

Communication (Special Issue on Electrocatalysis Transformation)

Cathode made of compacted silver nanoparticles for electrocatalytic carboxylation of 1-phenethyl bromide with CO₂

CrossMark

Hengpan Yang^a, Laxia Wu^b, Huan Wang^{a,*}, Jiaxing Lu^{a,#}

^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

^b School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, Anhui, China

ARTICLE INFO

Article history: Received 2 February 2016 Accepted 29 February 2016 Published 5 July 2016

Keywords: Electrocatalysis Electrocarboxylation Carbon dioxide Benzyl bromides Silver nanoparticles

ABSTRACT

Silver nanoparticles prepared by the direct reduction of AgNO₃ in aqueous solution were compacted into coins and used as the cathode for the electrocatalytic carboxylation of 1-phenethyl bromide with CO₂. The influences of the working electrode, charge, current density and temperature were investigated. Under optimized conditions, 98% yield of 2-phenylpropionic acid was obtained. The reaction was performed under very mild conditions and no added catalyst was required in the electrolyte. Yields that varied from moderate to excellent were also achieved with other benzyl bromides. This electrode has good stability and reusability, and the yield and selectivity of 2-phenylpropionic acid could be maintained during reuse for 10 times.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

 CO_2 is the main greenhouse gas linked to undesirable climate change. On the other hand, CO_2 is also a cheap, abundant and clean C1 feedstock [1]. In recent years, much effort has been made to develop effective processes for economical products by the fixation of CO_2 [2–8]. Among these products, phenylpropionic acids from the carboxylation of phenyl halides with CO_2 have commercial importance because of their extensive applications in pharmaceutical industry. They are used as intermediates for nonsteroidal antiinflammatory drugs (NSAIDs), like Ibuprofen, Naproxen, Ketoprofen and Flurbiprofen. Much attention has been paid to developing synthesis methods of phenylpropionic acids [9].

However, a homogeneous catalytic system for the synthesis of phenylpropionic acids involves the utilization of transition metal catalysts, such as cobalt, nickel and palladium complexes [10–12]. Although high yields have been reported by some workers, the disadvantages are also obvious, which are that the transition metal catalysts are both expensive and hardly recyclable, which cause difficulty in practical application. Electro-catalysis was also demonstrated to be an efficient method for the synthesis of phenylpropionic acids by us [13,14] and other workers [15,16]. It can be performed under mild conditions without a transition metal catalyst. For example, Isse and coworkers [15] reported a synthesis of benzoic acid by the electrocatalytic reduction of bromobenzene with CO₂ that gave benzoic acid yields of 80%.

In our former work, we investigated a route for the electrocatalytic asymmetric carboxylation of achiral 1-phenylethyl chloride with CO_2 in the presence of a chiral cobalt complex. Under optimized conditions, optically active 2-phenylpropionic

^{*} Corresponding author. Tel: +86-21-52134935; E-mail: hwang@chem.ecnu.edu.cn

[#] Corresponding author. Tel: +86-21-62233491; E-mail: jxlu@chem.ecnu.edu.cn

This work was supported by the National Natural Science Foundation of China (21203066, 21373090, 21473060).

DOI: 10.1016/S1872-2067(15)61075-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 7, July 2016

acid with 37% yield and 83% ee was obtained [17]. In addition, we also prepared a [Co]@Ag composite for asymmetric carboxylation of 1-phenylethyl bromide with CO₂. 2-phenylpropionic acid with 58% yield and 73% ee was achieved at normal pressure and temperature [18]. Although optically active products were obtained with a chiral cobalt catalyst, the yield was relatively low, which need further work.

In this work, silver nanoparticles (Ag NPs) were prepared by the direct reduction of $AgNO_3$ with hydrazine hydrate (N₂H₄·H₂O) in aqueous solution. A powder with typical metallic properties was obtained after filtration and drying. This can be easily compacted into a coin using a tablet press (Fig. 1) and used as the cathode for the electrocatalytic carboxylation of 1-phenylethyl bromide with CO₂. It should be noted that this coin was prepared from pure Ag NPs powder without a support or carrier. Both the synthesis of the Ag NPs cathode and carboxylation were performed under very mild conditions, and no other catalyst was needed.

For the synthesis of Ag NPs, 1.7 g AgNO₃ was dissolved in 100 mL deionized water. After 10 min stirring, 50 mL hydrazine hydrate solution (10%) was added, and the mixture was stirred at 25 °C for 4 h, and Ag NPs were precipitated immediately. The precipitate was filtered, and washed with 10 mL water and then 10 mL anhydrous ethanol for 4 times, and dried for 12 h at 35 °C under vacuum. Ag NP powder was pressed into a coin and used as the cathode for electrolysis.

Galvanostatic electrosynthesis was performed using a direct current regulated power supply (HY3002D, HYelec®, China). The product yield was determined by high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV (RS Variable Wavelength) detector. The microstructure and morphology of Ag NPs were analyzed using a Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM). X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K_{α} radiation ($\lambda = 0.15406$ nm). N₂ adsorption was carried out at -196 °C on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 300 °C.

The resulting material was characterized by many methods. Fig. 2(d) displays the XRD patterns of an Ag NPs coin. Typical diffraction peaks of the (111), (200), (220), (311) and (222) crystal faces were observed. It is also notable that no trace of



Fig. 1. Preparation of Ag NP electrode and electrocatalytic carboxylation of 1-phenethyl bromide with CO₂.



Fig. 2. Characterization results of Ag NPs. FE-SEM patterns of Ag NPs with magnifications of 5k (a), 20k (b), and after reuse for 10 times (c); (d): XRD patterns of Ag nanoparticles before (d-1) and after reuse for 10 times (d-2); FE-SEM patterns of Ag NPs with smaller particle size (e, f).

any other substance such as silver oxide was contained in this material. The FE-SEM patterns (Fig. 2(a), (b)) of the composite revealed that this Ag NP electrode has a hierarchical structure composed of metal nanocrystallites. These elementary particles were gathered into particles of 60 nm and aggregated further into a macroporous solid.

Besides the preparation and characterization of this Ag NP coin, we also showed its application in catalysis. As we mentioned above, the Ag NP powder was compacted into a coin with a 2 cm diameter, which can be used directly as the cathode for the electrocatalytic carboxylation of 1-phenylethyl bromide with CO2. Since galvanostatic electrolysis is often simpler and preferable for large scale applications, we therefore investigated the efficiency of the electrocatalytic carboxylation under galvanostatic conditions. A typical galvanostatic electrolysis was carried out in a mixture of 0.1 mol/L 1-phenylethyl bromide (1a), 0.1 mol/L tetraethylammonium iodide (TEAI) in 10 mL acetonitrile (MeCN) using an undivided glass cell with a Ag NP cathode and a sacrificial magnesium (Mg) anode. Each measurement was performed 3-4 times. After electrolysis, the products were detected quantitatively by HPLC, which showed that 2-phenylpropionic acid (2a) was the main product. The influences of electric charge (Q), current density, and the temperature were investigated to optimize the yield of 2a. The results of the electrolysis are summarized in Table 1.

In an electrochemical reaction, the electric charge passed during electrolysis strongly influenced the yield of product **2a** (Table 1, entries 1–4). The yield increased linearly with the charge from 1.5 to 2.5 F/mol. However, the yield did not increase further when the charge increased to 3.0 F/mol (Table

 Table 1

 Electrocatalytic carboxylation of 1-phenylethyl bromide under different conditions ^a.

Entry	Q (F/mol)	Current density (mA/cm ²)	<i>Т</i> (°С)	Yield b (%)
1	1.5	5	0	72
2	2.0	5	0	88
3	2.5	5	0	98
4	3.0	5	0	97
5	2.5	1	0	73
6	2.5	3	0	83
7	2.5	7	0	89
8	2.5	9	0	80
10	2.5	5	10	92
11	2.5	5	20	90
12	2.5	5	30	87
13 c	2.5	5	0	51
14 ^d	2.5	5	0	96

^a Electrolysis were carried out in an undivided cell, cathode: Ag NPs, anode: Mg, solvent: 10 mL MeCN, supporting electrolyte: 0.1 mol/L TEAI, substrate concentration: 0.1 mol/L. ^b Determined by HPLC. ^cCathode: Ag flake. ^dCathode: Ag NPs (20 nm).

1, entry 4), indicating that 1a was already consumed entirely when 2.5 F/mol electric charge was passed. As for the influence of the current density, the yield of 2a improved with the current density from 1 to 9 mA/cm², reaching a maximum (98%) at 5 mA/cm² (Table 1, entries 3, 5–8). Both low and high current densities led to lower yields. The reaction temperature was also a crucial factor, which influenced the overpotential and reaction rate of the electrolysis. The highest yield of 2a was obtained at 0 °C, a relatively low temperature. Increasing the temperature from 0 to 30 °C did not increase the yield of 2a. On the contrary, the 2a yield decreased from 98% to 87%. At a lower temperature, more CO2 was dissolved in MeCN, and CO2 is the key reagent in this reaction, which could explain this trend [19]. Although there was a slight decline, at least 90% yield of 2a could be achieved at 20 °C, which was room temperature. Hence, our Ag NP electrode generated very good results for the electrocatalytic carboxylation of 1-phenethyl bromide with CO₂ under very mild conditions. This was without the utilization of high CO₂ pressure or temperature.

Using the optimized conditions in Table 1, entry 3, different cathodes were also studied to show the superiority of our Ag NP cathode. Using Ag flake as cathode (Table 1 entry 13), only 51% yield of 2a was obtained, which was significantly lower than the 98% yield with the Ag NP cathode, indicating that our Ag NP cathode was much more effective for the electrocatalytic carboxylation of 1-phenethyl bromide with CO₂ than a common Ag flake cathode. This superiority can be attributed to the large specific surface area of Ag NPs. According to the N₂ adsorption isotherm, the Ag NP coin has an average specific surface area of 8.7 m²/g. Since 2 g Ag NPs powder was compacted into a 2 cm diameter coin, this gave this Ag NP cathode an actual surface area of 17.4 m². Hence, the real surface area of the Ag NP cathode is 5.5×10^4 times larger than that of a common Ag flake cathode, which would provide more active sites and accelerate the reaction rate. Since Ag NPs were more efficient than a common Ag flake cathode because of its nano-structure, can Ag NPs with smaller particle size lead to an even higher yield of

product? Further experiments were carried out to test this. We prepared Ag NPs with 20 nm particle size (Fig. 2(e), (f)) using the same method as the 60 nm Ag NPs except for the addition of polyethylene glycol in the reduction solution. Under the same conditions as Table 1, entry 3, 96% yield of **2a** was obtained at the Ag NP cathode with 20 nm particle size (Table 1 entry 14), which was obviously higher than that of the Ag flake cathode but almost the same as that of Ag NPs cathode with 60 nm particle size. This demonstrated again that nano-structure silver was beneficial to the electrocatalytic carboxylation of 1-phenethyl bromide with CO₂.

It should be noted that no other catalyst was needed in our synthesis system. In addition, this Ag NP cathode can be easily recycled and cleaned after an electrolysis. Under the electrolysis conditions of Table 1, entry 3, repeated tests of the electrocatalytic carboxylation of 1-phenethyl bromide with CO2 were carried out using the same Ag NP cathode. As shown in Fig. 3, the yield of **2a** was maintained at around 94% even after 10 runs, revealing that this Ag NP cathode has excellent reusability. XRD and SEM were used to further investigate the stability of the Ag NP electrode. According to the XRD patterns, the composition and crystal form of the Ag NPs did not change before and after electrolysis (Fig. 2(d)). Moreover, it retained its porous structures and had the same particle size (Fig. 2(c)). In other words, the Ag NPs electrode has excellent stability and reusability, and retained its catalytic activity after at least 10 times reuse.

Encouraged by excellent results obtained with 1-phenylethyl bromide (**1a**), the use of different substrates was further studied. Using the reaction conditions of Table 1, entry 3, a wide range of substituted bromides with both electron-withdrawing and electron-donating groups were tested for electrocatalytic carboxylation. The corresponding benzoic acids with moderate to good yields were obtained. As is obvious from the results summarized in Table 2, the Ag NP cathode can be applied to a wide range of substrates. Except for bromides, the Ag NP cathode was also effective for the carboxylation of 1-phenylethyl chloride, and 86% yield of



Fig. 3. Reuse of Ag NPs cathode. Reaction conditions are the same as Table 1, entry 3.

 Table 2

 Electrocatalytic carboxylation of different substrates with the Ag NP cathode ^a.

Entry	Substrate	Product	Yield ^b (%)
	Br	СООН	
1	la la	2a	98
2	Br 1b	COOH 2b	88
3	Br 1c	COOH 2c	73
	ÇOOH	СООН	
4	Br 1d	COOH 2d	67
5	Br 1e	COOH 2e	78
	Br	соон	
6	1f	2f	81
	ÇI	соон	
7	1g	2g	86

^a Electrolysis were carried out under the same conditions as Table 1, entry 3. ^b Determined by HPLC.

2-phenylpropionic acid was obtained using the same reaction condition as 1-phenylethyl bromide (Table 2, entry 7).

In conclusion, a compacted Ag NP cathode was prepared using a simple method without any support or carrier. This was effective for the electrocatalytic carboxylation of 1-phenethyl bromide with CO₂. Under optimized conditions, 2-phenylpropionic acid with 98% yield was obtained. Moderate to good yields of benzoic acids were achieved with other substrates. This Ag NP cathode has remarkable stability and reusability, shown by that the yield of 2-phenylpropionic acid did not decrease significantly after at least 10 times reuse. Considering its easy preparation, high effectiveness and excellent reusability, this Ag NP cathode has potential for practical application.

References

- [1] T. Sakakura, J. C. Choi, H. Yasuda, Chem. Rev., 2007, 107, 2365–2387.
- [2] C. A. Huff, M. S. Sanford, J. Am. Chem. Soc., 2011, 133, 18122–18125.
- [3] Z. F. Zhang, S. Q. Hu, J. L. Song, W. J. Li, G. Y. Yang, B. X. Han, *ChemSusChem*, 2009, 2, 234–238.
- [4] S. G. Liang, H. Z. Liu, T. Jiang, J. L. Song, G. Y. Yang, B. X. Han, Chem. Commun., 2011, 47, 2131–2133.
- [5] F. Shi, Y. Q. Deng, T. L. SiMa, J. J. Peng, Y. L. Gu, B. T. Qiao, Angew. Chem. Int. Ed., 2003, 42, 3257–3260.
- [6] B. Yu, H. Y. Zhang, Y. F. Zhao, S. Chen, J. L. Xu, C. L. Huang, Z. M. Liu, Green Chem., 2013, 15, 95–99.
- [7] O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, T. Cantat, *Chem-CatChem*, 2013, 5, 117–120.
- [8] M. North, R. Pasquale, C. Young, Green Chem., 2010, 12, 1514–1539.
- [9] A. A. Isse, A. D. Giusti, A. Gennaro, L. Falciola, P. R. Mussini, *Electrochim. Acta*, 2006, 51, 4956–4964.
- [10] P. L. Fabre, O. Reynes, *Electrochem. Commun.*, 2010, 12, 1360–1362.
- [11] A. Gennaro, A. A. Isse, F. Maran, J. Electroanal. Chem., 2001, 507, 124–134.
- [12] J. Damodar, S. R. K. Mohan, S. R. J. Reddy, *Electrochem. Commun.*, 2001, 3, 762–766.
- [13] L. X. Wu, H. Wang, Y. Xiao, Z. Y. Tu, B. B. Ding, J. X. Lu, *Electrochem. Commun.*, 2012, 25, 116–118.
- [14] Y. Xiao, B. L. Chen, H. P. Yang, H. Wang, J. X. Lu, *Electrochem. Commun.*, **2014**, 43, 71–74.
- [15] A. A. Isse, C. Durante, A. Gennaro, *Electrochem. Commun.*, 2011, 13, 810–813.
- [16] A. A. Isse, A. Gennaro, Chem. Commun., 2002, 2798-2799.
- [17] B. L. Chen, H. W. Zhu, Y. Xiao, Q. L. Sun, H. Wang, J. X. Lu, *Electro-chem. Commun.*, **2014**, 42, 55–59.
- [18] H. P. Yang, Y. N. Yue, Q. L. Sun, Q. Feng, H. Wang, J. X. Lu, Chem. Commun., 2015, 51, 12216–12219.
- [19] A. Gennaro, A. A. Isse, E. Vianello, J. Electroanal. Chem., 1990, 289, 203–215.

Page numbers refer to the contents in the print version, which include both the English version and extended Chinese abstract of the paper. The online version only has the English version. The pages with the extended Chinese abstract are only available in the print version.

