Research Article

Catalytic Oxidative Desulfurization of Dibenzothiophene Utilizing Composite Based Zn/Al Layered Double Hydroxide

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Abstract

In this study, the $Zn/Al-TiO_2$ and Zn/Al-ZnO was successfully synthesized. The catalysts were characterized by X-ray Diffraction (XRD), Fourier Transform Infra Red (FTIR), and Scanning Electron Microscope—Energy Dispersive X-ray Spectroscopy (SEM-EDS). The typical diffraction peaks of Zn/Al-LDH, TiO_2, and ZnO still appear in the $Zn/Al-TiO_2$ and Zn/Al-ZnO composites, indicating that the composite preparation did not change the form of precursors. FTIR spectra of $Zn/Al-TiO_2$ and Zn/Al-ZnO showed absorption band at 3448, 1627, 1381, 832, 779, and 686 cm^{-1}. The catalysts have an irregular structure where the percent mass of Ti and Zn on the composite at 10.6% and 55.6%, respectively. The acidity of Zn/Al-LDH composite increased after being composed with TiO_2 and ZnO. The percentage conversion dibenzothiophene on Zn/Al-ZnO, $Zn/Al-TiO_2$, ZnO, Zn/Al-LDH, and TiO_2 was 99.38%, 96.01%, 95.36%, 94.71%, and 91.92%, respectively. The heterogeneous systems of catalytic reaction was used for reusability. After 3 cycles catalytic reactions at 50 °C for 30 min, the percentage conversion of dibenzothiophene on Zn/Al-LDH, TiO_2, ZnO, $Zn/Al-TiO_2$, and Zn/Al-ZnO were 77.42%, 83.19%, 82.34%, 84.91%, and 89.71 %, respectively. The composites of $Zn/Al-TiO_2$ and Zn/Al-ZnO have better reusability test than Zn/Al-LDH, TiO_2, and ZnO, which proofing that $Zn/Al-TiO_2$ and Zn/Al-ZnO have a stable structure.

1. Introduction

Sulfur oxide (SOx) emissions from fossil combustion are recognized as one of the primary sources of air pollution [1]. The burning of sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and their derivatives, in fossil fuels into the atmosphere gradually causes acid rain, fog, smog, and other environmental problems [2]. As a result, the desulfurization of fuels has attracted much attention worldwide. Under strict regulations, it is necessary to reduce the sulfur content of the fuel below 10 ppm [3]. Therefore, strategies must be taken to remove sulfur compounds from fossil

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fuels. Hydrodesulfurization (HDS) is a conventional technique for reducing the sulfur component of liquid fuels [4]. However, the HDS technique is inefficient because it requires extreme operational conditions operating at high temperatures (320-380 ^{o}C), high pressures (3-7 MPa), and requires large amounts of H_2 [5,6].

Therefore, an environmentally friendly desulfurization system is needed. Several desulfurization technologies for benzothiophene compounds and their derivatives have been carried out, such as extractive desulfurization (EDS) [7], biodesulfurization (BDS) [8], photocatalytic desulfurization [9], desulfurization adsorptive [10], and oxidative desulfurization (ODS) [11]. Among these methods, oxidative desulfurization (ODS) by the catalyst is a promising strategy for the degradation of sulfur components in fuels. Oxidative desulfurization offers several advantages: no H_2 consumption and less extreme conditions (low atmospheric pressure and low temperature). ODS has two processes: oxidation and extraction [12,13]. In the presence of appropriate oxidants and catalysts, ODS includes several oxidative reactions that convert organosulfur to suitable sulfoxides and/or sulfones [14]. After that, the oxidized compounds are separated from the fuel through solvent extraction or adsorption [15]. Oxidative desulfurization of dibenzothiophene is shown in Figure 1.

A suitable catalyst can increase the oxidant activity in the ODS process. Several previously reported catalysts include polyoxometalate, metal oxides, titanate nanotubes, and layered double hydroxide. A suitable catalyst is a catalyst that can be made quickly, at a low cost, and with high efficiency [16]. In addition, the catalyst's separation and regeneration dramatically influence the type of catalyst. One of the catalysts that have the potential to be used is layered double hydroxide (LDH). LDH can be made quickly, at a low cost, and highly efficient [17]. In the catalytic process, LDH has been used for water remediation [18], n-heptane hydroconversion [19], and biodiesel production [20]. However, the disadvantage of LDH is easy to exfoliate [21]. To cover the disadvantage, it is composited with a metal oxide to strengthen the material. In the catalyst process, composit-
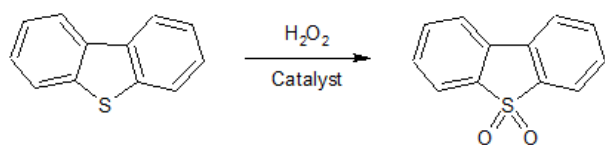
ed ZnAl-TiO$_2$/ZnO has been used for condensation of furfural [22], photocatalytic [23], and esterification catalysts [24]. The composited ZnAl-TiO$_2$/ZnO for oxidative desulfurization of dibenzothiophene not have been reported. This research is essential for developing LDH material in the desulfurization process. LDH can be made quickly, low cost, and highly efficient. However, the disadvantage of LDH is easy to exfoliate. The LDH is composed with a metal oxide to cover the disadvantage and strengthen the composite material. The composited ZnAl-TiO$_2$/ZnO for oxidative desulfurization of dibenzothiophene not have been reported.

In this study, Zn/Al-TiO$_2$ and Zn/Al-ZnO composites were prepared as catalysts. Characterization of catalysts used XRD, FTIR, and SEM-EDS to know the successful preparation of the catalysts. Optimizing the oxidative desulfurization of DBT was carried out with variations in time, UV-Vis spectrum, the catalyst dosage, temperature, solvent (n-pentane, n-hexane, and n-heptane), acidity test, heterogeneity test, and reusability of catalysts.

2. Materials and Methods

2.1 Materials

Analytical grade hydrogen peroxide (H_2O_2, Smart-Lab, MW= 34.01 g/mol), acetonitrile (CH_3CN, Merck, MW= 41.05 g/mol), pyridine (C_5H_5N, Merck, MW= 79.1 g/mol), zinc (II) nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, Sigma-Aldrich, MW= 297.49 g/mol), n-pentane (C_5H_{12}, Merck, MW= 72.15 g/mol), n-hexane (C_6H_{14}, Merck, MW= 86.18 g/mol), n-heptane (C_7H_{16}, Merck, MW= 100.21 g/mol), aluminum nitrate nonahydrate ($Al(NO_3)_2.9H_2O$, Sigma-Aldrich, MW= 375.13 g/mol), sodium hydroxide (NaOH, Sigma-Aldrich, MW= 40 g/mol), titanium(IV) oxide (TiO$_2$, Merck, MW= 79.87 g/mol), and zinc(II) oxide (ZnO, Merck, MW= 81.38 g/mol) were also directly used without further purification. Dibenzothiophene ($C_{12}H_8S$, MW= 184.26 g/mol) was obtained from Sigma-Aldrich. Pure water was supplied from PT. Bratachem, Indonesia.

2.2 Catalyst synthesis

2.2.1 Synthesis of Zn/Al Layered double hydroxide

Synthesis of Zn/Al-Layered double hydroxide was conducted: 0.75 M zinc (II) nitrate hexahydrate and 0.25 M aluminum nitrate nonahydrate dissolved in 100 mL of pure water, stirred for 10 min. Then slowly added 2 M sodium hydroxide to pH 8, stirred for 4 h at 70 ^{o}C,

Figure 1. Oxidative desulfurization of dibenzothiophene

filtered, and dried. The mass of Zn/Al-Layered double hydroxide was obtained 3.7 g.

2.2.2 Preparation of Zn/Al composite

Preparation of Zn/Al composite was conducted: 0.75 M zinc(II) nitrate hexahydrate and 0.25 M aluminum nitrate nonahydrate dissolved in 100 mL of pure water, stirred for 10 min. Then slowly added 2 M sodium hydroxide to pH 8. The mixture was stirred for 4 h at 70 °C, then added 3.7 g of TiO2/ZnO (ratio Zn/Al and metal oxide 1:1), and shaken for 3 h. The mixture was added 150 mL 0.37 M sodium hydroxide, shaken for 4 h at 70 °C, filtered, dried, and then calcinated at 300 °C for 7 h [25].

2.3 Characterization Methods

Characterization of the materials, instrumentation, such as X-Ray Diffractometer (Rigaku Miniflex-6000), UV-Vis Spectrophotometer (EMC-18PC-UV), Fourier Transfer Infra-Red (Shimadzu Prestige-21), and Scanning Electron Microscope Energy Dispersive Spectrometer (Quanta 650).

2.4 Oxidative Desulfurization Method

Dibenzothiophene with a concentration of 500 ppm was prepared in n-hexane and transferred to a two-pronged catalytic reaction flask. The flask is connected to a condenser to prevent the evaporation of n-hexane. 0.25 g Catalysts (Zn/Al-Oxide) followed by adding 1 mL of 30% hydrogen peroxide. The reaction was observed per 10 minutes time interval through extraction with acetonitrile followed by measuring using a UV-Visible spectrophotometer at 235 nm. The percentage conversion of DBT followed the equation (1):

$$\% \text{ Conversion of } DBT = \frac{(C_0 - C_f)}{C_0} x100 \qquad (1)$$

where, C_0 and C_f and are the initial and final concentrations of DBT, respectively.

The process of optimizing the oxidative desulfurization of DBT was carried out with variations in time (10-60 min), UV-Vis spectrum (220-250 nm), the dosage of catalyst (0.05-1.00 g), temperature (30-50 °C), solvent (n-pentane, n-hexane, and n-heptane), acidity test.

2.5 Heterogeneity Test

Heterogeneity test to determine homogeneous or heterogeneous catalysts. The heterogeneity test was carried out by desulfurizing DBT at 50 °C for 10 min, and the catalyst and DBT solution was separated. DBT solution continued with the desulfurization process for 20-30 min.

2.6 Reusability of catalyst

Reusability of catalyst is carried out by centrifugation of the reaction mixture after 1 h to recover the Zn/Al-oxide catalyst. After each cycle, the catalyst is recovered, dibenzothiophene desorbed using ultrasonic with n-hexane as a solvent, dried, and reused in oxidative desulfurization.

3. Results and Discussion

XRD powder diffraction of Zn/Al-LDH, TiO2, ZnO, Zn/Al-TiO2, and Zn/Al-ZnO is shown in Figure 2. XRD peaks of Zn/Al-LDH were analyzed from JCPDS No. 138-0486 [26]. Zn/Al-LDH peaks were detected at $2\theta = 10.29°$ (003), $20.07°$ (002), $34.02°$ (311), and $60.16°$ (013) (see Figure 2a). The diffraction peaks at $2\theta = 10.29°$ (003), and $60.16°$ (013) indicate crystal planes of Zn/Al-LDH [27]. Figure 2b shown diffraction of TiO2 at $2\theta = 25.59°$ (101), $37.09°$ (004), $48.16°$ (200), $54.03°$ (211), $55.26°$ (105), and $62.29°$ (204). Figure 2c shown diffraction of ZnO at $2\theta = 31.75°$ (100), $34.41°$ (002), $36.24°$ (101), $47.52°$ (002), $56.56°$ (110), and $62.84°$ (103). TiO2 and ZnO followed JCPDS No. 73-1764 and 36-1451, respectively [28]. The typical diffraction peaks of Zn/Al-LDH, TiO2, and ZnO still appear in the Zn/Al-TiO2 and Zn/Al-ZnO composites, indicating that the composite preparation did not change the form of precursors (see Figures 2d and 2e).
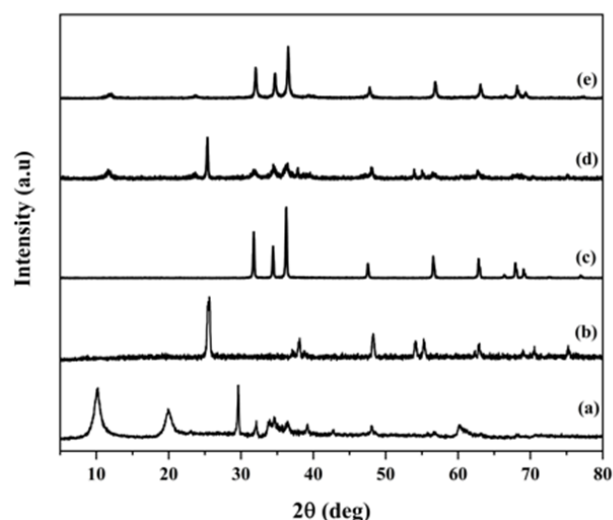

Figure 2. XRD powder diffraction of Zn/Al LDH (a), TiO2 (b), ZnO (c), Zn/Al-TiO2 (d), and Zn/Al-ZnO (e)

FTIR spectra of Zn/Al-TiO$_2$ and Zn/Al-ZnO absorption band at 3448, 1627, 1381, 832, 779, and 686 cm^{-1} (see Figure 3d and 3e). An absorption band at 3448 cm^{-1} was the O–H stretching vibrations in the hydroxyl layer [29]. 1627 and 1381 cm^{-1} as H–O–H and NO$_3^-$ stretching from Zn/Al-LDH [30]. The peaks at 832, 779, and 686 cm^{-1} can be assigned metal oxide in Zn/Al-LDH, TiO$_2$, and ZnO [31].

Figure 4 shows the morphology and EDS of Zn/Al-LDH, Zn/Al-TiO$_2$, and Zn/Al-ZnO. SEM image investigated the morphology of catalysts at 5000 times magnification. The catalysts have an irregular structure. EDS analysis in Table 1 shows the Zn, Al, Ti, and O atoms percentages. The Ti atom appears after composing into Zn/Al-TiO$_2$ composite, while %wt Zn atoms increase after being composed into Zn/Al-ZnO composite. The percent mass of Ti atom at 10.6%, while atom ZnO was from 41.2% to 55.6% after the preparation of the composite. Thus, the preparation of Zn/Al-TiO$_2$ and Zn/Al-ZnO has succeeded.

The acidity test was carried out using the gravimetric method with pyridine as the adsorbate base. The results of the determination of the acid site for each catalyst are shown in

Table 2. Zn/Al-LDH increased after being composed with TiO$_2$ and ZnO. the acidity of Zn/Al-LDH, TiO$_2$, ZnO, Zn/Al-TiO$_2$, and Zn/Al-ZnO were 0.399, 0.296, 0.714, 0.754, and 0.798 mmol/gram, respectively. The increase in the acidity of Zn/Al-LDH, because it has been reduced, tends to lack electrons so that it has a higher ability to absorb pyridine. Acid sites of catalysts are polyacid to convert DBT into DBT-sulfone [32,33].

Reaction time is one of the most influential factors in the desulfurization of dibenzothiophene. Figure 5 shows the profile of oxidative desulfurization by time-based double hydroxide catalysts. The increment reaction time increases the conversion of dibenzothiophene in catalysts. In line with this result, Ja'fari *et al.* [34] explained that increasing reaction time increases efficiency due to better interaction between two immiscible phases. The percentage conversion dibenzothiophene on Zn/Al-ZnO, Zn/Al-TiO$_2$, ZnO, Zn/Al-LDH, and TiO$_2$ was

Table 1. EDS characterization of catalysts

Element	Zn/Al-LDH (%wt)	Zn/Al-TiO$_2$ (%wt)	Zn/Al-ZnO (%wt)
Zn	41.2	10.7	55.6
Al	7.2	1.7	4.2
Ti	-	10.6	-
O	38.9	36.1	22.4

Table 2. The acidity characterization of the catalyst by pyridine adsorption

Catalyst	Acidity (mmol/g)
Zn/Al-LDH	0.399
TiO$_2$	0.296
ZnO	0.714
Zn/Al-TiO$_2$	0.754
Zn/Al-ZnO	0.798
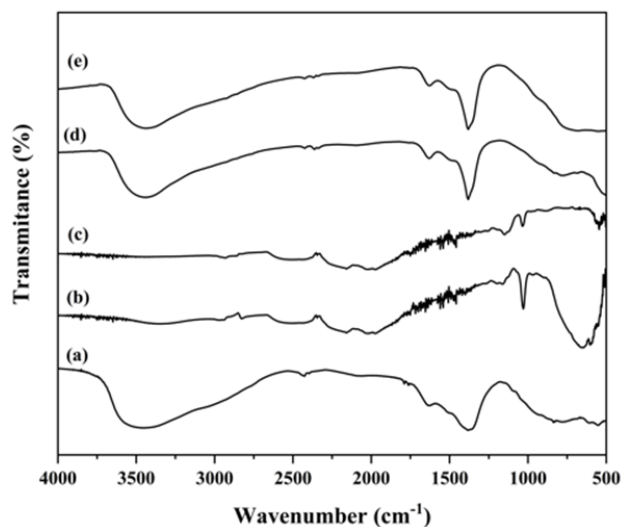
Figure 3. FTIR spectrum of Zn/Al LDH (a), TiO$_2$ (b), ZnO (c), Zn/Al-TiO$_2$ (d), and Zn/Al-ZnO (e)
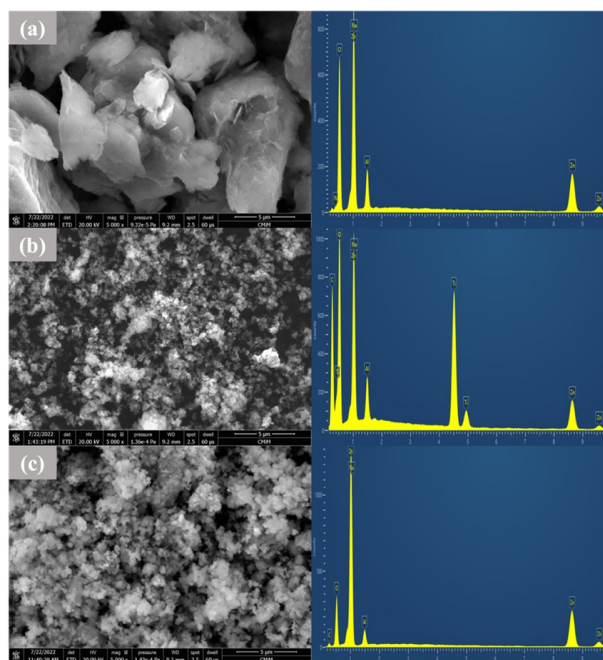

Figure 4. Morphology of Zn/Al-LDH (a), Zn/Al-TiO$_2$ (b), and Zn/Al-ZnO (c)

99.38%, 96.01%, 95.36%, 94.71%, and 91.92%, respectively. The optimum reaction time was chosen at 30 min. The reaction time in this study is relatively fast compared to other oxidative desulfurization. Desulfurization of dibenzothiophene using catalysts CoFeMo-MMO, FeNiMo/Al_2O_3, and MoO$_3$/V$_2$O$_5$/MCM-41 at time 3 h, 2 h, and 75 min, respectively [15,35,36].

Figure 6 shows the UV-Vis spectrum of oxidative desulfurization of dibenzothiophene. The maximum wavelength of dibenzothiophene is 235 nm. The absorbance of dibenzothiophene
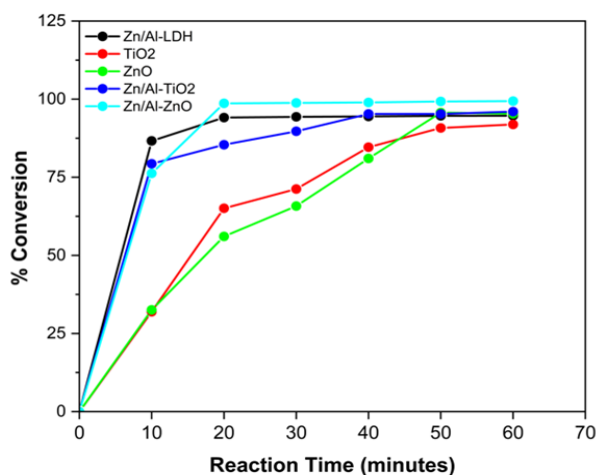

Figure 5. Profile of oxidative desulfurization by time-based layered double hydroxide catalysts

decreased with increasing reaction time. H_2O_2, as an oxidizing agent, is an essential factor in oxidative desulfurization for converting dibenzothiophene to sulfones [37,38]. At 30 min, conversion of DBT >90%, with the most significant reduction indicated by Zn/Al-ZnO. The extraction uses acetonitrile to remove oxidized sulfur compounds [39].

The effect of catalyst dosage on oxidative desulfurization of dibenzothiophene shows in Figure 7. The effect of catalyst dosage was studied for the initial concentration of dibenzothiophene 500 ppm at 50 °C for 30 min. The weight variations of the catalyst used were 0.05, 0.1, 0.25, 0.5, and 1 g. The most effective catalyst weight variation for Zn/Al-LDH, TiO$_2$, ZnO, Zn/Al-TiO$_2$, and Zn/Al-ZnO was 0.5 g, 0.25 g, 0.25 g, 0.1 g, and 0.05 g, respectively. The increment in dosage increases the catalytic site but also increases competition with oxidant molecules [40,41].

The reaction temperature dramatically affects the physical and chemical properties of the dibenzothiophene conversion [42]. Based on Figure 8, oxidative desulfurization of dibenzothiophene at 50 °C is faster than 30-40 °C. At higher temperatures, the oxidation of dibenzothiophene to sulfone is faster [43]. This proves that the higher the temperature, the faster the reaction rate. Ye *et al.* [44] reported that a temperature of 50 °C increases the con-
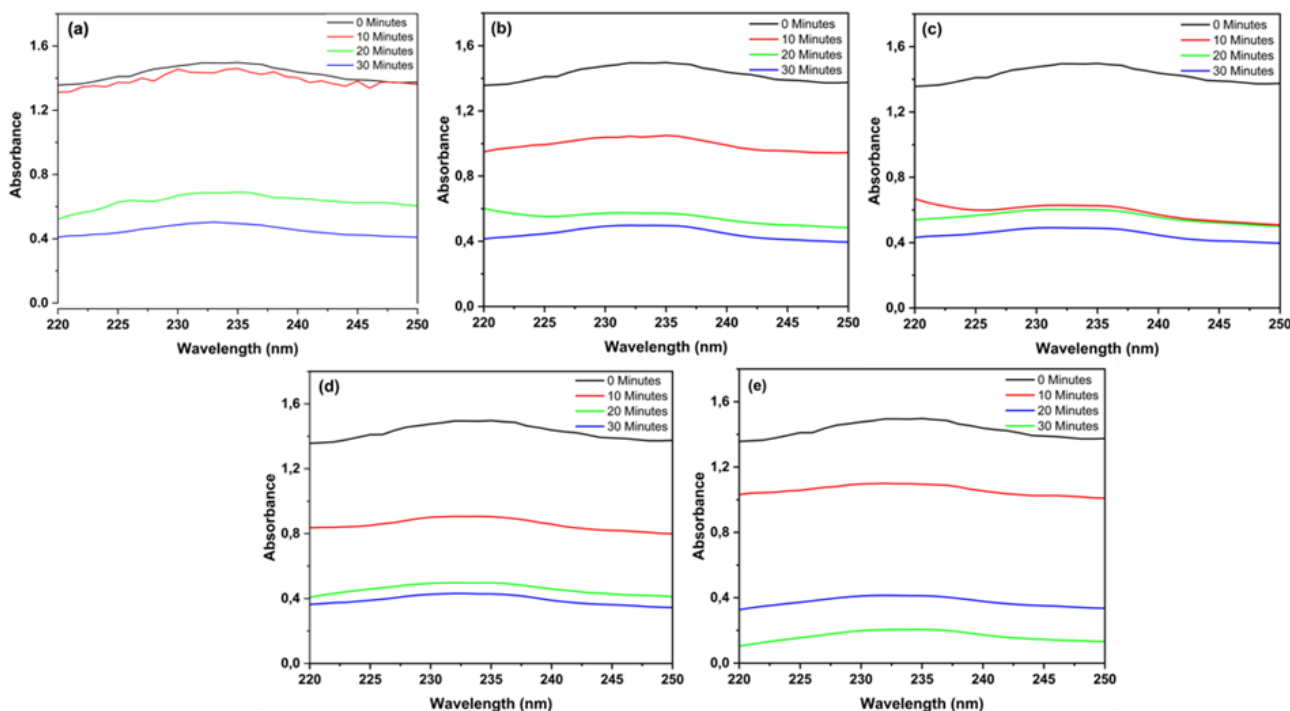

Figure 6. UV-Vis spectrum of oxidative desulfurization dibenzothiophene by catalysts Zn/Al LDH (a), TiO$_2$ (b), ZnO (c), Zn/Al-TiO$_2$ (d), and Zn/Al-ZnO (e)

version of dibenzothiophene. The effect of solvent was carried out to determine the best solvent in the oxidative desulfurization of DBT. N-pentane, n-hexane, and n-heptane were used as dibenzothiophene solvents. The solvent effect shows that n-hexane is better than n-pentane and n-heptane [33]. The results are compiled in Figure 9 showing the desulfurization of dibenzothiophene on Zn/Al-ZnO > Zn/Al-TiO$_2$ > Zn/Al-LDH > ZnO > TiO$_2$.

The heterogeneity test is a test to determine homogeneous or heterogeneous catalysts. Homogeneous catalysts are soluble in the reactants/products of the reaction, while heterogeneous catalysts are insoluble. The heterogeneity test was carried out at 50 °C for 10 minutes, and the catalyst and DBT solution was separated. The reaction process continued for 20-30 min without a catalyst. The unchanged DBT

concentration indicates a heterogeneous system. Figure 10 displays that Zn/Al-LDH, TiO$_2$, ZnO, Zn/Al-TiO$_2$, and Zn/Al-ZnO are truly heterogeneous catalysts. One advantage of heterogeneous catalysts is the easy separation of product and catalyst [45]. The other advantage of heterogeneous catalysts is that they can be used for reusability [46].

The reusability of the catalyst is important for the industry to save costs [47]. The reusability of catalysts was investigated using n-hexane as a solvent. After each cycle, the catalyst is recovered, dibenzothiophene desorbed using ultrasonic with n-hexane as a solvent, dried, and reused in oxidative desulfurization [48]. Figure 11 displayed the reusability of the catalyst after 3 cycles. After 3 cycles oxidative desulfurization, The percentage conversion of dibenzothiophene on Zn/Al-LDH, TiO$_2$, ZnO,
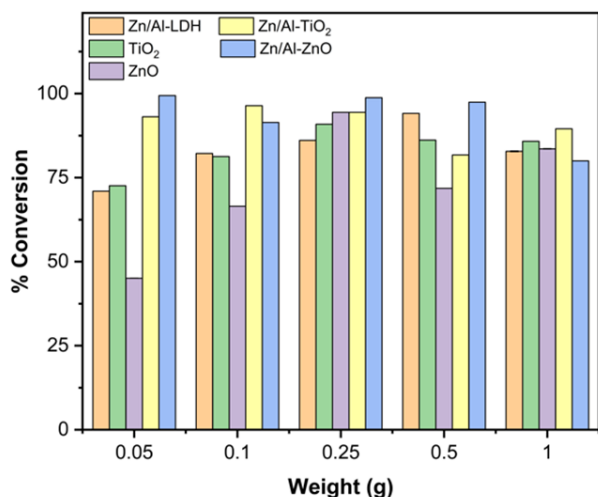
Figure 7. Effect of catalyst dosage on oxidative desulfurization of dibenzothiophene
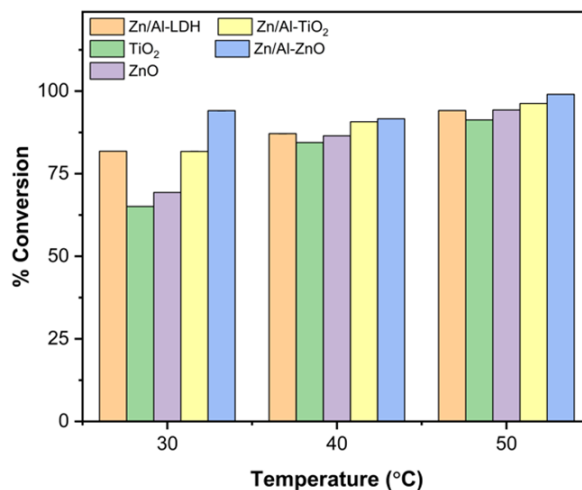
Figure 8. Effect of various temperatures on oxidative desulfurization of dibenzothiophene using composite catalysts
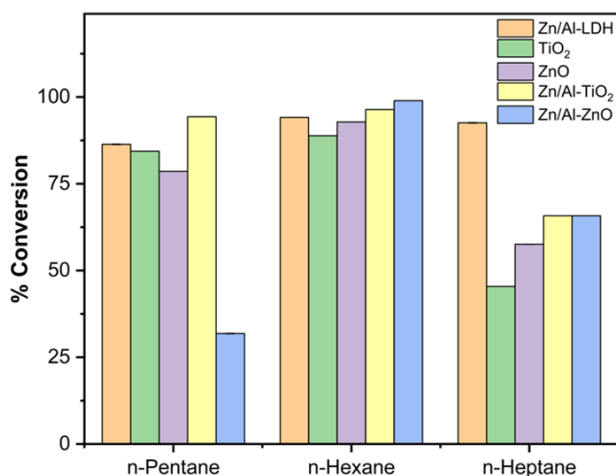
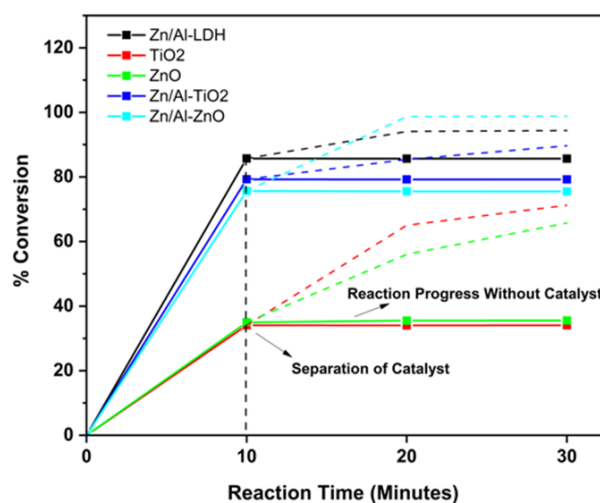Figure 9. Effect of solvent on oxidative desulfurization of dibenzothiophene by composite catalysts

Figure 10. Heterogeneity test of catalyst

Zn/Al-TiO$_2$, and Zn/Al-ZnO were 77.42%, 83.19%, 82.34%, 84.91%, and 89.71 %, respectively. Composited Zn/Al-TiO$_2$ and Zn/Al-ZnO have better reusability than Zn/Al-LDH, TiO$_2$, and ZnO. Reusability proves that Zn/Al-TiO$_2$ and Zn/Al-ZnO have a stable structure, because Zn/Al-LDH has been composed with TiO$_2$ and ZnO. To support this statement, the FTIR analysis was carried out to see changes in functional groups. Figure 12 shows that the FTIR and XRD of the composites with respect to before and after oxidative desulfurization of dibenzothiophene did not significantly change. So, the composited Zn/Al-TiO$_2$ and Zn/Al-ZnO have a stable structure and can be used for reusability.

4. Conclusion

In this study, the preparation of Zn/Al-TiO$_2$ and Zn/Al-ZnO was successful. The acidity of Zn/Al-LDH increased after being composed with TiO$_2$ and ZnO. The catalyst shows high

oxidative desulfurization of dibenzothiophene. The percentage conversion dibenzothiophene on Zn/Al-ZnO, Zn/Al-TiO$_2$, ZnO, Zn/Al-LDH, and TiO$_2$ was 99.38%, 96.01%, 95.36%, 94.71%,
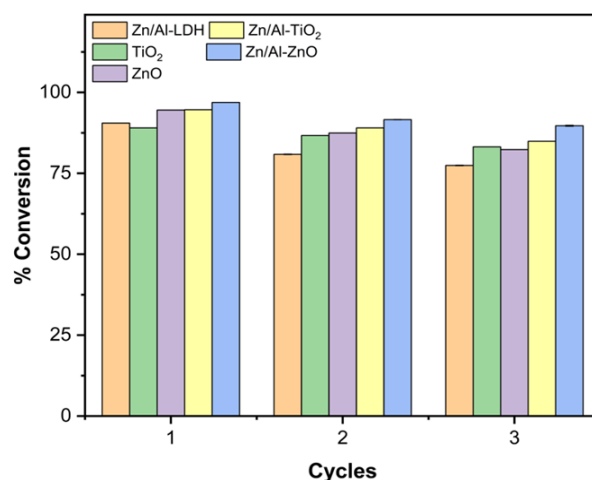

Figure 11. Reusability of catalyst on oxidative desulfurization of dibenzothiophene
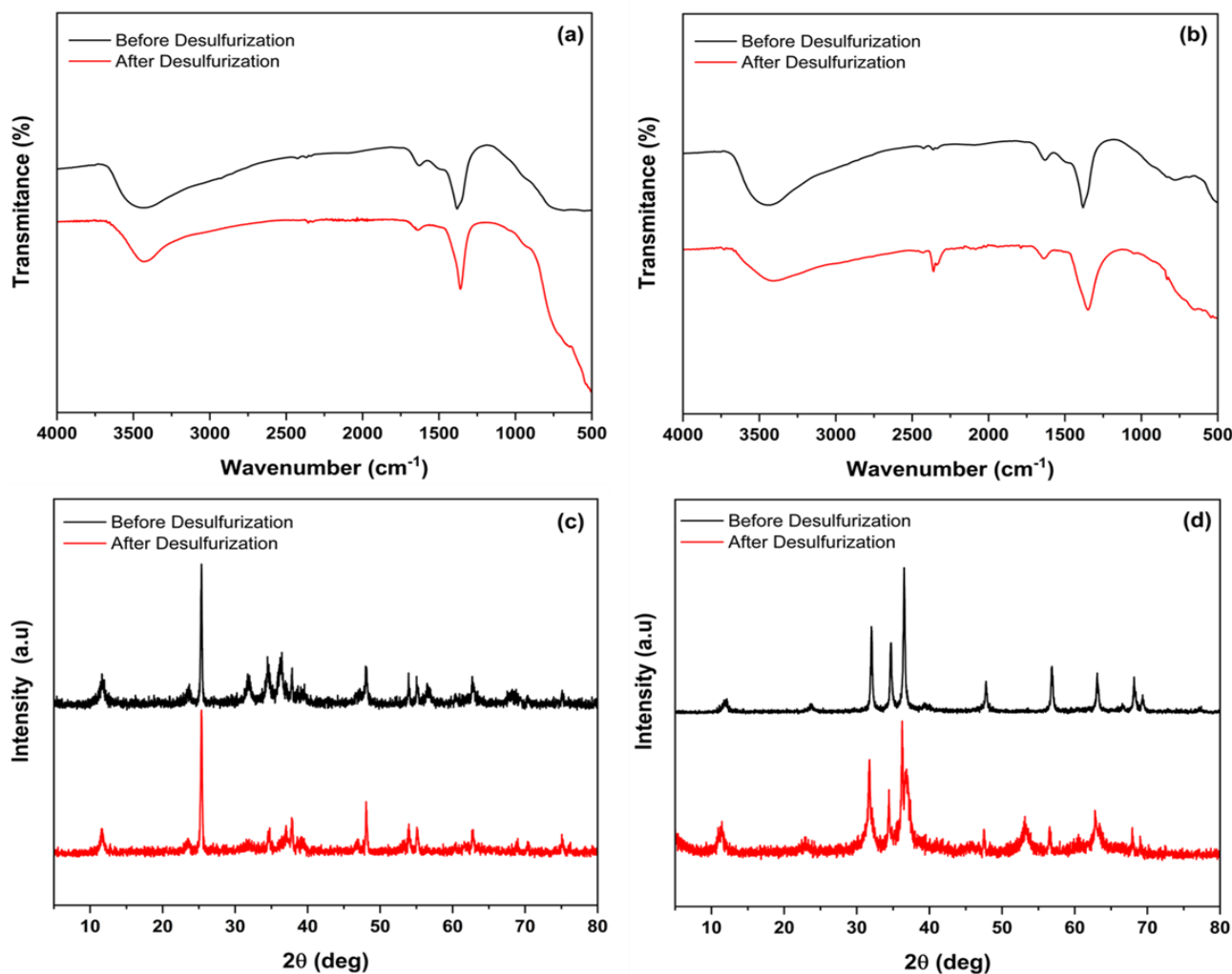

Figure 12. FTIR spectrum and XRD powder diffraction of Zn/Al-TiO$_2$ (a,c); Zn/Al-ZnO (b,d) before and after oxidative desulfurization of the third cycle

and 91.92%, respectively. The catalysts are heterogeneous systems, and the advantage is that they can be used for reusability. After 3 cycles of catalytic reactions at 50 $^{\circ}$C for 30 min, the composites Zn/Al-TiO$_2$ and Zn/Al-ZnO have better reusability than Zn/Al-LDH, TiO$_2$, and ZnO. Reusability proves that Zn/Al-TiO$_2$ and Zn/Al-ZnO have a stable structure.

Acknowledgement

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