Influence of the support on the catalytic performance of Mo, CoMo, and NiMo catalysts supported on Al_2O_3 and TiO_2 during the HDS of thiophene, dibenzothiophene, or 4,6-dimethyldibenzothiophene

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ABSTRACT

The activity and promoter effect of Co and Ni for MoS_2/Al_2O_3 and MoS_2/TiO_2 catalysts during the hydrodesulfurization of three sulfur containing molecules (thiophene, DBT and 4,6-DMDBT) that are transformed with different contributions of the direct desulfurization (DDS) or hydrogenation (HYD) reaction pathways was investigated. The results show that the greater activity displayed by Mo/TiO_2 comes from a moderate increase in the direct desulfurization capability but mostly from the increase in the hydrogenating character due to the stronger MoS_2 metallic character induced by TiO_2. Therefore, the HDS selectivity is strongly influenced by the support. MoS_2 supported on TiO_2 is not as effectively promoted by Co or Ni as MoS_2 supported on alumina, because it presents fewer defects and mostly exposes the Mo-edge, which is difficult to promote. The promoter incorporation benefits mainly the direct desulfurization route and the activity of the hydrogenation sites in MoS_2/TiO_2 is only weakly sensitive to the promotion.

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1. Introduction

The key to achieving deep hydrodesulfurization (HDS) of transport fuels is the removal of all the sulfur present in some molecules in the petroleum fraction used as feed [1]. However, this is a complex issue because industrial feeds contain many different sulfur-containing molecules, aromatics and nitrogen-containing compounds that compete for the same catalytic sites. Concerning the sulfur molecules, industrial feeds may contain simple molecules of high desulfurization reactivity such as thiophene (T), or complex molecules like dibenzothiophene (DBT) or its alkyl-substituted analogues, some of which display very low reactivity in catalytic HDS [1–3].

Depending on their complexity, sulfur-containing molecules are hydrodesulfurized through different reaction routes, mainly the direct desulfurization (DDS) and the hydrogenation (HYD) followed by desulfurization. The predominance of the reaction route depends strongly on the structure of the sulfur-containing molecule. For example, for the production of ultra-low sulfur gasoline from the hydrodesulfurization of naphthas, molecules of high

reactivity like thiophene or benzothiophene are hydrodesulfurized mainly through the direct desulfurization route [2]. In contrast, for the production of ultralow sulfur diesel molecules of intermediate or poor reactivity such as dibenzothiophene (DBT) or substituted DBT's like 4,6-dimethyldibenzothiophene (4,6-DMDBT), have to be desulfurized. Dibenzothiophenes and its alkyl-substituted analogs are transformed through two reaction routes, the direct desulfurization (DDS) route leading to biphenyl (or alkyl-substituted biphenyl), and the hydrogenation (HYD) route leading first to hydrogenated intermediates but finally, after a desulfurization step, to cyclohexylbenzene, CHB (or alkyl-substituted CHB) [2,4–8].

According to the accepted models for HDS catalysts, the direct desulfurization sites are coordinatively unsaturated sites located on the edges of the MoS_2 crystallites (CUS). On the other hand, it has been proposed that the hydrogenation sites are located on the top layer of the MoS_2 crystallites, either on the sulfur sites with metallic character located near the edge, called brim sites [9], or simply on the rim sites located on the upper top layer of MoS_2 crystallites (rim-edge model) [10]. It was shown recently using model Mo and CoMo catalysts supported on Au (1 1 1) that DBT can be adsorbed through its sulfur atom at sulfur vacancies on the MoS_2 nanocluster. In contrast, 4,6-DMDBT was found to adsorb only in a flat configuration on the so-called brim sites of the MoS_2, without the requirement of a nearby vacancy [11]. The results led the

authors to propose a two-site model where hydrogenation and sulfur extrusion takes place at different sites. These findings are important and emphasize the need to study in detail the desulfurization and hydrogenation steps for different catalytic systems and reacting molecules.

The modulation of the phase-support interaction is of great importance to achieve catalysts of high activity and selectivity. It has been established in the past that changing the support nature can lead to significant increases in HDS activity. For example, it has been reported that the activity of MoS_2 supported on titania is about four times greater than MoS_2 supported on alumina [12]. Moreover, it was also found that the promotional effect of Co was higher on alumina (7.6 times) than on titania (3.3). These results indicated that the main effect of the TiO_2 support was on the Mo and not on the promoter. Although several interpretations have been put forward to explain these results, the question is still open [13–17].

Understanding the origin of support effects is then of great importance to the design of new more active HDS catalysts. According to some theoretical studies, the higher activity of MoS_2 supported on titania is ascribed to the edge-wetting and ligand effects of anatase [16,17]. Edge wetting properties were also proposed as the cause for the differences in promotional effects observed in alumina and anatase-supported catalysts. However, further experimental evidence is still needed to fully understand the nature and origin of the support effects.

Changes in the initial activity and synergy during the HDS of 4,6-DMDBT were reported for MoS, CoMoS, NiMoS and CoNiMoS catalysts supported on Al_2O_3, SiO_2, TiO_2 and ZrO_2 [18]. No preferential promotion by Ni or Co of any of the edges in MoS_2 crystallites (Mo- or S- edge) was found. Nevertheless the results showed great differences in the promotional effect for both CoMoS and NiMoS catalysts when the support was changed from alumina or silica to titania or zirconia.

The phase-support interaction can lead two types of active sites in HDS catalysts: (1) poorly active type I sites in molybdenum sulfide particles bonded to the support through Mo-O-support bridges, and (2) highly active type II sites formed on well sulfided MoS_2 crystallites that do not interact with the catalyst support through oxygen bridges [19]. A theoretical study confirmed that the presence of oxygen linkages increases the energy required to form sulfur vacancies, and introduces changes in the metallic-like brim states [20].

The variations in the promotional effect depend not only on the support but on the molecule to be desulfurized and in the composition of the catalyst, as reported earlier [21], where changes in the promotional effects of Co and Ni on Mo/Al_2O_3 catalysts for the HDS of DBT and 4,6-DMDBT were observed. It was found that on Mo/Al_2O_3, DBT and 4,6-DMDBT had similar reactivity. However, over the promoted catalysts, DBT was 5–6 times more reactive than 4,6-DMDBT. From the variations in the DDS and HYD reaction rate constants it was proposed that the main effect of the promoter was to increase the rate of the C-S bond cleavage, which is the DDS reaction route, in the absence of steric hindrance effects. No similar work has been reported for titania-supported catalysts. Changes in the morphology and structure of the MoS_2 slabs in alumina-supported catalysts induced by the temperature of treatment have also an effect on the activity and selectivity. At high sulfidation temperatures (500–700 °C), well ordered MoS_2 particles display low desulfurization and hydrogenation activities as well as low DDS/HYD selectivity [22].

It seems then that the relative importance of the DDS and HYD reaction routes and the effectiveness in removing S atoms will depend on the type of feed molecule, on the composition of the active phase (Mo, CoMo or NiMo), and on the type of catalyst support (i.e. Al_2O_3, TiO_2). To enquire on these issues the present work analyzes the activity and promoter effect of Co and Ni for MoS_2/Al_2O_3 and MoS_2/TiO_2 catalysts during the hydrodesulfurization of three sulfur containing molecules (thiophene, DBT and 4,6-DMDBT) that are transformed with different contributions of the direct desulfurization (DDS) or hydrogenation (HYD) reaction pathways. Particular emphasis will be placed in elucidating why MoS_2/TiO_2 catalyst outperforms MoS_2/Al_2O_3 during the HDS of thiophene and if this difference in behavior is maintained for more complex molecules like DBT or 4,6-DMDBT. It will also be explored why for the Co(or Ni)Mo/TiO_2 catalysts the promoter effect is not as effective as in the case of the alumina supported counterparts. To make more evident the promoter effect some catalysts will also be prepared adding ethylenediaminetetraacetic acid (EDTA), which is known to improve the level of promotion [23]. To relate the catalytic activity with the catalyst properties, UV-Vis-NIR electronic spectroscopy and FTIR analysis of CO adsorbed will be used.

2. Experimental

2.1. Catalysts preparation

The Mo/Al_2O_3, $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, $CoMo-EDTA/Al_2O_3$, and $NiMo-EDTA/Al_2O_3$ (hereafter CoMo-E/Al_2O_3 and NiMo-E/Al_2O_3, respectively) catalysts were prepared using γ-alumina (Sasol, 207 m^2/g) as support and the required amount of ammonium heptamolybdate (AHM, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$, and nickel nitrate $(Ni(NO_3)_2 \cdot 6H_2O)$ to obtain 2.8 Mo atom/nm^2 and a Co(Ni)/(Co(Ni) + Mo) atomic ratio of 0.3.

Mo/Al_2O_3 was prepared by incipient wetness impregnation. The alumina support was impregnated with an aqueous solution of AHM, aged for 2 h in a closed container with water to maintain humidity, dried overnight at room temperature in a desiccator containing silica gel, then in an oven at 373 K (heating ramp ∼1 K/min), and finally calcined for 4 h at 773 K (heating ramp 5 K/min).

For the preparation of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$, alumina was successively impregnated (Mo first then Co (Ni)) following for each metal the same procedure described above for Mo/Al_2O_3. CoMo-E/Al_2O_3 and NiMo-E/Al_2O_3 was prepared by simultaneous incipient wetness impregnation. An NH_4OH-EDTA solution was contacted first with an aqueous solution of cobalt (nickel) nitrate, and finally with an NH_4OH-HMA solution (final pH 9). The change in color during the preparation of the impregnating solution was in accordance with the formation of a Co-EDTA (Ni-EDTA) complex. The impregnated alumina was aged for 2 h in a closed container partially filled with water to maintain humidity, dried first at room temperature for 12 h in a desiccator with silica gel, and then in an oven at 373 K (the calcination step was avoided).

The catalysts supported on TiO_2 (P-25 Degussa, 50 m^2/g) were prepared in a similar way to the alumina counterparts maintaining the same surface concentration of the metals.

The composition of the different catalysts is reported in Table 1.

Table 1
Catalysts composition.

	Mo (wt%)	Co (wt%)
Mo/Al_2O_3	8.45	–
$CoMo/Al_2O_3$	8.27	2.18
$CoMo-E/Al_2O_3$	7.14	1.88
$NiMo/Al_2O_3$	8.27	2.17
$NiMo-E/Al_2O_3$	7.14	1.87
Mo/TiO_2	2.28	–
$CoMo/TiO_2$	2.26	0.59
$CoMo-E/TiO_2$	1.98	0.52
$NiMo/TiO_2$	2.26	0.59
$NiMo-E/TiO_2$	1.98	0.52