

# Hydrodesulfurization of dibenzothiophene and 4,6-dimethyl-dibenzothiophene: Gallium effect over NiMo/Al<sub>2</sub>O<sub>3</sub> sulfided catalysts

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## Abstract

The influence of gallium on alumina-supported NiMo catalysts was investigated by correlating their physicochemical properties with the hydrodesulfurization (HDS) activity of model molecules. The Ga- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports were prepared by impregnation of Ga (0.6–5.9 wt%) on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The NiMo catalysts were prepared following the same method on calcined Ga-Al<sub>2</sub>O<sub>3</sub>. The N<sub>2</sub>-physisorption results showed that Ga did not affect the textural properties of both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. When the Ga-Al<sub>2</sub>O<sub>3</sub> supports were calcined at 723 K all Ga ions presented a high dispersion, forming a different structure than that observed in bulk Ga<sub>2</sub>O<sub>3</sub>. The XPS and the TPR-S showed that the Ga addition modified the structural properties of NiMo depending on the amount of Ga. In the HDS of DBT and 4,6-DMDBT, the Ga-Al<sub>2</sub>O<sub>3</sub> supported NiMo catalysts at loadings of Ga below to 1.2 wt% showed higher activity than that of a NiMo/Al<sub>2</sub>O<sub>3</sub> sample.

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## 1. Introduction

The current environmental regulations that impose very low sulfur content in diesel cuts have spurred research on hydrotreating catalysts. The commercial HDS catalysts consist of an active phase of molybdenum (Mo) promoted by nickel (Ni) or cobalt (Co) usually supported on alumina. Nevertheless, it has been recognized since the very first studies related to these solids (CoMo or NiMo/Al<sub>2</sub>O<sub>3</sub>) that alumina is not an inert carrier. On one hand, the promoter ion (Co or Ni) can react with the support and occupy octahedral or tetrahedral sites in external layers or even form an inactive phase such as CoAl<sub>2</sub>O<sub>4</sub> (NiAl<sub>2</sub>O<sub>4</sub>) depending on the preparation conditions [1]. On the other hand, the molybdates interact strongly with the support from the first steps of catalyst preparation through Mo–O–Al anchors [2,3]. Topsøe and Topsøe [4] and many other au-

thors have suggested that the improvement of HDS catalysts is closely related to the formation of the so-called “NiMoS” (CoMoS) phase. Thus the amount of the NiMoS phase should be increased by reducing the concentration of inactive species to improve the performance of HDS catalysts. As pointed out by several authors, the carrier plays a fundamental role, because strong interactions prevent NiMoS phase formation. Addition of a third metal as an additive may also influence the speciation of Ni and Mo and, consequently, HDS activity. Along this line, many papers have reported the influence of additives or modifiers, such as Mg [5–9], Ca [6,8,9], Ti [8], Fe [8], Mn [9] and Zn [5,10–13]. Unfortunately, the reports on the effects of these additives are rather conflicting. Martinez and Mitchell [5] showed that adding small amounts of Mg to CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts resulted in increased HDS activity, whereas adding large amounts of Mg resulted in decreased HDS activity. Muralidhar et al. [6] reported that adding 5% of Ca or Mg before or after Mo and Co impregnation decreased HDS activity. Hercules et al. [7] reported that Mg forms spinel-type species (MgAl<sub>2</sub>O<sub>4</sub>)

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or free oxides on the alumina surface, promoting Mo or W dispersion, and Saini et al. [8] reported that Ca cannot easily form  $\text{CaAl}_2\text{O}_4$  species due to its larger ionic radius compared with Mg ( $\text{Mg}^{2+}$ , 0.66;  $\text{Ca}^{2+}$ , 0.94). Transition metals (Me = Ti, Fe, or Mn) as additives scarcely form  $\text{MeAl}_2\text{O}_4$  species and have poor dispersion when they are impregnated on alumina and calcined around 773 K; therefore, these metals are not suitable for use in improving HDS activity. Martinez [5] showed that adding small amounts of Zn to the  $\text{CoMo}/\text{Al}_2\text{O}_3$  resulted in increased HDS activity, depending on the sequence of impregnation and on the calcination temperatures, in agreement with findings of other authors [11].

Gallium has been scarcely studied as an additive of HDT catalysts. However, some papers have been devoted to the characterization of Ga as an additive in alumina-supported  $\text{CoMo}/\text{Al}_2\text{O}_3$  and  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalysts. In early works, Cimino et al. [10] and Lo Jacono et al. [14] observed a high affinity of  $\text{Ga}^{3+}$  to the tetrahedral sites of alumina, modifying the ratio of tetrahedral/octahedral species of Ni ( $\text{Ni}_{\text{tet}}^{2+}/\text{Ni}_{\text{oct}}^{2+}$ ) in the  $\text{Ni}/\text{Al}_2\text{O}_3$  solid. A similar effect was observed when gallium was added to the  $\text{CoMo}$  catalyst, and these authors observed that the  $\text{Co}_{\text{tet}}^{2+}/\text{Co}_{\text{oct}}^{2+}$  ratio changed as a function of the metal loading (Ga, Co, and Mo) and of the impregnation sequence. As far as we know, these catalysts were not tested in HDS reactions; therefore, in this context, our experimental goals are aimed at investigating the additive effect of gallium. Indeed, recent results reported a positive effect of Ga as a second promoter to a  $\text{NiMo}$  catalyst in the pyridine hydrodenitrogenation (HDN) [15], and mixed gallium/aluminum oxides have been used as support for  $\text{CoMo}$  catalysts in the HDS of thiophene [16]. In this paper we report the study of a series of  $\text{NiMo}/\text{Ga}-\text{Al}_2\text{O}_3$  catalysts with a gallium content ranging from 0 to 5.9 wt%. These catalysts were tested in the HDS of dibenzothiophene and 4,6-dimethyl-dibenzothiophene, and a discussion of these results considering the characterization in the sulfided state by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and temperature-programmed reduction on the sulfided samples (TPR-S) is presented.

## 2. Experimental

### 2.1. Catalyst preparation

The supports were prepared by pore-filling impregnation of a commercial  $\gamma\text{-Al}_2\text{O}_3$  (high purity; BET surface area,  $240\text{ m}^2\text{ g}^{-1}$ ; pore volume ( $V_p$ ),  $0.63\text{ cm}^3\text{ g}^{-1}$ ; particle size, 80–100  $\mu\text{m}$ ) with an aqueous solution of  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (Aldrich Chemical) at constant pH of 5.4 to obtain supports with 0, 0.6, 1.2, 1.8, 2.9, and 5.9 wt% of metal. After 12 h, the obtained solids were dried at 393 K for 12 h and calcined at 723 K for 4 h under a flow of air ( $5.16 \times 10^{-3}\text{ mol min}^{-1}$ ) with a heating rate of  $1\text{ K min}^{-1}$ .

$\text{NiMo}$  catalysts were prepared by the pore-filling method on calcined  $\text{Ga}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  samples ( $\text{Ga}-\text{Al}_2\text{O}_3$ ) with aqueous solutions of ammonium heptamolybdate [AHM,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ; Merck] and nickel nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; Aldrich Chemical]. The loading of the metals was estimated per

$\text{nm}^2$  of initial surface area of alumina. For the molybdenum and nickel 2.8 and 1.2 at  $\text{nm}^{-2}$  were added, respectively, leading to an atomic Ni  $r = 0.3$ , with  $r = \text{Ni}/(\text{Ni} + \text{Mo})$ .

In a typical preparation, first a solution of AHM was prepared and the pH was adjusted to 8 by adding a basic solution ( $\text{NH}_4\text{OH}$ , Baker). Then, the support was impregnated and after 12 h, the solids were dried under a stream of air ( $5.16 \times 10^{-3}\text{ mol min}^{-1}$ ) at 393 K for 12 h, with a heating rate of  $3\text{ K min}^{-1}$ . The impregnation of nickel was performed with a solution of nickel nitrate at constant pH of 5.4. After 12 h, the obtained solids were dried at 393 K for 720 min and calcined at 673 K for 4 h under a stream of air ( $5.16 \times 10^{-3}\text{ mol min}^{-1}$ ) with a heating rate of  $1\text{ K min}^{-1}$ .

The oxide phases (mass of sample ca. 1 g) were sulfided at 673 K for 2 h with a mixture of  $\text{H}_2\text{S}/\text{H}_2$  (15%  $\text{H}_2\text{S}$ ) at a total flow rate of  $2.97 \times 10^{-3}\text{ mol min}^{-1}$  and a heating rate of  $5\text{ K min}^{-1}$ . After this step, the catalysts were cooled to room temperature and flushed with  $\text{N}_2$  for about 30 min and kept in sealed bottles under argon.

### 2.2. Characterization techniques

After the final calcination, the metal contents were determined by atomic absorption after appropriate dissolution of the solids samples; the results are presented in Table 1. This table also gives the nomenclature and specification of all of the catalysts. Elemental sulfur analyses were performed after combustion at 1623 K in a CS-mat 5500 instrument (Ströhlein). The emitted amounts of  $\text{SO}_2$  were analyzed by infrared spectroscopy.

Surface area, pore volume, and pore size distribution were obtained from  $\text{N}_2$  adsorption and desorption isotherms using the conventional BET and BJH methods. The samples were first dried at 393 K for 2 h and subsequently outgassed at 573 K under vacuum. Then  $\text{N}_2$  adsorption measurements were carried out at 73 K.

The XRD patterns of the calcined and sulfided catalysts were recorded on a Bruker D5005 diffractometer using  $\text{Cu-K}\alpha$  radiation (0.154184 nm) at 3–80° with a 0.02° step size and 1 s at every step.

XPS measurements were performed on a VG Instrument type ESCALAB 200R spectrometer equipped with an  $\text{Al-K}\alpha$  source ( $h\nu = 1486.6\text{ eV}$ ). The shifts of the peak core line due to the charge of the sample were corrected by taking the Al-2p line of the catalyst support,  $\gamma\text{-Al}_2\text{O}_3$  (Al 2p, 74.0 eV) as a reference. For the XPS measurements, the presulfided powder sample was introduced into an argon-filled glove box and pressed on indium foil fixed on the sample holder under the protection of inert Ar atmosphere. The sample holder was then transferred into the preparation chamber of the XPS equipment and passed into the analysis chamber after evacuation overnight ( $10^{-9}\text{ Pa}$ ). The XPS spectrum corresponds to the plot of the variation in the numbers of emitted electrons versus their kinetic energy values, that is, their binding energy values.

In the TPR-S experiments, an appropriate amount of the sulfided sample (50 mg) was maintained between two layers of quartz wool in a U-shaped quartz tube reactor with an outside

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