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Ethane Hydrogenolysis Catalyzed by W(100)

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The ability of the (100) face of tungsten to catalyze ethane hydrogenolysis has been investigated. At 573 K, methane is formed with a specific activity of 0.01 molecules per surface tungsten atom per second (100 Torr H_2, 1 Torr C_2H_6), with no evidence of catalyst deactivation even after several hundred turnovers. Hydrogenolysis is approximately first-order in ethane and half-order in dihydrogen, and displays an apparent activation energy of 27 kcal/mol. Negligible activity is displayed by clean tungsten; the true catalyst appears to be a monolayer of carbide which is formed on the surface of the tungsten on exposure to the reactants.

Tungsten is not commonly thought of as a good catalyst, perhaps because of the difficulty of reducing supported tungsten salts or complexes to the metallic state [see, for example Ref. (*1*)]. As the initial part of a study of model supported catalysts prepared in ultrahigh vacuum, the ethane hydrogenolysis activity of the (100) plane of oriented tungsten single crystals has been examined. The behavior of tungsten differentiates it from that of other materials in several ways, and some results of this examination thus are reported here.

Experiments on either of two tungsten single crystal disks (8 mm × 0.5 mm; spark cut from a (100) oriented rod obtained from Metal Crystals Ltd.[2]) with polished front and back faces were performed using a system similar to one previously described (*2*). Each sample was spot-welded to tungsten wires which were in turn held in massive molybdenum clamps, and could be translated between contiguous surface analysis (Auger electron spectroscopy, mass spectrometry) and high-pressure batch reaction chambers (10^{-10} Torr nominal base pressures in both). Resistive heating of the tungsten to a maximum temperature of 2100 K was monitored with a thermocouple (W-3%Re/W-25%Re) attached by spot-welding. Reaction rates were measured by periodic gas chromatographic analysis of aliquots of the reaction mixture, and showed agreement to within 20% under similar conditions on the two crystals.

Carbon and sulfur were removed from the bulk and from all faces of the tungsten crystals by extended heating at 1400 K in 10^{-7} Torr of dioxygen. Removal of surface oxygen (to <3% of monolayer coverage (*3*)) was effected by flashing several times to 2000 K; no other surface contaminants were detected by Auger electron spectroscopy. Matheson[2] research grade ethane was degassed by three freeze–pump–thaw cycles prior to use, and dihydrogen was purified by passage through palladium.

Methane is produced catalytically when a tungsten single crystal disk with polished (100) faces is heated in mixtures of dihydrogen and ethane (Fig. 1). After a period of several minutes during which little or no methane is formed, a constant turnover frequency (0.01 CH_4 per surface tungsten atom per second at 573 K) is attained. No decrease in this turnover frequency with time is observed, even after several hours: no self-poisoning of the catalyst occurs during the time of measurement.

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[2] Manufacturer is identified only for complete specification of experimental conditions; no endorsement by the National Bureau of Standards is implied.

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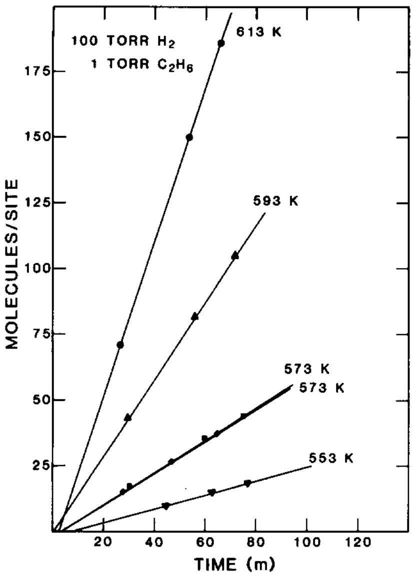

FIG. 1. Total methane accumulation per surface tungsten atom in the presence of 100 Torr of dihydrogen and 1 Torr of ethane; linear regression lines are shown.

If the crystal surface is carburized[3] before reaction, no induction period is observed, but catalytic activities otherwise are unchanged by this treatment. This may suggest that a surface carbide and not the clean tungsten surface is active for ethane hydrogenolysis. Based upon a steady-state ethane reaction probability of 10^{-8} per collision with the surface at 573 K and the estimated length of the induction period, roughly one monolayer of carbon may be deposited onto the tungsten crystal before any methane is formed.[4] In fact, Auger electron spectroscopic examination of the catalyst (either initially clean or carburized) once steady-state reactivity has been attained indicates the presence of a surface carbide [Fig. 2, Ref. (*4*)].[5] No change in the carbon Auger lineshape or peak-to-peak intensity is observed as a function of time, temperature, or reactant partial pressures. Formation of a stable carbidic surface phase is indicated under all conditions assayed, and formation of multilayer carbon deposits or of a bulk carbide is ruled out. Evidence for this last point lies in the finding that the oxygen dose needed to restore the crystal to cleanliness after reaction is appropriate to no more than approximately monolayer coverage of carbon.[6]

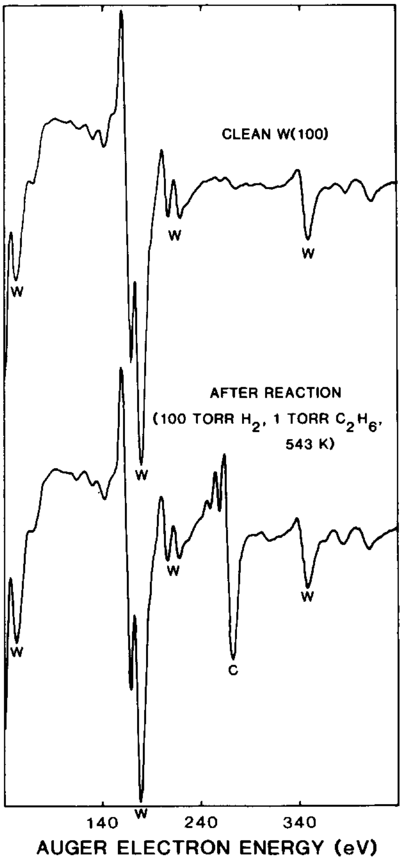

FIG. 2. Auger electron spectra of W(100) before and after reaction.

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[3] Sample is treated with ethane (1 Torr) at 800 K for several seconds; Auger spectroscopic analysis indicates approximately monolayer carbon coverage.

[4] This analysis assumes similar reaction probabilities for ethane on the clean and carbon-covered surfaces.

[5] Auger peak ratios are consistent with a near-monolayer coverage of carbon (*4*). Note that the lower instrumental resolution employed here relative to that used in other studies (*4a*, *6*) produces a slightly different lineshape.

[6] While treatment with hydrocarbon alone can produce bulk tungsten carbide [see, e.g., Ollis, D. F., and Boudart, M., *Surf. Sci.* **23**, 320 (1970)], the presence of dihydrogen apparently prevents multilayer carbide formation.

Together, these facts comprise compelling evidence that a surface carbide is the catalytically active species for ethane hydrogenolysis. The thesis that refractory carbides show such activity has been advanced previously (*5*). However, it has been claimed that formation of bulk carbides is necessary for full development of catalytic activity, which does not appear to be true in this case.

By independently varying the partial pressures of the two reactants at 573 K, it has been determined that methane production is nearly first-order in ethane (0.25–2.0 Torr) and half-order in dihydrogen (25–200 Torr):

$$\frac{dp_{\mathrm{CH_4}}}{dt} = 2kp_{\mathrm{C_2H_6}}^{0.80}p_{\mathrm{H_2}}^{0.45}.$$

In the absence of thermodynamic information on adsorption on the carbidic surface, it is not reasonable to draw mechanistic conclusions from these data. It is interesting to note, however, that the methanation of carbon monoxide on (carburized) W(110) is slightly greater than half-order in dihydrogen (*6*). Contrasted with this are the inverse dependences of many hydrogenolysis reactions on dihydrogen pressure (*7*, *8*), which may arise from differences in heats of adsorption on clean and carbon-modified metal surfaces (*4a*).

An apparent activation energy for ethane hydrogenolysis on the (100) surface of tungsten of 27 kcal mol^{-1} has been obtained (Fig. 3).[7] This number is identical with that previously reported on evaporated tungsten films (*9*). Methanation on the carbided (110) surface yields a much smaller value (14 kcal mol^{-1}) (*6*) suggesting that the two processes do not share a common rate-limiting step, e.g., reductive elimination of methane.

Comparison of the preceding results with those found for platinum is indicated, as this metal finds commercial use as a reforming catalyst and has been particularly well studied. Ethane hydrogenolysis on platinum films and supported particles proceeds with an apparent activation energy in excess of 50 kcal mol^{-1} (*9*). This value is reflected in a specific activity for methane formation 100 to 1000 times lower than that of tungsten. It is difficult to assess the source of this difference, no less as the putative catalyst is in one case a pure metal (*10*) and in the other a carbidic overlayer.

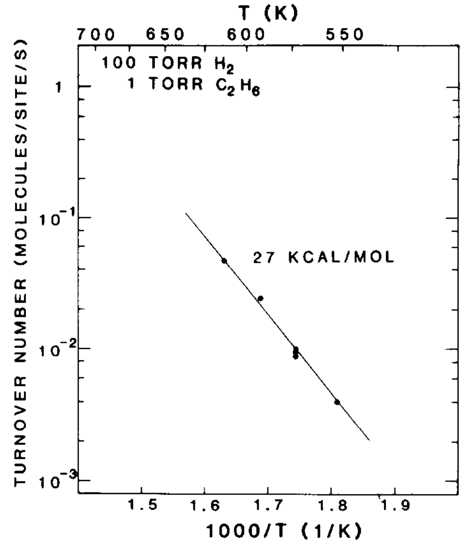

FIG. 3. Arrhenius plot of the turnover frequency for methane production (100 Torr dihydrogen, 1 Torr ethane); linear regression line is shown.

Equally striking in the context of a comparison between the metals is the catalytic stability of tungsten. Platinum exhibits a decreasing hydrogenolysis activity beginning with the earliest stages of reaction. This effect has been ascribed to surface site blocking by amorphous multilayer carbon deposits (*10*). Binding of adsorbates to the carbidic overlayer on tungsten must be sufficiently weak that alkane production is greatly favored relative to further dehydrogenation of bound species: no thick carbon deposits, and hence no self-deactivation, are observed.

It thus may be concluded that the (100) plane of tungsten is capable of catalyzing ethane hydrogenolysis. Important features of the carbidic overlayer which is the true catalyst are its relatively high activity and

[7] $A_{\mathrm{apparent}} = 1.1 \times 10^8\ \mathrm{s}^{-1}$.

its resistance to self-poisoning. That the hydrogenolysis ability of tungsten has not been generally recognized may be attributed to the difficulty of obtaining the tungsten in the metallic state: on dehydroxylated alumina, complete reduction of hexacarbonyltungsten at high temperature has given activities comparable to those reported here (*11*).

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