May, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53***, *1267—1270 (1980)* 1267

Polymer-protected Colloidal Nickel Boride in Ethanol and Its Catalytic Activity for Hydrogenation

Yukimichi NAKAO* and Shoei FUJISHIGE

Research Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba-gun, Ibaraki 305

(Received October 26, 1979)

Colloidal nickel borides were prepared in ethanol from nickel(II) chloride and sodium borohydride using a polymer as a protective colloid. For atmospheric hydrogenation of olefins such as acrylamide at 30 °C, the colloid prepared by using poly(vinylpyrrolidone) exhibited catalytic activity 15—60 times that of the usual nickel boride prepared without using a polymer. The high activity of colloidal nickel borides was found to be due to the polymers, soluble nylon being the most effective. The colloids are stable under oxygen-free hydrogen, decomposing immediately on exposure to air.

Reduction of nickel(II) chloride ($NiCl_2 \cdot 6H_2O$) with sodium borohydride ($NaBH_4$) in aqueous solutions gives a black precipitate of nickel boride which is catalytically active for the hydrogenation of olefinic compounds[1) and the hydrolysis of $NaBH_4$.[2) Many variations for the preparation of nickel boride have been reported.[3) Although the form of precipitated nickel boride varies according to the mode of preparation, most of them consist of a common unit Ni_2B.[3) In general, the activity of a solid catalyst such as nickel boride is primarily controlled by its effective surface area which is dependent upon both particle size and dispersion state. A number of reports[4) have appeared on the colloidal noble metals prepared from the corresponding metal salts by treatment with a reductant such as molecular hydrogen in aqueous solution. The coagulation of colloidal metals can be prevented by the presence of a polymer.

Hydrosol of nickel boride was prepared by the reduction of nickel(II) nitrate with potassium borohydride in the presence of a fairly large amount (5%) of a polymer such as acid gelatin and poly(vinyl alcohol).[5) Sols of metals in alcohol have been prepared in a similar manner.[6) An extremely fine colloid of rhodium (9 Å in diameter) was prepared from a methanolic solution of rhodium(III) chloride by treatment with sodium hydroxide in the presence of poly(vinylpyrrolidone) as a protective colloid. The colloidal rhodium was a very effective catalyst especially for the atmospheric hydrogenation of internal olefins. A clear nickel boride sol was prepared by the reduction of $NiCl_2 \cdot 6H_2O$ with $NaBH_4$ in ethanol under hydrogen in the presence of a small amount (0.01%) of poly(vinylpyrrolidone).[7) It exhibited a much higher activity for the hydrogenation of olefins such as acrylamide than that of the nickel boride precipitate prepared without using polymers. In the present paper, the effects of materials and the mode of preparation on the colloidal nickel boride as regards its catalytic activity and stability against oxygen are described.

Experimental

Chemicals. Hydrogen was of 99.999% purity. Liquid chemicals (reagent grade) for reaction medium were degassed by refluxing under argon before use. Solid chemicals (reagent grade) were used without further purification.

Preparation of Colloidal Nickel Boride. A typical procedure for the preparation of colloidal nickel boride is as follows. Nickel(II) chloride ($NiCl_2 \cdot 6H_2O$, 0.020 mmol) and poly(vinylpyrrolidone) (PVP-K30, degree of polymerization 360, 2.0 mg) were dissolved in ethanol (18 ml) under hydrogen. To the solution was added an ethanolic solution (1 ml) of sodium borohydride ($NaBH_4$, 0.040 mmol) prepared under argon with stirring at 30.0 °C and atmospheric pressure of hydrogen. Dark brown sol (19 ml) of nickel boride was obtained. The formation was followed by hydrogen evolution which ceased within 15 min.

Hydrogenation of Acrylamide. An ethanolic solution (1 ml) of acrylamide (0.25 mmol) prepared under argon was added to the nickel boride sol (19 ml) with stirring at 30.0 °C and atmospheric pressure of hydrogen, hydrogen uptake starting. The progress of hydrogenation was followed by means of the uptake volume of hydrogen. The hydrogenation product was found to be propionamide by means of infrared spectra.

Results

Formation of Colloidal Nickel Boride. Addition of an ethanolic solutions of $NaBH_4$ (0.040 mmol) to ethanolic solutions of $NiCl_2 \cdot 6H_2O$ (0.020 mmol) and PVP-K30 at 30 °C under hydrogen resulted in the formation of colloidal nickel boride. On adding $NaBH_4$, a short induction period of 1—2 s ended with the formation of a colloid. Colloidal nickel borides were obtained at 0 °C and −20 °C with induction periods 5 s and 25 s, respectively. Hydrogen evolution began immediately after the colloid formation, ceasing in 15 min. The total evolution volume was 2.55 ml (0.104 mmol).

Catalytic Activity for Hydrogenation. Addition of acrylamide[8) to colloidal nickel boride resulted in hydrogen uptake. Figure 1 shows the time-course of the hydrogen uptake. Equimolar amount of hydrogen with acrylamide was taken up until the hydrogenation was completed in 4 min. The initial rate of hydrogen uptake (r_i(acam)) was determined from the curve to be 167 H_2 mmol/Ni_2B mol s,[9) giving a measure of the catalytic activity of colloid.

Available Materials. Various nickel(II) salts, borohydrides, and solvents were examined for the preparation of colloidal nickel boride using PVP-K30. The results are given in Table 1. Nickel(II) sulfate and nickel(II) acetate also give colloidal nickel borides with an almost equal activity to that from $NiCl_2 \cdot 6H_2O$. On the contrary, a black colloidal solution from nickel(II) nitrate exhibits a much lower activity.

The use of water as a solvent gives a gray turbid solution which is not so effective as the clear sol pre-

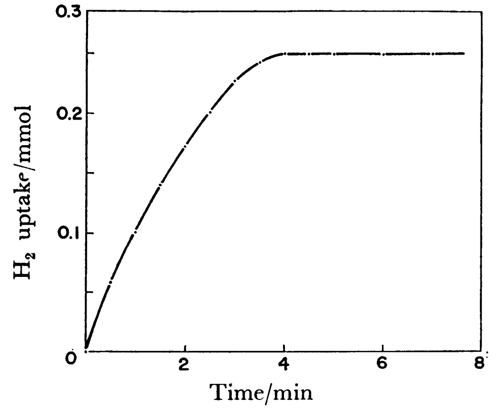

Fig. 1. Atmospheric hydrogenation of acrylamide in ethanol at 30 °C catalyzed by colloidal nickel boride.

TABLE 1. CATALYTIC ACTIVITY OF COLLOIDAL NICKEL BORIDE[a)]

Ni(II) salt	BH_4 salt	Solvent	r_i(acam)[b)] (H_2 mmol/Ni_2B mol s)
$NiCl_2 \cdot 6H_2O$	$NaBH_4$	EtOH	167
$NiSO_4 \cdot 7H_2O$	$NaBH_4$	EtOH	168
$Ni(OAc)_2 \cdot 4H_2O$	$NaBH_4$	95%EtOH	165
$Ni(NO_3)_2 \cdot 6H_2O$	$NaBH_4$	EtOH	2
$NiCl_2 \cdot 6H_2O$	$NaBH_4$	H_2O	11
$NiCl_2 \cdot 6H_2O$	KBH_4	MeOH	245
$NiCl_2 \cdot 6H_2O$	$NaBH_4$	MeOH	218

a) Prepared by using poly(vinylpyrrolidone)-K30. b) Initial rate of hydrogenation of acrylamide.

pared in ethanol. Potassium borohydride (KBH_4) is almost insoluble in ethanol, but soluble in methanol. A sol prepared in methanol with KBH_4 is more effective than that prepared with $NaBH_4$.

Borohydride salts are known to react with methanol.[10)] Ethanolic and methanolic solutions of $NaBH_4$ were examined for their ability to produce active colloidal nickel boride. The dependence of the ability of both $NaBH_4$ solutions upon time after $NaBH_4$ dissolution at 17 °C is shown in Fig. 2. Ethanolic $NaBH_4$ is still able to produce a colloid after being left to stand for 18 h, the ability of methanolic $NaBH_4$ being completely lost within 1 h. When methanolic $NaBH_4$ was added to $NiCl_2 \cdot 6H_2O$–PVP-K30 solutions 20 min after its dissolution, a highly active colloid was obtained. KBH_4 reacted with methanol more slowly than $NaBH_4$.

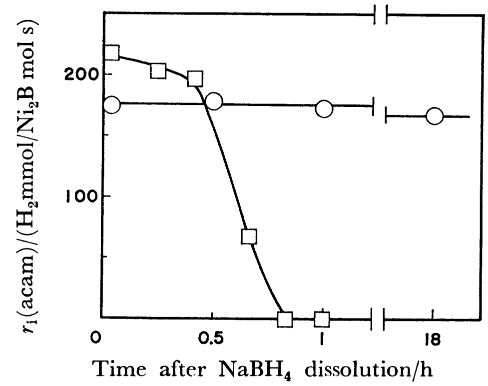

Fig. 2. Decrease in ability to produce colloidal nickel boride of ethanolic (○) and methanolic (□) $NaBH_4$ at 17 °C.

TABLE 2. CATALYTIC ACTIVITY OF COLLOIDAL NICKEL BORIDE[a)]

Polymer	r_i(acam)[b)] (H_2 mmol/Ni_2B mol s)
Poly(vinylpyrrolidone)-K30[c)]	167
Poly(vinylpyrrolidone)-K15[d)]	180
Poly(vinylpyrrolidone)-K90[e)]	156
Soluble nylon[f)]	377
Poly(methyl vinyl ether)[g)]	74
Ethyl hydroxyethyl cellulose	193
Poly(vinyl alcohol)[h)]	170[i)]

a) Prepared by using $NiCl_2 \cdot 6H_2O$ and $NaBH_4$ in ethanol. b) Initial rate of hydrogenation of acrylamide. c) Degree of polymerization (DP) = 360. d) DP = 90. e) DP = 3250. f) Ternary copolymer (6:66:610 = 3:4:3). g) DP = 570. h) DP = 500. i) Solvent = 95% EtOH.

A series of ethanol-soluble polymers were examined as a protective colloid using $NiCl_2 \cdot 6H_2O$, $NaBH_4$, and ethanol. Poly(vinylpyrrolidone)s, soluble nylon, and poly(vinyl alcohol) gave dark brown colloids, while poly(methyl vinyl ether) and ethyl hydroxyethyl cellulose gave black colloids. The catalytic activity of these colloids is shown in Table 2. Poly(vinylpyrrolidone)s of degree of polymerization 90 (PVP-K15) and 3250 (PVP-K90) give dark brown colloids with a nearly equal activity to that prepared with PVP-K30. The catalytic activity of colloid varies with the kind of polymer. Colloidal nickel boride with soluble nylon is the most active among those listed in Table 2, exhibiting about five times the activity of that with poly(methyl vinyl ether). *N*-methylpyrrolidone, a monomeric compound having the same functional group as poly(vinylpyrrolidone), gave no colloid but a black precipitate. Absence of a polymer also resulted in the precipitation of nickel boride.

Effect of $NaBH_4$ to $NiCl_2 \cdot 6H_2O$ Ratio. Colloidal nickel borides were prepared in ethanol with varying amounts of $NaBH_4$, and used as a catalyst after being stirred under hydrogen for 15 min. Figure 3 (solid line) shows the dependence of catalytic activity of colloidal nickel boride upon the molar ratio of $NaBH_4$ to $NiCl_2 \cdot 6H_2O$ (B/Ni). When less than equimolar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$ (B/Ni$<$1) was used, only unstable colloids were obtained. Thus, colloidal nickel boride, once formed on addition of $NaBH_4$, was gradually inactivated under hydrogen with fading of coloration during 15 min stirring. The catalytic activity of colloid increases remarkably with increase in the amount of $NaBH_4$ in the range of B/Ni ratio between 1 and 2, the dark brown coloration of the original solution remaining unchanged. By using not less than double molar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$ (B/Ni$\geqq$2), a colloid with an almost constant activity was obtained.

Reduction of $NiCl_2 \cdot 6H_2O$ with $NaBH_4$ in ethanol in the absence of a polymer gave a suspension containing visible particles of precipitated nickel boride. Suspen-

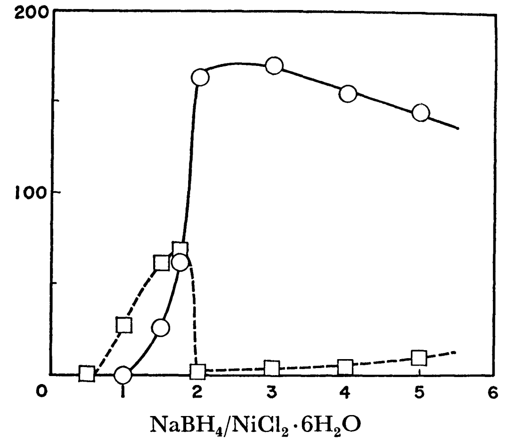

Fig. 3. Dependence upon $NaBH_4/NiCl_2\cdot 6H_2O$ ratio of the catalytic activity of colloidal (○) and precipitated (□) nickel borides.

sions prepared with varying amounts of $NaBH_4$ were examined for their catalytic activity. The dependence of the catalytic activity of precipitated nickel boride upon B/Ni ratio (Fig. 3, broken line), is compared with that of colloidal nickel boride. Maximal activity is obtained with B/Ni ratio in the region 1.5—1.7, in which fine particles of nickel boride appear. On the other hand, the use of not less than double molar $NaBH_4$ with $NiCl_2\cdot 6H_2O$ ($B/Ni \geqq 2$) gives only a coagulated mass with a much lower activity. In this range of B/Ni ratio, colloidal nickel boride showed 15—60 times the catalytic activity of the precipitate.

*Effect of the Amount of PVP-K*30. The reduction of $NiCl_2\cdot 6H_2O$ with $NaBH_4$ was carried out in ethanol in the presence of varying amounts of PVP-K30. As shown in Fig. 4, the presence of more than 0.5 mg (25 ppm) of PVP-K30 is important for obtaining colloidal nickel boride, otherwise a precipitate of nickel boride with a low activity is formed. The catalytic activity of colloidal nickel boride is nearly constant in the range of amount of PVP-K30 2—80 mg.

Decomposition by Oxygen. On exposure to the air, a dark brown solution of colloidal nickel boride was immediately converted into a light yellow inactive solution. In contrast, the colloid was stable under hydrogen and could be stored for 110 h with no change in coloration. The stored colloid exhibited 1.29 times the catalytic activity of the initial. Colloidal nickel boride was obtained under oxygen-free argon as well. Hydrogen was evolved by the hydrolysis of $NaBH_4$. So long as more than 4 vol% of evolved hydrogen was present in the atmosphere, the colloid was stable for a long period, exhibiting a considerable activity (r_i(acam) = 150 H_2 mmol/Ni_2B mol s). Under argon containing less than 0.1 vol% of hydrogen, the colloidal nickel boride catalyst was completely inactivated within 1 h.

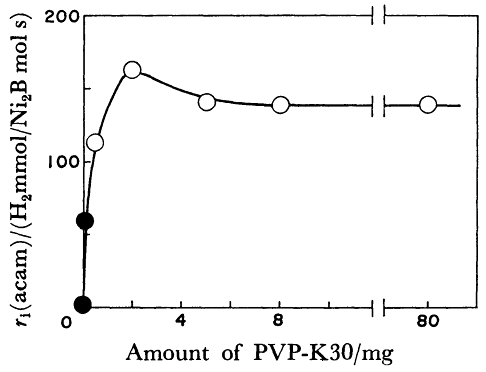

Fig. 4. Dependence upon the amount of PVP-K30 of the catalytic activity of nickel boride (○, colloidal; ●, precipitated).

Colloidal nickel borides prepared under hydrogen with 2 mg and 80 mg of PVP-K30 were exposed to the air at room temperature (20 °C). Decomposition of the colloids was followed by decrease in optical density at 750 nm of the colloidal solutions. The colloid with 80 mg of PVP-K30 always decomposed at a faster rate than that with 2 mg of PVP-K30.

Hydrogenation of acrylamide catalyzed by colloidal nickel borides with 2 mg and 80 mg of PVP-K30 was carried out in the presence of varying amounts of additional oxygen. The colloidal catalyst with 80 mg of PVP-K30 was inhibited more strongly than that with 2 mg of PVP-K30, the former being more sensitive to oxygen than the latter.

Discussion

The following stoichiometry was proposed for the progress of reduction of nickel(II) chloride with $NaBH_4$ in aqueous solution.[11]

$$NiCl_2 + 2NaBH_4 + 4.5H_2O \longrightarrow 0.5Ni_2B + 1.5H_3BO_3 + 6.25H_2 + 2NaCl \qquad (1)$$

A similar process performed in ethanol under nitrogen gave a nickel boride precipitate having the formula $(Ni_2B)_2\cdot H_3$.[12] It seems that colloidal nickel borides prepared in ethanol under hydrogen in the presence of a polymer contains a common structural unit Ni_2B. In the present case, the molar ratio of evolved hydrogen to $NiCl_2\cdot 6H_2O$ charged was calculated to be 5.2, being smaller than that expected from Eq. 1. This gap between observed and theoretical amounts of evolved hydrogen is caused by the adsorption of hydrogen on the surface of colloidal nickel boride. Colloidal nickel borides were stable only in an oxygen-free atmosphere containing hydrogen. This indicates that the adsorption of hydrogen on the colloid surface might take part in the stability of the colloid. A black colloid prepared from nickel(II) nitrate was almost inactive (Table 1). On the other hand, colloidal nickel boride from $NiCl_2\cdot 6H_2O$ was gradually inactivated when an alternative nitrate salt such as ammonium nitrate was added. In both cases, the inactivation process might be attributed to the loss of adsorbed hydrogen by oxidation with nitrate ion.

A reaction scheme involving $Ni(BH_4)_2$ intermediate was proposed for the process of nickel boride formation in aqueous solution.[11] During the induction period preceeding the formation of colloidal nickel boride, the conversion of $NiCl_2\cdot 6H_2O$ into $Ni(BH_4)_2$ might occur.

In aqueous solution, nickel(II) hydroxide may be formed in preference to nickel boride on account of the considerable basicity of the $NaBH_4$ solution. White turbidity appearing in the process using aqueous media (Table 1) might be due to polymeric nickel(II) hydroxide. However, nickel boride was predominantly produced in aqueous media when the reaction was carried out at low temperature (0 °C)[11] or in the presence of a large amount of polymers such as poly(vinyl alcohol)[5] owing to suppression of the formation of polymeric nickel(II) hydroxide.

The particle size of a colloidal catalyst is essential for the estimation of its turnover frequency. However, colloidal nickel boride was so unstable in a high vacuum as well as under hydrogen-free argon that the particle size of the colloid could not be determined by electron microscopy.

A precipitated nickel boride catalyst prepared without using polymers ($B/Ni=1.5$) was *ca.* 50% inhibited by the addition of 80 mg of PVP-K30. It seems that PVP-K30 acts as an inhibitor through locating on the catalytic surface of precipitated nickel boride. Polymers such as PVP-K30 existing in the solution of colloidal nickel boride are assumed to act as a protective colloid through covering the surface of colloidal particles.[13] Polymers existing in the solution of colloidal nickel boride are presumed to lower the catalytic activity to some extent. The widely varied activities of colloids prepared with a variety of polymers (Table 2) can be explained in terms of inhibition by polymers.

The degree of inhibition of a precipitated nickel boride catalyst increased with increase in the amount of PVP-K30. In contrary, the catalytic activity of colloidal nickel boride was independent of the amount of PVP-K30 (Fig. 4). A similar relationship was observed in the case of colloidal rhodium prepared by using poly(vinyl alcohol).[14] The discrepancy might be attributed to the variation of the size of colloidal particles with the amount of the polymer used.

The well-dispersed state of colloidal nickel boride due to the presence of PVP-K30 as a protective colloid is primarily responsible for its high activity. On the other hand, precipitated nickel boride formed with more than double molar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$ gradually coagulated into a black mass with a very low activity. Well-dispersed suspension of precipitated nickel boride ($B/Ni=1.5$) coagulated on further addition of $NaBH_4$. Nickel borides were found to be very active catalysts for the hydrolysis of $NaBH_4$.[2]

$$NaBH_4 + 2H_2O \xrightarrow{Ni_2B} NaBO_2 + 4H_2 \qquad (2)$$

It seems that excess or additional $NaBH_4$ is hydrolyzed to yield $NaBO_2$ which causes the coagulation of nickel boride precipitates.

Colloidal nickel borides prepared by using less than double molar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$ exhibited a considerable activity when used immediately after preparation. Thus, acrylamide was hydrogenated at an initial rate of 46 H_2 mmol/Ni_2B mol s with the colloid which had been prepared 1 min before its use by using equimolar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$. However, the colloid once formed was completely inactivated in 15 min with stirring under hydrogen (Fig. 3). The inactivation mechanism of the colloid under hydrogen has not been clarified.

References

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

2) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953).

3) R. C. Wade, D. G. Holah, A. N. Hughes, and B. C. Hui, *Cat. Rev.*, **14**, 211 (1976), and the references cited therein.

4) For example, R. Zsigmondy, *Z. Anal. Chem.*, **40**, 697 (1901); C. Paal and C. Amberger, *Ber.*, **37**, 124 (1904); A. Skita, *Ber.*, **42**, 1627 (1909); W. P. Dunworth and F. F. Nord, *Adv. Cat.*, **6**, 125 (1954).

5) K. N. Machalov, A. T. Groisberg, and N. A. Palikhov, *Tr. Kazan. Khim.—Tekhnol. Inst.*, **1969**, 150; through *Chem. Abstr.*, **75**, 40844h (1971).

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

7) Y. Nakao and S. Fujishige, *Chem. Lett.*, **1979**, 995.

8) Acrylamide was used as a substrate, since it is very soluble in both alcohols and water.

9) Since the stoichiometry of colloidal nickel boride is as yet unknown, a common unit of Ni_2B reported for precipitated nickel boride was applied for convenience to the molecular formula of colloidal nickel boride.

10) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York (1967), p. 1050.

11) N. N. Mal'tseva, Z. K. Sterlyadkina, and V. I. Mikheeva, *Zh. Neorg. Khim.*, **11**, 720 (1966); through *Chem. Abstr.*, **65**, 1751f (1966).

12) P. C. Maybury, R. W. Mitchell, and M. F. Hauthorne, *J. Chem. Soc., Chem. Commun.*, **1974**, 534.

13) Y. Glazman and Z. Blashchuk, *J. Colloid Interface Sci.*, **62**, 158 (1977).

14) H. Hirai, Y. Nakao, and N. Toshima, *J. Macromol. Sci., Chem.*, **A12**, 1117 (1978).