

Effect of the type of precursor and the synthesis method on thiophene hydrodesulfurization activity of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides

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Abstract

In this work it is studied the effect of the type of precursor (sulfate vs. nitrate of promotor) and the synthesis method (conventional vs. carbothermal carbiding) on the thiophene hydrodesulfurization (HDS) activity of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides. Catalytic precursors were prepared by co-impregnation of the support with solutions of ammonium heptamolybdate and the promotor salt. Conventional carbiding consists of a temperature-programmed treatment under a CH_4/H_2 (1:4) atmosphere, while the carbothermal method employs pure H_2 . The passivated carbided solids were characterized by XRD and XPS. The presence of metals and $\text{Fe}_3\text{Mo}_3\text{C}$ or $\text{M}_6\text{Mo}_6\text{C}_2$ phases ($\text{M} = \text{Co}$ or Ni) in samples from sulfate precursors and of $\beta\text{-Mo}_2\text{C}$ and metals in those from nitrate precursors was verified by XRD, whereas XPS showed the presence at the surface of $\text{Mo}^{\delta+}$ ($0 \leq \delta \leq 2$), Mo^{4+} , Mo^{6+} , Fe^{3+} , Co^{2+} , Ni^0 and Ni^{2+} species. The bimetallic carbides obtained from sulfate precursors retained sulfur on the surface, as shown by signals in the S 2p region, at 169 and 162 eV, assigned to S^{2-} and SO_4^{2-} , respectively. Prior to the catalytic reaction, the passivated carburized forms of carbon supported catalysts were presulfided *in situ*. The catalytic activity of carbides was strongly influenced by the type of precursor and slightly by the synthesis method. The activity of carbides obtained by the carbothermal method and with sulfate precursors was greater than that of the solids obtained by the conventional method and with nitrate precursors. The carbides obtained from nitrates showed increased catalytic activity when presulfided, suggesting that the carbides with sulfided surfaces or mixed carbo-sulfide species could be the active phase in HDS on carbide catalysts. The catalysts derived from sulfates showed higher activity than those obtained from nitrates, even without presulfiding, suggesting that sulfide from the precursor sulfate results in more active species than those obtained after presulfiding. © 2007 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Carbides; Precursor effect; Sulfided surface; Synthesis method effect; Thiophene hydrodesulfurization

1. Introduction

The high demand of hydrocarbons in the world during the last century has resulted in the exhaustion of most of the light oil reserves; therefore the petroleum used nowadays is increasingly contaminated with sulfur, which upon combustion of fuels produces sulfur oxides [1]. The current generation of hydrodesulfurization catalysts are sulfides of Co(Ni)-Mo supported on alumina, and although they are very active for conventional oil, they exhibit low activity towards highly refrac-

tory sulfur compounds [2]. The quality of fuels prescribed by the new environmental regulations can be attained using the current catalysts, but only after significant modifications of refining operations. At certain point, these modifications would cause negative effects on the catalyst life and would increase the costs of the processes [2]. In the last decades, efforts have been made to develop novel catalysts that can fulfill these regulations, and the transition metals carbides and nitrides have been identified as potential catalysts for such applications [3]. In this regard, the Mo based solids have been receiving most of the attention [3–14]. The catalytic properties of carbide materials strongly depend on their surface structure and composition, which are closely associated with the preparation methods [15]. When employing bimetallic precursors, there exist the possibility that the resulting carbides (nitrides) consist either of the separated

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monometallic phases or of the mixed Co(Ni)-Mo-C(N) ones. While in unsupported solids the presence of such compounds as $\text{Co}_3\text{Mo}_3\text{C}$ or $\text{Ni}_2\text{Mo}_3\text{N}$ has been shown by XRD, in supported systems it is not easy to observe such mixed phases, and only the monometallic carbides are generally detected [16]. In a few works, bimetallic phases supported on alumina have been observed [17,18]. Nevertheless, it is clear that regardless of the observation or not of the bimetallic phases, the mixed metal catalysts are more active than the catalysts consisting only of Mo carbide/nitride [5,16,18–21].

The transition metals carbides as catalysts are still in development and the type of support is a variable to be studied in order to improve the hydrotreating process efficiency. Activated carbon has received attention as a carrier for HDS catalysts for several reasons (variable amount of surface functional groups, large specific surface area with an easily controlled pore volume and relatively lower coking activity) [22–25].

In the preparation of carbides of catalytic interest, the conventional preparation method is the temperature-programmed reaction between oxide precursors and a flowing mixture of H_2 and carbon-containing gases [26]. However, some problems exist in this method of preparation, namely, the resultant carbide surface is usually contaminated by polymeric carbon from the pyrolysis of the carbon-containing gases [27,28]. Recently, Mordenti and co-workers developed a novel synthesis route to preparing high surface area carbides by employing the carbothermal method using H_2 , which can avoid the formation of carbon residues on the surface [29]. Liang et al. tried to optimize the carbothermal hydrogen reduction varying the H_2 flow and the load of precursor in order to obtain supported Mo_2C and bimetallic carbides [30]. Sayag, using the carbothermal H_2 method prepared supported Mo_2C , modifying the chemical surface of the support and obtained excellent results in HDS [31].

The exact nature of the active sites in these systems is still a matter of debate. It is believed that the carbide particles may simply serve as a template on which a strained or highly dispersed, sulfided phase is formed. In this sense, carbon could be considered as a textural promoters, acting to increase the number of active sites instead of their activity [14]. It has been suggested that during hydrotreating, these catalysts form a new active site (MoS_xC_y), which can enhance the HDS activity [32,33]. Aegerter et al. [13] observed sulfidation of Mo_2C during HDS of thiophene and proposed that a thin layer of highly dispersed MoS_2 is present on the surfaces of the carbide. This model is further supported by Bussell and co-workers [14,18]. Oyama et al. found an increase in the HDS activity of molybdenum carbides during hydrogenation reactions in presence of thiophenic compounds [5,34]. Szymanska-Kolasa et al. showed in recent studies, the sulfidation at the surfaces of Mo_2C during the HDS process [35]. Sundaramurthy et al. confirmed by DRIFTS of adsorbed CO that the surface of NiMo carbides are partially sulfided during the hydrotreating reaction as a result of the sulfidation [33].

In the present work we have studied the effect of the type of precursor salt and the carbiding method (conventional vs. carbothermal) on the thiophene hydrodesulfurization activity of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo. To our

best knowledge, this is the first report on the preparation of bimetallic carbides from *sulfate* precursors, showing an effect of sulfur derived from the precursor salt in the HDS of thiophene.

2. Experimental

2.1. Preparation of precursors and carbides

The bimetallic precursors were supported on a commercial activated carbon (Merck, $899\text{ m}^2/\text{g}$) by one-step co-precipitation. Aqueous solutions of ammonium heptamolybdate (Merck, 99%) and iron, cobalt or nickel nitrates (Riedel de Haen, typically 98%) or sulfates (Aldrich, typically 98%) were prepared with M/Mo molar ratio 1:1 and kept at 80°C , and only then were simultaneously added dropwise to a flask containing the support, under stirring. The impregnation was performed at pH 7. A slight excess of the solution was used to provide an uniform coating of the activated carbon surface. The impregnation step lasted until removal of the solvent by evaporation. The mass obtained was further dried at 120°C for 12 h overnight, and then the solids were transferred to a quartz reactor, deposited on a quartz fiber bed. A tubular electrical furnace controlled by a temperature programmer (Thermolyne 21100) was used to heat the reactor. The amount of the sample was about 2 g/batch. Either pure H_2 or a CH_4/H_2 (1:4, v:v) mixture was passed through the sample at a total flow rate of $100\text{ cm}^3\text{ min}^{-1}$. 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. The samples were quenched to room temperature and then passivated by a 1% O_2/Ar mixture for 1 h. The activated carbon supported carbides will be identified as MMo-P-m, where M, P, and m are, respectively, the type of metal promotor (Fe, Co, Ni), type of precursor (S = sulfate, N = nitrate), and synthesis method (CM = conventional; CTH = carbothermal with H_2).

2.2. Catalyst characterization

The activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and elemental CHNS analysis. XRD analysis of the samples was carried out using a SIEMENS D-5005 diffractometer with a Cu $\text{K}\alpha$ (1.5456 \AA) radiation source, within a range $10^\circ \leq 2\theta \leq 90^\circ$. The identification of the different phases was made using the JCPDS library [36] for Mo_2C (card No. 11-0680), Fe (card No. 06-0696), Co (card No. 15-0806), Ni (card No. 04-0850), $\text{Fe}_3\text{Mo}_3\text{C}$ (card No. 47-1191), $\text{Co}_6\text{Mo}_6\text{C}_2$ (card No. 80-0339) and $\text{Ni}_6\text{Mo}_6\text{C}_2$ (card No. 80-0337). The surface composition (XPS) of the carbides was determined with a VG ESCALAB 220 i-XL photoelectron spectrometer equipped with a dual (non monochromatic) Mg/Al anode, operated at 400 W. The Al $\text{K}\alpha$ radiation (1486.6 eV) was employed for the experiments reported here. All measurements were performed under UHV, better than 10^{-8} Torr. Calibration of the instrument was done employing the Au $4f_{7/2}$ line at 83.9 eV . Quantitation of the XPS signals and curve fitting of the spectra was carried out with the XPSPEAK 4.1 and XPS GRAPH routines after baseline subtraction by the Shirley

method, employing typically a 80% Gaussian-20% Lorentzian combination and tabulated atomic sensitivity factors. Due to the relatively insulating character of samples, internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV. Binding energies reported in the current study were accurate to within 0.2 eV. Analysis of sulfur content in selected catalyst samples was carried out by oxidation at 1000 °C and chromatographic separation of the resulting gases using an EA 1108 Carlo Erba CHNS-O instrument.

2.3. Catalytic test

Prior to the catalytic reaction, the carburized and passivated forms of activated carbon supported catalysts were activated *in situ* under a 1 vol% CS₂/H₂ mixture at 400 °C for 2 h, in order to remove the passivation layer and attain a stable and reproducible state at the surface. Tests of thiophene HDS were carried out in a fixed bed, continuous flow reactor, at 400 °C and atmospheric pressure. The test conditions were: 250 mg of catalyst, flow 100 cm³ min⁻¹ of the thiophene (2.27 mol%)/H₂ mixture. Reaction products were analyzed by means of gas chromatography, with sampling of the gas effluent occurring at 10 min intervals. After stabilization (≈3 h), the catalytic activities of Fe-Mo, Co-Mo and Ni-Mo catalysts were determined.

3. Results and discussion

3.1. XRD analysis

Fig. 1 show selected results of the analysis by XRD. Indifferently from the used synthesis method, the supported carbides obtained from sulfate precursors showed diffraction peaks due to mixed Fe₃Mo₃C or M₆Mo₆C₂ phases (M = Co or Ni) plus peaks due to the metals. On the other hand, the carbides obtained from nitrate precursors showed the presence of β-Mo₂C and metallic phases. All figures show narrow and defined diffraction peaks suggesting that these supported phases have good crystallinity.

Fig. 1(a) and (b) show XRD patterns of FeMo samples obtained from different precursors. In Fig. 1(a), the peaks at 2θ = 42.11, 39.60, 46.05, 71.85, 35.09, 73.58, 32.12, 64.24, 49.06, 54.60 are due to the Fe₃Mo₃C phase, and those at 2θ of 44.67, 65.02, and 82.33 correspond to metallic iron. Interestingly, the peaks due to Fe are more intense than those of similarly prepared samples of the Co and Ni promoted carbides (Fig. 1(c) and (e)). No peaks due to sulfur containing phases were observed. Fig. 1(b) shows peaks at 2θ = 39.49, 37.93, 34.47, 52.23, 69.64, 74.74, 61.65 and 44.67, 65.02, 82.33 due to β-Mo₂C, and also the signals due to iron.

The XRD patterns of CoMo carburized with different synthesis method and precursors are shown in the Fig. 1(c) and (d). Fig. 1(c) shows peaks at 2θ = 42.30, 39.89, 46.39, 72.44, 35.34, 32.35, 87.71, 64.67, 69.49, 59.64, 49.39, 74.11, 78.75 due to the Co₆Mo₆C₂ phase, while the other diffraction peaks at 2θ of 44.22, 51.52, and 75.85 correspond to cobalt metal. Fig. 1(d) shows diffraction peaks corresponding to Mo₂C and cobalt metal. Although, the diffraction patterns of FeMo and CoMo carbides obtained by the carbothermal method (Fig. 1(b)

and (d)) show predominant peaks of Mo₂C and metals, the presence of small amounts of the mixed Fe₃Mo₃C and Co₆Mo₆C₂ phases is evident from the less intense peaks at 42.11 and 42.30, respectively.

The XRD patterns of activated carbon supported Ni-Mo carbides are shown in the Fig. 1(e) and (f). Fig. 1(e) shows peaks of Ni₆Mo₆C₂ at 2θ = 43.11, 40.53, 47.16, 35.91, 73.74, 75.52, 60.66, 32.86, 68.90, 55.25, and metallic Ni at 2θ = 44.51, 51.85, and 76.37, while Fig. 1(f) shows diffraction peaks corresponding to Mo₂C and nickel.

3.2. XPS analysis

X-ray photoelectron spectroscopy was used to obtain the surface composition of the carbides and the chemical environment of Mo, Fe, Co and Ni, which was estimated by curve fitting of the Mo 3d, Fe 2p, Co 2p and Ni 2p spectra. Fig. 2(a)–(d) show the Mo 3d spectra of the activated carbon supported Fe-Mo carbides obtained with different synthesis method and type of precursor. These figures are typical of those obtained with the rest of Mo-containing catalysts. Regardless of the passivation procedure, they show the presence at the surface of a signal between 228.0 and 228.5 eV that can be attributed to a Mo 3d_{5/2} peak from a carbide phase. Previously, a similar peak denoted as Mo^{δ+} has been assigned to low oxidation state species (0 ≤ δ ≤ 2) [37], and also to Mo²⁺ species derived from allyl precursor on silica support [38]. Table 1 presents the B.E. of the Mo 3d_{5/2} signals and the percent distribution of Mo oxidation states that were obtained by deconvolution of the Mo 3d envelopes. The presence of Mo⁴⁺ (229.3–230.4 eV), and Mo⁶⁺ (232.0–232.5 eV) species can be identified, respectively, with Mo (IV) (oxy-) carbide and Mo (VI) oxide [37,39]. The use of nitrate precursors, indifferently from the used synthesis method, generated a greater proportion of high oxidation state species, Mo⁴⁺ and Mo⁶⁺. The same is true of the use of the CTH method with sulfate precursors, but the CM with sulfates generated a larger proportion of Mo^{δ+} species. This may be due to a higher

Table 1

Distribution of Mo oxidation states in activated carbon supported Fe-Mo, Co-Mo, and Ni-Mo carbides obtained with different synthesis method and type of precursor

Catalyst*	Mo 3d _{5/2}		
	Mo ^{δ+} /eV (%)	Mo ⁴⁺ /eV (%)	Mo ⁶⁺ /eV (%)
FeMo-S-CM	228.4 (15.07)	229.5 (45.49)	232.5 (39.44)
FeMo-N-CM	228.4 (32.51)	230.4 (10.66)	232.5 (56.83)
FeMo-S-CTH	228.4 (12.13)	229.5 (33.05)	232.5 (54.82)
FeMo-N-CTH	228.4 (5.68)	230.2 (7.14)	232.4 (87.19)
CoMo-S-CM	228.3 (14.96)	229.3 (47.76)	232.5 (37.28)
CoMo-N-CM	228.2 (25.33)	229.3 (18.59)	232.4 (56.08)
CoMo-S-CTH	228.3 (14.23)	229.5 (54.98)	232.5 (30.79)
CoMo-N-CTH	228.2 (19.63)	229.3 (22.19)	232.4 (58.18)
NiMo-S-CM	228.1 (61.70)	229.3 (10.85)	232.2 (27.45)
NiMo-N-CM	228.4 (78.15)	230.4 (8.96)	232.3 (12.89)
NiMo-S-CTH	228.0 (28.51)	229.3 (16.36)	232.4 (55.13)
NiMo-N-CTH	228.0 (34.90)	229.3 (17.57)	232.2 (47.53)

* S = sulfate; N = nitrate; CM = conventional method; CTH = carbothermal method.

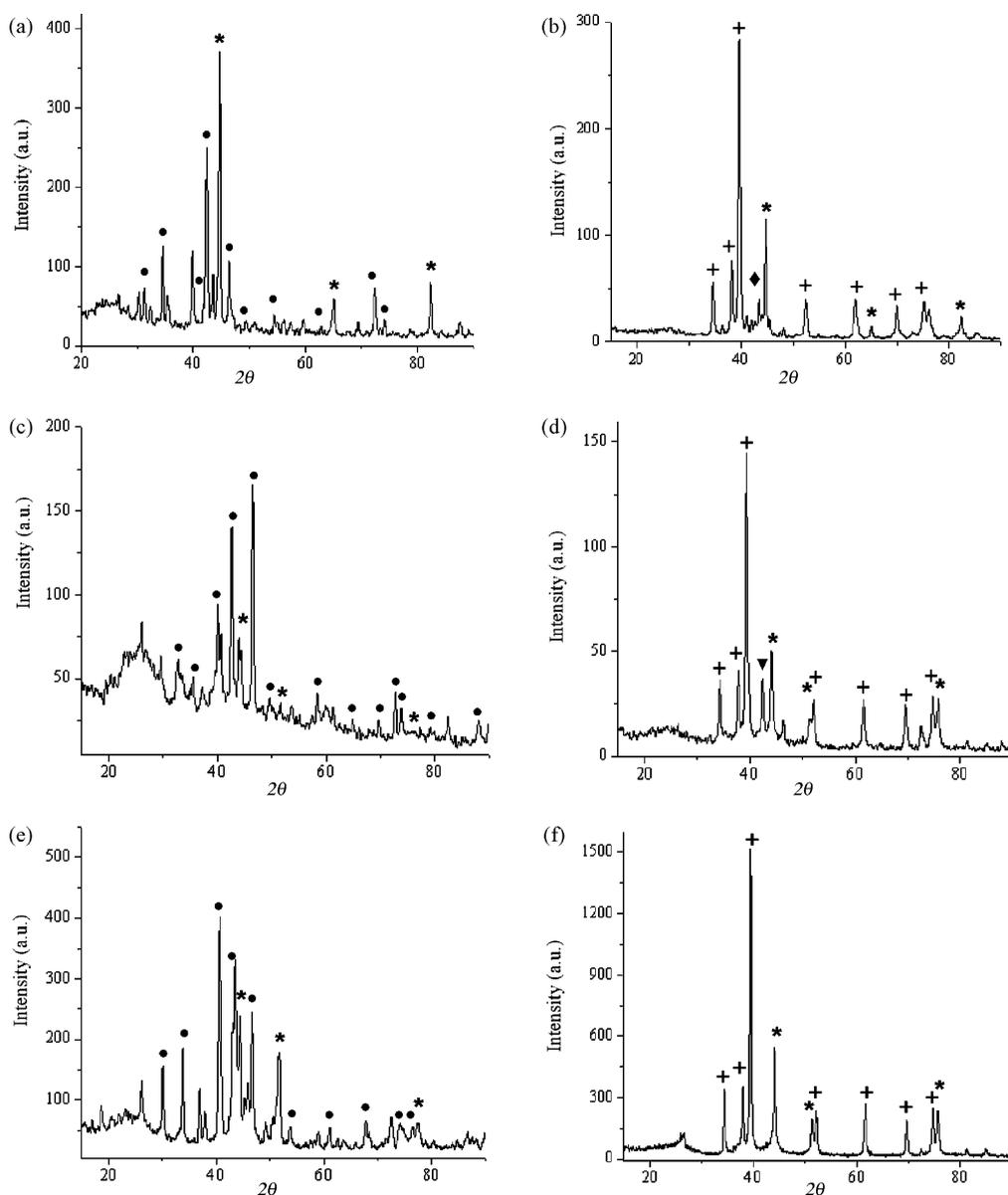


Fig. 1. XRD of activated carbon supported M-Mo carbides synthesized by the conventional (CM) and carbothermal (CTH) methods: (a) Fe-Mo from CTH and sulfate precursor— $\text{Fe}_3\text{Mo}_3\text{C}$ (●) and Fe (*); (b) Fe-Mo from CTH and nitrate precursor— $\beta\text{-Mo}_2\text{C}$ (+), Fe (*) and $\text{Fe}_3\text{Mo}_3\text{C}$ (◆); (c) Co-Mo from CM and sulfate precursor— $\text{Co}_6\text{Mo}_6\text{C}_2$ (●) and Co (*); (d) Co-Mo from CTH and nitrate precursor— $\beta\text{-Mo}_2\text{C}$ (+), Co (*) and $\text{Co}_6\text{Mo}_6\text{C}_2$ (▼); (e) Ni-Mo from CTH and sulfate precursor— $\text{Ni}_6\text{Mo}_6\text{C}_2$ (●) and Ni (*); (f) Ni-Mo from CTH and nitrate precursor— $\beta\text{-Mo}_2\text{C}$ (+) and Ni (*).

reducibly induced by the conventional method that consists of a temperature-programmed treatment under a CH_4/H_2 (1:4) mixture together with the support, both acting as sources of carbon atoms, while the carbothermal method employs only the support as source of carbon atoms.

The bimetallic carbides obtained from sulfate precursors retained sulfur on the surface, as suggested by a quite visible shoulder at 226.5 eV (Fig. 2(a) and (b)) close to the Mo 3d region, and confirmed by the presence of two bands in the S 2p region, at 169 and 162 eV (Fig. 3), assigned to S^{2-} and SO_4^{2-} [39]. This suggests that the carbides possess sulfided surfaces or mixed carbo-sulfide species present on the surface of the catalysts. Fig. 3 is typical of those obtained with the rest of Mo-containing catalysts synthesized from sulfate precursors. Table 2 shows the

amounts of sulfur, expressed as atomic %, obtained from XPS data and from elemental analysis for several catalyst samples, including in the case of the latter technique samples submitted to a sulfiding pretreatment. It can be seen that for samples derived from sulfate precursors (not presulfided) the amount of sulfur at the surface ($\%S_{\text{XPS}}$) is consistently higher than that in the bulk ($\%S_{\text{CNHS}}$). This suggests that the sulfide species tend to segregate towards the surface of the carbided phases.

Fig. 4(a) shows the Fe 2p spectrum of the activated carbon supported Fe-Mo carbide carburized by conventional method and sulfate precursor. Independently from the used synthesis method and type of precursor, the XPS analysis in the Fe 2p region shows a peak between 710.9 and 711.5 eV, with a strong shake-up line at 717 eV. These signals correspond to Fe^{3+} typi-

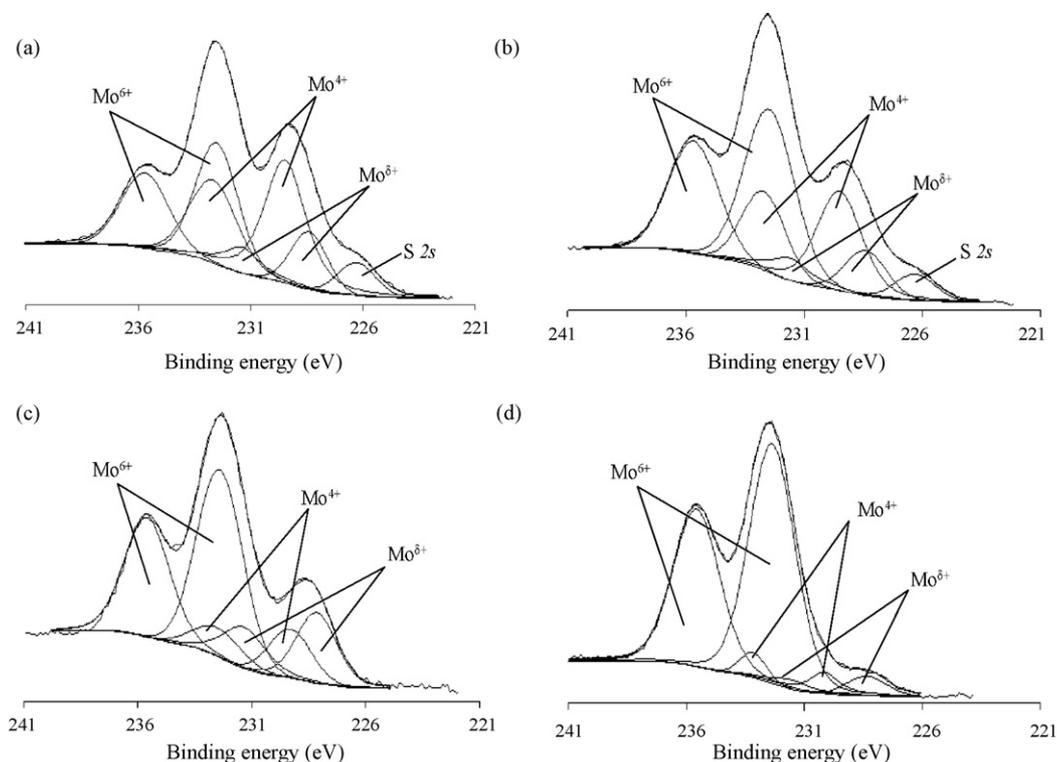


Fig. 2. X-ray photoelectron spectra (Mo 3d region) of the activated carbon supported Fe-Mo carbides: (a) synthesized by CM from sulfate precursor; (b) synthesized by CTH from sulfate precursor; (c) synthesized by CM from nitrate precursor; (d) synthesized by the CTH from nitrate precursor.

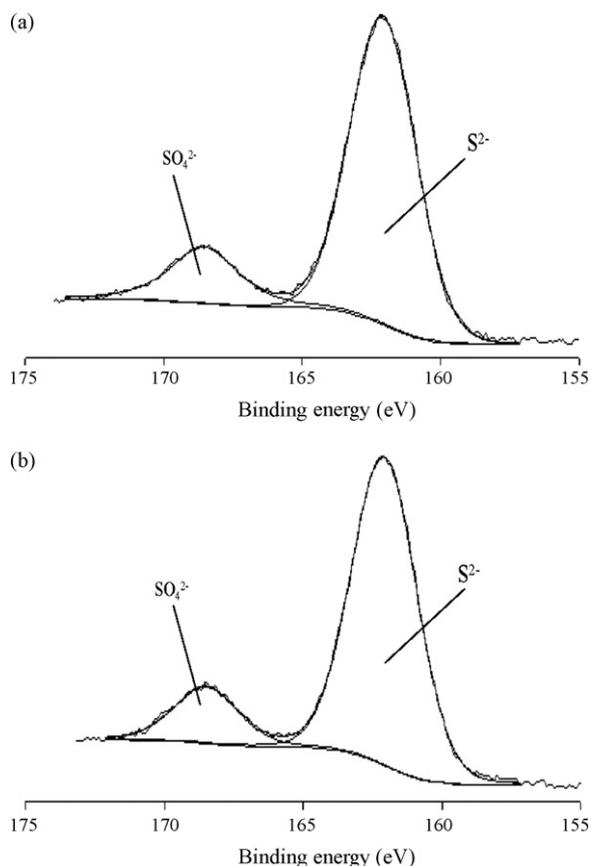


Fig. 3. X-ray photoelectron spectra (S 2p region) of the activated carbon supported Fe-Mo carbides synthesized from sulfate precursors: (a), CM; (b), CTH.

cal of a Fe_3O_4 structure [40], suggesting that the Fe species in the surface of the carbide are easily oxidized. On the other hand, the XPS analysis of the activated carbon supported Co-Mo carbide obtained by CM and sulfate precursor in the Co 2p region (Fig. 4(b)) shows a peak between 781.5 and 781.8 eV, together with a strong shake-up line at 786 eV, characteristic of Co^{2+} species. The Co $2p_{3/2}$ band corresponding to Co^{2+} is typical, e.g., of a CoMoO_4 structure [39], a possible precursor for the formation of “Co-Mo-S” species involved in the catalytic activity of hydrodesulfurization reactions [41]. The Co-Mo carbides have shown similar species on the surface indifferently from the used synthesis method and type of precursor.

The major XPS features for the activated carbon supported Ni-Mo carbides (Fig. 4(c) and (d)) are the peaks between

Table 2

Sulfur content (as atomic %) measured by XPS (S_{XPS}) and by chemical analysis (S_{CHNS}) of selected catalyst samples

Catalyst*	Non presulfided		Presulfided % S_{CHNS}
	% S_{XPS}	% S_{CHNS}	
FeMo-S-CM	6.3	3.2	15.4
FeMo-S-CTH	6.7	–	–
CoMo-S-CM	13.4	–	–
CoMo-S-CTH	13.7	3.1	13.9
NiMo-S-CM	5.7	–	–
NiMo-S-CTH	5.2	3.5	14.4
CoMo-N-CM	–	–	12.0
CoMo-N-CTH	–	–	11.0

* S = sulfate; N = nitrate; CM = conventional method; CTH = carbothermal method.

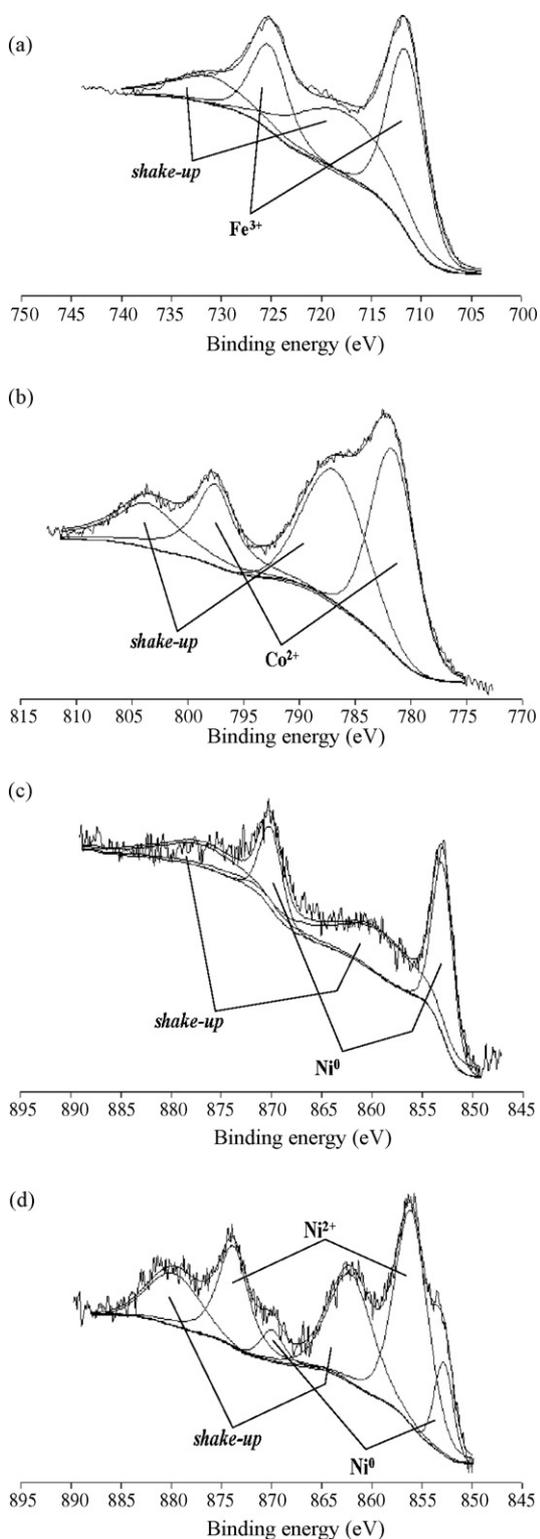


Fig. 4. X-ray photoelectron spectra (M 2p regions for M=Fe, Co and Ni) of activated carbon supported bimetallic carbides: (a) Fe-Mo carbide synthesized by CM from sulfate precursor; (b) Co-Mo carbide synthesized by CM from sulfate precursor; (c) Ni-Mo carbide synthesized by CM from nitrate precursor; (d) Ni-Mo carbide synthesized by CM from sulfate precursor.

852.7–852.8 and 856.1–856.7 eV, which correspond to metallic Ni and Ni^{2+} , respectively [42]. The strong shake-up line that appears at 862.0 eV in these spectra is associated to the Ni^{2+} species. The nitrate precursor generated a greater proportion of metallic Ni, while the sulfate precursor generated a larger abundance of Ni^{2+} species, which may be due to the lower thermal stability of the nitrate precursors, as compared to the sulfates, that results in generation of metallic Ni at low temperature due to the reducing effect of the carbon support. Additionally, this precludes the union between the nickel and molybdenum atoms in a mixed phase such as NiMoO_4 in the precursor and NiMo carbide or NiMoS in the working catalyst. The sulfate moiety, being more thermally stable, possibly allows maintaining the bonding between Mo and Ni in a more extended range of temperature. It is important to mention that Fig. 4 is similar to those obtained with the rest of Fe, Co and Ni-containing catalysts.

3.3. Catalytic HDS activity

Thiophene HDS activities are reported as pseudo-first-order rate constants for thiophene disappearance in units of moles of thiophene converted to products per gram of catalyst per minute (mol Th/g cat min) after ≈ 3 h of reaction time (steady state). The samples were presulfided before the activity tests in order to remove the passivation oxidic layer and to attain a reproducible and stable initial state of the catalytic surface, assuming that in the absence of any pretreatment oxygen surface species would eventually be exchanged for sulfur in the feed. It has been reported that passivated carbide or nitride catalysts submitted to presulfidation attain higher HDS activities than those submitted to either degassing in inert atmosphere or prereduction [18]. Table 2 shows that the amounts of sulfur in presulfided samples are four to five times higher than those originally present in the non presulfided, sulfate-derived samples. However, the amount of sulfur is lower for the samples obtained from nitrates than for those synthesized from sulfate precursors.

Figs. 5 and 6 show the effect of the type of precursor and the synthesis method on the thiophene hydrodesulfurization activity of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides. These figures show that the activity of carbides obtained

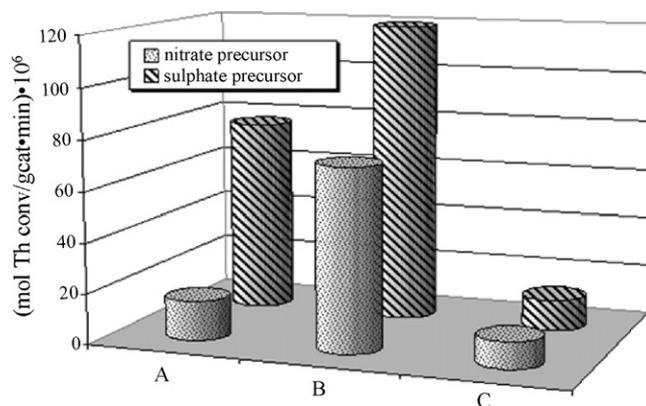


Fig. 5. Thiophene hydrodesulfurization activity at steady state of activated carbon supported bimetallic carbides prepared by the conventional method: (A) Fe-Mo, (B) Co-Mo, and (C) Ni-Mo.

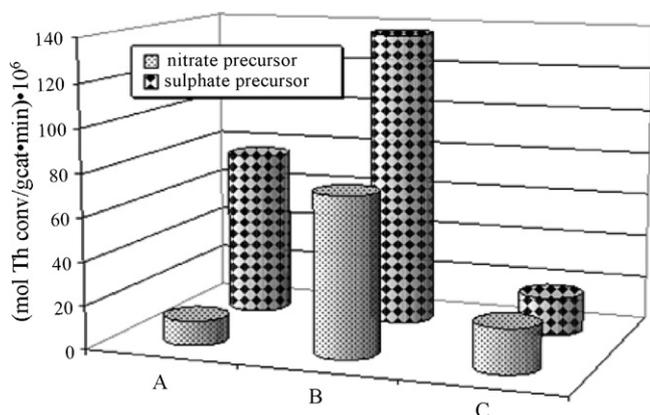


Fig. 6. Thiophene hydrodesulfurization activity at steady state of activated carbon supported bimetallic carbides prepared by the carbothermal method: (A) Fe-Mo, (B) Co-Mo, and (C) Ni-Mo.

from sulfate precursor was greater than that of solids obtained from nitrates. The differences in activity between conventional and carbothermal hydrogen reduction methods were less significant. The Fe-Mo and Co-Mo carbide catalysts obtained from sulfates showed thiophene HDS activities around five and two times higher, respectively, than those of Fe-Mo and Co-Mo carbides obtained from nitrate precursor, while both Ni-Mo carbides have similar catalytic activities, independently from the used synthesis method and type of precursor.

The results of catalytic activity obtained in this work may be correlated with the presence at the surface of molybdenum species, such as Mo^{4+} (Table 1), which could be identified with molybdenum in an oxo-carbide (or sulfo-carbide) environment or coordinatively unsaturated (anionic vacancy) sulfide centers; therefore the Mo^{4+} species could be the active centers [14]. The overall rate of the HDS of thiophene was found to increase as follows: $\text{NiMo-N-CM} < \text{FeMo-N-CM} < \text{NiMo-S-CM} < \text{FeMo-S-CM} < \text{NiMo-N-CTH} < \text{FeMo-N-CTH} < \text{NiMo-S-CTH} < \text{FeMo-S-CTH} < \text{CoMo-N-CM} < \text{FeMo-S-CM} < \text{CoMo-N-CTH} < \text{FeMo-S-CTH} < \text{CoMo-S-CM} < \text{CoMo-S-CTH}$; a sequence that almost parallels the increase of Mo^{4+} species content as shown in Table 1. The same molybdenum oxidation state was suggested by Manoli [43] to be the active site for HDS, his work showed the presence of molybdenum atoms mainly as Mo^{4+} , assigned to molybdenum oxycarbide; these catalysts displayed a high desulfurization rate in the 4,6-DMDBT hydrodesulfurization that was assigned to the Mo^{4+} abundance.

The results shown above demonstrate that the Ni-Mo carbides exhibited the lowest catalytic activities; this observation is contradictory with the results obtained for conventional sulfide catalysts. These results suggest that the nickel metal present on the surface of Ni-Mo carbides caused deactivation during the reaction, possibly due to the deposition of coke on the catalyst surface, since this coke covers the active sites and deactivates the catalysts [44].

The activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides obtained from the sulfate precursors retained sulfur on the surface, as shown by XPS analysis (Figs. 2 (a and b) and 3(a and b) and Table 2). This behavior may be related

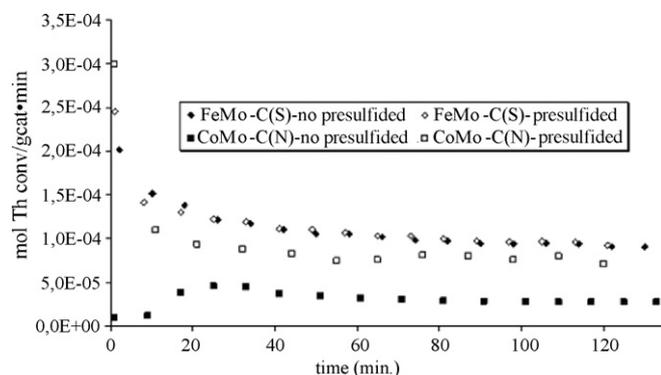


Fig. 7. Thiophene hydrodesulfurization activity as a function of time of activated carbon supported bimetallic carbides synthesized by the carbothermal method: Fe-Mo (from sulfate) and Co-Mo (from nitrate), presulfided and non presulfided.

to the increased HDS activities of the nitrate catalysts when they were presulfided (Fig. 7), showing that there is a change in the nature of surface active sites of these catalysts during HDS reaction. This points to the formation of a different active site, which can enhance the HDS activities of carbide catalysts, suggesting that the carbides with sulfided surfaces or mixed carbo-sulfide species could be the most active ones in HDS on carbide catalysts. On the other hand, the activity differences between carbides prepared with sulfate precursor (either presulfided or not) were not significant (Fig. 7).

The partial sulfidation of these carbide catalysts has been evidenced in a variety of studies [32–36,45]. These works showed that, it is possible that the carbide catalysts react with the H_2S gas produced during the HDS reaction and get sulfided. As a result of sulfidation, there is a possibility that “MMoS” phase ($\text{M} = \text{Fe}, \text{Co}, \text{or Ni}$) could be formed on the surface of carbide catalysts. The “MMoS” are the most active species in sulfide catalyst for HDS reactions [46,47]. The “MMoS” phases formed on the carbide surface are beneficial for hydrotreating and would enhance the HDS activities of carbide catalysts. Gaseous H_2S , produced during the pretreatment with CS_2/H_2 , carries out the sulfidation on the surface, and that way this treatment allows to have mixed carbo-sulfide species at the beginning of HDS reaction.

Fig. 7 shows that non presulfided, sulfate-derived samples present identical behavior in HDS of thiophene than the corresponding presulfided samples. Thus, for sulfate-derived samples, the relatively low sulfur content already present after carbiding (~ 3 atom %) seems to be the optimum content. The large excess observed after presulfiding (~ 15 atom %) is probably being retained in the microporous structure of the support, by means of a “sink effect” as proposed by Laine and co-workers [48]. Thus, sulfur added by means of presulfiding does not necessarily result in an optimum sulfo-carbide active phase in the case of nitrate precursors. In line with this, the amount of sulfur in catalysts derived from nitrates is slightly lower than that in catalysts obtained from sulfates (Table 2). These effects might be related to the observation by several workers (see, e.g., [15]) of irreversible loss of activity of carbide catalysts after passivation as compared with catalysts not submitted to passivation procedures.

4. Conclusions

The influence of the type of precursor (sulfate vs. nitrate of Fe, Co, or Ni promotor) and the synthesis method (conventional vs carbothermal carbiding) of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides was determined by XRD and XPS, and also evidenced in thiophene hydrodesulfurization (HDS) activity. The XRD analysis showed that the carbides obtained with sulfate precursors generated Fe₃Mo₃C or M₆Mo₆C₂ phases (M = Co or Ni), while the solids obtained from nitrate precursors formed β-Mo₂C and metals. XPS showed the presence at the surface of Mo^{δ+}, Mo⁴⁺, Mo⁶⁺, Fe³⁺, Co²⁺, Ni⁰ and Ni²⁺ species. All the carbides show similar species of Fe, Co, and Ni on the surface, however the relative proportions of Mo species depends on the synthesis method and/or type of precursor. Thus, the catalytic activity was influenced by the proportion of molybdenum species at the surface. The carbothermal method and nitrate precursor indifferently from the used synthesis method generated a greater proportion of high oxidation state species (Mo⁴⁺ and Mo⁶⁺), while the conventional method generated a larger proportion of reduced species (Mo^{δ+}). The results of catalytic activity could be correlated with the presence at the surface of Mo⁴⁺, which shows an increase in the proportion of these species on carbides prepared from the sulfate precursors. In consequence, the activity of carbides obtained by the carbothermal method and with sulfate precursors was higher than that of the solids obtained by the conventional method and with nitrate precursors. However, no significant differences in catalytic activity were found for the Ni-Mo carbides. From these results, it appears possible to correlate the Mo⁴⁺ content to HDS activity. The bimetallic carbides obtained from sulfate precursors retained sulfur on the surface, as shown by XPS and chemical analysis. Generally, the carbides showed greater catalytic activity when they were presulfided, suggesting that the carbides with sulfided surfaces or mixed carbo-sulfide species could be the active phase in HDS on carbide catalysts. In the present work it is shown that the use of sulfate precursors provides such mixed carbo-sulfide species prior to the catalytic reaction, even without the need of presulfidation, and that these phases are more active than those obtained by presulfidation.

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