ELSEVIER

Catalysis Today 24 (1995) 151–156

CATALYSIS TODAY

Liquid phase catalytic hydrogenation under potential control of the catalyst

E. Lamy-Pitara *, I. Belegridi, J. Barbier

LACCO, URA 350, Université de Poitiers,40, Avenue du Recteur Pineau, Poitiers 86022, France

Abstract

The hydrogenation of olefins in acidic aqueous solutions was studied on platinum catalysts under potential control. This control was achieved by an external device or was spontaneously established in the presence of the reactants. It is found that the catalytic activity does not depend on the way of potential control, or on the source of hydrogen (gaseous hydrogen or reduced protons). This result implies the same mechanism in the case of catalytic and electrocatalytic hydrogenation of olefins. Moreover the same type of active hydrogen species is involved in these reactions, identified as a weakly bound one. In competitive hydrogenations of methyl substituted olefins, high selectivities can be obtained by control of the potential of the catalyst at rather positive values.

1. Introduction

Platinum catalysts are largely used in catalytic hydrogenation reactions. This metal activates molecular hydrogen by dissociative chemisorption (reaction 1), which is an elementary step in the mechanism of catalytic hydrogenations [1]. This reaction occurs also in the process of electrocatalytic oxidation and evolution of hydrogen (reaction 2), [2,3].

$H_2 \rightleftarrows 2H_{ad}$ (reaction 1)

$H_2 \rightleftarrows 2H^+ + 2e^-$ (in acidic media) (reaction 2)

Reaction 2 is fast on platinum and in presence of H^+ and H_2 an equilibrium potential is reached. This potential can be calculated by the Nernst's law:

$$E = 0.058 \cdot \log(H_3O)^+ - 0.029 \cdot \log(p_{H_2})$$

So, at a constant pH, the potential depends on the effective pressure of hydrogen in the vicinity of the catalyst surface, which determines the hydrogen coverage, Θ_H.

Otherwise, the control of the catalyst potential by an external device, allowing the control of Θ_H, would influence the catalytic activity and selectivity in hydrogenation reactions. In this work the effect of the potential of platinum catalysts on their catalytic activity and selectivity for the hydrogenation of unsaturated diacids (maleic, methylmaleic and dimethylmaleic acids) in aqueous acid media was investigated. This test-reaction was largely studied as a model in liquid phase catalytic hydrogenations [4–12].

The potential of the catalyst was either controlled by an external device (in presence or in absence of gaseous hydrogen) or spontaneously set by the fast equilibrated reaction 2. The results, obtained by these three different experimental processes, were compared, to allow a definition of the role of the catalyst's potential and eventually

---

* Corresponding author.

SSDI 0920-5861(95)00017-8

to point out a possible 'non-Faradaic electrochemical modification of catalytic activity' (NEMCA effect) discovered by C. Vayenas et al. [13,14] in the case of organic compounds' oxidation.

2. Experimental

A platinized platinum wire (Lyon-Alemand-Louyot, 99.995%) was used as a model catalyst. A large active platinum area, equal to about 800 cm^2, was obtained by electrochemical deposition of platinum [8].

The solvent was an aqueous H_2SO_4 0.5 M solution prepared with suprapure Merck sulphuric acid and ultrapure water (of a resistivity equal to 18 MΩ·cm). Maleic, methylmaleic and dimethylmaleic acids were analytical grade (Merck-Schuchardt). The progress of reactions was followed by HPLC analysis with a Biorad Aminex 87H column and a UV detector.

Before each experiment, the platinum surface was cleaned by electrochemical potential cycling between 0 and 1.5 V/RHE. Then the effective surface area of the platinum catalyst was evaluated 'in situ' by linear potential sweep cyclic voltammetry (LPSCV) [15]. This evaluation is based on the measure of electricity, Q_H°, exchanged during the underpotential adsorption or the desorption of a monolayer of hydrogen (Fig. 1), following the reaction:

$$H^+ + e^- \rightleftarrows H_{ads} \qquad \text{(reaction 3)}$$

A classical three-electrode reaction cell is used for the characterization of platinum surface. For catalytic hydrogenations at controlled potentials the counter-electrode compartment was separated from the reaction-compartment by a Nafion membrane (type 417 Aldrich) in order to avoid the migration and the electrochemical reaction of the organic compound on the counter electrode.

2.1. Determination of the diffusion rate of hydrogen

The catalytic hydrogenations in liquid media are known to be often limited by the diffusion of gaseous hydrogen to the catalyst surface.

In this work, the diffusion rate of hydrogen was evaluated by the measure of the limiting current,

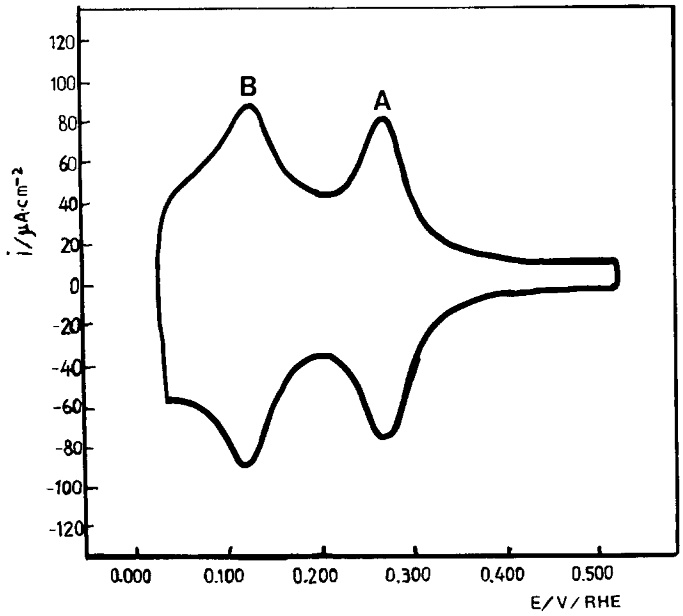

Fig. 1. Voltammogram of platinized Pt in the potential region of under-potential adsorption of hydrogen (reaction: $H^+ + e^- \rightleftarrows H_{ads}$). $v = 50$ mV/s, 0.5 M H_2SO_4, 299 K.

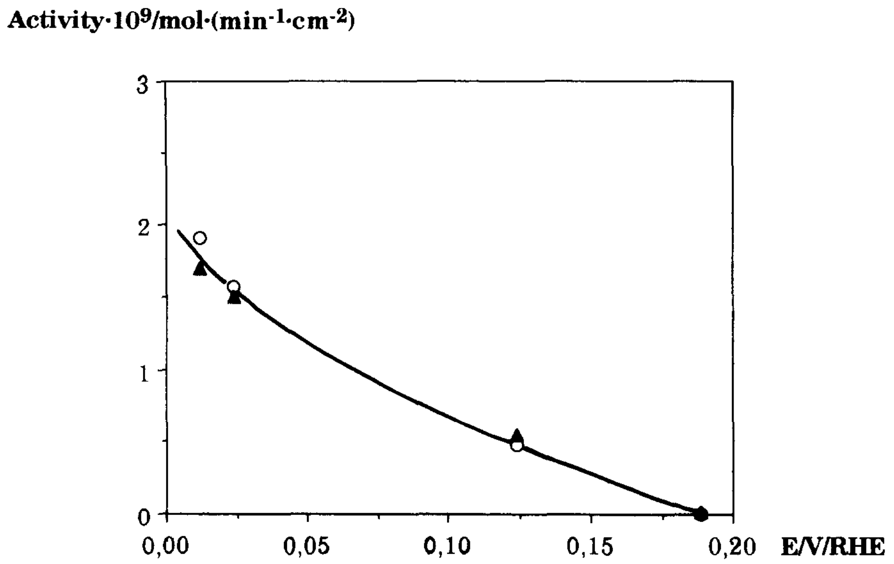

Fig. 2. Evolution of the catalytic activity of platinized Pt as a function of potential, spontaneously set by different partial pressures of hydrogen, (▲), or controlled by a potentiostat, (○). $C_{M.A.} = 2 \cdot 10^{-2}$M, $H_2SO_4 = 0.5$ M, $p_{H_2} = 1$ atm.

i_L, corresponding to the electrocatalytic oxidation of hydrogen (reaction 2, in the oxidation sense).

In the case of a rough platinum surface, i_L is equal to the maximum diffusion current ($i_L = i_{diff.max}$, [16]), allowing the determination of the diffusion rate of hydrogen: $v_{diff} = i_{diff.max}/(n \cdot F \cdot S)$ ($n = 2$, $F = 96500$ C and S = real surface area of platinum).

The diffusion rate of hydrogen, v_{diff}, measured in the experimental conditions used in this work is always higher than the hydrogenation rate, a, by a factor of 4 to 9 (for example, with $p_{H_2} = 1$ atm, $v_{diff} = 8.6 \cdot 10^{-9}$ mol·min^{-1}·cm^{-2} and $a = 1.7 \cdot 10^{-9}$ mol·min^{-1}·cm^{-2}).

3. Results

3.1. Hydrogenation of maleic acid at different potentials of platinum catalysts and at different hydrogen pressures

In Fig. 2 is presented the evolution of the catalytic activity of platinum, for the hydrogenation of maleic acid, in function of the potential of the catalyst controlled by an external device (*potentiostat*). The catalytic activity decreases with increasing potentials and becomes equal to zero at a potential value near + 180 mV/RHE.

On the other hand, during a conventional catalytic hydrogenation of maleic acid, with different hydrogen pressures, the potential of the catalyst is spontaneously set at different values (third column, Table 1).

The comparison of the catalytic activities obtained by catalytic hydrogenations (Table 1) with those obtained by an external control of the potential points out that the activities are equal for the same values of the potential of the catalyst (Fig. 2).

3.2. Electrocatalytic reduction of maleic acid

Maleic acid can be electrochemically reduced (in absence of gaseous hydrogen) following the global reaction:

$$HOOCCH{=}CHCOOH + 2H^+ + 2e^- \rightarrow HOOCCH_2CH_2COOH. \quad \text{(reaction 4)}$$

The intrinsic catalytic activity of platinum can be calculated either from the current–potential sta-

Table 1
Hydrogenation rates obtained at different potential values spontaneously set with different p_{H_2} (reaction: $H_2 \rightleftarrows 2H^+ + 2e^-$)

pH_2/atm	$E(H_2)$/mV/RHE	$E(H_2+M.A.)$ mV/RHE	Activity$\cdot 10^9$ mol/(min$\cdot$cm^2)
1.00	0	12	1.70
0.63	6	24	1.50
0.11	34	128	0.50
0.01	59	184	0.11

tionary curve, associated to the electroreduction of maleic acid, or by the decrease of the concentration of this compound.

The obtained catalytic activities were compared with those of hydrogenation at controlled potentials in the presence of gaseous hydrogen (Fig. 3). It can be remarked that the same activities are obtained for the same values of the potential of the catalyst (Fig. 3).

3.3. Effect of the nature of the olefin on the catalytic hydrogenations at controlled potentials of the catalyst

In order to investigate the influence of the nature of the olefin in catalytic hydrogenations at controlled potential, methylmaleic acid was hydrogenated at different hydrogen pressures and at different potentials and the obtained curve A (Fig. 4) is compared to curve B, corresponding to the hydrogenation of maleic acid. It appears that, for the same potential of the catalyst, higher activities are obtained for maleic acid than for methylmaleic acid. This result is confirmed by the rates of electrocatalytic reduction of maleic (M.A.), methylmaleic (M.M.A.) and dimethylmaleic (DM.M.A.) acids (Table 2), which decrease with increasing methyl substitution:

$a_{M.A.} > a_{M.M.A.} > a_{DM.M.A.}$

Moreover, the starting reduction potential is more negative for more substituted olefins (Table 2). This remark permits to control the selectivity, $S_{M.A./M.M.A.}$, in competitive hydrogenations of maleic and methylmaleic acid by imposition of different potentials ($S_{M.A./M.M.A.} = a_{M.A.}/a_{M.M.A.}$) (Table 3). Indeed, at + 170 mV/RHE the selectivity, $S_{M.A/M.M.A.}$ is equal to 50, whereas it is equal to 2 at 0 mV/RHE, pointing out that the selective hydrogenation of maleic acid, in a mixture of maleic and methylmaleic acid, is possible.

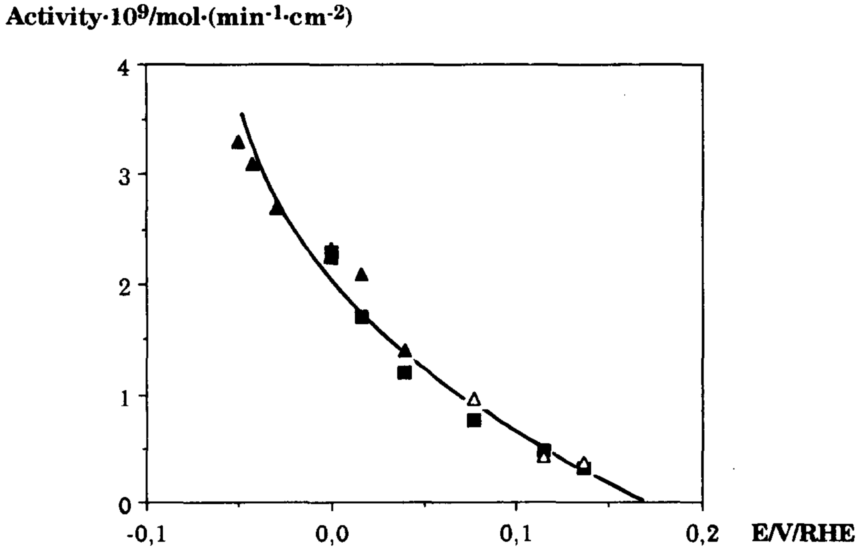

Fig. 3. Comparison of the catalytic activity of platinized Pt as a function of potential, for the electroreduction (absence of gaseous H_2), (▲,△) and the hydrogenation of maleic acid at different controlled potentials (presence of gaseous H_2, $p_{H_2} = 1$ atm), (■). $C_{M.A.} = 2\cdot 10^{-2}$ M. (△) activity calculated from the values of electroreduction currents (i_{t-0}); (▲) activity calculated from the decrease of $C_{M.A.}$.

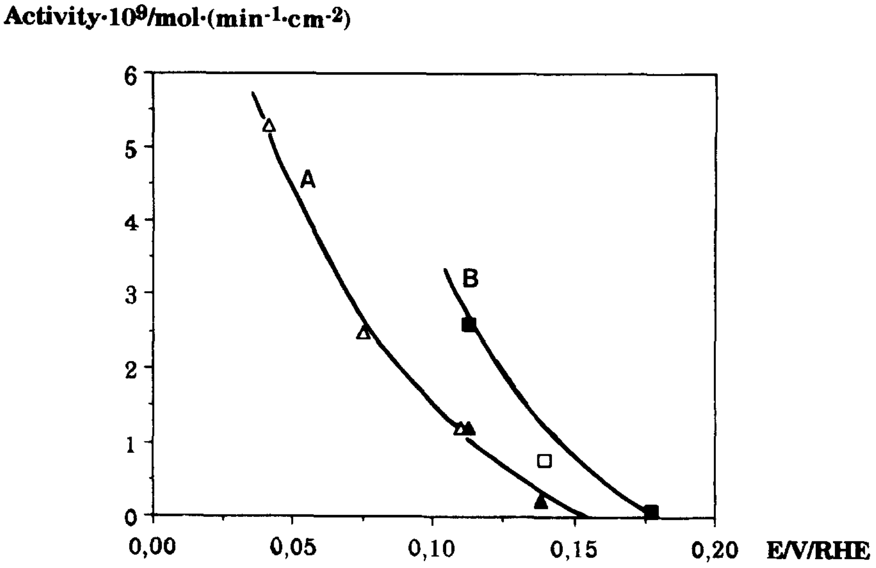

Fig. 4. Evolution of the catalytic activity of platinum in hydrogenations of maleic (curve B) and methylmaleic (curve A) acids, in function of the potential: (■,▲) imposed potential; (□,△) spontaneously set potential. $C_{M.A.}=C_{M.M.A.}=2\cdot10^{-2}$ M.

Table 2
Comparison of activities of platinum catalysts at different potentials, in electrocatalytic reduction of maleic (M.A.), methylmaleic (M.M.A.) and dimethylmaleic (DM.M.A.) acids ($c=10^{-3}$ M/l)

Potential mV/RHE	Activity · 10^9/mol/(min · cm^2)		
	M.A	M.M.A.	DM.M.A.
254	0.00	0.00	0.00
204	0.00	0.00	0.00
184	0.06	0.00	0.00
154	0.09	0.07	0.00
124	0.21	0.16	0.06
103	0.23	0.19	0.16
93	0.29	0.22	0.19

Table 3
Variation of the selectivity, $S_{M.A./M.M.A.}=a_{M.A.}/a_{M.M.A.}$, in competitive hydrogenation of maleic and methylmaleic acid as a function of potential ($c_{M.A.}=c_{M.M.A.}=10^{-3}$ M)

Potential/mV/RHE	Selectivity ($S_{M.A./M.M.A.}$)
9	1.7
69	3.1
150	7.0
171	50.0

3.4. Active hydrogen in catalytic hydrogenation of olefins

The changes of catalytic activities as a function of the potential of platinum catalyst (Figs. 2–4, Tables 1–2) can be compared with the voltammogram associated to the adsorption of hydrogen (Fig. 1) (reaction 3).

It can be remarked that, for the three studied olefins, the hydrogenation reaction occurs only at potentials lower than 200 mV/RHE, in the range of '*weakly*' adsorbed hydrogen (peak B in Fig. 1). However, as it is obvious on the voltammogram (Fig. 1), at this potential, about 35% of platinum surface is still occupied by the '*strongly*' adsorbed hydrogen (peak A). So, it can be concluded that only '*weakly*' adsorbed hydrogen species are active in catalytic hydrogenation of olefins [17].

4. Conclusion

The obtained results allow to conclude that:

— In liquid phase catalytic hydrogenation of olefins the activity of platinum catalyst depends mainly on the value of the potential of these catalysts. It doesn't depend on the way of potential control: by a potentiostat or by different hydrogen pressures following the equilibrium reaction 2.

— The same catalytic activities of platinum are obtained in electrocatalytic and in catalytic reduction of olefins, at the same potential values of the catalyst. This result points out that the same mechanism occurs in both processes and it proves that the nature of the active adsorbed hydrogen is the same, independently of its origin: *gaseous hydrogen* or *reduced protons* of the acid solution in agreement with the literature [5]. No promotion of the activity of platinum by electrochemical control of its potential is found in our experiment conditions, unlike in the case of the catalytic oxidation of hydrogen by oxygen, reported recently by S.G. Neophytides et al. [14].

— Only *weakly* adsorbed hydrogen species are involved in the catalytic hydrogenation of olefinic compounds on platinum catalysts. Similar explanations were proposed in the literature by P. Marécot et al. and P. Fouilloux et al. [18,19] in the case of Ni catalysts and also by I. Willner et al., P.C. Aben et al. [20,21] and J. Barbier et al. [22] in the case of Pt catalysts.

— High selectivities in competitive hydrogenations of methyl substituted olefins can be reached by control of the potential of the catalyst at values between 0.15 V and 0.2 V/RHE.

References

[1] J. Horiuti and M. Polanyi, Trans. Far. Soc., 30 (1934) 1164.

[2] A.N. Frumkin in P. Delayay (Editor), Advances in Electrochemical Engineering, Vol. 3, Interscience, N. York, pp. 287–385.

[3] J.O'.M. Bockris and A.K.N. Reddy, Modern Electrochemistry, Vol. 2, Plenum Press, New York, 1970, pp. 1153–1157.

[4] D.V. Sokolskii, Hydrogenation in Solutions, Academy of Sciences of the Kazakh SSR, transl. from Russian, Israel Program for Scientific Translations, Jerusalem, 1964, pp. 10, 64, 159, 483.

[5] (a) Yu.B. Vassiliev, V.S. Bagotzky, O.A. Khazova, U.V. Cherny and A.M. Meretsky, J. Electroanal. Chem., 98 (1979) 253; (b) ibid, 98 (1979) 273.

[6] J. Barbier and M.E. Gonzalez, J. Chim. Phys., 76 (1979) 219.

[7] I. Paseka, J. Catal., 121 (1990) 349.

[8] E. Lamy-Pitara, L. Bencharif and J. Barbier, Appl. Catal., 18 (1985) 117.

[9] E. Lamy-Pitara, L. Lghouzouani, M. Piktas and J. Barbier, Appl. Catal., 44 (1988) 261.

[10] E. Lamy-Pitara, L. Lghouzouani, C. Sieiro and J. Barbier, J. Chim. Phys., 87 (1990) 179.

[11] E. Lamy-Pitara, L. El Ouazzani-Benhima, J. Barbier, M. Cahoreau and J. Caisso, Appl. Cat., 81 (1992) 4.

[12] E. Lamy-Pitara, L. El Ouazzani-Benhima and J. Barbier, J. Electroanal. Chem., 335 (1992) 36.

[13] C.G. Vayenas, S. Bebelis, I.V. Yentekakis and H.G. Lintz, Catal. Today, 11 (3) (1992) 303–442.

[14] S.G. Neophytides, D. Tsiplakides, P. Stonehart, M.M. Jaksic and C.G. Vayenas, Nature, 370 (1994) 45.

[15] R. Woods in A.J. Bard (Editor), Electroanalytical Chemistry, Marcel Dekker Inc., New York, 1976, Vol. 9, Ch. 1, pp. 1–162.

[16] M. Rosen and S. Schuldiner, J. Electrochem. Soc., 117 (1) (1970) 35.

[17] E. Lamy-Pitara, I. Belegridi, L. El Ouazzani-Benhima and J. Barbier, Catal. Lett., 19 (1993) 87.

[18] P. Marécot, E. Paraiso, J.M. Dumas and J. Barbier, Appl. Catal., 74 (1991) 261.

[19] F. Hochard, G. Clugnet, J. Massardier, H. Jobic, A.J. Renouprez, J. Jenck and P. Fouilloux, Gecat-93, Giens 7–10 June, 1993.

[20] I. Willner, M. Rosen and Y. Eichen, J. Electrochem. Soc., 138 (2) (1991) 434.

[21] P.C. Aben, Van Der Eijk and J.M. Oelderik, in J.W. Hightower (Editor), Catalysis, Vol. 1, Proc. 5th Intern. Congress on Cat., North-Holland Publ. Company, 1973.

[22] J. Barbier and E. Lamy-Pitara, Gecat-90, Lozari, Corse, 1990.