

PREPARATION OF WC CATALYSTS WITH CARBON DEFICIENT CRYSTAL LATTICE

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A series of tungsten carbides was prepared by carburating tungsten and its oxygen compounds with carbon monoxide at varying conditions. The highest catalytic activity for oxidation of hydrogen in an acid electrolyte was found in WC prepared from white modification of tungstic acid $\text{WO}_3 \cdot x \text{H}_2\text{O}$ by reduction with hydrogen and by following carburation with carbon monoxide at 700 and 900°C, respectively. The activity was ascribed to a high carbon deficiency in the lattice.

It is known¹ that the activity of catalysts increases as their structure or stoichiometry deviates from perfectly ordered basic compounds. For instance Böhm and coworkers² found an increased catalytic activity in WC which was defective in carbon content. Goretzki and coworkers³ observed that a defective TiC reacted readily with hydrogen whereas no reaction proceeded on a stoichiometric TiC. Kulčický and Petrdlík⁴ observed, when preparing WC for high-speed cutting steels, that mechanical properties of the product were poorer if admixtures of white modification of tungstic acid, $\text{WO}_3 \cdot x \text{H}_2\text{O}$, were present in the yellow modification H_2WO_4 used as initial material. By further investigations they found that anhydrous WO_3 prepared from the yellow modification and that prepared from the white modification exhibited large differences with respect to their physical structures and the particle habitus. H_2WO_4 yielded WO_3 with a perfect crystalline structure whereas WO_3 prepared from $\text{WO}_3 \cdot x \text{H}_2\text{O}$ consisted of crystallites which were very irregular. High temperatures smoothed out the differences but if W or WC were prepared from the respective materials at temperatures below 1000°C, all the characteristic properties were transferred into the product.

Although these observations suggest that the white modification of tungstic acid might be a promising material for preparing electroactive WC, it has so far not been employed for this purpose. It was the aim of the present work to check this possibility.

EXPERIMENTAL

A series of WC catalysts was prepared by carburating tungsten or its oxygen compounds with CO at 900°C for 3.5 hours; the rate of flow of CO was 9.5 l/h. The following raw materials were used: tungsten trioxide, anal. grade (Lachema, Prague), tungsten powder, stated grain size below 0.3 μm (H. Starck, Berlin), and white modification of tungstic acid prepared by the method of Kulčický and coworkers⁵ (precipitation with HCl from dilute ammoniacal solutions at low

temperatures). Syntheses were made in a flow-through tube oven of 40 mm inner diameter. The carburization was preceded by reduction under hydrogen at 700°C for 3 hours, flow-rate 12 l/h. The conditions of the syntheses were optimized by a series of experiments performed with the white modification as may be seen from Tables I to III. The products were controlled by measuring the surface area by adsorption of argon, and by X-ray and chemical analyses. The activity of the catalysts was evaluated from polarization curves of porous electrodes operating on hydrogen in 1N-H₂SO₄ at 60°C. Double layer electrodes were prepared by pressing the catalyst with Teflon powder at 1000 kg/cm² and by subsequent sintering at 300°C for 70 min under nitrogen. The Teflon to catalyst ratio was 0.4 : 1.25 and 0.2 : 1.25 by weight. The electrodes had a diameter of 3 cm, their thickness varied between 0.8 and 1 mm according to the nature of the catalyst. No supporting skeleton and no current collector were used. No efforts were made to raise the performance of the electrodes by modifying their structure. The potential was measured against a Hg/Hg₂SO₄ reference electrode in the same electrolyte; in the figure and the tables, it is converted to the standard hydrogen scale. The electrode was placed into an acid-resistant steel holder which served at the same time also for feeding the gas and collecting the current. A lead grid behind a separator, both from a lead acid storage battery, served as counter electrode. Hydrogen was fed into the gas compartment of the holder under a small overpressure of 10 cm H₂O. The potential was read off five minutes after attaining a stationary value on loading the electrode with a constant current. As was verified by substituting hydrogen with argon, no measurable corrosion current was yielded by the electrode or the holder in the given potential range.

TABLE I

Influence of Rate of Flow of CO at 900°C and Carburization Time 3.5 Hours

Catal. No	Flow l/h	E, mV at 30 mA/cm ²	Surf. area, m ² /g
83	1.2	382	2.32
82	3.5	285	2.60
80	9	239	6.08
84	12	277	4.25

TABLE II

Influence of Carburization Time (*t_c*) at 900°C and Rate of Flow 9 l/h

Catal. No	<i>t_c</i> , h	E, mV at 30 mA/cm ²	Surf. area, m ² /g
104	1.5	274	8.16
91	3.5	177	8.40
103	5.5	234	5.90

RESULTS AND DISCUSSION

Fig. 1 compares the performances of a catalyst prepared from WO_3 with one prepared from the white modification of tungstic acid at equal conditions. Either curve is an average of values obtained on three electrodes, each of them containing a catalyst prepared from a different charge of the initial material. As is evident from the plot, the white modification proved to be a very good material; difficulties were, however, encountered with respect to the reproducibility of its preparation. In spite of strictly following the preparation procedure, structural differences were found in individual charges of $\text{WO}_3 \cdot x \text{H}_2\text{O}$ by X-ray analyses. The patterns contained several ill-defined diffuse lines, whose position and intensity varied from one batch to the next, testifying to a different degree of recrystallization. As was observed by Kulčický and coworkers⁵ the $\text{WO}_3 \cdot x \text{H}_2\text{O}$ gel prepared from ammoniacal solutions is very unstable and tends to form aggregates which pass readily into a crystalline form binding NH_4^+ ions. Although in general higher activities were obtained with $\text{WO}_3 \cdot x \text{H}_2\text{O}$ than with WO_3 , the degree of recrystallization influenced the quality of the final product; the matter will, therefore, require further investigation.

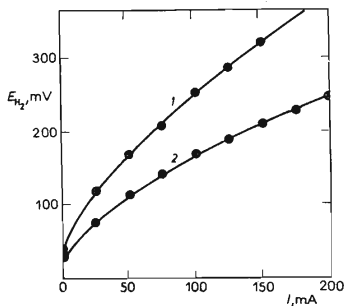


FIG. 1

Polarization Curves of Hydrogen Electrodes with WC Catalysts Prepared by Carburating
1 WO_3 and 2 $\text{WO}_3 \cdot x \text{H}_2\text{O}$ with Carbon Monoxide, in 1N- H_2SO_4 at 60°C

During the syntheses, white fumes of NH_4Cl were liberated at 400°C and above. Since chlorides are known⁶ to have a catalytic effect on the reaction $\text{W} + 2 \text{CO} = \text{WC} + \text{CO}_2$, two samples of $\text{WO}_3 \cdot x \text{H}_2\text{O}$ were prepared, differing only in the degree of washing the precipitate. One was just centrifuged off the parent solution retaining 12% NH_4Cl , the other was washed to neutral reaction and contained 1.8% NH_4Cl . Catalysts prepared from them confirmed the catalytic effect of ammonium chloride (performances 30 mA/cm² at 220 and 320 mV, resp.). To distinguish between

the contribution of NH_4Cl and that of the initial material, NH_4Cl was added to chloride-free materials.

TABLE III

Influence of Carburation Temperature (T_c) at Rate of Flow 9 l/h and Carburation Time 3.5 h

Catal. No	T_c , °C	E , mV at 30 mA/cm ²	Surf. area, m ² /g
106	800	382	7.20
91	900	177	8.40
105	1 000	232	5.13

TABLE IV

Influence of Addition of 10% NH_4Cl on the Catalytic Activity of WC Prepared at 900°C, 9 l/h CO and 3.5 hours Carburation Time

Catalyst No 91, included in the table for comparison, contained 4.2% NH_4Cl .

Catal. No	Initial material	E , mV at 30 mA/cm ²	Carbon content	Surf. area, m ² /g
66	WO_3	332	6.13	2.81
96	$\text{WO}_3, \text{NH}_4\text{Cl}$	312	5.68	3.46
60	W	216	5.77	4.87
94	W, NH_4Cl	192	5.28	5.42
91	$\text{WO}_3 \cdot x\text{H}_2\text{O}$	177	4.56	8.40

Table IV suggests that an addition of chlorides leads to an increase in surface areas and at the same time to a drop in the carbon content (free carbon was practically absent). This is understandable in view of the fact that mass transfer takes place in WO_3 particles (or in the WO_3 surface film if W is used as initial material) at temperatures of 800°C and above⁷ whereas no changes occur in WC at these temperatures. Therefore, the more rapid the carburation reaction, the finer the resulting powder. Also, the increased rate of carburation fixes the characteristic properties inherent in the raw material. On this basis, the decrease in the carbon content (as compared to stoichiometry) could be used as an indicator of the catalytic activity, since only WC phase was found by X-ray analysis.

Comparing the results it could be stated that the white modification of tungstic acid proved to be a very good material for preparing active WC, probably due to the capability to keep its structural irregularities throughout further reactions. Additional investigations will, however, be necessary aimed at preparing $\text{WO}_{3 \cdot x} \text{H}_2\text{O}$ with a definite fully reproducible structural composition.

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