



Article Highly Efficient Electrocatalytic Carboxylation of 1-Phenylethyl Chloride at Cu Foam Cathode

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Abstract: A simple and efficient electrocatalytic carboxylation of benzyl chloride with CO_2 is described. The reaction operates under 1 atm CO_2 and room temperature in an undivided cell with Cu foam cathode and Mg sacrificial anode without any additional catalyst. For the model compound 1-phenylethyl chloride, the influence of cathode material, solvent, charge, current density and temperature were investigated. Under optimized conditions, 99% yield of 2-phenylpropionic acid could be obtained. Moreover, reasonable yields were also achieved with other benzyl chlorides.

Keywords: electrocatalytic; carboxylation; carbon dioxide; benzyl chlorides; Cu foam

1. Introduction

 CO_2 reutilization is regarded as a plausible strategy to recycle the waste CO_2 emissions from energy-intensive industrial activities [1,2]. Therefore, a number of strategies for CO_2 fixation are being developed, despite its thermodynamic stability and kinetic inertness [3–7]. CO_2 can be used as a simple renewable feedstock for various high-value-added chemicals such as methanol, formic acid, methane, urea, organic carbonates, and carboxylic acid derivatives [3]. Among them, carboxylic acids have widespread applications, which are widely used in the synthesis of bioactive compounds and value-added chemicals [8].

Conventionally, organometallic nucleophiles such as Grignard reagents were used to synthesize carboxylic acids from CO₂. However, such reaction processes generate a large amount of waste regents [6,7]. Electrocarboxylation may use clean electricity for the synthesis of carboxylic acids, providing a worthy alternative [9–22]. The electrocatalytic reduction of organic halides on different cathodes (Pt, Zn, Hg, Sn, Bi, Pb, Au, Cu, Ag) had been studied by Bellomunno and coworkers [23], who showed that the group 11 metals have good catalytic properties towards this reduction process. Many researchers also demonstrated that a silver electrode has extraordinary electrocatalytic effect for carboxylation of halogenated compounds [14–20], which was also confirmed by our previous work [14,15]. In the subsequent research, it was found that silver nanoparticles (Ag NPs) exhibit better electrocatalytic activity than silver flakes [16]. On the other hand, Cu, being low cost compared to noble metals, is one of the most effective electrodes for CO₂ reduction reaction [24,25]. The potential use of Cu electrode for the electrocarboxylation of organic chlorides has not been demonstrated before.

In this work, we report the electrochemical carboxylation of 1-phenylethyl chloride (1a) with Cu foam electrode, avoiding the use of noble metals and catalysts (Figure 1). We showed that CO_2 can be converted into carboxylic acids on the Cu foam electrode under mild conditions. In addition, Ag–Cu dendrite electrode was used for the first time in the electrocarboxylation of 1-phenylethyl chloride to study the effect of cathode material.



Figure 1. Electrocatalytic carboxylation of 1-phenylethyl chloride with CO₂ at Cu foam.

2. Results and Discussion

2.1. Characterization of Electrode Materials

The Cu foam and bimetallic Ag–Cu electrode were characterized by many methods. Figure 2b displays the XRD patterns of Cu foam, the (111), (200) and (220) crystal faces were observed. It is notable that no trace of any other substance such as copper oxide or cuprous oxide was contained in this material. The FE–SEM patterns (Figure 2a) of the Cu foam revealed that this electrode has a porous network structure, indicating large active area. The SEM pattern of bimetallic material Ag–Cu obtained at 10 mM AgNO₃ for 10 min was shown in Figure 2c; the dendrites uniformly formed and almost covered the whole electrode surface, which had been confirmed by energy dispersive X-Ray fluoresence spectrometer (EDX, Figure 2d).



Figure 2. Characterization of Cu foam and Ag–Cu: SEM of Cu foam (**a**) and Ag–Cu (**c**); XRD of Cu foam (**b**); EDX of Ag–Cu (**d**).

2.2. Electrocarboxylation of 1-Phenylethyl Chloride

The typical electrocatalytic carboxylation was carried out in 0.05 M 1-phenylethyl chloride (1a, as model substrate) in 10 mL CO₂-saturated tetraethylammonium iodide–acetonitrile (TEAI–MeCN) solution, with Cu foam as the cathode and sacrificial magnesium (Mg) as the anode (Figure 1). After electrolysis, the products were detected quantitatively by HPLC. The results showed that 2-phenylpropionic acid (2a) was the main product. The effects of various parameters on the process such as cathode material, the solvent, the current density (*J*), the charge passed (*Q*) and the temperature (*T*) were investigated. The results of the electrolysis are summarized in Table 1.

To study the effect of the electrode material, the reaction was firstly carried out at Cu foam electrode. 73% yield of 2a can be obtained (Table 1, entry 1). Since it is reported that Ag-based nanocatalysts [26–31] were efficient in the one-electron reductive cleavage of C–X bonds [31], the Ag–Cu dendrite electrode was synthesized and applied to the reaction. The yield of 2a obtained with Ag–Cu dendrite electrode was higher than that with Ag flake electrode (Table 1, entries 2, 3), which is consistent with our previous study [16]. However, it is lower than that with Cu foam electrode (Table 1, entries 1, 2). In order to explain this phenomenon, cyclic voltammetry (CV) was used to study the reaction.

The cyclic voltammograms were recorded in 0.1 M TEABF₄–MeCN solution at a sweep rate of 0.1 V s⁻¹ (Figure 3). Firstly, the CV of the background was scanned on the Ag electrode, and oxidation–reduction peaks have not been found (curve a). Then, 1-phenylethyl chloride (1a, 4 mM) was added into the electrolyte solution, an irreversible reduction peak appeared which corresponds to $2e^-$ reduction of 1a [17]. Compared to the reduction of 1a on Ag disk electrode (curve b), a more positive onset potential was observed on Cu disk (curve c), which indicates that the reduction occurs more easily at Cu electrode. To some extent, this result can explain the above phenomena. However, the specific reasons are still in further study.

Entry	Cathode	J (mA/cm ²)	Q (F/mol)	Т (°С)	Yield ^b (%)
1	Cu foam	5	2.0	18	73
2	Ag–Cu	5	2.0	18	64
3	Ag flake	5	2.0	18	57
4 ^c	Cu foam	5	2.0	18	6
5	Cu foam	7	2.0	18	77
6	Cu foam	8	2.0	18	84
7	Cu foam	9	2.0	18	87
8	Cu foam	11	2.0	18	78
9	Cu foam	13	2.0	18	75
10	Cu foam	9	1.0	18	45
11	Cu foam	9	1.5	18	68
12	Cu foam	9	2.5	18	92
13	Cu foam	9	3.0	18	93
14	Cu foam	9	2.5	35	83
15	Cu foam	9	2.5	0	94
16	Cu foam	9	2.5	-10	99

Table 1. Electrocarboxylation of 1-phenylethyl chlorides under different conditions. ^a

^a Electrolyses were carried out in undivided cell, Mg anode, electrolyte solution: MeCN (10 mL)–TEAI (0.1 M)–substrate (0.05 M). ^b Determined by HPLC. ^c Dimethylforamide DMF as solvent.

The CVs also showed that Ag electrode has a greater current density, indicating a greater electroreduction rate at Ag electrode. To increase the reaction rate at Cu electrode, Cu foam instead of Cu flake was used. Greater reaction rate on Cu foam than that on Cu flake has been confirmed by constant potential electrolysis. Constant potential electrolysis was carried out under peak potential of 1-phenylethyl chloride reduced on Cu electrode (ca. -1.18 V) with Cu foam and Cu flake cathode, respectively. After the consumption of 70 C charges, the current was switched off. The resulting *Q*-*t* curves (Figure 4) show that the time required on the Cu foam is shorter, about 4/5 of that on the Cu

flake electrode. In addition, a slightly higher yield of the target product was obtained on the Cu foam electrode (Table S1). Hence, Cu foam was used as cathode in the next study.



Figure 3. Cyclic voltammograms of 4 mM 1-phenylethyl chloride recorded at different cathodes in 0.1 M TEABF₄–MeCN solution at a sweep rate of 0.1 V s⁻¹ at 18 °C saturated with N₂ (a) background; (b) Ag disk; (c) Cu disk.



Figure 4. *Q*–*t* curve on different cathode (a) Cu foam, (b) Cu flake.

Solvents have their own physical chemical and electrochemical properties, and many electrochemical reactions are affected by the nature of the solvents. Thus, the influence of solvent has been studied. The electrolysis was conducted in both MeCN and DMF (Table 1, entries 3, 4). The results show that higher 2a yield was obtained in MeCN which may be attributed to the larger solubility of CO_2 in MeCN compared with DMF [32].

The current density and charge passed during electrolyses also influenced the yield of 2a. In fact, both low and high current densities led to lower yields (Table 1, entries 3, 5–9). The results obtained at low current densities can probably be ascribed to side reactions such as the reduction CO_2 to C1 or C2 compounds [33,34]. The results at high current densities can be ascribed to a lower current efficiency with increased ohmic component. The highest yield of 2a was achieved with 9 mA/cm² current density and 2.5 F mol⁻¹ charge of 1a (92%, Table 1, entry 12). With further increase of consumed charge, the yield of 2a increased insignificantly.

The temperature can be a key factor for this reaction, which mainly affect the thermodynamics and kinetics of the reaction as well as the solubility of CO_2 [32]. Therefore, the effects of the reaction temperature were examined (Table 1, entries 12, 14–16). Increasing the temperature from -10 °C to 35 °C, the yield of 2a decreased. The highest yield of 2a was obtained at -10 °C (99%, Table 1, entry 16), a relatively low temperature. That is mainly because carbon dioxide is one of the raw materials of the reaction, and its solubility increases with decreasing temperature. It is worth emphasizing that the Cu foam cathode generated very good results for electrocatalytic carboxylation of 1-phenethyl chloride. Even at room temperature 18 °C, normal pressure, 92% yield of 2a could be achieved (Table 1, entry 12).

The results of this work may be comparable with literature data on the electrocarboxylation of ArCH(CH₃)Cl. We have previously reported on the electrocarboxylation of 1-phenethyl bromide with CO₂ at a Ag NP electrode [16]. Best yield (98%) of 2a was obtained at 273 K using 5 mA cm⁻² current density and 2.5 F mol⁻¹ charge. Under the optimized conditions, with 1-phenethyl chloride as substrate, the yield of 2a was 86%. Isse and coworkers studied the electrocatalytic reduction of arylethyl chlorides at silver cathodes in the presence of carbon dioxide, the acid yields were 70–81% at 273.15 K [18]. They also reported electrochemical carboxylation of arylethyl chlorides catalysed either by nickel(I) Schiff base complexes or by radical anions derived from aromatic esters, and yielded acids in the range of 26–88% [22]. Tateno and coworkers developed a novel electrochemical carboxylation system for CO₂ fixation to benzyl halides using a microreactor. In this system, 52–98% yield of acids was obtained with Pt anode [12]. The acid yields reported in this work are well comparable with these data. On the other hand, the use of noble metals and catalysts were avoided.

2.3. Electrocarboxylation of Other Benzyl Chlorides

Encouraged by excellent results obtained with 1-phenethyl chloride (1a), the reaction was further studied under the conditions of Table 1 entry 12, with the following organic halides: chlorodiphenylmethane (1b), benzyl chloride (1c), 2-methylbenzyl chloride (1d), 3-methylbenzyl chloride (1e), 4-methylbenzyl chloride (1f), 4-methoxybenzylchloride (1g), 4-trifluoromethylbenzyl chloride (1h), chlorobenzene (1i) and 2-chloronaphthalene (1j). The results are reported in Table 2.

In the case of 1b, 80% yield of 2b was obtained (Table 2, entry 2), lower than that of 2a (Table 2, entry 1). That is mainly due to the larger steric hindrance of the phenyl group as compared to a methyl group. When the methyl group of 1a was substituted by a H atom, namely 1c, 83% yield of 2c was achieved (Table 2, entry 3). The lower yield of 2c might be attributed to a side reaction (e.g., dimerization) of 1c.

To study the effect of different substituted positions on the reaction, three isomers of o-, m- and p-methylbenzyl chloride (1d–1f) were used as substrate, and the corresponding carboxylic acid yields were 85%, 88% and 72%, respectively (Table 2, entries 4–6). The yields of 2d (entry 4) and 2e (entry 5) are comparable to that of 2c (entry 3), whereas the yield 2f (entry 6) is lower than that of 2c. This indicates that the electron-donating group located at the ortho and meta positions of the halo group has little effect on the reactivity of the C–X bond, while it has a passivation effect on the reactivity of the C–X bond, while it has a passivation effect on the reactivity of the C–X bond at the para-position. In order to confirm this conclusion, benzyl chlorides substituted by an electron-donating group (–OCH₃) and an electron-withdrawing group (–CF₃) at the para positions have been studied (entries 7, 8). Low yield was obtained with the electron-donating group (–OCH₃), while high yield was achieved with the electron-withdrawing group (–CF₃). The results are consistent with the above conclusion.

As for chlorobenzene (1i) and 2-chloronaphthalene (1j), no supposed carboxylic acid (2i, 2j) could be detected (entries 9, 10). That is mainly because the C–X bonds of 1i and 1j were not easily broken (p, π -conjugate effect), and because of the unfavourable reaction to form carboxylic acid.

Entry	Substrate		Product	Product	
1	CI	1a	Соон	2a	92
2	CI	1b	СООН	2b	80
3	CI	1c	Соон	2c	83
4	CI	1d	СООН	2d	85
5	CI	1e	СООН	2e	87
6	CI	1f	Соон	2f	72
7	H ₃ CO	1g	Н3СО СООН	2g	76
8	F ₃ C CI	1h	F ₃ C COOH	2h	88
9	CI	1i	СООН	2i	_
10	CI	1j	СООН	2j	—

Table 2. Electrocatalytic carboxylation of different substrates on Cu foam cathode.^a

^a Electrolyses were carried out under the same conditions as Table 1, entry 12. ^b Determined by HPLC.

3. Materials and Methods

3.1. Materials and Instruments

All benzyl chlorides and acids were commercially available from J&K Chemical Co. (Beijing, China). MeCN and DMF were kept over 4-Å molecular sieves. All other reagents were used as received. Galvanostatic electrosynthesis was performed using a digital direct current-regulated power supply (HY3005MT, Hangzhou, China). Voltammetric measurements were conducted using the CHI650C electrochemical station (Chenhua, Shanghai, China) in a conventional three-electrode cell. The product yield was determined by high-performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) (Thermo Scientific, Germering, Germany) equipped with a UV (RS Variable Wavelength) (Thermo Scientific, Germering, Germany) detector. Microstructure and morphology of Cu foam and Ag–Cu were analyzed using Hitachi SU8000/S4800 field-emission scanning electron microscope (FE–SEM) (Hitachi, Tokyo, Japan) equipped with an energy dispersive X-Ray fluoresence spectrometer (Ametek, Oxford, UK). X-ray diffraction (XRD) (Rigaku Corporation, Tokyo, Japan) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K α radiation (k = 1.5406 Å).

3.2. General Procedure of Electrode Treatment and Preparation

Cu foam was cut into a circle (d = 2 cm) by mould and then cleaned successively with HCl (2 M), acetone and deionized water in an ultrasound reactor for 5 min. After drying, the Cu foam could be used as working electrode.

The Ag–Cu dentrite was prepared according to literature [35]. The treated Cu foam was immersed in 10 mM AgNO₃ solution without any surfactant for 10 min in the dark avoiding Ag photoreduction.

The resulting dendritic Ag–Cu was washed with deionized water and ethanol 3 times, then dried for 24 h at 35 °C under vacuum. After that, dendritic Ag–Cu was used as the cathode for electrolysis.

3.3. General Process of Cyclic Voltammetry

Cyclic voltammetric studies were undertaken with CHI650C electrochemical workstation (Chenhua, Shanghai, China). A conventional three-electrode cell was employed with Cu (r = 1 mm) and Ag (r = 1 mm) disk working electrode, a platinum sheet (1 cm \times 2 cm) counter electrode and a Ag/AgI/0.1 mol L⁻¹ TBAI reference electrode, scanning for the electrochemical behavior of 1-phenylethyl chloride (4 mM) at different cathodes with a sweep rate of 0.1 V s⁻¹ in a nitrogen atmosphere.

3.4. General Electrolysis Procedure

A typical galvanostatic electrolysis was carried out in a mixture of 1-phenylethyl chloride (50 mM), supporting electrolyte TEAI (0.1 M) and 10 mL MeCN saturated with CO₂ (1 atm) in an undivided glass cell equipped with a sacrificial magnesium (Mg) rod anode and Cu foam cathode (r = 1 cm). Continuous CO₂ flow was maintained throughout the duration of the whole electrolysis process. After consuming a charge of 2.0 F mol⁻¹, the current was switched off. MeCN was removed by rotary evaporation, then the rest was hydrolyzed with HCl (0.2 M, 15 mL) and extracted with Et₂O (20 mL) 3 times, and the organic layers were washed with H₂O, dried over MgSO₄, and then evaporated. The main features of the aimed products were identified by HP 6890/5973N GC/MS (Agilent, USA) and the yields were determined by high-performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump).

3.5. General Process of Constant-Potential Electrolysis

The potentiostatic electrolysis was carried out in a mixture of 1-phenylethyl chloride (50 mM), supporting electrolyte TEAI (0.1 M) and 10 mL MeCN saturated with CO_2 (1 atm) in an undivided glass cell equipped with a sacrificial magnesium (Mg) rod counter electrode, Cu flake (1.5 cm × 2 cm) and Cu foam working electrode (r = 1 cm), and Ag/AgI/0.1 mol L⁻¹ TBAI reference electrode. Continuous CO_2 flow was maintained throughout the duration of the whole electrolysis process. Electrolytic potential is the peak potential of 1-phenylethyl chloride reduction on Cu electrode (ca. -1.18 V); after the consumption of 70 C charges, the current was switched off. Post-processing and detection are the same as galvanostatic electrolysis.

4. Conclusions

In conclusion, a Cu foam electrode was effective for the electrocatalytic carboxylation of 1-phenylethyl chloride. 99% yield of 2-phenylpropionic acid was obtained under optimized conditions. Moderate-to-good yields were also achieved with other benzyl chlorides. Considering the high effectiveness, the economic benefits and the bigger availability of Cu foam cathode, we believe that the synthesis method described in this study has good potential for practical applications.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/7/273/s1, Figure S1: Cyclic voltammograms of 4 mM 1-phenylethyl chloride recorded at different cathodes in 0.1 M TEABF4-MeCN soultion at a sweep rate of 0.1 V s⁻¹ at 18 °C saturated with N2 (a) background; (b) Ag disk; (c) Cu disk. Table S1: Constant potential electrolysis on different cathode ^a.

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