ADSORPTION AND ELECTROOXIDATION OF THE SIMPLEST CARBON COMPOUNDS ON TUNGSTEN CARBIDES

R. A. Radzhiev, V. Sh. Palanker, and D. V. Sokol'skii

UDC 541.138:541.135.8-183:547

Tungsten carbide as a catalyst of the electrooxidation of hydrogen is interesting primarily in that it is practically not poisoned by impurities contained in technical hydrogen, obtained by the conversion or pyrolysis of hydrocarbons [1]. But until the present time, the causes of the stability of tungsten carbide to substances that poison all the known electrocatalysts in the region of potentials where hydrogen is adsorbed and oxidized had not been investigated. Therefore, it was unclear whether the stability of tungsten carbide is associated with the fact that carbon monoxide and hydrocarbons are not adsorbed on WC or with the fact that these substances are oxidized on tungsten carbide in the same potential region as hydrogen.

In this work we attempted first of all to investigate the adsorption on tungsten carbide of all the basic impurities contained in technical hydrogen: carbon monoxide and carbon dioxide and the simplest hydrocarbons, of which we selected ethylene and acetylene. (The adsorption of hydrogen sulfide was reported in [2].) The electrolyte was 1 N H_2SO_4; the purity of all the gases used was verified chromatographically.

Reversible charging curves and potentiodynamic curves in the region of potentials up to 0.35 V can be obtained on tungsten carbide. The charging curve and potentiodynamic curve on WC powder were first taken in pure 1 N H_2SO_4 according to the method described in [3], and then the solution was saturated with one of the gases enumerated above at various potentials, maintained with a potentiostat. When the potentiostat was turned off, the potential was not displaced in a solution of all these gases; therefore, it was possible to conduct washings with pure sulfuric acid with an open circuit. After washing, the charging curve or potentiodynamic curve was again recorded from the initial potential.

It was suggested that, just as in the case of platinum metals, when these carbon compounds are adsorbed, either the decrease in the amount of electricity on account of the displacement of hydrogen will be appreciable or, if the products are oxidized in the hydrogen region, the charging curves will be more extended. However, within the limits of the experimental accuracy, no changes in the shape of the charging curve or potentiodynamic curve in comparison with the background were observed. For carbon monoxide the potentiodynamic curves are shown in Fig. 1 (curves 1 and 2). Up to 250 mV, there is no difference between the curves in Ar and in CO, but then, on account of the oxidation of WC, the reproducibility of the curves becomes poorer, and the small difference that is visible in Fig. 1, as was shown by numerous experiments, cannot be associated with the adsorption of carbon monoxide.

Hence, the conclusion is built up that CO, CO_2, C_2H_4, and C_2H_2 are not adsorbed (in any case, with displacement of hydrogen) and are not oxidized in the hydrogen region on tungsten carbide. Then the question arose: are carbon compounds of any other classes absorbed on WC? We investigated methanol, formaldehyde, and formic acid by the method described above. Methanol behaves just like hydrocarbons and carbon monoxide (Fig. 1).

It was shown in [4, 5] that formaldehyde and formic acid are oxidized on tungsten carbide in the hydrogen region; other aldehydes are oxidized at a lower rate than formaldehyde [4]. But it is not known

Institute of Organic Catalysis and Electrochemistry, Academy of Sciences of the Kazakh SSR, Alma-Ata. Translated from Élektrokhimiya, Vol. 11, No. 9, pp. 1340-1343, September, 1975. Original article submitted September 18, 1974.

©1976 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

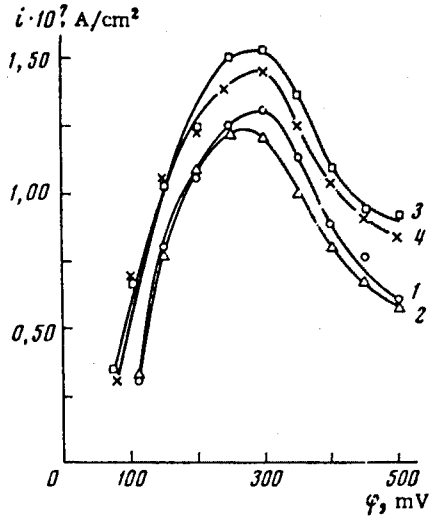


Fig. 1

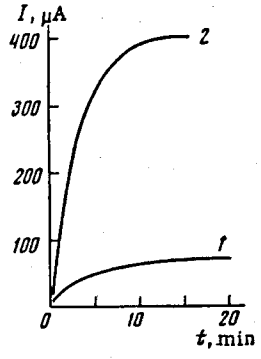


Fig. 2

Fig. 1. Potentiodynamic curves on two samples of tungsten carbide: 1, 3) pure 1 N H_2SO_4; 2) after adsorption of CO; 4) 1 N H_2SO_4 + 5 M CH_3OH; 1, 2) t = 50°C; 3, 4) t = 25°C. Rate of development of the potential 20 mV/min.

Fig. 2. Increase in anodic current on tungsten carbide after the introduction of 3 M solutions of organic substances into the cell: 1) CH_2O_2, t = 70°C, φ_r = 250 mV; 2) CH_2O, t = 50°C, φ_r = 150 mV.

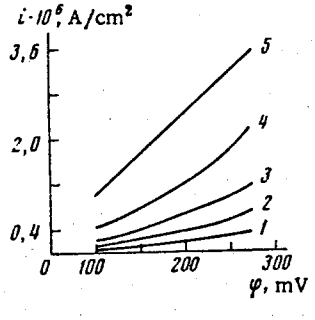


Fig. 3

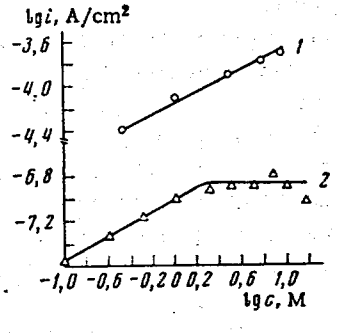


Fig. 4

Fig. 3. Static polarization curves on tungsten carbide in a solution of 1 N H_2SO_4 + 5 M CH_2O: 1) 40; 2) 50; 3) 60; 4) 70; 5) 80°C.

Fig. 4. Dependence of the rate of oxidation on the concentration of organic substances: 1) CH_2O, 90°C; 2) CH_2O_2, 70°C.

whether these processes proceed through a step of adsorption with sufficiently large coverage and through subsequent surface reactions, or whether there is a direct electrochemical oxidation of the substance passing through the electrode from solution.

If tungsten carbide is polarized to some positive potential and then, with the circuit open, formaldehyde or formic acid is introduced, the electrode potential decreases and becomes only 20-30 mV more positive than the hydrogen electrode. But if CH_2O and CH_2O_2 are introduced into solution, maintaining some sort of constant positive potential, then the current gradually increases (we used a liquid porous electrode) and reaches a static level (Fig. 2). In this case no nonstatic maximum of the current is observed, in contrast to the platinum metals, which is apparently evidence of the absence of destruction of organic matter with the appearance of adsorbed hydrogen on the surface. All attempts to determine the

adsorption of formaldehyde by the method of electrooxidation in an adsorbed layer after washing of the electrode with the supporting electrolyte solution did not give reproducible results: in some experiments no adsorption was detected, while in others, on the contrary, the amount of electricity consumed for electrooxidation was very large. This may be associated either with the fact that all the formaldehyde was not always washed out of the pores of the electrode, despite the substantial number of washings, or formaldehyde was weakly adsorbed on tungsten carbide and was desorbed to various degrees in the case of small fluctuations of the conditions of washing. The adsorption of formic acid could not be determined by electrochemical methods either. Radiochemical measurements of the adsorption of formaldehyde on smooth tungsten carbide were performed, and no adsorption was detected in this case.

The series of static polarization curves of the electrooxidation of formaldehyde is shown in Fig. 3. For formic acid the polarization curves take the same form, only the current density at the same φ is approximately three times lower. These measurements were made on a very thin liquid porous electrode. It was shown preliminarily that the electrode works in a purely kinetic system (when the weight of the catalyst sample is varied, the current is strictly proportional to the amount of the catalyst). The real activation energies of electrooxidation were calculated. At $\varphi_r = 250$ mV, in a solution of 1 N H_2SO_4 + 5 M CH_2O, E = 10.5 kcal/mole, while for 1 N H_2SO_4 + 5 M CH_2O_2, E = 11.4 kcal/mole. The dependence of the rate of the processes on the formaldehyde and formic acid concentrations is shown in Fig. 4. With formaldehyde these measurements were performed on a smooth rotating electrode, and with formic acid (on account of the low rate of the process) on a liquid porous electrode. For CH_2O in the entire investigated concentration region, all the way up to a saturated solution, the order of the reaction n = 0.5, and for CH_2O_2 up to a concentration of approximately 2 M, n = 0.5, but then the rate of the process becomes independent of the concentration of formic acid. The cause of this transition was not investigated in the present work. Since no appreciable coverage of the surface with adsorbed formaldehyde and formic acid is detected on tungsten carbide and electrooxidation proceeds in the hydrogen region of potentials, it can be assumed that the process occurs according to a mechanism of direct transfer of electrons from the reacting molecules to the electrode and not through surface chemical reactions with adsorbed oxygen.

In [1, 6] the static polarization curves were taken on electrodes of tungsten carbide in an atmosphere of CO, and it was found that at potentials more positive than 300 mV an anodic current is observed. From this the authors conclude that the electrooxidation of carbon monoxide occurs under these conditions. In [7] cyclic potentiodynamic curves on tungsten carbide in a solution of KOH in an atmosphere of inert gas and in an atmosphere of carbon monoxide were described. On the basis of the increase in the nonstatic current on the potentiodynamic curves in an atmosphere of CO it was concluded that electrooxidation of carbon monoxide proceeds at a significant rate even at potentials $\varphi_r = 100$ mV. We repeatedly recorded the polarization curves in an atmosphere of carbon monoxide and argon on various samples of tungsten carbide in acid and alkaline media and did not detect any appreciable difference in the shape of the polarization curves in CO and Ar. Actually, at temperatures above 50°C and a potential of 300 mV, a static anodic current is observed, but it is of the same magnitude in an atmosphere of carbon monoxide and argon and is associated with the oxidation of tungsten carbide itself under these conditions. It is impossible to speak of the electrooxidation of any substances at a low rate at $\varphi_r > 300$ mV, on account of the intensive corrosion of WC, and polarization measurements alone are insufficient to demonstrate the occurrence of any other anodic process.

The static polarization curves taken on a smooth rotating electrode of tungsten carbide according to the method developed earlier [8] in mixtures of H_2 + Ar and H_2 + CO coincide. Just as for pure hydrogen, in mixtures of H_2 + CO the ionization of hydrogen proceeds according to first order with respect to H_2. Thus, carbon monoxide does not participate in the electrochemical process and does not poison the electrode.

Let us express our deep gratitude to V. E. Kazarinov and V. N. Andreev for performing the radiochemical measurements.

LITERATURE CITED

1. H. Böhm and F. A. Pohl, Troisiémes Journees Internat. d'etude des piles a combustible, Compt. Rend. Bruxelles (1969), p. 183.
2. V. Sh. Palanker and R. A. Gadzhiev, Élektrokhimiya, 11, 1079 (1975).
3. D. V. Sokol'skii, V. Sh. Palanker, E. N. Baibatyrov, and E. A. Bogdanova, Élektrokhimiya, 8, 1754 (1972).
4. H. Binder, A. Kohling, W. Kuhn, and G. Sandstede, Angew. Chemie, Internat. Ed., 8, 757 (1969).

5. D. Baresel, W. Gellert, J. Heidemeyer, and P. Scharner, Angew. Chemie, 83, 213 (1971).
6. L. Baudendistel, H. Böhm, G. Louis, and F. A. Pohl, 23rd Meeting of ISE, Extend. Abstrs., Stockholm (1972), p. 424.
7. K. V. Benda, H. Binder, W. Faul, and G. Sandstede, Chem. Ingr. Techn., 43, 1223 (1971).
8. E. N. Baibatyrov, V. Sh. Palanker, and D. V. Sokol'skii, Élektrokhimiya, 10, 158 (1974).