CHEMISTRY LETTERS, pp. 673-676, 1980.

SODIUM HYDROXIDE-ACTIVATED CATALYST OF COLLOIDAL NICKEL BORIDE FOR ATMOSPHERIC HYDROGENATION OF KETONES AND ALDEHYDES

Yukimichi NAKAO* and Shoei FUJISHIGE
Research Institute for Polymers and Textiles,
Yatabe-Higashi, Tsukuba-gun, Ibaraki 305

Addition of sodium hydroxide to colloidal nickel boride in ethanol resulted in a marked enhancement of its catalytic activity for atmospheric hydrogenation of acetone at 30°C by a factor of more than 20. Other ketones and aldehydes with bulky substituents were smoothly hydrogenated by the activated colloidal catalyst.

Nickel borides (Ni_2B) prepared from nickel(II) chloride ($NiCl_2 \cdot 6H_2O$) or nickel(II) acetate by reduction with sodium borohydride ($NaBH_4$) in aqueous solution are known to be effective for catalytic hydrogenation of olefins.1,2) Well-dispersed suspension of nickel boride is obtained from nickel(II) acetate in 95% ethanol,3) being an effective hydrogenation catalyst for ketones especially in the pH range 10–12.4) It has been reported that colloidal nickel boride prepared by reduction of $NiCl_2 \cdot 6H_2O$ with $NaBH_4$ in ethanol in the presence of poly(vinylpyrrolidone) as a protective colloid exhibited a high activity for hydrogenation of acrylamide.5) In this report, a marked enhancement of the catalytic activity of the colloidal nickel boride for hydrogenation of acetone by addition of sodium hydroxide (NaOH) and the application of the activated colloidal catalyst for hydrogenation of various ketones and aldehydes are described.

A typical procedure is as follows. An ethanolic solution (5 ml) of $NaBH_4$ (0.20 mmol) was added dropwise with stirring to an ethanolic solution (14 ml) of $NiCl_2 \cdot 6H_2O$ (0.10 mmol) and poly(vinylpyrrolidone) (degree of polymerization 360, 10 mg), resulting in the formation of a dark brown-colored clear solution containing fine colloidal nickel boride. Then an ethanolic solution (1 ml) of NaOH (0.40 mmol) was added to the solution. After further stirring for about

15 min, acetone (0.0184 ml, 0.25 mmol) was added to the colloidal solution, at that time hydrogen uptake started. The hydrogenation reaction to produce 2-propanol was completed in 15 min. In the course of the reaction, no precipitate of nickel boride was formed. The catalytic activity was evaluated by the initial rate of hydrogen uptake (r_i). All operations for the preparation and the hydrogenation were performed at 30.0°C under the atmospheric pressure of hydrogen. Ethanol was degassed by refluxing under argon before use.

Effects of the addition of NaOH to the colloidal nickel borides on their catalytic activity for hydrogenation of acetone are illustrated in Fig. 1. The catalytic activity increases with increasing the amount of added NaOH and attains a plateau at 0.3 mmol NaOH. The activity of the colloid with NaOH of 0.3 mmol or above is more than 20 times that without NaOH. The addition of NaOH to nickel boride suspension, however, results in 4–6-fold enhancement of activity for hydrogenation of methyl ethyl ketone[4)] and furfural.[1)]

Hydrogenation of various ketones and aldehydes was performed over the colloidal nickel boride activated by 0.4 mmol NaOH. The initial rates of hydrogenation are compared in Table 1. The hydrogenation rate of ketones catalyzed by the NaOH-activated colloidal nickel boride is affected to a small extent by the number of alkyl carbon atoms in contrast to the case of nickel boride suspension. Thus, the relative hydrogenation rates of acetone, methyl ethyl ketone, methyl n-propyl ketone, and methyl isobutyl ketone over the NaOH-activated colloidal nickel boride are 100, 99, 96, and 73, respectively, while over the nickel boride suspension they are 100, 57, 31, and 15, respectively.[6)] It has been reported[7)] on the catalytic hydrogenation of internal olefins that the double bonds are far less sterically hindered on the catalytic surface of very fine colloidal rhodium of 8.8 Å diameter than on the surface of rather large one of 34.3 Å diameter. In the present case, the carbonyl groups are assumed to be less sterically hindered by the adjacent substituents on the catalytic surface of the small particles of colloidal nickel boride. Cyclic ketones are more rapidly hydrogenated than linear ketones. Aldehydes are also hydrogenated by the NaOH-activated colloidal catalyst at a significant rate. Ketones and aldehydes of which the carbonyl groups are adjacent to bulky phenyl groups are smoothly hydrogenated.

Ethanol-insoluble base such as anhydrous potassium carbonate was also effective for the activation of colloidal nickel boride. On adding NaOH to $NiCl_2 \cdot 6H_2O$-

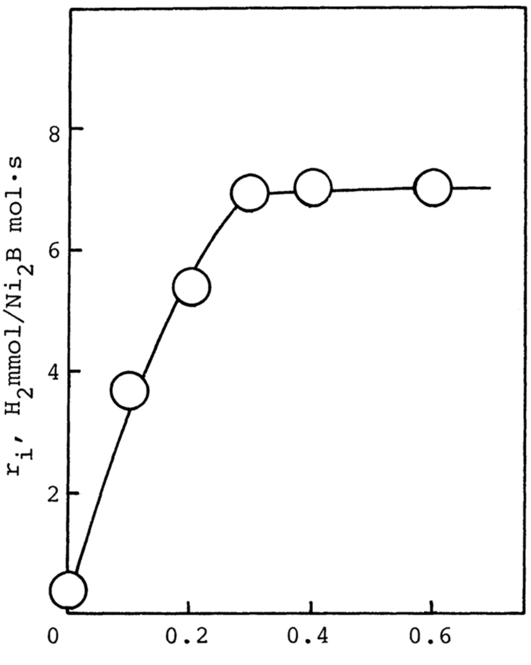

Fig. 1. Dependence of the catalytic activity of colloidal nickel boride upon the amount of added NaOH. ($NiCl_2 \cdot 6H_2O$=0.1 mmol, $NaBH_4$=0.2 mmol)

Table 1. Hydrogenation of ketones and aldehydes catalyzed by NaOH-activated colloidal nickel boride[a)]

Substrate	r_i[b)]
Acetone	7.1
Methyl ethyl ketone	7.0
Methyl n-propyl ketone	6.8
Methyl isobutyl ketone	5.2
Cyclopentanone	7.7
Cyclohexanone	8.4
Acetophenone	5.9
Benzophenone	5.2
Butyraldehyde	9.5
Benzaldehyde	12.6
Furfural	17.4

a) Prepared using 0.4 mmol NaOH.

b) Initial rate of hydrogenation (H_2mmol/Ni_2B mol·s) under conditions; temp. 30.0°C, press. 1 atm, substrate = 0.25 mmol.

poly(vinylpyrrolidone) solutions prior to $NaBH_4$, only nickel(II) hydroxide was formed as a white turbidity. On the other hand, addition of potassium carbonate gave an active colloidal catalyst of nickel boride, even if added prior to $NaBH_4$. The NaOH-activated colloidal nickel boride catalyst was inactivated by the addition of hydrochloric acid equimolar with added NaOH. However, the resulting colloid was reactivated by further addition of NaOH. This indicates that the catalytic activity of colloidal nickel boride for hydrogenation of acetone is essentially dependent on the pH of the solution.

When exposed to air, the NaOH-activated colloidal nickel boride decomposed to complete inactivation as well as that without NaOH.5)

References

1) R. Paul, P. Buisson, and N. Joseph, Ind. Eng. Chem., 44, 1006 (1952).

2) C. A. Brown and H. C. Brown, J. Am. Chem. Soc., 85, 1003 (1963).

3) H. C. Brown and C. A. Brown, ibid., 85, 1005 (1963).

4) Y. Murakami, S. Kishida, T. Imanaka, and S. Teranishi, Nippon Kagaku Zasshi, 89, 263 (1968).

5) Y. Nakao and S. Fujishige, Chem. Lett., 1979, 995; idem, Bull. Chem. Soc. Japan, 53, 1267 (1980).

6) S. Kishida, Y. Murakami, T. Imanaka, and S. Teranishi, J. Catalysis, 12, 97 (1968).

7) H. Hirai, Y. Nakao, and N. Toshima, Chem. Lett., 1978, 545.

(Received February 22, 1980)