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Effect of the activation process on thiophene hydrodesulfurization activity of activated carbon-supported bimetallic carbides

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ABSTRACT

The effect of passivation and presulfidation after carbiding of activated carbon-supported Fe–Mo, Co–Mo and Ni–Mo catalysts on their thiophene HDS activity was evaluated. Catalytic precursors were prepared by co-impregnation of the support with solutions of ammonium heptamolybdate and the promotor nitrates or sulfates. Carbiding was achieved by means of the carbothermal method, employing pure H_2 as reductant and the support as the carbon source. Carbided samples were submitted to one out of three types of procedures before HDS tests: (a) passivation at room temperature followed by presulfiding; (b) presulfiding (no passivation); and (c) neither passivation nor sulfiding before HDS. Samples of passivated catalysts prepared from the sulfates of Fe, Co or Ni contained variable amounts of sulfur, as shown by XPS and elemental analysis, while XRD showed only metals and mixed Fe_3Mo_3C or η-$M_6Mo_6C_2$ (M=Co, or Ni) phases. The nitrate-derived catalysts only presented β-Mo_2C and metals (XRD). Sulfur containing catalysts showed high initial activities although deactivate strongly during the first 40 min on the reaction stream, while the unsulfided nitrate-derived samples showed a more stable behavior and lower activities during the 2–3 h of testing. In general, samples submitted to passivation followed by presulfiding showed the higher steady state activities and those neither passivated nor sulfided were the less active. The results show the benefits of a passivating treatment on these carbon-supported catalysts, and point out to the importance of sulfided surface phases in HDS on carbides of transition metal catalysts.

1. Introduction

The need to upgrade low quality feedstocks explains the still increasing interest in the process of hydrodesulfurization (HDS), mainly aiming at the design of new catalysts that could serve as an alternative to the currently employed formulations, in order to meet the environmental standards on emissions of sulfur. Since the pioneering work by Levy and Boudart [1], early transition metal carbides (TMCs) of the 4–6 groups have attracted attention as potential catalysts for use in the HDS process, because they exhibit hydrogenating properties similar to those of noble metals [1] and at the same time they are sulfur-tolerant [2]. Initially, these interstitial compounds were found to show similar properties as the platinum-group metals for transformation of hydrocarbons reactions [1,3,4]. Later, they showed to be very active for other types of reactions, such as hydrotreatment (HDT) (*i.e.*, hydrodesulfurization, HDS; hydrodenitrogenation, HDN; hydrogenation, HYD) [4,5], conversion of methane to synthesis gas [6], methanol or higher alcohol synthesis [7], etc. Indeed, it has been reported by several authors [8–11] that these materials could exhibit similar or higher HDS activity than sulfided Mo/Al_2O_3 or $Co(Ni)Mo/Al_2O_3$.

For catalytic applications, TMCs are generally synthesized by means of temperature programmed reaction between oxide precursors and a flowing mixture of hydrogen and carbon-containing gases (generally light hydrocarbons, *e.g.*, methane, ethylene, or carbon monoxide) [12]. This type of procedure allows to obtain the desired phases at relatively low temperatures and, thus, with higher surface areas than the conventional ceramic-type methods. However, the resulting carbide surface is usually contaminated by polymeric carbonaceous species produced from the pyrolysis of the reactants [13,14]. As an alternative, Mordenti et al. developed a procedure for preparing high surface area carbides by employing the carbothermal method using H_2, which can avoid the formation of carbon residues on the surface [15]. In this route of synthesis, the carbon source is the catalyst carrier, either a carbonaceous material itself or a preconditioned conventional support (*e.g.*, by pyrolysis of a surface-bound polymer).

After preparation by either synthesis route, the obtained carbides are highly reactive towards oxygen, being in general pyrophoric. Before exposing the obtained catalysts to the normal atmosphere, a passivation treatment is customarily applied which

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consists in exposing for a given time the freshly prepared samples to a gaseous current containing a low oxygen concentration (typically, 1 vol.% O_2 in inert gas). Exposure to O_2 profoundly affects the surface composition and catalytic properties of the catalysts. Thus, the reactivity for hydrogenation/hydrogenolysis of hydrocarbons is strongly decreased or eliminated by surface oxidation, and this effect is irreversible in the sense that a reduction pretreatment will not fully recover the catalytic activity and/or selectivity shown by the fresh catalysts [16]. In agreement with this, Wu et al. reported an irreversible effect of passivation on the noble metal-like functionalities of carbides which parallels the behavior of CO adsorption on fresh and passivated-reduced Mo_2C/Al_2O_3 [17]. On the other hand, the catalytic performance can be enhanced by surface oxidation in such reactions as alkane isomerization, which could be related to the presence of very active mixed oxo-carbide species [18].

In the case of the HDT reactions, where most studies concern Mo-based monometallic or bimetallic (NiMo, CoMo) carbides, passivated samples are generally pre-reduced with H_2 at the reaction temperature before catalytic reaction tests. The purpose of such treatment is to remove the surface oxidic layer and restore the carbides to their previous condition. As indicated above, the passivated and reduced catalysts show a distinct reactivity than the initial carbides, which probably stems from the fact that reduction with H_2 of passivated carbides not only reduces the oxides, but that also carbidic C is removed from the surface [19]. In addition, it has to be taken into account the possibility that either the passivated surfaces or the pre-reduced ones could eventually become transformed into sulfides under the reaction atmosphere (or if a presulfiding treatment is purposely employed before reaction), thus generating carbo-sulfided phases. In the same way as the mixed oxo-carbide modified surface species exhibit new and interesting catalytic functionalities [18,20], it can be anticipated that mixed sulfo-carbides could show distinct properties than the carbidic original phases. From this point of view, the carbide particles may serve as a template on which a strained or highly dispersed sulfided phase is formed, and carbon could be considered as a textural promoter, acting to increase the number of active sites instead of their intrinsic activity [21].

In a previous article [22] it was reported that activated carbon-supported bimetallic A–Mo carbides (A = Fe, Co, Ni) derived from sulfate precursors showed high HDS activity, even without a sulfiding pretreatment, while similar catalysts prepared from nitrates required presulfiding in order to attain good activity levels. All these catalysts were passivated after synthesis.

The objective of the present work is to study the effects of applying or not the passivation and presulfiding treatments to the synthesized carbide catalysts on their thiophene HDS activity. To attain this goal, the carbides were subjected to one of three different protocols, under controlled conditions, before submitting them to the measurement of HDS activity, in order to vary the content and origin of sulfur.

2. Experimental

2.1. Preparation of precursors and carbides

The preparation of the precursors of the catalysts has been reported previously [22]. Briefly, the hydrated molybdates of composition $AMoO_4 \cdot nH_2O$ (A = Fe, Co, Ni) were co-precipitated on a commercial activated carbon (Merck), by mixing aqueous solutions of ammonium heptamolybdate with iron, cobalt or nickel salt solutions, either nitrates or sulfates, keeping the pH at 7. In all cases the nominal Mo content was 20 wt% and the A:Mo molar ratio was 1:1. After solvent evaporation and drying at 120 °C, the solids were transferred to a quartz reactor, and submitted to a carbothermal treatment under pure H_2. The temperature was increased at a linear rate of 5 °C min^{-1} to the final temperature (700 °C), which was held for 1 h. Generally, especially for characterization purposes, samples were quenched to room temperature and then passivated with a 1% O_2/Ar mixture. Alternatively, samples for some catalytic reaction experiments were synthesized in the same way, but excluding the passivating treatment. In this case, the samples were cooled to 400 °C before starting presulfiding and/or reaction (see below). Samples obtained from the A nitrates will be identified as AMo(N), while those obtained from sulfates will be labelled AMo(S).

2.2. Catalyst characterization

Sulfur elemental analysis was carried out by means of a combustion method employing a Fisons EA 1108 CHNS-O analyzer. The textural properties were determined by means of the adsorption of N_2 at 77 K using a Micromeritics ASAP-2010 instrument. Powder X-ray diffraction measurements were carried out with a Siemens D-5005 diffractometer employing Cu Kα radiation in the range $5^\circ < 2\theta < 90^\circ$. Identifications of phases was made using the JCPDS library, specifically for β-Mo_2C (card No. 11-0680); Ni (card No. 04-850); and Ni_3C (card No. 06-0697) [23].

2.3. Catalytic test

Before reaction, most samples were submitted to a sulfiding pretreatment, but in the case of some samples not passivated, the presulfiding was skipped. These protocols will be labelled as: *Carb-Ox-Sulf-HDS*, meaning carbided, passivated, presulfided and reacted in HDS; *Carb-Sulf-HDS*, carbided (not passivated) pre-sulfided and reacted; and *Carb-HDS*, carbided and reacted (without passivation nor sulfiding). Passivation was accomplished by cooling down to room temperature the fresh carbided sample and exposing it to a 1 vol.% O_2 in Ar flow of 50 cm^3/min for 2 h. Presulfiding was carried out under a 1 vol.% CS_2/H_2 mixture at 400 °C for 2 h. Tests of thiophene HDS were performed in a fixed bed, continuous flow reactor, at 400 °C and atmospheric pressure. Test conditions were: 250 mg of catalyst, flow of 100 cm^3/min of the thiophene (2.27 mol%)/H_2 mixture. Reaction products were analyzed by means of FID gas chromatography, with sampling of the gas effluent occurring at about 10 min intervals. After stabilization (~2 h), the steady state catalytic activities of Fe–Mo, Co–Mo and Ni–Mo catalysts were determined. Catalytic activity is reported as pseudo-first-order rate constant for thiophene disappearance in units of moles of thiophene converted to products per gram of catalyst per minute (mol Th $g_{cat}{}^{-1}$ min^{-1}) after 2 h of reaction time.

3. Results and discussion

Figs. 1 and 2 show the thiophene HDS activity as a function of time of NiMo(S) and NiMo(N) catalysts, respectively, submitted to the different pretreatment protocols. In general, sulfur-containing samples (*i.e.*, those presulfided but also the non-presulfided ones derived from sulfates) show high initial activities that slowly decrease until about 40 min. After this time, a stationary state is reached. Samples prepared from nitrates and submitted to presulfiding treatments have much higher initial activities but they deactivate strongly. The non-presulfided, nitrate-derived catalyst show almost the same activity level during the 2 h of the experiment. On the other hand, all the sulfate-derived samples showed deactivation, although in less extent than the presulfided NiMo(N) samples. Generally, the FeMo and CoMo supported samples showed similar trends as those shown in Figs. 1 and 2.

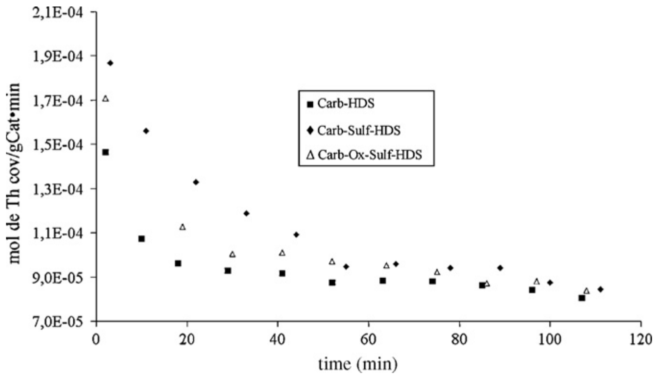

Fig. 1. Thiophene hydrodesulfurization activity as a function of time of activated carbon-supported NiMo catalysts derived from sulfates and submitted to different pretreatment procedures.

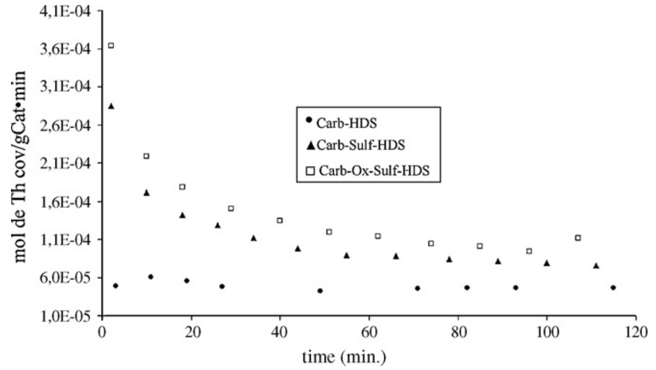

Fig. 2. Thiophene hydrodesulfurization activity as a function of time of activated carbon-supported NiMo catalysts derived from nitrates and submitted to different pretreatment procedures.

Fig. 3 presents the steady state activities of all the tested catalysts after the different activation procedures. Catalysts submitted to passivation followed by presulfidation show the higher activities, while those samples reacted after carbiding without further pretreatments (the *Carb-HDS* ones) were the less active. Samples prepared from sulfates showed higher activities than those derived from nitrates, including those submitted to the *Carb-HDS* protocol. As reported previously [22], the NiMo combination showed lower activities than the FeMo and specially the CoMo catalysts, but this seems to be an artifact of the synthesis conditions, as NiMo catalysts prepared at lower or higher pH values than 7 present higher catalytic activities [24].

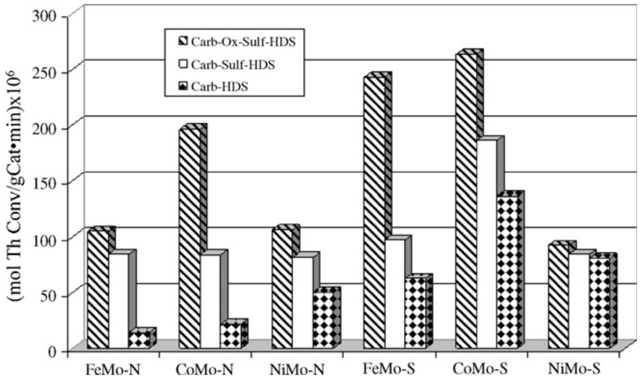

Fig. 3. Thiophene hydrodesulfurization activity at steady state of activated carbon-supported bimetallic carbides submitted to different pretreatment procedures.

Table 1
BET surface area of the activated carbon and the activated carbon-supported M–Mo carbides (M = Fe, Co, Ni). The catalysts were passivated after carbiding.

Solid	Precursor	Surface area (m^2/g)
Activated carbon	–	881
FeMo	Sulfate	548
FeMo	Nitrate	305
CoMo	Sulfate	342
CoMo	Nitrate	266
NiMo	Sulfate	400
NiMo	Nitrate	317

In Table 1, it is shown an effect of the precursor type on surface area after carbothermal hydrogen reduction. Depending on the preparation conditions, after the impregnation and carburization the surface areas ranged between 266 and 548 m^2/g. The surface areas of the carbide samples obtained from nitrate precursors were lower than those obtained from sulfate precursors. This difference may be attributed to the thermal stability of the sulfates compared to nitrates and/or to the greater oxidant power of nitrates, leading to greater support gasification [25].

Table 2 shows the steady state activities expressed per square meter. When compared on this basis, the CoMo catalysts are still the most active catalysts (especially that derived from sulfate), their activities being two- or even threefold those of the remaining samples. On the other hand, differences between the FeMo and NiMo catalysts decrease sharply, suggesting some similarity between these two systems. Catalysts of the same composition submitted to passivation show similar activities, indicating that the precursor effect (sulfate vs nitrate) is less important than suggested by the activity values on weight basis. Thus, *e.g.*, the abnormally high activity (on weight basis) of the FeMo(S) sample reflected in Fig. 3 is an artifact due to the very high surface area of this sample.

Carbided and passivated samples of the catalysts were characterized by means of XRD, confirming the results reported elsewhere [22], *i.e.*, the diffractograms of supported carbides obtained from sulfate precursors present narrow peaks that could be assigned to mixed η-Fe_3Mo_3C, η-Co_6Mo_6C, or η-Ni_6Mo_6C phases plus signals due to the promotor metals, while the carbides obtained from nitrate precursors showed signals due to β-Mo_2C and Fe, Co or Ni metallic phases. No peaks that could be assigned to oxides (or sulfur containing compounds) were found in the passivated catalysts. Liang et al. [26] reported that CoMo/C catalysts prepared from cobalt nitrate showed the presence of bimetallic CoMo carbides, but only if carbiding was carried out up to 600 °C, while separation into Co metal and β-Mo_2C occurred if the carbiding temperature was increased above 700 °C. In the present study, carbides prepared from sulfates were able to keep the CoMo bonding when carbiding was performed at this latter temperature. The presence of mixed phases in catalysts obtained from sulfates could be attributed to a role as "chelating agent" of the sulfate ions which would protect the Mo-promotor bonding

Table 2
Steady state activities, expressed per surface area, of activated carbon-supported M–Mo carbides (M = Fe, Co, Ni) submitted to different post-carbiding treatments.

Catalyst	Steady state activity ($\times 10^7$ mol Th conv m^{-2} min^{-1})		
	Carb-Ox-Sulf-HDS	Carb-Sulf-HDS	Carb-HDS
FeMo(N)	3.28	2.62	0.49
FeMo(S)	4.38	1.64	1.00
CoMo(N)	7.33	3.01	0.76
CoMo(S)	7.46	5.26	3.80
NiMo(N)	3.15	2.52	1.42
NiMo(S)	2.25	2.00	1.88

Table 3
Sulfur content, as measured by elemental analysis, in activated carbon-supported M–Mo carbides (M = Fe, Co, Ni) submitted to different post-carbiding treatments.

Catalyst	Sulfur content (at.%)		
	Carb-Ox-Sulf-HDS	Carb-Sulf-HDS	Carb-HDS
FeMo(N)	18.279	13.631	4.326
CoMo(N)	12.356	10.71	3.487
NiMo(N)	9.858	10.541	12.41
FeMo(S)	14.760	17.240	15.150
CoMo(S)	17.081	15.826	15.385
NiMo(S)	13.169	13.509	14.172

during thermal treatment. On the other hand, nitrates being more sensitive to heating and additionally being more oxidant, would favour the formation of the separated phases during carbiding at high temperatures.

It was previously shown by both XPS and elemental analysis that, after carbide generation and passivation, samples prepared from sulfate precursors retain sulfur [22]. The surface sulfur content detected by XPS was higher than that measured by elemental analysis, suggesting segregation of sulfur species to the surface of the carbides. After presulfiding, the sulfur contents of samples prepared from sulfates measured by elemental analysis show a fivefold increase as compared to those of the non-presulfided samples [22]. Table 3 shows the results of elemental analyses of samples submitted to the thiophene HDS reaction carried out for 2 h after the three post-carbiding procedures indicated above. The results shown in Table 3 for samples submitted to the *Carb-Ox-Presulf-HDS* procedure agree with those of presulfided non-reacted samples in the previous report [22], indicating stability under HDS conditions of the sulfur contents of presulfided catalysts. The presence of sulfur in Mo carbide catalysts employed for thiophene HDS was reported by Bussell and co-workers [11,21] who proposed that a thin layer of “sulfided Mo” forms on top of the carbide particles.

Sulfided, post-reaction samples of catalysts were also studied by XRD. Fig. 4 shows the diffractogram of the NiMo(N) post-reacted sample submitted to the *Carb-Ox-Presulf-HDS* procedure, presenting the peaks of β-Mo_2C at 2θ = 39.49, 34.45, 37,91, 52.2, 61.65, 69.65, 74.75. Three nickel carbide peaks were also observed, but no peaks due to sulfides or nickel metal were present, which is interesting as nickel carbide has shown to be easily decomposed to the metal in conditions similar to those of the HDS tests [27]. The reacted samples showed similar XRD signals as the fresh ones, proving that the crystalline structures of the carbides are stable in the reaction conditions employed. Thus, any active, sulfur-containing phases should exist at the catalyst surface and very well dispersed. These experiments, especially the ones carried out with reacted catalysts, were done with small amounts of samples, thus the lower intensity and noisier baseline as compared to diffractograms of the fresh (carbided and passivated) samples [22].

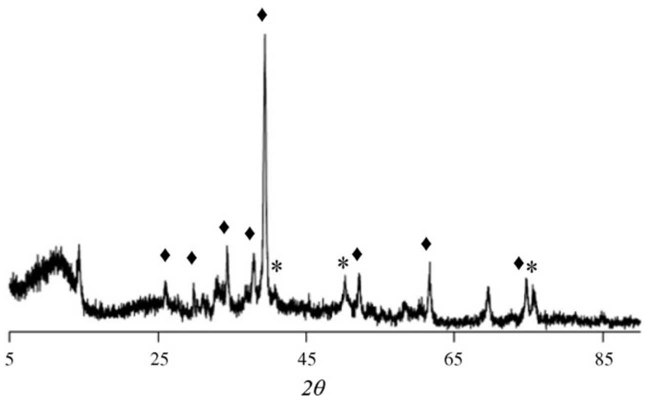

Fig. 4. X-ray diffraction patterns of activated carbon-supported NiMo(N) carbide after reaction, submitted to passivation and presulfiding pretreatments; keys: β-Mo_2C (◆) and NiC (*).

Interestingly, catalysts that do not contain sulfur at the start of reaction show a more stable activity behavior while those with sulfur (both presulfided and sulfate-derived) suffer initially a strong deactivation. Elsewhere [22] it was also found that passivated samples prepared from nitrates and not presulfided did not show the initial deactivation characteristic of samples that contain sulfur. This fact suggests that changes of the active phases of the presulfided carbides take place during the first minutes of reaction. In our previous work it was found that the amount of sulfur of passivated samples prepared from sulfates increases from about 3 to 14–15 at.% upon presulfiding [22]. Results in Table 3 show that even samples derived from nitrates and not presulfided retain sulfur after reaction, in general lower amounts than catalysts prepared from sulfates.

It is worth noting that the amounts of metals in these catalysts are about 3.1 at.% each. Thus, in most cases, the amounts of sulfur shown in Table 3 duplicate or even triplicate the metal amounts. This would imply almost full sulfidation of the metals, however, XRD of sulfided and reacted samples (Fig. 4) do show that the crystalline structure of the carbides is kept after presulfiding and reaction. It is possible that the major part of the sulfur retained by the samples could be trapped into the micropores of the activated carbon support. A “sink effect” that allows activated carbon supports to retain elemental sulfur and deliver it to the sulfided active phases as needed has been proposed by Laine et al. [28]. Most likely, sulfur species associated to the catalytically active phases exist as well dispersed surface phases supported on the carbides, as proposed by Bussell and co-workers [21]. In fact, recent TEM measurements on the present catalysts showed that the sulfided samples contain particles of the bimetallic carbides closely surrounded by MoS_2 fringes, showing that sulfide and carbide phases co-exist in these samples after presulfiding [29].

Fig. 5 shows plots of the activity per square meter against sulfur content after reaction for all the samples. It can be seen that the results of the catalysts prepared from sulfates follow a linear plot that cuts the *Y* axis at around 13.5–14 wt% S. This probably means that the amount of sulfur not related to the active phases is around 14 wt%, which would be in agreement with the low sulfur amounts expected from dispersed surface phases. The results for samples derived from nitrates are very scattered, the logarithmic trend line shown in that figure only pertains the CoMoN samples. It must be

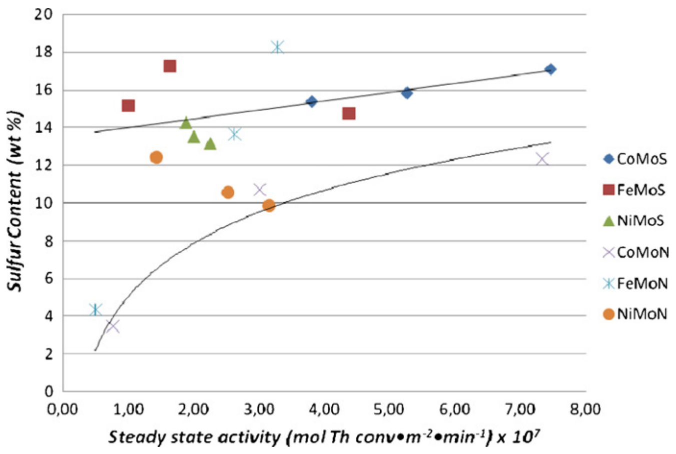

Fig. 5. Steady state HDS activity of activated carbon-supported bimetallic carbides as a function of sulfur content. The linear plot at the top concerns all the samples produced from sulfates, AMo(S) (A = Fe, Co, Ni); the logarithmic plot at the bottom pertains only the CoMo(N) samples.

remembered that the nitrate-derived samples are distinct from the sulfate-ones, as bimetallic carbide phases are present in the latter but not in catalysts prepared from nitrates. There is a coarse relationship between sulfur content and activity, as samples with lower sulfur amounts are the less active, while the most active samples show consistently high sulfur levels. However, a high amount of sulfur not necessarily means a highly active sample, given that most sulfur is unrelated to the active phases.

Sundaramurthy et al. [30], reported increasing HDN and HDS activities of supported, P-promoted NiMo/γ-Al_2O_3 carbide catalysts submitted to precooking with the LGO feed, which stabilized after 3 days on stream. On the other hand, when the same authors submitted these catalysts to presulfiding, the behavior was more close to that of sulfide-based catalysts, *i.e.*, the catalysts showed higher initial activity and deactivated slightly during precooking [31]. They attributed this behavior to the formation of very active "NiMoS" phases on the surfaces of the carbides, a gradual process with precooking activation and a faster one when presulfiding was purposely made. The opposite view for the case of sulfide catalysts, *i.e.*, the formation of "CoMoC" type phases, had been advanced by Chianelli and co-workers [32]. In any case, it is well known that incorporation of C atoms into the active phases of sulfides, *e.g.*, by pretreatment with CS_2 instead of H_2S [33], benefits the catalyst properties for hydrotreatment. In the present work, although there are not clear cut correlations between HDS activity and sulfur content, samples with lower sulfur amounts, *i.e.*, FeMo(N) and CoMo(N) submitted to the *Carb-HDS* treatment, are the less active ones, while the more active catalysts show high sulfur contents, resulting from presulfiding after a passivation treatment. These results point to an important role of sulfur in the generation of the active phase of carbon-supported carbide catalysts.

4. Conclusions

A study of the effects of applying or not the passivation and presulfiding treatments to the synthesized carbide catalysts on their thiophene HDS activity was performed in order to contribute to the understanding of the role of sulfur in the catalytic properties of these materials. Samples that contain sulfur either from sulfate precursors or from presulfiding, show high initial activities that slowly decrease over time until a pseudo-stationary state is reached, while those that initially do not posses sulfur attain lower activity levels and show a more stable behavior with time of reaction. Samples prepared from nitrates and submitted to presulfiding treatments have high initial activities but deactivate strongly. All the sulfate-derived samples showed deactivation, although in less extent than the presulfided NiMo(N) samples. The catalysts submitted to passivation followed by presulfidation show the higher activities, while those samples reacted after carbiding without further pretreatments were the less active. On the other side, the sulfur content of samples submitted to the *Carb-Ox-Presulf-HDS* procedure agree with those of presulfided unreacted samples indicating stability under HDS conditions of the sulfur contents of presulfided catalysts. The correlation between HDS activity and sulfur content is not clear, due to the fact that large amounts of sulfur are retained by the support. In general, however, the samples with lower sulfur amounts are the less active ones, while the more active catalysts show high sulfur contents. These results point to an important role of sulfur in the generation of the active phase of carbon-supported carbide catalysts.

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