

ELECTROCHEMICAL INVESTIGATION OF METAL CATALYSTS IN LIQUID PHASE

É. POLYÁNSZKY, T. MALLÁT and J. PETRÓ

Department of Organic Chemical Technology,
Technical University, H-1521 Budapest

Received July 1st. 1987

Abstract

Different electrochemical methods have been developed for studying dispersed metal hydrogenation catalysts in liquid phase. Metal-hydrogen systems can be investigated by galvanostatic and potentiodynamic method by which the amount of sorbed hydrogen, its bonding energy and the surface area of the catalyst can also be determined. By measuring the excess free energy, important information can be obtained about the energetic state of the catalyst. Measuring the electrochemical potential of the catalyst in the course of hydrogenation, the progress of the reaction can be monitored as well as the ageing of the catalyst.

The investigation and application of hydrogenation metal catalysts is one of the most important fields of catalysis research. Electrochemical methods have exceptional importance in studies on these catalysts. The basis of these methods is the measurement of the electrochemical potential of a good conductor metal catalyst. The main advantage of electrochemical methods is that valuable information about catalysts can be obtained at room temperature, with some milligram of substance, in a two- or three-electrode polarizing apparatus (Fig. 1), in the medium of a liquid electrolyte.

Noble metals and transition metals containing hydrogen on the surface behave as a reversible hydrogen electrode and therefore the amount and the bond strength of hydrogen sorbed on the catalyst can be determined by electrochemical measurement. On the other hand, after eliminating the sorbed hydrogen, information can be obtained about the metal surface energy.

Since electrochemical phenomena proceed at boundary layers, these methods provide specific information about the surface of a catalyst which has a distinguished role in catalytic processes. This aspect means a special relationship between catalysis and electrochemistry.

For electrochemical studies on supported and unsupported metal catalysts, the following methods have been developed:

- measurement of the excess free energy,
- galvanostatic and potentiodynamic polarization for the investigation of metal-hydrogen systems,
- measurement of the electrochemical potential of working catalyst during the hydrogenation reaction.

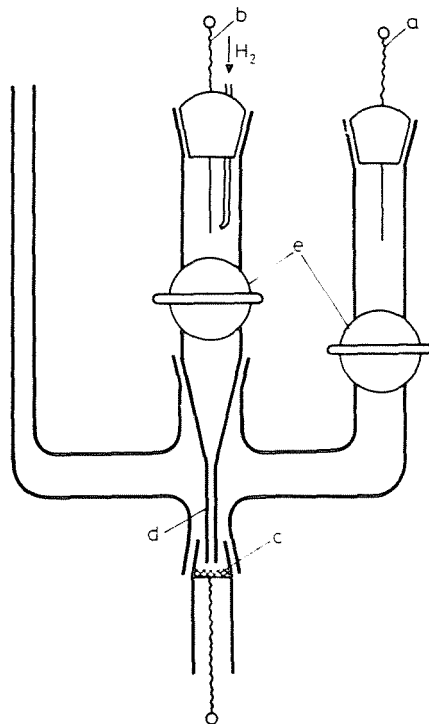


Fig. 1. Design of an electrochemical cell for powder catalysts; a) Pt sheet polarizing electrode; b) platinized Pt/H₂ reference electrode; c) catalyst/Pt sheet working electrode; d) Luggin capillary; e) ground-glass stopcocks

1. Determination of the excess surface free energy

The excess free energy is the additional energy which accumulates on the catalysts during preparation. This energy is important from the point of view of catalysis. Due to this excess energy the dispersed metal is not in a thermodynamic equilibrium state. The principle of the measurement is the determination of the electrochemical potential difference measurable between the unstable catalyst and the stable metal, while both are immersed into the solution of their ions [1, 2]. Before measuring, hydrogen or other gases adsorbed on the surface have to be eliminated by polarization [3].

By investigating supported and unsupported noble metal catalysts it has been established that from among the causes of the excess free energy accumulation (dispersity, chemical, physical and lattice defects), dispersity is the decisive factor. According to our results [4], the excess surface free energy changes in parallel with the dispersity.

2. Galvanostatic and potentiodynamic polarization

Metal catalysts containing hydrogen on the surface behave as reversible hydrogen electrodes and their electrochemical potential can be described by the Nernst equation. Hydrogen can be removed by galvanostatic or potentiodynamic polarization and its amount and nature can be investigated by this method.

In *galvanostatic polarization*, the catalyst (measuring electrode) is polarized with a constant current. By plotting the electrode potential as a function of the charge passing through the system, the galvanostatic (charging) curve can be obtained [5]. The characteristic charging curve of dispersed palladium can be seen in Fig. 2. Starting from the state saturated with hydrogen (0 to 0.05 V), the ionization of hydrogen dissolved terminates at 0.1 V, that of

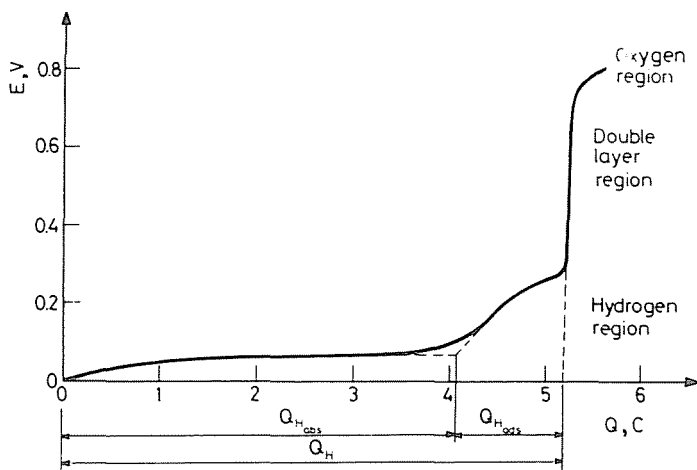


Fig. 2. Galvanostatic curve of dispersed Pd catalyst in 0.5 M sulphuric acid ($m = 10$ mg; $i = 2.5$ mA)

the adsorbed hydrogen at 0.3 V [6]. Then the potential suddenly increases due to the recharging of the double layer and at ca. 0.7 V the adsorption of oxygen sets in.

The amount of the two different hydrogen species as well as the area of catalyst surface can be calculated by measuring the quantity of coulombs passing through the electrode.

In *potentiodynamic polarization* (alternative names are "linear sweep voltammetry" or "cyclic voltammetry"), the potential of the catalyst (measuring electrode) is changed with respect to the reference electrode at a constant rate, and the current passing through the cell is simultaneously recorded. This curve is, in fact, a differential adsorption isotherm as a function of potential. Various kinds of hydrogen bonded with different sorption energy on the

catalyst surface can be seen as distinct maxima on the curve. By selecting appropriate conditions of measurement the amount of the hydrogen as well as its bonding energy and the surface area of the catalyst can be calculated from the curve [7, 8].

Figure 3 shows the hydrogen region of the potentiodynamic curve of unsupported dispersed palladium catalyst (6), where the first larger maximum

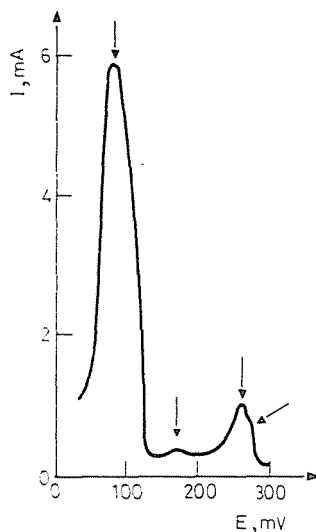


Fig. 3. Potentiodynamic curve of a dispersed Pd catalyst in 0.5 M sulphuric acid ($m = 1$ mg; sweep rate = $100 \text{ mV} \cdot \text{min}^{-1}$)

can mainly be attributed to dissolved hydrogen, while the second characteristic peak and the small shoulder correspond to the different adsorbed hydrogen species. This curve is similar to that obtained by thermodesorption.

By extending the method to supported catalysts, it has been established that not only the area of the surface grows as a consequence of greater dispersity, but also the nature of the surface capable of hydrogen sorption differs significantly. By studying the hydrogen sorption on carbon-supported palladium catalyst it has been found that when the amount of Pd in the catalyst decreases from 100% to 1% and the surface area of the metal increases simultaneously to more than three times the original area, the amount of strongly bonded (adsorbed) hydrogen increases due to the increased surface area, and thus the share of weakly bonded (dissolved) hydrogen decreases from 87% to 30% with respect to the total amount of hydrogen (Table 1). Simultaneously, the hydrogen content becomes more homogenous in energy [9, 10].

The ageing of catalysts and surface structure changes can also be monitored by this method.

Table 1

Hydrogen sorption on carbon supported Pd catalyst			
Pd content (%)	Total amount of sorbed H (cm ³ /g metal)	Ratio of weakly bonded and total amount of H (%)	Metal surface area (m ² /g Pd)
1	60	30	170
10	64	50	130
100	100	87	53

3. Measurement of the catalyst potential in the course of hydrogenation

In addition to the characterization of catalysts, the catalytic process itself can also be investigated by electrochemical methods, e.g. by checking the electrochemical potential of a working metal powder catalyst in the course of a catalytic hydrogenation process. Since the potential change of the catalyst sensitively reflects the processes taking place on the surface, the progress of the hydrogenation reaction can be monitored, the potential range of reversible operation can be determined and the selectivity and ageing of catalyst can also be investigated by potential measurement.

References

- MÜLLER, F.: *Z. Ang. Chem.* 54, 334 (1941)
- ROGINSKII, S.: *Z. Acta Phys. Chim. URSS*, 4, 729 (1936)
- PETRÓ, J., POLYÁNSZKY, É., CSÜRÖS, Z.: *J. Catal.* 35, 289 (1974)
- POLYÁNSZKY, É., MALLÁT, T., PETRÓ, J., SÁRKÁNY, A.: *Acta Chim. Acad. Sci. Hung.* 104, 337 (1980)
- FRUMKIN, A. N., SHLIGIN, A. J.: *Dokl. Akad. Nauk. SSSR*, 2, 173 (1934)
- MALLÁT, T., POLYÁNSZKY, É., PETRÓ, J.: *J. Catal.* 44, 345 (1976)
- PETRÓ, J., POLYÁNSZKY, É.: *Acta Chim. Acad. Sci. Hung.* 87, 385 (1975)
- POLYÁNSZKY, É., PETRÓ, J., SÁRKÁNY, A.: *Acta Chim. Acad. Sci. Hung.* 104, 345 (1980)
- POLYÁNSZKY, É., MALLÁT, T., PETRÓ, J.: *Acta Chim. Acad. Sci. Hung.* 92, 147 (1977)
- MALLÁT, T., PETRÓ, J., POLYÁNSZKY, É.: *Magyar Kémikusok Lapja*, 36, 642 (1981)

Dr. Éva POLYÁNSZKY }
 Dr. Tamás MALLÁT } H-1521 Budapest
 Dr. József PETRÓ }