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Ultrasound assisted synthesis of nanometric Ni, Co, NiMo and CoMo HDS catalysts

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Abstract

In the present work, ultrasound assisted synthesis of NiS, CoS, NiMoS and CoMoS was studied. Solids thus obtained were characterized by X-ray diffraction, confocal microscopy, chemical analysis, surface area determinations, and their activities in thiophene and benzothiophene hydrodesulfurization (HDS) were also evaluated. It was found that NiMo catalyst was 5 and 2.4 times more active than NiS, in thiophene and benzothiophene HDS, respectively, while CoMo was 6.4 and 3.2 more active than CoS for the same reactions. It is proposed that the high activity for bimetallic solids is due to the precipitation of a mixed sulfide in nanometric size particles.

Keywords: Ultrasound; Nanometric sulfides; HDS

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1. Introduction

Due to stringent legislation concerning sulfur content in fuels [1] there is a need for more active and selective hydrotreating catalysts. Also, as light crude oils reserves dwindle processing and upgrading heavy an extra heavy crude oil and tar sands is important.

The use of unsupported catalysts, which could be used either dispersed in a heavy feedstock [2], or in the preparation of bulk metal catalyst for a conventional process, is considered to be a promising way to improve HDS/Hydrotreating (HDT) process efficiency [3].

Different methods have been reported for the preparation of Mo sulfide nanoparticles [4–8], and the use of ultrasonic irradiation have proven to be an effective way for their synthesis [4–6]. In particular, the sonochemical approach has been found to produced active Mo sulfide nanoparticles [4–6], and the use of simple organic precursors in aqueous solution, instead of $Mo(CO)_6$ in organic solvent [4,5], have successfully been explored [6].

However, in spite of the well-known promotion of Mo by Ni or Co leading to more active HDT catalysts, there are not reports in the literature on the preparation of NiMo or CoMo nanometric sulfides. All preparations of NiMo or CoMo bulk sulfides, where particle sizes can be estimated, lead to high surface area porous particles of several microns or higher in diameter [9,10]. Only Ye et al. [11] have synthesized $NiMoO_2S_2$ nanoparticles (≈13 nm), using a microemulsion systems, but they were intended to be used as lubricant additives.

Ultrasound has also been used in the preparation of CoMo and NiMo sulfides supported on alumina or Al-MCM-41, starting from $Mo(CO)_6$, sulfur, isodurene or decaline, and $Co_2(CO)_8$ or $Co(CO)_3NO$, or $Ni(CO)_4$ [12,13].

In a previous work [14] FeMo and NiMo nanometric bimetallic sulfides were prepared from thermal decomposition of emulsions, and their activities tested in thiophene HDS.

The present work deals with the preparation of nanometric Co, Ni and CoMo and NiMo sulfides, from ultrasonic irradiation of aqueous solutions of simple metallic salts, and its use in thiophene and benzothiophene HDS.

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2. Experimental

2.1. Catalysts preparation

Catalysts were prepared according to the method reported by Wang et al. [15,16], for the preparation of Ni and Cu sulfides. Thus, in a typical preparation 0.9 g (0.012 mol) of thioacetamide (TAA), 0.20 g of polyvinylpyrrolidone (PVP), 5 cm^3 of triethanolamine and 0.01 g at. of metal (as Ni or Co acetate) were dissolved in 100 cm^3 of distilled water. PVP is used to reduce particle agglomeration, since it has been shown that it acts as stabilizer in the preparation of nonosized iron particles [17]. Then the solution was submitted to high intensity ultrasonic irradiation (20 kHz, $\approx$80 W/cm^2) for 50 min, with an ultrasonic processor (Sonics & Materials) using a titanium tip of 1 cm^2.

For the bimetallic sulfide preparation ammonium heptamolybdate (AHM) was added together with the Ni or Co salt, and the total amount of g at. of metal was kept constant and equal to 0.01.

Once the irradiation time was over, the sample was submitted to ageing for different periods of time. Finally, the solids were recovered by filtration through a porous frit, washed with water, ethanol and acetone, and vacuum dried for 24 h at 80 °C.

2.2. Characterization

2.2.1. X-ray diffraction

Diffraction patterns were obtained in a Phillips (PW 1830) apparatus with a Cu (λ = 1.5418) anode. Working voltage was set at 50 kV and the intensity at 35 mA.

2.2.2. Elemental analysis

Catalysts were analyzed for Mo, Ni and Co by atomic absorption in the ‘‘Centro de Química Analítica (Facultad de Ciencias, Universidad Central de Venezuela)’’ utilizing a GBC-Avanta instrument.

2.2.3. Confocal microscopy (CFM)

Microscopic images of the suspensions of the solids after ultrasonic irradiation were obtained with a home made confocal microscope [18]. The light source consisted of a tungsten lamp. The samples were observed with a 40× objective (10,000× magnifications). The microscope is equipped with a CCD camera (640 × 480 pixels). Reflected light can be directed to the CCD camera in order to acquire total image, an aperture placed before of the CCD produce the confocal effect and permits to obtain an image with enhance spatial resolution of less than 300 nm ($\approx$100 nm).

2.2.4. Surface area

Surface area determinations (BET method, nitrogen adsorption) were carried out, on the air-exposed non-presulfided samples, in a Flow Sorb II 2300 Micromeritics device. All samples were outgassed at 200 °C for 1.5 h.

2.2.5. Catalytic activity

All the solids were presulfided prior to reaction in a 15% (v/v) H_2/H_2S mixture (1.5 $cm^3\ s^{-1}$) at 400 °C for 4 h. This are standard conditions for the sulfidation of bulk sulfides [6,19,20], and for ultrasonically prepare Mo sulfide, a similar procedure lead to a fully sulfided solid (as evidenced by XPS) [6].

2.2.6. Thiophene HDS

The reaction was carried out in a Pirex continuous flow micro reactor at 300 °C and atmospheric pressure. A solution of thiophene in heptane (10%, v/v) was feed to the reactor ($2.7 \times 10^{-4}\ cm^3\ s^{-1}$) through a syringe metering pump, and the reaction products analyzed with a PerkinElmer Auto System XL chromatograph equipped with a flame ionization detector. Only *n*-butane, 1-butene, *cis*-2-butene and *trans*-2-butene were detected as reaction products. Hydrogen flow rate was 0.1 $cm^3\ s^{-1}$. Catalyst weight was varied in order to keep conversion low (<35%). Steady state activity (three consecutive measurements were the same within 1%) are reported.

Activity was taken as moles of thiophene converted by second and by gram of catalyst, and was calculated multiplying the thiophene molar flow rate by the conversion.

2.2.7. Benzothiophene HDS

Benzothiophene HDS were carried out batchwise in a high pressure Parr reactor at 55 bar of H_2 and 300 °C for 6 h. Initially the reactor is fed with 30 cm^3 of 2% (w/v) BT in *n*-heptane solution, and 0.100 g of catalyst. Reaction products were analyzed by gas chromatography (PerkinElmer Auto System XL chromatograph equipped with a flame ionization detector).

Activity was taken as moles of BT converted by second and by gram of catalyst.

3. Results and discussion

For every preparation, but for the ones carried out with AHM alone, a darkening of the solutions were observed immediately after ultrasonic irradiation started, which is indicative of sulfide (Ni or Co) formation, even though, no solids were observed. However, if the solutions were allowed to stand for several days after the ultrasonic treatment, solid agglomeration was observed which allowed them to be separated by filtration.

The preparation method used in this work was exactly the same as the one reported by Wang et al. [15], except for the addition of PVP, and they obtained particles of 17 ± 3 nm for NiS. We can then assume that the NiS and CoS particles prepared in this work are of the same order of magnitude. However, in order to recover and characterize the solids it was necessary to age the solutions for a week or more, during which time the solids agglomerated (as suggested by confocal microscopy results) and it was possible to separate them by filtration.

For the experiences carried out with AHM (without Co or Ni) the solution turned yellowish after ultrasonication, and no solids were obtained even after several weeks of ageing.

According to Wang et al. [15] the reaction process for the sonochemical formation of metallic sulfide nanoparticles can be summarized as follows:

Step 1 $M^{2+} + x\text{TEA} \rightarrow (M(\text{TEA})_x)^{2+}$ (M = Cu or Ni)
Step 2 H_2O))) $H^\bullet + {}^\bullet OH$
Step 3 $CH_3CSNH_2 + 2H^\bullet \rightarrow CH_3(NH_2)C^\bullet + H_2S$
Step 4 $M^{2+} + H_2S \rightarrow MS + 2H^+$
Step 5 $n\text{MS} \rightarrow (\text{MS})n$

Due to the elevated pressures and temperatures generated by ultrasonic irradiation water molecules are dissociated to form $H^\bullet$ and ${}^\bullet OH$ radicals (Step 2) inside the cavitation bubbles. $H^\bullet$ radicals react with TAM (which, due to cavitation conditions, is volatized inside the bubbles) to form H_2S (Step 3). Finally, the H_2S thus obtained reacts with metallic ions, which are forming a complex with the TEA, at the bubbles interface to give the corresponding sub micrometric metallic sulfides (Step 4).

Wang et al. [15] also propose a second possible pathway in which the sonochemical cleavage of water (Step 2) could be linked with the addition across the C=S bond to give $CH_3C(NH_2)(OH)SH$ (Step 6). Repeating this process would result in the formation of H_2S and $CH_3C(NH_2)(OH)_2$ (Step 7) which would immediately lose water to give CH_3CONH_2 (Step 8). The released H_2S reacts with M^{2+} to yield MS (Steps 4 and 5).

Step 6 $CH_3CSNH_2 + H^\bullet + {}^\bullet OH \rightarrow CH_3C(NH_2)(OH)\text{-}SH$
Step 7 $CH_3C(NH_2)(OH)\text{-}$
$SH + H^\bullet + {}^\bullet OH \rightarrow CH_3C(NH_2)(OH)_2 + H_2S$
Step 8 $CH_3C(NH_2)(OH)_2 \rightarrow CH_3CONH_2 + H_2O$

Even though the effect of the TEA as complexing agent is not well explained, when experiments were carried out without the use of this reagent metal sulfides precipitation was not possible.

It is clear that metallic sulfide formation has to take place at the interface between the bubbles and the liquid media which surrounds them, since the metallic salt used is not volatile enough to enter the vacuumed bubbles, thus H_2S and the metal can only be in contact at this interface.

When the reacting solution contains AHM and Co or Ni salt, solid formation was observed after 1 or 2 weeks of ageing, and the final solution was clear and not yellowish, as for AHM alone experiences, which means that Mo is co-precipitating with Co or Ni. In fact, chemical analyses of the solid obtained after ageing for 1 week and sulfided in H_2S/H_2 (Table 1) reveal the presence of variable quantities of Mo. As can be seen Mo was co-precipitated with Ni or Co, however, Mo content in the NiMoS catalyst is a lot smaller than for CoMoS catalysts. The origin of this difference is not clear at the moment.

Also, the filtration and drying might not completely eliminate any organic precursor that could remain with the precipitated solids, but the sulfiding procedure (treatment at 300 °C for 4 h in H_2/H_2S flow) should. However, the presence of organic and/or carbonaceous material that could be formed from the decomposition of the organic reagents used in the preparation of the metallic sulfides cannot be ruled out.

All solids prepared show low surface areas in the order of $4\ m^2\ g^{-1}$. Even though this value may appear to be too low for nanoparticles, a review of the literature reveals that no many work report surface areas of sulfides nanoparticles. Thus, Wang et al. [14], Marchand et al. [8], Boakye et al. [7] and Ye et al. [11] report the preparation of Ni, Cu, Mo and NiMoO sulfides, but not surface areas are given for their obtained solids. Mdleleni et al. [4] report the synthesis of Mo sulfide assisted by ultrasound, and they obtained a porous agglomeration of clusters of spherical particles with an average diameter of 15 nm, and $55\ m^2\ g^{-1}$. However, carbon contamination on this Mo sulfide could be responsible for the relatively high surface area.

X-ray diffraction pattern for NiS (Fig. 1) shows peaks at 2.771, 2.507, 2.221 and 1.860 Å, that can be assigned to the formation of Ni sulfide millerite (JCPDF 12.41), which is in agreement with Wang et al. [15] XRD results, and peaks at 2.929, 2.578, 1.975 and 1.695 Å which corresponds to synthetic Ni sulfide (JCPDF 2-1280). For de NiMoS solid only signals that can be assigned to synthetic Ni sulfide (JCPDF 2-1280) were observed (Fig. 2), which is not surprising since the amount of Mo in this solid was very low, according to the elemental analysis.

For CoS and CoMoS solids no diffraction signals were obtained. Possibly, the solids were too amorphous to produce any signal.

Confocal microscopy carried out in the suspension immediately after the ultrasonic irradiation, for NiS and CoS preparations, showed only a few particles (see Fig. 3 for NiS), even though the darker color of the suspension indicated that a significant amount of particles have been formed. Since the detection limit of this technique is around 100 nm, it can be safely assumed that the particles have sizes of less than 100 nm, which would be in agreement with Wang et al. [15,16] observations. Some of the few particles that can be observed have the appearance of being agglomerates of smaller particles (Fig. 3), and the smaller ones have diameters between 200 and 300 nm.

For solids which were aged for 1 day a higher number of particles are observed (see Fig. 4 for CoMoS) and particle sizes are in the range of 300–1500 nm. As for NiS some of the bigger particles have the appearance of being aggregates of smaller size particles.

Table 1
Metal content for mono and bimetallic sulfides

Catalyst	Ageing time (weeks)	Mo (wt.%)	Co (wt.%)	Ni (wt.%)	M/(M + Mo)[a] (atomic)
CoS	1	–	47		1.00
Co-Mo-S	1	21	27		0.68
NiS	1	–		38	1.00
Ni-Mo-S	1	4		30	0.92

[a] M = Co or Ni.

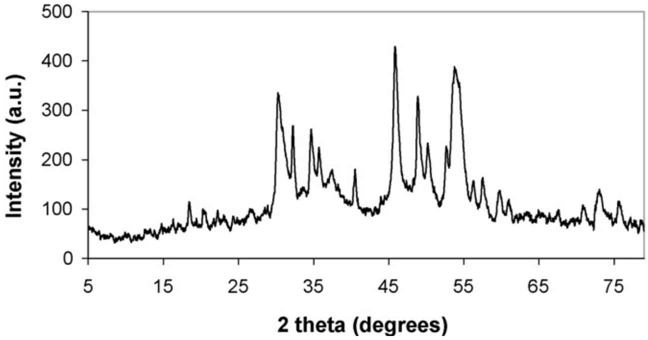

Fig. 1. X-ray diffraction pattern for NiS catalyst.

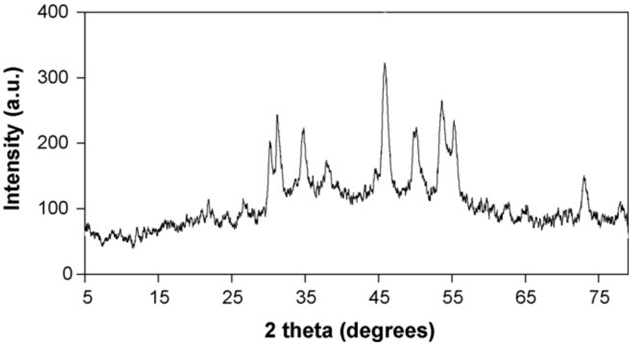

Fig. 2. X-ray diffraction patterns for NiMoS catalyst.

For CoMoS and NiMoS (Figs. 5 and 6, respectively) bigger and more numerous of particles are obtained, for the suspensions just after ultrasonic irradiation. Particularly, for NiMoS (Fig. 6) particles are very homogeneous and with sizes between 250 and 500 nm, even though some of them looked like aggregates.

Besides, Mo seems to have an important influence in the particles size, since for NiMoS and CoMoS a higher number of particles, larger in size, than for NiS and CoS, are obtained just after ultrasonication (compare Figs. 5 and 6 to Fig. 3).

Table 2 shows thiophene and benzothiophene HDS activities, for solids which have been aged for different periods of time. Also, for the sake of comparison, the activity for Mo sulfide prepared by a sonochemical method, and by thermal decomposition of ammonium tetrathiomolybdates (taken from Ref. [6]) have also been added to Table 2.

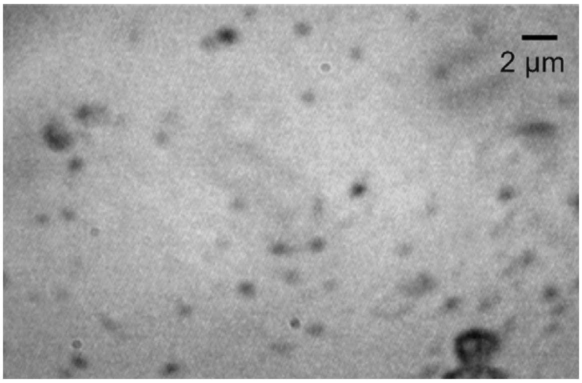

Fig. 3. Confocal image of suspension for NiS preparation, immediately after sonication.

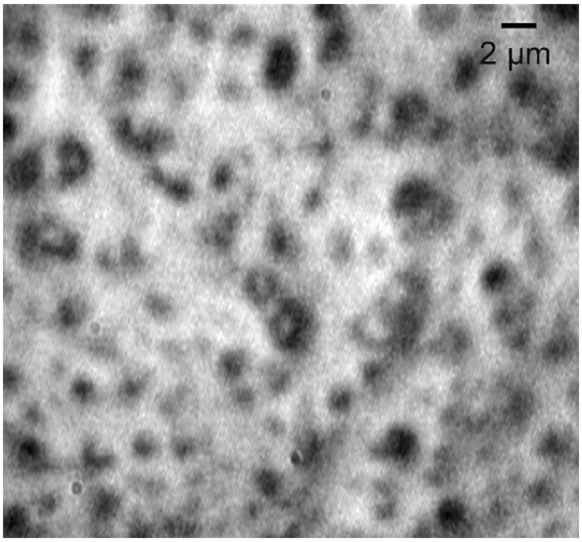

Fig. 4. Confocal image of suspension for CoS preparation, after 1 day of aging.

NiMoS and CoMoS catalyst are more active that their NiS and CoS counterparts for both reactions, which indicates that Mo is effectively coprecipitating with Co or Ni to form nanometric bimetallic sulfides with enhanced HDS activity. Since preparations with Mo alone did not yield any solid, there is no way to compare with a Mo sulfide catalyst prepared by a similar procedure, however, it is observed (Table 2) that when

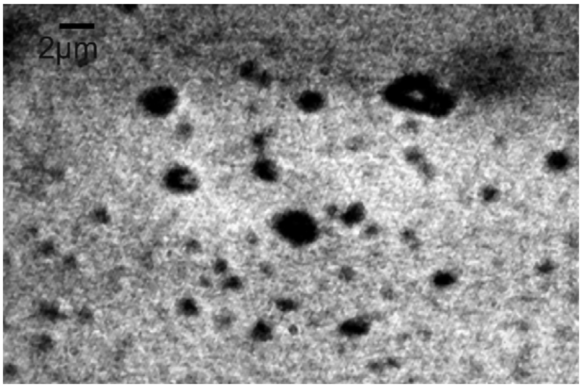

Fig. 5. Confocal image of suspension for CoMoS preparation, immediately after sonication.

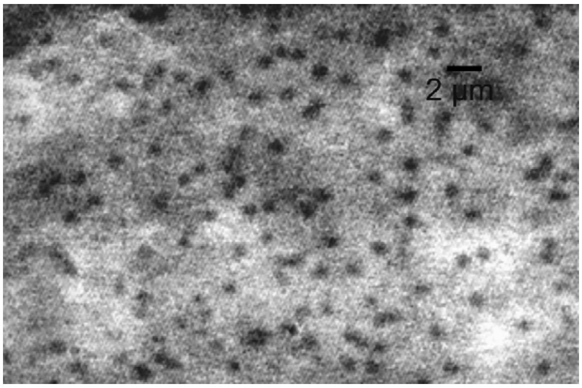

Fig. 6. Confocal image of suspension for NiMoS preparation, immediately after sonication.

Table 2
Thiophene and benzothiophene HDS, for sulfides aged for different periods of time

Catalyst	Activity (10^{-7} mol g^{-1} s^{-1})			
	Aging time (weeks)	Surface area (m^2 g^{-1})	Thiophene HDS	Benzothiophene HDS
CoS	1	4 ± 1	0.0	6.0
CoMoS	1	4 ± 1	6.4	18.8
NiS	1	4 ± 1	0.4	8.4
Ni-Mo-S	1	4 ± 1	1.9	19.4
NiMoS	4	–	14.4	–
MoS_2 sono[a]	–	4.7	4.13	–
MoS_2 ATTM[a]	–	67.7	4.25	–

[a] MoS_2 sono: prepared by a sonochemical method and MoS_2 ATTM: prepared by thermal decomposition of ammonium tetra thiomolybdate (from Ref. [6]).

compared to the activities for thiophene HDS reported in the literature [6] a promotion factor (activity of Mo promoted/ activity of unpromoted Mo) of 1.5 and 3.5, for CoMoS and NiMoS (aged for 4 weeks), respectively, is obtained, which is an indication that bimetallic sulfides were obtained.

Also, it is clear that ageing time has a drastic effect in the catalytic activity of bimetallic sulfides. Possibly, the initial Ni or Co sulfide particles formed during the ultrasonic irradiation serve as nucleation point for Mo, producing nanometric NiMo or CoMo mixed sulfides, provided the samples are aged for a period of time sufficiently large as to precipitate Mo together with Ni or Co.

For thiophene HDS CoMoS catalyst is more active than NiMoS (both aged for 1 week) which may be due to the smaller amount of Mo present in the NiMoS catalyst. However, for benzothiophene HDS both catalyst show similar activities.

Chianelli and Berhault [21], in their symmetrical synergism model, have proposed that Mo could also promote Co (or Ni) sulfide, so in this case we could be in the presence of such promotion of Ni by Mo, which is then more marked for benzothiophene than for thiophene HDS.

Fig. 7 shows the selectivity for NiMoS and CoMoS catalysts. Even though the conversions are different with both NiMoS and CoMoS catalysts (7 and 23%, respectively) they are low, and some general trends could be observed. Thus, CoMoS shows a higher production of *n*-butane than NiMoS, which may be due to the difference in composition between the two, which makes CoMoS catalysts more hydrogenating than NiMoS.

For the HDS of dibenzotiophene only ethyl benzene was obtained for both catalysts (NiMoS and CoMoS).

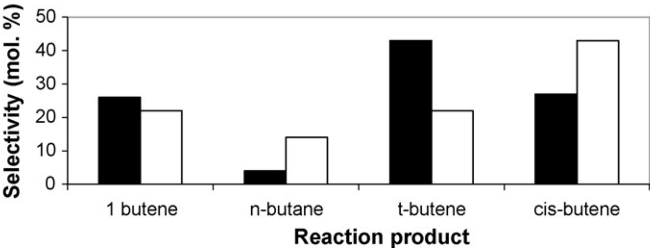

Fig. 7. Selectivity for thiophene HDS with NiMoS (■) and CoMoS (□).

In summary, all the results here shown suggest that ultrasonic irradiation of Ni or Co acetates, and ammonium heptamolybdate solutions (plus thioacetamide, polyvinylpyrrolidone and triethanolamine) leads to the formation of NiMoS and CoMoS nanometric particles with enhanced HDS activity.

4. Conclusions

The feasibility of the use of ultrasonic irradiation for the synthesis of nanometric NiMoS and CoMoS, have been shown. To the best of our knowledge nobody has reported the preparation of nanometric mixed sulfides to be used as hydrotreating catalysts. Thus, NiMo catalyst was 5 and 2.4 times more active than NiS, in thiophene and benzothiophene HDS, respectively, while CoMo was 6.4 and 3.2 more active than CoS for the same reactions. For thiophene HDS they were also more active than Mo sulfide. The high activity for bimetallic solids is due to the precipitation of a mixed sulfide in nanometric size particles.

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