



Electrocatalytic hydrogenation of organic compounds using current density gradient and sacrificial anode of nickel

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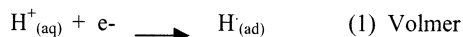
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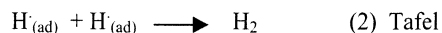
Abstract—Preparative electrocatalytic hydrogenation (ECH) of some organic compounds were performed: cyclohexene, 2-cyclohexen-1-one, benzaldehyde, acetophenone, styrene, 1,3-cyclohexadiene, *trans-trans*-2,4-hexadien-1-ol, citral, linalool and geraniol. H₂O/MeOH (1:1), NH₄OAc or NH₄Cl (0.2 M) were used as solvent and supporting electrolyte. A sacrificial anode of nickel allowed the use of an undivided cell, with a cell voltage varying between 2.3 and 1.3 V, depending on the supporting electrolyte. A current density gradient was applied to diminish the time of reaction and obtain a good electrochemical efficiency. An in situ prepared cathode of nickel deposited on iron provided a highly efficient ECH process, and the constant deposition of nickel on the electrode surface avoided catalyst poisoning. The ECH system was somewhat selective, hydrogenating conjugated olefins in good yield. © 2003 Elsevier Science Ltd. All rights reserved.

Electrochemical generation of hydrogen provides an interesting means to hydrogenate organic compounds.¹ The technique was improved by the development of various specific electrodes, which allowed for selective hydrogenation of different classes of organic compounds.² The discoveries of influencing parameters such as: supporting electrolyte,³ solvent,⁴ surfactant⁵ and the presence of inert gas,⁶ were important advances in electrocatalytic hydrogenation (ECH).

The success of the ECH is related to a conjugation of two mechanisms: the electrochemical generation of hydrogen and the catalytic hydrogenation.² The first one, also named hydrogen evolution reaction (HER),⁷ is classically based on a primary discharge step giving atomic hydrogen, which remains on the metal surface by chemical adsorption:^{8–10}



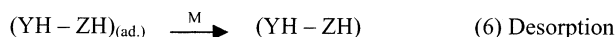
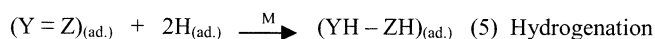
the following step is the combination of either two adsorbed hydrogen atoms:



or of a proton and an H atom (electrochemical desorption):



The ECH process involves three more steps,^{1,2} the adsorption of the olefin on the metal surface (4), the hydrogenation of the unsaturated group (5), and the desorption of the hydrogenated product from the metal surface (6):



Both processes, atomic hydrogen generation and catalytic hydrogenation, are cathode material dependent (M).² The ECH efficiency is determined by competition among hydrogenation of the unsaturated substrate, H₂ evolution, and, in some cases, the direct reduction of the substrate on the electrode surface.² The relative rates of these processes are not only affected by chemisorbed hydrogen activity, but also by the current density and the presence of any molecule (solvent, supporting electrolyte, surfactants) or reagent adsorbed on the cathode (catalyst) surface.^{6,11} The synergetic effect of a metal deposited on a matrix has been recently studied, and the behavior of a deposit is different from a pure solid material.¹²

Keywords: electrocatalytic hydrogenation; current density gradient; sacrificial anode.

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In this work we describe an efficient hydrogenation method for conjugated organic systems including olefins, aldehydes and ketones, using an electrochemical device made of an undivided cell fitted with a sacrificial anode of nickel, a cathode of iron and ammonium salt as supporting electrolyte. A current density gradient was implemented to increase the time/efficiency relation during electrolysis.

ECHs were carried out with 0.1 M substrate concentration, dissolved in 50 mL H₂O/MeOH (1:1). A sacrificial anode of nickel simplifies the procedure making possible the use of an undivided cell (Fig. 1),¹³ at the same time nickel is responsible by activation of the cathode (catalyst).¹⁴ Increasing cell voltage was observed during electrolyses, using 0.2 M NH₄OAc ($\Delta E = 2.3$ – 2.5 V) or NH₄Cl ($\Delta E = 1.3$ – 1.5 V) as supporting electrolyte. A current density gradient was applied by using initially 350 mA dm⁻².¹⁴ After passage of the first half charge necessary to a total theoretical hydrogenation, the current density was decreased to 306 mA dm⁻², and successively to 262, 219 and 175 mA dm⁻², at this point the current was maintained until total hydrogenation of the substrate was achieved. In Table 1 are shown ECHs of organic substrates using NH₄OAc as a supporting electrolyte in a first group, and NH₄Cl in a second one. Interesting results, like the unreactivity of non-conjugated substrates, were observed in the NH₄OAc group reactions. Cyclohexene, geraniol (Table 1, entries 1 and 19), and linalool showed a low yield of 30% (Table 1, entry 17), while 2-cyclohexen-1-one, benzaldehyde and styrene (Table 1, entries 3, 5 and 9) were hydrogenated with yields over 90% and electrochemical efficiencies[†] of 69, 35 and 48%, respectively. Acetophenone (Table 1, entry 7) was not reactive under these conditions. The

conjugated olefins, 1,3-cyclohexadiene and *trans-trans*-2,4-hexadien-1-ol (Table 1, entries 11 and 13), were hydrogenated in good yields but with different reactivity and selectivity. The former was more reactive giving cyclohexane (88%) as the major product, while the latter was less reactive, giving a mixture of dihydrogenated products (mixture of isomers, 52%) and tetrahydrogenated product (1-hexanol, 31%). The electrochemical efficiency was also different with values

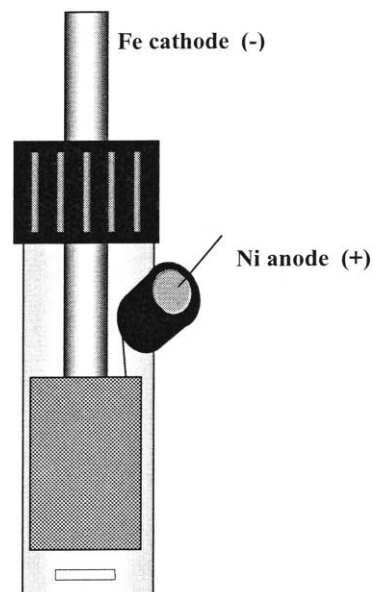


Figure 1. Electrochemical cell used in ECH reactions using sacrificial anode of nickel. (1) Cathode (nickel deposited on Fe⁰ bar); (2) anode (Ni⁰). Electrodes are dropped into a solution containing water/co-solvent and supporting electrolyte, constant stirring is necessary.

Table 1. Electrocatalytic hydrogenation of some organic substrates using H₂O/MeOH (1:1) solvent, 0.2 M NH₄OAc or NH₄Cl supporting electrolyte and current density gradient^a from 350 to 175 mA dm⁻². Inert atmosphere (N₂) was used only for NH₄OAc electrolyses group

Entry	Substrate (0.1 M)	Yield (%) / ee (%) ^b	Charge (C) / (F mol ⁻¹) ^c	Yield (%) / ee (%) ^b	Charge (C) / (F mol ⁻¹) ^c
1, 2	Cyclohexene	0/(0)	960/(1.0)	0/(0)	960/(1.0)
3, 4	2-Cyclohexen-1-one ^c	94, 1, 1/(69)	1288/(1.4)	96, 1, 1/(82)	1190/(1.2)
5, 6	Benzaldehyde	94/(35)	2553/(2.7)	99/(50)	1920/(2.0)
7, 8	Acetophenone	0/(0)	960/(1.0)	85/(33)	2547/(2.6)
9, 10	Styrene	95/(48)	1920/(2.0)	97/(65)	1450/(1.5)
11, 12	1,3-Cyclohexadiene ^d	12, 88/(94)	1920/(2.0)	11, 88/(94)	1920/(2.0)
13, 14	<i>trans-trans</i> -2,4-Hexadien-1-ol ^e	52, 31/(42)	2559/(2.7)	56, 38/(66)	1920/(2.0)
15, 16	Citral ^f	15, 36, 6, 9/(46)	2149/(2.2)	5, 70, 8, 14/(84)	1920/(2.0)
17, 18	Linalool	30/(15)	1920/(2.0)	93/(66)	1390/(1.4)
19, 20	Geraniol	0/(0)	960/(1.0)	22/(11)	1920/(2.0)

^a Current density gradient applied: 1–350 mA dm⁻² to the first half charge (480 C); 2–306 mA dm⁻² to the second half charge (240 C); 3–262 mA dm⁻² to the third half charge (120 C); 4–219 mA dm⁻² to the fourth half charge (60 C); 5–175 mA dm⁻² until reaction end.

^b Electrochemical efficiency was determined from the yield of total hydrogenation products.

^c Hydrogenation products: cyclohexanone, 2-cyclohexen-1-ol and cyclohexanol, respectively.

^d Hydrogenation products: cyclohexene, cyclohexane, respectively.

^e Hydrogenation products: mixture of hexen-1-ol isomers and 1-hexanol, respectively.

^f Hydrogenation products: citronellal, citronellol, nerol and geraniol, respectively.

^g Charge passed during electrolyses, and the corresponding faraday number per mol of reduced double bond (theoretical).

[†] Relation between hydrogen electrochemical generation ($Q = n \text{ (mol)} \times e \times 96487 \text{ (C mol}^{-1}\text{)}$) versus hydrogenated substrate yield. Electrical charge passed is $Q = I \text{ (A)} \times t \text{ (s)}$.

of 94 and 42%, respectively. We can observe here a different behavior for the hydrogenation of a conjugated (1,3-cyclohexadiene) and non-conjugated system (cyclohexene). This may occur due to differences in adsorption strength of substrates on the catalyst surface. Citral, with a conjugated double bond, showed low reactivity (Table 1, entry 15).

The exchange of supporting electrolyte from NH_4OAc to NH_4Cl allowed for lower cell voltages and elimination of oxygen during electrolysis.¹⁴ As a result, higher yields could be obtained in most cases, along with higher electrochemical efficiencies. Cyclohexene remained unreactive (Table 1, entry 2), while acetophenone (Table 1, entry 8) was hydrogenated in a yield of 85% (33% of electrochemical efficiency). This may be explained by acetate anion interference on acetophenone adsorption on the electrode surface.³ 2-Cyclohexen-1-one, benzaldehyde and styrene (Table 1, entries 4, 6 and 10) were again hydrogenated with yields over 90%, however, with better electrochemical efficiencies (82, 50 and 65%, respectively). The yields of 1,3-cyclohexadiene and *trans-trans*-2,4-hexadien-1-ol (Table 1, entries 12 and 14) hydrogenations were unchanged. In the group of terpenes, a considerable increase of yield was observed. Citral (Table 1, entry 16) gave citronellol as the principal product of hydrogenation with 70%, and 84% of electrochemical efficiency. Linalool and geraniol (Table 1, entries 18 and 20) also were hydrogenated in increased of 93 and 22%, respectively.

The results described herein illustrate ECH selectivity for various conjugated and non-conjugated double bonds. Substrates containing a conjugated system are more easily hydrogenated. NH_4Cl supporting electrolyte showed proportionate yield increase for all substrates hydrogenated, diminishing the cell potential and increasing the electrochemical efficiency in the major cases. These results show that ECH, improved by a current density gradient and sacrificial anode of nickel provides a good tool for hydrogenation of some classes of organic compounds, without the necessity of a H_2 supply.

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13. **Preparative electrolyses:** The controlled current preparative electrolyses were carried out in a Princeton Applied Research (PAR) 273A potentiostat/galvanostat, using undivided cells of 50 mL. Ni foam (or plate) was used as sacrificial anode (4.0×8.0 cm). The cell potential (cathode versus anode) may be monitored by using a multimeter. An iron bar (0.8 dm diameter; 0.1828 dm² surface) was used as the working electrode, and may be reused several times, after cleaning the nickel deposit by polishing. The electrolytic cell was charged with the solvent ($\text{H}_2\text{O}/\text{MeOH}$, 1:1) and 0.2 M supporting electrolyte. An inert atmosphere (N_2) is necessary when NH_4OAc is used as supporting electrolyte to expulse some O_2 produced on the anode. A pre-electrolysis is necessary to deposit nickel on the Fe electrode; 175 mA dm⁻² constant current was applied until consumption of 58 C. The substrate was added to the electrochemical system and the electrolysis continued, following the current density gradient program (it may be executed manually by calculating the charge passed, $Q = \text{current (A)} \times \text{time (s)}$). The reaction may be followed by GC analysis. At the end, the hydrogenated substrate was extracted with diethyl ether 3×15 mL, washed with water and dried with Na_2SO_4 . Gas chromatogram/mass spectra were taken with a Varian 3380 GC or Finnigan GC-MS instrument, fitted with a 30 m capillary CP-SPL5CB Chrompack column, using 60–200°C temperature range (10°C min⁻¹). Hydrogenation products and reagents were compared with authentic samples and were confirmed by GC/MS.
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