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Electrochemical Study of Palladium Powder Catalysts

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Electrochemical studies on the palladium–hydrogen system are described. The objective was to extend the potentiodynamic method, used so far with compact electrodes, to powder catalysts. The palladium catalyst was prepared by reduction with hydrogen, formic acid, formaldehyde, or sodium borohydride. The amount and nature of hydrogen sorbed on the catalyst was studied using galvanostatic and potentiodynamic methods, in various electrolytes. By selecting appropriate conditions of sample weight and rate of potential change, potentiodynamic measurements were extended to the dissolved hydrogen range hitherto uninvestigated on palladium. It is shown that the shape of the potentiodynamic curves and the number of hydrogen maxima depend on the age of the catalyst and on the electrolyte. The mode of catalyst preparation affects the ratio of adsorbed and dissolved hydrogen but has no effect on the position and shape of the characteristic peaks.

INTRODUCTION

Some very exact physico-chemical methods are now known for investigating the surface and active centers of catalytically active solids. However, many of these are suited only for the study of single crystals, whereas most "living" catalysts are polycrystalline substances. Furthermore, many of the new methods require pretreatments (e.g., gas removal in high vacuum by heating, irradiation, etc.) that may also change structural and catalytic properties of the "living" polycrystalline catalyst. In the case of metals, the application of electrochemical methods is useful, even though the results obtained are related to the state of the metal surface only indirectly. By studying the amount and nature of hydrogen on metal catalysts, indirect information on active centers is obtained. Some modification in the catalyst structure can take place during the electrochemical measurement, but it is a fact that even after finishing the measurement the catalyst is still "living", that is, it is active or can be activated very easily.

For studying hydrogen sorption on metal electrodes, galvanostatic and potentiodynamic methods are now being widely used. Many researchers have investigated noble metal catalysts in great detail using galvanostatic methods. Thus Burstein and co-workers (*1*) have measured hydrogen and oxygen adsorption on palladium and the effect of the electrolyte on the shape of the charge curve. Up to now, however, potentiodynamic polarization has mainly been used for studying compact electrodes. Our objective was to extend these measurements to powder catalysts. We already succeeded in carrying out such measurements on dispersed platinum (*2*). In this paper we report studies related to the palladium–hydrogen system which was found to be much more problematic. Particular stress was laid on the region of dissolved hydrogen. This has not yet been studied by potentiodynamic methods even with compact electrodes.

Potentiodynamic measurements on smooth or black electrodes, because of the large amounts of hydrogen dissolved in the palladium, are either carried out by polarizing at such high rates of potential change that absorption cannot take place (*3*, *4*), or polarization is started from 120–150 mV (*5–8*).

Will (*3*), Tarasewich (*4*, *5*), and Rubeš (*6*) and their co-workers, working with smooth and black palladium electrodes, found that adsorbed hydrogen was homogeneous in sulphuric acid and in potassium hydroxide. Sokolsky and co-workers (*7*), working with a black electrode, succeeded, by raising the temperature from 20 to 60°C, to separate the single, broad hydrogen peak appearing at 0.26 V into two sharply distinguishable peaks at 0.22 and 0.28 V. Khomchenko and co-workers (*8*) found three maxima above 150 mV on a black electrode in 1 *N* sulphuric acid (175, 255, and 285 mV, respectively).

EXPERIMENTAL

Catalyst Preparation

Palladium catalysts were prepared by reduction with formic acid, hydrogen, sodium borohydride, or formaldehyde.

The reagents used were analytical grade. Distilled water was used. Preliminary purification of Pd was carried out by twice-repeated precipitation with dimethylglyoxime and digestion. In this manner, impurities could be reduced to a level below 0.1%.

Reduction with formic acid. The pH value of 200 ml of a H_2PdCl_4 solution containing about 2 g of palladium was adjusted to 4–5 using a 20% NaOH solution. Twenty milliliters of concentrated HCOOH were added under agitation, and the pH was adjusted to 8–9 with NaOH. A further 10 ml of concentrated HCOOH was added in order to compact the catalyst by means of the hydrogen evolved. The substance obtained was filtered, washed with 500 ml of distilled water, 300 ml of 0.2 *N* sulphuric acid, and about 4 liters of distilled water, and it was dried at 105°C to constant weight.

Reduction with hydrogen. To a solution of 55 g of $NaHCO_3$ in 1500 ml of distilled water at 60°C, 300 ml of a H_2PdCl_4 solution containing 10.5 g of Pd were added in the course of 2–3 min under agitation. The pH value of the $NaHCO_3$ solution was initially 8.5–9.0 and became 8.0–8.5 after the addition. The mixture was intensely agitated for 0.5 hr at 60–62°C and subsequently hydrogenated at a pressure of 1 atm. The substance was decanted and filtered, washed for 4 hr with 2 liters of distilled water, and dried to constant weight in a vacuum desiccator at ambient temperature.

Reduction with sodium borohydride. Five-hundred milliliters of an aqueous H_2PdCl_4 solution containing 1 g of Pd were neutralized with 1 *N* NaOH, and the solution of 2.25 g of $NaBH_4$ in 25 ml of water was added under agitation at 20–25°C. The catalyst was filtered off, washed for 3 hr with about 3 liters of distilled water, and dried to constant weight in a vacuum desiccator at ambient temperature.

Reduction with formaldehyde. Twenty-five milliliters of a 35% formaldehyde solution were added to 100 ml of a H_2PdCl_4 solution containing 5 g of Pd, and a solution of 40 g of NaOH in 50 ml of distilled water was added dropwise in the course of 50 min at 50°C. Subsequently the mixture was kept at 60°C for 15 min. The catalyst was filtered off, washed for 2 hr with about 2.5 liters of distilled water, and dried to constant weight in a vacuum desiccator at ambient temperature.

Galvanostatic Measurements

The three-electrode polarizing cell reported in an earlier paper (*9*) was employed. The measuring electrode and the polarizing electrode are made of platinum sheet, while the reference electrode is platinized Pt/H_2. A Luggin capillary stretches from the reference electrode to the catalyst powder, which was placed on the horizontal Pt sheet polarizing electrode.

The charge curves were obtained with 10 mg of catalyst at ambient temperature, in solutions of analytical grade 1 *N* perchloric acid, 1 *N* sulphuric acid, 1 *N* sodium hydroxide, and 5 *N* potassium hydroxide at a current of 2.5 mA.

The samples stored in air adsorbed oxygen. Therefore we first saturated the catalyst with hydrogen by cathodic polarization and subsequently recorded the anodic curve.

Potentiodynamic Measurements

The same cell was used as in the galvanostatic measurements. The three electrodes were connected to an AMEL potentiostat which, following a preset program, automatically changed the potential of the measuring electrode against that of the reference electrode.

The tested electrolytes were 1 *N* sulphuric acid, 1 *N* hydrochloric acid, 1 *N* perchloric acid, and 5 *N* potassium hydroxide. The measurements were made at ambient temperature, with 1–3 mg of catalyst.

RESULTS AND DISCUSSION

In our galvanostatic and potentiodynamic studies, we primarily investigated hydrogen sorption on palladium catalysts obtained using different methods of preparation. From galvanostatic results we determined the amount of hydrogen sorbed on the catalyst and the surface area, while potentiodynamic results were used to attempt to draw conclusions on the nature of the hydrogen sorbed.

In plotting the *galvanostatic* curves, resistance polarization (determined by the current break method) was taken into account. The part of the curve below 50 mV was obtained by extrapolation.

TABLE 1

Galvanostatic Study of Catalysts Prepared with Different Reducing Agents

Reducing agent	Electrolyte	V_{total} (cm³/g)	V_{ads} (cm³/g)	V_{diss} (cm³/g)	F_H (m²/g)
HCOOH	1 *N* H_2SO_4	78.9	6.2	72.7	25
H_2	1 *N* H_2SO_4	89.4	17.0	72.4	69
	1 *N* NaOH	99.8	12.9	86.9	52
$NaBH_4$	1 *N* H_2SO_4	60.6	12.6	48.0	51
	1 *N* $HClO_4$	48.6	9.4	39.2	38
	5 *N* KOH	52.3	7.3	45.0	30
HCHO	1 *N* H_2SO_4	64.0	3.8	60.2	15
	1 *N* $HClO_4$	56.5	3.0	53.5	12

For determining the amount of adsorbed hydrogen, we adopted the method proposed by Burstein *et al.* (*1*), according to whom adsorption on palladium is negligible as compared to the large amount of dissolved hydrogen in the range of 0–90 mV, whereas dissolved hydrogen can be neglected in the range of 90 to 300–400 mV. Hence we assumed the first wave of the charge curve to be proportional to dissolved hydrogen, and the second to adsorbed hydrogen. We also used this approach in the following for dividing the hydrogen range into two parts. This does not, however, imply that no adsorption occurs in the so-called "dissolved hydrogen" range, and vice versa.

From the knowledge of the amount of adsorbed hydrogen, the surface area was calculated by means of the usual assumptions (*10*).

Amounts of hydrogen sorbed and surface areas determined from the charge curves measured in 1 *N* sulphuric acid, 1 *N* perchloric acid, 1 *N* sodium hydroxide, and 5 *N* potassium hydroxide, with the four catalysts prepared with different reducing agents, are summarized in Table 1.

The data in the table indicate that the amounts of hydrogen and the surface areas obtained from galvanostatic measurement data depend very much on the nature of the electrolyte. One of the reasons for this

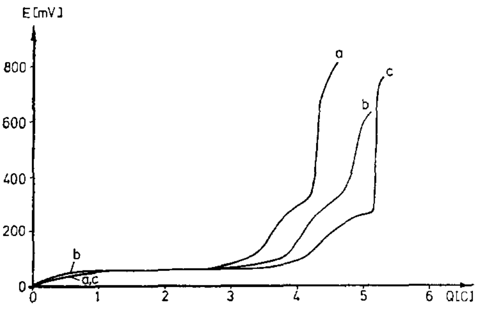

FIG. 1. Galvanostatic curves of catalyst prepared with sodium borohydride ($m = 10$ mg, current $= 2.5$ mA). (a), 1 N perchloric acid; (b), 5 N potassium hydroxide; and (c), 1 N sulphuric acid.

is presumably the inaccuracy of the approach used to distinguish between dissolved and adsorbed hydrogen. This dependence is clearly demonstrated in Fig. 1, representing the charge curves of the catalyst prepared by reduction with sodium borohydride measured in 1 N sulphuric acid, 1 N perchloric acid, and 5 N potassium hydroxide. Hence, only measurements in one and the same electrolyte are suited for comparisons of hydrogen contents in catalysts prepared in different ways.

Galvanostatic studies carried out in 1 N sulphuric acid indicate the following sequence of catalyst surface areas depending on the reducing agent: $H_2 > NaBH_4 > HCOOH > HCHO$. This sequence of active surface area is probably due, among other factors, to the effect of the deposited decomposition products of the reducing agents.

TABLE 2

Potentiodynamic Study of Catalysts Prepared with Different Reducing Agents

Reducing agent	Electrolyte	Location of peaks in the hydrogen range mV
HCOOH	1 N H_2SO_4 1 N HCl	60,[a] 165, 255, 265[b] 60, 150
H_2	1 N H_2SO_4 1 N HCl	60,[a] 170, 255, 265[b] 60, 150
$NaBH_4$	1 N H_2SO_4 1 N $HClO_4$	65, 75,[b] 180, 265 65, 75,[b] 180,[b] 290
HCHO	1 N H_2SO_4 1 N $HClO_4$	65, 75,[b] 160, 265 65, 75,[b] 180, 295

[a] The position of the shoulder could not be located.

[b] Shoulder instead of peak.

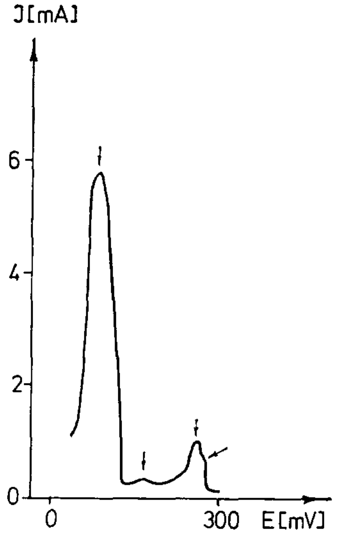

FIG. 2. Potentiodynamic curve of catalyst prepared by hydrogenation. Electrolyte, 1 N sulphuric acid; voltage = 100 mV/min; $m \cong 1$ mg.

In earlier studies, researchers did not succeed in carrying out *potentiodynamic* measurements with palladium electrodes in the dissolved hydrogen range. In our opinion, their failure was due to excessively large quantities of palladium (and, hence, of dissolved hydrogen) and to relatively high rates of potential change.

Our studies on platinum catalysts (*2*) demonstrated that, with powder catalysts, the rate of potential change must be significantly reduced as compared to the rate used for the polarization of compact electrodes. In the present measurements with palladium powder catalysts, the rate was further reduced and very small amounts of catalyst (1–3 mg) were used. In this manner, we succeeded in performing measurements over the total hydrogen range.

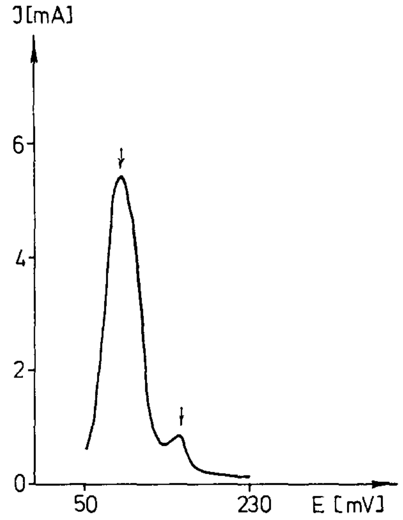

FIG. 3. Potentiodynamic curve of catalyst prepared by hydrogenation. Electrolyte, 1 N hydrochloric acid; voltage = 50 mV/min; $m \cong 1$ mg.

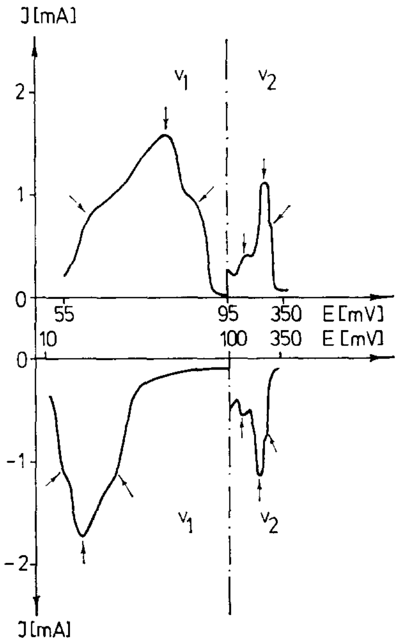

FIG. 4. Potentiodynamic curve of catalyst prepared by hydrogenation. Electrolyte, 1 N sulphuric acid; $v_1 = 10$ mV/min; $v_2 = 100$ mV/min; $m \cong 1$ mg.

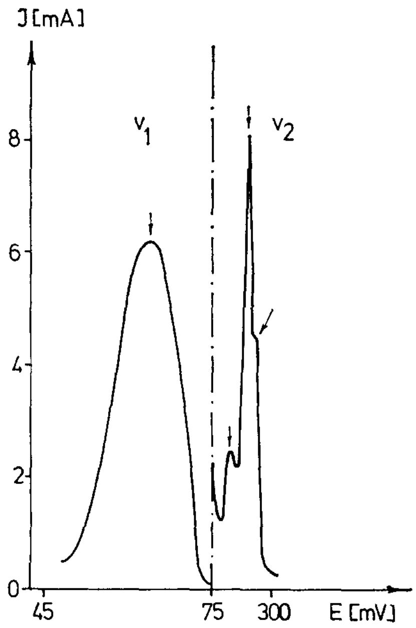

FIG. 5. Potentiodynamic curve of catalyst prepared by hydrogenation, 1 month after preparation. Electrolyte, 1 N sulphuric acid; $v_1 = 2$ mV/min; $v_2 = 50$ mV/min; $m \cong 3$ mg.

In determining the potential values belonging to individual maxima, we started from the observation of Will and Knorr (*3*) who found that, on platinum, the potential corresponding to maximum hydrogen ionization is independent of the rate of potential change, provided that the latter is relatively small as compared to the rate constants of the reaction in both directions. Presuming that this is true for palladium too, the curves used for determining the potentials belonging to individual hydrogen peaks were measured at rates of potential change that were reduced to the required extent. In the marginal cases the difference between the potentials of the anodic and cathodic peaks was 5–15 mV. The approximate value of the ohmic potential drop was considered in the determination of the peak potentials by using the current break method.

The results obtained with our different catalysts in different electrolytes are summarized in Table 2.

Polarization was carried out in two modes: either in the usual manner, at a relatively great rate of potential change, from about 50 mV up to the double layer

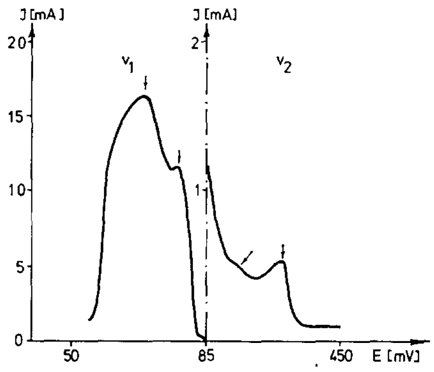

FIG. 6. Potentiodynamic curve of catalyst prepared with formaldehyde. Electrolyte, 1 *N* perchloric acid; v_1 = 2 mV/min, v_2 = 100 mV/min; $m \cong 2$ mg.

region (Figs. 2 and 3) or, after removing at low rate the major part of the dissolved hydrogen, at an increased rate of potential change up to 300–500 mV. In the latter case, adsorbed hydrogen was, as it were, magnified as compared to dissolved hydrogen (Figs. 4–7).

The dissolved hydrogen peak could be observed on all catalysts and in all four electrolytes between 60 and 65 mV (in 5 *N* potassium hydroxide (Fig. 7) the peak could not exactly be determined with the method mentioned above of initially reducing the rate of the potential change, owing to high resistance polarization). In sulphuric acid and perchloric acid, the single peak was split into two, only slightly separated maxima by selecting appropriate experimental conditions (Fig. 6). With the catalyst prepared by reduction with hydrogen, even a third maximum can be well discerned (Fig. 4). Splitting of the dissolved hydrogen peak can be detected not only on the anodic curve but also on the cathodic curve.

It is interesting to note that about 1 month after catalyst preparation, only a single dissolved hydrogen maximum could be detected at 60–65 mV with all catalysts (Fig. 5).

Splitting of the peak obtained between 0 and 150 mV can be explained by two assumptions: On the one hand, our approach that adsorption is negligible in this range may be erroneous, and, on the other hand, it is conceivable that dissolved hydrogen is not homogeneous energetically. This phenomenon had not hitherto been observed in studies of the palladium–hydrogen system.

Our results obtained above 100 mV in 1 *N* sulphuric acid are partly in agreement with data reported in the literature concerning black electrodes (*8*). With palladium catalysts obtained by reduction with hydrogen or formic acid, three peaks were found, whereas with the other two catalysts only two peaks or shoulders could be distinguished.

Similar to sulphate, the perchlorate anion is weakly adsorbed below 300 mV, and, correspondingly, hydrogen adsorption in 1 *N* perchloric acid and 1 *N* sulphuric acid is largely similar with respect to number, position, and proportion of peaks. In 1 *N* hydrochloric acid, however, a single adsorption maximum could only be detected at 150 mV, in agreement with the concept that chloride ions, being more strongly adsorbed, will displace hydrogen with higher bond energy (*1*). In 5 *N* potassium hydroxide, adsorption of two hydrogen species was observed at higher potentials than those measured in perchloric acid, since sorption of hydroxide

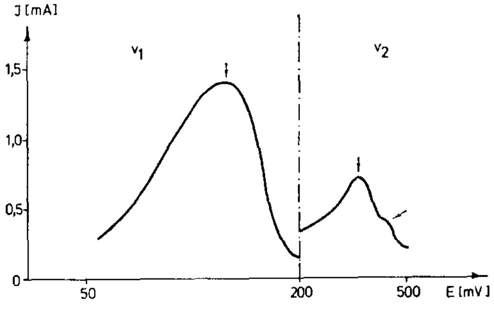

FIG. 7. Potentiodynamic curve of catalyst prepared with formaldehyde. Electrolyte, 5 *N* potassium hydroxide; v_1 = 5 mV/min; v_2 = 100 mV/min; $m \cong 1$ mg.

groups will primarily affect adsorption of weakly bound hydrogen.

Catalysts prepared in different ways yielded essentially identical results in identical electrolytes as to the nature of the sorbed hydrogen, except for some maxima difficult to separate (e.g., in sulphuric acid, the smaller maximum at 265 mV could be separated from the sharp peak at 255 mV only for the catalysts reduced with hydrogen or formic acid).

CONCLUSIONS

Potentiodynamic polarization, a method that has proved very satisfactory for studying smooth and black palladium electrodes, was extended, by selecting appropriate experimental conditions, to studies of palladium powder catalysts.

The range below 500 mV (the so-called hydrogen range) of the potentiodynamic curve was studied in detail. The qualitative results obtained on hydrogen sorption were complemented by quantitative data obtained from galvanostatic curves.

In the range below 100 mV, hitherto not studied potentiodynamically on palladium, two or three maxima were found which could not be completely separated. Ageing of the catalyst resulted in the disappearance of the multiple character. The presence of several peaks in the dissolved hydrogen range may be attributed to the presence of low bond energy adsorption besides absorption or to dissolution at sites with different energies.

Results obtained in the adsorbed hydrogen range were similar to those reported in the literature on black electrodes.

The curves obtained in different electrolytes greatly differ, owing to ion adsorption. The mode of preparation of the catalyst did not essentially change the potential dependence of hydrogen sorption, i.e. its nature, but affected quantitative relations.

The most detailed splitting-up of hydrogen peaks (six in all) was obtained with the catalyst prepared by hydrogenation, with measurements in 1 *N* sulphuric acid.

REFERENCES

1. Burstein, R. H., Vilinskaya, V. S., and Tarasevich, M. R., *Elektrokhimiya* **3**, 349 (1967); **6**, 1497 (1970).
2. Petró, J., and Polyánszky, É., *Acta Chim. Hung.*, **87**, 385 (1975).
3. Will, F. G., and Knorr, C. A., *Z. Elektrochem.* **64**, 258; 270 (1960).
4. Vilinskaya, V. S., Lentsner, B. I., Knots, L. L., and Tarasevich, M. R., *Elektrokhimiya* **7**, 1763 (1971).
5. Tarasevich, M. R., Vilinskaya, V. S., and Burstein, R. H., *Elektrokhimiya* **7**, 1200 (1971).
6. Rubeš, I., and Bilyková, H., *Collect. Czech. Chem. Commun.* **37**, 715 (1972).
7. Churina, D. H., Zakumbaeva, G. D., and Sokolsky, D. V., *Elektrokhimiya* **6**, 1039 (1970).
8. Shcherev, G. I., Glozhashka, Zh. D., and Khomchenko, G. P., "Kataliticheskie reaktsii v zhidkoy faze," (Tr. Vses. Konf. Katal. Reakts. v Zhidk. Faze), p. 137. Izd. Nauka Kazakhshkoy S. S. R., Alma Ata, 1972.
9. Petró, J., Polyánszky, É., and Csürös, Z., *J. Catal.* **35**, 289 (1974).
10. Sokolsky, D. V., "Gidrirovanie v rastvorakh." Izd. Akad. Nauk Kazakhskoy S. S. R., Alma Ata, 1962.