

Catalytic activity of trimetallic sulfided Re-Ni-Mo/ γ -Al₂O₃ toward deoxygenation of palm feedstocks

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ABSTRACT

Catalytic activities of trimetallic ReNiMo sulfide supported on γ -Al₂O₃ toward the deoxygenation of oleic acid, palm fatty acid distillate (PFAD), refined palm stearin (RPS) and refined palm olein (RPO) were studied. Relevant monometallic and bimetallic (i.e. Mo-, W-, Re-, ReMo-, ReW-, NiMo-) sulfides were also tested for comparison. Experiments revealed that, among all catalysts, ReNiMo sulfide catalyst exhibited the highest diesel yield of 76.5% from oleic acid, 72.5% from PFAD, 69.7% from RPS and 69.5% from RPO. Furthermore, the catalyst could maintain constant diesel yield level for at least six consecutive runs, whereas significant deactivation was observed from other catalysts due to high carbon deposition. Importantly, glycerol was also successfully employed as a hydrogen donor for deoxygenation reaction over this catalyst. From the catalyst characterizations, additional of Re increased the NiMo surface area by 20.4%, furthermore, it reduced the metal particle size and promote the metal dispersion on the support.

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1. Introduction

Nowadays, the replacement of fossil fuels with renewable fuels is an important global concern. It has been reported that diesel fuel demand has been dramatically increasing from 26 million barrels per day in 2012 to around 36 million barrels per day in 2035 [1]. Therefore, extensive researches on diesel fuel production from various feedstocks and technologies have been widely carried out in the recent years [2–7]. Among various raw materials, palm derivatives are promising renewable feedstocks for synthesizing diesel-like hydrocarbons via deoxygenation reaction [1,8,9]. Diesel-like hydrocarbons contain a mixture of hydrocarbon molecules that range in size from 8 to 21 carbon atoms, mainly C₁₇ (heptadecane) and C₁₈ (octadecane) [2]. A fatty acid is a carboxylic acid with a straight aliphatic chain and found in plant oils and animal fats. The differences of fatty acid compositions in plant oils mainly depend on species and quality of the source and also geographical location in which the plant grows [10]. Oleic acid (C_{18:1}), linoleic acid (C_{18:2}),

linolenic acid (C_{18:3}), stearic acid (C_{18:0}), and palmitic acid (C_{16:0}) are the principal compositions of free fatty acids in most vegetable oils [2,8,11].

The deoxygenation of fatty acids is an alternative process for the production of diesel-like hydrocarbons or green diesel from renewable sources by removing oxygen atoms from fatty acid molecules in form of H₂O or oxides of carbon (CO_x). The process can be carried out in the presence of H₂ or H₂-free atmosphere environment [9]. Reaction pathways for the deoxygenation of fatty acids consist of decarboxylation (DCO₂), decarbonylation (DCO), or hydrodeoxygenation (HDO) [1,9]. In detail, DCO₂ produces CO₂ and n-alkanes with the loss of one carbon atom (C_{n-1}) from the original fatty acid feedstock (C_n). The major advantage of DCO₂ is due to no H₂ requirement for producing n-alkanes. In case of DCO, both CO and water are lost from the original fatty acid feedstock while alkenes are generated. Meanwhile, HDO removes oxygen in form of water and produces the alkanes (C_n) with the same number as the corresponding fatty acid chain [1,9,11,12]. Because this process can generate gaseous CO and CO₂ as well as the presence of H₂ inside the reaction system, other possible reactions such as water gas shift, methanation, and hydrogenation should be considered [1,12].

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From the practical perspective, tuning of the hydrocarbon composition product is very important, which can be achieved via operating conditions and catalysts [1,2,9]. Typically, the suitable catalysts for deoxygenation of triglycerides and fatty acids are metal catalysts in a reduced state [4,12–14], metal phosphide, carbide, and nitride catalysts [15,16] and metal sulfide catalysts [5,12,16–20]. Many literatures have reported on deoxygenation process using noble metal catalysts in the reduced form such as Pd, Pt, and Ru [2,4,14,21]. However, noble metal catalysts are more expensive than non-noble metal catalysts. Moreover, the cost factor limits the applicability of noble metals for green diesel production process [2,18,20,22]. Non-noble metal catalysts such as Ni and Co demonstrate high activity but their basic drawback is the quick deactivation [18,23]. Metal phosphide and carbide catalysts show high performance in the removal of oxygen atoms from oxygenated biomass feedstocks and selectivity for diesel-range alkanes. However, the preparation processes of metal phosphide or carbide catalysts are complicated and most of them have a very short lifetime [2,24,25]. Transition metal sulfides show high catalytic performances in the production of green diesel and cost-effective application for large-scale production [26–28]. The effect of operating parameters and catalysts was explored in previous works. Based on some earlier works, Ruinat et al. and co-workers [29] studied the deoxygenation of ethyl heptanoate catalyzed by unsupported MoS_2 , Ni_3S_2 , and Ni-promoted MoS_2 (with various Ni/Mo ratios) in a fixed-bed reactor. They reported that the MoS_2 was highly selective for HDO while the Ni_3S_2 was highly selective for DCO and DCO_2 pathways. The Ni/Mo ratio impacted the HDO/DCO selectivity. Dragu and co-workers [21] studied influence of preparation method of Pd/mesoporous carbon nanocatalysts on activity and product distribution of oleic acid deoxygenation. They found that activity and product distribution depend on the synthesis route and reaction conditions, namely, batch and flow conditions. Kubička [30] prepared the sulfided Ni, Mo, and NiMo catalysts supported on commercial Al_2O_3 and tested at 260–280 °C, 3.5 MPa and 0.25–4 h^{-1} in a fixed-bed reactor. The bimetallic NiMo sulfide catalysts had a higher activity than a monometallic Mo and Ni sulfide catalysts. In our previous studies, a series of nickel catalysts i.e. nickel sulfide, nickel phosphide and nickel carbide was investigated for deoxygenation of spent coffee oil to produce bihydrotreated fuel [31]. From our previous work, it can be concluded that the production of the gasoline fraction was favored by nickel carbide, while the diesel fraction was favored by nickel sulfide. Then, we also have studied and compared NiMo/ $\gamma\text{-Al}_2\text{O}_3$ sulfide catalyst and Pd/C reduced catalyst for production of green diesel from spent coffee grounds [16]. We found that NiMo/ $\gamma\text{-Al}_2\text{O}_3$ sulfide catalyst showed higher catalytic activity than Pd/C reduced catalyst under the reaction time of 2 h with operating temperature of 400 °C. Moreover, the conversions of crude palm oil, degummed palm oil, and palm fatty acid distillate were tested [12]. The experiments were done by using NiMo/ $\gamma\text{-Al}_2\text{O}_3$ sulfide catalyst and Pd/C reduced catalyst. The results revealed that Pd/C is more suitable for use in free fatty acid feedstock while sulfided NiMo/ $\gamma\text{-Al}_2\text{O}_3$ is preferred for triglyceride feedstock. Nowadays, hydrogen donors such as glycerol, formic acid and alcohol are employed successfully as a solvent and hydrogen donor in hydrogenation and dehydrogenation reactions [32–34]. For instance, Vardon and co-workers [33] studied the use of Pt-Re/C for hydrogenation and deoxygenation of oleic acid using glycerol for in situ hydrogen production. They found that the addition of Re on Pt/C could improve deoxygenation performance at low temperature.

In the present work, the catalytic performance of sulfided ReNiMo supported on $\gamma\text{-Al}_2\text{O}_3$ toward catalytic deoxygenation of oleic acid for diesel-like hydrocarbon production was studied and compared to other common monometallic and bimetallic (i.e. Mo-,

W-, Re-, ReMo-, ReW- and NiMo-) sulfide catalysts. The effect of operating parameters (i.e. reaction temperature, time and hydrogen donor) was examined in order to determine suitable operating condition. Next, catalyst reusability test was also performed. Importantly, the catalytic activity toward the conversions of palm fatty acid distillate (PFAD), refined palm olein (RPO), and refined palm stearin (RPS) were also applied after optimized catalyst and operating condition. The characterizations of sulfided catalysts were evaluated using BET technique, X-ray diffraction analysis (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS), and H_2 -chemisorption and temperature-programmed oxidation (TPO) to study the relation between their catalytic activity and physical-chemical properties.

2. Experimental section

2.1. Materials

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium (para) tungstate hydrate ($(\text{NH}_4)_{10}\text{H}_2(\text{W}_2\text{O}_7)_6 \cdot x\text{H}_2\text{O}$), and ammonium perhenate (NH_4ReO_4) were purchased from Sigma-Aldrich. Ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was obtained from Carlo Erba. The $\gamma\text{-Al}_2\text{O}_3$ with 1.8 mm diameter was purchased from Sasol Company. The ASTM D2887-12 calibration standard of $\text{C}_5\text{-C}_{44}$ linear hydrocarbon compounds was supplied by Restek Corporation. N-hexane and formic acid were purchased from Fisher Scientific. Oleic acid and glycerol were supplied by Sigma-Aldrich. Ethanol was purchased from RCI Labscan Ltd. Glycerol was purchased from Sigma-Aldrich.

The raw materials i.e. palm fatty acid distillate (PFAD), refined palm olein (RPO), and refined palm stearin (RPS) were adopted from Pathum Vegetable Oil, Co., Ltd. (Thailand). PFAD is a by-product of physical refining of crude palm oil products while refined palm olein (RPO) and refined palm stearin (RPS) obtain by the fractionation of palm oil after crystallization. PFAD consists of 93 wt.% free fatty acid, whereas RPO and RPS consist of triglyceride higher than 99 wt% and 97 wt%, respectively. Palmitic acid and oleic acid are the major fatty acids in PFAD, RPO and RPS feedstocks, as shown in Table 1.

2.2. Catalyst preparations

Monometallic (10%Mo, 10%W, and 3%Re), bimetallic (3%Re-10%Mo, 3%Re-10%W, and 3%Ni-10%Mo), and trimetallic (1%Re-3%Ni-10%Mo) sulfide catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ were prepared by impregnation technique. The commercial $\gamma\text{-Al}_2\text{O}_3$ was crushed and sieved to obtain 0.42 mm particle size. The metal precursors were calculated by desired weight and dissolved in deionized water. Then, the metal aqueous solutions were impregnated on $\gamma\text{-Al}_2\text{O}_3$ followed by drying overnight in an oven at 105 °C and calcined with a ramping rate of 10 °C min^{-1} from room temperature to 500 °C in air and held for 5 h. Before testing reaction, the prepared catalysts were sulfided at 400 °C for 4 h under a flow of 4 L h^{-1} of $\text{H}_2\text{S}/\text{H}_2$ (10/

Table 1

Composition of PFAD, RPO, and RPS feedstocks from palm oil industry for biodiesel production.

Fatty acid	PFAD (wt.%)	RPS (wt.%)	RPO (wt.%)
C16:0 (Palmitic acid)	47.1	58.9	39.8
C18:0 (Stearic acid)	4.5	4.7	4.4
C18:1 (Oleic acid)	35.7	27.4	42.5
C18:2 (Linoleic acid)	9.3	6.9	11.2
Others	3.4	2.1	2.1

90) mixture.

2.3. Catalyst characterizations

Nitrogen adsorption-desorption of the samples was measured at -196°C on a Belsorp-max Bel Japan equipment. Prior to the measurements, the samples were degassed at 150°C for 3 h in the degas port before starting N_2 adsorption. The surface area and pore size distribution were determined using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

A scanning electron microscope (SEM) connected with an Energy Dispersive X-Ray Spectrometer (EDS) analyzer (JEOL, JSM-6610 LV, Japan) was applied to characterize the morphology and elemental composition of the sulfided catalysts.

An X-ray diffraction (XRD, Philips X'Pert, Netherlands) patterns of the alumina support and sulfided catalyst samples were obtained at 40 kV and 30 mA with $\text{CuK}\alpha$ radiation at a scanning rate of $0.02^{\circ}\text{min}^{-1}$ in the range of 20 – 80° , which are applied to provide detailed information on the crystallographic structure (phase and chemical composition). X-ray photoelectron spectroscopy (XPS) analysis of the studied samples was performed using AXIS Supra™ from Kratos Analytical (Shimadzu Corporation).

H_2 chemisorption analysis was performed on Micromeritics Pulse ChemiSorb 2700 (USA) to determine dispersion of sulfided catalyst samples. 100 mg of the sample placed in a quartz sample cell and the sample was first degassed under flowing He at 400°C to remove the moisture. Next, the sample was reduced under H_2 flow at 400°C for 2 h. After the reduction, the sample was purged in flowing He to remove hydrogen and cooled to 100°C . Subsequently, the sample was placed to temperature programmed desorption (TPD) with He at the heating rate of $10^{\circ}\text{C min}^{-1}$ to 800°C . The metal surface area and metallic dispersion was calculated from the

inner volume of 125 cm^3 , from which 25 cm^3 of feedstock (i.e. oleic acid, PFAD, RPS, or RPO) and 0.5 g sulfided metal catalyst were loaded into the reactor. Then, H_2 was loaded to raise the reactor pressure to 4 MPa. Next, the reactor was heated to desired temperature (300 – 400°C). The reaction time (1–3 h) was counted after the inside temperature of reactor reached the desired temperature. After reaching the reaction time required, the reaction was stopped instantly by quenching the reactor in an ice-cool water bath. The liquid and gas samples taken from the reactor were quantitatively analyzed by various techniques while the spent catalyst was collected to reuse. All the experiments were performed in triplicate, with the average value reported.

2.5. Product analysis

The liquid products were diluted with *n*-hexane prior to analyze with GC-FID (Shimadzu GC-2014) equipped with Agilent DB-1HT column. The amount of each of *n*-alkane compounds (*n*- C_8 to *n*- C_{18}) in the liquid samples were determined using calibration curve. The liquid product identifications were confirmed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A) with a DB-1HT column. The composition of gas products (H_2 , CO, CO_2 , CH_4 , C_2H_4 , and C_2H_6) obtained from experiments were collected and analyzed by GC Shimadzu GC-2014 with Supercol 60/80 Carboxen 1000 column coupled with FID and TCD detectors. Moreover, the water content in the liquid products was determined by Karl Fisher titrator (model 870 KF Titrino plus, Metrohm Co., Ltd.).

The equations for calculation of conversion of oleic acid and/or triglyceride, liquid fraction, gas fraction, product yield, and hydrocarbon product distribution are shown in Eqs. (1)–(5), respectively. The liquid hydrocarbon products were classified into 2 fractions: C_8 – C_{12} was defined as gasoline range and C_{13} – C_{18} is defined as diesel range. The hydrocarbon product distribution was defined as the

$$\text{Conversion}(\%) = \left(\frac{\text{Weight percent of FA and/or TG in feed} - \text{Weight percent of FA and/or TG in product}}{\text{Weight percent of FA and/or TG in feed}} \right) \times 100 \quad (1)$$

volume of H_2 adsorbed by assuming a H_2 to metal atom of 1:1.

After catalyst testing, the post-temperature programmed oxidation (TPO) was applied to indicate the amount of coke deposited on the surface of the catalyst by flowing $10\%\text{O}_2/\text{He}$ ($10^{\circ}\text{C min}^{-1}$) and the temperature increased from room temperature to 1000°C . The amount of coke deposited on the surface of the catalyst was calculated by measuring the amounts of CO and CO_2 desorbed from the spent catalyst samples by online mass spectrometer (Thermostar GSD 301 T).

2.4. Reaction procedure

The reactions were carried out in a batch-type reactor with

ratio of weight of single compound with total weight of hydrocarbon product (C_8 – C_{18}).

$$\text{Liquid fraction} = \frac{\text{Weight of liquid product}}{\text{Weight of feedstock}} \quad (2)$$

$$\text{Gas fraction} = 1 - \frac{\text{Weight of liquid product}}{\text{Weight of feedstock}} \quad (3)$$

$$\text{Product yield}(\%) = \left(\frac{\text{Total weight percents of desired hydrocarbons, } \text{C}_8 - \text{C}_{12} \text{ or } \text{C}_{13} - \text{C}_{18}}{\text{Weight percent of FA and/or TG in feed}} \right) \times \text{liquid fraction} \times 100 \quad (4)$$

$$\text{Hydrocarbon product distribution}(\%) = \left(\frac{\text{Weight percent of single component hydrocarbon}(\text{C}_i)}{\text{Total weight percents of desired hydrocarbons}(\text{C}_8 - \text{C}_{18})} \right) \times 100 \quad (5)$$

The hydrodeoxygenation (HDO), decarbonylation (DCO), and decarboxylation (DCO₂) were major reaction pathways for deoxygenation process. In the case of pure oleic acid as a feedstock, the proportion of HDO and DCO_x (i.e. DCO and DCO₂) reactions were calculated based on weight balance using following equations:

$$\text{HDO}(\%) = \left(\frac{\text{Weight percent of C}_{18} \text{ in product}}{\text{Weight percent of C}_{17} \text{ and C}_{18} \text{ in product}} \right) \times 100 \quad (6)$$

$$\text{DCO} \times (\%) = \left(\frac{\text{Weight percent of C}_{17} \text{ in product}}{\text{Weight percent of C}_{17} \text{ and C}_{18} \text{ in product}} \right) \times 100 \quad (7)$$

3. Results and discussion

3.1. Catalyst characterization

The BET surface area, total pore volume, mean pore diameter, and metal dispersion of γ -Al₂O₃, sulfided 3%Ni-10%Mo/ γ -Al₂O₃, and 1%Re-3%Ni-10%Mo/ γ -Al₂O₃ were characterized, as presented in Table 2. The BET surface area, total pore volume, and mean pore diameter of the sulfided samples were smaller than those of alumina support. The alumina support had a specific surface area of 167.8 m² g⁻¹. After loading Ni (3%) and Mo (10%), the surface area decreased from 167.8 to 117.0 m² g⁻¹ by approximately 30%. The decreasing of surface area after metal loading is due to the metal spreading over alumina support and blocking of pores by metal. Moreover, it is evident that the addition of Re could increase the surface area of sulfided 3%Ni-10%Mo/ γ -Al₂O₃. The surface area of sulfided 1%Re-3%Ni-10%Mo/ γ -Al₂O₃ increased from 117.0 to 140.8 m² g⁻¹ by approximately 20.4% after loading 1%Re into sulfided 3%Ni-10%Mo/ γ -Al₂O₃. From mean pore diameter data, γ -Al₂O₃ support and synthesized catalysts are mesopore materials having pore diameter between 2 and 50 nm. Furthermore, it was found that percentage of metal dispersion of trimetallic ReNiMo sulfide catalyst from H₂-TPD analysis was higher than those of bimetallic NiMo sulfide catalyst (see in Table 2). Therefore, it can be concluded that the presence of Re promoter on sulfided NiMo could facilitate high dispersion of Ni on γ -Al₂O₃ support.

The SEM images of sulfided 3%Ni-10%Mo/ γ -Al₂O₃ and 1%Re-3%Ni-10%Mo/ γ -Al₂O₃ are shown in Fig. 1. 3%Ni-10%Mo/ γ -Al₂O₃ showed large aggregates of metal sulfide particles. On the other hand, 1%Re-3%Ni-10%Mo/ γ -Al₂O₃ exhibited a highly dispersed nature (see in SEM images). Moreover, the EDS analysis reveals the elemental distributions of elements (i.e. Ni, Mo, Re, S, O, and Al) and %wt of the elements in each sample. We observed that elemental distributions of Ni and Mo particles on γ -Al₂O₃ support in case of using Re as a promoter (ReNiMo) were more homogenous distribution than those of NiMo catalyst. Element compositions of Ni, Mo, and S over sulfided 3%Ni-10%Mo/ γ -Al₂O₃ were 2.7, 7.8, and 8.1 wt%, respectively whereas the compositions of Ni, Mo, Re, and S over sulfided 1%Re-3%Ni-10%Mo/ γ -Al₂O₃ were 3.6, 9.3, 0.9, and 10.1 wt%, respectively. Therefore, it can be suggested from this study that Re should be applied as promoter along with Ni and Mo

to reduce the cluster size of metal sulfide particles and improve the metal dispersion over support. These benefits of Re promoter could improve the catalytic activity of various reactions such as partial oxidation of methane [35], cracking/reforming of biomass tar [36], and water gas shift reaction [37].

XRD method has been used to identify about the phase of sulfided samples. From XRD patterns of alumina support and sulfided samples in Fig. 2, we found that all of the samples presented diffraction peak at $2\theta = 37.5^\circ$, 45.7° , and 66.6° , which correspond to γ -Al₂O₃ (JCPDS no. 00-029-0063). Wang et al. [38] used XRD analysis to characterize phases of sulfided NiMo/ γ -Al₂O₃ catalysts. They found that NiMoS₄ phase appeared at $2\theta = 38^\circ$ and MoS₂ phase appeared at $2\theta = 33^\circ$ and 59° . However, no diffraction peaks of NiMoS₄ and MoS₂ showed in two sulfided NiMo and ReNiMo samples in our work. It could be due to all observed diffraction peaks were overlapped by three dominated γ -Al₂O₃ peaks and the low content, small fine particle size, or well dispersion of metals [35,38,39].

In addition, XPS experiments were used to identify phases of the elements i.e. Ni, Mo, and Re on a surface of the two sulfided catalysts. The XPS results of Ni 2p, Mo 3d, and Re 4f regions for sulfided NiMo/ γ -Al₂O₃ and ReNiMo/ γ -Al₂O₃ catalysts are shown in Fig. 3. For the analysis of surface Ni species over sulfided NiMo/ γ -Al₂O₃ and ReNiMo/ γ -Al₂O₃ catalysts (as shown in Fig. 3(a) and (c)), XPS shows the characteristic core-level of Ni 2p_{3/2} and Ni 2p_{1/2} at 853.1 and 870.3 eV, respectively. The binding energy at 853.1 eV corresponded to the NiS_x sulfide phase (i.e. Ni₂S₃, Ni₉S₈, or NiS) and NiMoS phase [40,41]. For the binding energy at 870.3 eV was assigned to the nickel metal (Ni⁰) species [42]. The peaks at 855.8, 860.1, and 876.1 eV were assigned to satellites of Ni 2p.

As shown in Fig. 3(b) and (d), the Mo 3d spectrum is composed of Mo(IV) 3d_{3/2}, Mo(IV) 3d_{5/2}, Mo(VI) 3d_{3/2}, Mo(VI) 3d_{5/2}, S²⁻, and S₂²⁻ at 232.1, 229.0, 235.2, 232.2, 226.0, and 227.8, respectively. The stronger peaks at 232.1 and 229.0 eV indicate the dominance of Mo⁴⁺ whereas weak peak at 235.2 and 232.2 eV presents a small amount of a Mo oxide phase (MoO_x or NiMoO₄, Mo⁶⁺). Moreover, two peaks at 226.0 and 227.8 eV relate to S²⁻ (MoS₂) and S₂²⁻ (MoO_xS_y), respectively [40].

For the analysis of surface Re species over ReNiMo/ γ -Al₂O₃ catalyst, the binding energies of Re 4f at 46.5 and 48.7 eV are assigned to Re 4f 3d_{7/2} and Re 4f_{5/2} of Re⁷⁺ (Re₂O₇) [35]. From the results indicate that Re could not be reduced and sulfided at sulfidation condition in this work (at 400 °C for 4 h under H₂S/H₂ mixture). The phenomenon corresponds to Claridge et al. [43] and Simchi et al. [44], who found that Re oxide was reduced to Re metal at temperatures above 900 °C [43] and then Re metal could be converted to Re sulfide phases under disulfur (S₂) at 10⁻⁵ bar and 750 °C [44].

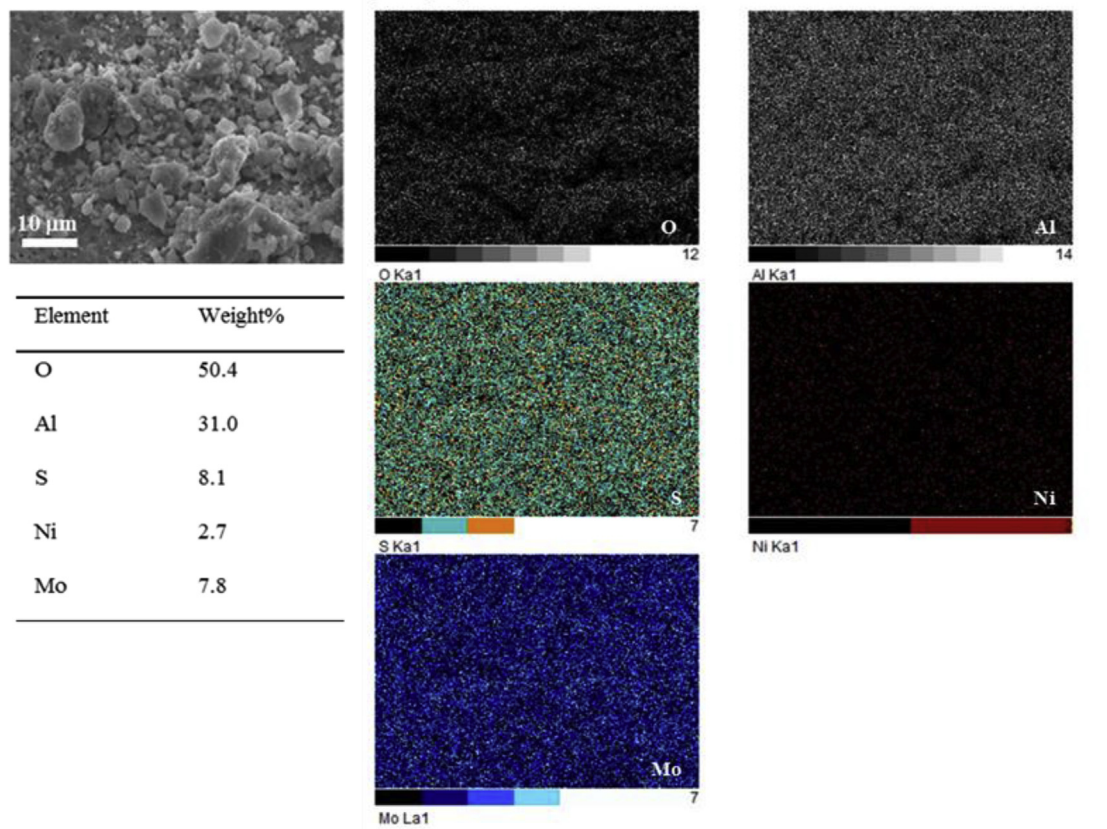
3.2. Effects of temperature and time over mono- and bimetallic sulfide catalysts

Firstly, the effects of reaction temperature and time on catalytic deoxygenation of oleic acid over synthesized monometallic 10%Mo, 10%W, 3%Re and bimetallic 3%Re-10%Mo, 3%Re-10%W, 3%Ni-10%Mo sulfide catalysts were studied by varying the reaction temperatures

Table 2
Physicochemical properties of the alumina support and sulfided catalyst samples.

Catalyst	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)	Metal dispersion (%)
γ -Al ₂ O ₃	167.8	0.45	10.77	—
3%Ni-10%Mo/ γ -Al ₂ O ₃	117.0	0.25	8.68	6.9
1%Re-3%Ni-10%Mo/ γ -Al ₂ O ₃	140.8	0.30	8.54	7.2

(a) Sulfided 3%Ni-10%Mo/ γ -Al₂O₃



(b) Sulfided 1%Re-3%Ni-10%Mo/ γ -Al₂O₃

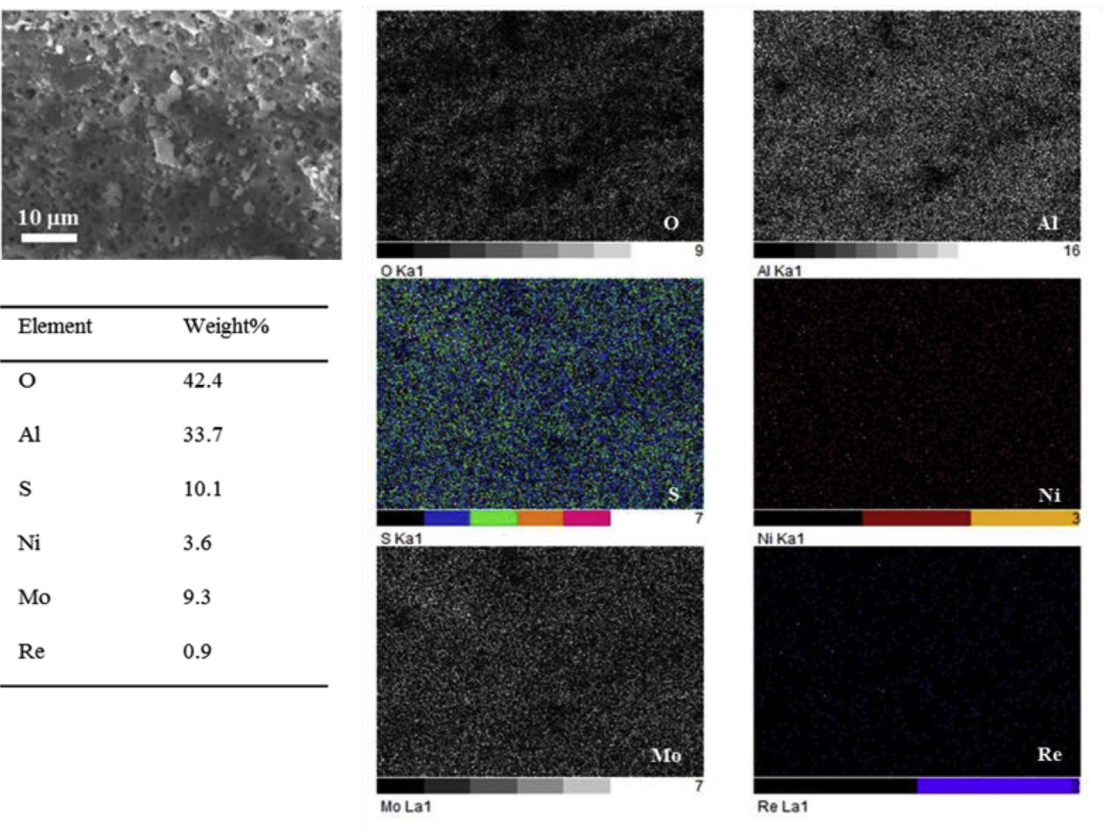


Fig. 1. SEM-EDS analysis of (a) sulfided 3%Ni-10%Mo/ γ -Al₂O₃ and (b) sulfided 1%Re-3%Ni-10%Mo/ γ -Al₂O₃.

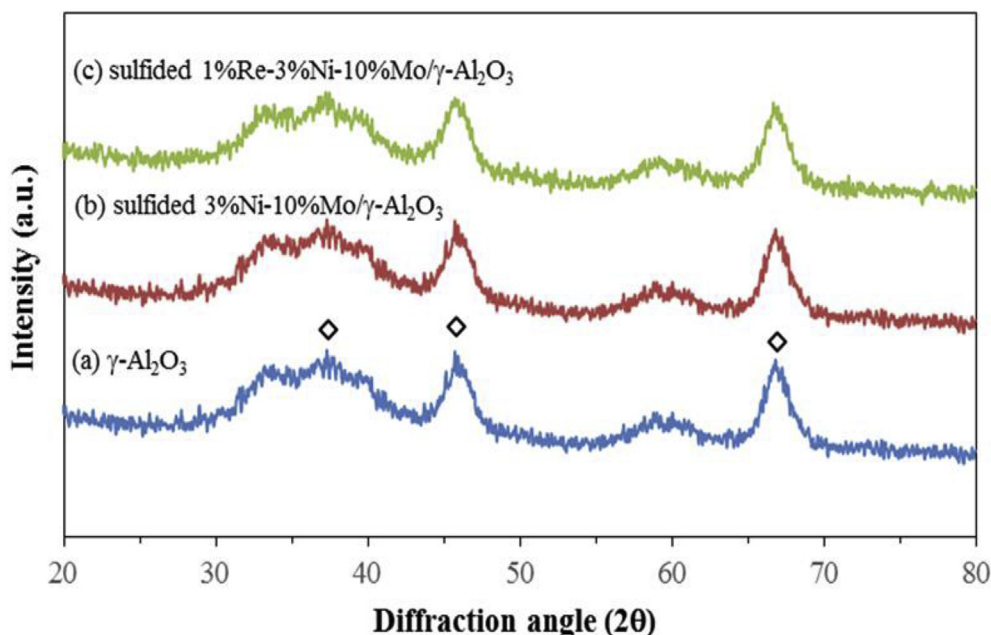


Fig. 2. X-ray diffraction patterns of (a) γ - Al_2O_3 , (b) sulfided 3%Ni-10%Mo/ γ - Al_2O_3 , and (c) sulfided 1%Re-3%Ni-10%Mo/ γ - Al_2O_3 .

from 300, 370 and 400 °C and the reaction times from 2 to 3 h under H_2 pressure of 4 MPa. Their performance in terms of oleic acid conversion, product yield, %HDO, % DCO_x (i.e. DCO and DCO_2), and hydrocarbon product distribution were evaluated and presented in Table 3 and Fig. 4.

The oleic acid conversion from the reaction in the presence of monometallic Mo, W, Re and bimetallic ReMo, ReW, NiMo sulfide catalysts at 300 °C for 2 h were within the range of 30.63–41.19% (see in Table 3). The n-alkane products obtained from all synthesized sulfide catalysts fell in the C_{15} to C_{18} range (Fig. 4). Among all the catalysts studied, NiMo sulfide catalyst was more active for deoxygenation of oleic acid than Mo, W, Re, ReMo, and ReW sulfide catalysts. Product yields were 4.94%, 3.76%, 2.04%, 2.66%, 4.37%, and 10.18% over Mo, W, Re, ReMo, ReW, and NiMo sulfide catalysts, respectively. Besides the n-alkane products (C_{15} – C_{18}) and remaining reactant (oleic acid, $\text{C}_{18:1}$), there were significant formations of stearic acid ($\text{C}_{18:0}$) and a little intermediate chemicals of octadecanal ($\text{C}_{18\text{-al}}$) and octadecanol ($\text{C}_{18\text{-ol}}$) over synthesized sulfide catalysts at 300 °C for 2 h (confirmed by GC-MS analysis). From experimental data, we therefore propose a possible mechanism for deoxygenation process that the double bond of oleic acid was hydrogenated directly to stearic acid. Then, stearic acid was deoxygenated to heptadecane via DCO_x pathways. Alternatively, HDO pathway of stearic acid to octadecane could proceed via an intermediate aldehyde (octadecanal) and alcohol (octadecanol). Moreover, the cracking reaction of long-chain alkanes could generate short-chain alkanes (C_{15} – C_{16}). In addition, small quantities of lower saturated fatty acids i.e. palmitic acid and myristic acid were also identified. These experiments indicated that cracking reaction of stearic acid occurred. The similar result was reported by Dragu et al. [21], Vardon et al. [33] and Hermida et al. [1].

Comparing the results for different temperatures (at 300 and 370 °C for 2 h), the results of this work indicated that temperature significantly impacted on the product yield and selectivity of diesel-like hydrocarbons. We found that higher temperature increased conversion and total product yield (C_8 – C_{18}) of oleic acid deoxygenation. The major product of almost all sulfided catalysts was C_{17} hydrocarbon, which contains one carbon atom shorter than the total length of the oleic acid feedstock, as shown in Fig. 4(a and

b). According to experimental results, DCO_x reaction pathway was main route for deoxygenation of oleic acid under the conditions studied. The results also suggest that DCO_x reaction pathway was favored at higher temperature (370 °C) whereas HDO was favored at lower temperature (300 °C). The proportion of C_{18} (%HDO) decreased with increasing temperature from 300 to 370 °C. Furthermore, it can be seen that lighter hydrocarbons obviously increased with increasing temperature. Among all synthesized catalysts, sulfided NiMo at 370 °C for 2 h provided the highest total product yield (61.82%) with C_{17} as the main product. When considering the gas product distribution (see in Fig. 5), we observed that the product gas contained remaining H_2 , CO, CO_2 , and CH_4 . We found that H_2 much remained after the reaction because we added an excess of H_2 . Methanation could not be ignored for all catalysts as presence of trace amount of methane. Therefore, it is beneficial for all catalysts that H_2 was consumed from hydrogenation of unsaturated fatty acid (oleic acid), DCO, and HDO routes, not methanation. The methanation was negligible. It implies that the CO/ CO_2 ratio was unaffected by methanation reaction. However, some aspects of water gas shift reaction depending on catalysts types were assumed to be occurred [16].

From Fig. 5 (370 °C for 2 h), it can be seen that gas fraction distribution of CO predominated over that of CO_2 over sulfided Mo catalyst. Therefore, it suggested that DCO was favorable than DCO_2 over sulfided Mo catalyst. When considering both sulfided Re and ReMo catalysts, the distribution of gas fraction of CO and CO_2 was the same. On the other hand, the gas fraction of CO_2 was more than the gas fraction of CO over sulfided W, ReW, and NiMo catalysts. This may indicate that the catalytic deoxygenation of oleic acid occurred through 3 reactions i.e. DCO_2 , DCO, and water gas shift reaction.

For the effect of reaction time (at 370 °C for 2 and 3 h), it was observed that the conversion of all synthesized sulfide catalysts increased with increasing reaction time. The diesel-range alkanes, C_{13} to C_{18} hydrocarbons, increased over W, Re, ReMo, and ReW at longer reaction time (3 h) at 370 °C whereas the results over Mo and NiMo showed a tendency in the opposite direction (see in Table 3). Compared to the shorter reaction time (2 h), the remaining hydrogen at longer reaction time (3 h) was decreased from 31.85-

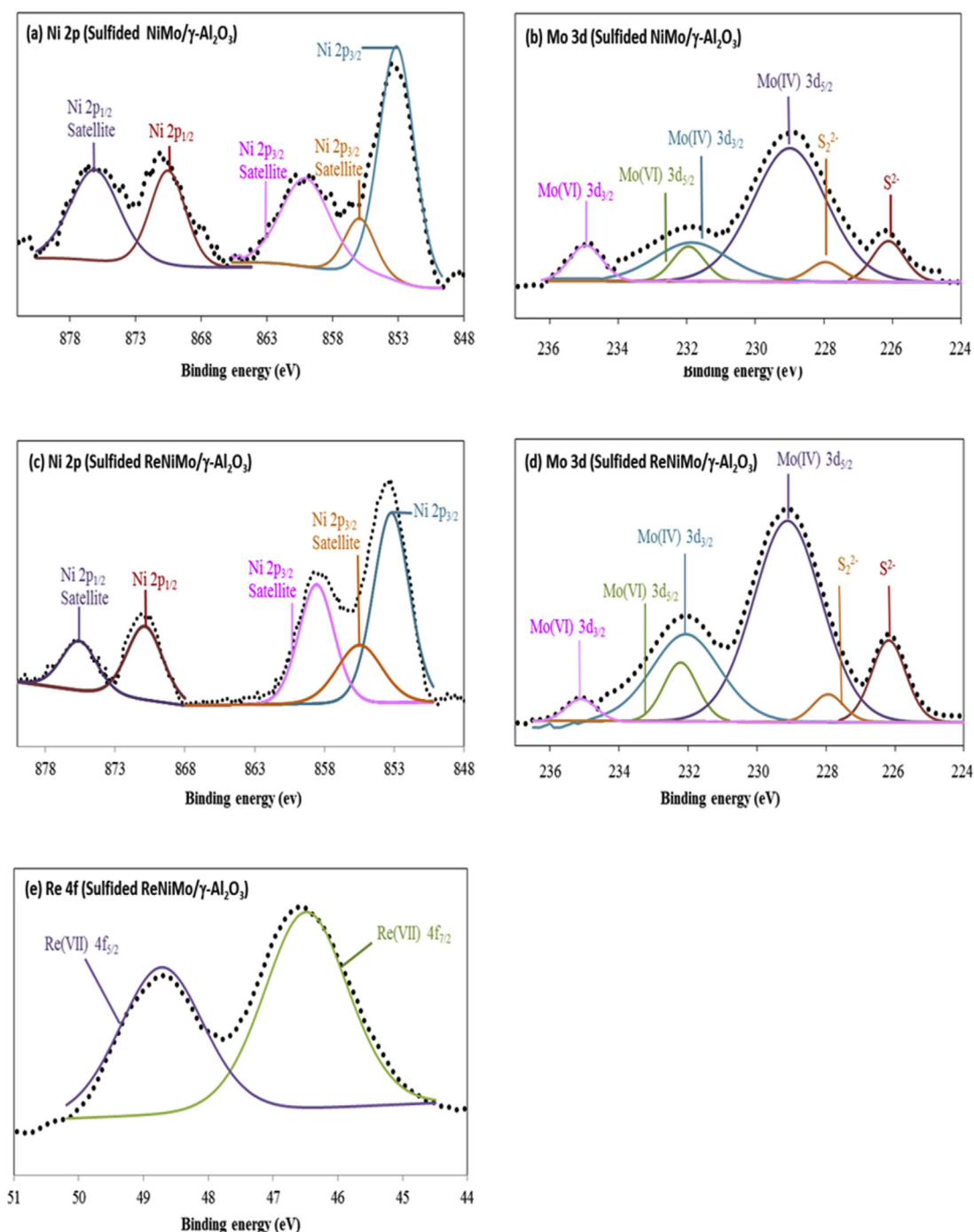


Fig. 3. XPS spectra of (a–b) sulfided NiMo/ γ -Al₂O₃ and (c–e) sulfided ReNiMo/ γ -Al₂O₃.

74.50% to 18.93–53.04%. It suggested that the HDO and DCO reactions proceeded more to consume hydrogen at long reaction time. Moreover, we found that gas fraction of CO₂ increased. These results suggest that the increase in the reaction time could improve the formation of products through HDO, DCO, and DCO₂.

At long reaction time and higher temperature (400 °C for 3 h), the conversion from the reaction in the presence of all catalysts exceeded 93.0%. Moreover, hydrocarbon products in gasoline range were also increased as presented in Table 3 and Fig. 4(d). At this condition, C₁₈ (via HDO route) and C₁₇ (via DCO/DCO₂ route) decreased while proportion of C₈–C₁₆ increased, as shown in Fig. 4(a–d). This could be due to the increase of cracking reaction

since some short-chain hydrocarbons i.e. CH₄ (0.87–3.04%), C₂H₄ (0.49–1.25%) and C₂H₆ (1.31–2.86%) were also observed in gaseous product under this reaction condition. Additionally, remaining H₂ increased when increasing reaction temperature from 370 to 400 °C. This may be because the HDO was not favorable at high temperature.

Among all monometallic and bimetallic catalysts studied, NiMo sulfide showed the greatest performance toward the deoxygenation reaction, providing high activity and product distribution in diesel range at moderated temperature (370 °C). Rhenium sulfide in hydrotreating was studied by Escalona et al. [45]. They found that rhenium sulfide showed high catalytic activity and sometimes was

Table 3

Effect of reaction temperature and time on conversion and product yield over mono- and bimetallic sulfide catalysts.

Catalyst	Conversion (%)	Product yield (%)		HDO (%),	DCO _x (%),
		C ₈ -C ₁₂	C ₁₃ -C ₁₈	C ₁₈	C ₁₇
Reaction condition: 300 °C and 2 h					
10%Mo	38.05	0	4.94	78	22
10%W	30.63	0	3.76	52	48
3%Re	30.74	0	2.04	74	26
3%Re-10%Mo	30.77	0	2.66	80	20
3%Re-10%W	30.75	0	4.37	50	50
3%Ni-10%Mo	41.19	0	10.18	36	64
Reaction condition: 370 °C and 2 h					
10%Mo	91.39	4.55	42.22	42	58
10%W	79.03	5.21	18.29	5	95
3%Re	76.66	2.16	19.68	44	56
3%Re-10%Mo	83.90	4.63	31.87	40	60
3%Re-10%W	80.05	3.98	17.62	23	77
3%Ni-10%Mo	93.06	2.49	59.33	13	87
Reaction condition: 370 °C and 3 h					
10%Mo	93.09	8.63	35.67	29	71
10%W	98.66	2.39	23.52	24	76
3%Re	79.95	2.57	20.63	48	52
3%Re-10%Mo	87.51	6.84	38.84	41	59
3%Re-10%W	93.41	7.19	24.04	40	60
3%Ni-10%Mo	98.67	2.66	54.53	13	87
Reaction condition: 400 °C and 3 h					
10%Mo	97.91	21.80	19.32	35	65
10%W	98.66	17.29	16.17	21	79
3%Re	97.83	23.26	17.04	42	58
3%Re-10%Mo	93.39	15.55	20.36	26	74
3%Re-10%W	99.69	13.66	11.32	28	72
3%Ni-10%Mo	99.21	20.89	29.89	15	85

better than industrial CoMo/Al₂O₃ and NiMo/Al₂O₃. From previous works, many researchers have reported that the use of Re as a promoter can improve the activity of many reactions. For instances,

Iida and Igarashi [46] studied the catalytic activity of Pt-Re catalyst toward water gas shift reaction (WGS). They found that the addition of Re can improve catalytic activity over Pt catalyst. Murata et al. [14] studied the catalytic activity of Pt-Re/H-ZSM-5 catalyst toward hydrotreatment of Jatropha oils for production of synthetic diesel. Vardon et al. [33] studied the catalytic activity of Pt-Re/C for the hydrothermal deoxygenation of stearic acid and oleic acid. They found that the addition of Re into Pt/C not only improved the dispersion of metals on carbon surface support but also reduced the crystallites. Therefore, the addition of Re to NiMo sulfide catalyst was further studied as presented in the next session.

3.3. Effect of Re promoted on bimetallic NiMo sulfide catalyst

To compare the catalytic performance of bimetallic NiMo and trimetallic ReNiMo sulfide catalysts, the sulfided catalysts were tested at 370 °C for 1 h. From our previous works, we studied the effect of Re over Ni by varying the ratio of Re:Ni at several proportions i.e. 1:9, 3:7, 5:5, 7:3 and 9:1 toward partial oxidation of methane [35] and cracking/reforming of biomass tar [36]. Among all proportions, the highest catalytic activity and stability were achieved from Re-Ni with Re:Ni ratio of 3:7. Therefore, in this work we selected 1 wt% Re additional over 3wt% Ni–10wt% Mo. The Re:Ni ratio at 1:3 in this work is close to the ratio at 3:7 (or 1:2.3) from previous our experiments.

As shown in Table 4, we found that the addition of Re to NiMo sulfide catalyst had a significant effect on the yield of liquid products and gas fraction distribution. It was observed that the presence of Re over NiMo sulfide catalyst could improve total product yield (C₈–C₁₈) from 61.63% to 79.59%. When considering %HDO and %DCO_x of NiMo and ReNiMo sulfide catalysts, we found that the distribution of %HDO and %DCO_x showed a similar trend. The percentage of DCO_x was much higher than that of HDO. It is indicated

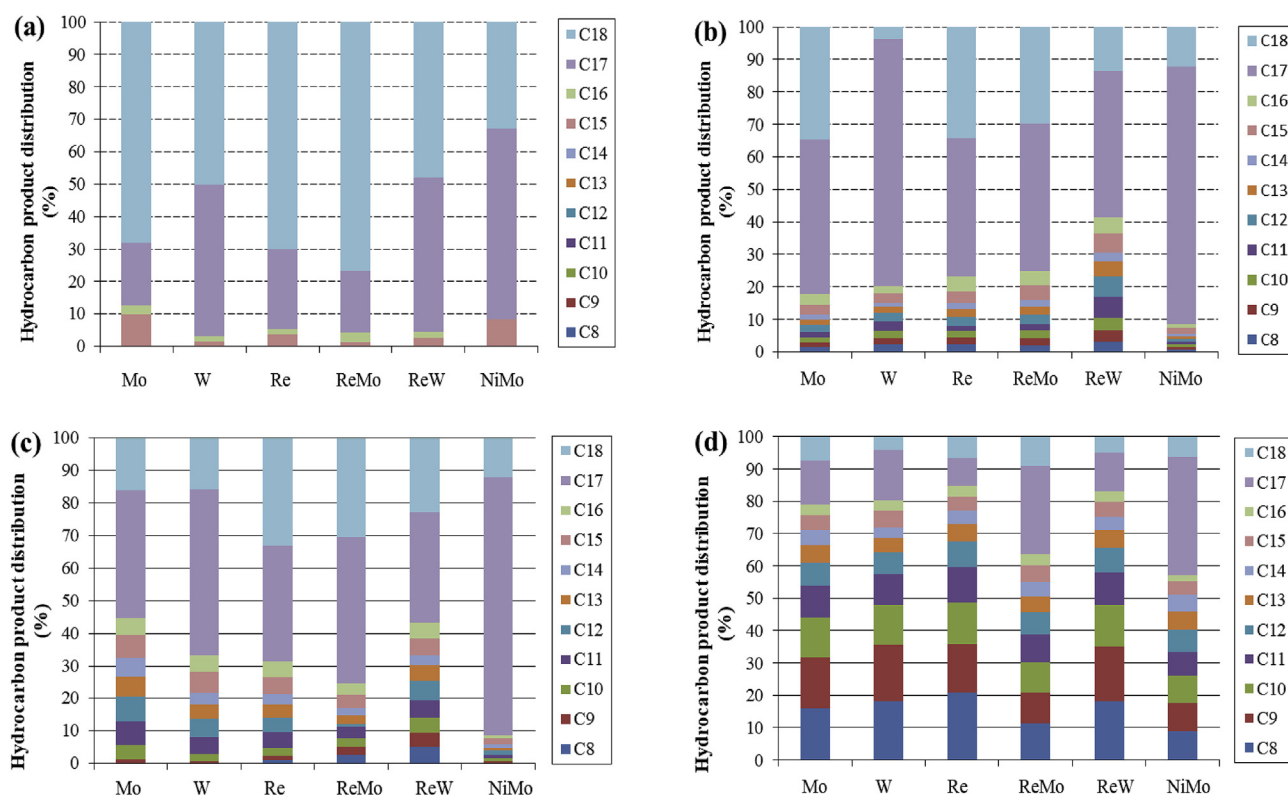


Fig. 4. Effects of reaction temperature and time on hydrocarbon product distribution at (a) 300 °C for 2 h, (b) 370 °C for 2 h, (c) 370 °C for 3 h, and (d) 400 °C for 3 h over monometallic Mo, W, Re and bimetallic NiMo, ReW, ReMo sulfide catalysts supported on γ -Al₂O₃.

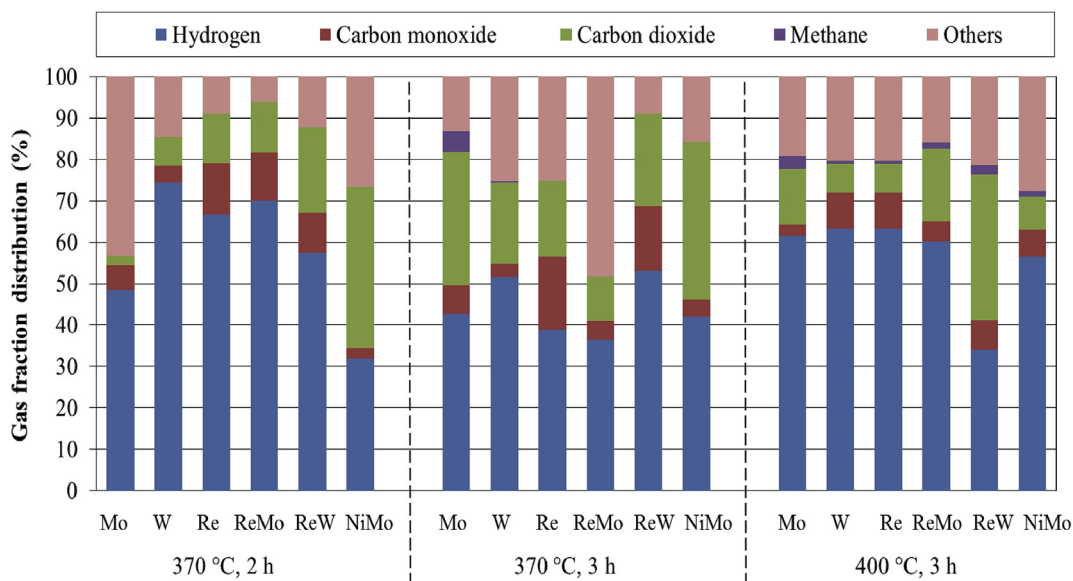


Fig. 5. Gas fraction distribution over monometallic Mo, W, Re and bimetallic NiMo, ReW, ReMo sulfide catalysts supported on γ -Al₂O₃.

Table 4

Summary of conversion, product yields of liquid and gas, and gas fraction distribution over bimetallic NiMo and trimetallic ReNiMo sulfides supported on γ -Al₂O₃ at 370 °C for 1 h.

Catalyst	Conversion (%)	Liquid fraction yield (wt.%)	Yield of liquid products (%)		HDO (%), C ₁₈	DCO _x (%), C ₁₇	Gas fraction yield (wt.%)	Gas fraction distribution (%)				
			C ₈ -C ₁₂	C ₁₃ -C ₁₈				H ₂	CO	CO ₂	CH ₄	Other
NiMo	100	85.35	3.52	58.11	11	89	14.65	50.58	2.58	30.12	ND	16.72
ReNiMo	100	84.37	5.09	74.50	13	87	15.63	60.33	6.41	16.66	ND	16.60

ND = not detectable.

that both sulfide catalysts favored DCO_x route. Therefore, main product obtained was the C₁₇ hydrocarbon. Moreover, it is worth to note that ReNiMo sulfide catalyst consumed less hydrogen than NiMo sulfide catalyst. The CO₂ fraction predominated over that of CO in both catalysts. It is indicated that DCO₂ was favored over DCO. The DCO₂ did not need hydrogen for alkane production as the DCO. The HDO and DCO reactions removed oxygen in form of water. From the study, the content of water in liquid products was 3.58% for NiMo and 6.77% for ReNiMo. It is implied that the presence of Re over NiMo could help promote DCO and HDO routes. Moreover, we observed that the addition of Re into NiMo sulfide catalyst not only increased C₈-C₁₈ alkanes but also increased C₁₅-C₁₇ isoparaffins (confirmed by GC-MS). This may be due to ReNiMo sulfide favored isomerization reaction. The amount of C₁₅-C₁₇ isoparaffins catalyzed over ReNiMo and NiMo sulfide catalysts could be estimated as 7.3 wt% and 5.2 wt%, respectively. The increasing of the degree of

isomerization provided lower cloud point [27].

The theoretical yields of liquid products depend on the types of feedstock (i.e. amount of triglycerides and/or fatty acids and their fatty acid chain length) and their reaction pathways (i.e. HDO, DCO, and DCO₂). In case of oleic acid feedstock, the maximum theoretical yields assuming without cracking and other side reactions were calculated. The theoretical yield obtained through DCO_x (DCO + DCO₂) and HDO were 84.0 wt% and 87.6 wt%, respectively. In addition, maximum theoretical yields of water were calculated, providing the yield of 6.40 wt% from DCO pathway and 12.4 wt% from HDO pathway. Moreover, the maximum theoretical yields of CO and CO₂ from DCO and DCO₂ routes were 9.9 wt% and 15.58 wt%, respectively.

Table 5 presents oleic acid conversion, yields of liquid and gas products, contributions of HDO and DCO_x (DCO + DCO₂) of liquid products and product distribution of gas phase over trimetallic

Table 5

Oleic acid conversion, yield and contributions of HDO and DCO_x of liquid products, and product distribution of gas phase over trimetallic ReNiMo sulfide supported on γ -Al₂O₃.

Temp. (°C)	Time (h)	Conversion (%)	Liquid fraction yield (wt.%)	Yield of liquid products (%)		HDO (%), C ₁₈	DCO _x (%), C ₁₇	Gas fraction yield (wt.%)	Gas fraction distribution (%)				
				C ₈ -C ₁₂	C ₁₃ -C ₁₈				H ₂	CO	CO ₂	CH ₄	Other
330	1	100	86.95	3.39	72.56	14	86	13.05	68.10	7.24	14.89	ND	9.77
350	1	100	86.27	3.89	76.51	13	87	13.73	70.93	7.32	14.58	ND	7.17
370	1	100	84.37	5.09	74.50	13	87	15.63	60.33	6.41	16.66	ND	16.60
370	2	100	84.72	8.51	67.75	25	75	15.18	60.52	4.68	16.79	ND	18.01
370	3	100	84.75	8.93	65.99	22	78	15.25	63.32	3.83	19.42	ND	13.43
400	1	100	78.44	14.88	16.07	10	90	21.56	66.91	7.68	13.35	1.24	10.82

ND = not detectable.

ReNiMo sulfide supported on γ -Al₂O₃ at 330–400 °C. It was found that the conversion of oleic acid was 100% under these studied conditions, which is significantly higher than those from the reaction over mono- and bimetallic sulfide catalysts as earlier reported. In addition, the total product yield (C₈–C₁₈) was incremented as temperature increased, from which the total yield of 79.59–80.40% was peaked at 350–370 °C. At temperature higher than 370 °C, lower diesel yield was obtained. This is due to a domination of cracking reaction at high reaction temperature. When considering gas phase, we found that CH₄ was generated along with CO and CO₂ at high temperature (400 °C). It is also noted that water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) and methanation reaction ($\text{CO}_x + \text{H}_2 \rightarrow \text{CH}_4$) could also occur due to the presences of CO, CO₂, water, and hydrogen.

Moreover, Table 5 also shows the effect of reaction time (1–3 h) on the catalytic deoxygenation reaction at 370 °C over ReNiMo sulfide catalyst. From the study, the maximum yield of diesel-like hydrocarbons was obtained at 370 °C for 1 h. These results suggest that the increase of the reaction time promoted the decomposition of deoxygenated liquid product into gasoline and light hydrocarbon. It is clear that among all studied catalysts, ReNiMo sulfide catalyst showed the highest catalytic activity toward the deoxygenation of oleic acid, providing diesel yield of 74.50–76.51% and gasoline yield of 3.89–5.09% at 350–370 °C for 1 h. Compared with NiMo at the same condition (370 °C for 1 h), the diesel yield of NiMo (58.11%) was lower than ReNiMo (74.50%).

For practical application, various feeds i.e. PFAD, RPS, and RPO were deoxygenated using ReNiMo sulfide catalyst at 370 °C under 5 MPa of H₂ for 1 h. In this study, it was found that the conversion of PFAD, RPS, and RPO was complete at 100% under reaction test. The diesel yield (C₁₃–C₁₈) increased in the order PFAD (72.52%) > RPS (69.74%) > RPO (69.47%), as shown in Fig. 6. PFAD showed the highest product yield because composition of PFAD consisted of free fatty acid (e.g. palmitic acid, oleic acid, and linoleic acid) higher than 93 wt% which easily converted to alkane when compared to RPO and RPS which were mainly triglycerides. Our results demonstrated that C₁₅–C₁₈ alkanes were the main components in

the liquid products of all feeds, as shown in Fig. 6. Therefore, it can be concluded that deoxygenation of fatty acids or triglycerides in feeds occurred via 3 major pathways, including DCO, DCO₂, and HDO.

3.4. Catalyst reusability and effect of in situ hydrogen donor

Reusability of ReNiMo sulfide and NiMo sulfide were compared in six consecutive runs without any intermediate treatment under optimal reaction condition. As shown in Fig. 7, it can be seen that the catalytic activity of ReNiMo sulfide catalyst remained constant in the first to third runs and slightly decreased after fourth run. Furthermore, diesel yield could be maintained to be higher than 71% after the sixth runs. In contrast with ReNiMo sulfide, the conversion and product yield over NiMo sulfide was dramatically decreased following the number of running. From the post-reaction characterization, the TPO analysis was applied to determine the amount of carbon formed on catalyst surface after six consecutive runs. It was found that addition of Re into NiMo sulfide catalyst enhance better resistance toward carbon deposition (2.35 mmol·g_{cat}^{−1} of carbon deposition for ReNiMo sulfide compared to 3.76 mmol·g_{cat}^{−1} for NiMo sulfide). The good catalytic activity of ReNiMo sulfide catalyst could be due to high dispersion of Ni and Mo particles when adding Re as promoter. Additional Re could also reduce particle agglomeration and enhanced the growth of metal crystalline, which consistent with H₂-TPD measurement (see in % metal dispersion) as shown in Table 2. Moreover, this could be due to the role of Re as stabilizer to prevent deactivation of catalyst. The result was in agreement with reports by our previous work [36], Baranowska et al. [47] and Johnson et al. [48].

The hydrogen consumption is one of the important limitations in hydrotreating process. However, hydrogen gas presents storage and transportation limitations. Thus, hydrogen donor agents become much more interesting. Therefore, several organic compounds have been investigated as hydrogen donors to replace the use of hydrogen gas for hydrogenation reaction [32–34,49]. Yang et al. [49] studied catalytic hydroconversion of C₁₈ fatty acids with

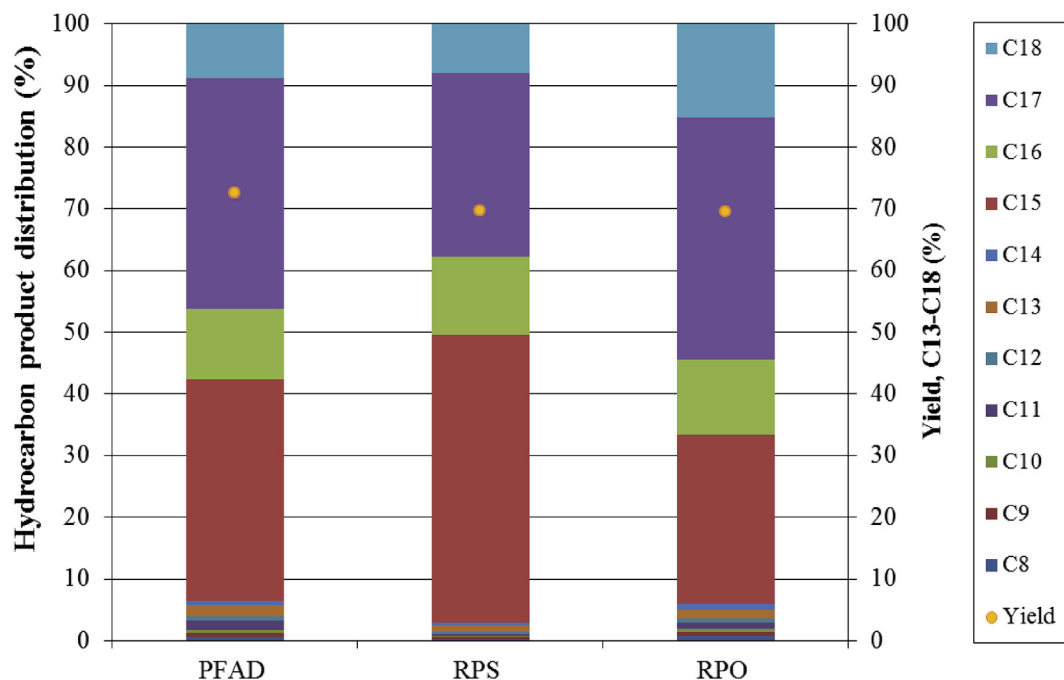


Fig. 6. Effect of feedstock types over trimetallic ReNiMo sulfide catalyst supported on γ -Al₂O₃ at 370 °C for 1 h under 4 MPa of H₂.

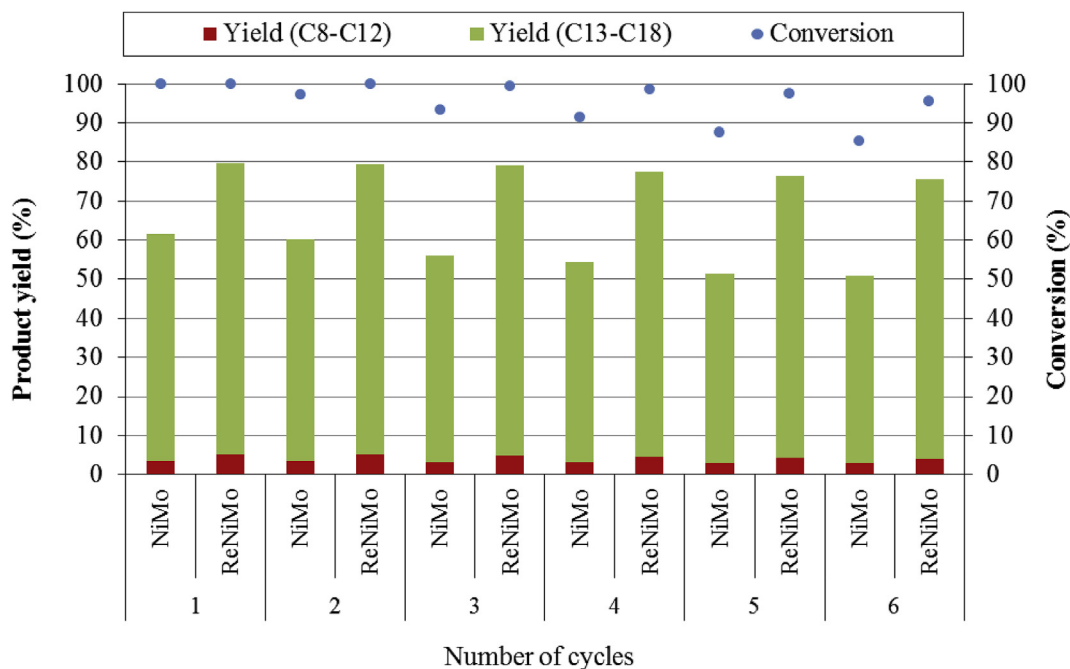


Fig. 7. Effect of reusability on conversion and product yield in six consecutive runs over NiMo and ReNiMo sulfide catalysts supported on γ -Al₂O₃ at 370 °C for 1 h.

different H-donors. They found that alcohols i.e. butanol, isopropanol and ethanol significantly improve the selectivity for C₁₈ hydrocarbon but suppress the selectivity for C₁₇ hydrocarbon. Vardon et al. [33] studied catalytic hydrothermal processing of oleic acid to hydrocarbons and succeeded in developing the method to replace the use of hydrogen gas. The results showed that the hydrogenation and deoxygenation of oleic acid to heptadecane (C₁₇) can be achieved within 2 h with a net-zero H₂ consumption using a 1:3 glycerol-to-fatty acid ratio.

In this work, we selected formic acid, ethanol, and glycerol as H-donors due to their availability and low cost under similar reaction conditions. The H-donor was added in the reaction system instead

of hydrogen gas (excess). The H-donor-to-oleic acid mole ratio was 1:1. The experimental condition was that filling gas is nitrogen instead of hydrogen at a pressure of 4 MPa. Fig. 8 shows the influences of different H-donors on the conversion and hydrocarbon yield over trimetallic ReNiMo sulfide supported on γ -Al₂O₃ compared with without H₂ donor and hydrogen gas at 370 °C for 1 h. In case of without H-donor, considerably lower oleic acid conversion and total product yield of 49.82 and 35.12% were obtained, respectively. In our reaction system tested under hydrogen gas at 4 MPa, the conversion showed high value of 100% and total product yield was achieved at relative high value of 79.59%. Formic acid, ethanol, and glycerol were used as an in situ source of

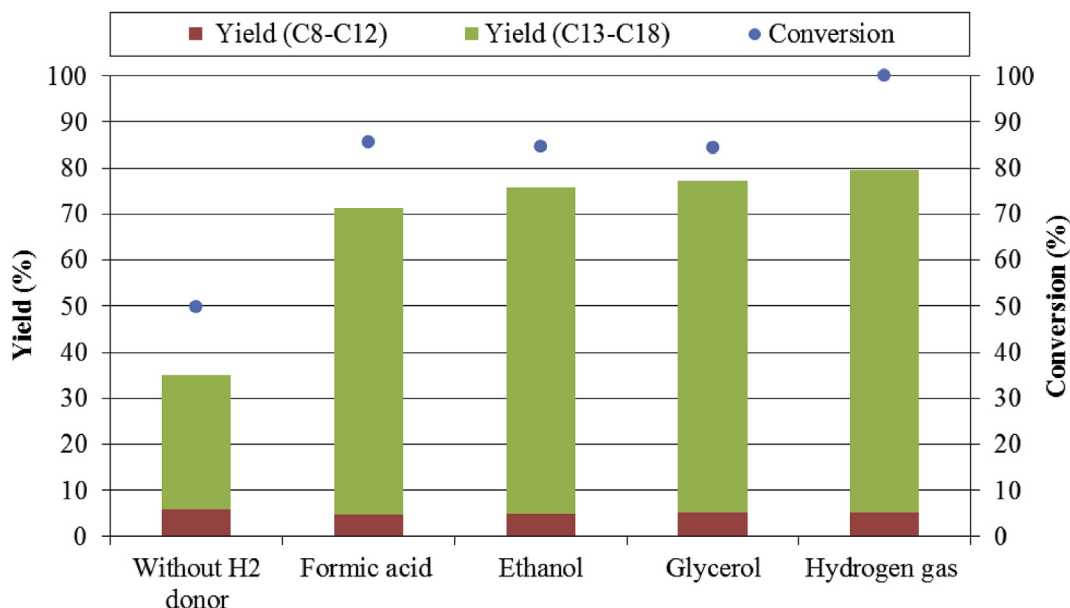


Fig. 8. Effect of in situ H₂ donor on conversion and product yield over trimetallic ReNiMo sulfide supported on γ -Al₂O₃ at 370 °C for 1 h.

hydrogen for the deoxygenation of oleic acid feedstock in this work. Results show that the presence of H-donors significantly could improve the conversion, selectivity, and total product yield when compared with without H-donors. The addition of H-donor solvents into deoxygenation reaction of oleic acid increased the total product yield from 35.12% as high as 71.16–77.23%. Glycerol exhibited the best performance with the highest diesel-like hydrocarbon production.

4. Conclusions

Addition of Re into sulfided NiMo catalyst can greatly improve the catalytic activity toward the deoxygenation of palm feedstocks (i.e. oleic acid, palm fatty acid distillate (PFAD), refined palm stearin (RPS), and refined palm olein (RPO)). Experiments revealed that the reaction exhibited different product distributions and strongly depended on operating parameters (i.e. reaction temperature and time). At 350–370 °C under 4 MPa H₂ pressure, sulfided ReNiMo catalyst provided high diesel yield (C₁₃–C₁₈) of 74.5–76.5% from oleic acid. It can also gain high diesel yield from the reaction over PFAD (72.52%), RPS (69.74%), and RPO (69.47%). It was then observed that sulfided ReNiMo/ γ -Al₂O₃ show good reusability, from which the diesel yield can be maintained to be higher than 71% after six consecutive runs. In addition, glycerol was also successfully employed as a hydrogen donor in deoxygenation reaction over this catalyst.

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