



## Hydroprocessing on chromium-containing metal sulfide catalysts

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### ABSTRACT

We showed previously that unsupported catalysts prepared from amine thiomolybdates incorporated with bivalent metals (Fe, Ni, Co) are highly active for hydrodenitrogenation (HDN) and hydrodesulfurization (HDS). In particular, an iron-promoted molybdenum sulfide catalyst gives a much higher HDN-to-HDS activity ratio than commercial supported catalysts. The present study examines trivalent chromium as a promoter for MoS<sub>2</sub>. The catalyst precursors are synthesized via two routes: one involves olation, the other chelation. Tests with a catalytic cycle oil show that the behaviors of the Cr-containing catalysts prepared from the two routes are qualitatively similar. Chromium is a more effective HDN promoter than iron. The Fe<sub>0.5</sub>Cr<sub>0.5</sub>Mo<sub>y</sub> (1 ≤ y ≤ 1.5) trimetallic sulfide is more active and selective for HDN than FeMo and CrMo<sub>y</sub> bimetallic sulfides. The predominant phase in the chromium-containing catalysts comprises nanocrystalline MoS<sub>2</sub> and amorphous Cr<sub>2</sub>S<sub>3</sub>.

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### 1. Introduction

Hydroprocessing is an integral part of fuels and lubes refining. Most refinery streams are hydroprocessed. Depending on the severity of the reaction conditions, the reactions taking place in a hydroprocessing reactor include hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodearomatization (HDA), and hydrocracking. Collectively, these reactions reduce air pollution, protect catalysts in downstream processing, and improve product quality and stability. The global demand for middle distillates (200–370 °C boiling range; diesel, jet fuel, etc.) is expected to escalate in coming decades. Concomitant with this trend are the growing need to process heavy oils and the increasingly stringent environmental regulations on transportation fuels. The nitrogen content in crude oils increases with boiling point [1]. Little wonder that the past several years have seen a significant increase in the nitrogen content of hydroprocessing feedstocks [2]. Indigenous organonitrogen species are potent inhibitors to HDS, HDA, hydrocracking, and catalytic cracking. As a result, the objectives of many refining processes cannot be achieved unless the nitrogen level is reduced to a sufficiently low level [3,4]. For instance, in hydrocracking a stand-alone, high-pressure reactor is used solely for HDN. A high-HDN-low-HDS catalyst is desirable in lubricating oil

hydroprocessing because nitrogen species are pro-oxidants while sulfur species are anti-oxidants. Developments of new or improved HDN catalysts and processes have been and will continue to be important in the years ahead [4].

The catalysts commonly used in hydroprocessing comprise molybdenum or tungsten sulfides that are promoted by Co and/or Ni [5]. The precursors to these catalysts are mixed metal oxides supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. An essential step in the catalyst preparation is high-temperature calcination in air followed by sulfiding with a sulfur-bearing stream. Great strides have been made to develop new hydroprocessing catalysts via organometallic modeling approaches [6]. A basic tenet is that properly prepared organometallic complexes and clusters may mimic some salient features of hydroprocessing active sites. Lots of studies have been done on the effects of bivalent metals as promoters. But relatively few have been done on trivalent metals or combined bi- and trivalent metals.

Previously, we discussed the preparation of unsupported transition metal sulfide catalysts using heterometallic sulfur or oxygen coordination compounds as precursors [7–11]. The formation of catalytically active sites from such compounds does not involve calcination in air. An example is the metal amine thiomolybdate/thiotungstate (MAT) family, which can be represented by M<sub>x</sub>M'<sub>1-x</sub>(amine)<sub>6/n</sub>Mo<sub>y</sub>W<sub>1-y</sub>S<sub>4</sub> (0 ≤ x, y ≤ 1) with M and M' being bivalent promoter metals such as Ni, Co, Fe, and Mn. The total denticity of the amine chelating ligand is six, so the subscript *n* is the total number of nitrogen atoms in the amine. The amines used here are ethylenediamine (en) and diethylenetriamine (dien) [7–11]. The synthesis can be extended to include more than two

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