

# Preparation, characterization of Mo catalysts supported on Ni- containing calcium deficient hydroxyapatite and reactivity for the thiophene HDS reaction

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**Abstract.** Ni-containing Calcium Hydroxyapatite (NiCaHAp; 3.31 wt.% Ni) was synthesized by coprecipitation and used as catalyst support. Molybdenum was supported on NiCaHAp by impregnation using ammonium heptamolybdate. The prepared catalysts Mo(x)/NiCaHAp (x: 2 to 8 wt % in Mo) were characterized by elemental analysis, XRD, FT-IR, N<sub>2</sub> adsorption-desorption and TEM-EDX. The catalysts were sulfided *in-situ* at 673 K under flowing H<sub>2</sub>S/H<sub>2</sub> (15 Vol.% H<sub>2</sub>S) and tested in hydrodesulfurization (HDS) of thiophene at 673 K. The main XRD peaks of hydroxyapatite CaHAp phase were observed in all samples and a peak due probably to crystalline MoO<sub>3</sub> phase was also identified from the results. However, no crystalline phase of NiO was found for the catalysts, which showed its Ni species were highly dispersed. The sulfided catalysts Mo(x)/NiCaHAp presented are active in HDS of thiophene, despite the presence of some large MoO<sub>3</sub> crystallites and incomplete sulfidation. This activity may be due to interaction of NiO and MoO<sub>3</sub> on CaHAp resulting in the formation of Ni-Mo-S phase under flowing H<sub>2</sub>S/H<sub>2</sub>. When the molybdenum content increased the HDS activity increased slightly, which was caused by the agglomeration of MoO<sub>3</sub>. The Mo(8)/NiCaHAp catalyst is about two times less active for thiophene HDS than the commercial NiMoP/Al<sub>2</sub>O<sub>3</sub>.

## 1. INTRODUCTION

It is currently known that a great part of natural phosphates adopts a crystalline structure similar to that of synthetic hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> [1]. The composition of natural phosphates is very complex. Indeed, the apatitic lattice allows various anionic and cationic substitutions.

Despite their low cost and their availability in the market, the use and application of apatite in catalysis is still a subject of relatively scarce investigations. For example, calcium hydroxyapatite containing transition metals were found to be very active in the methane dry reforming [2], the hydrogenolysis of S-containing substrates [3], the propane oxidative dehydrogenation [4] and the epoxidation of olefin [5]

Within our research team, we have been looking for some new catalytic applications for apatitic compounds with a special interest for hydroxyapatite. Most of these studies are focused on the hydrodesulfurization (HDS) of petroleum distillate fractions for the reduction of atmospheric pollution due to the emission of hazardous compounds such as SO<sub>2</sub>.

Previously, we have shown that hydroxyapatite containing small amounts of carbonate species, with a Ca/P molar ratio around 2, can be used as a support for hydrodesulfurization sulfide catalysts since it exhibits the required textural properties and a good thermal stability [6].

In the present work, we studied the use of nickel-containing calcium deficient hydroxyapatite Ni-CaHAp (3.31 wt% Ni) prepared by coprecipitation at pH basic and calcined at 773 K, as a support for molybdenum catalysts during the hydrodesulfurization of thiophene. Molybdenum supported catalysts were prepared by impregnation using ammonium heptamolybdate (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O.

The prepared catalysts were characterized using several experimental techniques such as X-ray diffraction,

FT-IR spectroscopy, nitrogen adsorption at 77 K and transmission electron microscopy combined with energy-dispersive X-ray analysis (TEM-EDX). Meanwhile, the hydrodesulfurization catalytic activity was assessed at atmospheric pressure using thiophene as a probe molecule.

## 2. EXPERIMENTAL

### 2.1. Synthesis of catalysts

#### 2.1.1. Synthesis of Ni-containing CaHAp

The nickel-containing calcium hydroxyapatite (noted as NiCaHAp) precursor was synthesized using the following precipitation method: an ammoniacal solution of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> ( $m = 11.75$  g dissolved in 1000 ml of distilled water + 100 ml of 25% aqueous ammoniac) was poured into a second solution (100 ml) of calcium nitrate ( $m = 18.51$  g) and nickel nitrate ( $m = 5.75$  g) while stirring at 353 K. The pH was maintained at 9 during mixing. After the dropwise addition (3 h), the mixture was kept at 353 K for 1 h. After this time, the yellow solid was separated by filtration, washed with distilled hot water, dried overnight at 393 K and calcined at 773 K. The Ca/P atomic ratio of Ni-CaHAp obtained was 1.51 indicating that the material is calcium deficient hydroxyapatite with a chemical formulae: Ni(3.31 wt%)-Ca<sub>9.1</sub>(HPO<sub>4</sub>)<sub>0.9</sub>(PO<sub>4</sub>)<sub>5.1</sub>(OH)<sub>1.1</sub>

#### 2.1.2. Synthesis of Mo(x)/NiCaHAp

Molybdenum was loaded on the NiCaHAp by pore volume impregnation. Before impregnation, 2 g of the Ni-CaHAp was calcined under dry air flow, at 773 K, for 2 h, and then added to 1 cm<sup>3</sup> of an aqueous solution of ammonium

**Table 1.** Chemical composition, textural and structural characteristics of catalysts Mo(x)/NiCaHAp.

Catalysts	Chemical analysis				Textural properties			
	Ca Wt.%	P Wt.%	Ni Wt.%	Mo Wt.%	Ca/P at./at.	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	D <sub>p</sub> (nm)
NiCaHAp	35.74	18.35	3.31	—	1.51	114	0.56	20.0
Mo(2)/NiCaHAp	33.37	17.15	3.28	2.20	1.51	90	0.51	22.6
Mo(5)/NiCaHAp	32.48	16.93	3.24	4.62	1.49	83	0.48	23.2
Mo(8)/NiCaHAp	—	—	2.88	8.32	—	54	0.33	24.6

heptamolybdate with the required concentration. The obtained slurry was left at room temperature for about one hour, and then evaporated at 333 K. All the prepared catalysts were dried overnight at 393 K in an oven, and finally calcined at 773 K for 2 h under ambient atmosphere. All catalyst will be referred to as Mo(x)/Ni-CaHAp, where x (expressed in wt.%) represents the weight percentage of Mo in the catalyst. The prepared catalysts contain loads varying from 2 to 8 wt% in molybdenum.

## 2.2. Characterization techniques

XRD patterns were obtained using a PW 1716 diffractometer, which utilizes Ni-filtered Cu (K<sub>α</sub>) radiation (λ: 1.5405 Å). Samples were run as fine powders mounted on glass slides.

Fourier transform infrared spectroscopy (FT-IR) studies were carried out on the Vertex 70 spectrometer in the range 400–4000 cm<sup>-1</sup>. The transmission technique was applied and the samples were prepared as standard KBr pellets (2%).

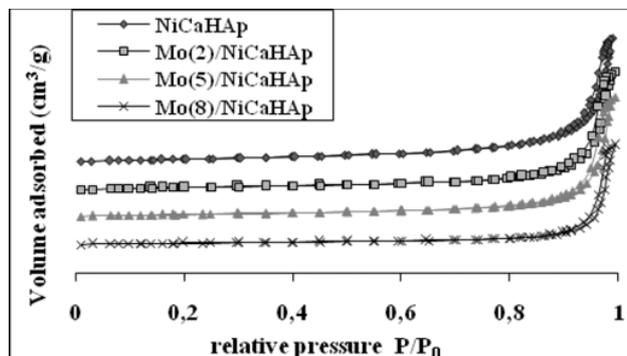
The textural properties of all the catalysts were carried out in an ASAP 2000 Micrometrics instrument by means of nitrogen adsorption and desorption at 77 K. Before analysis, all the samples were evacuated at 573 K under vacuum.

The transmission electron microscopy (TEM-EDX) analyses were performed in a Tecnai G<sup>2</sup>-FEI operated at 120 KV. TEM specimens were prepared by depositing a few drops of catalysts dispersed in acetone on a carbon-coated copper grid.

## 2.3. HDS catalytic measurements

The thiophene hydrodesulfurization reaction was carried out in a fixed bed flow reactor. Before the reaction, the oxide precursor (50 mg) was pretreated at 773 K under ambient atmosphere, and then *in-situ* sulfided at 673 K under flowing H<sub>2</sub>S/H<sub>2</sub> (15 Vol.% H<sub>2</sub>S) for 2 h 30 min at atmospheric pressure. Finally, the feed (thiophene 7.5 mol%, H<sub>2</sub>S 2 mol%, and H<sub>2</sub> 90.5 mol%) was supplied to the reactor and the HDS reaction was monitored at 673 K under atmospheric pressure. In these conditions, the total conversion of thiophene was kept below 15% to operate in differential regime. Thus, the catalytic activity could be estimated from the pseudo-first order rate constant k<sub>HDS</sub>:

$$k_{\text{HDS}} = -(F/CW) * \text{Ln}(1 - X). \quad (1)$$



**Figure 1.** N<sub>2</sub> adsorption-desorption isotherms of the Ni-CaHAp and the Mo(x)/NiCaHAp.

Where F is the thiophene molar flow (mol/h), W is the weight of the sulfide catalyst (g), X is the total conversion of thiophene, and C the concentration of thiophene in the feed (mol/l).

The hydrodesulfurization reaction products were separated on a gas chromatograph (GC) using an OV1 column and analyzed with a thermal conductivity detector (TCD). Besides un-reacted thiophene, the reaction products are, H<sub>2</sub>S and C4 (1-butene, trans-2-butene, cis-2-butene and butane). Thiophene conversion data were collected at 60 min intervals during 3 hours, and the values reported here are those obtained when the steady state is reached.

## 3. RESULTS AND DISCUSSION

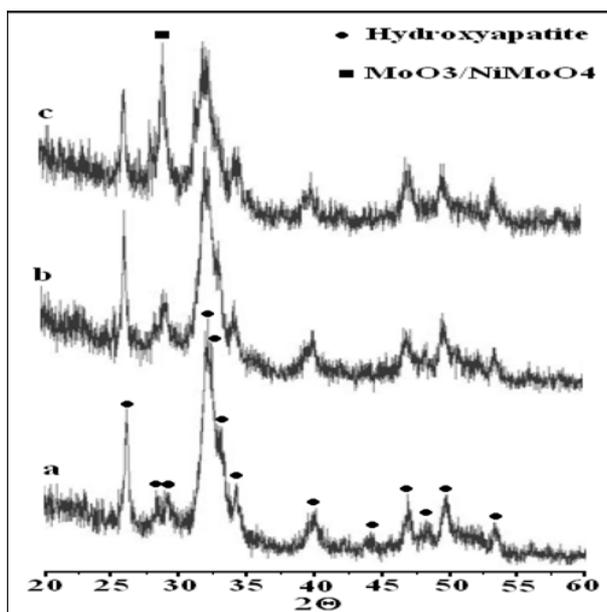
### 3.1. Characterization of catalysts

#### 3.1.1. BET surface area and elemental analysis

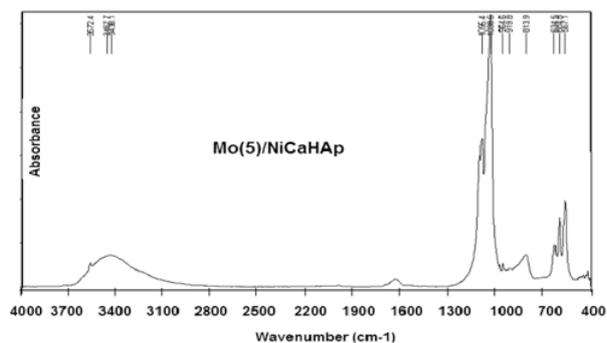
Table 1 summarizes the physicochemical parameters of the catalysts. Chemical analysis revealed a Ca/P molar ratio ranging from 1.51 to 1.49, compatible with calcium-deficient hydroxyapatite [7].

Figure 1 shows the N<sub>2</sub> adsorption-desorption isotherms of the NiCaHAp and Mo(x)/NiCaHAp catalysts. All samples showed a type IV isotherm with a type H2 hysteresis loop, indicating the presence of well-developed mesoporosity in all the samples.

The BET surface area for NiCaHAp was 114 m<sup>2</sup>/g. For the supported catalysts, an increase in molybdenum loading results in a decrease in the surface area probably due to pore blockage, since a similar pattern is observed for pore volume measurements (Table 1). There was a



**Figure 2.** XRD patterns of NiCaHAp (a), Mo(2)/NiCaHAp (b) and Mo(8)/NiCaHAp (c).



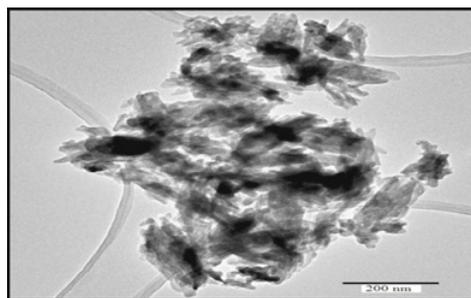
**Figure 3.** Infrared vibration spectrum of the Mo(5)/NiCaHAp.

minimal increase of the pore diameter with an increase in the molybdenum loading.

It should be noted that the changes in pore volume, pore diameter and BET surface area decreased abruptly when the Mo exceeded 5wt.%, which is attributed to the agglomeration of molybdenum oxide.

### 3.1.2. Powder X-ray diffraction

The powder XRD patterns of NiCaHAp and Mo(x)/NiCaHAp catalysts in the angular range  $2\theta$  of 10–70° are presented in Fig. 2. The NiCaHAp sample containing 3.31 wt.% Ni showed only diffraction lines belonging to calcium-hydroxyapatite CaHAp (JCPDS 09-0432), suggesting that the added nickel is amorphous and well dispersed on its surface. The diffraction peaks of CaHAp were clearly observed with all the Mo(x)/NiCaHAp catalysts. The diffraction peaks of CaHAp were weak, which was probably due to the small size of the particles [8]. Besides the peaks characteristic of calcium hydroxyapatite, we note the presence of a diffraction peak around  $2\theta \approx 29^\circ$  for high Mo loadings (8 wt.% Mo). This



**Figure 4.** TEM image of the Mo(5)/NiCaHAp catalyst.

peak can be probably attributed to the presence of bulk  $\text{MoO}_3$  [9,10]. Formation of a small amount of  $\text{NiMoO}_4$  (the strongest peak being at  $2\theta \approx 29^\circ$ ) is not excluded [11,12].

### 3.1.3. Infrared spectroscopy

Figure 3 depicts the FT-IR spectrum of Mo(5)/NiCaHAp catalyst, diluted in KBr (2%), in the 400–4000  $\text{cm}^{-1}$  wavenumber range. We can see that the FT-IR spectra of the catalyst investigated here exhibit the presence of vibration bands characteristic of  $\text{OH}^-$  groups (stretching mode at 3572  $\text{cm}^{-1}$  and vibrational mode at 634  $\text{cm}^{-1}$ ),  $\text{PO}_4^{3-}$  groups ( $\nu_3$ : 1095 and 1040  $\text{cm}^{-1}$ ,  $\nu_1$ : 965  $\text{cm}^{-1}$ ,  $\nu_2$ : 605 and 567  $\text{cm}^{-1}$ ) and the broad bands at 3435  $\text{cm}^{-1}$  and at 1630  $\text{cm}^{-1}$  were due to adsorbed  $\text{H}_2\text{O}$ . The bands assignments are according to literature data [13].

Meanwhile, we note the presence of a vibration band at 814  $\text{cm}^{-1}$ , which would correspond to the oxygen atom vibrations in Mo-O-Mo in which Mo represents hexavalent molybdenum [14].

### 3.1.4. Transmission electron microscopy

The micrograph of Mo(5)/NiCaHAp is shown in Fig. 4. Dark particles of metal oxide with a size distribution of 20–80 nm existed on the surface of CaHAp. EDX data show a Ni/Mo ratio of 1.07 which correlates with the value from elemental analysis (Table 1).

## 3.2. Catalytic tests

The thiophene hydrodesulfurization (HDS) model reaction has been used to establish the performance of the sulfided Mo(x)/NiCaHAp catalysts,  $k_{\text{HDS}}$  values are plotted as a function of time on-stream (TOS) in Fig. 5. As can be seen, the sulfided Mo(x)/NiCaHAp catalysts, which initially display a high thiophene HDS activity, undergo a strong deactivation during the first hour. This behaviour is attributed to a loss of sulfur atoms from the active NiMoS phase during reaction with thiophene [15]. The Mo(x)/NiCaHAp catalysts show a much higher HDS activity than the sulfided NiCaHAp ( $k_{\text{HDS}} = 0.781/\text{hg}$ ; 3.31 wt% Ni) and Mo/CaHAp ( $k_{\text{HDS}} = 1.641/\text{hg}$ ; 2.1 wt% Mo) catalysts, which is attributed to the promoting effect of  $\text{Ni}^{2+}$  ions in the mixed NiMo sulfided materials.

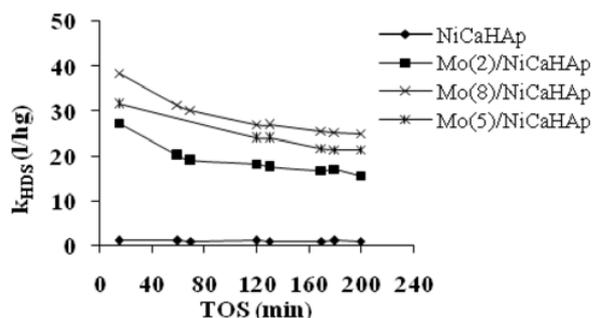


Figure 5.  $k_{HDS}$  of Mo(x)/NiCaHAp catalysts with TOS.

Table 2. Rate constants  $k_{HDS}$  and degree of sulfidation S/(Ni + Mo) of catalysts.

Catalysts	$k_{HDS}$ (l/hg)	S/(Ni + Mo) at./at.
Mo(2)/NiCaHAp	16.7	0.50
Mo(5)/NiCaHAp	21.4	0.87
Mo(8)/NiCaHAp	25.3	0.76
NiMoP/Al <sub>2</sub> O <sub>3</sub>	50.0	–

It is worth noting that the activity of sulfided Mo(x)/NiCaHAp catalysts slightly increases with Mo loading, because the higher Mo loading will result in more and larger MoO<sub>3</sub> particles and consequently the degree of sulfidation will be lower (Table 2). Among the catalysts tested, the Mo(5)/NiCaHAp catalyst showed better sulfidation than other catalysts. This may be due to a well dispersion of MoO<sub>3</sub> particles on NiCaHAp (Table 2).

The HDS activity of Mo(8)/NiCaHAp ( $k_{HDS}$  = 25.3l/hg; Ni/(Ni + Mo) = 0.36) is lower than that of commercial NiMoP/Al<sub>2</sub>O<sub>3</sub> ( $k_{HDS}$  = 50l/hg; Ni/(Ni + Mo) = 0.38) [10]. Compared to the cited catalyst, the relatively lower activity of Mo(8)/NiCaHAp catalyst is caused by the agglomeration of MoO<sub>3</sub> particles.

#### 4. CONCLUSION

The agglomeration of MoO<sub>3</sub> and the incomplete sulfidation may explain the relatively low activity of the

Mo(x)/NiCaHAp catalysts in hydrodesulfurization of thiophene compared to the commercial NiMoP/Al<sub>2</sub>O<sub>3</sub> in the same experimental conditions.

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