# *Studies on the Silk-platinum Catalyst. I. Its Preparation and Activity*

By Akira AKAMATSU, Yoshiharu IZUMI and Shiro AKABORI

(Received January 19, 1961)

Recently, Izumi¹⁾ reported on an entirely new type of palladium hydrogenation catalyst, which is unique in that its carrier is fibers of silk-fibroin. Parlladium chloride was easily coordinated with the silk-fibroin protein and then the resulting silk-palladium chelate was hydrogenated to give the catalyst. It is assumed that the metal in the catalyst is highly dispersed and tightly fixed to the micelle structure of silk-fibroin in a finely devided state, and consequently the active surface of the metal is considerably increased. Furthermore, the catalyst has a number of characteristics due to the nature of the carrier silk-fiibroin fibers.

In addition to these characteristics, other interesting properties were expected to be found, when palladium was replaced by platinum. A brown hair-like silk-platinum chelate was successfully formed, when silk-fibroin fibers were boiled with an aqueous solution of potassium tetrachloroplatinate ($K_2PtCl_4$). Activation of this chelate by hydrogenation gave the black-colored silk-platinum catalyst.

This catalyst was found to catalyze the hydrogenation of various compounds, as will be reported in the following papers of this series²⁾. In general it showed the highest hydrogenation activity for aromatic nitro compounds. In the hydrogenation of nitrobenzene to aniline, its activity was about two hundred and fifty times as high as that of a platinic oxide catalyst containing the same amount of platinum metal. Further advantages of this catalyst, as of a silk-palladium catalyst, are the facility with which it can be mixed with reactants and separated from the reaction mixture without detachment of the metal from the carrier, and the fact that it can be stored for a long period in air-dried conditions without undergoing spontaneous combustion.

The present paper describes the conditions used for the preparation of this catalyst, and its activity and stability.

## Results and Discussion

**Conditions for Preparation of the Chelate.**— In order to obtain a catalyst with high activity, as well as to minimize expensive loss of platinum, the platinum content of the chelate preparation must be increased. In the previous paper¹⁾ Izumi reported on an "easily detachable form" of metal in the silk-palladium catalyst, which did not contribute to the activity. It is probable that this "easily detachable form" is free metal which has been reduced without forming a chelate. Similarly, platinum in the chelate is assumed to consist of "coordinated" and "not coordinated" platinum. The latter is simply deposited on the silk-fiboin fibers as the free metal. It is possible that the former is readily soluble in concentrated hydrochloric acid while the latter is insoluble. Optimal conditions not only for "the

---

1) Y. Izumi, This Bulletin, 32, 932 (1959).

2) A. Akamatsu, Y. Izumi and S. Akabori, in preparation.

total platinum content", but also "the coordinated platinum content" were studied; the latter estimated as the concentrated hydrochloric acid soluble part. The results are shown in Fig. 1. (a) Four hundred milligrams of silk-fibroin fibers were boiled with an aqueous solution of potassium tetrachloro-platinate. The ratio of crystalline potassium tetrachloro-platinate to silk-fibroin in the solution, and the boiling time were constant. The concentration of the solution was varied by changing the volume of the solvent. Thus, the optimum concentration was found to be about 0.75%. (b) The boiling time was also kept constant and the volume of the 0.75% aqueous solution of potassium tetrachloro-platinate was varied. Comparatively high contents of platinum were obtained using more than 20 ml. of solution. (c) An adequate boiling time was found to be 14 to 20 min. Thus, the most desirable result was obtained when 400 mg. of silk-fibroin fibers were boiled with 20 ml. of a 0.75% aqueous solution of potassium tetrachloro-platinate for 14 to 20 min. This preparation was used for the work described in the following sections of this paper. Prolonged boiling of more than 20 min. only resulted in an increase in the "not coordinated part". Another good result was obtained, when a suspension of silk-fibroin in potassium tetrachloro-platinate solution was heated at 55°C in an air bath for 17 hr., instead being boiled.

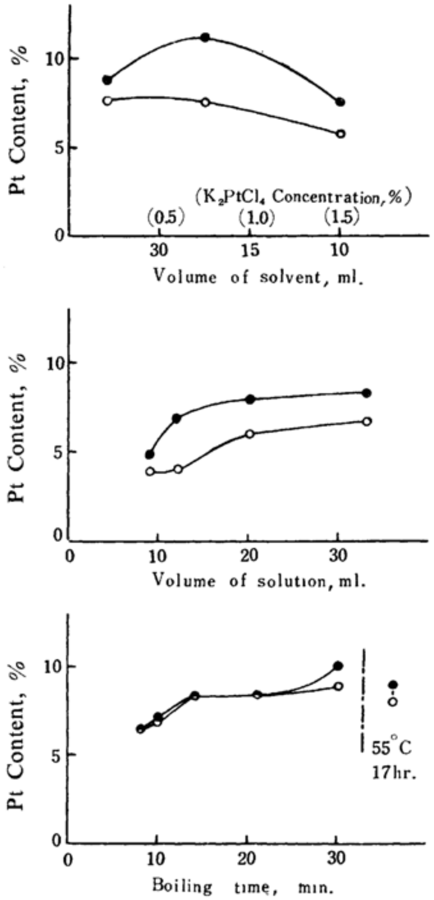


Fig. 1. Platinum content of chelate prepared under various conditions.

● Total platinum content, ○ Coordinated platinum
400 mg. of silk-fibroin was boiled (a) in an aq. solution containg 150 mg. of $K_4PtCl_4$ for 14 min., (b) in a 0.75% $K_2PtCl_4$ aq. solution for 14 min., and (c) in 20 ml. of a 0.75% $K_2PtCl_4$ aq. solution.

In the preparations described above, about 50% of the platinum in solution was used up in formation of the chelate. The remainder in the mother liquor was recovered and used for subsequent preparations.

**Conditions for Activation of the Chelate.**—The above chelate was converted to the active catalyst by reducing it with ca. 90 kg./cm$^2$ of hydrogen in an autoclave. To find the optimal conditions for activity, the hydrogenation reaction was carried out in various solvents at various temperatures for different periods. Representative experiments are summarized in Tables I to IV, in which the activity of the resulting catalysts are represented by their reaction velocity ($v$) during the hydrogenation of nitrobenzene to aniline using the same amount of catalyst in each case, and by their activity yield ($y \cdot v$.) which means their activity on the basis of the same amount of the metal in the catalyst. $v$ was calculated according to the equation; $v = 100/t$, where $t$ is the time in minutes required for 70% hydrogen uptake. $y \cdot v$ was calculated as the product of the reacion velocity ($v$) and the gravity yield[1] ($y$). The decrease in the gravity yield is due to destruction of the carrier fibroin fibers. In general, activation at high temperatures resulted in a high activity yield and low gravity yield. The former is not due only to an increase in the metal content resulting from destruction of the carrier.

When water was used as solvent during activation (Table I), carrier fibers were broken to pieces at above 150°C, and almost completely destroyed and dissolved in the solvent at 200°C. Activation for two hours gave a comparatively active catalyst. The most active catalyst was obtained at 160°C.

With diethyl succinate or methanol, less active catalysts were obtained with the silk-platinum catalyst (Table II), though in the

---

[1] For example, when 100 mg. of the chelate is hydrogenated to give 50 mg. of the active catalyst, the gravity yield is 50%.

TABLE I. ACTIVATION OF THE CHELATE IN 50 ml. OF WATER

| Cat. No. | Precursor chelate, mg. | Temp. °C | Time hr. | Grav. yield $y$, % | React. vel. at 32°C, $v$ | Act. yield $y \cdot v$ |
|---|---|---|---|---|---|---|
| 1 | 250 | 80 | 1 | 88 | 2.1 | 1.8 |
| 2 | | | 2 | 91 | 2.5 | 2.3 |
| 3 | | 100 | 1 | 84 | 2.6 | 2.2 |
| 4 | | | 2 | 84 | 2.7 | 2.3 |
| 5 | 200 | 150 | 1 | 73 | 5.4 | 3.9 |
| 6 | | | 2 | 69 | 5.9 | 4.1 |
| 7 | | | 3 | 62 | 4.5 | 2.9 |
| 8 | | 178 | 2 | 44 | 11.5 | 5.0 |
| 9 | | 200 | 1 | — | — | — |
| 10 | 100 | 160 | 2 | 61 | 9.5 | 5.8 |

TABLE II. ACTIVATION OF THE CHELATE (200 mg.) FOR 2 hr. IN METHANOL AND DIETHYL SUCCINATE

| Cat. No. | Solvent 50 ml. | Temp. °C | Grav. yield $y$, % | React. vel. at 32°C, $v$ | Act. yield $y \cdot v$ |
|---|---|---|---|---|---|
| 11 | Methanol | 100 | 90 | 2.9 | 2.6 |
| 12 | | 150 | 83 | 3.4 | 2.8 |
| 13 | diEt. Succ. | 100 | 95 | 0.4 | 0.4 |
| 14 | | 150 | 94 | 1.8 | 1.7 |
| 15 | | 200 | 81 | 4.0 | 3.2 |

TABLE III. ACTIVATION OF THE CHELATE AT 160°C FOR 2 hr. IN DILUTE ACETIC ACID

| Cat. No. | Solvent 50 ml. | Precursor chelate, mg. | Grav. yield $v$, % | React. vel. at 32°C, $v$ | Act. yield $y \cdot v$ |
|---|---|---|---|---|---|
| 16 | 1% AcOH | 100 | 52 | 19.3 | 10.0 |
| 17 | 2.5% AcOH | | 55 | 11.8 | 6.5 |
| 18 | 5% AcOH | | 54 | 17.9 | 9.7 |
| 19 | 1% AcOH | 2000 | 56 | 3.6 | 2.0 |

TABLE IV. REPEATED ACTIVATION OF CATALYST No. 19 FOR 1 hr.

| Cat. No. | Method | Solvent ml. | Precursor catalyst, mg. | Grav. yield $y \cdot y'$ | React. vel. at 32°C, $v$ | Act. yield $y \cdot y' \cdot v$ |
|---|---|---|---|---|---|---|
| 20 | Reduction at 160°C | 1% AcOH (30) | 300 | 31 | 60.0 | 18.8 |
| 21 | Heating at 160°C | 1% AcOH (50) | 100 | 35 | 34.9 | 12.5 |
| 22 | Boiling in flask | 1% AcOH (50) | | 51 | 3.0 | 1.5 |
| 23 | Reduction at 160°C | 1% $NH_3$ (50) | | 25 | 7.5 | 1.9 |

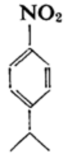
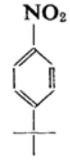
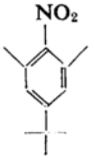
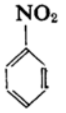
TABLE V. STABILITY OF CATALYST

| Storage time weeks | React. vel. at 32°C, $v$ |
|---|---|
| 0 | 60.7 |
| 2 | 50.5 |
| 5 | 89.0 |
| 12 | 85.8 |

case of the silk-palladium catalyst, an exceedingly active catalyst was obtained with diethyl succinate (Table VI).

However, the use of dilute acetic acid as a solvent (Table III), increased the activation. One per cent acetic acid was the most effective among the other solvents tested. But increasing the amount of the precursor chelate in proportion to that of the solvent, failed to give satisfactory results (Cat. No. 19). So, for the repeated activation of this catalyst, the various conditions shown in Table IV were tested. Repeated hydrogenation under the same conditions resulted in an extremely high activity. Heating in an autoclave without hydrogen also gave a very active catalyst though it was less

TABLE VI. REACTION VELOCITY IN HYDROGENATION OF ALKYL NITROBENZENES

| Substrate |  |  |  |  |  |
|---|---|---|---|---|---|
| | 4 g. | 5.4 g. | 5.9 g. | 6.3 g. | 4 g. |
| Solvent | Dioxane | | | | Methanol |
| Silk-Pt 40 mg. | 13.0 (52°C) | 11.4 (52°C) | 6.90 (55°C) | 0.18 (50°C) | 37.7 (23°C) |
| [Ratio] | [1.00] | [0.86] | [0.53] | [0.01] | |
| $PtO_2$ 15 mg. | 0.15 (50°C) | 0.15 (50°C) | 0.11† (50°C) | 0.03† (100°C) | 0.15 (17°C) |
| [Ratio] | [1.00] | [1.00] | [0.73] | [0.18] | |
| Silk-Pd 140 mg. | 3.30 (100°C) | 0.90 (100°C) | 0.65 (100°C) | 0 | 3.42 (18°C) |
| [Ratio] | [1.00] | [0.27] | [0.20] | [0.00] | |
| Silk-Pd-DES 54 mg. | 5.03 (52°C) | 1.07 (50°C) | — | — | 15.6 (18°C) |
| [Ratio] | [1.00] | [0.21] | | | |

† Calculated value

active than the former. However, boiling in a flask with 1% acetic acid was not effective. Repeated hydrogenation with 1% aqueous ammonia was not effective for increasing the total activity yield $(y \cdot y' \cdot v)$, but it did increase the reaction velocity.

The present results show that the activity of the catalyst is influenced very much by the solvent used, and the temperature and time of activation. The destruction of the carrier and the increase in the metal content of the catalyst are evidently effected by these conditions, and indeed might contribute to some extent to the activity represented by the activity yied. But a low gravity yield was not always accompanied by a high actvity yield as shown by comparison of catalysts Nos. 9 and 16. It may be that these conditions directly and independently influence the activity. The solvent especially is an important factor in the activation, as Hartung et al.[3] reported concerning the effect of certain organic anions on the preparation of the palladium-charcoal catalysts. It was proved in this work that regardless of the extent of the gravity yield, use of acetic acid resulted in a very good activity, while methanol, diethyl succinate, and aqueous ammonia were not effective.

It does not seem unreasonable, as Hartung pointed out, to attribute these solvent effects on the arrangement of the crystalline structure or the spacing of the active centers on the catalyst. It should also be noted that the ratio of the volume of solvent to the amount of the precursor-chelate used influenced the activity to a large extent, though such a phenomenon was not seen in the case of the silk-palladium catalyst.

**Stability of the Catalyst.** — In Table V are shown the reaction velocities observed in the hydrogenation of nitrobenzene to aniline, using the final catalyst*2 both immediately after its activation and after storage of the dry catalyst for several weeks in a stoppered bottle. The results clearly show the silk-platinum catalyst can be stored for a long period without loss and even with some increase of activity. No spontaneous combustion took place during the storage period.

**Activity with Aromatic Nitro Compounds.** — The activity of the silk-platinum catalyst*2 in the hydrogenation of various alkyl derivatives of nitrobenzene to the corresponding amines was compared with that of platinic oxide catalyst, silk-palladium catalyst (activated in methanol) and silk-palladium-DES catalyst (activated in diethyl succinate)*3. Table VI shows the reaction velocities for the hydrogenation of the same amount (1/30 mol.) of the various compounds, using catalysts, each of which contains the same amount (13 mg.) of metal. The silk-platinum catalyst showed the highest activity of all the catalysts with all the compounds tested. Notably in the hydrogenation of nitrobenzene in methanol, the reaction velocity was 254 times as fast as that with the platinic oxide catalyst. When methanol was used as a solvent, the reaction velocity for the silk-platinum and the silk-palladium-DES catalyst was faster than when dioxane was used, in spite of the low reaction temperature.

The ratios of the reaction velocity of alkyl nitrobenzenes to that of non-substituted nitrobenzene were calculated and are shown in

---

[3] W. H. Hartung et al., *J. Org. Chem.*, 21, 999 (1956).

*2 This catalyst was prepared under the same conditions as that for catalyst No. 20 in Table IV. See Experimental.

*3 See Experimental.

brackets in Table VI. In the series of alkyl nitrobenzenes the ratios decreased as the alkyl groups increased in substituents and branching. This decrease is distinguishable with catalysts in which the carrier is silk-fibroin fibers. It is possible that, not only the bulkiness of the reactants, but also the characteristic structure of carrier silk-fibroin[4] exerts some steric hindrance retarding the hydrogenation.

## Experimental

**Determination of Platinum.** — Platinum was measured by the iodine method[5], after the chelated sample had been treated as follows;

*1) For Estimation of the Total Platinum Content.* —About 15 mg. of the chelated sample were accurately weighed in a crucible and heated with 0.5 ml. of concentrated nitric acid on a steam bath for 20 min. The mixture was evaporated to dryness and the residue was strongly heated to ash over a burner. After the ash had been dissolved in 0.5 ml. of aqua-regia, the soluion was evaporated to dryness. One milliliter of concentrated hydrochloric acid was added to the residue and evaporated off twice to remove the nitrate. The residue was then dissolved in water and the solution diluted to 50.0 ml. Exactly 5.00 ml. of the solution was used for each determination.

*2) For Estimation of Coordinated Platinum.* — About 15 mg. of the chelated sample were accurately weighed in a test tube and heated with 2.0 ml. of 30% hydrochloric acid on a steam bath for 30 min. The mixture was filtered through filter paper and the filter paper was washed with water. The combined filtrates were transferred to a crucible and ashed by evaporation and strong heat. Then the ash was treated in the same way as described above for the estimation of the total platinum content.

**Reaction Vessel.**—The same autoclave as described in the previous paper[1] was used for activation of the chelate and for hydrogenation reactions.

**Measurement of the Reaction Velocity.** — One thirtieth of a mole of the substrates (for nitrobenzene, 4 g.) dissolved in 50 ml. of methanol and the catalysts to be tested (for silk-platinum catalyst, 40 mg.) were placed in the autoclave, into which hydrogen was then introduced to a pressure of 90 kg./cm$^2$. The initial pressure was read after shaking to allow equilibration, and then the shaking was continued until 70% of the theoretical amount of hydrogen had been taken up.

**Preparation of Catlysts.**—*1) Silk-platinum Catalyst.*—The catalyst, used in investigations of stability and activity, was prepared by the following method; a) Twenty grams of sik-fibroin fibers previously washed with boilng water were mixed with 1 l. of an 0.75% aqueous solution of potassium tetrachloroplatinate and the mixture was boiled for 18 min. The silk-platinum chelate obtained was filtered off, washed with water, methanol and then ether, and finally dried in vacuo. b) Twenty grams of the chelate were suspended in 500 ml. of 1% acetic acid reduced with hydrogen (80 kg./cm$^2$) at 160°C for 2 hr. in a 1 l. autoclave. The catalyst obtained was filtered off, washed with water, methanol and ether, and dried in vacuo (12 g., 60%). The reaction velocity ($v$) with nitrobenzene at 16°C was 1.8. Repeated hydrogenation of 4 g. of this catalyst by the same method for 1 hr. gave the final catalyst (2.6 g., 66%). The reaction velocity ($v$) of this catalyst at 32°C was 60.7.

*2) Platinic Oxide Catalyst.*—This was prepared by the method of Ref. 6.

*3) Silk-palladium Catalyst.*—This was prepared as described in the previous paper[1].

*4) Silk-Palladium-DES Catalyst.* — Two hundred milligrams of the silk-palladium chelate[1] were suspended in 50 ml. of diethyl succinate and reduced with hydrogen (80 kg./cm$^2$) at 220°C for 2 hr. in a 100 ml. autoclave. The resulting catalyst was washed with methanol and dried in vacuo.

**Isolation of Products.** — The products on the hydrogenation of nitrobenzene and of its alkyl derivatives were isolated as follows:

*Aniline.* — This was isolated as described previously[1].

*p-Aminoisopropylbenzene, p-Amino-tert-butylbenzene.* —The reaction mixture was filtered and the filtrate distilled in vacuo. The amines obtained were acetylated and the crude acetyl derivatives were recrystallized from alcohol: *p*-Aminoisopropylbenzene; b. p. 112°C/19 mmHg (lit.[7] 225°C/760 mmHg). *p*-Amino-*tert*-butylbenzene; b. p. 117∼119°C/15 mmHg (lit.[8] 120∼132°C/15 mmHg). *p*-Acetaminoisopropylbenzene; m. p. 105°C (lit.[9] 105∼106°C). *p*-Acetamino-*tert*-butylbenzene; m. p. 171°C (lit.[8] 171∼172°C).

*3,5-Dimethyl-4-amino-tert-butylbenzene.*—The crude amine was converted to its 2-nitro derivative and this was recrystallized; m. p. 86°C (lit.[10] 88∼89°C).

## Summary

1. A silk-platinum chelate, which had the highest platinum content, involving both the total platinum content and the coordinated platinum, was obtained when 400 mg. of silk-fibroin was boiled with 20 ml. of a 0.75% aqueous solution of potassium tetrachloroplatinate for 14 to 20 min.

2. The most active silk-platinum catalyst was obtained when reduction of the chelate was pepeated twice in 1% acetic acid with 90 kg./cm$^2$ of hydrogen at 160°C. The activity was much influenced by the solvent, temperature and time used for its activation.

3. The catalyst could be stored for a long

---

[4] S. Akabori, S. Sakurai, Y. Izumi and Y. Fujii, *Nature*, **178**, 323 (1956); S. Akabori, Y. Izumi, Y. Fujii and S. Sakurai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1374 (1956); S. Akabori, Y. Izumi and Y. Fujii, ibid., **78**, 886 (1957); Y. Izumi, This Bulletin, **32**, 942 (1959).

[5] E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York (1950), p. 493.

[6] "Organic Synthesis", Coll. Vol. **1**, 463 (1948).

[7] M. S. Carpenter et al., *J. Org. Chem.*, **16**, 586 (1951).

[8] B. M. Wepster et al., *Rec. trav. chem.*, **71**, 321 (1952).

[9] B. M. Wepster et al., ibid., **71**, 340 (1952).

[10] M. S. Carpenter et al., *J. Org. Chem.*, **19**, 77 (1954).

period in the dry state and even showed some increase in activity during storage.

4. The most active catalyst had about two hundred and fifty times as much activity as that of a platinic oxide catalyst in the hydrogenation of nitrobenzene to aniline.

5. The characteristic structure of the carrier seems to exert some steric hindrance on the hydrogenation of highly branched aromatic nitro compounds.

The authors wish to express their gratitude to Dr. S. Yamada for his suggestion concerning the platinum complex, to Mr. S. Watarai for supplying various alkyl nitrobenzene derivatives and to Mr. T. Kojima for his technical assistance in this investigation. They are also greately indebted to the Gunze Seishi Co., Ltd. for supplying the silk fibers.

*Division of Organic Chemistry*
*Institute for Protein Research*
*Osaka University*
*Nishi-ku, Osaka*