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Carbon nanofibres coated with Ni decorated MoS_2 nanosheets as catalyst for vacuum residue hydroprocessing

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ABSTRACT

Catalysts based on functionalised carbon nanofibers (FCNF) coated with Ni-decorated MoS_2 nanosheets were obtained by direct decomposition of ammonium thiomolybdate and nickel nitrate impregnated on the FCNF under controlled temperature conditions in inert atmosphere. The catalysts were characterised by X-ray diffraction (XRD), N_2 adsorption, Raman spectroscopy, temperature programmed reduction of sulfur species (TPR-S), NH_3 temperature programmed desorption (NH_3-TPD) and transmission electron microscopy (TEM). Decomposition temperature was found to have a paramount importance in the formation of uniform MoS_2 slabs, as revealed by the TEM study: at 600 °C, non-uniform covering of the carbon nanofiber (CNF) was observed together with the presence of small round-shaped metal particles (ca. 20 nm). On the other hand, at 450 °C CNF appeared homogeneously covered by amorphous MoS_2 slabs decorated with Ni, resulting in higher amount of coordinated unsaturated sites (CUS), as determined by TPR-S. Catalysts were tested in the hydroprocessing of a vacuum residue and the results were compared against a benchmark alumina-supported NiMo catalyst. Higher asphaltene conversions were obtained for the CNF-supported catalysts prepared at 450 °C, which overperformed the Al_2O_3-supported benchmark catalyst. However, the catalytic performance in hydrodesulfurisation and hydrodemetallisation of the CNF-based catalysts was slightly lower than that of the benchmark catalyst.

1. Introduction

Carbon materials have been extensively studied as catalytic support due to their outstanding textural properties and tunable chemical nature [1,2]. The discovery of carbon nanotubes (CNT) by Iijima [3] increased the interest in carbon nanofilaments, including CNT and carbon nanofibers (CNF). These structures of ca. 10–100 nm in diameter and several micrometres in length are formed by graphitic planes (graphenes) disposed with different arrangements. CNT and CNF are typically produced by the decomposition of various fossil hydrocarbons [4] or renewable sources such as biogas [5,6] on catalysts based on transition metals (Ni, Fe and Co) supported on different metal oxides [4]. Different chemical structures of CNT (single wall and multi wall) and CNF (platelet, fishbone and ribbon) can be obtained [7,8]. The carbon nanofilament morphology depends on variables such as the metal used in the catalyst, metal crystal size, carbon gas source and synthesis conditions [4].

Carbon nanofilament aggregates are characterised by having extremely open morphology with minimal or no microporosity, relatively large pore volumes generated by the empty space between the tubular structures, as well as significantly high surface area, mainly derived from the external wall surface area of the nanofilaments. These characteristics make them promising catalyst supports for liquid phase reactions, since mass transfer limitations are prevented due to the availability of the active sites on the outer section of the carbon nanofilaments [9]. In addition, some studies indicated higher hydrodesulfurisation (HDS), hydrodenitrogenation (HDN) and hydrodemetallisation (HDM) activity of carbon-supported catalysts compared to those supported on Al_2O_3, as reviewed in [10]. This higher activity was attributed to a more efficient activation of metal sites and transfer of hydrogen to reactant molecules [11,12]. Additionally, the lower metal–support interaction compared to typical acid supports such as alumina and zeolites makes a larger fraction of active phase available to the reactants. This fact allows an easier and deeper metal oxide reduction and sulfidation [13–15].

Catalysts supported on CNF have been used in fuel cell applications [16], chemical synthesis such as hydrogenation [17], higher alcohol synthesis [18] and Fischer–Tropsch reactions [19]. Some examples that show the potential of these materials in hydroprocessing reactions of both model compounds and real feeds can

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be found in the literature. Multi-walled CNT (MWCNT) supported catalysts were studied in the HDS of thiophene [14] and dibenzothiophene [20] and in the HDN of pyrrole [14]. Fishbone and platelet CNF were studied in the HDS of thiophene [15]. However, studies with real feeds using catalysts supported on nanostructured carbon (NC) are scarce. CNT impregnated with Co and Mo were used as catalysts for vacuum residue (VR) hydrocracking [21]. NiMo supported on acid-treated MWCNT were tested with a light gas oil (LGO) derived from Athabasca bitumen [13]. It was observed that CNT or CNF-supported catalysts yielded significantly less amount of coke than an Al_2O_3-supported catalyst under the same reaction conditions. This is commonly attributed to the lower acidity of the carbon-nanofilament-based catalysts. However, their performance may also depend upon factors such as the feed and type of reactor used. To the best of our knowledge, asphaltene upgrading and HDM activity using CNF- or CNT-based catalysts towards real feeds have not been addressed in the literature.

In this work, fishbone CNF were coated with MoS_2 nanosheets decorated with Ni. This was achieved by thermally decomposing the CNF impregnated with ammonium thiomolybdate (ATM) and nickel nitrate in an inert atmosphere. The effect of the decomposition temperature on the uniformity and homogeneity of the MoS_2 slabs was evaluated. These catalysts were characterised by a number of techniques such as N_2 adsorption, X-ray diffraction, Raman spectroscopy, temperature programmed reduction of sulfur species and transmission electron microscopy. Catalyst performance in heavy oil hydroprocessing was investigated using a real oil-derived feed, a vacuum residue from a Maya oil. Results in terms of liquid product upgrading (asphaltenes and fraction with boiling point above 450 °C), HDM (nickel and vanadium) and HDS conversions are presented and compared against a benchmark NiMo/Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst support synthesis

2.1.1. CNF synthesis and functionalisation

Fishbone-like CNFs were produced at large scale in a rotary bed reactor described elsewhere [22] using a Ni/Al_2O_3 catalyst. The as-prepared CNF will be referred to as CNF in this work. Hydrocarbon feedstock was composed by a mixture of CH_4:CO_2 (1:1). Synthesis conditions used were 700 °C and a weight hourly space velocity of 30 L·(g_{cat} h)$^{-1}$. More details about the catalyst properties and process conditions can be found elsewhere [6]. CNF functionalisation was performed by reflux in concentrated HNO_3 (Panreac, 65%) during 30 min. Finally, functionalised CNF (FCNF) were filtered, washed with distilled water until the pH was above 6 and dried at 100 °C overnight.

2.1.2. Mesoporous alumina synthesis

An alumina support with large surface area and pore volume was synthesised according to a procedure [23] modified from the literature [24].

2.2. Catalyst synthesis

Carbon-based catalysts were prepared by the incipient wetness impregnation method. Successive impregnations of the precursor salts, $(NH_4)_2MoS_4$ and $Ni(NO_3)_2$ were performed with intermediate drying steps at 80 °C for 12 h. The dilution calculations were based on the wettability of the supports for the following concentrations: 9.3 wt% Mo and 2.4 wt% Ni. After impregnation, catalysts were tempered either at 450 or 600 °C in a tubular reactor electrically heated under flowing N_2 at 50 mL min^{-1} for 4 h, in order to allow the decomposition of the metal precursors and simultaneously avoid the oxidation of the CNF that would take place during the typical calcination step in air. Catalysts are denoted as NiMo/FCNF-T hereafter, where T refers to the decomposition temperature.

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/Al_2O_3.

2.3. Characterisation techniques

The textural properties of the carbonaceous support and NiMo catalysts were measured by N_2 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 N_2 adsorption isotherms and the pore size distribution was calculated by the BHJ 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 CO_2 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 CO_2 released was calculated by integrating the area under of the concentration curve versus volume.

The remaining content of the Ni/Al_2O_3 used to grow the CNF was analysed in the CNF and FCNF by temperature programmed oxidation (TPO). This was obtained in a Setaram Thermogravimetric Analyzer by heating the sample under air flow at a rate of 10 °C min^{-1}. Ni oxidation was taken into account to calculate the catalyst content in the as-prepared carbon nanofibers.

Powder X-ray diffraction patterns of fresh and tempered catalysts were acquired in a PANalytical diffractometer equipped with a Ni-filtered Cu $K\alpha$ radiation and a secondary graphite monochromator, using a θ–2θ configuration.

Raman spectra of the carbonaceous materials were obtained with a Horiba Jobin Yvon HR800 UV microspectrometre using the green line of an argon laser (λ = 532 nm) as the excitation source.

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 H_2 (10%)/Ar mixture.

NH_3-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.

Transmission Electron Microscopy was carried out on a Jeol 2011 microscope equipped with a LaB_6 gun and operating at 200 kV. The samples were first finely grounded, dispersed in ethanol and a drop of solution was then deposited on a standard TEM copper grid, previously covered by a lacey amorphous carbon film.

Carbonaceous deposits on the spent catalysts were determined with a Pyris TGA1 thermogravimetric analyser. Samples of approximately 3 mg were combusted from 50 to 900 °C at a rate of 10 °C min^{-1} with an air flow of 40 mL min^{-1}. The samples were held at isothermal conditions for the initial and final temperatures to allow the weight to stabilise. Coke deposits were determined as