

New Hydrogenation Catalysts

POSSIBILITIES OF PROTEIN FIBRES AS BASES

A new type of palladium hydrogenation catalyst developed in Japan at Osaka University has silk as its carrier material. Early work by S. Akabori, Y. Izumi, Y. Fujii and S. Sakurai resulted in a silk-palladium catalyst which was effective for the asymmetric reduction of certain unsaturated compounds. The catalyst was prepared by co-ordinating palladium chloride with silk fibroin fibres and then hydrogenating the complex. Because of its low density, high ignition point and the ease with which it may be handled, the silk-palladium has characteristics which recommend it as a general hydrogenation catalyst. It is easily mixed with reacting substances and may be separated from them by simple filtration. The silk may be prepared as sheets, cloths or wool by spinning and weaving.

In three recent papers Y. Izumi describes an investigation into the suitability of the silk-palladium catalyst for general hydrogenation reactions (*Bull. Chem. Soc. Japan*, 1959, **32**, (9), 932-945). The preparation and stability, properties and physicochemical characterisation of the catalyst were studied. At the same time, a 6-Nylon-palladium catalyst was prepared and assessed.

Although the original silk-palladium complex was prepared by boiling silk fibroin fibres with an aqueous solution of palladium chloride, Izumi found a 5 per cent palladium content may be obtained by using a dilute acetic acid solution of the palladium salt. The resulting chelate is activated by reduction with hydrogen in an autoclave. Both the catalyst and its precursor, the silk-palladium chelate, are quite stable and may be stored for a long period without loss of activity. A value of 14.5 kcal/mol is quoted for catalyst activation energy in the hydrogenation of nitrobenzene to aniline. 6-Nylon-palladium prepared by a similar method has a lower

palladium content (2.3 per cent) but also shows a high activity; its activity is proportional to its palladium content.

The activity of the catalyst was examined with a variety of unsaturated compounds. In contrast to the original catalyst prepared from an aqueous palladium chloride solution, it does not achieve asymmetric catalysis. However, aliphatic C=C double bonds are reduced at low temperatures in a selective reaction in which carbonyl groups remain unattacked even at higher temperatures. Therefore, the catalyst is particularly suitable for the preparation of saturated aldehydes and ketones from the corresponding unsaturated compounds. Aromatic C=C bonds are inert to the catalyst. Although aliphatic carbonyl groups (with the exception of α -ketoglutarate) are not susceptible, aromatic carbonyl groups are attacked. Aldehyde, nitrile and nitro groups attached to aromatic rings are catalytically hydrogenated as are azobenzene and some oximino groups, but there is a weak catalytic effect for aliphatic nitro groups. After one run the activity of the silk-palladium catalyst is considerably increased and this higher activity persists for at least four more runs.

Toxicity tests carried out during the hydrogenation of nitrobenzene and diethyl maleate showed that the silk catalyst is more seriously poisoned by ethyl mercaptan than is a palladium-carbon catalyst; however, no palladium is extracted from the silk-palladium in contrast to a carbon catalyst. The mercaptan probably inhibits the catalyst by direct blocking of the active palladium. Acetylation and the presence of ferric and cupric ions greatly lower the activity. It is thought that the metal ions form chelate linkages with the protein, thus blocking the active palladium atoms distributed inside the

fibroin micelles; acetylation may have a similar effect. Treatment with EDTA reactivates the catalyst poisoned by ferric or cupric ions; in fact, EDTA treatment produces a more active catalyst. Also, treatment of silk fibroin with acetic anhydride prior to the preparation of the catalyst gives a strongly active product.

In an attempt to determine the mechanism of catalytic asymmetric reactions, silk fibroin, its palladium chloride chelate, the silk-palladium catalyst and 6-Nylon catalyst were examined by X-ray diffraction and infrared spectrophotometry. The reaction of the palladium in the silk complex with *p*-nitrosodimethylaniline was also observed.

Infra-red absorption measurements indicate that the NH, OH, COOH and CONH groups of the fibroin participate in the chelate formation. On reduction, the chelate linkages are broken and the palladium is then present in an atomic form. Studies by X-ray diffraction suggest that chelate formation

does not significantly alter the arrangement of the fibres. Distinct patterns due to palladium atoms are observed after hydrogenation of the complex. Chemical reaction with *p*-nitrosodimethylaniline confirms the presence of some of the palladium of the complex in a readily reactive state while the remainder appears to be dispersed in the fibre structures.

It is concluded that part of the palladium atoms in the catalyst are assembled in fine crystalline particles and the remainder probably becomes regularly arranged in the micelle structures of the fibres. There is a possibility, also, that certain regular structures emerge in the protein carrier itself.

No definite explanation of the mechanism of catalytic asymmetric reduction is given although it is suggested that it is related to the structure of the carrier. The lack of activity in this type of reaction of catalysts prepared in acetic acid is so far not understood.

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PLATINUM METALS IN POTENTIOMETERS

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The example illustrated is a miniature sine-cosine potentiometer intended mainly for use in airborne equipment. This has a flat Corundite former wound with either 10 per cent rhodium-platinum or 20 per cent copper-platinum wire according to the resistance required. The face of the winding is swept in a circular track by brushes of platinum-gold-silver alloy wire, soldered end-on to beryllium-copper blades so that the contact area does not increase with wear. Slip rings of copper-palladium are used with platinum-gold-silver brushes.

Only 1-5/8 inch in diameter, the potentiometer provides 18° revolution and 0.5 per cent sine law accuracy, with life expectation exceeding half a million revolutions.

