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# Partial Hydrogenation of Acetylenes on Modified Nickel Boride Catalysts

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**Synopsis.** Ni–B catalysts modified with a small amount of copper(II) salt have a higher selectivity than palladium and modified Raney nickel catalysts for partial hydrogenation of phenylacetylene, 1-heptyne, 1-ethynylcyclohexene, and propargyl alcohol.

Our previous paper[1)] reported that cobalt boride catalyst (Co–B), especially when modified with a small amount of metal salts, are much more effective than nickel boride catalyst (Ni–B) for selective hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols; however, for selective hydrogenation of acetylenes to olefins Ni–B is more selective than Co–B. This work investigated modifications of Ni–B by addition of a small amount of metal salts with a view to increasing the selectivity for the partial hydrogenation of acetylenes.

Although palladium has almost completely displaced nickel to be used as catalyst of choice for the partial hydrogenation of acetylenes, the lower price of nickel will make it more useful than palladium if equal or higher selectivity is to be obtained with it.[2)] Thus it is worthwhile to study the partial hydrogenation on Ni–B which is very simple to prepare and to use and which is, in activity, equal to or, in some cases, superior to Raney nickel catalyst (R-Ni) for hydrogenation of many kinds of organic functions. With R-Ni, Elsner and Paul[3)] reported that deactivation of the catalyst with copper(II) salt in ethanol might provide a selective catalyst for partial hydrogenation of octadecynes, without presenting any information on quantitative compositions of the products.

## Experimental

*Catalyst.* Ni–B and R-Ni were prepared according to the method described previously.[4)] Copper boride catalyst (Cu–B) and Co–B were prepared, respectively, with copper(II) chloride and cobalt acetate in a manner similar to that for Ni–B. The copper-modified nickel boride catalyst (Cu-modified Ni–B) was prepared by stirring Ni–B (0.2 g, by the P-1 method[4,5)]) in a solution of copper(II) chloride (2—10 mol% of Ni) in 99% ethanol (10 ml) at 30 °C for 10 min. The copper-modified Raney nickel catalyst (Cu-modified R-Ni) was prepared in the same way by using R-Ni (0.2 g) activated at 70 °C. The coprecipitated nickel copper boride catalyst (Ni–Cu–B) was prepared by reducing a mixture of measured amounts of nickel acetate and copper(II) chloride with $NaBH_4$ in water.

*Hydrogenation.* Acetylenes (0.2 ml) were hydrogenated at 30 °C in ethanol or in cyclohexane (10 ml) under atmospheric pressure of hydrogen. The olefin selectivity of a catalyst was defined as the mol% of olefin in olefin plus paraffin determined by a GLC method at 30% conversion of acetylene. Selectivities of the catalysts were almost independent of the conversion of acetylenes up to 90%. The other experimental details are the same as those described in our previous paper.[1)]

## Results and Discussion

Selectivities of boride catalysts in the partial hydrogenation of phenylacetylene fell in the order Cu–B>Ni–B>Co–B, which is considered to be reverse to the order of the strength of adsorption of the acetylene on the catalyst surface as based on the surface *d*-electron density.[1,8)] 1-Phenyl-1-propyne, which is supposed to be adsorbed more weakly than phenylacetylene because of the steric hindrance of methyl group, was hydrogenated to the olefin more selectively than phenylacetylene on Ni–B. These facts support the idea, presented in our previous paper[1)] concerning the selectivity of Co–B, that the stronger the adsorption bond between the C≡C bond and the metal, the lower the olefin selectivity.

The selectivity of Ni–B was enhanced by the modification with a small amount of copper(II) chloride even to such an extent as exceeds that of Cu–B or polymer-bound Pd complex catalyst (93%),[6)] although the hydrogenation rate decreased considerably. In the case of R-Ni, it was necessary to add a larger amount of the copper(II) salt to obtain as high a selectivity as that of Cu–B, probably because of the larger surface area of R-Ni. The selectivity of a coprecipitated nickel copper boride catalyst was lower than those of Ni–B and Cu–B. This fact again shows

Table 1. The olefin selectivity($S$) of various catalysts in the hydrogenation of acetylenes

| Catalyst | Cu/Ni[a)] | Reactant | $S$/% |
|---|---|---|---|
| Ni–B (P-1)[b)] | — | Phenylacetylene | 90.0 |
| Ni–B (P-2)[b)] | — | Phenylacetylene | 91.3 |
| R-Ni | — | Phenylacetylene | 88.0 |
| Cu–B | — | Phenylacetylene | 92.0 |
| Co–B | — | Phenylacetylene | 79.0 |
| Cu-modified Ni–B | 0.02 | Phenylacetylene | 96.3 |
| Cu-modified Ni–B | 0.05 | Phenylacetylene | 97.7 |
| Cu-modified Ni–B | 0.10 | Phenylacetylene | 98.3 |
| Cu-modified R-Ni | 0.05 | Phenylacetylene | 84.1 |
| Cu-modified R-Ni | 0.10 | Phenylacetylene | 83.8 |
| Cu-modified R-Ni | 0.20 | Phenylacetylene | 93.2 |
| Ni–Cu–B | 0.10 | Phenylacetylene | 88.9 |
| Ni–B (P-1) | — | 1-Phenyl-1-propyne | 92.3 |
| Ni–B (P-1) | — | 1-Heptyne | 72.5 |
| R-Ni | — | 1-Heptyne | 78.5 |
| Cu-modified Ni–B | 0.05 | 1-Heptyne | 89.7 |
| Cu-modified R-Ni | 0.05 | 1-Heptyne | 70.7 |
| Cu-modified Ni–B | 0.10 | 1-Ethynylcyclohexene | 94±1 |
| Ni–B (P-1) | — | Propargyl alcohol | 68.0 |
| Cu-modified Ni–B | 0.10 | Propargyl alcohol | 80.3 |

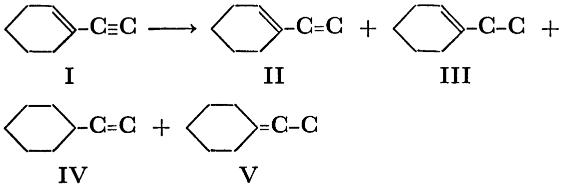
a) Molar ratio of copper(II) salt to nickel salt. b) Prepared in water (P-1) or in 95% ethanol (P-2).

that the coprecipitation method for preparing binary boride catalysts is ineffective for increasing the catalytic selectivity, as already shown for the selective hydrogenation of α,β-unsaturated aldehydes in our previous paper.[1]

The addition of zinc or iron(II) salts instead of copper(II) salts to the Ni–B catalyst raised the selectivity only slightly.

The Cu-modified Ni–B was highly selective also for the partial hydrogenation of 1-heptyne, while Cu–B was almost inactive towards 1-heptyne. XPS studies on Cu-modified Ni–B and R-Ni indicated that the copper(II) ion was deposited as copper metal on the catalyst surface. From these facts, the high selectivity of Cu-modified Ni–B is supposed to be due to the synergetic effect between copper and nickel metals on the catalyst surface, where copper atoms adsorb acetylenes rather weakly but do not adsorb olefins in outer surface or at the top of rugged surface and where nickel atoms activate hydrogen in inner pores or at the bottom of rugged surface.

As an instance of partial hydrogenation of conjugated acetylenes, 1-ethynylcyclohexene was hydrogenated over the Cu-modified Ni–B in cyclohexane. After all reactant I had been exhausted, no further uptake of hydrogen was observed; compositions of the products were as follows: II 94±1%, III+IV *ca.* 3%, and V and the others *ca.* 3%. Ethylcyclohexane was not detected. The yield of II was reported to be 86% at 94% conversion on the Lindler catalyst,[7] and to be 81% at 100% conversion on polymer-bound Pd complex catalyst.[6]



Propargyl alcohol was selectively hydrogenated to allyl alcohol on the Cu-modified Ni–B catalyst in ethanol without being accompanied by hydrogenolysis of the hydroxyl group.

These findings suggest that we can regard Cu-modified Ni–B as superior to the Lindler catalyst for the partial hydrogenation of acetylenes if we take into account both the ease of preparation and separation and the moderate price of nickel.

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