

On the catalytic activity of tungsten carbide in anodic oxidation of CHO compounds in acid electrolyte

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The electrodes were made of tungsten carbide and their activity in the electrooxidation of some carbonaceous fuels dissolved in acid electrolyte was tested by recording the polarization curves. It was found that the most active WC catalyst could be obtained by low-temperature carburization of fine-grained powdered tungsten with carbon monoxide.

Tungsten carbide has been known for several years especially as a catalyst of anodic oxidation of hydrogen in acid medium [1]. Attempts to oxidize some simple organic compounds (HCHO, CH₃CHO, HCOOH, and CO) on this catalyst have been also described [2, 3].

This paper is concerned with the attempts to oxidize CHO compounds on some differently prepared catalysts, namely tungsten carbide WC.

Experimental

The electrodes were prepared by moulding a mixture consisting of WC and powdered polytetrafluoroethylene (Hostafion; 8–12%), or by moulding and sintering a mixture of metallic tungsten (Starck, Berlin; mean grain size $0.4 \pm 0.1 \mu\text{m}$, purity 99.87%) and carbon (carbon black, spectral graphite or activated carbon). The compacts of W–C mixture were sintered in protecting hydrogen atmosphere for 3 hours at 1250°C [4].

The electrochemical measurements were carried out in a vessel with three-electrode arrangement [5]. The activity of electrodes was tested according to the galvanostatic polarization curves which were taken at different temperatures of the solutions containing H₂SO₄ and HCHO or H₂SO₄ and HCOOH.

Results and discussion

The galvanostatic polarization curves of oxidation of formaldehyde on tungsten carbide (Starck, Berlin; mean grain size $1 \mu\text{m}$, purity 99.7%) are presented in Fig. 1. It is obvious that the concentration of HCHO has a considerable influence on its electrochemical conversion. At the polarization of $\sim 350 \text{ mV/RHE}$ the current densities of 23, 33, and 37 mA cm⁻² were achieved in electrolytes containing 1, 2, and 3 moles of HCHO, respectively. The electrodes subsequently activated according to [2, 3] (anodically in the presence of reducing agent) showed practically equal activity.

As an electrochemical conversion of HCHO occurs on these electrodes, the electrooxidation of formic acid was also investigated. The results are in Fig. 2. In comparison with the electrochemical conversion of HCHO, the current densities attained in the case of anodic oxidation of HCOOH were very low.

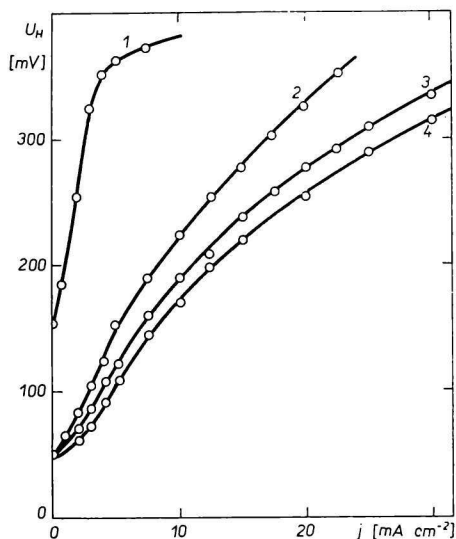


Fig. 1. Galvanostatic polarization curves obtained with an electrode made of WC catalyst (Starck).

Effect of the concentration of fuel in an electrolyte on its electrochemical conversion. Temperature of electrolyte 70°C.

1. 0 M-HCHO; 2. 1 M-HCHO;
3. 2 M-HCHO; 4. 3 M-HCHO.

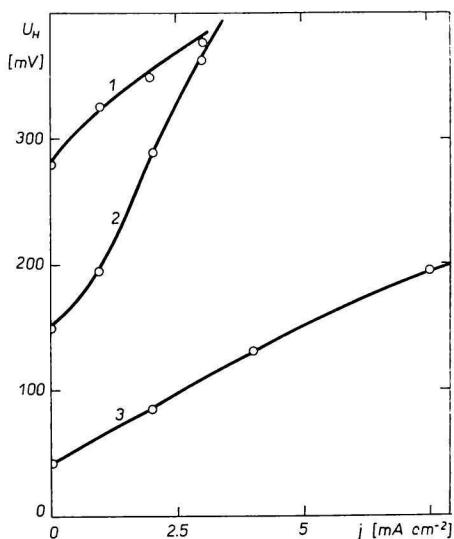


Fig. 2. Polarization curves obtained in different electrolytes with an electrode made of WC catalyst (Starck).

Temperature of electrolytes 70°C.

1. H₂SO₄; 2. H₂SO₄ + HCOOH;
3. H₂SO₄ + HCHO.

The activity of electrodes made from tungsten carbide (prepared from metallic tungsten and activated carbon) is comparable with that of the electrodes made from commercial tungsten carbide (Starck). At the polarization of 350 mV/RHE the current densities of 20 mA cm⁻² were measured in an electrolyte consisting of 1 M-H₂SO₄ and 1 M-HCHO at 72°C.

At the polarization of 280 mV/RHE the current densities of 75 mA cm⁻² were obtained provided that the oxidation of HCHO took place on tungsten carbide prepared by AEG — Telefunken, Frankfurt/Main (Fig. 3). According to preliminary measurements the corrosion of this tungsten carbide sets in at potentials exceeding 420 mV/RHE. Therefore the catalyst may be loaded with high polarization currents. The current densities obtained are approximately four times higher than those attained on the WC catalyst (Starck).

Still more marked difference appears between the activity of the WC catalyst (AEG) and other catalysts under study during the electrochemical conversion of HCOOH. While the currents obtained by oxidizing HCOOH on the WC catalyst (Starck) were minimum, the WC catalyst (AEG) gave the following values at 72°C:

Polarization [mV/RHV]	100	150	200	250	300
Current density [mA cm ⁻²]	2	3.5	5	7	8.5

When an attempt to oxidize methanol on tungsten carbide (AEG) was made only the current density of 1 mA cm⁻² was obtained at the polarization of 300 mV/RHE.

From among the three kinds of tungsten carbide tested as catalysts for the anodic

oxidation of CHO compounds it was only tungsten carbide prepared by AEG which gave real currents. Similarly as in the case of electrooxidation of hydrogen, the difference in the activity of catalysts may be explained by different conditions used for the preparation of tungsten carbide. As reported by the firm H. C. Starck, Berlin, their tungsten

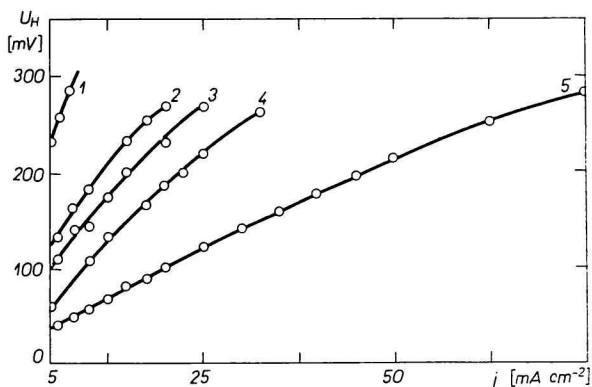


Fig. 3. Galvanostatic polarization curves obtained in an electrolyte consisting of 1 M-H₂SO₄ and 3 M-HCHO with an electrode made of WC catalyst (AEG — Telefunken).

Temperature dependence.

1. 22°C; 2. 45°C; 3. 50°C; 4. 57°C; 5. 72°C.

carbide was prepared from a mixture of powdered tungsten reduced with hydrogen (mean grain size 0.7 μm) and carbon black which was mixed vigorously and afterwards heated to 1400–1500°C in a protecting atmosphere. Tungsten carbide formed in that process was ground and sieved. The conditions used in that procedure are similar to those given in [4] which were employed in the preparation of tungsten carbide in this study. On the other hand, tungsten carbide prepared by AEG — Telefunken, was synthesized by carburizing the powdered tungsten with carbon monoxide in rotating quartz furnace at 850°C [6]. According to [7] a strongly active WC catalyst for anodic oxidation of hydrogen in H₂SO₄ was prepared from commercial powdered tungsten (Starck, Berlin; mean grain size 0.4 μm) by carburization with carbon monoxide at 800–900°C. The surface of tungsten was deprived of oxide layers by reduction with hydrogen immediately before carburization and thus tungsten was ready for the reaction with carbon monoxide. The temperature of reduction plays an important role: if the optimum temperature is exceeded, the recrystallization of tungsten occurs and makes the crystallite cluster in particles greater than 1 μm (even 5 μm).

Conclusion

On the basis of experiments with different WC catalysts it may be concluded that a low-temperature carburization of powdered tungsten with carbon monoxide according to [6] is one and only procedure known up to now which yields a highly active catalyst available for the electrooxidation of carbonaceous fuels dissolved in acid electrolytes.

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