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# Effect of the amount of citric acid used in the preparation of NiMo/SBA-15 catalysts on their performance in HDS of dibenzothiophene-type compounds



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# ABSTRACT

In the present work, NiMo catalysts supported on SBA-15 were prepared with the addition of different amounts of citric acid (CA) in the impregnation solutions. The aim of this study was to inquire into the effect of the amount of citric acid on the activity and selectivity of the NiMo/SBA-15 catalysts in deep hydrodesulfurization (HDS). Catalysts were prepared by coimpregnation of Ni and Mo species from acidic aqueous solutions containing citric acid without further adjusting the solution's pH. The amount of citric acid used in the catalyst preparation was varied from CA:Mo molar ratio 0.5 to 2.0. In addition, a reference NiMo/SBA-15 catalyst was prepared without citric acid. After the impregnation, catalysts were dried  $(100 \circ C, 6h)$  and calcined  $(500 \circ C, 4h)$ . The prepared catalysts were characterized by nitrogen physisorption, small-angle and powder X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (DRS), temperature-programmed reduction (TPR), high resolution transmission electron microscopy (HRTEM) and tested in simultaneous HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in a batch reactor at 300 °C for 8 h. XRD, DRS and TPR characterizations showed that Ni and Mo oxide species were well dispersed in all catalysts prepared with CA. In contrast, a NiMoO<sub>4</sub> crystalline phase was detected by XRD in the reference NiMo/SBA-15 catalyst prepared without citric acid. Addition of citric acid to the impregnation solutions used for the catalyst preparation also resulted in an increase in the degree of sulfidation and in the dispersion of catalytically active MoS<sub>2</sub> phase (elemental analysis, HRTEM). In accordance with this, HDS activity of the NiMo catalysts prepared with the addition of citric acid resulted to be significantly higher than that of the reference NiMo/SBA-15 sample for both sulfurcontaining compounds tested (DBT and 4,6-DMDBT). It was found that the optimum amount of citric acid, which allows achieving the highest catalytic activity, corresponds to CA:Mo molar ratio equal to 1. Further increase in the amount of citric acid resulted in a slight decrease in the HDS activity. Regarding selectivity, addition of small amounts of CA, in general, resulted in an increase of the hydrogenation ability of the NiMo/SBA-15 catalysts. However, some differences in the selectivity of the catalysts were observed with different amounts of citric acid used.

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# 1. Introduction

Nowadays, the demand for high quality petroleum-derived transportation fuels continues growing. Low and ultra-low sulfur content fuels are particularly desired in order to solve environmental problems induced by  $SO_x$  emission and to improve air quality [1,2]. The main industrial process to accomplish this purpose is hydrodesulfurization (HDS), in which S-containing molecules react with hydrogen at high temperature and pressure in the presence

of a heterogeneous catalyst. In order to attend the demand of production of lower contaminating diesel fuel, many efforts are aimed to develop novel hydrotreating catalysts, highly active and selective especially for HDS of the refractory polyaromatic sulfur compounds.

Among different approaches used in the last decade to improve traditional HDS catalysts based on Mo(W) sulfide promoted by Ni(Co) and supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [3,4], one of the most promising is related to the use of novel mesostructured materials, such as MCM-41, SBA-15 and KIT-6 as supports. These materials have different advantages in comparison with alumina, namely, they possess appropriate physicochemical properties, large surface area, tunable pore size, good thermal and mechanical resistance and



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the ability to disperse well NiMoS and CoMoS active phases leading to attractive HDS catalysts [5-7]. In our group, good results were obtained with NiMo and NiW catalysts supported on SBA-15, especially when this silica material was modified by the incorporation of different heteroatoms (Ti, Zr, Al) [8–13]. It was shown that heteroatoms incorporated on the SBA-15 surface serve as anchoring sites for the deposited Mo and W active species, significantly improving by this means catalysts' performance compared to pure silica SBA-15-supported analogs [11]. When SBA-15 silica with no incorporated heteroatoms is used as a support for the HDS catalysts, other approaches can be used to modify and improve catalytic activity. This can be achieved, for example, by the correct selection of metal precursors and solvents, or by the addition of different additives and organic ligands. Thus, the use of Keggin-type heteropolyacids ( $H_3PMo_{12}O_{40}$  and  $H_3PW_{12}O_{40}$ ) as distinct precursors for NiMo and NiW catalysts supported on SBA-15 has also led to good results [14]. Another option consists on the addition of different types of organic acids to modify the characteristics of HDS catalysts, among them nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), cyclohexanediaminetetraacetic acid (CyDTA), citric acid (CA), etc. [15-21]. It is well-known that, under the appropriate experimental conditions (solution pH, metal and ligand concentrations, temperature, etc.), organic or inorganic acids are able to interact with metal precursors and thus increase solubility and stability of the metal species used for the preparation of supported catalysts leading to a better catalytic performance. Among different organic additives, citric acid attracted our attention, because it is cheap, easily available and easy to handle.

In works [22,23], citric acid was employed to synthesize  $Co_2[Mo_4(C_6H_5O_7)_2O_{11}]$  complex in aqueous solution at acidic pH which then was used as a precursor of the CoMoS phase. CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared from this complex showed improved activity for deep HDS. Catalysts prepared with citric acid and supported on metal oxides other than Al<sub>2</sub>O<sub>3</sub> or alumina modified with zeolites were found to be active in hydrodesulfurization of refractory compounds such as dibenzothiophene (DBT) and 4,6dimethyldibenzothiophene (4,6-DMDBT). For example, attractive results were obtained with the CoMoP/HY-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with CA [24]. Addition of CA to this catalyst resulted in a considerable increase in activity when commercial diesel was used. This was ascribed to a better dispersion of the active phase and the prevention of the sulfidation of Co at low temperatures. Citric acid was also used in the preparation of  $CoMo/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with boron [16]. Addition of citric acid increased the dispersion of Co and Mo species, resulting in a larger amount of Co-Mo-S phase after sulfidation without active-site blocking by cobalt sulfide clusters [25]. NiMo catalysts supported on wide-pore ZrO<sub>2</sub>-TiO<sub>2</sub> prepared at acidic pH with the addition of EDTA or CA, and sulfided without previous calcinations, showed high catalytic activity in dibenzothiophene hydrodesulfurization [26]. For citric acid, better activity results were obtained for the Ni:CA molar ratio equal to 1:2, although no selectivity modifications were observed for any molar ratio.

In our group, a series of NiMo catalysts supported on SBA-15 were prepared with citric acid and tested in hydrodesulfurization of DBT [27,28]. In work [27], NiMo/SBA-15 catalysts were prepared by varying the pH of the impregnation solution and conditions of the thermal treatment after the impregnation step. We observed that these two factors modified activity and selectivity of the catalysts in HDS of DBT. A detailed kinetic study undertaken in this work confirmed this result. In the following work [28], NiMo/SBA-15 catalysts were prepared using basic impregnation solutions (pH 9) containing different amounts of citric acid. These catalysts were sulfided without previous calcination and showed very high selectivity for the direct desulfurization of DBT. In the more recent work [29], we compared behavior of the NiMo/SBA-15 catalysts prepared

with the addition of a constant amount of citric acid to the impregnation solution, but varying the pH value and conditions of the subsequent thermal treatment, in simultaneous HDS of DBT and 4,6-DMDBT. It was found that the catalyst prepared from acidic impregnation solution (pH 1) containing citric acid and calcined at 500 °C for 4 h before sulfidation showed the best catalytic activity in HDS of both model compounds tested. This exceptional behavior was attributed to a high hydrogenation ability of this catalyst, which is an important feature for the HDS of DBT-type compounds with alkyl-substituents in positions 4 and 6 of the molecule, reacting preferentially through the hydrogenation pathway of HDS [30]. In the present work, following up on our previous research, we tried to inquire on the effect of the amount of citric acid used in the preparation of the NiMo/SBA-15 catalysts from acidic impregnation solutions (pH 1 or below) on their activity and selectivity in deep hydrodesulfurization (HDS). We were interested in determining if varying the amount of citric acid can bring further improvement in activity and selectivity of these catalysts in deep HDS. For this aim, NiMo catalysts supported on SBA-15 were prepared with different amounts of citric acid, characterized and tested in simultaneous HDS of two model compounds (DBT and 4,6-DMDBT). This is the last work of this series dealing with the search for the optimum experimental conditions (solution pH, amount of citric acid and thermal treatment) for the preparation of active NiMo/SBA-15 catalysts with desired selectivity for HDS of DBT-type compounds.

# 2. Experimental

#### 2.1. Catalyst preparation

SBA-15 silica with hexagonal *p6mm* structure was prepared according to a reported procedure [31,32] using the triblock copolymer Pluronic P123 ( $M_{av}$  = 5800, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Aldrich) as the structure-directing agent and tetraethyl orthosilicate (TEOS, Aldrich, 99.999%) as the silica source. Pluronic P123 copolymer (4 g) was dissolved in water (30 g) and 2 M HCl (120 g) solution at 35 °C. Then TEOS (8.5 g) was added into the solution. The mixture was stirred at 35 °C for 20 h and then aged at 80 °C for 48 h without stirring. The solid product was recovered by filtration, washed with deionized water and air-dried at room temperature. Calcination was carried out in static air at 550 °C for 6 h.

NiMo catalysts supported on SBA-15 were prepared by a standard incipient wetness co-impregnation technique reported elsewhere [33]. The calcined support was co-impregnated using aqueous solutions of ammonium heptamolybdate, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Merck, 99%), nickel nitrate, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Baker), and citric acid, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O (Merck, 99.5%). Amounts of citric acid used corresponded to CA:Mo molar ratios between 0.5 and 2.0. All impregnation solutions had acidic pH (pH 1 or below) which was not adjusted to any specific value. In addition, a reference NiMo/SBA-15 catalyst was prepared by co-impregnation of nickel nitrate and ammonium heptamolybdate, without CA addition. After co-impregnation, all catalysts were dried first at room temperature, then at 100 °C for 6 h, and calcined at 500 °C for 4h in static air atmosphere. The nominal composition of the catalysts was 12 wt.% of MoO<sub>3</sub> and 3 wt.% of NiO, which corresponds to the Ni:Mo molar ratio = 1:2. As all catalysts were supported on SBA-15, hereinafter, we will denote them just as NiMo and NiMoCA(x), where x represents CA:Mo molar ratio used in the catalyst preparation (*x* = 0.5, 1.0, 1.5, 2.0).

#### 2.2. Support and catalyst characterization

SBA-15 support and NiMo(CA)/SBA-15 catalysts were characterized by  $N_2$  physisorption, small-angle and powder Xray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (DRS), temperature-programmed reduction (TPR), and high resolution transmission electron microscopy (HRTEM). Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020 automatic analyzer at liquid N2 temperature. Prior to the experiments, the samples were degassed  $(p < 10^{-1} \text{ Pa})$  at 270 °C for 6 h. Specific surface areas  $(S_{\text{BET}})$  were calculated by the BET method, the total pore volume  $(V_p)$  was determined by nitrogen adsorption at a relative pressure of 0.98 and pore size distributions were obtained from the adsorption isotherms by the BIH method. The mesopore diameter  $(D_P)$  corresponds to the maximum of the pore size distribution. The micropore area ( $S_{\mu}$ ) was estimated using the correlation of t-Harkins & Jura (*t*-plot method). XRD patterns were recorded from 3° to  $80^{\circ}$  (2 $\Theta$ ) on a Bruker D8 Advance diffractometer, using Cu K $\alpha$ radiation ( $\lambda = 1.5406$  Å) and a goniometer speed of  $1^{\circ}(2\Theta)$  min<sup>-1</sup>. Small-angle XRD ( $2\Theta = 0.5 - 10^{\circ}$ ) was performed on a Bruker D8 Advance diffractometer using small divergence and scattering slits of 0.05°. UV-vis electronic spectra of the samples were recorded in the wavelength range of 200-800 nm using a Varian Cary 100 Conc spectrophotometer equipped with a diffuse reflectance attachment. Polytetrafluoroethylene was used as a reference. TPR experiments were carried out in a Micromeritics AutoChem II 2920 automatic analyzer equipped with a TC detector. Before TPR experiments, the samples were pretreated in situ at 400 °C for 3 h under air flow and cooled in an Ar stream. The reduction step was performed under a stream of a H<sub>2</sub>/Ar mixture (10/90 mol/mol and 50 mL/min), with a heating rate of 10°C/min up to 1000°C. Elemental analysis of calcined and sulfided NiMo(CA) catalysts was performed on an automatic Perkin-Elmer 2400 Series II CHNS/O analyzer with TC detector. HRTEM studies of sulfided catalysts were performed using a Jeol 2010 microscope (resolving power 1.9Å). The solids were ultrasonically dispersed in *n*-heptane and the suspension was collected on carbon coated grids. Slab length and layer stacking distributions of MoS<sub>2</sub> crystallites in each sample were established from the measurement of at least 300 crystallites detected on several HRTEM micrographs taken from different parts of the same sample dispersed on the microscope grid.

#### 2.3. Catalytic activity

The HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h with constant stirring. Prior to the catalytic activity evaluation, the catalysts were sulfided ex situ in a tubular reactor at 400 °C for 4 h in a stream of 15 vol.% of H<sub>2</sub>S in H<sub>2</sub> under atmospheric pressure. The sulfided catalysts (0.15 g) were transferred in an inert atmosphere (Ar) to a batch reactor (Parr) with 40 mL of *n*-hexadecane solution containing both DBT (Aldrich, 1300 ppm of S) and 4,6-DMDBT (Aldrich, 500 ppm of S). The course of the reaction was followed by withdrawing aliquots each hour and analyzing them in an Agilent 6890A chromatograph. To corroborate product identification, the product mixture was analyzed in a Hewlett Packard GC–MS instrument.

# 3. Results

## 3.1. Characterization of support and catalysts in their oxide form

The textural properties of NiMo(CA) catalysts are given in Table 1. The SBA-15 support had a BET surface area of  $801 \text{ m}^2/\text{g}$ , micropore area of  $127 \text{ m}^2/\text{g}$ , total pore volume of  $1.04 \text{ cm}^3/\text{g}$  and pore diameter of 7.8 nm. All NiMo(CA) catalysts showed lower specific textural characteristics. Thus, the NiMo catalyst prepared without citric acid had surface area of  $598 \text{ m}^2/\text{g}$  and pore volume of  $0.78 \text{ cm}^3/\text{g}$ . This decrement can be related to an increase in the sample's density after the incorporation of Ni and Mo precursors

in the SBA-15 support and, probably, to some pore blockage by the agglomerated Ni and Mo oxides species. Pore diameter also decreased from 7.8 nm in the starting SBA-15 support to 7.4 nm in the NiMo catalyst, which supports our supposition about the agglomeration of Ni and Mo species inside the mesopore channels of the support. Regarding calcined NiMoCA(x) catalysts, their textural properties varied with the amount of citric acid used in the synthesis. Thus, the sample prepared with small amount of citric acid (x = 0.5) showed significantly better textural characteristics ( $S_{\text{BET}}$  and pore volume equal to 662 m<sup>2</sup>/g and 0.88 cm<sup>3</sup>/g, respectively) than the reference NiMo catalyst prepared without CA. This illustrates that the addition of a small amount of citric acid to the impregnation solution resulted in about 10-13% increase in the specific textural characteristics of the catalyst. The possible explanation for this can be an increase in the dispersion of the deposited Ni and Mo species in the NiMoCA(0.5) catalyst in comparison with the analog prepared without CA. However, further increase in the amount of citric acid used in the catalysts' preparation resulted in a slight decrease in the textural characteristics (Table 1). The catalyst prepared with CA:Mo molar ratio equal to x = 2.0 showed textural characteristics similar to those of the reference NiMo sample. This fact, possibly, is related to different degrees of agglomeration of Ni and Mo oxide species, and subsequently in a change in the dispersion of metal oxide particles over the SBA-15 support, or to the fact that not all citric acid was eliminated from the NiMoCA(x) catalysts upon calcinations, thus giving rise to an increase in the amount of residual carbon with increasing the amount of CA used. Elemental analysis performed to confirm this supposition showed the presence of 0.3 wt.% of carbon in the calcined NiMoCA(2.0) catalyst.

The nitrogen adsorption-desorption isotherm of the SBA-15 support and NiMo(CA) catalysts are shown in Fig. 1(a). They all correspond to a type IV isotherm characteristic of mesoporous materials, with a H1 hysteresis loop characteristic of a well-formed SBA-15 silica [31,32]. The shape of the isotherm and of the hysteresis loop did not suffer important changes after the incorporation of NiMo(CA) species. Isotherms of all catalysts shown in Fig. 1(a), prepared with or without citric acid, maintain the characteristic shape of the SBA-15 support. This indicates that the characteristics of the original pore structure of the SBA-15 support were conserved in the catalysts. However, all NiMo(CA) catalysts showed a decrease in the amount of adsorbed nitrogen, which is in line with textural characterization results from Table 1. Pore size distributions of the SBA-15 support and NiMo(CA) catalysts are shown in Fig. 1(b). All they show a monomodal pore size distribution with a maximum between 7 and 8 nm. Only a slight decrease in the pore diameter and in the intensity of the peaks can be observed in this figure after the incorporation of Ni and Mo species in the SBA-15 support.

Fig. 2 shows small-angle XRD patterns of the SBA-15 support and NiMo(CA) catalysts. All of them exhibit diffraction patterns characteristic of SBA-15 material with three well-resolved peaks corresponding to (100), (110) and (200) reflections associated with p6mm hexagonal symmetry of mesopores. The presence of these three signals in the XRD patterns of the NiMo(CA) catalysts points out that the long-range pore arrangement of the SBA-15 support was maintained in all catalysts after deposition of Ni and Mo species and citric acid. Results from the calculation of the pore wall thickness for the SBA-15 support and NiMo(CA) catalysts (Table 1, last column) indicate a small increase in the thickness of the pore walls of the starting SBA-15 support after the impregnation of Ni and Mo species. This increase was slightly higher for the reference NiMo catalysts prepared without CA (~0.2 nm) than for the catalysts of the NiMoCA(x) series ( $\sim$ 0.1 nm). This confirms that the metal species mentioned above were deposited mostly inside the SBA-15 mesopore channels and that their dispersion was better in the catalysts prepared with the addition of citric acid.

## Table 1

Textural and structural cl	haracteristics of SBA-15	5 support and NiMo	(CA) catalysts.
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Sample	$S_{\text{BET}}^{a}$ (m <sup>2</sup> /g)	$S_{\mu}^{b}(m^{2}/g)$	$V_p^c$ (cm <sup>3</sup> /g)	$D_p^d$ (nm)	$a_0^e$ (nm)	$\delta^{f}(nm)$
SBA-15	801	127	1.04	7.8	10.4	2.6
NiMo	598	83	0.78	7.4	10.2	2.8
NiMoCA(0.5)	662	87	0.88	7.5	10.2	2.7
NiMoCA(1.0)	617	76	0.84	7.5	10.2	2.7
NiMoCA(1.5)	610	99	0.82	7.5	10.2	2.7
NiMoCA(2.0)	592	90	0.81	7.5	10.2	2.7

<sup>a</sup> Specific surface area calculated by BET method.

<sup>b</sup> Micropore area estimated using the correlation of *t*-Harkins & Jura (*t*-plot method).

<sup>c</sup> Total pore volume determined at a relative pressure of 0.98.

<sup>d</sup> Pore diameter corresponding to the maximum of the pore size distribution calculated from the adsorption isotherm by the BJH method.

<sup>e</sup>  $a_0$ , unit-cell parameter estimated from the position of the (100) diffraction line ( $a_0 = d_{100} \times 2/\sqrt{3}$ ).

<sup>f</sup> Pore wall thickness ( $\delta = a_0 - D_p$ ).

Fig. 3 shows powder XRD patterns of the SBA-15 support and NiMo(CA) catalysts. The diffraction pattern of the SBA-15 support has the shape characteristic for this amorphous silica material [14]. In the case of the reference NiMo catalyst prepared without addition of citric acid, signals corresponding to NiMoO<sub>4</sub> crystalline phase (JCPDS 33-0948) were observed. Similar results have already been reported previously for the catalysts prepared by co-impregnation of ammonium heptamolybdate and nickel nitrate on SBA-15 and Al-SBA-15 supports [34]. It was shown that an Anderson-type heteropolymolybdate (NH<sub>4</sub>)<sub>4</sub>[Ni(OH)<sub>6</sub>Mo<sub>6</sub>O<sub>18</sub>]·4H<sub>2</sub>O was rapidly formed in the impregnation solution, and within a few minutes crystallites of this phase were precipitated. Low solubility of this ammonium salt led to the precipitation of the crystallites of this compound in and outside the porosity of the support. Calcination of the catalyst resulted in the elimination of NH4<sup>+</sup> cations and formation of MoO3 and NiMoO4. The above explains why the NiMoO<sub>4</sub> crystalline phase was detected in the reference sample prepared without citric acid. Regarding the catalysts prepared with citric acid, in all cases no signals of any crystalline phase were detected. It is worth to mention, that results obtained by XRD for the reference NiMo sample are consistent with results obtained for this catalyst by nitrogen physisorption, where a decrease in the  $S_{\text{BFT}}$  value and pore volume after Ni and Mo deposition makes us suppose the possibility of some pore blocking by the agglomerated Ni and Mo oxide species. As expected, addition of citric acid to the impregnation solutions increased solubility and stability of Ni and Mo precursors used, avoiding the formation of an Anderson-type heteropolymolybdate and increasing the dispersion of Ni and Mo oxide species deposited on the SBA-15 surface.

In order to obtain more information regarding the dispersion of Ni and Mo oxide species in the catalysts prepared with citric acid, UV-vis diffuse reflectance spectroscopy (DRS) and temperatureprogrammed reduction (TPR) were used. UV-vis DR spectra for NiMo(CA) catalysts supported on SBA-15 are shown in Fig. 4. In these spectra, absorption bands observed in the 200-400 nm region correspond to ligand-to-metal charge transfer (LMCT)  $O^{2-} \rightarrow Mo^{6+}.$ As it was described previously, the exact positions of these bands depend on the coordination around Mo(VI) cations, which can be octahedral (Oh) or tetrahedral (Td), and the size of the agglomerated Mo oxide species [35]. In the spectrum of the reference NiMo catalyst prepared without CA (Fig. 4, curve (a)), signals corresponding to different types of Mo species can be clearly observed. Thus, the absorption band with the maximum at 250 nm evidences the presence of tetrahedral Mo species, whereas the absorption at 280-330 nm is characteristic for agglomerated octahedrallycoordinated polymolybdate species. The latter ones showed a UV absorption edge energy  $(E_g)$  of 3.3 eV (Table 2), which is close to the previously reported values for ammonium heptamolybdate and small MoO<sub>3</sub> clusters [35]. This result is well in line with powder XRD results for this catalyst. Thus, the signal corresponding to tetrahedral Mo species can be associated with the formation of a NiMoO<sub>4</sub> crystalline phase evidenced by XRD, in which Mo(VI) cations are coordinated tetrahedrally. At the same time, small MoO<sub>3</sub> clusters, the formation of which can be expected as a result of the decomposition of an Anderson-type precipitate upon calcination and which



Fig. 1. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of SBA-15 support, NiMo and NiMoCA(x) catalysts.



Fig. 2. Small-angle XRD patterns of SBA-15 support, NiMo and NiMoCA(x) catalysts.



**Fig. 3.** Powder XRD patterns of SBA-15 support, NiMo and NiMoCA(*x*) catalysts. \*Signals of NiMoO<sub>4</sub> crystalline phase, JCPDS card 33-0948.

Table	2
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Absorption edge energy  $(E_g)$  and reduction behavior of NiMo(CA) catalysts.

Sample	$E_g^{a}(eV)$	H <sub>2</sub> consumpti		$\alpha_R^{c}$	
		200–650°C	650-1000°C	Total	
NiMo	3.3	1.38	0.48	1.86	0.64
NiMoCA(0.5)	4.0	1.55	1.00	2.55	0.88
NiMoCA(1.0)	4.0	1.67	0.83	2.50	0.86
NiMoCA(1.5)	3.9	1.51	0.78	2.29	0.79
NiMoCA(2.0)	3.8	1.31	0.79	2.10	0.73

<sup>a</sup>  $E_g$  values were determined from UV–vis DRS spectra of the catalysts [35].

<sup>b</sup> Hydrogen consumption determined from TPR results.

 $^{c}$   $\alpha_{R}$ , degree of the reduction of Ni and Mo oxide species determined from total H<sub>2</sub> consumption of each sample and the theoretical value corresponding to their complete reduction (2.90 mmol/g).



**Fig. 4.** UV-vis diffuse reflectance spectra of the catalysts: (a) NiMo, (b) NiMoCA(0.5), (c) NiMoCA(1.0), (d) NiMoCA(1.5) and (e) NiMoCA(2.0).

were not detected by XRD because of their small size, can be responsible for the absorption band corresponding to octahedrally coordinated Mo oxide species. The signals which can be observed in the spectra of the NiMo catalysts prepared with the addition of citric acid (curves (b)–(e), Fig. 4) can be ascribed to tetrahedral or well-dispersed octahedral Mo species.  $E_{\sigma}$  values determined for the catalysts of the NiMoCA(x) series varied between 3.8 and 4.0 eV (Table 2), which points out to a better dispersion of octahedral Mo species in the catalysts prepared with citric acid in comparison with the reference NiMo sample. An interesting behavior was observed between  $E_g$  values and the amount of citric acid used in the catalyst preparation; namely, catalysts prepared with small amounts of citric acid (x = 0.5 and 1.0) had higher  $E_g$  values (4.0 eV) than the samples prepared with larger amounts of CA (x = 1.5 and 2.0). It seems that when a small amount of citric acid is added to the impregnation solution containing both Ni and Mo precursor salts, dispersion of octahedral Mo species increases. However, when the amount of citric acid increases, there is a contrary effect consisting in an increase in the size of polymolybdate species.

TPR characterization results for NiMo(CA) catalysts supported on SBA-15 are shown in Fig. 5. It can be appreciated that the NiMo catalyst prepared without citric acid shows a complex TPR profile. A low-temperature reduction peak with a maximum at 386 °C has two shoulders at about 360 and 432 °C. The presence of three overlapped peaks in the 300-500 °C region points out to the coexistence in this sample of octahedral Mo species of different degrees of agglomeration [36–38]. These low temperature reduction peaks can be attributed to the first step of reduction from Mo<sup>6+</sup> to Mo<sup>4+</sup> of octahedral Mo species deposited on the SBA-15 surface. The signal at 610 °C can be attributed to the second step of reduction of octahedral Mo species (from Mo<sup>4+</sup> to Mo<sup>0</sup>) and to the first step of reduction of small MoO<sub>3</sub> clusters. Finally, low-intensity hydrogen consumption in the 700-1000 °C region corresponds to the reduction of tetrahedral Mo species detected by XRD as a NiMoO<sub>4</sub> crystalline phase. TPR profiles obtained for the NiMo catalysts prepared with the addition of citric acid were significantly different from the above-described one of the reference NiMo/SBA-15, especially in the low temperature region (below 650 °C). Thus, only one well-defined peak was observed between 300 and 450 °C for all NiMoCA(x) catalysts. The exact position of the maximum of this peak changed with the amount of citric acid used in the synthesis.



Fig. 5. TPR profiles of NiMo and NiMoCA(x) catalysts supported on SBA-15.

Thus, the addition of a small amount of citric acid to the impregnation solution (x = 0.5) resulted in a decrease in the temperature of the maximum to 369 °C. However, further increase in the amount of citric acid was accompanied by a slight increase in the position of the maximum, which was observed at 373, 378 and 385 °C for NiMoCA(1.0), NiMoCA(1.5) and NiMoCA(2.0) catalysts, respectively. In addition, the first reduction peak became more intense and symmetric than in the TPR profile of the reference NiMo sample, which points out to a more homogeneous distribution of octahedral Mo species in the samples prepared with citric acid.

Results from the quantification of the amount of hydrogen consumed during the reduction of the catalysts in low (200–650 °C) and high-temperature (650–1000 °C) regions, as well as the total hydrogen consumption are shown in Table 2. It can be seen that the reduction of the samples prepared with citric acid proceeds with higher total consumption of hydrogen than of the reference NiMo catalyst. Degrees of reduction ( $\alpha_R$ ) of NiMoCA(x) samples were in the range of 0.73–0.88, which indicates that the majority of Ni and Mo oxide species were reduced in the TPR experiments. For comparison, NiMo catalyst showed  $\alpha_R$  value equal to 0.64. The above results show that the addition of small amounts of citric acid (x = 0.5 and 1.0) during catalyst preparation not only results in a decrease in the temperature of reduction of Ni and Mo oxide species (Fig. 5), but also makes their reduction more complete. This fact can be explained by a better dispersion of Ni and Mo oxide species in the catalysts prepared with citric acid and an increase in the proportion of Mo<sup>6+</sup> ions in octahedral coordination, which can be reduced much easier than the corresponding tetrahedral ones.

## 3.2. Characterization of sulfided catalysts

Sulfided NiMo(CA)/SBA-15 catalysts were characterized by HRTEM in order to obtain more information about the dispersion of MoS<sub>2</sub> crystallites in the catalysts prepared with the addition of different amounts of citric acid. Representative micrographs of selected catalysts are shown in Fig. 6. The typical fringes due

#### Table 3

Results from the characterization of the sulfided NiMo(CA) catalysts: average length (*L*) and average stacking degree (*N*) of MoS<sub>2</sub> crystallites, estimated  $f_{Mo}$  fraction<sup>a</sup> and sulfur contents.

Catalyst	HRTEM			Chemical analysis		
	L(nm)	Ν	f <sub>Mo</sub>	S (wt.%)	$\alpha_{S}^{b}$	
NiMo NiMoCA(0.5) NiMoCA(1.0) NiMoCA(1.5) NiMoCA(2.0)	7.1 5.2 4.3 4.5	4.1 2.4 2.2 2.1 2.7	0.17 0.23 0.28 0.26 0.24	5.59 6.71 6.48 6.41 6.26	0.84 1.01 0.98 0.97	

<sup>a</sup>  $f_{Mo}$ , estimated fraction of Mo atoms on the edge surface of MoS<sub>2</sub> crystallites [12]. <sup>b</sup> Degree of the sulfidation of Ni and Mo species determined from elemental analysis results and the theoretical value corresponding to their complete sulfidation (6.62 wt% S).

to MoS<sub>2</sub> crystallites with 0.61 nm interplanar distances and some features of the SBA-15 mesopore structure were observed in micrographs of the sulfided catalysts. Reference NiMo catalyst prepared without citric acid showed MoS<sub>2</sub> crystallites with lengths between 2 and 10 nm and with variable stacking degrees (the number of stacking layers changed between 2 and 8). Addition of citric acid during catalyst preparation, in general, resulted in a better dispersion of MoS<sub>2</sub> particles. As it can be seen in Fig. 6 (b), NiMoCA(1.0) catalyst, prepared from the impregnation solution containing citric acid at CA:Mo molar ratio equal to 1.0, had smaller (2-6 nm) and less stacked (1-3 layers) MoS<sub>2</sub> particles. However, when the amount of citric acid was increased to x = 2.0, some more stacked MoS<sub>2</sub> particles were detected in addition to the well-dispersed Mo active phase (micrograph (d), Fig. 6). This qualitative observation was confirmed by calculation of length and stacking degree distributions for NiMo(CA) catalysts (Fig. 7), and by the determination on their basis of average morphology (average length and number of layers) of MoS<sub>2</sub> crystallites in different catalysts (Table 3). Fig. 7 clearly shows a decrease in MoS<sub>2</sub> slabs length and stacking for all catalysts prepared with CA. NiMoCA(1.0) catalyst showed MoS<sub>2</sub> particles of the shortest length (4.3 nm) among all the prepared samples, formed in average by 2.2 layered MoS<sub>2</sub> slabs. The above HRTEM observations seem to be in line with previously described results of characterization of the catalysts in their oxide form. Thus, it was described above that the addition of small amounts of citric acid (x=0.5 and 1.0) improves dispersion of Ni and Mo precursor species in calcined NiMoCA(x) catalysts, and in accordance with this, the same NiMoCA catalysts in their sulfided state also showed a better dispersion on the SBA-15 surface than the reference samples prepared without CA (Table 3).

Results from the HRTEM characterization of sulfided NiMo(CA) catalysts were used to determine the average fraction of Mo atoms on the edge surface of  $MoS_2$  crystallites ( $f_{Mo}$ , Table 3), which can be considered an indicator of the amount of sulfided Mo species located on the catalytically active surface of MoS<sub>2</sub> particles [39]. The  $f_{Mo}$  fraction was calculated using equations reported in [12], assuming that the MoS<sub>2</sub> crystallites are perfect hexagons. The  $f_{Mo}$  values reported for NiMo(CA) catalysts in Table 3 show a noticeable increase in the proportion of Mo species on the catalytically active surface of the sulfided catalysts prepared using citric acid. The highest value of the  $f_{MO}$  fraction (0.28) was found for the NiMoCA(1.0) catalyst. In addition, sulfur content was determined if the sulfided NiMo(CA) catalysts by elemental analysis in order to determine their degree of sulfidation ( $\alpha_s$ , Table 3). The reference NiMo catalyst prepared without citric acid was sulfided in 84%, whereas all catalysts prepared with citric acid showed higher amounts of sulfur and degrees of sulfidation corresponding to almost completely sulfided Ni and Mo species.



Fig. 6. HRTEM micrographs of sulfided catalysts supported on SBA-15: (a) NiMo, (b) NiMoCA(1.0), (c) NiMoCA(1.5) and (d) NiMoCA(2.0).

# 3.3. Catalytic activity

Catalytic behavior of the synthesized and characterized NiMo(CA) catalysts supported on SBA-15 was evaluated in simultaneous hydrodesulfurization (HDS) of two model compounds, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). These S-containing aromatic molecules were selected because they are representative for diesel fuel and have quite different reactivity toward two possible routes of HDS. It is well known that HDS of dibenzothiophene-type compounds can occur by the two parallel reaction routes. Fig. 8 shows the reaction scheme of HDS of DBT-type molecules. In the first route, called the direct desulfurization pathway (DDS), sulfur is eliminated through hydrogenolysis of C—S bonds, yielding biphenyl-type compounds. In the second route, called the hydrogenation pathway (HYD), desulfurization occurs after hydrogenation of one of the aromatic rings of dibenzothiophene molecules with the formation of tetrahydro- and hexahydrogenated intermediates, which after desulfuration resulted in the products with one aromatic and one hydrogenated rings (cyclohexylbenzene or methylcyclohexyltoluene). Nowadays, it is well known that unsubstituted DBT can react through any one of the reaction routes (the DDS or the HYD) depending on the catalyst used, whereas 4,6-DMDBT, one of the most refractory sulfur compounds in diesel fuels, has a clear



Fig. 7. Length and stacking distributions of MoS<sub>2</sub> crystallites in sulfided catalysts: (a) NiMo, (b) NiMoCA(0.5), (c) NiMoCA(1.0), (d) NiMoCA(1.5) and (e) NiMoCA(2.0).



Fig. 8. Reaction network for hydrodesulfurization of dibenzothiophene-type compounds.

#### Table 4

Conversions of DBT obtained over NiMo(CA) catalysts at different reaction times and overall pseudo-first order rate constant ( $k_{\text{DBT}}$ ).

Catalyst	DBT c	onversior	n (%)	$k_{\rm DBT}  imes 10^4 ~({ m s}^{-1} ~{ m g}_{ m cat}{}^{-1}$ )	
	2 h	4 h	6 h	8 h	
NiMo	21	42	58	68	2.4
NiMoCA(0.5)	36	66	86	95	4.8
NiMoCA(1.0)	40	69	87	96	5.3
NiMoCA(1.5)	33	63	85	94	4.4
NiMoCA(2.0)	27	61	81	92	4.1

preference for the HYD route, which is attributed, in general, to the steric hindrance because of the presence of two alkyl substituents in positions 4 and 6 of this molecule [40,30].

The DBT conversions obtained over NiMo(CA) catalysts at 2, 4, 6 and 8 h reaction time are shown in Table 4. The lowest conversion (68% at 8 h reaction time) was obtained with the NiMo catalyst prepared without citric acid. All NiMoCA(x) catalysts prepared with citric acid showed higher catalytic activity than the reference NiMo sample; especially, the catalyst prepared from impregnation solutions with CA: Mo molar ratio x = 1. This can be clearly observed from DBT conversions obtained at different reaction times and values of overall pseudo-first order rate constants shown in Table 4. Thus, 96% of DBT conversion was obtained with this catalyst at 8 h, and the corresponding rate constant was more than twice higher than that of the reference NiMo sample. Further increase in the amount of citric acid used to x = 1.5 and 2.0 resulted in a slight decrease in the catalytic activity. The above results show, in general, that the addition of citric acid in the impregnation solutions used in the preparation of NiMo HDS catalysts had a beneficial effect on their activity. However, the best results were obtained with the NiMoCA(1.0) catalyst having equimolar CA:Mo ratio.

#### Table 6

Conversions of 4,6-DMDBT obtained over NiMo(CA) catalysts at different reaction times and overall pseudo-first order rate constant ( $k_{\text{DMDBT}}$ ).

Catalyst	4,6-DMDBT conversion (%)				$k_{\rm DMDBT}  imes 10^4  ({ m s}^{-1}  { m g}_{\rm cat}^{-1})$
	2 h	4 h	6 h	8 h	
NiMo	13	30	43	56	1.6
NiMoCA(0.5)	23	47	74	89	2.8
NiMoCA(1.0)	25	54	80	92	3.4
NiMoCA(1.5)	21	45	67	84	2.6
NiMoCA(2.0)	18	41	60	75	2.3

Table 5 shows the reaction product distributions obtained with different NiMo(CA) catalysts at 50% of DBT conversion. As it was expected, biphenyl (BP) and cyclohexylbenzene (CHB) were the principal reaction products accompanied by small amounts of tetrahydrodibenzothiophene (4HDBT) and dicyclohexyl (DCH). However, the proportion of CHB and BP in the reaction products changed depending on the catalyst. Thus, the reference NiMo catalyst prepared without citric acid, NiMoCA(1.5) and NiMoCA(2.0) showed similar selectivities toward both routes of HDS, the DDS and the HYD, leading to the formation of comparable amounts of BP and CHB (Table 5). At the same time, two other catalysts prepared with smaller amounts of citric acid (x=0.5 and 1.0), showed much higher hydrogenation ability and larger amounts of cyclohexylbenzene in comparison with biphenyl. The highest CHB/BP ratio was obtained with the NiMoCA(1.0) sample.

Table 6 shows the results obtained in hydrodesulfurization of 4,6-DMDBT over prepared NiMo and NiMoCA(x) catalysts. It can be seen in Table 6 that conversions obtained for 4,6-DMDBT were lower than those of DBT (Table 4), which is due to the fact that 4,6-DMDBT has lower reactivity in comparison with unsubstituted DBT. In addition, a significant difference in the catalytic activity of the tested samples in HDS of 4,6-DMDBT was observed. However, trends similar to those obtained with DBT were found. Namely, the NiMo catalyst prepared without citric acid showed the lowest activity among all catalysts tested (56% of 4,6-DMDBT conversion at 8h reaction time). Catalysts prepared with small amounts of citric acid, NiMoCA(0.5) and NiMoCA(1.0) showed good performance in the hydrodesulfurization of 4,6-DMDBT (89 and 92% of conversion at 8 h, respectively). Further increase in the amount of citric acid to x = 1.5 and 2.0 resulted in a decrease in the catalytic activity: 84 and 75% of 4.6-DMDBT conversion were obtained with NiMoCA(1.5) and NiMoCA(2.0) catalysts, respectively (Table 6). The above results, as well as the pseudo-first order rate constants shown in Table 6, confirmed again that better catalytic performance was obtained with the catalysts prepared with small amounts of citric acid (x = 0.5 and 1.0). The most active NiMoCA(1.0) catalyst showed 4,6-DMDBT conversions and a  $k_{\text{DMDBT}}$  value almost twice higher that those of the reference NiMo catalyst. A comparison of the catalytic activity results from Tables 4 and 6 points out that the NiMoCA(1.0) catalyst resulted to be the most active for HDS of both DBT and 4,6-DMDBT, which indicates that the amount of citric acid used in the preparation of this catalyst was the optimum. This catalyst seems to be a promising one for deep HDS of diesel, since it

#### Table 5

Composition of products obtained in hydrodesulfurization of DBT over NiMo(CA)/SBA-15 catalysts (at 50% of DBT conversion).

Catalyst	Product <sup>a</sup> (%)				Product ratios		
	BP	4HDBT	СНВ	DCH	BP: 4HDBT	4HDBT: CHB	CHB: BP
NiMo	47.3	4.5	45.2	3.0	10.51	0.099	0.96
NiMoCA(0.5)	39.5	4.5	52.6	3.4	8.78	0.086	1.33
NiMoCA(1.0)	37.3	4.0	55.4	3.3	9.33	0.072	1.49
NiMoCA(1.5)	43.6	5.5	47.3	3.6	7.93	0.116	1.08
NiMoCA(2.0)	49.6	5.2	42.5	2.7	9.54	0.122	0.86

<sup>a</sup> BP, biphenyl; 4HDBT, tetrahydrodibenzothiophene; CHB, cyclohexylbenzene; DCH, dicyclohexyl.

Catalyst	Product <sup>a</sup> (%)		Product ratios				
	DMBP	4H	6H	MCHT	DMBCH	(4H+6H): MCHT	MCHT: DMBP
NiMo	6.7	17.0	8.5	53.1	14.7	0.48	7.9
NiMoCA(0.5)	6.7	16.3	4.6	57.8	14.6	0.36	8.5
NiMoCA(1.0)	6.6	12.5	3.8	60.7	16.4	0.27	9.2
NiMoCA(1.5)	5.9	13.6	8.6	56.3	15.6	0.39	9.5
NiMoCA(2.0)	5.6	11.5	7.0	60.1	15.8	0.31	10.7

Composition of products obtained in hydrodesulfurization of 4,6-DMDBT over NiMo(CA) catalysts (at 50% of 4,6-DMDBT conversion).

<sup>a</sup> 4H, tetrahydro-4,6-dimethyldibenzothiophene (4H-4,6-DMDBT); 6H, hexahydro-4,6-dimethyldibenzothiophene (6H-4,6-DMDBT); DMBP, dimethylbiphenyl; MCHT, methylcyclohexyltoluene; DMBCH, dimethylbicyclohexyl.

is able to eliminate sulfur from different types of sulfur-containing aromatic molecules contained in this fraction of petroleum.

Product distributions obtained for different catalysts at 50% of 4,6-DMDBT conversion are shown in Table 7. The preferential pathway of HDS, as expected, was found to be the HYD route. Methylcyclohexyltoluene (MCHT) was the main desulfurized product obtained with all catalysts tested. Other products of the HYD route: pre-hydrogenated S-containing intermediates (tetrahydro-4,6-dimethyldibenzothiophene, 4H-4,6-DMDBT, and hexahydro-4,6-dimethyldibenzothiophene, 6H-4,6-DMDBT) and dimethylbicyclohexyl (DMBCH) were also obtained in smaller proportions. Dimethylbiphenyl (DMBP), the desulfurized product of the DDS route, was formed in a much smaller amount (5.6-6.7%) for all catalysts tested (Table 7). The highest proportion of DMBP (6.7%) was obtained with the reference NiMo and NiMoCA(0.5) catalysts. Further increase in the amount of citric acid used in the catalysts' preparation resulted in a progressive decrease in the proportion of DMBP in the reaction products and, consequently, in an increase in the MCHT/DMBP ratio. The most active NiMoCA(1.0) catalyst showed an intermediate value of MCHT/DMBP ratio between the tested samples, but it also had a smallest ratio of the amount of pre-hydrogenated intermediates (4H+6H) to the corresponding desulfurized product (MCHT), Table 7. It seems that the high catalytic activity of this catalyst is due to the optimum ratio between the catalytically active sites responsible for the hydrogenation of the starting 4,6-DMDBT molecule and the ones responsible for their further desulfurization.

# 4. Discussion

In the present work, NiMo catalysts supported on high surface area SBA-15 silica were prepared by co-impregnation of Ni and Mo precursor salts from aqueous solutions containing different amounts of citric acid. All impregnation solutions containing citric acid had acidic pH values (pH below 1). In addition, a reference NiMo/SBA-15 catalyst was prepared without citric acid. After the impregnation, all catalysts were dried and calcined in air atmosphere. The aim of this study was to inquire into the effect of the amount of citric acid on the activity and selectivity of the NiMo/SBA-15 catalysts in the simultaneous HDS of two model compounds, DBT and 4,6-DMDBT. We tried to follow the relationship between the characteristics of the Ni and Mo oxide species present in the prepared catalysts after drying and calcination, their characteristics after sulfidation and the catalytic performance of the prepared formulations in HDS.

Characterization of the reference NiMo and NiMoCA(x) catalysts by nitrogen physisorption and powder XRD showed that, in general, dispersion of the deposited Ni and Mo oxide species was better in all catalysts prepared with citric acid than in the reference NiMo sample. When citric acid was used, no formation of a crystalline NiMoO<sub>4</sub> phase (detected in the reference NiMo catalyst) was observed (Fig. 3). In addition, NiMoCA(x) catalysts had better textural characteristics than the sample prepared without

citric acid (Table 1 and Fig. 1). However, further characterization of the catalysts by diffuse reflectance spectroscopy and temperature programmed reduction showed that the effect of citric acid was not linear with its amount used in the catalyst preparation. Thus, addition of a small amount of citric acid to the impregnation solution (x = 0.5 and 1.0) resulted in a noticeable increase in the dispersion of Ni and Mo oxide species, which was evidenced by an increase in the absorption edge energy ( $E_{\sigma}$ , Table 2) and a decrease in the temperature of reduction of octahedral Mo species (Fig. 5). When the amount of citric acid used in the preparation was increased to x = 1.5 and 2.0, this tendency changed. DRS and TPR results showed an increase in the agglomeration of the deposited Mo oxide species with an increase in the amount of citric acid used. Therefore, results from the characterization of the catalysts in their oxide form showed that a better dispersion of metal oxide precursors in calcined NiMoCA catalysts supported on SBA-15 was reached when the amount of citric acid was small (x=0.5-1.0). Results from the characterization of the sulfided catalysts were well in line with the above observations for calcined catalysts. Once again, an increase was found in the dispersion of the sulfided Mo species for the catalysts prepared with a small amount of citric acid, reaching maximum for the NiMoCA(1.0) sample, and a decrease in the dispersion of MoS<sub>2</sub> particles in the samples prepared with larger amounts of CA. This can be clearly seen in the values of the  $f_{Mo}$ fraction reported in Table 3. Catalytic activity tests also revealed an increase in the HDS activity of the catalysts of the NiMoCA(x) series to x = 1.0, and a further decrease for x values of 1.5 and 2.0. Interestingly, similar trends in the activity of the catalysts with the change in the amount of citric acid were found for both model compounds used, DBT and 4,6-DMDBT, in spite of some differences in the reactivity of these molecules and their preferences for particular reaction pathways of HDS.

The above results allow us to assume that the mechanism of action of citric acid is somewhat different when it is added in small or large amounts to the solutions used for the catalyst preparation. It is well documented in the literature [22–26] that the addition of citric acid improves activity of HDS catalysts. In general, it was ascribed to a stabilization of the impregnation solutions and a better dispersion of the active phase in presence of citric acid. In appropriate conditions citric acid can act as a chelating additive able to form complexes with Ni(II) or Co(II) and prevent the sulfidation of these promoters at low temperatures, leading to an increase in the amount of Ni(Co)-Mo-S phase after sulfidation [16,25]. In addition, a bimetallic Co<sub>2</sub>[Mo<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>O<sub>11</sub>] complex was synthesized in aqueous impregnation solution at acidic pH, which was employed for the preparation of active HDS catalysts supported on alumina [22,23]. However, formation of the complexes as described above strongly depends on the solution pH, and, as it was shown in our previous work [29], upon experimental conditions used by us (Ni and Mo concentrations and pH below 1), no complexes can be formed between citric acid and Ni(II) or Mo(VI) precursors. In some works [28,29,41], it was observed that citric acid can act as a source of a small amount of carbonaceous residues in HDS catalysts which

Table 7

can affect morphology of the MoS<sub>2</sub> or WS<sub>2</sub> slabs. However, in the present work NiMoCA catalysts were calcined in air atmosphere prior to sulfidation, and only small amount of carbon was found in them by elemental analysis (for example, 0.3 wt.% of carbon in the NiMoCA(2.0) sample). So, it seems that the presence of such a small amount of carbon in these catalysts cannot explain the changes in their catalytic behavior. In our opinion, when a small amount of citric acid is used in the NiMoCA catalyst preparation, the role of citric acid can consist in the stabilization of the impregnation solution. separation of Ni and Mo species in the solution, which avoids their interaction leading to the formation of a NiMoO<sub>4</sub> crystalline phase in the calcined catalysts, and probably in an increase in the solution viscosity. According to previous report [42], homogeneous distributions and high dispersions of the supported metal oxide species can be obtained from aqueous solutions containing citrate, acetate, EDTA, etc. Upon solvent evaporation when drying the catalysts, a steep increase in viscosity is observed, which inhibits redistribution of the impregnated solution upon drying of the support body. In addition, a gel-like phase can be formed that favors high dispersion of the active phase even after full drying and calcination. In order to confirm this supposition, we determined viscosity of the solutions used for the preparation of our catalysts. It was found that the viscosity of the aqueous solution containing only nickel nitrate and ammonium heptamolybdate was equal to  $0.715 \times 10^6 \text{ m}^2/\text{s}$ . When citric acid was added to this solution, its viscosity increased almost linearly with the amount of citric acid used, reaching a value of  $0.905 \times 10^6$  m<sup>2</sup>/s for CA:Mo molar ratio x = 2.0. Further increase in the viscosity can be expected upon drying of the impregnated catalysts. Formation of a gel-like phase was observed by us upon drying of the catalyst prepared with the largest amount of citric acid (x = 2.0).

On the other hand, when a large amount of citric acid was used in the preparation of our catalysts (x = 1.5 and 2.0), a decrease in the dispersion of oxide and sulfided Mo species was observed. We think that this contrary effect of citric acid can be related with the interaction of an excess of citric acid with the SBA-15 support. Recently, it has been reported for the case of alumina-supported NiW catalysts [41], that citric acid preferentially reacts with basic and neutral OH groups of alumina surface so as to moderate the interaction between tungsten species and the support. We suppose that similar interaction of citric acid with the SBA-15 surface groups can result in a decrease of a number of anchoring points for deposited Mo species, which can suffer agglomeration and loss of dispersion during the calcination of the catalysts prepared with large amount of citric acid.

Finally, it should be mentioned that the activity and selectivity trends obtained in the present work for the NiMoCA(x) catalysts prepared from acidic impregnation solutions with different amounts of citric acid can be compared with those found previously for similar catalysts, but prepared from basic impregnation solutions (pH 9) and sulfided without previous calcination [28]. In both cases, catalysts prepared with a small amount of citric acid showed higher catalytic activity than those prepared with a large amount of CA. However, the effect on selectivity the amount of citric acid used had, was significantly different depending on the pH of the impregnation solution and the thermal treatment (drying or drying-calcination) of the catalysts before sulfidation step. Thus in the work [28], a progressive increase in the selectivity of the NiMo/SBA-15 catalysts toward the direct desulfurization pathway of DBT HDS was observed with increasing the amount of CA used. On the contrary, in the present work all the catalysts prepared with CA showed high hydrogenation ability for both DBT and 4,6-DMDBT model compounds used. The best activity results were obtained with the NiMoCA(1.0) catalyst indicating that the amount of CA used in the preparation of this catalyst was the optimum.

#### 5. Conclusion

In the present work, NiMo catalysts supported on SBA-15 were prepared by coimpregnation of Ni and Mo species from acidic aqueous solutions (pH below 1) containing different amounts of citric acid (CA). The aim of this study was to inquire on the effect of the amount of citric acid on the activity and selectivity of the NiMo/SBA-15 catalysts in simultaneous hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene. The amount of citric acid used in the catalyst preparation was varied from CA:Mo molar ratio 0.5 to 2.0. In addition, a reference NiMo/SBA-15 catalyst was prepared without citric acid.

XRD, DRS and TPR characterizations showed that Ni and Mo oxide species were well dispersed in all catalysts prepared with citric acid. No presence of a NiMoO<sub>4</sub> crystalline phase, detected in the reference NiMo/SBA-15 catalysts prepared without citric acid, was found for the NiMoCA(x) catalysts. However, the maximum dispersion of deposited metal species was achieved for the intermediate amounts of citric acid used (x = 0.5 and 1.0). Further increase in the amount of citric acid to x = 1.5 and 2.0 resulted in some agglomeration of octahedral Mo oxide species (DRS, TPR). Similar changes in the dispersion of the sulfided MoS<sub>2</sub> active phase were observed by HRTEM. The NiMoCA(1.0) catalyst showed the best dispersion of MoS<sub>2</sub> particles and the highest fraction of Mo atoms located on the catalytically active surface ( $f_{Mo}$  fraction, Table 3). In line with results from the catalyst characterization, HDS activity of the NiMo catalysts prepared with the addition of citric acid resulted to be significantly higher than that of the reference NiMo/SBA-15 sample for both DBT and 4,6-DMDBT. It was found that the optimum amount of citric acid, which allows achieving the highest catalytic activity, corresponds to CA:Mo molar ratio equal to 1. Further increase in the amount of citric acid resulted in a slight decrease in the HDS activity. We think that this behavior is due to two opposite effects of citric acid. On the one hand, addition of citric acid to the impregnation solution increases its stability and viscosity, especially upon drying of the catalyst, leading to an increase in the dispersion of Mo species on the catalyst surface. On the other hand, when the amount of citric acid used in the catalyst preparation is large enough (x = 1.5)and 2.0), an excess of citric acid can react with the support surface groups decreasing the amount available for the interaction with Mo species from the solution and leading to the agglomeration of Mo species upon calcination.

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