CHARGING CURVES OF POWDERED CATALYSTS AND ADSORBENTS

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Up to now, the method of charging curves, which was proposed by A. I. Shlygin and A. N. Frumkin [1], has only been used for studying the properties of metals in the compact state. There is definite interest in the application of this method to the study of powdered catalysts and adsorbents, as the latter are widely used in industry. For the solution of this problem, we developed and used two procedures [2]. In the first of these, which we called the "sieve method," a sample of powder was introduced into a fine platinum sieve in a cell for obtaining charging curves, which were plotted by the usual method [3]. We used the "sieve method" for studying the properties of platinum and palladium blacks and Raney nickel.

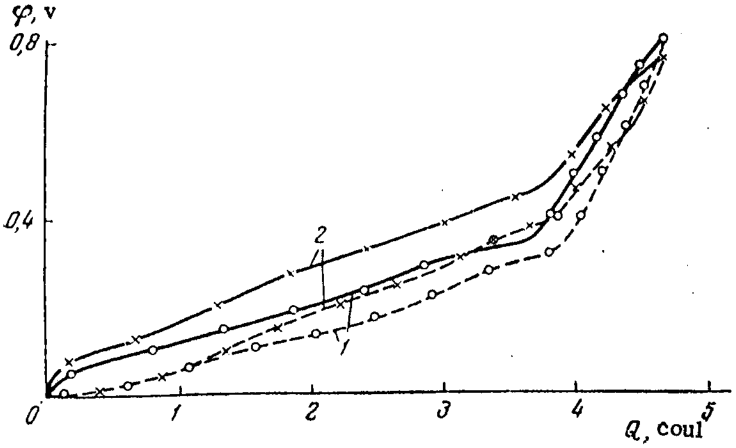

Fig. 1. Charging curves of platinum black. 1) In 0.1 N H_2SO_4 2) in 0.1 N NaOH.

Figure 1 shows charging curves of 0.1 g of platinum black in 0.1 N H_2SO_4 and 0.1 N NaOH. (In this figure and all subsequent ones showing charging curves, the amount of electricity Q is plotted along the abscissa and the potential relative to a reversible hydrogen electrode, φ, along the ordinate.) As Fig. 1 shows, the curves obtained do not differ in principle from the corresponding charging curves of platinized platinum (broken lines). The surface of freshly prepared disperse platinum precipitates, calculated from the slope of the charging curve in the zone of the double layer, was found to equal 40-45 m^2/g.

Figure 2 shows charging curves of 0.1 g of palladium black (solid line) and a palladized electrode (broken line) in 0.1 N H_2SO_4. A comparison of the curves shows that while the properties dependent on the over-all mass of the precipitate remain unchanged (for example, the adsorption capacity for hydrogen), the properties dependent on the surface atoms differ substantially; palladium black has a much greater surface (of the order of 65 m^2/g) and there is also considerable adsorption of oxygen (1 oxygen atom per surface palladium atom), which is not characteristic of palladized electrodes [4, 5].

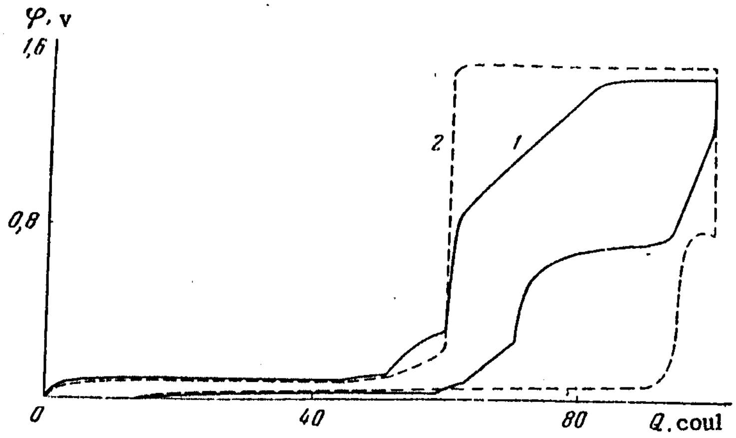

Fig. 2. Charging curves of palladium in 0.1 N H_2SO_4. 1) Palladium black (solid line); 2) palladized electrode (broken line).

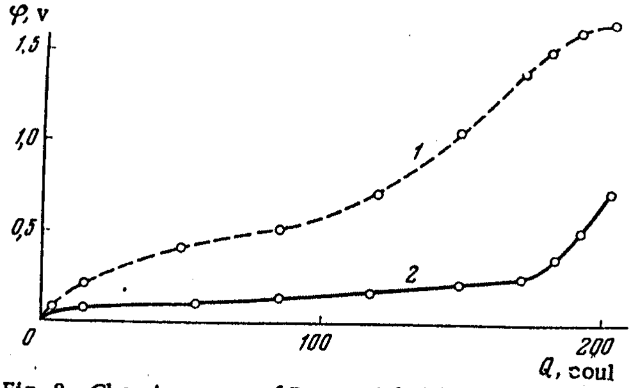

Fig. 3. Charging curve of Raney nickel in 0.1 N NaOH. 1) Nonequilibrium curve; 2) equilibrium curve.

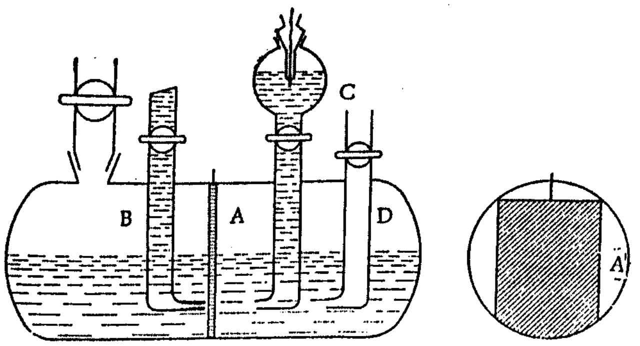

Fig. 4. Vessel for obtaining charging curves by the "impact method." A) Smooth platinum electrode; B) electrolytic connection to comparison electrode; C) auxiliary electrode for polarization; D) inlet for introducing gases into the system.

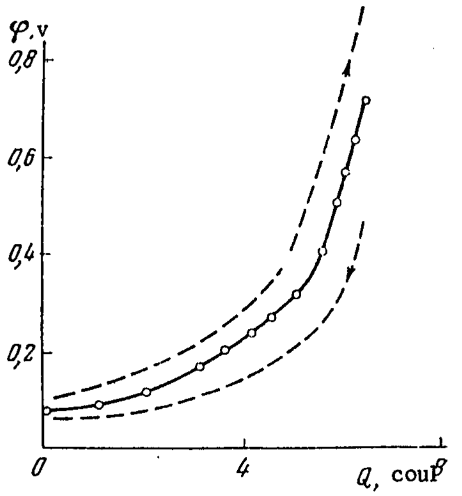

Fig. 5. Charging curve of platinum black obtained by the "impact method."

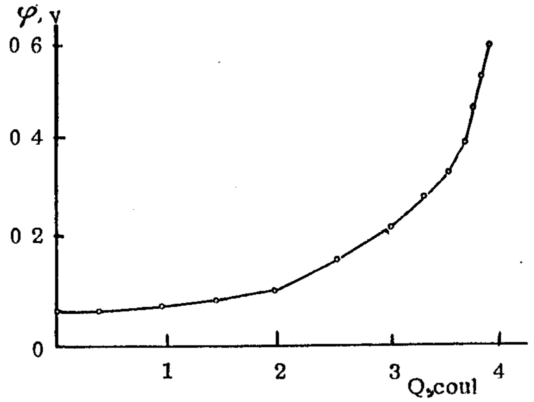

Fig. 6. Charging curve of platinized silica gel in 0.1 N H_2SO_4.

Figure 3 shows the equilibrium charging curve of 0.1 g of Raney nickel in 0.1 N NaOH. From this curve it was found that in freshly prepared Raney nickel the ratio between the number of atoms of nickel and adsorbed hydrogen equals 1 : 1.

In the second method, which we called the "impact method," the charging of the powder particles is achieved as a result of continuous impacts of the latter against a large smooth platinum electrode, polarized by an external current [2]. D. V. Sokol'skii and V. A. Druz' were the first to use in their investigations the possibility of imposing the potential of a powder suspended in an electrolyte onto an arbitrary electrode (immersed in the electrolyte) by shaking the system [6]. In our work [7] it was shown that the reliability of the measurement of the powder potential depends on the experimental conditions (amount of powder in the system, shaking intensity, etc.).

Charging curves were plotted by the "impact method" in the vessel illustrated in Fig. 4. The charging curve of 0.15 g of platinum black, obtained by this method in 0.1 N H_2SO_4 with shaking at a thousand unidirectional vibrations per minute with an amplitude of 30 mm, is shown in Fig. 5. The broken lines show polarization curves with a charging current strength of 1 ma, while the solid line shows the equilibrium charging curve of platinum black. The equilibrium curve is essentially identical to the charging curves of platinum black studied by the "sieve method" and platinized platinum, differing from the latter in a somewhat greater surface, corresponding to 50 m^2/g.*

In principle, the "impact method" offers the possibility of investigating metals deposited on carriers of a nonmetallic nature. In actual fact, with intensive shaking the particle of a catalyst may strike the polarized electrode with various parts of its surface, including those on which the metallic phase is deposited, and consequently the latter may be charged.

For the investigation we used platinized silica gel with 50% of the surface, covered with platinum on which a further 0.0472 g of platinum was deposited by reduction of chloroplatinate in a hydrogen atmosphere (weight of original silica gel 0.2253 g) for further coarsening and consolidation of the disconnected particles of the metallic phase. The charging curve obtained in 0.1 N H_2SO_4 is shown in Fig. 6. From the slope of the curve in the region of the double layer, the surface of the platinum on the given sample was found to equal 3.47 m^2, which gives a value of the order of 24 m^2 per g of platinum on the silica gel (under the experimental conditions).

In our opinion, the mechanism of charging of powder particles by the "impact method" consists of the transfer of electrons from the particles to the polarized electrode (or, the reverse, depending on the sign of the polarization) by a tunnel mechanism.

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* When our work was complete, there appeared in the press the work of D. V. Sokol'skii and Yu. P. Skopina [8], which was carried out by a method similar to the "impact method." The authors found the surface of 1 g of platinum black to equal 260 m^2/g.

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