

Electrocatalytic asymmetric hydrogenation of α,β -unsaturated acids in a PEM reactor with cinchona-modified palladium catalysts



Atsushi Fukazawa^a, Kenta Tanaka^a, Yasushi Hashimoto^b, Yasushi Sato^b, Mahito Atobe^{a,*}

^a Graduate School of Science and Engineering, Yokohama National University, 79-1 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

^b R&D Solution Center, JXTG Nippon Oil & Energy Co., 8 Chidoricho, Naka-ku, Yokohama 231-0815, Japan

ARTICLE INFO

Keywords:

Electrosynthesis
Proton-exchange membrane (PEM) reactor
Electrocatalytic asymmetric hydrogenation
 α,β -Unsaturated acids
Cinchona-modified palladium catalysts

ABSTRACT

We have developed an electrocatalytic asymmetric hydrogenation reaction using a proton-exchange membrane (PEM) reactor that employs a polymer electrolyte fuel cell and industrial electrolysis technologies. Reasonable enantioselectivities and excellent current efficiencies were obtained in the asymmetric hydrogenation of α -phenylcinnamic acid under mild conditions without adding a supporting electrolyte. The current density was crucial to achieving the improved results observed.

1. Introduction

The asymmetric catalytic hydrogenation of prochiral unsaturated acids is a widely used method for the preparation of optically pure chiral carboxylic acids [1–4]. These compounds are mainly used in the synthesis of chiral pharmaceuticals. However, the majority of these reactions are homogeneously catalysed by transition metal complexes which are always expensive and typically non-recyclable [5–7]. Replacement of these highly efficient soluble catalysts by heterogeneous catalytic systems results in several economic and technical advantages [8]. The major advantage of heterogeneous catalysts is their easy recovery from reaction mixtures by simple filtration and recycling [9]. Therefore, the asymmetric hydrogenation of unsaturated acids using heterogeneous catalysts is one of the most challenging topics not only for fundamental scientific research but also for practical applications. Cinchona-modified palladium is well known to be an effective catalyst for the asymmetric hydrogenation of α,β -unsaturated acids such as α -phenylcinnamic acid (PCA) [10–12]. In fact, using this catalyst, Sugimura and co-workers have successfully demonstrated the asymmetric hydrogenation of PCA derivatives with excellent enantioselectivities (up to 92% ee) [12].

Organic electrochemical reactions driven by electrical energy can generally be carried out under mild conditions (room temperature and ambient pressure) without any oxidant or reductant [13–16]. Therefore, organic electrochemical synthesis has recently attracted attention as an environmentally friendly process [17]. In addition, the electrical energy can be provided from renewable energy sources such as solar and wind, thus making the electrochemical synthesis sustainable [18].

However, electrosynthesis also has some drawbacks. Since the reaction only proceeds at the electrode surface, the area for electron transfer is limited [19]. Consequently, the productivity of an electrosynthesis is generally inferior to that of chemical homogeneous reaction systems. In addition, a large amount of supporting electrolyte is usually required to make the solution conducting. Therefore, the availability of solvents is limited by the necessity for dissolution of a supporting electrolyte. The presence of a supporting electrolyte often leads to difficulties with subsequent product purification and unwanted side reactions [20]. These problems of conventional electrochemical synthesis can be overcome by the use of a proton-exchange membrane (PEM) reactor.

Although the PEM reactor was originally developed for water electrolysis and fuel cells [21,22], this reactor system possesses many characteristics designed to overcome the disadvantages of conventional electrosynthetic processes [23]. In fact, in our previous work, we successfully demonstrated the highly efficient and selective electrocatalytic semihydrogenation of alkynes to Z-alkenes in a PEM reactor without adding any supporting electrolyte to the substrate solutions [23]. This is the first report of product selectivity and stereoselective control in fine chemical syntheses using a PEM reactor.

Electrochemical asymmetric synthesis has been extensively investigated by many researchers. The transformation of achiral organic substrates into chiral products by electrosynthetic methods requires the active participation of an external source of chirality [24]. Various chiral sources such as chiral supporting electrolytes [25], chiral solvents [26], chiral electrodes [27–29], and chiral catalysts [30] have been used for enantioselective recognition. With regard to the electrochemical asymmetric hydrogenation of alkenes, moderate

* Corresponding author.

E-mail address: atobe@ynu.ac.jp (M. Atobe).

<https://doi.org/10.1016/j.elecom.2020.106734>

Received 7 April 2020; Received in revised form 17 April 2020; Accepted 17 April 2020

Available online 20 April 2020

1388-2481/© 2020 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

enantioselectivities (43–63% ee) have been reported by several groups [31,32]. However, these reactions were carried out by a conventional electrosynthetic method, and hence suffered from some of the drawbacks of electrosynthetic processes.

Herein, we report the first electrocatalytic asymmetric hydrogenation of α,β -unsaturated acids in a PEM reactor with chiral-modified electrocatalysts under mild conditions without a supporting electrolyte. Controlling factors such as the current density and the chiral modifier were optimized to establish a highly efficient and reasonably enantioselective hydrogenation system.

2. Experimental

2.1. General procedure

Gas chromatography (GC) analyses were performed using a Shimadzu gas chromatograph (GC2014) equipped with a Cyclosil-B (Agilent Technologies, Inc.) Helium was used as a carrier gas for GC analyses. High-performance liquid chromatography (HPLC) analyses were performed with a LC pump (LC-20 AD, Shimadzu Co.), a UV detector (SPD-20A, Shimadzu Co.), and a chiral column (OD-H 250-4.6, Daicel, Co. Inc.) under isothermal (25°C) conditions using a mixture of *n*-hexane/IPA and TFA as a mobile phase. Potentiostatic and galvanostatic electrolyses were carried out using a potentiostat (Hokuto Denko HABF-501A). Potential changes were monitored using a voltammetric data logger (VR-71, T&D Co.). AC impedance measurements were performed using an electrochemical analyzer (660E, BAS. Inc.).

2.2. Preparation of MEA

The MEA was prepared as described in our previous work [23]. The MEA was fabricated with 0.5 mg cm² of metal loading. The catalyst ink consisted of fuel cell catalyst (Pt/C, 46.0 wt% or Pd/C, 29 wt%), deionized water, Nafion® perfluorinated resin solution, and 1-propanol. Pt was used as the anode catalyst material and Pd was used as the cathode catalyst material.

2.3. Synthesis of PCA derivatives and its characterization

PCA derivatives were synthesized using the Perkin reaction [12]. A mixture of a substituted phenylacetic acid (5.0 g), a substituted benzaldehyde (1.0–1.2 equiv.), triethylamine (0.7 equiv.), and acetic anhydride (2.9 equiv.) was heated at 120 °C for 48 h. After cooling, water (50 mL) and then 6 N KOH aqueous solution (15 mL) were added. After vigorous stirring overnight, the mixture was washed with ether ($\times 2$), and the resulting aqueous solution was neutralized by the addition of

2 N HCl (100 mL). After 30 min, the precipitate was collected by filtration, dissolved in ethyl acetate with active charcoal, and the filtrate was concentrated and recrystallized using a mixture of ethanol and water.

¹H NMR spectra were recorded on a Bruker Avance 500 spectrometer at ambient temperature.

E-2-(4-methoxyphenyl)-3-(4-methoxyphenyl)acrylic acid(4) [12]

White solid; yield: 39%; ¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H), 3.79 (s, 3H).

E-2-(4-trifluoromethylphenyl)-3-(4-trifluoromethylphenyl)acrylic acid(5) [33]

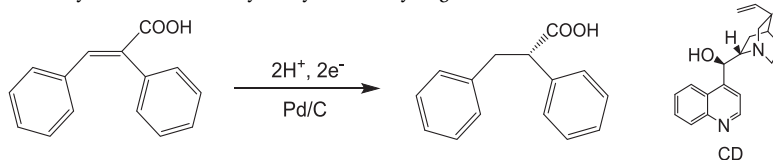
White solid; yield: 43%; ¹H NMR (500 MHz, CDCl₃) δ 8.06 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H).

2.4. Electrocatalytic asymmetric hydrogenation procedure

We took the asymmetric hydrogenation of PCA to 2,3-diphenylpropionic acid (DPPA) as a model reaction (see reaction scheme in Table 1) and performed galvanostatic electrocatalytic asymmetric hydrogenation in a PEM reactor. To conduct the electrosynthesis in a PEM reactor, humidified hydrogen gas was introduced directly to the anodic chamber (flow rate: 50 mL min⁻¹) and electrocatalytically oxidized at the Pt anode catalyst to produce protons, as shown in Fig. 1. In this case, the anodic reaction was hydrogen oxidation, the potential of which is almost same as the reversible hydrogen electrode (RHE); therefore, the anode functioned not only as the counter electrode but also as a RHE reference electrode [34]. Subsequently, the produced protons were transported through the proton-conducting polymer. At the cathode, protons penetrating through the polymer were reduced to monoatomic hydrogen species on the metal (Pd) catalyst surface, and then reacted with the substrate to give the corresponding hydrogenated product. During the electrosynthesis, a 1,4-dioxane solution of PCA (0.3 mmol) and cinchonidine (CD) (19 μ mol) as the substrate and the chiral modifier, respectively, were introduced to the cathodic chamber by a circulator pump (MSP101-00, Yamazen Corporation) in a closed system (total volume of 1,4-dioxane solution: 5.0 mL, flow rate: 1.25 mL min⁻¹) (Fig. 1). The hydrogenated products were analysed by GC or HPLC. In this work, 1,4-dioxane was selected as a solvent for the electrocatalytic hydrogenation due to its better solubility for the substrate acids. Although 1,4-dioxane is miscible with water, the Nafion part of the MEA and its proton conductivity were less affected during the electrolysis. The cell voltage was stable and kept constant during the electrolysis.

Table 1

The current efficiency and enantioselectivity of the electrocatalytic asymmetric hydrogenation of PCA with and without BA addition in a PEM reactor.^a



Entry	Additive	Pretreatment ^b	Current efficiency ^c (%)	Optical yield ^c (%ee)
1	none	without	27	2
2	BA (1eq.)	without	66	30
3	BA (1eq.)	with	87	44

^a Reaction conditions: anode catalyst, Pt; cathode catalyst, Pd; charge passed, 0.5 F mol⁻¹; cell temperature, r.t.; concentration, 0.06 M in 1,4-dioxane; substrate solution, 5 mL; addition amount of CD, 19 μ mol; current density, 0.4 mA cm⁻²; flow rate of substrate solution, 1.25 mL min⁻¹; flow rate of hydrogen, 50 mL min⁻¹.

^b For the pretreatment of Pd catalysts, 1,4-dioxane without PCA, BA and CD was provided to the cathodic chamber by a circulator pump and a potential of 0 V vs. RHE was applied for 1 h.

^c Determined by chiral HPLC

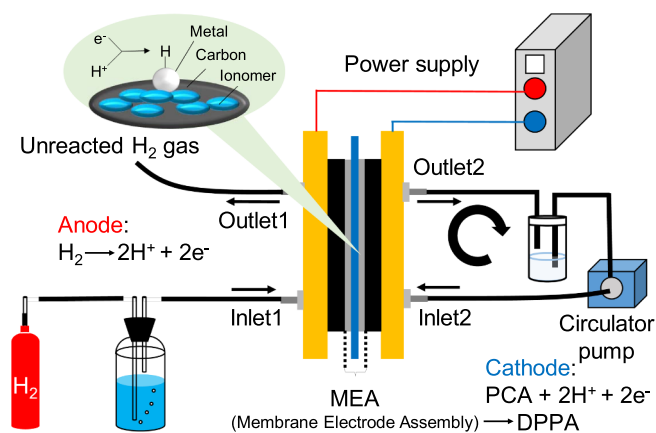


Fig. 1. Schematic image of a PEM reactor.

3. Results and discussion

Nitta reported that the addition of benzylamine (BA) increased the reaction rate and the enantioselectivity in the conventional asymmetric hydrogenation of PCA with a heterogeneous cinchona-modified palladium catalyst [11]. The author proposed that the rate enhancement might be due to facilitating the desorption of the product acids via an acid–base interaction. In addition, it was suggested that BA also contributes to a dynamic change in the adsorption configuration of the chiral modifier on the Pd surface and leads to a better stereochemically defined surface [35]. Based on the above information, we conducted electrocatalytic asymmetric hydrogenation of PCA in a PEM reactor with and without BA (Entries 1 and 2, Table 1). In the case without BA, the current efficiency and the enantioselectivity were very low, but were much improved on the addition of BA. Thus, BA addition was also effective for electrocatalytic asymmetric hydrogenation in a PEM reactor. Both the efficiency and the selectivity were further improved by using a pretreated catalyst (Entry 3). The pretreatment was conducted by electroreducing an oxide film on the catalyst surface at 0 V vs. RHE for 1 h before the electrocatalytic asymmetric hydrogenation. This operation cleaned the catalyst surface and the BA and the chiral modifier were adsorbed effectively on the surface.

In this reaction system, the hydrogen evolution reaction via the coupling of monoatomic hydrogen species is the main side electrochemical reaction. Therefore, it is expected that the current density would influence the efficiency of the desired hydrogenation reaction. Fig. 2 shows the influence of the current density on the current efficiency and the optical yield in the electrocatalytic asymmetric hydrogenation of PCA. The average cathode potential during each electrolysis is also shown in Fig. 2. Excellent current efficiencies were obtained at lower current densities. The efficiency decreased as the current density increased because the hydrogen evolution reaction became dominant at higher densities. In addition, we confirmed that no product formation was observed at zero current. This fact indicates that hydrogen crossover did not take place in our system. Therefore, the asymmetric hydrogenation proceeded by electrocatalytic reduction. In the present system, a hydrogen oxidation reaction was employed as the anodic process so that the anode was used not only as the counter electrode but also as the RHE reference electrode. However, the use of hydrogen gas may be a disadvantage for practical applications. In principle, this is not a problem as long as the anodic process of the PEM reactor is a proton-providing reaction such as water oxidation [23].

With regard to the enantioselectivity, the optical yield increased with an increase in the current density, reaching 50% at 0.8 mA cm^{-2} , but decreased at current densities higher than 1.5 mA cm^{-2} . Several groups have reported the adsorption and desorption behaviours of quinoline derivatives at various potentials [36,37]. Based on their

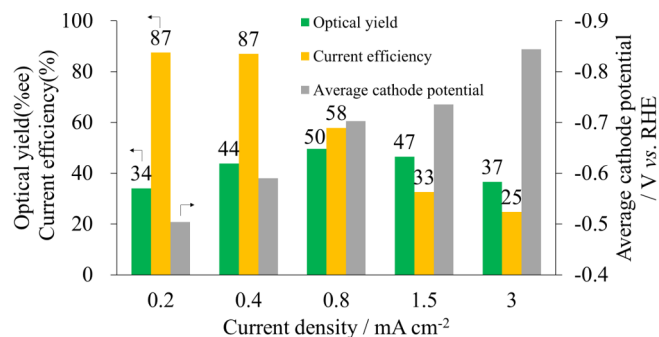


Fig. 2. The effect of current density on current efficiency and optical yield in electrocatalytic asymmetric hydrogenation of PCA with CD in a PEM reactor. Reaction conditions: anode catalyst, Pt; cathode catalyst, Pd; charge passed, 0.5 F mol^{-1} ; cell temperature, r.t.; concentration, 0.06 M in 1,4-dioxane; substrate solution, 5 mL ; amount of BA addition, 1 eq. to PCA; amount of CD addition, $19 \mu\text{mol}$; flow rate of substrate solution, 1.25 mL min^{-1} ; flow rate of hydrogen, 50 mL min^{-1} . For the pretreatment of Pd catalysts, 1,4-dioxane without PCA, BA and CD was introduced to the cathodic chamber by a circulator pump and a potential of 0 V vs. RHE was applied for 1 h. Current efficiency and optical yield were determined by chiral HPLC. The potential values were corrected for the IR drop determined by the impedance measurement.

experimental results, they indicated that at less negative potentials, the adsorbed quinoline derivatives were arranged with the plane of the quinoline ring parallel to the electrode surface, in which orientation the π -orbitals of the ring could interact with the electrode surface. However, at more negative potentials, the adsorbed quinoline ring was raised due to the repulsive interaction between the π -orbital of the quinoline ring and the negative surface charge. Finally, quinoline derivatives began to desorb from the electrode surface at larger negative potentials. CD, which is a chiral modifier used in this work, is a quinoline derivative. Therefore, along the same lines as the adsorption and desorption behaviours, the dependence of the optical yield on the current density may be hypothetically explained as follows. As illustrated in Fig. 3, the quinoline moiety of CD can adsorb flat on the electrode surface at lower current densities (at less negative potentials). As the current density increases, the cathode potential should be more negative, and hence the parallel adsorbed CD species is raised by the repulsive interaction. Rodríguez-García et al. reported that raised CD species lead to significantly more efficient enantiodifferentiation in their cinchona-modified catalyst system [38]. Based on their report, this reorientation may provide ideal chiral recognition sites and result in an increase in the optical yield. However, at higher current densities (at even more negative potentials), CD begins to desorb from the electrode surface, and hence the optical yield is decreased.

The choice of chiral modifier is also crucial to the high enantioselectivity observed in this study. We conducted electrocatalytic asymmetric hydrogenation of PCA in a PEM reactor with various chiral alkaloid modifiers (Table 2). Although the current efficiency was very high, only the racemic product was obtained in the case without a chiral modifier (Entry 1). When cinchonine (CN) was used as a chiral modifier, the optical yield was less than that obtained with CD (Entries 2 and 3). Sugimura et al. reported that the enantio-differentiating ability of CN was lower than that of CD [39], in agreement with our results. In addition, it should be noted that the *R*-isomer was obtained in excess when using CN. This can be ascribed to a difference in the absolute configurations of C9 and C8 between CD and CN. The use of quinine (QN) gave low enantioselectivity due to its weak adsorption strength on the Pd catalyst surface, which originates from the steric hindrance of the methoxy substituent at C6 (Entry 4) [39]. In the case with the α -isocupreine (α -ICPN) modifier, a high current efficiency was observed, but the enantioselectivity was very low (Entry 5). α -ICPN has a hydroxy substituent at C6, and therefore the low enantioselectivity of the α -ICPN-modified catalyst is ascribed to a low surface coverage of α -

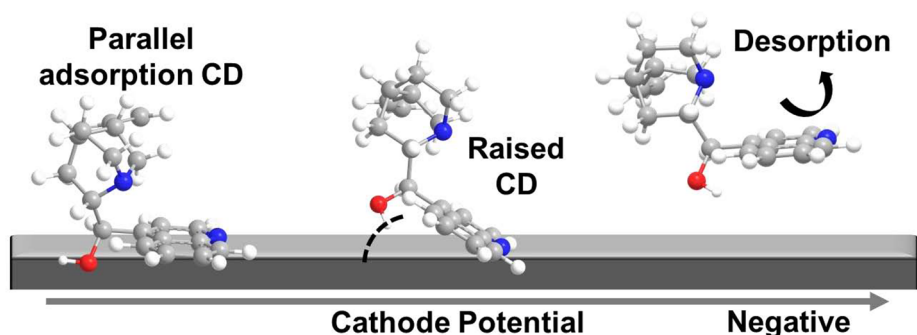


Fig. 3. Plausible adsorption and desorption behaviours of CD on the Pd electrocatalyst surface at various cathode potentials.

Table 2

Electrocatalytic asymmetric hydrogenation of PCA in a PEM reactor with various alkaloid modifiers.^a

Entry	Chiral modifier	Current efficiency ^b (%)	Optical yield ^b (%ee)
1	none	91	–
2	CD	87	44 (S)
3	CN	78	19 (R)
4	QN	65	13 (S)
5	α -ICPN	80	4 (R)
6	QQVM	30	3 (S)

^a Reaction conditions: anode catalyst, Pt; cathode catalyst, Pd; charge passed, 0.5 F mol⁻¹; cell temperature, r.t.; concentration, 0.06 M in 1,4-dioxane; substrate solution, 5 mL; amount of BA addition, 1 eq. to PCA; amount of chiral modifier addition, 19 μ mol; current density, 0.4 mA cm⁻²; flow rate of substrate solution, 1.25 mL min⁻¹; flow rate of hydrogen, 50 mL min⁻¹. For the pretreatment of Pd catalysts, 1,4-dioxane without PCA, BA and CD was provided to the cathodic chamber by a circulator pump and the potential of 0 V vs. RHE was applied for 1 h.

^b Determined by chiral HPLC.

ICPN. Both current efficiency and enantioselectivity were quite low in the case with the (*S*)-*N*-8-quinolinesulfonyl-(quinolin-4-yl)-(8-vinylquinuclidin-2-yl)methanamine (QQVM) modifier (Entry 6). This modifier has two quinoline moieties and hence may adsorb strongly on the catalyst surface. However, there is little space for access of PCA to the chiral centre of QQVM due to its large steric hindrance. Therefore, it can be stated that, of the samples tested, CD is the best chiral modifier for electrocatalytic asymmetric hydrogenation of PCA in a PEM reactor.

Finally, to demonstrate the general applicability of this reaction

system, we carried out the electrocatalytic hydrogenation of various α,β -unsaturated acids using a PEM reactor with a CD modifier (Fig. 4). By comparison of the results, it was found that the phenyl group at the α -position was crucial to the high enantioselectivity observed in this reaction system. The α -phenyl group is twisted from the olefinic plane of PCA. The steric hindrance provided by this twist seems to enhance the enantiomeric recognition. When carboxylic acid **3** was used as a substrate, the current efficiency was decreased because acid **3** is less reducible than the other carboxylic acids. On the other hand, the

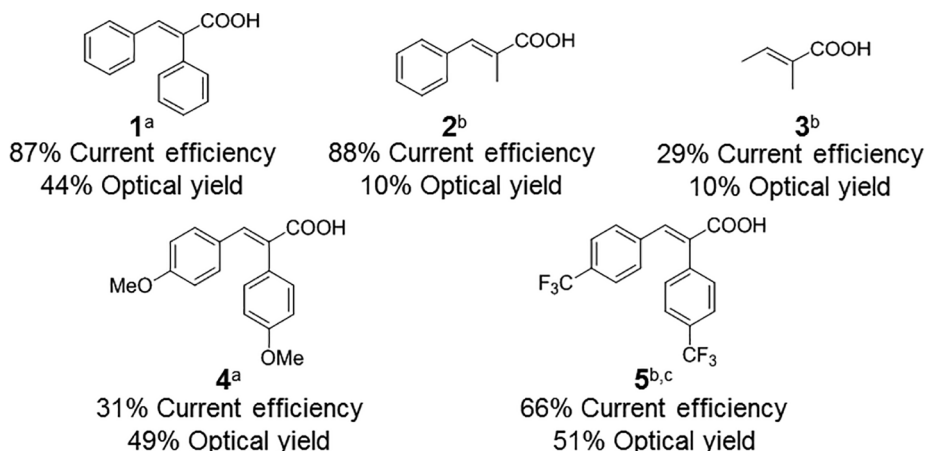


Fig. 4. The current efficiency and enantioselectivity for the electrocatalytic asymmetric hydrogenation of α,β -unsaturated acids in a PEM reactor. Reaction conditions: anode catalyst, Pt; cathode catalyst, Pd; charge passed, 0.5 F mol⁻¹; cell temperature, r.t.; concentration, 0.06 M in 1,4-dioxane; substrate solution, 5 mL; amount of BA addition, 1 eq. to PCA; amount of CD addition, 19 μ mol; current density, 0.4 mA cm⁻²; flow rate of substrate solution, 1.25 mL min⁻¹; flow rate of hydrogen, 50 mL min⁻¹. For the pretreatment of Pd catalysts, 1,4-dioxane without PCA, BA and CD was provided to the cathodic chamber by a circulator pump and a potential of 0 V vs. RHE was applied for 1 h. ^aCurrent efficiency and optical yield were determined by chiral HPLC. ^bCurrent efficiency and optical yield were determined by chiral GC. ^cMethyl esterification of the product was conducted before the analysis.

introduction of an electron-donating group on the phenyl moieties resulted in a decrease in the current efficiency. This can be ascribed to an increase in the electron density on the C = C double bond. In contrast, the efficiency was improved to some extent by the introduction of an electron-withdrawing group such as a trifluoromethyl group, but it was still lower than that of carboxylic acid **1**. This may be ascribed to the difficulty of accessing the catalyst surface due to the steric hindrance of the trifluoromethyl group. On the other hand, the introduction of a methoxy or trifluoromethyl group on the phenyl moieties resulted in an increase in the optical yield compared with the carboxylic acid **1**, with carboxylic acid **5** giving the best optical yield of 51% ee. This observation suggests that steric factors rather than the polarity of the substrate play a significant role in increasing the optical yield in our reaction system.

4. Conclusion

We have demonstrated the first electrocatalytic asymmetric hydrogenation of α,β -unsaturated acids in a PEM reactor under mild conditions, without a supporting electrolyte. The current density was crucial to achieving the better enantioselectivities and high current efficiencies observed in this reaction system. CD was found to be the best chiral modifier among all the cinchona alkaloids tested. In addition, it was found that the α -phenyl group of the α,β -unsaturated acids was necessary to obtain better enantioselectivity. We expect that this research will lead to the development of various fine chemical synthetic processes using a PEM reactor.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was financially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 2707: Middle Molecular Strategy) and JST CREST Grant No. JP65R1204400, CREST, Japan.

References

[1] Gy. Szöllösi, B. Hermán, F. Fülöp, M. Bartók, *J. Catal.* 276 (2010) 259–267.

- [2] M. Breuer, K. Dittrich, T. Habicher, B. Hauer, M. Kessler, R. Stürmer, T. Zelinski, *Angew. Chem., Int. Ed.* 43 (2004) 788–824.
- [3] J.A.F. Boogers, U. Felfer, M. Kotthaus, L. Lefort, G. Steinbauer, A.H.M. de Vries, J.G. de Vries, *Org. Process Res. Dev.* 11 (2007) 585–591.
- [4] H.-U. Blaser, B. Pugin, F. Spindler, *J. Mol. Catal. A: Chem.* 231 (2005) 1–20.
- [5] H.P. Yang, H. Wang, J.X. Lu, *Electrochem. Commun.* 55 (2015) 18–21.
- [6] W. Tang, X. Zhang, *Chem. Rev.* 103 (2003) 3029–3069.
- [7] C. Jäkel, R. Paciello, *Chem. Rev.* 106 (2006) 2912–2942.
- [8] Gy. Szöllösi, B. Hermán, K. Felföldi, F. Fülöp, M. Bartók, *J. Mol. Catal. A: Chem.* 290 (2008) 54–59.
- [9] R. Sen, D. Saha, S. Koner, *Catal. Lett.* 142 (2012) 124–130.
- [10] F. Meemken, A. Baiker, *Chem. Rev.* 117 (2017) 11522–11569.
- [11] Y. Nitta, *Chem Lett* 28 (1999) 635–636.
- [12] T. Sugimura, T. Uchida, J. Watanabe, T. Kubota, Y. Okamoto, T. Misaki, T. Okuyama, *J. Catal.* 262 (2009) 57–64.
- [13] M. Yan, Y. Kawamata, P.S. Baran, *Chem. Rev.* 117 (2017) 13230–13319.
- [14] J.-I. Yoshida, A. Shimizu, R. Hayashi, *Chem. Rev.* 118 (2018) 4702–4730.
- [15] T. Fuchigami, T. Tajima, *Electrochemistry* 74 (2006) 585–589.
- [16] M. Yan, Y. Kawamata, P.S. Baran, *Angew. Chem., Int. Ed.* 57 (2018) 4149–4155.
- [17] T. Raju, S. Manivasagan, B. Revathy, K. Kulangiappar, A. Muthukumar, *Tetrahedron Lett.* 48 (2007) 3681–3684.
- [18] J.A. Lopez-Ruiz, U. Sanyal, J. Egbert, O.Y. Gutiérrez, J. Holladay, A.C.S. Sustain. Chem. Eng. 6 (2018) 16073–16085.
- [19] A.A. Folguez-Amador, T. Wirth, *J. Flow Chem.* 7 (2017) 94–95.
- [20] Z. Ogumi, K. Nishio, S. Yoshizawa, *Electrochim. Acta* 26 (1981) 1779–1782.
- [21] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, *Int. J. Hydrogen Energy* 38 (2013) 4901–4934.
- [22] B. Smitha, S. Sridhar, A.A. Khan, *J. Membr. Sci.* 259 (2005) 10–26.
- [23] A. Fukazawa, J. Minoshima, K. Tanaka, Y. Hashimoto, Y. Kobori, Y. Sato, M. Atobe, A.C.S. Sustain. Chem. Eng. 7 (2019) 11050–11055.
- [24] M. Ghosh, V.S. Shinde, M. Rueping, *Beilstein Journal of Organic Chemistry* 15 (2019) 2710–2746.
- [25] L. Horner, D. Degner, *Tetrahedron Lett.* 9 (1968) 5889–5892.
- [26] D. Seebach, H.A. Oei, *Angew. Chem., Int. Ed.* 14 (1975) 634–636.
- [27] Y. Kashiwagi, F. Kurashima, S. Chiba, J. Anzai, T. Osa, J.M. Bobbitt, *Chem. Commun.* 1 (2003) 114–115.
- [28] S. Assavapanumat, M. Ketkaew, A. Kuhn, C. Wattanakit, *J. Am. Chem. Soc.* 141 (2019) 18870–18876.
- [29] G.A. Attard, A. Ahmadi, D.J. Jenkins, O. Hazzazi, P.B. Wells, K.G. Griffin, P. Johnston, J.E. Gillies, *ChemPhysChem* 4 (2003) 123–130.
- [30] K.L. Jensen, P.T. Franke, L.T. Nielsen, K. Daasbjerg, K.A. Jørgensen, *Angew. Chem., Int. Ed.* 49 (2010) 129–133.
- [31] N. Schoo, H.-J. Schäfer, *Liebigs Ann. Chem.* 6 (1993) 601–607.
- [32] S. Abe, T. Nonaka, T. Fuchigami, *J. Am. Chem. Soc.* 105 (1983) 3630–3632.
- [33] M.C. Fu, R. Shang, W.M. Cheng, Y. Fu, *ACS Catal.* 6 (2016) 2501–2505.
- [34] S. Mitsushima, Y. Takakuwa, K. Nagasawa, Y. Sawaguchi, Y. Kohno, K. Matsuzawa, Z. Awaludin, A. Kato, Y. Nishiki, *Electrocatalysis* 7 (2016) 127–131.
- [35] F. Meemken, N. Maeda, K. Hungerbühler, A. Baiker, *ACS Catal.* 2 (2012) 464–467.
- [36] S. Bordin, G. Papaschi, *J. Electroanal. Chem. Interfacial Electrochem.* 20 (1969) 297–309.
- [37] K. Motobayashi, R. Tomioka, T. Uchida, M. Osawa, *Chem. Lett.* 44 (2015) 770–772.
- [38] L. Rodríguez-García, K. Hungerbühler, A. Baiker, F. Meemken, *Catal. Today* 283 (2017) 66–73.
- [39] M. Nakatsuji, T. Misaki, Y. Okamoto, T. Sugimura, *Bull. Chem. Soc. Jpn.* 89 (2016) 1187–1191.