INVESTIGATION OF HYDROGEN ADSORPTION ON TUNGSTEN CARBIDE BY MEANS OF THERMAL DESORPTION AND CHARGE CURVES

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UDC 541.13

The catalytic activity of tungsten carbide in the electrolytic oxidation of molecular hydrogen, the reversibility of the charge curves at potentials φ_r between 0 and +0.4 V and the large total specific surface charge, and also the adsorption of hydrogen on tungsten carbide from the gas phase, all allow us to suppose that tungsten carbide chemisorbs hydrogen from solution in the above potential range [1,2]. However, though very forcible, all these arguments, which are founded on an analogy with platinum-group metals, are nevertheless only indirect evidence for the above hypothesis. It would be extremely interesting to obtain direct evidence for the adsorption of hydrogen on tungsten carbide and to find out what proportion of the total charge is due to hydrogen adsorption.

With this aim, we used a method involving the thermal desorption of gases from the surface [3,4] in conjunction with the quantitative analysis of the gas collected during desorption. Before thermal desorption, we endeavored to treat the catalyst in the same way as before – plotting the charge curves. Tungsten carbide powder was placed in a quartz vessel, a small amount of 0.01 N H_2SO_4 poured over it, and the powder then saturated with pure hydrogen for 1 h. Some samples only acquired a stable hydrogen-electrode potential after cathodic reduction. In this case, the powder was subjected to a preliminary cathodic polarization in the same vessel, after which most of the liquid was poured off and the sample, moistened with the solution, was purged with hydrogen for 1 h. The hydrogen stream was then replaced by a stream of pure argon, which passed at a fixed rate through the vessel containing the catalyst and through a chromatograph. The water entrained by the argon stream was completely absorbed in a column of phosphorus pentoxide, which was placed in front of the chromatographic detector. The chromatograph registered a gradual reduction in the concentration of hydrogen in the gas, until it reached practically zero. This took 30-40 min, as it did in the intense purging in the charge curve method. After this, a furnace which increased the temperature of the catalyst linearly with time was switched on, the desorption of the chemisorbed gas was recorded on the chromatograph, and the gas was collected at the same time for analysis at the outlet of the instrument.

The method was checked on platinum black; a clear desorption peak was recorded, and analysis of the gas showed that it was pure hydrogen. Thermal desorption was then carried out with several samples of

TABLE 1

Sample No.	Surface charge, C/g		$\frac{Q_H}{Q}$	Sample No.	Surface charge, C/g		$\frac{Q_H}{Q}$
	from charge curve Q	from thermal desorp. Q_H			from charge curve Q	from thermal desorp. Q_H	
1	7,5	5,4	0,72	4	4,0	1,3	0,33
2	3,6	2,1	0,59	5	0,16	0,17	1,06
3	5,7	3,3	0,58				

Institute of Organic Catalysis and Electrochemistry, Academy of Sciences of the KazakhSSR, Alma-Ata. Translated from Élektrokhimiya, Vol. 9, No. 6, pp. 854-856, June, 1973. Original article submitted October 9, 1972.

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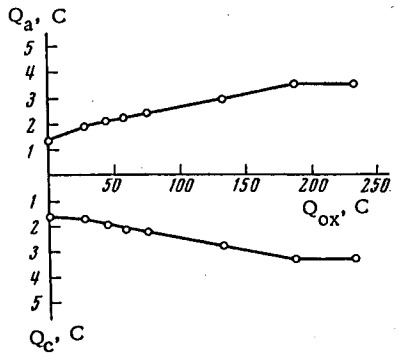


Fig. 1. Dependence of the charge calculated from anodic (Q_a) and cathodic (Q_c) charge curves on the quantity of electricity passed during the electrolytic oxidation of a tungsten carbide sample.

tungsten carbide. Under these conditions, the desorption gas was also pure hydrogen. The amount was determined both from the area of the desorption peak and by analyzing all the gas collected. The surface charge calculated from the amount of hydrogen desorbed is compared in Table 1 with the charge calculated from the anodic charge curves in 1 N H_2SO_4* for the same samples at potentials between +0.04 and +0.35 V. The method used to plot the charge curves for tungsten carbide has been described previously [2].

Only in one case is the ratio Q_H/Q equal to 1, but this experiment was less reliable than the others, owing to the very small absolute quantity of hydrogen desorbed. In the other cases, the charge associated with the adsorbed hydrogen is between one-third and three-quarters of the total surface charge. Of course, these data cannot as yet be regarded as being definitive characteristics of the tungsten carbide surface, since the liquid-phase variant of the thermal desorption method has not yet been mastered sufficiently, and the errors involved in these experiments may be quite high. Nevertheless, we can conclude that the coverage of the surface of tungsten carbide with chemisorbed hydrogen in solutions of acids is considerable.

However, there are already experimental data indicating that the shape of the charge curves for tungsten carbide powders may not be explained completely by the ionization of adsorbed hydrogen and the charging of the electrical double layer, even at potentials between 0 and +0.35 V. Surface oxidation and reduction processes have a considerable effect. To obtain a stable hydrogen potential, several of the samples of tungsten carbide have to be subjected to preliminary cathodic polarization, the more negative the cathode potential, the shorter the minimum polarization time. When this is done, a slow reduction of the surface oxides evidently takes place, since oxide phases are not detected in these samples by x-ray analysis. After switching the electrode from a cathodic potential (φ_r = −50 or −100 mV) to φ_r = +40 mV for 3-4 h or more, a small anodic current (tens of μA) flows on intensively purging with argon, the current gradually falling and changing, as must be the case when φ_r = +40 mV, into the small anodic current associated with hydrogen evolution in an inert gas atmosphere. This anodic current cannot be connected only with the ionization of the hydrogen evolved at the negative potential, since the hydrogen dissolved in the liquid is removed by the inert gas stream in a period of time which is less than the indicated time by a factor of 10. There cannot be any great kinetic barriers to the ionization of the dissolved hydrogen either, since the electrolytic oxidation of H_2 on tungsten carbide proceeds at a fairly high rate. The slow fall in the anodic current on changing from negative potentials to a small positive potential may be connected with the slow oxidation of the reduced surface. This oxidation evidently continues on further plotting the anodic charge curve, but in the cathodic range, reversible reduction of the oxides does not take place. Thus, for some samples, a difference is observed in the lengths of the anodic and cathodic charge curves, reaching approximately 30% in our experiments.

In a number of works [5-7], it is shown that the partial oxidation of tungsten carbide leads to its activation as a catalyst in the electrolytic oxidation of hydrogen and organic compounds. We have investigated how the electrochemical oxidation of tungsten carbide is reflected in the shape of its charge curves.

Figure 1 shows the dependence of the charge calculated from the charge curves on the quantity of electricity consumed in the electrolytic oxidation of one of the tungsten carbide samples. The degree of oxidation at which the charge curve stops changing corresponds to the conversion of a considerable part of the tungsten carbide into oxide, which is revealed directly by x-ray analysis. It is interesting to note that the reversibility of the charge curves for an oxidized sample of tungsten carbide is observed to be very good, and the lengths of the anodic and cathodic curves are observed to coincide completely. We have yet to determine whether the lengthening of the charge curve is connected with an increase in the specific adsorption of hydrogen or with an increase in the actual surface area of the sample.

*By means of a separate experiment, it was shown that the charge curves for tungsten carbide in 0.01 N and in 1 N H_2SO_4 differ only slightly in the total charge.

The thermal desorption experiments were carried out on laboratory oxidation apparatus from our own institute, for which we express our profound gratitude to the laboratory supervisor N. M. Popova. We are sincerely grateful to N. G. Mishanin for carrying out the gas analyses.

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