Studies on the Silk-platinum Catalyst. II. General Properties

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(Received February 27, 1961)

In the previous paper[1] of this series, the preparation of a silk-platinum catalyst, and its activity and stability were reported. This catalyst is extremely active for the hydrogenation of aromatic nitro compounds.

In the present work it was found that this catalyst was relatively less active for the hydrogenation of other compounds, and showed behaviors in the catalytic reactions, quite unlike the so far known reactions of other platinum catalysts. It is probable that the difference is mainly due to the nature of the carrier silk-fibroin in this catalyst. Various reactions of this catalyst with poisons of catalysts are also described in the present paper.

Catalytic Efficiency with Various Compounds

In order to examine the catalytic efficiency of the silk-platinum catalyst[1], various compounds were tested for their power of reduction of 200 mg. of the catalyst per mole of hydrogen theoretically taken up, with 90 kg./cm^2 of hydrogen, in a 100 ml. autoclave. The results are summarized in Table I, in which are recorded the conditions used for the hydrogenation reaction, the ratios of hydrogen taken up to the theoretical amount, and reaction products and their yields.

Hydrogenation of Ketones.—This catalyst was found to be capable of catalyzing the hydrogenation of acetone and ethyl methyl ketone to the corresponding alcohols, but was quite inactive for the cardonyl groups of mesityloxide and acetophenone. In general, it is probable that simple aliphatic ketones can be reduced in the presence of this catalyst, while reduction of carbonyl groups, conjugated with the C=C double bonds and attached to aromatic rings, may be impossible.

Hydrogenation of Aldehydes.—A very interesting phenomenon was observed on the hydrogenation of both acetaldehyde and benzaldehyde in the presence of this catalyst. When hydrogen was introduced into the reaction vessel before the reactant had been heated to the reaction temperature, reduction of these aldehydes did not take place. But, when previously heated reactant was shaken with hydrogen (indicated by an asterisk* in the

1) A. Akamatsu, Y. Izumi and S. Akabori, This Bulletin, 34, 1067 (1961).

TABLE I. CATALYTIC REACTIONS WITH VARIOUS COMPOUNDS

Substrate (g.)	Solvent (ml.)	Cat. mg.	Temp. °C	H_2-Uptake %	React. time min.	Product	Yield %
Acetone (29)		100	85	100	376	Isopropyl alcohol	79
Ethyl methyl ketone (36)		100	85	100	207	*sec*-Butyl alcohol	89
Acetophenone (24)		40	85	12	201	—	—
Acetaldehyde (22)		100	50	0	—	—	—
Acetaldehyde (22)		100	50*	92	451	Ethyl alcohol	90**
Benzaldehyde (27)		100	50	0	—	—	—
Benzaldehyde (27)		100	15	140	310	Benzyl alcohol Toluene	87** 10**
Benzaldehyde (27)		100	60*	130	66	Benzyl alcohol Toluene	92** 6**
Allyl alcohol (29)		100	100	71	253	*n*-Propyl alcohol	70
Maleic acid (12)	aq. NaOH (65)	20	165	95	106	Succinic acid	81
Mesityloxide (25)		100	13	88	1475	Isobutyl methyl ketone	60**
Acrolein (28)		100	100	20	917	—	—
Crotonaldehyde (35)		100	70*	0	—	—	—
Nitromethane (6)	$(CH_3CO)_2O$ (50)	60	45*	100	196	Methyl acetamide	90
Diethyl nitro malonate (21)	$(CH_3CO)_2O$ (50)	60	78	100	68	Diethyl acetaminomalonate	64
Acetophenoxime (14)	CH_3OH (50)	40	70	95	934	α-Phenethyl amine α, α′-Diphenethyl amine	72 20
Ethyl cyanide (11)	CH_3OH (50)	80	60	0	—	—	—
α-Ketoglutaric acid (7)	CH_3OH (35) 28% aq. NH_3 (15)	10	100	0	—	—	—

* Hydrogen was introduced into the autoclave, after the reactant had been heated to this temprature.

** Estimated directly by gas-chromatography of the reaction mixture.

table), the reaction occurred. Moreover, benzaldehyde could be reduced even at room temperature. As a matter of further interest, it was found that the catalyst which was recovered after having failed to catalyze the reduction of benzaldehyde, showed a considerable increase in activity to hydrogenate nitrobenzene. Its reaction velocity (v)[1] was 100 at 21°C.

Unlike the case with ketones, this catalyst seems to be more active for the reduction of aromatic aldehydes than for that of aliphatic aldehydes, as shown by comparison of the reduction of acetaldyde and benzaldehyde shown in the table. With the aliphatic aldehyde groups conjugated with the C=C double bonds in acrolein and crotonaldehyde, hydrogen uptake hardly occurred.

Hydrogenation of the C=C Double Bonds.—Tests on the redudtion of allyl alcohol and maleic acid showed that this catalyst is rather active in hydrogenating the C=C double bonds. In the hydrogenation of allyl alcohol, the reaction velocity was influenced by the pressure of hydrogen. The reaction proceeded slowly at a low pressure of hydrogen. On the other hand, it was somewhat difficult to reduce the C=C double bonds conjugated with the carbonyl groups in mesityloxide, acrolein and crotonaldehyde. The double bonds in benzene rings were not reduced in the presence of the catalysts.

Reduction of Aliphatic Nitro Compounds.—This catalyst was found to be extremely active in hydrogenating nitro groups attached to aromatic rings, as described in the previous paper[1]. However, nitromethane and diethyl nitro malonate in acetic anhydride were both reduced much more slowly to give methyl acetamide and diethyl acetaminomalonate, respectively.

Reduction of Acetophenoxime.—Hydrogenation of acetophenoxime took place rather slowly with this catalyst, yielding α-phenethyl amine and some α, α′-diphenethyl amine.

Reduction of Ethyl Cyanide.—Ethyl cyanide could not be reduced at all in the presence of this catalyst.

Reductive Amination of α-Ketoglutaric Acid.—It was expected that this catalyst would convert α-ketoglutaric acid to glutamic acid in the presence of ammonia and hydrogen, but the result was negative.

As seen in the results described above, the catalytic reactions effected by the silk-platinum catalyst are quite different from the known reductions effected by other platinum catalysts. It may be inferred that the difference is due to

the characteristic spacing of the active centers on the silk-platinum catalyst, which are the result of the structure of the carrier fibroin protein.

The difference between the catalytic efficiency of the silk-platinum and that of the platinic oxide catalyst in the hydrogenation of aromatic nitro compounds, was described in the previous paper[1] of this series.

Poisoning of the Catalyst

The silk-platinum catalyst was found to be sensitive to poisonous substances or to chemical treatments. But the behavior towards catalytic poisons were somewhat different from that of the silk-palladium catalyst[2]. In examining these inhibitory effects, hydrogenation of nitrobenzene to aniline was adopted as the test system and the reaction velocity (v) was calculated as previously described[1].

Inhibition by Carbon Monoxide.—Activity of the silk-platinum catalyst in hydrogenating nitrobenzene in the presence of carbon monoxide was tested in comparison with that of the silk-palladium catalyst. For this purpose, carbon monoxide was mixed with hydrogen in various proportions, and introduced into the reaction system. The results obtained are shown in Table II.

Table II. Inhibition by carbon monoxide

Catalyst	Addition of CO %	Temp. °C	React. vel. v
Silk-Pt (40 mg.)	0	19	41.7*
	0.1	23	8.3*
	0.1	50	35.7
	5.0	21	0
	replaced with pure H_2	21	8.2
	5.0	110	5.0
	10.0	100	0
	(recovered cat.) 0	16	15.0
Silk-Pd (200 mg.)	0	30	11.1
	0.1	30	0.12**
	replaced with pure H_2	30	0
	1.0	80	0.34

* See Fig. 1. ** Calculated value.

The silk-palladium catalyst was much more inhibited by carbon monoxide than the silk-platinum catalyst. The silk-platinum catalyst that had no catalytic action in the presence of carbon monoxide, recovered its activity to some extent in the absence of carbon monoxide. Furthermore, when little carbon monoxide was added (0.1%), the activity was restored even in the course of the reaction, as shown in Fig. 1. It is probable that carbon monoxide is adsorbed by the active metals, sometimes

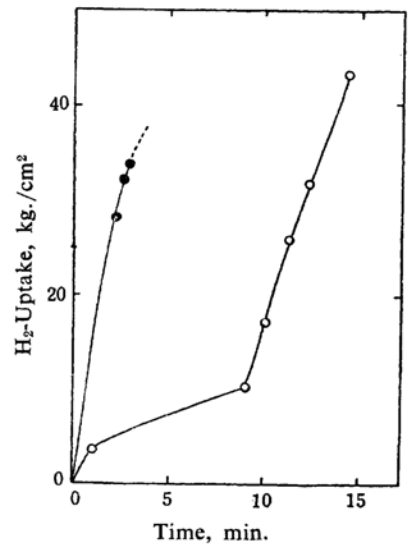

Fig. 1. Hydrogenation of nitrobenzene,
● in the absence of CO, at 19°C,
○ in the presence of 0.1% CO, at 23°C.

forming coordinate linkages, thus preventing the catalytic action. The activity may be restored when the adsorption is partially removed by hydrogenation of the carbon monoxide (as in the case shown in Fig. 1), or by washing the poisoned catalysts with methanol. It seems that palladium adsorbs carbon monoxide more easily than platinum, and thus the silk-palladium catalyst was more inhibited than the silk-platinum catalyst.

Inhibition by Benzyl Mercaptan.—As shown in Table III, treatment of the catalyst with benzyl mercaptan and its addition to the substrate resulted in a remarkable decrease in the catalytic activity in hydrogenating nitrobenzene. It is probable, that the mercaptan inhibits the catalyst by directly blocking active platinum, as in the case of the silk-palladium catalyst[2].

Table III. Inhibition by benzyl mercaptan

Treatment	Addition	React. vel. v at 32°C
—	—	48.2
CH_3OH	—	33.8
$C_6H_5CH_2SH$*/CH_3OH	—	1.5
—	$C_6H_5CH_2SH$ 2 mg.**	1.1

* 1 mol. per mol. of platinum in the catalyst used.

** 0.25 mol. per mol. of platinum in the catalyst used.

Inhibition by Metal Ions.—In the case of the silk-palladium catalyst[2], the activity was greatly lowered in the presence of ferric and cupric ions supplied as nitrates. Cupric ion

2) Y. Izumi, ibid., 32, 936 (1959).

was somewhat more toxic than ferric ion. The silk-platinum catalyst was scarcely inhibited by ferric ion, as shown in Table IV. Cupric ion inhibited this catalyst considerably. The catalyst could not be reactivated by treatment with ethylenediamine tetra-acetic acid (EDTA). When the silk-palladium catalyst was similarly treated, however, it showed very powerful catalytic activity. These metal ions may form chelate linkages, though in a manner different from that of the silk-palladium catalyst, with the carrier protein to prevent the reactant from approaching the active platinum atoms.

TABLE IV. INHIBITION BY METAL IONS

Metal ion		React. vel. v at 32°C
—		48.2
$Fe(NO_3)_3 \cdot 12H_2O$	8 mg. (10^{-4} mol.)	36.8
	40 mg.	26.5
$Cu(NO_3)_2 \cdot 3H_2O$	5 mg. (10^{-4} mol.)	20.3
	10 mg.	8.8
	(treated with EDTA)*	2.6
	25 mg.	1.0

* The catalyst was recovered (80%) and treated with 0.5% ethylenediamine tetra-acetic acid.

Effect of Acetylation.—The activity of this catalyst remained unaffected by acetylation; the reaction velocity (v)[1] with an acetylated silk-platinum catalyst was 33.0 at 32°C. This is not the case with the silk-palladium catalyst[2].

Experimental

Preparation of the Catalyst.—The catalysts used in this work were prepared by the method of Ref. 1 for the silk-platinum, and Ref. 3 for the silk-palladium catalyst.

Isolation of the Products.—*Reduction of Acetone.*—The reaction mixture was filtered and the filtrate was distilled; b. p. 80~82°C. The product was identified as isopropyl alcohol by means of gaschromatography.

Reduction of Ethyl Methyl Ketone.—The product was isolated as above (b. p. 97.5~98.5°C), and identified as *sec*-butyl alcohol by gaschromatography.

Reduction of Acetaldehyde.—The reaction mixture was filtered and the filtrate was treated by gaschromatography. The product was identified as ethyl alcohol, and the yield estimated.

Reduction of Benzaldehyde.—The products were identified as benzyl alcohol and toluene and their yields were estimated by gaschromatography.

Reduction of Allyl Alcohol.—The product distilling at 97~98°C was identified as *n*-propyl alcohol by means of gaschromatography.

Reduction of Maleic Acid.—An aqueous solution of maleic acid adjusted to pH 7.0 with sodium hydroxide was subjected to reduction. The reaction mixture was filtered and the filtrate evaporated to 20 ml. It was then acidified with 20 ml. of concentrated hydrochloric acid. After standing overnight, 9.5 g. of succinic acid (m. p. 184°C) was obtained. It was confirmed by ultraviolet spectroscopy that the product was devoid of unsaturated bonds.

Reduction of Mesityloxide.—The reaction mixture was filtered and the filtrate was subjected to gaschromatography. The product was identified as methyl isobutyl ketone, and the yield estimated. Unreacted mesityloxide was also detected.

Reduction of Nitromethane.—After filtration of the reaction mixture, the filtrate was fractionally distilled under reduced pressure. The product, boiling at 95~96°C/17 mmHg, was identified as methyl acetamide by gaschromatography and infrared spectroscopy.

Reduction of Diethyl Nitro Malonate.—The reaction mixture was filtered and the filtrate evaporated to 20 ml. Thirty milliliters of water were added. After standing overnight, 14 g. of diethyl acetamino malonate (m. p. 93~95°C) was obtained.

Found: N, 6.41. Calcd. for $C_9H_{15}O_5N$: N, 6.45%.

Reduction of Acetophenoxime.—The reaction mixture, from which the catalyst had been removed, was evaporated to 30 ml. To this was added 15 ml. of concentrated hydrocholoric acid and then 30 ml. of ether. After standing the solution in a refrigerator overnight, the crystals were filtered off, recrystallized from water, and identified as α, α'-diphenethyl amine hydrochloride (sublimed above 240°C).

Found: C, 73.52; H, 7.73; N, 5.22; Cl, 13.56. Calcd. for $C_{16}H_{20}NCl$: C, 73.55; H, 7.66; N, 5.32; Cl, 13.47%.

The filtrate was evaporated to dryness and the residue dissolved in 20 ml. of methanol, to which was added 30 ml. of ether. After standing overnight, α-phenethyl amine hydrochloride was obtained. It was recrystallized from alcohol and ether; m. p. 158°C.

Found: C, 61.04; H, 7.80; N, 8.75, Cl, 22.45. Calcd. for $C_8H_{12}NCl$: C, 60.95; H, 7.68; N, 8.89; Cl, 22.49%.

Poisoning of the Catalyst.—The reaction velocity (v) of the hydrogenation of nitrobenzene to aniline was measured and calculated by the method of the previous paper[1].

Inhibition by Carbon Monoxide.—Carbon monoxide was mixed with hydrogen in varying proportions and introduced into the reaction system.

Preparation of Inhibited Catalyst.—Two hundred milligrams of the silk-platinum catalyst (containing 1/3000 mol. of platinum) was suspended in 100 ml. of methanol or in 100 ml. of 0.04% benzyl mercaptan methanol solution (containing 1/3000 mol. of mercaptan), stirred for 15 min. washed with methanol and ether, and then dried in vacuo. Forty milligrams of this catalyst was used for the test.

Treatment of the Inhibited Catalyst by Ethylenediamine Tetra-acetic Acid (EDTA).—The inhibited catalyst was boiled with a 0.5% aqueous solution of EDTA for 5 min., filtered, washed with water, methanol, and then ether, and finally dried in vacuo; 32 mg. (80%).

3) Y. Izumi, ibid., 32, 932 (1959).

Acetylation of the Catalyst.—One hundred milligrams of the catalyst was boiled with 50 ml. of acetic anhydride for 2 hr., filtered, washed with ether, and dried in vacuo. Forty milligrams of this catalyst was used for the test.

Summary

1. The silk-platinum catalyst showed quite different behaviors with various compounds from that of other platinum catalysts. The difference is probably due to the characteristic spacing of the active centers on the silk-platinum catalyst, due to the structure of the carrier silk-fibroin protein.

2. The catalyst was found to catalize the hydrogenation of some aldehydes, unconjugated aliphatic ketones and C=C double bonds, aliphatic nitro groups and oxime, more weakly, than that of the aromatic nitro groups.

3. Carbon monoxide, benzyl mercaptan and cupric ion poisoned the catalyst, and the activity of the catalyst inhibited by cupric ion, was not recovered by treatment with ethylenediamine tetra-acetic acid.

4. Ferric ion scarcely inhibited the catalyst and acetylation of the catalyst scarcely decreased its activity, unlike that of the silk-palladium catalyst.

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