



Tetraalkylthiomolybdates-derived Co(Ni)Mo/ γ -Al₂O₃ sulfide catalysts for gas oil hydrotreating

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ABSTRACT

Bimetallic γ -Al₂O₃-supported CoMo and NiMo sulfide catalysts were prepared using ammonium thiomolybdate (ATM), tetramethylammonium thiomolybdate (TMATM), tetrabutylammonium thiomolybdate (TBATM), cetyltrimethylammonium thiomolybdate (CTMATM) as precursors for MoS₂. The CO chemisorption study showed better dispersion of MoS₂ on γ -Al₂O₃ support in the catalysts prepared from the thiosalts precursor than the catalysts obtained from the oxides precursor. Among the catalysts derived from tetraalkylammonium thiomolybdates, Co(Ni)Mo/ γ -Al₂O₃ catalysts derived from CTMATM precursor showed higher CO uptake. The presence of molybdenum carbide phase in the Co(Ni)MoS₂ catalysts formed from the tetraalkylammonium thiomolybdates is evidenced by NEXAFS study. DRIFT spectra showed lesser amount of partially sulfided molybdenum species in thiosalts-derived catalysts compared to those catalysts prepared by the conventional oxide precursors. The HDN and HDS activities of Co(Ni)Mo/ γ -Al₂O₃ sulfide catalysts with coker light gas oil (KLGO) feed at temperature, pressure and LHSV of 350 °C, 8.8 MPa and 1.5 h⁻¹ were studied. The activity of thiosalts-derived catalysts is significantly higher than the respective oxides precursor catalysts. The presence of carbo-sulfide phases promotes the HDN and HDS activities of tetraalkylammonium thiomolybdates derived NiMo and CoMo catalysts. In both NiMo and CoMo series, catalyst prepared by *in situ* decomposition CTMATM showed a maximum HDN and HDS activities as result of better dispersion of active phase on the support via microemulsion.

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1. Introduction

The conventional methods of hydrotreating catalysts preparation consist of supporting the transition-metal salts (Mo or W plus Co or Ni) onto γ -Al₂O₃, followed by calcination to produce the stable oxidic materials that must be sulfided either prior to or during the start-up of the hydrotreating process. The strong interaction of the molybdenum or tungsten oxide with the γ -Al₂O₃ makes the incomplete sulfidation of the conventional catalysts. On the other hand, the ammonium thiomolybdates, which have sulfur already bound to the metal atoms in a tetrahedral coordination, and their decomposition is expected to lead more completely sulfided catalysts. The thiosalt decomposition method has been widely used in the preparation of molybdenum and tungsten sulfide catalysts. The metal sulfide catalysts formed by decomposition of the thiosalts showed higher catalytic activity than the catalysts prepared by the conventional techniques [1,2]. The cobalt and nickel act as effi-

cient HDN and HDS promoter for conventionally prepared MoS₂ or WS₂ catalysts. The cobalt promoted unsupported hydrotreating catalysts prepared from the decomposition of thiosalts have shown higher catalytic activities than the unpromoted catalyst and also other catalysts prepared by conventional techniques [3–5].

Alonso et al. [6–8] produced the unsupported MoS₂ catalysts from carbon-containing thiosalts of the type (NR₄)₂MoS₄ (where R = alkyl group), and observed greater catalytic activities than those obtained from the ammonium thiomolybdate. Increasing attention has been paid to the role of carbon in the activity of MoS₂ and RuS₂ catalysts, with some studies suggesting that the active phase of these compounds involves a high surface area MoS_{2-y}C_z compounds, where 0.01 ≤ y ≤ 0.5 and 0.01 ≤ z ≤ 3 [9]. The first claims of the importance of carbon in these catalysts are made with regard to the synthesis of RuS_{2-x}C_x compounds, where carbon atoms substituting surface sulfur atoms were detected [9,10].

Exchange of thiomolybdate ammonium cation with the methyl, butyl, hexylammonium cations resulted in MoS₂ phases with high-surface area and mesoporous structure [11]. The HDS of dibenzothiophene is strongly affected by the nature of alkylammonium groups, and highest activity observed with the catalyst formed from butylammonium group. The effect of exchange of

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ammonium cation with bulk cetyltrimethylammonium cation is unknown. Further most of the catalysts prepared by thiosalt decomposition method are unsupported catalysts and their activity was studied with model compounds. Only fewer studies related to supported catalysts have been reported in the literature due to difficulties involved in understanding the effect of the support, and also in their characterization [12–15]. The study on the γ - Al_2O_3 -supported thiosalt-derived bimetallic sulfide catalysts is scarce in literature. The aims of this work are to prepare the γ - Al_2O_3 supported NiMo and CoMo sulfides by using thiosalts as precursor for MoS_2 and study their hydrotreating activity with the real feedstock. Ammonium thiomolybdate (ATM), tetramethylammonium thiomolybdate (TMATM), tetrabutylammonium thiomolybdate (TBATM) and cetyltrimethylammonium thiomolybdate (CTMATM) were selected as the precursors for preparation of NiMo and CoMo series of catalysts. The properties of these samples were compared with those prepared by conventional oxide precursors.

2. Experimental

Ammonium hydroxide solution of ammonium heptamolybdate was bubbled with H_2S gas at room temperature to get crystals of ammonium thiomolybdate. The aqueous solution of ammonium thiomolybdate was mixed with methanol solution of tetraalkylammonium bromide to get tetraalkylammonium thiomolybdate precursors, $(\text{NR}_4)_2\text{MoS}_4$ (R = methyl, butyl, and cetyl). Supported bimetallic catalysts were prepared by wet co-impregnation of γ -alumina with methanol–water solutions containing appropriate amounts of tetraalkylammonium thiomolybdate and nickel nitrate (99.9%, BDH) or cobalt nitrate (99.9%, BDH). The γ - Al_2O_3 supported unpromoted Mo catalyst was prepared by following the same method as above using only ammonium thiomolybdate. The samples were vacuum dried at 120°C for 2 h. The conventional NiMo and CoMo catalysts were prepared through incipient wetness co-impregnation method using aqueous solution containing the appropriate amounts of ammonium heptamolybdate, nickel nitrate or cobalt nitrate. The impregnated samples were dried at 120°C for 5 h and then calcined at 500°C for 5 h in air.

The contents of Ni, Co, and Mo samples were determined by plasma atomic emission method (ICP). The carbon content of sulfided catalysts was carried out using CHNSO analyzer (Elementar Americas Inc.) The BET surface area, pore diameter and pore volume of *in situ* sulfided samples were measured by means of the adsorption of N_2 at 78 K. The carbon monoxide (CO) uptake on sulfided catalysts was measured using the Micromeritics ASAP 2000 instrument. Before chemisorption measurement, 200 mg of sample was sulfided *in situ* with 10% $\text{H}_2\text{S}/\text{H}_2$ at 400°C for 2 h, and then evacuated until the static pressure remained less than 6.6×10^{-4} Pa. Pulses of CO were passed over the sample to measure the total gas uptake at 35°C . X-ray powder diffraction (XRD) patterns for sulfided catalysts were recorded on a Rigaku diffractometer using monochromatic $\text{Cu K}\alpha$ radiation in step scanning mode, in the range $10^\circ < 2\theta < 80^\circ$.

Near-edge X-ray absorption fine structure (NEXAFS) measurements of selected sulfided catalysts were carried out at the high resolution spherical grating monochromator (SGM) beamline of the Canadian Light Source at University of Saskatchewan. The powder samples were pressed into a stainless steel sample holder and spectra were recorded near the K-edge of the C by measuring the fluorescence electron yield. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) experiments were performed using a PerkinElmer Spectrum GX instrument equipped with DTGS detector and a KBr beam splitter. Approximately 30 mg of sample was loaded into a sample cup inside a Spectrotech diffuse

Table 1
Characteristics of KLG0 derived from Athabasca bitumen

Characteristic	KLGO
Nitrogen (ppm)	2439
Sulfur (ppm)	23,420
Density (g/ml)	0.95
Boiling point distribution	
IBP ($^\circ\text{C}$)	169
FBP ($^\circ\text{C}$)	548
Boiling range ($^\circ\text{C}$)	
IBP–250	6
250–300	22
300–350	31
350–400	23
401–450	9
450–500	6
500–FBP	3

reflectance *in situ* cell equipped with ZnSe windows and a thermocouple mount that allowed direct measurement of the sample surface temperature. The oxide form of conventional catalysts were degassed at 200°C for 2 h with He flow and spectra were recorded at room temperature. Both conventional and thiomolybdates samples were sulfided *in situ* in a Spectrotech diffuse reflectance cell with 10% $\text{H}_2\text{S}/\text{H}_2$ ($30\text{ cm}^3/\text{min}$) at 400°C for 2 h. The spectra were recorded at 30°C with He flow. For the CO adsorption, the sulfided sample was exposed to CO (99% pure) at a flow rate of $30\text{ cm}^3/\text{min}$ for 30 min. The spectra for each experiment were averaged over 64 scans with a nominal 8 cm^{-1} resolution. The sample loaded in the sample cup was weighed after the experiment. The bands intensity was corrected for the differences in the weight of the sample and normalized to 30 mg.

Hydrotreating experiments were performed in a trickle bed reactor under typical industrial conditions. The coker light gas oil (KLG0) derived from Athabasca bitumen is used as a feed for hydrotreating studies. The feed properties are given in Table 1. The high-pressure reaction setup used in this study simulates the process that takes place in industrial hydrotreaters. The details of reaction setup and catalyst loading into the reactor are described elsewhere [16]. Appropriate amount of catalyst precursor, which would yield 3.8 g of catalyst after sulfidation, was loaded into the reactor. The precursor sample was *in situ* sulfided to get active sulfide phase at 400°C for 8 h in the presence of 10% $\text{H}_2\text{S}/\text{H}_2$ (v/v). Following sulfidation, the catalyst was precoked (stabilized) with KLG0 for 5 days at a temperature of 370°C , pressure of 8.8 MPa, and LHSV of 1.5 h^{-1} . After precoking, HDN and HDS activities of catalysts were studied at 350°C for 48 h by maintaining pressure, H_2/feed ratio and LHSV at 8.8 MPa, 600 ml/ml and 1.5 h^{-1} , respectively. The products were collected at 12 h intervals. The products were stripped with N_2 for removing the dissolved NH_3 and H_2S . The total nitrogen content of the liquid product was measured by combustion/chemiluminescence technique following the ASTM D4629 method, and the sulfur content was measured using combustion/fluorescence technique following the ASTM 5463 method. The sulfur and nitrogen were analyzed in an Antek 9000 NS analyzer.

3. Results and discussion

3.1. Chemical composition and textural properties

The CoMo/ γ - Al_2O_3 sulfide catalysts derived from the ammonium thiomolybdate, tetramethylammonium thiomolybdate, tetrabutylammonium thiomolybdate, cetyltrimethylammonium thiomolybdate are named as CoMo-1, CoMo-2, CoMo-3 and

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