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Nanometric bimetallic sulfides prepared via thermal decomposition of Ni and Fe heteropolymolybdate emulsions

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NiMo and FeMo nanometric particles were prepared by thermal decomposition of water in oil emulsions, where the aqueous phase was a solution of iron or nickel heteropolymolybdates. Decomposition experiments were carried out at 573 K and 70 Bar of hydrogen, with carbon disulfide added to the emulsions. Solids were characterized by X ray diffraction, confocal microscopy and BET surface area. Thiophene hydrodesulfurization was performed in a continuous flow microreactor at 553 K and 1.0 Bar. Particles with diameters between 370 and 560 nm were obtained, and thiophene HDS was in the order NiMoS > MoS ≈ FeMoS > NiS > FeS. The feasibility of using thermal decomposition of emulsions to obtain nanometric bimetallic sulfides particles was shown.

KEY WORDS: nanometric sulfides; HDS; thiophene; NiMoS; FeMoS.

1. Introduction

Due to actual and forthcoming stringent legislation concerning sulfur content in fuels [1] there is a strong incentive for much more active and selective hydrodesulfurization (HDS) catalysts. Also, as light crude oils reserves dwindle there is a need for processing and upgrading heavy an extra heavy crude oil and tar sands, which are found in vast abundance in different places, thus, for instance the heavy oil and tar sands bitumen in the Alberta Province of Canada and in the Orinoco Belt of Venezuela are each as large as the oil deposits in Saudi Arabia [2].

The use of unsupported catalysts, which could be used either dispersed on a heavy feedstock [3], or in the preparation of bulk metal catalyst for a conventional process, is considered to be a promising way to improve hydrotreatment (HDT) process efficiency [4]. Then, the preparation of nanoparticles of Mo sulfide has gathered great attention recently, and different methods have been reported for its synthesis [5–9]. 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 particles of several microns or higher in diameter [10–12]. Only Ye et al. [12] have synthesized $NiMoO_2S_2$ nanoparticles (≈ 13 nm), using a microemulsion systems, but they were intended to be used as lubricant additives.

In the present work the preparation of nanometric particles, from thermal decomposition of water (aqueous solution of heteropolymolybdates) in oil emulsions, and its used in thiophene HDS, has been explored.

2. Experimental

2.1. Heteropolycompounds preparation

Heteropolymolybdates (HPM) were prepared according to the method reported by Nomiya et al. [13], thus to a boiling aqueous solution of ammonium heptamolybdate (5 g. dissolved in 80 cm^3 of water), a solution of iron or nickel sulfate ($3.1\ 10^3$ mol in 20 cm^3) was added. The resulting solution was further heated, evaporated, and filtered while hot. Finally, the solution was cooled down and the crystal formed separated by filtration. Obtained crystals were characterized by IR spectroscopy and the spectra were similar to those reported in the literature for this compounds [13].

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2.2. Emulsions preparation and thermal decomposition

Water in oil (w/o) emulsions were prepared by adding a surfactant mixture (20% tween 80, 75% span 80 and 5% hexanol) to decahydronaphtalene (1:10 by weight) and the resulting solution was stirred using a Rushton turbine for 5 min. To this organic solution an aqueous solution of the corresponding HPM (ammonium heptamolybdate, or nickel or iron nitrate for monometallic solids) was added and then further stirred (the quantities used are reported in table 1). To the emulsions thus obtained carbon disulfide was added, followed by thermal decomposition in a 300 cm^3 Parr autoclave at 573 K and 70 bar of H_2. A small portion (about 5 cm^3) of the solids suspended in the liquid product was separated for confocal microscopy analysis. Finally the solids were recovered by centrifugation and washed with toluene.

2.3. Catalysts characterization

X-ray diffraction (XRD) patterns were obtained on a Phillips PW1840 diffractometer, equipped with a Cr anode (Cr$k\alpha$). All samples were exposed to air for this analysis.

Surface area determinations (BET method, nitrogen adsorption) were carried out, on the air-exposed samples, in a Flow Sorb II 2300 Micromeritics device. All samples were outgassed at 473 K for 90 min.

Microscopic images of the suspensions of the solids after thermal decomposition of the emulsions were obtained with a laboratory designed confocal microscope [14]. The light source consisted of a tungsten lamp. The samples were observed with a 40 × objective (10000 × magnifications). The microscope is equipped with a charged couple device (CCD) camera (640 × 480 pixels). Reflected light can be directed to the CCD camera in order to acquire total image, an aperture placed before the CCD produces the confocal effect and permits to obtain an image with enhance spatial resolution of less than 300 nm (≈ 100 nm).

2.4. Catalytic activity

A continuous flow microreactor, working at atmospheric pressure, was used for catalytic determinations. Reactions were performed using a liquid feed composed of 10% (v/v) of thiophene in n-heptane (2.7 10^{-4} cm^3 s^{-1}), and H_2 (0.25 cm^3 s^{-1}), at 553 K. The system was covered with a heating mantle (423 K) in order to avoid any condensation of the reaction products. Catalysts were used without presulfiding. Reaction products were injected to a Perkin-Elmer (AutoSystem XL) gas chromatograph equipped with a flame ionization detector. Only *n*-butane, 1-butene, cis-2-butene and trans-2-butene were detected as reaction products. Reported steady state activity and conversion are the result of three consecutive measurements within 1% variation.

Table 1
Molar quantities of metals in the aqueous solution used in emulsions preparations

Compound	Mo (mmol)	*M (mmol)	Total (mmol)
$(NH_4)_3[NiMo_6O_{24}]7H_2O$	6.4	1,1	7,5
$(NH_4)_3[FeMo_6O_{24}]7H_2O$	6.4	1,1	7,5
$(NH_4)_6[Mo_7O_{24}]7H_2O$	7.5	–	7,5
$Ni(NO_3)_2\ 6H_2O$	–	7,5	7,5
$Fe(NO_3)_3\ 9H_2O$	–	7,5	7,5

*M = Nickel or Iron.

3. Results and discussion

XRD results show that all solids present poorly crystallized structures. For NiS and MoS samples the XRD patterns can be assigned to Ni_9S_8 and MoS_2 respectively. The diffractograms for NiMoS and FeS did not show any peak at all; while the diffraction pattern for FeMoS was similar to that of MoS (i.e. only peaks that could be assigned to MoS_2 were obtained). Even though, diffractograms were obtained for air exposed samples, no peaks for metal oxides were observed.

This results show that the decomposition of the emulsions in presence of hydrogen and carbon disulfide (which decomposes to produce hydrogen sulfide) is an effective method for obtaining the corresponding metallic sulfides, since only peaks due to sulfide structures were obtained.

The fact that no peaks that could be assigned to any form of iron sulfide, and in particular to pyrrhothite ($Fe_{1-x}S$) which is usually found in homogeneous precipitation of iron sulfides [15–19], were obtained for the FeMoS sample, seem to indicate that, either iron sulfide particles are to small to diffract X rays, or iron is in interaction with molybdenum in the MoS like phase. Confocal microscopy results seem to favor the latter explanation.

BET surface areas determined for all solids were very small (3–10 m^2 g^{-1}) and in the order of bulk precipitated sulfides [15–20].

Figure 1 shows selected confocal pictures for the suspensions obtained after thermal decomposition of the emulsions. In all of them some agglomeration of the particles is observed. However, in spite of the relatively high temperature used in the decomposition of the emulsions (573 K) particles are very homogeneous and small in size (see table 2). All solids present particle sizes of the same order (400–600 nm), except for FeS which gave particles with little higher diameters.

After centrifugation, separation from the liquid, washing and HDS reactions, particles agglomerate considerably, as observed in figure 2, giving apparent larger particle size (table 2).

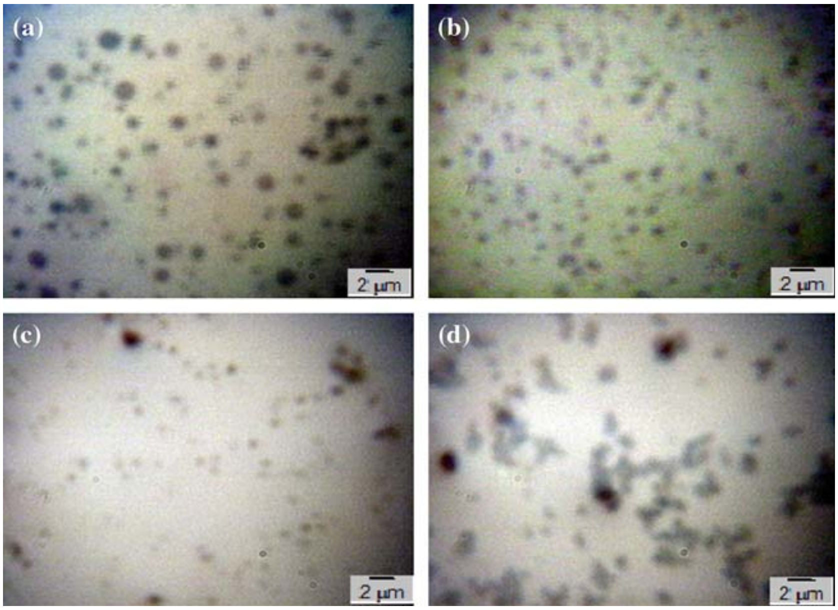

Figure 1. Confocal images of suspensions for: a) FeS; b) FeMoS; c) MoS; and d) NiMoS.

Table 3 shows HDS conversion, catalytic activity and product distribution for the different solids. HDS activity for conversion of thiophene is higher for NiMoS than for MoS or NiS. This effect can not be attributed to differences in particle size since they are of the same order (in fact NiMoS particles are a bit larger than that of MoS particles). The enhanced activity is then due to the formation of nanometric particles of a mixed NiMoS phase.

To the best of our knowledge nobody has reported the preparation of nanometric mixed sulfides to be used as HDT catalysts. Thus, Ye et al. [12] have synthesized $NiMoO_2S_2$ nanoparticles ($\approx$ 13 nm) using a microemulsion systems, and tested them as lubricant additives, Genuit et al. [11] have reported one-step preparation, and HDS activity, of NiMo sulfide using surfactants, but the sulfide particles seem to have sizes of the order of a few microns. The preparation of unsupported Ni(Co)MoW [10] by ex situ decomposition of alkylthiomolybdotungstates have also been reported, but particle sizes are well over 1 μm.

The fact that FeMoS catalyst shows similar activity to that of MoS catalyst, suggests that Fe is not promoting Mo. However, product distribution for FeMoS and MoS are different (table 3), which may be an indication that iron is indeed interacting with molybdenum but the

Table 2
Particle size for sulfides prepared by thermal decomposition of emulsions, determined from confocal images

Catalyst	Average Particle Diameter (nm)/Standard deviation in parenthesis.	
	Before HDS	After HDS
NiMoS	483 (173)	5415 (4679)
MoS	587 (287)	
FeMoS	371(103)	3027 (1818)
NiS	558 (224)	5091 (3560)
FeS	865 (554)	

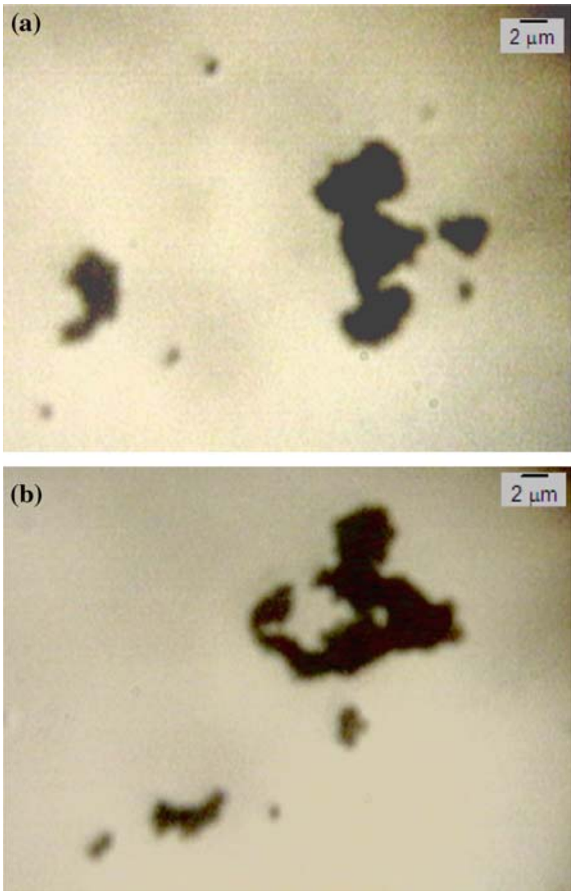

Figure 2. Confocal images of solid catalysts after HDS reactions: a) NiMoS; and b) MoS.

Table 3
Thiophene HDS conversion, activity and selectivity

Catalyst	Conversion (%)	Activity (10^{-5}mol g^{-1} s^{-1})	Selectivity (mol. %)			
			1-butene	*n*-butane	Trans-2-butene	Cis-2-butene
NiMoS	17.9	2.22	19.0	16.9	39.4	24.7
MoS	17.0	1.49	21.1	29.3	24.5	25.2
FeMoS	16.0	1.47	24.2	10.0	40.0	25.8
NiS	5.5	0.53	11.1	37.0	38.4	13.0
FeS	5.0	0.35	33.0	13.2	32.5	21.3

amount of Fe is not enough to induce an appreciable activity increase. The M/(M + Mo) atomic ratio (M = nickel or iron) for bimetallic solids is limited by the HPM stoichiometry and is equal to 0.14. This ratio is below the one usually reported for catalysts with a maximum activity in HDS (see for example references 19, 21–23), which is in the range of 0.25–0.50. Then NiMo and FeMo nanometric bimetallic sulfides were obtained but the increase in activity, in relation to the monometallic parent sulfides, is small (null for FeMo) due to the low M/(M + Mo) atomic ratio. We are currently working on ways to increase this atomic ratio.

4. Conclusions

In conclusion, it has been demonstrated that it is possible to prepare nanometric bimetallic FeMo and NiMo sulfides with enhanced catalytic properties, by thermal decomposition of w/o emulsions at high hydrogen pressure and temperatures (were the aqueous phase is a solution of Fe or Ni heteropolymolybdates) and in the presence of carbon disulfide. Using this procedure, particles of Mo, Ni, Fe, NiMo and FeMo sulfides, with diameters in the order of 370 to 560 nm, were obtained. To the best of our knowledge nobody has reported the preparation of nanometric bimetallic sulfides to be used as hydrotreating catalysts.

Acknowledgments

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