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Oxidative carbonylation of glycerol to glycerol carbonate catalyzed by $PdCl_2(phen)/KI$

Jianglin Hu^a, Jinjin Li^a, Yanlong Gu^{a,b}, Zhenhong Guan^a, Wanling Mo^a, Youming Ni^a, Tao Li^{a,b}, Guangxing Li^{a,b,*}

^a School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan, Hubei 430074, PR China ^b Hubei Key Laboratory of Material Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, PR China

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ABSTRACT

We present a direct and highly efficient approach for synthesizing glycerol carbonate, via the catalytic oxidative carbonylation of glycerol, using $PdCl_2(phen)$ (phen = 1,10-phenanthroline) as catalyst with the aid of KI. The palladium catalyst loading as low as 0.25 mol% is sufficient for high conversion (92%) and selectivity (99%) at the reaction condition: 2.0 MPa CO, 1.0 MPa O₂, 140 °C, 2 h. The turnover frequency (TOF) reaches 184 h⁻¹. Furthermore, using crude glycerol, we achieved 85% conversion of glycerol. We discuss in detail a plausible mechanism based on PdI₂(phen) as an intermediate. We propose that there is synergistic effect of I⁻ and 1,10-phenanthroline on the performance of the Pd complex catalyst. Based on the cyclic voltammograms, the reduction of $PdI_2(phen)$ occurred at a more positive potential than that of $PdCl_2(phen)$. This may explain why the catalytic activity of $PdI_2(phen)$ was more effective than that of $PdCl_2(phen)$.

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1. Introduction

The large surplus of bio-glycerol generated by the biodiesel industry has gained considerable attention. Using bio-glycerol as a raw material for the production of value-added chemicals may extend and broaden the practical applications of biomass energy sources. Therefore, it is both important and desirable [1–3]. It is possible to transform glycerol into various glycerol derivatives, including acrolein [4], glycerol ether [5], and 1,2-propanediol [6]. Glycerol can also be used directly as a solvent [7]. However, further research is needed to in order to develop new and innovative processes using glycerol.

Glycerol carbonate, an important glycerol derivative, can be polymerized or reacted with isocyanates or acrylates for use in coatings, adhesives and lubricants [8]. Glycerol carbonate's low toxicity, low evaporation rate, low flammability, and moisturizing properties make it ideal for use as a solvent in cosmetics, personal care items, and medicine [9]. Furthermore, glycerol carbonate is a valuable intermediate for the production of glycidol, used in resins, plastics, and throughout the pharmaceutical and cosmetics industries [10]. Glycerol carbonate may also be used in place of ethylene and propylene carbonates as a main ingredient of an electrolyte of secondary batteries, like lithium ion batteries [11].

Several methods for the synthesis of glycerol carbonate have been described. These methods are commonly based on the reaction of glycerol with carbonyl sources like phosgene [12], dialkyl carbonate [13–15], alkylene carbonate [16], urea [17], and CO_2 [18,19]. However, transesterification is not entirely appropriate because alkylene carbonate is typically prepared through a petrochemical process. The direct carboxylation of glycerol with CO_2 is an interesting process that can transform two waste products into a valuable product. However, it produces a low glycerol carbonate yield. Therefore, finding a new, direct and highly efficient approach for synthesizing glycerol carbonate is important.

Oxidative carbonylation is one of the most important reactions in the field of organic transformations. The reaction can produce a variety of oxygen-containing compounds, particularly carbonates [20–24]. The wide availability of CO and the attractiveness of the process in light of its high atom economy and environmental friendliness merit further study.

Herein, we report a direct and highly efficient approach for synthesizing glycerol carbonate via the oxidative carbonylation of glycerol using $PdCl_2(phen)$ (phen = 1,10-phenanthroline) as catalyst with the aid of KI (Scheme 1). In addition, we evaluate the mechanistic pathway using the possible intermediate $Pdl_2(phen)$ as a direct catalyst in the catalytic cycle. To the best of our knowl-

^{*} Corresponding author at: School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan, Hubei 430074, PR China. Tel.: +86 27 87543732; fax: +86 27 87544532.

E-mail address: ligxabc@163.com (G. Li).

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Scheme 1. Catalytic oxidative carbonylation of glycerol to glycerol carbonate.

edge, this promising result has not previously been reported for the synthesis of glycerol carbonate in the literature.

2. Experimental

2.1. Catalyst preparation

2.1.1. PdCl₂(phen)

PdCl₂(phen) was synthesized according to the literature [25] with some modifications. The mixture of a suspension of PdCl₂ (1.46 mmol) and KCl (2.92 mmol, 2 eq.) in methanol (10 mL) was stirred at room temperature overnight, and a brown yellow solid (K_2 PdCl₄) was generated. Then, 10 mL of water was added and the solid was dissolved. Finally 1,10-phenanthroline monohydrate(phen·H₂O) (1.46 mmol) was added, and the pH adjusted to 4.47 with hydrochloric acid (37 wt%). The resulting

pinkish yellow suspension was stirred at 40 °C for 1 h, then filtered, washed with cold water, and dried in a vacuum. A light yellow complex was obtained.

2.1.2. $PdI_2(phen)$ and $[Pd(phen)_2][PF_6]_2$

 $Pd(OAc)_2$ (0.25 mmol) dissolved in ethanol/H₂O (10 mL, 1:1, v/v) was mixed with a 10 mL ethanol solution containing KI (0.60 mmol; I/Pd = 2.4) and phen·H₂O (0.25 mmol). After 30 min the resulting precipitated pinkish brown product was filtered, washed with ethanol, and dried in a vacuum [25]. The [Pd(phen)₂][PF₆]₂ was synthesized according to the literature [26].

2.2. Catalytic oxidative carbonylation of glycerol

The catalytic reactions were carried out in a 250 mL stainless steel autoclave lined with Teflon and equipped with a mechani-



Fig. 1. GC–MS chromatogram of silylated sample obtained after oxidative carbonylation of glycerol: (a) GC chromatogram; (b) MS, 1,2,3-Tris-(trimethylsilyloxy)- propane (silylated glycerol); (c) MS, 4-(((trimethylsilyl)oxy)methyl)-1,3-dioxolan-2-one(silylated glycerol carbonate); (d) MS, bis(2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonan-5-yl) carbonate (silylated bis(1,3-dihydroxypropan-2-yl) carbonate).

Table	1

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Entry	Catalyst	Glycerol:catalyst molar ratio	Conversion (%)	Selectivity ^b (%)	TOF^{c} (h^{-1})
1	CuCl	10	4.4	93	0.22
2 ^d	CuCl/phen	10	6.8	95	0.34
3 ^d	CuI/phen	10	8.4	95	0.42
4	PdCl ₂	200	47	96	47
5	PdCl ₂ (phen)	200	36	96	36
6 ^e	PdCl ₂ (phen)/PPh ₃	200	42	98	42
7 ^f	PdCl ₂ (phen)/CuCl ₂	200	56	97	56
8 ^g	PdCl ₂ (phen)/KI	200	92	>99	92
9 ^g	PdCl ₂ (phen)/KI	400	92	99	184
10 ^g	PdCl ₂ /KI	200	58	96	58
11 ^{g,h}	PdCl ₂ (phen)/KI	400	85	98	170

^a Reaction conditions: solvent DMF 30 mL, glycerol 4.60 g (50 mmol), CO 2.0 MPa, O₂ 1.0 MPa, 140 °C, 2 h, stirring speed 800 rpm.

^b The possible byproduct was bis(1,3-dihydroxypropan-2-yl) carbonate (see Fig. 1d).

^c TOF (mol converted glycerol/mol cat. h).

^d Cu:phen = 1:1 (molar ratio).

^e Pd:PPh₃ = 1:1 (molar ratio).

^f Pd:CuCl₂ = 1:5 (molar ratio).

^g Pd:KI = 1:10 (molar ratio).

^h Using industrial grade glycerol 5.75 g (80 wt% glycerol, generally contains about 15 wt% of water and 5 wt% of soap).

cal stirrer. In the experiment, 44.7 mg (0.125 mmol) PdCl₂(phen), 207.5 mg (1.25 mmol, 10 eq.) KI, 30 mL N,N-dimethyl formamide (DMF) solvent, and 4.60 g (50 mmol) glycerol were loaded into the reactor. The autoclave was purged three times with CO and then pressurized to 3.0 MPa with CO and O_2 (*P*(CO):*P*(O_2)=2:1) at room temperature. The reaction was carried out at 140 °C for 2 h. During the reaction, the CO and O_2 mixture was added to maintain a total pressure of 3.0 MPa. After the reaction, the reactor was cooled to room temperature and depressurized.

Safety advice: Although oxidative carbonylation of methanol has been industrialized by ENIchem for 30 years [20] and no security incident has been reported up to date, high-pressure carbonylation experiments with compressed gases represent a significant safety risk and should only be conducted in conjunction with the use of suitable equipment and special care.

Gas chromatography analyses were performed in an Agilent GC 1790 apparatus equipped with a HP-5 ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu \text{m}$) capillary column and a flame ionization detector (FID). The sample taken after reaction of 0.50g was weighed into 5 mL tubes with caps. 2.00g of silyl reagent (a 3:1:9 hexamethyldisilazane, trimethylchlorosilane, and pyridine mixture) was added and the tubes were closed, gently agitated for 5 min and allowed to incubate at room temperature for 30 min. A white, NH₄Cl precipitate was formed, and 40 mg of cumene was added as an internal stan-



Fig. 2. Effect of temperature on oxidative carbonylation catalyzed by $PdCl_2(phen)/KI$, glycerol/Pd = 400 molar ratio, CO 2.0 MPa, O_2 1.0 MPa, 2 h, stirring speed 800 rpm. (a) Conversion of glycerol and (b) selectivity of glycerol carbonate.

dard. The mixture was centrifuged at 2500 rpm for 5 min and the clear supernatant was analyzed with gas chromatography.

GC-MS analyses were performed in an Agilent 6890/5973 GC-MS apparatus equipped with a split/splitless injection system and a flame ionization detector (FID). The capillary column was an Agilent HP-5MS, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu \text{m}$. Oven temperature started at 50 °C and was increased to 260 °C at a rate of 20 °C/min. Helium was used as the carrier gas (1.0 mL/min). The GC-MS chromatogram of silvlated samples is shown in Fig. 1. MS (m/z) (1) silylated glycerol: 293 (M⁺-CH₃), 263 (M⁺-3CH₃), 218 (M⁺-6CH₃), 205 (M⁺-CH₂OSi(CH₃)₃), 191 (M⁺-CH₂OSi(CH₃)₃-2CH₃), 175 (M⁺-CH₂OSi(CH₃)₃-3CH₃), 147 (M⁺-CH₂OSi(CH₃)₃-Si(CH₃)₃), 117 $(M^{+}-Si(CH_{3})_{3}), 103 (CH_{2}OSi(CH_{3})_{3}^{+}), 101 (M^{+}-OSi(CH_{3})_{3}^{+}), 89$ $(OSi(CH_3)_3^+)$, 73 $(Si(CH_3)_3^+)$; (2) silvlated glycerol carbonate: 189 (M⁺-1), 175 (M⁺-CH₃), 160 (M⁺-2CH₃), 145 (M⁺-3CH₃), 131 (M⁺-Si(CH₃)₂), 116 (M⁺-Si(CH₃)₃), 103 (CH₂OSi(CH₃)₃⁺), 101 $(M^+-OSi(CH_3)_3^+)$, 89 $(OSi(CH_3)_3^+)$, 73 $(Si(CH_3)_3^+)$. The bis(1,3dihydroxypropan-2-yl) carbonate byproduct was also detected (see Fig. 1d).

2.3. Electrochemical properties

Cyclic voltammetry (CV) was utilized to elucidate the electrochemical behavior of the palladium complexes. CV measurement was performed in DMF using tetrabutylammonium tetrafluoroborate (n-Bu₄NBF₄, 0.1 M = 0.1 mol L⁻¹) as the supporting electrolyte with an Electrochemical Workstation CS300 at 20 °C. A conventional three-electrode system was employed. A stationary platinum-disk served as the working electrode, and a large platinum foil was used as the counter electrode. A commercial saturated calomel electrode (SCE) was used as the reference electrode. Current-voltage curves were measured at 0.1 V s⁻¹. All potentials were reported in volts *vs* SCE. The palladium complex's concentration was 1 mM. All measurements were performed in well-deaerated solutions under nitrogen atmosphere.

3. Results and discussion

3.1. The catalytic performance of different catalysts

Glycerol carbonate was prepared by oxidative carbonylation of glycerol with CO (2.0 MPa) and O₂ (1.0 MPa) using different catalyst systems, in presence of a DMF solvent at 140 °C. The results are presented in Table 1. Initially, CuCl was employed as the catalyst. The catalytic efficiency was very low (TOF was only 0.22 h^{-1}), even

when using a nitrogen-containing ligand (1,10-phenanthroline, phen) that has proven effective in promoting both the activity and selectivity of the CuCl-based system for the synthesis of dimethyl carbonate [24]. This result was consistent with the work of Teles et al. reported in a US patent in 1994 [27].

Recently, a number of oxidative carbonylation reactions have been achieved with various palladium catalysts [21,23], perhaps the most active and versatile in organic synthesis [28]. Therefore, a simple palladium salt, PdCl₂, and its 1,10-phenanthroline complex PdCl₂(phen), were adopted. Remarkably, we observed a considerable improvement in the conversion of glycerol compared with that of CuCl-based system (Table 1, entries 4 and 5). It should be noted that decomposition of the catalyst, i.e., reduction of Pd²⁺ to Pd⁰, occurred in the case of PdCl₂. Palladium black was deposited on the bottom of the Teflon tube after the reaction. However, it was not observed in the case of PdCl₂(phen), which may be attributed to the ligand phen. The ligand may prevent Pd⁰ from being deposited as the bulk metal palladium black [29]. Furthermore, when PPh₃ and CuCl₂ were introduced into the PdCl₂(phen) system as cocatalysts, the conversion and selectivity were moderately enhanced. When the reaction was performed on 0.5 mol% PdCl₂(phen) with the aid of KI, we observed a considerable improvement in the reaction rate along with a high conversion of glycerol (92%) and selectivity of glycerol carbonate (>99%). Moreover, with a catalyst loading as low as 0.25 mol%, high conversion and selectivity were achieved, and the TOF reached 184 h⁻¹. To the best of our knowledge, this attractive result has not yet been reported for the synthesis of glycerol carbonate. For comparison, the PdCl₂/KI catalyst system [30] was also examined in this reaction. We found that 58% glycerol was converted, considerably lower than occurred when using PdCl₂(phen)/KI.

Considering the possible commercial uses of this process, we also carried out the reaction using industrial grade, crude glycerol, which is more economical and eco-friendly. Fortunately, the impurities present in crude glycerol do not significantly change its physical properties or the activity of the palladium catalyst. We obtained a very good result using crude glycerol: the conversion and selectivity were 85% and 98%, respectively (Table 1, entry 11).

Table 2

Effect of pressure on oxidative carbonylation of glycerol catalyzed by $\mbox{PdCl}_2(\mbox{phen})/\mbox{Kl}^a.$

Entry	P_{total} (MPa)	$P(CO)/P(O_2)$	Conversion (%)	Selectivity (%)	$TOF^{b}(h^{-1})$
1	2.0	2:1	23	97	46
2	2.5	2:1	67	98	134
3	3.0	2:1	92	99	184
4	3.5	2:1	94	99	188

^a Reaction conditions: solvent DMF 30 mL, glycerol 4.60 g (50 mmol), PdCl₂(phen) 0.125 mmol (glycerol/Pd = 400 molar ratio), KI 1.25 mmol, 10 eq., 140 °C, 2 h, stirring speed 800 rpm.

^b TOF (mol converted glycerol/mol cat. h).

3.2. Effect of temperature on the oxidative carbonylation of glycerol

We also studied the effect of varying the temperature from $110 \,^{\circ}$ C to $160 \,^{\circ}$ C (Fig. 2). Below $120 \,^{\circ}$ C, only a small amount of glycerol carbonate was obtained. From $120 \,^{\circ}$ C to $140 \,^{\circ}$ C, the conversion and yield increased rapidly, reaching a maximum value at $140 \,^{\circ}$ C. Above $140 \,^{\circ}$ C, the conversion and selectivity decreased. Stahl reported that at higher temperatures the palladium complex was prone to rapid decomposition that consequently decreased the activity [28]. Indeed, we found that the palladium black was deposited at the bottom of the Teflon tube after the reaction when it was carried out at $160 \,^{\circ}$ C, resulting in the low catalytic activity.

3.3. Effect of pressure on the oxidative carbonylation of glycerol

The results obtained by varying the pressure are shown in Table 2. We found that there is a significant relationship between the conversion of glycerol and total pressure. Since the total pressure varied from 2.0 to 3.5 MPa at the same CO/O_2 ratio, using 0.125 mmol PdCl₂(phen)/1.25 mmol KI, the glycerol conversion increased notably from 23% to 92%. After 3.0 MPa, increasing the pressure had little impact on the conversion rate.



Fig. 3. Proposed mechanism for oxidative carbonylation of glycerol.

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Table 3 Comparison of different Pd-catalysts in oxidative carbonylation^a

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P				
Entry	Catalyst system	Conversion (%)	Selectivity (%)	TOF ^b (h ⁻¹
1 ^c	PdCl ₂ (phen)/KI	92	99	184
2	PdI ₂ (phen)	65	99	130
2d	PdI ₂ (phen)/KI	87	99	174

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^a Reaction conditions: solvent DMF 30 mL, glycerol 4.60 g (50 mmol), palladium catalyst 0.125 mmol (glycerol/Pd = 400 molar ratio), CO 2.0 MPa, O₂ 1.0 MPa, 140 °C, 2 h, stirring speed 800 rpm.

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^b TOF (mol converted glycerol/mol cat. h).

 $[Pd(phen)_2][PF_6]_2$

^c Pd:KI = 1:10 (molar ratio).

^d Pd:KI = 1:8 (molar ratio).

4. Proposed mechanism

Taking into account what we know about the Pd-catalyzed oxidative carbonylation reaction mechanism [21,30], we propose a plausible mechanism for the oxidative carbonylation of glycerol to glycerol carbonate catalyzed by PdCl₂(phen)/KI (Fig. 3). In this catalytic cycle, formation of an intermediate PdI₂(phen) species I takes place through the halide anion exchange of PdCl₂(phen) with KI, which may be transformed into the ((1,3-dihydroxypropan-2-yl)oxy)palladium(II) iodide 1,10-phenanthroline complex II via the abstraction of H⁺ from the glycerol OH group. The glyceroxycarbonyl intermediate III is generated by reaction of II and CO. The species III then undergoes intramolecular nucleophilic displacement by the second hydroxyl group and is convert into the palladiouscycle derivative IV by eliminating of HI. Reductive elimination eventually leads to the final product, glycerol carbonate, and [Pd⁰(phen)] species V. [Pd⁰(phen)] is then reoxidized to PdI₂(phen), involving the initial oxidation of HI by O₂ to give I₂ followed by the oxidative addition of the latter to [Pd⁰(phen)].

The additional experiments using $PdI_2(phen)$ $[Pd(phen)_2][PF_6]_2$ as catalysts were carried out in the oxidative carbonylation of glycerol. As summarized in Table 3, PdI₂(phen) exhibited high catalytic activity and a 65% conversion rate. This percentage increased to 87% when KI was used as a cocatalyst. This was comparable to the percentage obtained with PdCl₂(phen)/KI. However, $[Pd(phen)_2][PF_6]_2$, an excellent catalyst in the carbonylation of styrene [26] or nitrobenzene [29], had low catalytic activity in this reaction. It is worth mentioning that a long induction period (about 30 min) was observed when the reaction was carried out using PdCl₂(phen)/KI as the catalyst. This can be explained by the slow halide anion exchange of PdCl₂(phen) with KI. With these results in hand, we consider the proposed mechanism was reasonable. Indeed, iodide is one of the "softest" ligands, binding more strongly to soft metals (low oxidation state, polarizable, and electron rich, such as the later transition metals), than do the other halides. Hence in a catalytic cycle that includes these metals in low oxidation states, the metal is less likely to precipitate and will be removed from the cycle in the presence of I- when compared with most other ligands [31]. Furthermore, the 1,10-phenanthroline ligand significantly enhances the oxidation rate of palladium(0), i.e., $[Pd^{0}(phen)]$ by I₂. Therefore, the synergistic effect of I⁻ and 1,10-phenanthroline in the PdCl₂(phen)/KI system ultimately causes in the high catalytic performance in the reaction, whereas $[Pd(phen)_2][PF_6]_2$ does not.

Finally, in the cyclic voltammograms of $PdCl_2(phen)$ and $PdI_2(phen)$, 1 mM in DMF, we observed two set of reduction peaks: at ca. -1.0V vs SCE (R_1) and -1.4V vs SCE (R_2) attributed to $PdCl_2(phen)$ (Fig. 4a), and at ca. -0.9V vs SCE (R_1') and -1.2V vs SCE (R_2') attributed to $PdI_2(phen)$ (Fig. 4b). The reduction of $PdI_2(phen)$ had a more positive potential than that of $PdCl_2(phen)$. Similar results was obtained for $PdX_2(PPh_3)_2$ (X = Cl, I) [32]. These



Fig. 4. Cyclic voltammogram performed in DMF $(0.1 \text{ M} n-Bu_4\text{NBF}_4)$ at a stationary platinum-disk electrode with a scan rate of 0.1 V s^{-1} , at $20 \degree \text{C}$: (a) PdCl₂(phen)(1 mM) and (b) Pdl₂(phen) (1 mM).

results could explain why the catalytic activity of PdI₂(phen) was more effective than that of PdCl₂(phen) [33].

5. Conclusion

In conclusion, we showed that glycerol carbonate can be readily synthesized via the catalytic oxidative carbonylation of glycerol using PdCl₂(phen) as catalyst with the aid of KI, even when using crude glycerol. Excellent conversion (92–94%), selectivity (>99%), and TOF(184–188 h⁻¹) were achieved using 2.0 MPa CO, 1.0 MPa O₂ at 140 °C with a very low dosage of palladium catalyst (0.25 mol%). We discussed in detail a plausible mechanism using PdI₂(phen) as an intermediate, and the I⁻ and 1,10-phenanthroline ligands have a synergistic effect on the catalytic performance of palladium. In general, the catalytic oxidative carbonylation of glycerol to glycerol carbonate would not only present a new platform to valorize glycerol but also offer an attractive way to conduct environmentally friendly organic synthesis.

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