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Journal of Catalysis 245 (2007) 191–197
JOURNAL OF CATALYSIS
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Electrocatalysis over Pd catalysts: A very efficient alternative to catalytic hydrogenation of cyclohexanone

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Received 21 July 2006; revised 3 October 2006; accepted 5 October 2006

Abstract

Electrocatalytic reaction was examined as an alternative method for the catalytic hydrogenation of cyclohexanone over Pd catalysts. The behavior of Pd/alumina catalyst and finely divided Pd catalyst in the electrocatalytic and catalytic hydrogenation of cyclohexanone in aqueous solution were investigated as a comparative study. The role of the pH of the solution was studied both in electrocatalytic and catalytic hydrogenation over Pd/alumina catalyst using acetic acid as a supporting electrolyte. High current yields were obtained for the electrocatalytic process, whereas, as expected from the literature, the catalytic hydrogenation was inefficient.

Keywords: Functionalized Pd composite material; Cyclohexanone; Cyclohexanol; Electrocatalytic hydrogenation; Catalytic hydrogenation; pH dependence

1. Introduction

From a synthetic standpoint, catalytic hydrogenation (CH) represents a very important reaction in organic chemistry and has been extensively studied in the gas phase and liquid phase. CH is generally carried out in mild to hard conditions of temperature (from ambient to 400 °C) and hydrogen pressure (from 1 to 350 atm) over high-surface area catalysts (supported or nonsupported transition or noble metals, Raney-type metals) [1]. Electrocatalytic hydrogenation (ECH) provides an alternative way to hydrogenate organic molecules under mild conditions (ambient temperature and normal pressure); the success of this method is related to a conjugation of two mechanisms: the electrochemical generation of hydrogen and the catalytic hydrogenation, both processes being cathode material-dependent. The main difference between CH and ECH processes lies in the method of generating atomic hydrogen. The CH process involves an external source of gas [Eq. (1)], whereas in the ECH process, electroreduction of hydronium ion leads to in situ generated atomic hydrogen [Eq. (2)] [2]. This species reacts with organic unsaturated molecules [Eq. (6)] adsorbed on the catalyst matrix [Eq. (5)] [3]. The hydrogenation step [Eq. (6)] is in competition with the hydrogen electrochemical and chemical desorption [Eqs. (3) and (4), respectively] to form H_2. The last step in the ECH and CH process is the regeneration of the adsorption sites by desorption of the hydrogenated compound. Equations (5)–(7) describe the hydrogenation mechanism over a composite (electro)catalyst that is composed by metallic nanoparticles supported on larger nonconductive material particles. Because steps (1)–(7) are surface reactions, the nature of both catalyst matrix [3] and metal [4] plays a key role in the kinetics of the reaction. Hydrogenation reaction depends on the surface coverage by adsorbed hydrogen and by the adsorbed organic substrate, fast and strong adsorption, and desorption of the organic substrate, increasing the efficiency of the ECH and CH processes. The ECH efficiency is also determined by competition among hydrogenation of the unsaturated substrate, H_2 evolution, and, in some cases, the direct reduction of the substrate on the electrode surface [5]. The chemisorbed hydrogen generated in ECH process is very reactive and has the same nature as in CH process. Equations (5)–(7) are common to both processes.

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doi:10.1016/j.jcat.2006.10.010

$$H_2 + 2M \leftrightarrow 2MH_{ads}, \quad (1)$$

$$H_3O^+ + e^- + M \leftrightarrow MH_{ads} + H_2O \quad \text{(Volmer reaction)}, \quad (2)$$

$$H_3O^+ + MH_{ads} + e^- \leftrightarrow M + H_2 + H_2O \quad \text{(Heyrovsky reaction)}, \quad (3)$$

$$2MH_{ads} \leftrightarrow 2M + H_2 \quad \text{(Tafel reaction)}, \quad (4)$$

$$Y{=}Z + A \leftrightarrow (Y{=}Z)_{ads}A, \quad (5)$$

$$(Y{=}Z)_{ads}A + 2MH_{ads} \leftrightarrow (YH\text{–}ZH)_{ads}A + 2M, \quad (6)$$

$$(YH\text{–}ZH)_{ads}A \leftrightarrow YH\text{–}ZH + A. \quad (7)$$

Here, M represents the metallic sites (Pd), where atomic hydrogen is formed (MH_{ads}), Y=Z describes the organic unsaturated molecule (cyclohexanone), $(Y{=}Z)_{ads}A$ is the adsorbed organic unsaturated molecule (cyclohexanone), and YH–ZH represents the organic saturated molecule (cyclohexanol). The target molecule is adsorbed on the adsorption sites (A) located on the catalyst matrix (alumina). Increasing the density of the target molecule in the immediate vicinity of the adsorbed hydrogen facilitates the overall hydrogenation process.

An interesting property of Pd (electro)catalyst is that it can adsorb and absorb hydrogen. This material is usually used supported on a carrier (catalyst matrix), but is occasionally used as palladium oxide or finely divided palladium particles. The popularity of this (electro)catalyst is due to the fact that it is the best catalyst usable for the hydrogenation of olefins and acetylenes as well as for most hydrogenolysis reactions [6–8].

The studies of Cleghorn and Pletcher [6,7] showed that Pd on Ni electrodes in methanol containing acetic buffer absorbs much less hydrogen than pure Pd does, but is a much more selective electrocatalyst for the conversion of nitrobenzene to aniline than Pd on graphite. The same studies demonstrated that alkynes and alkenes are reduced, but none of the studied carbonyl compounds (cyclohexanone, benzophenone, octyl aldehyde), cyclohexene, or naphthalene undergoes electrocatalytic hydrogenation in short time-scale electrolysis. The ability of a metal to promote ECH of a specific type of bond is not well understood, but the work of Dubé et al. [9] demonstrated that the electrocatalytic activity of metals dispersed on alumina matrix in ECH of cyclohexanone decreases in the order Rh > Pt = Pd > Ru. In some cases, the activity of a catalyst is the same, independent of the method used for hydrogenation of unsaturated molecules (ECH or CH). The work of Osa et al. [10,11] demonstrated that when using hydrogen active powder electrodes (Pd/C, Pt/C, and Ra–Ni) for the selective (electro)catalytic hydrogenation of some conjugated enones (unsaturated ketones), the ECH and CH processes have similar reactivities. On one hand, selectivity of the ECH process of unsaturated ketones depends significantly on the electrolysis conditions, especially on the nature of cathode materials. On the other hand, with electrodeposited Ni, Cu, or Co electrodes, the selectivity (ratio between yield of cyclohexanone and conversion) for the ECH of 2-cyclohexen-1-one to cyclohexanone reaches its maximum (100%) at a given charge, corresponding to $2\ \mathrm{F\,mol^{-1}}$ (theoretical charge to hydrogenate the α, β C=C bond) for a conversion rate of 69–80% [12]. In a comparative study of electrocatalytic and catalytic hydrogenation of 4-t-butylcyclohexanone on Pd-black cathodes and catalysts, the ketonic functional group is hydrogenated on Pd-black cathodes only in strongly acidic medium (1 M H_2SO_4–CH_3OH 1:1, v/v) to give 4-t-butylcyclohexanol with only 30% yield [13]. No 4-t-butylcyclohexanol is formed in acidic or basic medium (2 M NaOH–CH_3OH 1:1, v/v) using Pd-black catalysts.

Aliphatic and aromatic ketones are usually hydrogenated without difficulty to the corresponding alcohols over most of the transition metal catalysts under relatively mild conditions unless the ketones are highly hindered. Hydrogenation of unsaturated aliphatic ketones generally proceeds with preferential saturation of the olefinic function. Aromatic ketones can undergo hydrogenation in two paths: hydrogenation of only the ketonic functional group, resulting in formation of the corresponding alcohol, and hydrogenation of the aromatic ring, giving rise to saturated alcohol or ketone. Palladium, for instance, is a poor catalyst for hydrogenation of saturated aliphatic ketones but excellent for hydrogenation of aromatic ketones. It is the most widely used of the Pt group catalysts for hydrogenolysis of aromatic ketones, because it combines good activity for hydrogenation and hydrogenolysis of the ketone with low activity for hydrogenation of the aromatic ring. The rate of reduction of aliphatic ketones depends markedly on the catalyst and solvent used. Breitner et al. [14] studied the hydrogenation of cyclohexanone, cyclopentanone, and isobutylketone with Pd, Pt, Rh, and Ru on carbon in various solvents, but the Pd catalyst was ineffective in all solvents for hydrogenation of the ketones studied. In a recent study [15], a new concept—in situ functionalized materials for electrochemical processes—was introduced to enhance ECH efficiency. New catalysts based on the in situ modification of the alumina surface by the adsorption of aliphatic monocarboxylic acids as carboxylate were designed. Adsorption properties of the target molecule are influenced by the nature of these adsorbed chains. St.-Pierre et al. [16] carried out a similar study using silica-functionalized electrocatalysts and cyclohexanone as the target molecule. As in reverse-phase chromatography [17], adsorption phenomena of the target molecule on the stationary phase (cyclohexanone on the functionalized electrocatalyst in our study) can be controlled by the mobile-phase (solvent) polarity. This process influences overall ECH efficiency by increasing the target molecule density at the adlineation point [3].

This paper reports a comparative study of the ECH and CH of cyclohexanone with supported and nonsupported Pd catalysts in aqueous medium using phosphoric and acetic acid as supporting electrolytes. We show that the alumina surface is modified by the adsorption of acetic acid, a process that depends on the pH of the solution. This surface modification influences the adsorption phenomena and enhances the overall hydrogenation process. The ECH of cyclohexanone occurs efficiently with Pd/alumina catalyst in slightly acidic solution (acetic acid at pH 5 and 6), whereas the CH process is ineffective. We explain the ECH results by functionalization of the catalyst coupled with activation of the C=O bond by the polarization of the metallic aggregates.

2. Experimental

2.1. Chemicals

Cyclohexanone, cyclohexanol, and 3-methylcyclohexanol (all purchased from Aldrich) were of 99+% purity and used as received. High-purity water (from a Milli-Q unit) was used to prepare the solutions, and chloroform (Fisher, spectrophotometry grade) was used for liquid–liquid extraction. Reticulated vitreous carbon (RVC; 100 pores per inch) purchased from Electrolytica was used as cathode; commercial 10% Pd on alumina powder reduced (40 µm APS; Aldrich) and finely divided Pd (1.1–2.0 µm APS, Alfa Aesar) were used as catalysts. The solutions were prepared using glacial acetic acid (from Caledon, HPLC grade), H_3PO_4 (85% solution), and NaOH solution (10 N).

2.2. Electrocatalytic hydrogenation procedure

Electrolysis was carried out at ambient temperature using two-compartment electrochemical cells as described previously [18]. The cathode compartment was filled with 29 mL of a 0.5 M solution of acetic acid or phosphoric acid in water. The pH was previously adjusted with 10 M NaOH solution. The catalyst (200 mg of 10% Pd/Al_2O_3 powder or finely divided Pd) was suspended in solution and dynamically circulated through the RVC cathode in the electrochemical cell. The anodic compartment was filled with 10 mL of acetate or phosphate buffer solution (1 M). The ECH process was performed under galvanostatic conditions ($I = 20$ mA) using an Agilent galvanostat/potentiostat (model 6634 B). The electrode was polarized for 42 min under an applied constant current of 20 mA, with a corresponding charge of 50 C. After polarization, the coulometer was reset, a 1-mL solution of cyclohexanone (final concentration, 8.9 mM) was added in the cathode compartment, and a 0.5-mL aliquot of mixed solution was immediately removed as a reference sample (0 C) and treated as described in Section 2.4.

2.3. Catalytic hydrogenation procedure

The CH experiments were carried out at ambient temperature under atmospheric pressure of hydrogen. To a 29-mL solution of 0.5 M of acetic acid or phosphoric acid in water, a 1-mL solution of cyclohexanone (final concentration, 8.9 mM) was added. The catalyst (200 mg of 10% Pd/Al_2O_3 powder or finely divided Pd) was suspended in solution and stirred at constant rate.

2.4. Product analysis

Quantitative analyses were carried out by gas chromatography (GC) for ECH and high-pressure liquid chromatography (HPLC) for CH. GC analyses were performed on an Agilent 6890 Series chromatograph equipped with a MS detector and an HP-5HS capillary column (30 m × 0.250 mm × 0.25 µm). Aliquots of 0.5 mL were removed from cathode compartment at different times during electrolysis and were treated as follows: 25 mg of NaCl and 1 mL chloroform were added to a 0.5-mL aliquot, shaken together, and allowed to settle. The organic phase was removed and dried on Na_2SO_4. At 0.4 mL of the organic phase, 0.1 mL of an external standard solution was added, and the mixture was injected in the chromatograph.

HPLC analyses were carried out on a HPLC Agilent 1100 series chromatograph equipped with an Agilent Zorbax Eclipse X DB-C8 4.6 × 150 mm, 5-µm column and a G1362A RID detector. Aliquots of 0.5 mL were removed from the bulk at different times during the reaction, filtered with Millipore filters (0.45 µm), and directly injected.

2.5. DRIFT spectra

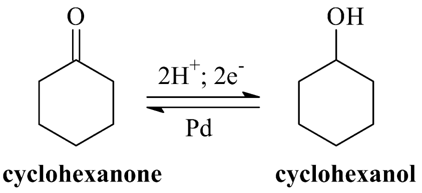
Diffuse reflection infrared Fourier transform (DRIFT) spectra of the electrocatalytic powders were recorded on a Nicolet Nexus 470 FTIR spectrometer equipped with a Harrick DRIFT accessory and a MCT-A detector. All data were collected with a resolution of 4 cm^{-1}, a moving mirror speed of 1.98 cm/s, and Happ–Ganzel apodization; typical spectra required 256 mirror scans. To exclude atmospheric interferences and to minimize sample contamination, the sample compartment and the optical bench were purged with Ar. The powders were immersed in the supporting electrolyte solutions containing acetic acid (0.5 M) at pH 5 and 10. The suspensions were filtered, and the powders were washed with methanol and water to remove all soluble compounds and salts. After drying at 50 °C for 8 h, the catalyst powders were probed by DRIFT using a powder not exposed to the organic acids as a reference.

2.6. Zeta potential measurements

Zeta potential analyses were performed using a Zeta Probe Analyzer from Colloidal Dynamics. Diluted 1-wt% Pd/alumina suspensions containing acetic acid or phosphoric acid and deionized water were prepared for zeta potential measurements. NaOH (10 N) was used as a titrant to adjust the pH.

3. Results and discussion

In the present study, we are interested in the ECH and CH of cyclohexanone. The ketonic group of cyclohexanone is hydrogenated in a two-proton and two-electron process to form the hydroxylated compound (Scheme 1). According to the literature data, catalytic and electrocatalytic hydrogenation of cyclohexanone on Pd supported or nonsupported catalysts are difficult to carry out [13,14].



Scheme 1. Reaction scheme for the hydrogenation of cyclohexanone to cyclohexanol.

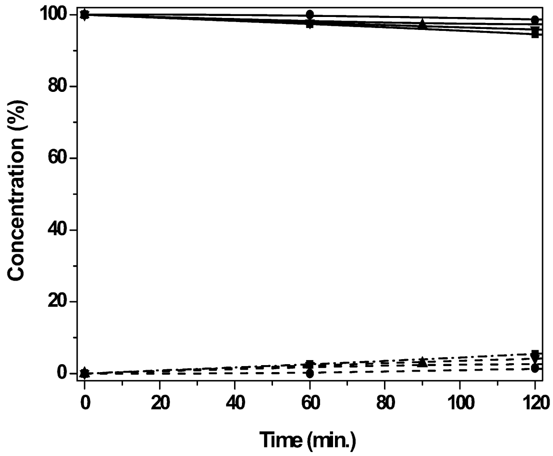


Fig. 1. Cyclohexanone (solid line) depletion to cyclohexanol (dash line) in CH process: (■) 10% Pd/alumina + acetic acid; (▼) 10% Pd/alumina + phosphoric acid; (▲) finely divided Pd + acetic acid; (●) finely divided Pd + phosphoric acid.

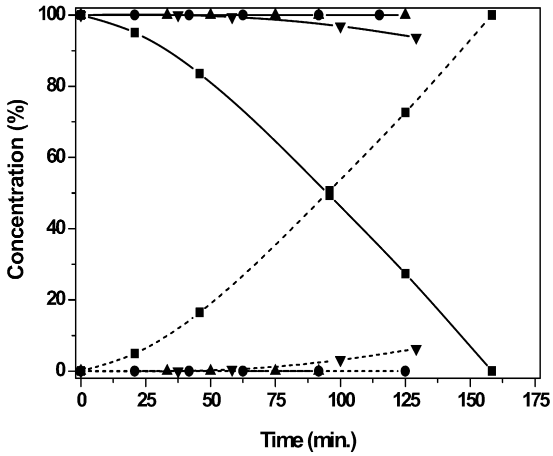


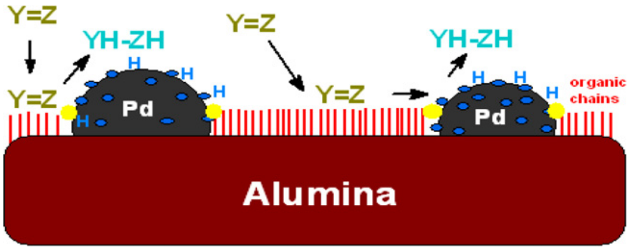
Fig. 2. Cyclohexanone (solid line) depletion to cyclohexanol (dash line) in ECH process: (■) 10% Pd/alumina + acetic acid; (▼) 10% Pd/alumina + phosphoric acid; (▲) finely divided Pd + acetic acid; (●) finely divided Pd + phosphoric acid.

Generally, the hydrogenation process is greatly affected by the preparative procedure of the catalyst [19]. Therefore, in this comparative study of ECH and CH on Pd-supported or unsupported catalysts, the experimental conditions are identical in both processes. The only experimental parameter that differs for these processes is the method of generating the chemisorbed atomic hydrogen. Fig. 1 presents the results obtained in the CH of cyclohexanone with Pd/alumina and Pd finely divided catalysts in water. To ensure the same experimental conditions as in ECH, an equivalent of 0.5 M acetic or phosphoric acid was added, and the pH was adjusted to 5. A very slight tendency was observed for cyclohexanone transformation with all catalysts, regardless of the acid used. Under these experimental conditions, cyclohexanol can be obtained only with a poor yield. These results corroborate those of Breitner et al. [14] suggesting blockage of the hydrogenation process by the strong adsorption of the studied ketones on Pd, hence deactivation of the catalyst by poisoning.

To compare the results for CH with those for ECH, the conversion rate is represented as a function of time. Because the electrocatalytic process was conducted at a constant current density, the charge consumed was converted into time.

The ECH results, obtained in a solution of 0.5 M of supporting electrolyte (acetic acid or phosphoric acid adjusted to pH 5) are presented in Fig. 2. We can see unexpected activity with the Pd/alumina catalyst in the presence of acetic acid; cyclohexanone is quantitatively transformed to cyclohexanol with a good current efficiency. In contrast, with the finely divided Pd catalyst, the reaction does not occur. Very poor conversion is observed with Pd/alumina catalyst using phosphoric acid (pH 5) as the supporting electrolyte. Clearly, under our experimental conditions, the supporting electrolyte intervenes in the electrocatalytic process.

One explains these results using a concept recently introduced by our group: in situ functionalized materials [15]. We showed that when alumina is immersed in a solution containing aliphatic carboxylic acids, the surface is modified by the adsorption of carboxylate. An organic layer is thus formed in a process called in situ functionalization. In our experimental conditions, cyclohexanone adsorption occurs on the new modified surface. We suggest that cyclohexanone is adsorbed according to its van der Waals interactions with the organic layer, but the transport across this surface at the adlineation point (yellow circles in Scheme 2) is achieved by the 2D diffusion. By using solvents of different polarities (water, methanol, or a mixture of both) and various organic acids (short- or long-chain acids), the adsorption of the target molecule can be modulated [Eq. (5)], as can the overall ECH process [15].



Scheme 2. Schematic representation of the ECH process for an unsaturated molecule on the in situ functionalized electrocatalyst.

The electrocatalytic process is also controlled by the adsorption step of organic unsaturated molecules, which depends on the functionalization of alumina. Whereas steps (5)–(7) are common to both processes, a difference in behavior is observed when comparing the CH (Fig. 1) and ECH (Fig. 2) processes. Conversion after 160 min practically reached 100% with the Pd/alumina catalyst in the presence of acetic acid in the ECH. To explain this inequality, we suggest that at the adlineation point, cyclohexanone behaves following different pathways. In the ECH process, the negative polarization of the Pd aggregates can exert a significant effect on the C=O functional group. In fact, a partial oxygen–palladium bonding can be formed, resulting in weakening of the ketonic bonding group, and, consequently, the adsorbed hydrogen transfer can be facilitated. This reasoning is in agreement with the literature on the catalytic and the electrocatalytic hydrogenation of some ketones [13]. Using phosphoric acid as the supporting electrolyte (pH 5), the alumina surface is modified by the phosphate adsorption; an inner-sphere surface complex is formed by a direct chemical bond between adsorbing anions (Lewis base) and the metal ions at the surface (Lewis acid) [20]. This new modified surface damages the cyclohexanone adsorption [Eq. (5)] at the interface and blocks the transport of the molecule at the adlineation point, giving rise to a slower reaction (Fig. 2). When the alumina surface is organically modified, the adsorption of the cyclohexanone and its transport across the interface are facilitated, increasing the reaction rate. In the ECH, activation of the C=O bond due to the polarization of palladium aggregates aids hydrogen transfer, enhancing the overall efficiency. When the palladium aggregates are not polarized (in the case of catalytic process), activation of the C=O bond cannot occur, and the CH yield diminishes because the reaction (6) becomes the rate-determining step. CH and ECH of cyclohexanone were also performed in ethanol solution, using Pd/alumina catalyst and acetic acid as the supporting electrolyte (pH 6). We observed a drastic loss of ECH efficiency, whereas the CH process remained ineffective (data not presented here). This behavior can be explained by the change in polarity of the solvent. In the solution containing 90% ethanol in water, the polarity mixture diminishes [17], affecting the adsorption of cyclohexanone, resulting in loss of ECH efficiency. To conclude, the yield of cyclohexanol is influenced by the catalyst functionalization and the polarization of Pd aggregates, which aid hydrogen transfer.

Because the pH of the solution can influence the hydrogenation reaction, we were interested in studying its role in the CH and ECH of cyclohexanone with a Pd/alumina catalyst in solution containing acetic acid. The solutions were prepared in the same manner as above, over a pH range of 3–7.

Although we know that the pH can change during the electrocatalytic process due to the hydroxyl ions formation by the reduction of water, but for some solutions (pH 4–6), its values remain constant during the electrocatalytic reaction because of the buffer capacity. For the solution of pH 3, a slight change was observed during the electrocatalytic process, whereas for the solution of pH 7, the change was significant (initial pH 7; final pH 10). In the catalytic process, the pH is not subject to change, because no species able to modify the pH is formed. Fig. 3 shows that the catalytic hydrogenation of cyclohexanone using Pd/alumina catalyst in solutions of various pH followed the same tendency independent of the pH of the solution; however, the yield of the catalytic process remained weak. Surprising results were obtained in the electrocatalytic process using the Pd/alumina catalyst and acetic acid as supporting electrolyte at pH 3–7 (Fig. 4).

For pH 3 and 4, the cyclohexanone conversion reached 6–10% after 160 min with all catalysts used, whereas at pH 5 and 6, the conversion reached 100% after 160 and 82 min, respectively. It is interesting to point out that at pH 7, the conversion diminished, being between the values obtained for pH 4 and 6, as depicted in Fig. 4. This variant behavior can be justified by the different modifications of the alumina surface. Because acetic acid is a weak acid, its degree of dissociation in an aqueous solution (Fig. 5) and adsorption on alumina are greatly affected by pH [21]. At pH 3 and 4, the acetic acid was practically undissociated, whereas at pH 5 and 6, the dissociation degree changed drastically. The protonated form, which is dominant at pH 3 and 4, is weakly adsorbed on alumina, whereas the unprotonated form is more strongly adsorbed, with greater adsorption energies [22].

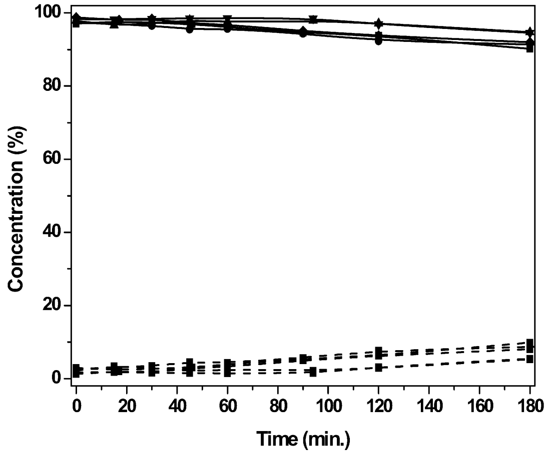


Fig. 3. Cyclohexanone depletion to cyclohexanol in CH process over 10% Pd/alumina catalyst in acetic acid solution: (■) pH 3; (●) pH 4; (▲) pH 5; (▼) pH 6; (◆) pH 7.

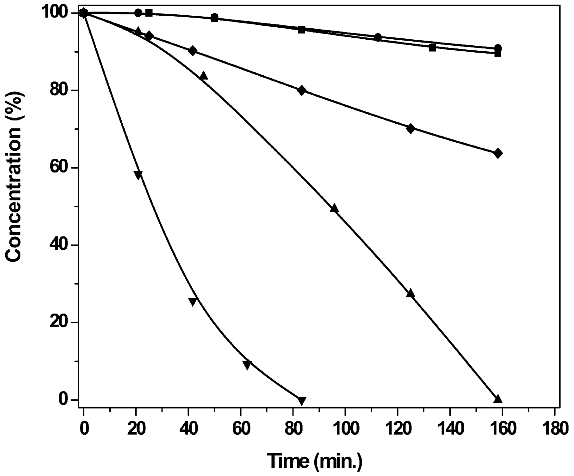


Fig. 4. Cyclohexanone depletion to cyclohexanol in ECH process over 10% Pd/alumina catalyst in acetic acid solution: (■) pH 3; (●) pH 4; (▲) pH 5; (▼) pH 6; (◆) pH 7.

Because adsorption of acetic acid is weak below pH 4, it can be concluded that the alumina surface is not functionalized. This phenomenon affects the adsorption and the diffusion of the cyclohexanone across the interface; in the absence of a high adsorbed cyclohexanone density at the adlineation point, the electrocatalytic process is kinetically limited, which explains the slight efficiency obtained at pH 3 and 4. At pH 5 and 6, the modified surface is stable in these experimental conditions, as shown elsewhere [15], and the adsorption phenomena are enhanced. This stability is facilitated by the favorable interactions of the acetate ions with the alumina surface. The dissociation degree of acetic acid is 33% greater at pH 6 than at pH 5, implying better coverage of the surface at pH 6. This better coverage of the alumina surface by the organic phase is equiv-

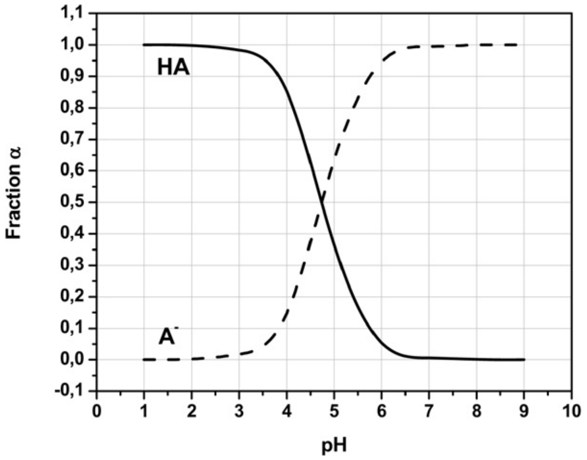


Fig. 5. Calculated dissociation diagram for acetic acid ($pKa = 4.76$ at 25 °C).

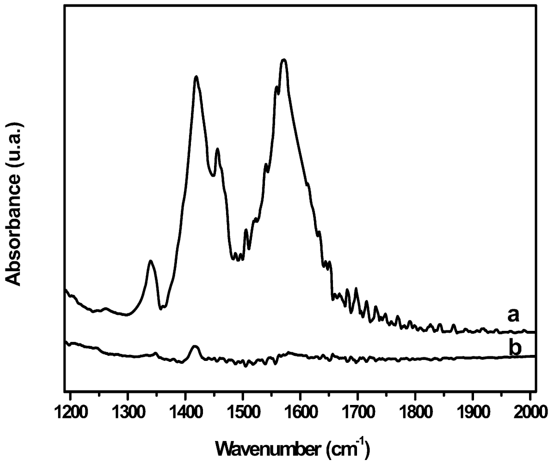


Fig. 6. FT-IR spectra of Pd/alumina catalyst subjected to aqueous solutions of acetic acid: (a) pH 5; (b) pH 10.

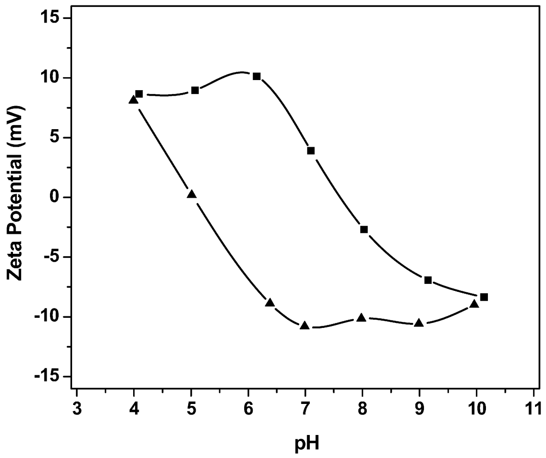


Fig. 7. Zeta potential vs pH for Pd/alumina in solution containing 0.1 M of (■) acetic acid and (▲) phosphoric acid.

alent to an increase in specific sites that support the adsorption and diffusion of cyclohexanone across the interface. Increasing the density of adsorbed cyclohexanone at the adlineation point enhances the ECH efficiency, as shown in Fig. 4. The result obtained at pH 7 is surprising, especially because better coverage of the alumina was expected at this pH, because the acetate form is predominant. This can be explained by the drastic change in pH observed during the ECH at pH 7; the pH reached a value of 10 few minutes after the reaction started.

The pH change affects alumina functionalization, and the competition to occupy the alumina sites supports the hydroxyl ions, which are dominant in basic solution. To support this hypothesis, we analyzed the alumina surface by infrared spectroscopy after functionalization in solutions at different pH. As shown in Fig. 6 (curve a), the presence of antisymmetric and symmetric stretching of COO^- at 1750 cm^{-1} and 1418 cm^{-1}, respectively, indicates that acetic acid is adsorbed as acetate onto alumina at pH 5 [15]. The loss of these bands when the catalyst is immersed in the solution at pH 10 (Fig. 6, curve b) indicates that no adsorption of acetate occurs in basic solution. In this manner, the functionalization of alumina surface is damaged during the ECH process; the adsorption and the diffusion of cyclohexanone across the interface are affected, which explains the loss of efficiency when the electrocatalytic hydrogenation is carried out at pH 7. A high stability of the modified surface ensures a constant covering of the alumina surface, which supports the adsorption and diffusion of the target molecule at the interface. To probe in situ the alumina surface in solution containing acetic or phosphoric acid (0.1 M), zeta potential measurements were conducted. The magnitude of the zeta potential gives an indication of the potential stability of the alumina suspension. If the particles in suspension have a large negative or positive zeta potential, then they will tend to repel each other, and there is no tendency to agglomerate. However, a low value of zeta potential indicates that there is no force preventing the particles from coming together, and thus they can flocculate. The stability of alumina particles in aqueous suspension is closely related to its electrophoretic properties; a well-dispersed suspension can be obtained with high surface charge density to generate strong repulsive forces. The isoelectric point (IEP) of untreated alumina is at pH 9.1, but adding a dispersant can shift this value [23]. Fig. 7 shows the effect of pH on the zeta potential of Pd/alumina powder in solution containing 0.1 M acetic or phosphoric acid.

The Pd/alumina particles exhibited different behavior, depending on the acid used. A quick diminution in zeta potential occurred with phosphoric acid solution up to pH 7, followed by a stagnant value beyond this pH. In acetic acid solution, up to pH 6, the zeta potential remained constant and underwent a drastically decrease in neutral and basic solution. The IEP shifted toward acidic values for acetic acid (7.5) and was more pronounced for phosphoric acid (5.2). Reverse of the zeta potential sign indicates that ions are specifically adsorbed at the alumina surface [24]. Our results reveal that Pd/alumina particles behaved differently depending on the acid solution, suggesting that the alumina surface was modified by the interaction with both acids. We can also conclude that modification of the alumina surface was modulated by the pH of the solution. From the foregoing discussion, it becomes clear that the supporting electrolyte (acetic or phosphoric acid) intervenes in the ECH and CH processes due to the modification of the catalyst matrix (alumina surface), which influences the adsorption and the diffusion of cyclohexanone toward the adlineation point, where hydrogenation occurs. The concept of in situ functionalized (electro)catalyst [15] can explain the results obtained in the present study. As demonstrated experimentally, the ECH process occurs very efficiently over the acetate-functionalized Pd/alumina catalyst at pH 6, due to the organic stable interface, which enhances cyclohexanone density at the adlineation point, and due to the effect of the polarized Pd aggregates on the C=O bond. This in situ functionalized electrocatalyst was used in the ECH of other organic molecules (octyl-aldehyde, benzophenone), which are known as nonhydrogenable with Pd catalyst, and satisfactorily results were obtained.

4. Conclusion

The present work shows that organic compounds containing C=O functional group can be efficiently hydrogenated by electrocatalytic hydrogenation using an organically modified Pd/alumina catalyst. It was demonstrated that the Pd/alumina catalyst in the presence of phosphoric acid as the supporting electrolyte is ineffective in electrocatalytic and catalytic hydrogenation but becomes very efficient in the electrocatalytic process when used in acetic acid solution at slightly acidic pH. Moreover, the importance of the catalyst matrix is evidenced by the comparison between supported and nonsupported Pd catalyst in ECH and CH. Electrocatalytic hydrogenation is a suitable way to efficiently transform the cyclohexanone into cyclohexanol with a palladium-supported catalyst.

Acknowledgments

The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Fond Quebecois de la Recherche de la Nature et les Technologies (FQRNT).

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