A DIRECT METHOD FOR THE STUDY OF THE ADSORPTION OF HYDROGEN ON ELECTRODES, AND ITS APPLICATION TO TUNGSTEN CARBIDE

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On the basis of the electrocatalytic activity of tungsten carbide in the ionization of molecular hydrogen [1], the reversibility of the charging curve as far as 0.4 V, and the large total specific charge, it has been suggested [2, 3] that hydrogen undergoes chemisorption on WC. In [4] this suggestion was confirmed by the direct thermal desorption of hydrogen from tungsten carbide in H_2SO_4 solution. These last measurements were not carried out very rigorously, however, so that only approximate data were obtained on the quantity of adsorbed hydrogen, and these data relate only to a potential close to $\varphi_r = 0$. The errors in the thermal desorption determinations were associated chiefly with the fact that the passage of gaseous hydrogen for the saturation of tungsten carbide and the subsequent removal of hydrogen from the cell by means of an inert gas were carried out without objective control of the degree of saturation of the surface with hydrogen, and the only conditions observed were that the time taken for these operations was approximately the same as in the charging-curves method.

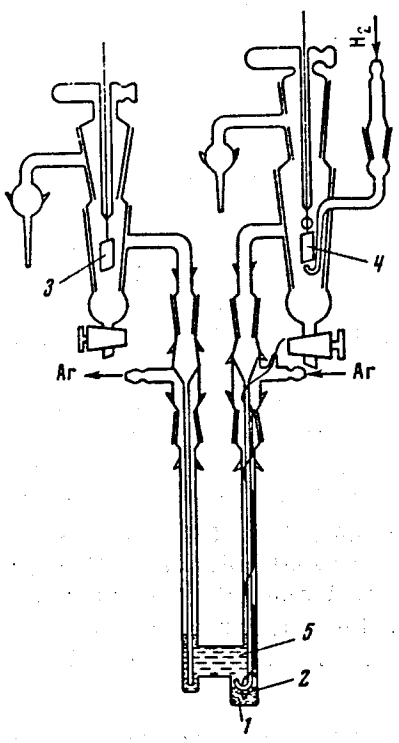


Fig. 1. Cell for thermal desorption with an electrolyte: 1) catalyst being studied; 2) platinum contact; 3) auxiliary electrode; 4) reference electrode; 5) electrolyte.

We recently developed a method for the thermal desorption of hydrogen in the presence of an electrolyte at any given potential. The construction of the cell is shown in Fig. 1. This three-electrode cell does not differ fundamentally from the usual electrochemical cell; the only difference is that it is elongated considerably in a vertical direction, so that the lower part can be heated to a temperature of several hundred degrees without heating the upper part. The required potential is applied by means of a potentiostat to the electrode catalyst for a time interval required for the establishment of equilibrium. An inert gas, thoroughly purified from oxygen, is passed through the cell at a low rate. The potentiostat is then disconnected, and from this moment all the gas leaving the cell when its lower part is heated is collected. The final temperature of the thermal desorption and the time required for complete desorption are established experimentally. When the thermal desorption is complete, the collected gas is analyzed quantitatively for its hydrogen concentration; this can be very conveniently carried out by a chromatographic method.

It is possible to record directly on the chromatograph the hydrogen desorbed when the cell is heated, as is done in the thermal desorption without a liquid phase [5]. The vigorous effervescence of the electrolyte, however, usually interrupts the uniform flow of gas through the chromatograph, and this distorts the chromatogram considerably and makes the rigorous quantitative determination of the desorbed hydrogen impossible. Water does not reach the detector of the chromatograph and does not interfere in the determination, since a column containing an absorbing agent, for example, P_2O_5 is placed in the gas line.

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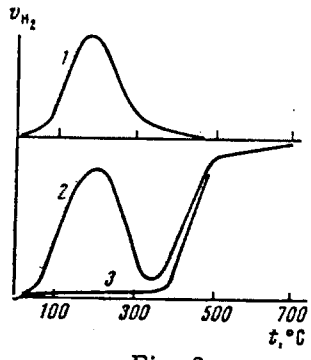


Fig. 2

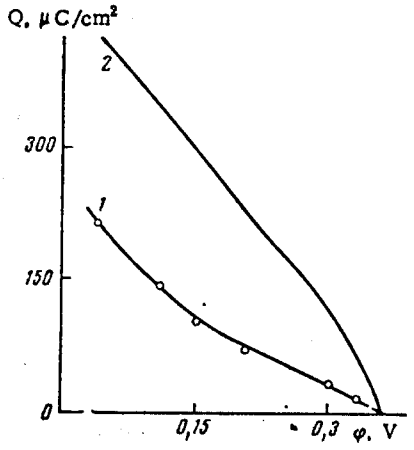


Fig. 3

Fig. 2. Curves giving the thermal desorption of hydrogen from tungsten carbide: 1) without electrolyte; 2, 3) with 0.01 N H_2SO_4 solution (2 – WC saturated with hydrogen, 3 – without saturation of WC by hydrogen). The rate of desorption of hydrogen (axis of abscissae) was not calibrated in these experiments.

Fig. 3. Dependence of the adsorption of hydrogen on tungsten carbide on the potential (1). Charging curve (2) in 0.1 N H_2SO_4 at a temperature of 25° C.

The method developed was applied to the determination of the chemosorption of hydrogen on tungsten carbide in a solution of sulfuric acid. It was established beforehand by the thermal desorption of hydrogen from tungsten carbide without an electrolyte that the thermal desorption is complete at a temperature of approximately 450° C, but the main quantity (more than 90%) is desorbed up to 350° C (curve 1 in Fig. 2). In the direct recording of the thermal desorption of hydrogen from WC in the presence of H_2SO_4 solution on the chromatograph, it was shown that the desorption is also for the most part complete before 350° C, but with further increase in temperature, another rising section is observed (curve 2 in Fig. 2). To establish the nature of this rising section, dry tungsten carbide was heated without degassing, in a stream of argon, to 800° C, after which it was cooled, and a degassed solution of electrolyte was introduced, while the system was kept hermetically sealed. The cell was then heated again, and the collected gas was analyzed. Up to a temperature of 350° C it was possible to detect only very small quantities of hydrogen, amounting to not more than 5-7% of the total quantity of hydrogen desorbed from the same weight of WC previously kept at a potential φ_T = 50 mV. On heating above 400-450° C, the quantity of hydrogen was considerable. This hydrogen evidently appears as a result of the reaction of WC with electrolyte still remaining, possibly in the adsorbed state. We restricted ourselves to an upper temperature of thermal desorption equal to 350° C, although not all of the hydrogen is desorbed from WC at this temperature. Thus, the results given below represent the lower limit of the adsorption of hydrogen on tungsten carbide.

The adsorption was studied on WC powder obtained by the reaction of WO_3 with CO at 1000° C. The thermal desorption was carried out at the potentials indicated by the points in Fig. 3. In these experiments we also used a cell without separation of the cathode and anode compartments. When equilibrium was established, however, the current was so low that when argon was blown continuously through it, the oxygen remaining in the cell could be neglected, just as the concentration of hydrogen in the gaseous phase and in the solution, maintained by the same current, is neglected. The volume of desorbed hydrogen was recalculated as the charge, and is compared with the charging curve in the same figure. By extrapolation of the hydrogen-adsorption curve to its intersection with the axis of abscissae, we found that the range in which the adsorption of hydrogen predominates over the adsorption of oxygen finishes at a potential of approximately 0.35 V.*

* The method described here makes it possible to determine only the excess of hydrogen above oxygen in the layer next to the surface, since equivalent quantities of hydrogen and oxygen may react with one another on heating.

This coincides approximately with the potential of the minimum of the potentiodynamic curves and with the end of the reversible region of the charging curves [2, 3], which provides direct confirmation of the views which we previously put forward regarding the limit of the hydrogen range on tungsten carbide.

For the charging curve (Fig. 3), the charge at a potential of 0.35 V is unknown, and we conditionally took it from zero. It is therefore possible to compare only the change in the total charge and the charge corresponding to the adsorbed hydrogen. It can be seen from Fig. 3 that the adsorption of hydrogen is equivalent to approximately half of the change in the charge in the range of potentials indicated. The rest corresponds to the change in the charge of the double layer, and possibly to some oxidation-reduction processes which take place in the same range, reversibly or almost reversibly, so that the overall almost completely reversible charging curve is obtained.

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