# On the efficiency of phenol and cyclohexanone electrocatalytic hydrogenation — Effect of conditioning and working pH in acetic acid solution on palladium/fluorine-doped tin dioxide supported catalyst

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**Abstract:** The electrocatalytic hydrogenation (ECH) of phenol and cyclohexanone was performed on a conductive Pd/SnO<sub>2</sub>:F catalyst. The catalyst was obtained by the impregnation method. We studied the influence of the pH of the supporting electrolyte, the conditioning pH, and the quantity of the conditioning charge passed before hydrogenation. Fourier transform infrared spectroscopy analysis showed that the functionalization of the catalyst surface by the acetic acid electrolyte depends on the pH. A direct correlation was observed between the efficiency of the hydrogenation, the pH of the electrolyte, and the electrode conditioning charge. Phenol hydrogenation was favored in acidic media, whereas cyclohexanone hydrogenation needed an acidic medium for conditioning and a basic medium for hydrogenation. The ECH rate appeared to depend on the functionalization of the catalyst surface, the adsorption of the target organic molecule on the catalyst, and its structural modification with the pH.

Key words: electrocatalytic hydrogenation (ECH), functionalization, phenol, cyclohexanone, tin dioxide catalyst.

**Résumé :** L'hydrogénation électrocatalytique (HEC) du phénol et de la cyclohexanone a été réalisée avec un catalyseur de Pd sur SnO<sub>2</sub>:F conducteur obtenu par imprégnation. Les effets du pH de l'électrolyte support, du pH de conditionnement et de la quantité de charge utilisée pour le conditionnement ont été examinés. La spectroscopie infra rouge par transformée de Fourier a montré que la fonctionnalisation de la surface du catalyseur avec l'acide acétique dépend du pH de l'électrolyte. Une corrélation directe entre l'efficacité d'hydrogénation, le pH de l'électrolyte et la charge de conditionnement a été démontrée. L'hydrogénation du phénol est favorisée en milieu acide tandis que celle de la cyclohexanone nécessite un conditionnement en milieu acide et une HEC en milieu basique. Le taux d'HEC dépend ainsi de la fonctionnalisation de surface du catalyseur, de l'adsorption de la molécule cible sur la surface fonctionnalisée et de la structure de cette molécule en solution dépendamment du pH.

*Mots-clés* : hydrogénation électrocatalytique (HEC), fonctionnalisation, phénol, cyclohexanone, catalyseur de dioxyde d'étain.

### Introduction

Electrocatalytic hydrogenation (ECH) of organic compounds is industrially exploited to produce molecules that have applications as chemical intermediates.<sup>1,2</sup> This hydrogenation method is gradually replacing the catalytic hydrogenation (CH) process because of its easy implementation. Indeed, the reactions are carried out at ambient temperatures and pressures by producing chemisorbed hydrogen at a cathode and by electrolyzing water. This method is applicable to hydrogenation of all kinds of unsaturated molecules, including aromatic rings, carbonyl, nitro, and nitrile compounds.<sup>3</sup>

The efficiency of the ECH is dependent on numerous parameters, such as the unsaturated molecule to be hydrogenated, the catalytic metal, the support of the metal, the supporting electrolyte and its pH, the presence of organic cosolvent or surfactant, and the current density.<sup>4</sup> Each of

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**Fig. 1.** X-ray diffraction patterns of Pd/SnO<sub>2</sub>:F catalyst (a) before and after ECH process at (b) pH 3 and (c) pH 12. ( $\blacklozenge$ ) SnO<sub>2</sub>:F, cassiterite structure; ( $\blacklozenge$ ) tetragonal PdO peaks at  $2\theta = 33.89$ , 46.66, 54.76, and 71.48 in diffractogram (a) are superposed to the SnO<sub>2</sub>:F peaks; ( $\blacklozenge$ ) metallic Pd.



Scheme 1. Conversion of phenol into cyclohexanol via cyclohexanone.



these parameters has an influence on the mechanism of the ECH described below.

[1a] 
$$H_3O^+ + e^- + M \rightarrow MH_{ads} + H_2O$$
 Volmer reaction

$$[1b]$$
  $H_2O + e^- + M \rightarrow MH_{ads} + OH^-$ 

$$[2] \qquad Y{=}Z + A \underset{\overline{K_{des}}}{\overset{K_{ads}}{\rightleftharpoons}} (Y{=}Z)_{ads} \ A \quad Adsorption$$

[4] 
$$(YH-ZH)_{ads} A \stackrel{K_{des}}{\underset{K_{ads}}{\longrightarrow}} YH-ZH + A$$
 Desorption

$$[5a] \qquad H_2O + MH_{ads} + e^- \rightarrow M + H_2 + OH^-$$
  
Heyrovsky reaction

$$[5b] \qquad H_3O^+ + MH_{ads} + e^- \rightarrow M + H_2 + H_2O \\ He yrovsky reaction$$

$$[6] \qquad 2MH_{ads} \rightarrow 2M + H_2 \quad Tafel reaction$$

In this mechanism, three groups of reactions can be observed. The first one (reactions 1a and 1b) is relative to the production of the chemisorbed hydrogen ( $MH_{ads}$ ) on the metallic surface (M) by the electroreduction of water (acidic or basic medium); the second (reactions 2–4) concerns the hydrogenation reaction, which starts with the adsorption of the unsaturated molecule (Y=Z) on the support (A), which further reacts with the chemisorbed hydrogen; the last group of reactions (reactions 5 and 6), which concerns the hydrogen evolution reaction, is a competition reaction with hydrogenation. Depending on the parameters cited above, either the hydrogenation process or the hydrogen evolution will be predominant.

The behavior of a supported metal is different from the bulk metal, and the synergy effect of a metal supported on a matrix has been recently studied.<sup>5</sup> The adsorption of the unsaturated organic molecule is a key step. For the supported catalysts, this adsorption takes place on the support,<sup>6</sup> thus the efficiency of the ECH is relative to the nature of the catalyst matrix. To control both the adsorption of the unsaturated compound and the desorption of the hydrogenated product, recent studies have introduced new concepts: ex situ<sup>7</sup> and in situ functionalized<sup>8</sup> materials. They consisted of a modification of the catalyst matrix with organic functional molecules before and during the ECH process, respectively. These modifications controlled the adsorption of the target molecule as in reverse chromatography. It was demonstrated that the in situ modification of alumina surface depended on the pH of the electrolyte when acetic acid was used.<sup>9</sup>

Before the introduction of these new concepts, several studies had focused on phenol and cyclohexanone. On RaNi electrode, in alkaline media (pH > 13), ECH of cyclohexanone led to excellent chemical yields and current efficiencies, the best results being obtained with NaOH 0.14 mol/L. However, when an acetate buffer was used, no hydrogenation took place.<sup>10</sup> The studies of Dubé et al.<sup>11</sup> in a phosphate buffer (KH<sub>2</sub>PO<sub>4</sub> + NaOH), pH 7, showed that Pd dispersed on both alumina and activated carbon presented a bad electrocatalytic activity compared with the other metals of the Pt group. They also demonstrated that the yield of cyclohexanone electrohydrogenation was strongly dependent on the nature of the non-conductive matrix used to disperse Ni nanoparticles. Santana et al.12 found that the pH had no influence on the hydrogenation of 2-cyclohexen-1-one when a nickel sacrificial anode was used. This study concluded that the ECH of conjugated olefins or carbonyl groups is efficient, whereas for non-conjugated substrates (the case of cyclohexanone), it is not.

Fichter and al.<sup>13</sup> reported a poor yield for the reduction of phenol to cyclohexanol in 2 N H<sub>2</sub>SO<sub>4</sub> at a platinized Pt electrode. On the contrary, Misra et al.<sup>14</sup> showed that phenol was reduced electrochemically in a divided cell at a Pt cathode in 2 N HClO<sub>4</sub>, in the presence of tetraethylammonium, with a 82.7% yield. More recently, the effect of pH on the kinetics of phenol ECH was investigated with BaSO<sub>4</sub> as the adsorbent. The rate of reaction was considerably lower at pH 14, and remained unchanged between acidic and neutral media.<sup>15</sup> In acidic media (H<sub>2</sub>SO<sub>4</sub>), Martel et al.<sup>4</sup> found that the phenol ECH depended on the catalyst material, whereas in neutral media the results were linked to the supporting electrolyte, i.e., the nature of ions in solution.

Current density also influences the hydrogenation product yield. This parameter acts as a balance between the two

**Fig. 2.** ECH of phenol on Pd/SnO<sub>2</sub>:F in aqueous solution of acetic acid (0.5 mol/L) as a function of the electrolyte pH and total charge: ( $\blacktriangle$ ) pH 12, ( $\blacksquare$ ) pH 6, ( $\blacklozenge$ ) pH 5, and ( $\blacklozenge$ ) pH 3; *I* = 20 mA.



**Fig. 3.** FTIR spectra of SnO<sub>2</sub>:F powder subjected to aqueous solutions of acetic acid at (a) pH 3, (b) pH 6, and (c) pH 12.



competitive reactions (3 and 5a, 5b). A high current density favors the hydrogen evolution reaction, whereas a low current density improves the hydrogenation efficiency.<sup>16</sup>

This paper reports the results of a study on the effect of the pH (3 to 12) on the efficiency of phenol and cyclohexanone ECH in acetic acid as electrolyte using Pd deposited on conductive fluorine-doped tin dioxide (SnO<sub>2</sub>:F) as catalyst. Effectively, the ECH process implied a pH variation during its proceeding as stated by the mechanism (reactions 1 and 5), and also the functionalization of the catalyst is a pH-depending phenomenon.<sup>9</sup>

**Fig. 4.** ECH of cyclohexanone on Pd/SnO<sub>2</sub>:F in aqueous solution of acetic acid (0.5 mol/L) as a function of the total charge, at different starting pH values without controlling the pH during the reaction: ( $\blacksquare$ ) pH 5, ( $\blacklozenge$ ) pH 6, ( $\blacklozenge$ ) pH 8, and ( $\blacktriangle$ ) pH 12; *I* = 20 mA.



As shown by the ECH mechanism, the efficiency of hydrogenation is linked to the production of chemisorbed hydrogen (reactions 1a and 1b) by electroreduction of water. Here, we present a study of the effect of quantity of charge used for the conditioning of the catalyst, before the ECH process, which determines the available quantity of chemisorbed hydrogen. We show that the ECH efficiency depends on the pH and the conditioning charge.

#### **Experimental**

#### Chemicals

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Conductive fluorine-doped tin dioxide (SnO<sub>2</sub>:F) of ( $\rho < 5$   $\Omega$ cm,  $S_{\text{BET}} = 6-10 \text{ m}^2 \text{ g}^{-1}$ ) was purchased from Keeling & Walker Limited. Also, Pd(OOCCH<sub>3</sub>)<sub>2</sub> as Pd precursor was purchased from Aldrich.

Phenol, cyclohexanone, cyclohexanone-oxime, cyclohexanol, and 3-methylcyclohexanol (Aldrich) were of +99%grade of purity and were 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 the solubilization of Pd(OOCCH<sub>3</sub>)<sub>2</sub> and the liquid–liquid extraction. Reticulated vitreous carbon (RVC, with 100 pores per inch) was purchased from Electrolytica Inc. and used as cathode. The electrolyte was prepared using glacial acetic acid from Aldrich.

#### **Catalyst preparation**

Pd/SnO<sub>2</sub>:F catalyst was prepared by impregnating com-

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		Startin	Starting pH			
Charge passed (C)		3	5	6	8	12
Conditioning	7	3.0	5.0	6.1	10.0	12.0
	50	3.0	5.1	6.7	12.0	12.0
HEC process	20	3.1	5.1	11.2	12.1	12.0
	50	3.1	5.2	12.1	12.3	12.0
	100	3.1	5.2	11.9	12.0	12.1
	150	3.1	5.4	11.9	12.1	12.1

**Table 1.** Evolution of the pH as a function of the starting pH andthe quantity of charge passed.

**Fig. 5.** ECH of cyclohexanone on Pd/SnO<sub>2</sub>:F in aqueous solution of acetic acid (0.5 mol/L) as a function of the total charge, at different starting pHs with pH control during the reaction: ( $\blacksquare$ ) pH 5, ( $\blacklozenge$ ) pH 6, ( $\bigcirc$ ) pH 8, and ( $\blacktriangle$ ) pH 12; *I* = 20 mA.



mercially available SnO<sub>2</sub>:F. Pd(OOCCH<sub>3</sub>)<sub>2</sub> was first solubilized in chloroform and poured in a flask containing SnO<sub>2</sub>:F. After 1 h of stirring, the chloroform was evaporated at low temperature. Water was added to the flask and it was maintained at 80 °C until the complete evaporation of water. The prepared catalyst with a nominal concentration of 10% of Pd was dried overnight at 90 °C in a stove.

#### **Catalyst characterization**

Previous MEB characterization of the catalyst has been described elsewhere.<sup>17</sup> X-ray measurements were performed using an X'pert Pro MRD of Panalytical diffractometer with Cu K $\alpha$  (wavelength = 1.5406 Å) radiation. Diffractograms of powders were recorded in 2 $\theta$  scan configuration, in the 10–80 ° 2 $\theta$  range, at a fixed incident angle of 0.02 °. Fourier transform infrared spectroscopy (FTIR) of the SnO<sub>2</sub>:F pow-





ders was recorded on a Bruker IFS 25 with a resolution of  $4 \text{ cm}^{-1}$ . The powders were immersed in the aqueous supporting electrolyte solutions containing acetic acid at pH 3, 6, and 12. These pHs were adjusted with a NaOH (10 N) solution. The suspensions were filtered, and the powders were washed with water. After drying at 50 °C for 15 h, the powders were probed by FTIR using powder not exposed to the supporting electrolyte as a reference. The samples were dispersed in a KBr matrix and pressed in self-supporting disks.

Measurements of adsorption isotherms were carried out as described below. Cylindrical vials (25 mL) were thoroughly cleansed, rinsed with high purity water (from a Milli-Q unit), and dried. SnO<sub>2</sub>:F powder (1 g) was added to each vial, except to the vials serving as blanks, 10 mL of acetic acid solutions (0.5 mol/L) adjusted to pH 5 and 12 was added to each vial. After 1 h of stirring in the presence of SnO<sub>2</sub>:F powders, some of the vials at pH 5 were adjusted to pH 12. To each of these vials, cyclohexanone solution was added to obtain the desired concentrations. The total volume in each vial was 15 mL. The SnO<sub>2</sub>:F powders – cyclohexanone suspensions were then stirred with an orbital shaker at 320 trs/min and at ambient temperature (23  $\pm$  2 °C). Adsorption isotherms were measured after 3 h (time required for one ECH experiment). A 0.5 mL aliquot was withdrawn from each vial, filtered, and analyzed by GC chromatography to determine cyclohexanone concentration.

#### Electrocatalytic hydrogenation procedure

All electrocatalytic experiments were carried out in a twocompartment dynamic cell<sup>18</sup> under galvanostatic conditions at ambient temperature. The cathode compartment was filled with 29 mL of 0.5 mol/L solution of acetic acid in water at the desired pH. The anodic compartment was filled with the same solution. Prior to the ECH process, 200 mg of the catScheme 2. Reaction scheme for the hydrogenation of cyclohexanone-oxime to cyclohexanone.



alyst was suspended in the catholic solution and dynamically circulated ( $\approx 1$  L/min) through the reticulated vitrous carbon cathode. The catalyst was then conditioned by passing a known quantity of charge. This quantity of charge served to reduce Pd(II) in the catalyst after preparation into metallic Pd and to saturate the cathode material with chemisorbed hydrogen. For our catalysts, containing theoretically 10% of Pd, 31 °C was normally necessary to reduce the oxidized Pd, assuming that Pd is totally in its oxidized form in the catalyst before conditioning. The reduction of oxidized Pd is kinetically faster than the formation of chemisorbed hydrogen.19

For phenol electrohydrogenation, the quantity of conditioning charge was fixed to 50 C for all the pH values, whereas for cyclohexanone this quantity varied from 5 C to 75 C.

After conditioning, the coulometer was reset to zero; a volume of 1 mL of an aqueous unsaturated organic compound solution (25.2 mg/mL of phenol or 26.3 mg/mL of cyclohexanone) was then added to the cathodic compartment, giving a total volume of 30 mL and an unsaturated compound concentration of 8.94  $\times$  10<sup>-3</sup> mol/L. During the ECH process, the constant current applied was 20 mA for phenol hydrogenation, 20 and 5 mA for cyclohexanone hydrogenation.

After passing different quantities of charge, 0.5 mL aliquots were withdrawn from the catholyte and added to 1 mL of chloroform, saturated with NaCl, and shaken together for the extraction of the organic compounds. The organic phase was removed and dried on Na<sub>2</sub>SO<sub>4</sub>. Finally, an internal standard chloroform solution was added to 0.4 mL of the organic phase, mixed, and 1µL of this solution was injected in the gas chromatograph. The GC analyses were carried out using an Agilent 6890 series chromatograph equipped with an MS detector and 5HS capillary column (30 m  $\times$  0.250 mm  $\times$  0.25  $\mu$ m). Since hydroxide ions are produced (reaction 1) during the electrolysis, the pH can change depending on the quantity of charge, so we followed this pH in situ, or maintained its value using a concentrated acetic acid solution.

#### Chemisorbed hydrogen quenching procedure

The quantity of chemisorbed hydrogen produced during the conditioning was estimated using cyclohexanone-oxime as a quencher. Open-circuit hydrogenation (catalytic hydrogenation)<sup>3</sup> of cyclohexanone oxime was done to determine the quantity of active atomic hydrogen in solution or adsorbed. After conditioning, the current was switched off, and 1 mL of cyclohexanone-oxime solution (30 mg/mL in 50/50 (v/v) water/methanol) was added to the cell. An aliquot was withdrawn from the cell at each hour, extracted with diethyl ether, and injected to GC chromatograph to measure the quantity of cyclohexanone-oxime that disappeared from the solution in the cell.

#### **Results and discussion**

As we study the influence of the pH on the ECH efficiency of phenol and cyclohexanone, we have to ensure that the properties of our catalysts are not modified by changing pH values. Indeed, XRD measurements carried out on the Pd/SnO<sub>2</sub>:F catalyst after the ECH process at pH 3 and pH 12 (Fig. 1) showed no change in the catalyst support (SnO<sub>2</sub>:F) structure, demonstrating that the catalyst support remained stable in acidic and basic media. The only change in the XRD peaks is linked to the electrochemical reduction of Pd(II) to metallic Pd during the process. As a result, SnO<sub>2</sub>:F is a good matrix, which allows the study of the pH effect in a large range, contrary to alumina for example, which is deteriorated in basic medium.<sup>15</sup>

Conversion of phenol can lead to cyclohexanone formation and eventually to cyclohexanol (Scheme 1), depending on the reaction conditions.

The ECH of phenol conducted on Pd/SnO<sub>2</sub>:F in acetic acid solution mainly led to the formation of cyclohexanone and presented different behaviors depending on the working pH (Fig. 2). Two observations can be made. First, at pH 12, the process was inefficient. Second, at pH 6 and below, the more acidic the pH, the more efficient the ECH process became. Considering the functionalization of the SnO2:F surface as a function of pH, the IR spectra were recorded. If functionalization of the catalyst by the acetic acid had occurred, three bands at 1654, 1563, and 1466 cm<sup>-1</sup> would appear. Figure 3 shows that this was not the case at pH 12. Therefore, it can be concluded that there was no acetic acid on the catalyst surface. That absence of functionalization at pH 12 is due to the competitive adsorption of the hydroxyl anions,<sup>20,21</sup> whereas at pH 3 and 6 (no excess of hydroxyl ions in solution), SnO2:F surface is well-functionalized. As shown by Cirtiu et al.,8 the functionalization phenomenon enhances the hydrogenation process by improving the adsorption of the unsaturated molecule. That means that at pH 12, the catalyst surface is unable to adsorb phenol moleculesbecause of the absence of functionalization. As shown in the ECH mechanism, the adsorption is an important step that will be the limiting reaction at this pH.

However, one also must take into account that the structure of phenol is pH-dependent, as its  $pK_a$  is 9.96. Thus, at pH 12, phenol exists as phenolate in solution. As ECH is totally inefficient at this pH, we suppose that this form (phenolate) does not adsorb onto the non-functionalized SnO<sub>2</sub>:F at all. Such a strong decrease in hydrogenation rate at high pH was pointed out by Wismeijer et al.<sup>22</sup> in the catalytic hydrogenation (CH) process when Pd/C was used. They attributed this effect to the absence of adsorption of the phenolate

Experimental conditions	pH	Entries	Theoretical H• quantity formed (mol) $N = Q/nF$	Cyclohexanone-oxime starting quantity (mol)	Cyclohexanone formed after 3 h (mol)	H• quantity available (mol)
With catalyst + 50 C charge	5	1	$5.18 \times 10^{-4}$	$2.27 \times 10^{-4}$	$2.20 \times 10^{-4}$	$4.40 \times 10^{-4}$
	12	2	$5.18 \times 10^{-4}$	$2.27 \times 10^{-4}$	$1.50 \times 10^{-4}$	$3.10 \times 10^{-4}$
Without cata- lyst, without charge	5	3	0	$2.27 \times 10^{-4}$	$0.45 \times 10^{-4}$	$0.90 \times 10^{-4}$
U	12	4	0	$2.27 \times 10^{-4}$	0	0

Table 2. Quantity of H<sup>•</sup> available (mol) as a function of the charge passed for the conditioning.

on the catalyst. Phenolate molecules are preferably found in the aqueous phase because of the electrostatic repulsion with the negatively charged carbon surface due to the OH<sup>-</sup> ions. At pH < 10, we observed that the ECH process of phenol becomes efficient. Moreover, we showed that the more acidic the solution, the more efficient the hydrogenation. As there is a significant difference between conversion of phenol at pH 6 and at pH 3, we suggest the most acidic medium is favorable for phenol electrohydrogenation. Indeed, it is well-known that in a strong acid solution, the hydrogenation of phenol is facilitated by some decrease in its resonance stabilization energy.<sup>23</sup> Also, the rate of enhancement of aromatics hydrogenation in superacidic solutions was attributed to the removal of the aromatic resonance stabilization energy by Feiring<sup>24</sup> and Mador.<sup>25</sup>

Therefore, the ECH process of phenol on Pd/SnO<sub>2</sub>:F in an acetic solution will work, provided that the catalyst has been previously functionalized at a pH  $\leq$  6, and it will be more optimal in a more acidic medium. The pH values affected the catalyst/solution interface that has a great influence on the adsorption/desorption steps of the ECH process.

Cyclohexanone is the intermediate product in the complete ECH of phenol into cyclohexanol (Scheme 1), and it is interesting to study its reactivity as a function of pH when it is the starting product to see the influence of its adsorption and reactivity on the ECH efficiency. If we consider the ECH conducted at several pHs without controlling the pH (Fig. 4), we observe that the maximal efficiency is obtained for a starting pH equal to 6. Nevertheless, it is important to notice that, apart from the starting pH 5 and 12. which remained stable during the process, the other starting pH 6 and 8 change during the experiment for a final pH equal to 12 (Table 1). Maintaining the pH is especially important for values higher than 5.5 due to the loss of the buffer capacity of acetic acid, which has a  $pK_a$  of 4.76. The speed of pH change increases when the starting pH increases (Table 1).

As observed for phenol hydrogenation, pH 12 is inefficient, owing to the non-functionalization of the catalyst surface. Surprisingly, pH 5 is the less efficient medium, although the surface is functionalized. In fact, Breitner et al.<sup>26</sup> had made the same observation in the CH process for rhodium and ruthenium catalysts, which hydrogenated carbonyl compounds rapidly in neutral and basic solutions and slowly in acid solutions. They also noted that palladium was ineffective to hydrogenate aliphatic ketones, but this becomes possible in our case by the ECH process. A starting pH of 6 with final pH equal to 12 seemed to be the best condition for ECH of cyclohexanone. Indeed, for a starting pH of 6, it remained slightly acidic at the end of the conditioning and went up to basic pH after a few quantity of charge (20 C) was passed for the ECH. When starting with a pH 8, only 7 C was sufficient to bring the pH to the basic range during the conditioning (Table 1).

Then, we decided to control the pH of the solution to know exactly the best working pH for cyclohexanone hydrogenation. We realized ECH of cyclohexanone at these different pHs with in situ control of the pH (Fig. 5), and we observed that the maximal efficiency was obtained for pH 8 and that it was near 50%. As a result, a starting pH of 6 was not the only reason for the ECH efficiency without pH control (Fig. 4) because this process was kinetically limited when the electrolyte was constantly maintained at pH 5 and 6. Even if the catalyst surface was functionalized at these pHs (Fig. 3), the process remained inefficient, which means that the functionalization is not the only sufficient condition.

Comparing Fig. 4 and Fig. 5, we can suppose that the starting pH must be acidic, whereas the working pH must be basic to get the best efficiency. This is the reason why the process is divided into two steps: the conditioning and the working parts. We verified the impact of the conditioning pH by conducting ECH of cyclohexanone with two different procedures (Fig. 6): First, we conditioned the catalyst at pH 5 during 50 C, and then adjusted the working pH to 12 before adding cyclohexanone. Second, we used pH 12 both in conditioning and working conditions. Figure 6 perfectly shows that catalyst must be conditioned at pH 5 to be able to convert cyclohexanone into cyclohexanol.

Then, it is important to know if there is a difference in the quantity of chemisorbed hydrogen produced in acidic and basic media. We know that the chemisorbed hydrogen's production kinetics depends upon the metal<sup>27</sup> and also the medium (acidic or basic).<sup>19</sup> To quantify the number of moles of  $H_{ads}$  produced by the conditioning in acidic versus basic medium we used an H<sup>•</sup> quencher, which completely reacts with all the H<sup>•</sup> available. Before that, one must take into account that during the conditioning, some electrons are used to reduce the oxidized Pd and some to produce chemisorbed hydrogen (reaction 1). To determine the quantity of chemisorbed hydrogen produced during the conditioning, we made an open-circuit hydrogenation of cyclohexanone-oxime, which was added to the catholyte after switching off the current at the end of the conditioning. After a total time

**Fig. 7.** Adsorption isotherm for cyclohexanone after 3 h in contact with F-doped SnO<sub>2</sub> powders in aqueous solution of acetic acid (0.5 mol/L) as a function of the initial pH: ( $\blacktriangle$ ) pH 12, ( $\blacklozenge$ ) pH 5, ( $\blacksquare$ ) 1 h of electrolyte–SnO<sub>2</sub>:F suspension stirring at pH 5 before adding cyclohexanone at pH 12.



of 4 h, the cyclohexanone-oxime CH ended, i.e., its reaction with active chemisorbed was total.

We calculated the theoretical quantity of H<sup>•</sup> formed during conditioning according to Scheme 2. Then, experiments were conducted in the presence and absence of a catalyst, and we determined the available quantities of active hydrogen (Table 2). This was done at a charge of 50 C during conditioning. Table 2 shows that the maximum quantity of H• produced is  $4.4 \times 10^{-4}$  mol (Table 2, entry 1) at pH 5 and 50 C conditioning of the electrocatalysis. We observed that at pH 12 (Table 2, entry 2), the available quantity of H<sup>•</sup> was less important. However, it is interesting to remark that without either a catalyst or a charge, little reactivity of cyclohexanone was observed at pH 5 (Table 2, entry 3), whereas no reaction at all took place at pH 12 (Table 2, entry 4). Consequently, we assume that only  $3.5 \times 10^{-4}$  mol of H• (corresponding to 33.7 C) are really produced at pH 5 on the catalyst over 50 C. In these conditions, the quantity of active hydrogen available at pH 5 or pH 12 is in the same range and the observed differences are in the experimental error range. Then, experimentally, a maximum of 20 C is used for the reduction of Pd(II) into Pd(0), which means that all the Pd is not in Pd(II) form in the catalyst before conditioning. We can assume that this quantity is always the same whatever the quantity of charge passed for conditioning.

From these observations, we can conclude that the difference in the efficiency of the ECH process due to the conditioning pH is not linked to the available quantity of  $H_{ads}$ because this quantity is the same in acidic and basic media. We can suppose that basic pH allows cyclohexanone to be activated and this activated form of cyclohexanone may have affinity with functionalized catalyst after conditioning in acidic medium (no functionnalization in basic medium). Indeed, adsorption of cyclohexanone on  $SnO_2$ :F in presence of acetic acid (Fig. 7) is more favored at pH 5 than at pH 12. Above that, its adsorption is maximal when the catalyst is conditioned at pH 5 (functionalization) and when cyclohexanone is introduced at pH 12. Hence, the activated cyclohexanone has a good adsorption onto the functionalized catalyst. This activation of cyclohexanone may be due to the solvation, which differs in acidic and basic environments. The keto-enol equilibrium is also more favorable in alkaline medium. Indeed, it was demonstrated that the alkene group is more reactive than the carbonyl group in the ECH process.<sup>12,26</sup> The increase in the rate of hydrogenation of cyclohexanone in KOH solution in the CH process was also observed by Wismeijer et al.<sup>22</sup> It was assumed that the promoted effect came from the reactive enolate anions or ionized hydrated cyclohexanone species formed in the presence of OH<sup>-</sup>. In our case, the FTIR spectrum (not presented) of cyclohexanone at pH 12 shows an additional band compared with that of cyclohexanone at pH 5, that band was attributed to the enolate ion.

As pointed out by Dubé et al.,<sup>11</sup> the efficiency also depends on the kinetics of the transfer of a monoatomic hydrogen ( $H_{ads}$ ) from the metal site to the  $\pi$ -bond of the adsorbed organic molecule. This transfer can differ from acidic to basic medium depending on the configuration of the substrate in solution.

Because the quantity of the available  $H_{ads}$  can influence the hydrogenation, we were interested in studying its role in the ECH of cyclohexanone on the same catalyst in acetic acid electrolyte. For this study, the conditioning pH was 5 and the working pH was 12. To improve the efficiency of the reaction, the constant current applied after conditioning was 5 mA. As seen in the quenching of  $H_{ads}$ , the experimental quantity of charge necessary to reduce all the Pd(II) to Pd(0) was around 20 C. Then, we can estimate the approximate quantity of  $H_{ads}$  as a function of conditioning charge (Table 3). This table shows that if the quantity of  $H_{ads}$  available

Charge $Q$ passed for conditioning (C)	Experimental quantity of charge $Q_{Pd}$ necessary to reduce Pd(II) into Pd(0) (C)	Experimental quantity of charge $Q_{\text{Hads}}$ for chemisorbed hydrogen production with $Q_{\text{Hads}} = Q - Q_{\text{Pd}}$	Theoretical H <sup>•</sup> quantity <i>N</i> formed and available (mol) with $N = Q_{\text{Hads}}/(nF)$ and $n = 1$
5	20	0	None
25	20	5	$5.18 \times 10^{-5}$
50	20	30	$3.11 \times 10^{-4}$
75	20	55	$5.70 \times 10^{-4}$

Table 3. Theoretical quantity of H<sup>•</sup> formed and available (mol) as a function of the conditioning charge.

**Fig. 8.** ECH of cyclohexanone on Pd/SnO<sub>2</sub>:F in aqueous solution of acetic acid (0.5 mol/L) as a function of the total charge for different quantities of conditioning charge: ( $\blacksquare$ ) 5 C, ( $\blacktriangle$ ) 25 C, ( $\bigcirc$ ) 50 C,



**Fig. 9.** CH of cyclohexanone on Pd/SnO<sub>2</sub>:F in aqueous solution of acetic acid (0.5 mol/L) as a function of the total charge for different quantities of conditioning charge: ( $\blacktriangle$ ) 25 C, ( $\bigcirc$ ) 50 C, and ( $\diamondsuit$ ) 75 C; *I* = 5 mA; conditioning pH = 5 and working pH = 12.



increases. Indeed, the more the charge passed before the beginning of ECH, the faster the reaction (Fig. 8), which shows that the kinetics of cyclohexanone hydrogenation is affected. This observation can explain why a difference is noticed in the ECH process according to the nature of the metal used<sup>27</sup> or the conductivity of the matrix supporting the metallic nanoaggregates.<sup>17</sup> Indeed, the quantity of  $H_{ads}$ generated is linked to these parameters.

To study only the influence of the conditioning charge directly on cyclohexanone hydrogenation, CH of cyclohexanone was conducted at the end of each conditioning (Fig. 9). Cyclohexanone was added to the catholyte after the conditioning, i.e., in the presence of chemisorbed  $H_{ads}$ (demonstrated by the quenching), and then we verified whether or not it was hydrogenated after 100 min. Surprisingly, Fig. 9 shows that cyclohexanone hydrogenation took place and the quantity of H• (Table 3) produced during conditioning played an important role on the CH process. This result demonstrated that when chemisorbed hydrogen is produced (by the electroreduction of water), cyclohexanone could catalytically be hydrogenated on Pd catalyst. Never-

theless, the catalytic hydrogenation of cyclohexanone, and most of aliphatic ketones, was impossible on palladium catalyst when hydrogen gas was used as source of chemisorbed hydrogen.<sup>12,26</sup> This is explained by the kinetic barrier (related to the low solubility and low dissociation of molecular hydrogen (H<sub>2</sub>)) that is too high.<sup>28</sup> So, it can be said that the production of chemisorbed hydrogen is not systematic in CH conditions. The ECH offers soft conditions of work<sup>11</sup> in which the production of chemisorbed hydrogen is obvious as it was shown by the quenching. Additionally, in the ECH process, the polarization of the catalyst<sup>29</sup> and the cyclohexanone C=O bond takes place.<sup>9</sup>

## Conclusion

The in situ functionalization of the catalyst support affects the electrocatalytic hydrogenation of phenol and cyclohexanone. This functionalization takes place in an acidic medium (pH  $\leq$  6) with acetic acid as electrolyte. The effect of the pH on the ECH process is explained by the catalyst functionalization, which affects the catalyst/solution interface also by the structural changes of the target molecule.

Hydrogenation of phenol to cyclohexanone increases as the medium becomes more acidic. When the support surface is functionalized, cyclohexanone is hydrogenated only in a basic medium. For a complete hydrogenation of phenol with good kinetics, it would be interesting to conduct the first step of hydrogenation, i.e., the formation of cyclohexanone in an acidic medium and then increase the pH to basic values to facilitate the formation of cyclohexanol. The conditioning charge influences the amount of chemisorbed hydrogen available for the hydrogenation of the organic compound. This work has identified yet another advantage of ECH versus CH, owing to the fact that the production of chemisorbed hydrogen is systematic in the ECH process.

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