

On the Possibility of Metal Borides for Hydrodesulfurization

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We have explored cobalt and nickel boride-based catalysts for the hydrodesulfurization (HDS) of thiophene and evaluate their overall catalytic activity, mode of desulfurization, and stability to sulfo-reductive reaction conditions. While the prepared cobalt and nickel borides promote hydrodesulfurization, flow-reactor studies measuring the catalytic activity show that, in actuality, these materials are unstable with respect to the metal sulfides under HDS conditions. In fact, the observed catalytic HDS results from the conversion of the metal boride, and any impurity oxides, to the corresponding metal sulfide. These results include confirmation from characterization of the used catalysts by EDX, powder XRD, and elemental analysis.

Introduction

As the world's petroleum supply becomes more limited, coal liquefaction and the efficient upgrading of heavy oil fractions to usable fuel will become essential. Catalytic hydrotreating of such fractions is necessary to upgrade the oil and remove environmental pollutants.¹ This conversion requires moderate temperatures (300–450 °C) and high H₂ pressures (20–100 bar). Typically, supported metal sulfides are used as they are resilient under these sulfo-reductive refining conditions; improvements in catalyst activity, lifetime, and diffusion rates,² however, are desired, particularly as environmental controls on fuel sulfur content become increasingly restrictive.¹ To improve such catalysts, most research has emphasized the role of supports and promoters in catalysis.

Supported MoS₂ has been found to be a highly active, affordable catalyst able to withstand the harsh hydrotreating conditions of HDS. To improve this catalyst system, promoters such as nickel or cobalt have been added to the active phase.³ Support effects have also been considered, most commonly, the interaction between MoS₂ and alumina, silica, titania, or carbon supports.⁴ The influence of support additives such as phosphorus, boron, and fluorine has also been examined.⁵ There has been, however, little deviation

from the use of metal sulfides for HDS, with the notable exceptions of molybdenum carbide and nitride⁶ and more recently metal phosphides.⁷

The possibility of metal borides for HDS upgrading of oil⁸ has been suggested in the literature; their refractory nature,⁹ reported resistance to sulfur poisoning,¹⁰ and known desulfurization ability in organic synthesis¹¹ make metal borides potentially desirable catalysts. The few HDS experiments reported with metal borides, however, do not provide quantitative activity measurements, analysis of the active HDS phase, or thorough characterization of both the new and used catalyst. The work reported here demonstrates for the first time that under HDS conditions, conventionally synthesized cobalt and nickel borides, which promote HDS, are in fact not stable as prepared and undergo extensive sulfiding of both the surface and bulk material. Molybdenum boride was not included in this study, in part because commercial sources are not readily available and in part because prior syntheses report only very low surface area materials (<1 m²/g), not relevant to catalytic applications.

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Experimental Section

Boride Syntheses. Cobalt and nickel boride were prepared by conventional solution chemistry techniques.¹² To 50 mL of 0.1 M aqueous solutions of either $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, excess aqueous NaBH_4 stabilized with NaOH was added dropwise over 30 s while stirring. A constant flow of air flushed the reaction vessel of generated hydrogen. The black precipitates were collected by vacuum filtration and washed with water and then ethanol to remove NaCl , $\text{B}(\text{OH})_3$, and any slightly soluble cobalt borate phases. Samples were vacuum-dried at 110 °C for 12 h and heat treated at 450 °C for 12 h in a flow of helium at 30 cm^3/min . Heat-treated samples were stored in a N_2 glovebox (oxygen <0.2 ppm as determined by a Teledyne oxygen meter) until use.

Catalyst Characterization. Elemental analysis was performed at the University of Illinois Microanalytical Laboratory. Scanning electron microscopy (SEM) was conducted with a Hitachi S-4700 microscope operating at 10 kV. The microscope was equipped with an energy-dispersive X-ray spectroscopy system (EDX) manufactured by Oxford Instruments. Powder X-ray diffraction was conducted with a Rigaku D-Max using $\text{Cu K}\alpha$ radiation. Crystallite sizes were determined using the Jade X-ray analysis software package. Surface area measurements were obtained by BET analysis of N_2 isotherms (at -196 °C) from Quantachrome Instruments Nova 2200e surface area and pore analyzer.

Catalysis Studies. Catalytic studies were performed at 1 bar in a single-pass glass microreactor. Freshly prepared, heat-treated metal borides were used for each catalysis study. Catalysts were transferred to the reactor in air. A control, however, was run in which exposure to air was eliminated; catalysis results were the same indicating that brief exposure to oxygen does not alter the degree of surface passivation likely induced during catalyst preparation. Thiophene vapors were carried at a constant partial pressure of 0.075 bar by a flow of hydrogen (27.5 cm^3 (STP)/min). The reaction products were analyzed by gas chromatography–mass spectrometry (Agilent 6890/5973 GC–MS); the GC was fitted with a 30 m (35%-phenyl)-methylpolysiloxane fused-silica capillary column.

Results and Discussion

As detailed by Glavee et al.,¹³ the conditions used to synthesize metal borides can greatly influence the final product's composition, leading to a mixture containing small amounts of impurities in the Co_2B , e.g., Co_3B , metallic Co, cobalt oxides, and $\text{Co}(\text{BO}_2)_2$. The methodology employed here was selected to minimize both the production of pure metal and metal oxyborides by suppressing the formation of the borate anion from the hydrolysis of borohydride. As prepared, the initially synthesized powders are amorphous according to powder XRD. The heat treatment of the powders used to prepare samples for catalytic evaluation induced crystallization, whose XRD (included in Figure 4) correspond to cobalt boride, Co_2B ,^{14a} and nickel boride, Ni_3B ,^{14b} no metal oxide or boron oxide phases were observed, indicating that any oxide or oxyboride formation is minimal or limited to the surface of the boride and not the bulk material. Due to the broadened nature of the XRD peaks and the close

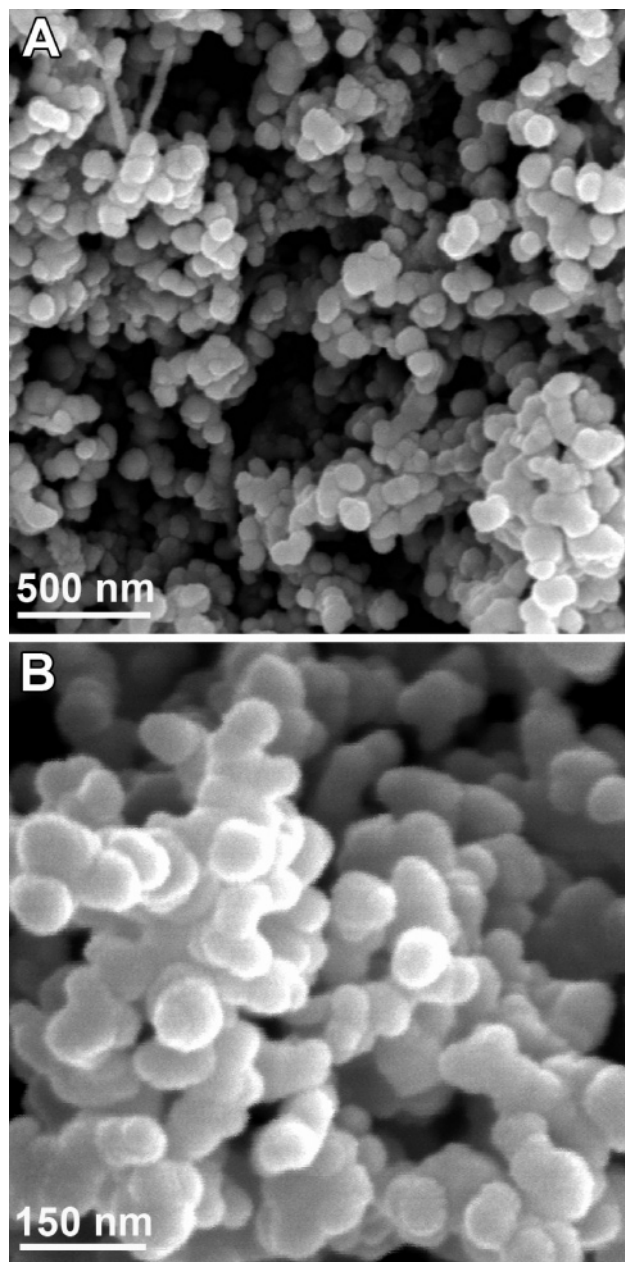


Figure 1. SEM images of (A) Co_2B and (B) Ni_3B after heat treatment.

proximity of the most intense Co peak^{14c} to characteristic Co_2B and Co_3B ^{14d} diffraction peaks, it is difficult to rule out the presence of small amounts of elemental Co in the samples; however, other prominent Co diffraction peaks are absent in the spectra. No elemental Ni is indicated in the XRD pattern of the heat-treated Ni_3B sample. The average crystallite size for Co_2B and Ni_3B was 10 and 20 nm, respectively. Elemental analysis of the heat-treated samples indicated a Co to B ratio of 1.9 and a Ni to B ratio of 2.7. Contamination from carbon, hydrogen, and nitrogen were all less than 0.25 wt %. Oxygen, determined by difference, varied from 2 to 5 wt % depending on the sample. Sodium and chlorine were effectively removed from the samples by washing.

Figure 1 shows SEM images of the heat-treated Co_2B and Ni_3B catalysts used in this study. Both borides are composed of ~ 100 nm sized particles fused together into larger agglomerates. Due to the agglomeration of particles, the

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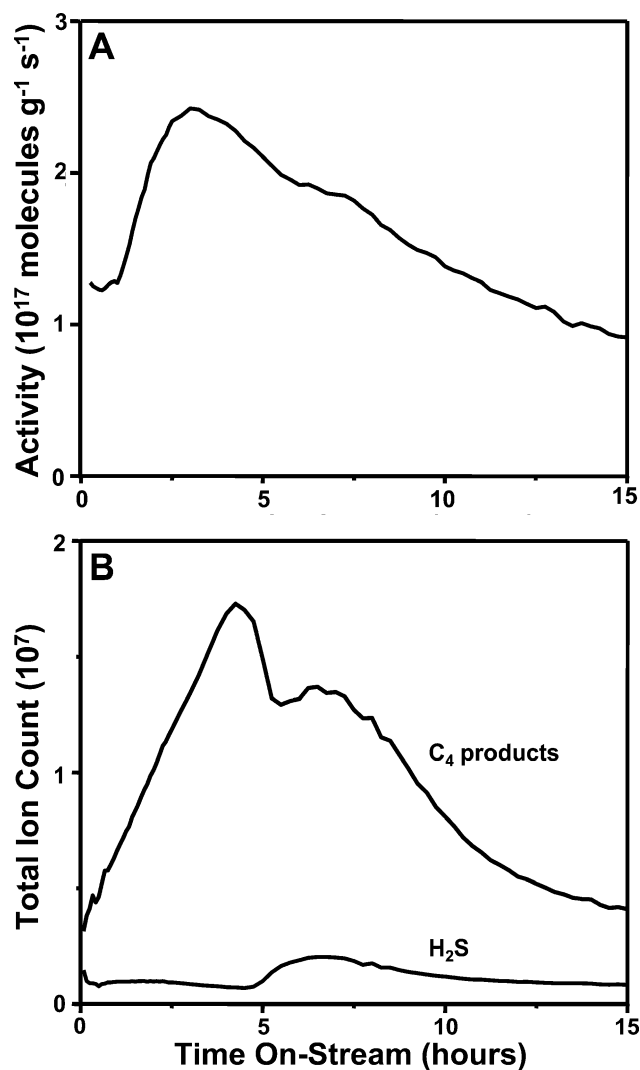


Figure 2. (A) Thiophene HDS activity measurement for pretreated Co_2B as a function of time at 450 °C. (B) Product formation as a function of time on-stream at 450 °C for Co_2B .

resulting materials are relatively nonporous, with only moderate surface areas (Co_2B 30 m^2/g , Ni_3B 20 m^2/g).

The HDS catalysis studies reported in the literature on cobalt or nickel borides rely on batch reactors to assess the overall catalytic activity. While this is a valid and common technique for evaluating the activity of a known catalyst system, with a new system such as the metal borides, characterization of the used catalyst is essential to ensure that the observed activity is indeed due to the starting material. Unfortunately, characterization of such boride catalysts after use has not been reported. Flow reactors are better equipped to assess the onset of catalytic activity because changes in substrate concentration and the formation of reaction products are continuously monitored over the entire duration of the study.¹⁵

Relatively (but not exceptionally²) high temperatures (i.e., 450 °C) were used in these catalytic studies, partly to mimic the conditions needed for HDS of heavier feedstocks and partly to simulate the effects created by multimonth use of catalysts in real applications. Figure 2A contains a repre-

sentative plot of the observed activity for the HDS of thiophene using Co_2B as the catalyst in a flow microreactor at 450 °C; only traditional HDS products, C_4 hydrocarbons and H_2S , were observed during catalysis runs. No tetrahydrothiophene or hydrocracking products were observed. Interestingly, the catalytic activity increases with time on-stream (“lining-out”), reaches a maximum (2.5×10^{17} molecules $\text{g}^{-1} \text{s}^{-1}$, compared with Co_9S_8 (20 m^2/g) $> 10^{17}$ molecules $\text{g}^{-1} \text{s}^{-1}$ and MoS_2 (40 m^2/g) $> 10^{18}$ molecules $\text{g}^{-1} \text{s}^{-1}$ at 450 °C), and then begins to decrease. For Ni_3B at 450 °C (Supporting Information Figure 1A), the catalytic activity increases over the entire duration of the experiment. Such behavior is in contrast to typical flow-reactor catalysis studies in which appropriately prepared catalysts display short or no lining-out period, with the observed activity starting high and decreasing with time on-stream due to catalyst deactivation mechanisms.^{15,16} An initial increase in catalytic activity is generally indicative of some chemical or physical change occurring to the catalyst. At catalysis temperatures below 450 °C, both Ni_3B and Co_2B catalysts show increasing catalytic activity over the entire duration of the experiment suggesting that physical and/or chemical changes to the catalyst are incomplete.

In looking at the product distribution for the HDS of thiophene as a function of time on-stream, the observed lining-out behavior can be explained. For Co_2B (Figure 2B), C_4 hydrocarbon production increases as the HDS activity increases, as expected. Interestingly, however, the observed hydrogen sulfide, H_2S , production is constant at first, and then increases once the C_4 production and HDS activity begin to decrease. This observation suggests that the initially observed HDS activity and mechanism for HDS is through sulfiding of the metal boride and any impurities, thus suppressing H_2S production. Once the impurities and bulk metal boride are sulfided, H_2S production tracks with C_4 production and HDS activity, since the H_2S is now liberated from the thiophene and not trapped by reaction with the surface. For Ni_3B , C_4 production increased during the entire time on-stream while H_2S production remained constant, suggesting that even after 15 h, surface sulfiding was incomplete (Supporting Information Figure 1B). This behavior is also observed when the catalysis temperature is lowered below 450 °C for both Ni_3B and Co_2B catalysts. The observed increase in HDS activity is likely due to the formation of a more intrinsically active metal sulfide phase, such as Co_9S_8 or Ni_9S_8 ,¹⁷ initially dispersed on the corresponding metal boride.

Characterization of the used catalyst confirms sulfiding of the initial material. A prominent sulfur peak centered at 2.38 eV is observed in the EDX spectra of both used cobalt and nickel boride catalysts (Figure 3), which was not present in the initial catalyst (boron of course cannot be analyzed by EDX). XRD was used to characterize the sulfur phases formed. Figure 4A shows the *complete conversion* of Co_2B to Co_9S_8 after 20 h on-stream. After 20 h at 350 °C, only the Co_2B phase is observed for the used catalyst, but at 400

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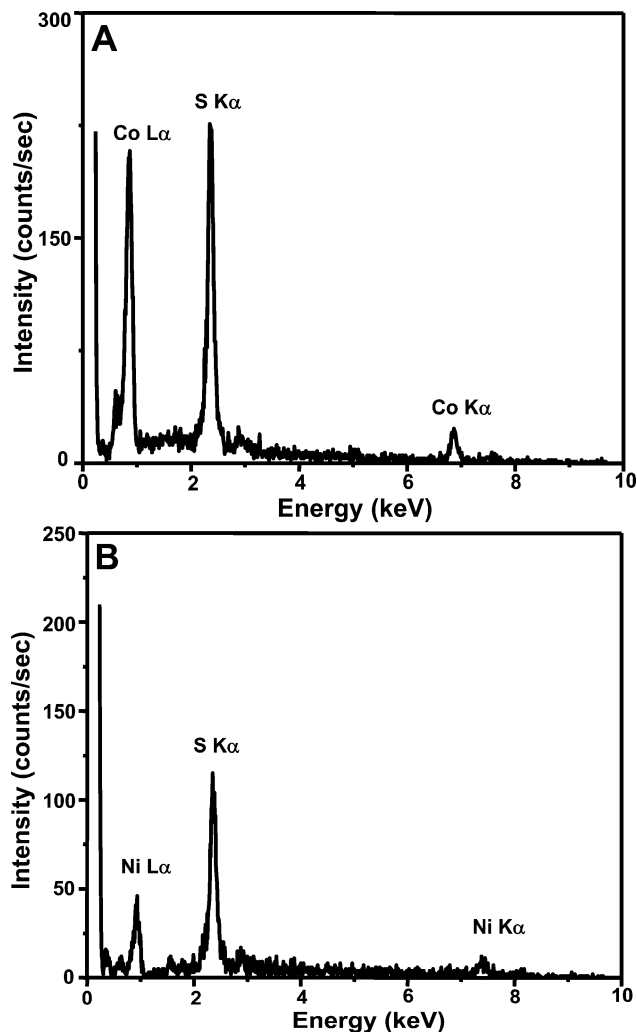


Figure 3. EDX spectra of used (A) Co_2B and (B) Ni_3B catalysts.

$^\circ\text{C}$ both Co_2B and Co_9S_8 phases are observed after 20 h. The catalyst used at 450°C shows complete conversion to Co_9S_8 . Ni_3B also undergoes sulfiding, albeit somewhat slower (Figure 4B); after 20 h on-stream at 450°C , both Ni_9S_8 and Ni_3B phases are observed. More rigorous sulfiding conditions (i.e., $30\text{ cm}^3/\text{min}$ of 10% $\text{H}_2\text{S}/\text{H}_2$ at 450°C for 12 h) convert Ni_3B fully to Ni_9S_8 . Elemental analysis indicates that boron is still present in the sulfided catalysts (for sulfided Co_2B , 5.8% B, and for sulfided Ni_3B , 3.2% B).

Very little thermodynamic data on the heats of formation of metal borides is available,¹⁸ so prediction of the relative stability of metal borides to the corresponding metal sulfides under HDS conditions could only have been speculative. Given the presence of surface impurities (notably oxides) from the preparation of the metal borides, such sites may serve as nucleation sites for the conversion to the metal sulfides under catalytic conditions. Regardless of detailed mechanism, however, the issue of importance for catalytic applications is the *complete conversion of the metal borides to the metal sulfides*, which are certainly active HDS catalysts. Moreover, this conversion is rapid, at least with respect to required catalyst lifetime in real world application.

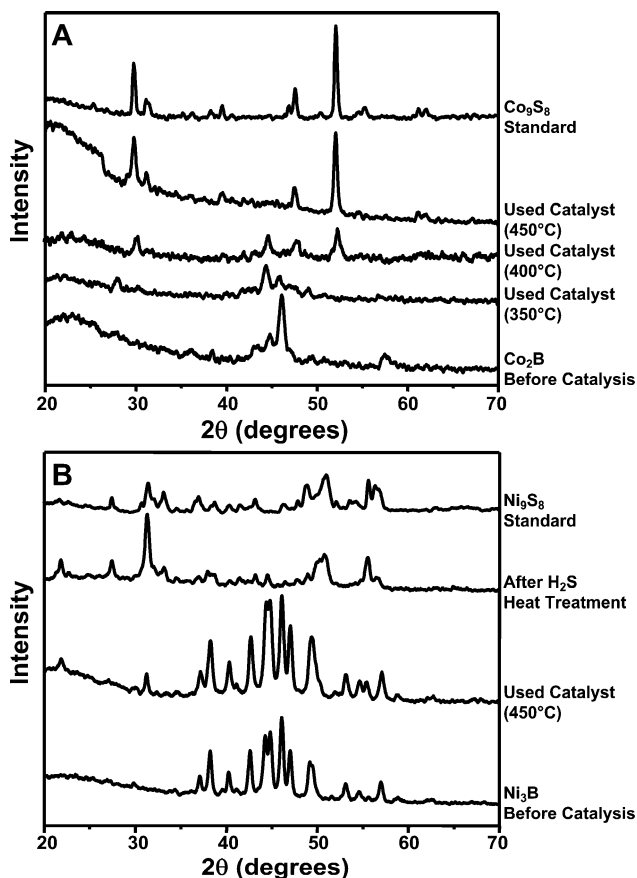


Figure 4. (A) Powder XRD patterns of Co_2B before catalysis, after catalysis (for 20 h at 350 , 400 , and 450°C), and of a Co_9S_8 standard. (B) Powder XRD patterns of Ni_3B , from bottom to top: (i) before catalysis, (ii) after catalysis (for 20 h at 450°C), (iii) after more rigorous heat treatment with H_2S (i.e., $30\text{ cm}^3/\text{min}$ of 10% $\text{H}_2\text{S}/\text{H}_2$ at 450°C for 12 h), and (iv) of a Ni_9S_8 standard.

Similar sulfiding behavior has been observed with metal carbides and nitrides. For example, sulfiding of the surfaces of both Mo_2C and Mo_2N catalysts has been reported and confirmed by TEM and IR-chemisorption studies of catalysts after catalytic use;¹⁹ conversion of the bulk material to molybdenum sulfide, however, has not been observed. Similarly, new metal phosphide catalyst systems, which show promise as stable HDS catalysts, also undergo surface sulfiding. The surfaces of both nickel and molybdenum phosphide catalysts do become sulfided in HDS reactions, but the interior of the metal phosphide particles remain intact, as confirmed by IR-chemisorption studies.^{7,20}

While both Co_2B and Ni_3B display HDS activity, the use of a flow reactor to measure the activity shows that, in actuality, the metal borides display relatively low desulfurization activity. In fact, the primary mode for desulfurization is from catalysis after sulfiding of the boride phase and any impurities, such as surface oxides or elemental Co/Ni, by the sulfur-containing substrate. Upon conversion to metal

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sulfide, the observed catalytic activity behaves like that of the metal sulfide. So, while both cobalt and nickel boride are respectable catalysts for the desulfurization of organic substrates, characterization of the used catalyst shows that the borides are not left intact by the harsh hydrotreating conditions employed in petroleum refining but in fact are completely converted to the metal sulfides.

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Supporting Information Available: Thiophene hydrodesulfurization data for Ni₃B at 450 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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