Preparation of NiMoS nanoparticles for hydrotreating

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ABSTRACT

NiMo sulfide nanoparticles were prepared by precipitation using water in oil (w/o) microemulsions, and were characterized by X-ray diffraction (XRD), Dynamic Light Scattering (DLS), X Ray Photoelectron Spectroscopy (XPS) and nitrogen adsorption (BET). They were also tested in the HDS of vacuum gas oil (VGO). Nanoparticles of 3-5 nm which produced 50% HDS conversion of a Vacuum Gas Oil (VGO), as well as an enhanced HDN activity (when compared to a NiMo/Al_2O_3 catalyst), were obtained. After sulfidation of the solids the Ni, at the surface, is mainly decorating the edges of the MoS_2 slabs (90 at.%), however, an important proportion of the Ni segregates out of this position during the reaction (39%).

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1. Introduction

Due to metal sulfides and coke deposition in the support's pore mouth the use of supported catalysts for the hydroprocessing of heavy oils and heavy oil fractions is limited. The development of supports with high proportion of macropores partly solves this problem [1–3], however, even when macroporous supports are used these catalysts have a short life span, which varies depending on the characteristics of the feed.

The use of unsupported catalysts which could be used dispersed on a heavy feedstock (also called ultra-dispersed catalysts, UDC) is considered to be a promising way to improve the catalytic hydrotreating of heavy feedstocks [4]. When using a bulk metallic catalyst there is not support and only the active phase is present, then, instead of the reacting molecules going to the site where the active phase is located (mostly inside the pores for supported catalysts), the active site goes where the reacting molecules (hydrogen and hydrocarbons) are. In order to increase the efficiency of the catalytic particles during the reaction they have to be as small as possible, and nanoparticles (i.e. diameter <100 nm) are preferred.

The use of very small bulk particles presents several advantages:

- High surface areas (the smaller the particles, the higher the external surface area).
- Deactivation problems are greatly reduced.
- Diffusional problems are avoided or totally reduced.
- High density of particles per unit volume of feed to be treated and lower inter-particle distances that increases the probability of active phase interacting with the reactants.
- Less settling tendency [5–7].

Normally, Mo promoted by Co or Ni is the catalyst used for these applications. Several works have been published on the preparation of MoS_2 nanoparticles, however, there are few reports in the literature concerning the preparation of NiMo or CoMo nanometric sulfides. Thus, Ye et al. [8] synthesized $NiMoO_2S_2$ nanoparticles (13 nm) using a microemulsion system, and the particles were tested as lubricant. FeMo and NiMo sulfide particles (400–600 nm and 30–100 nm) have been prepared [9,10] by thermal decomposition of emulsions, and tested in HDS of Thiophene or Vacuum Gas Oil. Also, using ultrasonic irradiation, NiMo and CoMo sulfide particles (250-500 nm) were synthesized and tested in the HDS of Thiophene and Benzothiophene [11]. Trikalitis et al. [12] prepared CoMoS and NiMoS type spherical particles ($\approx$ 150-200 nm) by reacting $MoS_4{}^{2-}$ with Ni^{2+} or Co^{2+} in formamide in the presence of alkyl-pyridinium surfactant molecules, however, no catalytic

activity for these particles was reported. More recently, Chenguang et al. [13] reported the preparation of oil soluble NiMoS nanoparticles by surfactant assisted solvothermal method. Nanoparticles ($\approx$7.6 nm average particle diameter) with high naphthalene hydrogenation activity were obtained.

In the present work NiMo sulfide nanoparticles were prepared by a very simple methodology, consisting of precipitation of the sulfide using water in oil (w/o) microemulsions. The particles thus obtained were characterized by X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS), X Ray Photoelectron Spectroscopy (XPS) and nitrogen adsorption (BET surface area). Their catalytic activity for the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) of a vacuum gas oil (VGO), was also tested.

2. Experimental

Catalyst preparation: 4 cm^3 of ammonium sulfide (40–48 wt.%) were added to a solution of ammonium heptamolybdate hydrate (0.9180 g in 4 cm^3 of water) and the resulting mixture was aged for 5 h. Then, 5 g of sodium sulfosuccinate (AOT) were dissolved in 85 g of deca hydronaphtalene (DHN) at 313 K, with stirring. An emulsion was formed by adding, drop-wise, the Mo solution to the DHN-surfactant one (maintained at 313 K) with vigorous stirring. The obtained Mo-DHN emulsion was allowed to stand for 15 min and then a nickel nitrate hydrate solution containing 0.664 g of nickel nitrate in 2 cm^3 of water, was added. The initially orange-red emulsion immediately turned black. The resulting mixture was heated to 338–343 K for 2 h and finally heated under reflux at 439-443 K for a further 6 h. Particles were separate by centrifugation (6000 rpm for 30 min), washed several times with toluene and vacuum dried at 353 K overnight (NiMoS-BS). The method for precipitating the NiMoS solids resembles the "Homogeneous Sulfide Precipitation" (HSP) previously reported [14].

Particle Characterization: The size of the particles was determined by Dynamic Light Scattering (DLS) using a Zetasizer Nano S (Malvern Instruments) equipped with a 4.0 mW He–Ne laser (633 nm) and operated at an angle of 173° and a temperature of 298 K to obtain the average diameter (Z-Ave). The particles were suspended in a base lubricant oil by adding a suspension of the prepared particles in toluene to the base oil in such a proportion as to have approximately 1 × 10^{-3} g/l, and then treating it in a laboratory ultrasonic bath for 1 h.

XRD patterns were obtained with a Rigaku X-ray diffractometer with a scanning speed of 0.8°/min and a step size of 0.02° (2 theta) with Cu Kα radiation and 40 KV. The XRD patterns were referenced to the powder diffraction files (International Centre for Powder Diffraction PDF 2005) using the pattern processing analysis software JADE from Materials Data Inc.

A PHI VersaProbe 5000-XPS was used to record XPS spectra. The spectra were taken on samples pressed on double sided tape, using monochromatic Al source, 1486.6 eV, with a 49.3 W of power and beam diameter of 200.0 μm. A double neutralization, i.e., a low energy electron beam and low energy Ar$^+$ beam, were used during spectrum recording to avoid non-uniform charging. Binding energies relative to C1S at 284.8 eV, are reported. Data analysis was performed using MultiPak software developed by Physical Electronics and provided with the XPS instrument.

Surface areas were determined by N$_2$ adsorption at 77 K in a Micromeritics TriStar apparatus. Prior to the adsorption measurements, the samples were out gassed overnight at 423 K. Nitrogen isotherms were obtained in both adsorption and desorption modes. The surface areas were determined by the BET method.

Catalytic Activity: Even though the type of catalsts produced in this work is intended for treatment of heavy feedstocks (like heavy oil, bitumen and vacuum residue) were the solids are dispersed in the heavy hydrocarbon, hydrotreating of a VGO was used as catalytic test since this type of feed is easier to analyze. The particles produced were first sulfide in a 100 cm^3 batch Parr reactor using a solution of carbon disulfide (CS$_2$) in decahydronaphthalene (20 vol% of CS$_2$) at 523 K for 6 h, under 500 psi of hydrogen. The sulfide solid was washed with toluene, separated by centrifugation and dried in vacuum at 353 K overnight (NiMoS-S). VGO HDS was then performed in the same reactor under 800 psi of hydrogen at 653 K during 6 h. The reactor was first loaded with the VGO ($\approx$20,000 g) and then $\approx$0.200 g of catalysts (NiMoS-S) were added. The reactor was tested for leaks and purge with hydrogen, before heating was started at 20 K min^{-1} and the stirring set at 500 rpm. Hydrogen inlet was kept open during the test in order to avoid pressure dropping due to hydrogen consumption. Once the reaction time was completed, the reactor was cooled down, opened, and the liquid products were separated from the catalysts by centrifugation (NiMoS-AR). The amount of liquid recovered represented 95.7% of the original VGO, the difference being attributed to the liquid that remained attached to the reactor walls (due to the viscosity of the products) and gases formed, which could not be determined since the hydrogen inlet was kept opened during the experiment. Characterization of the hydrotreated VGO was performed using high temperature simulated distillation (HTSD) and the sulfur and nitrogen content, of the original VGO and reaction products, were determined on an Antek 9000 NS elemental analyzer.

3. Results and discussion

XRD patterns for the as prepared (BS), sulfided (S) and after reaction (AR) solids are shown in Fig. 1.

For the particles before sulfidation, very broad lines characteristic of amorphous materials, together with some crystalline phase(s), are observed. For the sulfided (S) and after reaction (AR) samples, very broad lines due to MoS$_2$ are obtained. The (0 0 2) basal plane peak for MoS$_2$, observed in the sulfided and after reactions samples, shows very low intensity indicating low stacking and highly disordered packing of the MoS$_2$ slabs. Other broad peaks at higher angle (2θ > 30°), also characteristic of MoS$_2$ are also seen. Sharper peaks that can be assigned to Ni sulfide (hexagonal NiS PDF file # 01-075-0612) can be seen as well. Similar diffraction signals are obtained for the sample after reaction (AR) along with additional peaks that can be assigned to and orthorhombic Ni$_9$S$_8$
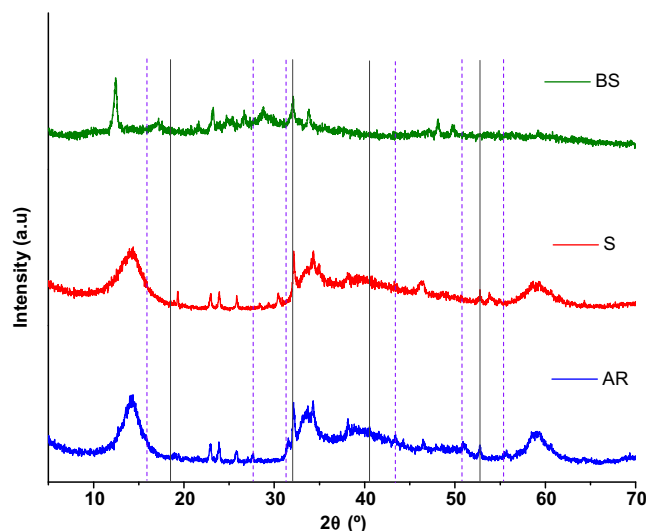

Fig. 1. XR diffractograms of the NiMoS solids: BS as prepared; S; sulfided; AR: after reaction. — Hexagonal NiS; - - - ortho Ni$_9$S$_8$.