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Cu-Ni Alloy Catalyzed Electrochemical Carboxylation of Benzyl Bromide with Carbon Dioxide in Ionic Liquid 1-Butyl-3-methylimidazolium tetrafluoroborate

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A novel, direct and efficient electroreduction method of benzyl bromide in ionic liquid $BMIMBF_4$ has been developed by potentiostatic electrolysis. Under the atmospheric pressure of CO_2, the electrosynthesis was performed in an undivided cell with Cu-Ni cathode and Al anode. A moderate yield (39.4%) of ethyl phenylacetate **1** as the principal product was obtained, accompanied astonishingly by yield (4.6%) of benzyl ether **2**. Synthetic factors such as electrode material, working potential and electric charge were found to influence the carboxylation yields. The results indicate that the porous structure Cu-Ni alloy electrode with different adsorption energies for CO_2 and benzyl bromide played an ensemble effect role in the reaction efficiency and products distribution. Moreover, the ionic liquid was successfully recycled and a plausible reaction mechanism was proposed.

Keywords: Benzyl bromide; Carbon dioxide; Ionic liquid; Electrocarboxylation; Cu-Ni alloy

1. INTRODUCTION

Since the first industrial revolution, the global average temperature has raised by approximately 0.6℃ and is projected to continue its grow rapidly [1,2]. Carbon dioxide is a largest cutthroat for the global warming, and a great deal of carbon dioxide has been continuously emitted into atmosphere from increasing consumption of fossil fuel and expansion of industrial processes, which is becoming a serious environmental issue today. Thus, utilization or removing CO_2 from industrial emissions have attracted considerable attention and become an interesting topic in the whole world [3-7]. From an environmental viewpoint, CO_2 is an attractive C1 building block in organic synthesis because it is an abundant, inexpensive, nontoxic, and nonflammable carbon resource that can sometimes replace toxic chemicals such as phosgene, isocyanates or CO [8-10]. However, the direct synthesis process remains impractical and insufficient because of activation thermodynamic limitations (ΔG_f^o=-396KJ/mol) and kinetic inertness of CO_2 [11-13]. In contrast to conventional chemical reactions, an electrochemical method has become one of the efficient routes because CO_2 activation could be easily achieved via electrochemical reaction at mild conditions.

Ethyl phenylacetate is an important compound which had been widely used as intermediate in the chemical, medicinal and agricultural industries because of its excellent physicochemical property and low toxicity [14,15]. In classical organic synthesis, synthesis methods of ethyl phenylacetate requiring toxic and harmful reagents under high temperature and pressure have many drawbacks [16,17]. Electrocarboxylation of benzyl halide has been studied by several researchers, but their reaction solvents are usually selected from organic solvents such as CH_3CN and DMF [18-20]. Their reaction yields may be high, but the disadvantages of these methods are the difficulty in handing toxic solvent residues. In addition, with the growing demand of environmental sustainable development, any effort should be devoted to avoid the use of toxic and damaging solvents.

In recent years, ionic liquids have received considerable attention as “green” reaction media in catalysis, material, energy, extraction process and organic synthesis because they exhibit appreciable advantages such as good solvent power, negligible volatility, low toxicity, thermal and chemical stability [21-25]. However, to the best of our knowledge, systematic studies concerning the electrochemical reduction of benzyl bromide with CO_2 in ionic liquids have not been reported yet. In this paper, for the first time, we report the approach of electrosynthesis of ethyl phenylacetate from benzyl bromide and CO_2. We have unexpectedly found benzyl ether besides ethyl phenylacetate in the synthetic products. The electroreduction of CO_2 occurred at a mild potential in the presence of $BMIMBF_4$ and a plausible reaction mechanism was proposed.

2. EXPERIMENTAL

2.1 Chemicals and reagents

$BMIMBF_4$ (99%) was purchased from Chengjie ionic liquid company of Shanghai (China). The ionic liquid prior to use was dried over basic alumina for at least 6 hours, then transferred into vacuum drying box at 120 °C for 12 hours, until cyclic voltammogram result indicated that there was not detectable water. Benzyl bromide (Reagent Plus, 99%) was purchased from Xiyu Chemical Reagent Co., Ltd. Other solvents and conducting salts were purchased from Sinopharm Chemical Reagent Co., Ltd. The purity of CO_2, N_2 and argon (Ar) was 99.995%. Unless otherwise noted, the reagents and solvents were used as received from commercial suppliers without further purification.

2.2 Apparatus and voltammetric measurements

Potentiostatic electrolysis was carried out in an undivided cylindrical geometry tank glass equipped with a gas inlet and outlet. The volume of the ionic liquid $BMIMBF_4$ was 5 mL. The transient voltammetric measurement with a standard three-electrode cell was performed by using a CHI660 electrochemical workstation (Shanghai Chenhua Instruments Company). The electrolysis was carried out in an undivided glass cell equipped, a sliver electrode as the reference electrode, a copper (Cu), silver (Ag), Cu-Ni alloy, stainless steel (Ss) and nichel (Ni) electrode (area = 1cm^2) as the working electrode, respectively. An aluminum rod (Al) and magnesium rod (Mg) were used as the sacrificial anode. The Cu-Ni alloy electrode was prepared in accordance with Cu and Ni mass ratio three to one by high temperature melting and sintering method. Fig.1 presents the diffraction pattern (a) by X-ray diffraction (XRD) and the morphology and size of Cu-Ni alloy (b) by scanning electron microscopy (SEM). Prior to the cyclic voltammetry experiment, the electrodes were polished with aqueous Al_2O_3 slurry of 0.05-0.1μm grain size on a polishing cloth, then cleaned by diluted hydrochloric acid and carefully washed with distilled water and acetone, and finally dried under a flow of nitrogen before use.

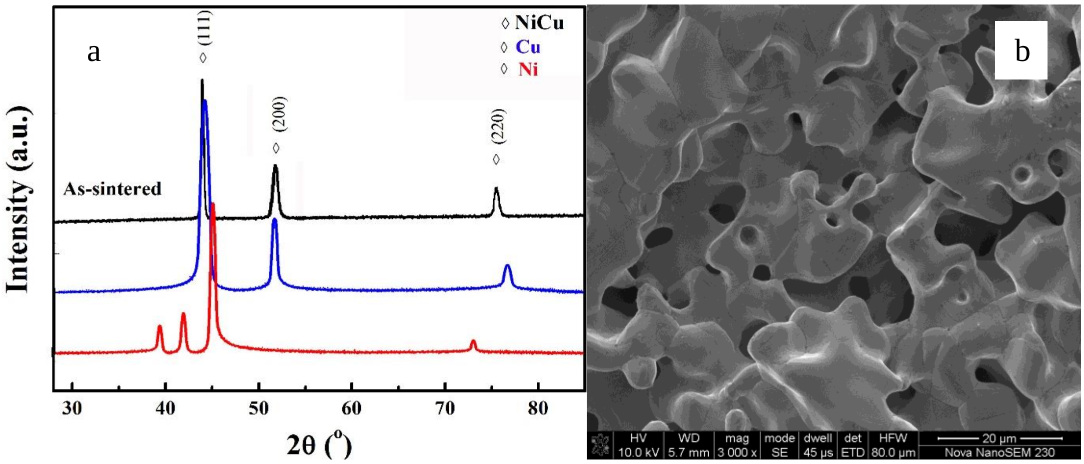

Figure 1. Characterization results of Cu-Ni alloy electrode. a: XRD; b: SEM.

2.3 Bulk electrolysis and product analysis

As can be seen from Fig.2, dried $BMIMBF_4$ (20mL) and benzyl bromide (3.5mL) were added to the cell in turn as electrolyte. Before electroreduction of CO_2, carbon dioxide was bubbled into electrolyte ionic liquid $BMIMBF_4$ at the desired pressure for 30 minutes to ensure saturated [26]. A slow stream of CO_2 was provided during the whole electrolysis process in order to maintain a constant concentration of CO_2. The electrosynthesis was performed under a continuous stirring condition until 3 F·mol^{-1} of charge was passed under atmospheric pressure. At the end of the electrosynthesis, the reaction mixture was esterified in ionic liquid $BMIMBF_4$ by adding anhydrous K_2CO_3 (1mmol) and CH_3CH_2Br (2mmol) with stirring the mixture at 60 ℃ for 6 h. The products were separated from ionic liquid by extraction with diethyl ether. Then the solvent was distilled off in vacuum, leaving a viscous residue. The residue was well stirred in 50 mL of aqueous HCl of 2 mol·L^{-1} for 3 h and filtered. The solution was extracted four times with diethyl ether (20mL×4). The ether phase was washed twice using distilled water. After evaporation of ether, the obtained crude product was further purified by column chromatography, with a mixture of petroleum ether and ethyl acetate (volume ratio 1:1) as the eluent.

Gas chromatograph mass spectra (GC-MS) and liquid chromatograph (LC) were recorded with HP 6890/5973GC-MS an Agilent 1100 series.

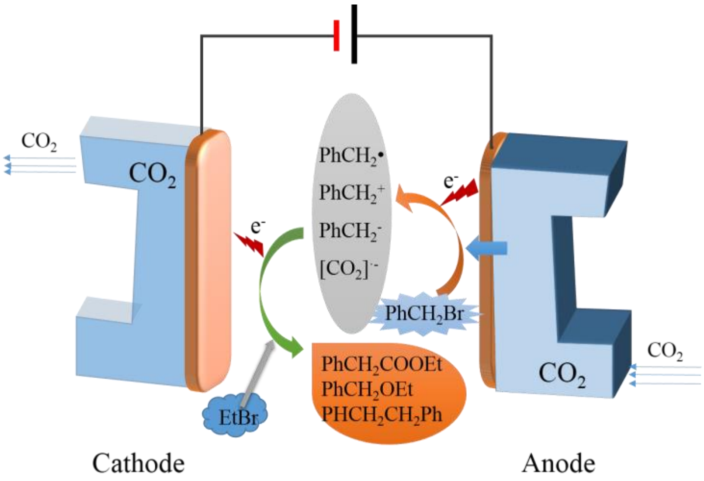

Figure 2. Electrocarboxylation reaction in a one-compartment electrochemical cell.

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry of benzyl bromide in BMIMBF$_4$

Cyclic voltammetric measurements were initially undertaken at a scan rate of 100mV·s^{-1} in an undivided cell with Ag as counter electrode and Cu-Ni alloy as working electrode. Fig.3a presents the cyclic voltammetry curve in N_2 saturated ionic liquid BMIMBF$_4$. Cyclic voltammetry of BMIMBF$_4$ illustrates that no any reduction peak could be observed in the scan range between -0.6 and -2.2 V. It also can be observed that the current starts to increase at around -2.0V, which could be due to the polarization of the BMIMBF$_4$ [27]. As can be seen from Fig.3b, a single irreversible reduction small peak can be observed at -1.23V for CO_2-saturated neat BMIMBF$_4$, which generated an anion radical ($CO_2^{\bullet-}$) by one-electron irreversible reduction of CO_2 [28]. For comparison, CO_2 reduction in ionic liquid BMIMBF$_4$ is relatively easier than in organic solvents [29-31]. Another, a much higher reduction peak current of CO_2 with Cu-Ni alloy electrode shows that the porous structure can increase active centers where the reduction of CO_2 carried on [32]. After addition of benzyl bromide (0.1mol) to the neat BMIMBF$_4$, a single irreversible reduction small peak is observed at -1.45V (Fig.3c), which is formed by reduction of $PhCH_2Br$ to $PhCH_2$•. Under a CO_2 saturated BMIMBF$_4$ (Fig.3d), the benzyl bromide reduction peak current increased obviously compared with the curve *c* and the peak potential shifted positively to -1.38V. Consequently, the voltammetic changes in the presence of CO_2 imply the production of new chemical reaction.

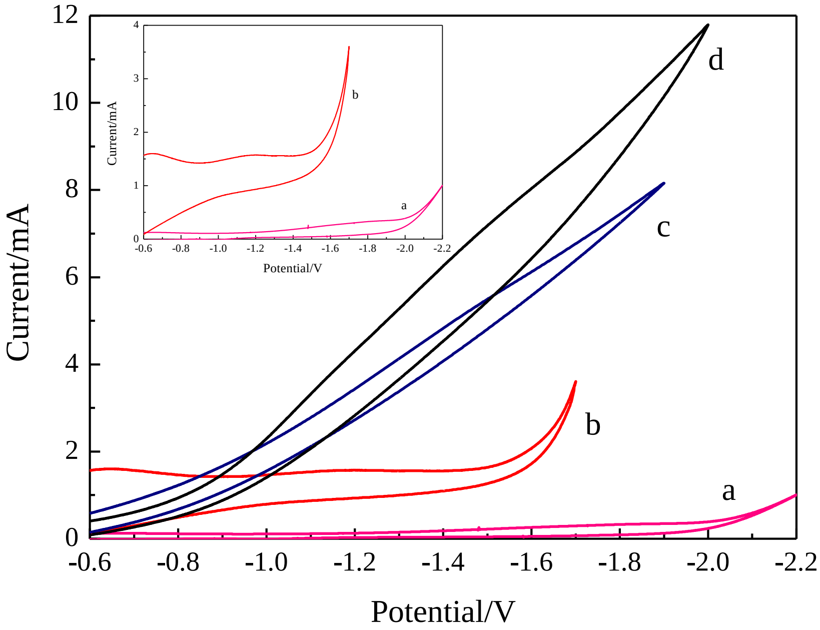

Figure 3. Cyclic voltammograms recorded on Ag electrode, at 100 mV·s^{-1} and room temperature, in $BMIMBF_4$ solution. (a) neat $BMIMBF_4$; (b) $BMIMBF_4$ saturated with CO_2; (c) $BMIMBF_4$ containing 0.1mol·L^{-1} benzyl bromide; (d) as (c) saturated with CO_2.

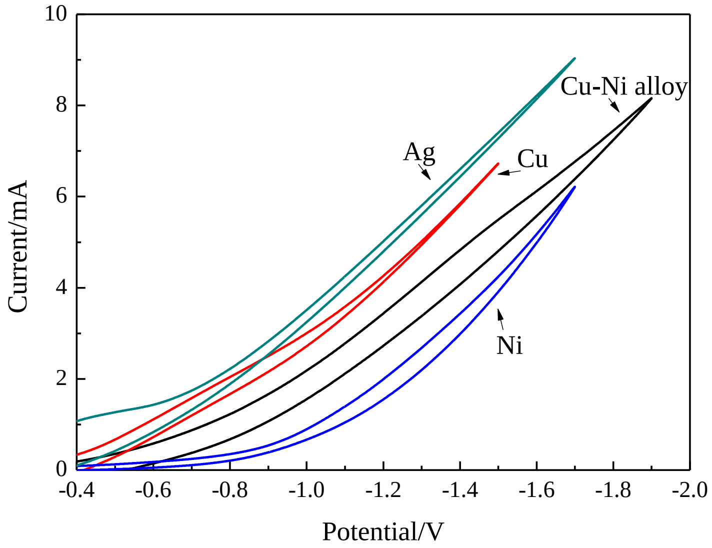

Figure 4. Cyclic voltammograms of 0.1mol benzyl bromide in $BMIMBF_4$ record at the Ag, Cu, Ni, Cu-Ni alloy electrodes, v=0.1V·s^{-1},T=25°C.

In order to study the effect of metal electrode on the reduction of benzyl bromide, the voltammetry behaviors of benzyl bromide in ionic liquid $BMIMBF_4$ were also investigated at the most commonly used cathodes such as, Cu, Ni, and Ag (Fig.4). As can be seen from the Fig.4, Ag electrode is conducive to the occurrence of the reaction because of high current density and lower over-potential, but there is not thoroughly reduction peak in the -0.6 ~ -2.0V. Over-potential of Cu electrode is slightly higher than the Ag electrode. Ni electrode has a small reduction peak though the current density is the smallest at the comparison electrodes. Nevertheless, the current density of Cu-Ni alloy electrode is much higher than Cu and Ni electrode. Furthermore, there is an obvious reduction peak at -1.43V which indicates porous structure Cu-Ni alloy can increase a great deal of active centers for benzyl bromide and CO_2 [33]. In general, the reduction of benzyl bromide takes place on surface of electrode during electrolyses [34]. Herein, the higher yield could be achieved when much contact opportunity between benzyl bromide and $CO_2^{\bullet-}$ was provided for the nature of the electrode material [35]. In other word, Cu-Ni alloy electrode exhibits more excellent electrochemical catalytic performances than Cu, Ni, and Ag electrodes because of their porous structure and ensemble effect.

3.2 Experimental investigations on the electrochemistry of benzyl bromide

Potentiostatic electrolysis for electrosynthesis ethyl phenylacetate from CO_2 and benzyl bromide was performed in CO_2-saturated $BMIMBF_4$ solution. The synthesis was carried out at a potential of -1.4V with a charge consumption of 2.5 $F\cdot mol^{-1}$ at room temperature. In our experiments, the aim of optimizing the yields, we have focused our attention on various influence parameters such as electrode materials, the working potential and the passed charge.

Gas chromatograpy-mass spectra (GC-MS) and liquid chromatography (LC) were recorded with HP 6890/5973 GC-MS and Agilent 1100 series. Spectroscopic data of the prepared compounds were given as follows.

Ethyl phenylacetate **1:** GC-MS (m/z, %) 150 (M^+, 54), 119 (4), 108 (36), 91 (100), 86 (2), 79 (25), 65 (13), 51 (10); ^{1}HNMR ($CDCl_3$): δ 1.32 (t, J=8Hz, 3**H**), 3.80 (s, 2**H**), 4.51 (q, J=9Hz, 2**H**), 7.23-7.50 (m, 5**H**).

Benzyl ether **2:** GC-MS (m/z, %) 136 (M^+, 11), 91 (100), 86 (2), 79 (28), 65 (10), 51 (5); ^{1}HNMR ($CDCl_3$): δ 1.16 (t, J=7Hz, 3**H**), 3.64 (q, J=8Hz, 2**H**), 4.85 (s, 2**H**), 7.35-7.47 (m, 5**H**).

1, 2-diphenylethane **3:** GC-MS (m/z, %) 182 (M^+, 55), 165 (4), 152 (2), 104 (4), 91 (100), 77 (5), 65 (13), 51 (3); ^{1}HNMR ($CDCl_3$): δ 2.96 (s, 4**H**), 6.99-7.42 (m, 10**H**).

3.2.1 Influence of cathode materials

The influence of cathode materials on electrochemical carboxylation of benzyl bromide was investigated. Under benzyl bromide at 0.1mol, the ionic liquid $BMIMBF_4$ at 15mL, CO_2 saturated, the electrosynthesis was performed with a sliver electrode as the reference electrode, a copper (Cu), silver (Ag), Cu-Ni alloy, stainless steel (Ss) and nichel (Ni) electrode (area = $1cm^2$) as the cathode materials, respectively. An aluminum rod (Al) and magnesium rod (Mg) were compared as the sacrificial anode, respectively. Cyclic voltammetric measurements were initially undertaken at a scan rate of $100mV\cdot s^{-1}$ and the scan range between -0.6 and -2.2 V. The charge passed the cell increased gradually from 1.0 to 3.0 $F\bullet mol^{-1}$. The results are reported in Table 1 (entries 1-14). After esterification, the yields of the carboxylated products decreased in the order Cu-Ni alloy(39.4%)>Ag(28.7%)>Ni(18.5%)>Cu(15.3%)>Stainless steel(10.4%). The results showed porous structure Cu-Ni alloy cathode could get higher yield of ethyl phenylacetate than Ag, Ni and Cu cathodes. Different adsorption energies between Cu-Ni alloy atoms and intermediates of CO_2 and $PhCH_2Br$ play an “ensemble effect” role in electrochemical carboxylation [33]. The porous structure Cu-Ni alloy cathode is advantageous for electro-reduction of CO_2 as it ensures sufficient contact area between the electrode and the electrolyte. Particularly, similar potentiostatic electrolysis found about 5% of benzyl ether in reaction products. The yield of benzyl ether on Mg electrode is lower than Al electrode (entries 1, 6). The possible reason is that solubility product constant of Al^{3+} and CO_3^{2-} is larger than one of Mg^{2+} and CO_3^{2-} in ionic liquid $BMIMBF_4$ [36]. As a result, this is advantageous for electroreduction of CO_2 as it ensures sufficient opportunities to contact between benzene methyl positive ion and the CO_3^{2-}. The yield (39.4%) of ethyl phenylacetate **1** as the principal product can be obtained, accompanied astonishingly by yield (4.6%) of benzyl ether **2** with the porous structure Cu-Ni alloy electrode as the cathode, Al as the anode. In summary, the products distribution and product yields depend remarkably on the nature of the electrode material.

Table 1. Electrocarboxylation of benzyl bromide with CO_2 under various conditions.[a]

Entry	Cathode	Anode	$Q/F\cdot mol^{-1}$	Potential/V	Product yield[b]/%		
					1	**2**	**3**
1	Cu-Ni alloy	Al	2.5	-1.4	39.4	4.6	12.5
2	Cu	Al	2.5	-1.4	15.3	2.1	8.9
3	Ni	Al	2.5	-1.4	18.5	1.8	10.3
4	Ag	Al	2.5	-1.4	28.7	1.2	15.7
5	Stainless Steel	Al	2.5	-1.4	10.4	0.4	13.3
6	Cu-Ni alloy	Mg	2.5	-1.4	39.7	2.8	11.6
7	Cu-Ni alloy	Mg	1.0	-1.4	20.8	2.3	5.1
8	Cu-Ni alloy	Al	1.5	-1.4	29.5	3.1	8.6
9	Cu-Ni alloy	Al	2.0	-1.4	35.8	4.0	11.5
10	Cu-Ni alloy	Al	3.0	-1.4	36.9	3.2	11.3
11	Cu-Ni alloy	Al	2.5	-1.2	35.3	3.8	12.8
12	Cu-Ni alloy	Al	2.5	-1.3	37.2	3.9	12.4
13	Cu-Ni alloy	Al	2.5	-1.5	38.9	4.2	12.6
14	Cu-Ni alloy	Al	2.5	-1.6	33.9	2.4	10.2

[a] Benzyl bromide at 0.1mol, $BMIMBF_4$ at 15mL, CO_2 saturated.
[b] GC yield. The yield based on starting benzyl bromide.

3.2.2 Influence of charge passed

Charge passed number (Q) has a great important impact on the yield of ethyl phenylacetate because charge of reduce CO_2 into $CO_2^{\bullet -}$ with electrochemical method strongly depended on electrodes electronic supply [37]. The influence of different amounts of charge passed has been studied. The corresponding results are illustrated in Table 1 (entries 1 and 7-10). As shown, the yield of ethyl phenylacetate first increased and then decreased dramatically with the increase of charge passed amount from 1.0 to 3.0 F•mol^{-1}. The yield of ethyl phenylacetate reaches the maximum of 39.4% at 2.5 F•mol^{-1} charge. The increased yield of ethyl phenylacetate less than 2.5 F•mol^{-1} charge suggests that the enhanced concentration of electrogenerated intermediate $CO_2^{\bullet-}$ in the ionic liquid $BMIMBF_4$ is driven by increasing the charge consumption. The best yield was achieved at 2.5 F•mol^{-1} charge because the amount of electrogenerated intermediate $CO_2^{\bullet-}$ was equal to amount of benzene methyl positive ion. With too large charge passed amount, it may produce excessive electrogenerated intermediate $CO_2^{\bullet-}$ where corresponding $CO_2^{\bullet-}$ reacts itself and is converted into by-products by dimerization [38]. Therefore, it can be concluded that the charge passed is significantly depended on the critical concentration of electrogenerated intermediate $CO_2^{\bullet-}$ in the ionic liquid $BMIMBF_4$. On the basis of the above investigations, the appropriate charge passed was 2.5 F•mol^{-1}.

3.2.3 Influence of electrolysis potential

Several electrolysis experiments were carried out using different electrolysis potential. The results are presented in Table 1(entries 1 and 11-14). Further analysis results showed that the yield of ethyl phenylacetate first increased, and then decreased by shifting the potential to more negative value. The optimized applied potential was achieved at -1.4 V with the highest yield of carboxylation product. The chemical reactivity of molecules can not meet demand when the electrolysis potential is too small. The more negative the electrolysis potential is, the larger the current density is. Accordingly, more electrogenerated intermediate $CO_2^{\bullet-}$ will be produced as electrolysis potential slowly become more negative. But a potential more negative than -1.4 V will be disadvantageous for the yields of ethyl phenylacetate **1**. Firstly, the ionic liquid $BMIMBF_4$ will easily be polarized at more negative potential. Secondly, the electrode is easily passivation and the reaction electrode is denatured if the electrolysis potential between cathode and anode is too large [39]. Herein, an appropriate electrolysis potential of 1.4 V for this electrolysis experiment was chosen finally.

3.3 The electrochemical reaction mechanism

The plausible electrochemical reaction mechanism of benzyl bromide and CO_2 is proposed according to our experimental results and cyclic valtammograms (Fig. 2). In potentiostatic electrolysis, three kinds of products were obtained (Fig. 5) after 2.5 F•mol^{-1} charge passed the cell. The major products were identified as 150 m/e $PhCH_2COOEt$, 135 m/e $PhCH_2OEt$ and 182 m/e $PhCH_2CH_2Ph$ by comparison with the GC-MS and cyclic voltammetry characteristics. These results are consistent with a proton coupled electron transfer reaction (Fig. 6). In the ionic liquid, a proton may be derived from a trace impurity (e.g. H_2O) or the C-2 hydrogen in $[BMIM]^+$ [40,41].

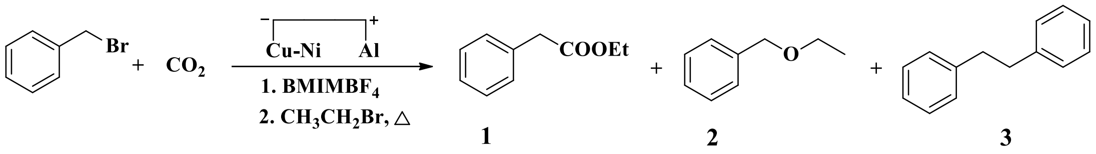

Figure 5. Electrocarboxylation of benzyl bromide under a CO_2 atmosphere.

As shown in Fig. 6, $PhCH_2Br$ is reduced to $PhCH_2$• radical at -1.4V, which can be further electronically converted into $PhCH_2^-$ anions and can also be coupled to form dimer product $PhCH_2CH_2Ph$ **3**. Simultaneously, $PhCH_2$• radical can also occur disproportionation reaction to produce $PhCH_2^+$ cation and $PhCH_2^-$ anion. The interaction intermediate plays a significant role in electrochemical carboxylation. The CO_2 electroreduction rate is determined by the first electron transfer to form $CO_2^{\bullet -}$ [42]. In general, CO_2 is electron-generated $CO_2^{\bullet -}$ radical anion, which can form $PhCH_2COO^-$ with $PhCH_2^-$ anion. The $CO_2^{\bullet -}$ radical anion can also occur coupling reactions to form CO and CO_3^{2-} ions ($2CO^2+2e^- \rightarrow CO+CO_3^{2-}$) [28,43]. $PhCH_2^+$ cation mediate could normally react with CO_3^{2-} ions to form $PhCH_2OCOO^-$, which may further react with CH_3CH_2Br to produce benzyl ether product **2**. Based on the proposed electrocarboxylation scheme from Fig. 6, ethyl phenylacetate **1** could be obtained by two pathways. Both $PhCH_2^-$ anion with CO_2 and $PhCH_2$• radical with $CO_2^{\bullet -}$ radical anion can firstly form $PhCH_2COO^-$ anion, which may further occur esterification reaction with CH_3CH_2Br to obtain ethyl phenylacetate **1**.

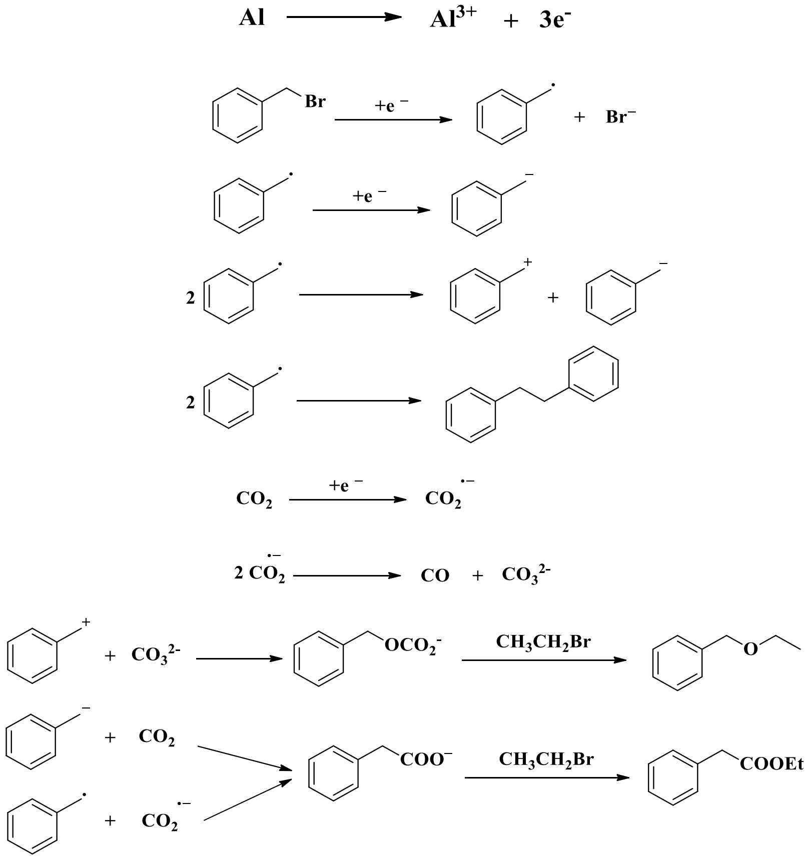

Figure 6. Plausible electrochemical reaction mechanism of benzyl bromide and CO_2.

3.4 Reuse of ionic liquid

The CH_2Cl_2 was added to $BMIMBF_4$ after the solution was extracted with diethyl ether. The solvent was filtered in order to eliminate K_2CO_3. The mixture was frequently washed with distilled water until precipitate was not found in aqueous solution detection with silver nitrate. After this step, the organic layer was evaporated and corresponding ionic liquid $BMIMBF_4$ was dried under vacuum. As show in Fig. 7, the obtained carboxylation yield was slightly lower than the fresh ionic liquid when the ionic liquid $BMIMBF_4$ was used for the second time. In the subsequent two cycles, the carboxylation yield was over 38%. But the cycle to the fourth, carboxylation yield decreased obviously because the structure of ionic liquids may have been destroyed [29,44]. In general, the ionic liquid can well be reused for electrochemical reduction.

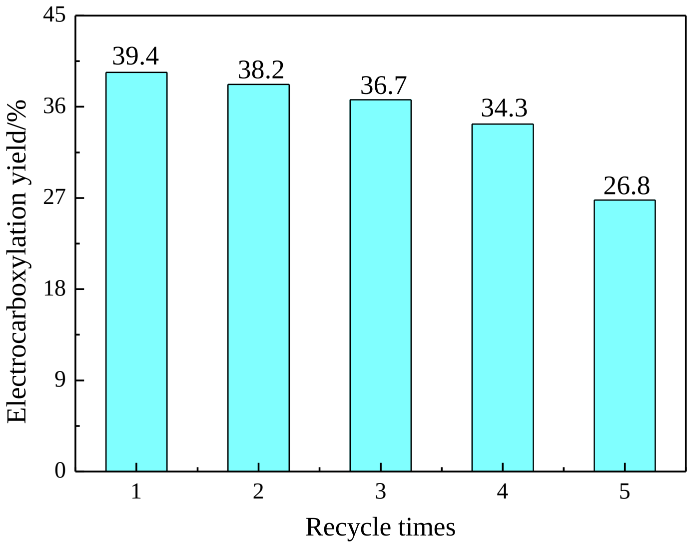

Figure 7. Reuse of $BMIMBF_4$ in the electrocarboxylation of benzyl bromide.

4. CONCLUSIONS

This study is a detailed investigation of the electrochemical carboxylation of benzyl bromide with carbon dioxide on Cu-Ni cathode and Al anode in ionic liquid $BMIMBF_4$. The electrocarboxylation was carried out under mild condition and a moderate yield was obtained. The influences of electrode material, working potential and electric charge on the yield were investigated. The results show that the yields of ethyl phenylacetate and benzyl ether were mainly due to the porous structure and the ensemble effect of Cu-Ni alloy electrode. This study can avoid the use of toxic and volatile solvents and catalysts. Simultaneously, ionic liquid could be successfully recycled at least three times. A plausible electrochemical reaction mechanism was proposed. The present approach has obvious significance for study and practical application because it not only can synthesis useful and valuable chemicals but also may be helpful for the utilization of CO_2.

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