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EVALUATING THE FUNCTIONALITIES OF $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ CATALYSTS IN NAPHTHALENE HYDRODEAROMATIZATION AND DIBENZOTHIOPHENE HYDRODESULFURIZATION

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ABSTRACT

The aim of this work is to contribute to the current understanding on the role of the support's acidic properties in the hydrogenating function of $NiMo/\gamma\text{-}Al_2O_3$ type catalysts during hydrodearomatization (HDA) and dibenzothiophene (DBT) type molecules desulfurization. $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts of different B_2O_3 (0, 2, 3, 6 and 8 wt.%) contents were prepared and tested in independent and simultaneous naphthalene (NP) HDA and DBT hydrodesulfurization (HDS) reactions. For HDA the catalytic activity as a function of the B_2O_3 content followed a volcano-shape trend, with a maximum around 3 wt.% of B_2O_3. In DBT desulfurization boron was found to have a positive effect in the development of the HYD route of desulfurization possibly due to an increase in total acidity. Conversely, the direct desulfurization route (DDS) was negatively affected by boron addition. The presence of NP during the HDS of DBT was found to have a significant effect in neither total HDS activity nor the HYD/DDS selectivity. The findings in this paper are significant for ultra-deep HDS of heavy oil cuts where increasing in the selectivity to HYD is a must because highly refractory alkyl-DBTs mostly react by this reaction route.

Keywords: *$NiMo/\gamma\text{-}Al_2O_3$, hydrotreatement, direct desulfurization route, HYD function.*

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RESUMEN

El objetivo de este trabajo es contribuir a entender el papel de la acidez de los soportes sobre la función hidrogenante de catalizadores tipo $NiMo/\gamma\text{-}Al_2O_3$ durante la hidrodesaromatización (HDA) y la desulfuración de moléculas tipo dibenzotiofeno (DBT). Se prepararon catalizadores $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ con diferentes contenidos de B_2O_3 (0, 2, 3, 6 y 8% en peso) y se ensayaron independiente y simultáneamente en la HDA del naftaleno (NF) y la hidrodesulfuración (HDS) del DBT. La actividad catalítica en HDA en función del contenido de B_2O_3 siguió una curva tipo volcán con un máximo alrededor de 3% de B_2O_3. En la HDS del DBT, se encontró que el boro tiene un efecto positivo sobre el desarrollo de la ruta de hidrogenación (HID) de la desulfurización, posiblemente debido al aumento en la acidez total. Por el contrario, la ruta de desulfurización directa (DDS) fue negativamente afectada por la adición de boro. También se encontró que la presencia de NF durante la HDS de DBT no tiene un efecto significativo sobre la actividad total de HDS ni sobre la selectividad HID/DDS. Los hallazgos realizados en este estudio son importantes para los procesos de desulfurización profunda de cortes pesados de refinería; en los cuales se requiere aumentar la selectividad hacia la ruta HID que es la vía de reacción de las moléculas tipo alquil-DBTs que son altamente refractarias al proceso.

Palabras clave: *$NiMo/\gamma\text{-}Al_2O_3$, ruta de desulfurización directa, hidrotratamiento, función hidrogenante.*

1. INTRODUCTION

Burning of fossil fuels produces pollutants such as CO_2, CO, SO_x and NO_x. Nevertheless, the world's energy global market is sustained by this non-renewable resource. To lessen the environmental cost of fossil fuels consumption stringent governmental legislation has been imposed particularly on their sulfur and aromatic contents. Both the US Environmental Protection Agency (EPA, 2008) and the European Directive (1998) have fixed a 10 ppm concentration limit for the sulfur content in diesel oil for 2008-2009, namely Ultra-Low Sulfur Diesel (ULSD). ULSD requires either the development of new refining units combined with more active desulfurization-hydrogenation catalysts (Leliveld & Eijsbouts, 2008). The benefit of high hydrogenating selective catalysts is that their use allows sulfur removal from sterically hindered 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) and parent molecules (Pérot, 2003). Moreover, parallel saturation of aromatic rings (HDA) and hydrodenitrogenation (HDN) can be highly competitive hydrogenation (HYD) reactions (Leliveld & Eijsbouts, 2008). It has been recognized that the acidic function of sulfided *CoMo* and $NiMo/\gamma\text{-}Al_2O_3$ catalysts plays a key role in the hydrodesulfurization (HDS) of refractory 4,6-DMDBT (Pérot, 2003). A simple and economic way to increase the acidity of the alumina support consists in boron impregnation, to obtain mixed $\gamma\text{-}Al_2O_3\text{-}B_2O_3$ type oxides (Sibeijn, Vanveen, Bliek, & Moulijn, 1994; Usman, Takaki, Kubota, & Okamoto, 2005; Torres-Mancera, Ramírez, Cuevas, Gutiérrez-Alejandre, Murrieta, & Luna, 2005; Lewandowski & Sarbak, 2000; Sato, Kuroki, Sodesawa, Nozaki, & Maciel, 1995). By means of this procedure, Torres-Mancera *et al.* (2005) prepared *CoMo* and $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts exhibiting good activity in the HDS of 4,6-DMDBT. This effect is related to the development of the catalyst's ability to isomerize the methyl substituents of the 4,6-DMDBT molecule, surpassing steric hindrance, (Pérot, 2003; Torres-Mancera *et al.*, 2005).

Though a huge amount of studies have been carried out to understand the relationship between the acidic function and the isomerization and cracking functionalities of HDT catalysts, the relationship between acidity and the selectivity either to the direct desulfurization (DDS) or HYD route of desulfurization is not fully understood (Pérot, 2003). In the case of $\gamma\text{-}Al_2O_3\text{-}B_2O_3$ supports such relationship is more complicated to establish because as boron loading increases catalyst's acidity also increases, but due to structural changes of the boron oxide species the *Co*(*Ni*)-*Mo*-alumina interaction is affected modifying the active sites of the sulfided phases (Usman *et al.*, 2005; Torres-Mancera *et al.*, 2005; Lewandowski & Sarbak 2000; Sato *et al.*, 1995; Li, Sato, Imamura, Shimada & Nishijima, 1998; Li, Sato, Imamura, Shimada, & Nishijima, 1997; Usman, Kubota, Hiromitsu, & Okamoto, 2007; Ferdous, Dalai, & Adjaye, 2006). Though the structural changes induced by B on the active phase of sulfided *CoMo* and *NiMo* have been studied with certain detail (Usman *et al.*, 2005; Li *et al.*, 1998; Usman *et al.*, 2007), few reports have dealt with B effect on the functionalities of such catalysts in HDA and HDS. Furthermore, contradictory results have been presented mainly due to differences in the reaction conditions used in each of these studies (Lewandowski & Sarbak, 2000; Ding, Zhang, Zheng, Ring, & Chen, 2006).

This work aims to contribute to the current understanding on the role of the support's acidic properties in the HYD function of $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ type catalysts during aromatics HDA and dibenzothiophene (DBT) type molecules desulfurization. DBT was chosen as a model molecule instead of 4,6-DMDBT because it allows a direct measurement of HYD/DDS selectivity as referred to the removal of the sulfur heteroatom from the thiophenic ring against DBT aromatic backbone saturation (Pérot, 2003). Both molecules share similar desulfurization reaction pathways (Mijoin, Pérot, Bataille, Lemberton, Breysse, & Kasztelan, 2001). Moreover, parallel cracking and isomerization reactions are ruled out. Reactions conditions were selected to avoid thermodynamic constraints in either the HDA or the HYD route of desulfurization of DBT, (Cooper & Donnis, 1996; Ho, 2004).

2. EXPERIMENTAL

Catalysts preparation

A series of $\gamma\text{-}Al_2O_3\text{-}B_2O_3$ supported *NiMo* catalysts of various B_2O_3 contents were prepared by the sequential incipient-wetness method. Procatalyse alumina, D_p = 0,3-0,6 mm, was calcined in air flow at 773 K for

4 h before boron impregnation. Alumina support was first impregnated with a H_3BO_3 solution, followed by sequential impregnation of *Mo* and *Ni* precursors, respectively. The precursors used were ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}•4H_2O$ (Merck), and niquel nitrate $Ni(NO_3)_2•6H_2O$ (Aldrich). The amounts of each precursor were calculated from the desired contents of MoO_3, 9 wt.%, and *NiO*, 4,5 wt.%. After each impregnation step, the solids were aged by 24 h. Afterwards, the impregnated solids were dried (393 K for 12 h) and calcined (773 K for 4 h) in air flow. B_2O_3 nominal contents were: 0, 2, 3, 6 and 8 wt.%. Catalysts were labeled as *NiMo-B(x)*; where, *x* referred to the B_2O_3 nominal content.

Catalysts activation

All of the catalysts (approximately 0,5 g) were *in situ* activated with a gaseous mixture of H_2S (15 vol.%) in H_2, at 673 K and atmospheric pressure, during 3 h. The activation mixture flow was (100 mL/min) kept until reaching reaction temperature and beginning H_2 pressurization of the reaction system.

Catalysts characterization

BET surface area (S_{BET}), pore volume (V_P) and average pore diameter (D_P) were measured by the conventional nitrogen adsorption-desorption technique in a NOVA 1200 (Quantachrome) apparatus.

NH_3 TPD analysis was used to determine total acidity of the catalysts. A Chembet 3000 (Quantachrome) apparatus was used. Previous to each test, catalyst activation was performed at the same conditions mentioned in the precedent section. Activation was followed by N_2 evacuation (15 min) at 373 K. NH_3 was adsorbed at this temperature by flowing it during 15 min. Once adsorption step was completed, the evacuation of the system was carried out for 2 h. NH_3 TPD analysis was performed by heating the sample (at 10 K/min) until 773 K under N_2 flow and, then, collecting desorbed ammonia in a 0,4 vol.% H_3BO_3 solution. The amount of desorbed NH_3 (μeq NH_3/g cat.) was calculated by titrating with H_2SO_4.

Catalytic tests

Catalytic tests were performed in a continuous high-pressure fixed-flow reactor. The volume of the catalytic bed was c.a. 2 mL and it was composed of 0,5 g of catalyst diluted in borosilicate glass-beads. Three types of catalytic tests were performed: (i) naphthalene (NP) HDA, under an H_2S atmosphere, (ii) DBT hydrodesulfurization, and (iii) simultaneous DBT hydrodesulfurization and naphthalene HDA. The composition of the liquid feed was 3 wt.% of NP and/or 2 wt.% of DBT respectively, and 2 wt.% of hexadecane, as GC internal standard, diluted in ciclohexane. To generate the H_2S atmosphere during the HDA tests, dimethyldisulfide was added to the liquid feed in such a concentration as to obtain 4074 wppm of H_2S. Reaction conditions were: T = 563 K for HDA, and T = 583 K for the HDS and the simultaneous HDS and HDA, P = 5 MPa, liquid feed flow of 30 mL/h and an H_2/liquid feed flow ratio of 500 NL/L. Under such conditions, the absence of diffusion limitations was verified. Reaction products were identified using an HP 6890 GC, provided with an FID detector and an HP-1 (100 m x 0,25 mm x 0,5 µm) column. All catalytic tests were conducted until steady state (approximately 5 h). The catalytic activity was expressed as the fraction of reactant conversion (X) and as the yield (y_j) of products (*Equation 1*):

$$y_j = \frac{n_j}{n_{DBT,0}} \tag{1}$$

Where n_j are the moles of different reaction products: cyclohexylbenzene (CHB) and biphenyl (BP) and $n_{DBT,0}$ are the feed moles of DBT.

3. RESULTS AND DISCUSSION

Catalysts characterization

Table 1 shows the textural characteristics and total acidity of the prepared catalysts.

The results of the textural characterization show that the effect of boron on the catalysts S_{BET} depends on the boron concentration, without causing significant changes in the porous structure (V_p and D_p). As compared to the *NiMo* catalyst, an increase in S_{BET} is observed for the catalysts containing an amount of B_2O_3 up to 3 wt.% whereas a decrease in S_{BET} is observed for those with higher B_2O_3 wt.%. Usman *et al*. (2005) showed that at low boron concentration, B_2O_3 is well dispersed on the alumina support without significantly changing its textural properties. Torres-Mancera *et al*.

Table 1 Textural properties and acidity of *NiMo-B(x)* catalysts

Catalyst	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)	Total acidity (μeq NH_3/g cat.)	Specific acidity (μeq NH_3/m^2)
$\gamma\text{-}Al_2O_3$	220	0,62	11,6	N.D.	N.D.
NiMo	185	0,50	10,8	329	1,78
NiMo-B(2)	205	0,51	11,2	389	1,90
NiMo-B(3)	191	0,46	10,9	397	2,08
NiMo-B(6)	166	0,43	11,1	465	2,80
NiMo-B(8)	126	0,37	11,3	576	4,57

S_{BET}: Surface area, V_P: pore volume and D_P: average pore diameter.
NiMo-B(x): x is the B_2O_3 nominal content (wt.%).

(2005) ascribed the effect of boron on the support's textural properties to a partial dissolution of alumina during H_3BO_3 impregnation. Thus, at low boron concentrations, S_{BET} increases whereas at higher boron load, the boron oxide causes a blocking of the pores.

The trend registered for total acidity (Table 1) agrees with previous reports (Sibeijn *et al*., 1994; Usman *et al*., 2005; Torres-Mancera *et al*., 2005; Lewandowski & Sarbak, 2000; Sato *et al*., 1995; Li *et al*., 1998). There is an increase in catalyst's total acidity after boron incorporation. It has been demonstrated that such acidity increase is due to the generation of Brønsted acidic sites. In addition, it has been observed that the amount of Lewis acidic sites slightly increase at B_2O_3 concentrations up to 3 wt.%. Such Lewis sites tend to decrease and disappear at B_2O_3 concentrations higher than 5 wt.%. Sibeijn *et al*. (1994) showed that boron does not bond to alumina Lewis sites, yet it rather links to its OH^- groups. Due to this observation, significant changes in the structure of the sulfided catalyst take place (Usman *et al*., 2005 and 2007), as it will be discussed later. Sato *et al*. (1995) studied the acidity of $\gamma\text{-}Al_2O_3\text{-}B_2O_3$ supports by pyridine TPD. Their results indicate that the amount and strength of Brønsted acidic sites of such materials is related to the presence of BO_4 species, which increases with the load of boron. Similar trends have been reported for $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts (Lewandowski & Sarbak, 2000). Lewandowski and Sarbak (2000) found, by means of model reactions, that boron addition to $NiMo/\gamma\text{-}Al_2O_3$ catalysts leads to the formation of Brønsted acidic sites of intermediate strength. The above mentioned evidence leads to believe that the increase in the total acidity of the *NiMo-B(x)* catalysts due to boron incorporation can present two main zones of distribution of acidic sites: at low B_2O_3 concentrations there is an equilibrium between the number of Brønsted and Lewis acidic sites, and at higher boron concentrations, Lewis acidic sites tend to disappear and, thus mostly Brønsted sites are present on the catalyst's surface. Such Brønsted sites would possess an intermediate acidic strength, which increases with the amount of BO_4 species.

Catalyctic Activity

Naphthalene HDA

Figure 1 shows the effect of boron concentration in the catalytic performance in naphthalene HDA along with the change in the total acidity of *NiMo-B(x)*. It is observed that the promoting effect of boron in HDA is a

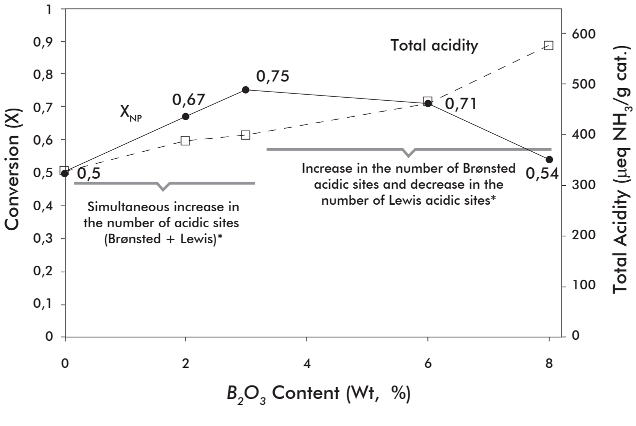

Figure 1 Steady state performance of $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts during naphthalene HDA under an H_2S atmosphere as a function of the B_2O_3 wt.%. Reaction conditions: T = 563 K, P = 5 MPa, liquid feed flow 30 mL/h, H_2/liquid feed ratio = 500 NL/L, additional H_2S concentration in the reaction atmosphere c.a. 4074 wppm.
*Acidic sites distribution as presented by Sato *et al*., (1995)

function of the B_2O_3 content of the catalysts. In general, a volcano-shape plot is observed. For B_2O_3 contents up to 6 wt.% there is an activity increase compared to the *NiMo* catalyst, whereas for a content of 8 wt.% no significant change is registered. The observed trend has been reported before. Li *et al*. (1998) reported a volcano-type behavior for the HDA of 1-methylNP for $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts. The corresponding maximum was around 1 wt.% of B_2O_3. They ascribed this behavior to a better dispersion of the oxidic *NiO* and MoO_3 precursors at low boron concentration. Other authors have established that the dispersion and the structure of the active phase of $Al_2O_3\text{-}B_2O_3$ supported HDT catalysts is affected by the B_2O_3 concentration due to changes induced by the conformation of borate ions present in the alumina surface (Sibeijn *et al*., 1994; Usman *et al*., 2005). Sato *et al*. (1995) proved the existence of tetrahedral BO_4 monomeric species over the alumina surface at low boron concentrations. Sibeijn *et al*. (1994) showed that the B_2O_3 is attached to the hydroxyl groups of Al_2O_3 and after saturation B_2O_3 polymeric species are formed. Such species tend to form a monolayer at the alumina surface. The presence of these polymeric species reduces the interaction between *Mo* and the alumina support, thus increasing the size of the *Mo* oxide clusters. As a result, a less dispersed MoS_2 active phase is formed after sulfidation (Usman *et al*., 2005). Usman *et al*. (2007) assuming the *Co-Mo-S* active phase proposed by Topsøe (2007), suggested a change in the structure of the *Co-Mo-S* mixed sulfide phase due to a decrease in the number of *Co* atoms decorating the edges of the MoS_2 phase. Nevertheless, these authors could not correlate such effect to the catalytic performance of $CoMo/Al_2O_3\text{-}B_2O_3$ catalysts in HDT reactions. On the other hand, Li *et al*. (1997) used XRD, XPS and EXAFS to characterize $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts and showed that the main effect of boron is to modify the dispersion of the MoS_2 active phase and the *Ni*, as well as the textural properties of the catalysts. Considering such evidence, it can be said that the HDA trend registered results from a combination of two main effects induced by boron addition to the alumina support. The first would be the conformational structure of B_2O_3 which modifies the dispersion of the MoS_2 active phase and *Ni*, and the second corresponds to the acidity increase of the catalysts. In this last regard, it seems that not only acidity increase is important but also the distribution and strength of Brønsted and Lewis acidic sites (Figure 1). Considering the work of Sato *et al*. (1995) it can be speculated that along with the appropriated dispersion of B_2O_3, MoS_2 and *Ni*, the best catalytic performance of $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ in HDA reactions is related to an appropriated balance between the relative concentration of Brønsted and Lewis acidic sites of intermediate acidic strength.

Dibenzothiophene HDS

Figure 2 shows the influence of *B* content in the behavior of *NiMo-B(x)* catalysts in the HDS of DBT as well as over the total acidity. As observed, boron addition at low concentrations does not significantly impact DBT conversion, but at higher boron concentration HDS activity decreases. Other authors have reported similar trends (Lewandowski & Sarbak, 2000; Ferdous *et al*., 2006). Lewandowski and Sarbak (2000) found that boron addition to *NiMo* catalysts did not affected the HDS activity of liquid carbon. Ferdous *et al*. (2006) investigated the effect of the B_2O_3 concentration in $NiMo/Al_2O_3$ catalysts in the HDS of heavy gas-oil, without detecting any effect. A volcano type behavior has been reported for HDS in agreement with the trends registered in HDA in the present work. However, the activity increase reported in such references is not as high as the one reported here (Li *et al.* 1997 and 1998). Therefore, the overall changes in HDS activity can be ascribed mainly to changes in the dispersion of the MoS_2 active phase.

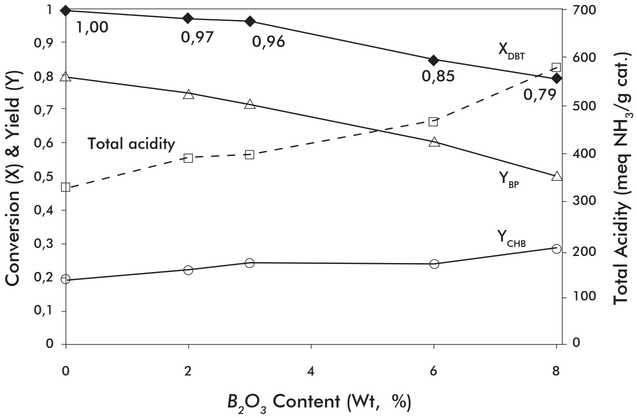

Figure 2 Steady state performance of $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts during dibenzothiophene (DBT) HDS as a function of the B_2O_3 wt.%. Reaction conditions: T = 583 K, P = 5 MPa, liquid feed flow 30 mL/h, H_2/liquid feed ratio = 500 NL/L.
BP: biphenyl; CHB: cyclohexylbenzene

It is much more interesting to analyze the changes in reaction product distribution during DBT hydrodesulfurization as presented in Figure 2. Under the present reaction conditions, biphenyl (BP), resulting from the DDS route, and cyclohexylbenzene (CHB), from the HYD reaction route, were mainly the only detected products. Partially hydrogenated tetrahydro-DBT and hexahydro-DBT intermediates were detected only in very small traces. It is assumed here that no significant further conversion of BP to CHB takes place during DBT hydrodesulfurization (Mijoin *et al*., 2001). It is observed that boron incorporation has a negative effect in DDS. Conversely, HYD selectivity increases to some extent. Such opposite trends confirm that BP is not being hydrogenated to CHB. Contrary to the present results, Li *et al*. (1997 and 1998) found an increase in the conversion to BP, with a simultaneous decrease to CHB with the increase in the boron concentration of $NiMo/\gamma$-Al_2O_3-B_2O_3 catalysts. The differences between their results and ours can be ascribed to the higher temperature employed by those authors (733 K). Under such conditions, thermodynamic limitations for HYD reaction have been predicted (Cooper & Donnis, 1996; Ho, 2004). On the other hand, the trend observed in Figure 2 agrees with the hypothesis that an increase in Brønsted acidic sites of the support of MoS_2 based catalysts favors the HYD route of desulfurization (Pérot, 2003). Comparatively, the increase in HYD selectivity, as a function of acidity and B_2O_3 content, is not as high as the one obtained in HDA. This can be ascribed to the lower aromaticity of the fused rings of NP, as compared with those of DBT. This makes the latter more refractory to HYD (Cooper & Donnis, 1996). Therefore, it is also likely that the development of the HYD route of desulfurization of DBT type molecules over conventional MoS_2 based catalysts is more related to the presence of Brønsted sites of higher acidic strength compared to those required for NP hydrogenation.

Simultaneous dibenzothiophene HDS and naphthalene HDA

According to the catalytic results in HDS and HDA as well as to the measured acidic properties for the series of $NiMo/\gamma$-Al_2O_3-B_2O_3 catalysts prepared, the catalyst labeled as *NiMo-B(6)* was chosen to perform this test. Figure 3 shows the evolution of the catalytic performance with time on stream for the simultaneous HDS and HDA reaction. The results show only slight differences with those registered for the independent tests. This behavior is in agreement with the generally accepted idea of the existence of different active sites for HDS and HYD (Topsøe, 2007; Grange & Vanhaeren, 1997). Besides, it should be noticed that there are no changes in the selectivity to the desulfurization pathway of DBT. The HYD/DDS selectivity is related to the differences in the adsorption mode of the DBT molecule over the MoS_2 active phase (Cristol, Paul, Payen, Bougeard, Hutschka, & Clémendot, 2004; Nag, 1984; Egorova & Prins, 2004). Cristol *et al*. (2004) theoretically showed that during DDS, the DBT molecule is linked to the coordination unsaturated sites (CUS) of the MoS_2 active phase via direct sulfur $\eta^1 S$ adsorption (or σ-mode). Conversely, flat $\pi-$mode of adsorption of one of the aromatic rings of DBT is required to develop HYD route. The formed $\pi-$complex between the benzene ring of DBT and the CUS of MoS_2 leads to a hydrogenation-dehydrogenation-sulfur atom bond scission equilibrium resulting in CHB formation (Mijoin *et al*. 2001; Baldovino-Medrano, Eloy, Gaigneaux, Giraldo, & Centeno, 2009). In agreement with Cristol *et al*. (2004) and Egorova and Prins (2004) proposed that the *C-S-C* bond scission step in HYD proceeded only after desorption and re-adsorption of the partially hydrogenated intermediates over the same active site.

The results of this work are pertinent for deep HDT. In that case, the effect of parallel HDN reactions must also be considered. Works in this sense will be performed in the near future.

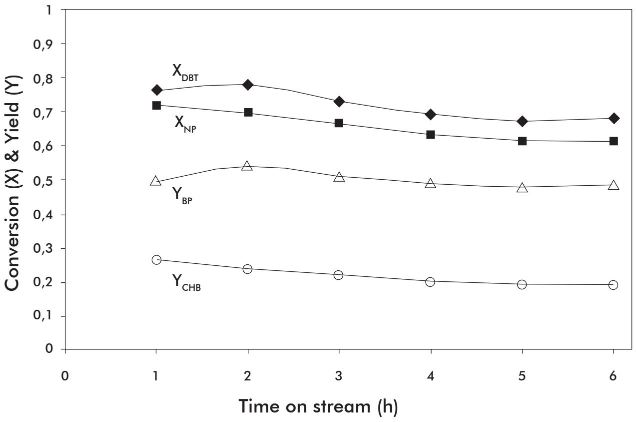

Figure 3 Catalytic performance of *NiMo-B(6)* during simultaneous naphthalene (NP) HDA and dibenzothiophene (DBT) HDS with time on stream. BP: biphenyl; CHB: cyclohexylbenzene

4. CONCLUSIONS

The main conclusions of this work are:

- The activity of the $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$ catalysts in HDA follows a volcano-type trend as a function of the boron content. The reason of this behavior is related to changes in the dispersion of the MoS_2 active phase, the textural characteristics of the support, and the proportion between the Brønsted and Lewis acidic sites generated by the addition of boron.

- Boron addition caused a decrease in the HDS of DBT activity, particularly at higher boron contents. It was determined that boron presence slightly increases conversion via HYD but negatively affects the DDS route of desulfurization. The latter effect is coherent with an increase in catalysts' acidity.

- No direct correlation between naphthalene hydrogenation and the HYD pathway was determined.

- A comparison of the results of the independent and simultaneous HDA and HDS catalytic tests indicated that the presence of naphthalene does not particularly hinder the development of the HYD route of desulfurization over $NiMo/\gamma\text{-}Al_2O_3\text{-}B_2O_3$.

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