

Comparison of product selectivity during hydroprocessing of bitumen derived gas oil in the presence of NiMo/Al₂O₃ catalyst containing boron and phosphorus

D. Ferdous^a, A.K. Dalai^{a,*}, J. Adjaye^b

^a *Catalysis and Chemical Reactor Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, Canada SK S7N 5A9*

^b *Syncrude Canada Ltd, Edmonton Research Center, 9421-17th Avenue, Edmonton, Alta., Canada T6N 1H4*

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Abstract

A detailed experimental study was performed in a trickle-bed reactor using bitumen derived gas oil. The objective of this work was to compare the activity of NiMo/Al₂O₃ catalyst containing boron or phosphorus for the hydrotreating and mild hydrocracking of bitumen derived gas oil. Experiments were performed at the temperature and LHSV of 340–420 °C and 0.5–2 h⁻¹, respectively, using NiMo/Al₂O₃ catalysts containing 1.7 wt% boron or 2.7 wt% phosphorus. In the temperature range of 340–390 °C, higher nitrogen conversion was observed from boron containing catalyst than that from phosphorus containing catalyst whereas in the same temperature range, phosphorus containing catalyst gave higher relative removal of sulfur than boron containing catalyst. Phosphorus containing catalyst showed excellent hydrocracking and mild hydrocracking activities at all operating conditions. Higher naphtha yield and selectivity were obtained using phosphorus containing catalyst at all operating conditions. Maximum gasoline selectivity of ~45 wt% was obtained at the temperature, pressure, and LHSV of 400 °C, 9.4 MPa and 0.5 h⁻¹, respectively, using catalyst containing 2.7 wt% phosphorus.

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1. Introduction

As the worldwide supply of light crude oil decreases, more attention is being paid to refining of bitumen derived gas oils and residues to lighter and more valuable liquid products [1]. The heavy oils and bitumens of Alberta are enormous potential resources which require considerable processing in order to substitute conventional petroleum [2]. Oil sand bitumen and the bitumen derived gas oil contain high levels of nitrogen and sulfur compounds. Thus, the products such as heavy gas oil obtained from the processing of bitumen also contain very high levels of nitrogen and sulfur. Catalytic hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) are the processes used commercially for reducing the level of nitrogen and sulfur content in these types of feed stocks. Because of high nitrogen and sulfur contents, HDN and HDS of this gas oil are more

difficult and less effective with conventional NiMo/Al₂O₃ catalyst. HDN and HDS are basically required for environmental reasons. Sulfur and nitrogen are sources of air pollution during combustion and play a significant role in poisoning of naphtha reforming and cracking catalysts [3]. HDN is also required to improve the gas–oil stability.

Several attempts have been taken earlier to modify NiMo/Al₂O₃ catalyst using boron and phosphorus or to develop new catalyst to improve catalysts' hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) activity. Alumina forms a system exhibiting acidic properties with the incorporation of boron in it, which was confirmed by Peil et al. [4] and Wang and Chen [5]. Moreover, borate ions brought about an increase in the activity of CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts in the reaction of HDS [6,7]. The performance of NiMo/Al₂O₃–B₂O₃ catalyst on the HDN of the mixture of light and heavy gas oil (3:1) was investigated by Lulic [8] and he concluded that the catalysts containing boron are more active than commercial HDN catalyst. DeCanio and Weissman [9] studied the characterization and activity of boron (0.3–1.8 wt%) modified commercial NiMo/Al₂O₃ catalyst. At higher boron loadings of over 1.8 wt% boron, poor catalytic

* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.
E-mail address: ajay.dalai@usask.ca (A.K. Dalai).

performance was observed due to the presence of bulk borate phase. Lewandowski and Sarbak [10,11] found that addition of boron did not change the pore volume significantly, however increased the pore radius to 20, 25, 30 and 40 Å in comparison with the unmodified catalyst.

The addition of small amounts of phosphorus in NiMo/Al₂O₃ catalyst has also showed positive effect on both their HDN and HDS activities and these catalysts are less susceptible to coking [12]. It has been reported that phosphorus enhances the solubility of the molybdate by the formation of phosphomolybdate complexes, which make the catalyst preparation easier and may lead to a different dispersion of the Mo and Co/Ni. Also, addition of phosphorus causes the formation of easily reducible and sulfided forms, such as multilayered molybdate, crystalline Al₂(MoO₄)₃ and MoO₃ on the catalyst surface [12–14]. On the other hand, phosphorus causes interactions of metal atoms with alumina support surface in case of sulfided cobalt and nickel [15]. However, Iwamoto and Grimblot [16] reported that phosphorus modifies the textural characteristic and acidity of the catalysts. From work on the unpromoted MoP/Al₂O₃ catalyst, they have shown that the thiophene HDS activity was not promoted by phosphorus loading while large amount of phosphorus decreased the catalytic performances, probably by formation of bulk MoO₃ in oxide precursor. Eijsbouts et al. [17] found beneficial effects of phosphorus in studies of quinoline HDN. They have suggested that, phosphorus may play a direct role in C–N bond cleavage. On the other hand, Lewis et al. [14] and Eijsbouts et al. [17] did not find any positive effect of phosphorus during hydrodesulfurization of thiophene. Jian et al. [18] found no effects in the HDN of piperidine and pyridine over NiMo/Al₂O₃ catalyst. But in the presence of phosphorus the HDN activity decreased as the phosphorus content in the catalyst increased. They have concluded that phosphorus has a negative effect on the C–N bond cleavage in piperidine, as well as on the subsequent hydrogenation of the C₅ alkene intermediates.

In order to clarify these discrepancies, Ferdous et al. [19,20] prepared a series of NiMo/Al₂O₃ catalyst containing boron and phosphorus. The initial activity and stability of these catalysts for HDN and HDS of heavy gas oil derived from Athabasca bitumen was tested in a trickle-bed reactor at the temperature, pressure, LHSV and H₂/feed ratio of 385 °C, 8.7 MPa, 1 h⁻¹ and 600 mL/mL, respectively. They concluded that the total (TN), basic (BN) and non-basic nitrogen (NBN) conversions increased from 61.9 to 78.0 wt%, from 78.9 to 93.0 wt% and from 52.8 to 70.0 wt%, respectively, with the increase in boron concentration from 0 to 1.7 wt% to NiMo/Al₂O₃ catalyst. Similarly, TN, BN and NBN conversions increased from 61.9 to 78.4 wt%, from 78.9 to 91.0 wt%, and from 52.8 to 71.6 wt% with the addition of 2.7 wt% phosphorus to NiMo/Al₂O₃ catalyst. Diaz-Real et al. [21] studied the HDN of Athabasca bitumen-derived heavy gas oil over Ni–Mo, Ni–W and Co–Mo catalysts supported on zeolite. Maximum nitrogen and sulfur conversions of 75 and 99 wt% were obtained at the temperature pressure, LHSV and H₂/feed ratio of 425 °C, 6.89 MPa, 2 h⁻¹ and 890 mL/mL, respectively.

The boiling point (BP) distribution is one of the critical properties for the evaluation of product qualities.

The distribution curve of any hydrocarbon mixture is important because it indicates the quantities of the useful fractions to refiner [2]. As the importance of production of synthetic crude oil from oil sands is increasing day by day, in addition to the removal of nitrogen and sulfur, it is also important to study the selectivity, yield and quality of different liquid products such as naphtha, gasoline, diesel, kerosene and light cycle oil (LCO). To our knowledge no literature is available on the effect of operating variables on the product distribution and selectivity from hydrotreatment of bitumen derived gas oil using NiMo/Al₂O₃ catalyst containing boron or phosphorus. In this work, a systematic study has been conducted to study the effect of operating variables on the HDN and HDS of bitumen derived gas oil. Boiling point distribution of products and product selectivity was also studied in this work.

2. Experimental

2.1. Catalyst preparation and characterization

In this work, three catalysts namely NiMo/Al₂O₃, NiMoB/Al₂O₃, and NiMoP/Al₂O₃ were prepared using incipient wetness coimpregnation method. Ni and Mo in all catalysts were maintained at 3 and 14 wt%, respectively. In this method, an ammoniacal solution (28 wt% concentrated NH₃) was prepared using required amount of ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] and nickel nitrate [Ni(NO₃)₂·6H₂O]. NiMoB/Al₂O₃ catalysts were prepared by impregnating appropriate solutions of boric acid (H₃BO₃) on to a NiMo/Al₂O₃ catalyst. Boron concentration in the catalyst was maintained at 1.7 wt%. Phosphorus concentration in NiMoP/Al₂O₃ catalyst was maintained at 2.7 wt% using appropriate amount of phosphoric acid. The detailed preparation procedure is given elsewhere [19]. All catalysts were characterized extensively using inductivity coupled plasma (ICP), BET surface area, pore volume and pore size measurement, temperature programmed reduction (TPR), temperature programmed desorption (TPD), scanning electron microscopy (SEM), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), transmission electron microscopy (TEM), X-ray photo electron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The detail description on these analyses is given elsewhere [19].

2.2. HDN and HDS studies

Hydrotreating studies of bitumen derived gas oil using NiMoB/Al₂O₃ and NiMoP/Al₂O₃ were performed in a micro scale trickle bed reactor using 5 mL of catalyst. Experiments were performed at the temperature and LHSV of 340–420 °C and 0.5–2 h⁻¹, respectively. Pressure and H₂ flow rate were maintained constant at 9.4 MPa and 50 mL/min, respectively, in all cases. The feed material was characterized with respect to boiling range, sulfur and nitrogen content, basic nitrogen, non-basic nitrogen content, aromatics content and density. The detailed experimental procedures and set-up are given

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