTEM (e) images of the $PdCl_2/Cu\text{-}Cu_2O$ catalyst synthesized using 10 mmol glucose.

SEM images (Fig. 6(a–c)) of $PdCl_2/Cu\text{-}Cu_2O$ catalysts made with varying amounts of glucose were acquired, and all the catalysts displayed a sphere-like morphology. The low-magnification TEM image in Fig. 6(d) shows the morphology of $PdCl_2/Cu\text{-}Cu_2O$ nanoparticles generated using 10 mmol glucose. Fig. 6(e) is a high-resolution TEM (HRTEM) image taken from the red sphere region in Fig. 6(d), showing that the plane spacings of 0.24 and 0.18 nm correspond to the *d* spacings of $Cu_2O(111)$ and Cu(111), respectively.

The entire XPS spectrum of the $PdCl_2/Cu\text{-}Cu_2O$ catalyst made with 10 mmol glucose is shown in Fig. 7(a), in which both Cu 2*p* and O 1*s* peaks are observed. Fig. 7(b) shows a high resolution view that emphasizes the main Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks of the catalyst. The broad Cu $2p_{3/2}$ peak has been divided into two peaks, attributed to Cu [41] and Cu_2O [42], respectively. It has been reported that $PdCl_2$ plays an important role in catalytic reactions [12], although a metallic Pd peak is not clearly observed in Fig. 7(a) because of the low $PdCl_2$ concentration in the catalyst. Hence, high resolution XPS spectra of the Pd 3*d* (Fig. 7(d)) and Cl 2*p* (Fig. 7(e)) regions of the catalyst are presented to illustrate the presence of $PdCl_2$.

4. Conclusions

Both CuO and $Cu\text{-}Cu_2O$ nanoparticles were successfully synthesized by a simple hydrothermal method and subsequently used as supports to prepare catalysts for the gas phase synthesis of DEC. The results of this work show that catalysts prepared with 5 mol/L NaOH exhibit better catalytic performances because of their low extent of powder agglomeration. It is noteworthy that the $PdCl_2/Cu\text{-}Cu_2O$ showed better catalytic performance than $PdCl_2/CuO$ made at the same NaOH concentration. In Pd(II)-Cu(II) ($PdCl_2/CuO$) catalysts, there is an induction period, during which Pd(II) is reduced to Pd(0), that must occur prior to electron transfer between Pd and Cu, and this can slow the catalytic reaction. To further pinpoint the active species, $PdCl_2/Cu\text{-}Cu_2O$ catalysts with different Cu_2O contents were prepared by controlling the dosages of glucose. XRD, TG and catalytic performance data all

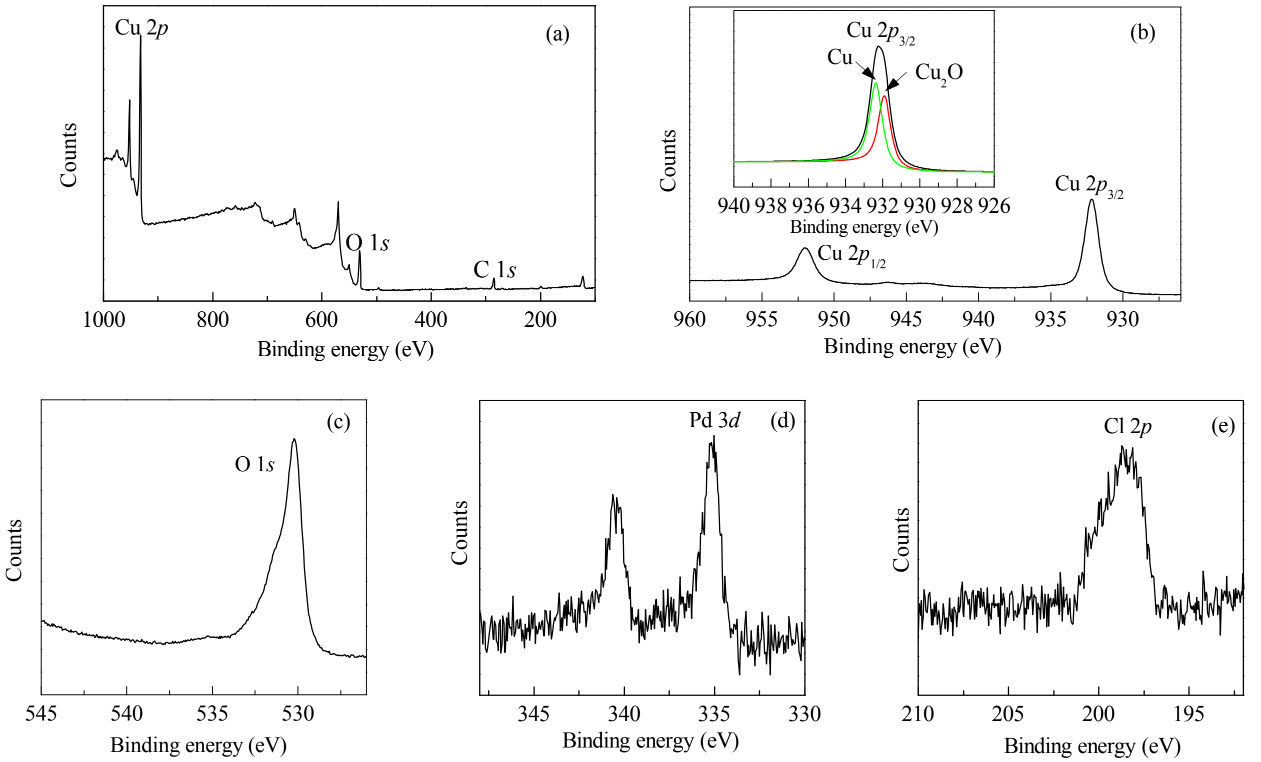


Fig. 7. (a) The complete XPS spectrum and the high-resolution XPS spectra for the (b) Cu 2*p*, (c) O 1*s*, (d) Pd 3*d* and (e) Cl 2*p* regions for $PdCl_2$/Cu-Cu_2O catalysts made with 10 mmol glucose.

indicate that the $PdCl_2$/Cu-Cu_2O catalyst prepared with 10 mmol glucose had more Cu^+ and also showed better catalytic performance. The selectivity for DEC based on EtOH reached 97.9%, together with an EtOH conversion value of approximately 7.2% and a STY for DEC of 151.9 $mg \cdot g^{-1} \cdot h^{-1}$. The higher concentration of Cu^+ in the $PdCl_2$/Cu-Cu_2O catalyst evidently lowered the Pd^{2+} concentration and limited the CO oxidation side reaction, thus DEC selectivity was increased and catalytic performance was enhanced. From the above results, it can be concluded that the active species in the synthesis of DEC is Cu^+. However, it would still be beneficial to study $PdCl_2$/Cu_2O catalysts without Cu in the future to obtain a more complete understanding of this catalyst system.

References

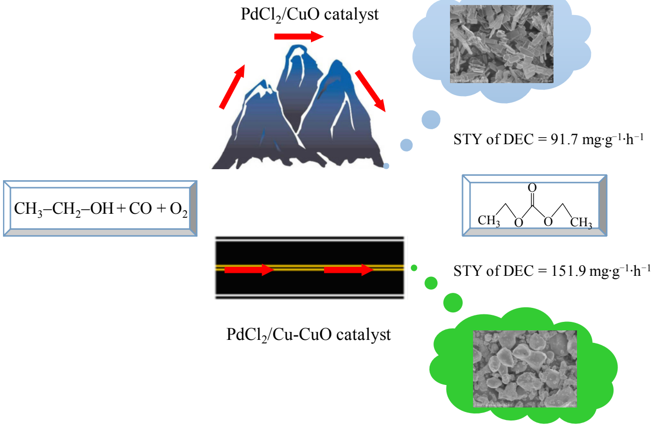
[1] Pacheco M A, Marshall C L. *Energy Fuels*, 1997, 11: 2
[2] Horvath I T. *Green Chem*, 2008, 10: 1024
[3] Moumouzias G, Ritzoulis G, Siapkas D, Terzidis D. *J Power Sources*, 2003, 122: 57
[4] Herstedt M, Stjerndahl M, Gustafsson T, Edstrom K. *Electrochem Commun*, 2003, 5: 467
[5] Muskat I E, Strain F. US Patent 2379250. 1945
[6] Mo W L, Li G X, Zhu Y Q, Xiong H, Mei F M. *Chin J Catal*, 2003, 24: 3
[7] Zielinska-Nadolska I, Warmuzinski K, Richter J. *Catal Today*, 2006, 114: 226
[8] Zhang Z, Ma X B, Zhang J, He F, Wang S P. *J Mol Catal A*, 2005, 227: 141
[9] Gao X C, Ma X B, Wang S P, Li Z H. *Chin J Catal*, 2007, 28: 720
[10] Ryu J Y. US Patent 5902894. 1999
[11] Tomishige K, Sakaihori T, Ikeda Y, Fujimoto K. *Catal Lett*, 1999, 58: 225
[12] Dunn B C, Guenneau C, Hilton S A, Pahnke J, Eyring E M, Dworzanski J, Meuzelaar H L C, Hu J Z, Solum M S, Pugmire R J. *Energy Fuels*, 2002, 16: 177
[13] Briggs D N, Lawrence K H, Bell A T. *Appl Catal A*, 2009, 366: 71
[14] Briggs D N, Bong G, Leong E, Oei K, Lestari G, Bell A T. *J Catal*, 2010, 276: 215
[15] Zhang P B, Huang S Y, Wang S P, Ma X B. *Chem Eng J*, 2011, 172: 526
[16] Zhang P B, Ma X B. *Chem Eng J*, 2010, 163: 93
[17] Huang S Y, Wang Y, Wang Z Z, Yan B, Wang S P, Gong J L, Ma X B. *Appl Catal A*, 2012, 417-418: 236
[18] Zhang P B, Zhang Z, Wang S P, Ma X B. *Catal Commun*, 2007, 8: 21
[19] Zheng H Y, Ren J, Zhou Y, Niu Y Y, Li Z. *J Fuel Chem Technol*, 2011, 39: 282
[20] Richter M, Fait M J G, Eckelt R, Schreier E, Schneider M, Pohl M M, Fricke R. *Appl Catal B*, 2007, 73: 269
[21] Huang S Y, Chen P Z, Yan B, Wang S P, Shen Y L, Ma X B. *Ind Eng Chem Res*, 2013, 52: 6349
[22] Huang S Y, Zhang J J, Wang Y, Chen P Z, Wang S P, Ma X B. *Ind Eng Chem Res*, 2014, 53: 5838
[23] Zhang Y H, Drake I J, Briggs D N, Bell A T. *J Catal*, 2006, 244: 219
[24] Li Z, Wen C M, Zheng H Y, Xie K C. *Chem J Chin Univ*, 2010, 31: 145
[25] Ding X S, Dong X M, Kuang D T, Wang S F, Zhao X Q, Wang Y J. *Chem Eng J*, 2014, 240: 221
[26] Zhang R G, Liu H Y, Zheng H Y, Ling L X, Li Z, Wang B J. *Appl Surf Sci*, 2011, 257: 4787
[27] Zhang R G, Zheng H Y, Wang B J, Li Z. *Chem J Chin Univ*, 2010, 31: 1246
[28] King S T. *Catal Today*, 1997, 33: 173

Graphical Abstract

Chin. J. Catal., 2013, 34: 2036–2043 10.1016/S1872-2067(15)60973-1

Catalytic synthesis of diethyl carbonate with supported Pd-Cu bimetallic nanoparticle catalysts: Cu(I) as the active species

Pingbo Zhang, Yan Zhou, Mingming Fan *, Pingping Jiang
Jiangnan University



The catalytic performances of PdCl$_2$/Cu-Cu$_2$O materials were found to be superior to those of CuO catalysts. The primary reason is believed to be that Cu$^+$ promotes electron transfer between Pd and Cu without the requirement for an induction period, which could potentially enhance the catalytic reaction.

[29] Yan B, Huang S Y, Wang S P, Ma X B. *ChemCatChem*, 2014, 6: 2671
[30] Chen Z W, Jiao Z, Pan D Y, Li Z, Wu M H, Shek C H, Wu C M L, Lai J K L. *Chem Rev*, 2012, 112: 3833
[31] Lignier P, Bellabarba R, Tooze R P. *Chem Soc Rev*, 2012, 41: 1708
[32] Park J C, Kim J, Kwon H, Song H. *Adv Mater*, 2009, 21: 803
[33] Chanda K, Rej S, Huang M H. *Chem Eur J*, 2013, 19: 16036
[34] Li L L, Nan C Y, Peng Q, Li Y D. *Chem Eur J*, 2012, 18: 10491
[35] Zhong Z Y, Ng V, Luo J Z, Teh S P, Teo J, Gedanken A. *Langmuir*, 2007, 23: 5971
[36] Neupane M P, Kim Y K, Park I S, Kim K A, Lee M H, Bae T S. *Surf Interface Anal*, 2009, 41: 259
[37] Cao M H, Hu C W, Wang Y H, Guo Y H, Guo C X, Wang E B. *Chem Commun*, 2003: 1884
[38] Zhang Z, Ma X B, Zhang P B, Li Y M, Wang S P. *J Mol Catal A*, 2007, 266: 202
[39] Zheng X B, Bell A T. *J Phys Chem C*, 2008, 112: 5043
[40] Engeldinger J, Domke C, Richter M, Bentrup U. *Appl Catal A*, 2010, 382: 303
[41] Radi A, Pradhan D, Sohn Y, Leung K T. *ACS Nano*, 2010, 4: 1553
[42] Ghodselahi T, Vesaghi M A, Shafiekhani A, Baghizadeh A, Lameii M. *Appl Surf Sci*, 2008, 255: 2730

Page numbers refer to the contents in the print version, which include both the English version and extended Chinese abstract of the paper. The online version only has the English version. The pages with the extended Chinese abstract are only available in the print version.