

# The effect of phosphorus on hydrotreating property of NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nitride catalyst

V. Sundaramurthy<sup>a</sup>, A.K. Dalai<sup>a,\*</sup>, J. Adjaye<sup>b</sup>

<sup>a</sup> *Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK S7N 5A9, Canada*

<sup>b</sup> *Syncrude Edmonton Research Centre, Edmonton, AB T6N 1H4, Canada*

Received 23 July 2007; received in revised form 7 November 2007; accepted 8 November 2007

Available online 22 November 2007

## Abstract

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported P-doped nickel molybdenum (NiMo) nitride hydrotreating catalysts with 12 wt.% of Mo, 3 wt.% Ni and 0–2.5 wt.% P were synthesized by means of temperature-programmed reaction, and characterized by BET surface area analysis, elemental analysis, CO uptake titration, DRIFT study of adsorbed CO, temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) of NH<sub>3</sub>. The activity of the nitride catalysts was studied in a trickle-bed reactor operated at 8.8 MPa and 385 °C in the hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of heavy gas oil (HGO) derived from Athabasca bitumen. The CO uptakes measurement showed that P addition to NiMo nitride improves the dispersion. DRIFT spectra of CO adsorption evidenced that the number of Mo<sup>2+</sup> sites on the surface of NiMo nitride increases with increasing P concentration and reaches optimum with 2.0 wt.% of P. TPD of NH<sub>3</sub> indicated an increase of strong acid sites and also strengthening of moderate acid sites in NiMo nitride on P doping. All the nitride catalysts have suffered partial sulfidation during initial period of hydrotreating of HGO. HDN activity of NiMo nitride was promoted greatly by the phosphorus content, reached a maximum with P content of 1.6 wt.%. An increased acidity of P-doped NiMo nitrides accelerated C–N bond breaking and thus enhanced the HDN activity. No significant change was observed in HDS of HGO over NiMo/Al<sub>2</sub>O<sub>3</sub> nitride catalyst on P doping.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:**  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support; NiMo nitride; Phosphorus doping; DRIFT of CO adsorption; Hydrodesulfurization; Hydrodenitrogenation; Heavy gas oil

## 1. Introduction

As light crude oil supplies diminish, there is increasing interest in the conversion of oil sand bitumen derived heavy gas oils into transportation fuels. Bitumen derived heavy gas oils contain high levels of nitrogen and sulfur compounds. Because of high nitrogen and sulfur content, hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) of this heavy gas oils are more difficult and less effective with conventional NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sulfide catalyst. Current commercial hydrotreatment catalysts are typically optimized for the removal of sulfur from light crudes. So, novel catalysts are required to be effective in reducing the nitrogen and sulfur contents with less catalyst deactivation and H<sub>2</sub> consumption. Transition bimetallic nitrides, NiMo and CoMo [1–10] have been recently studied

as an alternative to CoMo and NiMo sulfide catalysts for the hydrotreating. The NiMo nitride catalyst showed higher HDN activity than NiMo sulfide catalysts [4].

Phosphorus is used as a third element in conventional NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sulfide catalyst to increase hydrotreating activity. P doping promotes both HDN [10–14] and HDS [15–19] activities of NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sulfide catalyst. But few studies [20,21] showed that phosphorus doping did not affect the HDS activity of NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sulfide catalyst, whereas it promoted the HDN activity. These phosphorus effects in NiMo/Al<sub>2</sub>O<sub>3</sub> sulfide catalyst were explained in terms of dispersion of the metal salts on the support, modification of acid sites, or formation of a new active phase. Analogous to the Mo sulfide catalyst, the P addition to monometallic nitride, especially, Mo nitride promotes the HDN of indole and HDS of benzothio-*phene* [22,23], and hydrogenation of propene [24]. Only one report is available on phosphorous-doped bimetallic NiMo nitrides [25]. This study illustrates that P doping in NiMo and CoMo nitrides promotes the HDS of dibenzothiophene.

\* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.

E-mail address: [ajay.dalai@usask.ca](mailto:ajay.dalai@usask.ca) (A.K. Dalai).

However, information available on the effect of P on structural properties of NiMo nitride is very limited. The effect of P on HDN activity of NiMo nitride is unknown either with model compound or real feed. In this investigation, a series of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported NiMo nitrides with various loadings of P were synthesized. The effect of P loading on NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nitride with respect to structural properties and HDN and HDS activities using Athabasca heavy oil (HGO) as feed stock were studied.

## 2. Experimental

### 2.1. Catalyst preparation

The preparation of the nitride catalyst involves: (i) the preparation of oxide precursors of desired composition by an incipient wetness co-impregnation and (ii) the nitridation of oxide precursors by temperature-programmed reaction (TPRe). A series of P-doped NiO·MoO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> precursors (12 wt.% Mo and 3.0 wt.% Ni) with various amount of P (0–2.5 wt.%) were prepared by coimpregnation of precalcined  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (500 °C, air) with an aqueous solution (pH 4) containing the appropriate amounts of ammonium heptamolybdate (99.9%, Aldrich), nickel nitrate (99%, BDH) and phosphoric acid (AnalaR, BDH). The wet samples were dried at 120 °C for 5 h and then calcined at 500 °C for 5 h in air.

The nitriding of P-doped NiO·MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> samples were carried out in an inconel reactor using NH<sub>3</sub> (99.9%, Praxair). In a typical synthesis, 10 ml of oxide precursors sample was heated to 400 °C at rate of 3 °C/min in flowing He (flow rate 50 cm<sup>3</sup>/min). At this temperature, the flow was switched to NH<sub>3</sub> at a flow rate of 50 cm<sup>3</sup>/min and then the temperature was ramped at 1 °C/min from 400 °C to 700 °C. After 4 h at 700 °C, the sample was cooled to room temperature in flowing He, and then passivated in a mixture of 1% O<sub>2</sub>/He to avoid the mass oxidation of the nitride. The prepared nitride catalysts are in the form of extrudates of 1 mm diameter and 8 mm length.

### 2.2. Catalyst characterization

Metallic content in the nitride samples was determined by plasma atomic emission method (ICP). Nitrogen content of nitride catalysts was carried out using CHNSO analyzer (Elementar Americas Inc.). BET surface area, average pore volume, and CO uptake of nitrides were determined using Micromeritics ASPA-2000. Prior to the analysis, the passivated nitride catalysts were *in situ* reduced in flowing H<sub>2</sub> at 450 °C and degassed in vacuum at 200 °C until the static pressure remained less than  $6.6 \times 10^{-4}$  Pa. BET surface area, average pore volume and average pore diameter were measured by means of the adsorption of N<sub>2</sub> at 78 K. The CO uptake of nitride catalysts was measured at 35 °C. The XRD patterns of the passivated samples were taken on a Bruker diffractometer using Cu K $\alpha$  radiation. H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) of the samples was carried out using a ChemBET-3000 instrument. A 0.25 g of each sample was placed in a U-shaped quartz cell and purged with He at 400 °C for 1 h in order to

remove impurities on the surface of the sample. After the sample was cooled to room temperature in flowing He, TPR was carried out in 3% H<sub>2</sub>/N<sub>2</sub> (v/v) mixture with a flowing rate of 30 ml/min. The heating rate was 5 °C/min from room temperature to 600 °C. TPR profiles were recorded with a thermal conductivity (TC) detector.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO adsorption experiments were performed using a PerkinElmer Spectrum GX instrument equipped with DTGS detector and a KBr beam splitter. Prior to the CO adsorption, the nitride catalyst was *in situ* reduced in Spectrotech diffuse reflectance cell with H<sub>2</sub> at 450 °C for 2 h. At this temperature, the flow was switched to He at a flow rate of 50 cm<sup>3</sup>/min and the temperature was decreased to 30 °C and then background spectrum was recorded. The adsorption process was carried out at 30 °C by introducing CO into the system for 30 min. After adsorption, the system was subsequently purged with He at a flow rate of 50 cm<sup>3</sup>/min for 20 min. The spectra were collected in He flow with a resolution of 4 cm<sup>-1</sup> and 64 scans in the region 4000–1000 cm<sup>-1</sup>, and the background spectrum was subtracted from the post-adsorption spectra.

Temperature-programmed oxidation (TPO) of the nitride samples were performed by TG/DTA instrument (Pyris Diamond, PerkinElmer). In a typical experiment, 30 mg of sample was heated to 600 °C with a heating rate of 5 °C/min in the presence of air flow (50 cm<sup>3</sup>/min), and the weight change caused by reactions was measured. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) experiments were carried out in ChemBET-3000 system equipped with a TC detector. Before NH<sub>3</sub> adsorption, the samples were *in situ* reduced with H<sub>2</sub> at 450 °C, and cooled to room temperature in He flow, and contacted with a 3% NH<sub>3</sub>/He (v/v) mixture for 1 h. The ammonia adsorbed sample is purged for 30 min with He (30 cm<sup>3</sup>/min) at room temperature and desorption of NH<sub>3</sub> was performed in flowing He (30 cm<sup>3</sup>/min) with a heating rate of 5 °C/min.

### 2.3. Hydrotreating test

The hydrotreating tests were carried out under steady-state operation in a trickle-bed reactor in down-flow mode. The system consists of liquid and gas feed sections, a high-pressure reactor, a heater with temperature controller for precisely controlling the temperature of the catalyst bed, a scrubber for removing the ammonium sulfide from the reaction products, and a high pressure gas–liquid separator. The high pressure reaction set up used in this study simulates the process that takes place in an industrial hydrotreater. The reactor is made of an inconel tube. The length and internal diameter of the reactor are 240 mm and 14 mm, respectively. The 5 cm<sup>3</sup> of nitride catalyst (3.8 g) diluted with silicon carbide of 90 mesh was loaded into the reactor. The detail of catalyst loading is described elsewhere [26]. The heavy gas oil used in this study contains 0.31 wt.% of N and 4 wt.% S and other details are given in elsewhere [26].

Prior to the catalytic run, the passivated nitrides were reduced in flowing H<sub>2</sub> at 450 °C for 4 h to remove passivating

Download English Version:

<https://daneshyari.com/en/article/43681>

Download Persian Version:

<https://daneshyari.com/article/43681>

[Daneshyari.com](https://daneshyari.com)