Colloidal nickel boride on rare earth oxides for hydrogenation of olefins

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An extremely active and colloidal nickel boride was prepared by using rare earth oxide as a support in the presence of polyethylene glycol (PEG) at room temperature which could act as a catalyst in the hydrogenation of olefinic compounds, such as 4-(4′-hydroxyphenyl)-3-buten-2-one.

Keywords: colloidal nickel boride; rare earth oxides; polyethylene glycol; hydrogenation of olefins

1. Introduction

Nickel boride, precipitated from the reaction of nickel salt with sodium borohydride in an ethanolic solution, is an active and selective catalyst for the hydrogenation of olefins [1,2] and the α,β-olefinic double bond in unsaturated aldehydes [3,4]. Polymer-protected colloidal nickel boride [5] and magnesium hydroxide supported nickel boride [6] would be improved catalysts for hydrogenation in microscale. Although the colloidal nickel borides are active in the hydrogenation of olefinic compounds, however, they are rather tedious and troublesome in the experimental operations. The rare earth oxides have been reported to be active catalysts in the hydrogenation of 1,3-butadiene at relatively high temperature [7,8]. Thus, for the first time, the preparation of supported colloidal nickel borides was done from nickel chloride and sodium borohydride on rare earth oxides in the presence of polyethylene glycol at room temperature (25°C) and atmospheric pressure. Such catalyst would facilitate the hydrogenation of olefinic compounds to take place extremely rapid within a very short period and would be filtered off conveniently and completely after the reaction (table 1).

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Table 1
Hydrogenation of olefinic compounds catalyzed by supported colloidal nickel boride [a]

No.	Catalyst [b]	Olefinic compound	Initial rate (H_2ml/min g-atomNi)	Conversion time (min)	Yield [d] (%)
1	Ni_2B	$C_6H_5CH=CH_2$	152	36	99
2	Ni_2B/Nd_2O_3	$C_6H_5CH=CH_2$	196	35	98
3	Ni_2B/PEG	$C_6H_5CH=CH_2$	340	20	99
4	Ni_2B/Nd_2O_3-PEG	$C_6H_5CH=CH_2$	537	8	99
5	Ni_2B/La_2O_3-PEG	$C_6H_5CH=CH_2$	472	16	98
6	Ni_2B/Er_2O_3-PEG	$C_6H_5CH=CH_2$	478	12	99
7	Ni_2B/Dy_2O_3-PEG	$C_6H_5CH=CH_2$	512	10	99
8	Ni_2B	$CH_2=CH\text{-}COOH$	145	32	99
9	Ni_2B/Nd_2O_3-PEG	$CH_2=CH\text{-}COOH$	290	14	99
10	Ni_2B	$CH_2=CH\text{-}CH_2OH$	138	36	98
11	Ni_2B/Nd_2O_3-PEG	$CH_2=CH_2\text{-}CH_2OH$	308	14	99
12	Ni_2B	*p*-$HOC_6H_4CH=CHCOCH_3$ [c]	60	170	96
13	Ni_2B/Nd_2O_3-PEG	*p*-$HOC_6H_4CH=CHCOCH_3$ [c]	290	16	99
14	Pd/C	*p*-$HOC_6H_4CH=CHCOCH_3$ [c]	90	160	96

[a] Hydrogenation of 40 mmol olefinic compound at 25°C, 1 atm H_2, 50 ml ethanol, over 5.0 mmol of nickel boride catalyst.

[b] Polyethylene glycol (PEG, MW = 400, 1.6 g, 40 mmol).

[c] Product is raspberry ketone 4-$HOC_6H_4CH_2CH_2COCH_3$.

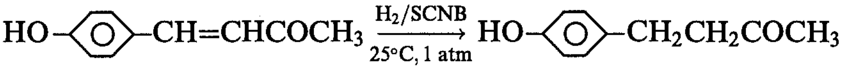
[d] Product isolated.

2. Results and discussion

Nickel boride is comparable to Raney nickel and Pd/C (table 1) in the catalytic activities for hydrogenation. It would likely improve the dispersion and increase the surface area of the catalyst prepared whether in the presence of polymers such as polyvinylpyrrolidone in ethanol or on support (e.g., Mg $(OH)_2$). It was proved that the catalytic activity of nickel borides was improved [5,6]. In the hydrogenation of styrene, polyethylene glycol was a protective polymer and increased the activity of colloidal nickel boride. The initial rate enhancement of nickel boride was about two-fold. The data in table 1 show that the rare earth oxides used as catalytic support are catalytic activators; the rate enhancement would be up to about 30%. However, the rate enhancement of nickel boride, whether in the presence of PEG or on the rare earth oxides, was not very obvious. If the supported colloidal nickel boride was prepared in the presence of polyethylene glycol and on rare earth oxide, the initial rate enhancement for such system would be tremendous (table 1).

The results in table 1 illustrate that neodymium oxide is the best catalytic support among these rare earth oxides being on colloid nickel boride and could be used in the hydrogenation of other olefinic compounds besides styrene.

What deserved to be mentioned was the supported colloidal nickel boride (Ni_2B/Nd_2O_3-PEG), which provides both high catalytic activity and selectivity in the hydrogenation of the α,β-olefinic double bond of unsaturated ketones such as 4-(4′-hydroxyphenyl)-3-buten-2-one ($4\text{-}HOC_6H_4CH{=}CHCOCH_3$) to give fragrant raspberry ketone ($4\text{-}HOC_6H_4CH_2CH_2COCH_3$) in high yield, e.g.,



The selectivity for saturated ketone was 99% on SCNB, which is comparable with that of nickel boride (99% selectivity) and Pd / C (99% selectivity).

3. Experimental

IR spectra were recorded on a Perkin-Elmer 684 spectrometer. NMR spectra were recorded on an IBOL FX-90Q spectrometer. Gas chromatography was performed on a Varian model 920 instrument using 10% Carbowax 20M on 60–80 Chromosorb W and HPLC using a Diacel Chiral column. Elemental analyses were done on a Carlo Erba-1106 instrument. All the reagents used were of the highest purity available. Prior to use, each compound was purified and analyzed by gas–liquid chromatography to check the purity, and kept in a closed vessel under N_2 atmosphere before use.

General procedure: preparation of supported colloidal nickel boride catalyst and hydrogenation of styrene. To a four-necked 100 ml round-bottomed flask equipped with an electromagnetic stirrer (2 cm Teflon-coated rod rotating at 900–1000 rpm) two 10 ml dropping funnels with pressure equalization and a gas duct, immersed in a constant temperature water bath of 25°C, were charged with nickel chloride ($NiCl_2{\cdot}6H_2O$, 5 mmol, 1.19 g) and polyethylene glycol (PEG, MW = 400, 4 mmol, 1.6 g) and 40 ml absolute ethanol. To the stirred clear solution, neodymium oxide (Nd_2O_3, 1.0 g) was added and the flask was connected to the hydrogenation apparatus which was similar to that mentioned in literature [1]. To the stirring reaction mixture, which was saturated with hydrogen, a solution of sodium borohydride ($NaBH_4$, 10 mmol, 0.38 g) in ethanol (10 ml) was dropwisely added over a period of 30 s; a black solution containing the supported colloidal particles of nickel boride (SCNB) resulted. A further stirring for 15 min completed the hydrolysis of $NaBH_4$ with the evolution of hydrogen. Then, styrene (40 mmol, 4.16 g) was added to this solution from another dropping funnel in a very short period. The hydrogenation was completed in 8 min, as equimolar amount of hydrogen with styrene had been taken up. The initial rate of hydrogen uptake was found from the curve to be 537 H_2ml/min g-atom Ni, giving a measure of the catalytic activity of supported colloidal nickel boride catalyst. After the catalyst was filtered off, the clear and colorless filtrate was distilled in vacuum to give the product (ethyl benzene, yield 90%). The product is characterized by GC, with *n*-hexadecane as the internal standard.

Synthesis of raspberry ketone using the supported colloidal nickel boride catalyst.

Hydrogenation of 4-(4′-hydroxyphenyl)-3-buten-2-one under the above conditions in the general procedure in 16 min gave the product raspberry ketone: yield 99%, selectivity 99%. MP 82–83°C. IR (film) ν 3385, 1690, 1610, 1590, 1510, 1435, 1225, 830 [1]. H NMR ($CDCl_3$) δ 2.15 (3H, s, CH_3), 2.80 (4H, t, $(CH_2)_2$), 5.35 (1H, s, OH), 6.9 (4H, m, C_6H_4). Anal. calculated for $C_{10}H_{12}O_2$: C, 73.15; H, 7.34; found: C, 73.32; H, 7.20.

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