BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1447—1449 (1969)

Liquid-phase Selective Hydrogenation of an Aliphatic α,β-Unsaturated Aldehyde over Raney Cobalt Catalyst Modified with Ferrous Chloride

Kazuhiko HOTTA and Teruo KUBOMATSU

The Osaka Municipal Technical Research Institute, Kita-ku, Osaka

(Received August 10, 1968)

It is comparatively difficult to hydrogenate selectively an α,β-unsaturated aldehyde to an unsaturated alcohol by heterogeneous catalytic reaction. This hydrogenation can, however, be performed over the noble metal catalysts or over less active catalysts under severe conditions.[1–6] Hydrogenation under mild conditions, however, was not successful over Raney-type catalysts, except over the Raney zinc and the Raney zinc-copper catalysts.[7,8]

The present authors have studied the selectivities of Raney-type catalysts modified with various compounds. It has been found that no unsaturated alcohols can be obtained by the hydrogenation of such unsaturated aldehydes as 2-methyl-2-pentenal and cinnamaldehyde over the Raney nickel catalyst, and that the addition of such modifiers as ferrous chloride, cadmium chloride, cobalt chloride, and citric acid was not effective in producing unsaturated alcohols.[9]

On the other hand, it is interesting that unsaturated alcohols was obtained over the Raney *cobalt* catalyst under the normal hydrogen pressure at 55°C, and that the addition of ferrous chloride to the reaction mixture increased the yield of the unsaturated alcohol.

Experimental

A commercial Raney cobalt-aluminum alloy (Co: 50 wt%) was developed with a 15% sodium hydroxide solution at 50°C, and the resulting catalyst was washed with water and then with 2-propanol. The catalyst thus prepared was stirred with ferrous chloride in 2-propanol under a hydrogen atmosphere, then the substrate was added to the solution and the mixture was stirred with a magnetic stirrer under the normal pressure of hydrogen at 55°C. 2-Methyl-2-pentenal, used as the substrate, was prepared from propionaldehyde; its purity was indicated to be more than 99% by gas chromatography. The reaction products were analyzed by gas chromatography. The amount of hydrogen adsorbed on the catalyst was estimated by methods described previously.[10,11]

Results and Discussion

The selectivity of the catalyst, which is defined as the mole percent of the unsaturated alcohol in all the products, depended on the temperature at which the development of the Raney cobalt alloy was carried out. The best selectivity was obtained with the catalyst developed at 50°C, so this catalyst was used for this hydrogenation.

The hydrogenation of 2-methyl-2-pentenal (UD) is shown in Fig. 2. 2-Methyl-2-pentene-1-ol (UA) was obtained as the main product. The rate of

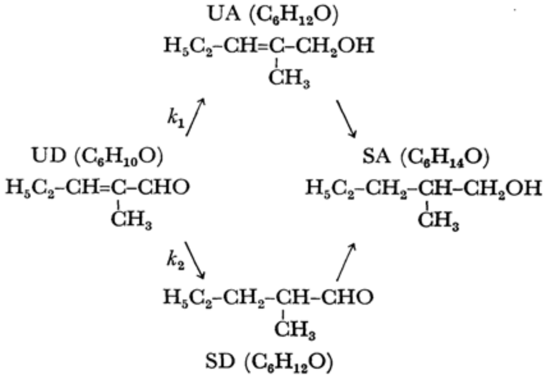

Fig. 1. Hydrogenation scheme of 2-methyl-2-pentenal.

---

[1] H. S. Broadbent, G. C. Campbell, W. J. Bartley and J. H. Johnson, *J. Org. Chem.*, **24**, 1847 (1959).

[2] W. F. Tuley and R. Adams, *J. Am. Chem. Soc.*, **47**, 3061 (1925).

[3] P. N. Rylander, N. Himelstein and M. Kilroy, *Engelhard Ind. Tech. Bull.*, **4**, 49 (1963).

[4] W. J. Peppel, U. S. Pat. 2448047 (1948).

[5] S. Yada, T. Yamauchi and S. Kudo, *Shokubai* (*Catalyst*), **5**, 2 (1963).

[6] K. Yamagishi, S. Hamada, H. Arai and H. Yokoo, *Yukigosei Kagaku Kyokai-shi* (*J. Org. Synth. Chem. Soc.*), **24**, 54 (1966).

[7] Kh. Freidlin, A. S. Sultanov and M. F. Abidova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1958**, 378.

[8] Kh. Freidlin and V. I. Gorshkov, *ibid.*, **1959**, 2027.

[9] K. Hotta and T. Kubomatsu, Preprints for the 20th Annual Meeting of the Chem. Soc. Japan (Tokyo, 1967), No. 11303.

[10] K. Tarama, T. Kubomatsu and S. Kishida, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **82**, 1633 (1961).

[11] K. Tarama, S. Teranishi, T. Kubomatsu and S. Kishida, *Shokubai* (*Catalyst*), **7**, 289 (1965).

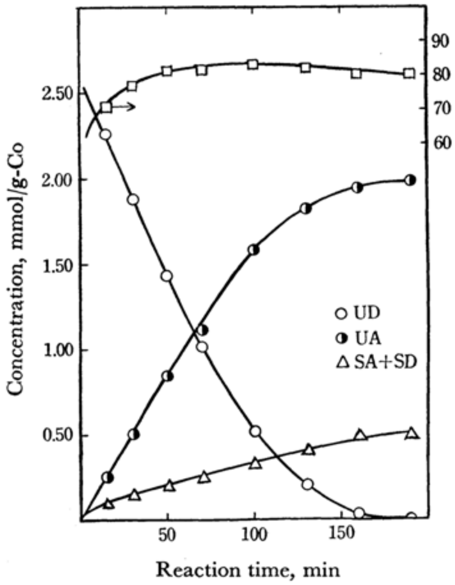

Fig. 2. Hydrogenation of 2-methyl-2-pentenal. Catalyst: 1.0 g cobalt, solvent: 2-propanol 5 m*l*, concentration of substrate: 2.60 mmol/g-Co, amount of ferrous chloride added: 0.18 mmol/g-Co.

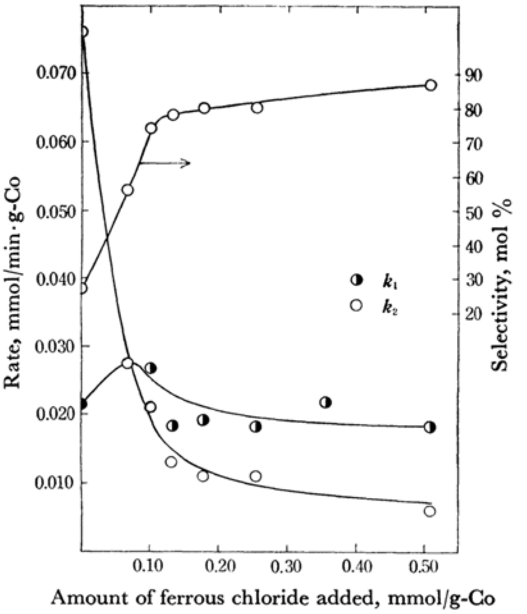

Fig. 3. Dependence of selectivity and initial rate on amount of ferrous chloride added. Catalyst: 1.0 g cobalt, solvent: 2-propanol 5 m*l*, concentration of substrate: 2.60 mmol/g-Co.

the production of UA was constant during the first period of the reaction, and the total rate of the production of the saturated compounds, 2-methylpentan-1-ol (SA) and 2-methylpentanal (SD), which were obtained as the by-products, decreased gradually. A similar situation was observed when ferrous chloride of less than 0.36 mmol/g-Co was added. The rate of the production of UA showed a progressive decrease in the course of the reaction when more than 0.51 mmol/g-Co of ferrous chloride was added.

Each hydrogenation step is supposed to be irreversible, judging from the fact that the dehydrogenation of the produced alcohols did not occur under these conditions. The isomerization of UA to SD almost did not occur at all and SD was consumed preferentially on the hydrogenation of a mixture of UA and SD. Judging from the facts mentioned above, the produced SD is readily hydrogenated to SA and the produced UA does not react further; thus, most of the SA is supposed to be produced through SD.

The yield of UA increased with an increase in the amount of ferrous chloride added, as is shown in Fig. 3. It is also shown in Fig. 3 that the rate of the hydrogenation of the carbon-carbon double bond (C=C), k_2, decreased remarkably, and that the rate of the hydrogenation of the aldehyde group, k_1, decreased only slightly, with an increase in the amount of ferrous chloride added. Thus the promotion of the selectivity of the catalyst in the hydrogenation of the unsaturated aldehyde seems to be caused by the decrease in the rate of the hydrogenation of the carbon-carbon double bond.

It was found that the color of the reaction solution changed to the blue of the cobalt(II) ion when it was stirred for about 5 min. This indicates that the cobalt of the catalyst was substituted rapidly by the iron when ferrous chloride was added. A part of the remaining ferrous chloride might be adsorbed on the catalyst surface and might react further with the Raney cobalt catalyst, judging from the fact that the concentration of ferrous chloride decreased gradually during the last period of the reaction.

It has been found that there are two types of hydrogen on the Raney nickel catalyst.[10,11] One of these is the hydrogen adsorbed weakly on the catalyst, and the other is the strongly-adsorbed hydrogen, the amount of which is termed the hydrogen content of the catalyst. These two types of adsorbed hydrogen were also found on the Raney cobalt cotalyst. The weakly-adsorbed hydrogen decreased to 40% of the original value, and the hydrogen content of the catalyst decreased to 8%, when 0.18 mmol/g-Co of ferrous chloride was added.

It seems that the selective hydrogenation could be carried out because the addition of ferrous chloride to the reaction mixture decreased the amount of the strongly-adsorbed hydrogen more than that of the weakly-adsorbed hydrogen, and thus the decrease in the rate of hydrogenation became much greater for the carbon-carbon double bond than for the aldehyde group, assuming that the carbon-carbon double bond reactes more readily with the strongly-adsorbed hydrogen than with the weakly-adsorbed hydrogen, as has been reported by Takeuchi and Asano.[12]

A more detailed discussion will be reserved until the results of experiments now in progress are available.

---

[12] T. Takeuchi and T. Asano, *Z. Physik. Chem., N.F.*, **36**, (1/2) 118 (1963).