IMPROVED MOLIBDENUM SULPHIDE NANODISPERSED CATALYST FOR HYDRO PROCESSING, PREPARED VIA MICROEMULSIONS

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Introduction

Due to environmental restrictions as well as to limitations of performance of traditional fixed bed catalysts for hydro processing extra heavy feedstocks, the generation of micro-nano size catalyst particles within the feed at conditions close to the ones available in the reaction zone is an important alternative. It has allowed the proposition of a set of many different new processes that could be considered the third generation hydro processing of residues and bitumen.

Oil soluble compounds of those transition metals catalytically active for hydro processing yield very good results [1] but their preparation is expensive. Most of the inorganic forms of these transition metals are much less expensive, for instance, ammonium heptamolibdate is perhaps the least expensive form of Mo with the highest metal proportion within the salt. Nevertheless its insolubility in the reaction media prevents from obtaining a good dispersion of the metal, which makes necessary to incorporate significant amounts of the compound to get sufficient catalysis.

Traditionally more considered for heavy crude oils transporting [2] the use of emulsions and micro emulsions are an alternative way of incorporating well dispersed catalysts for heavy feedstocks hydro processing. In this paper the preparation of micro/nano dispersed Mo particles by thermal decomposition of ammonium heptamolibdate emulsions was studied. The effects of nature and quantity of pre-sulphuring agents dissolved in the emulsion as well as the effect of surfactant were some of the variables determined by using a Design of Experiment method.

Experimental

Emulsions preparation

1-metilnaphtalene (1-MN), an oil lubricant base and a Light Vacuum Gas oil were all used as different oil basis for the preparation of the emulsions. The aqueous phase was prepared containing ammonium heptamolibdate (7.5% Mo) with or without ammonium sulphide at two different concentrations (3 and 10%). Also different percentages of surfactant were used from 1 to 10%.

Thermal decomposition of the emulsions

The emulsions were decomposed in two different reactor set-ups, an autoclave reactor and a continuous reactor, in a temperature range between 200 and 300C at either atmospheric pressure or at 1000 psig., In the case of using autoclave a mechanical stirring was set at 300 rpm. In the autoclave the emulsion was entered into the reactor once the temperature and pressure conditions were reached. After 5 minutes, the thermally decomposed solid is recovered by centrifuging, washing several times with toluene and dried at 125C during 4 hours.

Solids Characterization

X Ray Photoelectron spectroscopy (XPS)

A Leybold-Heraeus equipment model LH-11 was used. The radiation was provided with an Al anode (1486.6 eV) and a power of 350 watts. Pass energy at 50 eV. The C_{1s} line (284.6 eV) was used as reference for calibration of Binding Energies (BE) for the different elements as well as for charge effects correction.

X Ray Diffraction (XRD)

A diffractometer DRX Philips model PW3710 at powder was used, employing a graphite monochromator. An APD program from Phillips was used for detection and recording. A scintillate detector was used. Continuous scan of the diffraction angles was performed from 5.00 until 75.69° (2θ). A Cu anode Kα1 emission line was used.

Surface area

The samples were pretreated in a degasifier VacPrep 061 from Micromeritics at 120°C, desorbed under vacuum (1×10^{-4} torr) for 2 hours. Specific surface area is determined by adsorption-desorption of nitrógeno following the standard BET method. The microporous volume was determined with the t method, the pore radii distribution by the method of Roberts with the cylinder pores model. Additionally a pore distribution was performed on some solids using the BJH method (Barret, Joyner, Hallenda).

Results and Discussion

In figure 1 are shown the XRD analysis of some solids prepared by thermal decomposition of the emulsions prepared using 1-Methyl Naphthalene as the oil phase. It can be observed that these solids are poorly crystallized showing a pattern of amorphous Molybdenum Disulfide. The main reflections observed are the ones corresponding to the faces 002, 100, 103 and 110. Nevertheless, differences are perceived regarding the intensities of the reflections in particular that of the face 002.

Based on the intensities of the face 002, the solids obtained from the decomposition of emulsions containing 3% ammonium sulphide were the ones showing higher piling. It seems that the use of a higher proportion of ammonium sulphide decreases the piling. In addition, the use of higher proportions of surfactant also resulted in reduced ray intensities particularly in the phase 002. Apparently a lower drop size in the emulsion conduces to a lower extent of crystals growing and to a higher disorder of lamellas when the progression is done from macro emulsions (1% surfactant) toward micro emulsions(10%).

In figure 2, are shown the XPS spectra obtained for the solids prepared via flashing and decomposition of the emulsions. The signal centred at 226.3 eV is assigned to the binding energy of the sulphur 2s orbital. As observed each spectrum is the result of the overlapping of signals corresponding to the principal oxidation states of Mo, which are centred at 229.1 and 232.3 eV, representing the doublets 3d, $3d_{5/2}$ and $3d_{3/2}$. These results suggest that Mo is mostly present under the oxidation state +4, even though the intensities do not correspond with the existence of a unique oxidation state.

In table 1 the BET areas of some of the solids obtained and their corresponding catalytic activity for the hydrodesulphurisation of Thiophene are presented. The solids prepared with the higher proportion of surfactant, which implies lower drop size (micro emulsions) present higher surface area as well as much higher catalytic activity for the desulphurisation of Thiophene.

The results presented were very similar to the ones obtained by preparation of the ultra dispersed solids in a continuous decomposition set-up, in which the conditions were implemented to produce nano particles of both Mo oxide as well as Mo Sulphide.

This second solid was also obtained by incorporating to the aqueous Mo solution different proportions of ammonium sulphide. Thus the pre-sulphuring at an early emulsion preparation stage eliminates the need for addition of pre-sulphuring agents as required when Mo oxide is first obtained.

Reduced nano particle size, increased disordered lamellar nano particles and consequently enhanced catalytic activity were obtained by this continuous method which simulates at lab scale a real on line incorporation of the catalyst occurring in a slurry type hydro conversion processing of hydrocarbon residues.

Conclusions

Nano particles of Mo oxide and Mo sulphide were produced via thermal decomposition of emulsions and micro emulsions containing Mo Heptamolibdate in the aqueous phase by using both a batch and a continuous reaction set-up. The solids obtained presented differences in the pre-sulphuring level due to the proportions of ammonium sulphide incorporated to the aqueous solutions. The solid produced from micro emulsions, prepared with increased amounts of surfactants were found the more dispersed and active toward the Thiophene HDS reaction test. No significant differences were found for the two different preparation set-ups employed.

References

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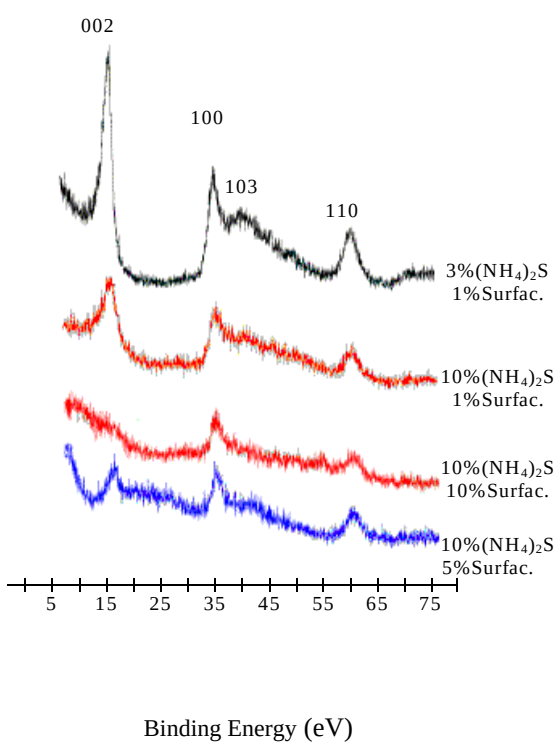

Figure 1. Diffractograms of different solids prepared

Table 1. BET Area and Catalytic Activity

Sample	Area (m^2/g.)	Rel.Activity
3%$(NH_4)_2S$/1%Surf.	3	1
10%$(NH_4)_2S$/1%Surf.	5	4
10%$(NH_4)_2S$/5%Surf.	10	49
10%$(NH_4)_2S$/10%Surf.	38	54

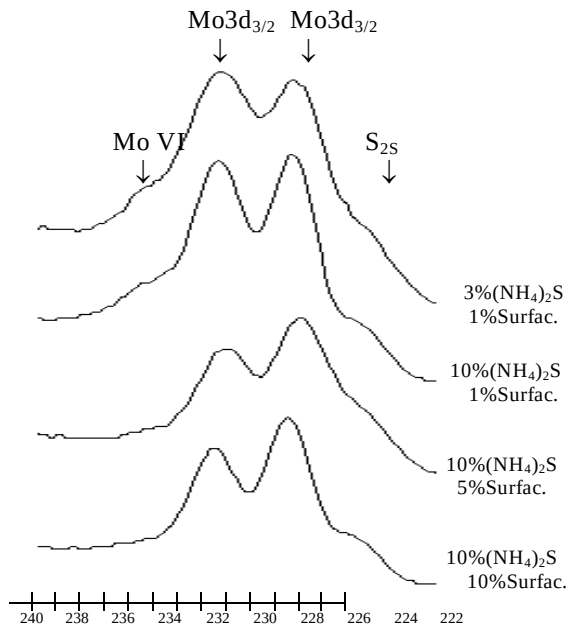

Figure 2. XPS spectra of the different solids.