



# Catalytic hydrotreatment in reverse microemulsions under microwave irradiation



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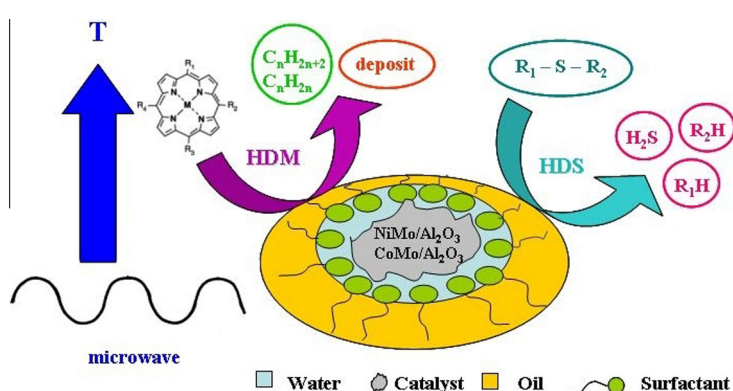
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## HIGHLIGHTS

- The catalytic hydrotreatment is much more effective under microwave radiation.
- The HDS and HDM on the model compounds were highly efficient.
- The synthesized catalysts were highly effective in developing the process.
- The heavy oil microemulsion allows establishing the catalytic reaction mechanisms.
- The Perovskite-like arrangement in microemulsion facilitates the hydrotreatment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 23 January 2013

Received in revised form 30 April 2013

Accepted 2 May 2013

Available online 2 June 2013

### Keywords:

Hydrodemetallization

Hydrodesulfurization

Reverse microemulsion

Microwave irradiation

NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>

## ABSTRACT

This report describes a hydrocatalytic process developed in a reverse microemulsion using microwave irradiation. The catalysts used, CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>, were synthesized in the laboratory. The effectiveness of the procedure was tested with model compounds such as nickel (II) phthalocyanine tetrasulfonate tetrasodium salt (NiPcTSNa<sub>4</sub>), nickel tetraphenylporphyrin (NiTPP) and thiophene. The first two model compounds were demetallized to a percentage around 85% and 60% respectively, while desulfurization of the latter was greater than 90%. These values are higher than most of the values reported in the literature for this type of process. We also applied this catalytic hydrotreating to a real sample, Venezuelan heavy oil (Hamaca), achieving high conversion in a relatively short time. In this case, the hydrodesulfurization was above 59%, while the hydrodemetallization of organic compounds containing nickel and vanadium was greater than 35% and 47%, respectively. The results demonstrate the advantage of using this type of hydrotreating in less extreme conditions and in a shorter time than that used in other hydrocatalytic procedures.

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## 1. Introduction

Catalytic hydroprocessing is a commonly used method for treating oil residues. The catalysts used for hydroprocessing

usually consist of molybdenum or tungsten accompanied by promoters such as nickel or cobalt supported on alumina [1]. The catalysts promote elimination of undesirable heteroatoms such as sulfur, nitrogen and metals. Removal of such elements from crude oil is called hydrodesulphurization (HDS), hydrodenitrogenation (HDN) and hydrodemetallization (HDM), respectively. However, such catalysts tend to deactivate rapidly due to residual coke and metals generated in the process (in crude oil mostly V and Ni), which are deposited on the catalytic surface poisoning

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their active sites [1,2]. Water present in the medium may also ruin the catalysts. The negative effect of water on catalyst is avoided when an appropriate surfactant stabilizes the micelles where such water is confined. However, when the amount of water is small the catalyst activity may even improve. Additionally, such amount of water is an in situ source of  $H_2$ , which facilitates hydrogenation [3] and form suspensions that often decrease viscosity. This is convenient when dealing with high-viscosity oils.

Catalyst pore size is a basic parameter in catalytic hydrotreatment [4,5]. The addition of  $TiO_2$  to the alumina support promotes a structural change that improves catalytic activity. However, the usual method of incorporating the oxide typically has the effect of decreasing pore size, which favors hydrodesulfurization (HDS) but prevent hydrodemetallization (HDM). The latter requires a larger pore size to ensure a high catalytic activity [4,5]. The kind of synthetic process developed to produce the catalyst is very important because it determines their textural properties (specific area, pore volume and average pore diameter). Synthesis and catalytic activity of those materials remains a very active research area [4,5]. When  $SiO_2$  is incorporated into the catalyst support, the textural properties and acidity of the catalyst changes [2]. The results obtained using the modified support indicated that HDS of crude oil is related to the number of active metal sites present in the catalyst. However, HDM presented a complex behavior, indicating that the process is affected by the dispersion of the sulfide phase and by the porosity and acidity of the catalyst [2].

HDS and HDM are necessary to refine crude oil. Venezuelan crude oils are characterized by high concentrations of sulfur and metals, especially nickel and vanadium, as well as asphaltene and resins [6,7]. The techniques for demetallization and desulfurization of crude oil are still under investigation. Some of the methods used to remove sulfur compounds are reactive adsorption (based on a metal oxide catalyst that incorporates sulphide), adsorption on charcoal or alumina (a non-destructive physical procedure), alkylation and polymerization (to alter the boiling point of the compounds), precipitation of salts from a matrix and electrochemical methods [8,9]. Porphyrins are usually removed through catalytic hydroprocessing at high temperatures and high pressures of gaseous hydrogen [10–12]. On the other hand, phthalocyanines, important constituents in effluents of the textile industry, are removed with methods such as adsorption on activated carbon, ultra-filtration, reverse osmosis, chlorination, biodegradation, ozonation and photo- and/or electro-catalysis [13–16].

Even though, highly active catalysts are in use nowadays, the researchers are paying increasing attention towards heavy oil hydroprocessing. The catalysts used to treat heavy oils are entirely different. Ultra-deep HDS and HDM catalysts has become the focus of a large number of studies. The researchers are looking for the right formulation as well as the best processing designing [17,18]. Homogeneous precipitation is a common route to prepare catalysts, alumina support prepared by urea hydrolysis gives a better pore size distribution and higher pore volume, which is convenient to produce a better metal deposition and diffusion of metalloporphyrins [19].

Some techniques, such as, acidic or basic leaching from the ashes of coke, hydrotreatment with catalysts present, hydrotreating in non-equilibrium plasma, ultrasound and hydrotreating under microwave irradiation without catalysts, are time consuming and require drastic operating conditions [6,7]. The asphaltenes and resins are heavier petroleum fractions, which are responsible for serious problems in the oil production (they generate organic deposits that adhere to the wells and the storage and transport containers, etc.). Asphaltenes limit the efficiency of hydroprocessing causing increased production of coke and a more rapid deactivation of the catalysts [14]. Soluble oil amphiphilic (surfactants) provided the most practical and economical solution to treat such deposits or to prevent them from forming. Natural organic acids

(linoleic, palmitic and caprylic) and dodecylbenzenesulfonic acid are the most effective, which confirms the importance of acid-base interactions to develop those kinds of processes [22]. Depending on the ratio between surfactant and water, various conformations of microemulsion or micelle solutions are obtained.

Microwave energy is an irradiation source that favors the generation of chemical reactions. Therefore, microwave irradiation can also be applied to catalytic hydrotreatment since it requires, besides the presence of hydrogen, a sufficiently high temperature that microwave energy may provide [6–13]. This kind of irradiation has been proposed for hydrodesulfurization of thiophene and hydrodemetallization of porphyrins, which are compounds usually present in heavy oil [6–10].

The issues discussed so far address the proposal of development catalytic hydrotreatment involving both microwave energy and microemulsion, hoping to improve the hydrotreatment conditions because of the combined advantages involved. Therefore, in this study, we used microwave irradiation to increase the temperature of reverse microemulsions prepared with different surfactants. These microemulsions are formed by micelle suspensions of water nanodrops in a continuous oil phase. Such arrangement allows the contact among the catalyst, the in situ hydrogen-generating substance and the selected organometal or organosulfur, which is going to be transformed. The catalysts used to develop the experiments were synthesized by homogeneous precipitation ( $NiMo/Al_2O_3$  and  $CoMo/Al_2O_3$ ). The cosurfactant, used to stabilize the microemulsion, 1-pentanol, was also an additional source of hydrogen required in the hydrotreatment. The compounds selected to develop the hydrocatalytic procedure were nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt, nickel tetraphenyl porphyrin and thiophene. According to the high efficiency obtained for the demetallization and desulfurization of the model compounds, the method described was applied to transform samples of heavy oil, producing high levels of demetallization and desulfurization.

## 2. Experimental

### 2.1. Reagents

Sodium dodecyl sulfate (SDS,  $C_{12}H_{25}NaO_4S$ , 99%), sodium dodecyl benzene sulfonate (SDBS,  $C_{18}H_{29}NaO_3S$ , 99%), cobalt nitrate hexahydrated ( $Co(NO_3)_2 \cdot 6H_2O$ , 99%) and aluminum nitrate nonahydrated ( $Al(NO_3)_3 \cdot 9H_2O$ , 99%) were purchased from Riedel-de Haën. Nickel nitrate hexahydrated ( $Ni(NO_3)_2 \cdot 6H_2O$ , 99%), molybdcic acid ( $MoO_4H_2$ , 99%) and urea ( $CO(NH_2)_2$ , 99%) from Fisher Scientific. 1-pentanol ( $C_5H_{12}O$ , 99%), tetrasodium salt of nickel (II) phthalocyanine tetrasulfonate acid ( $NiPcTSNa_4$ ,  $C_{32}H_{12}N_8NiO_{12}S_4 \cdot 4Na$ ,  $\geq 99\%$ ), 5,10,15,20-tetraphenyl-21H, 23H-porphyrin nickel (II), ( $NiTPP$ ,  $C_{44}H_{28}N_4Ni$ ,  $\geq 99\%$ ), thiophene ( $C_4H_4S$ ,  $\geq 99\%$ ) and n-tetradecane ( $C_{14}H_{30}$ ,  $\geq 99\%$  from Sigma-Aldrich. The standard solutions for the atomic absorption analysis (1.004 mg/ml of Mo in water, 1.004 mg/ml of Al in 2%  $HNO_3$ , and 0.999 mg/ml of Ni 2%  $HNO_3$ ) were obtained from SPEX Standard and from Merck (1.000 g of Co in 1000 ml water). The crude oil used to apply the new hydrotreatment method was the one known as Hamaca. All other chemicals were reagent grade. The solutions were prepared in distilled and demineralized water, filtered through a demineralizer system of Milli-Q Water System Reagent, with a resistance greater than 15 M  $\Omega$  cm.

### 2.2. Apparatus

The pH of the solutions was determined using a pH meter Orion model 420A and its conductivity was measured with a conductimeter OAKLON conductivity/TDS/C/F CON 510 m series.

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