

Enhancement of Desulfurization Process for Light Gas Oil Using New Zinc Oxide Loaded Over Alumina Nanocatalyst

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Abstract

This work reports the removal of dibenzothiophene (DBT) via an oxidative desulfurization (ODS) process over Zn/Al₂O₃ catalyst utilizing H₂O₂ as an oxidizing agent. The influence of operating parameters, such as reaction temperature, time was investigated. Results clarified that recognizably high DBT elimination of 93.781% has been achieved within 80 min using 0.1 g (9% Zn/Al₂O₃) catalyst at 90 °C reaction temperature. It was observed that an overall ODS catalytic efficiency order of: 9% ZnO/γ-Al₂O₃ > 6% ZnO/γ-Al₂O₃ > 3% ZnO/γ-Al₂O₃. Discernment of the surface morphology and textural properties of prepared nano-catalysts were characterized utilizing X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared (FTIR) and BET surface area analysis, which assisted in evaluating the performance of the prepared nano-catalysts. Owing to its highly effective nature, operation at moderate conditions and cost-effectiveness, this work can be conceived as an efficient methodology for the ODS operation of fuel oils on an industrial scale.

Keywords: Nano-catalyst, Gamma alumina, Zinc oxides, Oxidative desulfurization, Diesel fuel

1 Introduction

Emissions produce via the combustion of petroleum fractions, such as SO₂ and NO_x. These harmful emissions contribute to acid rain, which increases environmental pollution and global warming effects [1]–[4]. Rising ecological worries for a clean environment and gradually more strict legislations on organosulfur contents

presented in fuels, make desulfurization technologies so necessary. Minimizing the concentration of sulfur compounds in transportation fuels and petroleum fractions considers a persistent necessity to protect the ecosystem [5]–[9]. Organosulfur found in liquid fuels mostly be as DBT. So, it was predominantly employed as a model in order to exemplify organosulfur found in real oil. To eliminate organosulfur from liquid fuel,

several technologies such as hydrodesulfurization (HDS), extractive desulfurization (ODS), oxidative desulfurization, bio-desulfurization (BDS) and adsorptive desulfurization have been studied [10]–[14]. HDS carried out at severe operation conditions (temperature and pressure), is efficient only to aliphatic sulfur compounds comprising hydrocarbons and less effective to refractory organosulfur, such as benzothiophene (BT), DBT and 4,6-dimethyl dibenzothiophene [10], [15]–[20]. Conversely, oxidative desulfurization is a catalytic process that can effectively eliminate DBT compounds and their derivatives, at moderate process conditions [10], [21], [22]. In ODS reactions, organosulfur found in fuel are converted into highly polarized sulfones by utilizing appropriate oxidizing agents such as H_2O_2 ozone, Nitrogen oxides, hypochlorite or potassium permanganate [15], [23]–[26]. Gamma-alumina ($\gamma-Al_2O_3$) is commonly utilized as a support of catalyst for several processes due to its mechanical strength leads to make the catalyst become stable under harsh operating conditions. The alumina has a good porosity and large surface area, and its structure involves acidic sites [27]–[31]. Also, $\gamma-Al_2O_3$ can readily be structured into the desirable shape; furthermore, it is comparatively low-cost support [32]. Two reported studies in the literature utilized (zinc oxide (ZnO)/ $\gamma-Al_2O_3$) as heterogeneous catalysts in order to accelerate the removal of organosulfur compounds. For instance, previous work studied the sulfur compounds elimination from kerosene fuel via ODS in the existence of air as oxidant and (18% ZnO)/ $\gamma-Al_2O_3$) as a catalyst with a specific surface area of 159.2676 m^2/g . The removal of sulfur compounds was carried out under moderate conditions and the sulfur removal was 70.5% [33]. Abdulateef *et al.* [34] studied the ODS process by employing air as oxidant and in the presence of (12.5% ZnO –12.5% MgO)/ $\gamma-Al_2O_3$ as a catalyst with a surface area of 107.4292 m^2/g , where 84.6% sulfur compounds were removed at 190 °C and 45 min employing the batch reactor. The novelty of the present work was focused on the development of a new oxidative desulfurization process using various amounts of zinc oxide as active metal oxide loaded over efficient large surfaces are gamma alumina nanoparticles as catalyst support. So, the enhancement of the ODS performance was studied by promoting the properties of the catalyst ($ZnO/\gamma-Al_2O_3$) via using high surface area gamma alumina. Also, the effect of various

loading of active metal (ZnO) on the elimination of organosulfur compounds was detected.

2 Materials and Methods

2.1 Materials

The chemicals and material utilized in this work were zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), $\geq 99\%$, (Sigma), Dibenzothiophene {(DBT), 98%, (Aldrich), Deionized water and gamma alumina ($\gamma-Al_2O_3$) nanoparticles. The gamma alumina ($\gamma-Al_2O_3$) nanoparticles specifications are presented in Table 1.

Table 1: Gamma Alumina gamma alumina ($\gamma-Al_2O_3$) nanoparticle specifications

Specifications, Unit	Values
Bulk density, g/m^3	0.333
Surface area, m^2/g	500
Pore volume, cm^3/g	1.5
Pore size, nm	20

Hydrotreated light gas oil (HLGO) fraction supplied from Pendik-Istanbul-Turkey produced by OMV Company was employed to evaluate the prepared catalyst by catalytic ODS process. This HLGO contains 9 ppm sulfur content.

2.2 Catalyst preparation

The catalysts with various loading of ZnO were synthesized by utilizing the impregnation technique [10], [35], [36]. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was employed to load ZnO nanoparticles on gamma alumina ($\gamma-Al_2O_3$). At first, zinc acetate was suspended in deionized water with mixing for 1 h in order to achieve regular dispersion of zinc acetate. Afterward, $\gamma-Al_2O_3$ added leisurely to the prepared zinc acetate solution and then mixed at 25 °C for 12 h. The produced impregnated solution was dried for 16 h in an oven at 60 °C, and finally calcined by using a furnace for 4 h at 550 °C to obtain nanocatalysts ($ZnO/\gamma-Al_2O_3$) with various amount of ZnO loaded.

2.3 Catalysts characterization

Structural phase analysis of the synthesized nanocatalysts ($ZnO/\gamma-Al_2O_3$) has been performed by

utilizing powder X-ray diffraction (XRD) (SHIMADZU, Japan) utilizing CuK α radiation Nickel filter with wavelength ($\lambda= 1.5406 \text{ \AA}$) and the results are recorded for 2 theta range from 5–60 degree at scanning speed of 5 degree/min. Fourier transform infrared (FTIR) has been utilized for (ZnO/ γ -Al $_2$ O $_3$) samples (SHIMADZU, Japan). The surface morphology of synthesized nanocatalysts has been studied by utilizing scanning electron microscopy (SEM) (Zeiss-EM10C-100 KV). Pore volume and surface area (textural analysis) have been estimated by employing Brunauer–Emmett–Teller (BET) type (micromeritics, USA).

2.4 Catalytic ODS process

The performance of the prepared (ZnO/ γ -Al $_2$ O $_3$) nanocatalyst was evaluated by utilizing the batch ODS process. The feedstock of ODS process is prepared by dissolving DBT in HLGO at a concentration of 611 ppm. Catalytic ODS experiments were performed in a flask (capacity of 500 mL) by using 100 mL feedstock, 1 g catalyst and 4 mL H $_2$ O $_2$ (1 M), which were stirred and heated on a heating mantle stirrer. Also, catalytic ODS reactions were carried out at various operation conditions, such as reaction temperature (30–90 °C), reaction time (20–80 min) and stirring speed at 600 rpm. All ODS experiments are performed twice to confirm the validity of the experimental data. The sulfur concentration in light gas oil was evaluated by X-ray fluorescence (EDXRF) (RX-360SH, Tanaka Scientific, Ltd, Japan) analyzer based on ISO 9454 and ASTM D4294-03.

3 Results and Discussion

3.1 Characterization of (ZnO/ γ -Al $_2$ O $_3$) catalyst

The BET test revealed the textural properties of the synthesized nano-catalysts. Table 2 summarizes the BET results of the synthesized nano-catalysts. The results of BET analysis indicated that with increasing the loading of zinc oxide, the pore volume and specific surface area diminish whereas the pore size increases. The results show that with increasing the loading of active metal (ZnO), the pore volume and surface area diminished due to the occupancy of ZnO in some areas in the prepared nano-catalysts [37].

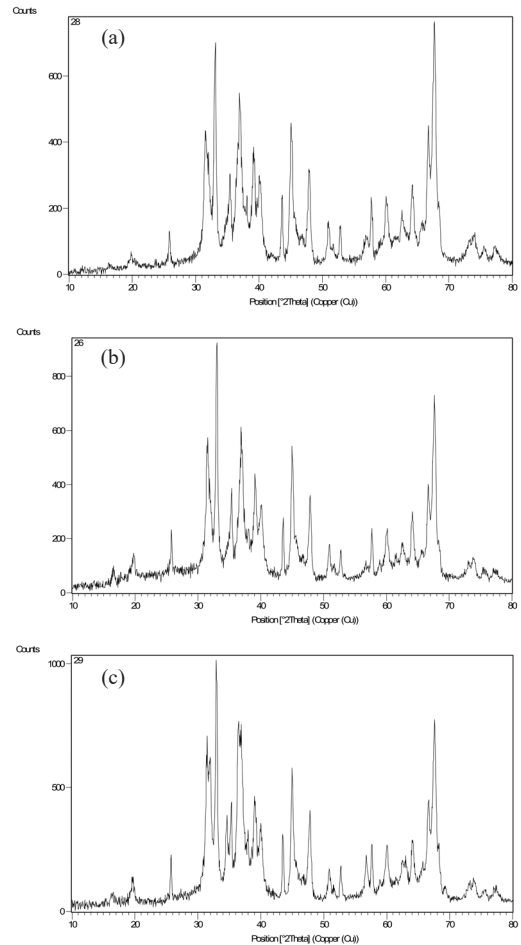


Figure 1: XRD patterns for the prepared for (a) 3% ZnO/ γ -Al $_2$ O $_3$, (b) 6% ZnO/ γ -Al $_2$ O $_3$ (c) 9% ZnO/ γ -Al $_2$ O $_3$ nanocatalysts.

Table 2: BET results of prepared catalysts

Sample	Specific Surface Area (m 2 /g)	Pore Volume (cm 3 /g)	Pore Size (nm)
γ -Al $_2$ O $_3$	500	1.5	20
3% ZnO/ γ -Al $_2$ O $_3$	457.5	0.634	27.2
6% ZnO/ γ -Al $_2$ O $_3$	413.2	0.295	33.2
9% ZnO/ γ -Al $_2$ O $_3$	388.8	0.085	39.5

Figure 1 presents the powder XRD patterns for the prepared ZnO/ γ -Al $_2$ O $_3$ nano-catalysts. The usual diffraction peaks for pure γ -alumina are located at 35.5°, 45.7° and 66.6°, and for ZnO at 31.8°, 34.5°, 36.3°, 47.6°, 56.7°, 62.9°, 66.4°, 67.9°, 69.2° and 77°

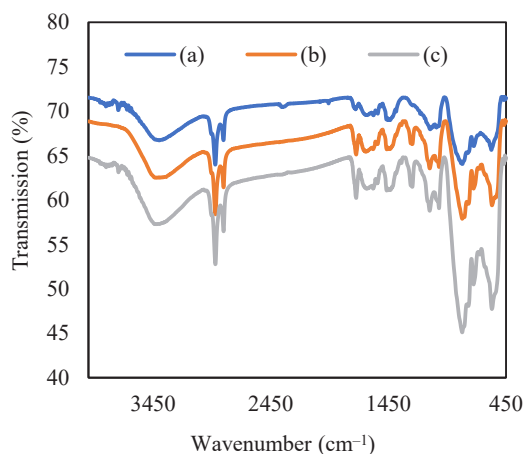


Figure 2: FT-IR spectra for (a) 3% ZnO/ γ -Al₂O₃, (b) 6% ZnO/ γ -Al₂O₃ (c) 9% ZnO/ γ -Al₂O₃ nanocatalysts.

[38]–[40]. As presented in Figure 1, after loading of ZnO on the γ -Al₂O₃, the characteristic peaks corresponding to γ -Al₂O₃ drops while the diffraction peak intensities of ZnO increase.

Synthesized ZnO/ γ -Al₂O₃ nano-catalysts were subjected to FT-IR analysis to reveal the several characteristic functional groups related to the synthesized nano-catalysts. Figure 2 displays the results of FT-IR analysis for the prepared nano-catalysts. The bands at about 3400 cm⁻¹ corresponds to –OH groups stretching vibrations and the bands at about 1700 cm⁻¹ are imputed to the H–O–H symmetric bending vibration of water molecules adsorbed on the catalysts surface [41]. The bands at about 1100 and 1000 cm⁻¹ are the consequence of the bending vibration of Al–O–H group and the band at wavenumbers of 820 cm⁻¹ is the result of the symmetrical bending vibration of Al–O [41], [42]. The absorption peak at 570 cm⁻¹ are associated with the stretching vibration of zinc oxide [43]. It was observed that with increasing the ZnO loading, the peak at about 790 cm⁻¹ has increased.

The SEM test describes the nature of the surface for the synthesized ZnO/ γ -Al₂O₃ nanocatalysts. Figure 3 displays the SEM images of the catalysts. Generally, the high surface area of γ -Al₂O₃ supports the dispersion of nanomaterials of small sizes [32].

These results of catalyst characterization gave a good indication for the high dispersion of ZnO-supported compounds on the surface of synthesized nanocatalysts.

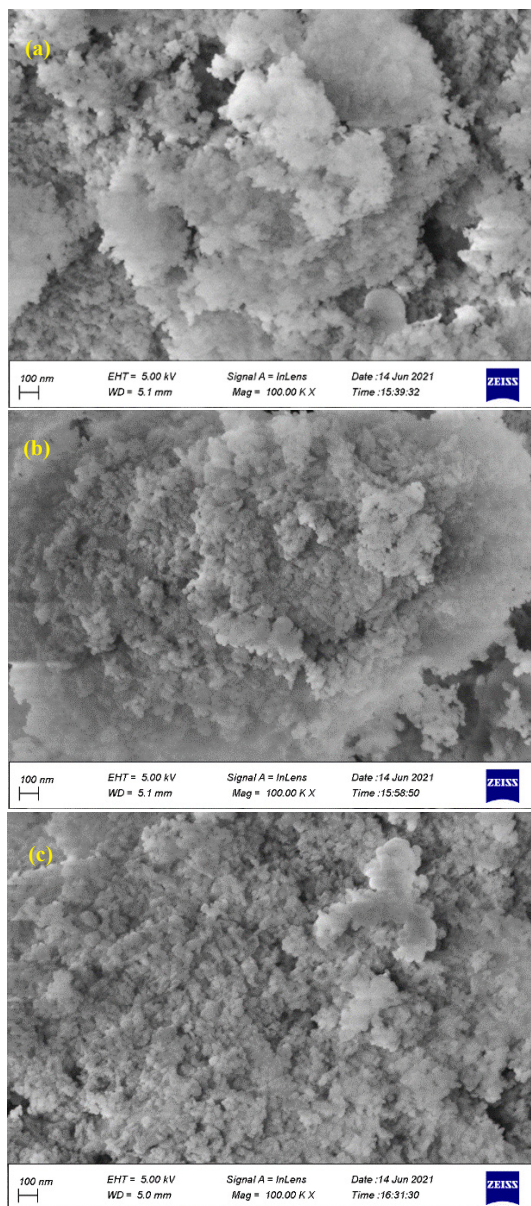


Figure 3: Scanning electron microscopy images for (a) 3% ZnO/ γ -Al₂O₃, (b) 6% ZnO/ γ -Al₂O₃ (c) 9% ZnO/ γ -Al₂O₃ nanocatalysts.

3.2 Catalytic activity tests

The activity of the synthesized nano-catalyst has been experimented by studying the influences of various operation conditions involving time of reaction, reaction temperature and the amount of active metal loaded.

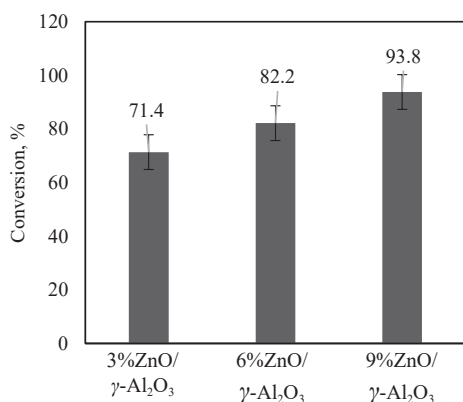


Figure 4: The influence of amount of loading ZnO on the activity of ODS reaction.

3.2.1 Influence catalyst support

The nano-catalysts have been produced by loading ZnO over a high surface area γ -Al₂O₃ in order to study the influence of catalyst support on the performance of the catalyst in ODS operation. The results of ODS process show that the catalyst support has a significant role in promoting the efficiency of ODS process compared to related previous studies [33], [34]. The high specific surface area of catalyst support (γ -Al₂O₃) promotes the distribution of nanomaterials of small sizes [32]. On the other hand, the γ -Al₂O₃ supplies a larger interaction area contact for the DBT to oxidize by the oxidizing agent causing higher elimination of DBT. As well as, the large specific surface area of γ -Al₂O₃ enhances the DBT diffusion to the active sites on the catalyst surface [21].

3.2.2 Influence of ZnO loaded

The impact of ZnO loaded on the performance of ODS process was studied by loading various amounts of ZnO over the surface of the catalyst. Three nanocatalysts containing various amounts of zinc oxide (3%, 6% and 9%) were prepared. Figure 4 explains the impact of the amount of ZnO loaded on the DBT conversion. The DBT conversion improved with increasing the loading of ZnO owing to the availability of active sites on the catalyst surface that lead to increases in the oxidation probability of DBT compounds by the oxidant in these sites. The performance of the oxidation reaction was also improved by enhancing the activity of the

prepared catalyst by increasing the quantity of ZnO over γ -Al₂O₃ support due to enhancing the adsorption capacity toward DBT compounds [35], [36].

3.2.3 Influence reaction temperature

Figure 5 present the impact of reaction temperature on the activity of ODS process. For all synthesized nano-catalysts, the results show that the DBT conversion rises with increasing temperature of reaction. This increase is owing to the following [37], [44]–[46]: Based on Arrhenius's equation, the increase in the temperature of reaction leads to promote the DBT conversion, where the reaction rate constant is positively influenced. Therefore, the average kinetic energy of molecules increases with increasing in reaction temperature, so the number of molecules that have activation energy increases, the chances of collision increase, and the rate of the reaction increases. At higher reaction temperatures, the most strongly adsorbed sulfones will be easily eliminated from the catalyst surface.

3.2.4 Influence reaction time

The impact of interaction time on the conversion of DBT compounds is illustrated in Figure 6. In general, it was found that the conversion of DBT compounds rises with the interaction time. The long interaction time leads to an increase in the contact time among the reactants in the active site on the surface of the catalyst and enhances the chance of reaction between DBT compounds and the oxidant [36], [47]–[50].

The comparison between the activity of the ZnO/ γ -Al₂O₃ nanocatalyst for ODS process in the present work and the previous works are summarized in Table 3.

Table 3: comparison between the activity of the ZnO/ γ -Al₂O₃ nanocatalyst for ODS process in the present work and the previous works

Sulfur Model	System, Oxidant/ Catalyst	Conversion	Reference
DBT	Kerosene, 12.5%ZnO and 12.5%MgO/ γ -Al ₂ O ₃	84.6%	[34]
DBT	Kerosene, 18% ZnO/ γ -Al ₂ O ₃	70.52%	[33]
DBT	Light gas oil, 9% ZnO/ γ -Al ₂ O ₃	93.781%	Present study

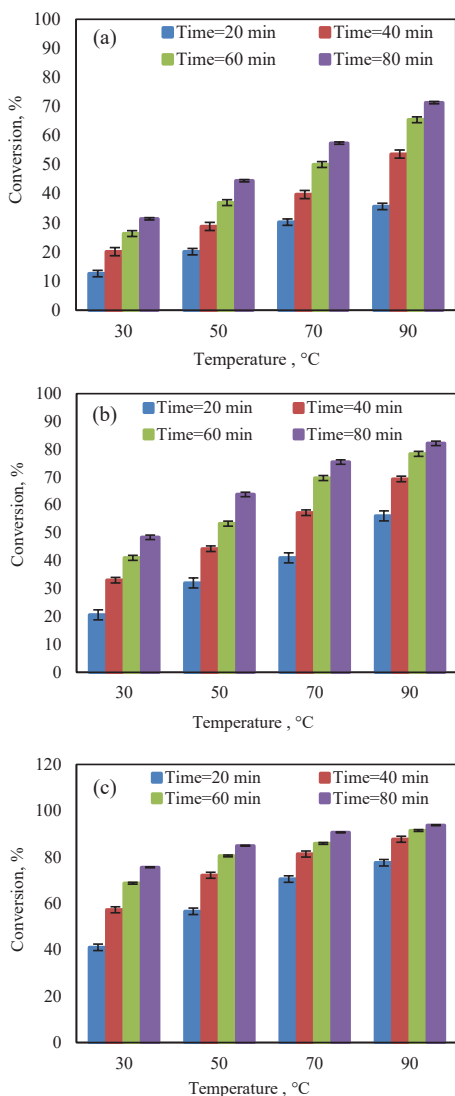


Figure 5: The influence of reaction temperature on the activity of ODS reaction for (a) 3% ZnO/γ-Al₂O₃ (b) 6% ZnO/γ-Al₂O₃ (c) 9% ZnO/γ-Al₂O₃.

3.3 ODS cycles (Deactivation study)

The activity of the new 9% ZnO/γ-Al₂O₃ nanocatalyst was determined after six ODS cycles at the best experimental parameters. The conversion of DBT after these cycles was summarized in Figure 7. ZnO/γ-Al₂O₃ catalyst attained a peripheral decrease in conversion after six cycles. The result proved the high stability of the employed nanocatalyst. The small decrease in the

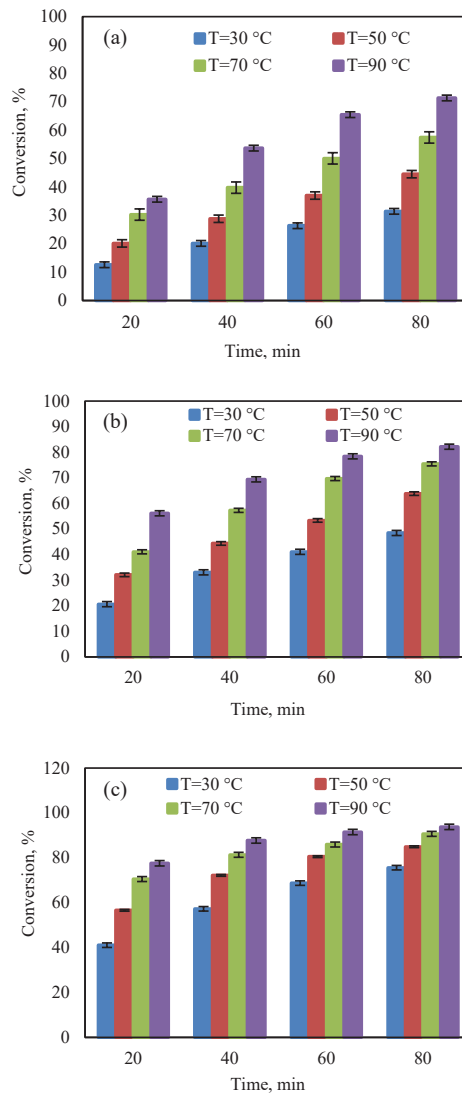


Figure 6: The influence of reaction time on the activity of ODS reaction for (a) 3% ZnO/γ-Al₂O₃ (b) 6% ZnO/γ-Al₂O₃ (c) 9% ZnO/γ-Al₂O₃.

catalyst activity may be owing to some active sites losing through during ODS cycles.

3.4 The Mechanism for nano catalytic oxidative desulfurization process

Figure 8 explained the mechanism for nano catalytic oxidative desulfurization in presence of ZnO/γ-Al₂O₃ and H₂O₂ is illustrated in. ODS reactions were achieved

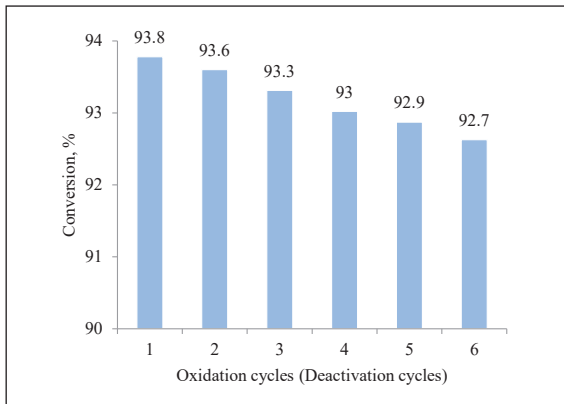


Figure 7: ODS cycles for 9% ZnO/ γ -Al₂O₃ catalyst at the best conditions.

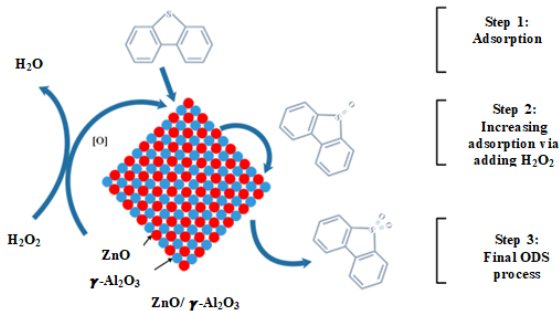


Figure 8: Mechanism of nan catalytic oxidative desulfurization.

as follows: in the first step, the DBT was absorbed into the pore channel of ZnO/ γ -Al₂O₃ through the adsorption step. The oxygen released from H₂O₂ oxidizes the DBT molecules into sulfoxides (DBTO) in the second step. After that, sulfoxides (DBTO) were oxidized to sulfones (DBTO₂), which are more polar than DBT in the third step. The sulfoxides/sulfones were migrated from the fuel phase (non-polar phase) to the polar aqueous phase [7], [51]. After that, the reaction products were allowed to separate. The sulfur content was tested in the fuel phase sample.

4 Conclusions

This work focused on investigating the effect of using high surface area catalyst support on the performance of the nano-catalyst. A nano-catalysts (ZnO/ γ -Al₂O₃) have been synthesized, characterized (SEM, powder XRD, FTIR and BET analysis methods), and utilized

for the ODS of DBT compounds found in LGO fraction under mild process conditions. The catalyst characterization indicated that a high dispersion of ZnO-supported compounds on the surface of synthesized nanocatalysts was achieved. The results of the prepared nano-catalysts evaluation display that the use of high surface area catalyst support significantly affected the elimination of DBT compounds. Also, The loading amount of active metal positively influenced the catalytic activity, where over the course of all reaction parameters, catalytic activity followed an order as: 9% ZnO/ γ -Al₂O₃ > 6% ZnO/ γ -Al₂O₃ > 3% ZnO/ γ -Al₂O₃. The highest removal of DBT compounds contained in light gasoil has (93.781%) over (9% ZnO/ γ -Al₂O₃) catalyst at 90 °C and 80 min.

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Author Contributions

A.A.A.: conceptualization, investigation, reviewing and editing; J.I.H.: investigation, methodology, writing an original draft; G.S.A.: research design, data analysis; A.T.J.: conceptualization, data curation; M.A.A.: writing—reviewing and editing; W.S.A.: project administration. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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