Selective Catalytic Behaviour of Tungsten Carbide in the Liquid-phase Hydrogenation of Organic Compounds

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The catalytic activity of tungsten carbide for liquid-phase hydrogenation has been studied in acidic (H_2SO_4) media at 40—90 °C. Tungsten carbide proved to be a selective catalyst, easily promoting the reduction of aromatic nitro-compounds and quinones. However, the saturation of double and triple bonds, aromatic nuclei, and oxo-groups did not occur under these conditions. The effect of temperature and the composition of the liquid phase on the rate of hydrogen uptake have been studied. Some problems concerning the mechanism of hydrogenation are discussed.

VARIOUS workers[1-3] have studied the electrocatalytic properties of tungsten carbide (WC) in anodic reactions of H_2, CO, and other fuels. They proved the suitability of tungsten carbide electrodes for fuel cells with acidic electrolytes. It seems, however, that their observations might have considerable importance not only in electrochemistry but also in other areas of chemistry.

From the study of the electrocatalytic behaviour of tungsten carbide in the promotion of the anodic oxidation of hydrogen the conclusion can be drawn that WC should be a catalyst in the liquid-phase hydrogenation of some types of organic compounds. This concept was outlined in a communication[4] which presented some preliminary results proving that tungsten carbide is a catalyst for the liquid-phase hydrogenation of aromatic nitro-compounds. The same result was obtained for the hydrogenolysis of iodoacetic acid.

This paper gives a detailed account of these studies and presents some results which might have preparative importance.

EXPERIMENTAL

The procedure was that commonly used for liquid-phase hydrogenations. A hydrogenation vessel (50 ml) with a thermostatted jacket and shaking apparatus was used at atmospheric pressure between 40 and 90 °C. The hydrogen uptake was measured by a gas burette.

The reactions were generally carried out with tungsten carbide (1—4 g) in aqueous 2N-H_2SO_4 (20—30 ml) (variations are mentioned as they occur). The solubility of the organic compounds in the aqueous phase is very low and most of the substrate remained undissolved. This heterogeneity, however, did not influence the rate of hydrogenation.

Two types of tungsten carbide were used. The first was

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[1] F. A. Pohl and H. Böhm, ' Proceedings of the III. Journées Internationales d'Etude des Piles á Combustible Brussels, 1969, p. 180; *Wiss. Ber. AEG-Telefunken*, 1968, **41**, 46; H. Böhm, *Electrochim. Acta*, 1970, **15**, 1273.

[2] H. Binder, A. Köhling, W. Kuhn, W. Lindner, and G. Sandstede, *Energy Conversion*, 1970, **10**, 29; *Nature*, 1969, **224**, 1299.

[3] D. Baresel, W. Gellert, J. Heidemeyer, and P. Scharner, *Angew. Chem.*, 1971, **83**, 213.

[4] G. Horányi, G. Vértes, and Gy. Fézler, *Z. phys. Chem.* (*Frankfurt*), 1973, **83**, 322.

commercial (Found: bound C, 6·05—6·10; free C, 0·1; O, 0·1%; mean particle size 5 μm). The other was an AEG-Telefunken sample (for which we are indebted to Professor A. Pohl and Dr. H. Böhm) specified elsewhere.[5]

RESULTS

The rate of hydrogenation is independent of the amount of substrate present. There is no significant change in the rate of hydrogen uptake during the hydrogenation except at the very end of the process.

The various substances give roughly similar results. If the hydrogenation proceeds at a measurable rate its extent varies generally within 10—12 ml g^{-1} h^{-1} uptake of hydrogen. The rate was directly proportional to the weight of catalyst over the range 0·5—5·0 g. The results are summarized in Table 1.

TABLE 1

Hydrogenation in the presence of WC * in 2N-H_2SO_4 at 80 °C

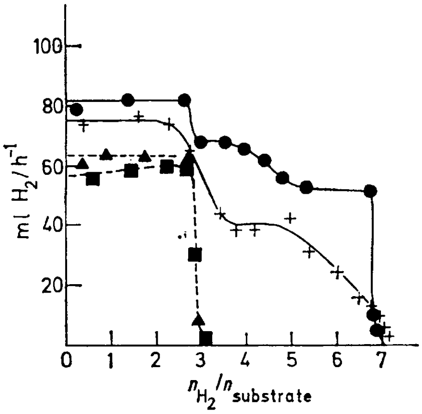
	Substrate	Hydrogen uptake (mole H_2 per mole substrate)	Reaction rate [ml H_2 h^{-1} (g catalyst)$^{-1}$]
(1)	Fe^{3+}	½	12
(2)	*p*-Quinone	1	12
(3)	Isatin	1	5
(4)	Nitrobenzene	3	11 (60 †)
(5)	*p*-Nitrophenol	3	11
(6)	*p*-Nitrosophenol	2	8
(7)	3,4-Bis-2-methylpropoxy-benzene	3	8 (45 †)
(8)	*p*-Nitrobenzoic acid	3	12
(9)	*p*-Nitrobenzamide	3	11
(10)	*m*-Dinitrobenzene	6	18
(11)	Nitroethane		2·5
(12)	Acetone		None
(13)	Benzaldehyde		<1
(14)	*N*-(*p*-Methoxybenzylidene)-aniline		None
(15)	Maleic acid		None (None †)
(16)	But-2-ene-1,4-diol		None
(17)	But-2-yne-1,4-diol		<1
(18)	Cinnamic acid		None
(19)	*p*-Nitrocinnamic acid	3	10
(20)	4-(3-Nitrophenyl)but-3-en-2-one	3	11 (60 †)
(21)	Trichloroacetic acid		None
(22)	Iodoacetic acid	1	10
(23)	β-Bromopropionic acid		1
(24)	Iodobenzene		None
(25)	Benzonitrile		None

* Commercial WC. † AEG WC. The substrates used were puriss grade commercial ones. Compounds (14) and (20) were obtained following H. H. Keasling and F. W. Schueler, *J. Amer. Pharm. Assoc.*, 1950, **39**, 87 and R. Sorge, *Ber.*, 1902, **35**, 1068, respectively.

Table 1 shows that unsaturated compounds do not react with hydrogen in the presence of tungsten carbide. If nitro-groups and double bonds or oxo-groups are present simultaneously the reaction proceeds selectively. The extent of hydrogen uptake corresponds to the reduction of the nitro-groups only.

The selective behaviour of tungsten carbide is clearly shown by comparison with that of platinum. The extent of hydrogenation of such simple compounds as *p*-nitrophenol or *p*-nitrocinnamic acid differed significantly in the two cases as shown in the Figure. In the presence of platinum the hydrogen consumption corresponded to 7 moles H_2 per mole substrate (*i.e.* the aromatic nucleus and the double bond was saturated in the case of the acid and the OH group was eliminated in the case of *p*-nitrophenol).

Comparison of the initial rates of hydrogenation (using AEG tungsten carbide) with those observed in the presence of platinum powder allows the estimation of the catalytic activity of tungsten carbide. The Figure shows that the catalytic activity of tungsten carbide in our experiments is lower than that of platinum by a factor of ten. (The specific surface area of both catalysts was nearly the same.)



Comparison of the hydrogen consumption in presence of platinum and tungsten carbide (at 80 °C): + Pt (0·1 g), *p*-nitrocinnamic acid; ● Pt (0·1 g), *p*-nitrophenol; ▲ WC (1·0 g) (AEG), *p*-nitrophenol; ■ WC (1·0 g) (AEG), *p*-nitrocinnamic acid. $n_{H_2}/n_{substrate}$ = moles H_2 uptake per mole substrate

The apparent temperature dependence of the rate of hydrogenation has been studied to find the optimal temperature for the reaction of a given system. Upon increasing the temperature the vapour pressure of water above the solution increases. As the total pressure is constant (1 atm) the partial pressure of hydrogen decreases. So the temperature dependence of the rate of hydrogen uptake given in Table 2 is an apparent one. Data in Table 2 are, however, convenient for practical purposes. The rate of hydrogen uptake decreases above 80 °C as at 90 °C the partial pressure of hydrogen is very low corresponding to the high vapour pressure of water.

TABLE 2

Temperature dependence of the hydrogenation of nitrobenzene on WC (AEG) in 2N-H_2SO_4 solution

t/°C	Rate of hydrogenation [ml H_2 h^{-1} (g catalyst)$^{-1}$]
50	5
60	7
70	10
80	12
90	11

The composition of the liquid phase influences the rate of hydrogen uptake (Table 3) in the case of nitrobenzene and 3,4-bis-2-methylpropoxy-1-nitrobenzene. In nonpolar solvents the rate decreases sharply. In alcohols containing a few percent of water the rate is much lower than in aqueous solutions. Increasing the concentration of water and hydrogen ions results in an increase in the rate. The effect of an increase of hydrogen ion concentration may also be observed in the case of 70% acetic acid.

The quality of the catalyst plays an important role. The AEG tungsten carbide (results in parentheses in Table 1) is a better catalyst than the commercial one. It

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[5] J. D. Voohries, *J. Electrochem. Soc.*, 1972, **119**, 219.

is known[1-3] that the mode of preparation and the composition of the catalyst have great influence on its activity.

TABLE 3

The effect of the composition of the liquid phase on the rate of hydrogen uptake

Substrate	Solvent	Reaction rate [ml H_2 h^{-1} (g catalyst)$^{-1}$]
Nitrobenzene	2N-H_2SO_4	12
	2N-H_2SO_4 in 2% ethanol	12
	2N-H_2SO_4 in 50% ethanol	8
3,4-Bis-2-methylpropoxy-1-nitrobenzene	2N-H_2SO_4	8
	Toluene	1
	n-Propanol	1·5
	70% Acetic acid	2
	0·1N-H_2SO_4–70% acetic acid	4
	1N-H_2SO_4–70% acetic acid	5

DISCUSSION

Tungsten carbide acts as a hydrogenation catalyst for aromatic nitro-, nitroso-, and aliphatic nitro-compounds and for quinones.

It is known[6] that the hydrogenation of an organic compound on noble metal catalysts in aqueous solution may occur (1) by a sequence of non-electrochemical reactions involving adsorbed hydrogen atoms and organic radicals as intermediates (radical mechanism) and (2) by the ionization of hydrogen and consecutive reduction of the compound by transfer of electrons originating from the ionization of hydrogen (ionic mechanism).

The hydrogenation of the compounds mentioned above belongs to the second group and in the case of tungsten carbide a similar mechanism may be assumed. The 'hydrogenation' of Fe^{3+} ions and quinones serves as a justification of this assumption.

Tungsten carbide is a selective catalyst. Hydrogenation of oxo-groups and double and triple bonds does not occur and thus nitro-compounds and quinones containing such groups may be hydrogenated without any precautions. The mechanism of hydrogenation of compounds containing double and triple bonds, *etc.* differs significantly from the ionic mechanism, as they react by the radical mechanism in the presence of noble metal catalysts, *i.e.* hydrogenation takes place by reaction of adsorbed substrate and adsorbed hydrogen. The adsorption of the reacting species on tungsten carbide presumably differs from that on noble metals (at the temperatures under consideration) and this may be a reason for the phenomena observed.

The rate-determining step of hydrogenation is presumably the diffusion or activation of hydrogen. For this the following arguments may be put forward. (*a*) The rate of the reaction does not depend on substrate concentration. (*b*) For different substrates similar rates were found. It is, however, difficult to decide whether the diffusion or the activation of hydrogen is the rate-determining step.

The difference found between the rates of WC and Pt powder of similar surface area indicates that the role of diffusion control may be excluded on the assumption that there are similarities of particle and pore size and distribution. In contrast the poor dependence of the rate upon temperature may be an argument for the rate-determining role of diffusion.

It must be mentioned that in the electrochemical oxidation of hydrogen the activation step is rate determining[1] and results obtained from the comparison of the activity at Pt and WC are similar to ours. The problem of the rate-determining step, however, is not yet clear and further studies are needed to solve it.

This problem, however, does not affect the practical applications of tungsten carbide. An advantage of tungsten carbide is that it can be used in strong acid as can the noble metal catalysts. This cannot be achieved *e.g.* with Raney nickel. Since tungsten carbide is cheaper than noble metals and its activity is more lasting, it may have practical importance. Studies in this direction are in progress.

[3/257 *Received, 5th February,* 1973]

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[6] C. Wagner, *Electrochim. Acta*, 1970, **15**, 987.