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Novel Metal Borides with Catalytic Reactivity for Hydrodesulfurization and Coal Liquefaction[‡]

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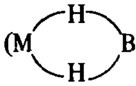
Introduction

Relatively few compounds survive reaction conditions typically required to liquefy coal and upgrade heavy oils; 1000–3000 psig, H_2, 350–450 °C, with high heteroatom levels, commonly 1% sulfur, 3–7% oxygen and up to 1% nitrogen [1, 2]. Thus metal sulfides and oxides, which tend to be more resistant under the above reaction conditions, are commonly used as catalysts for such conversions. With current emphasis on the development and evaluation of new classes of catalysts for fossil energy conversions, we have been involved in investigating the application of new types of metal catalysts. In this search we have been limited to compounds which will retain chemical integrity under the necessary reaction conditions. There were predictions in the literature that certain metal borides might exhibit high chemical stability particularly towards sulfidation [3] in addition to the well-established [4] thermal stability properties.

Scattered in the patent and open literature are indications that group III hydride derivatives can effect hydrodesulfurization of heavy feedstocks [5] and promote direct hydrogenolysis of ether and thioether linkages with simpler substrates [6]. Furthermore, recent advances with hydride-derived metal boride catalysts [7] had indicated considerable potential in hydrogenation reactions, with turnovers similar to active noble metals reported in some cases [8].

Results and Discussion

We wish to report the preparation, composition and some chemical properties of a new type of metal boride which catalyzes hydrodesulfurization (HDS) and promotes liquefaction of coal. These borides are produced through reactions of borane anions with transition metal salts at 400 °C and 2000 psi H_2. The most active catalysts have been prepared from the pentaborane anion. Thus a one hour reaction of 4.3 g (20 mmol) anhydrous cobalt bromide and 40 mmol NaB_5H_8 [9] produces 5.3 g of a black powder which analyzes [10] as Co 14.8%, B 17%, C 4.1%, Br 32.5%, H 1.6%*; Na 8.7%. An analogous nickel boride can be prepared in a similar manner using the same metal halide to borane ratio; Ni 15%, B 12.4%, C 1.2%, H 1.7%, Br 36.4%, Na 8.0%.

Samples of the new cobalt and nickel borides were finely ground under nitrogen and infrared spectra recorded using a multiple internal reflectance accessory. Both samples exhibited weak absorptions at 2950, 2920, 2960 cm^{-1} (νCH) and 2505 cm^{-1} ($\nu BH_{terminal}$). Strong broad absorptions were centered at 1400 cm^{-1} and 1375 cm^{-1} for the cobalt and nickel compounds respectively. By analogy with tetrahydroborate metal complexes [12], these seem most likely due to bridge stretching of bidentate  $(M\overset{H}{\underset{H}{\rightleftarrows}}B)$ structures in the compound. Other absorptions were observed at 1190, 1020 (w, both compounds), 720–790 s, vbr and 640 m, br 540 (w, br) (cobalt derivative), and 710 m, br 800 (w, br) (nickel derivative). Absorptions at 1020 and 800 cm^{-1} regions are possibly due to $\delta BH_{2(terminal)}$ and $\nu BH_{2(bridging)}$ B [13].

The boride catalysts are stable in air and are relatively inert, dissolving (slowly) only in hot nitric acid or aqua regia. The catalysts are unaffected by boiling hydrochloric or hydrofluoric acids.** However at 400 °C under 1900–2000 psi hydrogen pressure the catalysts actively promote hydrodesulfurization. For example with thiophene, a widely accepted model for an organic sulfur structure in coal and heavy crudes [14] ninety minute reactions above 400 °C resulted in 99 and 95% hydrodesulfurization to butane, and H_2S, with the pentaborane-derived cobalt and nickel catalysts respectively. Under similar conditions the commercially available borides Co_2B–Co_3B and NiB both cleaved only 35% of the thiophene, while also producing 19 and 12% tetrahydrothiophene respectively. The new catalysts are thus the most active borides for hydrodesulfurization yet established. Systems are at least twice as active as Raney nickel which hydrodesulfurized thiophene at 32% levels under the same reaction conditions, while

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*Pyrolysis of this catalyst at 1050 °C [11] yielded 0.4 weight percent H (collected as H_2 with a Toepler pump).

**This chemical resistance is similar to higher transition metal borides and elemental boron, see reference 3 above.

producing 7% tetrahydrothiophene. Early in the project we established that high temperatures were required for efficient rates of reaction. For example, reaction of the new nickel boride with thiophene, carried out at 254 °C for an extended period (16 hours) resulted in only 33% cleavage products and 22% simple hydrogenation to tetrahydrothiophene.

Under the same reaction conditions the new borides catalyzed liquefaction of a medium volatile bitmunious Virginia coal*. Thus 1.5 g of the catalyst derived from $CoBr_2$ and NaB_5H_8 converted 45 g of coal to 19.2% cyclohexane-soluble oils, 20.4% toluene-soluble asphaltenes, and 60.3% preasphaltene plus char [15]. Reactions without catalyst and reactions using a commercial $CoO-MoO_3$ catalyst** produced 8 and 15% oils, 34 and 28% asphaltenes with 56% and 57% preasphaltenes plus char respectively. While the levels of toluene insoluble (char plus preasphaltene) were similar in all reactions, the relative levels of oils to asphaltenes are affected considerably using different catalysts.

The nickel and cobalt borides derived from pentaborane are the most active HDS and coal liquefaction boride catalysts we have established to date. We are continuing to investigate other borides produced with different metals and borane anions. However, this preliminary work has shown that this type of compound has considerable potential in important energy-related areas.

Experimental

Thiophene was supplied by Columbia Chemicals, cobalt boride (Co_2-Co_3B), nickel boride (NiB), nickel(II) bromide, cobalt(II) bromide and Raney nickel were supplied by Alfa-Ventron, and pentaborane was purchased from Callery Chemicals.

IR spectra were recorded on a Perkin-Elmer 283 spectrometer, mass spectra on a Finnigan 1020 (GC/MS) and Bendix (TOF) instrument. NMR spectra were recorded using a Varian FT 80A spectrometer with a broadband probe; observe frequencies were 20.0 MHz (^{13}C) and 79.8 MHz (^{1}H). Gas chromatography was carried out using a 5% Carbowax 20M/TPA column (GC/MS system), phenylisocyanate/Porasil C (vent gases) and OV 101 (Varian Vista 44).

Reactions were carried out in an Aminco 4 3/8 O.D. vessel. After introduction into a preheated jacket on the rocker-shaker assembly, and pressurization, the vessel took five hours to heat to 400 °C. Reactions were continued for a further 90 minutes after this temperature, before the vessel was removed and quenched on ice. Cooling to 100 °C took six minutes. Gases were vented into a 42 liter tank and were sampled directly (IR, GC, mass spectrometry), before removal of liquid nitrogen condensables (butane, H_2S). Unreacted thiophene, and tetrahydrothiophene were removed by conventional vacuum distillation from the vessel and identified [16] by ^{13}C NMR spectroscopy.

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*C 76.92%; H 5.11%; N 1.57%; S 1.52% (Huffman Laboratories, Inc., Wheat Ridge, Colorado); Coal samples were ground under nitrogen using a Spex mixer-mill inside a glovebox.

**3.5% CoO–10% MoO_3 on alumina supplied by Strem Chemicals.

N.Y. and Atlantic Microlabs, Atlanta, Georgia. Halogen levels in catalysts would be expected to interfere with the C analysis in particular. Another part of the residual composition is pressued due to metal-bound oxygen. This oxygen (and the carbon) would arise through destruction of coordinated tetrahydrofuran remaining from the initial borane anion preparation.

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