

# Palladium-on-Charcoal Catalysts

## SOME EFFECTS OF VARIABLES ON HYDROGENATION ACTIVITY

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*The performance of charcoal-based catalysts cannot be described simply in terms of their mesh size and noble metal content, as many factors can cause wide variations in activity, selectivity and resistance to poisoning. It is possible, however, by close collaboration between catalyst manufacturer and user, and by suitable choice of base and production technique, to provide a range of such catalysts tailored to meet the needs of a particular industrial reaction.*

Catalysts of the type commonly described as palladium-on-charcoal find extensive use in the chemical and pharmaceutical manufacturing industries as hydrogenation catalysts for a wide variety of reactions.

Basically, charcoal supported catalysts are comprised of powdered activated charcoal having a particle size of the order of 200 mesh impregnated with a solution of a palladium salt which is subsequently reduced to metallic form.

Since charcoal is essentially a natural product, wide variations in its physical structure, in its purity, in its content of trace elements, and indeed in its properties generally are to be expected. More than this, the activity of palladium-on-charcoal catalysts is, somewhat surprisingly, susceptible to extraordinarily wide variation according to the method chosen to introduce palladium into the structure and to absorb it on the surface of the charcoal particles. In addition, the resistance of a palladium-on-charcoal catalyst to certain types of poisoning can be influenced both by method of manufacture and by various after-treatments.

It thus becomes possible, by suitable choice of charcoal and by the use of appropriate manufacturing techniques, to make palladium-on-charcoal catalysts that differ widely in their performance, in their activity as hydrogenation

catalysts, in their selectivity and in their resistance to particular forms of poisoning in use. It cannot be emphasised too strongly that the activity of any palladium hydrogenation catalyst cannot be expressed generally but only as it is related to specific hydrogenation reactions or groups of reactions.

### Nature of Charcoal Base

Charcoal bases for catalysts are nearly always selected from the group known as "activated" charcoals. The raw material from which "activated" charcoal is made is a carefully selected natural product which may be hard wood, nutshells, peat, or a blend of particular grades of coal and anthracite. After carbonising by heating in retorts to about 600°C, the charcoal is "activated" to develop the required pore structure by heating again in a controlled atmosphere, usually of steam. The control of this stage is normally by means of an absorption or decolourising test using a suitable dyestuff such as methylene blue.

The extent to which the activity of palladium-on-charcoal catalysts in specific reactions is dependent on the nature of the charcoal base may be illustrated by a simple example.

Two charcoals, impregnated with the same proportion of palladium by the same technique, were used as catalysts in two well-

*Determining the activity of a palladium-on-charcoal catalyst in the Johnson Matthey research laboratories by measuring the rate of hydrogen absorption in a hydrogenation reaction at room temperature*



known hydrogenation reactions—one of crotonic acid and the other of nitrobenzene—both at room temperature and atmospheric pressure. The relative rates of uptake of hydrogen were found to be as follows:

	Crotonic Acid	Nitrobenzene
Charcoal A	100	55
Charcoal B	105	3

It is clear that these two charcoals are fundamentally different in their performance as catalyst bases. A catalyst made with Charcoal B is slightly more active than one made with Charcoal A in promoting the hydrogenation of crotonic acid, yet it is very nearly inactive for the hydrogenation of nitrobenzene, for which the catalyst made with Charcoal A is over 17 times more active.

Similar wide variations in the characteristics of palladium-on-charcoal catalysts may be deliberately achieved by modifying the procedure by which the charcoal is impregnated with palladium. The extent to which activity can be varied in different reactions by

this means is well shown by the following test results, all relating to catalysts containing 3 per cent of palladium on the same type of charcoal.

	Relative Activity in Hydrogenation of Nitrobenzene	Activity in an Industrial Hydrogenation Reaction
Made by Procedure A	100	Good
„ „ B	46	Poor
„ „ C	24	Good
„ „ D	118	Good

### Percentage of Palladium

The amount of palladium incorporated in a catalyst mass of the type under discussion is, in general, of less importance than the way in which it is applied or the nature of the charcoal base. Provided that more than a minimum amount is present, the actual palladium content is generally not very critical.

The effect of varying the palladium content on the properties of one type of palladium-on-charcoal catalyst (all other factors being kept constant) is shown in the table over page.

Effects of Variations in Palladium Content on the Activity of a Charcoal-base Catalyst		
Per cent palladium in catalyst	Relative Rates of Hydrogenation of Nitrobenzene	
	Using constant weight of catalyst (1.00g.)	Using sufficient catalyst to contain 0.03 g. Pd
0.5	22	44
1.0	59	84
2.0	88	88
3.0	100	100
4.0	112	110
5.0	116	115
6.5	118	97
8.0	118	96

It follows from these results (at least under the test conditions employed, in which a mechanical shaker was used to maintain

vigorous interaction between the catalyst, the liquid and the gaseous hydrogen) that it is not possible to compensate for a low palladium content simply by using more catalyst. The activity of the catalyst in this and in many other reactions appears to rise sharply to a maximum corresponding to around 4 to 5 per cent of palladium and then to remain constant or to decline slowly as the palladium content is increased. This conclusion applies equally whether activity is judged in terms of the weight of catalyst or of the weight of palladium in the circuit.

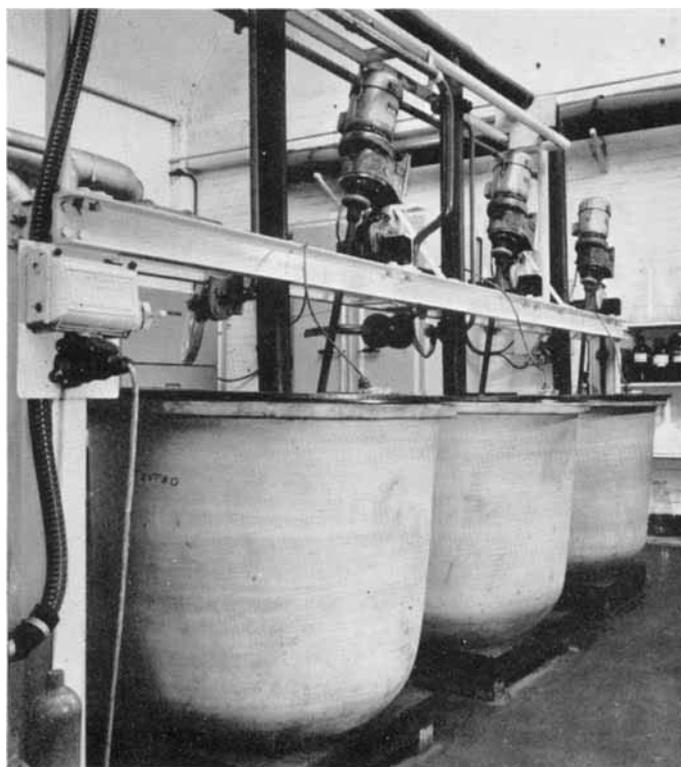
### Poisoning of Catalysts

General poisoning of charcoal-base catalysts, resulting in an overall loss of activity, may of course often occur in service. It is not so generally appreciated that poisoning may occur during storage in industrial atmospheres. Traces of sulphur dioxide, in particular, may render an active catalyst completely inactive in the course of a few minutes, and for this reason the protection of catalysts in storage needs particular care and consideration to ensure that their initial high activity is maintained until the time comes for their use. Charcoal-base catalysts are accordingly packed in airtight containers and these should be stored in clean, dry and uncontaminated surroundings. The original packings should not be opened until immediately



*A constant temperature autoclave for the investigation of hydrogenation reactions over charcoal-base catalysts at elevated temperatures and pressures*

*Equipment for the impregnation of charcoal supports in the production of Johnson Matthey catalysts to meet special requirements in the pharmaceutical industry*



before the catalyst is required for use.

In some instances it is of advantage to supply the catalyst as a damp paste rather than as a dry powder, for ease in transport and handling.

It is sometimes possible to develop charcoal-base catalysts which will selectively promote one of two or more possible hydrogenation reactions in certain systems. This may be achieved by selectively poisoning the catalyst, presumably thereby occupying those active sites on the catalyst surface which would normally be responsible for the unwanted hydrogenation reactions. Controlled quantities of base metal salts, of quinoline or of certain sulphur compounds, added during catalyst manufacture, are examples of selective poisons which have been used for the control of industrial hydrogenation processes.

Finally, the active life of a charcoal-base catalyst in some hydrogenation reactions has sometimes been prolonged, and its resistance

to poisoning in service increased, by selectively pre-poisoning it during manufacture. The original activity is by this treatment somewhat reduced, but an appreciably more stable catalyst is produced.

The examples quoted above have been confined to palladium-on-charcoal catalysts, but the discussion applies with equal force to platinum-on-charcoal and to charcoal-base catalysts impregnated with ruthenium or other platinum metals. The performance of none of these is to be described simply in such general terms as mesh size of the charcoal and the noble metal content. There is an almost unlimited field for the development of an immense range of catalysts differing in activity, selectivity, and service life, and one which can be explored only by the closest collaboration between the manufacturer of catalysts on the one hand and the user—whether research chemist, development engineer or plant operator—on the other.