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Article

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

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ABSTRACT

Cupric oxide (CuO) and copper-cuprous oxide (Cu-Cu₂O) 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 PdCl₂/CuO and PdCl₂/Cu-Cu₂O 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 PdCl₂/Cu-Cu₂O catalysts were the most active, especially the PdCl₂/Cu-Cu₂O catalyst prepared with 10 mmol glucose and having a higher Cu₂O concentration. In Pd(II)-Cu(II) (PdCl₂/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, PdCl₂/Cu-Cu₂O catalysts with different Cu₂O contents were prepared by controlling the dosages of glucose. The maximum DEC yield obtained with these catalysts was 151.9 mg·g⁻¹·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 Pd²⁺ 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.

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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 (C₂H₅ONO) [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

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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 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 $\text{Cu-Cu}_2\text{O}$ 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 $\text{Cu-Cu}_2\text{O}$ 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 $\text{Cu-Cu}_2\text{O}$ nanoparticles were prepared by hydrothermal synthesis based on literature methods [36,37]. In a typical synthesis, 20 mL of a 1 mol/L $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 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 $\text{Cu-Cu}_2\text{O}$ nanoparticles containing various Cu_2O species. In our previous work, the special roles of Pd and Cu in $\text{PdCl}_2/\text{Cu-HMS}$ catalysts were investigated in detail [16,18]. Therefore, in the present work, catalysts were also prepared by impregnating the CuO or $\text{Cu-Cu}_2\text{O}$ 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 $\text{Cu-Cu}_2\text{O}$.

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 $\text{Cu } K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of $2^\circ/\text{min}$ from $2\theta = 10^\circ$ 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 $10^\circ\text{C}/\text{min}$ 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 $\text{PdCl}_2/\text{Cu-Cu}_2\text{O}$ 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 PdCl₂/CuO and PdCl₂/Cu-Cu₂O 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-Cu ₂ O	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, O₂ 10 mL/min, CO 80 mL/min, N₂ 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-Cu₂O, possibly resulting in some powder agglomeration and partial coverage of the active sites. In addition, at the same NaOH concentration, the PdCl₂/Cu-Cu₂O exhibits better catalytic performance than the PdCl₂/CuO. As previously reported [8], in the case of Pd(II)-Cu(II) (PdCl₂/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 Cu⁰ 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 (111), (111) and (202) 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°,

Fig. 2. TG patterns of PdCl₂/CuO (1–3) and PdCl₂/Cu-Cu₂O (4–6) catalysts synthesizing using different NaOH concentrations. (1, 4) 2.5 mol/L; (2, 5) 5 mol/L; (3, 6) 10 mol/L.

42.30°, 61.34° and 73.53° and these are assigned to the (111), (200), (220) and (311) reflections of cubic Cu₂O (JCPDS 05-0667). Even when employing different NaOH concentrations, the PdCl₂/CuO catalysts exhibit similar XRD patterns, as do the PdCl₂/Cu-Cu₂O materials, suggesting that the same crystal structures are present, with major crystal planes diffracting at essentially the same 2θ angles.

To assess the thermal stability of the catalysts throughout the reaction, TG analysis was performed under O₂ and the resulting data are summarized in Fig. 2. It is evident that there were no mass changes associated with any temperature for the PdCl₂/CuO catalysts, while the PdCl₂/Cu-Cu₂O 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 Cu₂O.

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 PdCl₂/CuO (a) and PdCl₂/Cu-Cu₂O (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 PdCl₂/CuO (a–c) and PdCl₂/Cu-Cu₂O (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 PdCl₂/CuO catalysts, while the PdCl₂/Cu-Cu₂O 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 PdCl₂/Cu-Cu₂O exhibited better catalytic performance than the PdCl₂/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 PdCl₂ 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 PdCl₂ [12]. For this reason, ICP analyses were performed to assess the PdCl₂-loadings. The resulting data showed that the PdCl₂/CuO and PdCl₂/Cu-Cu₂O catalysts both had similar PdCl₂ concentrations, at 0.15% and 0.16%, respectively.

Based on the above analysis, it was concluded that the PdCl₂/Cu-Cu₂O catalyst exhibited better catalytic performance than the PdCl₂/CuO, although the main factors responsible for the differing catalytic performance between Cu⁰ and Cu⁺ remained unknown. Therefore, catalysts with different Cu⁰ and Cu⁺ contents were prepared for comparison purposes by varying the glucose concentration applied during synthesis. The catalytic performances over the PdCl₂/Cu-Cu₂O catalysts are summarized in Table 2. From these data, it is evident that the PdCl₂/Cu-Cu₂O prepared with 10 mmol glucose showed high catalytic performance. The STY for DEC obtained with this

material was 151.9 mg·g⁻¹·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. Cu⁰ 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 Cu⁰. Ding et al. [25] has reported that a higher ratio of Cu⁺ can reduce the Pd²⁺ concentration and limit the CO oxidation side reaction, thus increased the DEC selectivity. This could explain the higher catalytic performance of the PdCl₂/Cu-Cu₂O 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⁺.

Figure 4 displays the XRD patterns of the PdCl₂/Cu-Cu₂O catalysts. It is well known that glucose is a strong reducing agent, and so Cu₂O 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 PdCl₂/Cu-Cu₂O catalysts synthesized with varying amounts of glucose. (1) 10 mmol; (2) 15 mmol; (3) 20 mmol.

Table 2

Catalytic performances of PdCl₂/Cu-Cu₂O catalysts synthesized with varying concentrations of glucose (5 mol/L NaOH).

Dosage of glucose (mmol)	Conversion of EtOH (%)	STY of DEC (mg·g ⁻¹ ·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, O₂ 10 mL/min, CO 80 mL/min, N₂ 50 mL/min.

Fig. 5. TG data for PdCl₂/Cu-Cu₂O 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 Cu₂O (JCPDS 05-0667), respectively. The relative intensities of the Cu₂O diffraction peaks are seen to decrease with increasing glucose amounts, indicating that the PdCl₂/Cu-Cu₂O catalyst prepared with 10 mmol glucose contained more of the Cu₂O, in accordance with its improved catalytic performance (Table 2). That is to say, the PdCl₂/Cu-Cu₂O catalyst prepared with 10 mmol glucose had a higher Cu₂O content showed better catalytic performance. Accordingly, Cu⁺ was the more active species in comparison with Cu⁰.

The thermal stability of each PdCl₂/Cu-Cu₂O catalyst was assessed by TG between 25 and 800 °C in under O₂, 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 Cu₂O, respectively. That is to say, supposing that the catalyst was composed purely of Cu₂O, the theoretical mass gain rate can be calculated by the chemical equation 2Cu₂O + O₂ → 4CuO with the same holding true for Cu, in which case the equation is 2Cu + O₂ → 2CuO. Theoretical weight gain rate of Cu is 25.11% and that of Cu₂O is 11.12%. If the theoretical mass gain rate based on Cu₂O is closer to the actual rate, this suggests that the catalyst contained a greater proportion of Cu₂O. The PdCl₂/Cu-Cu₂O catalyst prepared with 10 mmol glucose had an experimental mass gain rate of 13.89% which was closer to the calculated rate based on Cu₂O of 11.12%, compared with the other catalysts. Thus, the PdCl₂/Cu-Cu₂O catalyst prepared with 10 mmol glucose had more Cu₂O, which resulted in better catalytic performance, as further confirmed by the XRD analysis.

SEM images (Fig. 6(a–c)) of PdCl₂/Cu-Cu₂O 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 PdCl₂/Cu-Cu₂O 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

Fig. 6. SEM images of PdCl₂/Cu-Cu₂O catalysts synthesized with varying amounts of glucose. (a) 10 mmol; (b) 15 mmol; (c) 20 mmol. TEM (d) and HRTEM (e) images of the PdCl₂/Cu-Cu₂O catalyst synthesized using 10 mmol glucose.

that the plane spacings of 0.24 and 0.18 nm correspond to the *d* spacings of Cu₂O(111) and Cu(111), respectively.

The entire XPS spectrum of the PdCl₂/Cu-Cu₂O 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 2*p*_{3/2} and Cu 2*p*_{1/2} peaks of the catalyst. The broad Cu 2*p*_{3/2} peak has been divided into two peaks, attributed to Cu [41] and Cu₂O [42], respectively. It has been reported that PdCl₂ 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 PdCl₂ 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 PdCl₂.

4. Conclusions

Both CuO and Cu-Cu₂O 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 PdCl₂/Cu-Cu₂O showed better catalytic performance than PdCl₂/CuO made at the same NaOH concentration. In Pd(II)-Cu(II) (PdCl₂/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, PdCl₂/Cu-Cu₂O catalysts with different Cu₂O 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 2p, (c) O 1s, (d) Pd 3d and (e) Cl 2p regions for PdCl₂/Cu-Cu₂O catalysts made with 10 mmol glucose.

indicate that the PdCl₂/Cu-Cu₂O 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·g⁻¹·h⁻¹. The higher concentration of Cu⁺ in the PdCl₂/Cu-Cu₂O catalyst evidently lowered the Pd²⁺ 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 PdCl₂/Cu₂O catalysts without Cu in the future to obtain a more complete understanding of this catalyst system.

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Graphical Abstract

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Catalytic synthesis of diethyl carbonate with supported Pd-Cu bimetallic nanoparticle catalysts: Cu(I) as the active speciesPingbo Zhang, Yan Zhou, Mingming Fan*, Pingping Jiang
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The catalytic performances of PdCl₂/Cu-Cu₂O 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.

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负载型Cu-Pd双金属纳米氧化物催化剂催化合成碳酸二乙酯： Cu(I)作为活性中心

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摘要: 催化反应活性与催化剂活性组分的存在价态密切相关, 所以探讨催化剂在反应过程中的活性中心及其价态变化, 对于催化反应机理和催化剂的研究都显得十分重要。目前对于氧化羰基合成碳酸二甲酯催化剂的机理的探讨很多, 主要存在的争议是Cu⁺还是Cu²⁺作为活性中心, 以及铜物种的配位状态。大多体系都是以分子筛为载体的铜基催化剂, 其活性中心的研究存在铜离子在分子筛中的定位问题, 而且催化活性也会受到分子筛结构的影响。采用这种方法研究活性中心的影响因素较多, 存在一定的局限性。因此, 直接制备纳米级的铜基氧化物用于本催化体系, 有利于更直观简单地探索其活性中心。

纳米级金属氧化物材料是一种新型的功能性材料, 而纳米铜基氧化物(CuO和Cu₂O)因其独特的物化性质和结构而引起广泛关注。我们采用水热法制备纳米CuO及其它氧化物, 研究了NaOH浓度对催化剂的催化性能的影响; 葡萄糖是一种还原性较强的还原剂, 其用量必定会对所制备的氧化物的物种有所影响。为了探究Cu⁰和Cu⁺在本体系中的作用, 采用不同葡萄糖用量制备了具有不同Cu₂O含量的PdCl₂/Cu-Cu₂O催化剂。

在上述研究基础上, 我们采用X射线衍射、场发射扫描电子显微镜、热重分析、等离子体原子发射光谱等表征手段研究了负载型纳米铜基氧化物催化剂在合成碳酸二乙酯反应中催化性能差异的原因, 旨在直接考察活性中心主要是Cu⁺还是Cu²⁺, 避免分子筛等体系中载体结构的影响, 研究结果更具参考性。

结果发现, NaOH浓度为5 mol/L时制备的PdCl₂/CuO和PdCl₂/Cu-Cu₂O催化剂的性能优于其他浓度下制备的催化剂, 这可能是由于不同浓度的碱溶液会对铜离子的沉淀过程产生不同的影响; 相同NaOH浓度下制备的催化剂中, PdCl₂/Cu-Cu₂O催化剂的催化性能明显优于PdCl₂/CuO催化剂, 这可能是由于PdCl₂/Cu-Cu₂O催化剂更有利于反应过程中电子的传递, 从而表现出更好的催化

性能, 我们推测 Cu^0 和 Cu^+ 可能更有利催化乙醇氧化羰基合成DEC; 表征分析发现 PdCl_2/CuO 和 $\text{PdCl}_2/\text{Cu-Cu}_2\text{O}$ 均具有很好的热稳定性, 两种催化剂中 PdCl_2 负载量几乎相同, 因此, 主要影响催化性能的因素是载体 CuO 和 $\text{Cu-Cu}_2\text{O}$ 中铜的价态.

采用不同葡萄糖用量制备了含有不同 Cu_2O 含量的 $\text{PdCl}_2/\text{Cu-Cu}_2\text{O}$ 催化剂, 其中, $\text{PdCl}_2/\text{Cu-Cu}_2\text{O-2}$ 催化剂中含有更多的 Cu_2O , 在反应中乙醇转化率达到7.2%, DEC的选择性为97.9%, DEC的时空收率可达到 $151.9 \text{ mg}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. 由此可见在乙醇气相氧化羰基合成DEC体系中, Cu^+ 是主要的活性中心.

关键词: 氧化铜; 铜-氧化亚铜; 碳酸二乙酯; 氢氧化钠浓度; 葡萄糖用量; 活性中心

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