CHEMISTRY LETTERS, pp. 995-996, 1979. Published by the Chemical Society of Japan

PREPARATION AND CATALYTIC ACTIVITY OF COLLOIDAL NICKEL BORIDE DISPERSED IN ETHANOL

Yukimichi NAKAO and Shoei FUJISHIGE
Research Institute for Polymers and Textiles,
Sawatari, Kanagawa-ku, Yokohama 221

Colloidal nickel borides in ethanol were prepared by the reaction of nickel(II) chloride with sodium borohydride in the presence of a polymer like poly(vinylpyrrolidone). The colloid was effective for the hydrogenation of acrylamide at 30°C under an atmospheric hydrogen pressure.

The reaction of nickel(II) salts with sodium borohydride ($NaBH_4$) in aqueous solution results the precipitation of nickel boride, Ni_2B, which is comparable to Raney nickel in the catalytic activity for hydrogenation.1) An improved procedure involving the reaction of nickel(II) acetate with $NaBH_4$ in 95% ethanol supplies much finer particles of nickel boride, termed the P-2 nickel boride.2) As previously reported, a colloidal dispersion of extremely fine rhodium particles was prepared by reduction of rhodium(III) chloride with methanol in the presence of poly(vinyl alcohol) as a protective colloid, and exhibited more than four times the catalytic activity of the commercial catalyst of rhodium supported on charcoal.3) In this communication, the preparation of colloidal nickel boride using polymers and the catalytic activity for hydrogenation are described.

The typical procedures are as follows. Nickel(II) chloride ($NiCl_2.6H_2O$, 0.020 mmol) and poly(vinylpyrrolidone) (2.0 mg) was dissolved in ethanol (18 ml) under hydrogen. To the solution, a solution of $NaBH_4$ (0.040 mmol) in ethanol (1 ml) was added dropwise with stirring, resulting in a clear dark-brown solution containing the colloidal particles of nickel boride. After further stirring for 15 min to complete the hydrolysis of $NaBH_4$ accompanied by hydrogen evolution, a solution of acrylamide (0.25 mmol) in ethanol (1 ml) was added to the colloidal solution, whereupon hydrogen began to be taken up. Being soluble in ethanol-water as well as in ethanol, acrylamide was used as a substrate (see Table 1, No.5 and 7). The product was identified to be propionamide by infrared spectra. The catalytic activity of the colloid was evaluated by the initial rate of hydrogen uptake. All operations of preparation and hydrogenation were performed at 30°C in a flask in which the atmosphere was previously replaced with hydrogen. Ethanol was degassed by refluxing under argon before use.

The use of some other polymers also gave dark-brown or black colored clear solutions containing colloidal nickel boride. Table 1 (No.1-5) shows the catalytic activities of the colloids. This indicate that the catalytic activity of the colloidal nickel boride is dependent upon the kinds of polymers used. Among the

Table 1. Catalytic activity of colloidal nickel boride[a)]

No.	Polymer	Solvent	Dispersion of nickel boride	Catalytic activity[b)] (H_2mmol/Ni mol.sec)
1	Poly(vinylpyrrolidone)[c)]	EtOH	Dark-brown clear solution	167
2	Soluble nylon[d)]	"	"	377
3	Poly(methyl vinyl ether)[e)]	"	Black clear solution	74
4	Ethyl hydroxyethyl cellulose	"	"	193
5	Poly(vinyl alcohol)[f)]	95%EtOH[h)]	"	170
6	none	EtOH	Black coagulated mass	3
7	none[g)]	95%EtOH[i)]	Black suspension	119

a) Prepared from $NiCl_2.6H_2O$. b) Initial rate of hydrogenation under conditions; temp. 30.0°C, press. 1 atm, [Ni]=1.0 mM, [acrylamide]=12.5 mM, reaction vol.=20 ml. c) Degree of polymerization (DP)=360. d) Ternary copolymer(6:66:610=3:4:3). e) DP=570. f) DP=500. g) Suspension (P-2 nickel boride) prepared from $Ni(OAc)_2.4H_2O$.[2)] h) Water was required for the dissolution of the polymer. i) Water was required for the dissolution of $Ni(OAc)_2.4H_2O$.

colloids, the one prepared using soluble nylon is the most effective catalyst. Table 1 (No.6) also shows that, in the absence of a polymer, the reaction of $NiCl_2.6H_2O$ with $NaBH_4$ produces only a black coagulated material with a much lower activity than colloidal nickel boride. These results suggest that the hydrogenation rate is determined by the catalytic surface area which is dependent upon both the dispersion state and particle size of nickel boride. On the other hand, a well-dispersed suspension (P-2 nickel boride) is prepared from $Ni(OAc)_2.4H_2O$ even without using polymers, exhibiting a considerable activity (Table 1, No.7), which may be ascribed to acetate ion generated from $Ni(OAc)_2.4H_2O$.

Colloidal nickel boride prepared using poly(vinylpyrrolidone) was stable under hydrogen for more than several months, but decomposed immediately on exposure to air.

References

1) R. Paul, P. Buisson and N. Joseph, Ind. Eng. Chem., 44, 1006 (1952).
2) H. C. Brown and C. A. Brown, J. Amer. Chem. Soc., 85, 1005 (1963).
3) H. Hirai, Y. Nakao, N. Toshima and K. Adachi, Chem. Lett., 1976, 905.

(Received June 7, 1979)