



Acid treated carbon nanofibers as catalytic support for heavy oil hydroprocessing



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ABSTRACT

The catalytic performance of functionalised CNF coated with Ni-decorated MoS₂ slabs on the hydroprocessing of a Maya vacuum residue was studied and compared with a benchmark alumina-supported NiMo catalyst. NiMo/CNF catalysts were characterised by N₂ adsorption, X-ray diffraction and temperature programmed reduction of sulfided species (TPR-S). It was found that thermal cracking mainly controlled the conversion of the fraction with boiling point above 450 °C (X₄₅₀₊), and that catalytic cracking influenced the asphaltene conversion. MoS₂ slabs morphology was varied by modifying the CNF surface chemistry. The amount of coordinately unsaturated sites determined by TPR-S was related to the MoS₂ slabs morphology, although its relationship with the catalytic activity was not straightforward. Higher hydrogenation activity of the CNF supported catalysts allowed to obtain relatively high metal and sulphur conversions, despite the lack of carbon surface acidity. This helped suppress coke formation, at the expense of a less deep cracking into lighter molecules. Overall, CNF-supported catalyst yielded results comparable to the Al₂O₃-supported catalyst, implying that they have a high potential in heavy oil hydroprocessing.

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1. Introduction

Heavy oils (API gravity < 20°) are characterised by low hydrogen to carbon (H/C) ratios, high viscosities, and high concentrations of metals and heteroatoms, and yield a larger proportion of heavy fractions, such as atmospheric and vacuum-distillation residues, which are of relatively little commercial value and highly contaminant [1,2]. Heavy oil production is expected to reach a peak production of 12.3 mbd in the year 2020 [3] triggered by the decrease in conventional oils and the development of novel technologies for extraction and processing of heavy feeds. Therefore, there is a need to maximise refinery output by converting these heavy residues into lighter, more valuable feedstocks, which can be used as a source of chemicals and transport fuels. Hydroprocessing (HP) is commonly used to upgrade heavy oils [4]. However, this technology presents many challenges related to the activity and resistance

to deactivation of the catalysts employed due to the peculiar characteristics of the heavy oil fraction composition [5,6].

Carbon materials have extensively been studied as catalytic support in hydroprocessing reactions because of their textural properties and chemical nature [7]. Advantages of carbon-supported catalysts with respect to the counterparts prepared with Al₂O₃ include a more efficient activation and transfer of hydrogen to reactant molecules, lower tendency to coke formation, and weaker metal-support interaction, which allows a deeper sulfidation of the active phase [8–10]. Particularly, nanofilamentous carbons (NC), including carbon nanofibers (CNF) and carbon nanotubes (CNT), possess highly desirable surface properties, since the porous architecture can be considered as the inverse replica of a conventional support [11], thus avoiding mass transfer limitation of particular relevance in gas–liquid reactions [12]. Upgrading of heavy oils using NC or NC-supported catalysts has been addressed in the literature [13,14].

In previous works, the synthesis of novel catalytic systems based on CNF coated with Ni decorated MoS₂ slabs was reported [14,15]. These structures were formed upon decomposition of ammonium tetrathiomolybdate (ATM) impregnated on the support under inert atmosphere. The decomposition temperature [14] and surface chemistry of the CNF [15] were revealed to significantly affect the MoS₂ morphology, which in turn determined the catalytic

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activity. Low decomposition temperature allows the formation of MoS₂ slab-like structures coating the CNF surfaces [14]. The length and stacking degree of the MoS₂ slabs increased with the functionalisation treatment, affecting negatively the hydrogenation activity in experiments carried out with an aromatic model compound (anthracene) [15]. The presence of a certain amount of oxygen surface groups, however, was necessary to provide the impregnation of well-dispersed thiomolybdate ions.

In an attempt to further expand previous works on CNF-based catalysts, this study focused on the effect of MoS₂ morphology on catalytic performance using a real refinery feedstock, vacuum residue (VR) from a Maya oil. An exhaustive characterisation of the CNF supported catalysts and the hydroprocessed oil obtained is presented.

2. Experimental

2.1. Catalyst preparation

Fishbone-like CNF were produced by catalytic decomposition of methane, as described in [14]. CNF were subjected to different functionalisation treatments in liquid phase obtaining three supports with well-differentiated surface chemistry [15]: HNO₃ (65%) at boiling temperature either during 30 min or 120 min (denoted as CNF_{N30} or CNF_{N120}, respectively) or in a mixture of HNO₃ (65%) and H₂SO₄ (96%) during 30 min (CNF_{NS-30}). Finally, functionalised CNF were filtered, washed with distilled water and dried at 100 °C overnight. The metallic catalysts were prepared by the incipient wetness impregnation method with successive impregnation of the precursor salts, (NH₄)₂MoS₄ and Ni(NO₃)₂, with intermediate drying steps at 70 °C for 12 h. The dilution calculations were based on the support wettability for the following concentrations: 9.3% wt Mo and 2.4% wt Ni. After impregnation, catalysts were tempered at 450 °C in a tubular reactor electrically heated under flowing N₂ at 50 mL min⁻¹ for 4 h. The catalysts are denoted as NiMo/CNF_X, where X is the type of acid treatment as defined above (N30, N120 or NS30).

The alumina-supported catalyst used as a benchmark was prepared following the same procedure described for the carbon-based catalysts. The metal loading for this catalyst was the same as for the carbon-supported ones. After impregnation, the catalyst was calcined in a muffle furnace at 500 °C for 4 h under air flowing at 200 mL min⁻¹. This catalyst is denoted as NiMo/Al₂O₃.

2.2. Characterisation techniques

Powder X-ray diffraction (XRD) patterns of fresh and reduced catalysts were acquired in a PANalytical diffractometer equipped with a Ni-filtered Cu K α radiation and a secondary graphite monochromator, using a θ -2 θ configuration. The powder XRD patterns were further processed using the accompanying software in the equipment, X'Pert Highscore Plus, to get refined structural parameters of crystal domain sizes of C through the application of Rietveld methods.

The textural properties of the carbonaceous support and NiMo catalysts were measured by N₂ adsorption at -196 °C in a Micromeritics Tristar apparatus. The specific surface areas and pore volumes were calculated by applying the BET method to the respective N₂ adsorption isotherms and average pore diameters were calculated by the BJH method based on the desorption branch of the isotherm.

The determination of the amount of surface oxygen created during the functionalisation treatments was carried out by temperature programmed desorption (TPD) in an AutoChem II 2920 apparatus. The profiles of released CO and CO₂ were obtained in a

quartz reactor heated under a constant flow of Ar (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹, up to a temperature of 1000 °C. The eluted gas was analysed by mass spectroscopy. The total amount of CO and CO₂ released was calculated by integrating the area under the concentration versus volume curve.

Temperature programmed reduction of sulfided samples (TPR-S) was performed in a PulseChemisorb 2700 apparatus equipped with a thermal conductivity detector (TCD). The amount of sample used was approximately 200 mg. Temperature was increased from room temperature to 600 °C at a rate of 10 °C min⁻¹ under a flow rate of 50 mL min⁻¹ of a H₂ (10%)/Ar mixture.

NH₃-temperature programmed desorption of the fresh catalysts was carried out in the same apparatus used for the TPR-S analysis. The catalyst (200 mg) was outgassed in argon flow, heated to 600 °C at a rate of 10 °C min⁻¹, and kept at 600 °C for 1 h. The sample was cooled down to 50 °C and allowed to adsorb ammonia. After purging the physically adsorbed ammonia, the system was heated to 600 °C under Ar flow. The amount of chemisorbed ammonia was detected with a TCD.

2.3. Hydroprocessing experiments

A microbomb batch reactor based on a 1/2 in. bored-through Swagelok union-T with both ends plugged and connected to a control line was used for the hydroprocessing reactions. A detailed description of the reactor can be found elsewhere [16]. The feed used was a vacuum residue from a Maya oil with high asphaltene (33.6% wt.), sulphur (7% wt.) and metal (320 ppm wt/wt) content (properties available in Table S1). Feed to catalyst ratio was 4:1 (wt/wt), with 0.5 g of feed used in each experiment. Reactions took place at 18.5 MPa of H₂ and 425 °C. The reactor was kept at reaction temperature for 1 h and then quickly quenched in cold water to terminate reactions. In all tests, 0.1 mL of CS₂ was added to the reactor. This allowed in-situ sulfidation of the NiMo/Al₂O₃ catalyst and it ensured that the catalysts (NiMo/Al₂O₃ and CNF-based catalysts) remained in the sulfided state during the runs.

2.4. Reaction product characterisation

The reaction products were recovered from the reactor using a solvent mixture of CHCl₃/CH₃OH 4:1 vol/vol. The product recovery procedure is described in detail in [16]. Briefly, catalysts were separated from liquid products by filtration. The latter were fractionated into their maltene (heptane soluble) and asphaltene (heptane insoluble, toluene soluble) fractions. Afterwards, the maltene fraction was analysed by gas chromatography (GC) fitted with a flame ionisation detector (FID) to quantify the boiling point distribution below 450 °C in the maltene fraction following the ASTM 2887 method. A calibration using Standard Gas Oil (Sigma-Aldrich) was performed to evaluate the percentage of elution of the material. Thermogravimetric analysis (TGA) was used to determine coke content in the catalysts, considered as the materials which were combusted between 300 and 500 °C.

The expression used to calculate the conversion of materials boiling above 450 °C (X_{450+}) and the conversion of the asphaltene fraction (X_A) can be found as Supplementary Information. These conversion definitions take into account carbonaceous deposits on the catalysts as unconverted feed. This allows for a distinction between active catalysts and catalysts that merely lead to large carbon deposits [17]. The procedure and expressions used to calculate the conversion of sulphur (X_S), nickel (X_{Ni}), vanadium (X_V) and metals (Ni + V) can also be found as Supplementary Information.

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