

Ultrasound-assisted electrocatalytic hydrogenation in water

Josinete Angela da Paz^a, Ayrlane Sales^{b,c}, Larissa Dias da Silva^b,
Émerson Felipe Mendonça da Silva^{b,c}, José Angelo Peixoto da Costa^b, Marcelo Navarro^a,
Frederico Duarte de Menezes^b, Márcio Vilar^{b,*}

^a Departamento de Química Fundamental, Universidade Federal de Pernambuco, Cidade Universitária, CEP 50670-901, Recife PE, Brazil

^b Departamento de Controle e Processos Industriais, Instituto Federal de Educação, Ciência e Tecnologia de Pernambuco, Cidade Universitária, CEP 50740-540, Recife PE, Brazil

^c Departamento de Engenharia Química, Universidade Federal de Pernambuco, Cidade Universitária, CEP 50740-521, Recife PE, Brazil

ARTICLE INFO

Keywords:

Electrocatalytic hydrogenation
Ultrasound
Sonochemistry
Catalysis
Pulegone

ABSTRACT

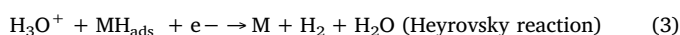
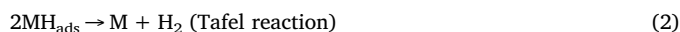
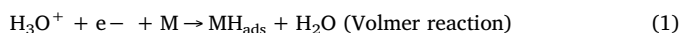
The optimum conditions for the electrocatalytic hydrogenation of (R)-(+)-pulegone in water, using ultrasound (continuous or pulsed mode) and a nickel sacrificial anode have been determined. The continuous ultrasound (14 W), without temperature control, showed to be a most effective technique if compared with pulses of 0.2 s applied after each second. The sonication of the reaction solution presented a slight stereochemical effect on the product distribution, and its magnitude depends on both the ultrasound power and the mode. Simultaneous ultrasound irradiation during electrochemical process showed a synergetic effect, able to generate H radical from water H–O bond rupture, in addition to the H radicals formed by the electrochemical reduction of water on the electrode surface, increasing both current efficiency and conversion yields. Chitosan microspheres were used in the removal of nickel ions of the aqueous medium showing an adsorption efficiency of 64%.

1. Introduction

Catalytic hydrogenation (CH) is one of the most useful and important catalytic methods used in synthetic organic chemistry. It has been largely studied in both laboratory and large-scale production [1,2]. The CH process technology is well established and the laboratory experiment scale up presents low difficulty levels. In most cases, extreme conditions (high pressure and temperature) are necessary to accelerate the process, leading to by-products and a significant increase of the operating costs [1,3,4]. The main reason for the increase in operating costs is related to the production and storage of the molecular hydrogen, since it is mostly produced from fossil fuels. It is estimated that 49% of the hydrogen production comes from natural gas sources, and only 4% is resulting from electrolysis processes [5]. Otherwise, the electrochemistry is a clean technology that allows *in situ* hydrogen generation for the CH process; this technique will henceforth be referred to as electrocatalytic hydrogenation (ECH). The ECH provides an alternative synthetic route for the hydrogenation of some organic molecules under mild conditions (room temperature and normal pressure) and is considered an attractive process because it dispenses a molecular hydrogen supply, since atomic hydrogen is produced on the electrode surface and also eliminates inconveniences such as catalyst poisoning

[6–9]

The main difference between the CH and ECH processes concerns the generation of chemisorbed hydrogen. Hydrogen is a clean and environmentally friendly energy carrier that can be produced by means of hydrogen evolution reaction (HER) during water electrolysis. According to classical theory [10], overall HER on the metal (M) surface may proceed via elementary steps. At the first step, the catalyst surface undergoes a primary discharge (Eq. (1)) in which the reduction of hydronium ions form atomic chemisorbed hydrogen (MH_{ads}). This discharge step is believed to be fast and followed by both desorption and/or recombination steps (Eqs. (2) and (3)).

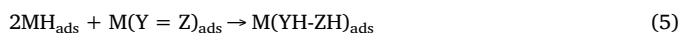


Either reaction, Heyrovsky or Tafel, is considered to be a rate-limiting step. Thus, the HER mechanism may be represented as Volmer–Heyrovsky or Volmer–Tafel [10]. In the ECH process, the chemisorbed hydrogen (MH_{ads}) reacts with unsaturated organic molecules (Y = Z) (Eqs. (4) and (5)) adsorbed on the catalyst (cathode) surface, followed by desorption of the hydrogenated product (Eq. (6))

* Corresponding author.

E-mail addresses: marciovilar@recife.ifpe.edu.br, marcio.vilar@globo.com (M. Vilar).

and regeneration of the adsorption sites [11–14].



The electrocatalysis is a procedure exploring the rates of electrochemical reactions as a function of the electrode surface properties. Thus, a metal is considered catalytically active if it is able to chemisorb both atomic hydrogen and unsaturated bonds of the substrate. The most important classes of metals with catalytic activity are those in Groups 8–11 of the Periodic Table, *i.e.* Fe, Co, Ni and Cu groups. The choice of cathode material is a difficult task and is generally governed by economic factors. In the last decades, extensive studies have been carried out on this subject, looking for efficient, robust, and low-cost catalysts for the ECH [6,13,14,15–22], which could potentially replace the widely used Pd and Pt electrocatalysts. Nickel is among the most abundant transition elements in the Earth's crust and is, for instance, 100-fold and more than 130-fold cheaper than Ru and Pd, respectively [23]. This makes its use as catalyst for both ECH and HER extremely attractive. For example, Navarro et al. [11] investigated the development of an ECH system using undivided cells and Ni as the sacrificial anode (referred as to ECHSA), which permits a fine deposit of Ni during ECH process. In other work [24], the optimum conditions for the ECHSA of benzaldehyde in water, using β -cyclodextrin (β CD) as inverse phase transfer catalyst (IPTC) were determined. The morphology of the nickel deposited on the cathode matrix (Cu, Fe, Ni or Fe/Ni alloy (64:36)) during a pre-electrolysis was investigated. The results showed that the hydrogenation yields for the cathode matrices of Fe:Ni alloy, Fe, and Cu were the same, remaining within the experimental error.

Substrates like olefins [25], arenes [26], aromatic and aliphatic nitriles [27], unsaturated aldehydes [28] and ketones [29] have been hydrogenated by the electrocatalytic process. However, the use of insoluble substrates leads to an overall yield drop of the ECH method, due to the mass-transport limitation between the bulk solution and the electrode surface. Consequently, the use of co-solvent is generally the only alternative wishing to hydrogenate highly hydrophobic substrates in water. However, the ECH field have a marked tendency for using different co-solvents making recycling difficult owing to cross contamination [9,11–14,16–19,22]. Although co-solvents might solve the mutual insolubility problem, they can also cause certain disadvantages such as competing hydrolysis pathways and difficulties in their purification and removal. The absence of the solvent should be the ideal situation, once it implies efforts and energy to remove it from the reactional system [30,31]. Therefore, a promising alternative to circumvent the aforementioned disadvantages is the use of ultrasound (US) in the ECH process.

US has been recognised as a key technique for green and sustainable synthetic processes, allowing the use of non-active metals and crude reagents as well as aqueous media [32]. The sonoelectrochemistry is the science that couples US to electrochemistry and provide a powerful combination for the surface activation of materials toward HER [33,34]. The first application of US in an electrochemical procedure dates back to the 1930s, when Moriguchi [35] showed that under sonication, the water electrolysis (Pt electrode) took place at lower voltages and faster rates than under normal (silent) conditions. The many benefits of US in electrochemical process are well known. The particular advantages which accrue from the use of sonoelectrochemistry include: 1) the enhancement of the mass transport to/from an electrode and in bulk solution, which affects concentration-dependent phenomena; 2) the diminution of the diffusion layer, which affects electron transfer; 3) the modification of the electrode surface phenomena (adsorption/desorption), the diminution of the electrode fouling and removal of electrode coatings [28,30,31].

When US is applied to a liquid, several processes can occur that

often create unusual physical conditions: acoustic streaming, turbulent convection, microstreaming in the presence of oscillating bubbles and cavitation [36,37]. The chemical and physical effects of US arise from a cavitation phenomenon, which produces localized extreme conditions (short-lived hot spots). Cavitation is the origin of sonochemical effects. The significance of cavitation to sonochemistry is not so much on how the bubbles form, but rather what happens when they collapse. Cavitation arises from the rapid compression and rarefaction phases of the longitudinal sound wave propagating through the liquid. When cavitation occurs in a liquid close to a solid surface (*e.g.* a cathode matrix/electrode), the dynamics of the cavity collapse is rather asymmetric and produces high-speed jets of liquid, termed “microjets”. The impact of the jets on the surface is very strong causing damages and leading to cleaning, ablation and, sometimes, fracture of the structure, increasing the number of edges, crevices and kinks that expose fresh and highly active surfaces [37–40].

Ultrasound-enhanced electrochemical systems with different electrodes have been widely reported for oxidation of variety of organics such as chlorinated organics [41], dyes [42] and phenolic substances [43]. The US-assisted chemical reduction method has been successfully applied in the preparation of amorphous alloys with homogeneous particle sizes [44]. However, the number of articles in the field of ECH reporting the use of US is limited. For instance, US was used as a pre-electrolytic treatment in the ECH of benzaldehyde, in water using a Ni electrode, leading to an increase of 5% in the hydrogenation yields [24].

In this context, the present investigation explored the use of US in the ECH of α,β -unsaturated ketones and aldehydes in water using a simple undivided cell with a sacrificial anode (US-ECHSA). (R)-(+)-Pulegone ((+)-(1)) was adopted as the standard substrate. This study is relevant from both sonoelectrochemistry and green standpoint because, besides meeting the principles 2, 3, 5, 6, 7 and 9 of sustainable and green chemistry [31], no study have yet been reported concerning the use of US to assist the ECHSA of (+)-(1) in water.

2. Experimental

2.1. Chemicals

(+)-(1) (96%) was purchase from Acros. Diethyl ether, ammonium chloride (supporting electrolyte), acid chloride, sodium hydroxide and sodium sulphate were purchased from Vetec. Acetylcyclohexene, 2-cyclohexen-1-one, isophorone, (S)-(+)-carvone, β - and α -ionone, 2-methyl-2-cyclopenten-1-one, mesityl oxide, chitosan, polyvinyl alcohol and glutaraldehyde were purchase from Aldrich and used as received. Water was of Milli-Q® grade.

2.2. Procedures

2.2.1. Electrochemical procedure

The controlled current preparative electrolyses were carried out with an Autolab PGSTAT101 potentiostat/galvanostat, using a 30 mL undivided cell. A cylindrical nickel rod was used as sacrificial anode (0.1 dm diameter; 0.078 dm² area). Another Ni bar (0.1 dm diameter; 0.078 dm² area) was also used as the working electrode, which can be reused several times after removing the nickel deposit by abrasion and polishing processes. Water was the solvent in all electrochemical experiments. A Bandelin Sonopuls ultrasonic homogenizer HD 2070 was used for the approach of ultrasound-assisted electrolyses.

The basic setup consists of a 30 mL undivided electrochemical cell (Fig. 1), which was filled with the 25 mL of 0.2 M of the supporting electrolyte and 0.5 mmol of substrate. The ultrasonic irradiation at a frequency of 20 kHz \pm 500 Hz was used for passage of ultrasound into the reaction mixture through a titanium cylindrical horn, submerged 3.0 cm into reaction mixture. Ultrasonic horn had a diameter of 13 mm and maximum rated power output of 70 W. The probe was connected

Download English Version:

<https://daneshyari.com/en/article/6497150>

Download Persian Version:

<https://daneshyari.com/article/6497150>

[Daneshyari.com](https://daneshyari.com)