Characterization of active hydrogen in catalytic double bond hydrogenations

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The catalytic hydrogenation of a C–C double bond was studied in the liquid phase as a function of the electrochemical potential of the catalyst, which was controlled by an external device or set spontaneously by the redox system: $H_2 \rightleftharpoons 2H^+ + 2e^-$ at various hydrogen partial pressures. It was found that the catalytic activities depend only on the electrochemical potential, not on the mode of control of the potential. The comparison of obtained catalytic activities with voltammetric curves related to adsorption and desorption of hydrogen on platinum, leads us to the conclusion that only some weakly adsorbed hydrogen species are involved in the catalytic hydrogenation of olefinic compounds on platinum catalysts.

Keywords: Catalytic hydrogenation; potential control; platinum catalyst; active hydrogen

1. Introduction

Metal catalysts of the platinum group (VIIIA) are known for their activity in hydrogenation reactions. These catalysts are also able to activate the electrocatalytic oxidation of molecular hydrogen, following the equilibrated reaction

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad \text{(in acid medium)}, \qquad (1)$$

leading to the establishment of an equilibrium potential. This potential, at a given pH, depends on the hydrogen pressure, following the Nernst law: $E = 0.058 \log(H_3O^+) - 0.029 \log pH_2$ (at 298 K).

During a liquid phase catalytic hydrogenation in a protonic solvent, the potential of the platinum catalyst is spontaneously set at a value which is mainly determined by equilibrium reaction (1). This potential can also be controlled by an external device, which allows to vary the effective pressure near the catalyst in a large range of values.

Various kinds of hydrogen adsorbed on platinum have been characterized, depending on the structure of the catalyst, the experimental conditions (temperature, pressure) and the electrochemical potential [1–4].

The purpose of this work was to study the catalytic hydrogenation of maleic acid on platinum, at different electrochemical potentials, therefore at different hydrogen coverages, in order to define which kind of adsorbed hydrogen is active during this reaction.

2. Experimental

The catalyst used was a high purity platinum wire (Lyon-Alemand-Louyot, 99.995%). Its surface was developed by electrochemical deposition of platinum [5].

The solvent was an aqueous H_2SO_4 0.5 M solution prepared with sulphuric acid (suprapure Merck) and ultrapure water (of a resistivity equal to 18 M Ω cm).

We used the hydrogenation of maleic acid (Merck-Schuchardt) as a test reaction. The progress of the reaction was followed by high performance liquid chromatography (HPLC) analysis.

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 measured in situ by the integration of voltammetric peaks associated with the adsorption or desorption of one monolayer of hydrogen [5,6] (fig. 1).

The reaction cell used for the characterization and for the hydrogenation reaction is similar to that described previously [5], except for the counter-electrode com-

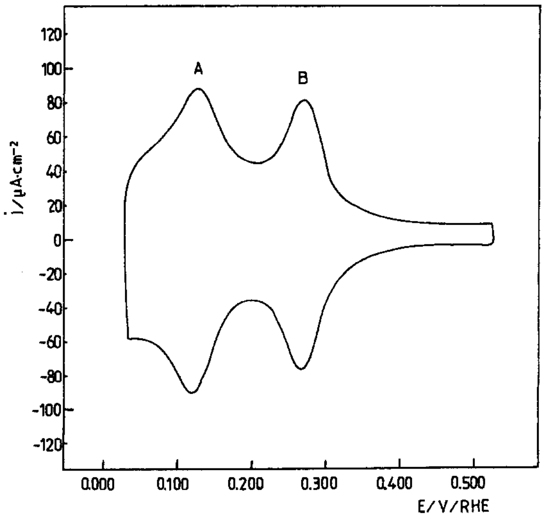

Fig. 1. Voltammogram of platinized platinum in the potential region of adsorption–desorption of hydrogen ($v = 50\,mV/s$, 0.5 M H_2SO_4 solution, 299 K).

partment which is separated from the reaction compartment by a Nafion membrane (in order to avoid the migration and the electrochemical reaction of the organic substrate on the counter electrode during the catalytic hydrogenations at controlled electrochemical potentials).

3. Results and discussion

3.1. CHARACTERIZATION OF ADSORBED HYDROGEN BY CYCLIC VOLTAMMETRY

It is possible to characterize the adsorbed hydrogen on polycrystalline platinum by linear potential sweep cyclic voltammetry (LPSCV). In an acid solution (0.5 M H_2SO_4) the adsorption of hydrogen occurs in the potential range 0–0.4 V/RHE, following the fast reaction

$$\mathrm{Pt} + \mathrm{H}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Pt\,H_{ads}}\,. \tag{2}$$

On the voltammogram two main reversible peaks appear associated respectively with the adsorption–desorption of the so-called "weakly" adsorbed hydrogen (peak A at ~ 0.15 V) and of the "strongly" adsorbed hydrogen (peak B at ~ 0.25 V) (fig. 1).

On the energy scale, the peak of the weakly adsorbed hydrogen corresponds to 14.5 kJ/atom-gram adsorbed H ($E = 0.15$ V; $\Delta G \approx -FE$) and the peak of the strongly adsorbed hydrogen to 24 kJ/atom-gram adsorbed H ($E = 0.25$ V; $\Delta G = -FE$). A small intermediate peak, located between the two main peaks, is attributed to interactions with adsorbed anions, and is more important on some particular stepped surface sites of the type [m(111) × n(111)] [7]. Several studies with different faces of Pt single crystal have shown that voltammetric curves depend on the surface structure [4,6,7]. Moreover, the voltammogram of the polycrystalline platinum can be simulated mainly by that of [100] Pt face (corresponding to the "strongly" adsorbed hydrogen) and that of [110] Pt face (corresponding to the "weakly" adsorbed hydrogen), the (111) face being less stable and easily reconstructed [4].

3.2. HYDROGENATION OF MALEIC ACID AT VARIOUS POTENTIALS

The evolution of the catalytic activity of platinum, for the hydrogenation of maleic acid, as a function of the electrochemical potential (controlled by an external source (potentiostat)), is shown in fig. 2. On the same curve the electrochemical potential was converted to hydrogen pressure by using the Nernst's law.

In another set of experiments the potential variation was achieved by different partial pressures of hydrogen, introduced in mixture with nitrogen. In this case, the

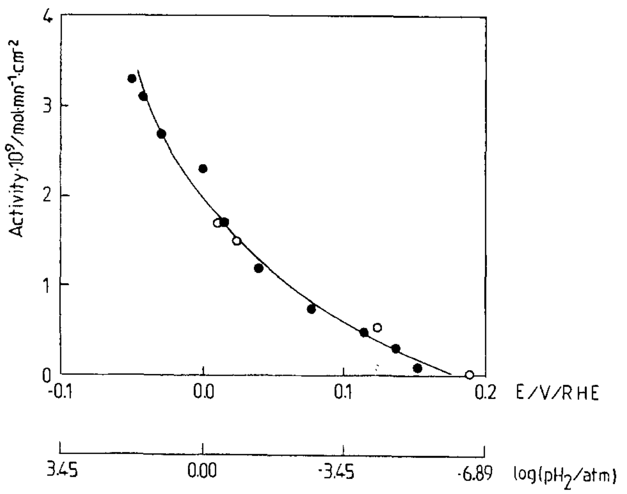

Fig. 2. Evolution of the catalytic activity of platinum, for the hydrogenation of maleic acid ($C_M = 2 \times 10^{-2}$ M), as a function of potential applied by a potentiostat (●), or fixed spontaneously by variation of p_{H_2} (○)($T = 299$ K).

potential was fixed spontaneously following Nernst's law; furthermore the rate of the reaction follows an apparent kinetical law: activity $= k(p_{H_2})^{0.5}$.

The evolution of the specific catalytic activities, as a function of the effective potential (fixed spontaneously near the catalyst surface in the presence of maleic acid and gaseous hydrogen), are comparable to those obtained by an external control of the potential (fig. 2). Moreover, at potential values higher than 0.15–0.20 V/RHE, the hydrogenation rates become very low, nearly equal to zero (fig. 2).

Some other experiments confirm this result: if the hydrogenation reaction is carried out without stirring of the solution, i.e. under conditions controlled by the diffusion rate of hydrogen (being in a concentration 20 times lower than the concentration of maleic acid), the potential is spontaneously fixed at +162 mV/RHE and the reaction rate is equal to zero.

The comparison of the results of hydrogenation of maleic acid at controlled potentials (or spontaneously fixed potentials) with the voltammetric data related to the adsorption of hydrogen points out that at potential lower than 0.2 V/RHE only weakly adsorbed hydrogen is consumed and so only weakly adsorbed hydrogen species are active in catalytic hydrogenation reactions. Indeed, at potentials higher than 0.2 V/RHE about half of platinum surface is covered by strongly bound hydrogen species.

So, it can be concluded that, during the liquid phase hydrogenation reactions of C=C bonds, only weakly bonded hydrogen species are active, setting a question on the structure insensitivity of catalytic hydrogenation reactions, mainly when the metallic surface area has been evaluated by "irreversibly" adsorbed hydrogen.

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