Catalytic Hydrogenation over Platinum Metals

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PART I

Catalysts, Equipment, and Conditions

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1

Platinum Metal Catalysts

I. PLATINUM METALS

The six elements in the platinum metals group (Table I) are all hydrogenation catalysts. Palladium and platinum catalysts have been widely used for decades. Rhodium and ruthenium also make excellent hydrogenation catalysts, but their merits are not yet so widely appreciated (most references to these catalysts date from the middle fifties). Iridium and osmium have found still less use. Osmium hydrogenation catalysts do not appear to have exceptional merit; whether this is due to some intrinsic property of osmium or to inadequate procedures in the catalyst preparation is not yet known. Iridium, on the other hand, makes a fair catalyst and its lack of use stems partly from neglect and partly from the fact that some platinum metal has usually proved more suitable whenever a comparison was made.

The platinum metals make exceptionally active hydrogenation catalysts, and most functional groups can be reduced under mild conditions over one or another of these catalysts. Many industrial hydrogenation processes are carried out at elevated pressure and/or temperature, however, to make more

TABLE I

PLATINUM METALS[a]

Element	Symbol	Atomic number	Atomic weight
Ruthenium	Ru	44	101.07
Rhodium	Rh	45	102.905
Palladium	Pd	46	106.4
Osmium	Os	76	190.2
Iridium	Ir	77	192.2
Platinum	Pt	78	195.09

[a] A review of the physical properties of the platinum metals and gold and silver has been published in *Engelhard Ind. Tech. Bull.* **6**, 61 (1965).

efficient use of the metal and hydrogenation equipment. The most effective metal varies with each substrate, but enough data have accumulated to permit a satisfactory selection of catalyst and conditions for successful reduction of most substrates without undue difficulty.

II. TYPES OF CATALYST

Platinum metal hydrogenation catalysts are of two types—supported and unsupported, with the latter group being further divided into those for use in slurry processes and those for use in fixed-bed operation. In batch-type hydrogenations the support is usually a fine powder. Occasionally a coarser support is used, so that on completion of the reaction the catalyst settles and can be recovered by decantation rather than filtration. Catalyst supports for use in fixed-bed operation are usually in the form of cylinders, spheres, or granules with particle size of roughly $\frac{1}{4} - \frac{1}{32}$ inches.

A. Unsupported Catalysts

Early in the century, platinum metal catalysts were usually in the form of finely divided metal or metal oxide (Sabatier, 1923). The metals are referred to as blacks, and, if stabilized in solution by substances such as gum arabic (Skita, 1912) or polyvinyl alcohol (Rampino and Nord, 1941), as colloidal catalysts. Platinum metal oxides and blacks are still widely used and may be preferred to supported catalysts with compounds difficult to hydrogenate, or when substantial yield losses occur through absorption of products by the catalyst support (Barnes and Fales, 1953), or when overly strong adsorption on the support poisons the catalyst. Unsupported metal is used less efficiently than supported metal and recovery losses are likely to be higher.

B. Supported Catalysts

Supported platinum metal catalysts have a number of advantages over unsupported catalysts. The support permits greater efficiency in use of the metal by increasing the active metal surface and by facilitating metal recovery. Also, supported catalysts have a greater resistance to poisoning. Perhaps the greatest value of a support is that it provides a further control over selectivity.

Platinum metals have been supported on a variety of materials, including such diverse substances as carbon, alumina, silica, alkaline earth carbonates and sulfates, zinc, asbestos, and silk. The list could be extended greatly. One gathers that almost any material of suitable form and stability can be used

as a catalyst support. The relationship between performance and support is extremely complex for, among other things, performance is related to the particular sample of support examined (Maxted and Elkins, 1961), to the precise method of metal deposition, and to the system in which the catalyst is used. Among the physical properties of a support that may influence performance are total surface area, average pore size, pore size distribution, and particle size, insofar as these properties affect the metal dispersion and control the transport of reactants and products to and from the catalyst surface.

Relatively little effort has been made in liquid phase catalysis to disentangle the multiple contributions, both chemical and physical, of a support to catalyst performance, but in special instances particular characteristics have been singled out. For instance, the activity differences found in platinum-on-alumina, platinum-on-zirconia, and platinum-on-chromium sesquioxide, when used for hydrogenation of cyclohexene and ethyl crotonate, have been related to mean pore radius of these supports; correlations between activity and surface area of the platinum metal (Maxted and Elkins, 1961), or in supported palladium catalysts between activity and surface area of the support, were not evident (Maxted and Ali, 1961). On the other hand, the marked difference in isomer distribution obtained on hydrogenation of hexahydroxybenzene over colloidal palladium and over 10% palladium-on-carbon was attributed to the greater surface area of the latter (Angyal and McHugh, 1957). The products of hydrogenation may also change with the support, inasmuch as various supports, for whatever reason, give catalysts of differing activities and consequently different levels of hydrogen availability at the catalyst surface (Zajcew, 1960; Augustine, 1963). Supports, or the catalyst as a whole, may also influence the product insofar as they contain trace quantities of free acid or alkali.

1. *Agglomeration*

Supports may affect catalyst activity, as the support partly determines the tendency of a catalyst to agglomerate or to stick to the reactor walls. The factors determining the degree of agglomeration are indeed subtle, for the extent of agglomeration may change markedly with the support, the reaction, and minor changes in the reaction system. Catalyst clumping is a common cause of unsatisfactory results. This difficulty can usually be overcome by a change of support, amount of catalyst, agitation, solvent, or even reactor size.

2. *Resistance to Poisoning*

Metals on different supports vary in resistance to poisoning by extraneous contaminants and by products of the reduction. The effect that a product

of reduction may have on the catalyst is illustrated by hydrogenation of nitrobenzene in cyclohexane solvent over 5% palladium-on-carbon and 5% palladium-on-alumina. Both catalysts had the same initial rate, and over the carbon-supported catalyst the reaction continued unabated almost until completion. However, over the alumina catalyst the rate declined sharply to one sixth of the original rate when the reaction was about 30% complete. When water, equal to the amount formed at this point, was added initially the reduction began at and maintained this lower rate. In this system, palladium-on-calcium carbonate tended to stick to the walls of the reactor and was largely unavailable for use (Rylander *et al.*, 1965). The support may also influence the course of reduction and the amount of various inhibiting by-products.

In general, supported catalysts show a greater resistance to poisoning than nonsupported catalysts, probably because the support increases the active surface (Germain *et al.*, 1961). Also, the support itself may sop up catalyst poisons and inhibitors; the performance of unsupported catalysts can often be improved by adding a catalyst support, such as high surface carbon, to the reaction mixture.

3. *Effect of Particle Size on Activity*

The activity of a catalyst is related to the particle size of the support, as illustrated by the data of Table II (Rylander *et al.*, 1965). A 1% platinum-on-carbon catalyst was divided by screening into five portions, and an equal weight of each portion was used in hydrogenation of nitrobenzene dissolved in acetic acid. Only part of the marked increase in rate with decreasing particle size can be attributed to the higher percentages of metal found on the smaller particles; most of the increase must be attributed to better transport of reactants to the catalysts. The rate advantages obtained by

TABLE II

EFFECT OF PARTICLE SIZE ON RATE OF HYDROGENATION[a]

(Hydrogenation of Nitrobenzene in Acetic Acid)

Particle size	Percent Pt on support	Relative rates based on equal weights of catalyst
40–60 mesh	1.0	1.0
60–80 mesh	1.0	1.6
80–100 mesh	1.02	1.9
100–150 mesh	1.07	2.5
through 150 mesh	1.43	5.9

[a] 100 mg platinum-on-carbon catalyst, room temperature, atmospheric pressure.

using very fine particles are in practice offset by increasing catalyst cost and by difficulties in filtration. The best catalysts combine a sufficiently fast rate with easy recovery. Rampino and Nord (1941) have examined the complex relationship between particle size and rate of hydrogenation over palladium and platinum-polyvinyl alcohol colloidal catalysts.*

4. *Economical Use of Metal*

In general, supported catalysts provide much more economical use of the metal. For example, hydrogenation of heptaldehyde over equal weights (on a metal basis) of 5% platinum-on-carbon and over platinum oxide proceeded about eight times more rapidly over the former (Rylander and Kaplan, 1961). Similar comparisons are common. In addition, supported catalysts may be more easily filtered, and mechanical losses of the metal will be proportionately less when handling a metal diluted by a support.

5. *Concentration of Metal*

Platinum metal catalysts for use in batch processing usually contain about 1–10% by weight of metal, although special purpose catalysts containing as much as 30–40% by weight of metal are made and used commercially. Fixed-bed catalysts contain generally about one tenth as much metal as powdered catalysts. The percentage of metal on a catalyst has, with a number of exceptions, little effect on the product, and the question of appropriate metal concentrations is determined in most instances more by economic than technical considerations. More efficient use is made of the metal as the concentration of the metal is lowered (Table III) (Karpenko, 1964), but the

TABLE III

HYDROGENATION OF NITROBENZENE IN ACETIC ACID[a]

Catalyst	Catalyst (mg)	Pd (mg)	Relative rate
1% Pd-on-carbon	500	5	7.6
3% Pd-on-carbon	166	5	3.5
5% Pd-on-carbon	100	5	1.8
10% Pd-on-carbon	50	5	1.2
30% Pd-on-carbon	16.6	5	1.0

[a] Each experiment was carried out at room temperature and atmospheric pressure with 500 mg total carbon carrier present. Not all substrates show as large a variation in rate with percent metal as shown here; the magnitude of the change depends among other things on the substrate (Young and Hartung, 1953).

* Manufactured by Engelhard Industries, Newark, N.J.

increased efficiency is offset by increasing catalyst costs. Since the platinum metal is ordinarily reclaimed, the metal cost is not the major factor in the total cost of the catalyst. In the United States, 5% metal-on-powdered carrier catalysts are used widely, the economics being such that metal concentrations in this range will give the most product per dollar of total catalyst cost. When the metal is recovered, 10% metal-on-carrier catalysts are only slightly more expensive to use than 5%. In England, where labor costs are different, 3% catalysts are more popular.

6. *Asymmetric Supports*

Asymmetric syntheses may be achieved by catalytic hydrogenations carried out over a platinum metal deposited on an asymmetric surface, as *d*- or *l*-quartz or silk fibroin, but the optical purity is usually not high. Optically active phenylalanine was obtained in 25% optical purity by the hydrogenation of ethyl α-acetoximino-β-phenylpyruvate over palladium-on-silk fibroin at 70°C and 1350 psig pressure, followed by acid hydrolysis of the product. Optically active phenylalanine was also derived by hydrogenation of 4-benzylidene-2-methyloxazol-5-one under similar conditions over a palladium-on-silk catalyst (Akabori *et al.*, 1956, 1957). There is some evidence that catalyst sites may be asymmetric and present with an equal number of the mirror images. In support of this suggestion was the observation that an optically active compound was not reduced as fast as the racemic mixture (Beamer *et al.*, 1960).

7. *Choice of Support*

The rate and, at times, the products of reduction vary with the catalyst support. The literature records many examples (Rylander *et al.*, 1965) where one catalyst support was preferred to another, but guiding principles for choice have yet to be developed. An understanding of the influence of carrier on the rate and course of reduction from preferences recorded in the literature is particularly difficult to achieve, because one is never certain whether it was the support itself, the method of catalyst preparation, or some unknown factor that was responsible for the differential results. Even in controlled studies it is difficult to disentangle effects produced by the support itself from various other factors involved in the comparison. For instance, optimum catalysts are not produced if all catalysts are prepared by the same technique regardless of support, but if the technique is altered an additional variable will be introduced.

In practice it is usually not difficult to pick a satisfactory support. Unless there is evidence to the contrary, either carbon or alumina is an excellent first choice and either will prove adequate for most reductions. Beyond this

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