

Hydroprocessing catalysis on metal sulfides prepared from molecular complexes

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Abstract

This article gives an overview of preparation, characterization, and activity/selectivity of bulk and dispersed metal sulfide catalysts prepared from two families of molecular complexes. New promoter metals are identified. Behavioral features of these molecular-complex-derived catalysts for different hydroprocessing applications are discussed. These catalysts share some common characteristics that make them distinct from conventional Al_2O_3 -supported catalysts. Examples are given to show the importance of understanding catalyst–feedstock interactions and balancing catalyst hydrogenation and hydrogenolysis functionalities.

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1. Introduction

Hydroprocessing catalysis has been and will continue to be an active research area in the coming years. The key drivers are the tightening environmental regulations, dwindling supply of high-quality crude oils, and growing demands for transportation fuels and lubes. The increasingly large incentive for high-performance catalysts has stimulated the development of novel catalytic materials. A case in point is the recent commercialization of the Nebula catalyst, which is an unsupported (bulk) mixed metal sulfide [1]. Its performance justifies its higher manufacturing cost compared to that of conventional Al_2O_3 -supported catalysts.

Bulk metal sulfides have been part of our laboratory's hydroprocessing research portfolio for decades. The first part of this article is a brief review of selected parts of the portfolio whose objective was to develop new catalysts with greater control of activity and/or selectivity relative to conventional catalysts. Specifically, it highlights the preparation and properties of two classes of molecular complexes, which upon thermal decomposition and sulfiding yield highly active and/or selective metal sulfide catalysts for various hydroprocessing applications involving very different feedstock types. Also

highlighted are significant observations made in the course of dispersing these catalyst precursors on oxide supports. The exploitation of these molecular-complex-derived catalysts led to the discovery of new synergistic promoter metals that perhaps would not otherwise be identified.

The second part of this article gives an account of kinetic characterization of conventional and experimental catalysts, aiming at gaining a better understanding of process chemistry. The emphasis is on the competition between hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Examples are given to show the benefit of conducting model-compound experiments alongside with real-feed studies. A case is made for probing reaction dynamics under transient conditions. The results obtained from model-compound and real-feed experiments, taken together, provide insights into the interactions between catalyst hydrogenation/hydrogenolysis functionalities and feedstock composition. The article concludes with a summary of general characteristics of bulk metal sulfide catalysts.

2. Metal amine thiometallates as catalyst precursors

2.1. Bivalent promoter metals

Metal amine thiometallates (MAT) are a family of transition metal/sulfur complexes that have been exploited

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as hydroprocessing catalyst precursors [2–4]. The compositions of these precursors can be systematically varied. As an example, a doubly promoted system can be represented by $M_xM'_{1-x}(\text{amine})_{6/b}\text{Mo}_y\text{W}_{1-y}\text{S}_4$ in which M and M' are different bivalent metal promoters, $0 \leq x, y \leq 1$, and b is the total number of nitrogen atoms in the amine chelating ligand. The amine ligand used in the present study is ethylenediamine (en) or diethylenetriamine (dien). Examples of M and M' are Ni, Co, and Fe. The presence of two promoter metals can generate a synergistic effect [5–8]. It is straightforward to extend the synthesis to include more than two promoter metals. The preparation of the MAT-based bulk catalysts does not involve calcination in air; the final catalysts are obtained from thermal decomposition of MAT in a sulfur-bearing stream (e.g., 10% H_2S in H_2) at temperatures typically between 320 and 400 °C. Varying decomposition procedures would lead to different catalytic properties. After the decomposition and sulfiding treatment, the bulk metal sulfides generally contain small amounts of carbon and nitrogen. The BET (with N_2) surface areas of the resulting bulk catalysts typically range between 5 and 15 m^2/g .

Many of the MAT-derived bulk sulfide catalysts have higher volumetric HDS and/or HDN activities than commercial sulfided $\text{CoMo}/\text{Al}_2\text{O}_3$ and $\text{NiMo}/\text{Al}_2\text{O}_3$ catalysts [2–11]. This family of catalysts shows a strong effect of metal composition. For illustration, Fig. 1 shows that the HDN activity of the FeMo sulfide catalyst can be significantly increased by copromotion with Ni or Co [6]. These doubly promoted molybdenum sulfides are more effective for HDN than their singly promoted counterparts. Activity and selectivity data were obtained in tests with light catalytic cycle oil (LCO), a most refractory class of feedstocks rich in aromatics and five-membered ring nitrogen heterocycles such as alkylcarbazoles [5].

We next explore the extent to which the foregoing strong metal composition effect can be carried over to trivalent chromium as a promoter or copromoter.

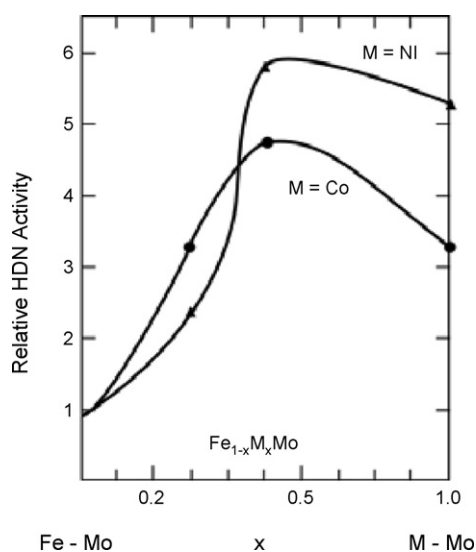
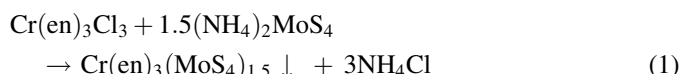


Fig. 1. Effects of metal composition on relative HDN activities of $\text{Fe}_{1-x}\text{Ni}_x\text{Mo}$ (▲) and $\text{Fe}_{1-x}\text{Co}_x\text{Mo}$ (●) sulfides.

2.2. Bulk Cr-promoted catalysts

To extend the synthesis to include chromium, some modifications are necessary. This leads to two routes for preparing chromium-containing catalysts [8–11]: one involves the aforementioned chelation chemistry; the other is related to the ololation process [12]. In the former case, the formation of chromium–amine thiomolybdate salt is not kinetically favored over hydrolysis. So an essential step in the chelation route entails isolating Cr^{3+} via the formation of $\text{Cr}(\text{en})_3\text{Cl}_3$ in a non-aqueous environment. This is done by slowly adding anhydrous CrCl_3 to en, resulting in a yellow precipitate which is filtered and recovered. $\text{Cr}(\text{en})_3\text{Cl}_3$ is soluble and stable in water, so $[\text{Cr}(\text{en})_3]_2(\text{MoS}_4)_3$ can be prepared by metathesis in the presence of en, leading to an orange-red precipitate, as summarized below [8–10].



The synthesis involving ololation is illustrated by the following example. Forty grams of ammonium thiomolybdate $(\text{NH}_4)_2\text{MoS}_4$ was dissolved into 82 ml of dien. The resulting dark red solution was cooled to 0 °C in an ice bath. In a separate flask, 27.56 g of $\text{Cr}(\text{OH})_3 \cdot 6\text{H}_2\text{O}$ was dissolved into 250 ml of distilled water. To this solution was added dien, leading to the formation of a precipitate. The resulting slurry was allowed to stand for 2–3 h and then added slowly to the $(\text{NH}_4)_2\text{MoS}_4/\text{dien}$ solution. This resulted in the formation of a bright orange precipitate which was separated by filtration, washed with water and ethanol and dried at ambient temperature under vacuum. Ninety-one grams of the catalyst precursor was obtained, with the empirical formula $[\text{Cr}(\text{OH})_3 \cdot 1.5\text{H}_2\text{O}](\text{H}_2\text{dien})_{1.1}(\text{MoS}_4)_{1.1}$.

The Cr-containing catalysts prepared from the ololation route were tested with LCO at 325 °C and 3.15 MPa (8–10). Their relative (hence dimensionless) volumetric HDS and HDN activities and selectivities are compared with those of commercial Al_2O_3 -supported CoMo and NiMo catalysts (Catalysts A and B, respectively) and those of the MAT-derived bulk FeMo catalyst. Table 1 summarizes the results. The HDN selectivity is defined as the ratio of the rate constant of HDN to that of HDS, that is, $S_N = k_{\text{HDN}}/k_{\text{HDS}}$. Referring to Table 1, the HDN activity of Cr-containing catalysts can be significantly increased by copromotion with Ni or Fe, whereas their HDS activity can be promoted by Co. For reference, also shown in Table 1 is the bulk FeMo catalyst. Comparing the present results with those in Fig. 1 indicates that there exists a synergism between Cr and Fe as copromoters, an important finding to which we will refer again. Catalysts prepared from the chelation route show similar trends, with their activities being somewhat lower than those shown in Table 1 [8,11].

The foregoing results indicate that the MAT-derived catalysts give rise to an unusual combination of high HDN and low HDS compared to commercial supported catalysts. This appears to be a general characteristic of many bulk metal sulfides. To put this observation in perspective, we next

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