

Elimination of polycyclic aromatic hydrocarbons in light cycle oil via hydrogenation over NiMo-based catalysts

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ABSTRACT

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Light cycle oil (LCO) is a by-product obtained from the fluid catalytic cracking unit in petroleum refineries. Since LCO has a high content of organosulfurous compounds and polycyclic aromatic hydrocarbons (PAHs), which adversely affect the environment and animals, LCO cannot be directly applied in combustion engines. To utilize LCO as a higher value-added chemical, this work aimed to transform the PAHs in LCO into aromatics with a lower toxicity, such as BTX (benzene, toluene, and xylene), tetralins, and decalins, via hydrogenation over nickel (Ni)–molybdenum (Mo)-based catalysts. The effect of the catalyst's support on the hydrogenation efficiency was investigated using γ -alumina (γ -Al₂O₃), KIT-6, and β -zeolite. The results showed that the NiMo/KIT-6 catalyst exhibited the highest ability for hydrogenation of PAHs (49.6% removal of PAHs) and produced alkylbenzenes, decalins, and tetralins at 12.0, 0.22, and 36.4% selectivity, respectively, when the reaction was conducted under 40 bar hydrogen pressure at 350°C for 3 h with a stirring rate of 300 rpm. This study proposed an alternative way to produce value-added chemicals from a by-product stream derived from the petroleum refinery process, thereby expanding the options for sustainable development.

Keywords: hydrogenation; light cycle oil; polycyclic aromatic hydrocarbons; catalysts

1. INTRODUCTION

The increasing demand for energy, depletion of petroleum resources, and increasing global warming has led to more stringent environmental standards and the increased importance of using alternative energy resources, such as

biomass, municipal solid wastes, and by-products from the petroleum industry. Light cycle oil (LCO) is one of the by-products obtained from the fluid catalytic cracking unit in the oil refinery process to convert heavy petroleum fractions into lighter hydrocarbon products (Cha et al., 2012). The LCO can be blended with diesel or fuel oil or

used as a feedstock for manufacturing diesel-fuel (Karakhanov et al., 2018). However, the high contents of polycyclic aromatic hydrocarbons (PAHs) and organosulfurous compounds give LCO a very low cetane number and an adverse environmental impact, resulting in a low market demand (Rigutto et al., 2007).

With respect to the PAH content, LCO is comprised of more than 90% w/w total aromatics and a PAH fraction (two or more aromatic rings) exceeding 70% (Oh et al., 2019). Although PAHs are ubiquitous in the environment, they raise significant concerns due to their toxicity, as they can induce carcinogenic and mutagenic effects, respiratory problems, and metabolic abnormalities (Abdel-Shafy and Mansour, 2016; Venkatraman et al., 2024). Moreover, LCO also contains 0.2 to 2.5% w/w organosulfurous compounds depending on the quality of the feedstock (Pasadakis et al., 2011). This high sulfur content can cause corrosion, deactivation of the catalyst, and emissions of toxic pollutants into the atmosphere (Kondyli and Schrader, 2021). According to the enhanced (more stringent) environmental requirements, the amounts of PAHs and sulfur species in fuels have been strictly limited in diesel fuel to < 8% w/w and 10 ppm, respectively, under the Euro 5 standard (Thansettakij, 2023).

There are several methods to utilize LCO, such as solvent extraction and selective ring opening. However, these methods are constrained by the high level of pollution they can create and the relatively low stability of the catalyst (Miao et al., 2020). In the latest refinery configurations, hydrogenation has been considered for upgrading the LCO fraction to obtain high-quality fuels and petrochemicals (Laredo et al., 2018). This process also has a high performance in converting PAHs into less toxic compounds, such as tetralin and decalin, which can be applied as high-boiling-point solvents and chromatography reagents, and can also be used in coal direct liquefaction and biomass liquefaction (Su et al., 2020). Non-noble metal-based catalysts, such as nickel (Ni) and cobalt (Co) are widely used as catalysts in the hydrotreating process due to their lower cost than that of noble metal-based catalysts, making their use more economically feasible. The addition of promoters is also required to provide the resistance to sulfur compounds during hydrodesulfurization (HDS). Kingputtpong et al. (2022) studied the efficiency of Ni supported on a gamma-alumina ($\text{Ni}/\gamma\text{-Al}_2\text{O}_3$) catalyst promoted by molybdenum (Mo), tungsten (W), or platinum (Pt) for the hydrogenation of naphthalene (a PAH model compound) and PAHs in a real waste tire pyrolysis oil (WTPO). The results showed that $\text{NiPt}/\gamma\text{-Al}_2\text{O}_3$ had an extremely low sulfur tolerance compared to the $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ and $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$ catalysts. The $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst could also achieve a 98.4% sulfur removal with a maximum PAH removal of 52.1% in the hydrogenation of PAHs in WTPO dissolved in decane, whereas the $\text{NiW}/\gamma\text{-Al}_2\text{O}_3$ catalyst provided the highest maximum PAH removal level of 69.4% with a lower efficiency for HDS due to its lower acidity and reducibility. Since the catalyst's support has an important role in any catalytic reaction, three different supports ($\gamma\text{-Al}_2\text{O}_3$, KIT-6, and β -zeolite) were examined as supports for the NiMo catalyst used in the hydrogenation of LCO. Currently, $\gamma\text{-Al}_2\text{O}_3$ is widely used as a support for various catalysts and catalytic applications due to its low cost, high specific surface area, and good thermal stability (Henpraserttae et al., 2023). The Lewis acid sites of $\gamma\text{-Al}_2\text{O}_3$ can promote the

adsorption of aromatic molecules to form intermediates, which are then hydrogenated to produce the saturated compounds (Wang et al., 2000). Considering KIT-6, it is classified as an ordered three-dimensional (3D) mesoporous silica (SiO_2) material with a highly accessible porous structure that provides a higher mass diffusion and prevents pore clogging (Chai et al., 2023; Huang et al., 2022). Moreover, KIT-6 has a high surface area and pore volume along with a high thermal resistance (Huang et al., 2022). Thus, KIT-6 has been applied as the support for the Ni-based catalyst in the hydrogenation of α -pinene (Huang et al., 2022) and nitrobenzene (Zhou et al., 2020) as well as in HDS (Wu et al., 2014; Soni et al., 2009). In the case of zeolites, they can be employed as supports for metal bifunctional catalysts in the selective hydrocracking of PAHs (Brito et al., 2021). The Brønsted acid sites in the zeolites also facilitate the dealkylation of alkyl PAHs resulting in the ease of hydrogenation to form alkanes and aromatic compounds (Katada et al., 2017). Among the zeolites used as supports for commercial catalysts in the hydrocracking process, β -zeolite is generally used due to its high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio with a 3D porous structure (Wei et al., 2019). Yu et al. (2023) revealed that the combination of $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ and the appropriate content of β -zeolites enhanced the hydrocracking of naphthalene to obtain the highest BTX (benzene, toluene, and xylene) selectivity of 62.8% with 98% naphthalene conversion.

Therefore, this research focused on a comparative investigation of the effects of catalyst supports having different structures and acidity as well as the reaction parameters on the hydrogenation of PAHs in LCO to obtain higher value-added chemicals such as monoaromatics, tetralins, and decalins. This research is expected to contribute to the sustainable development of the oil refinery process by providing a method to utilize LCO more effectively.

2. MATERIALS AND METHODS

2.1 Preparation and characterization of LCO solution

The LCO, obtained from the IRPC Public Company Limited (Thailand), was diluted in n-decane to 10% w/w LCO. The composition of the LCO solution was analyzed using gas chromatography coupled with mass spectrometry (GC-MS; Shimadzu, model GCMS-QP2020NX). Before analysis, the LCO solution was dissolved in n-hexane to 6,000 ppm LCO. The selectivity of the chemical composition in the LCO solution before and after hydrogenation was calculated based on the percentage of the peak area in the GC-MS chromatograms. The result showed that the initial LCO mainly consisted of PAHs (85.3% w/w) with 0.55% w/w organosulfurous compounds.

2.2 Preparation of catalysts

With respect to the supports for the NiMo-based catalyst, commercial $\gamma\text{-Al}_2\text{O}_3$ (Merck, Germany) and β -zeolite (930NHA; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 27$ by mole, TOSOH Co., Ltd.) were first calcined at 550°C for 6 h before use as catalyst supports. KIT-6 was synthesized as previously described (Kleitz et al., 2003). Briefly, 2 g Pluronic P123 ($M_n \sim 5,800$, Sigma-Aldrich) was dissolved in 2 M hydrochloric acid solution (19 g) and 57 g deionized (DI) water followed by the addition of 2.52 g n-butanol (KEMAUS, Australia). This

mixture was stirred at 35°C for 1 h and then 6.42 g tetraethyl orthosilicate (Sigma-Aldrich) was added and continuously stirred at 35°C overnight. The product mixture was further crystallized in an autoclave at 100°C overnight. The sample was collected, washed with DI water, dried at 100°C, and then calcined at 550°C for 6 h at a heating rate of 0.75°C/min.

The bimetallic NiMo-based catalysts containing 13.12% w/w Ni and 3.55% w/w Mo were prepared by the incipient wetness impregnation method using nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ajax Finechem Pty Ltd., Australia) and ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Macron Fine Chemical™, USA) as the metal precursors (Kingputtpong et al., 2022). The mixture of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in the presence of citric acid (molar ratio of Ni/citric acid = 1) were impregnated onto the $\gamma\text{-Al}_2\text{O}_3$, KIT-6, and β -zeolite supports to obtain the NiMo/ $\gamma\text{-Al}_2\text{O}_3$, NiMo/KIT-6, and NiMo/ β -zeolite catalysts, respectively. Thereafter, the water was removed from the prepared catalysts using a rotary evaporator and dried overnight at 110°C before calcination at 550°C for 3 h at a heating rate of 10°C/min to obtain the catalysts in the oxide form. Before hydrogenation, all catalysts were reduced in the presence of a H_2 gas stream at a flow rate of 40 mL/min at 550°C for 2 h and then passivated using 5/95 vol% oxygen(O_2)/nitrogen (N_2) mixed gas at a flow rate of 0.12 L/h at room temperature overnight.

2.3 Catalysts characterization

Textural properties of all catalysts were analyzed by N_2 adsorption/desorption using a surface area analyzer (3P Instrument, Micro 300). The catalyst sample (40 mg) was degassed at 300°C under vacuum to remove the adsorbed moisture prior to analysis. The specific surface area was estimated following the Bruanuer-Emmett-Teller (BET) equation, while the Barrett-Joyner-Halenda (BJH) desorption cumulative volume and average pore diameter were also considered.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES; PerkinElmer, Avio 200) analysis was performed to determine the metal contents in the prepared catalysts. Briefly, a catalyst sample (20 mg) was digested in 10 mL of aqua regia (~ 2,000 ppm) and then diluted to 16 ppm in DI water before analysis. The amount of Ni and Mo was then estimated by multipoint calibration curves prepared from plasma-grade standards of each element.

The phase composition of the supports and active metals in the passivated catalysts was evaluated using X-ray diffractometry (XRD; Bruker D8 Advance) analysis. The sample was characterized using Cu K-alpha radiation ($\lambda = 1.54 \text{ \AA}$) at a 40 kV and 40 mA operating X-ray power. The 2θ spectra were collected between 5° and 80° with a 10°/min step size.

The H_2 -temperature-programmed reduction (H_2 -TPR) was recorded on a Belcat-Basic Chemisorption analyzer (Belcat II). The calcined catalyst (50 mg) was pretreated at 110°C for 1 h to remove moisture. The sample was then analyzed using a 5/95% v/v H_2 /argon gas mixture (30 mL/min) from ambient temperature to 900°C at a heating rate of 10°C/min and then held at 900°C for 20 min.

The acidity of the prepared catalysts was analyzed using ammonia temperature-programmed desorption (NH_3 -TPD) using a Belcat-basic chemisorption analyzer (Belcat II). Briefly, the calcined catalysts (50 mg) were reduced under a 5/95% v/v H_2 / N_2 gas mixture at 550°C for 2 h and then cooled down to 50°C. For the NH_3 adsorption step, a 10:90 vol% NH_3 /helium (He) gas mixture was introduced to the system at a flow rate of 30 mL/min for 30 min. The amount of adsorbed NH_3 in each catalyst sample was analyzed by desorption by increasing the oven temperature from 50 to 600°C at 10°C/min.

2.4 Hydrogenation of LCO

The hydrogenation of LCO was performed in a 300-mL stainless-steel high-pressure reactor (Parr, model 4843). The reduced catalyst (0.3 g) and LCO solution (33 g) were added into the reactor. After purging the reactor with H_2 for 10 min to remove the air, the reactor was then pressurized with H_2 to the desired initial pressure and heated to the targeted reaction temperature under a stirring rate of 300 rpm for the given time interval. The liquid product from the reaction was then collected and analyzed using GC-MS as per Section 2.1. The catalyst type providing the highest PAH removal efficiency was then selected for further study.

3. RESULTS AND DISCUSSION

3.1 Catalysts characterization

The obtained N_2 -adsorption/desorption isotherm and pore size distribution (Figure 1) were used to analyze the textural properties of the NiMo-based catalysts over three different supports ($\gamma\text{-Al}_2\text{O}_3$, KIT-6, and β -zeolite). The N_2 -adsorption/desorption isotherm for each catalyst had a hysteresis loop (Figure 1a), which represents a mesoporous structure (Sing et al., 1985). The BJH desorption data (Figure 1b) of the NiMo/KIT-6 catalyst exhibited two major peaks, whereas the other two catalysts had only one major peak. The specific surface areas, average pore diameters, and pore volume of all the catalysts are summarized in Table 1. The NiMo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst had the lowest surface area with the largest pore diameter. The NiMo/KIT-6 catalyst had the largest surface area with a medium pore size, while the NiMo/ β -zeolite catalyst had a medium surface area with the smallest pore diameter reflecting the presence of the micropores.

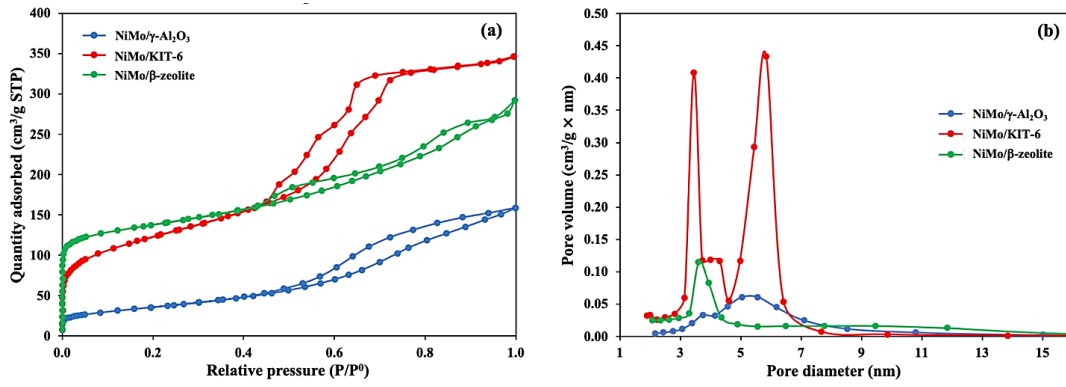


Figure 1. (a) N₂-adsorption/desorption isotherms and (b) BJH pore size distribution of the NiMo/γ-Al₂O₃, NiMo/KIT-6, and NiMo/β-zeolite catalysts

Table 1. Textural properties of the prepared catalysts

Catalysts	Surface area (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)	Element composition ^a (% w/w)	
				Ni	Mo
NiMo/γ-Al ₂ O ₃	128	7.59	0.259	11.9	4.1
NiMo/KIT-6	505	4.84	0.582	12.6	3.5
NiMo/β-zeolite	471	3.74	0.323	13.7	3.9

Note: ^aEstimated by ICP-OES analysis

The actual Ni and Mo contents in the studied catalysts were evaluated by ICP-OES analysis, with the results summarized in Table 1. The XRD patterns of the passivated catalysts are shown in Figure 2. For the NiMo/γ-Al₂O₃ catalyst (Figure 2a), the reflection signals of metallic Ni were indicated at a 2θ of 44.3°, 51.5°, and 75.7° (Yao et al., 2018), while the signals at a 2θ of 37.7°, 46.3°, and 66.8° were attributed to the γ-Al₂O₃ support Vo (2023). In the case of the NiMo/KIT-6 catalyst, a weak and broad peak was observed at a 2θ of 23°, ascribed to the amorphous SiO₂ of the KIT-6 support (Boulaoued et al., 2012). No typical XRD peaks of metallic Ni were observed in the NiMo/KIT-6 catalyst, suggesting that the Ni species have been well dispersed on the surface of the mesoporous silica KIT-6 (Liu et al., 2012). The order of the mesoporous structure of KIT-6 was also confirmed by the low angle XRD pattern (Figure 2b). The NiMo/KIT-6 catalyst exhibited a sharp intense peak at a 2θ of

1.03°, corresponding to the reflection from the (211) crystalline plane (Lan et al., 2017), and a hump peak at a 2θ of 1.17° that was attributed to the (220) reflection (Delgado et al., 2018). This result indicated that the NiMo/KIT-6 catalyst had a mesoporous structure belonging to the bicontinuous cubic Ia3d space group (Boulaoued et al., 2012). For the NiMo/β-zeolite catalysts, the diffraction peaks for metallic Ni were observed at a 2θ of 44.2° and 51.6° (Yao et al., 2018), while the peaks at a 2θ of 7.68° and 22.4° were attributed to the zeolite support (Torres-Rodríguez et al., 2012). The absence of Mo species in the XRD patterns of each catalyst was possibly due to the low content of Mo and the high dispersion of Mo species on the supports (Boulaoued et al., 2012). Moreover, the crystallite size of metallic Ni in the NiMo/γ-Al₂O₃ and NiMo/β-zeolite catalysts (Table 2) was 6.31 and 3.04 nm, respectively, which corresponded to the average pore diameter of each support (Table 1).

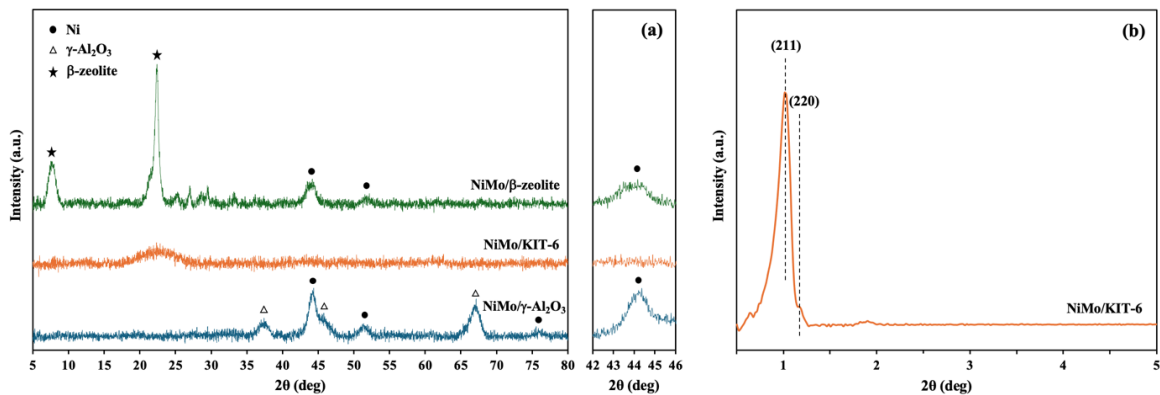


Figure 2. (a) Wide angle XRD patterns of the NiMo/γ-Al₂O₃, NiMo/KIT-6, and NiMo/β-zeolite catalysts and (b) low angle XRD pattern of the NiMo/KIT-6 catalyst

Table 2. Total H₂ consumption and total acidity of the prepared catalysts

Catalysts	Ni crystallite size ^a (nm)	Total H ₂ consumption ^c (mmol/g)	Total acidity ^d (μmol NH ₃ /g)
NiMo/γ-Al ₂ O ₃	6.31	1.43	333
NiMo/KIT-6	n.d. ^b	1.80	307
NiMo/β-zeolite	3.04	1.80	703

Note: ^a Evaluated from the XRD analysis at a 2θ of 44.3° following Scherrer's equation [36]; ^b not detected; ^c obtained from the peak area of H₂-TPR profiles; and ^d evaluated by NH₃-TPD analysis

The H₂-TPR profiles of the NiMo-based catalysts are comparatively shown in Figure 3. The H₂ consumption peaks in each sample mainly involved the reduction of Ni and Mo species. For all three catalysts, two main reduction peaks were superimposed between 400–600°C. The first peak at 400–500°C was attributed to the reduction of MoO₃ (Khrouz et al., 2013), while the second peak at 500–600°C was assigned to the reduction of NiO (Singh and Kunzru, 2016). In the case of the NiMo/KIT-6 catalyst, a small peak located at ca. 356°C was also observed. This implied that some portions of the NiO particles deposited on the KIT-6 surface had a weaker metal-support interaction than others. This phenomenon was also previously observed when the amount of Ni was increased in Ni/KIT-6 catalysts (Lv et al., 2018). Noteworthy, a small broad peak at a high reduction temperature of 630°C was detected when using the NiMo/γ-Al₂O₃ catalyst. This peak might correspond to the reduction of the NiO species that have a strong interaction with the Al₂O₃ support (El Doukkali, 2017). To compare the reducibility of these catalysts, the total H₂ consumption was also evaluated and is summarized in Table 2. The NiMo/γ-Al₂O₃ catalyst had the lowest H₂ consumption level (1.43 mmol/g), whereas both the NiMo/KIT-6 and NiMo/β-zeolite catalysts had a higher H₂ consumption (1.80 mmol/g). Thus,

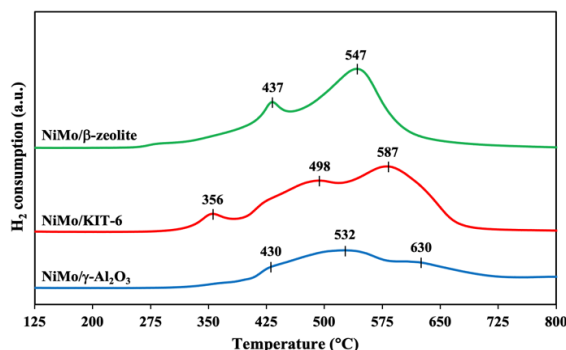
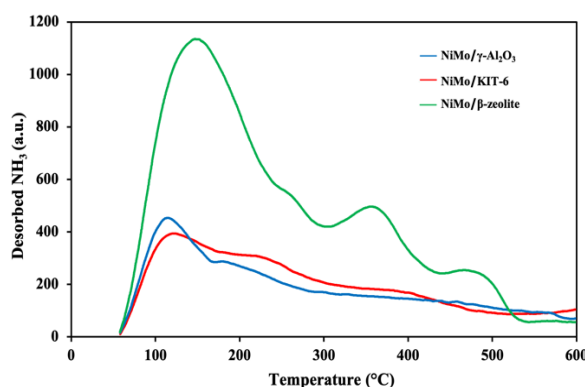
the NiMo/KIT-6 and the NiMo/β-zeolite catalysts clearly had a higher reducibility than the NiMo/γ-Al₂O₃ catalyst.

The acidity of a catalyst is crucial for its hydrocracking performance. This property was calculated from the desorption peak area obtained from NH₃-TPD profile (Figure 4), and is summarized in Table 2. The NiMo/β-zeolite showed the highest total acidity (703 μmol NH₃/g) due to the combination of Lewis and Brønsted acid sites in the zeolite structure (Huber et al., 2022). The NiMo/γ-Al₂O₃ and NiMo/KIT-6 catalysts exhibited a lower acidity of 333 and 307 μmol NH₃/g, respectively.

3.2 Hydrogenation of LCO

3.2.1. Chemical compositions of LCO before and after hydrogenation

The components in the LCO solution before hydrogenation were identified by GC-MS analysis (Figure 5a), and are summarized in Table 3. They were classified into three groups: saturated compounds (decalin and alkyldecalins), partially saturated compounds (tetralin, alkyltetralins, and indane derivatives), and unsaturated compounds (alkylbenzenes, naphthalene, alkyl naphthalenes, dihydronaphthalenes, indene derivatives, fluorene, and biphenyls).

**Figure 3.** Comparative H₂-TPR profiles of the NiMo/γ-Al₂O₃, NiMo/KIT-6, and NiMo/β-zeolite catalysts**Figure 4.** Comparative NH₃-TPD profiles of the NiMo/γ-Al₂O₃, NiMo/KIT-6, and NiMo/β-zeolite catalysts

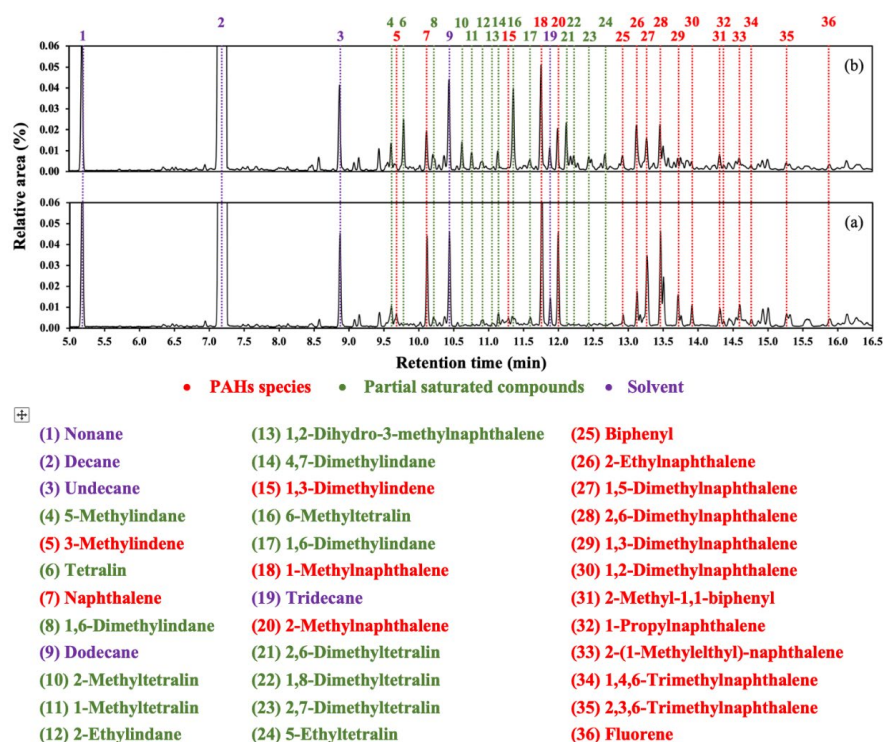


Figure 5. Representative GC-MS chromatograms of the (a) LCO solution and (b) LCO-NiMo/KIT-6

Table 3. Selectivity for different chemical compositions in the LCO solution before and after hydrogenation over the NiMo-based catalysts

Compounds	LCO ^a	LCO-NiMo/ γ -Al ₂ O ₃ ^b	LCO-NiMo/KIT-6 ^b	LCO-NiMo/ β -zeolite ^b
1. Selectivity to the compositions in the liquid product (%) ^c				
<i>Saturated compounds</i>				
Decalin	-	-	0.10	-
Alkyldecalins	-	-	0.12	-
<i>Partially saturated compounds</i>				
Tetralin	-	3.11	4.38	2.95
Alkyltetralins	-	22.7	32.0	22.3
Indane derivatives	8.41	9.03	8.11	9.61
<i>Unsaturated compounds</i>				
Alkylbenzenes	5.71	10.2	12.0	9.96
Naphthalene	7.40	5.09	3.49	5.02
Alkyl-naphthalenes	67.0	44.1	34.1	43.6
Dihydronaphthalenes	0.41	0.09	0.29	0.09
Indene derivatives	3.40	0.65	0.33	0.76
Fluorene	1.03	0.93	0.69	0.85
Biphenyls	6.09	4.17	4.10	4.86
Total PAHs	85.3	55.0	43.0	55.2
PAH removal (%)	-	35.5	49.6	35.3
2. Sulfur content (%)	0.55	-	-	-
3. Liquid yield (%)	-	84.6	86.9	55.4

Note: ^aLCO solution (10% w/w LCO in n-decane); ^bcondition for hydrogenation: T = 350°C, initial H₂ pressure = 40 bar, and reaction time = 3 h.; and ^ccalculated from the %relative area obtained from the GC-MS chromatograms

The selectivity to each species was calculated from the relative peak area in the GC-MS chromatograms and is summarized in Table 3. It was found that the starting LCO solution (10% w/w LCO in n-decane) consisted of 8.41% partially saturated compounds, 91.0% unsaturated compounds, and 0.55% sulfur species. Among these components, the PAH content (naphthalene, alkyl naphthalenes, dihydronaphthalenes, indene derivatives, fluorene, and biphenyls) was 85.3%, and so were the predominant fraction in the LCO solution.

After hydrogenation, only the hydrogenated liquid product obtained from the system using the NiMo/KIT-6 catalyst (LCO-NiMo/KIT-6) exhibited saturated compounds, such as decalin and alkyldecals, (Figure 5b and Table 3). The content of partially saturated compounds in all the hydrogenated LCO products increased from 8.41% in the starting LCO solution to 34.8, 44.5, and 34.9% for the LCO-NiMo/ γ -Al₂O₃, LCO-NiMo/KIT-6, and LCO-NiMo/ β -zeolite catalysts, respectively, with a reduction in the level of unsaturated compounds. The overall PAH fraction of all the hydrogenated products also decreased, giving a PAH removal level of 35.5, 49.6, and 35.3% for the LCO-NiMo/ γ -Al₂O₃, LCO-NiMo/KIT-6, and LCO-NiMo/ β -zeolite catalyst, respectively. Moreover, sulfurous compounds could not be detected after hydrogenation, which was due to the HDS catalytic ability of the applied catalysts.

To study the influence of the support type on LCO hydrogenation, the efficiency of the NiMo/ γ -Al₂O₃, NiMo/KIT-6, and NiMo/ β -zeolite catalysts were comparatively investigated when the LCO hydrogenation was performed under 40 bar initial H₂ pressure at 350°C for 3 h. The NiMo/KIT-6 catalyst exhibited the highest catalytic performance, yielding 49.6% PAH removal and increasing contents of tetralins and decalins. It was possible that the ordered 3D mesopore structure of the NiMo/KIT-6 catalyst facilitated the dispersion of active metals and mass diffusion of reactants and products. This could induce a higher catalytic performance in the

hydrogenation of PAHs. In contrast, the NiMo/ γ -Al₂O₃ catalyst, which had the largest pore size, showed the lowest level of PAH removal. This was due to its lowest surface area and reducibility. Although the NiMo/ β -zeolite catalyst showed a similar PAH removal efficiency to the NiMo/ γ -Al₂O₃ catalyst, it provided the lowest liquid product yield due to its highest total acidity that promotes side reactions, such as solvent hydrocracking or coke formation, which are competitive reactions that occur simultaneously during hydrogenation (Choi et al., 2015; Munir et al., 2020; Lu et al., 2022).

3.2.2. Effect of the hydrogenation parameters on the removal of PAHs in the LCO solution

To obtain a better understanding on the LCO hydrogenation, the influence of the reaction temperature and initial H₂ pressure on the removal of PAHs in the LCO solution using the NiMo/KIT-6 catalyst was evaluated at a central condition of 350°C and 40 bar initial H₂ pressure for 3 h (Table 4).

The level of PAH removal increased from 20.3 to 53.5% when the reaction temperature was increased from 300 to 400°C (Entries 1–3). It is likely that the greater average energy of the molecules at higher reaction temperatures promoted an enhanced rate of chemical reactions (Kotz et al., 2012). Although the reaction performed at 400°C provided the highest level of PAH removal, the obtained hydrogenated products did not support the formation of decalins. Thus, the high reaction temperature possibly promoted hydrocracking that led to the lower hydrogenation efficiency to transform tetralins to decalins (Gutiérrez et al., 2012). For the effect of the initial H₂ pressure (Table 4; Entry 2 and Entry 4), the higher initial H₂ pressure promoted a markedly higher hydrogenation performance. The initial H₂ pressure at 40 bar achieved 49.6% PAH removal, while an initial H₂ pressure of 20 bar resulted in only 14.2% PAH removal without the formation of decalins in the liquid product.

Table 4. Effect of the reaction temperature and initial H₂ pressure on the selectivity to tetralins and decalins, and the %PAH removal, in the hydrogenation of the LCO solution over NiMo/KIT-6 catalyst

Entry	Temperature (°C)	Initial H ₂ pressure (bar)	Selectivity (%)		PAH removal (%)
			Tetralins	Decalins	
1	300	40	12.2	-	20.3
2	350	40	36.4	0.22	49.6
3	400	40	38.0	-	53.5
4	350	20	6.98	-	14.2

Note: Central condition of 350°C, 40 bar initial H₂ pressure, and 3 h

4. CONCLUSION

This research studied the effect of three catalyst supports (γ -Al₂O₃, KIT-6, and β -zeolite) for the elimination of PAHs in a LCO solution via hydrogenation over NiMo-based catalysts. The total acidity of all catalysts decreased in the order NiMo/ β -zeolite > NiMo/ γ -Al₂O₃ > NiMo/KIT-6. The NiMo/KIT-6 catalyst (mesoporous silica) had the highest surface area and provided the highest PAH removal level at 49.6%. The NiMo/ β -zeolite catalyst had the highest total acidity and gave the lowest liquid product yield, although it had a similar efficiency for reducing the level of PAHs as the

NiMo/ γ -Al₂O₃ catalyst. In addition, the NiMo/ γ -Al₂O₃ catalyst, which had the largest pore diameter and the lowest reducibility, provided a PAH removal of 35.5%. The increase in the reaction temperature to 400°C promoted the highest PAH removal level (53.5%) with a 38.0% selectivity to tetralins. Elevation of the initial H₂ pressure from 20 to 40 bar significantly enhanced the catalytic performance and so increased the level of PAH removal from 14.2 to 49.6%. This study expanded the possibilities for sustainable development by proposing an alternate method for converting a petroleum refinery process by-product stream to value-added chemicals with less toxicity.



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