Synthesis layered material of MnO\(_2\) and TiO\(_2\) as the support of molybdenum catalyst for bio-crude oil upgrading process

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Abstract. Layered materials are attractive for many applications because of their unique structure consisting of stacked sheets that can be controlled and modified. In this work, various synthetic layered materials (SLMs) i.e., Na-MnO\(_2\), H-MnO\(_2\), and Cs-TiO\(_2\) have been successfully prepared as the support for molybdenum (Mo)-based catalyst and applied for bio-crude oil hydrodeoxygenation (HDO) process. A commercial Mo/Al\(_2\)O\(_3\) catalyst will also be utilized as a benchmark. The physical and chemical properties of the catalysts were characterized by using an X-ray diffractometer, X-ray fluorescence, surface area analyzer, \(\text{NH}_3\)-temperature-programmed desorption, and scanning electron microscopy. The characterization results showed that the interlayer ion exchange of Na\(^+\) ions with H\(^+\) ions was successful for MnO\(_2\) support. The impregnation of the MoO\(_3\) into SLMs increased the surface area, pore-volume, average pore size, and total acidity. The HDO of bio-crude oil using MoO\(_3\)/Na-MnO\(_2\) catalyst produced a higher HHV value of 38.75 MJ/Kg and a DOD value of 82.75% compared to other prepared catalysts or even the MoO\(_3\) commercial catalyst.

1. Introduction

The global energy demand has been increased due to the increase in population growth and economic developments. On the other hand, the availability and sustainability of fossil fuels have led to major global concerns. It encourages the need for sustainable energy sources and liquid fuels or bio-crude oil produced from biomass become promising fuels in the future [1-3]. However, direct bio-crude oil cannot be directly used because of its high corrosiveness, high viscosity, high oxygen and water contents, and low high heating value (HHV). Thus, bio-crude oil needs upgrading to remove the high oxygen content (10-40 wt%) which affects the homogeneity, polarity, high heating value (HHV), viscosity, and acidity of the oil [4-13].

Catalytic hydrodeoxygenation (HDO) is an important process to remove oxygen from the bio-crude oil and produce a high-grade oil product equivalent to fuels [13-17]. Supported MoO\(_3\) catalyst is already known its effectiveness in the hydrodeoxygenation (HDO) reaction that can selectively cut C-O bonds in various derivatives of organic compounds to produce olefin and aromatic hydrocarbons with high activity and selectivity [18]. The reactivity and stability of different supported MoO\(_3\) catalysts (SiO\(_2\), \(\gamma\)-Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\), and CeO\(_2\)) were also investigated for HDO of m-cresol. ZrO\(_2\) and TiO\(_2\) support promoted the catalytic activity and improved stability of MoO\(_3\) catalyst compared with unsupported MoO\(_3\) catalyst [19]. Therefore, the support role of the catalyst is also important that different support could significantly affect the catalyst activity.
Layered materials still developed for many applications due to their unique structure consisting of stacked sheets [20]. These materials can be modified their structural, textural, and compositional depend on their applications. Layered materials allow a fine-tuning and control of the catalytic reactivity [21,22], therefore very interesting for many catalytic applications. Nakamura et al. [23] reported monolayered titanium, tungsten, and manganese oxides synthesized by exfoliation of the nanocrystals through aqueous solution processes at room temperature. The results showed that the exfoliation of the nanocrystals generated the monolayered structures without changes in the lateral size. This monolayered nanodots with morphological control and tuning properties can be applied as a building block of composites at a molecular level and comprehensive applications. Honda et al. [24] have discovered the synthesis path of MnO$_2$ synthetic layered material (SLM) and TiO$_2$ synthetic layered material to enhance their ability as the catalyst.

Due to synthetically layered material (SLM) has significant potential to develop on the catalyst system with high porosity and activity [21], therefore, in this research, various SLMs, such as Na-MnO$_2$, H-MnO$_2$, and Cs-TiO$_2$ were prepared as the support of MoO$_3$ catalyst. The physicochemical properties of SLM before and after supported by MoO$_3$ supported were characterized. The catalytic performance of prepared catalysts was investigated on the catalytic HDO reaction of bio-crude oil. The supported MoO$_3$ commercial catalyst was also utilized as a comparison.

2. Experimental

2.1. Materials

The chemicals employed in this research were manganese chloride tetrahydrate (MnCl$_2$·4H$_2$O), Aldrich), disodium dihydrogen ethylene-diamine tetraacetate (EDTA, Merck), sodium hydroxide (NaOH, Merck), rutile titanium oxide (TiO$_2$, Aldrich), cesium carbonate (Cs$_2$CO$_3$, Aldrich), hydrochloric acid (HCl, Merck), ammonium heptamolybdate heptahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Merck), H$_2$ gas, carbon disulfide (CS$_2$, Merck), ethyl acetate (C$_4$H$_8$O$_2$, Merck), and MoO$_3$/Al$_2$O$_3$ commercial catalyst (15% wt MoO$_3$). The bio-crude oil used in this work was produced from pyrolysis of palm kernel shell, a naturally abundant lignocellulosic biomass waste obtained from a local palm oil plant in Sumatera.

2.2. Synthesis of Na-MnO$_2$ SLM

Na-MnO$_2$ SLM was synthesized by the chelation-mediated approach reported before Honda et al. [24]. An amount of typically 5 mmol/dm$^3$ (0.58 g) EDTA and 20 mmol/dm$^3$ (1.58 g) MnCl$_2$·4H$_2$O into a polypropylene container which contains 400 mL of distilled water, then stir until all powder dissolved. After dissolved, 200 mmol/dm$^3$ (3.2 g) NaOH in 400 mL distilled water was prepared and added into the solution. The solution was maintained under stirring for five days at room temperature. The black precipitate obtained was filtered and dried at room temperature.

2.3. Synthesis of H-MnO$_2$ SLM

The H-MnO$_2$ SLM synthesized by the ion-exchange method. 1 g of the synthesized Na-MnO$_2$ SLM was added into 100 mL of 1M HCl solution. The mixture was stirred for one day at room temperature. The precipitates were collected and dried at room temperature [24].

2.4. Synthesis of Cs-TiO$_2$ SLM

Synthesis of Cs-TiO$_2$ SLM was carried out in solid-state conditions reported by Honda et al. [24]. 1.5 g of TiO$_2$ rutile powder and 1 g of Cs$_2$CO$_3$ are mixed and calcined at 800 °C for 20 hours in argon gas flow. Then, the powder was cooled until room temperature.

2.5. Impregnation of MoO$_3$

The SLMs were impregnated with MoO$_3$ through the wet impregnation method from the ammonium heptamolybdate (AHM) precursor [25,26]. A total of 13% wt MoO$_3$ (0.275 g) AHM was dissolved in 5
mL distilled water then added to the solution contained 1.5 g of the synthesized layer material in 10 mL distilled water. The mixture was stirred and heated around 80 °C until dry. The powder results were dried overnight in oven 100 °C and calcined at 550 °C for 3 hours.

2.6. Catalyst characterization

X-Ray Diffractometer (XRD) of the catalysts was analyzed using MAX Science MXP3V, with Cu Kα radiation at 40 kV and 25 mA, and a secondary graphite monochromator.

Brunauer-Emmett-Teller (BET) adsorption method of the catalysts was conducted using Tristar II 3020 Micromeritics Instrument to obtain the specific surface area of the samples through nitrogen adsorption-desorption isotherms, performing at -196 °C on liquid nitrogen after degassing the sample at 200 °C for 2 h.

NH₃-Temperature Programmed-Desorption (NH₃-TPD) of the catalysts was conducted using Micromeritics 2900. The analysis was carried out from 100 to 450 °C at a heating rate of 10 °C/min with a flow rate of Helium (He) gas of 15 mL/min. After each TPD measurements, the amount of ammonia adsorbed was determined from the calibration curve obtained from varying volumes of ammonia in He. The total acidities of the catalysts were measured by comparing the NH₃-TPD spectra to that of the reference material.

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-IT300 electron microscope. The samples are fixed on the holder with conductive adhesive and coating with gold for 90 s to improve the conductivity of the samples.

X-Ray Fluorescence (XRF) of the catalysts was performed using Thermo Niton XL3t. About 1 gr sample is placed on the sample holder and was measured on the inert condition using He gas.

2.7. Catalyst sulfidation

All prepared catalysts were sulfided before the HDO reaction by the same procedure as reported by Jiang et al. [26,27]. 0.3 g of catalyst was placed into the U tube reactor and flowed by N₂ gas at a pressure of 1 bar. The temperature was maintained at 150 °C for 1.5 h. Then, the catalyst was cooled to room temperature. The sulfidation was continued with 1 bar of H₂ gas that flows over CS₂ at 400°C for 2 h. The catalyst was cooled to room temperature and applied for hydrodeoxygenation (HDO) of bio-crude oil.

2.8. Catalytic performance test

0 g of bio-crude oil and 3% w/w of catalyst were placed into an autoclave reactor, HDO reaction was carried out at 300°C for 4 h under 60 bar of H₂ [26]. The MoO₃/Al₂O₃ commercial catalyst was used as a benchmark. The liquid product was collected and analyzed using a CHON analyzer to measure the high heating value (HHV). The HHV results were compared with the HHV of commercial diesel fuel.

3. Result and discussion

3.1. Characterization of catalysts

The crystal structure of supports and supported Mo catalysts was observed using XRD to ensure the diffraction pattern of the synthesized catalyst were appropriate to the diffraction pattern of the target material. The diffraction pattern of prepared catalysts is shown in figure 1.

For Na-MnO₂ SLM (figure 1.1-a), the dominant peaks at 20 of 12.40°, 24.90°, and 35.60° (ascribed to the diffraction by the (001), (002), (200) planes) might be described to typical of birnessite-type of sodium manganite which is compatibility with JCPDS 43-1456. H-MnO₂ SLM (figure 1.1-b) shows some dominant peaks which are similar to Na-MnO₂ with a lower intensity. Some peaks diminished and a new peak observed at 20 of 23.1°. It indicates that Na⁺ ions in the interlayer of Na-MnO₂ SLM have been exchanged by H⁺ ions from HCl and produced H-MnO₂ SLM. Moreover, the XRD pattern of Cs-TiO₂ SLM shows the 20 of 10.2°, 20.5°, 27.9°, and 30.5° (ascribed to the diffraction by the (020), (040), (130), (011) planes) which revealed to Cs₅Ti₆O₁₃ according to JCPDS 38-0170. The diffraction pattern
also observed in the region of $2\theta = 27.4^\circ; 36.0^\circ; 54.3^\circ$ with Miller indexes (110), (101) and (211) under JCPDS 21-1276 which is a diffraction pattern of rutile TiO$_2$ that from material precursors. Although Cs-TiO$_2$ SLM was obtained with TiO$_2$ as the main layer and Cs ions found in between layers [28], it is suggested that only a small formation of Cs-TiO$_2$ SLM was formed, due to the diffraction pattern of rutile TiO$_2$ still be observed (figure 1.1-c). All XRD pattern results were obtained in figure 1 is the same observed on Honda et al. [24], it is described that preparation of synthesis layer materials of Na-MnO$_2$, H-MnO$_2$, and Cs-TiO$_2$ are obtained successfully. For impregnated MoO$_3$ in SLMs support (figure 1.2), the peaks observed at $2\theta = 12.8^\circ, 23.3^\circ, 25.3^\circ$, and $27.3^\circ$ (ascribed to the diffraction by the (020), (110), (040), (021) planes) indicates the existence of orthorhombic phase of MoO$_3$ (JCPDS 35-0609). The presence of MoO$_3$ peaks on the SLMs shows that the impregnation of the MoO$_3$ into SLMs was successful. However, this result is also described that Mo structure on SLM supports is mostly in MoO$_3$ crystal and indicated poor dispersion of Mo on the SLM support [29].

The surface area, pore-volume, and average pore diameter of the supports and supported Mo catalysts are summarized in table 1. The impregnation of MoO$_3$ increased the surface area, pore-volume, and average pore size of SLMs. It is suggested that some of MoO$_3$ is not dispersed on the pore of SLM support after impregnation but also modified the stacked sheets of SLM acting as the pillar [30-32], thus increasing surface area and pore diameter. Moreover, the average pore diameter of Na-MnO$_2$ (17.384 nm) is lower than H-MnO$_2$ (12.803 nm). It indicates the success of ion exchange of Na$^+$ ions with H$^+$ ions in the interlayer of MnO$_2$ which decreased the distance between layers.

| Sample                  | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Average Pore diameter (nm) | Total Acidity (mmol/g) |
|-------------------------|------------------------|------------------------|----------------------------|------------------------|
| Na-MnO$_2$              | 6.273                  | 0.027                  | 17.384                     | 1.03x10$^4$            |
| MoO$_3$/Na-MnO$_2$      | 11.980                 | 0.060                  | 20.098                     | 3.03x10$^4$            |
| H-MnO$_2$               | 10.039                 | 0.032                  | 12.803                     | 2.64x10$^4$            |
| MoO$_3$/H-MnO$_2$       | 14.353                 | 0.069                  | 19.174                     | 6.12x10$^5$            |
| Cs-TiO$_2$              | 1.736                  | 0.012                  | 26.869                     | 1.56x10$^4$            |
| MoO$_3$/Cs-TiO$_2$      | 5.425                  | 0.030                  | 22.044                     | 7.30x10$^5$            |

The acidity properties of catalysts were evaluated through NH$_3$-TPD analysis as also shown in table 1. The total acidity of Na-MnO$_2$ (1.025x10$^4$ mmol/g) is higher than H-MnO$_2$ (2.64x10$^4$ mmol/g). It
means the interlayer ion exchange of Na\textsuperscript{+} ions with H\textsuperscript{+} ions that contribute to the increase of the acidity sites was successful \cite{30}. The impregnation of MoO\textsubscript{3} into MnO\textsubscript{2} SLM support also increased the total acidity significantly from 1.025x10\textsuperscript{-4} to 3.03x10\textsuperscript{-4} mmol/g. On the other hand, the impregnation of MoO\textsubscript{3} into H-MnO\textsubscript{2} and Cs-TiO\textsubscript{2} SLMs support decreased the total acidity from 2.64x10\textsuperscript{-4} to 6.12x10\textsuperscript{-5} mmol/g and from 1.56x10\textsuperscript{-4} to 7.30x10\textsuperscript{-5} mmol/g, respectively. This decrease in total acidity after impregnation is suggested that the acidity of H-MnO\textsubscript{2} and Cs-TiO\textsubscript{2} SLMs is higher compare to MoO\textsubscript{3} metal. Therefore, during the impregnation proses, some of the MoO\textsubscript{3} metal was exchanged ion H\textsuperscript{+} and Cs\textsuperscript{2+} and acting as the pillar between the stacked sheets, thus decrease the acidity. This result is similar to the surface area and average pore diameter in table 1 that also showed a decrease after the impregnation.

**Figure 2.** Surface morphology of (a) Na-MnO\textsubscript{2}, (b) H-MnO\textsubscript{2}, (c) Cs-TiO\textsubscript{2}, (d) MoO\textsubscript{3}/Na-MnO\textsubscript{2}, (e) MoO\textsubscript{3}/H-MnO\textsubscript{2}, and (f) MoO\textsubscript{3}/Cs-TiO\textsubscript{2} (Bar scale: 1\textmu m)

SEM analysis was carried out to identify surface morphology and the distribution of components on the synthesized catalysts as shown in figure 2. It can be seen that the surface morphology of Na-MnO\textsubscript{2} SLM (figure 2a) is mostly hollow tubes structure and stacked. Moreover, after ion-exchanged with H\textsuperscript{+}, the surface morphology of H-MnO\textsubscript{2} (figure 2b) is different from Na-MnO\textsubscript{2}, the structure of H-MnO\textsubscript{2} SLM becomes small agglomerate particles composed of the thin layers stack. This morphological change confirms that the interlayer exchange Na\textsuperscript{+} ions with H\textsuperscript{+} ions were successful. For Cs-TiO\textsubscript{2} SLM, the surface structure is mostly small distributed particles. The addition of MoO\textsubscript{3} into the Na-MnO\textsubscript{2} and H-MnO\textsubscript{2} supports (figure 2d and 2e) also changed the surface morphology. All surface structures of MoO\textsubscript{3}/Na-MnO\textsubscript{2} and MoO\textsubscript{3}/H-MnO\textsubscript{2} become similar to the H-MnO\textsubscript{2} structure and even smaller agglomerate particles. It indicates that MoO\textsubscript{3} particles filled the pores and decreased the particle size. On the other hand, Cs-TiO\textsubscript{2} does not show significant differences in the surface morphology after impregnated by MoO\textsubscript{3}, but it seems to become smaller particles after the impregnation.

XRF analysis is conducted to determine the composition of metal elements in prepared catalysts both qualitatively and quantitatively. The results of the qualitative measurement of chemical composition are shown in table 2. It can be observed that the composition of Na in the H-MnO\textsubscript{2} sample disappeared. It confirms that Na\textsuperscript{+} ions in the Na-MnO\textsubscript{2} sample are exchanged successfully by H\textsuperscript{+} ions. The impregnation of MoO\textsubscript{3} shows a decrease in the Mn composition and the appearance of Mo metal content in the material. The presence of Mo shows that the MoO\textsubscript{3} metal was successfully impregnated into the SLM supports. However, it is different for the Cs-TiO\textsubscript{2} sample. The amount of Mo is slightly small observed than Na-MnO\textsubscript{2} and H-MnO\textsubscript{2} after the impregnation. It is indicated that only a minor amount of MoO\textsubscript{3}
could disperse and exchange with Cs ion as the pillar on Cs-TiO$_2$ SLM support. This phenomenon is also supported by the SEM analysis result (figure 2), which showed that the surface structure of Cs-TiO$_2$ SLM is not significantly altered after the impregnation.

### Table 2. Element compositions by XRF analysis.

| Sample                  | Na | Mn | Cs | Ti | Mo |
|-------------------------|----|----|----|----|----|
| Na-MnO$_2$              | 1.5| 98.2| -  | -  | -  |
| MoO$_3$/Na-MnO$_2$      | 0.5| 69.2| -  | -  | 29.6|
| H-MnO$_2$              | -  | 98.2| -  | -  | -  |
| MoO$_3$/H-MnO$_2$      | -  | 78  | -  | -  | 21.7|
| Cs-TiO$_2$           | -  | -   | 36.3| 43.8| -  |
| MoO$_3$/Cs-TiO$_2$     | -  | -   | 31.8| 40.9| 9.6|

### 3.2. Catalytic performance of MoO$_3$ supported catalysts

HDO reaction of bio-crude oil was conducted in a batch reactor and products were analyzed using the CHON analyzer to determine a high heating value (HHV) and degree of deoxygenation (DOD) of the product. The results were summarized in Table 3.

### Table 3. CHON analysis results.

| Samples         | %, wt | HHV (MJ/Kg) |
|-----------------|-------|-------------|
|                 | N     | C   | H   | O   |     |
| Bio-crude oil   | 0.45  | 58.18| 7.79| 33.58| 24.8 |
| MoO$_3$/Al$_2$O$_3$| 0.59 | 72.84| 7.95| 18.62| 32.7 |
| MoO$_3$/Na-MnO$_2$| 0.75 | 82.55| 8.30| 8.40 | 38.3 |
| MoO$_3$/H-MnO$_2$| 0.56 | 70.58| 7.80| 21.06| 31.3 |
| MoO$_3$/Cs-TiO$_2$| 2.31 | 71.86| 7.41| 18.42| 31.6 |
| Diesel oil      | -     | 87.00| 13.00| -   | 44.91 |

All of the catalyst samples show the decrease in oxygen content of bio-crude oil from 33.58% to below 22% after HDO. On the other hand, the carbon content of bio-crude oil increased from 58.18% to more than 70% after HDO. Consequently, HHV of bio-crude oil increased after HDO using MoO$_3$/Na-MnO$_2$, MoO$_3$/H-MnO$_2$, and MoO$_3$/Cs-TiO$_2$, which is from 24.8 MJ/Kg to 38.3 MJ/Kg, 31.3 MJ/Kg and 31.6 MJ/Kg, respectively. It indicates that the HDO process was successfully diminished the oxygen content and improve the quality of bio-crude oil even though the quality obtained was still below diesel fuel. The commercial MoO$_3$/Al$_2$O$_3$ catalyst was used as a benchmark in this study. It is observed that our prepared catalysts were closed to the activity of MoO$_3$/Al$_2$O$_3$ commercial catalyst or even higher, especially on the MoO$_3$/Na-MnO$_2$ catalyst. The HHV value of the MoO$_3$/Na-MnO$_2$ catalyst is superior compared with the commercial catalyst.

The DOD value indicates the percentage of oxygen lost during the HDO reaction takes place. The higher DOD value means a higher catalytic activity on breaking the C-O bond in the deoxygenation reaction [33]. Table 4 shows the DOD value of bio-crude oil products produced by HDO. It is observed that the MoO$_3$/Na-MnO$_2$ catalyst produced the highest decrease in the O/C ratio with a DOD value of 82.75%. Meanwhile, MoO$_3$/Cs-TiO$_2$ catalyst and commercial catalyst MoO$_3$/Al$_2$O$_3$ showed the same value of 55.17%. The MoO$_3$/H-MnO$_2$ catalyst showed the lowest DOD value of 48.28%. This decrease in the O/C ratio confirms that the deoxygenation reaction was successful. It is shown that the MoO$_3$/Na-MnO$_2$ SLM catalyst was superior on the catalytic performance compared to the other prepared catalysts instead of the commercial MoO$_3$ catalyst.
Table 4. DOD value of HDO products.

| Sample                  | O/C  | H/C  | DOD (%) |
|-------------------------|------|------|---------|
| Bio-crude oil           | 0.58 | 1.32 | -       |
| MoO₃/Al₂O₃              | 0.26 | 0.86 | 55.17   |
| MoO₃/Na-MnO₂            | 0.10 | 0.64 | 82.75   |
| MoO₃/H-MnO₂             | 0.30 | 0.92 | 48.28   |
| MoO₃/Cs-TiO₂            | 0.26 | 0.86 | 55.17   |

Topsøe et al. [34] describe there are several properties of the MoO₃ catalyst are affected on the hydrotreating reaction of crude oil, such as surface area, pore diameter, acidity, porous catalyst, dispersion of active metal on the surface support, the interaction between active metal catalysts and the surface support, and additive component [34-40]. Based on the characterization data above, it is suggested that the total acidity of catalyst is one of the crucial points to obtain a high catalyst activity next to the surface area, pore-volume, and pore diameter. Surface area, pore-volume, and pore diameter of MoO₃/Na-MnO₂ is similar to MoO₃/H-MnO₂ (table 1), and the surface morphology of both catalysts also showed as the porous material with small agglomerate particles composed of the thin layers stack (figure 2). However, the MoO₃/Na-MnO₂ catalyst is more acid compare to other catalysts (table 1). Table 4 showed that O/C and H/C values of MoO₃/Na-MnO₂ are very narrow compared to the other catalysts, especially the MoO₃ commercial catalyst, which is indicated that the ability of deoxygenation and hydrogenation reactions is more active of MoO₃/Na-MnO₂ catalyst. The activity catalyst on the hydrotreating process could be increased by using the support with a high acidity [34-37]. Thus, the acidity factor is concluded as significant properties to obtain a high HHV and DOD values after the HDO reaction of bio-crude oil in this study.

4. Conclusion

Synthetic layered materials of Na-MnO₂, H-MnO₂, and Cs-TiO₂ have been successfully prepared and characterized as support for MoO₃ catalyst. MoO₃/Na-MnO₂ catalyst showed superior in the HDO activity compared with other catalysts, especially the MoO₃ commercial catalyst. The highest HHV and DOD values were obtained of 38.3 MJ/Kg and 82.75%, respectively, although this value was still lower than diesel fuel properties. It is suggested that the acidity factor is the primary characteristic next to the surface area, pore-volume, and average pore diameter to obtain a high HHV and DOD values after the HDO reaction of bio-crude oil.

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