$(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ as Versatile Catalysts for Hydrogenation, Hydrogenolysis, and Methanation Reactions

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Summary The hydrogen adducts $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ have been found to be active catalysts for the hydrogenation and hydrogenolysis of *cis*-but-2-ene and also for the reduction of carbon monoxide to methane.

We have noted[1] that the interaction of cobalt(II) chloride or nickel(II) chloride with $NaBH_4$ leads to products with approximate stoicheiometries $(Co_2B)_5H_3$ and $(Ni_2B)_2H_3$ respectively. We have now prepared rhodium containing species whose elemental analyses confirm the stoicheiometries $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$. These substances were obtained by interaction of 1M ethanolic Co^{II} or Ni^{II} chloride containing 5 molar % $RhCl_3.3H_2O$ with a 4-fold molar excess of $NaBH_4$ under N_2. The products were found to be pyrophoric in air when dry, and were stored under ethanol until required for catalytic purposes. It should be noted that treatment of Co^{II}, Ni^{II} or Rh^{III} chloride with BH_4^- independently does not produce species that are active catalysts in these reactions. Although nickel boride obtained by reduction of Ni^{II} salts with BH_4^- has been shown to act as a hydrogenation catalyst in liquid phase reactions[2] and in one instance[3] when supported on silica gel for CO reduction, there seems to be no report in the literature where substances obtained by this method have been used unsupported, as catalysts in gas-phase reactions.

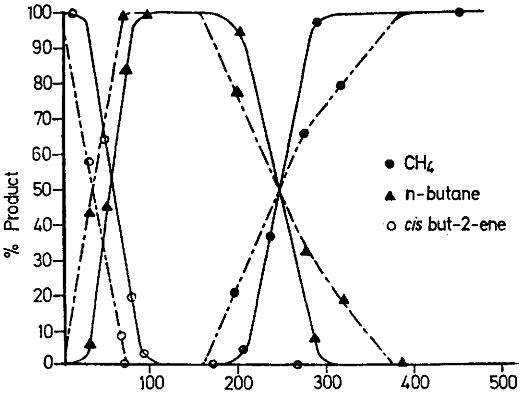

Figure Catalytic hydrogenation and hydrogenolysis of *cis*-but-2-ene (1·2 mole %) in hydrogen by, - - - $(Co_2B)_{10}RhH_6$ (151 mg), ——— $(Ni_2B)_{10}RhH_{15}$ (140 mg). Flow rate 40 cm^3 min^{-1}.

We now discuss our preliminary findings on the catalytic nature of the species $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$.

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For catalytic hydrogenation and hydrogenolysis of gaseous alkenes, notably *cis*-but-2-ene, the catalysts were supported on a glass wool plug in an 8 mm diameter Pyrex glass tube and dried in a stream of H_2 at 100 °C for 6 h. A mixture of *cis*-but-2-ene (1·2 mole %) in hydrogen was admitted at a flow rate of 40 $cm^3 min^{-1}$ at 1 atm pressure. The catalyst temperature was monitored over a wide range (25—500 °C) ± 1° and the exhaust gas analysed for hydrocarbon content by flame ionisation gas chromatography using a 5 m, 1/8 in diameter Porapak Q column (80—100 mesh) at 140 °C. On no occasion did we find *trans*-but-2-ene or but-1-ene. At 62 °C the Ni species gave almost 50% hydrogenation to n-butane increasing to *ca.* 100% at 90 °C. At 200 °C hydrogenolysis started and was quantitative at 300 °C yielding *ca.* 100% methane (Figure). Both the Co and Ni catalysts showed no loss in activity with time (48 h) and at temperatures up to 500 °C. Unsupported Raney nickel under identical reaction conditions was found to behave similarly, producing *ca.* 100% CH_4 at 400 °C but below 200 °C apart from n-butane, up to 10 mole % of isomerised *trans*-but-2-ene and but-1-ene was detected.

TABLE

Catalytic activity of $(Ni_2B)_{10}RhH_{15}$ for the methanation of CO

Mole CO conversion

T/°C	CH_4	C_2H_6	C_2H_4	C_3H_8	C_4H_{10}	C_6H_{14}
100	0·01	b	–	b	b	–
220	0·43	0·05	b	0·03	0·01	b
300	6·63	0·14	–	0·02	b	–
350	27·86	0·20	–	b	b	–
400	34·39	0·08	b	b	b	–
450	51·37	b	–	–	–	–
480	52·67	–	–	–	–	–
490	59·64	–	–	–	–	–

[a] Includes isobutane, *cis*-and *trans*-but-2-ene and but-1-ene; [b] <0·01%. Feed gas H_2:CO ratio of 3:1 at 66·7 $cm^3 min^{-1}$ at 1 atm. Catalyst weight 410 mg.

For carbon monoxide methanation, the catalysts were supported and dried as above, and carbon monoxide (25 mole %) in hydrogen was admitted at 66·7 $cm^3 min^{-1}$ at 1 atm pressure. The Co species was *ca.* 70% as active for methane formation as the Ni species at all temperatures up to 500 °C. The Table gives methanation data using the more active Ni species, showing that mole % CO to CH_4 conversions of up to 60% have been achieved using this catalyst. As noted above, both catalysts showed no loss in activity with time (48 h) at temperatures up to 500 °C.

The species $(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ have been shown to be effective catalysts for three very important gas-phase transformations. More work is required in this field to elucidate the role that the bound hydrogen in these substances plays (if any) in such catalytic reactions involving hydrogen.

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