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Research Article

Recycle Performance of Heterogeneous Catalyst Metal Oxides-Based Layered Double Hydroxide for Oxidative Desulfurization Process of 4-methyldibenzothiophene

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Abstract

The desulfurization of oil must be resolved as soon as possible due to a variety of issues, including environmental contamination and protection regulations. It was believed that oxidative desulfurization (ODS) was the most promising method. In this research, metal oxide-based layered double hydroxides (TiO_2@Ni-Al and ZnO@Ni-Al) were effectively synthesized for the ODS of 4-methyldibenzothiophene (4-MDBT). TiO_2@Ni-Al and ZnO@Ni-Al exhibited superior catalytic performance and high recycling capacity, achieving a 99% removal rate after five reactions in 30 min. The heterogeneous catalyst TiO_2@Ni-Al/ZnO@Ni-Al is easy to separate and recover from a reaction system. Increased temperature facilitates the transformation of 4-MDBT into 4-MDBTO$_2$. The influence of H_2O_2's rapid decomposition rate, which can inhibit oxidation reactions, reduces the catalytic activity as the temperature increases. 4-MDBT Sulphur removal on TiO_2@Ni-Al and ZnO@Ni-Al is 99.48 and 99.51%, respectively. TiO_2@Ni-Al and ZnO@Ni-Al have great potential for use in the industry based on these results.

Keywords: Recycle catalyst; oxidative desulfurization; heterogeneous; metal oxide; 4-methyldibenzothiophene

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1. Introduction

Fossil fuels will continue to be the mainstay of energy supply for several years to come due to rising populations and worldwide industrial development [1,2]. A number of environmental issues include SO_2 emissions from engines, generators, vessels, and factories [3,4]. The removal of sulfur-based substances from fossil fuels has assumed great significance [5]. In addition, governments across the world have implemented progressively strict rules concerning the highest allowable amount of sulfur in fossil fuels [6]. Hence, the creation of novel ultra-deep desulfurization methods is currently at the frontier of

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both research and practice in order to satisfy forthcoming and future fuel sulfur requirements.

The most common desulfurization process, hydrodesulfurization (HDS), operates at high temperatures and hydrogen pressures over catalysts supported by alumina [7]. Benzothiophene and their derivatives are resistant polycyclic aromatic sulfur heterocycles (PASHs), but HDS is extremely effective at desulfurizing aliphatic and some thiophenes organosulfur despite these drawbacks [8]. As a result, numerous identical high-performance ultra-deep desulfurization technologies have been investigated, such as adsorptive desulfurization, biodesulfurization, photocatalytic desulfurization, and oxidative desulfurization, the last of which is thought to be one of the most efficient and potential techniques [9–12].

Sulfones are created when molecules containing sulfur are oxidized by an oxidant during the oxidative desulfurization (ODS) process [13,14]. H_2O_2, O_2, and air are a few examples of the several oxidants that have been used [15]. Because of their high reactivities, H_2O_2 has been regarded as the most potent oxidant [16,17]. Water is a by-product of H_2O_2, an oxidant that cannot dissolve in oil. Due to the reduced mass transfer across the interface between the oil and water phases as a consequence of this, the rate of ODS is decreased in a two-liquid-phase reaction mixture [18]. The sulfones may be extracted from non-polar hydrocarbon streams using liquid-liquid extraction and polar solvents because they have greater polarities than their progenitors [19].

The ODS process heavily relies on the use of a suitable catalyst, which is thought to increase the activity of oxidants [20,21]. As a result, many different kinds of catalysts, including polyoxometalates and their composites, supported metal oxides, phase-transfer catalysts, two-dimensional (2D) catalysts with a hexagonal structure, titanate nanotubes, as well as organic acids, have been created and assessed in earlier studies [22]. Researchers from all around the world pay particular attention to layered double hydroxide (LDH), a subcategory of layered materials, because of their exceptional qualities. The metal hydroxide layers in LDH have an interesting structure that is similar to that of brucite. The features of the LDH, such as layer spacing, active site, and surface charge, can be simply adjusted by modification with other materials [23,24].

Metal oxides support layered double hydroxide to increase the active site in the ODS process. Metal oxide catalysts are low-cost, have a high oxidizing capacity, and have gained significant interest in the degradation and oxidation of environmental pollutants [25]. Generally, it is acknowledged that the most crucial elements for a suitable catalyst are excellent performance, cheap cost, and ease of repair [26,27]. Additionally, the economics of the ODS process may be significantly impacted by the separation and recyclability of catalysts [28,29]. Due to the difficulties in obtaining homogeneous catalysts at the last step of the process, heterogeneous catalysts are thus more beneficial and cost-effective [30].

In this case, the 4-methyldibenzothiopehe by ODS was carried out using the metal oxides-based LDH. It investigated how the catalyst's recycle catalyst behavior was affected by the reaction circumstances. To comprehend the outstanding ODS process of catalysts, effect a kinetic study was carried out. Investigated was how well the catalysts performed throughout consecutive desulfurization and recycle catalyst performances.

2. Materials and Methods

2.1 Materials and Instrumental

Without further purification, analytical grade sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), zinc(II) / nickel(II) / magnesium nitrate hexahydrate ($Zn/Ni/Mg(NO_3)_2.6H_2O$), acetonitrile (CH_3CN), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), titanium(IV) oxide (TiO_2), zinc(II) oxide (ZnO), and distilled water were also used. Various analytical techniques were used to characterize the physicochemical characteristics of the synthesized materials. X-ray diffraction (XRD; Rigaku Miniflex-6000; constructed with Cu-Kα radiation, 5–70°) was used to study the crystal phases. FTIR spectra were used to determine the chemical groups of catalysts. The samples were produced using the KBr pellet technique, and the results were recorded using a Shimadzu Prestige-21, 500-4000 cm^{-1}. Scanning Electron Microscope (SEM, Quanta 650) was carried out at 250 times magnification.

2.2 Catalyst Preparation

First, M^{2+}/Al-LDH (M= Zn, Ni, Mg) was synthesized by following a literature method [31,32]. TiO_2/ZnO@M^{2+}/Al-LDH (M= Zn, Ni, Mg) was prepared by adding TiO_2 or ZnO to M^{2+}/Al-LDH (M= Zn, Ni, Mg) solution with ratio 1.0. Afterward, 150 mL NaOH 0.37 M was added and stirred at 150 rpm for 24 h at 80 °C.

Then, the mixture was calcinated for 10 h at 300 °C and stored.

2.3 ODS Process of Catalyst

The 4-MDBT was dissolved in n-hexane with a concentration of 500 mg/L. A 250 mL chemical flask with two holes was used to oxidize 4-MDBT with H_2O_2 whilst under atmospheric pressure. The chemical flask with two holes was first filled with a particular quantity of H_2O_2 (2 mL). Next, around 0.25 g of the catalyst and 25 mL of 4-MDBT were added, respectively, to the center of the reactor. With the use of an oil bath, the reactor was heated to a range of consistent temperatures of 50 °C while being magnetically agitated. After the reaction had been going for 60 min, the liquid was cooled and separated. In order to ensure that all sulfur was eliminated, the clear mixtures were then extracted twice with 2 mL of acetonitrile. For catalyst recycle performance, the separated catalysts from each reaction might be used again after being cleaned and dried for 12 h in a vacuum oven at 60 °C. For the purpose of ensuring that the findings were reproducible, each experiment was performed three times. The percentage of 4-MDBT conversion followed the Equation (1) [33]:

$$4-\text{MDBT}\ Conversion\ (\%) = \left(\frac{C_0 - C_t}{C_0}\right)\times 100 \qquad (1)$$

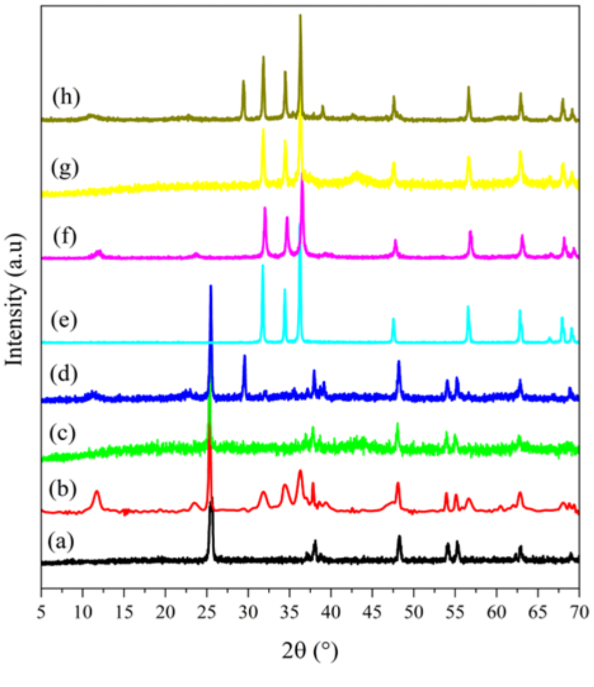

Figure 1. XRD pattern of TiO_2 (a), TiO_2@Zn-Al (b), TiO_2@Ni-Al (c), TiO_2@Mg-Al (d), ZnO (e), ZnO@Zn-Al (f), ZnO@Ni-Al (g), ZnO@Mg-Al (h).

where, C_0 and C_t are the initial and concentrations of 4-MDBT after t time, respectively.

3. Results and Discussion

The X-ray diffraction pattern of TiO_2, TiO_2@Zn-Al, TiO_2@Ni-Al, TiO_2@Mg-Al, ZnO, ZnO@Zn-Al, ZnO@Ni-Al, and ZnO@Mg-Al are shown in Figure 1. The typical reflections (101), (004), (200), (105), (204), and (116) of TiO_2 are shown by the peaks of diffraction at 2θ = 25.19°, 38.01°, 48.37°, 54.09°, 62.85°, and 68.94°, (JCPDS card No. 021-1272) [34]. On the other hand, the ZnO primary peak values were observed at 2θ = 31.69°, 34.33°, 36.36°, 47.55°, 56.53°, 62.84, 66.50°, 67.91°, and 69.13° which represent to the typical reflections (100), (002), (101), (102), (110), (103), (200), (112), and (201) (JCPDS card No. 36-1451) [35,36]. Whereas the peaks of layered double hydroxide (Ni-Al, Mg-Al, and Zn-Al) at 2θ = 9–12° and 60–62° as shown layered materials.

The functional groups adhered to the surfaces of TiO_2, TiO_2@Zn-Al, TiO_2@Ni-Al, TiO_2@Mg-Al, ZnO, ZnO@Zn-Al, ZnO@Ni-Al, and ZnO@Mg-Al are all interpreted using an FTIR instrument (Figure 2). The peaks at 655 and 556 cm^{-1} for TiO_2 and ZnO were the vibrations of Ti−O and Zn−O, respectively [37]. The bending vibration of H−O−H was attributed to the bands at 3415-3481 cm^{-1} and 1634-1656 cm^{-1} for metal oxide-layered double hydroxide

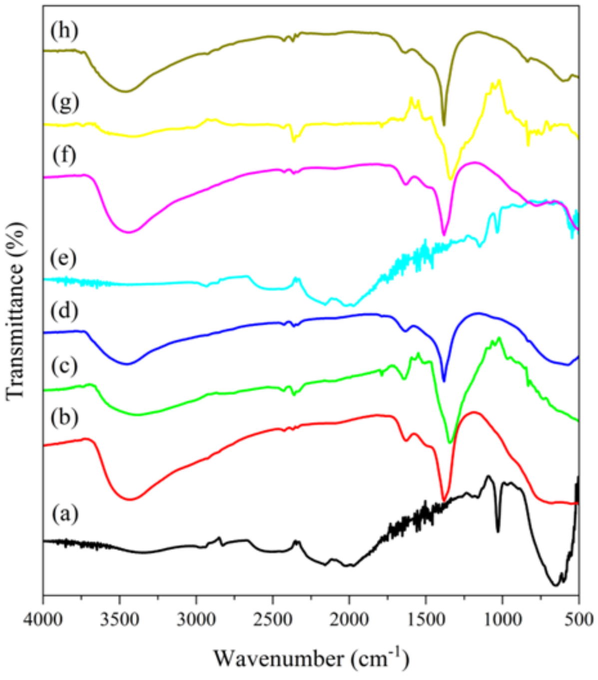

Figure 2. FTIR spectra of TiO_2 (a), TiO_2@Zn-Al (b), TiO_2@Ni-Al (c), TiO_2@Mg-Al (d), ZnO (e), ZnO@Zn-Al (f), ZnO@Ni-Al (g), ZnO@Mg-Al (h).

[38]. NO_3^- stretching was related to the strong band at 1325-1391 cm^{-1} [39,40]. Additionally, the M−O−M, M−O, and O−M−O vibration modes had peaks below 1000 cm^{-1} [41]. TiO_2@Zn-Al, TiO_2@Ni-Al, TiO_2@Mg-Al, ZnO@Zn-Al, ZnO@Ni-Al, and ZnO@Mg-Al all showed the typical peaks of metal oxides and layered double hydroxide, which proved the effective synthesis of the composites.

SEM images of TiO_2@Ni-Al and ZnO@Ni-Al are shown in Figure 3. The material's morphology reveals its surface is uneven and rough. In SEM images, roughness is defined as fluctuations, imperfections, or unevenness on the material's surface. When there is a lack of uniformity in SEM images, the surface characteristics or features are not constant throughout the entire sample. Roughness and non-uniformity can result from various factors such as the synthesis process, deposition methods, or inherent properties of the material itself.

The oxidative desulfurization is greatly influenced by the catalyst. Thus, the catalyst's ability to be recycled was studied. After every run, the catalyst was centrifuged. After multiple rinsing with n-hexane and ultrasound equipment, the previously used catalyst was desiccated overnight. For the next reaction, the

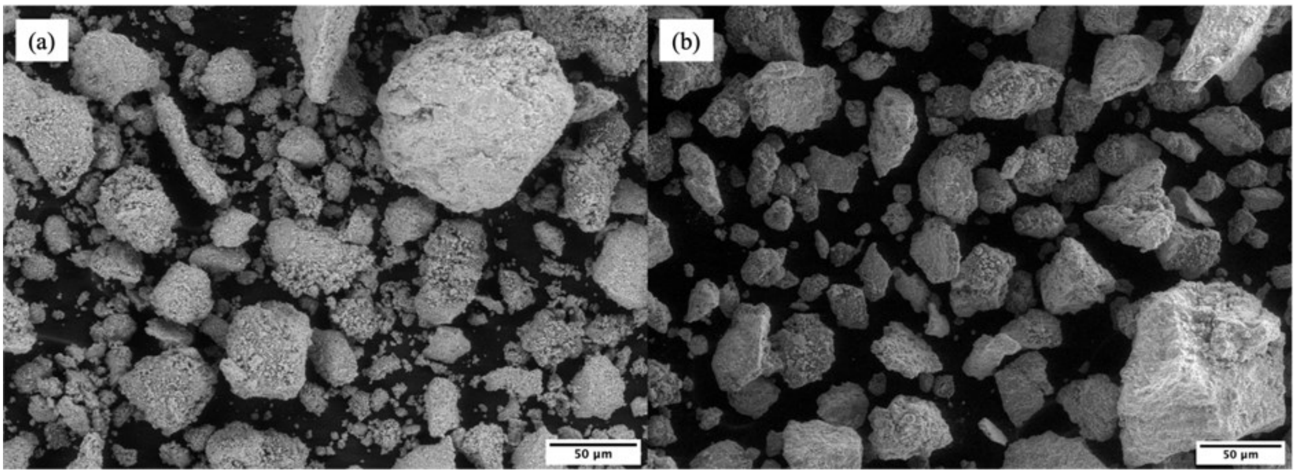

Figure 3. SEM image of TiO_2@Ni-Al (a) and ZnO@Ni-Al (b).

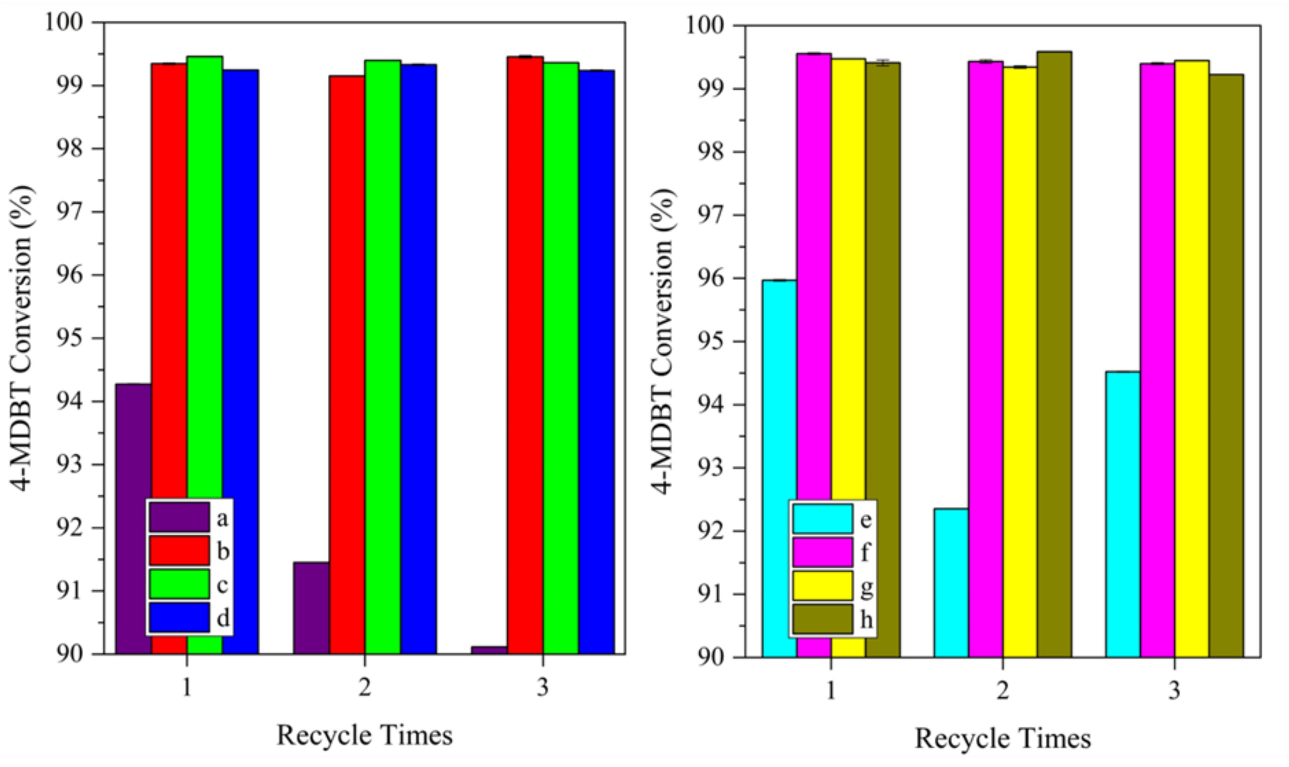

Figure 4. Recycle performances of TiO_2 (a), TiO_2@Zn-Al (b), TiO_2@Ni-Al (c), TiO_2@Mg-Al (d), ZnO (e), ZnO@Zn-Al (f), ZnO@Ni-Al (g), ZnO@Mg-Al (h).

recycled catalyst was treated with the new oxidant and extractant. When H_2O_2 is used as an oxidant, the produced H_2O is extracted with acetonitrile. Using acetonitrile, sulfones might be easily extracted from the 4-MDBT [42]. This confirms that the 4-MDBT has been completely purified of catalyst and oxidant residues. We thus look at the effects of materials based on metal oxides when H_2O_2 is used as an oxidant in the same circumstances. In Figure 4, the findings of TiO_2, TiO_2@Zn-Al, TiO_2@Ni-Al, TiO_2@Mg-Al, ZnO, ZnO@Zn-Al, ZnO@Ni-Al, and ZnO@Mg-Al in the ODS of 4-MDBT are shown. In comparison to other catalysts, TiO_2@Ni-Al and ZnO@Ni-Al demonstrated greater recycling performance.

Catalyst heterogeneity testing in the ODS process is a crucial phase in the development and selection of efficient catalysts for reducing sulfur content in fuel in an efficient and cost-effective manner. To determine whether a catalyst is homogeneous or heterogeneous, the heterogeneity test is crucial. Homogeneous catalysts consist of catalysts that are in the same phase as the reactants. Thus, the catalyst is completely dissolved within the reactant phase. Heterogeneous catalysts, on the other hand, are catalysts in a distinct phase from the reaction material [43]. In this investigation, a heterogeneity test was conducted by combining 0.25 g TiO_2@Ni-Al/ZnO@Ni-Al and 25 mL 4-MDBT. Separating the catalyst from the 4-MDBT solution after 10 min. Between 20 and 30 min were devoted to the ODS procedure. The ODS results are depicted in Figure 5, which demonstrates that there is no significant change in the sulfur content, indicating that TiO_2@Ni-Al/ZnO@Ni-Al is a heterogeneous catalyst. Because they exist in distinct phases, heterogeneous catalysts are simple to separate and recover from a reaction system [44]. After the reaction has been completed, the solid catalyst can be removed, cleaned, and utilized in the next cycle reaction.

The impact of reaction time on the oxidative desulfurization of 4-MDBT was examined during the course of 10–60 min at a temperature of 50 °C and a catalyst dose of TiO_2@Ni-Al and ZnO@Ni-Al was 0.25 g in order to optimize the following critical factors. Figure 6 shows that the elimination of 4-MDBT using H_2O_2 oxidant improves when response time increases from 10 to 60 min. Because they boost contacts between 4-MDBT and TiO_2@Ni-Al/ZnO@Ni-Al, which enhances conversion rates, longer reaction periods often improve the oxidation activity's kinetics and catalytic efficacy [45]. As a result of 4-MDBT molecules utilizing all active species and decreasing the likelihood of 4-MDBT oxidation on the catalyst surface, 4-MDBT conversion does not vary considerably after 30 min. As a consequence, it was decided that 30 min would be the appropriate response time for further research.

The effect of reaction temperature was examined, as indicated in Figure 7, ascribed to

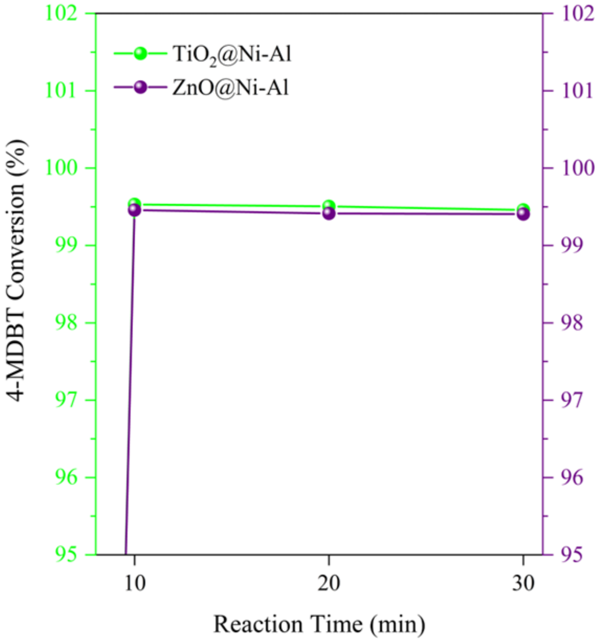

Figure 5. The heterogeneity of TiO_2@Ni-Al and ZnO@Ni-Al.

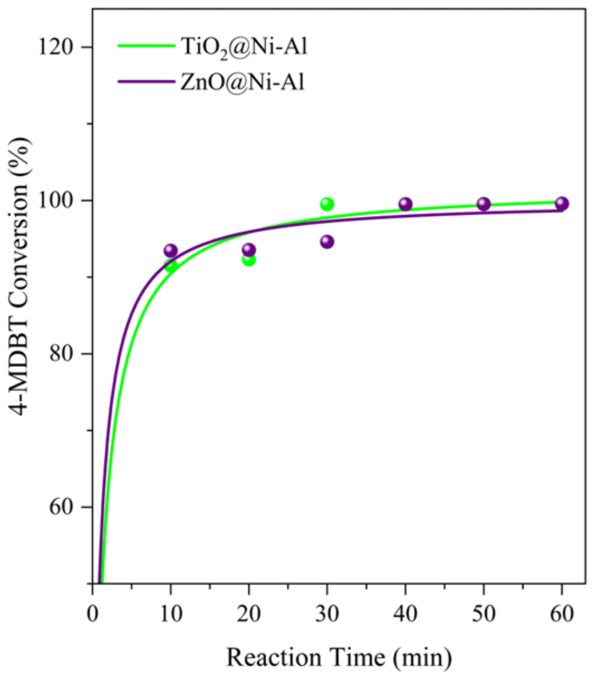

Figure 6. The influence of reaction time.

the significance of reaction temperature on ODS. It is clear that temperatures used could somewhat improve the catalytic activity. According to Wei *et al.* [46], oxidant availability might rise dramatically at higher temperatures, favoring the chemical interaction between 4-MDBT and the oxidant. In the current study, TiO_2@Ni-Al and ZnO@Ni-Al eliminating 99.48 and 99.51 % after 30 min was reported at 30 °C. As could be observed, the conversion of 4-MDBT occurred at 99.51 and 99.69 % for TiO_2@Ni-Al and ZnO@Ni-Al, respectively, when the reaction temperature was raised to 50 °C. These data demonstrate that increased temperature aids in the conversion of 4-MDBT to the associated 4-$MDBTO_2$. The influence of H_2O_2's rapid breakdown rate, which may stifle oxidation reactions, causes the catalytic activity to decline at temperature rises [47,48]. The outcome at 50 °C was effective for 4-MDBT conversion and beneficial for energy conservation.

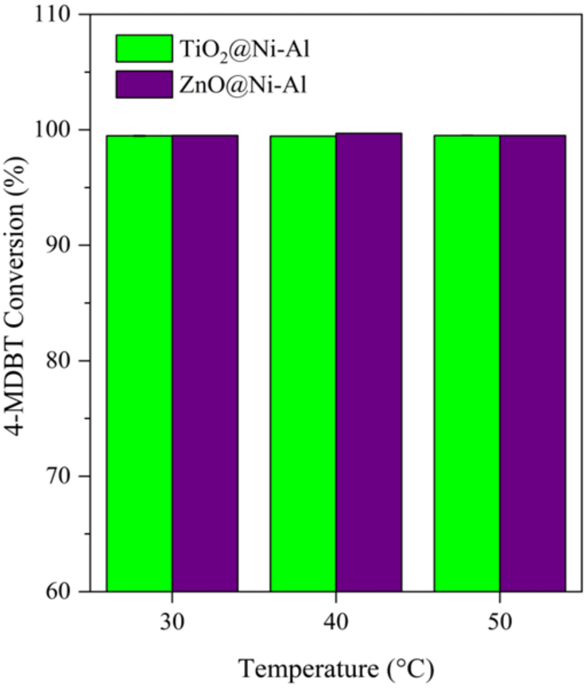

Figure 7. Temperature's effect on ODS.

The efficiency of ODS is greatly influenced by the kind and quantity of oxidant. H_2O, an ecologically friendly byproduct, was the oxidation product of H_2O_2. Furthermore, high oxidant concentrations create more oxidizing species, which quickens the conversion of 4-MDBT. To determine the appropriate oxidant dose, a desulfurization examination of 4-MDBT using the TiO_2@Ni-Al and ZnO@Ni-Al catalysts with varying oxidant doses was carried out. According to Figure 8, more H_2O_2/4-MDBT results in higher efficiency of ODS. This is due to an increase in the number of catalytically active peroxo molecules produced [49]. When H_2O_2 was added in amounts up to 2.5 mL, the effectiveness of 4-MDBT elimination increased. The activity can be hampered by the potential for entering water to collect on the catalyst surface.

The impact of catalyst dose on ODS performance was looked at since it is vital for use in the industry. The sulfur removal percentage

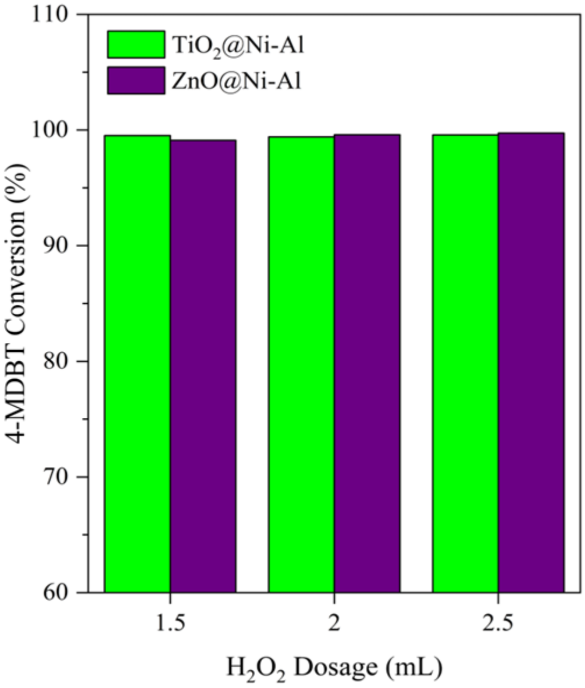

Figure 8. Effect of H_2O_2 dosage.

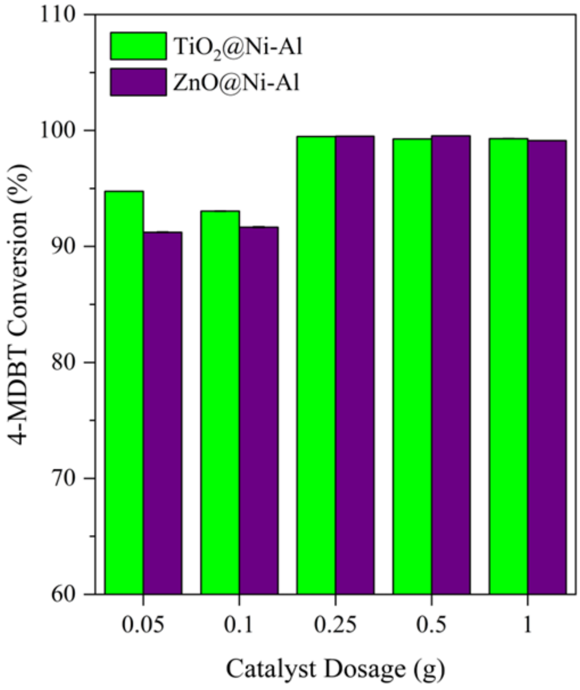

Figure 9. The influences dosage of the catalyst.

for 4-MDBT is greatly improved by increasing the catalyst quantity up to 1 g, as shown in Figure 9, due to an increase in the system's active sites. The catalyst's desulfurization activity did not, however, improve when the dose was raised to 1 g. Additionally, increasing the catalyst dose to 1 g decreased the sulfur removal percentage and, when accounting for the economic cost, might significantly increase the process cost [33]. As a consequence, the catalyst's recommended dosage was found to be 0.25 g. The sulfur removal percentage for 4-MDBT on TiO_2@Ni-Al and ZnO@Ni-Al is 99.48 and 99.51%, respectively. The proposed ODS mechanism for 4-MDBT is displayed in Figure 10. It has been proven that H_2O_2 intermediates frequently play a crucial part in catalysis during ODS reactions. This information led to the supposition that TiO_2@Ni-Al and ZnO@Ni-Al first interacted with H_2O_2 to create H_2O_2 complexes that might oxidize 4-MDBT into the appropriate 4-$MDBTO_2$.

4. Conclusion

To sum up, layered double hydroxides based on metal oxides were successfully synthesized. The meticulously characterized synthetic samples exhibited excellent catalytic ODS performance in 4-MDBT. The prepared catalyst demonstrates outstanding stability and performance in the recycling test, and Sulphur removal could still reach 99% after five reactions without additional treatment. In addition, TiO_2@Ni-Al and ZnO@Ni-Al are heterogeneous catalysts that are easy to recover from a reaction system. The effects of ODS reaction variables were investigated. The optimum requirements were 30 min of reaction time, 50 °C of operating temperature, 2.5 mL of hydrogen peroxide, and 0.25 g of catalyst. This research demonstrated the possibility of synthesizing TiO_2@Ni-Al and ZnO@Ni-Al composites with encouraging catalytic performance for the desulfurization of fuel oil, which could be advantageous to the petrochemical sectors.

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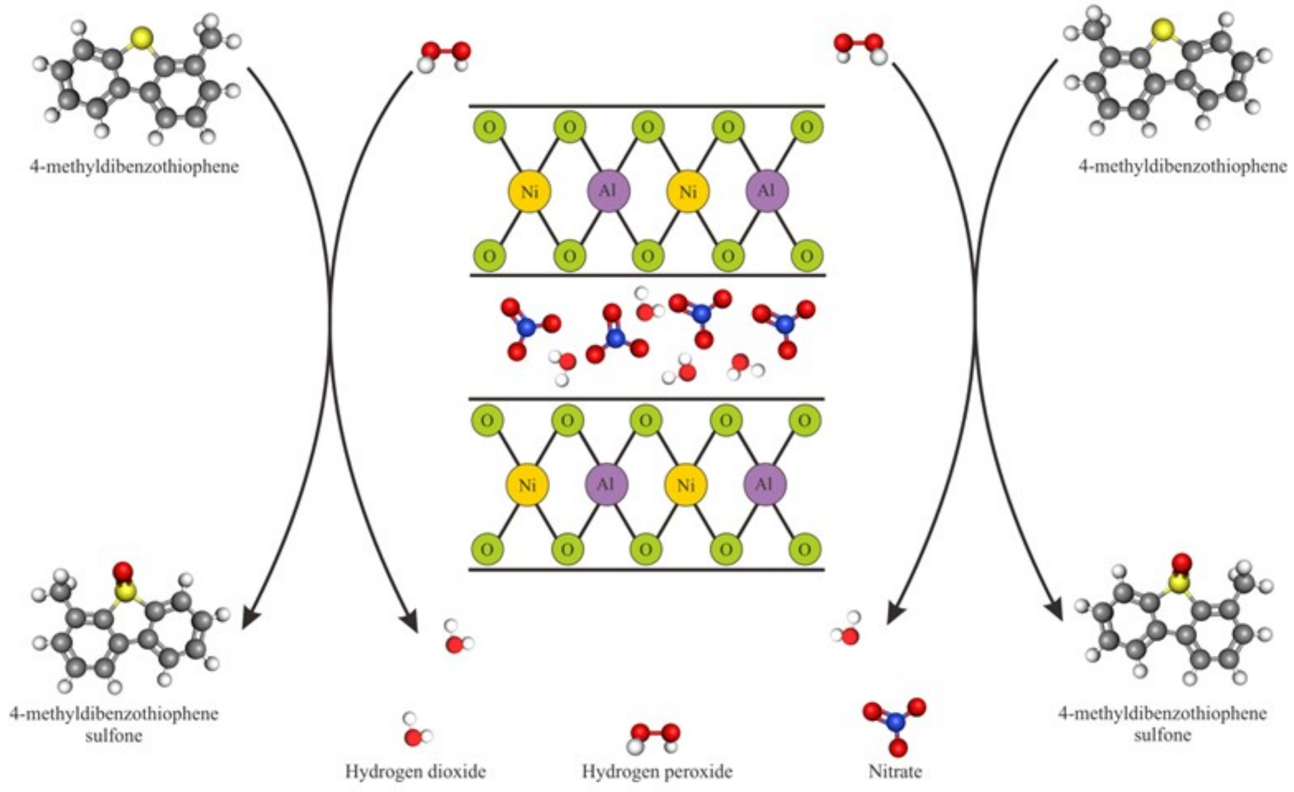

Figure 10. ODS mechanism for 4-MDBT.

CRediT Author Statement

Author Contributions: *N. Ahmad*: Investigation, Writing – Original draft; *R. Rohmatullaili*: Data curation, Software; *Y. Hanifah*: Visualization, Validation; *S. Wibiyan*: Investigation, Software; *A. Amri*: Investigation, Formal Analysis; *A. Wijaya*: Visualization, Formal Analysis; *M. Mardiyanto*: Data curation, Formal Analysis; *R. Mohadi*: Conceptualization, Methodology; *I. Royani*: Validation, Data curation; *A. Lesbani*: Conceptualization, Methodology, Writing – review & editing, Supervision. All authors have read and agreed to the published version of the manuscript.

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