

# Platinum Metals as Hydrogenation Catalysts

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The object of this paper is to survey the applications of the platinum metals as catalysts for hydrogenation reactions: their applications as oxidation catalysts will not be dealt with. There is an enormous and continually growing literature of this subject, but it is proposed to stress the more recent advances. Only leading literature references will therefore be given.

## Metallic Structure and Activity

On theoretical grounds, maximum activity in hydrogenation processes is expected to be shown by metals in Group VIII of the Periodic Table, and especially by metals in the palladium and platinum triads. Two distinct but related quantities have been recognised as determining catalytic activity: these are respectively the so-called electronic and geometric factors. For the easy chemisorption of gases on metallic surfaces, it is necessary for the metal to possess vacant d-orbitals which can accept electrons from the reactants. If, however, the number of such vacant orbitals is large (as is the case

with metals in Groups III to VII), the gases are strongly chemisorbed, and their removal during reaction is correspondingly difficult. If there are no vacant d-orbitals (as is the case with metals in Group IB), chemisorption is almost impossible, and catalytic efficiency is low. Maximum activity is therefore expected for those metals having the smallest possible number of vacant d-orbitals, i.e. by metals in Group VIII. This is the electronic factor in catalysis.

A further requirement for efficient catalysis is that the metal atoms in the surface should be so arranged and spaced that the transition-state complex of the reaction has the lowest possible energy. This implies a minimal activation energy for the reaction, and hence reaction at the lowest possible temperature. It appears to be little more than a lucky chance that metals which are electronically suitable also have atoms spaced and ordered conveniently. This second requirement is termed the geometric factor in catalysis. The two factors are related in that metallic radii in the transition series metals decrease to a

Values of percentage d-bond character, metallic radii and lattice type for the platinum metals

	Ru	Rh	Pd	Os	Ir	Pt
Percentage d-bond character, $\delta$ , % ..	50	50	46	49	49	44
Metallic radius, $r$ , Å .. .. .	1.34	1.34	1.37	1.35	1.36	1.39
Lattice type .. .. .	C.p. hex	F.c. cube	F.c. cube	C.p. hex	F.c. cube	F.c. cube

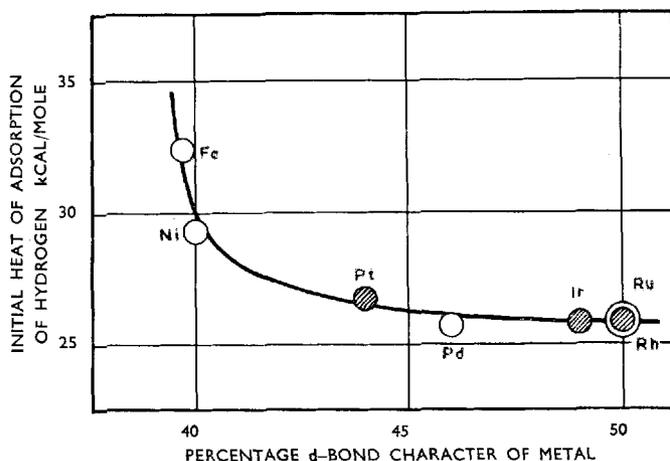


Fig. 1 The dependence of initial heats of adsorption of hydrogen on  $\delta$  for platinum metals. Open circles, on evaporated metal films; hatched circles, on reduced silica-supported metals.

minimum in Group VIII with the number of added d-electrons, but it remains a coincidence that both factors are optimal for catalysis in Group VIII.

The number of vacant d-orbitals possessed by any metals is a quantity which is difficult to measure experimentally. However, Pauling (1) has described the calculation of the percentage d-bond character (given the symbol  $\delta$ ) of metal-metal bonds in the solid. This quantity therefore measures the degree of filling of d-orbitals. Values of  $\delta$  range

between about 20 per cent in Group IIIA to 40 to 50 per cent in Group VIII, so that  $(100-\delta)$  gives an indication of the number of vacant d-orbitals which a metal has. The table gives the values of  $\delta$  for the platinum metals, together with data on their geometric properties. From this table it is seen that high values of  $\delta$  and small metallic radii are shown in particular by ruthenium, rhodium, osmium and iridium, and these metals should thus be more active than the more commonly employed palladium and platinum.

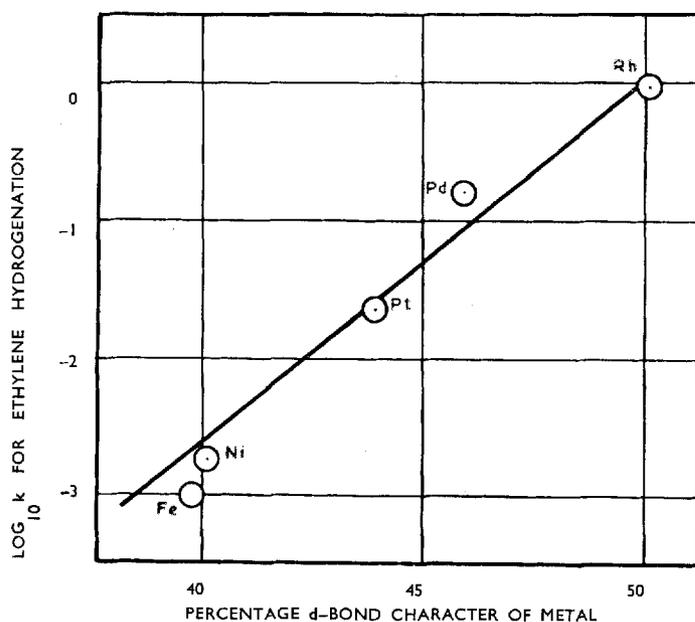


Fig. 2 The dependence of the log of the velocity constant for ethylene hydrogenation on  $\delta$  for evaporated films of platinum metals.

In agreement with the foregoing expectations, it has been found (2) that initial heats of adsorption of hydrogen and of ethylene decrease with increasing values of  $\delta$ , and the relevant data for the adsorption of hydrogen on the platinum metals are shown in Fig. 1. However, the change between rhodium and platinum is not large, and is probably only just outside experimental error. Similarly the activity of evaporated films of platinum metals has been found (3) to increase with increasing values of  $\delta$ , and the relevant data are plotted in Fig. 2. It is worth noting that the change in activity between rhodium and platinum is relatively much greater than the change in their heats of hydrogen adsorption.

### **Physical Forms and the Role of the Support**

Platinum metals are employed catalytically in a wide variety of physical forms. For vapour-phase reactions, it is common to use a massive form, such as wire, wire gauze or foil. Evaporated metal films have a great advantage for fundamental work in that surfaces can be prepared reproducibly and clean. The active area of a massive metal can be very greatly increased by the electrolytic deposition of a thin film of metal on its surface. The metal "black" so formed is extremely porous and has a high surface area: electron micrographs of electro-deposited platinum have shown the existence of clearly observable dendritic growths (4). While highly active, such catalysts are very susceptible to poisoning and have to be protected from mercury and traces of tap-grease.

Catalysts prepared by the reduction of a supported metal salt are far less readily poisoned (4). For work in the liquid phase, it is convenient to use a colloidal form of a metal, either dispersed in the liquid medium or supported by an inert carrier such as calcium carbonate or barium sulphate.

The value of supporting the metal on an

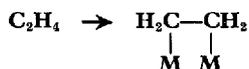
inert carrier has long been recognised, although the precise role of the carrier is not clearly understood. It first enables the metal to be thinly spread and so to expose the maximum surface area: secondly, it is likely that supported metals are less readily sintered than unsupported ones, although no quantitative work seems to have been done on this point. There is, however, growing evidence of a specific chemical interaction between a metal and its support, of a kind which it is not easy to explain. Thus for example the reaction between ethylene and deuterium has been studied (4) over colloidal platinum supported in various insulator oxides, and distinct but fairly minor differences were noted, particularly in the temperature- and partial pressure-dependence of the product distributions. The unique behaviour of Group VIII metals on an acid-support is the basis of the catalyst now widely employed in the reforming of petroleum to give products of greater octane rating. Here the specific interaction between the metal and its support is very marked, since metals supported on insulating oxides do not effect the necessary isomerisation, but the precise nature of the interaction is not known.

Metals of the platinum group have been supported on synthetic polymers, and such catalysts are very effective for certain purposes. Polyvinyl alcohol is particularly suitable as a support (5).

### **The Hydrogenation of Carbon-Carbon Double Bonds**

As has been mentioned previously, metals of the platinum group are highly active for the hydrogenation of olefinic double bonds (6, 7), more so than nickel, although fewer studies on reaction mechanisms have been carried out using platinum metals than using nickel. It is, however, likely that olefines are relatively less strongly adsorbed on platinum than on nickel, and it has been estimated that ethylene is about ten times more strongly

adsorbed than hydrogen on the former (4). Olefines are probably associatively adsorbed, that is to say, the  $\pi$ -bond of the olefine is broken and two carbon-metal bonds are formed:

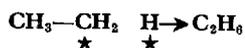
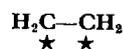
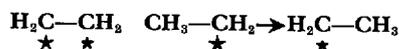
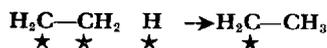
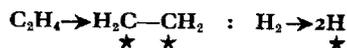


Hydrogen will be present on the surface as adsorbed atoms, but the mechanism is more complicated than the simple one-stage addition of two adsorbed hydrogen atoms to an adsorbed ethylene molecule to form ethane.

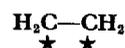
Much detailed information has come from the use of deuterium in place of hydrogen and the subsequent mass-spectrometric analysis of the reaction products (4, 6). The following are the principal results which show the complexity of the process:

- (1) The saturated product is not simply (and sometimes not even chiefly) dideuteroethane, but ethanes containing from nought to six deuterium atoms are also formed.
- (2) Deuterium atoms are introduced into the ethylene, although more slowly with platinum than with nickel.
- (3) Hydrogen is introduced into the deuterium, although again more slowly over platinum than over nickel.

These two latter processes are termed the olefine exchange and hydrogen exchange reactions respectively. From these observations it is possible to construct a plausible reaction mechanism, as follows: asterisks indicate bonds to the metal.



or



It is frequently found that the yields of the deuterated ethanes decrease logarithmically with increasing deuterium content, so that by plotting the log of the yield against the number of deuterium atoms a straight line is obtained. From the slope of this line, a mean value of the ratio

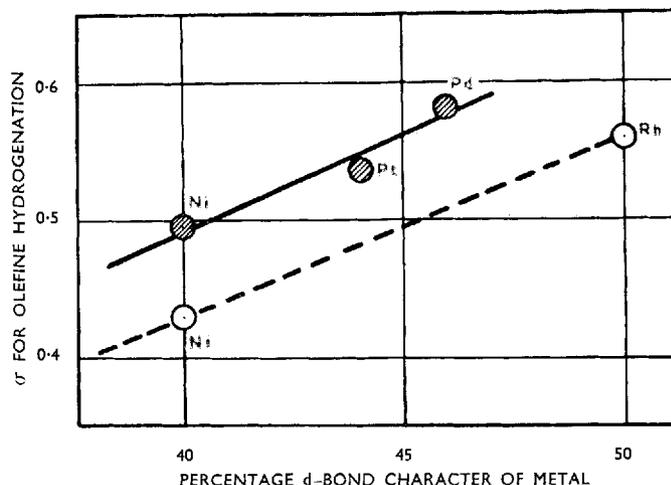
$$\sigma = \frac{[\text{C}_2\text{H}_6-x \text{D}x+1]}{[\text{C}_2\text{H}_6-x \text{D}x]}$$

where  $x=2 \dots 5$

can be calculated. Fig. 3 shows the dependence of  $\sigma$  for the ethylene-deuterium reaction on  $\delta$ , the percentage d-bond character of the metal. Values are known both for supported metal catalysts and also for evaporated metal films (8). Values for nickel are included for comparison. It is concluded that  $\sigma$  increases with  $\delta$  and therefore with basic activity, although the values for different types of catalyst are not identical. A method of determining catalytic efficiency without reference to rates of reaction is therefore available.

Metals of the platinum group are also efficient catalysts for the hydrogenation of cyclopropane, although here the situation on the surface is somewhat different from that existing during the hydrogenation of olefines. Cyclopropane is more weakly adsorbed than hydrogen, and during the reaction there are a relatively few propyl radicals surrounded by a large number of hydrogen atoms. When deuterium is used in place of hydrogen, the hydrogen atoms of the propyl radicals are readily replaced by deuterium atoms, and the major product is then perdeuteropropane. A study of the available results (9) has shown that the

Fig. 3 The dependence of  $\sigma$  in olefine hydrogenation on the percentage d-bond character of metals. Open circles, evaporated metal films; hatched circles, supported metal catalysts.



efficiency of multiple exchange in this system increases with increasing  $\delta$  and hence also with basic hydrogenating activity. This work showed that iridium is a slightly more efficient metal for multiple exchange than is rhodium, although its  $\delta$  value is slightly smaller. This is of particular interest, since iridium has been little studied in fundamental work on catalytic hydrogenation.

A similar correlation between multiple exchange activity and  $\delta$  can be derived from studies of the exchange reaction between deuterium and the hydrogen atoms in saturated hydrocarbons. For example, the ethane-deuterium reaction has been followed over evaporated films of a number of metals (10), and whereas on metals such as tungsten, zirconium and vanadium mono-deuteroethane is the chief product, per-deuteroethane is the chief product over the platinum metals.

### The Hydrogenation of Carbon-Carbon Triple Bonds

Problems of a somewhat different nature from those met with in olefine hydrogenation are encountered in the hydrogenation of acetylenic bonds catalysed by metals of the platinum group (11, 12). First, this is a two-stage process, and considerable interest attaches to the selective production of the intermediate olefine. Secondly the catalytic

hydrogenation of, in particular, acetylene is accompanied by a hydropolymerisation reaction leading to butanes, hexanes and higher hydrocarbons, while thirdly the reduction of the acetylenic bond is often stereospecific, leading chiefly to the formation of the corresponding cis-olefine.

**Selectivity.** The selective production of olefines in the hydrogenation of acetylenes can only be explained in terms of the stronger adsorption of the latter. Once an olefine molecule has been formed and has desorbed, it cannot re-adsorb and be further reduced until most of the acetylene has been removed. Any fully saturated product which is formed in the initial stage of the reaction must therefore arise from the further reduction of olefine which does not desorb after its initial formation. Selectivity is therefore closely related to the ease of olefine desorption. That the stronger adsorption of the acetylene is responsible for the failure of desorbed olefine to react further is shown by the fact that in many cases the olefine separately reacts faster than does the acetylene.

Selectivity depends markedly on the physical form of the catalyst, and varies widely from metal to metal within the platinum group. Thus platinum and palladium "blacks" are generally non-selective, while

colloidal palladium is highly selective. Supported palladium catalysts increase in selectivity with continued use, but this is largely because they become poisoned with respect to their ability to hydrogenate olefines. Rhodium has been reported to be highly selective and iridium of very low selectivity.

**Hydropolymerisation.** Although not nearly as marked as over Group VIII metals in the first triad, this process is none the less significant over metals of the platinum group. C<sub>2</sub> hydrocarbon yields from acetylene are only 70 to 85 per cent over the face-centred cubic platinum metals; C<sub>3</sub> recoveries from methylacetylene are higher except over palladium. The mechanism of the reaction is as follows: reaction between an adsorbed hydrogen atom and an adsorbed acetylene molecule leads to an adsorbed vinyl radical which may exist in either a "normal" or a free-radical form, viz.



The free-radical form then initiates vinyl-like polymerisation with either "normal" vinyl radicals or with chemisorbed acetylene molecules. The larger interatomic distances in the platinum group metals as against those in the first Group VIII triad lead to less efficient polymerisation over the former

metals. The steric hindrance caused by the methyl group in methylacetylene also makes for less efficient polymerisation.

**Stereospecificity.** The degree of stereospecificity in a given system is probably more dependent on reaction time and temperature than on the particular metal used. The adsorption of acetylene as a cis-ethylene complex  $\text{HC}=\overset{\star}{\text{C}}\text{H}$  necessarily leads to the formation of a cis-olefine if the free-radical form of the vinyl radical does not intervene. Stereospecificity in the hydrogenation of acetylene over nickel is low, indicating the importance of the vinyl free-radical in this system.

Before leaving acetylene hydrogenation, it is worth noting a very marked geometric factor in this reaction over Group VIII metals. While the face-centred cubic metals are quite active, the close-packed hexagonal metals ruthenium and osmium are inactive, as they do not have the necessary interatomic spacing for the adsorption of acetylene.

## The Hydrogenation of Other Unsaturated Functions

Platinum metals are efficient catalysts for the reduction of a variety of other unsaturated functions, and also for the hydrogenolysis of, for example, alkyl halides. Platinum

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and palladium will reduce acetone to propane, with or without the intervention of iso-propyl alcohol. Thus, for example, perdeuteropropane has been made by the catalytic reduction of perdeuteroacetone with deuterium over palladium at 100°C. The  $-\text{NO}_2$  group is readily reduced to  $-\text{NH}_2$  by hydrogen with the aid of platinum metals, and oxygen is easily reduced to water by the same method. This latter procedure is employed for the

removal of traces of oxygen from hydrogen.

Ruthenium and osmium efficiently catalyse the decomposition of ammonia to nitrogen and hydrogen, while the platinum metals catalyse the replacement of the hydrogen atoms in ammonia by deuterium. Platinum metals catalyse the hydrogenation of benzene to cyclohexane, although palladium is less active than expected, perhaps because of the poisoning action of dissolved hydrogen.

## Electron Microscopy of Crystal Lattices

Since the classical work of G. I. Taylor in 1934 it has been accepted that the failure of metals to reach their theoretical strength and their behaviour in fracture, fatigue or creep are explained by the existence of defects or dislocations in their crystal lattices. Such defects, of atomic or molecular dimensions, have not hitherto been observed directly, but a significant step in this direction has recently been reported by Dr. J. W. Menter of the Tube Investments Research Laboratories, Hinxton Hall, Cambridge.

Working on the principle that provided a crystal lattice were sufficiently large to be resolvable in the electron microscope it should be possible not only to follow the propagation of a crack but to observe directly various types of imperfections in the lattice,

Dr. Menter chose crystals of metal phthalocyanines for examination. In particular platinum phthalocyanine was thought to have suitable crystal dimensions and to have planes lying in a suitable orientation.

A preliminary survey of this work (*Proc. Roy. Soc.*, 1956, **236A**, 119) includes a number of quite remarkable electron micrographs, one of which is reproduced below. This shows part of a crystal of platinum phthalocyanine, magnified 1,500,000 times, and exhibiting perfect structure, but numerous other micrographs illustrate various types of imperfections and their propagation.

This technique opens up a rich new field yet to be explored in the study of crystal lattices, more especially of materials whose bulk properties are already known.

*Part of a perfect crystal of platinum phthalocyanine seen under the electron microscope with a magnification of 1,500,000 times. The well-defined parallel lines represent the edge projections of individual sheets of molecules, separated in the crystal by a distance of  $12 \text{ \AA}$  ( $0.00000012 \text{ cm.}$ )*

