

On the study of the catalytic transfer hydrogenation reaction: The hydrogenation of 3-buten-1-ol on a Pd-black film

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Abstract

The spontaneous catalytic transfer hydrogenation (CTH) was investigated using the H_2PO_2^- ion as the H-donor, 3-buten-1-ol as the model organic molecule and a Pd-black film as the catalyst. A pre-evaluation of the competitive ability of the unsaturated alcohol and H-donor to co-adsorb on the surface was performed by cyclic voltammetric experiments. The performance of the CTH was characterized in terms of the reaction selectivity, H-donor efficiency, material yield, reactant conversion, reaction rate and catalyst stability in successive hydrogenation reactions. The effect of the H-donor concentration on these parameters was also analysed. Evidence was given for the modification of the surface catalyst during the course of the hydrogenation but no effect on the catalytic activity was observed. The prospective ability of this catalyst material to be pre-charged in a hypophosphite solution and to operate as a source of hydrogen for the catalytic hydrogenation was demonstrated. For comparison, the electrocatalytic hydrogenation was also studied using the same organic compound and catalytic material as in the CTH.

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1. Introduction

The hydrogenation is one of the most important reactions in synthetic and industrial chemistry. Among the several methodologies available for the addition of hydrogen to unsaturated organic compounds, the use of hydrogen gas in liquid-phase (also known as catalytic hydrogenation) is still the most familiar method to organic chemists [1]. However, several drawbacks are displayed by this hydrogenation methodology: it requires the handling of a highly flammable gas and pressurized conditions. In addition, molecular hydrogen has low water solubility, which limits its applications in aqueous solutions. Promising alternatives to this methodology are the electrocatalytic hydrogenation (ECH) and the catalytic transfer hydrogenation (CTH) reactions. These processes also rely on a heterogeneous reaction, but are performed on much more attractive experimental conditions, under atmospheric pressure and at room temperature.

In the ECH process the chemisorbed hydrogen is produced *in situ* by the electroreduction of water [2]. Once this

specie is formed it reacts with coadsorbed unsaturated organic compounds to form the hydrogenated organic products. The generation of chemisorbed hydrogen can be controlled by adjusting the electrode potential or the current density, which makes the reaction easy to handle. Even so, the need of having special equipment and some experience on dealing with electrochemical systems has limited the application of such procedure among organic chemists.

In the last three decades an increased interest in the CTH has been observed [3–7]. This methodology relies on the *in situ* formation of atomic hydrogen from a hydrogen donor, and its transfer to an organic or inorganic acceptor, through the use of an appropriate catalyst. It is very attractive for small-scale production since it does not require special equipment and involves an easy-to-handle procedure. The compounds used as hydrogen donors are easy to store, handle and transport, unlike hydrogen gas under pressure. The most commonly used hydrogen donors are hydrazine, formic acid, sodium formate, ammonium formate and hypophosphite ion.

Concerning the use of the hypophosphite ion, its use on the hydrogenation of alkynes into alkenes [8], alkenes into alkanes [9], aromatic nitriles into the corresponding aldehydes [10], aromatic nitro groups into amines [11,12], nitroolefins into

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enamines [13], carboxylic acids into aldehydes [14], reductive desulfurization [15,16] and dehalogenation reactions [17,18] have already been reported. From the overall work reported in the literature it is clear that characterization of the CTH performance has been restricted to the determination of the reaction yield for established experimental conditions. No information regarding its selectivity, H-donor efficiency, catalyst stability, whether or not it loses activity during the hydrogenation reaction or when re-used, has ever been given. In addition, the performance of the CTH was never compared to other hydrogenation methodologies and systematic studies on the effect of the experimental variables (such as temperature, H-donor concentration, catalyst) are scarce, incomplete and are often merely qualitatively reported. For example, the effect of modified palladium catalyst on the chemoselectivity of some CTH reactions has been analysed by Johnstone and Wilby [8], but the catalyst characterization, in terms of its structure, morphology and effective composition was not performed. On account that the reaction yield, chemical and stereo selectivity of the CTH are probably ruled by the adsorption characteristics of the organic molecule and hydrogen donor, which are themselves dependent on the catalyst surface properties, it is essential that the performance of the CTH reaction is evaluated in parallel to the surface catalyst characterization.

The present study aims to provide a comprehensive investigation on the catalytic transfer hydrogenation using of 3-buten-1-ol as the unsaturated organic compound and a Pd-black film as the catalyst. The choice of 3-buten-1-ol as a model compound was justified by two practical reasons: the high solubility in aqueous solution and the small number of hydrogenation products that could be formed.

The performance of the CTH will be characterized using the following parameters: selectivity, conversion, yield, H-donor efficiency, hydrogenation rate and stability of the catalytic substrate in successive experiments. Characterization of the catalyst will be performed by cyclic voltammetry and SEM/EDS. To gain further insight into this system, the open circuit potential (OCP) evolution will be followed during the hydrogenation reaction and the effect of the H_2PO_2^- ion concentration on the CTH performance will be analysed. For comparison, the electrocatalytic hydrogenation of 3-buten-1-ol will be also studied in the same electrolyte and using the same catalyst as in the CTH.

2. Experimental and methods

2.1. Pd-black preparation and characterization

The Pd-black mesh was prepared by open-circuit immersion of a Ni mesh (15 mm × 50 mm; 0.73 mm nominal aperture, 0.25 mm wire diameter, Goodfellow) in a 0.5% (w/v) $\text{PdCl}_2 + 1 \text{ M HCl}$ solution for 8 min. Deaeration of this solution was not performed (the spontaneous deposition of palladium occurs either in deoxygenated and oxygenated solutions). Unless otherwise stated, a new deposit is formed on the Ni mesh before the beginning of each experiment. The Pd-black electrode used on the cyclic voltammetric experiments was prepared in a similar way but a Ni rod electrode ($\varnothing = 5 \text{ mm}$), previously abraded

with carbide paper 600 (to provide surface roughness), was used as the metal substrate. The morphology of the Pd-black surface was characterized by SEM/EDS (FEI Quanta 400 microscope). Voltammetric experiments were performed on a classical three-compartment cell using a saturated calomel electrode and a Pt foil as the reference and counter electrode, respectively. All the voltammetric data was obtained by initiating the potential scan in the negative direction ($\nu = 10 \text{ mV s}^{-1}$) in solutions previously deaerated with N_2 .

The effective electrode area of the Pd-black film on the disk ($5.16 \pm 0.8 \text{ cm}^2$) and on the mesh ($503 \pm 128 \text{ cm}^2$) substrates was determined by plotting the charge associated with the Pd oxide reduction for different upper anodic limits and assuming that the inflection point of the obtained curve occurs at a potential close to the monolayer coverage with oxygen atoms [19]. The amount of Pd-black deposited on the disk was ($30 \mu\text{g}$ or $153 \mu\text{g/cm}^2$), which was determined by electrothermal atomization after dissolving it in a 20% (v/v) $\text{HNO}_3 + 2\%$ (v/v) HCl solution.

2.2. Catalytic transfer hydrogenation and electrocatalytic hydrogenation

The CTH and electrocatalytic hydrogenation experiments were carried out in one compartment cell having a Pt mesh counter electrode. The solution, containing a 10 mM 3-buten-1-ol + 0.1 M NaOH (+ NaH_2PO_2 in the CTH runs), was thermostated at 25.0°C and stirred with a magnetic bar. The electrode potential was controlled by an Autolab potentiostat model 100 and is referred to a saturated calomel electrode (SCE).

The progress of the hydrogenation reaction was monitored by gas-chromatography (GC) analysis on a Dani model 1000 gas-chromatograph equipped with a FID detector and a DB-1701 capillary column (30 m long, 0.53 diameter). 0.5 mL of the electrolyte solution was extracted with ethyl ether and was immediately analysed by GC. An internal standard (1-pentanol) was used on the quantification. The reaction products were identified by comparing their retention time with that of authentic samples and by GC-MS (GCQ mass spectrometer coupled to a CE instruments GC Trace).

Calculation of the material yield was based on the amount of 1-butanol formed and on the initial amount of 3-buten-1-ol. Determination of the reactant conversion was based on the amounts of 3-buten-1-ol consumed. Selectivity was calculated by the ratio of yield to conversion. The H-donor efficiency of the catalytic hydrogenation was defined as the ratio of $n_{1\text{-butanol}}$ (formed)/ $n_{\text{hypophosphite}}$ (consumed). Quantitative determination of the hypophosphite ion concentration at the end of the hydrogenation reaction was performed by the iodometric method [20]. Current efficiency was calculated on basis of the amount of 1-butanol formed and the charge passed on the cell.

3. Results and discussion

3.1. Pd-black characterization

The use of a Pd-black film as the catalytic material is an interesting alternative to powder catalysts, which are less practical

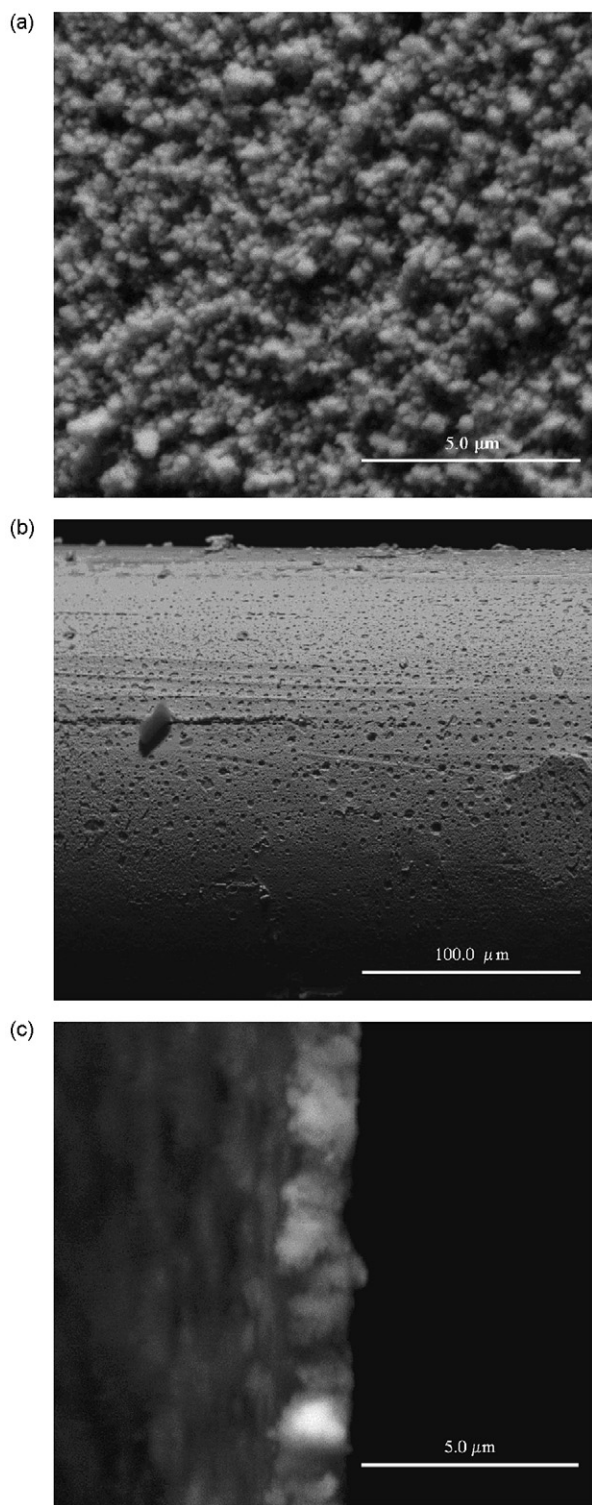


Fig. 1. SEM images of (a) as-deposited Pd-black surface; (b) as-deposited Pd-black on the Ni mesh; (c) cross-sectional of the Pd-black film.

and rather hazardous to employ. The methodology used for the preparation of the Pd-black films gave a black deposit visible to naked eye, which showed very good adherence to the Ni mesh. The analysis of the surface electrode by scanning electron microscopy (SEM), Fig. 1a, showed that the surface is fully

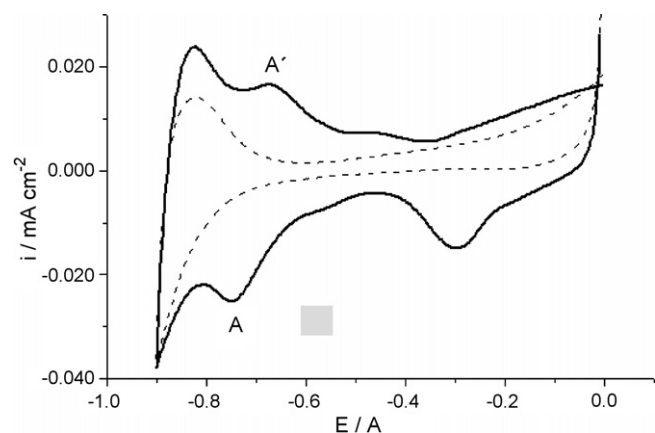


Fig. 2. Cyclic voltammograms of the Pd-black electrode in 0.10 M NaOH (solid line) and 0.10 M NaOH + 10 mM 3-buten-1-ol (dashed line). $\nu = 10 \text{ mV s}^{-1}$.

covered with a uniform compact layer of spherical crystallites in a coral-like shape. However, some pits along the surface can be detected, particularly upon a lower magnification, Fig. 1b. These are probably formed by the evolved gas that is observed during the Ni mesh immersion in the Pd^{2+} solution. The thickness of the Pd-black film, estimated from SEM analysis is approximately 0.9–1.2 μm , Fig. 1c. EDS analysis allowed to conclude that no other metal than palladium was present on the surface electrode (there is no contamination by nickel).

3.2. Cyclic voltammetry

Prior to the catalytic hydrogenation experiments, the cyclic voltammetry technique provides the first diagnostic tool to evaluate the competitive ability of 3-buten-1-ol and hypophosphite to co-adsorb on the catalytic substrate. The adsorption of the organic molecule, a pre-requisite of any catalytic hydrogenation reaction, can be appraised from the cyclic voltammogram of a Pd-black electrode in 0.1 M NaOH solution (Fig. 2). In effect, previous studies [21] revealed that hydrogen adsorption–desorption peaks (peak A and A', respectively) can be depicted in the hydrogen region of the voltammogram. The disappearance of this peak in the presence of 10 mM 3-buten-1-ol is indicative of the blocking action of the alcohol due to its adsorption. Nonetheless, it is important that adsorption of the organic molecule is not too strong; otherwise, the adsorption of the H-donor species, the hypophosphite ions, could not take place. The cyclic voltammogram recorded for the Pd-black electrode in 0.30 M $\text{H}_2\text{PO}_2^- + 0.10 \text{ M NaOH}$ solution, in the presence or not of 10 mM 3-buten-1-ol, Fig. 3, reveals that the hypophosphite ion oxidation occurs even in the presence of the organic molecule, which is a strong indicator for the non hindrance effect by the adsorption of 3-buten-1-ol.

3.3. Catalytic transfer hydrogenation

Fig. 4a and b show, respectively, the 3-buten-1-ol conversion and 1-butanol yield as a function of hydrogenation time, for different hypophosphite concentrations. It was found that:

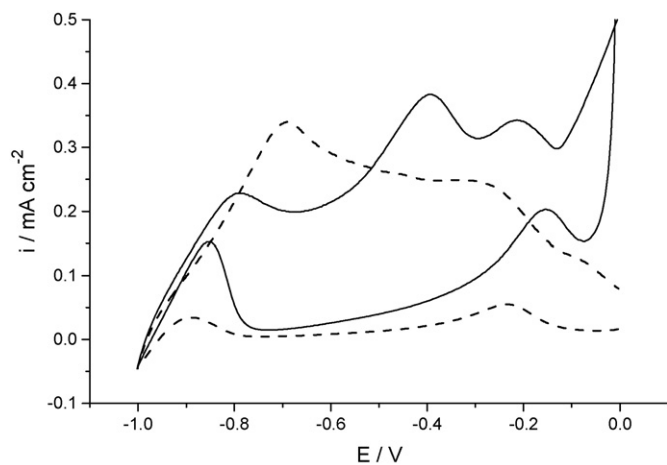


Fig. 3. Cyclic voltammograms of the Pd-black electrode in 0.10 M NaOH + 0.30 M H_2PO_2^- (solid line) and 0.1 M NaOH + 0.30 M H_2PO_2^- + 10 mM 3-buten-1-ol (dashed line). $\nu = 10 \text{ mV s}^{-1}$.

- (i) Broadly, the conversion and reaction yield increase linearly with time. The hydrogenation rate, evaluated from the slope of the time course of 1-butanol production was found to be 6.0, 4.3, 3.8 and $2.2 \mu\text{mol h}^{-1} \text{ dm}^{-2}$, for the 0.05, 0.1, 0.15 and 0.3 M H_2PO_2^- solutions, respectively. This trend is consistent with the competition between hypophosphite

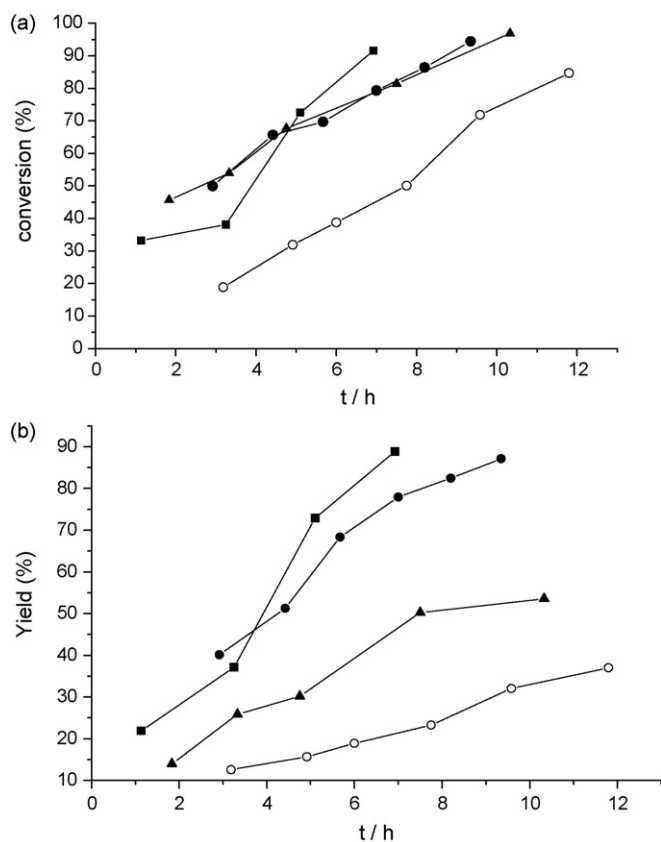
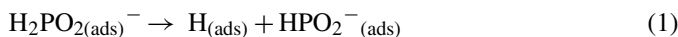


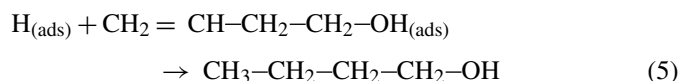
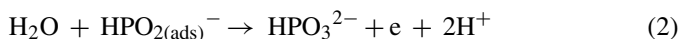
Fig. 4. Evolution of (a) 3-buten-1-ol conversion and (b) butan-1-ol yield in solutions of different hypophosphite concentration: (■) 0.05 M; (●) 0.10 M; (▲) 0.15 M; (○) 0.30 M.

ions and the organic molecule to adsorb on the Pd-black surface. As the hypophosphite ion concentration increases, the amount of adsorbed hypophosphite increases as well (up to the threshold value) [22], hindering the adsorption of 3-buten-1-ol, and consequently, leading to a decrease in the rate of reaction.

- (ii) The divergence between the reaction yield and reactant conversion data is indicative that other reaction products, than 1-butanol have been formed, despite its non detection by GC. This discrepancy is more prominent on the more concentrated hypophosphite solutions. In effect, 98% and 52% selectivity was found, respectively for 0.05 M and 0.30 M H_2PO_2^- solutions. This behaviour may be explained on basis that an increasing hypophosphite concentration yields an increasing amount of H and HPO_2^- radicals, very reactive species that are formed upon the H–P bond breakdown on the H_2PO_2^- ion [23,24]:



In addition to reactions (2)–(5),



these radicals species may participate on other side reactions. In effect, some authors advocate that sodium hypophosphite can be oxidized by alcohols in the presence of palladium, giving rise to sodium monoalkenylphosphites [25]. It was shown that this reaction occurs via the formation of adsorbed radicals, followed by their recombination.

The CTH was not performed with hypophosphite solutions below 0.05 M because the spontaneous oxidation of hypophosphite was not able to occur at such conditions. Despite it is not the intention of the present study to investigate the hypophosphite oxidation mechanism, this finding may be interpreted on the assumption that repulsion forces between hypophosphite ions in the catalyst/electrolyte interface are responsible for triggering the spontaneous dehydrogenation of the hypophosphite ion on the Pd-black surface. For a better understanding of this phenomenon, further fundamental and theoretical investigations are required.

The dependence of the H-donor efficiency on the hypophosphite concentration was also found to follow the same trend than selectivity: 13.0, 8.5 and 5.5% are displayed, respectively by the 0.05, 0.1 and 0.15 M H_2PO_2^- solutions. The low efficiency can be attributed to the hydrogen absorption by Pd-black (reaction (4)) and to the recombination of chemisorbed hydrogen (reaction (3)), which are favourable routes on high hydrogen coverage electrodes, at the expense, in part, of the hydrogenation route (reaction (5)). Despite no hydrogen evolution was detected during the experiments performed in the 0.05 M H_2PO_2^- solu-

tion, gaseous hydrogen may be formed and occluded in the films defects, which could explain its non detection. This hypothesis is consistent with the high H/Pd loading ratio previously reported on these films [21]. In the more concentrated hypophosphite solutions the gas evolution was clearly detected, which is in agreement with the CTH efficiency data.

These results clearly illustrate the importance of appropriate hypophosphite/organic ratio in CTH reactions. By regulating the H-donor concentration, a high selectivity and a not much low H-donor efficiency can be achieved.

According to previous work, an open circuit potential of approximately -1.15 V is spontaneously established on a Pd-black electrode in hypophosphite solution [21]. It has been showed that, at this potential, β -PdH is spontaneously formed. On account that the OCP evolution reflects the catalyst ability to generate spontaneously atomic hydrogen, the CTH experiments were also followed by recording the OCP, Fig. 5a. The OCP profiles, in the various hypophosphite solutions, reveal that during a rather long period (6–9 h) a potential of, -1.18 to -1.12 V (dependent on the hypophosphite concentration) remains approximately stable. This behaviour, concomitant to the progressive 3-buten-1-ol conversion to 1-butanol, is indicative that hydrogen formation is self-sustained in the present

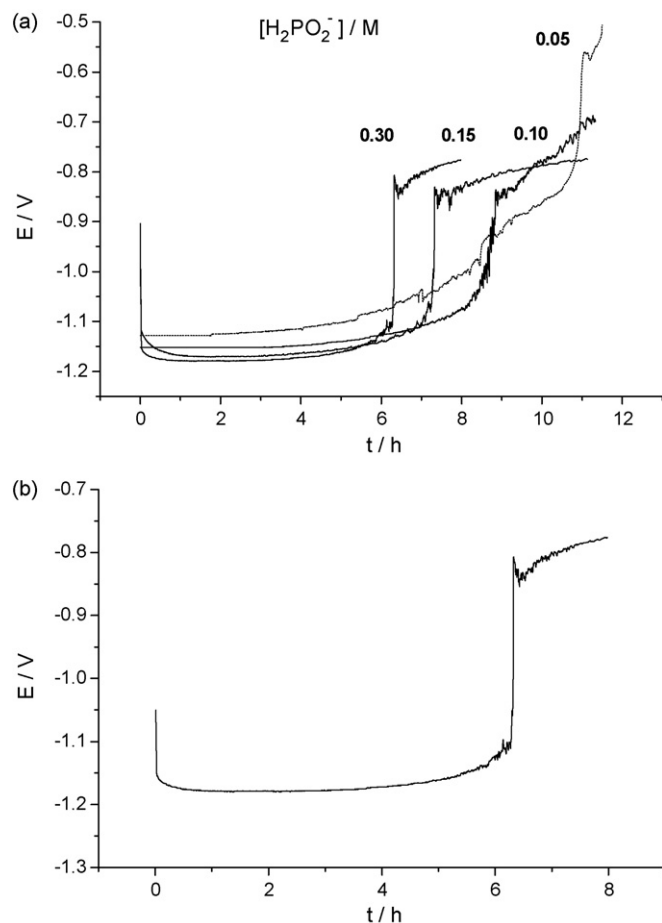


Fig. 5. OCP profile of the Pd-black electrode in (a) 0.1 M NaOH + 0.30 M H_2PO_2^- + 10 mM 3-buten-1-ol solution; (b) in a 3-buten-1-ol free-solution.

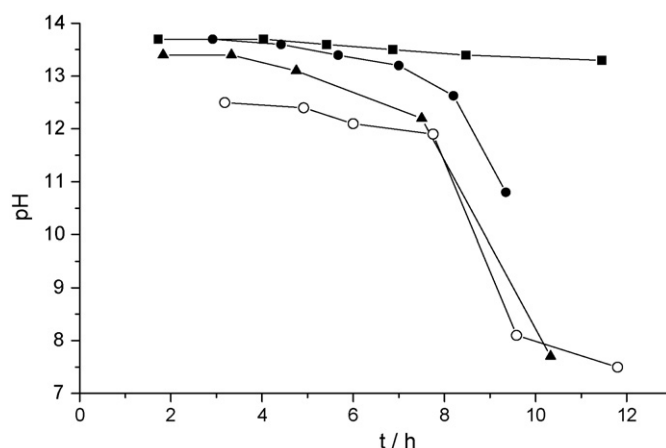


Fig. 6. Plot of the pH solution as a function of the time in solutions of different hypophosphite concentration: (■) 0.05 M; (●) 0.10 M; (▲) 0.15 M; (○) 0.30 M.

experimental conditions. Afterwards, a strong and sharp shift of the electrode potential towards $\cong -800$ mV is depicted (except in the 0.05 M solution where the potential drops to -550 mV). This behaviour is observed in the Pd-black/ H_2PO_2^- system as well (Fig. 5b), suggesting that it is not related to the presence of the organic substrate in solution. In effect, the progress of the hydrogenation reaction is not affected by such potential shift. In order to evaluate whether this behaviour could be related to a variation in the solution pH, this parameter was monitored during the hydrogenation reaction, Fig. 6. Despite a pH decrease after the potential decay is observed, this variation ($\Delta_{\text{max}} \text{pH} = 5$) occurs within a large time lag, $\cong 2$ h (in a stirring solution), which is not consistent with the abrupt potential shift observed. This incongruence suggests that two different effects may be responsible for the pH decrease in the bulk of the solution:

- (i) The generation of H^+ upon the hypophosphite oxidation reaction in a non-buffered solution (reaction (2)). This would explain the slow acidification of the bulk solution and the ΔpH dependence on the hypophosphite concentration.
- (ii) The instantaneous increase of H^+ in a layer adjacent to the electrode. A possible explanation for this phenomenon could be the electrode discharge that occurs on an electrode loaded by hydrogen. Although it is known that the maximum hydrogen loading occurs upon 5 min in OCP in similar experimental conditions [21], the hydrogen would remain absorbed for 6–8 hours and, for some reason that is not clear for the moment, would be released. This proposal would explain on one hand, an abrupt pH decrease in the layer adjacent to the surface electrode and, therefore, the high magnitude of the potential decay, and on another hand, the fact that the potential drop is not dependent on the hypophosphite concentration.

This explanation is corroborated by the results obtained upon removing the Pd-black electrode from the 0.30 M H_2PO_2^- + 0.1 M NaOH solution in two distinct points of the OCP profile, A and B (i.e. before and after the potential decay),

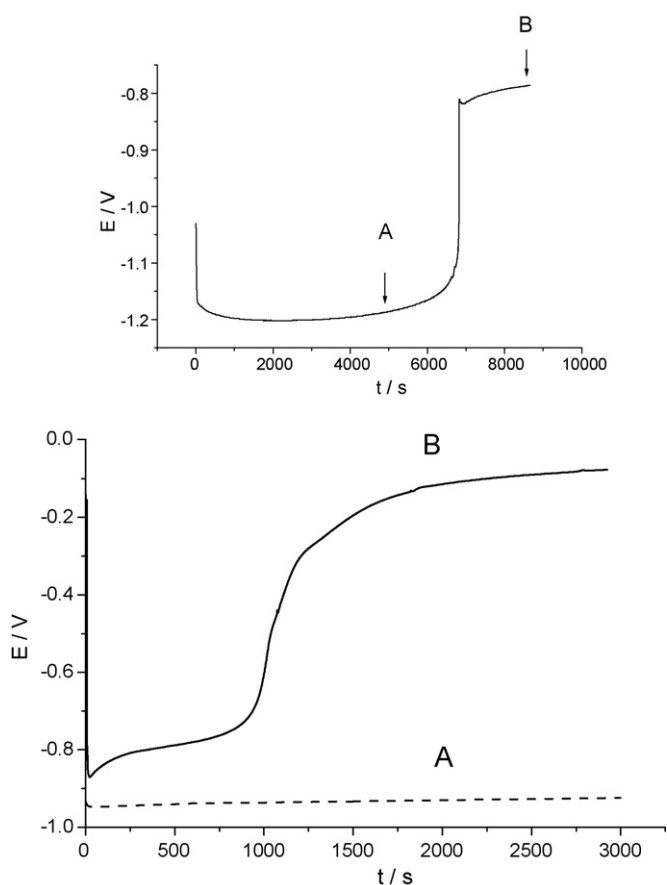


Fig. 7. OCP evolution, in 0.10 M NaOH solution, of a Pd-black electrode, which has been, removed from a 0.30 M H_2PO_2^- + 0.10 M solution, in two distinct zones (A and B). Inset identification of zones A and B.

followed by its immersion in a 0.1 M NaOH solution, Fig. 7. The constant and rather negative potential (-0.95 V) displayed by the electrode removed before the potential decay is indicative that the modified surface is very stable, probably by the formation of stable hydrides that are able to rest on the surface (and maybe subsurface) even after the electrode removal from the hypophosphite solution. This behaviour contrasts with the OCP curve developed when the electrode is removed after the potential drop; the potential rests at approximately -0.80 V for some minutes and then falls to nearly 0 V, which is the OCP characteristic of as-prepared Pd-black electrode in a 0.1 M NaOH solution. In this case, it is shown that even if some hydrides remain on the electrode surface (or subsurface) after the potential drop, these are rapidly released giving rise to a fresh surface electrode.

Regarding these results a modified CTH experiment, on which the pre-charged Pd-black operates as a hydrogen source for the catalytic hydrogenation in a hypophosphite-free solution, was tested. Hence, after loading the Pd-black electrode at OCP in 0.05 M H_2PO_2^- + 0.1 M NaOH solution for 1800 s, it was transferred to 10 mM 3-buten-1-ol + 0.1 M NaOH solution. Fig. 8 shows the OCP profile and the reaction yield data at two different points of the experiment. The results reveal that hydrogenation occurs promptly in the first minute of the experiment.

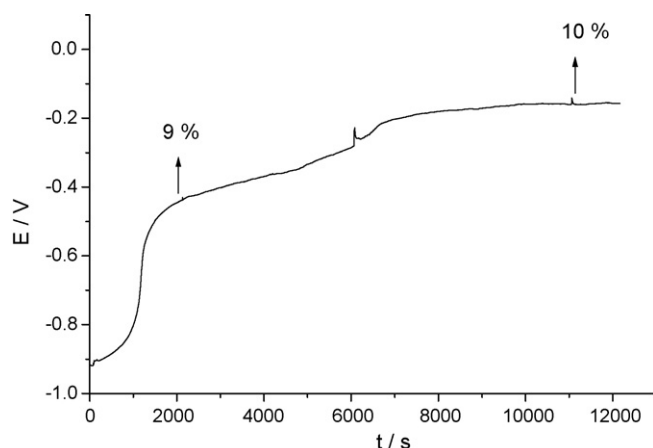


Fig. 8. OCP profile, in 0.1 M NaOH + 10 mM 3-buten-1-ol solution, of a pre-charged Pd-black film and the material yield obtained at two distinct points of the hydrogenation run.

Despite the rather low reaction yield obtained (constrained by the amount of hydrogen absorbed), this modified CTH undoubtedly brings a new insight on novel dehydrogenation/hydrogenation palladium membrane reactors devices.

In order to evaluate the performance of the same Pd-black electrode in successive CTH experiments, the reaction yield, selectivity, hydrogenation rate and surface morphology were analysed in three consecutive experiments performed in 0.05 M hypophosphite solutions, Fig. 9 and Table 1. It can be concluded that on reusing the same electrode the electrode catalytic activity remains stable for at least three hydrogenation runs, but the adherence of the Pd-black film is progressively lost. The film peeling, detected by the SEM images, must be attributed to the tension stresses generated by the Pd-black lattice expansion upon the hydrogen absorption. In effect, the volume of the Pd metal expands by approximately 11% when fully loaded with hydrogen, which is accompanied by the phase transition from α to β Pd hydride [26]. It is interesting to find that despite the film peeling, no intergranular cracks are observed, which seems to reveal that the lattice expansion was not followed by the lattice contraction. Development of contraction are usually associated to hydrogen desorption, which occurs preferentially on the grain boundaries of the metal film.

It is worthwhile to note that the hydrogenation rate appears to increase with the number of consecutive hydrogenation runs. This result may be attributed to the enhancement of the Pd-black surface area due to partial film detachment from the nickel

Table 1
Material yield, selectivity and hydrogenation rate in successive hydrogenation experiments in 0.1 M NaOH + 0.05 M H_2PO_2^- + 10 mM 3-buten-1-ol solution

Hydrogenation run	Yield (%)	Selectivity (%)	Reaction rate ($\mu\text{mol h}^{-1} \text{dm}^{-2}$)
1	89	97	6.0
2	92	92	7.2
3	95	95	9.0

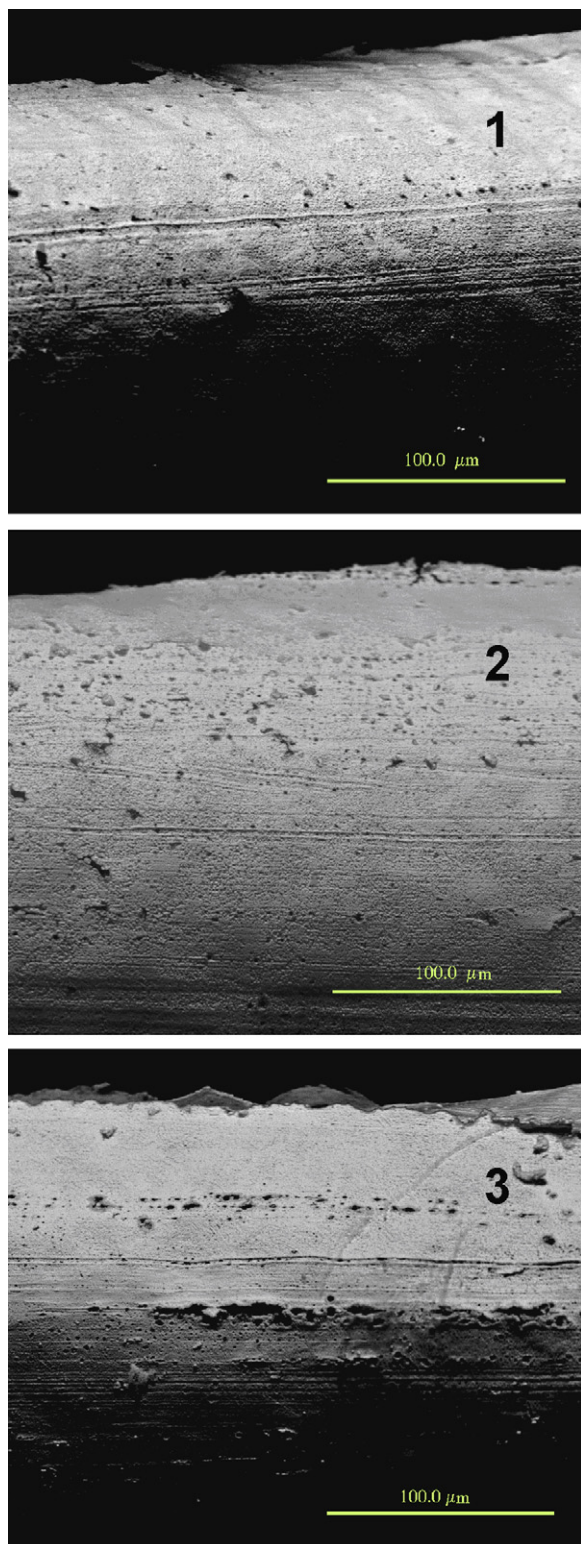


Fig. 9. SEM images of a Pd-black film after successive hydrogenation experiments in 0.1 M NaOH + 0.05 M H_2PO_2^- + 10 mM 3-buten-1-ol solution.

mesh. The nickel substrate, itself, is not responsible for this effect because no 3-buten-1-ol conversion was detected on performing the hydrogenation experiment on a non-coated nickel mesh.

3.4. Electrocatalytic hydrogenation

In order to evaluate the performance of the CTH compared to others hydrogenation methodologies, the electrocatalytic hydrogenation was carried out using the same catalyst, the same organic substrate (10 mM 3-buten-1-ol) and the same medium (0.1 M NaOH). The effect of the electrode potential on the chemical yield, selectivity, current efficiency and reaction rate was analysed at a charge corresponding to 4.9 F mol^{-1} (at 2 F mol^{-1} incomplete substrate conversion was obtained), Table 2. It is shown that selectivity and material yield are comparable at -1.0 and -1.1 V , but the best reaction rate is achieved at -1.1 V . At -0.95 V the selectivity decreases which is in agreement with the detection of other hydrogenation products, than 1-butanol, namely the *E* and *Z* isomers of 2-buten-1-ol. At potentials above -0.95 V , no conversion was detected.

Comparison of these results with the voltammetric data (Fig. 2) points out that no catalytic activity for the ECH is displayed in the adsorbed hydrogen region depicted in the -0.7 to -0.9 V potential range of the cyclic voltammogram. This effect may be attributed to a low surface coverage by 3-buten-1-ol at that potential range. Another explanation relies on the type of adsorbed hydrogen species, which may be inactive in hydrogenation reactions. The latter proposition is consistent with the conclusion of several investigators who advocate that the “strongly bound hydrogen” on the voltammogram of Pt was not the active specie for the ECH, but some weakly adsorbed hydrogen should be the active entity [27–29].

Although the low current efficiency suggests that competition between the hydrogenation step and the hydrogen evolution reaction occurred, no gas was evolved in any of these experiments. Alike the CTH experiments, this behaviour indicates that a substantial amount of hydrogen has entered into the palladium lattice (reaction (4)) and/or H_2 has been trapped by surface voids.

Upon reusing the same electrode for consecutive electrolysis no decrease of selectivity, chemical yield and current efficiency was observed, however, adherence of the Pd-black film to the Ni mesh was progressively lost, concomitant to the enhancement of the hydrogenation rate observed in the CTH experiments. In order to evaluate if exposed Ni was responsible for the hydrogenation of 3-buten-1-ol, an experiment was performed using Ni mesh as the cathode material, but no products were detected.

By comparison of the results obtained in these two series of experiments (CTH and EC), Table 3, it can be concluded that both methodologies are comparable with respect to their efficiency, selectivity, material yield and hydrogenation rate. From the economic point of view, the investment of the ECH is much higher than in the CTH, but the cost-effectiveness of the ECH experiments is significantly cheaper than in the CTH. However, on account that the CTH is technically less demanding than ECH, it is a very interesting alternative hydrogenation methodology for small scale production.

The most drawbacks of the present CTH methodology were found to be the low H-donor efficiency and poor film adhesion to the metal mesh; hence, future work will focus on the investigation of the CTH on other catalyst materials.

Table 2
The electrocatalytic hydrogenation of 10 mM 3-buten-1-ol in 0.1 M NaOH solution at a Pd-black film electrode

<i>E</i> (V)	<i>F</i> (mol ⁻¹)	Yield (%)	Selectivity (%)	Current efficiency (%)	Reaction rate (μmol h ⁻¹ dm ⁻²)
-0.95	4.9	40	61	12	3.4
-1.00	4.9	89	89	27	3.4
-1.10 ^a	4.9	84	85	26	5.8
-1.10 ^b	4.7	87	89	28	8.2
-1.10 ^c	5.6	90	91	24	–
-1.10 ^d	4.5	81	84	28	–

The effect of the electrode potential and number of hydrogenation runs on the material yield, selectivity and hydrogenation rate.

a–d: successive hydrogenation runs.

Table 3
Electrocatalytic vs. catalytic hydrogenation of 10 mM 3-buten-1-ol in 0.1 M NaOH solution at a Pd-black film

Characterization parameters	CTH (0.05 M H ₂ PO ₂ ⁻)	ECH (<i>E</i> = -1.1 V)
Yield (%)	89	84
Selectivity (%)	97	85
Efficiency (%)	26	26
Hydrogenation rate (μmol h ⁻¹ dm ⁻²)	6.0	5.8

4. Conclusions

Cyclic voltammetry revealed to be an adequate technique to pre-evaluate the ability of the organic unsaturated compound and H-donor to co-adsorb on the catalytic material.

It was found that the H-donor concentration affects strongly the selectivity, efficiency and reaction rate of the hydrogenation reaction. The best data was obtained with a 3-buten-1-ol/hypophosphite ratio of 0.2. It was demonstrated that the performance of the CTH, in terms of the material yield, selectivity and efficiency, was maintained during successive hydrogenation runs, however, the adhesion of the Pd-black film to the metal substrate was progressively lost. Under appropriate experimental conditions the performance of the ECH was found to be comparable with CTH.

By monitoring the CTH by the OCP evolution, it was concluded that during the hydrogenation course the observed hydrogen is abruptly released, without influencing the progress of the hydrogenation reaction. It was also shown that Pd-black could operate not only as a catalyst but also as a source of hydrogen, after being pre-loaded with hydrogen in a hypophosphite solution.

References

[1] G. Solomons, C. Fryhle, Organic Chemistry, seventh ed., John Wiley, New York, 2000, p. 801.

- [2] J. Lipkowski, P. Ross, Electrocatalysis, Frontiers in Electrochemistry, Wiley-VCH, New York, 1998, p. 307.
- [3] R. Johnstone, A. Wilby, I. Entwistle, Chem. Rev. 85 (1985) 129.
- [4] M. Tike, V. Mahajani, Chem. Eng. J. 123 (2006) 31–41.
- [5] K. Abiraj, B. Dinesh, G. Srinivasa, D. Gowda, J. Chem. Res. (2006) 534–535.
- [6] A. Sharma, V. Kumar, A. Sinha, Adv. Synth. Catal. 348 (2006) 354–360.
- [7] K. Abiraj, G. Srinivasa, D. Gowda, Synth. Commun. 35 (2005) 223–230.
- [8] R. Johnstone, A. Wilby, Tetrahedron 37 (1981) 3667–3670.
- [9] R. Sala, G. Doria, C. Passarotti, Tetrahedron Lett. 25 (1984) 4565–4567.
- [10] O. Backeberg, B. Stakun, J. Chem. Soc. (1962) 3961–3963.
- [11] I. Entwistle, A. Jackson, R. Johnstone, R. Telford, J. Chem. Soc. Perkin I 4 (1977) 443–444.
- [12] I. Entwistle, A. Jackson, R. Johnstone, T. Povall, J. Chem. Soc. Perkin I 13 (1975) 1300–1301.
- [13] D. Monti, P. Gramatica, G. Speranza, P. Manitto, Tetrahedron Lett. 24 (1983) 417.
- [14] L. Gooßen, K. Ghosh, Chem. Commun. (2002) 836–837.
- [15] K. Nishide, Y. Shigeta, K. Obata, T. Inoue, M. Node, Tetrahedron Lett. 37 (1996) 2271–2274.
- [16] M. Node, K. Nishide, Y. Shigeta, K. Obata, H. Shiraki, H. Kunishige, Tetrahedron 53 (1997) 12883–12894.
- [17] S. Boyer, J. Mckenna, J. Karliner, M. Nirsberger, Tetrahedron Lett. 26 (1985) 3677–3680.
- [18] S. Boyer, J. Mckenna, J. Bach, G. Jagdmann, J. Org. Chem. 50 (1985) 3408–3411.
- [19] A.N. Correia, L. Mascaro, S. Machado, L. Avaca, Electrochim. Acta 42 (1997) 493–495.
- [20] R. Jones, E. Swift, Anal. Chem. 25 (1953) 1272–1274.
- [21] M.C. Oliveira, Electrochem. Commun. 8 (2006) 647–652.
- [22] L.M. Abrantes, M.C. Oliveira, E. Vieil, Electrochim. Acta 41 (1996) 1515–1524.
- [23] Y. Zeng, S. Zhou, Electrochem. Commun. 1 (1999) 217.
- [24] Y. Zeng, Y. Zheng, S. Yu, K. Chen, S. Zhou, Electrochem. Commun. 4 (2002) 293–295.
- [25] Y. Dorfman, M. Aleshkova, Kinet. Catal. 39 (1998) 852–858.
- [26] D. Lawson, M. Tierney, I. Cheng, L. Dyke, M. Espenscheid, C. Martin, Electrochim. Acta 36 (1991) 1515.
- [27] E. Lamy-Pitara, S. Mouahid, J. Barbier, Electrochim. Acta 45 (2000) 4299–4308.
- [28] M. Quiroz, F. Córdova, E. Lamy-Pitara, J. Barbier, Electrochim. Acta 45 (2000) 4291–4298.
- [29] E. Lamy-Pitara, I. Belegri, L. Ouazzani-Benhima, J. Barbier, Catal. Lett. 19 (1993) 87–91.