# ELECTROCHEMICAL METHODS AND THEIR APPLICATION TO RANEY-NICKEL*

by

Z. CSŰRÖS, J. PETRÓ and É. POLYÁNSZKY

Department of Chemical Technology, Polytechnical University, Budapest

(Received March 15, 1968)

Electrochemical methods are extremely important in the study of liquid phase catalytic processes. They provide information about the properties of the catalyst, adsorption phenomena, reaction mechanism, etc. Electrochemical methods are useful in the selection of optimum conditions — e.g. the catalyst to substrate ratio, solvent, pH, temperature, stirring speed, etc. — for a reaction to be carried out as a part of a technological process. Under optimum conditions the lifetime of the catalyst is longer, i.e. the amount of products obtained on a given catalyst sample increases. In principle, electrochemical methods can be used for controlling the condition of the catalyst during continuous catalytic hydrogenation in chemical technology. The obvious theoretical and practical importance of the electrochemical methods is illustrated in several papers by SOKOLSKY [1].

The importance of these methods requires detailed studies of the limits of their applicability, including technological conditions. It should be noted that it is very difficult to create electrochemically well-defined conditions for a "living" catalyst even in the absence of a catalytic reaction. One of the reasons for this is the insufficient "purity" of many catalysts. During preparation very strong salt adsorption takes place on the surface, and occlusions can also be formed. These impurities are extremely difficult to remove even by intensive washing. The aging of the catalyst which is accompanied by a decrease in its surface area by shrinking, as well as by the disappearance of the active sites, in principle, results in a change in the electrochemical potential — another reason for the above mentioned difficulties. Several practically important catalysts are unstable during the catalytic reaction. To a first approximation, noble metals (Pt, Pd, etc.), being less susceptible to oxidation, are better models than the catalytically active transition metals (e.g. nickel). In water, and during reduction of oxygen-containing compounds nickel can be oxidized even under the conditions of hydrogenation [2], the extent of oxidation being greatly dependent on reaction conditions, e.g. the catalyst-substrate-hydrogen ratio.

---

* Presented at the II. Federal Conference on Liquid Phase Catalytic Reactions (Alma-Ata, Soviet Union, 1966).

The method of measurement can also affect unstable metals like nickel.

In the following, the measurement of the electrochemical potential of Raney-nickel will be discussed. It is clear from the above discussion that nickel is not the best model. It is not uniform due to its aluminium content and the presence of $Al_2O_3$ hydrated to a variable extent. Raney-nickel is prepared by removing Al by base from a nickel-aluminium alloy, resulting in strong adsorption of alkali on the surface in uncontrollable amounts. In spite of all these difficulties, we have selected Raney-nickel as a catalyst model because it is widely used in the Hungarian pharmaceutical industry. It follows from technological reasons that alcohol is frequently used as a solvent. The potential of the catalyst was, therefore, studied in water and dry alcohol, too.

## Experimental

The experimental results can be divided into two groups. The first group is concerned with technical problems: the factors that are most decisive for the electrochemical potential of Raney-nickel, and the conditions under which the potential is most reproducible, have been studied. The second group is an attempt at elucidating the correlation between the electrochemical potential and catalytic properties of Raney-nickel.

The potentials of catalyst samples prepared from alloys of the same grain size by an identical method (continuous flow of base) at different temperatures and NaOH concentrations are shown in Fig. 1. The potential was measured after washing the catalyst until neutral reaction (checked with indicator paper), using Pt and calomel electrodes, in distilled water. The Pt electrode was immersed in the catalyst powder, and the EMF determined with a vacuum tube voltmeter. The dependence of the EMF on the catalyst's past is obvious. The more concentrated the base used to dissolve Al, the larger the EMF which is also increased by increasing temperature during the treatment with NaOH.

In the following two series of measurements are presented, differing in the conditions during dissolving Al. The catalyst samples have been prepared from alloys of identical grain size. In series A aluminum was dissolved in a stream of 2% NaOH (at 95° C), followed by a treatment with 20% NaOH of the same temperature. The catalyst was washed until neutral reaction, and ground in a ball mill. Samples were taken at intervals. These samples are members of series A. The basic sample of series B has been prepared with 20% NaOH at 95° C. Instead of neutral reaction, this catalyst sample was washed until constant potential, followed by grinding under conditions identical to those used with series A.

Washing a catalyst until constant potential is a requirement more stringent than that of neutral reaction. Neutral reaction can often be reached after 5—10-fold decantation, while — depending on the grain size — 50—150-fold decantation may be necessary to achieve a constant potential. The EMF decreased during the washing procedure (e.g. 803 mV for the sample of series A showing neutral reaction prior to grinding, as opposed to 690 mV after washing until a constant potential has been reached). In order to obtain better reproducibility it is advisable to continue washing until constant potential. It has been observed that a neutral catalyst sample may either desorbe, or adsorbe base when placed in water or NaOH-solutions, depending on the base concentration. The critical concentration was found to be 0.01 N NaOH, desorption and adsorption of base being observed below and above this concentration, respectively. The optimum pH for storing the catalyst for a longer time is unknown as yet.

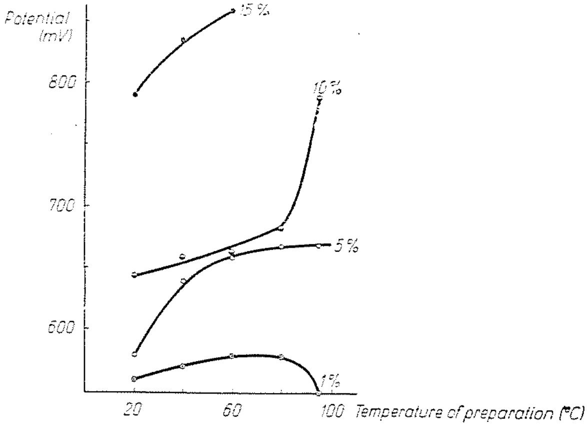

*Fig. 1.* The potentials of Raney-Ni samples as a function of temperature during Al-removal with 1, 5, 10 and 15% NaOH solutions

*Fig. 2/a* shows the potentials of the series A sample (measured in water) washed until constant potential as a function of the time of grinding. Curve *1* was obtained with Pt and calomel electrodes, the EMF being measured with a vacuum tube voltmeter. Curve *2* is a result of EMF-measurements in 0.01 M $NiCl_2(E^+)$ between two thermically matched Ni electrodes (purity 99.9999%) using a compensation technique [3]. No potential difference was observed between the two nickel plates used as electrodes in $NiCl_2$ solution. Therefore, upon immersing one of the plates into the catalyst powder, the potential could directly be read. Identical values were obtained with a vacuum tube voltmeter; these points are shown by asterisks. Curves *1* and *2* are parallel.*

---

* The potential measured on the way above mentioned seems to be mixed potential. There are at least two potential controlling steps: 1. $H \rightleftharpoons H^+ + e^-$ 2. $Ni \rightleftharpoons Ni^{2+} + 2e^-$

The potentials of series B samples washed until constant potential are shown in Fig. 2/b as a function of the time of grinding. The potentials were determined with Pt/calomel in water (curve *1*) and in dry alcohol after 10-fold decantation with dry alcohol (curve *2*). The fact that the two curves run parallel indicates that an electrochemical potential is measurable in dry alcohol — an important solvent used in organic chemistry. The difference between potentials measured in water and ethyl alcohol is quantitative rather than qualitative. The EMF values obtained in 0.01 M $NiCl_2$ with nickel electrodes using a vacuum tube voltmeter ($x$) and a compensation technique ($\Delta$) are the points on curve *3* $/E^{+}/$. The values obtained by different methods are in good agreement.

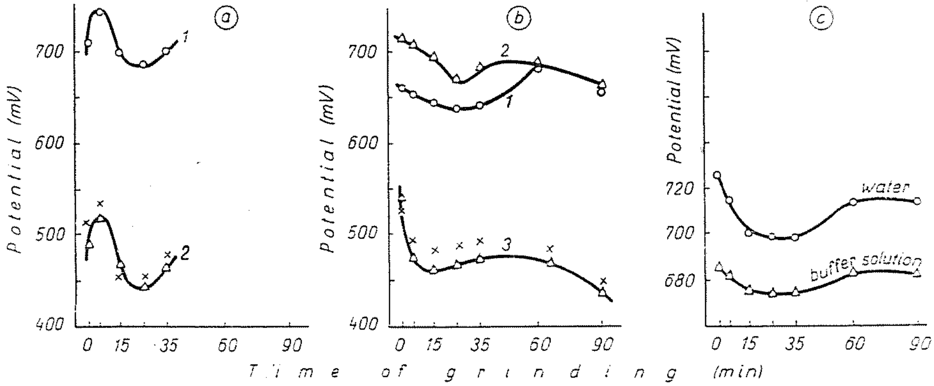

*Fig. 2/a.* The potentials of the series A samples in water (curve *1*) and in 0.01 M $NiCl_2$ measured with Ni electrodes (curve *2*)

*Fig. 2/b.* The potentials of the series B samples in water (curve *1*), in dry alcohol (curve *2*), and in 0.01 M $NiCl_2$ measured with Ni electrodes (curve *3*)

*Fig. 2/c.* The potentials of Raney-nickel samples in water and in $KH_2PO_4$—NaOH buffer (pH = 7)

The potentials of samples washed until constant potential are shown in Fig. 2/c, as measured in water (pH = 6.5) and a $KH_2PO_4$—NaOH buffer (pH = 7). The difference between the two curves is due to the pH values differing by 0.5 units.

The following is a study of the correlation between catalytic properties and the electrochemical potential measured by the above procedure.

The rates of hydrogen uptake in the presence of cyclohexene and nitrobenzene, measured simultaneously for all samples of series A in dry alcohol at atmospheric pressure and room temperature on a shaking machine, are shown in Fig. 3/a. For brevity's sake, the rate is called activity. Curve *1* in Fig. 3/b represents the excess of surface free-energy for the catalyst calculated from the EMF values according to

$$\Delta F = n \cdot 23060 \cdot E^{+} \text{ [cal/mole]}$$

where $n$ — the ion charge, and $E^{+}$ — the EMF (volts). There is no noticeable similarity to the activity curves. However, a parallelism is observed between the excess of the surface free-energy and the surface area determined by the BET method (curve *2* in Fig. 3/b).

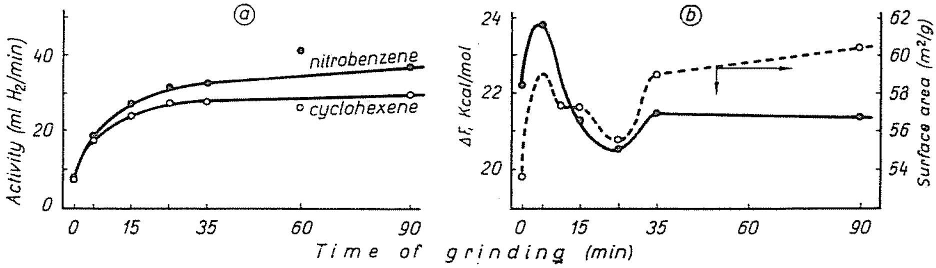

*Fig. 3/a.* The activities of series A catalyst samples in dry alcohol in the presence of cyclohexene and nitrobenzene

*Fig. 3/b.* The excess of surface free-energy (curve *1*) and the surface area determined by the BET method (curve *2*) for samples of series A

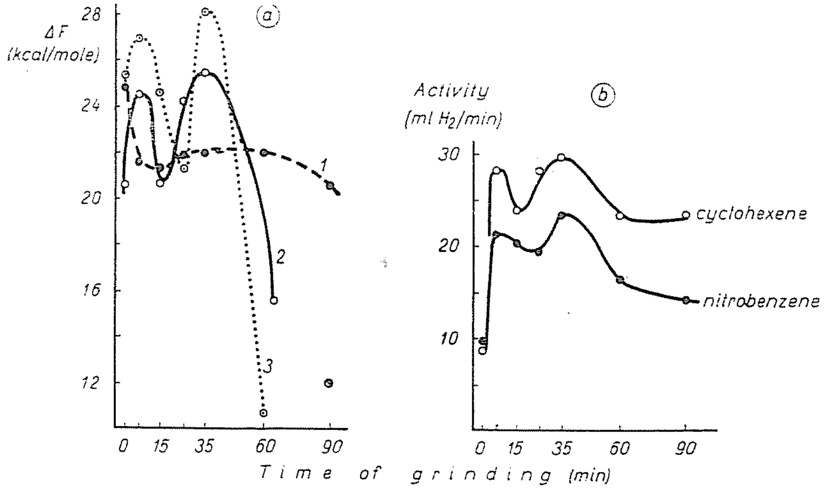

*Fig. 4/a.* Activities of the series B samples in dry alcohol in the presence of cyclohexene and nitrobenzene

*Fig. 4/b.* The excess of the surface free-energy for catalysts of series B before (curve *1*) and after hydrogenation of cyclohexene (curve *2*) and nitrobenzene (curve *3*)

The activity curves for the samples of series B in the presence of cyclohexene and nitrobenzene determined by the above procedure are shown in Fig. 4/a. Curve *1* in Fig. 4/b represents the excess of the surface free-energy. No correlation between excess surface energy or electrochemical potential shown in Fig. 2/b and activity can be observed.

In series B the reaction mixture was poured off at the end of the catalytic reduction and the catalyst samples were then washed with dry alcohol (tenfold decantation). The electrochemical potentials were measured in 0.01 M $NiCl_2$ using nickel electrodes. The excess of surface free-energy *after reduction* has been calculated from the potentials. The results are shown in Fig. 4/b, curves *2* and *3* referring to cyclohexene and nitrobenzene, respectively.

## Discussion

The following conclusions can be reached by comparing the curves in Figs 4/a and 4/b.

1) A marked parallelism is observed between the activity curves and the curves representing the *excess of surface free-energy after the catalytic reaction.* According to Dobichin and Hüttig [4, 5], the excess free-energies of catalytic surfaces are average values which also reflect energies of active sites that are of less, if any, importance in the catalytic reaction. This, presumably, is manifested in the lack of simple correlation between $\Delta F$ values and activities of freshly prepared catalyst samples. However, *during* the reaction catalytically active sites become predominant (the period of "formation" of the catalyst), and the excess of surface free-energy starts to reflect the average energy of these active sites.

2) A comparison of the $\Delta F$ curves for fresh (*1*) and used (*2*—*3*) catalysts shows that the excess of surface free-energy for coarse gained samples (larger surface area) may increase by as much as 4—6 kcal/mole, i.e. 20—30%, during reaction. The excess of surface free-energy for samples ground for 60 and 90 minutes, i.e. those with the largest surface area, can significantly decrease towards the end of the reaction, the decrease being larger with strongly oxidizing substrates. After the reduction of nitrobenzene $\Delta F$ values of 10.6 and

**Table 1**

Excess of the surface free-energy for Raney-nickel samples

| Time of grinding [min] | $\Delta F$ [kcal/mole] | | |
|---|---|---|---|
| | Fresh catalyst | After the measurement of activity | |
| | | Cyclohexene | Nitrobenzene |
| 0 | 25.0 | 20.8 | 24.9 |
| 5 | 21.9 | 24.7 | 27.0 |
| 15 | 21.5 | 20.9 | 24.6 |
| 25 | 22.0 | 24.4 | 21.7 |
| 35 | 22.0 | 25.6 | 28.1 |
| 60 | 22.0 | 15.7 | 10.6 |
| 90 | 20.6 | 23.4 | 10.0 |
| Inactive Raney-Ni | 10.2 | — | — |
| Ni powder of 99.9999% purity | 5.8 | — | — |

12 kcal/mole were measured which are very close to a value of 10.2 kcal/mole found for an inactive industrial catalyst. Under identical conditions the $\Delta F$ value for fine nickel powder of 99.9999% purity (not a catalyst) was found to be 5.8 kcal/mole (cf. *Table I*). These values are consistent with the observation that under technological conditions the reduction of nitrobenzene is optimum when coarse grained Raney-nickel (2—5 mm) is used. Nitro compounds poison (oxidize) finely ground catalysts, thus increasing the necessary amount of catalyst. On the basis of the above data, conclusions can be made whether or not a given catalyst sample is suitable for further use.

## Summary

The electrochemical potential of Raney-nickel can not be measured under conditions which would be clearly defined from an electrochemical point of view. In spite of this, data obtained with a suitable method both in water, and alcohol, can provide useful information about catalytic properties such as the excess of the surface free-energy which is related to the energy of the catalytically active sites on the surface. The problem requires further studies and is further investigated in this laboratory.

## References

1. SOKOLSKY, D. V.: Gidrirovanie v rastvorakh. Izd. A. N. Kaz. S. S. R., Alma-Ata. 1962.
2. NAGY, F., TELCS, I., HORÁNYI, GY.: Acta Chim. Hung. **37**, 295 (1963).
3. HÜTTIG, G. F., HERMANN, E.: Z. anorg. Chem. **247**, 221, 1941.
4. DOBICHIN, D. P.: Problemy kinetiki i kataliza, Izd. A. N. U. S. S. R., V, 1948.
5. HÜTTIG, G. F.: Handbuch der Katalyse VI. 318. Springer Verlag, Wien 1943.

Prof. Dr. Zoltán CSŰRÖS
Dr. József PETRÓ
Éva POLYÁNSZKY

Budapest, XI., Műegyetem rkp. 3. Hungary