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

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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 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.

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


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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-
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$_2$ [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$_2$ [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$_2$ 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$_3$[α-PW$_{12}$O$_{40}$]-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$_3$[α-PW$_{12}$O$_{40}$].nH$_2$O.

#### 2.4 Preparation of ZnAl-K$_3$[α-PW$_{12}$O$_{40}$]

K$_3$[α-PW$_{12}$O$_{40}$]-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$_2$ gas for 24 hours. Then the suspension is cooled, and the product is washed with water and dried.

#### 2.5 Characterizations

ZnAl-LDH, K$_3$[α-PW$_{12}$O$_{40}$]-polyoxometalate, and ZnAl-K$_3$[α-PW$_{12}$O$_{40}$] catalysts were characterized by Fourier transform infrared (Shimadzu, Japan) in wavenumber 4000 – 500 cm$^{-1}$, 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 H₂O₂ oxidizer was added, and catalysts ZnAl-LDH, K₃[α-PW₁₂O₄₀]-polyoxometalate, and ZnAl-K₃[α-PW₁₂O₄₀] 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 g), wavelength scan (220 – 250 nm), reaction time (10 – 60 min), solvent (n-heptane, n-heptane, and n-pentane), acidity test, heterogeneous test, and reusability of catalysts. The efficiency conversion of dibenzothiophene was evaluated by Equation 1:

\[
\text{% Conversion} = \frac{C_0 - C_i}{C_0} \times 100\%
\]  

where, \(C_0\) and \(C_i\) are the initial and final concentrations of dibenzothiophene, respectively.

3. Results and Discussion

X-ray diffraction of ZnAl-LDH, K₃[α-PW₁₂O₄₀]-polyoxometalate (PW), and ZnAl-K₃[α-PW₁₂O₄₀] (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 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, K₃[α-PW₁₂O₄₀]-polyoxometalate, and ZnAl-K₃[α-PW₁₂O₄₀]. FTIR spectra, the bands of ZnAl-PW in wavenumber 3276, 1637, 1363, 1050, 952, 887, and 667 cm⁻¹. The band at 3276 cm⁻¹ could be attributed to O-H stretching from the layer and interlayer of ZnAl-LDH. The absorption peaks at 1637 and 1363 cm⁻¹ were assigned to the hydroxyl and NO₃⁻ vibration [36]. The broad bands around 1050, 952, 887, and 667 cm⁻¹ 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.
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 easily activate the hydrogen atoms in H-bonds and liberate protons, hence increasing the amount of strong Brönsted acid sites. Second, transition metal oxides can induce a reaction through the formation of transition metal oxides with high surface area. The reaction occurs at the interface of transition metal oxides and PW anions, where the transition metal oxides react with PW anions to generate strong Brönsted acid sites.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acidity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAl-LDH</td>
<td>0.399</td>
</tr>
<tr>
<td>PW</td>
<td>1.635</td>
</tr>
<tr>
<td>ZnAl-PW</td>
<td>3.023</td>
</tr>
</tbody>
</table>

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. \( \text{H}_2\text{O}_2 \) 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)](image)

![Figure 5. Effect of contact time](image)

![Figure 7. Effect of catalyst dosage](image)
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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>% Conversion</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neam leaves</td>
<td>DBT = 800 ppm, t = 60 min, solvent = hexane, T = 303 K, dosage of catalyst = 0.8 g</td>
<td>65.80</td>
<td>[41]</td>
</tr>
<tr>
<td>V/HY Zeolite</td>
<td>DBT = 1000 ppm, t = 90 min, solvent = isooctane and toluene, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H₂O₂</td>
<td>100</td>
<td>[42]</td>
</tr>
<tr>
<td>alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TBOT</td>
<td>DBT = 1000 ppm, t = 10 min, solvent = n-octane, T = 298 K, dosage of catalyst = 0.2 g, oxidant = H₂O₂</td>
<td>99.60</td>
<td>[43]</td>
</tr>
<tr>
<td>Mo/MCM-41</td>
<td>DBT = 600 ppm, t = 180 min, solvent = isooctane, T = 363 K, dosage of catalyst = 0.6 g, oxidant = TBHP</td>
<td>94</td>
<td>[44]</td>
</tr>
<tr>
<td>Co/KIT-6</td>
<td>DBT = 400 ppm, t = 40 min, solvent = n-octane, T = 373 K, dosage of catalyst = 0.1 g, oxidant = CYHPO</td>
<td>98.68</td>
<td>[45]</td>
</tr>
<tr>
<td>ZnAl-LDH</td>
<td>DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.25 g, oxidant = H₂O₂</td>
<td>94.71</td>
<td>This study</td>
</tr>
<tr>
<td>PW</td>
<td>DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H₂O₂</td>
<td>95.88</td>
<td>This study</td>
</tr>
<tr>
<td>ZnAl-PW</td>
<td>DBT = 500 ppm, t = 30 min, solvent = n-hexane, T = 323 K, dosage of catalyst = 0.1 g, oxidant = H₂O₂</td>
<td>99.16</td>
<td>This study</td>
</tr>
</tbody>
</table>
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 homogeneous 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.

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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


