# New material of composite electrode for electrocatalytic hydrogenation

G. St-Pierre, H. Ménard, N.A. Bouchard, L. Brossard*

Département de chimie, Université de Sherbrooke,
Sherbrooke, Québec, J1K 2R1, Canada
*Institut de Recherche d'Hydro-Québec, 1800 Montée
Sainte-Julie, Varennes, Québec, J3X 1S1 Canada

## Introduction

The choice of electrode materials used for the electrocatalytic hydrogenation (ECH) of organic molecules is very important. It has been previously demonstrated that the support can infuence the activity of the catalyst [1]. This influence is the result of metal-support interactions [2-3]. Recent results show that the support (alumina, activated carbon) can also participate in the adsorption of organic molecules [4-5]

In this paper it is demonstrated that is possible to fabricate ECH electrodes from functionalized silica gel powders where the organic phase controls adsorption.

## Theory

The mechanism proposed for the ECH of unsaturated bonds is described by equations 1-4. First, electrosorbed hydrogen is formed on the metallic nanoaggregates by reduction of water (eq 1 where $(H)_{ads}M$ is the electrosorbed hydrogen)

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

Hydrogenation of the double bond then proceeds as in the catalytic hydrogenation, i.e., by the reaction of the adsorbed substrate onto the adsorbent with the electrosorbed hydrogen (eq 3, adsorption step shown in eq 2) at the triple phase boundary, followed by the desorption of the product (eq 4). The triple phase boundary (or adlineation point)[6,7] can be defined as the junction between the adsorbent (support), the metal and the solution; it is the site of the ECH process. For a given adsorbent, the larger the area related to the triple phase boundary , 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).

$$(H)_{ads}M + H_2O + M + e^- \rightarrow H_2 + 2OH^- \qquad (5)$$
$$(H)_{ads}M + (H)_{ads}M \leftrightarrow H_2 \qquad (6)$$

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

## Results and discussion

The results presented herein were obtained using silica gel powder (40~63 μm) for the substrate; these substrates were then functionalized by binding Diols, trimethylsilyl, $C_8$ , $NH_2$ groups to the surface. This powder, which is usually used in liquid chromatography as an strong adsorbent of organic species, were partially covered by nickel nanoaggregates. As in liquid chromatography, we have performed a study on ECH of cyclohexanone as a function of the methanol concentration in solution.

Figure 2 shows the efficiency of the ECH of cyclohexanone as a function of the methanol concentration. These results are in accord with adsorption isotherms obtained by liquid chromatography on these same powders (Figure 3) and thus confirm that the limiting step for the ECH is associated with the process defined by equation 2, and illustrated in Figure 1.

## Acknowledgments

Financial support from NSERC and FCAR is gratefully acknowledged.

## References

1. K. Amouzegar and O. Savadogo, *Electrichim. Acta,* **43**, 503-508 (1994)
2. V.S. Bagotsky and A.M. Skundin, *Electrochimica Acta*, **29**, 757 (1984)
3. N. H. Sagert and R.M. Pouteau, *Can. J Chem.*, **50**, 3686, (1972)
4. P. Dubé, L. Brossard, H. Ménard. *Can. J. Chem* **80**, 345-349 (2002).
5. P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Ménard, et J. Lessard.. Environ. Sci. Technol. 2000,34, 1265-1268
6. E.B. Maxted and S. Ali, *J. Am. Chem. Soc.*, **83**, 4137 (1961)
7. P. Chou and M. A. Vannice, *Journal of catalysis*, **107**, 129 (1987)

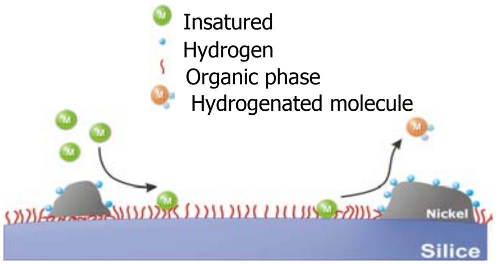

Figure 1 Schematic view of the ECH mechanism

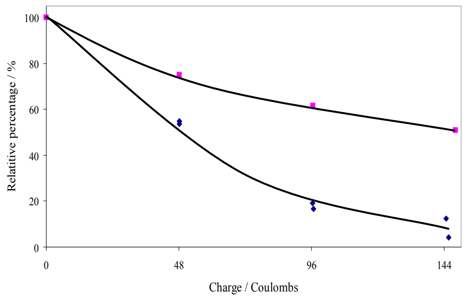

Figure 2 ECH of cyclohexanone in (■) 100% $H_2O$ , (♦) 20%$CH_3OH$ in $H_2O$

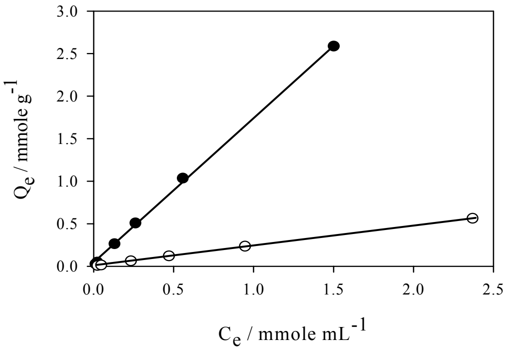

Figure 3 Adsorption isotherms of cyclohexanone in (●) 100% $H_2O$ , (○) 25%$CH_3OH$ in $H_2O$