An Excellent Nickel Boride Catalyst for the Selective Hydrogenation of Olefins

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Nickel boride prepared on borohydride exchange resin (BER) in methanol is an excellent catalyst for the selective hydrogenation of olefins. Thus, monosubstituted olefins and norbornene were hydrogenated quantitatively at 0 °C in 1 hour in the presence of disubstituted olefins and trisubstituted α,β-unsaturated acid derivatives, the disubstituted olefins in turn were hydrogenated at 65 °C in 1 hour without affecting trisubstituted olefins, benzene, and heteroaromatic compounds.

The selective hydrogenation of olefins is important in organic synthesis and is usually carried out by catalytic hydrogenation.[1] Among the catalysts reported, Brown's P-2 nickel[2] and Caubere's nickel complex reducing agent (NiCRA)[3] show very good selectivity in the hydrogenation of olefins. Some other systems, such as $NaBH_4$–$CoCl_2$,[4] FeCRA,[5] LiH–VCl_3,[6] and $LaNi_5H_6$,[7] have also been reported to be selective hydrogenation systems.

Recently, we have studied the reducing properties of borohydride exchange resin–nickel boride (BER–Ni_2B) in methanol, and have reported that this system is excellent for the selective reductions of aliphatic and aromatic halides,[8] nitro compounds,[9] and azides.[10] In the course of these studies, Ni_2B prepared on BER in methanol was found to be an excellent catalyst for the selective hydrogenation of olefins. We report here this application of BER–Ni_2B in methanol.

We have now studied the hydrogenation of various representative olefins, using the BER–Ni_2B in methanol and could classify these olefins into three groups. BER–Ni_2B in methanol does not require an external hydrogen supply since BER evolves hydrogen in methanol in the presence of Ni_2B. Monosubstituted olefins and norbornene (GROUP A) were hydrogenated quantitatively in methanol at 0 °C in 1 hour. However, 1,1-disubstituted olefins, 1,2-disubstituted olefins, and trisubstituted α,β-unsaturated acid derivatives (GROUP B) were not hydrogenated at 0 °C even after 6 hours, but were easily hydrogenated at 65 °C in 1 hour. Trisubstituted olefins, benzene, and heteroaromatic compounds (GROUP C) were not hydrogenated even after 6 hours at 65 °C. The classification is summarized in Table 1.

Next, we examined selective hydrogenation of several representative dienes and the competitive hydrogenation of various olefin mixtures to confirm the selectivity of this system. As shown in Table 2, monosubstituted olefins were selectively hydrogenated in the presence of disubstituted olefins at 0 °C; and disubstituted olefins were hydrogenated in the presence of trisubstituted olefins at 65 °C with complete selectivity. In several cases, the selectivities were compared with those of P-2 nickel and NiCRA catalysts (entries 1, 3, 4, 11, 15 and 16). These other catalysts also exhibited very good selectivity; but, the BER–Ni_2B in methanol always showed complete selectivity. For example, dec-1-ene was hydrogenated quantitatively in 1 hour at 0 °C, leaving 2-methylpent-1-ene, oct-2-ene, cyclohexene, and β-methylstyrene intact (entries 1–3 and 5). Whereas P-2 nickel[2] and NiCRA catalysts[3] showed 97 % and 98 % selectivities, the BER–Ni_2B in methanol hydrogenated 4-vinylcyclohex-1-ene to 4-ethylcyclohex-1-ene quantitatively (entry 4). Since the separation of hydrogenated products from substrates or byproducts is difficult in most cases, we believe that this complete selectivity is valuable. Competitive hydrogenations of α,β-unsaturated carboxylic acid derivatives also

Table 1. Classification of Olefins Regarding to Hydrogenation with BER–Ni_2B in Methanol[a]

GROUP A			
dec-1-ene	styrene	norbornene	ethyl acrylate
acrylonitrile	acrylamide	*N,N*-dimethylacrylamide	
GROUP B			
2-methylpent-1-ene	2,4,4-trimethylpent-1-ene	α-methylstyrene	oct-2-ene[b]
cyclohexene	3-hydroxymethylcyclohex-1-ene[c,d]		β-methylstyrene[b]
(*E*)-stilbene[c,d,e]	ethyl methacrylate	ethyl crotonate[b]	crotonitrile[b,e]
crotylamide[b]	methyl angelate		
GROUP C			
1-methylcyclohex-1-ene	α-pinene	benzene	2-hydroxymethylfuran
benzofuran	pyrrole	indole	2-hydroxymethylthiophene

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[a] Olefins (1 mmol) were hydrogenated with BER (1 mmol) and $Ni(OAc)_2$ (0.1 mmol) in MeOH at 0 °C or 65 °C. After 1 h, GC analysis showed the corresponding hydrogenated product in 100 % yield: GROUP **A** is hydrogenated quantitatively at 0 °C; GROUP **B** is not hydrogenated at 0 °C but is hydrogenated quantitatively at 65 °C; GROUP **C** is not hydrogenated even at 65 °C.

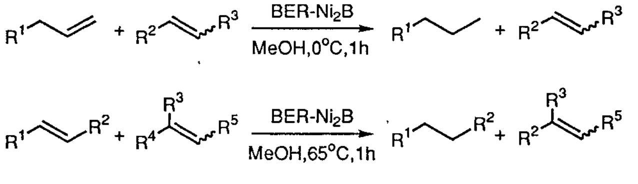
[b] Mixture of *cis* and *trans* isomers was used.

[c] Two equiv of BER were used.

[d] 3-Hydroxymethylcyclohexane and 1,2-diphenylethane were isolated in 97 % and 95 % yields, respectively.

[e] Reaction was carried out for 3 h, and butyronitrile (92 %) was obtained together with butylamine (8 %).

exhibited a complete selectivity (entries 7–10). 5-Ethylidene-2-norbornene and limonene were also hydrogenated selectively to give pure ethylidenenorbornane and *p*-menthene in isolated yields of 91 and 95 %, respectively (entries 11 and 13). 2,2,4-Trimethylpent-1-ene, oct-2-ene, and 3-hydroxymethylcyclohex-1-ene were also hydrogenated selectively in the presence of a trisubstituted olefin, 1-methylcyclohex-1-ene (entries 12, 14, and 15). Lastly, we examined two conjugated dienes, namely cyclohexa-1,3-diene and cycloocta-1,3-diene. Both cyclohexa-1,3-diene and cycloocta-1,3-diene were readily hydrogenated to cyclohexene and cyclooctene quantitatively at 0 °C (entries 16 and 17). Another advantage of BER–Ni_2B in methanol is that there is no need to interrupt the hydrogenation at the point of one equiv of hydrogen uptake.[2,3]



R = Alkyl, Aryl, COOR, CN, $CONR_2$

In conclusion, nickel boride catalyst prepared on BER in methanol is an excellent catalyst for the selective hydrogenation of olefins. BER–Ni_2B in methanol provides a convenient hydrogenation method which exhibits a complete selectivity between structurally different double bonds.

Table 2. Selective Hydrogenation of Dienes or Olefin Mixtures with BER—Ni_2B in Methanol[a]

Entry	Substrate	Temp (°C)	Product	Yield[b] (%)
1[c]	dec-1-ene	0	decane	100
	2-methylpent-1-ene		2-methylpentane	0
2	dec-1-ene	0	decane	100
	oct-2-ene		octane	0
3[e]	dec-1-ene	0	decane	100
	cyclohexene		cyclohexane	0
4[f]	4-vinylcyclohex-1-ene	0	4-ethylcyclohex-1-ene	100 (83)
5	dec-1-ene	0	decane	100
	β-methylstyrene[d]		isopropylbenzene	0
6	norbornene	0	norbornane	100
	cyclohexene		cyclohexane	0
7	dec-1-ene	0	decane	100
	ethyl crotonate[d]		ethyl butyrate	0
8	ethyl acrylate	0	ethyl propionate	100
	ethyl crotonate[d]		ethyl butyrate	0
9	acrylonitrile	0	propionitrile	100
	crotonitrile[d]		butyronitrile	0
10	acrylamide	0	propionamide	100
	crotylamide[d]		butyramide	0
11[h]	5-ethylidene-2-norbornene[g]	0	ethylidenenorbornane	100 (91)
12	2,4,4-trimethylpent-1-ene	65	2,4,4-trimethylpentane	100
	1-methylcyclohex-1-ene		methylcyclohexane	0
13	limonene	65	*p*-menthene	100 (95)
14	oct-2-ene[d]	65	octane	100
	1-methylcyclohex-1-ene		methylcyclohexane	0
15	3-hydroxymethylcyclohex-1-ene	65	hydroxymethylcyclohexane	100
	1-methylcyclohex-1-ene		methylcyclohexane	0
16[i]	cyclohexa-1,3-diene[j]	0	cyclohexene	100
17[k]	cycloocta-1,3-diene[j]	0	cyclooctene	100

[a] The mixtures of olefins (1 mmol each) or dienes (1 mmol) were hydrogenated with BER (1 mmol) and $Ni(OAc)_2$ (0.1 mmol) in MeOH at 0 °C or 65 °C for1 h. All hydrogenation products are known and were identified by GC and characterized by comparison with an authentic sample and spectral data (cf. experimental).

[b] GC yields. Isolated yields in parenthesis.

[c] Decane (96 %) and 2-methylpentane (6 %) were obtained with P-2 nickel (Ref. 2), and decane (93 %) and 2-decenes (7 %) were obtained with NiCRA (Ref. 3).

[d] A mixture of *cis* and *trans* isomers was used.

[e] Decane (98 %) and cyclohexane (4 %) were obtained with P-2 nickel, and decane (93 %) and dec-2-ene (7 %) were obtained with NiCRA.

[f] 4-Ethylcyclohexane was obtained in 97 % and 98 % yields with P-2 nickel and NiCRA, respectively.

[g] A mixture of *endo* and *exo* isomers.

[h] Ethylidenenorbornane was obtained in 96 % yield with P-2 nickel.

[i] Cyclohexene was obtained in 89 % and 98 % yields with P-2 nickel and NiCRA, respectively.

[j] The reaction was carried out for 3 h.

[k] Cyclooctene was obtained in 93 % yield with NiCRA.

Borohydride Exchange Resin (BER):
An aqueous solution of $NaBH_4$ (1 M, 500 mL) was stirred with wet chloride form of anion exchange resin (Amberlite IRA-400, 20-50 mesh, total exchange capacity: 3.8 meq/g dry, Fluka, 200 g) for 15 min. The resulting resin was washed thoroughly with distilled water (3 × 100 mL) and additionally washed with EtOH. The borohydride form anion exchange resin was dried in vacuo at r.t. for 12 h to give the dried borohydride exchange resin (BER); yield: 102 g. The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 2 N HCl, and the average hydride content of BER was found to be 3.0 mmol of BH_4^- per gram. The dried resin was stored under N_2 in refrigerator (~ 4 °C). The hydride content was constant over 6 weeks.

Selective Hydrogenation of Olefins with BER–Ni_2B in Methanol: *p*-Menthene; Typical Procedure:
BER (3.33 g, 10 mmol) was added to $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in MeOH (100 mL), and the mixture was stirred slowly at r.t. Immediately, a black coating of Ni_2B was observed. After 1 min, limonene (1.36 g, 10 mmol) was added, and the mixture was stirred under reflux for 1 h to complete the hydrogenation. Complete reaction was confirmed by GC, and the resin was removed by filtration. MeOH was evaporated under reduced pressure to yield pure *p*-menthene (1.31 g, 95%).

^1H NMR ($CDCl_3$): $\delta = 0.87$ (d, 3H, $J = 6.7$ Hz), 0.89 (d, 2H, $J = 6.7$ Hz), 1.19–1.27 (m, 2H), 1.42–1.52 (m, 2H), 1.65 (s, 3H), 1.71–1.79 (m, 1H), 1.94–2.18 (m, 3H), 5.30–5.39 (m, 1H).

MS (EI, 70 eV): m/z (relative intensity) = 138 (M^+, 35), 123 (16), 95 (100), 81 (17), 79 (21), 67 (83), 55 (37).

4-Ethylcyclohex-1-ene:

^1H NMR ($CDCl_3$): $\delta = 0.86$–0.93 (m, 3H), 1.12–1.36 (m, 3H), 1.51–1.77 (m, 4H), 2.00–2.04 (m, 2H), 5.65 (br s, 2H).

MS (EI, 70 eV): m/z (relative intensity) = 110 (M^+, 20), 95 (11), 81 (100), 67 (36), 54 (42).

Ethylidenenorbornane:

^1H NMR ($CDCl_3$): $\delta = 1.17$–1.37 (m, 4H), 1.48–1.69 (m, 5H), 1.74–1.86 (m, 1H), 2.02–2.20 (m, 1H), 2.32–2.38 (m, 1H), 2.61–2.67 (m, 1H), 5.02–5.30 (m, 1H).

MS (EI, 70 eV): m/z (relative intensity) = 122 (M^+, 45), 107 (30), 93 (100), 79 (28), 78 (27), 77 (79), 66 (20), 53 (10).

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