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Research Paper

Synthesis of Zn/Al-ZnO Composite Using Zn/Al-Layered Double Hydroxide for Oxidative Desulfurization of 4-Methyldibenzothiophene

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Abstract
Zn/Al-ZnO composites made from Zn/Al-Layered Double Hydroxide base material and ZnO as a precursor were successfully made in this study. Characterization analysis using SEM-EDS, XRD, and FTIR. The SEM analysis results show the Zn/Al-LDH has a smooth surface, overlapping, and is prone to aggregation, resulting in non-uniform particle size. However, it forms a uniform grain shape. Zn/Al-ZnO have rough surfaces with uniform particle shape and size, and the presence of pores on the particle surface. EDS analysis shows the Zn element which is more abundant in Zn/Al-ZnO. XRD analysis of Zn/Al-LDH showed the hydrotalcite. XRD analysis on ZnO showed the hexagonal wurtzite crystal structure. Zn/Al-ZnO composites at an angle of 2θ show the same peak of the base material and the precursor. FTIR analysis of the composite revealed the presence of O-H groups at wave numbers 3445 cm^{-1}, 1633 cm^{-1}, and 1504 cm^{-1}, indicating the presence of nitrate. Additionally, vibrations at wave numbers 1382 cm^{-1} corresponded to antisymmetric (*v3*) stretching of nitrate, while wave numbers 418 cm^{-1} and 606 cm^{-1} indicated metal-oxygen stretching vibrations. Of all the factors used in the desulfurization of 4-methyldibenzothiophene, Zn/Al-ZnO composites had the highest %conversion rate of both the base material and the precursor. The %conversion values of Zn/Al-ZnO at the time of contact were 99.40%, catalyst dosage 99.38%, solvent 99.10%, and temperature 99.56%, respectively. The catalyst is heterogeneous and reusable for the desulfurization of 4-methyldibenzothiophene.

Keywords
Desulfurization, 4-Methyldibenzothiophene, Zn/Al-Layered Double Hydroxide, ZnAl-ZnO

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1. INTRODUCTION

Crude oil, natural gas, liquefied natural gas, coal, and fossil fuels are widely recognized as the main energy sources to meet the growing global energy demand, representing more than 90% of the overall energy consumption on a global scale (Ahmad et al., 2023a). For numerous decades, individuals across the globe have heavily depended on fossil fuels for energy generation. Industries and transportation, in particular, heavily rely on these fuels to sustain daily operations. Nonetheless, these activities deplete fossil fuel reserves while inevitably contributing to air pollution (Azni et al., 2023).

One of the most toxic components in crude oil, which people use as fuel for a variety of activities, is sulphur, which can be found in various forms such as sulfides, thiophenes, and other compounds. The combustion of sulphur can result in toxic acid rain and photochemical smog, endangering both the ecological environment and human health (Zhu et al., 2020; Chen et al., 2020; Zhang et al., 2019; Smith et al., 2019; Tchalala et al., 2019). Prolonged or excessive exposure to SO_2 can result in respiratory ailments like asthma, emphysema, and chronic bronchitis. Additionally, it can contribute to the development of neurological disorders. SO_2 also irritates the skin and the mucous membranes of the eyes (Han et al., 2018). Moreover, the removal of sulphur compounds from petroleum has the potential to enhance the quality of petroleum-derived fuels and concurrently decrease environmental pollution resulting from the burning of fossil fuels. The elimination of sulphur compounds leads to a substantial reduction in the emission of SO_2 (Anqi, 2023). Sulphur, along with metals, is considered a primary contaminant in crude oil, and it is necessary to decrease their levels in the feed to meet the standard requirements (Tripathi et al., 2019). The content of sulphur in fuel should be below 10 ppm according to the guidelines stated by the United States Environmental Protection Agency and the European (Mahboob et al., 2022). The petroleum industry can effectively eliminate these compounds through appropriate separation techniques.

Separation techniques methods such as adsorptive desulfurization, extractive desulfurization, and oxidative desulfurization are employed in the petroleum industry for the thorough removal of sulphur from fuel in liquid form (Malani et al., 2021). Adsorptive desulfurization, which focuses on reducing sulphur compound levels, encounters difficulties in achieving high selectivity for sulphur removal. Conversely, hydrodesulfurization, another desulfurization technique, requires elevated temperatures and pressures (Abedini et al., 2021). Several transition metal-based catalysts, including Ni (Ahmad et al., 2022c), Mg (Ahmad et al., 2023b), and another catalyst like polyoxometalate (Ahmad et al., 2022a), red mud (Liu et al., 2023) and solvents as catalysts such as ionic liquid (Parhi and Misra, 2023) and alkanol amine (Chandran et al., 2019) can be utilized for catalytic oxidative desulfurization. Iron-based catalysts are highly appealing due to their affordability and the fact that they do not require high temperatures for operation (Bartoli et al., 2022).

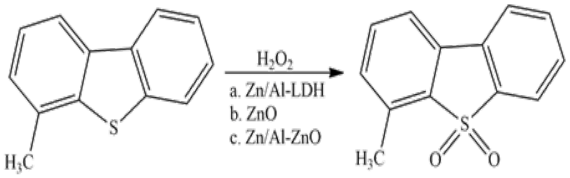

Figure 1. Oxidative Desulfurization Process of 4-Methyl dibenzothiophene by Zn/Al-LDH (a) ZnO (b), and Zn/Al-ZnO (c)

Layered Double Hydroxides (LDH) are a class of clay compounds that are well-suited for the aforementioned purposes (Li et al., 2022). These materials possess a layered structure with a positive charge, and the interlayer spaces are occupied by anions, as defined by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-}$. In this formula, M2+ represents a divalent metal such as Mg^{2+}, Zn^{2+}, Ca^{2+}, etc., and M^{3+} trivalent metal like Al^{3+}, Fe^{3+}, and others. A represents an anion, which can be CO_3^{2-}, NO^{3-}, Cl^{-}, or SO_4^{3-} (Wu et al., 2018). Their remarkable characteristics, including a wide range of chemical compositions, affordability, significant surface area values, excellent thermal stabilities, and high sorption capacities, contribute to the effectiveness of layer double hydroxides (LDHs). Moreover, LDHs possess the ability for structure reconstruction and exhibit efficient regeneration capabilities (Lozano-Lunar et al., 2023). LDH has various advantages due to its capacity to be produced quickly, cheaply, and efficiently (Palapa et al., 2021). The main aim of this study was to exploit the benefits of layered double hydroxide (LDH) and metal-based catalysts in the synthesis of a composite material. The composite material was produced by combining ZnO with Zn/Al-LDH as its base. The ultimate goal was to improve the efficiency of the composite material in desulfurization operations, with a particular emphasis on the successful elimination of 4-methyldibenzothiophene, a sulphur-containing compound. It was expected that this approach would considerably enhance desulfurization efficiency and aid in reducing pollution from sulphur compounds.

Synthesized Zn/Al-ZnO catalysts were used to remove sulphurs from 4-methyldibenzothiophene. Technical term abbreviations were fully explained when first used. The objective of this study was to desulfurize this selected sulfur-containing compound. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) were used to examine the catalysts for effective synthesis. Time variation, catalyst dosage, temperature, solvent option (n-pentane, n-hexane, and n-heptane), heterogeneity test, and catalyst regeneration were involved in the oxidative desulfurization of 4-methyldibenzothiophene. The material's shape, surface characteristics, and the present elements in Zn/Al-ZnO were analyzed through SEM-EDS.

2. EXPERIMENTAL SECTION

2.1 Chemical and Instrumental

Sigma-Aldrich provided 4-methyldibenzothiophene, which was used without additional purification. Hydrogen peroxide (H_2O_2), acetonitrile (CH_3CN), pyridine (C_5H_5N), zinc (II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), n-pentane (C_5H_{12}), n-hexane (C_6H_{14}), n-heptane (C_7H_{16}), aluminum nitrate nonahydrate ($Al(NO_3)_2.9H_2O$), sodium hydroxide (NaOH), and zinc (II) oxide (ZnO) can also be utilized directly without further purification. A Rigaku Miniflex-6000 X-ray diffractometer, a Shimadzu Prestige-21 Fourier transform infrared spectrometer, and Quanta 650 scanning electron microscope were used to examine the material properties. An EMC-18PC-UV UV-Vis spectrophotometer was used to measure the % sulphur conversion.

2.2 Preparation of Zn/Al-Layered Double Hydroxide

The procedure for preparing Zn/Al-layered double hydroxide (LDH) involved the combination of a 50 mL solution containing $Zn(NO_3)_2\cdot6H_2O$ at a concentration of 0.75 M with a 50 mL solution containing $Al(NO_3)_3\cdot9H_2O$ at a concentration of 0.25 M. The resulting mixture was then placed in a shaker and subjected to agitation for 2 hours. To attain a pH level of 10, NaOH were added to the mixture. The mixture was further shaken for 10 hours at a temperature of 80 °C. Following filtration and rinsing with distilled water, the LDH mixture was dried by placing it in an oven set at 110 °C, and subsequently, the weight of the LDH was measured (Lesbani et al., 2021).

2.3 Preparation of Zn/Al-ZnO Composite

The Zn/Al-ZnO is produced by dissolving 0.75 M $Zn(NO_3)_2\cdot 6H_2O$ and 0.25 M $Al(NO_3)_2.9H_2O$ in 100 mL of distilled water and stirring the solution for 2 hours. A 2:1 mixture of NaOH was gradually added until the pH reached 10. The mixture was then agitated for 17 hours at 70°C. The solution was then agitated for 3 hours with a 1:1 ratio of ZnO. The mixture was added 150 mL of 0.37 M NaOH and stirred at

70°C for 17 hours. The mixture was then filtered, dried, and calcined at 300°C for 7 hours (Yuliasari et al., 2022).

2.4 Oxidative Desulfurization Method

A 100 mL two-necked flask equipped with a condenser was used for the oxidative desulfurization reaction and stirred magnetically at 300 rpm. 4-methyldibenzothiophene with an initial concentration of 500 ppm and 30 mL of n-hexane used as solvent was added to the flask. After that, 0.25 g of Zn/Al-LDH, ZnO, and Zn/Al-ZnO composite catalysts were added to the mixture. To enhance the oxidation process, 1 mL of hydrogen peroxide was added as an oxidant, while 3 mL of acetonitrile was included as an extraction agent. The reaction was carried out at 50 °C, and the reaction was measured periodically every 10 minutes. The percentage of sulphur conversion of 4-methyldibenzothiophene was calculated using the following Equation 1.

$$\%\text{ Conversion of 4-MDBT} = \frac{(C_0 - C_f)}{C_0} \times 100\% \qquad (1)$$

The symbol C_0 indicates the initial concentration while C_f indicates the final concentration of the compound. These initial and final concentration values are used to calculate the sulphur conversion value of the desulfurization process. The parameters used in the desulfurization process were time variation (10-60 minutes), catalyst dosage (0.05-1 gram), temperature (30-50 °C), solvent type (n-pentane, n-hexane, and n-heptane), heterogeneity test, and catalyst regeneration. To see how the catalyst performed when reused, the desulfurized mixture was first centrifuged after 1 hour to recover the Zn/Al-LDH and its composite. After separation, the catalyst was washed using n-hexane. Then, the catalyst was dried and reused for desulfurization of 4-methyldibenzothiophene.

2.5 Heterogeneity Test

In the heterogeneous test, 500 ppm of 4-methyldibenzothio phene in 30 mL of n-hexane was used in the desulfurization process. The reaction was carried out for 10 minutes at a constant temperature of 50 °C. After the reaction, the catalyst was separated from the 4-methyldibenzothiophene solution and continued for 20 to 30 minutes, maintaining the temperature at 50 °C. An analysis was then conducted to determine how the sulphur conversion proceeded in the absence of the catalyst during the desulfurization process of the 4-methyldibenzothiophene.

3. Results and Discussion

The surface morphology of the catalyst can be seen in Figure 2. The surface morphology of Zn/Al-LDH in Figure 2 (a) explains that the surface shape of Zn/Al-LDH is smooth, piled up, and can aggregate into larger particles so that the size of the particles is not uniform, but the uniform shape forms grains. The surface morphology of Zn/Al-ZnO in Figure 2 (b) is rough and has a uniform particle shape and size and there are pores on the particle surface.

Table 1. Weight Percentage by EDS Analysis of Zn/Al-LDH and Zn/Al-ZnO

Element	Weight Percentage (Wt %)	
	Zn/Al-LDH	ZnAl-ZnO
O	36.8	21.4
Zn	32.7	54.4
C	14.7	12.5
Na	6.6	7.8
Al	3.7	4.0

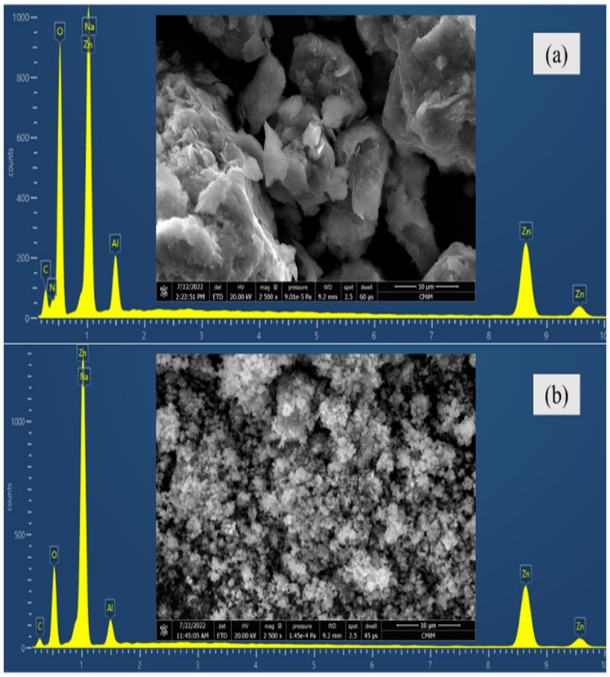

Figure 2. Surface Morphology and EDS Spectrum of Zn/Al-LDH (a), and Zn/Al-ZnO (b)

Table 1 explains that ZnAl-LDH has a weight percentage of O (36%), Zn (32.7%), C (14.7%), Na (6.6%), and Al (3.7%). In the Zn/Al-ZnO, composite the Zn element has increased in weight percentage from the Zn/Al-LDH base material with a weight percentage of 32.7% to 54.4% at the Zn/Al-ZnO. These results indicate that the synthesis of Zn/Al-ZnO composites was successfully carried out.

In Figure 3, the XRD diffraction patterns of Zn/Al-LDH, ZnO, and Zn/Al-ZnO are presented. Figure 3 (a) displays the XRD analysis of Zn-Al LDH, exhibiting distinct diffraction peaks at 2θ values of 11.52°, 23.25°, 34.45°, 39.11°, 46.53°, 59.93°, and 61.67°. These peaks correspond to the crystallographic planes (003), (006), (009), (015), (018), (110), and (113) of hydrotalcite-like LDH (JCPDS no. 38–0486). The presence of these well-defined peaks indicates the presence of crystalline structures in the Zn/Al-LDH sample (Mallakpour et al., 2023). Figure 3 (b) exhibits diffraction peaks at 31.76°, 34.42°, 36.26°, 47.54°, 56.56°, 62.82°, 66.38°, 67.92°, 69.04°, 72.82°, and 76.94°, confirming the hexagonal wurtzite crystal structure of ZnO. These peaks correspond to the wurtzite phase of ZnO (JCPDS No. 36-1451) (Zhang et al., 2021). The congruent 2θ angle values observed for the Zn/Al-ZnO in Figure 3 (c) composites, obtained from the base material Zn/Al-LDH and their ZnO precursor, indicate the successful synthesis of the composite materials.

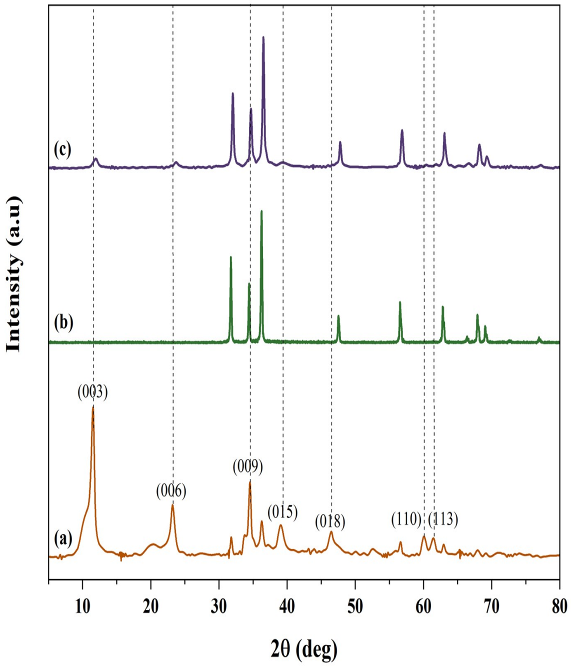

Figure 3. XRD Diffraction of Zn/Al-LDH (a), ZnO (b), and Zn/Al-ZnO (c)

FTIR analysis of the catalyst can be seen in Figure 4. The peak at wave number 3445 cm^{-1} indicates the O-H stretching band of hydroxyl groups and H_2O molecules (Priatna et al., 2023). Zn/Al-LDH is capable of incorporating nitrate ions into its structure, which is evidenced by the presence of characteristic bands in the infrared spectrum. Specifically, bands appear at approximately 1633 cm^{-1} and 1504 cm^{-1}, indicating the presence of H_2O bending vibration (Wibiyan et al., 2023). The peak at approximately 1382 cm^{-1} corresponds to the antisymmetric stretching vibration ($v3$) of nitrate anion. These spectral features confirm the incorporation of nitrate ions within the Zn/Al-LDH structure (Mahjoubi et al., 2017). The structure of LDH is characterized by the presence of positively charged metal cations, such as Zn^{2+} and Al^{3+}, that are coordinated with negatively charged hydroxyl and oxide ions. The bonding between the metal cations and oxygen atoms can be observed in the FTIR spectrum, where specific bands appear. In particular, the metal-oxygen stretching vibrations are reflected by bands at approximately 418 cm^{-1} and 606 cm^{-1}. These bands provide evidence of the metal-oxygen bonding within the LDH structure (Intachai et al., 2021).

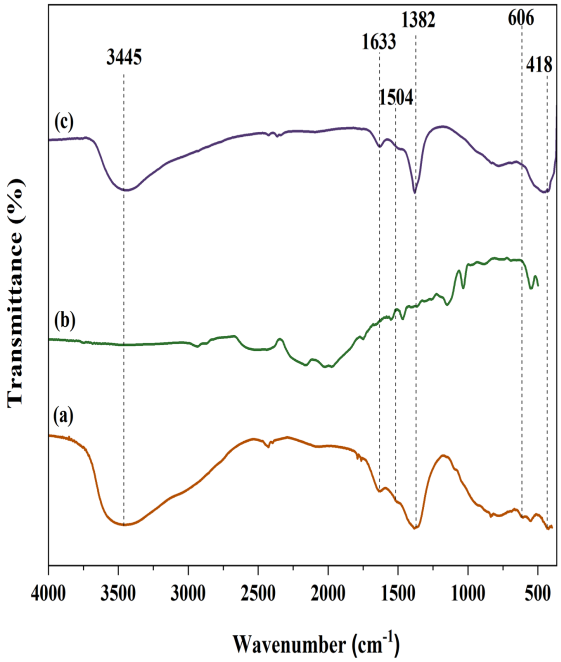

Figure 4. FTIR Spectrum of Zn/Al-LDH (a), ZnO (b), and Zn/Al-ZnO (c)

This heterogeneity study aims to find out the heterogeneity of the catalysts used in this study including Zn/Al-LDH, ZnO, and Zn/Al-ZnO catalysts. Heterogeneous catalysts have distinct advantages, with ease of separation and regeneration being key benefits. These catalysts exist in a different phase than the reactants and products, enabling simple separation through physical processes like filtration or decantation. Once separated, the catalyst can be reused, promoting cost-effectiveness and environmental sustainability. Moreover, heterogeneous catalysts can be regenerated through methods like heat treatment, washing, or surface reactivation, restoring their catalytic activity and extending their lifespan. The capacity to readily separate and regenerate heterogeneous catalysts makes them highly valuable in various industrial applications (Pei et al., 2023; Houda et al., 2018; Polikarpova et al., 2020). The heterogeneity test was conducted for 10 minutes at 50 °C. Afterward, the catalyst was separated from the 4-methyldibenzothiophene solution. The reaction process was continued for 20-30 minutes in the absence of the catalyst. Then the process was observed and showed that the percentage of sulphur conversion increased at 10 minutes, then after the catalyst was separated from the 4-methyldibenzothiophene solution the reaction proceeded linearly without any change in the percentage value of sulphur conversion indicating that the system showed heterogeneity which can be seen in Figure 5.

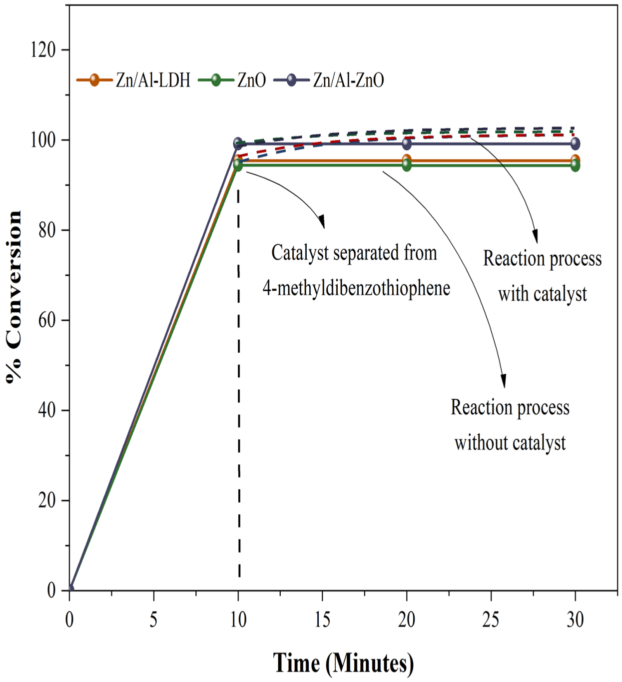

Figure 5. Heterogeneity Test of Catalyst Zn/Al-LDH, ZnO, and Zn/Al-ZnO

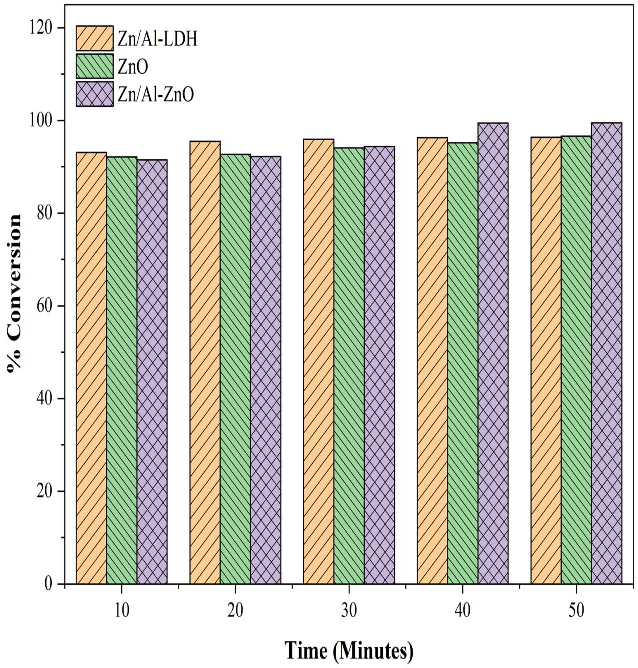

Figure 6. Oxidative Desulfurization of 4-Methyldibenzothio phene by Catalyst Zn/Al-LDH, ZnO, and Zn/Al-ZnO on Re action Time Effect

The desulfurization rate increases with the extension of the reaction time. As the reaction time increases, the reaction reaches equilibrium so that the reaction runs linearly (Lin et al., 2020). The graph effect of time reaction on oxidative desulfurization of 4-methyldibenzothiophene can be seen in Figure 6. The optimum time for Zn/Al-LDH, ZnO, and Zn/Al-ZnO catalysts to desulfurize 4-methydibenzotiophene minutes was 40. The %conversion values from the largest to the smallest are Zn/Al-ZnO (99.40%), Zn/Al-LDH (96.30%), and ZnO (95.20%), respectively.

The effect of catalyst dosage on oxidative desulfurization of 4-methyldibenzothiophene can be seen in Figure 7. In the absence of a catalyst, the desulfurization reaction rate is nearly zero. As the catalyst dosage is increased, the desulfurization rate progressively rises until it reaches its peak value. However, if the catalyst dosage is further increased beyond this optimal point, the reaction rate starts to decline. This decrease occurs because an excessive amount of catalyst saturates the system, leading to inadequate desulfurization. At this point, there are no more available catalyst surfaces to facilitate further desulfurization reactions (Chang et al., 2021). The optimum catalyst dosage for desulfurizing 4-methyldibenzothiophene of Zn/Al-LDH and ZnO was at 0.25 grams, while that of Zn/Al-ZnO catalysts was at 0.1 grams. Zn/Al-ZnO catalysts require less dose to reach the optimum point in desulfurizing 4-methyldibenzothiophene, indicating the success of the composite synthesis made because it has a better ability to desulfurize 4-methyldibenzothiophene. The %conversion values from largest to smallest are Zn/Al-ZnO (99.38), Zn/Al-LDH (96.70%), and ZnO (94.61%), respectively.

The solvents n-pentane, n-hexane, and n-heptane were used in this study to determine which solvent is more suitable for the desulfurization process of 4-methyldibenzotiophene. The effect of solvent on oxidative desulfurization of 4-methyl dibenzothiophene can be seen in Figure 8. In the desulfurization of 4-methyldibenzothiophene, it was found that the n-hexane solvent demonstrated superior effectiveness compared to n-pentane and n-heptane solvents when used with Zn/Al-LDH and Zn/Al-ZnO catalysts. The %conversion values obtained using n-hexane were 96.70% and 99.10%, respectively. However, in the case of the ZnO catalyst, the best solvent for desulfurization was found to be n-pentane, yielding a %conversion value of 95.94%. The n-hexane solvent is considered a more suitable solvent for the desulfurization of 4-methyldibenzohiophene as it involves selective extraction or chemical reaction to remove the sulphur contained in the 4-methyldibenzohiophene compound (Lesbani et al., 2017). The low polarity and non-reactive nature of n-hexane allow for efficient extraction or separation of 4-methyldibenzothiophene (Zhuang et al., 2018). Boiling point n-pentane lower than n-hexane and lower solubility for sulphur compounds compared to n-hexane may affect its effectiveness in the desulfurization of 4-methyldibenzothiophene. The different extraction efficiency or reaction kinetics are due to the higher

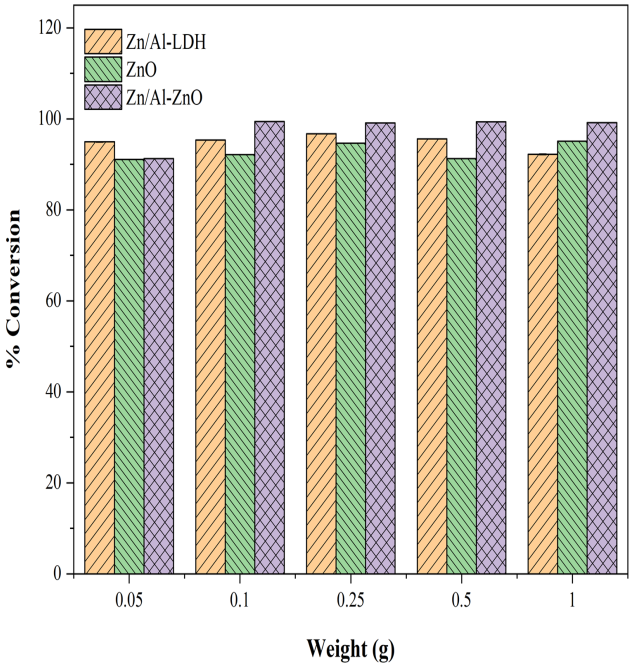

Figure 7. Oxidative Desulfurization of 4-Methyldibenzothio phene by Catalyst Zn/Al-LDH, ZnO, and Zn/Al-ZnO on Ca talyst Dosage Effect

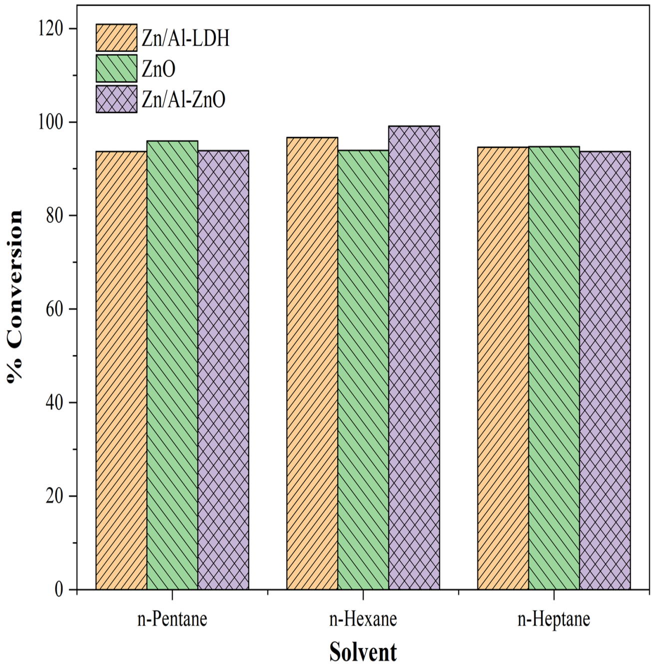

Figure 8. Oxidative Desulfurization of 4-Methyldibenzothio phene by Catalyst Zn/Al-LDH, ZnO, and Zn/Al-ZnO on Sol vent Effect

boiling point of n-heptane and slightly higher polarity than n-hexane. The solvent n-hexane is more suitable for the desulfurization of 4-methyldibenzothiophene due to its optimal balance of low polarity, good solvent properties, and compatibility with sulphur compounds, although n-pentane and n-heptane can also be used in the desulfurization process of 4-methyldibenzothiophene (Privat et al., 2010; Rohman, 2014; Ahmad et al., 2022b). This is further supported by the data from the results of this study.

Figure 9 explains the effect of temperature on the %conversion value of 4-methyldibenzothiophene desulfurization. The optimum temperature for the Zn/Al-LDH catalyst was 30 °C, with a %conversion of 96.70%. For the ZnO catalyst, the optimum temperature was found to be 40 °C, achieving a conversion percentage of 95.62%. Zn/Al-ZnO catalysts demonstrated exceptional performance at 40 °C, with conversion percentages of 99.56%. These findings highlight the significance of temperature in optimizing the desulfurization process for 4-methyldibenzothiophene using different catalysts. This finding indicates that increasing the temperature during the desulfurization process leads to higher %conversion values, implying enhanced efficiency in the desulfurization of 4-methyldibenzothiophene (Han et al., 2020). The %conversion values in the range of 90% and above indicate that the desulfurization process of 4-methyldibenzothiophene with these catalysts does not necessarily require high temperatures to achieve optimal conditions. This suggests that effective desulfurization can be achieved at relatively moderate temperatures, ensuring energy efficiency and practical applicability of these catalysts (Akopyan et al., 2020).

The catalyst reuse test was conducted to find out how good or can the catalysts Zn/Al-LDH, ZnO, and Zn/Al-ZnO be reused towards the desulfurization of 4-methyldibenzothio phene. After the first use and each cycle, the catalyst separated from 4-methyldibenzothiophene was reused repeatedly three times with n-hexane solvent with an ultrasonic system and measured the %conversion which can be seen in Figure 10. From the data obtained, the reuse of Zn/Al-LDH, ZnO, and Zn/Al-ZnO catalysts obtained effective results with the %conversion value decreasing by a small difference and the %conversion still in the 90% range and above after the third use. In industrial applications, achieving a rapid separation and efficient recycling of the catalyst after a catalytic reaction is crucial. These requirements play a significant role in reducing production costs and minimizing waste generation. By enabling quick and effective catalyst separation, the process becomes more streamlined and cost-effective. Additionally, efficient catalyst recycling ensures the utilization of available resources and reduces the environmental impact associated with catalyst waste. Thus, the ability to rapidly separate and recycle the catalyst is highly important for optimizing efficiency, cost-effectiveness, and sustainability in industrial processes (Miceli et al., 2021).

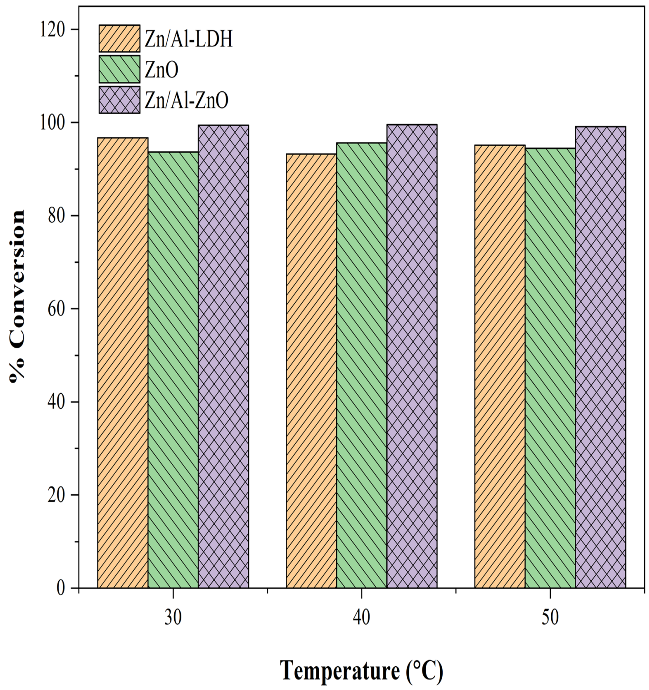

Figure 9. Oxidative Desulfurization of 4-Methyldibenzothi ophene by Catalyst Zn/Al-LDH, ZnO, and Zn/Al-ZnO on Temperature Effect

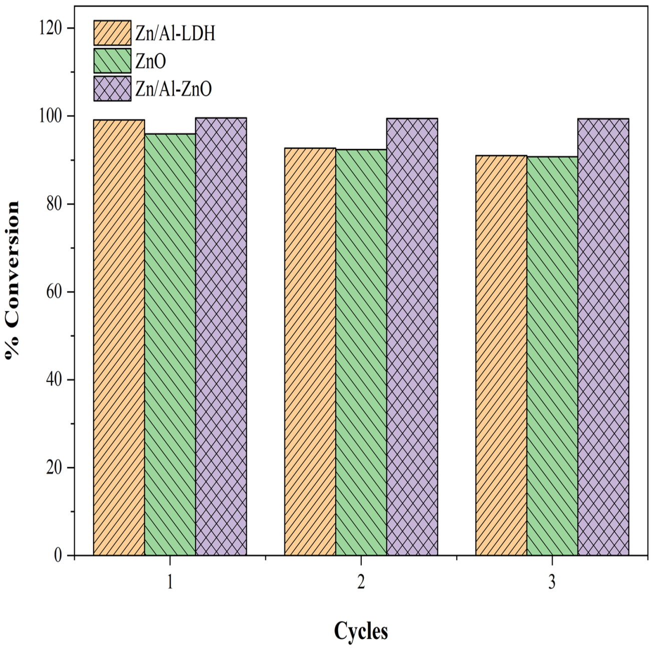

Figure 10. Reusability of Catalyst on Oxidative Desulfurization of 4-Methyldibenzothiophene

4. CONCLUSION

This research successfully synthesized Zn/Al-ZnO from Zn/Al-LDH base material with ZnO as the precursor. The success of this synthesis can be seen from the results of characterization analysis XRD, and surface morphology from SEM analysis, and element presence analysis from EDS. FTIR characterization results also support the success of the synthesis in this study. Zn/Al-ZnO composites have a better ability than the base material and its precursor towards the desulfurization of 4-methyldibenzothiophene seen from the %conversion value which is greater than all factors used in this study such as reaction time, catalyst dosage, solvent type, and reaction temperature. The catalyst used is also heterogeneous which can be easily separated from 4-methyldibenzothiophene so that it can be reused for the desulfurization of 4-methyldibenzothiophene. With the reusability, the effectiveness of the catalyst to desulfurize 4-methyldibenzothiophene is still very good after being used three times.

5. ACKNOWLEDGEMENT

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