Selective monocarboxylation of olefins at $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride cathode

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Abstract:

Metallic oxide conductor $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) electride with high affinity to CO_2 , a new candidate for the cathode material in electrochemistry, is used for the selective monocarboxylation of various olefins. The galvanostatic electrolysis was performed under carbon dioxide atmosphere without sacrificial anode in a divided cell. The monocarboxylic products were obtained in moderate to high yield (58–91%), which were significantly higher than those at Pt (9–83%) and glassy carbon (32–72%) cathode.

Keywords: Mayenite; Electride; Cyclic Voltammetry; Carboxylation; Carbon Dioxide

1. Introduction

Fixation of carbon dioxide into organic substrates for preparing valuable chemicals is an attractive goal in organic synthesis. The electrochemical method is one of the efficient routes which was used for the fixation of CO₂ to various organic compounds, including benzylic halides [1–5], ketones [6–8], imines [9,10], and olefins [11–17]. Conventionally, electro-carboxylation was performed in an undivided cell with Mg or Al sacrificial anode. For instance, the carboxylation of phenyl-substituted alkenes to form 1,2-dicarboxylic acids was achieved using Pt cathode and Mg anode in high yields [11]. However, electrochemical synthesis of monocarboxylic products from olefins always gave low yields [12–17]. Usually benzylic halides have to be used as starting materials to form the monocarboxylic products [1–5], or the Fe and Ni based catalyst were necessary for the monocarboxylation [18,19]. Hence, a halide-free and metal catalyst-free process for the monocarboxylic compounds synthesis is desirable from a viewpoint of green sustainable chemistry.

Recently we found that 12CaO•7Al₂O₃ (C12A7) electride could be used as cathode for the electro-reduction of oxygen to superoxide ions, which was used for organic synthesis [20]. C12A7 electride is a metallic conducting oxide with very low work function of 2.4 eV (comparable to metal potassium) and chemical inertness [21,22]. It was found that C12A7 electride is a good adsorbent and chemical activator of CO₂ [23]. The adsorbed CO₂ amount on C12A7 electride surface, which corresponds to that of surface electron concentration, is 2–3 times as large as that on glassy carbon (GC) surface [24]. Therefore, we expected that C12A7 electride cathode would be better for the carboxylation than other conventional electrodes. Here we report the highly efficient and selective carboxylation of olefins to form monocarboxylic products in a divided cell by using C12A7 electride cathode

(hereafter denoted as C12A7:e⁻ electrode) without sacrificial anode.

2. Experimental

The preparation of C12A7 electride has been described in detailed previously [20,25,26]. Briefly, CaCO₃ and γ -Al₂O₃ powders with a molar ratio of 12:7 were reacted at 1300 °C for 12 h in air to form C12A7 oxide. The product was crushed in ethanol solvent by planetary milling to obtain the fine powder. The pellets formed by cold-isostatic pressing the above powder at 200 MPa were sintered at 1350 °C for 24 h in dry oxygen atmosphere. The resultant translucent pellets with a relative density of >95% were obtained. These pellets were sealed in an evacuated silica glass tube with titanium metal shots and heated at 1100°C for 24 h to reduce C12A7 oxide and hence introduce electrons. After removing the surface TiO_x layer, the black C12A7 electride with an electron concentration of about $1.4 \times 10^{21} \text{ cm}^{-3}$ was attained. It was cut into columns (about 15×2×2 mm for cyclic voltammetry measurement) and plates (about 20×10×1 mm for galvanostatic electrolysis). Each side of these samples was polished to be a mirror surface. Then the samples were sealed in an evacuated silica glass tube and annealed at 950 °C for 10 min to form active surfaces [27].

CV measurements in an undivided cell and galvanostatic electrolysis in an H type divided cell separated by a G4 sintered glass filter were conducted in a 0.1 M Bu₄NClO₄-CH₃CN solution with the substrate concentration of 10 mM. For galvanostatic electrolysis, the volume for the catholyte and anolyte were both 16 ml, and the size for the exposed cathodes and Pt anode were 10×10 mm. CO₂ was bubbled during electrolysis. The catholyte after reaction was esterified by adding 5 mole fold of iodoethane or iodomethane and stirred at room temperature for 24 hours. The products extracted with diethyl ether were identified by ¹H NMR measurements with

nitromethane as an internal standard to calculate the crude yields.

3. Results and Discussions

The cathodic reactions of methyl cinnamate (**1a**) was performed by galvanostatic electrolysis with a current density of $5 \text{ mA} \cdot \text{cm}^{-2}$ using a C12A7:e⁻ electrode (Table 1). The products were dominantly α -carboxylic compound **2a**, with a few percent of α , β -dicarboxylic compound **4a** and saturated ester **5a**. Moreover, the β -carboxylic compound **3a** was not observed in present study, while it was obtained using electrosynthesis in single cell with Mg anode [16]. When $3 \times 96485 \text{ C} \cdot \text{mol}^{-1}$ of electricity was passed, **2a** was obtained in 91% yield. For comparison, Pt and GC electrodes were also used as cathode for the reaction. When the passed charge was $3 \times 96485 \text{ C} \cdot \text{mol}^{-1}$, the yield of **2a** was 82% at Pt electrode, which was little lower compared to C12A7:e⁻ electrode, while the yield at GC electrode was only 67%. As shown in Table 1, both yield and selectivity of **2a** in the present study were much higher than those obtained using sacrificial anode in a single cell [16,17].

Insert Table 1 here

To further check the activity of C12A7:e⁻ electrode, the same cathodic reduction was performed for various olefins, which are not substituted with electron-withdrawing group, and the results are summarized in Table 2. The dominant product was the monocarboxylic compound **2**, and C12A7:e⁻ electrode always gave the highest yield on **2** among present three electrodes for all substrates. Contrary to **1a**, the use of Pt cathode resulted in a low yield of **2b–2d**. For instance, the yields of **2b** are 83%, 22% and 60% for C12A7:e⁻, Pt and GC electrode, respectively.

Insert Table 2 here

To clarify the reduction characteristics at different electrodes, cyclic voltammetry measurement was performed by using SCE as reference electrode. At first, the CO₂ reduction at different electrodes was investigated for the CO₂ saturated 0.1 M Bu₄NClO₄-CH₃CN solution. An intense CO₂ reduction started at -1.9 V (curve a in Fig. 1) was observed at a Pt electrode. However, only a weak and broad reduction peak at around -2.6 V which is due to the reduction of CO₂ [13] was observed at C12A7:e⁻ electrode,. Comparing to Pt electrode, the reduction of CO₂ is suppressed greatly at C12A7:e⁻ electrode. The weak and broad reduction wave was also observed at GC electrode.

Insert Figure 1 here

Then, the reduction of **1a** and **1b** were investigated. Two clear reduction peaks at around -1.9 V and -2.4 V owing to the reduction of **1a** were observed at all electrodes when 10 mM **1a** was dissolved in 0.1 M Bu₄NClO₄-CH₃CN solution (curve b in Fig. 1), while the reoxidation peaks was not clearly observed. After adding CO₂ into above solution, the peak at -2.4 V was disappeared, and an intense reduction peak at around -1.9 V was observed with the onset potential shifted positively (curve c in Fig. 1). It indicates that **1a** is reduced to form radical anion at first, which then immediately reacts with CO₂ near the electrode surface, and further electron transfer occurs after the CO₂ combination.

Similar to **1a**, two reduction peaks were observed for **1b** at all electrodes (curve b in Fig. 2). After applying CO₂, the reoxidation and second reduction peaks disappeared and the first reduction peak became intense and shifted positively. Almost the same CV curves were observed at C12A7:e⁻ and GC electrode. However,

curve c and a almost overlapped at Pt electrode, only a shoulder peak was observed. It strongly suggests that the reduction of CO₂ to form CO₂^{•-} ion was the main process at Pt electrode when **1b** and CO₂ were simultaneously presented. It is consistent to the reduction potential of **1b** (−2.33 V vs SCE) which is more negative than that of CO₂.

Insert Figure 2 here

It was reported that the electrogenerated CO₂^{•-} ions reacted with olefins in the single cell, in which Mg²⁺ or Al³⁺ ions formed at sacrificial anode captured carboxylate ions to form stable metal-organic complexes [7,11]. However, the low yields at Pt electrode for **1b–1d** suggest that CO₂^{•-} ions does not react with neutral olefins without the existence of Mg²⁺ or Al³⁺ cations. Therefore, the suppression of CO₂ reduction is suitable for the efficient carboxylation without sacrificial anode. C12A7:e⁻ electrode, which showed weak CO₂ reduction and higher CO₂ adsorption, would be a good cathode for the monocarboxylation of olefins.

Based on the galvanostatic electrolysis results and CV measurements, we propose the following reaction mechanism as shown in Scheme 1. The substrate **1** closes to the electrode surface and gains one electron to form the radical anion intermediate **IM1**, which then reacts with the CO₂ molecule adsorbed on the cathode surface to form **IM2**. Additional one electron transfers to **IM2** to form the dianion intermediate **IM3**, which is easily protonated to form monocarboxylic anion **IM4** prior to further addition to CO₂ to form dicarboxylic product **4**.

Insert Scheme 1 here

4. Conclusion

In this work, we demonstrated the highly efficient electrochemical synthesis of monocarboxylic compounds from various olefins under atmospheric CO₂ in a divided cell without sacrificial anode. The yields of target products at C12A7:e⁻ electrode were significantly higher than those at conventional Pt and GC electrodes. Cyclic voltammetric analysis together with galvanostatic electrolysis provide evidence that the substrate is at first reduced at the cathode to generate the corresponding radical anion and then reacts with adsorbed CO₂ immediately. Our results indicate that C12A7:e⁻ electrode having excellent affinity to CO₂ and suppression of CO₂ reduction may be promising material for the efficient monocarboxylation of various olefins, which can not be achieved by using other electrodes. Furthermore, this electrochemical carboxylation does not require sacrificial metal anode, which means metal free electrosynthesis. Namely, this electrosynthesis is superior from a viewpoint of green sustainable chemistry.

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References

- [1] A.A. Isse, A. Gennaro, *Chem. Commun.*, 38 (2002) 2798.
- [2] A.A. Isse, M.G. Ferlin, A. Gennaro, *J. Electroanal. Chem.*, 38–45 (2005) 581.
- [3] M.D. Otero, B. Batanero, F. Barba, *Tetrahedron Lett.*, 47 (2006) 2171.
- [4] M. Tokuda, *J. Natural Gas Chem.*, 15 (2006) 275.
- [5] Y. Hiejima, M. Hayashi, A. Uda, S. Oya, H. Kondo, H. Senboku, K. Takahashi, *Phys. Chem. Chem. Phys.*, 12 (2010) 1953.
- [6] J. Harada, Y. Sakakibara, A. Kunai, K. Sasaki, *Bull. Chem. Soc. Jpn.*, 57 (1984) 611.
- [7] G. Silvestri, S. Gambino, G. Filardo, *Tetrahedron Lett.*, 27 (1986) 3429.
- [8] Q.J. Feng, K.L. Huang, S.Q. Liu, J.G. Yu, F.F. Liu, *Electrochim. Acta*, 56 (2011) 5137.
- [9] M.A. Casadei, A. Inesi, F.M. Moracci, L. Rossi, *Chem. Commun.*, 32 (1996) 2575.
- [10] D.F. Niu, L. Zhang, L.P. Xiao, Y.W. Luo, J.X. Lu, *Appl. Organometal. Chem.*, 21 (2007) 941.
- [11] H. Senboku, H. Komatsu, Y. Fujimura, M. Tokuda, *Synlett*, (2001) 418.
- [12] D.A. Tyssee, M.M. Baizer, *J. Org. Chem.* 39 (1974) 2819.
- [13] G. Filardo, S. Gambino, G. Silvestri, A. Gennaro, E. Vianello, *J. Electroanal. Chem.*, 177 (1984) 303.
- [14] S. Gambino, A. Gennaro, G. Filardo, G. Silvestri, E. Vianello, *J. Electrochem. Soc.*, 134 (1987) 2172.
- [15] D. Ballivet-Tkatchenko, J.C. Folest, J. Tanji, *Appl. Organometal. Chem.*, 14 (2000) 847.
- [16] H. Wang, K. Zhang, Y.Z. Liu, M.Y. Lin, J.X. Lu, *Tetraheron*, 64 (2008) 314.

- [17] H. Wang, G.R. Zhang, Y.Z. Liu, Y.W. Luo, J.X. Lu, *Electrochem. Commun.*, 9 (2007) 2235.
- [18] C.M. Williams, J.B. Johnson, T. Rovis, *J. Am. Chem. Soc.*, 130 (2008) 14936.
- [19] M.D. Greenhalgh, S.P. Thomas, *J. Am. Chem. Soc.*, 134 (2012) 11900;
- [20] J. Li, B. Yin, T. Fuchigami, S. Inagi, H. Hosono, S. Ito, *Electrochem. Commun.*, 17 (2012) 52.
- [21] S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, H. Hosono, *Science*, 301 (2003) 626.
- [22] Y. Toda, H. Yanagi, E. Ikenaga, J.J. Kim, M. Kobata, S. Ueda, T. Kamiya, M. Hirano, K. Kobayashi, H. Hosono, *Adv. Mater.*, 19 (2007) 3564.
- [23] Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P.V. Sushko, H. Hosono, *Nat. Commun.*, 4 (2013) 2378.
- [24] The adsorption of CO₂ was conducted in gas phase (1 atm CO₂) and liquid phase (CO₂ saturated CH₃CN) for C12A7:e⁻ and GC electrodes with the size of 10x10x1 mm. The amount of adsorbed CO₂ was measured using Q-MS in a thermal desorption spectrometry.
- [25] K. Hayashi, M. Hirano, H. Hosono, *J. Mater. Res.* 17 (2002) 1244.
- [26] S.W. Kim, S. Matsuishi, T. Nomura, Y. Kubota, M. Takata, K. Hayashi, T. Kamiya, M. Hirano, H. Hosono, *Nano Lett.* 7 (2007) 1138.
- [27] Y. Toda, Y. Kubota, M. Hirano, H. Hiramaya, H. Hosono, *ACS Nano*, 5 (2011) 1907.

Table

Table 1. Carboxylation of methyl cinnamate (**1a**) with CO₂ at different electrodes.

Cathode	Charge passed $n \times 96485$ $\text{C}\cdot\text{mol}^{-1}$	Yields 2a	3a	4a	5a
* C12A7:e ⁻	2	63%	0	3%	2%
* Pt	2	57%	0	3%	2%
* GC	2	50%	0	3%	3%
* C12A7:e ⁻	3	91%	0	5%	3%
* Pt	3	82%	0	4%	3%
* GC	3	67%	0	5%	4%
# Ti	2.8	41%	10%	15%	0
& Stainless steel	2	35%	0	0	32%

* Present results which performed in divided cell using CH₃CN as solvent.

Reported in Ref. 16 which performed in single cell using CH₃CN as solvent and Mg as a sacrificial anode.

& Reported in Ref. 17 which performed in single cell using ionic liquid as solvent and Mg as a sacrificial anode.

Table

Table 2. Carboxylation of various olefins with CO₂ at different electrodes.

Substrate	Cathode	$E_{\text{peak}}^{\text{red}*}$ (V vs SCE)	Yields	
			2	4
1b	C12A7:e ⁻	-2.32	83%	8%
1b	Pt	-2.33	22%	2%
1b	GC	-2.35	60%	5%
1c	C12A7:e ⁻	-2.71	63%	5%
1c	Pt	-2.44	14%	2%
1c	GC	-2.75	47%	4%
1d	C12A7:e ⁻	-2.82	58%	6%
1d	Pt	-2.57	9%	1%
1d	GC	-2.88	32%	4%

* The peak for the first reduction wave without the supply of CO₂.

Figure Captions

Fig. 1. Cyclic voltammograms in 0.1 M Bu₄NClO₄-CH₃CN solution at different electrodes for (a) saturated CO₂, (b) 10 mM methyl cinnamate **1a** and (c) 10 mM **1a** with saturated CO₂. The sweep rate is 100 mV·s⁻¹.

Fig. 2. Cyclic voltammograms in 0.1 M Bu₄NClO₄-CH₃CN solution at different electrodes for (a) saturated CO₂, (b) 10 mM *trans*-stilbene **1b** and (c) 10 mM **1b** with saturated CO₂. The sweep rate is 100 mV·s⁻¹.

Scheme 1. Possible reaction mechanism for the carboxylation of olefins in divided cell without sacrificial anode.

Figures

Fig. 1

Fig. 2

Scheme 1