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Colloidal Nickel Boride Catalyst for Hydrogenation of Olefins

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Colloidal nickel boride was prepared from nickel(II) chloride by reduction with sodium borohydride in the presence of polyvinylpyrrolidone in ethanol. Hydrogenation of various olefins was examined over the colloidal catalyst at 30°C and atmospheric pressure. The colloidal nickel boride was much more effective than the precipitated nickel boride prepared in the absence of polyvinylpyrrolidone as a hydrogenation catalyst, especially for isopropenyl compounds. Additional amines and sodium acetate were slightly inhibitive to the colloidal catalyst, while, being strongly promotive to the precipitated catalyst. The colloidal nickel boride was superior to the charcoal-supported metals of the platinum group in catalytic activity for α-methylstyrene.

INTRODUCTION

Colloidal metallic catalysts of the platinum group are prepared by the reduction of the corresponding metal salts in aqueous media in the presence of natural or synthetic polymer as a protective colloid, being employed in the hydrogenation of various unsaturated compounds (see, for example, (*1*)). The reduction of the metal salts of the platinum group with methanol gives very fine colloidal metals, among which colloidal rhodium is the most effective catalyst for hydrogenation of olefins (*2*). In the reaction with borohydride salts, metal ions of the platinum group are reduced to the metallic state as well (*3*), while nickel(II) and cobalt(II) ions are converted to the metal borides, exhibiting a catalytic activity for both hydrolysis of borohydride ion and hydrogenation of olefins (*4*). Therefore, the reduction of the metal ions of group VIII with potassium borohydride in aqueous media in the presence of a polymer such as acid gelatin gives colloidal metals of the platinum group or colloidal metal borides of nickel and cobalt (*5*). It has been previously reported (*6*) that colloidal nickel borides dispersed in ethanol are prepared by the reduction of nickel(II) salts with sodium borohydride ($NaBH_4$) under hydrogen in the presence of a polymer such as polyvinylpyrrolidone, exhibiting a high activity for catalytic hydrogenation of acrylamide.

In the present paper, the application of the colloidal nickel boride prepared from nickel(II) chloride ($NiCl_2 \cdot 6H_2O$) to a catalyst for hydrogenation of various olefins will be described.

EXPERIMENTAL

Materials. Reagent-grade $NiCl_2 \cdot 6H_2O$, $NaBH_4$, and polyvinylpyrrolidone (PVP-K30, degree of polymerization 360) were used without further purification.

Reagent-grade olefins to be subjected to hydrogenation were purified by distillation under argon or recrystallization. Hydrogen was of 99.999% purity. Reagent-grade ethanol for reaction medium was degassed by refluxing under argon. Reagent-grade amines were distilled under argon before use.

Catalyst preparation. Catalysts were prepared in a 50-ml round-bottomed flask connected to a gas burette, in which the atmosphere was previously replaced with hydrogen. In the flask, $NiCl_2 \cdot 6H_2O$ (20 μmol) and PVP-K30 (2.0 mg) were dissolved in ethanol (18.5 ml). An ethanol solution (1.5 ml) of $NaBH_4$ (60 μmol)

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freshly prepared and stored under argon at 0°C was added to the solution which was stirred by a magnetic stirrer (2-cm Teflon-coated rod rotating at 900–1000 rpm) at 30.0°C and atmospheric pressure. The colloid formation was followed by hydrogen evolution which ceased within 15 min. A dark-brown-colored clear solution (20 ml) of colloidal nickel boride (CNB) thus obtained was ready for the hydrogenation reaction.

A well-dispersed suspension (20 ml) of precipitated nickel boride (PNB) was prepared by the addition of an ethanol solution (0.75 ml) of $NaBH_4$ (30 μmol) to an ethanol solution (19.25 ml) of $NiCl_2 \cdot 6H_2O$ (20 μmol) in the absence of PVP-K30 under similar conditions to the CNB preparation.

As previously reported (6), the catalytic activity of PNB is largely affected by the molar ratio of $NaBH_4$ to $NiCl_2 \cdot 6H_2O$ (B/Ni). Thus, maximal activity is obtained with a B/Ni ratio of about 1.5. The use of three times molar $NaBH_4$ with $NiCl_2 \cdot 6H_2O$, however, gives only a coagulated mass with a much lower activity. On the other hand, maximal activity of CNB is obtained with a B/Ni ratio of 3.

Hydrogenation procedure. After completion of hydrogen evolution followed by the formation of CNB, hydrogenation reaction was initiated by injecting the substrate (250 μmol) to the CNB solution with a microsyringe under the same conditions as catalyst preparation. Solid substrates were dissolved in ethanol (1 ml) under argon before injection. The progress of hydrogenation was followed by measuring the volume of hydrogen uptake. The initial rate per unit nickel was determined from the time course of hydrogen uptake, giving a measure of the catalytic activity of CNB and PNB. In certain cases in which the hydrogenation rate was too high, 1, 2, or 10 ml of CNB solution was used after being diluted to 20 ml with ethanol under hydrogen in order to keep the rate of hydrogen uptake below 200 ml/hr. Hydrogenation over PNB was carried out in a similar manner.

RESULTS AND DISCUSSION

Hydrogenation of Cycloheptene over CNB and PNB

Ten preparations of CNB and PNB were performed in the presence and in the absence of PVP-K30, respectively. The ethanol solutions of $NaBH_4$ used were freshly prepared for each preparation. The hydrogenation rates of cycloheptene over CNB and PNB thus prepared are summarized in Table 1. CNB is superior to PNB not only in catalytic activity but also in reliability.

Comparison of CNB with PNB in Hydrogenation of Alkenes

In Table 2 are compared the hydrogenation of various linear and cyclic alkenes over CNB and PNB catalysts. The hydrogenation rates over CNB are higher than those over PNB by a factor of 16–420. The CNB solution with complete transparency is assumed to contain very fine particles, although the diameter of the particles has not been determined by direct measurement such as electron microscopy because

TABLE 1

Catalytic Hydrogenation of Cycloheptene over Colloidal and Precipitated Nickel Borides

No.	Initial rate (mmol/sec · g-atom Ni)	
	CNB[a]	PNB[b]
1	198	4.9
2	184	4.6
3	185	3.8
4	183	4.9
5	192	3.6
6	194	3.7
7	194	4.5
8	190	4.2
9	188	5.0
10	203	3.9
Average	191	4.3
Standard deviation	±6	±0.5

[a] Colloidal nickel boride (Ni = 10 μg-atom).
[b] Precipitated nickel boride (Ni= 20 μg-atom).

TABLE 2

Catalytic Hydrogenation of Alkenes over Colloidal and Precipitated Nickel Borides

Substrate	Initial rate (mmol/sec · g-atom Ni)		CNB/PNB ratio of initial rate
	CNB[a]	PNB[b]	
1-Hexene	680 (2)	10	68
cis-2-Hexene	24 (20)	0.2	120
trans-2-Hexene	34 (20)	0.2	170
Cyclopentene	230 (2)	7.9	29
Cyclohexene	21 (20)	0.05	420
Cycloheptene	191 (10)	4.3	44
Cyclooctene	33 (20)	2.1	16

[a] Coilloidal nickel boride, the amounts of nickel (μg-atom) in parentheses.

[b] Precipitated nickel boride (Ni = 20 μg-atom).

of the very labile nature of CNB in hydrogen-free atmosphere (*6*). The very large area of the CNB surface might be responsible for its much higher activity. 2-Hexenes are hydrogenated over both catalysts at a much lower rate than 1-hexene. This indicates that the hydrogenation rate of linear alkenes is strongly dependent upon steric hindrance by the *vic*-disubstituents around the C=C bond. The order of hydrogenation rate of cyclic alkenes is rather complicated. Over PNB, cyclohexene is hydrogenated at a much lower rate in agreement with the case over P-2 nickel boride (*7*), while it is hydrogenated over CNB at a moderate rate. In other words, the CNB/PNB ratio of initial rate is much greater for cyclohexene. The hydrogenation rates of other cycloalkenes over CNB and PNB decrease with increasing the number of carbon. This is in accord with the results reported on a silica-supported platinum catalyst (*8*).

Comparison in Hydrogenation of Vinyl and Isopropenyl Compounds

The hydrogenation of five couples of vinyl and isopropenyl compounds was carried out over CNB and PNB catalysts. The initial rates are compared in Table 3. Over PNB, similar to the case of linear alkenes, the hydrogenation rates of isopropenyl compounds are much lower than those of vinyl compounds. On the other hand, the rate of hydrogenation over CNB is less affected by the structure of the substrate, especially for couples of styrene–α-methylstyrene, methyl acrylate–methyl methacrylate, and acrylamide–methacrylamide. In other words, CNB is much more effective than PNB for hydrogenation of isopropenyl compounds. It has been reported (*9*) that in hydrogenation of isopropenyl compounds such as methyl methacrylate, the C=C bonds are not hindered on the catalytic surface of very fine colloidal rhodium (8.8 Å diameter) but are hindered when the particle is considerably larger (34.3 Å diameter). In the present case of CNB as well, the C=C bonds of the isopropenyl compounds are assumed to be less sterically hindered on the surface of the very small particles of CNB. A similar insensibility of the reaction rate to the substituent bulkiness has been reported (*10*) on hydrogenation of a series of ketones catalyzed by sodium hydroxide-activated CNB.

TABLE 3

Catalytic Hydrogenation of Vinyl and Isopropenyl Compounds over Colloidal and Precipitated Nickel Borides

Substrate	Initial rate (mmol/sec · g-atom Ni)		CNB/PNB ratio of initial rate
	CNB[a]	PNB[b]	
1-Hexene	680 (2)	10	68
2-Methyl-1-hexene	25 (20)	<0.05	>500
Styrene	1600 (1)	16	100
α-Methylstyrene	940 (2)	0.1	9400
Allyl alcohol	2070 (1)	94	22
Methallyl alcohol	370 (2)	4.0	93
Methyl acrylate	720 (2)	18	40
Methyl methacrylate	500 (2)	0.2	2500
Acrylamide	156 (10)	47	3.3
Methacrylamide	112 (10)	8.7	13

[a] Colloidal nickel boride, the amounts of nickel (μg-atom) in parentheses.

[b] Precipitated nickel boride (Ni = 20 μg-atom).

TABLE 4

Effects of Additive on the Catalytic Activity of Colloidal and Precipitated Nickel Borides for Hydrogenation of Cycloheptene

Additive[a]	Initial rate (mmol/sec · g-atom Ni)	
	CNB[b]	PNB[c]
None	191	4.3
Sodium hydroxide	174	3.7
Hydrochloric acid[d]	<0.1	0.6
n-Butylamine	10.5	0.3
Diisopropylamine	178	45
Triethylamine	183	34
Sodium acetate (anhydrous)	141	19

[a] The amounts of additive are 100 and 200 μmol for CNB and PNB, respectively.

[b] Colloidal nickel boride (Ni = 10 μg-atom).

[c] Precipitated nickel boride (Ni = 20 μg-atom).

[d] The amount of added HCl is 20 μmol for both CNB and PNB.

Effects of Additive

The effects of additive on the rate of hydrogenation over CNB and PNB catalysts were investigated. The results are shown in Table 4. The hydrogenation rates of cycloheptene over either catalyst are lowered by the addition of sodium hydroxide to some extent. On the contrary, the addition of sodium hydroxide to CNB enhances its catalytic activity for hydrogenation of acetone by more than 20-fold (*10*). The activity of CNB is strictly inhibited by hydrochloric acid. The resulting CNB was reversibly reactivated by the addition of sodium hydroxide. This indicates that the catalytic activity of CNB is affected by the pH of the solution. *n*-Butylamine is also inhibitory to both nickel boride catalysts. This is presumably because the amine is strongly adsorbed on the catalytic surface. On the other hand, both diisopropylamine and triethylamine are slightly inhibitory to CNB catalyst, while these enhance the catalytic activity of PNB by 8 to 10-fold. Sodium acetate has similar effects on the catalytic activities of CNB and PNB. The enhancement of the catalytic activity of PNB by the addition of these compounds might be attributed to their buffering capacity. The difference between CNB and PNB catalysts in the effects of additive suggests that the structures of the active species of the catalysts may be different from each other.

Comparison of CNB with Conventional Catalysts

Hydrogenation of 1-hexene and α-methylstyrene was performed in ethanol over a series of nickel borides and charcoal-supported metals of the platinum group, as compared in Table 5. For both substrates, the order of the activity of nickel borides was CNB > P-2 nickel boride > PBN. Superiority of P-2 nickel boride to PNB in catalytic activity can be explained by the term of the effect of acetate ion (Table 4). CNB is superior to the platinum group metals in catalytic activity for α-methylstyrene rather than for 1-hexene. The hydrogenation of α-methylstyrene to cumene is

TABLE 5

Catalytic Hydrogenation of 1-Hexene and α-Methylstyrene

Catalyst	Initial rate[a] (mmol/sec · g-atom Ni)	
	1-Hexene	α-Methylstyrene
CNB[b]	680 (2)	940 (2)
PNB[c]	10 (20)	0.1 (20)
P-2 nickel boride[d]	49 (20)	55 (20)
Pd/C(5%)[e]	230 (2)	700 (2)
Rh/C(5%)[e]	2120 (1)	270 (2)

[a] The amount of nickel (μg-atom) is designated in parentheses.

[b] Colloidal nickel boride.

[c] Precipitated nickel boride prepared from $NiCl_2 \cdot 6H_2O$.

[d] Precipitated nickel boride prepared from $Ni(OAc)_2 \cdot 4H_2O$ in 95% ethanol (*7*).

[e] Commercial 5% palladium or rhodium catalyst supported on active charcoal.

important especially for industrial phenol production.

Hydrogen Diffusion in the Hydrogenation

The possibility of hydrogen diffusion control in the hydrogenation was examined. The limiting rate of hydrogen dissolution into ethanol was estimated to be more than 370 ml/hr from the rate of hydrogen uptake in hydrogenation of 1-hexene by using a large amount (Ni = 10 μg-atom) of CNB. Each hydrogenation listed in Tables 1–5 was performed at a rate of hydrogen uptake below 200 ml/hr. The hydrogenations of allyl alcohol both over CNB and over PNB, which proceeded at a rate nearest to 200 ml/hr, were not affected by stirring efficiency, that is, the revolution rate of a magnetic stirrer in the range of 900–2200 rpm. These facts exclude the possibility that hydrogen diffusion limits the rate of hydrogenation.

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