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A HIGHLY ACTIVE SUPPORTED CATALYST FOR OLEFIN HYDROGENATION FROM COLLOIDAL NICKEL BORIDE

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Supported catalysts, which were prepared from colloidal nickel boride by immobilizing on inorganic substances such as $Mg(OH)_2$, exhibited higher activity for olefin hydrogenation than a sol-type catalyst of colloidal nickel boride protected by polyvinylpyrrolidone.

It has been reported[1] that a sol of polyvinylpyrrolidone-protected colloidal nickel boride (CNB-PVP) prepared from nickel(II) chloride ($NiCl_2 \cdot 6H_2O$) by reduction with sodium borohydride ($NaBH_4$) in ethanol exhibited more than ten times the catalytic activity of precipitated nickel boride prepared without using polymers for olefin hydrogenation. The sol-type catalyst, however, possesses a disadvantage in the difficulty encountered in separating it from the reaction mixture. We now report the preparation of supported nickel boride catalysts by immobolizing colloidal nickel boride on inorganic substances and their catalytic activity for the hydrogenation of various olefins.

Typical procedures for catalyst preparation and olefin hydrogenation are as follows. Reagent grade $Mg(OH)_2$ powder (10 mg) was charged in a 50 ml round-bottomed flask. After replacing the atmosphere of the flask with hydrogen, an ethanol solution (19.85 ml) of $NiCl_2 \cdot 6H_2O$ (2 μmol) was poured into the flask and stirred for 10 min with $Mg(OH)_2$ at 30°C and 1 atm. An ethanol solution (0.15 ml) of $NaBH_4$ (6 μmol) was added to the white suspension with stirring. At that time, the color of the suspension immediately turned to gray. The resulting suspension consisted of a gray-colored powder which was an active supported catalyst of colloidal nickel boride (CNB/$Mg(OH)_2$). After further stirring for 15 min, liquid olefin (0.25 mmol) was added with a micro-syringe, and then hydrogenation reaction started. The reaction was followed by hydrogen uptake which gave the rate of hydrogenation. The initial rate per unit nickel was used as a measure of catalytic activity.

In the usual procedures for the preparation of supported metal catalysts, metal ions are first attached on the surface of supports and then reduced to metallic state. In the case of CNB/$Mg(OH)_2$, however, nickel(II) ion was not adsorbed on the surface of $Mg(OH)_2$ but left in a solution phase. This suggests that colloidal nickel boride particles once formed in a solution phase are immobilized on the surface of $Mg(OH)_2$ to give a supported catalyst. Actually addition of $Mg(OH)_2$ to a nickel boride sol prepared without using protective colloid[2] also resulted in the formation of gray-colored suspension which exhibited a somewhat

Table 1. Hydrogenation of olefins catalyzed by supported and sol-type catalysts of colloidal nickel boride

No.	Olefin	r_i[a] (mol/sec·g-atom Ni)		
		$CNB/Mg(OH)_2$[b]	$CNB/CaCO_3$[c]	CNB-PVP[d]
1	1-Hexene	1.21	0.81	0.68
2	Cycloheptene	0.38	0.18	0.19
3	Styrene	3.09	2.73	1.60
4	α-Methylstyrene	2.23	1.90	0.94
5	1,1-Diphenylethylene	1.03	0.34	0.34
6	n-Butyl vinyl ether	0.41	0.24	0.19
7	Methyl acrylate	0.99	1.44	0.72
8	Methyl vinyl ketone	0.05	0.09	0.03
9	Acrylamide	0.23	0.39	0.16

a) Initial rate of hydrogenation. b) $Mg(OH)_2$-supported catalyst of colloidal nickel boride. c) $CaCO_3$-supported catalyst of colloidal nickel boride. d) Sol-type catalyst of polyvinylpyrrolidone-protected colloidal nickel boride.[1]

low catalytic activity for olefin hydrogenation.

Other reagent grade powders of ethanol-insoluble compounds such as MgO, MgF_2, $CaCO_3$, CaF_2, TiO_2, $Al(OH)_3$ and ZrO_2 were also available for the support of colloidal nickel boride, giving highly active catalysts. In Table 1 is given the catalytic activity of the representative ones, $CNB/Mg(OH)_2$ and $CNB/CaCO_3$, for olefin hydrogenation. Both supported catalysts are more effective than the sol-type catalyst, CNB-PVP, for almost all the olefins listed in Table 1. In the case of CNB-PVP, polyvinylpyrrolidone molecules located on the surface of colloidal nickel boride particles might exert inhibiting effects. For the olefins listed in Table 1 (No. 1-6), $CNB/Mg(OH)_2$ is more active than $CNB/CaCO_3$. The difference in activity between the two supported catalysts is particularly large for 1,1-diphenylethylene. On the contrary, $CNB/CaCO_3$ is more active than $CNB/Mg(OH)_2$ for the rest of the olefins, which contain carbonyl-conjugating C=C bond.

References

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