

Electrocatalytic hydrogenation of carbonylic compounds using an electrode with platinum particles dispersed in films of poly-[allyl ether *p*-(2-aminoethyl) phenol] co-polymerized with allyl phenyl ether

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Abstract

A modified electrode (ME) covered with poly-[allyl ether *p*-(2-aminoethyl) phenol] film containing platinum particles was prepared and used for the electrohydrogenation of several carbonylic compounds. Structural modifications on the film were made by co-polymerization with allyl phenyl ether, aiming to separate the ion-exchanger groups. The application of this new ME to the same reactions improved the product yield; enabling the use of a less negative potential for H[•] generation, the consequent increase in efficiency indicates an electrocatalytic hydrogenation route.

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1. Introduction

Electrocatalytic hydrogenation (ECH) is carried out since the beginning of the last century [1]. In the last decades, an increasing number of related works have been published with the formation of active hydrogen in powdered cathodes, particularly built on Raney-nickel, or palladium and platinum over carbon catalysts. Modified electrodes (MEs), by conducting redox polymeric films or by inactive polymeric films in which highly dispersed platinum or palladium particles were dispersed, also present good catalytic activity for proton reduction to H[•] and to hydrogen [2].

The outset of ECH is similar to catalytic hydrogenation—unsaturated molecules rich in π bonds are adsorbed by the empty orbitals of the transition metals surface and the hydrogen, also adsorbed, is transferred to the weakly π bonds. However, in the adsorption step the two methods are

different—the catalytic hydrogenation frequently needs high temperature and pressure to sustain the process and in the ECH, the H_{ads} is produced by protons discharge onto surface sites. Thus, the advantage of the ECH method is the in situ generation of atomic hydrogen in the surface of the electrode which can be directly used for the envisaged hydrogenation; alternatively, one can also use the hydrogen (g) subsequently formed with easy production control by potential or the current density adjustment, in mild experimental conditions (temperature and pressure) and minor catalyst poisoning by appropriate selection of the applied potential during electrolysis.

The limitation of the ECH method is the required large surface of the transition metal employed as working electrode. Several techniques were developed to improve the ECH [3–11].

The use of MEs for the ECH of several substrates has been largely reported in the last two literature decades [12–24]. To improve the activity and the selectivity of the electrode reactions, the surface of classical electrodes (e.g., noble metals, carbon, and semi-conductors) have been modified by the immobilization of species displaying given properties such

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as chemical [12], electrochemical [13–23], catalytical [24], photochemical [25] and optical [26].

Nowadays, electropolymerization is a common method for the preparation of MEs. It permits to cover the metallic electrode surface with an uniform polymeric film, chemically stable, and firmly attached. Furthermore, the amount of polymerized material is easily assessed by the control of the charge spent in the monomer oxidation [14].

The deposition of metallic particles has an increasing interest in electrocatalysis. To improve the ECH in aqueous solutions, platinum particles incorporation was carried out in viologen [27–29], cobaltocene (redox polymer) [30], poly-(vinylacetic acid) [31], poly-(2-methylthiophene) [32], poly-(4-vinylpyridine) [33,34], Nafion [35], polyaniline and poly-(mercaptohydroquinone) [36] and poly-(benzoquinone) [37].

Modified carbon electrodes with poly-(pyrroleviologen) bearing Pd, Pt, Rh or Ru particles have been reported as efficient electrodes for the ECH of unsaturated organic substrates, such as acids and ketones, nitro compounds, imines and nitriles [37]. Those metals can be incorporated in the porous polymeric matrix by a two-step procedure—ion-exchange from their salts followed by electrochemical reduction. The polymer matrix prevents large crystals growth or the aggregation of particles in clusters [15]. Polypyrrole films incorporating Ru, Rh and Ir display electrocatalytic activity for the hydrogenation of several conjugated ketones [14].

In spite of their advantages, polypyrrole films functionalized with ionic exchangers are difficult to prepare, requiring super dry solvent and inert atmosphere, and present low chemical and mechanical stability. At high oxidation potentials PPy can be overoxidized and loose its conductivity. Adherence problems have also been observed [38].

The preparation of ME with poly-(allyl ether *p*-benzenesulfonate) has been reported [39]. The film is chemically and mechanically very stable but poorly conductive. The incorporation of Ce(IV) salt, by ion-exchange, rendered the polymer electrocatalytic for the oxidation of several organic substrates [39]. In order to improve the cationic or anionic exchange, the main interest in the preparation of these electrodes is their versatility for the functionalization in the *para* position on benzene ring. Films containing ammonium groups are cationic exchangers and they can incorporate transition metal salts. The electrochemical reduction of these salts yield to metal particles and the so-modified electrodes can be used for ECH of organic substrates displaying better stability and being easier to prepare and more stable than those polymers based on polypyrrole. Films of poly-[allyl ether *p*-(2-aminoethyl) phenol] containing platinum particles were previously prepared and used in the ECH of an aldehyde and an olefin with hydrogen generated by electroreduction of H⁺ from acid solutions [40,41]. In this work the same ME is used for the ECH of carbonylic compounds with different structures. Structural modifications have shown a

positive effect in lowering the potential for the generation of atomic hydrogen.

2. Experimental

2.1. Equipment

Film preparation was carried out in a 50 ml one-compartment cell with a carbon vitreous plate (45 mm × 26 mm × 15 mm) as working electrode, a saturated calomel electrode (SCE) as reference and a platinum gauze with a 0.1 cm thick, 1.0 cm high and 80 cm long wire as an auxiliary electrode. This platinum gauze was rolled into a cylinder and the carbon plate was placed inside it in a symmetrical way.

Electrochemical experiments were also carried out in a 50 ml one-compartment cell, with the MEs as working electrode, SCE as reference and a platinum wire inside a sintered glass tube as an auxiliary electrode.

A PAR 273 Potentiostat/Galvanostat run by Electrochemical Analysis software Model 270 and a Potentiostat MQPG-01 were utilized.

Spectroscopic measurements were made in a 3.0 ml quartz cell using an 8453 HP spectrophotometer.

2.2. Reagents

All reagents and solvents were analytical grade and purified when necessary. A PK-4 polishing kit from Bioanalytical Systems Inc. (BAS) was used to clean the electrodes and to remove the films from the carbon vitreous support.

2.3. Analysis

Gas–liquid chromatography was performed with an Intralab 3300 chromatograph equipped with an OV-17 column, an ionisation flame detector and an Intralab 4290 recorder. Proton nuclear magnetic resonance (¹H NMR) spectra were obtained with a Brüker AC-80 (80 MHz) spectrometer.

2.4. Preparation of the monomer allyl ether *p*-(2-aminoethyl) phenol acetamide I

2.4.1. Tyramine acetylation

Preparation of the *p*-(2-aminoethyl) phenol acetamide was carried out according to reference [40].

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2.5. Hydrolysis of the allyl ether *p*-(2-aminoethyl) phenol acetamide (yielding I)

Preparation of the poly-[allyl ether *p*-(2-aminoethyl) phenol]–poly-(I) film on vitreous carbon electrode was carried out according to reference [40].

2.6. Preparation of the co-polymer (poly-allyl phenyl ether)–poly-(I) mixed-film covering carbon vitreous electrode

1.2 mmol (262 mg, 0.02 mol l^{-1}) of the allyl ether *p*-(2-aminoethyl) phenol acetamide was hydrolyzed as above described and added to 1 mmol (134 mg, 0.02 mol l^{-1}) of the co-monomer allyl phenyl ether. The electrochemical cell and the procedure for the polymerization were carried out according to reference [40] (Fig. 2).

2.7. Tetrachloroplatinate ion incorporation into the polymer films: electroreduction for the preparation of poly-(I) Pt and poly-mixed-I Pt modified electrodes

The carbon vitreous plates covered with the poly-(I) and poly-(I) mixed-films were initially dipped in a KCl solution, 0.5 mol l^{-1} , and then in a potassium tetrachloroplatinate solution, 0.01 mol l^{-1} , for 30 min in both cases. After treatment, these modified electrodes were washed carefully and transferred to a conventional electrolytic cell with KCl, 0.1 mol l^{-1} and subjected to potential scans within $+0.2$ to -1.0 V versus SCE interval at 10 mV s^{-1} scan rate (Fig. 3).

2.8. Modified electrodes characterization

2.8.1. Hydrogen generation from the H_2SO_4 solution

The current responses of the poly-(I) Pt and poly-mixed-I Pt MEs in $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution, in the potential domain $+0.2$ to -1.0 V versus SCE, 10 mV s^{-1} , were compared with the cathodic current generated in the same solution, by a platinum gauze with a surface of 164 cm^2 (18.2 g) used as working electrode (Table 1). The current density was calculated based on the current observed at -1.0 V (Fig. 4), taking into account the geometrical surface of the film that covered the electrode.

2.8.2. Platinum mass calculation of incorporated metal in the films

The mass of platinum incorporated in the film was evaluated stoichiometrically based on the number of Coulombs consumed by the voltammetric response corresponding to the reduction of the tetrachloroplatinate ions to metallic platinum (two electrons) after the ionic exchange. It was deduced that the charge generates by the pristine film (Table 1).

Table 1
Mass of Pt and the current densities at -1.0 V for the hydrogen generation for the two MEs and the platinum gauze electrode

ME	Mass (g cm^{-2})	Current density (mA cm^{-2}) ^a
Pt gauze	18.2 g (164 cm^2) ^b	7.9
Poly-I Pt	8.1×10^{-5}	14.1
Poly-mixed-I Pt	27.4×10^{-5}	23.1

^a Referred to the geometrical film area that covered the electrodes.

^b Total mass and total geometrical area of the platinum gauze electrode.

2.8.3. Electrochemical characterization of platinum particles in the films

Cyclic voltammograms of the poly-(I) Pt and poly-mixed-I Pt MEs were carried out between $+0.25$ and -0.05 V intervals versus SCE at a 5 mV s^{-1} scan rate (platinum oxides formation) and at $+0.25$ to $+0.05 \text{ V}$ intervals (reduction of the platinum oxides) in $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution.

2.8.4. Hydrogen volume evolved method

By connecting the conventional electrochemical cell to a graduated U-tube containing water, the gas exit was measured. The sintered compartment for the auxiliary electrode was kept out and all three electrodes were sealed with a tight-fitting glass stopper. A three-way plug was also connected to the cell to equalize the pressure during the experiment. A -0.9 V potential was applied to electrodes dipped in $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution, during 4 min. The volume of gas generated was measured in the U-tube every day for the period of one week (Fig. 5).

2.9. Electrocatalytic hydrogenation of substrates with the poly-(I) Pt and poly-mixed-I Pt MEs

1.0 mmol (0.02 mol l^{-1}) of each benzaldehyde, acetophenone, cyclohexanone, isophorone, 2-cyclohexen-1-one and 2.0 mmol of *n*-valeraldehyde (0.04 mol l^{-1}) substrates were added to 50 ml of a $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution, in the conventional electrolytic cell. Ethanol in the 1:1 proportion with the acid solutions (maintaining the acid concentration) was used to facilitate the dissolution of some immiscible substrates as acetophenone and isophorone. The MEs were polarized at -0.9 V versus SCE, under strong magnetic stirring, during at least 24 h. The evolution of hydrogen could be observed. In order to follow the reaction process, aliquots were taken during the process and were analyzed in the UV-Vis spectrometer.

To isolate the reaction products, the final solution was neutralized with NaHCO_3 and CH_2Cl_2 was used for the extraction of these. After solvent evaporation, the products were analyzed by GLC; comparison with pure samples helped its identification. Isophorone and 2-cyclohexen-1-one products were analyzed by $^1\text{H NMR}$.

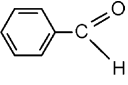
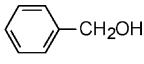
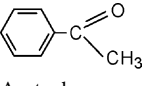
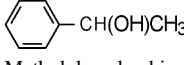
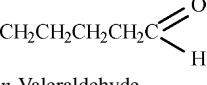
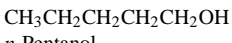

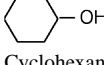

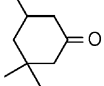

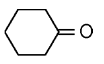
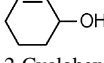
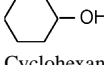
In a separated set of experiments, substrates were submitted to electrocatalytic hydrogenation at 0.6 V . The procedure was the same as above.

3. Results and discussion

Table 2 shows that the poly-(I) Pt ME works equally well for the ECH of several carbonylic compounds as aromatic, saturated or unsaturated aliphatic aldehydes and ketones, with different molecular volumes.

The film having an ethylene group prepared with the tyramine allyl ether yields more hydrogen than those prepared with the allyl ether of the *p*-aminophenol, likely due to the

Table 2
Yields of the ECH of the substrates using the MEs

Substrate	Product	ME poly-I Pt (–0.9 V) (% yield and reaction time h)	ME poly-mixed-I Pt (–0.9 V) (% yield and reaction time h)	ME poly-mixed-I Pt (–0.6 V) (% yield and reaction time h)
 Benzaldehyde	 Benzylic alcohol	94.7 (24)	81.0 (6.5)	95.3 (4.5)
 Acetophenone	 Methylphenylcarbinol	86.9 (24)	73.4 (7.0)	92.3 (5.5)
 <i>n</i> -Valeraldehyde	 <i>n</i> -Pentanol	53.0 (24)	70.6 (16)	65.3 (16)
 Cyclohexanone	 Cyclohexanol	65.3 (24)	78.3 (16)	88.5 (16)
 Isophorone	 3,5,5-Trimethyl-cyclohexanone	12.9 (24)	25.3 (24)	– –
 2-Cyclohexen-1-one	 Cyclohexanone	54.0	–	–
	 2-Cyclohexen-1-ol	23.3	90.2	92.6
	 Cyclohexanol	–	3.4 (8.0)	4.2 (6.0)
			(24)	

higher spacing between the ion-exchanger groups and the increase of the distance among the particles [40], which may facilitate the movement of the solvated H^+ ions. This observation has been the basis for the preparation of a mixed film with co-polymerized units of allyl phenyl ether and allyl ether *p*-(2-aminoethyl) phenol, aiming the increase of the permeability of the polymeric matrix to facilitate the movement of bulk molecules as isophorone and *n*-valeraldehyde and the increase of the ECH yields. The co-monomer was added in a proportion of 1:1, with the same initial amount of the monomer I, to ensure the same number of ion-exchanger terminals (Fig. 1). Preliminary studies showed that the increase of the co-monomer concentration increases the generation of hydrogen but proportion higher than 1:1 gives solubilization problems. A homogenous mixture of monomer and co-monomer oxidized electrochemically gives a radical cation that initiates a chain reaction that yields a polymer having units with and without ion-exchange groups.

Fig. 2 shows that the occurrence of a discharge for the first scan corresponds to the oxidation of the monomers. For the successive scans the current decreases as occurs with the polymerization of I [39], isolating the electrode. So, only one scan is sufficient to polymerize the mixture of allyl ethers.

After the incorporation of $PtCl_4^{2-}$ ions, their reduction to Pt (Fig. 3) originates a higher current than that observed for the film prepared from I, being deducted the charge generated by the pristine film, indicating a more efficient ion-exchange.

The presence of Pt particles in the film has been confirmed by cyclic voltammetry in H_2SO_4 . Anodic scan presented peaks at 0.07, 0.15 and 0.32 V and the cathodic scan at 0.15 and 0.22 V [41,42].

As expected from the increase in the amount of Pt particles incorporated in the film, the poly-mixed-I Pt modified electrode presents better electrocatalytic activity for hydrogen evolution when compared to the carbon vitreous plate and poly-(I) Pt (Fig. 4).

Table 1 shows the mass of Pt and the current densities for the hydrogen generation for the two MEs, comparing them with the platinum gauze electrode. The mixed film presents a metal content three times higher than poly-(I) Pt, and about 60% larger a current density for hydrogen generation. The increase of the metal mass can be due to the better permeability of the polymeric mesh for the $PtCl_4^{2-}$ mobility, favoring the displacement of the ion-exchange equilibrium.

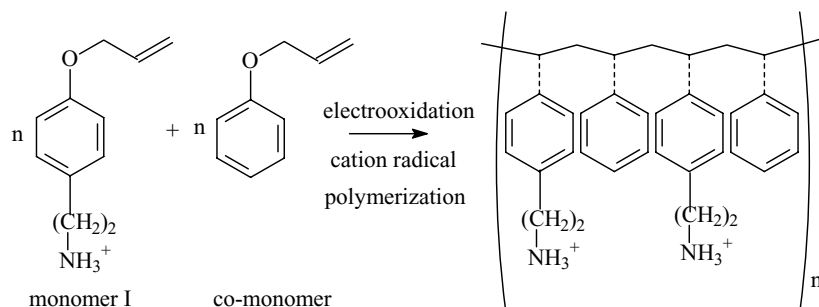


Fig. 1. Polymerization reaction scheme showing the 1:1 monomer I and co-monomer mixture and the correspondent polymer having alternated ion-exchanger groups.

The stability of the MEs has been tested by measuring the volumes of hydrogen formed in a modified cell during one-week. As shown by Fig. 5, ME-mixed-I Pt appears to be more stable than ME-I Pt. The charges calculated for a suitable volume of hydrogen generated during 4 min interval of time also showed that both electrodes are stable dur-

ing one-week: poly-(I) Pt: initial 14.2 mC, final 11.8 mC, decay of 2.4 mC and poly-mixed-I Pt: initial 17.8 mC, final 16.7 mC, decay of 1.1 mC (film surfaces).

Table 2 shows the performance of both MEs for the same hydrogenation processes: carbonyl function, isophorone (that gave a double bond hydrogenation product) and 2-cyclohexen-1-one where the double bond hydrogenation was partial.

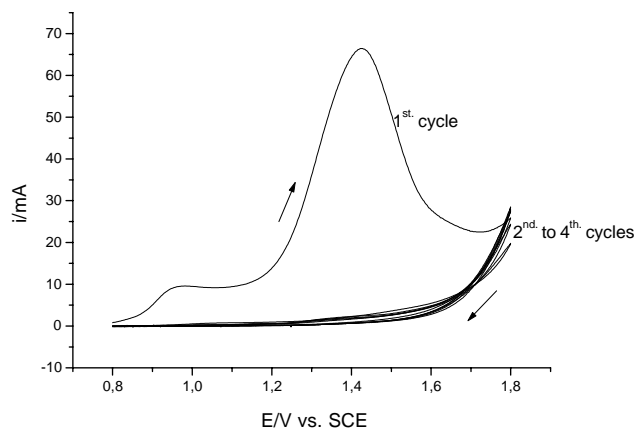


Fig. 2. Cyclic voltammograms at vitreous carbon electrode in 0.02 mol l^{-1} of monomer and 0.02 mol l^{-1} of co-monomer, dissolved in 3:7 t-butanol: perchloric acid 0.50 mol l^{-1} solution, scan rate 10 mV s^{-1} .

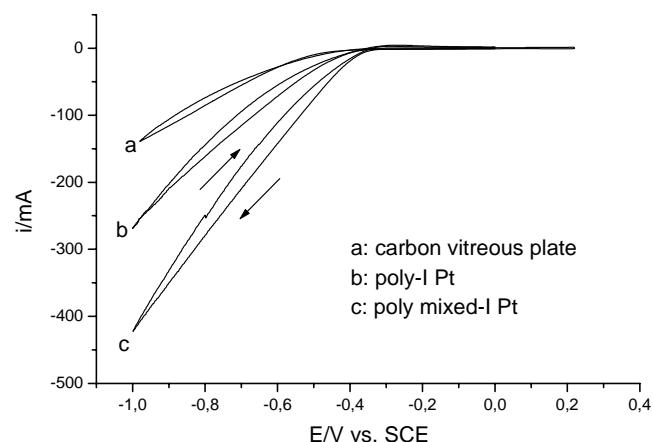


Fig. 4. Hydrogen generation by cyclic voltammograms for the two MEs, $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution, scan rate 10 mV s^{-1} .

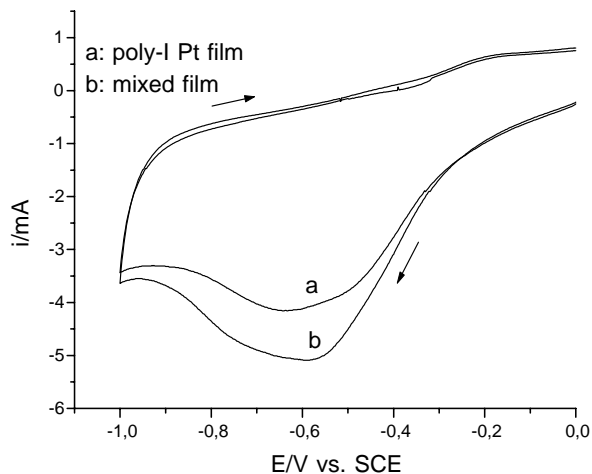


Fig. 3. Cyclic voltammograms for the two MEs. 0.10 mol l^{-1} of KCl solution, scan rate 10 mV s^{-1} .

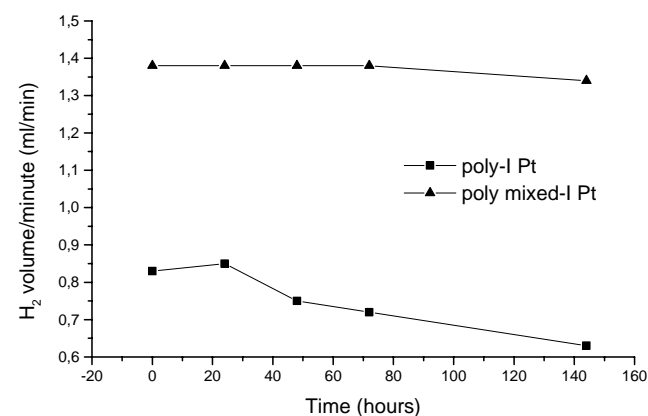


Fig. 5. Hydrogen volume generated during cathodic polarization at -0.9 V and step time of 4 min using the two MEs, $0.1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ solution.

The better efficiency of poly-mixed-I Pt is confirmed for all substrates. For *n*-valeraldehyde the yield in pentanol grows from 53 to 70.6% in 2/3 of the reaction time. The yield of 3,5,5-trimethyl-cyclohexanone from isophorone is double (13–25.3%), in spite of being low; it is likely that steric hindrance turns the adsorption of this large molecule difficult.

With both MEs, the aromatic substrates, benzaldehyde and acetophenone, present higher yields than observed for the correspondent aliphatic *n*-valeraldehyde and cyclohexanone, as expected by the superior capacity of adsorption on the Pt of molecules with extensive conjugation.

The results in Table 2 also show that both, the permeability of polymeric mesh and the Pt mass increase can improve the efficiency of the catalytic hydrogenations.

Surprising result was the different products for the ECH of 2-cyclohexen-1-one. With poly-(I) Pt a mixture of the hydrogenation of the double bond (principal product, as in the case of the hydrogenation of isophorone) and of the carbonyl has been obtained. Even with a reaction time longer than 24 h, the hydrogenation of cyclohexanone product to cyclohexanol does not occur in contrast with the result obtained when cyclohexanone is taken as substrate. For 8 h of reaction with poly-mixed-I Pt, the 2-cyclohexen-1-one gave a high yield of 2-cyclohexen-1-ol with no trace of cyclohexanone. Although the system deserves further investigation, this information suggests that the product, 2-cyclohexen-1-ol, is strongly adsorbed, poisoning the catalyst for the subsequent hydrogenation of the parallel cyclohexanone product formed.

Since a copious hydrogen evolution at the MEs surfaces may hinder the substrate adsorption, a study has been made for the same substrates but holding the electrode at different potentials, starting from -0.4 V, the onset of the cathodic current (see Fig. 4). The outstanding results displayed in Table 2, have shown that the hydrogenations can be efficiently achieved at -0.6 V with an increase of yield and decrease of the reaction time except for the *n*-valeraldehyde and for isophorone (isophorone react only at -0.9 V). In a shorter time, the conversion of benzyl alcohol and methylphenylcarbinol were almost complete; the formation of cyclohexanol from cyclohexanone was improved and the 2-cyclohexen-1-ol was also obtained with better yield. These results reinforce the electrohydrogenation character of these MEs. Indeed, the atomic hydrogen electrogenerated at -0.6 V promotes the hydrogenation at higher yields and lower reaction time than that promoted at -0.9 V.

4. Conclusion

The poly-(I) Pt ME runs efficiently the ECH of several carbonylic compounds giving good yields for products from benzaldehyde, acetophenone, cyclohexanone, 2-cyclohexen-1-one and medium to poor values in the case of *n*-valeraldehyde and isophorone. The poly-mixed-I Pt ME has been prepared by co-polymerization of allyl phenyl

ether with allyl ether *p*-(2-aminoethyl) phenol in a proportion of 1:1, and bearing the same number of ion-exchanger terminals. Separating the ion-exchanger groups by the insertion of a co-monomer has proven to permit the increase of the mobility of ions and molecules. Indeed, due to the higher permeability of PtCl_4^{2-} , the mass of Pt incorporated in this film increased three times and an increment of 60% on the current density for hydrogen generation from a H_2SO_4 solution has been observed. A significant increase in the ECH yields has been obtained for all studied substrates, with concomitant decrease in the reaction time, in spite of low yield for the isophorone product.

The same hydrogenation reactions carried out at potentials appropriate for the electrogeneration of H^\bullet have displayed even better yields and shorter reaction times, meaning that the so-prepared modified electrodes are adequate for electrohydrogenation of a wide variety of compounds.

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