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The Silicon on the Catalysis: Hydrodesulfurization of Petroleum Fractions

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Abstract

The use of silicon in hydrodesulfurization (HDS) catalysts has had an impact on some of the fundamental parameters for the performance of the HDS catalyst, such as dispersion of the active phase, the extent of sulfidation, or the level of promotion. Mesoporous silicates such as MCM-41, SBA-15, the modified surface of γ -alumina with silica, or mixed Al_2O_3 - SiO_2 support have showed to affect the metal-support interaction, favoring the so-called type II Co(Ni)-Mo(W)-S structures. The aim of this chapter is to elaborate an analysis on the recent advances in the synthesis design of silicon catalyst support for the hydrodesulfurization of petroleum fractions.

Keywords: type I and type II structures, HDS, metal-support interaction, sulfidation, mesoporous silicates, silica

1. Introduction

The air pollution is one of the main problems that the governments around the world have been concerned to mitigate in recent decades. The harmful gases found in the atmosphere are the product of the generation of energy through the combustion of hydrocarbons [1–3]. However, the hydrocarbons will continue to be used as the main source of energy in the next decades [4]; thus, it represents an environmental problem. The main pollutants generated by the combustion of fuels are SO_x , CO, NO_x , and traces of some heavy elements. The SO_x is considered particularly dangerous since SO_2 can be oxidized to SO_3 by several routes, depending on the particular conditions of the atmosphere. Once the SO_3 is formed, it is diluted in the water droplets that are present in the atmosphere, therefore generating the sulfuric acid (H_2SO_4), leading to the acid rain. Moreover, it produces a direct environmental damage to humanity, such as eye irritation and constriction of the respiratory tract, causing harm to the entire population, but especially to asthmatics and other sensitive people. It also contributes to vegetation damage, causing discoloration and lesions on the leaves. In addition, sulfur dioxide has been associated with steel corrosion, deterioration of concrete structures, paper, leather, historical monuments, and certain textiles. Based on the described problems,

countries have opted to make stringent environmental regulations to reduce the levels of air pollutant emissions. Worldwide legislations have been issued to reduce the amount of sulfur contents in the transport fuels close to zero sulfur ppm (ultralow sulfur fuels) [5]. This represents a challenge due to the declining trend of light oil supplies [6], leading to process heavy crudes with higher concentrations of sulfur, nitrogen, and metals. In this context, the hydrodesulphurization (HDS) is considered the most effective used process to produce ultralow sulfur transport fuels, for which the design and preparation of catalysts of high HDS performance are believed to be central factors [7, 8]. In the last decade, traditional HDS catalysts have usually been based on Mo or W sulfides promoted by Co or Ni supported on γ -alumina [9, 10]. Nonetheless, due to the need to process increasingly heavy crudes and in consequence with higher concentrations of sulfur as mention before, it is becoming more difficult to produce ultralow-sulfur transport fuels using traditional HDS catalysts [11, 12]. Therefore, it is necessary to design novel catalysts with higher performance in the HDS reaction. In order to achieve it, the HDS catalysts require (1) complete sulfidation of the molybdenum or tungsten and Co(Ni) precursor oxides phases, (2) high extent of promotion, and (3) high dispersion of the Co(Ni)Mo(W)S active phase. It is well known that the strength of interaction between the support and the Co(Ni)Mo(W)S active phase has an important effect on the above three parameters. Alumina interacts strongly with the Co, Ni, Mo, and W oxide-supported phases; therefore, new support materials with weaker metal-support interaction must be identified. This chapter will explain which factors can lower the reactivity for HDS in some sulfur compounds such as 4,6-DMDBT, as well as the models proposed to explain the nature of the active sites, and briefly summarize recent advances in the use the silicon in catalyst support with the aim of understanding the difference in HDS performance compared with the traditional catalyst supported on γ -alumina from the point of view of the strength of the interaction between the support and the active phase.

2. Hydrodesulfurization (HDS)

Hydrodesulfurization is one of the most important processes among the oil refining industry, whose purpose is to reduce pollutants in the fraction of the petroleum distillates. The operation conditions of HDS reaction are in a pressure range between 60 and 200 atm and temperatures higher than 280°C. On the other hand, the sulfur vacancies, called coordinatively unsaturated sites (CUS), present at the edge of the Mo(W)S₂ crystals are the active sites [13, 14].

Crude oil contains a complex mixture of sulfur compounds, which in turn have a different reactivity. It is known that for each type of fuel, the sulfur-containing molecules are different and the degree of reactivity of these sulfur compounds in HDS depends on its structure. The degree of reactivity for the removal of sulfur can vary in several magnitudes. Generally, acyclic sulfides such as sulfides, disulfides, and thiols are highly reactive in HDS compared to thiophene. The reactivities of sulfur compounds with 1–3 rings decrease in the following order thiophenes > benzothiophenes > dibenzothiophenes [14]. Similarly, the reactivity of alkyl-substituted compounds such as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) is much less reactive than other compounds. **Figure 1** qualitatively represents the relationship between the type and size of sulfur compound in different fractions of distillate and their relative reactivity. In the range of diesel, molecules such as dibenzothiophenes and alkyl-dibenzothiophenes predominate, which present low reactivity for HDS.

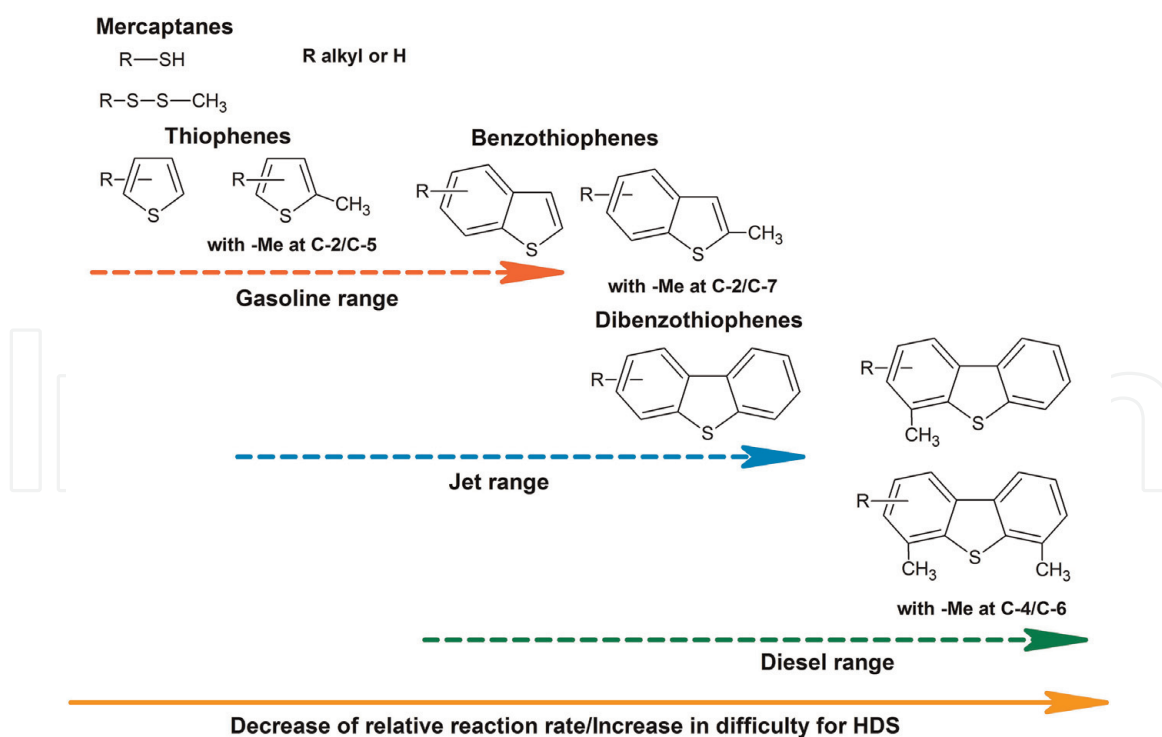


Figure 1.
 Relative reaction rate of organic sulfur compounds.

2.1 Reaction routes

The activity study of the catalysts for deep desulfurization has focused mainly on the most refractory molecules as can be observed in the literature [14, 15]. These molecules such as 4,6-dimethyldibenzothiophene (4,6-DDMBT), 4-methyldibenzothiophene (4-MDBT), and dibenzothiophene (DBT) have different reaction routes [16, 17], considering mainly the direct desulfurization route (DDS) and the hydrogenation route (HYD).

Desulfurization route (DDS). In the case of 4,6-DMBT, the DDS route is one in which the sulfur atom is removed from the structure and replaced by hydrogen, without carrying out the hydrogenation of any of the carbon-carbon double bonds present in the molecule. Some authors [17, 18] proposed that once it is adsorbed, the molecule on the active site, the DDS route begins with hydrogenation of one of the double bonds adjacent to the sulfur atom, to obtain a dihydrogenated product and then, the opening of the C—S bond through a process of elimination. **Figure 2** shows the mechanism for the C—S cleaving. According to the studies of the structure reactivity, the activity for the DDS reactions is attributed to sites located at the edges of the MoS_2 crystal [19], and it is suggested that the sites are sulfur anionic vacancies, called coordinatively unsaturated sites (CUS), which are created and regenerated during the reaction in the presence of hydrogen.

Hydrogenation route (HYD). In the HDS, the HYD route involves the hydrogenation of one of the aromatic rings, prior to the cleaving of the C—S bond: assuming that the cleavage of the C—S bond occurs through the β -elimination process, several explanations for the low reactivity of 4,6-DMBT have been proposed and discussed by Bataille et al. [17] such as: (a) steric hindrance of the methyl groups for the adsorption of the molecule hydrogenated, (b) steric hindrance of the methyl groups for the cleavage of the C—S bond, (c) the fact that only one atom of H is available for the cleavage of the C—S bond, and (d) an effect of the methyl group on the acidity of the H atom involved in the elimination process.

The mechanism of elimination E_2 (β -elimination) is described as following: a group S^- (nucleophile) subtracts a proton from the molecule with sulfur atom and the leaving group is the S atom from that molecule (**Figure 3**).

The favorable configuration for an elimination E_2 is to have both the sulfur atom and the hydrogen- β atom interacting with the surface of the active phase ($Mo(W)S_2$) at the same moment (**Figure 4a**). Then, the methyl group can hinder the process of elimination by blocking either the sulfur atom or the hydrogen- β atom as it approaches to catalytic center (**Figure 4b**). Moreover, the methyl group in 4,6-DMDBT molecule can also cause the hydrogen- β atom involved in the elimination process to be less acidic than the DBT molecule (**Figure 4c**). On the other hand, in the case of 4,6-DMDBT molecule, only one hydrogen atom is available for the elimination instead of two H atoms as occurs in DBT molecule. All of these factors can lower the reactivity of the 4,6-DMDBT compared to the DBT molecule.

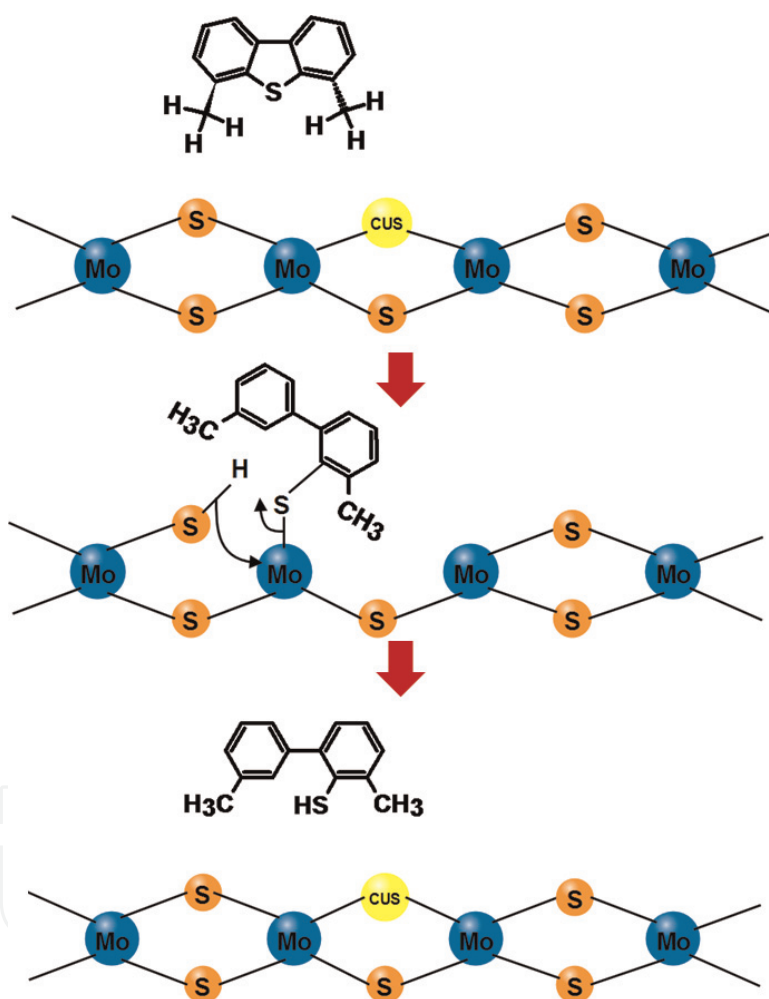


Figure 2.
Mechanism of the cleaving of the C—S bond in the DDS route.

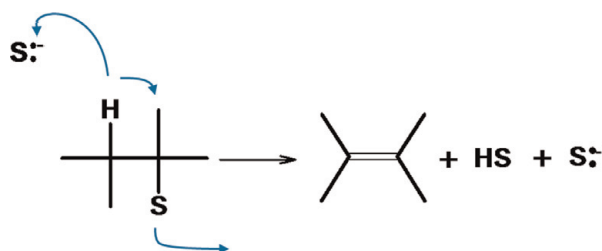


Figure 3.
Mechanism of elimination E_2 (β -elimination).

2.2 Active phase models

In the literature, there are some models that try to explain the structure and operation of the active phase. The models proposed by Daage and Chianelli [20] and Chianelli et al. [21] have named the sites located in the upper and lower edges of the crystal as “Rim site,” which are reactive to the reactions of HYD and the break of the C—S bond. While the “edge” sites are active only in the cleaving of the C—S. **Figure 5** depicts the location of these sites in the MoS₂ crystal.

Ramos et al. [22] have also showed for unsupported systems the existence of strong electron donation from Co to Mo and an enhanced metallic character associated to the Co₉S₈/MoS₂ interface. Berhault et al. [23] studied the structural role of cobalt, and the influence of support interactions on the morphology and catalytic properties of Mo and CoMo catalysts supported on alumina and silica.

On the other hand, another model called of the mixed phase “Co(Ni)-Mo(W)-S” combines studies of tunneling microscopy (STM) with calculations of density functional theory (DFT), identifying an area with high electron density in the upper part of the MoS₂ crystal that was called “BRIM site,” which have metal properties capable of efficiently carrying out the hydrogenation reactions [19, 24–26]. In the present chapter, the mixed phase model was used, since it is the most widely

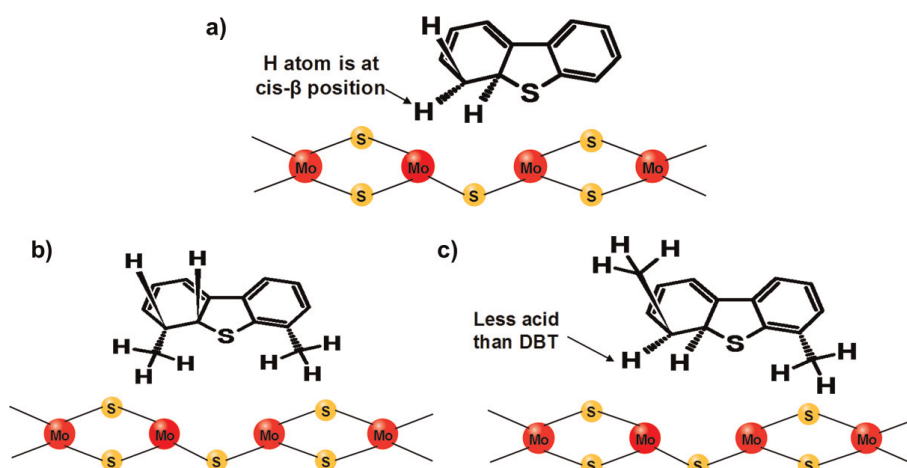


Figure 4. Approaching of: (a) DBT, (b) methyl group of the 4,6-DMDBT, and (c) hydrogen atom of the 4,6-DMDBT molecule to the catalytic center.

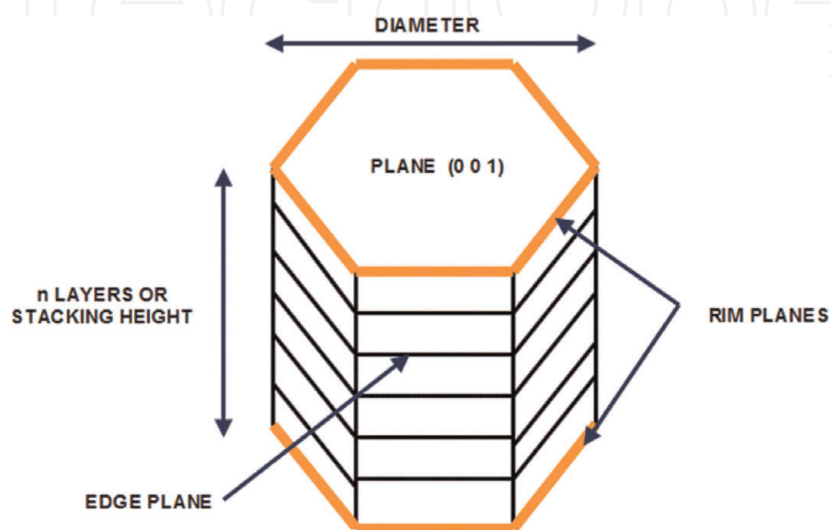


Figure 5. Model “Rim-edge” [21].

utilized in the literature. Based on this model, the catalytic properties of the sulfur vacancies at the edges of Mo(W)S₂ crystallites are strongly enhanced by the close presence of a promoter atom (Co or Ni) in the so-called Co(Ni)-Mo(S)-S structures [23, 26–28]. It has been reported that there are two types of structures that involve molybdenum or tungsten Co(Ni)-Mo(W)-S crystal, these structures were named types I and II [23, 27–29]. Type I structure has a strong interaction in the γ -alumina, since there is the presence of Mo-O-Al linkages and presents poor sulfidation. Type II structures are characterized by a weaker interaction with the γ -alumina, allowing to be full sulfided and exhibits high HDS activity. Therefore, it is important to find a way to weaken the interaction between the active phase and the support. One option is to use supports that present weak interaction with the active phase such as silica or carbon. On these supports (silica or carbon) “multilayer” MoS₂ structures are generated, thus the superior crystallites in the structure have a lower interaction with the support and form type II structures, which means that stacked or multilayer structures are type II and that single layer structures are type I, as shown in the **Figure 6**.

Nevertheless, it is also true that single layer structures that are type II can be obtained through a complete sulfidation of the oxidized phase and weaken the electronic interaction with the support. **Figure 7** illustrates the aforementioned.

The choice of a suitable support material is often dictated by the process conditions in which a catalyst has to operate. Although, one of the key features of a

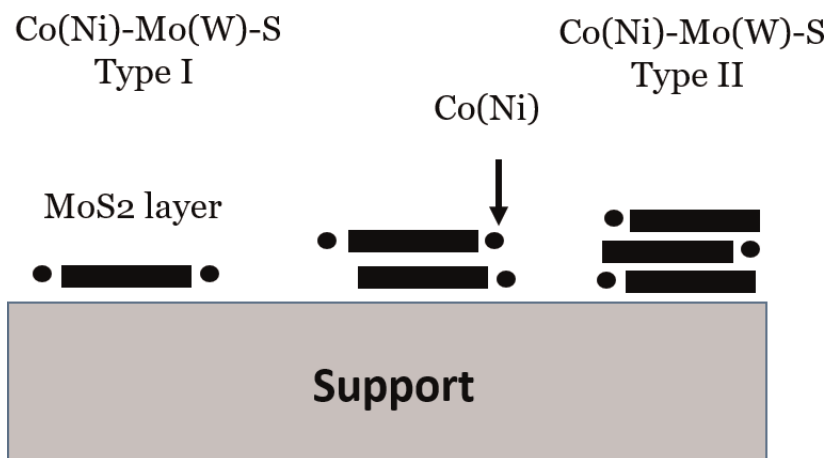


Figure 6. Structures Co(Ni)-Mo(W)-S types I and II.

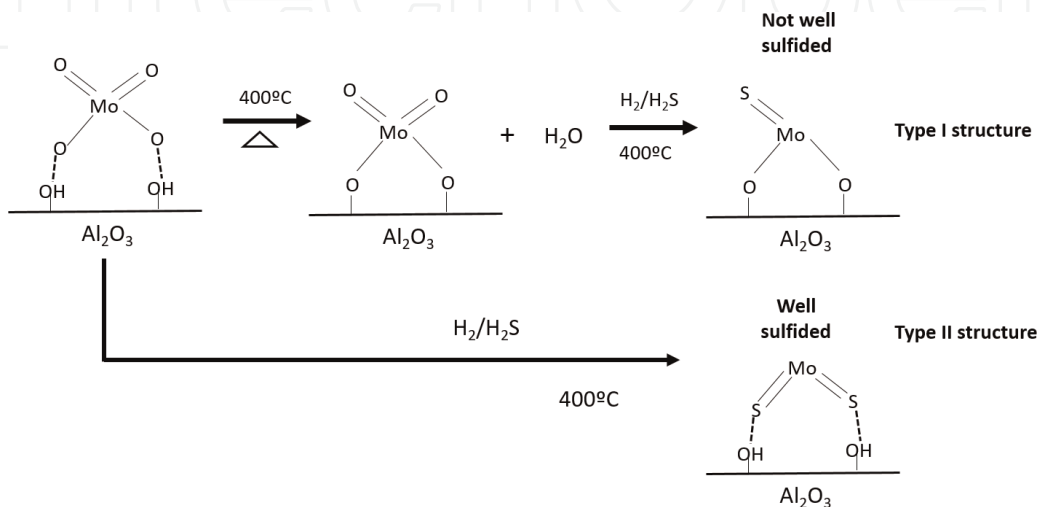


Figure 7. Sulfidation reaction in Mo/Al₂O₃ catalysts.

support for HDS catalysts is the presence of a large specific area in which the active phase Mo(W)S_2 presents a very high dispersion and/or present weak interaction support—active phase to generate more active structures (type II). Therefore, it is important to find a way to weaken the interaction between the active phase and the support. Therefore, the purpose of the next section is to make an overview of the recent investigations into the role of silicon in the generation of the type II structures (weak metal-support interaction), which present better HDS conversion.

3. HDS catalysts supported on mesoporous silicates

The mesoporous silicates such as MCM-41 and SBA-15 have received great attention in the last decades due to their excellent properties as catalyst support in hydrotreating reactions [30–36]. These catalysts have reported a high catalytic activity in the HDS of DBT than their counterpart supported on alumina. In the case of MCM-41, its low structural stability has limited its industrial use as support. It is also reported that the addition of Al_2O_3 stabilizes the structure of the MCM-41, but do not achieve the promoting effect of Ni [37].

In order to obtain a deep insight into how the preparation conditions of the MCM-41 have influence on the performance of the catalyst, Hernandez Cedeño et al. [38] did a detail study of UV-vis spectroscopy in order to find out how the pH (7 and 9) during the preparation of MCM-41 (MCM41) and Al_2O_3 (Al) supports as well as the effect of varying the molar ratio of Si/Al (10, 25, and 50) affect the coordination of the supported metals, and thus the metal-support interaction. The catalysts NiW were evaluated in the HDS of DBT. For the catalysts, $\text{W/Al}_2\text{O}_3$ at different pH presented well-defined bands at 423, 720–722 nm, which can be related to nickel in octahedral coordination [39, 40].

On the other hand, the catalysts NiW/MCM41 prepared at pH 7 with different Si/Al (10, 25 and 50) molar ratio presented bands in the range of 710–730 nm ascribed to octahedral nickel species [11, 49–51]. But also a band between 807 and 818 nm were detected, which was associated to nickel species with octahedral symmetry distorted; this latter may be related to an interaction Ni-W [41, 42]. In addition, the catalysts prepared at pH 9 bands at 804 and 820 nm ascribed to nickel with octahedral distortion were also detected similarly to the catalyst synthesized at pH 7 [43].

At pH of 9, the NiW/AMS50 prevails the band at 818 nm, related to nickel with distorted octahedral symmetry, while for the NiW/AMS10 using the same pH, no octahedral species were observed. An opposite behavior was observed with the pH 7 catalyst, which means the catalyst NiW/AMS10 presents more define bands related to nickel species in octahedral coordination with respect to the NiW/AMS 50.

Then, the catalyst with the highest reaction rate at pH 7 and pH 9 was the NiW/AMS10 and NiW/AMS50 catalysts, respectively. Therefore, there is a trend between the HDS activity and the bands in the range of 804–820 nm as well as the bands between 710 and 730 nm, which are related to the interaction of Ni-W and Ni species in octahedral coordination, respectively. Meanwhile, on the catalyst NiW/ Al_2O_3 prevailed the well-defined band between 720 and 775 nm associated to Ni^{2+} in octahedral symmetry, which is caused by the interaction between the metal and promoter, and leads to the formation of species NiWS type II, resulting in a better conversion of the DBT.

Although the incorporation of Al in the MCM41 framework improved the hydrothermal stability, the reaction rate decreases. According to the results of that work, the incorporation of Al in the MCM41 framework has a negative effect on the catalyst performance. On the other hand, in the NiW/AMS catalyst, both the pH

and the amount of alumina affect the reaction rate. In the case of the catalysts impregnated at pH 7, the highest reaction rate was achieved with the catalyst that contains the highest amount of alumina in its structure (NiW/AMS10). On the contrary for the catalysts impregnated at pH 9, the NiW/AMS50 catalyst (lowest amount of alumina) presented the highest reaction rate of this series.

Continuing with the influence of the preparation conditions of the support with Si on the performance of the HDS catalysts in terms of metal-support interaction, Gómez-Orozco et al. [44] analyzed the effect of modify the SBA-15 support with Ti on its physicochemical properties and its sulfidation behavior using NiMoW/SBA-15 catalysts in the HDS reaction of DBT. The amounts of Ti⁴⁺ ions incorporated during the direct synthesis of the SBA-15 support were varied using an Si/Ti molar ratio of 60, 40, and 20, and the nominal metals loading were 3.84, 13.83, and 17.33 wt% of Ni, Mo, and W, respectively. The supported catalysts were labeled as CAT/S15, CAT/60TiS15, CAT/40TiS15, and CAT/20TiS15 in agreement with the nominal Si/Ti ratio of 60, 40, or 20, respectively.

The coordination of Ni, Mo, and W ions was analyzed by UV-vis-DRS. It was observed that all the samples present a strong band in the range of 210–280 nm, which is ascribed to Mo and W ions in tetrahedral coordination, such as Mo(W)O₄²⁻. The intensity of this band (210–280 nm) was observed to follow the next trend: CAT/40TiS15 > CAT/20TiS15 > CAT/S15 > CAT/60TiS15. The catalysts CAT/40TiS15 and CAT/60TiS15 also showed an intense band at about 350 nm, which is related to Mo or W ions with octahedral coordination [45]. Furthermore, these catalysts present a band at 750 nm assigned to Ni²⁺ ions in octahedral coordination. In general, the population of octahedral W species and the W species in tetrahedral coordination was increased significantly upon Ti incorporation into S15. In addition, the incorporation of Ti did not decrease the catalytic activity in the HDS of DBT reaction except for Si/Ti = 40. The UV-vis analysis of the catalyst CAT/40TiS15 indicates a higher amount of tetrahedral species than its counterpart CAT/60TiS15. The lower amount of Ti in the catalyst (CAT/60TiS15) presented the highest hydrogenation capability among the catalysts studied (HYD/DDS = 0.81) (**Table 1**) despite the main route of DBT reaction was the direct desulfurization (DDS) pathway. Hence, the superior activity for CAT/60TiS15 and CAT/S15 samples was related to a higher dispersion of Mo(W)S₂ phase and a lower amount of tetrahedral species, which are not easy to reduce and sulfide (type I structure), which means that the catalysts CAT/60TiS15 and CAT/S15 possess a higher population of Mo(W)S₂ phase with type II structure.

The incorporation of Ti into the structure of the SBA-15 affected the catalytic properties of the sulfide catalysts. However, the Ti effect depends on its loading. In this study, the moderate Ti loading (Si/Ti = 40 molar ratio) was observed and had a negative effect in the catalytic activity, presenting the lower DBT conversion

Catalysts	DDS		HYD		DBT	
	BF (%)	CBH (%)	BCH (%)	THDBT (%)	HYD/DDS	Conversion (%)
CAT/S-15	22.34	13.47	1.11	3.08	0.79	91.57
CAT/60Ti-S15	22.16	13.05	1.05	3.75	0.81	96.86
CAT/40Ti-S15	23.99	12.3	0.1	3.6	0.65	80.15
CAT/20Ti-S15	22.86	13.23	0	3.58	0.75	82.36

THDBT, tetrahydrodibenzothiophene; BF, biphenyl; CBH, cyclohexylbenzene; and BCH, bicyclohexyl; calculated for batch reactor operating at $T = 320^{\circ}\text{C}$ and $P_{\text{H}_2} = 800$ psi for 5 h.

Table 1.

DBT conversion and selectivity HYD/DDS (at 40% of DBT conversion) [39].

(**Table 1**). One reason for the poor activity in the catalysts CAT/40TiS15 is the higher amount of tetrahedral species compared to their counterparts. In contrast, the catalyst CAT/60TiS15 (Si/Ti = 60 molar ratio) presented a lower amount of the tetrahedral species. Tetrahedral species are difficult to be reduced and sulfided, and therefore are not susceptible to develop the HDS active sites. Then, CAT/60TiS15 exhibited the highest HDS activity (96.98% of DBT conversion), the better performance for this catalyst is due to the small amount of tetrahedral species, the low staking, and high dispersion of Mo(W)S₂ phases. As it is observed, there is an optimal relationship of Si/Ti molar ratio in order to improve the HDS performance. Furthermore, the incorporation of certain amount of Ti into the structure of SBA-15 generates a high dispersion of the active phase, and a large number of structure type II.

4. HDS catalysts supported on SiO₂-Al₂O₃

As mentioned above, the type I structure with poor sulfidation has strong Mo-O-Al linkage with γ -alumina and presents low activity, whereas the type II structures with full sulfidation possess weak interaction with γ -alumina and exhibit high HDS activity. The surface modification of alumina with silica is an efficient way to weaken the metal-support interaction. Sanchez-Minero et al. [46] studied the effect of incorporate SiO₂ with a nominal loading of 10 wt% (SAC 10) onto the surface of alumina in NiMo/Al₂O₃-SiO₂(x) catalysts for the hydrotreatment of mixtures of 4,6-DMDBT-naphthalene-carbazole. An infrared analysis of the hydroxyl region was carried out, characteristics bands of Al₂O₃ hydroxyl groups were observed at 3790, 3775, 3740, 3730 and 3680 cm⁻¹ [47], and it can be noted from the IR spectrum of the alumina support (SAC). The most basic hydroxyl groups in alumina give rise to an IR band at 3775 cm⁻¹. When silica is incorporated to alumina (SAC 10), some changes in the bands intensity are observed. A new band localized in the region at 3725–3750 cm⁻¹ appears, which is assigned to isolated silanol groups [48, 49]. Furthermore, the bands corresponding to the most basic hydroxyl groups (3775 cm⁻¹) disappear. This behavior indicates that modifying the alumina surface with SiO₂ eliminates the most basic hydroxyl groups in alumina promoting that the sulfided NiMoSAC10 catalyst presented highly stacked MoS₂ crystallites with more than two layers (type II structure). These sites favor the hydrogenation route, being more active for 4,6-DMDBT HDS.

Recently, Romero-Galarza et al. [50] carried out a systematic study of the change in activity, selectivity, dispersion, sulfidation, and extent of promotion for CoMo and NiMo HDS catalysts supported on Al₂O₃ and SiO₂/Al₂O₃. They found for CoMo and NiMo catalysts that the grafting of the surface of alumina support with a 4.0 wt% of silica was enough to eliminate the most basic hydroxyl groups bonded to tetrahedral aluminum (IR band at 3767 cm⁻¹), and thus, this induces to have a higher proportion of Mo and Co(Ni) in octahedral coordination (DRS-UV-vis results), resulting in a better catalytic performance in the HDS of 4,6-DMDBT.

It was also found that the extent of promotion, determined by the XPS ratio of NiMoS/NiT, is larger for the Ni-promoted catalysts than for Co-promoted catalyst, which is in line with the fact that NiMo catalysts can incorporate the Ni promoter on three different edges of a dodecagonal NiMoS particle, in contrast to CoMo catalysts where the copromoter is incorporated only on the sulfur edge of a hexagonal CoMoS cluster [26, 27]. The origin of the better performance of the NiMoSAC catalyst over their alumina-supported counterparts, NiMoAl and CoMoAl, seems to be mainly related to the higher extent of promotion and sulfidation achieved in the catalysts with SiO₂ (type II structures). This fact is reflected with a good

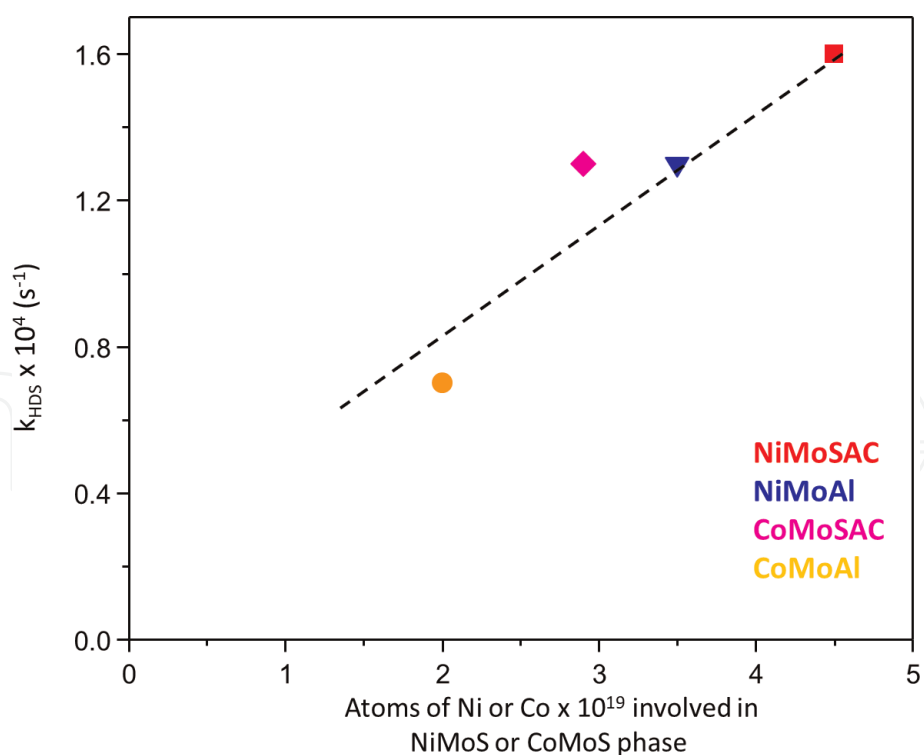


Figure 8.

Relationship between global HDS rate constant vs. Ni or Co atoms involved in the Co(Ni)MoS phase.

correlation between the degree of promotion with the hydrodesulfurization rate constant displayed in **Figure 8**, and agrees with the literature reports that indicate that promotion favors the appearance or brighter (more metallic) brim site, which can perform hydrogenating reactions [51], which is the main route for the HDS of 4,6-DMDBT.

On the other hand, Xu et al. [11] prepared a novel NiMo/SiO₂-Al₂O₃ catalysts with the improved stacking and good dispersion of supported active phase via gemini surfactant-assisted synthesis. In this method, polymolybdates anions were transformed into gemini surfactant-linked Mo precursor (GSMP), dispersing Mo species well and weakening the strong Mo-support interaction. The GSMP-based NiMo/SiO₂-Al₂O₃ (NiMo-GSHD) catalyst presents higher activity for the HDS of 4,6-DMDBT than its counterparts prepared via impregnation (NiMo-IM) and the cetyltrimethylammonium bromide-assisted hydrothermal method (NiMo-CTHD). To understand their different activities (**Table 2**), the HDS activities of the catalysts were correlated with the structure of their metal phase.

The reason for the higher HDS activity of 4,6-DMDBT (**Table 2**) exhibited in the catalyst NiMo-GSHD is related to the greater MoS₂ dispersion, a superior average stacking number determined by HRTEM and the higher extent of promotion (NiMoS) calculated by XPS and by NO-IR characterization, thus generating more Ni-Mo-S active sites with sufficient brim sites (type II structures). Such that, the prehydrogenation activity of NiMi-GSHD for 4,6-DMDBT with steric hindrance is markedly improved. The prehydrogenated products (4,6-THDMDBT and 4,6-HHDMDBT) without steric hindrance are much easier to be desulfurization via hydrogenolysis on the edge sites of Ni-Mo-S phases than initial 4,6-DMDBT. Therefore, NiMo-GSHD, with more edge sites due to its better metal dispersion, possesses higher 3,3'-MCHT selectivity than NiMo-IM and NiMo-CTHD.

According to the results showed in this section, the use of supports SiO₂-Al₂O₃ results in an improvement in the performance of the catalysts in the HDS reaction of the 4,6-DMDBT molecule. Grafting SiO₂ on the surface of γ -alumina generates two main effects. Increasing the extent of sulfidation and promotion, generating

Catalysts	$k_{\text{HDS}}^{\text{a}}$	$\text{TOF}^{\text{b}} \times 10^4$	Product ratio ^c	
	($10^{-7} \text{ mol g}^{-1} \text{ s}^{-1}$)	(s^{-1})	(TH + HH)/MCHT	MCHT/DMDBP
Mo-IM	0.32	1.72	0.33	1.85
Mo-CTHD	0.47	2.24	0.3	2.41
Mo-GSHD	0.7	2.83	0.27	3.07
NiMo-IM	3.16	5.62	0.16	2.04
NiMo-CTHD	4.18	7.34	0.13	2.72
NiMo-GSHD	5.78	9.21	0.11	3.67

TH, tetrahydrodimethylbenzothiophene; HH, hexahydrodimethyldibenzothiophene; MCHT, dimethylbicyclohexyl; and DMDBP, dimethylbiphenyl.
^aCalculated with the 4,6-DMDBT conversion at about 30%.
^bNumber of the reacted 4,6-DMDBT molecules per second and per Mo atom at the edge surface.
^cDetermined at about 50% of the total 4,6-DMDBT conversion by changing liquid hourly space velocity.

Table 2.
 HDS results of 4,6-DMDBT on different catalysts [47].

structures Co(Ni)-Mo-S type II, unlike the catalysts supported in γ -alumina where the structures type I predominate, which are not well sulfided due to a strong metal-support interaction. On the other hand, a different Mo precursor is used (gemini surfactant-linked) in conjunction with the use of a mixed Al₂O₃-SiO₂ support with a composition of 96.4 and 3.6 wt%, respectively, resulting in the formation of sulfide molybdenum (MoS₂) crystals with higher stacking, generating the so-called Ni-Mo-S type II, which are more active in HDS of 4,6-DMDBT molecule.

5. Conclusions

The metal-support interaction is one of the most important parameters in the design of HDS catalysts. The use of silicon in the preparation of HDS catalyst support has been showed to weak the metal interaction, generating type II Co(Ni)-Mo(W)-S structures, which are characterized by: (i) a complete sulfidation of the oxidized phase, weakening the electronic interaction with the support or (ii) stacked structures so that the upper crystallites in the structure Mo(W)S₂ have a low interaction with the support. The so-called type II Co(Ni)-Mo(W)-S structures are more active than the partially sulfide type I. The use of mesoporous silicates such as MCM-41 and SBA-15 has been proposed in the literature, with the intention to increase the active phase, acidity, the type II structures, and the dispersion of the active phase (Mo(W)S₂). In the case of the MCM-41 support, the preparation conditions such as pH and the Si/Al molar ratio increase the number of oxidized species in octahedral coordination, which are precursors of the type II structures. However, these materials did not show better HDS performance in the DBT molecule compared with the alumina support. It would be very useful to evaluate this type of catalyst support (MCM-41) in a molecule more refractory to HDS, such as 4,6-DMDBT, and see if it is possible to increase the catalytic performance compared to the catalyst supported in alumina, since the 4,6-DMDBT molecule is more sensitive to the geometry of the Co(Ni)-Mo(W)-S structure than the DBT molecule. On the other hand, SBA-15 mesoporous silicate doped with a certain amount of Ti (Si/Ti = 60 molar ratio) showed to improve the catalytic performance in the HDS of the DBT molecule, through generating a greater population of type II structures; therefore, these materials are useful as HDS catalyst support.

Grafting SiO₂ on the surface of γ -alumina or the use of mixed support (Al₂O₃-SiO₂) are other alternatives to promote the formation of so-called type II Co (Ni)-Mo(W)-S structures. It has been reported that a small amount of SiO₂ is enough to weaken the metal-support interaction and thus increase the extent of sulfidation and level promotion, which are fundamental parameters to improve the performance of HDS catalysts. So, it can be concluded that the use of silicon in the preparation of HDS catalyst support is a promising alternative to get better performance in HDS catalysts.

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