



Research Article

# Highly Efficient Catalytic Oxidative Desulfurization of Dibenzothiophene using Layered Double Hydroxide Modified Polyoxometalate Catalyst

Nur Ahmad<sup>1</sup>, Muhammad Badaruddin<sup>2</sup>, Nova Yuliasari<sup>1</sup>, Fitri Suryani Arsyad<sup>3</sup>, Aldes Lesbani<sup>1,2\*</sup>

<sup>1</sup>Graduate School of Mathematics and Natural Sciences, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia.

<sup>2</sup>Research Center of Inorganic Materials and Coordination Complexes, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia.

<sup>3</sup>Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Jl. Palembang Prabumulih Km.32 Ogan Ilir 30662, Indonesia.

Received: 4<sup>th</sup> November 2022; Revised: 5<sup>th</sup> December 2022; Accepted: 5<sup>th</sup> December 2022

Available online: 7<sup>th</sup> December 2022; Published regularly: December 2022



## Abstract

Layered double hydroxide-modified polyoxometalate (ZnAl-PW) was prepared and used for the oxidative desulfurization of dibenzothiophene. XRD patterns of ZnAl-LDH and PW are still present in ZnAl-PW. The bands of ZnAl-PW in wavenumber 3276, 1637, 1363, 1050, 952, 887, and 667  $\text{cm}^{-1}$ . The typical surface of ZnAl-LDH and ZnAl-PW can be observed not smooth in different sized with irregular shapes. The average diameter distribution of ZnAl-LDH and ZnAl-PW is 14 nm and 47 nm, respectively. For dibenzothiophene with 500 ppm, conversion on ZnAl-LDH, PW, and ZnAl-PW was 94.71%, 95.88%, and 99.16%, respectively. Conversion of dibenzothiophene in line with the acidity of ZnAl-LDH, PW, and ZnAl-PW were 0.399, 1.635, and 3.023 mmol/gram, respectively. The most effective catalyst dosage for the desulfurization of dibenzothiophene on ZnAl-LDH, PW, and ZnAl-PW is 0.25 g. The unchanged dibenzothiophene concentration indicates a heterogeneous system. ZnAl-LDH, PW, and ZnAl-PW are truly heterogeneous catalysts. After 3 cycles of oxidative desulfurization, the percentage conversion of dibenzothiophene on ZnAl-LDH, PW, and ZnAl-PW were 77.42 %, 65.98%, and 86.38%, respectively.

Copyright © 2022 by Authors, Published by BCREC Group. This is an open access article under the CC BY-SA License (<https://creativecommons.org/licenses/by-sa/4.0>).

**Keywords:** polyoxometalate; layered double hydroxide; oxidative desulfurization; dibenzothiophene

**How to Cite:** N. Ahmad, M. Badaruddin, N. Yuliasari, F.S. Arsyad, A. Lesbani. (2022). Highly Efficient Catalytic Oxidative Desulfurization of Dibenzothiophene using Layered Double Hydroxide Modified Polyoxometalate Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(4), 821-830 (doi: 10.9767/bcrec.17.4.16373.821-830)

**Permalink/DOI:** <https://doi.org/10.9767/bcrec.17.4.16373.821-830>

## 1. Introduction

Nowadays, producing environmentally friendly fuels involves the removal of sulfur compounds (dibenzothiophene and its derivatives) because these compounds are responsible for environmental problems such as acid rain [1]. Many countries have implemented strict environmental regulations and fuel standards by

producing low-sulfur fuels [2]. However, this is a challenge for every less-developed country. Therefore, reducing the sulfur content of the fuel is one way that can be done, which is called desulfurization [3]. Many desulfurization methods have been developed, such as bio desulfurization [4], adsorptive desulfurization [5], extractive desulfurization [6], and oxidative desulfurization [7].

Oxidative desulfurization (ODS) is one of the most studied methods of reducing sulfur com-

\* Corresponding Author.

Email: [aldeslesbani@pps.unsri.ac.id](mailto:aldeslesbani@pps.unsri.ac.id) (A. Lesbani)

pounds [8]. The advantages of ODS are that its operation does not require extreme conditions and has efficiency in converting sulfur compounds. In the ODS process, the catalyst is very influential in activating oxidants [9]. Thus, a high-efficiency catalyst is needed [10]. The catalysts have been reported in the ODS process include MIL-101(Cr)-NO<sub>2</sub> [11], ceramics [12], dioxomolybdenum(VI) [13], polyoxometalates [14], and layered double hydroxide [15].

A layered double hydroxide (LDH) is a group of versatile two-dimensional layered inorganic materials [16]. The advantages of LDH are its adjustable composition, large surface area, structural memory effect, low cost, and reusability [17]. LDH has been applied in various fields, including hydrogenation of CO<sub>2</sub> [18], supercapacitors electrodes [19], and catalysts [20]. To increase the active site of LDH, it must be modified in structure and physicochemical, one of them with polyoxometalate.

Polyoxometalates are mixed metal oxides attracting attention because of their unique properties and wide applications in electrocatalysts, adsorption, photodegradation, and catalysts [21]. Polyoxometalates have adjustable acid-base properties and good thermal and oxidative stability [22]. In addition, Polyoxometalates contain empty D-orbitals for electron capture [23]. Polyoxometalates consist of Keggin, Anderson, and Dawson types [24–26]. In recent years, type Keggin-polyoxometalate has been the most studied in this field. The research on polyoxometalate has been reported photocatalyst [27], adsorption [28], and dye-sensitized solar cells [29]. Composite layered double hydroxide modified type Keggin-polyoxometalate was used for photocatalytic dyes [30], hydrodeoxygenation of guaiacol [31], and esterification catalyst [32]. However, Oxidative desulfurization of dibenzothiophene on layered double hydroxide-modified type Keggin-polyoxometalate (ZnAl-PW) has not been reported.

In this study, layered double hydroxide-modified type Keggin-polyoxometalates (ZnAl-PW) were prepared and used for oxidative desulfurization. All oxidative desulfurization reactions were carried out with hydrogen peroxide as an oxidant and acetonitrile as an extraction agent. Process sustainability and system efficiency are optimized. After that, heterogeneous tests and reusability were investigated.

## 2. Materials and Method

### 2.1 Chemicals

All chemicals, i.e. zinc nitrate hexahydrate, aluminum nitrate nonahydrate, distilled water, sodium hydroxide, sodium phosphate, sodium tungstate, concentrated hydrogen chloride, N<sub>2</sub> gas, potassium chloride, dibenzothiophene, hydrogen peroxide, acetonitrile, n-hexane, n-heptane, n-pentane, and pyridine, were used without any further purification (pro-analysis, PA). All chemicals were obtained from Sigma-Aldrich and Merck.

### 2.2 Synthesis of ZnAl-LDH

Zinc nitrate (0.75 M) and aluminum nitrate (0.25 M) were dissolved in 50 mL of distilled water [33]. The mixture was poured into a beaker containing 20 mL of distilled water. Afterward, the mixture was added 2 M sodium hydroxide to pH 8 and shaken for 4 h at 343 K to obtain ZnAl-LDH.

### 2.3 Synthesis of K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate

Sodium phosphate (20 g) was dissolved in 100 mL of distilled water as solution A. 125 g of sodium tungstate was dissolved in 300 mL of hot water as solution B. Afterward, solution A was added to solution B, followed by the addition of 10 mL of concentrated 37% hydrogen chloride maintained at 323 K. This solution is filtered and dried. The addition of 50 g of potassium chloride formed a white precipitate of K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>].nH<sub>2</sub>O.

### 2.4 Preparation of ZnAl-K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]

K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate (1 g) in 50 mL distilled water was mixed into 2 g ZnAl-LDH in 25 mL sodium hydroxide 1 M. The mixture was stirred under N<sub>2</sub> gas for 24 hours. Then the suspension is cooled, and the product is washed with water and dried.

### 2.5 Characterizations

ZnAl-LDH, K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate, and ZnAl-K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] catalysts were characterized by Fourier transform infrared (Shimadzu, Japan) in wavenumber 4000 – 500 cm<sup>-1</sup>, X-ray diffractometer (Rigaku, Japan) in 2θ = 5° – 80°, scanning electron microscope (Quanta, England) in 2500 times magnification, and spectrophotometer UV-Visible (EMC, Germany) in wavelength 220 – 250 nm.

## 2.6 Oxidative Desulfurization of Dibenzothiophene

Oxidative desulfurization of dibenzothiophene is carried out in several stages. Prepared 30 mL of 500 ppm dibenzothiophene in a two-head flask connected to a condenser. After that, 1 mL of H<sub>2</sub>O<sub>2</sub> oxidizer was added, and catalysts ZnAl-LDH, K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate, and ZnAl-K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] were added. After stirring, the mixture was added 3 mL of acetonitrile to extract dibenzothiophene. The desulfurization process was carried out with variations in temperature ((303 – 323 K), a dosage of catalyst (0.0.5 – 0.5 g), wavelength scan (220 – 250 nm), reaction time (10 – 60 min), solvent (n-hexane, n-heptane, and n-pentane), acidity test, heterogeneous test, and reusability of catalysts. The efficiency conversion of dibenzothiophene was evaluated by Equation 1:

$$\% \text{ Conversion} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where,  $C_0$  and  $C_t$  are the initial and final concentrations of dibenzothiophene, respectively.

## 3. Results and Discussion

X-ray diffraction of ZnAl-LDH, K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate (PW), and ZnAl-K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>] (ZnAl-PW) was shown in Figure 1. PDF card of ZnAl-LDH and PW was ICDD#48-1023 and ICDD#01-072-9992, respectively [34,35]. The characteristic diffraction of ZnAl-LDH was located at 10.29°, 20.07°, 34.02°, and 60.16° corresponding to the lattice plane (003), (006), (012), and (110), respectively. The diffraction peaks of PW at 10.93°, 21.76°, 26.65°, 30.80°, 36.32°, 39.59°, and 65.12°, which

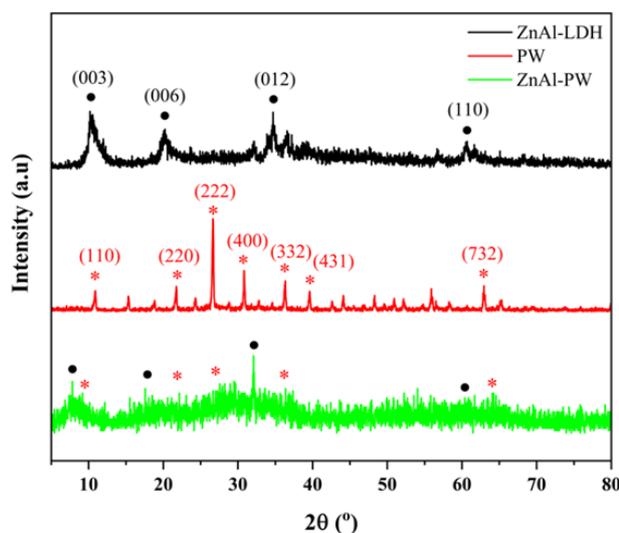


Figure 1. XRD diffraction of catalysts

correspond to (110), (220), (222), (400), (332), (431), and (732). The peaks of ZnAl-LDH and PW are still present in ZnAl-PW.

Figure 2 presents FTIR spectra of ZnAl-LDH, K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]-polyoxometalate, and ZnAl-K<sub>3</sub>[α-PW<sub>12</sub>O<sub>40</sub>]. FTIR spectra, the bands of ZnAl-PW in wavenumber 3276, 1637, 1363, 1050, 952, 887, and 667 cm<sup>-1</sup>. The band at 3276 cm<sup>-1</sup> could be attributed to O-H stretching from the layer and interlayer of ZnAl-LDH. The absorption peaks at 1637 and 1363 cm<sup>-1</sup> were assigned to the hydroxyl and NO<sub>3</sub><sup>-</sup> vibration [36]. The broad bands around 1050, 952, 887, and 667 cm<sup>-1</sup> correspond to asymmetric stretching of M-O and M-O-M (M = P, W, Zn, Al) from ZnAl-LDH and PW.

Figure 3 shows the surface morphology and diameter distribution of ZnAl-LDH and ZnAl-PW. The typical surface of ZnAl-LDH and ZnAl-PW can be observed not smooth in different sized with irregular shapes. The average diameter distribution of ZnAl-LDH and ZnAl-PW is 14 nm and 47 nm, respectively. The diameter distribution of ZnAl-LDH was smaller than that of ZnAl-PW. The band gap energy ( $E_g$ ) represents the spacing between the valence and conduction bands [37].  $E_g$  is essential for determining the absorption zone of the catalyst. As shown in Figure 4, the  $E_g$  values of ZnAl-LDH and ZnAl-PW samples were 3.14, 3.28, and 3.95 eV, respectively

Based on Table 1, the acidity of ZnAl-LDH, PW, and ZnAl-PW were 0.399, 1.635, and 3.023 mmol/gram, respectively. The acidity test of ZnAl-LDH, PW, and ZnAl-PW used pyridine as the adsorbate base. The acidity of catalysts is affected by the amount of pyridine adsorbed.

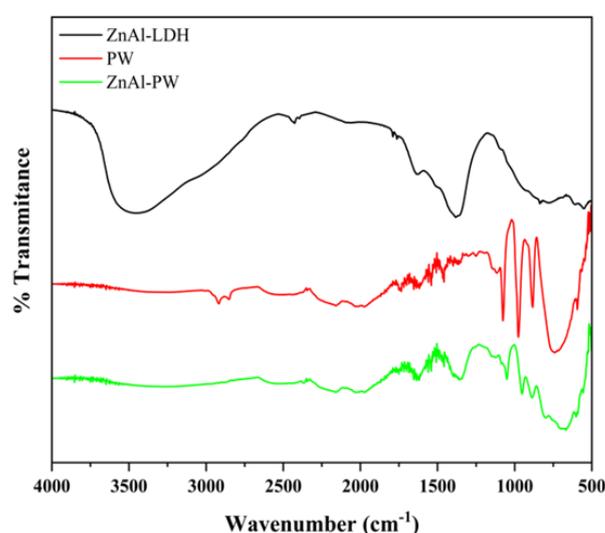


Figure 2. FTIR spectra of catalysts

Acid sites can accept electrons during the oxidative desulfurization process. Acid sites of catalysts are polyacid to convert dibenzothiophene to dibenzothiophene-sulfones [38,39]. Due to the abundance of oxygen in PW, H-bonds can be formed between PW anions and water in interlayer layered double hydroxide. The positively charged layered double hydroxide can create a strong electrostatic contact with highly negatively charged PW anions, which may easi-

ly activate the hydrogen atoms in H-bonds and liberate protons, hence increasing the amount of strong Brönsted acid sites. Second, transi-

Table 1. Acidity of catalyst

Catalyst	Acidity (mmol/g)
ZnAl-LDH	0.399
PW	1.635
ZnAl-PW	3.023

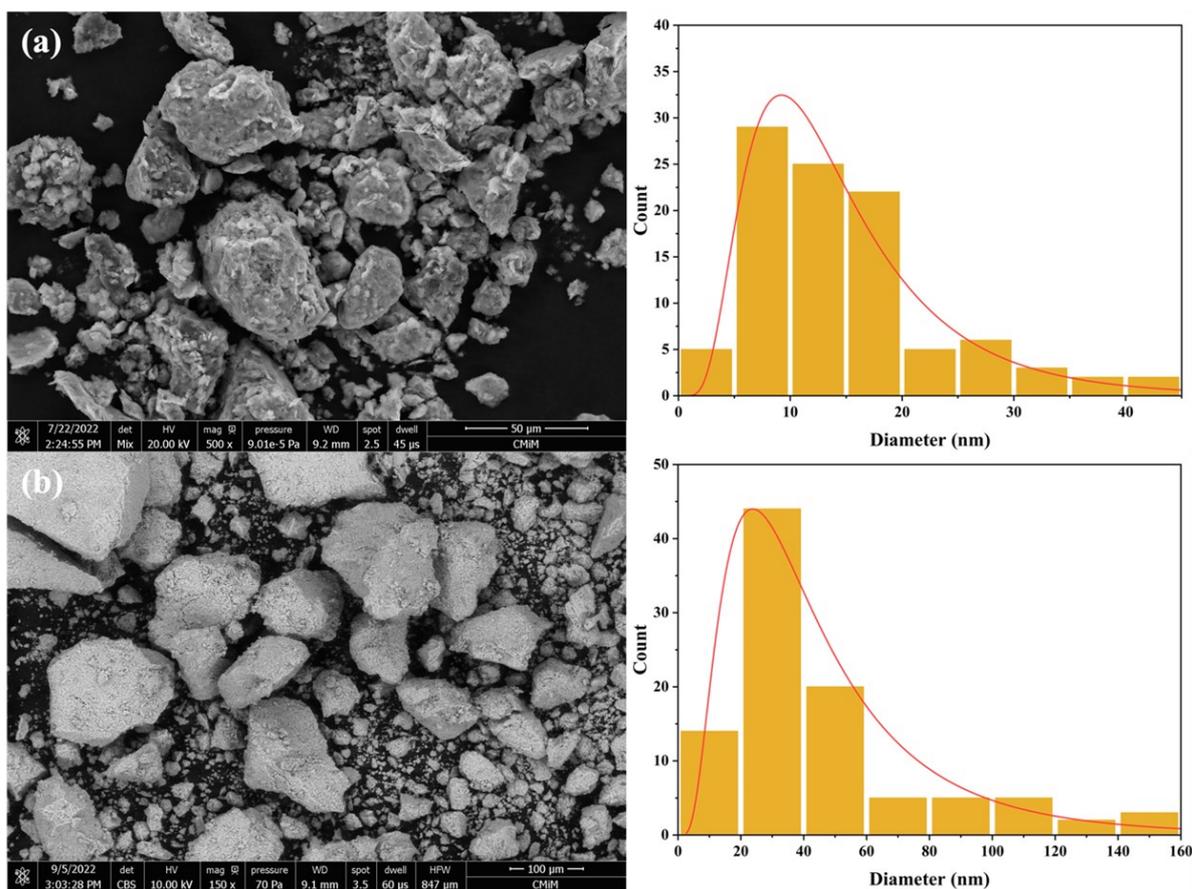


Figure 3. SEM pictures of ZnAl-LDH (a) and ZnAl-PW (b)

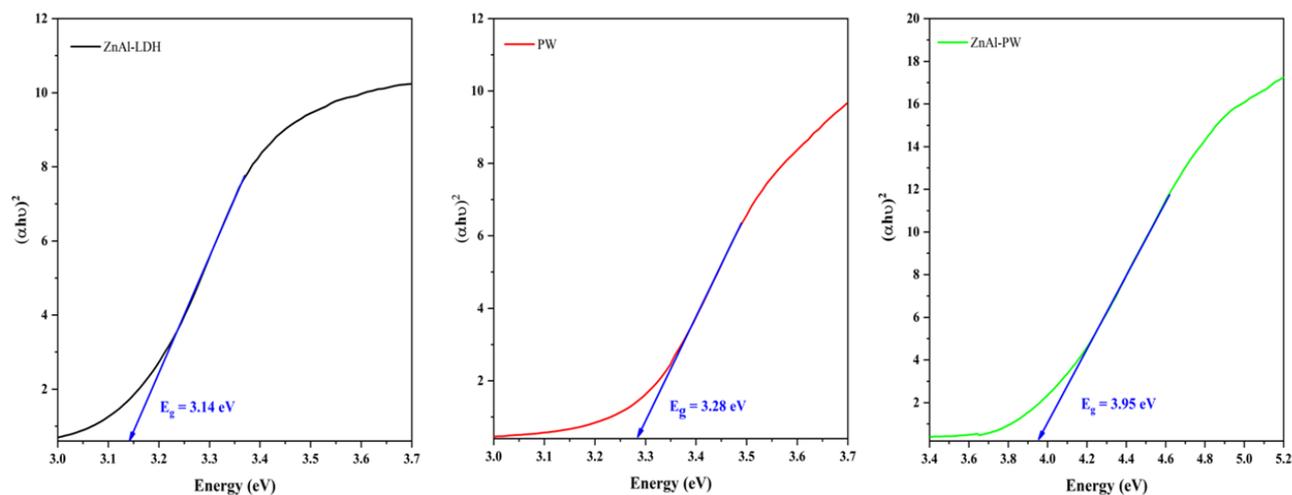


Figure 4. Band gap energy of catalysts

tion metal cations in PW and ZnAl-LDH in the sheets can both produce Lewis acid sites [32].

Figure 5 shows the reaction time used 10-60 min. In the oxidative desulfurization of dibenzothiophene, reaction time is one of the main factors impacting the conversion. The increment reaction time increases the conversion of dibenzothiophene in catalysts. For dibenzothiophene with 500 ppm, conversion on ZnAl-LDH, PW, and ZnAl-PW was 94.71%, 95.88%, and 99.16%, respectively. The optimum reaction time was 30 min. The increasing reaction time increases efficiency [40]. Several researches oxidative desulfurization of dibenzothiophene as shown in Table 2.

As observed in Figure 6, the maximum wavelength of dibenzothiophene is 235 nm. The wavelength scan desulfurization process was used at 220-250 nm. The absorbance of dibenzothiophene decreased with increasing reaction time. H<sub>2</sub>O<sub>2</sub> as an oxidizing agent, has a stimulating effect on converting dibenzothiophene to dibenzothiophene-sulfones [46,47]. Furthermore, acetonitrile was used as an extraction agent to remove oxidized sulfur compounds as

a final step in the oxidative desulfurization process [48].

The effect of catalyst dosage on oxidative desulfurization of dibenzothiophene was used in variations of 0.05, 0.1, 0.2, 0.25, and 0.5 g. The effect of catalyst dosage was studied for the initial concentration of dibenzothiophene 500 ppm at 323 K for 30 min. Based on the data shown in Figure 7, the most effective catalyst dosage for the desulfurization of dibenzothiophene on ZnAl-LDH, PW, and ZnAl-PW is 0.25 g, 0.1 g, and 0.1 g, respectively. The increment catalyst dosage increases the catalytic site but also increases competition with oxidant molecules [49,50].

Based on Figure 8, the optimum temperature for desulfurization of dibenzothiophene is 323 K. Oxidative desulfurization of dibenzothiophene at varying temperatures from 303 K to 323 K. The increasing temperature accelerates the rate of molecular diffusion and increases the contact between dibenzothiophene and catalysts, so that the desulfurization process becomes effective [51]. Thus, the oxidative desulfurization process is set at a temperature

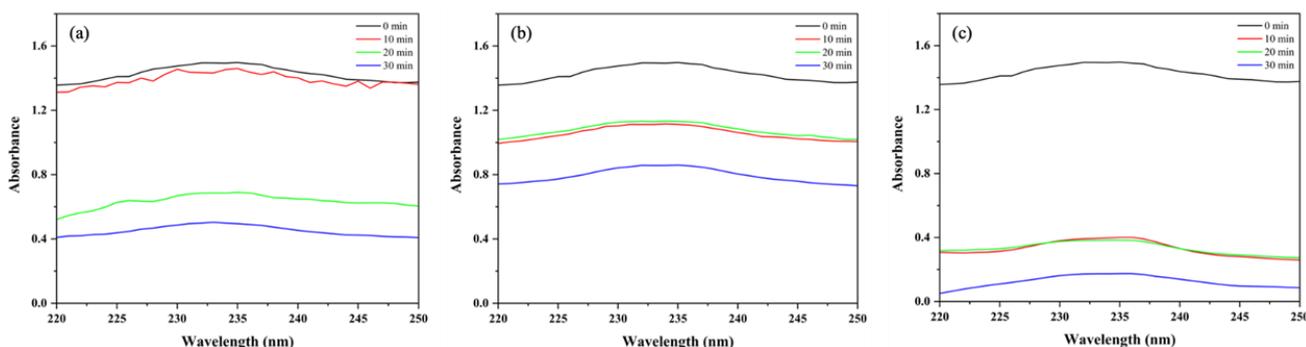


Figure 6. Wavelength scan of ZnAl-LDH (a), PW (b), ZnAl-PW (c)

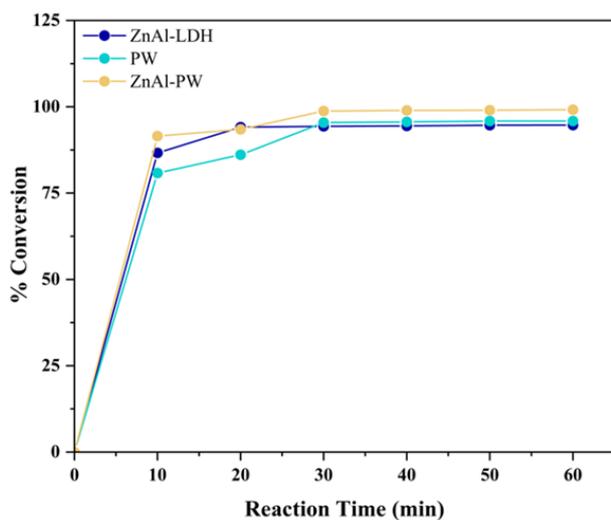


Figure 5. Effect of contact time

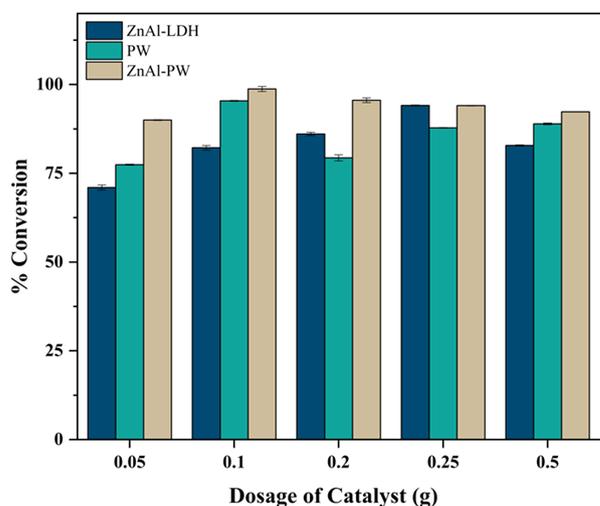


Figure 7. Effect of catalyst dosage

of 323 K. Furthermore, n-pentane, n-hexane, and n-heptane were used as dibenzothiophene solvents. The effect of solvent obtained by n-hexane is better than n-pentane and n-heptane [39]. As can be seen in Figure 9, the conversion of dibenzothiophene on ZnAl-LDH < PW < ZnAl-PW.

A heterogeneous test was carried out to know ZnAl-LDH, PW, and ZnAl-PW homogeneous or heterogeneous catalysts. The oxidative desulfurization process was used at a temperature of 323 K for 10 min, then the catalyst and dibenzothiophene were separated. The reaction

process continued for 20 and 30 min without a catalyst. The unchanged dibenzothiophene concentration indicates a heterogeneous system. As presented in Figure 10, ZnAl-LDH, PW, and ZnAl-PW are truly heterogeneous catalysts. The advantage of heterogeneous catalysts is that they can be used for reusability [52].

The reusability of the catalyst is essential for the industry to save costs [53]. The reusability of catalysts was investigated using n-hexane as a solvent. After each cycle, the catalyst is recovered, desorbed using ultrasonic, dried, and reused in oxidative desulfurization

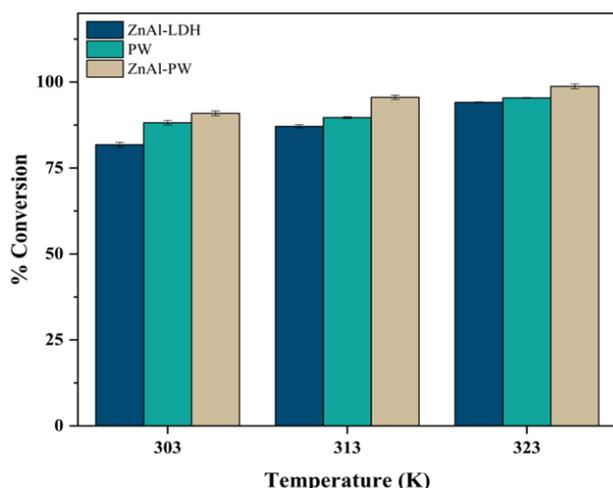


Figure 8. Effect of temperatures

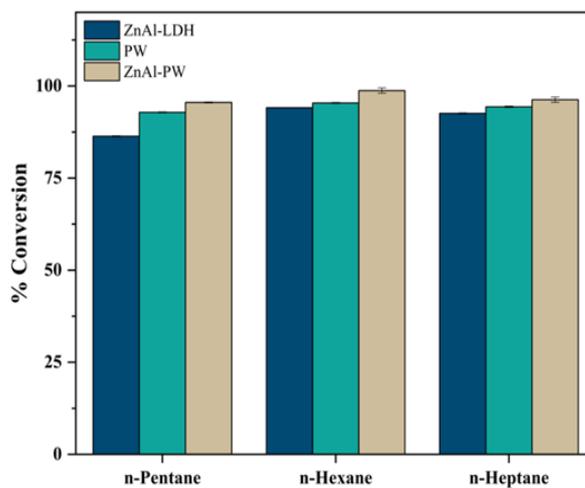


Figure 9. Effect of solvent

Table 2. Several researches oxidative desulfurization of dibenzothiophene

Catalyst	Reaction conditions	% Conversion	Reference
Neam leaves	DBT = 800 ppm, t = 60 min, solvent = hexane, T = 303 K, dosage of catalyst = 0.8 g	65.80	[41]
V/HY Zeolite alumina	DBT = 1000 ppm, t = 90 min, solvent = isooctane and toluene, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H <sub>2</sub> O <sub>2</sub>	100	[42]
TBOT	DBT = 1000 ppm, t = 10 min, solvent = n-octane, T = 298 K, dosage of catalyst = 0.2 g, oxidant = H <sub>2</sub> O <sub>2</sub>	99.60	[43]
Mo/MCM-41	DBT = 600 ppm, t = 180 min, solvent = isooctane, T = 363 K, dosage of catalyst = 0.6 g, oxidant = TBHP	94	[44]
Co/KIT-6	DBT = 400 ppm, t = 40 min, solvent = n-octane, T = 373 K, dosage of catalyst = 0.1 g, oxidant = CYHPO	98.68	[45]
ZnAl-LDH	DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.25 g, oxidant = H <sub>2</sub> O <sub>2</sub>	94.71	This study
PW	DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H <sub>2</sub> O <sub>2</sub>	95.88	This study
ZnAl-PW	DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H <sub>2</sub> O <sub>2</sub>	99.16	This study

[54]. Figure 11 displayed the reusability of the catalyst after 3 cycles. After 3 cycles of oxidative desulfurization, the percentage conversion of dibenzothiophene on ZnAl-LDH, PW, and ZnAl-PW were 77.42 %, 65.98%, and 86.38%, respectively.

#### 4. Conclusions

This study shows layered double hydroxide modified polyoxometalate (ZnAl-PW) was prepared and effective for oxidative desulfurization of dibenzothiophene. XRD patterns, FTIR spectra, and SEM images show the successful preparation of catalysts. For dibenzothiophene with 500 ppm, conversion on ZnAl-LDH, PW, and ZnAl-PW was 94.71%, 95.88%, and 99.16%, respectively. This study also conducts heterogeneous tests to know if ZnAl-LDH, PW, and ZnAl-PW are truly heterogeneous catalysts. After 3 cycles of oxidative desulfurization, the percentage conversion of dibenzothiophene on ZnAl-LDH, PW, and ZnAl-PW were 77.42 %, 65.98%, and 86.38%, respectively.

#### Acknowledgments

The authors thank Universitas Sriwijaya for funding this research through DIPA of Public Service Agency of Universitas Sriwijaya, Hibah Profesi SIP DIPA-023.17.2.677515/2022 on December 12, 2021, following the Rector degree number 0111/UN9.3.1/SK/2022 on April 28, 2022, for additional output research. We acknowledge the Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya for instrumental analysis and fruitful discussion.

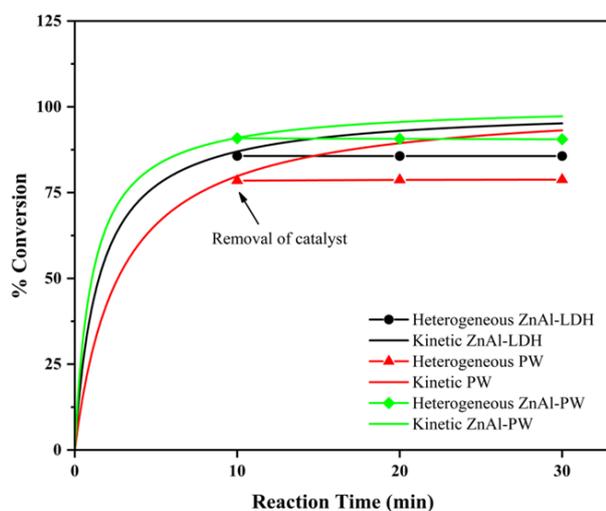


Figure 10. Heterogeneous test of catalyst

#### CRedit Author Statement

Author Contributions: N. Ahmad: Conceptualization, Investigation, Writing–Original draft, Software; M. Badaruddin: Formal analysis, Project administration, Resources; N. Yuliasari: Visualization, Data curation, Formal Analysis; F. S. Arsyad: Methodology, Validation, Visualization; A. Lesbani: Methodology, Conceptualization, Funding acquisition, Writing – review & editing, Supervision.

#### References

- [1] Ribeiro, S.O., Almeida, P.L., Pires, J., de Castro, B., Balula, S.S. (2020). Polyoxometalate@Periodic mesoporous organosilicas as active materials for oxidative desulfurization of diesels. *Microporous and Mesoporous Materials*, 302, 110193. DOI: 10.1016/j.micromeso.2020.110193.
- [2] Jiang, W., Dong, L., Liu, W., Guo, T., Li, H., Zhang, M., Zhu, W., Li, H. (2017). Designing multifunctional SO<sub>3</sub>H-based polyoxometalate catalysts for oxidative desulfurization in acid deep eutectic solvents. *RSC Advances*, 7(87), 55318–55325. DOI: 10.1039/c7ra10125b.
- [3] Fraile, J.M., Gil, C., Mayoral, J.A., Muel, B., Roldán, L., Vispe, E., Calderón, S., Puente, F. (2016). Heterogeneous titanium catalysts for oxidation of dibenzothiophene in hydrocarbon solutions with hydrogen peroxide: On the road to oxidative desulfurization. *Applied Catalysis B: Environmental*, 180, 680–686. DOI: 10.1016/j.apcatb.2015.07.018.
- [4] Mu, T., Yang, M., Xing, J. (2021). Performance and characteristic of a haloalkaliphilic bio-desulfurizing system using *Thioalkalivibrio verustus* D301 for efficient removal of H<sub>2</sub>S. *Biochemical Engineering Journal*, 165, 107812. DOI: 10.1016/j.bej.2020.107812.

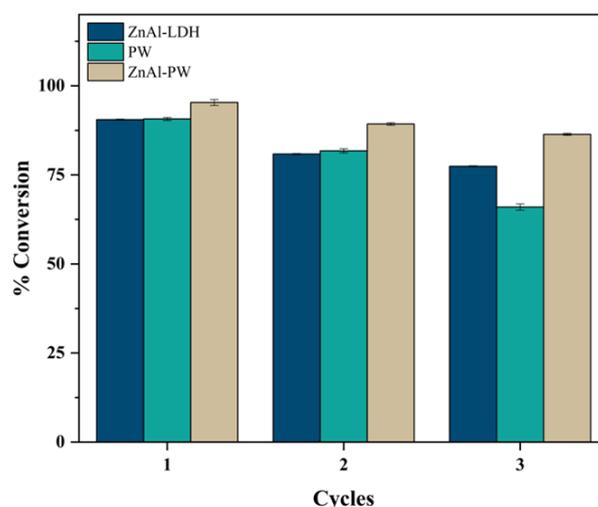


Figure 11. Reusability of catalyst

- [5] Huang, C., Zhao, Z., Ping, E., Zhang, L., Zhou, Y., Qin, L. (2021). Combination of coordinatively unsaturated metal sites and silver nano-particles in a Ni-based metal-organic framework for adsorptive desulfurization. *Microporous and Mesoporous Materials*, 323, 1 1 1 2 4 1 . DOI : 10.1016/j.micromeso.2021.111241.
- [6] Khan, N., Srivastava, V.C. (2022). Extractive desulfurization using ethylene glycol and glycerol-based deep eutectic solvents: engineering aspects and intensification using ultrasound. *Chemical Engineering and Processing - Process Intensification*, 180, 108973. DOI: 10.1016/j.cep.2022.108973.
- [7] Farghadani, M.H., Mahdavi, V. (2022). Novel synthesis of highly dispersed molybdenum oxide over nanorods cryptomelane octahedral manganese oxide molecular sieve (MoOx/nanorod-OMS-2) as a high performance catalyst for oxidative desulfurization process. *Fuel Processing Technology*, 236, 107415. DOI: 10.1016/j.fuproc.2022.107415.
- [8] Raeisi, A., Najafi Chermahini, A., Momeni, M.M. (2022). A novel photocatalytic and photoelectrocatalytic system for oxidative desulfurization of model fuel using BiVO<sub>4</sub>@HKUST-1 composite in powder and deposited on fluorine-doped tin oxide. *Journal of Photochemistry and Photobiology A: Chemistry*, 433, 114190. DOI: 10.1016/j.jphotochem.2022.114190.
- [9] Deng, C., Zhu, H., Huang, Y., Liu, H., Liu, P., Cui, P., Chao, Y., Liu, J., Wang, R., Wu, P., Zhu, W. (2022). High temperature oxidizing-resistant magnetic high entropy catalyst for efficient oxidative desulfurization. *Catal. Today*, 405-406, 66-74. DOI: 10.1016/j.cattod.2022.08.002.
- [10] Xun, S., Wu, C., Tang, L., Yuan, M., Chen, H., He, M., Zhu, W., Li, H. (2022). One-pot in-situ synthesis of coraloid supported VO<sub>2</sub> catalyst for intensified aerobic oxidative desulfurization. *Chin. J. Chem. Eng.* In Press. DOI: 10.1016/j.cjche.2022.07.005.
- [11] Vallés-García, C., Santiago-Portillo, A., Álvaro, M., Navalón, S., García, H. (2020). MIL-101(Cr)-NO<sub>2</sub> as efficient catalyst for the aerobic oxidation of thiophenols and the oxidative desulfurization of dibenzothiophenes. *Applied Catalysis A: General*, 590, 117340. DOI: 10.1016/j.apcata.2019.117340.
- [12] Elena Manríquez-Ramírez, M., Valdez, M.T., Castro, L. v., Flores, M.E., Ortiz-Islas, E. (2022). Application of CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> catalysts in the oxidative desulfurization of 4,6-dimethyl dibenzothiophene as a model reaction to remove sulfur from fuels. *Materials Research Bulletin*, 153, 111864. DOI: 10.1016/j.materresbull.2022.111864.
- [13] Julião, D., Gomes, A.C., Cunha-Silva, L., Pillinger, M., Gonçalves, I.S., Balula, S.S. (2022). Dichloro and dimethyl dioxomolybdenum(VI)-bipyridine complexes as catalysts for oxidative desulfurization of dibenzothiophene derivatives under extractive conditions. *Journal of Organometallic Chemistry*, 967, 122336. DOI: 10.1016/j.jorganchem.2022.122336.
- [14] Liu, Y., Zuo, P., Wang, F., Lv, Y., Wang, R., Jiao, W. (2020). Extraction combined oxidation desulfurization of dibenzothiophene using polyoxometalate-supported magnetic chitosan microspheres. *Journal of the Taiwan Institute of Chemical Engineers*, 117, 112–122. DOI: 10.1016/j.jtice.2020.12.003.
- [15] Song, Y., Bai, J., Jiang, S., Yang, H., Yang, L., Wei, D., Bai, L., Wang, W., Liang, Y., Chen, H. (2021). Co-Fe-Mo mixed metal oxides derived from layered double hydroxides for deep aerobic oxidative desulfurization. *Fuel*, 306, 121751. DOI: 10.1016/j.fuel.2021.121751.
- [16] Yu, Q., Li, C., Ma, D., Zhao, J., Liu, X., Liang, C., Zhu, Y., Zhang, Z., Yang, K. (2022). Layered double hydroxides-based materials as novel catalysts for gaseous VOCs abatement: Recent advances and mechanisms. *Coordination Chemistry Reviews*, 471, 214738. DOI: 10.1016/j.ccr.2022.214738.
- [17] Abdel-Hady, E.E., Mahmoud, R., Hafez, S.H.M., Mohamed, H.F.M. (2022). Hierarchical ternary ZnCoFe layered double hydroxide as efficient adsorbent and catalyst for methanol electrooxidation. *Journal of Materials Research and Technology*, 17, 1922–1941. DOI: 10.1016/j.jmrt.2022.01.042.
- [18] Fang, X., Chen, C., Jia, H., Li, Y., Liu, J., Wang, Y., Song, Y., Du, T., Liu, L. (2021). Progress in Adsorption-Enhanced Hydrogenation of CO<sub>2</sub> on Layered Double Hydroxide (LDH) Derived Catalysts. *Journal of Industrial and Engineering Chemistry*, 95, 16–27. DOI: 10.1016/j.jiec.2020.12.027.
- [19] Lv, H., Rao, H., Liu, Z., Zhou, Z., Zhao, Y., Wei, H., Chen, Z. (2022). NiAl layered double hydroxides with enhanced interlayer spacing via ion-exchange as ultra-high performance supercapacitors electrode materials. *Journal of Energy Storage*, 52, 104940. DOI: 10.1016/j.est.2022.104940.
- [20] van Everbroeck, T., Wu, J., Arenas-Esteban, D., Ciocarlan, R.-G., Mertens, M., Bals, S., Dujardin, C., Granger, P., Seftel, E.M., Cool, P. (2022). ZnAl layered double hydroxide based catalysts (with Cu, Mn, Ti) used as noble metal-free three-way catalysts. *Applied Clay Science*, 217(December 2021), 106390. DOI: 10.1016/j.clay.2021.106390.

- [21] Song, Y., Fang, W., Liu, C., Sun, Z., Li, F., Xu, L. (2020). Effect of mixed Mo/W polyoxometalate modification on photoelectrocatalytic activity of CdS nanocrystals for arsenic(III) oxidation. *Journal of Physics and Chemistry of Solids*, 141, 109395. DOI: 10.1016/j.jpcs.2020.109395.
- [22] He, R., Xue, K., Wang, J., Yan, Y., Peng, Y., Yang, T., Hu, Y., Wang, W. (2020). Nitrogen-deficient g-C<sub>3</sub>N<sub>4</sub>/POMs porous nanosheets with P-N heterojunctions capable of the efficient photocatalytic degradation of ciprofloxacin. *Chemosphere*, 259, 127465. DOI: 10.1016/j.chemosphere.2020.127465.
- [23] Xing, F., Zeng, R., Cheng, C., Liu, Q., Huang, C. (2022). POM-incorporated ZnIn<sub>2</sub>S<sub>4</sub> Z-scheme dual-functional photocatalysts for cooperative benzyl alcohol oxidation and H<sub>2</sub> evolution in aqueous solution. *Applied Catalysis B: Environmental*, 306, 121087. DOI: 10.1016/j.apcatb.2022.121087.
- [24] Tian, Y., Chang, Z.H., Zhang, Y.C., Wang, X.L., Chen, Y. zhen, Liu, Q. qian, Yu, L. (2021). Two Anderson-type POM-based metal-organic complexes as multifunctional materials for electrocatalytic sensing and zinc-ion batteries. *Polyhedron*, 204, 115245. DOI: 10.1016/j.poly.2021.115245.
- [25] Taghiyar, H., Yadollahi, B. (2020). Keggin polyoxometalates encapsulated in molybdenum-iron-type Keplerate nanoball as efficient and cost-effective catalysts in the oxidative desulfurization of sulfides. *Science of the Total Environment*, 708, 134860. DOI: 10.1016/j.scitotenv.2019.134860.
- [26] Liu, Y., Zuo, P., Wang, R., Liu, Y., Jiao, W. (2020). Covalent immobilization of Dawson polyoxometalates on hairy particles and its catalytic properties for the oxidation desulfurization of tetrahydrothiophene. *Journal of Cleaner Production*, 274, 122774. DOI: 10.1016/j.jclepro.2020.122774.
- [27] Huang, X., Liu, X. (2020). Morphology control of highly efficient visible-light driven carbon-doped POM photocatalysts. *Applied Surface Science*, 505, 144527. DOI: 10.1016/j.apsusc.2019.144527.
- [28] Zhang, H., Li, M., Liu, Z., Zhang, X., Du, C. (2022). Two Keggin-type polyoxometalates used as adsorbents with high efficiency and selectivity toward antibiotics and heavy metals. *Journal of Molecular Structure*, 1267, 133604. DOI: 10.1016/j.molstruc.2022.133604.
- [29] Cruz, H., Pinto, A.L., Lima, J.C., Branco, L.C., Gago, S. (2020). Application of polyoxometalate-ionic liquids (POM-ILs) in dye-sensitized solar cells (DSSCs). *Materials Letters: X*, 6, 100033. DOI: 10.1016/j.mlblux.2019.100033.
- [30] Xu, M., Bi, B., Xu, B., Sun, Z., Xu, L. (2018). Polyoxometalate-intercalated ZnAlFe-layered double hydroxides for adsorbing removal and photocatalytic degradation of cationic dye. *Applied Clay Science*, 157, 86–91. DOI: 10.1016/j.clay.2018.02.023.
- [31] Wang, Z., Wang, A., Yang, L., Fan, G., Li, F. (2022). Supported Ru nanocatalyst over phosphotungstate intercalated Zn-Al layered double hydroxide derived mixed metal oxides for efficient hydrodeoxygenation of guaiacol. *Molecular Catalysis*, 528, 112503. DOI: 10.1016/j.mcat.2022.112503.
- [32] Wu, Y., Liu, X., Lei, Y., Qiu, Y., Wang, M., Wang, H. (2017). Synthesis and characterization of 12-tungstophosphoric acid intercalated layered double hydroxides and their application as esterification catalysts for deacidification of crude oil. *Applied Clay Science*, 150, 34–41. DOI: 10.1016/j.clay.2017.09.007.
- [33] Badaruddin, M., Ahmad, N., Fitri, E.S., Lesbani, A., Mohadi, R. (2022). Hydrochar and Humic Acid as Template of ZnAl Layered Double Hydroxide for Adsorption of Phenol. *Science and Technology Indonesia*, 7(4), 492-499. DOI: 10.26554/sti.2022.7.4.492-499.
- [34] Vasiljević, B.N., Obradović, M., Bajuk-Bogdanović, D., Milojević-Rakić, M., Jovanović, Z., Gavrilov, N., Holclajtner-Antunović, I. (2019). In situ synthesis of potassium tungstophosphate supported on BEA zeolite and perspective application for pesticide removal. *Journal of Environmental Sciences (China)*, 81, 136–147. DOI: 10.1016/j.jes.2019.01.018.
- [35] Dinh, T.D., Zhang, D., Tuan, V.N. (2020). High iodine adsorption performances under off-gas conditions by bismuth-modified ZnAl-LDH layered double hydroxide. *RSC Advances*, 10(24), 14360–14367. DOI: 10.1039/d0ra00501k.
- [36] Utami, H.P., Ahmad, N., Zahara, Z.A., Lesbani, A., Mohadi, R. (2022). Green Synthesis of Nickel Aluminum Layered Double Hydroxide using Chitosan as Template for Adsorption of Phenol. *Science and Technology Indonesia*, 7(4), 530-535. DOI: 10.26554/sti.2022.7.4.530-535.
- [37] Flihh, S.M., Ammar, S.H. (2022). Zeolitic imidazolate framework grafted by cobalt tungstate as an efficient photocatalyst for photocatalytic oxidative desulfurization of dibenzothiophene. *Materials Science in Semiconductor Processing*, 149, 106894. DOI: 10.1016/j.mssp.2022.106894.

- [38] Trisunaryanti, W., Sumbogo, S.D., Novianti, S.A., Fatmawati, D.A., Ulfa, M., Nikmah, Y.L. (2021). ZnO-activated carbon blended as a catalyst for oxidative desulfurization of dibenzothiophene. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(4), 881–887. DOI: 10.9767/BCREC.16.4.11797.881-887.
- [39] Ahmad, N., Wijaya, A., Salasia Fitri, E., Suryani Arsyad, F., Mohadi, R., Lesbani, A. (2022). Catalytic Oxidative Desulfurization of Dibenzothiophene by Composites Based Ni/Al-Oxide. *Science and Technology Indonesia*, 7(3), 385–391. DOI: 10.26554/sti.2022.7.3.385-391.
- [40] Ja'fari, M., Ebrahimi, S.L., Khosravi-Nikou, M.R. (2018). Ultrasound-assisted oxidative desulfurization and denitrogenation of liquid hydrocarbon fuels: A critical review. *Ultrason Sonochem*, 40, 955–968. DOI: 10.1016/j.ultsonch.2017.09.002.
- [41] Sadare, O.O., Ayeni, A.O., Daramola, M.O. (2022). Evaluation of adsorption and kinetics of neem leaf powder (*Azadirachta indica*) as a bio-sorbent for desulfurization of dibenzothiophene (DBT) from synthetic diesel. *Journal of Saudi Chemical Society*, 26(2), 101433. DOI: 10.1016/j.jscs.2022.101433.
- [42] Akbari Moghadam, S., Mazloom, G., Akbari, A., Banisharif, F. (2022). Supported vanadium oxide catalyst over HY-zeolite-alumina composite fabricated by extrusion for oxidative desulfurization of dibenzothiophene. *Molecular Catalysis*, 532, 112731. DOI: 10.1016/j.mcat.2022.112731.
- [43] Li, X., Qi, H., Zhou, W., Xu, W., Sun, Y. (2019). Efficient catalytic performance of tetra-alkyl orthotitanates for the oxidative desulfurization of dibenzothiophene at room temperature. *Comptes Rendus Chimie*, 22(4), 321–326. DOI: 10.1016/j.crci.2018.11.008.
- [44] Sikarwar, P., Kumar, U.K.A., Gosu, V., Subaramaiah, V. (2018). Catalytic oxidative desulfurization of DBT using green catalyst (Mo/MCM-41) derived from coal fly ash. *Journal of Environmental Chemical Engineering*, 6(2), 1736–1744. DOI: 10.1016/j.jece.2018.02.021.
- [45] Wei, S., He, H., Cheng, Y., Yang, C., Zeng, G., Kang, L., Qian, H., Zhu, C. (2017). Preparation, characterization, and catalytic performances of cobalt catalysts supported on KIT-6 silicas in oxidative desulfurization of dibenzothiophene. *Fuel*, 200, 11–21. DOI: 10.1016/j.fuel.2017.03.052.
- [46] Xie, D., He, Q., Su, Y., Wang, T., Xu, R., Hu, B. (2015). Oxidative desulfurization of dibenzothiophene catalyzed by peroxotungstate on functionalized MCM-41 materials using hydrogen peroxide as oxidant. *Cuihua Xuebao/Chinese Journal of Catalysis*, 36(8), 1205–1213. DOI: 10.1016/S1872-2067(15)60897-X.
- [47] Lesbani, A., Agnes, A., Saragih, R.O., Verawaty, M., Mohadi, R., Zulkifli, H. (2015). Facile oxidative desulfurization of benzothiophene using polyoxometalate H4[ $\alpha$ -SiW<sub>12</sub>O<sub>40</sub>]/Zr catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 10(2), 185–191. DOI: 10.9767/brec.10.2.7734.185-191.
- [48] Akopyan, A.v., Plotnikov, D.A., Polikarpova, P.D., Kedalo, A.A., Egazar'yants, S.v., Anisimov, A.v., Karakhanov, E.A. (2019). Deep Purification of Vacuum Gas Oil by the Method of Oxidative Desulfurization. *Petroleum Chemistry*, 59(9), 975–978. DOI: 10.1134/S0965544119090019.
- [49] Kumar, S., Srivastava, V.C., Badoni, R.P. (2012). Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, 93(1), 18–25. DOI: 10.1016/j.fuproc.2011.08.017.
- [50] Qiu, L., Cheng, Y., Yang, C., Zeng, G., Long, Z., Wei, S., Zhao, K., Luo, L. (2016). Oxidative desulfurization of dibenzothiophene using a catalyst of molybdenum supported on modified medicinal stone. *RSC Advances*, 6(21), 17036–17045. DOI: 10.1039/c5ra23077b.
- [51] Cao, Y., Wang, H., Ding, R., Wang, L., Liu, Z., Lv, B. (2020). Highly efficient oxidative desulfurization of dibenzothiophene using Ni modified MoO<sub>3</sub> catalyst. *Applied Catalysis A: General*, 589, 117308. DOI: 10.1016/j.apcata.2019.117308.
- [52] Polikarpova, P., Akopyan, A., Shlenova, A., Anisimov, A. (2020). New mesoporous catalysts with Brønsted acid sites for deep oxidative desulfurization of model fuels. *Catalysis Communications*, 146, 106123. DOI: 10.1016/j.catcom.2020.106123.
- [53] Jiang, W., Zheng, D., Xun, S., Qin, Y., Lu, Q., Zhu, W., Li, H. (2017). Polyoxometalate-based ionic liquid supported on graphite carbon induced solvent-free ultra-deep oxidative desulfurization of model fuels. *Fuel*, 190, 1–9. DOI: 10.1016/j.fuel.2016.11.024.
- [54] Ribeiro, S.O., Granadeiro, C.M., Almeida, P.L., Pires, J., Capel-Sanchez, M.C., Campos-Martin, J.M., Gago, S., de Castro, B., Balula, S.S. (2019). Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: Biphasic versus solvent-free systems. *Catalysis Today*, 333, 226–236. DOI: 10.1016/j.cattod.2018.10.046.