CHARGING CURVES OF METALLIC POWDERS IN DIELECTRIC MEDIA

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One of the most widespread methods of studying the sorption properties of compact electrodes and dispersed catalysts with respect to electromotor-active gases in solutions of electrolytes, is the recording of the curves of charging of polarization by electric current or by unsaturated organic substances [1-4]. And yet, the hydrogenation of organic compounds is frequently conducted in dielectric media, the low conductivity of which has made it impossible to use potentiometry to investigate the sorption properties of powdered catalysts (for information on a conductometric study of metallic suspensions in hydrocarbons, see [2]).

Recently the authors succeeded in developing an essentially new method of measuring the potential of dispersed catalysts in liquid dielectrics [5-7]. In this work, the indicated method is used to take the polarization curves of platinum and palladium blacks and skeletal nickel with dimethylethynylcarbinol (DMEC) and p-benzoquinone in 0.1 N HCl and H_2SO_4, benzene and n-heptane. The potential of the suspension was measured with electrodes (1e and 1d), the design of which was described in detail in [7]. After saturation of the powder with hydrogen, the potential [9] was displaced with argon to 0.050-0.063 V (Pt) or 0.025-0.040 V (Pd, Ni). A solution of the unsaturated compound was dropped at a constant rate into the reaction vessel, which was constantly shaken [2,3].

Charging curves of platinum black in standard solutions of electrolyte [1] were preliminarily recorded with electrode 1d [7]. Figure 1 presents curves of $\varphi(Q)$ and $\varphi(\tau)$, where Q is the amount of electricity passed through,† τ is the time for Pt black in 0.1 N HCl and H_2SO_4 (20°C). The region of the electrical double layer on the polarization curve in 0.1 N H_2SO_4 (Fig. 1, curve 5, portion B) begins at 0.29 V (in 0.1 N HCl, 0.20 V) and ends at 0.68 V. The coincidence of curves 2 and 3, as well as the comparatively small hysteresis loop (see [7], Fig. 1b), is evidence that the desorption of hydrogen proceeds on an equilibrium basis. Moreover, the deviation of the polarization in the hydrogen region (Fig. 1, portion A) leads to a change in the potential of no more than 0.010 in 60 min.

The shape of the curves of $\varphi(Q)$ is identical with the charging curves described in the literature, recorded by polarization of platinized platinum or platinum black with current or unsaturated organic substances [1,2].

Figure 1b shows the forward and reverse paths of the curve of $\varphi(\tau)$ in n-heptane in anodic polarization with p-benzoquinone and cathodic polarization with a mixture of H_2: Ar (8 vol. % H_2). The nature of the curves of $\varphi(\tau)$ in electrolytes and dielectrics is practically the same (cf. curves 6 and 7), and therefore the latter may be considered as charging curves. When 0.1 N HCl is replaced by n-heptane, the extent of the portions A and B is somewhat changed, which is due to the influence of the solvent on the sorption properties of the catalyst.

An investigation of a skeletal nickel catalyst by the method of charging curves in electrolytes is hindered as a result of the easy oxidizability of metallic nickel in the region of anodic potential. In view of this, the results of different authors are ambiguous and contradictory [4,8-13].

The catalyst was prepared by leaching of powdered Ni—Al, an alloy (28% by weight Ni) consisting of $NiAl_3$ and Al [14]. The nickel content was determined according to the difference in the weight of the samples before and after leaching and practically coincides with the results of chemical analysis. In these experiments the potential of the powders was measured with electrode 1e [7]. It was found that at a rate of removal of hydrogen less than 0.08 ml/min, the curves coincide (Fig. 2). A cessation of polarization on the portion A leads to a shift of the potential by 0.008 V in 30 min. The charging curves of skeletal nickel in n-heptane and benzene are the same (Fig. 3, curves 3 and 4).

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†The amount of the unsaturated substance introduced was converted to electrical units according to Faraday's law.

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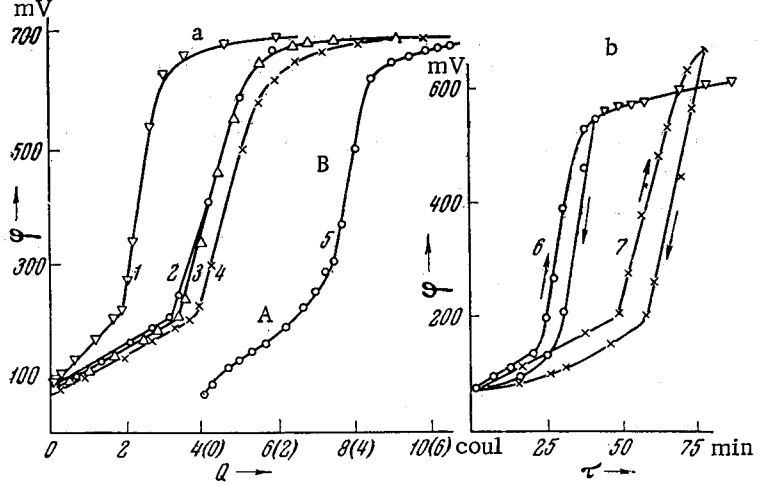

Fig. 1. Charging curves of platinum black in anodic polarization with p-benzoquinone. a) 0.1 N HCl (1-4); 0.1 N H_2SO_4 (5); b) n-heptane (6); 0.1 N HCl (7). Rate of removal of hydrogen: 1) 0.0018; 2) 0.0085; 3) 0.0044; 4) 0.0180; 5-7) 0.0085 ml H_2 per min.

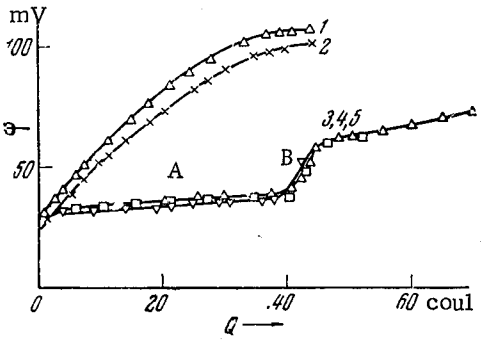

Fig. 2. Charging curves of a skeletal nickel catalyst with a solution of DMEC in benzene. Rate of removal of hydrogen: 1) 0.11; 2) 0.08; 3) 0.06; 4) 0.04; 5) 0.02 ml H_2 per min.

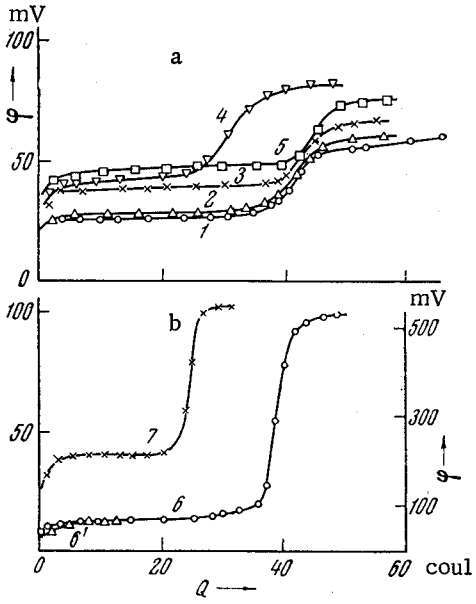

Fig. 3. Charging curves of skeletal nickel (1-6) and palladium black (7) with a solution of DMEC in benzene (1-4,7) and n-heptane (6 and 6'). 1-5) 0.13 g; 6,7) 0.10 g of catalyst.

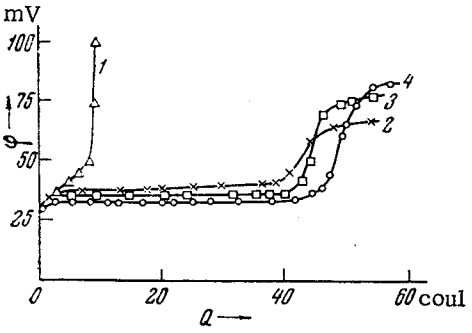

Fig. 4. Influence of temperature on the shape of the charging curve of a skeletal nickel catalyst in benzene in the case of polarization by DMEC: 1) 10°; 2) 20°; 3) 30°; 4) 40°.

When the initial potential varied from 0.025 to 0.040 V, the shape of the curves is unchanged (Fig. 3a). After a portion practically parallel to the x-axis, the potential is shifted in the positive direction, while analysis shows the appearance of unsaturated compound in solution. Figure 3b depicts the charging curves of a skeletal nickel catalyst (6) and palladium black (7), taken with electrode 1d. The shape of the curve of $\varphi(Q)$ for palladium is similar to that described in the literature [2,15]. Variation of the rate of removal of hydrogen from Ni with p-benzoquinone within the interval 0.0166 (not shown on the figure) to 0.0017 ml H_2 in 1 min (curve 6') enables us to find conditions under which desorption occurs on an equilibrium basis. In the first case, unique "harmonics" of the oscillations of the potential, previously

observed in aqueous and aqueous-organic media [2,3], are obtained; curves 6 (0.0040 ml H_2 in 1 min) and 6' coincide.

Replacement of DMEC by a compound with a higher redox potential, p-benzoquinone, increases the extent of the hydrogen region and of portion B. When the potential of the catalyst is measured with a platinized electrode 1e, the value Q still increases somewhat as a result of parallel desorption from the platinum applied to the surface of the glass to increase the rate of reaching of electrochemical equilibrium [6,7].

The charging curve at 10° is characterized by the absence of a portion parallel to the x-axis (Fig. 4). With increasing temperature, the amount of desorbed hydrogen increases.

Thus, the method developed permits a successful study of the sorption properties of powders in dielectrics, which is especially important in the case of readily oxidized catalysts.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
