Studies on the Silk-Palladium Catalyst. I.
Preparation and Stability

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A number of methods have so far been attempted in order to increase the active surface of hydrogenation catalysts of metal or metal oxide nature. Thus, for example, a method has been devised to deposit certain metals or metal oxides onto porous carriers such as carbon or Kieselguhr, to disperse them into colloidal states with the aid of various protective colloids, or to remove a constituent metal from an alloy by chemical treatments as in the case of preparation of Raney nickel. The other methods so far attempted are also based on physical or mechanical dispersion of catalyst metals into colloidal solutions or on the surface of porous substances.

A few years ago, Akabori et al.[1-3] for the first time reported an entirely new type of hydrogenation catalyst and showed that it was capable of catalyzing asymmetric reduction of certain unsaturated compounds. This catalyst was prepared by coordinating palladous chloride with silk fibroin fibers and then hydrogenating the resulting silk-$PdCl_2$ complex. Since palladous can form a chelate compound with silk fibroin, it is not unreasonable to assume that the palladium in the catalyst is firmly fixed to the asymmetric structure of the protein fibers in an almost atomic state. The capacity of asymmetric catalysis may be explained on the basis of the asymmetric structure of the carrier fibroin.

Although this catalyst was originally developed for the purpose of asymmetric synthesis, it also has a number of characteristics suitable for use as a general hydrogenation catalyst. Thus, it is quite easy to mix the catalyst with reacting substances because of its unusual low

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[1] S. Akabori, Y. Izumi, Y. Fujii and S. Sakurai, *Nature*, 178, 323 (1956).

[2] S. Akabori, Y. Izumi, Y. Fujii and S. Sakurai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 1374 (1956).

[3] S. Akabori, Y. Izumi, Y. Fujii and S. Sakurai, ibid., 78, 168 (1957).

density. The catalyst is also unique in that its carrier is a fibrous protein and therefore it can be spun or woven into sheets, cloth or fluffs. In hydrogenation catalysts hitherto devised, the metal is either bound to the carrier by simple mechanical attraction or finely dispersed as colloidal particles. Therefore, it is sometimes not very easy to separate the catalyst from the reaction mixture due to the detachment of the metal from the carrier or to the colloidal nature of the catalyst. With the silk-palladium catalyst, however, the catalyst can be readily separated from the reactants by simple filtration owing to the fact that the metal, though highly dispersed, is tightly held by the micelle structure of silk-fibroin.

The investigations to be reported in this and the following papers were undertaken with an object of obtaining some basic data concerning the applicability of this hydrogenation catalyst for general practical purposes. Also included in this series of papers are observations on the properties of a Nylon-palladium catalyst in which silk fibroin is replaced by the synthetic fiber, 6-Nylon, as the carrier.

Results and Discussion

Activity and Conditions of Preparation of Catalyst.—For the purpose of obtaining the catalyst of a high activity, optimum conditions were sought for the preparation of the catalyst. Table I records the palladium contents of various preparations prepared under different sets of conditions. As can be seen, the highest content was attained when 350 mg. of silk fibroin was boiled for 8 min. with 100 ml. of 0.1 N acetic acid containing 100 mg. of palladous chloride and the resulting chelate was reduced with hydrogen in an autoclave. These conditions were, therefore, used in preparing the catalysts studied in the following sections.

TABLE I. PALLADIUM CONTENTS OF CATALYSTS

Condition for preparation				Pd content in 50 mg. catalyst*
Medium	(ml.)	$PdCl_2$ (mg.)	Carrier (mg.)	(μg.)
Water	100	100	Fibroin 350	2590
N/5 HOAc	50	〃	〃	3950
N/10 〃	100	〃	〃	4600
N/10 〃	100	〃	6-Nylon 350	1165
N/15 〃	50	〃	Fibroin 350	3700
N/30 〃	100	〃	〃	4300

* Pd contents were determinated with *p*-nitrosodimethylaniline.

Prolonged boiling for more than 8 min. resulted in an increased palladium content in the catalyst, but this increase was found to be mainly due to an easily detachable form of palladium and did not contribute to the activity. Although the solubility of palladous chloride could be considerably increased by the addition of sodium chloride or sodium acetate to the aqueous solution, these salts were found to inhibit the chelate formation between palladous chloride and fibroin and consequently lead to less active preparations. When silk fibroin was boild with palladous chloride in distilled water, a preparation containing less palladium was obtained as compared with the preparation which was boiled in dilute acetic acid.

The silk-palladium chelate was usually converted into the active catalyst by reducing it with hydrogen in an autoclave. When this activation was carried out by means of formic acid, the resulting catalyst showed appreciably less activity as shown in Table III.

Capacity of Asymmetric Catalysis.—The asymmetric catalyst reported in previous papers was prepared by boiling silk fibroin with palladous chloride in water. This catalyst, as reported previously, was able to catalyze, for example, the asymmetric hydrogenation of 4-benzylidene-2-methyl-oxazol-5-one(4-benzylidenazlacton) to give optically active products. The catalyst prepared in 0.1 N acetic acid instead of in water, and mainly used in this investigation failed to achieve asymmetric catalysis despite its higher palladium content. The reason for such a peculiar behavior of the silk-palladium catalyst is not yet clear. In any event, it seems that the mechanism responsible for the asymmetric catalysis is of a quite delicate nature and can be profoundly affected by slight alterations of the system.

Stability of Catalyst.—Table II is a summary of an investigation in which the activity of the catalyst and its precursor, silk-palladium chelate, was examined both immediately after preparation and after storage for several days in methanol or under dried condition. The activity of the chelate was of course measured after activation. The activity in the table is expressed in terms of "70% reaction time (t)" and reaction velocity (v) observed in the hydrogenation of nitrobenzene to aniline. The results recorded in Table II clearly show that both the catalyst itself and its precursor chelate are quite stable and can be stored for a long period

TABLE II. STABILITY OF CATALYST AND PRECURSOR CHELATE UNDER VARIOUS CONDITIONS

Sample	Storage condition	Storage time	70% Reaction time (min.)	Reaction velocity	Reaction temp. (°C)
Silk-Pd·Cl_2* 350 mg.	In dry state	0	15.5	6.5	16～17
		12 d.	15.0	6.7	〃
Silk-Pd 350 mg.	In methanol	0	18.5	5.4	12～14
		5 d.	20.5	5.0	13～15
		11 d.	18.5	5.4	〃
	In dry state	0	2.1	47.5	40
			9.0	11.1	20～21
		19 h.	9.5	10.5	20
		14 d.	9.0	11.1	20～21
		30 d.	9.5	10.5	18～20

* The activity was measured after conversion to catalyst by hydrogenation.

without loss of activity. Furthermore, no spontaneous combustion took place even when the catalyst was stored in air dried conditions.

TABLE III. ACTIVITY OF CATALYST ACTIVATED WITH FORMIC ACID

Catalyst (mg.)	70% Reaction time (min.)	Reaction velocity	Reaction temp. (°C)
Silk-Pd (350) Activated with HCOOH	15.0	6.7	20

Activation Energy of Hydrogenation Reaction.—The catalytic hydrogenation of nitrobenzene to aniline in the presence of the silk-palladium catalyst was measured at various temperatures. In Fig. 1 is plotted logarithm of reaction velocity ($\log v$) against reciprocal absolute temperature ($^1/_T$). From this graph the activation energy of the catalyzed reaction was computed to be approximately 14.5 kcal./mol.

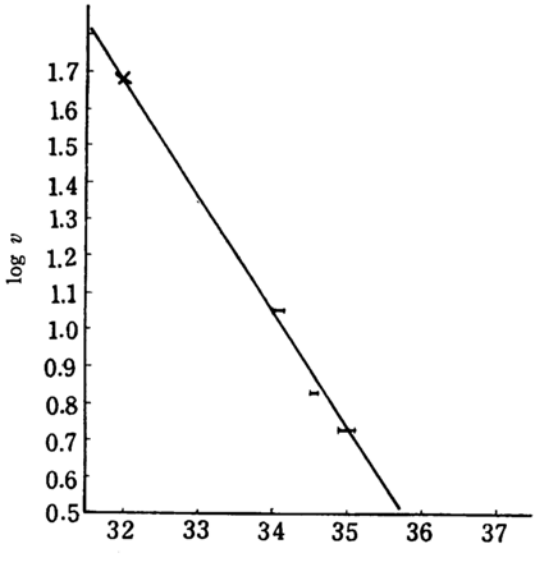

Fig. 1. Dependence of reaction velocity upon temperatures.

Nylon-Palladium Catalyst. — When 6-Nylon (caprolactam polymer) fibers were used as the carrier and treated in the same way as described for silk fibroin fibers, a 6-Nylon-palladium catalyst could be obtained. It was revealed, as shown in Table IV, that the Nylon-palladium catalyst also exhibits a high activity in catalyzing the hydrogenation of nitrobenzene. Nitrobenzene was readily reduced to aniline with hydrogen even at atmospheric pressure in the presence of this catalyst. It was found that the activity was proportional to the palladium content as shown in Table I.

TABLE IV. ACTIVITY OF NYLON-PALLADIUM CATALYST

Catalyst (mg.)	70% Reaction time (min.)	Reaction velocity	Reaction temp. (°C)
Nylon-Pd 350	65	1.5	10
Control (Silk-Pd)		4.9*	10

* Calculated value.

Experimental

I. Preparation of Catalyst. — *1) Palladous Chloridd Solutions.* — *a) Solution in water.*—One hundred milligrams of palladous chloride was added to 100 ml. of cold water and the mixture was stirred for 30 min. in the cold with the aid of a magnetic stirrer.

b) Solution in 0.1 N acetic acid.—One hundred milligrams of palladous chloride were dissolved at 60°C in 10 ml. of 1 N acetic acid and the solution was diluted 10-fold before use.

2) Silk-Palladium Chelate.—Three hundred and fifty milligrams of silk fibroin fibers previously cut into ca. 3 mm. pieces was mixed with 100 ml. of palladous chloride solution (palladous chloride, 100 mg.) and the mixture was boiled for 8 min. The fibers gradually became dense and brownish and finally precipitated as a dark brown mass. After cooling, the precipitated chelate was filtered, washed with water and then methanol, and finally air-dried.

3) *Silk-Palladium Catalyst*.—The chelate was converted to the active catalyst by the following two methods.

a) The chelate corresponding to 3.5 g. of silk fibroin was suspended in 50 ml. of methanol and reduced with hydrogen (80 kg./cm^2) at 100°C for 1 hr. in a 100 ml. autoclave. (80°C, 2 hr. for the Nylon catalyst).

b) The chelate corresponding to 350 mg. of fibroin was suspended in 30 ml. of 2% formic acid and boiled for 4 min. The chelate became black with vigorous evolution of hydrogen. In both cases, the catalyst, after cooling, was washed with water and methanol and then air-dried.

II. Determination of Palladium.—This was performed by the *p*-nitrosodiethylaniline method of Overholser[4].

III. Reaction Vessel.—A 100 ml. of autoclave was used as the vessel for hydrogenation reactions. The autoclave is illustrated in Fig. 2. The cap A was filled with absorbent cotton in order to prevent the catalyst from invading into the accessory parts of the autoclave. The apparatus was also so designed that the part B could be opened after the reaction. This device rendered it very easy to wash the inside of the tube. Although an aluminum packing was used at the interface between the lid and the vessel, silver packings were employed in other parts to minimize the unfavorable effects due to metal ions. The autoclave was shaken 100 times per min. with an inclination angle of 15°.

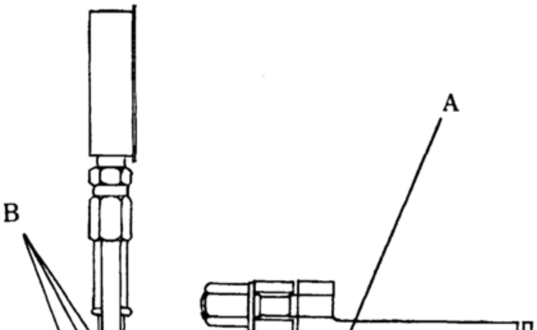

Fig. 2.

IV. Reaction Velocity Measurement.—*1*) *Reaction Conditions*.—Four grams of nitrobenzene dissolved in 50 ml. of methanol and the catalyst to be tested were placed in the autoclave and it was filled with hydrogen to 90 kg./cm^2. The initial pressure was read after 15 sec. shaking for equilibriation and the shaking was continued until the theoretical amount of hydrogen was taken up.

2) *Calculation of Reaction Velocity*.—The reaction velocity (v) was calculated according to the equation,

$$v=\frac{100}{t}$$

where t is the time in minutes required until 70% of the theoretical hydrogen uptake occurred ("70% reaction time").

V. Isolation of Product. — The reaction mixture was filtered and 10 g. of acetic anhydride was added to the filtrate. The mixture was then evaporated to dryness. On cooling the residue after treating with 10 ml. of water, 4.0 g. of crude acetanilide (m. p. 111°C) was obtained. Its melting point was increased to 113°C on recrystallization from water.

VI. Tests of Stability.—*1*) *Stability Test of Chelate*.—Silk-palladium chelate was dried at 40°C and stored in a stoppered bottle. After 12 days it was activated by hydrogen as described above and its activity for the reduction of nitrobenzene was measured.

2) *Stability Tests of Catalyst*.—The catalyst preparations prepared by reduction with hydrogen were stored either in methanol or in the dry state (in a stoppered bottle). After suitable periods of storage, their activities were measured as above.

Summary

1. The highest hydrogenation activity was obtained when the silk-palladium catalyst was prepared by boiling the silk fibroin fibers with 0.1% palladous chloride solution in 0.1 N acetic acid for 8 min. and then hydrogenating the resulting chelate.

2. The catalyst prepared as above was, however, devoid of the capacity of asymmetric catalysis, although the same catalyst prepared in distilled water (instead of dilute acetic acid) was able to achieve asymmetric reduction.

3. The catalyst and its precursor chelate could be stored in dry state without any loss of activity.

4. The synthetic fiber, 6-Nylon, could be successfully used as the carrier in place of silk fibroin.

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[4] L. G. Overholser and J. H. Yoe, *J. Am. Chem. Soc.*, **63**, 3224 (1941).

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