

Sorption of Hydrocarbons on Clean Metal Films

STUDIES WITH RHODIUM, IRIIDIUM AND PLATINUM

The study of catalyst behaviour at surfaces is making increasing demands on the experimental skill of investigators. In particular, when studying such mechanisms as the adsorption and decomposition of hydrocarbons on metal surfaces, it has become obvious that the presence of even a relatively few atoms of impurities may contaminate the surfaces and interfere with the progress of the reaction. When a metal surface is to be studied, it is essential that the experimenters can rely on it as being really clean.

For some years, R. W. Roberts and his colleagues, working in the General Electric Research Laboratory, Schenectady, New York, have been engaged in investigating these problems. They have been particularly interested in the application of ultra high vacuum techniques and mass spectroscopy for examining the absorption and desorption of simple hydrocarbons on clean metal films, and Roberts has recently published a summary of their results in a paper contributed to the Conference on the Sorption Properties of Vacuum Deposited Metals held at Liverpool in April (*British J. Applied Physics*, 1963, **14**, 485-487). This paper includes very careful observations of the reactions of ethane with numerous metal films, including those of the platinum metals as well as reactions of propane and butane on a more limited range of materials.

It is true that perfect cleanliness must be an unattainable ideal; but it has been established experimentally that if a metal surface is prepared in a vacuum of 1 ntorr (10^{-9} torr, i.e. 10^{-9} mm of mercury) it will remain free from detectable adsorbed contaminants (in other words, it will remain virtually clean) for several minutes or longer.

The ultra-high vacuum system used in this work has been described by Roberts (*Trans. Faraday Soc.*, 1962, **58**, 1159-1169), and is designed so that all parts can be baked at 400°C - metal parts inside the system being outgassed by electron bombardment or r.f. induction heating. The volume of the system is about 800 cc, and before an experiment is started the pressure inside is reduced to about 2×10^{-10} torr. Changes in the composition of the gas in the system were followed by the use of a small, sensitive mass spectrometer, which also could be baked and degassed before each experiment was started. A small portion of the gas phase was sampled periodically and the masses of the constituent molecules recorded.

The reactions of ethane with clean films of the platinum metals are of special interest when contrasted with their behaviour with films of such carbide-forming metals as tungsten, molybdenum and vanadium; in addition the great variations in catalytic activity, while not completely understood, are most striking.

All of the metals investigated, when clean, adsorb ethane; and of these platinum and palladium, as well as nickel, iron, and titanium yield no gaseous decomposition products either at 27°C or 100°C . The adsorbed species, however, is certainly strongly bound to the surface. The other metals all cause decomposition - either to methane only, to hydrogen only, or to mixtures of methane and hydrogen. Rhodium and iridium are in the first of these classes.

On clean rhodium surfaces, ethane is decomposed at temperatures as low as 0°C to yield gaseous methane and an adsorbed hydrocarbon residue. No hydrogen was

detected by the mass spectrometer, the sensitivity of which was estimated as 1 per cent.

On clean iridium surfaces adsorption and decomposition proceed in much the same fashion but at a slightly reduced rate. Moreover, at temperatures below 100°C, decomposition to methane is not complete; thus at 27°C the reaction yielded 37 per cent of methane, 27 per cent of hydrogen, and 36 per cent of C₂H₆ together with a solid residue identified as CH_{2.8}.

Rhenium, molybdenum and tungsten decompose ethane at 27°C to form hydrogen, and iron gives the same reaction at 350°C; whereas at 200°C palladium produces a mixture of methane and hydrogen.

The presence of only a trace of oxygen – sufficient to form a monolayer on the surface of the clean films – slows down the reactions

of ethane on rhodium by more than a hundredfold, and the major product is not methane but water. This effect will occur if the films are prepared in a vacuum of 10⁻³ torr, conditions which in the past have usually been accounted as excellent.

In considering the reactions of hydrocarbons with clean films, the interesting suggestion is made that the composition of the products may be related to the ease with which the metal will form carbides. This criterion places the platinum metals in a class of their own among those of high melting point, and these metals alone will react with ethane to form methane. Tungsten, molybdenum and vanadium, on the other hand, readily form carbides and on reaction with ethane yield hydrogen as the principal gaseous product.

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Electrodeposition of the Platinum Metals

COMPOSITION OF ELECTROLYTES AND PROPERTIES OF DEPOSITS

Of the six platinum metals, only platinum, palladium and rhodium have established applications for themselves in electrodeposited form, and of these rhodium has so far greatly outweighed the other two in importance. In the last few years, however, an increasing degree of attention has been given to platinum and rather more to palladium, stimulated in the one case by the development of cathodic protection techniques and in the other by the demands of printed circuitry. A considerable literature has now grown up covering electrolytes suitable for the deposition of these metals, and workers in this field will be grateful for a comprehensive survey prepared by F. H. Reid of the International Nickel Company (Mond) Limited and published by the Institute of Metals in their series of "Metalurgical Reviews" (1963, 8, (30), 167-211).

Not unnaturally rhodium receives a considerable share of attention in this review, and a mass of detail is well summarised concerning the preparation of electrolytes, formulation and operating conditions, the effects of operating conditions on the properties of

deposits, and on questions of contamination and purification of the electrolytes.

With both palladium and platinum plating, recent industrial demand has disclosed a paucity of systematic data, and investigations in this field are currently being actively pursued. However, the review surveys the several types of electrolytes that have been proposed for these two metals and the operating conditions recommended for their successful use.

Interest in the electrodeposition of the other three metals of the platinum group has been slight, and there is therefore very little literature to review. Ruthenium plating could, however, have an interesting future. Two other fields in which the author considers that advances might be expected during the next few years are those of alloy plating – possibly of rhodium-platinum or iridium-platinum alloys for high temperature protection – and of electroless deposition, which has obvious potentialities that have not as yet been at all fully explored. The review gives ninety-five references.

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