



Synthesis of NiMo/Al₂O₃ Hydrodesulphurization Nanocatalyst by One Pot Co-impregnation Route

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Abstract

Nano NiMo/ γ -Al₂O₃ catalysts was prepared by using the impregnation method of nickel chloride (as a source of nickel) and ammonium molybdate (as a source of molybdenum) on the alumina. Then, they were characterized and studied by many techniques, including X-ray diffraction (XRD), Fourier transform infrared (FTIR), field emission scanning electron microscope (FESEM) and thermo-gravimetric analysis (TGA). From X-ray diffraction (XRD) spectrometry, results showed that the particle size was (11.903 nm) for the prepared nano NiMo/ γ -Al₂O₃ catalyst and that the nickel and molybdenum atoms were incorporated into the mesoporous alumina channels. Finally, the shape of the particle is spherical or nearly spherical as seen in FESEM image.

Keywords: co-impregnation , catalyst, one pot synthesis, NiMo-alumina catalyst.

1. Introduction

The catalysts can be defined as materials that increases the reaction rate in which the chemical reaction is approaching the equilibrium in the reaction and can return to its original form without being destroyed or consumed at the end in reaction [1]. Requirements for a good catalyst is activity, selectivity and stability, the solid catalyst should have reasonably large surface area needed for reaction active sites [2]. Catalysis contributes the mechanism by which chemical transformations take place thus enabling the commercially viable creation of desired materials. By using catalysts manufacturing protocols one can be made thus more economic, green and sustainable [3]. The nano catalyst has collected the advantages of homogeneous and heterogeneous catalyst systems. The Nano catalytic system allows rapid and selective chemical transformations with an excellent product yield as well as easily catalyst and recovery [4]. Different support for hydrotreating catalysts has been studied. The most widely used alumina support for its mechanical properties and excellent inspection, as a general rule, active components are loaded on support using cobalt (nickel) nitrates and ammonium heptamolybdate solutions [5]. Alumina, zeolite, carbon, silicon, zirconia or clay materials are used as support and a catalytic metals used are nickel, platinum, palladium, molybdenum, cobalt, copper, iron. Many types of

(HDS) are now used in the oil industry depending on feed properties and reaction conditions. The most important factor in hydrotreating is catalytic action and performance [6,7, 8] .

CoMo/Al₂O₃ or NiMo/Al₂O₃ is widely used to remove sulfur, nitrogen, oxygen, metals and other contaminants from crude oil fraction under operating conditions. In these mixed catalysts, Mo can work as an active component enhanced by activity of Cobalt (Co) or nickel (Ni) present [8,9]. Different metals and materials such as aluminium, iron and titanium oxide, clay, and silica are used as catalysts in nanoscale for many years . Nano materials are experiencing a rapid development in recent years because of their current or potential applications in a wide range of technological areas such as electronics, catalysis, ceramics, magnetic data storage, structural components and so on to meet the technological requirements in these areas [10]. HDS Catalyst is a hydrotreating catalyst used in hydrotreater, which usually includes (catalysts for hydrodesulfurization, hydrodenitrogenation, hydrogenation of aromatics, and hydrodemetallization) [11]. Due to continuous changes in the legislative requirements on transport fuel, the process of Hydrodesulfurization (HDS) is currently more interested. Oil sources face challenge to meet new specifications by improving hydrotreating performance [12].

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The aim of the present work is the synthesis of NiMo/Al₂O₃ nanocatalyst using impregnation / incipient wetness route and characterize it.

2. Experimental

2.1 Materials : The samples, including nickel nitrate (Ni(NO₃)₂·6H₂O), were purchased from the company (Central Drug House(P)Ltd.) in purity (99.5%), ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O from the company (Thomas baker (chemicals) Pvt.Ltd.) in purity (99.9%), gamma alumina from (Changsha Santech Co. , Ltd.) with purity (99.5%) and anhydrous ethanol.

2.2. Catalyst preparation : The catalyst was prepared. (1.946 g) from (Ni(NO₃)₂·6H₂O) was used and dissolved in (20 ml) ethanol in a dry beaker. (1.226 g) of (NH₄)₆Mo₇O₂₄·4H₂O dissolved in another beaker in (20 ml) ethanol at room temperature. Then, they were mixed with vigorous stirring with the addition of alumina. The beaker was then covered with a polyethylene film and left at room temperature for at least (6 h) and then transferred to (60°C) drying oven for ethanol evaporation. After aging for two days, the prepared material became solid, resembling green foam. The product was calcined at (500°C) for (7 h) to obtain the desired material.

2.3. Characterization:

The ordered mesoporous NiMo/γ-Al₂O₃ catalyst were characterized by a series of techniques including X-ray diffraction (XRD-6000 CuKα) (λ=1.5406 Å), 220/50,Hz,SHIMADZU(japan). FTIR of catalyst was recorded at (4 cm⁻¹) accuracy, in a spectral range from (400 - 4000 cm⁻¹) with an FTIR spectrometer (Nicolet 380, Thermo Electron Co.). TGA (Instrument: SDT Q600 V20.9 Build 20) of the spent and virgin catalysts was carried out under a 40/60 ml/min N₂/air flow rate with a heating rate of (10 °C/min) in room, temperature to (900°C). Field emission scanning electron microscopy type (JSM-820, JEOL) was used to analysis of surface morphological of catalysts..

3. Results and discussion

3.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is used to examine and determine the crystalline phase of materials. There are three main wide diffraction peaks at 2θ values of (37°, 46°, 67°) with the X-ray diffraction pattern shown in figure (1) as well. The appearance of these peaks can be attributed to the presence of Mo species and varying degree of the peaks are the result of the difference in the degree of crystalline, as well as the effect of calcination at high temperatures which depends on the crystallinity of the nanoparticles. On comparing these results with the peaks in previously

reported that results are in agreement with the XRD of NiMo/γ-Al₂O₃ with her [23-26].

The most common NiO and Ni₂O₃ may also be present in the amorphous phase or microcrystals [13]. Moreover, it has been noted that both (Al₂O₃) and NiAl₂O₄ have a characteristic peak at (2θ = 37.7) . but this peak for the former is broad and weak, while for the latter it is relatively narrow and sharp [14]. As the calcination temperature increases, some Ni atoms enter the surface of the Al₂O₃ internal structure to form NiAl₂O₃ [15]. The peaks position and intensities are in a good agreement with those reported in joint committee on powder diffraction standards (JCPDS) file No.(20-0776) for prepared (NiMo/γ-Al₂O₃).

The particle sizes were calculated from Debye-Scherrer formula given below:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \dots\dots\dots(1)$$

In which:

D: is the crystallite size.

λ: is the wave length of radiation.

θ: is the Bragg's angle.

β: is the full width at half maximum (FWHM).

The estimated crystallite size of the prepared NiMo/γ-Al₂O₃ is (11.903) nm. The presence of sharp peaks in XRD pattern and particle size being less than (100) nm refers to the nano-crystalline nature of the prepared materials.

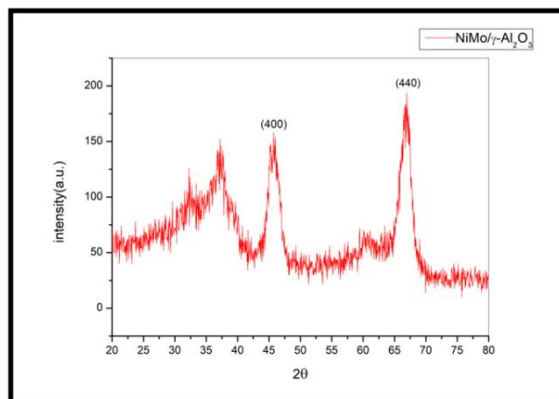


Figure 1. X-ray diffraction for prepared (NiMo/γ-Al₂O₃).

3.2. Thermo gravimetric analysis (TGA)

The (TGA) curves of new and spent catalyst are shown in Figure (2). According to (TGA) there are successive stages of weight loss in the sample. The reason for weight loss at room temperature up to (200°C) is the elimination of the water physically adsorbed on the surface of the sample and the partial decomposition of nickel and molybdenum., the second reason for weight loss is due to the total decomposition of the salts of nickel and molybdenum

as well as the decomposition of the remaining organic additives in the sample [16-18]. In nano catalysts, mass loss due to combustion reactions is (8.968 % , and 14.48%) respectively . In accordance with (TGA) proles, there is not loss of weight between (620 and 1000 °C), We can say that at temperatures above(620 °C) , all remaining volatile compounds were removed. The interfering signals in the (DTA) curves may be due to the endothermic evaporation, oxidative decomposition, and thermal adsorption [19] . Because of these interfering signals in the (DTA) curve, it is difficult to determine the endothermic or exothermic peak to a specific temperature [19,20]. TGA technology is a dissociation and component change technology where the dissociation of the catalyst represents loss of moisture and water and has nothing to do with the nano size and the nano size cannot be compared before and after preparation because the catalyst changed ,the purpose of the examination is to observe the phases of thermal dissociation ,So the temperature here has no effect on the size and shape of the nano composites.

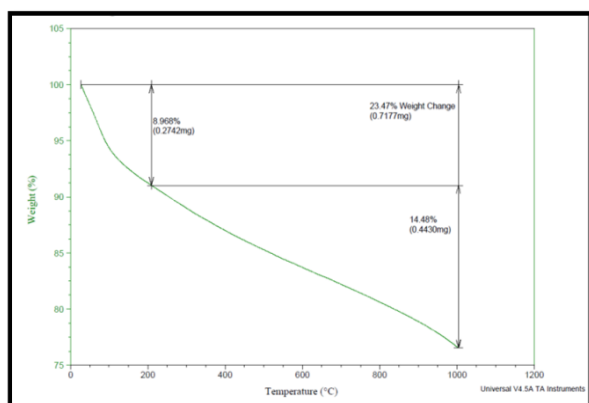


Figure 2. TGA for NiMo/ γ -Al₂O₃ catalyst prepared.

3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the prepared catalyst are shown in figure (3). Peak in the band (400-1050 cm⁻¹) corresponds to MoO₃ in (815.12). The absorption bands assigned to the Al-O vibration in (575.46 and 751.21) represent the aluminium ions octahedral and tetrahedral respectively [27,28]. These values found in the fingerprint region under 1000 cm⁻¹ arising from inter-atomic vibrations. These results are in agreement with NiMo/Al₂O₃ the previously reported FTIR spectrum [21,22]. When comparing these results with the peaks in figure (4) indicates that results are in agreement with the FTIR of NiMo/ γ -Al₂O₃ previously reported [23].

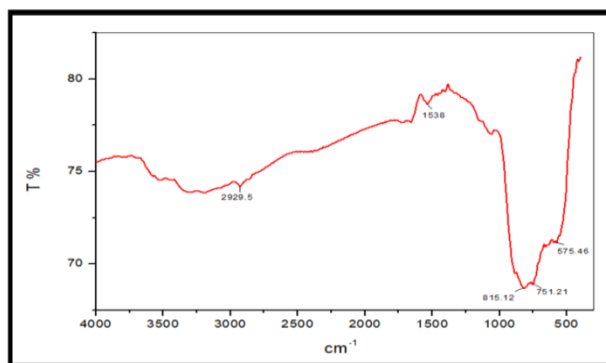


Figure 3. FTIR spectrum of prepared NiMo/ γ -Al₂O₃ catalyst.

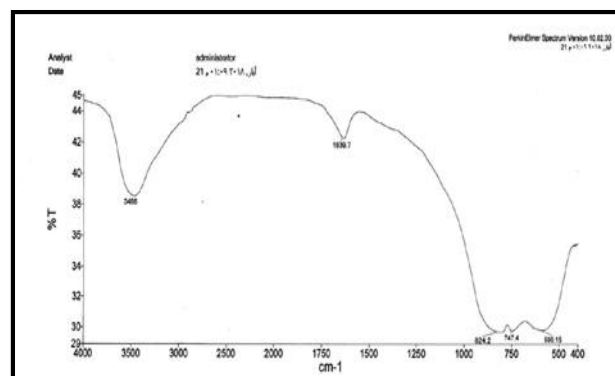


Figure 4. FTIR spectrum of prepared NiMo/ γ -Al₂O₃ catalyst previously reported [23].

3.4. Field emission scanning electron microscope (FESEM)

Figure (5) shows the FESEM images of the prepared (NiMo/ γ -Al₂O₃) catalyst, which shows its surface morphology and structural properties. From its observation, we note that the minimum and maximum and average particle size are (26.05, 48.38 and 33.80 nm) respectively and that the shape of the particle is spherical or nearly spherical and in the form of clusters distributed on the surface in a regular equal manner, indicating that the shape is regular and it is approximately in its forms to the FESEM image of the new catalyst shown in the figure (6).

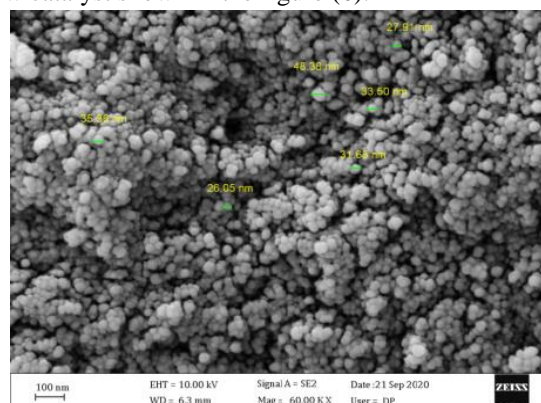


Figure 5. FESEM image of the prepared catalyst (NiMo/ γ -Al₂O₃)

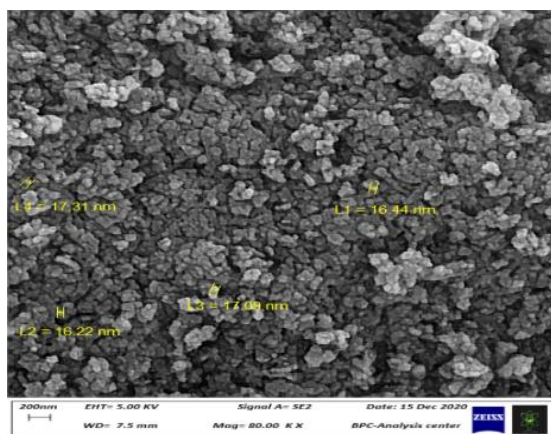


Figure 6. FESEM image of the new catalyst (NiMo/γ-Al₂O₃)

4. Conclusions

The nanocatalyst NiMo/γ-Al₂O₃ was synthesized by one pot co-impregnation route, using its corresponding salts and anhydrous ethanol as a solvent. Calcination of the as-synthesized NiMo-Al₂O₃ precursors at 500 °C completely removed the solvent, which leads to the formation of desired catalysts. The method is simple, very good and effective one for preparing NiMo/γ-Al₂O₃ Nano catalysts. The material prepared characterized by use of (XRD), (FTIR), (TGA) and (FESEM). The results show that the prepared sample particle size of NiMo/γ-Al₂O₃ nanoparticles was (11.903 nm). The FTIR spectra of the prepared nanocatalyst are in agreement with the previously reported NiMo/Al₂O₃ FTIR spectra. FESEM images show its surface shape and structural properties, and in clusters evenly distributed over the surface of the prepared nano NiMo/γ-Al₂O₃ catalyst and that the nickel and molybdenum atoms were incorporated into the mesoporous alumina channels and that the shape of the particle is spherical or nearly spherical one. This method of catalysts synthesis provide an alternative one for other used methods of preparation.

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