

Performance of unsupported Ni(Co,Fe)/MoS₂ catalysts in hydrotreating reactions

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Abstract

The catalytic performance of unsupported Me/MoS₂ catalysts (where Me = Co, Ni, Fe) in the hydrotreating reactions of furfurylamine (FA) and dibenzothiophene (DBT) in a dynamic micro-reactor was reported. The Me/MoS₂ samples were synthesized by the impregnated thiosalt decomposition (ITD) method and sulfided under a mixture H₂S/H₂ (20% v/v), at 400 °C for 4 h. In all samples the Me/(Me + Mo) atomic ratio was of 0.85. The samples were characterized by Chemical analysis by EDS, N₂ adsorption–desorption, X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. The Ni/MoS₂ sample showed higher catalytic activity in the hydrotreating reactions of FA and DBT in comparison with the Co/MoS₂ and Fe/MoS₂ samples. The selectivity in both FA and DBT reactions depends strongly on the presence of Me (Ni, Co or Fe). We found two interesting correlations between the catalytic activity of both FA and DBT reactions with the fraction sulfided of Me and Mo species and with the total sulfidation degree of the samples.

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1. Introduction

Hydrotreating of petroleum fractions is one of the most important processes in the refining industry due to the ever increasing amounts of heavier feeds and the severe restrictions imposed on the allowed percentage of sulfur and nitrogen containing compounds, as well as aromatics in the different distillates [1–5]. The growing interest of the scientific community for the processing of model feeds containing the nitrogen and sulfur compounds is well demonstrated in various reports [6–9]. Ni-based catalysts are generally more active in the hydrodenitrogenation hydro-treating (HDT) reactions than those cobalt-containing catalysts [6,10,11]. The need to produce clean engine fuels,

combined with the prospect of processing poor-quality petroleum feedstocks, has stimulated the development of high-performance HDT catalysts. The addition of phosphorous to the conventionally supported Co–Mo, Ni–Mo and Ni–W sulfides [12–18], and the development of new catalysts such as metal carbides, metal nitrides [19–21] have been described in the literature. Recently, the high-performance of the unsupported hydrotreating catalysts versus the supported hydrotreating catalysts has been reported in the literature [22–26]. The unsupported hydrotreating catalysts could be interesting due to their demonstrated high catalytic activity in comparison with the supported HDT catalysts.

It is well known that the elimination of N atoms in the N-containing ring molecules is carried out first by complete hydrogenation followed by hydrodenitrogenation step [27,28]. Then to decrease the active sites competence by the inhibition of N-containing ring molecules in HDS reactions, most hydrotreating catalysts have high hydrogenation

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ability. Also, it is known that the predominant compounds in the petroleum fractions are the sulfur and nitrogen compounds. Nevertheless, organic oxygen-containing compounds such as phenols and ethers are also present [6]. The hydrodeoxygenation over sulfided catalysts has been reported [6,27]. In general, the ethers are easy to convert, whereas the furans are the most difficult to convert [6]. Then the necessity to have multi-functional catalysts must be focused on to the synthesis of hydrotreating catalysts with HDS, HDN and HDO activities.

In the present work, the unsupported Me/MoS₂ catalysts (where Me = Ni, Co and Fe) were synthesized by the ITD method. The samples were characterized by Chemical analysis by EDS, N₂ adsorption–desorption, X-ray diffraction, X-ray photoelectron spectroscopy, and high-resolution transmission electron microscopy. For activity test, furfurylamine was selected as the probe molecule owing to its complex structure induced by the presence of amino group and the oxygen ions in the furan ring. Similarly, the DBT molecule was selected for the HDS reaction taking into account its complex structure and the presence of S ions in the thiophenic ring. The aim of this work was to establish the structure-activity and structure-selectivity correlations for the hydrotreating reactions of the furfurylamine and dibenzothiophene molecules over unsupported MoS₂ promoted with sulfided metals as Fe, Co and Ni ions.

2. Experimental

2.1. Synthesis of unsupported catalysts

The unsupported Me/MoS₂ (Me = Co, Ni or Fe) samples were prepared following the procedure described elsewhere [29,30]. Binary samples with atomic ratio $R = 0.85$, where $R = \text{Me}/(\text{Me} + \text{Mo})$, were prepared by adding drop-wise an acetone solution containing the precise amount of nickel nitrate hexahydrate, cobalt nitrate hexahydrate or iron nitrate non-hydrated to the (NH₄)₂MoS₄ thiosalt. The solution mixture was stirred for 3 h at 333 K, until the solvent was evaporated. Finally, the dried materials were treated at 673 K in hydrogen sulfide/hydrogen gas mixture (20 vol.% H₂S) with a flow of 0.7 ml/min for 4 h. The samples were stored under nitrogen atmosphere with the aim to avoid contact with air.

2.2. Characterization methods

2.2.1. Chemical analysis

The chemical analysis was made with a JEOL 5300 scanning electron microscope with a dispersive energy detector (EDS). Samples were placed on the sample holder using highly conductive graphite paint as adhesive to fix the samples.

2.2.2. Surface area

The surface area values of the samples were determined by N₂ adsorption–desorption isotherms at 77 K with Gem-

ini 2060 equipment from Micromeritics equipment. Prior to the experiments all samples were degassed at 473 K in vacuum for 5 h. The volume of adsorbed N₂ was normalized to standard temperature and pressure. Specific surface area (S_{BET}) was calculated by the B.E.T method.

2.2.3. X-ray diffraction

The X-ray diffraction (XRD) measurements of the samples were made in a Philips spectrometer model X'pert using the Cu K α radiation (40 kV, 30 mA) with wavelength of 0.154 nm. Interpretation of XRD data was made by comparing experimental patterns with those reported in the ICDD-PDF data bases [31].

2.2.4. X-ray photoelectron spectroscopy

A RIBER LDM-32 equipped and analyzer XPS with a hemispherical electron analyzer and a Mg K α ($h\nu = 1253.6$ eV) X-ray source was used. The samples were first placed in a copper holder mounted on a sample-rod in the pretreatment chamber of the spectrometer and then outgassed at 403 K for 1 h before transfer to the analysis chamber. All catalysts were outgassed at 10^{-5} mbar and then transferred to the ion-pumped analysis chamber, where residual pressure was kept below 1×10^{-9} mbar during data acquisition. The binding energies (BE) were referenced to the C 1s peak (284.9 eV) to account for the charging effects. The areas of the peaks were computed after fitting of the experimental spectra to Gaussian/Lorentzian curves and removal of the background (Shirley function). Surface atomic ratios were calculated from the peak area ratios normalized by the corresponding atomic sensitivity factors.

2.2.5. High-resolution transmission electron microscopy (HRTEM)

TEM images were collected on a JEOL 2010 instrument with an atomic resolution of 0.19 nm. The samples were suspended in heptane as solvent to be deposited on lacey carbon (440 Mesh) Cu grid holders.

2.2.6. Catalytic activity measurements in fixed-bed catalytic reactor

2.2.6.1. Catalytic activity measurement in the reaction of furfurylamine. The transformation of furfurylamine (FA) was performed in a dynamic micro-reactor model 150 HP In situ Research Instruments working under atmospheric pressure. The reactions were carried out in the vapor phase, the micro-reactor working in a differential mode, at 593 K. The total gas flow was 2.5 L h^{-1} , the partial pressure of furfurylamine was 5 mm of Hg (298 K) and the weight of catalyst was 0.1 g. The reactant was fed to the micro-reactor by H₂ flowing through a saturator containing liquid furfurylamine. High-resolution Supelcowax-10 capillary column (0.53 mm-diameter, 30 m-long) installed in a gas chromatograph (HP model 6890) was used to determine the products from the transformation of FA. The chromatograph uses nitrogen as carrier gas and is equipped with a flame ioniza-

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