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COLLOIDAL NICKEL BORIDE WITHOUT PROTECTIVE AGENT AND ITS CATALYTIC ACTIVITY FOR OLEFIN HYDROGENATION

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A stable dispersion of colloidal nickel boride was prepared from a dilute solution of nickel(II) chloride in ethanol by sodium borohydride reduction in the absence of protective colloid polymers. The colloid is superior to the conventional poly(vinylpyrrolidone)-protected one in the catalytic activity for the hydrogenation of styrenes and unsaturated carbonyl compounds.

Reduction of nickel(II) salt with sodium borohydride ($NaBH_4$) in aqueous or alcoholic solution gives a black precipitate of nickel boride which exhibits catalytic activity for hydrogenation.[1)] Recently,[2,3)] colloidal nickel boride has been prepared in the presence of poly(vinylpyrrolidone) (PVP) as a protective colloid, being found to be much more effective than precipitated one as a catalyst for olefin hydrogenation. We have found that $NaBH_4$-reduction of a very dilute solution of nickel(II) chloride ($NiCl_2.6H_2O$) in ethanol gives a stable dispersion of colloidal nickel boride even in the absence of protective colloid polymers. This report describes the preparation of the colloidal dispersion without using polymers and the characteristics of the colloidal nickel boride as a catalyst for olefin hydrogenation.

The dispersion of colloidal nickel boride without using polymers (nCNB = naked colloidal nickel boride) was prepared to be used as a catalyst for olefin hydrogenation at 30.0°C under 1 atm hydrogen in the following procedure. To an almost colorless ethanolic solution (19.85 ml) of $NiCl_2.6H_2O$ (2 μmol), an ethanolic solution (0.15 ml) of $NaBH_4$ (6 μmol) was added dropwise with stirring, resulting a black-colored clear solution (20 ml) of CNB. In a similar condition, however, the use of more than 6 μmol of $NiCl_2.6H_2O$ with three times $NaBH_4$ by molarity caused partial or entire precipitation of nickel boride. After stirring the nCNB solution for 15 min, liquid olefin (0.25 ml) was added to the solution with a micro-syringe, at that time hydrogen uptake started. For very smooth hydrogenation such as styrene, a nCNB solution (20 ml) prepared from $NiCl_2.6H_2O$ (1 μmol) and $NaBH_4$ (3 μmol) was used. Colloidal nickel boride protected by PVP (CNB-PVP) was prepared, for comparison, from $NiCl_2.6H_2O$ (20 μmol) and PVP (Degree of polymerization 360, 2 mg) in ethanol (20 ml) by reduction with $NaBH_4$ (60 μmol) and was used as a hydrogenation catalyst after diluting 1 or 2 ml of the CNB-PVP solution to 20 ml with ethanol.[3)] Ethanol for the preparation of both nCNB and CNB-PVP was previously deaerated by refluxing under argon before use.

Table 1. Hydrogenation of olefins catalyzed by colloidal nickel borides

Substrate	r_i[a] (mmol/s.g-atom Ni)	
	nCNB[b]	CNB-PVP[c]
1-Hexene	417	680
Cyclohexene	9	21
Cycloheptene	90	191
Styrene	2100[d]	1600[d]
α-Methylstyrene	1390	940
Methyl acrylate	1170	720
Diethyl maleate	1050	850
Diethyl fumarate	700	580

a) Initial rate of hydrogenation (Ni=2μg-atom). b) Colloidal nickel boride without protective colloid polymers. c) Colloidal nickel boride protected by PVP.[3] d) Ni=1μg-atom.

Table 1 shows the initial rates of hydrogenation of olefins catalyzed by nCNB, compared with those by CNB-PVP. All the hydrogenation reaction listed in the Table proceeded in a homogeneous liquid phase without precipitation. The rates by nCNB for 1-hexene and cyclic alkenes are lower than those by CNB-PVP. On the other hand, nCNB exhibited higher activity than CNB-PVP for the hydrogenation of styrenes and other olefins having carbonyl-conjugated C=C bonds. After the completion of the hydrogenation, nCNB could be precipitated by the addition of a small amount (below 0.5 μmol per 2 μg-atom Ni) of ethanol-soluble calcium(II) salt such as $CaCl_2$ to be separated from the solution of the product. On the contrary, CNB-PVP was not precipitated even in the presence of 1 mmol of $CaCl_2$ per 2 μg-atom Ni owing to the protective effect of PVP. The $CaCl_2$-deposited precipitate from nCNB exhibits more than 60% activity of the original authentic nCNB for the hydrogenation of methyl acrylate.

On exposing to air, nCNB loses its catalytic activity, while the solution color of nCNB remained black, being distinct from the CNB-PVP solution which was readily decolorized to air.[2]

References

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