# Considerations about phenol electrohydrogenation on electrodes made with reticulated vitreous carbon cathode

# François Laplante, Louis Brossard, and Hugues Ménard

**Abstract:** The electrocatalytic hydrogenation (ECH) of phenol was carried out in aqueous media with catalytic powders. The catalytic powders were composed of palladium nanoaggregates deposited on various substrates such as  $Al_2O_3$ ,  $BaSO_4$ , and  $BaCO_3$ . Composite powders are trapped (upon stirring) into a reticulated vitreous carbon (RVC) matrix, allowing a rapid in situ build-up of the electrode and alleviating the use of a binder, since the latter may have a detrimental effect on the ECH. For a given amount of noble metal (5% palladium by weight), it is observed that the ECH of phenol to cyclohexanol increases in the following order:  $Pd/BaCO_3 < Pd/BaSO_4 < Pd/Al_2O_3$ . It is deduced that the ECH rate is largely dependent on the adsorption of organic molecules on the nonmetallic substrate, and a model is considered to explain such a behavior. The ECH of phenol is also feasible at a reasonable rate with composite  $Pd/Al_2O_3$  (0.25% Pd by weight) powders fabricated by physical vapor deposition because the peripheral distribution of Pd nanoaggregates is favorable towards the ECH.

*Key words:* electrocatalytic hydrogenation (ECH) of phenol, reticulated vitreous carbon (RVC), alumina-based catalyst, agglomeration process, adlineation point, adsorption.

**Résumé :** On a effectué l'hydrogénation électrocatalytique (HEC) du phénol, en milieu aqueux, en présence de diverses poudres catalytiques. Ces poudres étaient formées de nanoaggrégats de palladium déposés sur divers substrats, tels que  $Al_2O_3$ ,  $BaSO_4$  et  $BaCO_3$ . Les poudres composites sont piégées (par agitation) sur une matrice de carbone vitreux réticulé (CVR) qui permet d'obtenir une accumulation rapide in situ de l'électrode, ce qui permet d'éviter d'avoir à utiliser un agglomérant puisque ceux-ci peuvent avoir un effet néfaste sur l'HEC. Pour une quantité donnée de métal noble (5 % de palladium en poids), on a observé que l'HEC du phénol en cyclohexanol augmente dans l'ordre suivant:  $Pd/BaCO_3 < Pd/BaSO_4 < Pd/Al_2O_3$ . On en déduit que la vitesse d'HEC dépend grandement sur l'adsorption des molécules organiques sur le substrat non métallique et on considère un modèle pour expliquer un tel comportement. L'HEC du phénol peut se faire à une vitesse raisonnable avec des poudres composites de  $Pd/Al_2O_3$  (0,25 % de Pd en poids) préparées par déposition physique de vapeur parce que la distribution périphérique des nanoaggrégats de Pd est favorable à l'HEC.

*Mots clés :* hydrogénation électrocatalytique (HEC) du phénol, carbone vitreux réticulé (CVR), catalyseur à base d'alumine, processus d'agglomération, point d'adlinéation, adsorption.

[Traduit par la Rédaction]

# Introduction

The electrode materials used for the electrocatalytic hydrogenation (ECH) of organic molecules are of paramount importance, since the kinetics of the electrohydrogenation process is quite dependent on the nature of the electrode materials (1). As far as the electrodes made with pressed metallic powder particles are concerned (1-3), their mechanical

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<sup>2</sup>Present address: Institut de recherche d'Hydro-Québec (IREQ), 1800 boul. Lionel-Boulet, Varennes, QC J3X 1S1, Canada. strength is generally weak without the use of a binding material (4). The electrohydrogenation process may also be carried out in the presence of composite metallic powder particles by an alternate method: the powder particles are trapped inside the pores of a porous electrode possessing a very high hydrogen (molecular or adsorbed) overpotential. Such electrodes are made by the entrapment of composite powder particles with nano-deposits of a metal at their surface, and thus the use of a binding material is not necessary (2, 5, 6). It is an attractive way to discriminate the ability of new powders for use in the electrohydrogenation process without changing their chemical and (or) physical characteristics.

Reticulated vitreous carbon (RVC) is particularly suitable, since this excellent electronic conductor is generally electrochemically stable and has a well-developed tridimensional network of large pores (7–11) (Fig. 1). The specific RVC surface is 66 cm<sup>2</sup> per cm<sup>3</sup> for a 100 pore-per-inch (1 inch = 25.4 mm) matrix with a void volume of 97% (7). The high **Fig. 1.** Electron scanning micrograph of a piece of reticulated vitreous carbon foam of 80 pores per inch (ppi).



porosity of the RVC offers a great number of large pores accessible to the composite powder particles. The electrolyte penetrates through the RVC by forced convection, and the electrocatalytic particles in suspension in the electrolyte are trapped inside the pores. Recently, papers dealing with the use of agglomerated electrodes in the dechlorination of polychlorophenol and the electrocatalytic hydrogenation of lignin showed the successful use of Pd–alumina and Rh–alumina electrocatalysts (2, 5, 6).

The rate of the electrohydrogenation process is largely dependant on several experimental parameters, particularly those connected to the electrode fabrication. The present paper deals with the key parameters for the successful entrapment of the electrocatalytic particles by the RVC, that is: the size of the particles, the applied current density during the agglomeration process, and the appropriate design of the electrochemical cell used for the agglomeration process. The reaction under consideration is phenol electrohydrogenation. In addition, different palladium powders supported on various adsorbents (substrates) were considered, to show that the adsorption of the phenol molecule may be the ratedetermining step of the ECH process for a given amount of palladium (5% w/w).

# **Experimental**

## The electrodes

The electrode was a piece of RVC foam (25 mm  $\times$  20 mm  $\times$  6 mm, 100 pores per inch (ppi), Electrosynthesis Co.). The electrode was mounted by inserting a glass rod (OD 5~6 mm, ID 3.5 mm) in the horizontal axis of a piece of RVC (20 mm  $\times$  40 mm  $\times$  6 mm). The excess of RVC was then removed and a copper wire was inserted into the RVC to be further cemented with silver epoxy (Epoxy Technology). Finally, the electrical contact zone on the RVC matrix was glued to the glass rod with epoxy, to isolate the electrical contact from the electro-active part of the electrode. The use of a nickel strip, as a contact with the RVC electrode, should be avoided because the activity of the nickel towards the electrocatalytic hydrogenation of ketone (12) may affect the data.

The physical embodiment of the composite material into the RVC occurred under moderate stirring of the catholyte (~450 rpm), and the catalyst powder particles were trapped into the RVC matrix pores spontaneously (provided that no sudden perturbation occurred); the RVC electrode was under cathodic polarization during the agglomeration process. The catalytic powder remained in the pores of the RVC electrode (without any apparent loss during polarization); it also remained cathodically polarized ( $J = 100 \text{ mA } \text{dm}^{-2}$ ) for the electrohydrogenation process and was in electrical contact with the matrix (Fig. 2). With this type of RVC, the diameter of the particle size should be between 15 and 43  $\mu$ m. The entrapment process is completed within 2 h, up to a charge of 50 C. The dimensions of the H-cell and those related to the other parts are given in Fig. 3. We observed that the agglomeration process was successful with this specific cell, since the process is closely dependent on the fluid dynamics. The powder characteristics are summarized in Table 1. Note that the average particle size refers to composite Pd support-particles when Pd is present.

## Electrolysis

The electrolysis was carried out in a two-compartment, jacketed glass H-cell (Fig. 3), having a Nafion-324 (E.I. Dupont de Nemours & Co) membrane as a separator. The cell temperature was fixed at 21°C during the electrohydrogenation process by a circulating thermostated bath (VWR 1160A); to prevent analyte evaporation, a water-cooled condenser was added to the top of the cell. Afterwards, the cathodic compartment was filled with a phosphate buffer (29 mL, 1 M KH<sub>2</sub>PO<sub>4</sub> + 1 M NaOH) previously adjusted to pH 7, and 200 mg of the composite powder was added to the catholyte. The electrode was built-up in situ, using the previously described technique. The anodic compartment was filled with a 1 M NaOH solution (Fisher); the counterelectrode was a platinum mesh. Prior to the electrohydrogenation process, 1 mL of a phenol solution in water  $(25 \text{ mg mL}^{-1})$  was added to the catholyte, giving a total volume of 30 mL and a phenol concentration of 8.8 mMol  $L^{-1}$ . Further, the electrocatalytic hydrogenation was performed under galvanostatic control (J = 100 mA  $dm^{-2}$ ) using an EG&G PAR model 273. All of the commercial powder particles considered in the present paper (Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/BaCO<sub>3</sub>, Pd/BaSO<sub>4</sub> 5 or 10 w/w %) were bought from Aldrich and used as received.

During the electrocatalytic hydrogenation process (ECH), 500 µL aliquots were withdrawn from the catholyte, further saturated with NaCl, acidified to pH 1 with HCl (HCl concn. 10 N), and then extracted with 1 mL ethyl acetate, to be further dried under sodium sulfate. After the completion of ECH, both the RVC electrode and the whole cell were rinsed with pure water. Internal standard (ISTD, 2-cyclohexen-1one) was added to the cell solution; further, the extraction was carried out twice  $(2 \times 20 \text{ mL})$  with distilled ethyl acetate. The organic layer was dried on sodium sulfate and filtered. The filtrate was collected in a 50 mL volumetric flask containing an external standard (ESTD, 3-methylcyclohexanol). The GC analyses were carried out on a Hewlett-Packard 5890 chromatograph equipped with an FID detector on a 30-m-long HP-5 column. The products were then identified by comparison with the retention time of the authentic compound, and the mass balance was obtained from the ISTD:ESTD ratio of the corrected peak surface area.

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**Fig. 2.** SEM micrograph of Pd–alumina (5%) entrapped in RVC pores ( $I_{app} = 5 \text{ mA}, T = 25^{\circ}\text{C}, \text{ pH 7}$ ).



#### **RVC** electrode plated with mercury

Mercury depositions on RVC were achieved in accordance with the method described by Armalis and Kubiliene (13).

#### **Catalyst synthesis**

Noncommercial catalyst synthesis was carried out according to the technique described by Fournier et al. (14).

#### Galvanostatic measurements

The potentials were recorded vs. standard calomel electrode (SCE). Reagents (NaOH 99.999% and  $KH_2PO_4$  99.99%) used for the galvanostatic measurements were provided by Aldrich, and high purity water from a Milli-Q unit was used for the preparation of solutions. A constant applied current (from 250 to 0.02 mA dm<sup>-2</sup>) with an applied current time of 10 s was used to record the galvanostatic traces.

## **Results and discussion**

### **Catalyst characterization**

Despite the presence of a small amount of metal deposited onto the surface of the powder particles, a disk made with pressed composite powder particles (commercially available) is characterized by a very high electrical resistance. However, those powder particles, when agglomerated inside the RVC pores, show an electrocatalytic activity. The beneficial effect of the composite powder particles entrapped in an RVC electrode on the evolution of hydrogen is illustrated in Fig. 4 (curve A and B). At a current density of 100 mA cm<sup>-2</sup>, the hydrogen overpotential is ~50 mV lower when Pd/Al<sub>2</sub>O<sub>3</sub> is present, as compared with the absence of any catalyst. To show that the current may circulate through the agglomerated composite powder particles - the latter being in electrical contact with the RVC electrode surface - mercury was electrodeposited on a bare RVC electrode. As anticipated, the overpotential for water reduction is very high on an Hg-RVC cathode (Fig. 4, curve C). The picture is completely different with Pd/Al<sub>2</sub>O<sub>3</sub> particles agglomerated on the Hg-RVC cathode (Fig. 4, curve D): the hydrogen overpotential is considerably lower. From the curves of Fig. 4, it is deduced that the agglomerated powder particles are in electrical contact with the RVC electrode.

Composite Pd/Al<sub>2</sub>O<sub>3</sub> powders were fabricated by physical vapor deposition (PVD) of Pd on alumina powder particles according to the method described in ref. 14. Palladium nanoaggregates are randomly distributed over the entire alumina particle surfaces (Fig. 5). In Fig. 6, galvanostatic traces show the influence of both powders (that is, commercially available or obtained through PVD) on the electrocatalytic activity towards the hydrogen evolution reaction. A tremendous beneficial effect is observed for the hydrogen-evolution reaction with the catalyst obtained by PVD (Pd/Al<sub>2</sub>O<sub>3</sub> 0.1% w/w) relative to the commercial catalyst (Pd/Al<sub>2</sub>O<sub>3</sub> 5% w/w). The overpotential shift of +410 mV at 100 mA dm<sup>-2</sup> is related to peripheral distribution of the palladium nanoaggregate (Fig. 5). Palladium deposited onto alumina by PVD favors an efficient electrical contact between the powder particles and the RVC matrix, since the preferential location of nanoaggregates is in the "skin" of the powder particles. Moreover, the electrolyte may easily reach the Pd nanoaggregates. On the other hand, the particles of the commercial Pd/Al<sub>2</sub>O<sub>3</sub> powder, which are obtained by an impregnation method, are most likely characterized by a large amount of Pd deposited deeply inside the pores of the alumina and in such a way that the contact with the Pd-RVC matrix is hindered.

#### Kinetics

The ECH process of phenol in the presence of commercially available Pd/Al<sub>2</sub>O<sub>3</sub> (5% w/w) results in the formation of cyclohexanone and, further, cyclohexanol (Fig. 7). The amount of cyclohexanone is at its maximum for a charge of ~200 C, with the phenol being almost completely exhausted. For a charge (Q) larger than 200 C, the larger the Q, the larger the amount of cyclohexanol and the lower the amount of cyclohexanone. If the amount of palladium is 10% w/w rather than 5% w/w, the current efficiency of the cyclohexanol production remains practically unchanged (Table 2).

The ECH of phenol, made with the catalytic powder produced by PVD (0.25% of Pd w/w), shows a significant activity despite the low amount of metal present at the surface. However, the rate of ECH is lower compared with that for the commercials powders (Fig. 8). The higher ECH yield observed with the commercial powder is attributed to lower hydrogen flow rate, the hydrogen evolution reaction being in competition with the ECH reaction.

Since alumina is slightly soluble in alkaline solution and BaSO<sub>4</sub> is not, the effect of pH over a range of 4.1 to 14.0 on the kinetics of phenol ECH was investigated with BaSO<sub>4</sub> as the adsorbent (Fig. 9). The rate of the reaction is considerably lower at pH 14.0 — by a factor of 25 — in comparison with the rates at pH 7.0 and 4.1. The adsorption ability of the matrix is linked to the nature of the molecules (ionized or not) present in the solution. In a basic media, phenol is in the phenolate form, which has a strong affinity for polar solvents, and the adsorption of phenol is sluggish; hence phenol adsorption becomes the rate-limiting step for the ECH process. The picture is different at pH 7.0 and below since phenol is principally in its molecular form  $(pK_a 9.9)$ , and the adsorption is greatly promoted. In addition, the phenolate form most likely induces the enhancement of the resonance, which in return renders the ECH of phenol more difficult.

# Fig. 3. Electrochemical cell and electrode design. Length: mm. Electrode (Side and front)



Table 1. Powder characteristics.

Entry	Particles <sup>a</sup>	BET surface (m <sup>2</sup> g <sup>-1</sup> )	Average particle size (10 <sup>-3</sup> mm)	Particle entrapment in RVC <sup>b</sup>
1	Alumina	119.0	11.5	None <sup>c</sup>
2	BaSO <sub>4</sub>	4.3	5.0	None
3	BaCO <sub>3</sub>	1.5	10.17	None
4	Pd/Al <sub>2</sub> O <sub>3</sub> (1% Pd)	237.2	68.5	Fair <sup>d</sup>
5	Pd/Al <sub>2</sub> O <sub>3</sub> (5% Pd)	78.3	12.4	Very good <sup>e</sup>
6	Pd/Al <sub>2</sub> O <sub>3</sub> (10% Pd)	85.3	42.6	Very good
7	Pd/BaSO <sub>4</sub> (5% Pd)	4.4	14.9	Very good
8	Pd/BaCO <sub>3</sub> (5% Pd)	4.9	16.8	Very good
9	Pd/Al <sub>2</sub> O <sub>3</sub> <sup>f</sup> (0.25% Pd)	98.0	16.0	Very good
10	RVC	$50.0^{g}$	—	_

<sup>a</sup>Commercially available from Aldrich.

<sup>b</sup>Step under galvanostatic control (5mA).

'No agglomeration. Those powders were not further used for the ECH process.

<sup>d</sup>The agglomeration was not complete in the sense that some particles were remaining in the solution. Those powders were not further used for the ECH process.

The particles were completely agglomerated in the electrode, i.e., the solution was becoming very clear.

<sup>f</sup>Catalyst synthesized by PVD.

<sup>g</sup>Specific surface calculated in cm<sup>2</sup> per cm<sup>3</sup>.

In acidic media, the rate of the phenol ECH is unchanged in comparison with the rate in neutral media. The difference recorded between the production of cyclohexanol and cyclohexanone can be explained by the hydrogen evolution reaction (HER), which is favoured in acidic media. Hence, the cyclohexanol production is retarded because the Heyrovsky and (or) the Tafel steps (eqs. [5] and [6] below) for the hydrogen evolution are easier.

In Table 2, the remaining concentration of phenol during its electrohydrogenation is expressed against Q for different electrode materials. The main features are: (i) in the presence of the bare RVC matrix, the rate of the ECH process is marginal; (*ii*) in the presence of an RVC electrode entirely covered with Pd metal, the rate of ECH is very slightly improved; (*iii*) the activity towards the ECH increases in the following order: Pd/BaCO<sub>3</sub> (5%) < Pd/BaSO<sub>4</sub> (5%) < Pd/Al<sub>2</sub>O<sub>3</sub> (5–10%). Alumina is recognized as an efficient adsorbent for organic molecules; this is ascribed to the presence of aluminum sites (15), which become the Lewis sites. For a given amount of palladium, it is deduced that the adsorption of organic compounds is lower for BaSO<sub>4</sub> and BaCO<sub>3</sub> in comparison with Al<sub>2</sub>O<sub>3</sub>.

It is generally admitted that the noble metals possess the ability to generate hydrogen and to adsorb unsaturated mole-

**Fig. 4.** Galvanostatic traces of agglomerated electrodes without any catalyst (curve A, ▲ and C, ●) and with  $Pd/Al_2O_3 5\%^*$ (curve B, ▲ and D, ●). Both curve C and D are RVC mercury plated. Solution  $T = 21^{\circ}$ C, pH 7, applied current time = 10 s. \*Commercially available.



Fig. 5. TEM micrograph of Pd on alumina deposited by PVD (0.1% of Pd).



cules (16). Since the phenol electrohydrogenation may not be carried out on a Pd foil, it is tentatively deduced that the adsorption of the unsaturated organic molecule on Pd is marginal.

Assuming that Pd deposited onto the oxide surface possesses marginal specific adsorptive properties, the choice of the adsorbent becomes of prime importance. The existence of such a discrimination between the adsorbent and the metal (adlineation point) in catalytic hydrogenation was previously suggested by Maxted and Ali (17). Later, Chou and Vannice (18) refer to the adlineation point to explain their

**Fig. 6.** Galvanostatic traces on RVC (80 ppi) electrodes without any catalyst (curve A,  $\bullet$ ), with Pd/Al<sub>2</sub>O<sub>3</sub> 5%<sup>\*</sup> (curve B,  $\blacksquare$ ), and with Pd/Al<sub>2</sub>O<sub>3</sub> 0.1% obtained by PVD (curve C,  $\blacktriangle$ ). Applied current time = 10 s. \*Commercially available.



**Fig. 7.** ECH of phenol through cyclohexanol with  $Pd/Al_2O_3 5\%^*$ , RVC 80 ppi,  $I_{app} = 5$  mA,  $T = 21^{\circ}C$ , pH 7. ( $\bullet$ ) Phenol, ( $\blacksquare$ ) cyclohexanone, and ( $\blacktriangle$ ) cyclohexanol. \*Commercially available.



results on the gas-phase hydrogenation of benzene. Similarly, in HEC, a discrimination between the adsorption sites (A) and the metallic sites (M) was proposed to explain the ECH process on composite materials, i.e., a metal deposited onto an oxide. The mechanism proposed for the electrohydrogenation of unsaturated bonds is described by eqs. [1]–[4]. First, electrosorbed hydrogen is formed on the metallic aggregates by reduction of water (eq. [1], where  $(H)_{ads}M$  is the electrosorbed hydrogen).

- $[1] \qquad 2H_2O + 2e^- + M \rightarrow 2(H)_{ads}M + 2OH^-$
- $[2] \qquad A + (Y=Z) \leftrightarrow (Y=Z)_{ads}A$
- $[3] \qquad 2(H)_{ads}M + (Y=Z)_{ads}A \rightarrow (YH-ZH)_{ads}A + M$
- $[4] \qquad (YH-ZH)_{ads}A \leftrightarrow YH-ZH + A$

Entry	Particles (% of metal)	Relative %			
		Phenol	Cyclohexanone	Cyclohexanol	Current efficiency
1	RVC	100	0	0	0
2	Pd/Al <sub>2</sub> O <sub>3</sub> 5%	2.2	19.7	78.1	26.3
3	Pd/Al <sub>2</sub> O <sub>3</sub> 10%	0.0	26.0	74.0	25.2
4	Pd/BaSO <sub>4</sub> 5% <sup>a</sup>	11.7	33.0	55.3	18.8
5	Pd/BaSO <sub>4</sub> 5% <sup>b</sup>	7.4	77.8	14.8	5.1
6	Pd/BaSO <sub>4</sub> 5% <sup>c</sup>	95.4	3.3	1.3	0.4
7	Pd/BaCO <sub>3</sub> 5%	87.6	12.4	0	0
8	Pd on $RVC^d$	94.9	3.4	1.7	0.6
9	Pd foil <sup>e</sup>	95.0	5.0	0	0
10	$Pd/Al_2O_3^{\ f} 0.25\%$	22.3	61.5	16	5.5

Table 2. Percentage of organic compound after the ECH of phenol (charge consumption = 450 C).

<sup>a</sup>Neutral media in a phosphate buffer at pH 7.

<sup>b</sup>Acid media, pH 4.1, in KH<sub>2</sub>PO<sub>4</sub> 1 M.

<sup>c</sup>Basic media (NaOH 1 M).

<sup>d</sup>Galvanic deposition of 105 mg of palladium deposited from a PdCl<sub>2</sub> solution.

 $e^{2} \times 2.5 \text{ cm}^{2}$ .

<sup>f</sup>Catalyst synthesized by PVD.

**Fig. 8.** ECH of phenol through cyclohexanol with  $Pd/Al_2O_3$  0.25% obtained by PVD, RVC 80 ppi,  $I_{app} = 5$  mA,  $T = 21^{\circ}C$ , pH 7. ( $\bullet$ ) Phenol, ( $\blacksquare$ ) cyclohexanone, and ( $\blacktriangle$ ) cyclohexanol.



**Fig. 9.** Phenol depletion ( $I_{app} = 5 \text{ mA}$ ,  $T = 25^{\circ}\text{C}$ ) through ECH with Pd/BaSO<sub>4</sub> 5% at different pH: ( $\bullet$ ) pH 7.0, ( $\blacktriangle$ ) pH 4.1, ( $\blacksquare$ ) pH 14.0.



Hydrogenation of the C=C bond then proceeds as in catalytic hydrogenation, i.e., by the reaction of the adsorbed substrate with the electrosorbed hydrogen (eq. [3], adsorption step shown in eq. [2]) at the adlineation point followed by the desorption of the product (eq. [4]). The adlineation point can be defined as the junction between the adsorbent and the metal; it is the site of the ECH process. For a given adsorbent, the larger the area related to the adlineation point, the higher the rate of the ECH reaction. It is relevant to point out that the efficiency of the ECH of a given organic compound depends also on the relative rates of the adsorption step, the hydrogenation step (eq. [3]), and the hydrogen desorption (eqs. [5] and [6]).

$$[5] \qquad (H)_{ads}M + H_2O + M + e^- \rightarrow H_2 + 2OH^-$$

$$[6] \qquad (H)_{ads}M + (H)_{ads}M \leftrightarrow H_2$$

The hydrogen desorption can be controlled by adjusting the current density at the electrode to optimize the current efficiency.

The effect of the adsorption process on the kinetics of the ECH is illustrated in Fig. 10. From the suggested ECH mechanisms, eq. [2], and the curves of Fig. 10, barium carbonate is considered a less efficient support for the adsorption of phenol than is barium sulphate. Both catalysts have the same amount of metal on the surface and have approximately the same specific surface area.

The use of a bare RVC matrix (Table 2, entry 1) shows no catalytic properties. The absence of metallic sites (M) and weak adsorptive properties between the RVC and phenol explain the poor yield of hydrogenation. We suspect that the phenol is practically not adsorbed onto vitreous carbon unless it is modified with an organic functional group (19–21).

By controlling the chemical nature of the adsorption sites and the metallic nanoaggregates, our goal is to tailor a cata**Fig. 10.** The effect of the adsorbent on the ECH of phenol  $(I_{app} = 5 \text{ mA}, T = 25^{\circ}\text{C}, \text{ pH } 7)$ . ( $\bullet$ , A) RVC matrix; ( $\blacktriangle$ , B) RVC + Pd (105.3 mg)–Pd foil; ( $\blacksquare$ , C) Pd/BaCO<sub>3</sub>; ( $\bullet$ , D) Pd/BaSO4,; ( $\bullet$ , E) Pd/Al<sub>2</sub>O<sub>3</sub> (5%); and ( $\blacktriangledown$ , F) Pd/Al<sub>2</sub>O<sub>3</sub> (10%), pH 7.



lyst that has some selectivity for targeted molecules. Adsorption sites determine catalyst selectivity and influence the chemical nature of the collected organic products; this is in agreement with the views of Neri et al. (22). Neri uses the idea that the catalytic support plays a predominant role in phenol hydrogenation. Moreover, it was stated that hydrogenation occurs through the phenol adsorption onto the adsorption sites followed by transfer of the chemisorbed hydrogen.

However, the catalyst performance remains highly influenced by the kinetics of hydrogenation, which is highly influenced by the nature of the metal used. In this case, the adsorption is not the limiting step; the rate-determining step is the hydrogen transfer itself from the metal surface to the unsaturated molecule (eq. [6]).

# Conclusion

The key parameters for the agglomeration process of catalytic powders are the catalyst particle size and the applied cathodic current. Composite electrode material powders of Pd nanoaggregates deposited onto oxide particles, which were different in nature, were characterized for the electrocatalytic hydrogenation of phenol. A model is proposed to explain the kinetics of the ECH, in which the sites for the adsorption of generated atomic hydrogen are the metallic sites (M) and the sites for the adsorption of the organic molecules to be hydrogenated are the oxide sites (A).

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