Studies on Modified Hydrogenation Catalyst. I. Selective Hydrogenation Activity of Modified Raney Nickel Catalyst for Carbonyl Group and C=C Double Bond

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Recently, Izumi et al.[1-3] developed an entirely new series of hydrogenation catalysts, which are unique in that silk fibroin serves as carrier for metals. These catalysts have highly selective hydrogenation activity, having high activity for unsaturated compounds and aromatic nitro compounds but no activity for aliphatic carbonyl compounds. It was suggested that the specificity of these catalysts resides in the special structure of the carrier, silk fibroin.

It therefore seemed possible that if Raney nickel (R-Ni) catalyst is treated with amino acid, peptide or protein, these modified R-Ni catalysts may possess selective hydrogenation activity similar to that of the silk-metal catalyst. Isoda and Ichikawa[4] have, in fact reported the occurrence of asymmetric hydrogenation with the use of R-Ni catalyst on which optically active amino acids had been adsorbed.

As is well known, enzymatic reactions are highly specific, but their velocities can be modified by means of various reagents. Accordingly, methods of competitive inhibition or antagonism in enzymology should also be applicable to the study of non-enzymatic catalytic reactions. On the basis of these conceptions, the hydrogenation activity of the R-Ni catalyst modified with amino acids and other chelating agents has been systematically studied.

R-Ni catalyst treated with these reagents had diminished hydrogenation activity only for the carbonyl group. In particular, R-Ni catalyst modified by various amino acids, possessed this property to a greater extent than that modified by other reagents. The present paper describes the hydrogenation activity and some characteristics of the modified R-Ni catalyst.

Results and Discussion

Allyl alcohol and ethyl methyl ketone were used as substrates for most of this investigation. As modifying agent, L-glutamic acid or its monosodium salt was generally used because of its selectivity.

As summarized in Table I, the hydrogenation activity of R-Ni catalyst for ethyl methyl

TABLE I. CONCENTRATION OF MODIFYING SOLUTION

Modifying reagent	Concn. %	Hydrogenation activity		
		EMK		AA
		10°C	60°C	10°C
Untreated	—	2	20	34
Untreated*	—	3	20	—
L-Glu	0.02	0.5	17	34
	0.5	0	3	34
	1.0	0	1.5	34
L-MSG	1.0	0	2	30
	2.0	0	2	30
	4.0	0	0.5	16
Gly-Gly	1.0	0	2	45
	2.0	0	0	21

* Allowed to stand for 5 hr. at room temperature

1) Y. Izumi, This Bulletin, **32**, 932, 936, 942 (1959).
2) A. Akamatsu, Y. Izumi and S. Akabori, ibid., **34**, 1067, 1302 (1961).
3) Y. Izumi, A. Akamatsu and S. Akabori, in preparation.
4) T. Isoda, A. Ichikawa and T. Shimamoto, *J. Sci. Res. Inst.* (*Riken hokoku*), **34**, 143 (1958).

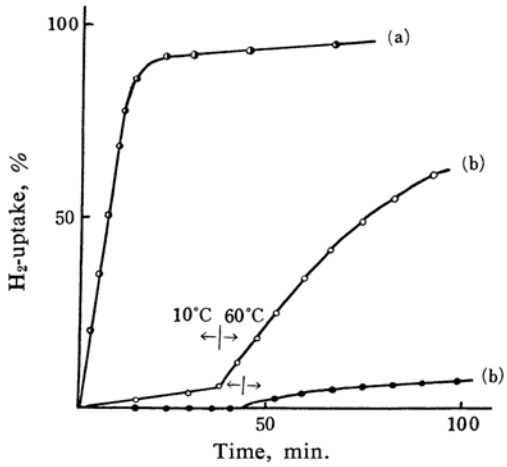

Fig. 1. Hydrogenation of allyl alcohol (a) at 10°C and ethyl methyl ketone (b) at 10°C and 60°C.
○ With unsaturated catalyst
● With modified catalyst (0.5% Glu)

ketone was almost lost at 10°C when the catalyst was treated with a solution of L-glutamic acid or sodium L-glutamate of greater concentration than 0.5%, and was greatly diminished at 60°C. On the other hand, no appreciable change in its hydrogenation activity for allyl alcohol occurred upon treatment with sodium L-glutamate solutions in concentration up to 4%. When the catalyst was treated with sodium L-glutamate at concentrations greater than 4%, the hydrogenation activity for ethyl methyl ketone was almost lost even at higher temperatures. Figure 1 shows a typical hydrogenation curve of ethyl methyl ketone (a) and allyl alcohol (b) carried out with untreated and modified R–Ni catalyst.

The effect of modifying the time of immersion of R–Ni catalyst in L-glutamic acid solution on hydrogenation activity is shown in Table II. Immersion for 15 min. was sufficient to cause a pronounced decrease in hydrogenation activity for ethyl methyl ketone. Further treatment resulted in a more gradual decrease in activity. It thus appears that most of the modifying effect of L-glutamic acid took place in the first 15 min. On the other hand, immersion of R–Ni catalyst in water as long as 5 hr. did not change its hydrogenation activity.

TABLE II. TIME OF MODIFYING

Modifying reagent	Time of immersion	Hydrogenation activity EMK 10°C	EMK 60°C	AA 10°C
0.5% L-Glu	15 min.	0	4	34
	2 hr.	0	3	—
	16 hr.	0	2	30
4% L-MSG	2 hr.	0	1	16
	16 hr.	0	0	14

Treatment with various other amino acids and some other types of compounds has been carried out, and the results are summarized in Table III. All of the amino acids tested gave selective hydrogenation activity to R–Ni catalyst. Dibasic amino acids and phenylalanine had the greatest effect among the α-amino acids tested to date. Other types of chelating agents had a lesser effect than amino acids.

An interesting finding was, that the hydrogenation activity of R–Ni catalyst for allyl alcohol was promoted by the treatment with dimethylglyoxime. As will be described below, it was observed, that the hydrogenation activity of the modified R–Ni catalyst increased to three times that of the untreated catalyst in the hydrogenation of nitrobenzene. The surface of the catalyst modified with dimethylglyoxime turned pink in color. This change suggests the formation of a chelated complex between nickel and dimethylglyoxime.

Table IV summarizes the results of the hydrogenation of various ketones and unsaturated compounds with the modified R–Ni catalyst. The catalyst in these experiments was prepared by immersion in 2% sodium L-glutamate solution for 2 hr. at 10°C. The hydrogenation activity at low temperature for ketones was lost by this treatment, and even at 60°C the activity decreased from one tenth

TABLE III. VARIOUS MODIFYING REAGENTS

Modifying reagent	Concn. %	pH	Hydrogenation activity EMK 10°C	EMK 60°C	AA 10°C
L-Glu	1.0	4	0	1.5	36
L-MSG	1.2	7	0	2	30
L-ASP	1.0	4	0	2	35
L-Leu	1.0	7	0	3.5	34
Gly	1.0	7	0	3	35
DL-Thr	1.0	7	0	3	35
L-Hypro	1.0	7	0	3	38
L-Phe	1.0	7	0	1–0.5	36
L-Arg	1.0	11	0	3.5	22
Gly-Gly	1.0	5	0	2	45
Gelatin*	0.5	6	0.5	1.5	38
EDTA·2Na	1.85	4	0.5	4	37
Succinic acid	1.3	3	0	3–3.5	25
Sodium acetate	0.5	5	2	6	—
Dimethyl-glyoxime**	0.8	—	0.5	5.5	(50)
Ethylenediamine hydrochloride	1.0	7	0	3	(52)

* Reaction was stopped at the hydrogen uptake of nearly half of the theoretical.
** In methanol

Table IV. Hydrogenation of various substrate

Substrate	Hydrogenation activity[a] 10°C Control	10°C Modified	60°C Control	60°C Modified
Ketone				
Acetone	5.7	0	55	8
Ethyl methyl ketone	2	0	20	2
Acetophenone	8	0	120	22
Cyclohexanone	1.8	0	24.3[b]	7
C=C Double bond				
Allyl alcohol	34	34		
Cinnamic acid	16	16		
Maleic acid	41	63		
Ethyl acrylate	5 min.[c]	3 min.		
Diethyl maleate	5 min.[c]	4 min.		
Mesityl oxide[d]	28	14	6	1
Cinnamic aldehyde	12.5	0.5	14	—

a) Hydrogenation activity is expressed by % hydrogen uptake in initial 30 min. in the case of ketone and in initial 5 min. in the case of C=C double bond.
b) This compound was reduced at 80°C.
c) Time of reaction finished.
d) Losses of carbonyl group in the products were 11% and 3%, respectively.

to one sixth of that of the untreated catalyst. Hydrogenation activity of R-Ni catalyst for unsaturated compounds was almost unchanged by this treatment, and the activity increased in the case of hydrogenation of maleic acid. Similarly, the rates of hydrogenation of ethyl maleate and of ethyl acrylate were increased by this treatment.

When mesityl oxide was the substrate of hydrogenation, hydrogen uptake ceased, when the uptake of hydrogen was one mol. per mol. of substrate, and isobutyl methyl ketone was obtained in high yield. This result shows that the C=C double bond was predominantly hydrogenated while the carbonyl group was almost unaffected when mesityl oxide was hydrogenated with this modified catalyst.

This conclusion was confirmed by examining the infrared spectrum and determining the carbonyl content of the hydrogenated products. The only negative result occurred with cinnamaldehyde. Neither its C=C double bond nor its carbonyl group was hydrogenation activity of R-Ni catalyst for nitrobenzene was depressed by treatment with amino acid as shown in Table V, but was increased two-fold by treatment with dimethylglyoxime.

The results thus for obtained suggest the possibility that the surface of activated R-Ni catalyst is inhomogeneous and that C=C and

Table V. Hydrogenation activity for nitrobenzene

Modifying reagent	Hydrogenation activity* 10°C	40°C
Untreated	9	16
2% L-MSG	2	8
0.8% Dimethylglyoxime	32	45

* % Hydrogen uptake (%) in initial 10 min.

C=O bonds are reduced at different hydrogenating centers on the surface. When the catalyst was modified with an amino acid capable of chelating with nickel ion, the hydrogenated centers for carbonyl compounds were inhibited, whereas the centers for C=C double bond remained unaffected.

In this investigation, carbonyl-containing substrates used were limited to some ketones, and the conditions of hydrogenation were also limited. In order to obtain further information concerning the mechanism of this modification and to provide a basis for its practical application, further studies are required. It is expected that such studies will shed some light on the mechanism of catalytic hydrogenation reactions.

Experimental

Preparation of Catalyst. — The catalyst used in this work, was prepared by the following method. One and a half grams of Raney nickel alloys (aluminum content 45%, manufactured by Kawakami Lab. Co. Ltd.,) was added to 20 ml. of 20% sodium hydroxide solution in small portions during a period of 5 min., and was allowed to stand for 45 min. at 80°C. The activated catalyst was washed several times with water. All of hydrogenation reaction in this work was carried out with this quantity of R-Ni catalyst.

Modification of Catalyst. — Fifty milliliters of an amino acid solution was added to the activated catalyst, and the mixture was allowed to stand with occasional shaking at room temperature (10~15°C) for 2 hr. After the modifying solution was removed by decantation, the catalyst was washed once with water and two times with methanol, and centrifuged. Dry weight of the catalyst was about 0.7 g. Glycylglycine hydrochloride and acetic acid were used after their solution were adjusted to pH 5 by dilute alkali. Dimethylglyoxime was used in methanol solution.

Reaction Vessel.—A shaking autoclave of 100 ml. capacity was used as the vessel for hydrogenation reaction.

Activity of Catalyst. — Hydrogenation activity was measured by the rate of hydrogen uptake at the initial period of reaction and was represented as percent of theoretical hydrogen absorption per specified period of time.

Hydrogenation Reaction. — *1) Hydrogenation of C=C Double Bonds. — a) Hydrogenation of Allyl Alcohol.*—Seventeen grams (0.3 ml.) of allyl alcohol

were hydrogenated with hydrogen 95 kg./cm² at 10°C with R-Ni prepared from 1.5 g. alloy. Reaction velocity was represented by percent hydrogen uptake in the initial 5 min.

b) Hydrogenation of Cinnamic Acid, Maleic Acid, Ethyl Acrylate and Diethyl Maleate.—7.5 g. cinnamic acid in 50 ml. methanol, 17.5 g. maleic acid in 50 ml. methanol, 15 g. ethyl acrylate in 40 ml. methanol and 17.2 g. diethyl maleate in 50 ml. methanol were hydrogenated by the same procedure as allyl alcohol.

2) Hydrogenation of Ketones.—a) Hydrogenation of Ethyl Methyl Ketone.—Twenty grams (0.3 mol.) of ethyl methyl ketone were hydrogenated with hydrogen (70 kg./cm²) at 10°C. Reaction velocity represented hydrogen uptake in the initial 30 min. Temperature of the reaction was initially maintained at 10°C for 3 hr. and then was raised to 60°C.

b) Hydrogenation of Acetone.—Acetone (11.6 g., 0.2 mol.) was hydrogenated by the same procedure as ethyl methyl ketone.

c) Hydrogenation of Acetophenone.—Twelve grams (0.1 mol.) of acetophenone dissolved in 50 ml. methanol were hydrogenated by the same procedure as ethyl methyl ketone.

d) Hydrogenation of Cyclohexanone.—Cyclohexanone (19.6 g., 0.2 mol.) was hydrogenated by the same procedure as ethyl methyl ketone, except that the hydrogenation at higher temperature was carried out at 80°C instead of 60°C.

3) Hydrogenation of Mesityl Oxide. — Mesityl oxide was purified by fractional distillation (128~130°C, b. p.) after being washed with dilute alkali to remove contaminating iodine. Purified mesityl oxide (19.6 g., 0.2 mol.) was hydrogenated with hydrogen 90 kg./cm² initially at 10°C. After the hydrogen uptake was 0.2 mol., temperature was raised to 60°C and reaction was continued still further for 2 hr. Reaction velocity was represented by hydrogen uptake in the initial 5 min. at 10°C and during the first 30 min. at 60°C and was expressed as percentage of the theoretical amount for each radical.

4) Hydrogenation of Nitrobenzene. — Four grams (0.03 mol.) of nitrobenzene dissolved in 50 ml. methanol were hydrogenated with hydrogen (80 kg./cm²). The temperature, which initially was 10°C, rose to 40°C during the reaction. Reaction velocity was presented by percent hydrogen uptake in the first 10 min.

Determination of the Carbonyl Group. — The carbonyl group was assayed by the hydroxylamine method after Fritz and Yamamura[5].

Summary

Hydrogenation activity of the Raney nickel catalyst for carbonyl compounds was greatly diminished, when the catalyst was treated with a solution of amino acid. On the other hand, no appreciable change in its hydrogenation activity for C=C double bonds occurred upon this treatment. When mesityl oxide was used as a substrate, selective hydrogenation was most clearly demonstrated.

The effect of conditions of modification, such as concentration of the modifying solution, immersion time and kind of modifying reagent on the activity of the modified catalyst, were investigated.

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