



Indigenous Materials as Catalyst Supports for Renewable Diesel Production in Malaysia

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Abstract: High energy demand from the market due to the rapid increment of the human population worldwide has urged society to explore alternatives to replace non-renewable energy. Renewable diesel produced from biomass could be the next potential energy source for its high stability, long-term storage, and comparable performance with diesel fuels. In producing renewable diesel, the application of catalyst is essential, and the catalyst support is synthesized with the catalyst to enhance the reaction rate and catalytic properties. In this review, the type of catalyst support will be reviewed along with a brief introduction to biodiesel and renewable diesel production, especially focusing on zeolites as the catalyst support. The enhancement of catalyst support will be critically discussed to improve the catalytic performance of support in renewable diesel production and important aspects such as the stability and recyclability of the supported catalyst are included. The application of the supported catalyst in increasing the selectivity and yield of renewable diesel is significant, in which the catalyst as a favorable substance to assist in enhancing renewable diesel yield could lead to a sustainable and greener future for the biofuel industry in Malaysia.

Keywords: catalyst support; renewable diesel; recyclability; stability; enhancement

1. Introduction

The high population over the world and on-going industrial activities for technology development, daily activities, etc. have contributed to the enormous energy demand and increased environmental pollution severity. The usage of non-renewable sources remains a major energy source in most developing countries and alternatives should be explored to overcome the current issues faced. To date, renewable sources such as lignocellulosic biomass, wastes, oilseeds, etc. have been utilized as biofuel feedstocks for their sustainability in reducing the carbon footprint throughout the cycle from up to downstream processing.

Aside from being a fuel source, renewable diesel (also known as green diesel) that is chemically identical to diesel is potentially substituting fossil fuels and securing the world's energy demand. Renewable diesel is different from biodiesel but producible using feedstocks such as waste cooking oil (WCO), lignocellulosic biomass, vegetable oils, etc. [1–3]. As renewable diesel is chemically identical to diesel, it contains no oxygen,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). allows stable storage in the long term, no compatibility modifications are required in diesel engines, and has outstanding performance in cold weather. On the other hand, the instability of biodiesel has been an issue as biodiesel degrades easily if it comes into contact with water. As biodiesel contains functional groups such as carbonyl groups (which contain oxygen), biodiesel is prone to oxidation at higher temperatures due to the formation of oxidation products. The drawbacks of biodiesel in storage and low performance under cold weather have urged the discovery of better alternatives to replace biodiesel. In addition, it was reported that renewable diesel has cleaner combustion due to its low aromatic content, which is less than 0.1 wt% and possesses a similar net heating value to conventional diesel [4,5]. Renewable diesel can be used in high concentrations compared to conventional biodiesel even as a standalone product in diesel engines, which has successfully gained attraction from fuel industries. Around 0.6 billion gallons per year of production capacity was reported at the end of 2020 for the United States [6]. The rapid expansion of renewable diesel plants in the United States shows the current trend of shifting energy production to renewable diesel production, where the production capacity is predicted to be 2.65 billion gallons over the next three years [7].

To produce renewable diesel, the selection and properties of catalysts are the key factors in optimizing the yield of end products in the catalytic reactions. Catalysts are commonly applied to perform catalytic upgrading into renewable diesel or aid in the hydroprocessing of renewable diesel production. Types of catalysts are categorized into supported and unsupported catalysts, where the supported catalysts have much higher surface areas as compared to unsupported catalysts which only range from 1 to 50 m² g⁻¹. For example, the specific areas of common supports such as active carbons, alumina, and silica can be up to 1000 m² g⁻¹ or more for active carbons, and range from 200 to 300 m² g⁻¹ for the latter [8]. The increment of specific areas in supports allows small catalyst particles to be widely dispersed on the surface of the support, thereby enhancing the catalytic reaction rate. The existence of supports provides stability and improves the interaction between catalysts and supports, especially for nano-sized and powdered catalysts [9]. In addition, the support in catalysts enables the efficiency of catalysts to be fully utilized as a catalytically active center and influences the characteristics of supported metal catalysts through the activation of supported metal by their physical and chemical properties [10].

With the advantages of supported catalysts as compared to unsupported catalysts, the exploration of the combination of the supports and catalysts type is required to determine the suitable combination in improving the selectivity and yield of target products. Yet, there is a lack of studies reviewing the interaction between supports and catalysts as well as their effect on renewable diesel production. This review focused on the latest update of supported catalysts applied in producing renewable diesel and their performances in the aspects of recyclability as well as stability. In addition, the enhancement of supports in improving the catalytic properties of catalysts is reviewed thoroughly to provide insights into high efficiency and reaction rates with environmentally friendly benefits. Lastly, the future prospect and challenges faced in this field are included as well.

2. Renewable Diesel and Biodiesel Production

Both renewable diesel and biodiesel are categorized as biofuel as they are produced from renewable feedstocks. To differentiate them, renewable diesel is also known as green diesel or hydrotreated vegetable oil. Although the feedstocks of renewable diesel and biodiesel are similar, the production process is varied as biodiesel is mainly produced by transesterification and renewable diesel is mainly produced by hydroprocessing (hydrocracking and hydrotreatment) with the presence of hydrogen. The molecular structure of renewable diesel, biodiesel, and petroleum diesel are varied and shown in Figure 1. (a) Petroleum diesel

(b) Biodiesel





Figure 1. Structure of (**a**) petroleum diesel, (**b**) biodiesel, and (**c**) renewable diesel. Adapted with permission from ref. [11]. 2022 Elsevier.

Transesterification is the most common method applied in the industries to produce biodiesel, e.g., alkyl esters and fats, as compared to other techniques such as microemulsion, blending with fossil diesel, and pyrolysis (thermal cracking) [12]. The mechanisms of transesterification are illustrated in Figure 2.



Figure 2. Mechanisms of transesterification. Adapted with permission from ref. [13]. 2019 Elsevier.

The history of biodiesel begins with the attempts of biofuel engine operation by Rudolph Diesel using peanut oil (1900) and vegetable oil (the 1930s) in running engines with no modifications conducted [14]. However, the high kinematic viscosity, low volatility, and large molecular mass of vegetable oil imply the impracticality of direct usage in the diesel engine as the performance of the engine is affected [15]. Hence, transesterification is applied to convert 1 mole of triglyceride into 3 moles of mono-alkyl ester and 1 mole of glycerol with the assistance of 3 moles of alcohol. Transesterification can be conducted with or without the presence of catalysts, where homogeneous catalysts are the traditionally used catalysts for industrial production [16]. However, the disadvantages of homogeneous catalysts such as difficulty in separation of catalysts and products as well as incapability of reusing catalysts have led to the application of heterogeneous catalysts in biodiesel production. A trimetallic oxide catalyst, SrO-CaO-Al₂O₃, was studied recently and successfully overcame the issue of active species leaching into the reaction solution while reusing CaO as catalyst [17]. In that study, the outstanding catalytic stability of the mentioned catalyst was discovered even after the fifth reused cycle and is capable of achieving a fatty acid methyl ester (FAME) yield of around 93%. Other than heterogeneous catalysts, biocatalysts such as immobilized lipase from Bacillus mycoides and Ophiostoma piceae strains, as well as fermented macaúba cake are used to assist in enzymatic transesterification [18–20]. Biocatalysts are studied as they are eco-friendly, generate minimal waste while consuming less energy, and function well under mild process conditions [20]. Other than the type of catalyst, the common alcohol used for biodiesel is methanol and ethanol as short-chain alcohol provides better conversion in the same reaction time [21]. The excess amount of alcohol is used in biodiesel production to make the reversible reaction favours the formation of biodiesel as the triglycerides react completely with the excess alcohol.

In the case of hydroprocessing, the oxygen content in the feedstocks is removed during the process, resulting in the product being chemically similar to fossil diesel. The end product of hydroprocessing is reported to be oxygen-, sulfur-, aromatics-, and nitrogenfree diesel with a high cetane number, which can be used as a standalone fuel in diesel engines without any modifications. Hydroprocessing can be performed in a simplified two-stage process: the first stage is hydrotreatment and the following stage is cracking or isomerization [22]. Hydrogen supply is required in the reactions of the first stage such as hydrogenation, deoxygenation, or decarboxylation, leading to the formation of saturated vegetable oil triglycerides and formation of fatty acids for hydrogenation as well as removing oxygen by either supplying more hydrogen (deoxygenation which produces water as a by-product) or without oxygen supply (decarboxylation which produces carbon dioxide as a by-product). Through the first stage, propane is produced as the by-product in hydrogenation and the following by-product varies depending on the later reactions mentioned after hydrogenation. Figure 3 shows the possible reaction pathway of hydroprocessing using the feedstock, vegetable oil.



Figure 3. Reaction pathway of hydroprocessing using vegetable oil to produce renewable diesel [23]. Adapted with permission from ref. [23]. 2019 MDPI.

The catalysts commonly applied in hydrotreatment are transition metal, for example, Ni- and CO-based catalysts as good conversion can be achieved [24–26]. The study by Liu et al. concluded that the Ni supported on a porous carbon matrix synthesized at 400 $^{\circ}$ C was able to obtain a high conversion up to 90% under reaction conditions at 320 °C, 3 MPa, and 4 h of reaction time in cyclohexane. The exceptional advantage is the catalyst can be recycled magnetically for the next cycle and effective for four consecutive cycles in the recycling study [27]. Another study showed the upgrading of biodiesel to renewable diesel using Ni supported on palygorskite, where the researchers concluded that the catalytic efficiency depended on the concentration of Ni species in the catalyst [28]. In addition, the synthesis method of catalyst has been proven to influence the catalytic efficiency of the catalyst. In the study by Fani et al., Ni supported on activated mordenite catalyst synthesized through deposition-precipitation had a higher amount of green diesel produced as compared to other methods such as incipient wetness impregnation, infiltration, and wet impregnation [29]. The resultant product from hydrotreatment was subjected to isomerization and cracking in the second stage. Isomerization was performed to rearrange the hydrocarbon molecules to enhance the octane rating of fuel, while cracking was conducted to break down the large hydrocarbon molecules into useful and smaller molecules through high operating temperature. The isolation of hydrocarbons ranging from C_{15} to C_{18} was achieved through fractional distillation performed for conventional diesel production. These processes are performed to improve the quality of the liquid products in meeting the standards set for conventional diesel. In the study by Ameen et al., the proposed mechanisms of renewable diesel production using sonochemically synthesized catalyst are illustrated in Figure 4, where the first reaction involved was hydrogenolysis followed by hydrogenation to convert propane, linoleic acid into oleic acid then stearic acid. Different pathways such as decarboxylation, decarbonylation, and hydrodeoxygenation were involved for stearic acid to produce the renewable diesel range of hydrocarbons with either further hydrogenation or other intermediate reactions.



Figure 4. Mechanism of hydrodeoxygenation for renewable diesel production using sonochemically synthesized catalyst. Adapted with permission from ref. [30]. 2019 Elsevier.

Table 1 shows the advantages and disadvantages of both processes on biodiesel and renewable diesel production as compared to other types of processes in producing the

same products. Even though transesterification for biodiesel production has been studied and commercialized for a long period, enhancement and improvement are still being investigated by researchers to overcome the issues mentioned. As for hydroprocessing, it was chosen in commercializing renewable diesel production as the process can be conducted using the existing refineries facilities of petroleum fractions and the technology is long established with varied feedstock (renewable sources).

Table 1. Advantages and disadvantages of transesterification and hydroprocessing for biodiesel and renewable diesel production as compared to other techniques [13,16,31–35].

Process	Advantages	Disadvantages
Transesterification	 Biodiesel produced does not need lubricant before usage Performs under mild conditions Applicable for industrial scale Able to perform with or without catalyst Established technology and conventional Friendly to environment (biocatalyst and supercritical fluid) 	 Soap formation using homogeneous catalyst High processing time Requires post treatment process (separation water washing and heating) More water is required to purify biodiesel Expensive cost for supercritical methanol (high temp and pressure)
Hydroprocessing	 No pre-treatment of feedstock is required No post-treatment required for the product to meet diesel standards Easily accomplished using the existing refineries facilities of petroleum diesel Able to perform using low-cost transition metal with supports 	 Requires hydrogen supply leading to costly process Maintenance of catalysts required Tailor-made catalysts are required to avoid rapid catalyst deactivation High operating conditions required Optimization required to favor reaction in forming the higher yield of C₁₅-C₁₈ hydrocarbons

3. Type of Supports

3.1. Activated Carbon

In renewable diesel production, utilization of carbonaceous source materials as the support of catalysts is widely studied. Carbonaceous source materials are treated into activated carbon to serve as the support as the tiny volume of pores produced during the treatment increases the surface area of the catalysts and subsequently enhances the catalytic properties of catalysts to allow a high yield of the end product. Aside from their high porosity, their chemical inertness without interfering with either catalysis activity or selectivity has made them excellent catalyst support even under harsh conditions such as alkali or acidic solutions [36]. The numerous active sites with good pore size distribution along with functional groups are their advantages as support; while the most common heteroatom in their functional groups is oxygen [37]. Other heteroatoms such as nitrogen, sulfur, and hydrogen are present in activated carbon (AC) but in a significantly lesser amount than oxygen as shown in Table 2. In past studies, the doping of different types of heteroatoms on the AC could be performed to establish different properties of AC as support, such as pre-treating it with sulfuric acid or doping it with nitrogen. The purposes of pre-treating AC with sulfuric acid are increasing the number of acid sites through functionalization of the sulphonic groups $(-SO_3H)$, enhancing the interface between active phase and support and acid strength of the acid sites via the covalent bonds formed on catalyst's surface through the post-sulfonation process, which leads to catalyst stability [1,38]. For nitrogen-doped (N-doped) AC, the conversion rate is higher compared to the catalyst without N-doping, along with a lower yield of light hydrocarbon compounds (C_8 – C_{14}). It also leads to favourable results such that high selectivity of $C_{15}-C_{18}$ was obtained due to the suppression of C–C bonds catalytic cracking by adding nitrogen [39]. Similarly, the addition of nitrogen alters the acidity/basicity of AC and the electronic density of catalyst. The doping of nitrogen into AC was reported to increase metal particles' stability and avoid

the re-oxidation of metal particles [40]. Yet, both micro- and mesopores' volumes were reduced in N-doped AC compared to AC.

AC, also known as activated charcoal or activated biochar, is producible from various types of waste and biomass such as coconut shells, wood, walnut shells, and more [41,42]. Pyrolysis is performed to convert these wastes and biomass into char under a nitrogen atmosphere, subsequently followed by an activation process performed under a steam atmosphere at a temperature varied according to the type of biomass to obtain activated carbon. AC produced from wheat straw pellets was activated at a temperature between 800 °C and 900 °C to enhance the char surface area which can be analyzed by the BET method [43,44]. The reuse of waste as a source of AC aids in reducing the amount of waste disposed of in the environment and transforms it into useful products in various fields, such as water and waste treatment, and food, chemical, and automobile industries.

AC works well as support with various types of metals. The catalyst, Pd/AC has successfully performed a molar yield of 35.4% pentadecane under optimized conditions and NiMo/AC with 3% Ni and 15% Mo leads to 99.7% of yield along with high selectivity towards C_{17} – C_{18} hydrocarbons [45,46]. The main products obtained using 5% of Pd/AC were pentadecane and heptadecane, which showed the catalyst was favorable towards hydrothermal decarboxylation in renewable diesel production [45]. The loading of the active phase, Ni and Mo also leads to reduction of the specific surface area of the support, from 1800 m^2/g to 1500 m^2/g [46]. In the same study, the temperature of maximum reduction peak (examined from hydrogen temperature-programmed reduction) reduced along with the increment of Ni amount, especially those catalysts with a low Mo amount, showing the reducibility process was favored by high Ni/Mo molar ratio at a temperature below 400 °C. The observed low reduction temperature peaks indicated the poor strength interaction between the reducible species of NiMo and AC support, which enhanced the formation of sulfided NiMo active phase [46]. It was reported that 90% of hydrocarbon yield along with significantly high selectivity of n-(C_{15} + C_{17}) were obtained using Co/AC with a concentration of 25 wt% Co [47]. However, the crystalline and amorphous phases of AC were substantially reduced due to the impregnation of Co and Mn with AC, indicating the intercalation of CoO and MnO. The embedded Co and Mn also have reinforced the scattering on the AC matrix, which is in agreement with the reduction of Co/AC and Mn/AC catalysts' crystalline size. In addition to the structural properties, the Co/AC possessed the largest total weak + medium (acidities of 2239.23 µmol/g) and strong acid site (acidities of 4295.94 μ mol/g) distributions as well as high basicity (2447.25 μ mol/g) compared to Mn/AC. The synergistic effect between CoO and AC was reported as the reason for the high basicity and acidity profile observed in Co/AC [47]. The high loading of Co (>10 wt%) has resulted in more formation of Co oxides, which subsequently blocked the reactant to access the active site of the catalyst, showing the importance of optimizing the amount of metal impregnated on the support [48]. Although the adaptability of AC as support is excellent with various metals, the selectivity to deoxygenation route rather than other reactions in hydrodeoxygenation varies depending on the type and the concentration of metal synthesized with AC. The study by Mayorga et al. concluded that 5% Rh/AC and 1% Pt/AC were able to obtain a higher conversion of feedstocks in hydrotreatment than 5% Ru/AC [49]. The synergistic interaction between AC support and Co was reported to produce strong acid-based sites, leading to higher renewable diesel yield via deoxygenation reaction compared to Mn [47]. The usage of Co and Fe catalysts with AC as support also showed compatibility in the study of Thangadurai and Tye. High conversion of palmitic (C_{16}) and oleic (C_{18}) acid were obtained using Co/AC while significant hydrocarbon yield of C_5 to C_{20} was gained by Fe/AC [48].

Type of S	Type of Support Elemental Surface Area Pore Volu		Pore Volume	Remarks	Reference	
AC		C: 90.03 % H: 0.557% N: 0.367% S: 0.069% O: 8.98% C/H: 161.6	Micropore: 775 m²/g External: 15 m²/g	Micro: 0.23 cm ³ /g Total: 0.26 cm ³ /g	Charcoals from Iwasaki kiln	[42]
AC		C: 80.71 % H: 1.146% N: 1.094% S: 0.078% O: 16.97% C/H: 70.4	Micropore: 1202 m ² /g External: 20 m ² /g	Micro: 0.39 cm ³ /g Total: 0.42 cm ³ /g	Charcoals from tube furnace	[42]
AC		-	BET: 1484.33 cm ² /g	Total: 1.038 cm ³ /g	Acid sites: 3.96 mmol NH ₃ /g catalysts	[50]
AC		-	BET: 266.1 m ² /g	Total: 0.17 cm ³ /g	Pre-treated with a nitric acid solution	[51]
AC		C: 88.57 wt% O: 8.01 wt% P: 3.42 wt%	BET: 350 m ² /g	Total: 1.88 cm ³ /g	Total acidity (144 °C): 1055.3 μmol/g Total acidity (852 °C): 2064.7 μmol/g Total basicity (902 °C): 1086.6 μmol/g	[52]
AC		C: 79.1 <i>w/w</i> % H: 0.9 <i>w/w</i> % N: 0.9 <i>w/w</i> % O: 19.2 <i>w/w</i> %	BET: 964 m ² /g	Micro: 77.92% Meso: 22.08% Total: 0.57 cm ³ /g	-	[53]
Type of support	Type of catalyst	Composition of the active phase	Surface area	Pore volume	Remarks	Reference
AC	NiP	Ni: 5.14 wt% P: 2.23 wt%	Micropore: 739 m ² /g External: 15 m ² /g	Micro: $0.22 \text{ cm}^3/\text{g}$ Total: $0.25 \text{ cm}^3/\text{g}$	Charcoals from Iwasaki kiln	[42]
AC	NiP	Ni: 4.66 wt% P: 2.24 wt%	Micropore: 851 m ² /g External: 16 m ² /g	Micro: $0.26 \text{ cm}^3/\text{g}$ Total: $0.31 \text{ cm}^3/\text{g}$	Charcoals from tube furnace	[42]
AC	Ni ₂ P	-	BET: 612 m ² /g	-	Total acidity: 1.3 mmol/g	[54]
AC	Ni	O (on the surface): 9.4%	BET: 807.26 cm ² /g	Total: 0.185 cm ³ /g	-	[50]
AC	Co-Fe	Co: 8.67 wt% Fe: 3.52 wt%	Micropore: 459.91 m ² /g	Micro: $0.22 \text{ cm}^3/\text{g}$ Total: $0.44 \text{ cm}^3/\text{g}$	-	[48]
AC	Mo ₂ C	Mo(II): 52% Mo(IV): 8% Mo(VI): 40%	Total: 417.02 m ² /g	Total: 0.22 cm ³ /g	-	[55]
AC	Mo ₂ C	Mo ₂ C (II): 52.17% MoO ₂ (IV): 8.2% MoO ₃ (VI): 39.63%	BET: 322.20 m ² /g	Total: 0.202 cm ³ /g	-	[51]

Table 2. AC as catalyst support for renewable diesel production.

Type of support	Type of catalyst	Composition of the active phase	Surface area	Pore volume	Remarks	Reference
AC	Co-Ag	C: 63.41 wt% O: 13.26 wt% P: 1.45 wt% Co: 9.57 wt% Ag: 12.31 wt%	BET: 793 m ² /g	Total: 1.67 cm ³ /g	Acidity: 8502.3 μmol/g Total basicity: 6220.2 μmol/g	[52]
AC	CoP	-	BET: 822.9 m ² /g	Micro: 68.79% Meso: 31.21% Total 0.43 cm ³ /g	Acidity: 52.5 μmol/g	[53]

Table 2. Cont.

Note: Basic and acid strength tests were performed using TPD-CO₂ and TPD-NH₃, respectively.

Oil Palm Wastes in Malaysia

In Malaysia, the abundance of oil palm wastes can be the main source of AC production. It was reported that palm oil constitutes only 10% and the majority is the oil palm biomass such as oil palm trunks (OPT), empty fruit bunch (EFB), mesocarp fiber (MF), palm kernel shell (PKS), oil palm shell (OPS), and oil palm fronds (OPF), showing an enormous number of hidden wastes generated with regard to the production of 19.14 million tons crude palm oil in 2020 [11,56]. These oil palm biomasses were high in fiber content and often reduced to smaller sizes through pelletizing, chipping, and shredding for converting into useful products. However, approximately 75% of OPT and OPF were left at plantations in their original form for nutrient recycling and mulching while 25% of MF, EFB, and PKS were burnt to produce electricity [57]. As Malaysia is the second-largest exporter of palm oil in global, continuous generation of oil palm wastes from the palm oil industry is expected as long as there is demand. The mismanagement of these biomass wastes can contribute to environmental pollution by either decomposing in plantation sites or utilizing them as boiler fuel. However, the negative image of the palm oil industry requires an alternative solution to drive sustainability and ensure the least impact caused. To handle these biomass wastes effectively, the conversion of oil palm wastes into a wide range of products is suggested and one of them is to convert them into catalyst support materials.

Past literature has shown the potential of oil palm biomass wastes as a precursor of catalyst support through the convincing results obtained in various reactions. The properties of oil palm biomass wastes are suitable for such application as they are easily available and consist of hemicelluloses, cellulose, and lignin. The presence of lignin aids in the formation of the internal structure of AC which is desired particularly in catalyst support materials [58]. It was reported that the unique characteristics of lignin-based catalyst support such as three-dimensional interpenetrating polymer network structure and aromatic units lead to favourable properties, outstanding catalytic performance, and good stability [59]. In the case of palm kernel shell, the synthesis of potassium hydroxide catalyst supported on palm kernel shell AC showed excellent performance in obtaining 98.03% biodiesel with 0.53 ppm of catalyst leaching [60]. The catalytic performance of palm kernel shell AC is varied depending on the chemical or physical activation method in the methane reforming reaction as reported by Liew et al. It was claimed that the chemically activated catalyst displayed better catalytic performance with regard to the conversions of CH₄ and CO₂ [61]. The microcrystalline cellulose support is producible from empty fruit bunch, allowing a high esterification rate of 92.1% when synthesized with γ -Fe₂O₃ [62]. The AC derived from corncob and bamboo were reported to have a slightly lower esterification rate (80.4% and 91%) than empty fruit bunch-derived support, with significant low recyclability (28.8% and 47% after 3 cycles for corncob and bamboo-derived catalyst, as compared to 77.6% after 5 cycles for EFB-derived support) [62–64].

Moreover, the palm male flower (PMF) which also exists in abundance as waste from the palm industry has been investigated as catalyst support by Kaewtrakulchai et al. The study reported 58% selectivity of renewable diesel with 26.9% selectivity of bio-jet fuel obtained through catalytic hydrotreatment using cobalt phosphate (CoP)/PMF-based porous carbon [53]. The improved acidity in the mentioned supported catalyst as compared to Co₂P has resulted in higher cracking activity, which can be optimized through temperature and liquid hourly space velocity (LHSV) of the reactor. It is also worth taking note that a lower LHSV and reaction temperature >420 °C led to a higher fraction of bio-jet fuel and a lower yield of renewable diesel range hydrocarbons [53]. Other than the type of oil palm waste, ammonia fiber explosion pretreatment was reported to be capable of altering the crystalline index as well as the linkage of lignin and carbohydrates of EFB through facilitating partial removal and relocating the lignin for higher sugar yield [65]. This treatment shows insight for its functional relocation of lignin, in providing better catalytic performance of EFB-derived catalyst support in hydrotreatment.

3.2. Metal Oxides

Metal oxides are well known as catalyst supports for industrial catalysts, for example, alumina, zirconia, and silica [66]. They often consist of a metal cation and oxide anion, which form bases through reaction with water and form salts through reaction with acids. The nature of metal oxides varied with the oxidation states, where the metal oxides are more stable and more acidic with higher oxidation states as compared to lower oxidation states. The properties of metal oxides such as stability, strength, and chemical nature are influenced by the type of metal/element as shown in the periodic table, with increasing basic nature and solubility of metal oxides observed down the column [67]. The metallic elements also dominate their wide range of attractive physicochemical properties, from the aspects of morphological, electronic, textural, structural, and redox [68].

The catalyst supports, alumina (Al_2O_3), also known as the aluminum oxides, are often found compatible with a mixture of catalysts (containing two or more than two types of catalysts). It was reported that the catalyst 4Pt-8MO_x (where M includes Sn, W, Mo, and Re) has exhibited improved catalytic activity on hydrodeoxygenation compared to "neat" Pt supported on alumina [69]. These metal oxides impregnated with Pt affected the electronic and textural properties of Pt, resulting in hydrodeoxygenation reaction rather than decarboxylation or decarbonylation reaction during deoxygenation. In the same study, the pore size distribution of metal oxides-Pt was found to be more in a smaller range of pore sizes compared to "neat" Pt, along with higher total acidity. The metal oxides such as MoO_x and ReO_x have higher weak (100–200 °C) and moderate (200–350 °C) acid sites than "neat" Pt, while the SnO_x and WO_x have less weak acid sites and higher strong (>350 $^{\circ}$ C) acid sites than the "neat" Pt. The obtained product selectivity towards C₁₈ was arranged in such order that $MoO_x > WO_x > ReO_x > SnO_x$ with the synergistic effect between Pt (as the catalyst) and Al_2O_3 (as catalyst support) with the function of reaction time (ranged from 41.1 wt% to 89.1 wt%) and temperature (ranged from 1.2 wt% to 92.5 wt%). The good compatibility of NiMo with Al_2O_3 was proven in another study as high product yield (80 wt%), with relatively stable activity if NiMo is sulfided even after 5 cycles of re-use [70]. The sulfided NiMo has a better performance compared to sulfided CoMo due to the amount of stronger sulfided sites and higher metal dispersion (75% higher than sulfided CoMo), while other characteristics such as pore volume, pore diameter, surface area, and reaction temperature at intermediate temperature did not vary significantly. The favorable reaction of these catalysts supported on y-alumina was decarbonylation/decarboxylation, where the carbon atom was released in the form of CO_2 or CO. Parameters such as reaction pressure and time possess a positive effect on the yield of the product while the negative effect was observed in temperature [70]. Other good matches of Pt-MoO_x and Pt-WO_x with Al_2O_3 as catalyst support also outstand Pt-ReO_x with similar support, where the selectivity of C_{18} exceeds 50 wt% after 3 cycles without significant decrement [69]. In the study by Sotelo-Boyás et al., the highest yield of renewable diesel was obtained using NiMo/ γ -Al₂O₃ as compared to Pt/H-Y and Pt/H-ZSM-5, constituted of mostly n-paraffins of C₁₅ to C₁₈, which contributed to poor cold flow properties [71]. The relationship between the yield of renewable/isomerization degree and acid sites' activity of catalysts directly influenced

the obtained cold flow properties of the product. On the other hand, the usage of zirconia (ZrO_2) as catalyst support was studied and reported in the literature. High conversion of palmitic acid (~99%) was reported using Ni/ZrO₂ for renewable diesel production, where a lower conversion rate was observed using AC and H-ZSM-5 under the same study [50]. Although AC as catalyst support has a higher BET surface area than ZrO₂, the total pore volume and average pore size of Ni/ZrO₂ were higher than Ni/AC. As for the surface, 35.8% of oxygen atoms were found on the surface of Ni/ZrO₂ and only 9.4% of oxygen atoms were found on the surface of ZrO₂. It also reported that the bimetallic (NiCu) with ZrO₂ as support is more effective than Ni alone as a catalyst

because the reduction of NiO was facilitated by the Cu during hydrodeoxygenation [72]. Other advantages to utilizing NiCu over Ni as catalyst supported with ZrO₂ were low choking and sintering observed after the reaction. The increasing Cu loading also enhanced the hydrodeoxygenation activity to 82% efficiency with a higher yield of crude bio-oil, using Cu loading up to 6.29 wt% and decreased yield observed thereafter.

The other type of metal oxides, silicon oxide, also known as silica (SiO₂), is utilized as catalyst support due to the uniform distribution of pores and pore sizes as well as its good chemical and thermal stability [73]. These features are important as catalyst support is utilized to improve the catalytic activity of reactions [74]. The arrangement of crystalline and noncrystalline silica varies and is shown in Figure 5, where the crystalline silica is in ordered arrangement and the noncrystalline silica (referred as silica glass) is in the disordered arrangement.



Figure 5. Arrangement of crystalline and noncrystalline silica. Adapted with permission from ref. [75]. 2004 Elsevier.

The conversion of vegetable oil and waste cooking oil using Ir-ReO_x/SiO₂ through hydrodeoxygenation is achievable under mild reaction conditions, with diesel-range alkanes yielding over 79 wt% [76]. It was reported that the high activity of Ir-ReO_x/SiO₂ was elucidated by the synergy effect between partially reduced ReO_x sites and Ir to achieve such yield using a Re/Ir molar ratio of 3. The comparable catalytic activity was also observed for such combination after being regenerated with calcination. For the combination of Ni-P/SiO₂, the variance of metal composition has led to varied competitive pathways in producing C_{15} and C_{16} from palmitic acid, either decarbonylation with/without water

formation, or the dehydration of hexadecanol intermediate pathway [77]. Higher Ni faction of Ni/SiO₂ (24.2 wt%) leads to the pathway of direct decarboxylation in forming C_{15} while the Ni₁₂P₅/SiO₂ catalyst with slightly lower Ni content (18.84 wt%) and P (5.91 wt%) produces C₁₅ with water formation via decarbonylation with dehydration of hexadecanol intermediate to produce C_{16} , and the yield of C_{15} was produced two times of C_{16} . In the case of Ni₂P with an almost similar fraction of Ni (10.19 wt%) and P (10.53 wt%), C_{15} was producible through both decarbonylation and dehydration, followed by direct decarbonylation without water formation. The characterization analyses showed that the metal dispersion and metal site concentration were reduced in the following order: $Ni_{12}P_5/SiO_2 > Ni/SiO_2 > Ni_2P/SiO_2$, which corresponded to the higher catalytic performance of $Ni_{12}P_5/SiO_2$ compared to others [77]. Aside from being a common metal catalyst, SiO_2 as support is suitable to be utilized with coal fly ash as a heterogeneous catalyst in renewable diesel production. The study by Pelemo et al. showed the mentioned catalyst was capable of tolerating high temperatures up to 950 °C with a thermal equilibrium of 700 °C. As compared to pure coal fly ash, the reinforcement of SiO_2 as its support enhanced the pore and micropore volume as well as BET surface area of coal fly ash [78]. The increment of quartz, mullite, and calcite in percentage in coal fly ash up to 87%, 39%, and 5% was also attributed to the reinforcement of SiO₂ which aids in the catalytic performance of the supported catalyst. As for the surface structure, the catalyst with SiO₂ reinforced was found to have hexagonal-shaped particles, regular surface structure, and more pores, compared to the catalyst without SiO₂, representing the high amount of SiO₂ that benefitted the catalysis efficiency. The combination showed good thermal stability as no further weight loss was observed at 700 °C and the thermal degradation was reported to be minimal due to the low composition of calcite (an unstable compound). Other types of metal oxides such as TiO_2 , ZnO, or CaO have the potential to be utilized as they are widely used as part of the catalyst in other applications, even biodiesel production. The properties of metal oxides as catalyst supports are tabulated in Table 3. However, these metal oxides are often utilized with other types of components and act as catalyst support in a combination of two or more components. The related studies will be presented in the sub-section of Section 4.

Type of	Support	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
γ-Al	₂ O ₃	-	BET: 352 m ² /g	Total: 0.68 cc/g	Total acidity: 0.99 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.40 mmol/g Moderate (200–350 °C): 0.21 mmol/g Strong (>350 °C): 0.37 mmol/g	[69]
SiC	D ₂	-	BET: 342 m ² /g	Total: 0.97 cm ³ /g	-	[77]
Ca	Ю	Ca: 98.91 atomic% Other (include S, Sr, Cu, Br, K, Fe): 1.09 atomic%	BET: 9.8 m ² /g	-	Basic sites: 548.52 µmol/g	[79]
Type of Support	Type of Catalyst	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
Al ₂ O ₃	Pt	-	BET: 292 m ² /g	Total: 0.66 cc/g	Total acidity: 1.27 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.56 mmol/g Moderate (200–350 °C): 0.63 mmol/g Strong (>350 °C): 0.07 mmol/g	[69]
Al ₂ O ₃	Pt-WO _x	Pt: 2.4 wt% Mo/W: 10.3 wt% Al: 42.7 wt% O: 44.4 wt%	BET: 240 m ² /g	Total: 0.23 cc/g	Total acidity: 1.39 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.55 mmol/g Moderate (200–350 °C): 0.47 mmol/g Strong (>350 °C): 0.37 mmol/g	[69]

Table 3. Metal oxide as catalyst support for renewable diesel production.

Table 3. Cont.

Type of Support	Type of Catalyst	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
Al ₂ O ₃	Pt-MoO _x	Pt: 3.4 wt% Mo/W:7.6 wt% Al: 43.2 wt% O: 45.8 wt%	BET: 269 m ² /g	Total: 0.19 cc/g	Total acidity: 1.70 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.64 mmol/g Moderate (200–350 °C): 0.80 mmol/g Strong (>350 °C): 0.25 mmol/g	[69]
Al ₂ O ₃	Pt-ReO _x	-	BET: 242 m ² /g	Total: 0.21 cc/g	Total acidity: 1.40 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.68 mmol/g Moderate (200–350 °C): 0.64 mmol/g Strong (>350 °C): 0.07 mmol/g	[69]
Al ₂ O ₃	Pt-SnO _x	-	BET: 187 m ² /g	Total: 0.16 cc/g	Total acidity: 1.26 mmol/g <u>Acid sites distribution</u> Weak (100–200 °C): 0.35 mmol/g Moderate (200–350 °C): 0.63 mmol/g Strong (>350 °C): 0.27 mmol/g	[69]
Al ₂ O ₃	Ni-Mo	NiO: 3.5 wt% Ni: 2.75 wt% MoO ₃ : 10.5 wt% Mo: 6.7 wt%	Micro: 262 m²/g External: 30.7 m²/g	Total: 0.7 cm ³ /g	External surface area is the metallic surface area Dispersion of CO: 7%	[70]
Al ₂ O ₃	Ni-Mo	S: 9.8 wt% C: 5.9 wt%	BET: 177 m ² /g	-	Desorbed NH ₃ : 98.3 mmol at maximum temperature, 167 °C	[80]
Al ₂ O ₃	Co-Mo	CoO: 4.4 wt% Co: 3.46 wt% MoO3: 11.5 wt% Mo: 7.67 wt%	Micro: 242 m ² /g External: 20.8 m ² /g	Total: 0.6 cm ³ /g	External surface area is the metallic surface area Dispersion of CO: 4%	[70]
SiO ₂	Ni	Ni: 2.82 wt% O: 54.93 wt% Si: 42.25 wt%	BET: 237 m ² /g	Total: 0.66 cm ³ /g	Active site: 0.03 mmol/g Metal exposed: 0.34%	[77]
SiO ₂	Ni ₁₂ P ₅	Ni: 5.22 wt% P: 2.06 wt% O: 56.90 wt% Si: 35.82 wt%	BET: 218 m ² /g	Total: 0.55 cm ³ /g	Active site: 0.03 mmol/g Metal exposed: 0.45%	[77]
SiO ₂	Ni ₂ P	Ni: 4.02 wt% P: 5.27 wt% O: 57.12 wt% Si: 33.59 wt%	BET: 88 m ² /g	Total: 0.38 cm ³ /g	Active site: 0.02 mmol/g Metal exposed: 0.26%	[77]
SiO ₂	Coal fly ash	-	External: 32.58 m ² /g BET: 35.11 m ² /g	Micro: 0.000852 cm ³ /g Total: 0.13 cm ³ /g	Micropore area: 2.53 m ² /g	[78]
SiO ₂	Ni-Mo	S: 15.6 wt% C: 5.6 wt%	BET: 343 m ² /g	-	Desorbed NH3: 108.1 mmol at maximum temperature, 160 °C	[80]
TiO ₂	Ni-Mo	S: 7.1 wt% C: 5.5 wt%	BET: 117 m ² /g	-	Desorbed NH ₃ : 54.1 mmol at maximum temperature, 195 °C	[80]
CaO	Со	Ca: 80.29 atomic% Co: 19.37 atomic% Other (include S, Sr, Cu, Br, K, Fe): 0.34 atomic%	BET: 7.46 m ² /g	-	Basic sites: 260.79, 307.77 μmol/g (603, 826 °C) Acid sites: 257, 486.91 μmol/g (488, 840 °C)	[79]
CaO	W	Ca: 83.04 atomic% W: 16.24 atomic% Other (include S, Sr, Cu, Br, K, Fe): 0.72 atomic%	BET: 7.48 m ² /g	-	Basic sites: 450.55 μmol/g (638 °C) Acid sites: 77.22, 10340.49 μmol/g (505, 734 °C)	[79]

Note: Basic and acid strength tests were performed using TPD-CO₂ and TPD-NH₃, respectively.

Tin in Malaysia

Malaysia is well known for its natural resources, including mineral resources, which accounts for a substantial portion of Malaysia's GDP. The major mineral ores are tin, iron,

copper, and bauxite (aluminum) [81]. It is reported that Malaysia produced approximately 3200 metric tons of tin in 2020, accounting for an adequate portion of the tin production of the Asia Pacific region [82]. Although the tin mining industry is not as popular as a few decades ago, the Water, Land and Natural Resources Minister, Dr Xavier Jayakumar, mentioned the intention of the Malaysia Government to go into tin mining again due to the large tin deposits and good revenues [83]. The abundance of tin ores in Peninsular Malaysia can be found in the three major areas of tin belts, namely the Western Tin Belt and two Eastern Tin Belts. The common applications of tin are as coating of other metals (e.g., tin cans to prevent corrosion), alloyed with niobium for superconducting magnets, used in manufacturing different alloys such as copper, bronze, pewter, etc., used in soldering to join electrical circuits or pipes, and more. This is because tin has high corrosion resistance, is ductile and malleable, has low toxicity levels, and is easy to melt. These properties of tin make it easy to be combined with other types of metal for various purposes. The principal tin mineral is cassiterite or known as tinstone (SnO₂) as it contains around 79.2% of tin, which is commonly deposited with iron. A further rewash process is required to concentrate the tin composition before selling to the smelting industry to produce ingots (tin in blocks) for ease of exportation [84].

In addition to for industry usage as mentioned above, SnO_2 has been widely applied as catalyst or catalyst support for biodiesel and biofuel additive production, in reactions such as etherification, esterification, and transesterification. In the study by Srinivas et al., the acidity and activity of catalyst depended on the dispersion and the amount of surface acidic sites of cesium exchanged tungstophosphoric acid (CsTPA) over SnO_2 , which subsequently affected the reaction conversion. The structure of the surface was affected by the amount of CsTPA on SnO_2 , such that a higher amount of CsTPA led to a lower surface area of the catalyst. A strong interaction between the Keggin unit of TPA and the SnO_2 surface was observed through corner-shared oxygen. However, the higher loading of CsTPA above 20 wt% leads to a decrement in acidity due to the bulk nature of support [85]. It was reported that the impregnation of MoO_3 on SnO_2 increased the overall acidity of catalyst, which the weak or moderate acid strength of acid sites changed to strong; hence, the product yield obtained from esterification [86].

Moreover, the organotin (IV) compounds such as *n*-butyltin trichloride (BuSnCl₃), di-*n*-butyltin dichloride (Bu₂SnCl₂), and di-*n*-butyl-oxo-stannane (Bu₂SnO) are reported to possess high selectivity and catalytic activities in glycerolysis, which are actively converting triglycerides to monoacylglycerols and diacyglycerols [87]. Organotin compounds are claimed as pollution components in the aqua environment and could be well-managed for a better purpose, utilizing them as catalyst support to maximize the yield of the end product [88]. The application of tin oxides for catalysis is possible with the successful completion using the synthesized platinum and tin oxides as a catalyst in producing renewable diesel through hydrodeoxygenation, obtaining favorable properties of a catalyst such as high distribution of 3–4 nm particle size, 1.26 mmol/g of total acidity, and 85 mol% conversions of oleic acid [69]. Hence, the further investigation of tin oxides as catalyst support should be deeply studied for their underneath potential in renewable diesel production.

3.3. Zeolite

In the context of catalyst support, zeolite has been outstanding support as it possessed high porosity, surface area, adsorption capacity, and ease of reactant and products separation [89]. As compared to activated carbon, zeolite deposits are not a renewable source as they are a type of mineral which exists naturally. However, they can be produced synthetically for various applications, especially in environmental improvement and renewable energy. The common types of zeolites utilized as the catalysts support are ZSM-5, HZSM-5, SAPO-11, MOR (mordenite), Y-, and β -zeolites. Each type of zeolite consists of a distinct structure and function when incorporated with catalysts. The discussion of natural and synthetic zeolites is included in the following sections and the types of catalyst support studied are summarized in Table 4.

3.3.1. Natural Zeolite

Natural zeolites are minerals formed as the low-temperature products of feldspathic rocks and volcanic, with silicon, aluminum, and oxygen in their framework [90]. The zeolite is formed by tetrahedral $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ in the three-dimensional network in which cations are positioned within materials' pores. Figure 6 illustrated the example of zeolite framework for LTA, FAU and NaA types. These porous aluminosilicate minerals have a variety of compositions, and the catalytic properties are affected by the cations which replace part of the silicon atoms [91]. Hence, different types of zeolites are observed, and they are categorized depending on their crystal structure, morphological characteristics, chemical composition, pore diameter etc. The general structural formula of zeolite is based on the following crystallographic unit cell [92,93]:

$$M^{2+}{}_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot wH_2O \tag{1}$$

where *M* represents the alkaline earth cation, *n* represents *M*'s oxidation state, *x* and *y* represent the number of their atoms per unit cell, and *w* represents the number of water molecules.



Figure 6. Different types of zeolite frameworks: (a) LTA type and (b) FAU type of zeolites' framework structures; (c) NaA type of zeolite's crystal structure in (100)-projection; (d) schematic diagram of α -cage and (e) β -cage. Adapted with permission from ref. [94,95]. 2017, 2013 Elsevier, Nature. The work, ref. [95] is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0/ (accessed on 10 December 2021).

The application of natural zeolites as catalyst support is cheaper than synthetic zeolites as natural zeolites can be mined and processed from natural ore bodies while synthesis of synthetic zeolites requires energy, equipment, and clean substrates, probably leading to a higher price of end product [96]. However, the formation of natural zeolite takes around 50 to 50,000 years at a reaction range from 27 °C to 55 °C and is often contaminated with other minerals, causing them to be excluded for significant commercial applications that require purity and uniformity [97].

The up-gradation of biodiesel to renewable diesel can be performed using zeolitesupported catalysts. The study by Fani et al. concluded that Ni catalysts supported on activated natural MOR led to the production of 25 wt% renewable diesel using the highest loading of Ni as catalyst [29]. The deposition-precipitation method is more favorable compared to other synthesis methods (incipient wetness impregnation, wet impregnation, and infiltration) for Ni/natural MOR due to the resulting better catalyst dispersion, specific surface area, and a lower amount of carbon deposits on the catalyst surface. The highest loading of Ni leads to the balanced amount of weak and strong acid sites along with the highest Ni surface area to produce the highest efficiency for renewable diesel production [29]. Another study reported on the application of Fe/natural zeolite (NZ) showed enhancement on catalytic properties and selectivity towards hydrocarbons with straightchain alkanes ($C_{15}-C_{18}$), and the presence of Fe did not change the morphology and crystal structure of zeolites supports [98]. The Fe particles were found to be well-dispersed on the natural zeolite support although the Fe/NZ tends to be agglomerated. It was observed that the impregnation of Fe on NZ led to reduced BET surface area and pore volumes due to the micropore blocking, which was in agreement with the study by Rostamizadeh et al. [98,99]. The mentioned study achieved 89% conversion of palm oil into renewable diesel using Fe/natural zeolites as compared to pure natural zeolites as catalysts (58%), showing the maleficent results of natural zeolites as catalyst support. With the high conversion rate, the total yield of renewable diesel obtained was 76.3% along with the highest selectivity to C_{15} (66.37%), followed by C_{16} (2.01%) and C_{18} (1.55%). As for the zeolite-Lampung, the main pathway of oxygenation removal is decarboxylation at 375 °C. The surface area of zeolite-Lampung was reduced but the pore volume increased after being impregnated with the catalyst, Pd. This is due to the removal of alkyl-metal impurities and salts within the pores of the catalyst through the activation process. A total conversion of 90.23% can be obtained using this combination of catalyst and catalyst support, with the highest yield of 34.87% and selectivity of 42.70% for the range of $C_{13}-C_{19}$ [100].

3.3.2. Synthetic Zeolite

On top of natural zeolites, synthetic zeolites with optimized structure and surface characteristics can be produced via a thermal process by controlling the composition of materials and process temperature during synthesis [101]. The synthesis of synthetic zeolites can be completed using natural raw materials such as diatomites, volcanic glasses, and clay minerals through various methods [96]. Methods used in synthesizing synthetic zeolites include microwave-assisted synthesis, dialysis, fusion method, ultrasonic method, molten salt method, alkali activation, and hydrothermal synthesis [102–104]. Synthetic zeolites are mainly manufactured for commercial applications such as ion exchange, separation, adsorption, and catalysts for catalytic reactions (molecular-sized microporosity) [96,105]. However, the synthesis of synthetic zeolites from the chemical source of alumina and silica is expensive. Therefore, the raw material namely kaolin was studied as a precursor of zeolite due to their silica and alumina ratio as discussed in the following sub-section.

Short synthesizing time, the versatility of catalytic properties in synthetic zeolites, and the possibility to generate desired zeolite structures are the advantages of synthetic zeolites over natural zeolites as catalyst support. Ni was found as versatile catalysts working well with synthetic zeolites as catalyst support. The compatibility of Ni with zeolites was found in agreement in the study by Li et al., where 79% to 90% of diesel range alkanes were produced using both H-ZSM-5 and H-MOR as catalyst support [106]. The desired properties of Ni/H-ZSM-5 to produce such as high yield of diesel range alkanes (90%) are moderate Ni dispersion (9%) with the acid amount of 1.15 mmol/g with a SiO_2/Al_2O_3 molar ratio of 25. In this case, the catalyst, Ni/H-MOR with a higher amount of acid sites, slightly lower value of SiO₂/Al₂O₃ molar ratio as well as low metal dispersion produced a lower yield of diesel range alkanes as compared to Ni/H-ZSM-5. The reported results were due to more hydrocracking and isomerization occurring over Ni/H-MOR, obtaining a higher yield of hydrocracking products and isomerized C_{14} alkanes [106]. For Pt/H-ZSM-5 catalyst, hydrotreating of rapeseed oil leads to the production of denoting quantities of green gasoline and renewable diesel, favouring *iso*-paraffins rather than *n*-paraffins [71]. It was reported that the performance of a similar combination of catalyst and catalyst support

was affected by the synthesis method. Other types of zeolites such as zeolite beta have good catalytic performance with the catalyst, La_2O_3 , producing diesel-ranged (C_{13} – C_{18}) products with high selectivity of 83% and excellent conversion rate up to 99% from the hydrodeoxygenation of oleic acid. It was contributed to by the textural properties of a catalyst that has large pore diameter, an appropriate amount of weak and medium acid sites, and synergistic interaction between La-Si-Al [107]. Other types of metals such as MgO, MnO, Fe₂O₃, ZnO, and Co₃O₄ also favor the production of diesel-like hydrocarbon, but with a lower conversion percentage (71–98%) and selectivity compared to La_2O_3 . With zeolite Y, the study by Choo et al. showed that transition metal oxides worked well with it to produce renewable diesel via deoxygenation without the presence of H₂ and solvent.

Kaolin Clay in Malaysia

Kaolin clay as a good precursor of zeolite should be explored by Malaysia Government to contribute to the renewable diesel industry and gain revenue from the mining sector. This is due to zeolite as catalyst support being widely applied with additional applications in gas separation and ion exchange, which play an important role in industrial application. Kaolin clay has been utilized in agricultural fields as a biopesticide to repel insects, bacteria, and fungi from fruits and vegetable crops as well as to reduce fungal disease. As for food application, kaolin clay has been used as the filter-aid agent during the brewing of fruit wine or beer. Other than these applications, it is used to create porcelain products in China and applied in skincare or hair products. Since kaolin clay is a natural resource, the kaolin deposits are varied according to geographical location. It was reported that the United States is the country to export the most kaolin, followed by Belgium, the United Kingdom, Brazil, and Ukraine for the top 5 kaolin exporting countries in 2015 [108].

In Malaysia, the abundance of total clay reserves (around 900 million tons) discovered is potential to be utilized for zeolite synthesis, while their elemental composition varies depending on the geographical origin [109]. The raw Malaysian kaolin with a composition of 21.41 wt% Al_2O_3 and 70.08 wt% of SiO₂ and the refined kaolin with a composition of 33.83 wt% Al_2O_3 and 53.44 wt% of SiO₂ are both suitable materials to produce zeolites due to the high composition of Al₂O₃ and SiO₂ [110]. Several studies have shown different synthesis methods in enhancing the production of zeolite from kaolin clay. Low-temperature calcination of crude kaolin can be performed at 600 °C, leading to the formation of metakaolin, subsequently undergoing hydrothermal synthesis to attain zeolite without additional silica and alumina [111]. The low-grade kaolin can be synthesized into zeolites with good crystallinity at a low temperature of 90 °C and improvement of raw material reactivity was observed under 700 °C for the metakaolinization process with a period of 2 h [112]. The favourable results obtained without the addition of a structural directing agent showed the suitability of kaolin as a zeolite precursor. In another study, the kaolin precursor was activated to produce metakaolin using 850 °C and achieved crystallization at 90 °C; then, a good grade of LTA type of zeolite was generated using the synthesized product and watermelon plant extract [113]. The Na-A type zeolite for bioethanol purification was successfully produced through hydrothermal reaction by using NaOH as the activator. The high intensity of peak observed in XRD has shown that the resulted zeolite contained high crystalline phases with a cubic crystalline system. The water adsorption ability from the resulted catalyst was enhanced as compared to conventional zeolite. However, the quartz phases observed in the products indicated the existence of impurities [114].

Type of S	upport	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
Zeol	ite	Si: 36.23 wt% O: 47.64 wt% Al: 8.95 wt% Fe: 1.07 wt%	BET: 55.41 m ² /g	Micro: 0.09 cc/g	-	[98]
H-ZSI	M-5	-	BET: 312.92 cm ² /g	Total: 0.047 cm ³ /g	Acid side amount: 1.39 mmol/g	[50]
Natural m	ordenite	-	BET: 16 m ² /g	Total: 8 m ² /g	-	[29]
Activated n	nordenite	-	BET: 156 m ² /g	Total: 131 m ² /g	Support activated by acid treatment	[29]
ZrC	D ₂	-	BET: 17.77 cm ² /g	Total: 0.053 cm ³ /g	Acid side amount: 2.13 mmol/g	[50]
Zeolit	re Y	Si/Al ratio: 2.14	Micro: 684 m ² /g External: 33 m ² /g BET: 717 m ² /g	Micro: 0.31 cm ³ /g Total: 0.31 cm ³ /g	Weak acidity: 0.83 mmol/g Mild acidity: 1.44 mmol/g Medium acidity: 3.01 mmol/g	[115]
Zeolite-La	mpung	-	BET: 51.9 m ² /g	Total: 0.0045 cc/g	-	[100]
Zeolite	beta	O: 51.6 wt% Al: 2.5 wt% Si: 38.1 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 4.1 wt%	BET: 648 m ² /g	Total: 0.22 cm ³ /g	Weak + medium acid strength: 1615 µmol/g Strong acid strength: 2883 µmol/g Weak + medium basic strength: 158 µmol/g Strong basic strength: 90 µmol/g	[107]
Type of support	Type of Catalyst	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
Zeolite	Fe	Si: 35.40 wt% O: 49.89 wt% Al: 7.58 wt% Fe: 4.47 wt%	BET: 51.26 m ² /g	Micro: 0.07 cc/g	-	[98]
Activated mordenite	Ni	-	BET: 96 m ² /g	Total: 21 m ² /g	20 wt% of Ni is synthesized with support.	[29]
ZrO ₂	Ni	O atoms (only on the surface): 35.8%	BET: 19.80 m ² /g	Total: 0.585 cm ² /g	The binding energy of NiO on ZrO2: 30.90%	[50]
H-ZSM-5	Ni	O atoms (only on the surface): 36.4%	BET: 321.21 m ² /g	Total: 0.114 cm ² /g	The binding energy of NiO on ZrO2: 32.16%	[50]
Zeolite Y	Ni	Si/Al ratio: 2.12 Metal content: 9.44%	Micro: 587 m ² /g External: 47 m ² /g BET: 634 m ² /g	Micro: 0.22 cm ³ /g Meso: 0.04 cm ³ /g Total: 0.26 cm ³ /g	Weak acidity: 1.18 mmol/g Mild acidity: 2.01 mmol/g Medium acidity: 2.72 mmol/g	[115]
Zeolite Y	Cu	Si/Al ratio: 2.13 Metal content: 8.90%	Micro: 583 m ² /g External: 28 m ² /g BET: 611 m ² /g	Micro: 0.21 cm ³ /g Meso: 0.03 cm ³ /g Total: 0.24 cm ³ /g	Weak acidity: 0.56 mmol/g Mild acidity: 2.22 mmol/g Medium acidity: 3.55 mmol/g	[115]
Zeolite Y	Со	Si/Al ratio: 2.12 Metal content: 9.80%	Micro: 564 m ² /g External: 39 m ² /g BET: 603 m ² /g	Micro: 0.22 cm ³ /g Meso: 0.04 cm ³ /g Total: 0.26 cm ³ /g	Weak acidity: 0.54 mmol/g Mild acidity: 3.80 mmol/g Medium acidity: 1.85 mmol/g	[115]
Zeolite Y	Zn	Si/Al ratio: 2.11 Metal content: 8.80%	Micro: 569 m ² /g External: 28 m ² /g BET: 597 m ² /g	Micro: 0.20 cm ³ /g Meso: 0.03 cm ³ /g Total: 0.23 cm ³ /g	Weak acidity: 0.58 mmol/g Mild acidity: 2.92 mmol/g Medium acidity: 1.48 mmol/g	[115]
Zeolite Y	Mn	Si/Al ratio: 2.20 Metal content: 9.40%	Micr566 m ² /g External: 32 m ² /g BET: 598 m ² /g	Micro: 0.20 cm ³ /g Meso: 0.04 cm ³ /g Total: 0.24 cm ³ /g	Weak acidity: 1.95 mmol/g Mild acidity: 2.10 mmol/g	[115]
Zeolite	Pd	Pd: 4.09 wt% O: 45.67 wt% Al: 8.26 wt% Si: 41.96 wt%	BET: 27.26 m ² /g	Total: 0.0139 cc/g	-	[100]

 Table 4. Zeolite as catalyst support for renewable diesel production.

Type of support	Type of Catalyst	Elemental Composition	Surface Area	Pore Volume	Remarks	Reference
Zeolite beta	La ₂ O ₃	O: 56 wt% Al: 1.7 wt% Si: 15.1 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 7.3 wt%	BET: 556.4 m ² /g	Total: 0.29 cm ³ /g	Weak + medium acid strength: 4700 µmol/g Strong acid strength: 1006 µmol/g Weak + medium basic strength: 97 µmol/g Strong basic strength: 145 µmol/g	[107]
Zeolite beta	Co ₃ O ₄	O: 63.4 wt% Al: 1.5 wt% Si: 24.3 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 8.5 wt%	BET: 556.4 m ² /g	Total: 3.6 cm ³ /g	Weak + medium acid strength: 2594 µmol/g Strong acid strength: 1202 µmol/g Weak + medium basic strength: 130 µmol/g Strong basic strength: 193 µmol/g	[107]
Zeolite beta	Fe ₂ O ₃	O: 65.7 wt% Al: 1.1 wt% Si: 21.9 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 6.2 wt%	BET: 574 m ² /g	Total: 3.8 cm ³ /g	Weak + medium acid strength: 2183 µmol/g Strong acid strength: 692 µmol/g Weak + medium basic strength: 95 µmol/g Strong basic strength: 185 µmol/g	[107]
Zeolite beta	MgO	O: 58.4 wt% Al: 1.8 wt% Si: 29.6 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 7.7 wt%	BET: 596.8 m ² /g	Total: 3.6 cm ³ /g	Weak + medium acid strength: 7763 µmol/g Strong acid strength: 4105 µmol/g Strong basic strength: 526 µmol/g	[107]
Zeolite beta	MnO	O: 48.6 wt% Al: 2.2 wt% Si: 32.7 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 9.7 wt%	BET: 440.3 m ² /g	Total: 4.7 cm ³ /g	Weak + medium acid strength: 7186 µmol/g Weak + medium basic strength: 105 µmol/g Strong basic strength: 232 µmol/g	[107]
Zeolite beta	ZnO	O: 57.1 wt% Al: 1.4 wt% Si: 29.2 wt% RM (La/Co/ Fe/Mg/Mn/Zn): 8.5 wt%	BET: 547.7 m ² /g	Total: 3.8 cm ³ /g	Weak + medium acid strength: 3508 µmol/g Strong acid strength: 521 µmol/g Weak + medium basic strength: 102 µmol/g Strong basic strength: 208 µmol/g	[107]

 Table 4. Cont.

Note: Basic and acid strength tests were performed using TPD-CO₂ and TPD-NH₃, respectively.

4. Enhancement of Supports

4.1. Pore Size in Nano-Meter Range/Nano-Sized Porous Support

The structural properties of catalyst supports are significant in assisting the catalytic activity of catalysts. Mesoporous materials are suitable candidates as catalyst support due to high surface area and pore volume as well as pore size distribution. As the synthesis of the catalyst with catalyst support leads to the dispersion of catalyst on the catalyst support, the pore size of catalyst support has to be analyzed as catalyst particles may go into the porous catalyst support, subsequently influencing the specific surface area and total pore volume of the catalysts. The textural parameters such as surface area, pore volume, and pore size are determined through N_2 adsorption/desorption.

Literature studies have presented the structural properties of various catalysts or catalyst supports in catalysis reactions for renewable diesel production. In the study of Abdulkareem-Alsultan et al., the nanosized AC catalyst support was synthesized by the walnut shell with $Co_3O_{4(x)}$ -La₂O_{3(y)} as a catalyst. The maximized catalytic activity was obtained using 20:20 wt/wt % of Co and La ratio, allowing high selectivity (~63%) to n-(C₁₅+C₁₇) via deoxygenation [116]. The acidity of the catalyst was enhanced by the Co species, ranging from 5 to 20 wt%, any value over the mentioned range has resulted in the decrement of strong acid sites. In addition, the high Co content possibly led to structural changes and damaged the mixed oxide structure. For the basicity, the interaction between

 Co_2 with strong basic sites was observed at the main desorption peak (at >500 °C) due to the synergistic effect of Co and La on the support's surface. Similarly, the basicity increased along with the increment of Co content up to 20 wt%. An interesting observation was reported where the needle-like structures of the catalyst deformed due to the aggregation as the Co loading increased [116]. It was reported that the pore size of the catalyst synthesized was affected by the pore size of the catalyst support, while the larger pore size of catalyst allowed high selectivity for gasoline to diesel products [117]. Results obtained from another study were in agreement as the highest conversion of palmitic acid (around 99%) into n-alkane was obtained using the 10% Ni/ZrO₂ (larger average pore size than 10% Ni/AC and 10% Ni/H-ZSM-5) and relatively high selectivity to n-pentadecane due to high amount of acid sites [50]. Aside from the renewable diesel, the main component produced in the gaseous product is methane gas from the methanation reaction, leading to the production of CO₂. The Ni particles were found to be stacked compactly on the ZrO₂ surface while Ni particles were found to be small and uniform in size supported on AC. In the study by Papageridis et al., the comparison of Al₂O₃, ZrO₂, and SiO₂ as support with Ni nanoparticles as catalyst was synthesized via wet impregnation and reported. The isotherms illustrated are of mesoporous materials where Ni/Al₂O₃ and Ni/SiO₂ corresponded to pores with non-uniform size/shape, and Ni/ZrO₂ corresponded to sharp pore size distribution. The highest operating temperature (375 °C) was required for Ni/Al₂O₃ and lowest (300 °C) for Ni/ZrO₂, favoring deoxygenation more than the hydrodeoxygenation pathway [118].

The characterization of a catalyst can be performed via X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy analysis (XPS), Raman analysis, transmission electron microscopy (TEM) image, Brunauer–Emmet–Teller (BET) analysis, etc. Using mesoporous AC as support, the TEM images showed that the molybdenum compounds are uniformly dispersed on Mo₂C/AC catalysts [55]. The results obtained in the study by Hongloi et al. were in agreement with the previous study as high dispersion was observed with Ni on AC support and smaller particle size were analyzed as compared to Ni on ZrO₂ and H-ZSM-5 as supports [50]. In addition to TEM images, the dispersion pattern of catalysts on support can be analyzed through XRD analysis. The dispersion of Co and Mn active metal oxides on nanosized AC was observed from the peak intensities of XRD analysis, as the amorphous and crystalline phases of AC were diminished after being synthesized with the carburization temperature. Higher temperature promotes the formation of metal carbides and produces WC at a temperature of more than 800 °C [55].

In addition, the repetition of catalyst usage changes the texture of both catalyst and catalyst support. The textural parameters of Mo₂C/AC were changed after the first and second cycle, the pore size was enlarged from 2.149 nm to 3.053 nm while the surface area and pore volume were decreased significantly due to coke deposition during hydrotreatment [55]. The catalyst support with nanosized pores often obtains good selectivity of hydrocarbon, for example, 92% of diesel range hydrocarbon selectivity using zeolite Y as support and 97% using NiMoC/zeolites USY for its higher specific surface area and pore volume [115,119]. The sulfided NiMo/ γ -Al₂O₃ works even better than the noble metal catalysts, 4.29 and 4.95 wt% Pd/ γ -Al₂O₃, respectively, as well as 3.06 wt% Ru/Al₂O₃ in the hydroprocessing conversion for renewable diesel production [120]. Aside from sulfided or co-precipitated catalysts, Al₂O₃ seems to work well with a combination of three metals, such that non-sulfided NiMoCe/Al₂O₃ can attain a high yield of C15–C18 alkanes with significant selectivity and conversion percentage under optimized conditions [121]. The bimetallic catalyst (Pt-MoO_x) supported on ZrO_2 allowed the conversion of fatty acids to renewable diesel at 200 °C, exhibiting superior catalytic activity at such low temperature [122]. ZrO_2 was found to be most effective acting as catalyst support for Ni to yield C15–C18 using palm oil and the least activity was found in Co at a similar reaction temperature [123]. The type of synthesis method was concluded to influence the surface area of ZrO₂. Moretti et al. stated that the sol-gel method allows high surface area while fast precipitation results in low surface area of ZrO₂ [124]. However, the surface area and pore

volume were significantly decreased after impregnation for the sol-gel method due to pore blockage and collapse of the structure.

4.2. Synthesis with Other Component(s)

The synthesis of additional component(s) to a type of catalyst support and applied as single catalyst support was explored to overcome particular difficulties faced during the catalytic reaction. Such synthesis can enhance the catalytic properties of catalyst support and subsequently aid in the catalytic performance of the catalyst. Studies of incorporating other components (metal or non-metals) on the conventional supports were performed to discover the potential combinations of catalyst support with varied catalysts, or the catalyst supports are phosphatized or sulfided for improvement.

 Al_2O_3 support as one of the conventional catalyst supports has been investigated and synthesized with other types of components in various catalytic reactions. As discovered by Papageridis and the team, the incorporation of lathana (La_2O_3) in Al_2O_3 support has improved the interaction of active phase and support as well as enhanced the active species dispersion on the support. Their studies not only contribute to the enhancement of biogas-reforming reaction and hydrogen production, but also even improve the continuous selective deoxygenation of palm oil in producing renewable diesel [125–127]. It was reported that the atomic concentration of Ni surface was increased (XPS) by using $La_2O_3 - Al_2O_3$ as support, leading to a larger population of acid sites in the catalyst which helps to avoid the coke formation and extended cracking in the process [127]. In addition to La_2O_3 , the Al_2O_3 support incorporated with β -zeolites was investigated for renewable diesel production through hydroisomerization of n-hexadecane as well. As hydroisomerization requires a bifunctional catalyst, the β -zeolites are chosen based on their good balance between acid and metal functions, and Al_2O_3 is used as a binder where the amount of zeolite influences the ratio of acid/hydrogenation activity [128]. It was reported that the optimum ratio of H- β zeolites and γ -Al₂O₃ binder was 40:60 wt% in the hydrodeoxygenation of vegetal oil without sulfur feed substitution using Pd and Pt as catalyst [129]. Although the deoxygenation rate was better using Pd/AC, Pt-Pd/ γ -Al₂O₃-H- β zeolites boosted the activity of hydrogenolysis and hydrogenation with the H₂ partial pressure as the key parameter for thermal decomposition of unsaturated triglycerides. Manganese (Mn) addition to the Al₂O₃ able to improve the catalytic performance under optimization as 5% of Mn added to the support formed free Mn^{2+} and Mn^{3+} species while 1% of Mn aided in good dispersion of catalyst [130].

Moreover, metal oxides are incorporated with alumina support as well. A recent study indicated that the SiO₂-Al₂O₃ supported Ni catalyst is highly selective and active in synthesizing hydrocarbon, especially *n*-C₁₅ and *n*-C₁₇ hydrocarbons where carbonyl groups were eliminated in reaction pathways [131]. High recovery of spent catalyst was obtained in the same study, but the catalytic performance was significantly reduced, indicating that room remains for improvement and future work for such incorporation of the catalyst support. Catalyst support with more than one component have been synthesized with multicomponent catalysts for either simulation studies or experimental studies. The study of RSM simulation also indicated that good dispersion of active metals (NiO-CaO₅) was observed in the SiO₂-Al₂O₃ support due to the existence of both acidic and basic active sites, leading to a total yield of >67% for hydrocarbons ranging from C₁₃ to C₂₀ [132]. The conversion of waste chicken fat into renewable diesel via deoxygenation using Ni-MoS₂/Al₂O₃-(15%) TiO₂ in the latest study by Hanafi et al. reported that the yield of diesel range products decreases along with the increasing reaction temperature, ranging from 1 to 4 h⁻¹ [133].

On the other hand, the researchers have studied the application of modified alumina support with metal oxides, phosphating agents, and pyrrole. The γ -Al₂O₃ support modified with CaO and MgO showed a high selectivity in renewable diesel production as the presence of CaO and MgO increased the active phase of Ni⁰, lowered the formation of carbon deposits, and suppressed the occurrence of sintering [134]. The phosphatized

alumina support was synthesized using phosphoric acid and compared with the catalyst without phosphatized catalyst support. The study reported that phosphatization enhanced the catalytic performance by eliminating the surface pair sites of $AI^{\oplus} - O^{\ominus}$ on the support's surface and better reactive bidentate carboxylates formation in triglyceride hydrodeoxygenation [135]. The n-doped AC support was synthesized using pyrrole to perform the deoxygenation of palm oil. In the study by Jin et al., the obtained results showed that the electric density of catalyst was altered by N atoms and subsequently led to the enhancement of decarbonylation and decarboxylation routes through the interaction of catalyst with electrophilic groups [39].

4.3. Multi-Walled Carbon Nanotube

Carbon nanotubes can be categorized into single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). SWCNT is formed by the rolled-up graphene sheet whereas MWCNT is formed by more than a SWCNT, where multiple SWCNTs are nested within each other or are combined by weak intermolecular forces. MWCNTs are intensively studied and investigated for various applications and have been utilized in the end-use industry such as electronics and semiconductors, energy and storage, medical, and structural composites. More research studies have been performed using MWCNTs compared to SWCNTs as MWCNTs are functionable under the highly corrosive condition with a low production cost per unit as well as better chemical and thermal stability. The unique properties of MWCNTs have led them to be the largest share of the carbon nanotube market in 2021, where they can be utilized to enhance the mechanical properties of materials without affecting the performances and reduce the CO₂ emissions for aircraft or automotive applications [136]. MWCNTs are high aspect ratio materials that possess excellent electrical conductivity, good tensile strength, and high chemical and thermal stability. Their mesoporous morphology provides the possibility of application in renewable diesel production as catalysis support.

In the study by Aliana-Nasharuddin et al., the nanotube structure of MWCNTs remained after synthesizing with the metal catalyst, and the formation of bulky dense aggregates was noticed only for Ni₁₀, not for those bimetallic catalysts such as Ni₁₀ - Mg₁₀, $Ni_{10} - Mn_{10}$, $Ni_{10} - Ce_{10}$, $Ni_{10} - Cu_{10}$. The introduction of another metal catalyst enhanced the homogeneity morphology and formation of small metal particles on the surface of MWCNTs, but at the expense of metal particles embedded inside the support as the actual amount of metal, particle traces were lower than the theoretical amount [137]. Similar results were observed for the EDAX mapping of Ni-HPW/MWCNT at various loading of HPW, as the experimental value of chemical element contents was lower than the theoretical values although they were homogeneously dispersed on MWCNT [138]. However, the metal loading of a particular metal type influences the degree of deoxygenation. The study of Asikin-Mijan et al. has concluded that the high dosages of Fe and Zn (in NiO-Fe₂O₃) and NiO-ZnO catalysts) contribute to inefficient deoxygenation, as the enhancement of $n-(C_{15}+C_{17})$ selectivity was observed in low metal loading with a large density of weak and medium acidic sites along with strong basic sites [139]. As from the study by Yang et al., the higher loading of HPW (i.e., 50 wt% and 60 wt%) led to lower total pore volume, specific surface area, and pore diameter as compared to low loading of HPW as the pores of support were clogged by excessive catalyst content [138].

In past literature, a high hydrocarbon yield of >75% was obtained using the optimum content of mixed metal catalyst with MWCNTs as support, along with high selectivity of n-(C₁₅+C₁₇) [137,139,140]. It was noticeable that the common metal type used to mix with other metal catalysts is Ni, exhibiting good catalyst activity to produce high quality renewable diesel. The highest conversion of 97.7% was reported by Yang et al., with a total of 51.9 wt% for the yield of <C₁₅ alkenes to process jatropha oil via hydroprocessing using 40 wt% of HPW in Ni-HPW as catalyst [138]. The processing of jatropha oil using 20 wt% NiO-5 wt% Fe₂O₃ also led to a favorable conversion of hydrocarbon, yielding 89% hydrocarbon with a selectivity of 79% n-(C₁₅+C₁₇). Therefore, the optimum catalyst loading

to be synthesized with MWCNT is required to obtain maximize reaction efficiency and catalyst activity.

5. Recyclability and Stability of Supported Catalysts

5.1. Recyclability

To produce renewable diesel on a commercial scale, the performance of catalysts involved in the reaction is of utmost important. The determination in the recyclability of supported catalysts is often conducted by researchers from the view of economics and sustainability as more cost can be saved and the process is greener if the efficiency of catalysts remains after multiple runs of production. The catalysts utilized for renewable diesel production without support are difficult to recycle, especially for those that are nanosized. Therefore, supported catalysts are more advantageous than unsupported catalysts for their stability and ease of recovery. As the catalysts take up a considerable amount of operating cost, the loss of catalyst has to be minimized and it is favorable to have long lifetime catalysts to reuse and recycle for several runs.

To examine the recyclability of used catalysts, the catalysts can be recovered through filtration and being washed by solvent to remove the traces of contaminants on catalyst surface or recalcination or re-reduction method as the treatment method. The study by Malins reported the catalyst activity of recovered spent catalyst was gradually decreased after each run, and the treatment by washing spent catalyst with acetone and drying led to lower product yield compared to the spent catalyst treated with recalcination and rereduction. Through the later method, a total amount of 53.6 wt% hydrocarbon content was obtained in the fifth run of the experiment using the spent NiMo/SiO₂-Al₂O₃ catalyst as recalcination eliminates the organic contaminants (carbon deposits). However, the ratio of $n-C_{18}/n-C_{17}$ content was altered after each treatment and experiment cycle due to the change in catalyst structure [141]. For the derivation of renewable diesel from waste cooking oil, the catalyst, CaO-La₂O₃/nanorode AC also exhibited excellent reusability as it was able to yield >63% for 5 cycles of studies with high selectivity of n-C₁₅ by washing the spent catalyst with hexane multiple time prior reusing it [142]. The reusability of NiO- Fe_2O_3 with MWCNT as support has a higher yield (70–89%), even used for six consecutive runs, and only showed noticeably decreased deoxygenation activity after the fifth run of the experiment [139]. However, in the study by Khalit et al., the selectivity of $n-(C_{15}+C_{17})$ was significantly reduced without remarkable influence on the hydrocarbon yield after reusing the catalyst for four consecutive runs of experiment [1].

The recyclability of the spent catalyst may perform well from the aspect of products yield or selectivity, but the coking activity of the catalyst is subjected to different operating conditions. Coke deposition on the catalyst is studied as it is believed the occurrence leads to catalyst deactivation through the coke deposition on the active sites of the catalyst. The application of La_2O_3 as catalyst supported by HZSM5 has the issue of coking activity as the catalyst active sites were reduced in each run, leading to catalyst deactivation. The coking activity was analyzed through TGA analysis, where soft and hard coke (12 wt% and 7 wt%, respectively) was detected in the La_2O_3 /HZSM5 [143]. A total coke formation of 16% using Ni/AC was reported and the addition of other catalysts into Ni/AC was suggested to reduce the coke activity of catalysts [1]. However, the application of a bimetallic catalyst, CaO-La₂O₃, with a similar support (AC) resulted in negligible coke formation due to the anti-coking properties of the catalyst [142]. In other words, the occurrence of coke deposition is related to the combination of the type of catalyst and catalyst support used for renewable diesel production.

5.2. Stability

The lifespan of supported catalysts not only depends on their reusability; their stability is one of the important characteristics. The interaction between catalyst and the support defines the stability of supported catalysts, as higher stability of supported catalysts is achieved with stronger interaction. The catalytic stability of supported catalysts can be determined with longer reaction time under optimum processing conditions of other parameters (e.g., pressure or H₂/feed ratio etc.), or multiple runs (related to recyclability); while the stability of supported catalysts can be analyzed using characterization tests such as transmission electron microscopy (TEM), high resolution-transmission electron microscopy (HR-TEM), Raman analysis, x-ray diffraction (XRD), thermogravimetric analysis (TGA), and more. It was reported that the catalytic stability of Ni with a different type of support, such as ZrO₂, Al₂O₃, and SiO₂, has been studied for an on-stream experiment lasting up to 20 h at the optimum conditions. The observed outcome from the mentioned supported catalysts was a significant reduction of conversion (32–45%) in the first few hours (6–8 h), with less decrement observed in Ni/ZrO₂ compared to others [118]. Another reported incredible performance of Ni-WC/AC was that the change of catalytic activity and carbon activity was insignificant during the 24 h continuous hydrodeoxygenation, implying its potential to substitute noble catalysts like Pt/AC and Pd/AC with comparable catalytic activity [144]. Other than Ni with different supports, the stability of Pt/SAPO11R was reported after 4 re-uses in hydroisomerization of deoxygenated palm oil [145].

In addition, the study by Papageridis et al. reported characterization tests and carbon analysis for spent catalysts, Ni/Al and Ni/LaAl, where the spent Ni/LaAl had better stability characteristics than the other ones due to less sintering as compared to Ni/Al. One of the favourable results was that the coke formation on the catalyst surface was very thin and no clear carbon structures were viewable using transmission electron microscopy (TEM) [127]. However, another study conducted by Papageridis et al. further investigated the spent catalysts: Ni supported on SiO2, ZrO2 and Al2O3 using HR-TEM after the first attempt using TEM due to undetectable carbon deposits. The results of HR-TEM showed that a thin graphitic carbon shell covered the catalysts with a thickness ranging from 2.2 to 4.2 nm [118]. From the EDX study, the differences between fresh and spent catalysts were increment of carbon, reduction of oxygen, and sulfur and nickel content for Ni/AC. The decrement of Ni was due to the coke coverage and the obtained higher carbon content was ascribed to coke formation [1]. Other than the analysis mentioned above, the XRD study was used to examine the quality of catalysts' structure and chemical and thermal stability. Nur Azreena et al. reported outstanding properties of $La_2O_3/HZSM5$ as no diffraction peaks were observed due to its good chemical stability and structural qualities. This supported catalyst also exhibited excellent thermal stability because only a minor peak increase was observed after usage [143]. The loss of acid and base sites in the spent catalyst due to coking and metal phase transformation can be further confirmed using XRD. It was reported that the active sites of Ni⁰ were dominant in fresh catalysts, which would be easily transformed into inactive Ni₃C after exposure to CO environment [1].

6. Challenges and Future Prospects

The discussion above has demonstrated the importance of catalyst support's properties in reactions to function at their maximum efficiency. Particular properties are required according to the objective of the study being performed, while the synthesis condition of catalyst and catalyst support is one of the main challenges to obtaining desired properties. This is due to similar synthesis conditions leading to different properties depending on the type of catalyst and catalyst support used to synthesize. The efficiency of the catalyst is influenced by the properties obtained through synthesis, and subsequently affects the yield of the end product, reusability/recyclability as well as stability of the catalyst. Most studies reported that the higher acidity or basicity with more amount of acid or basic sites, the high surface area of the catalyst and high pore volume demonstrated good catalytic performance towards renewable diesel production. However, the synergistic effect between catalyst and catalyst support does affect the catalytic performance and may lead to a higher or lower yield of the end-product. Another major challenge is the suitable combination of the type of catalyst and catalyst support in sustaining the catalytic performance after several runs as well as the stability of catalyst during the process. Various types of combinations have been researched for their recyclability and stability in repeating usage for economical

purposes and the quality of renewable diesel obtained. A supported catalyst with good recyclability and stability is always favourable to get comparable quality of end-product without high amount of coke formation, which easily leads to catalyst deactivation. The recyclability of the supported catalyst was affected by the treatment method before the second run of the experiment. The coke formation can be reduced by using bimetallic catalysts on the same catalyst support compared to a single type of metal catalyst. The stability of the supported catalyst is important as well to keep the catalytic activity under various experimental conditions, to ensure the composition of hydrocarbons obtained is corresponding to renewable diesel range. Characteristic analysis can be performed to compare the fresh and spent support catalysts in investigating their respective stability and recyclability. Therefore, the appropriate type of supported catalyst has to be applied as subjected to the type of feedstocks used to produce renewable diesel. These challenges have to be addressed before applying the supported catalyst for renewable diesel production on industrial scale.

For renewable diesel production, the research works conducted focus on supported metallic catalysts such as transition metal and noble metal-supported catalysts. The coke formation on transition metal-supported catalysts such as Ni is an issue in the recyclability of supported catalysts to use for repeated applications. Although the noble metal-supported catalysts have higher stability, the expensive cost of noble metal is another challenge for commercial application despite the good efficiency. More investigation for different types of supported catalysts can be performed to study their efficiency in producing renewable diesel and overcoming undesired side reactions as well as coke formation during the process. In addition to chemical catalysts, the potential of supported biocatalysts can be explored and studied in renewable diesel production as there are success cases in producing biodiesel using biocatalysts and the feedstocks for both biodiesel and renewable diesel are similar. The renewable diesel industry is in progress and not as established as biodiesel production worldwide, hence an improvement of process and development of new protocols are required especially for developing countries. Technology maturity is essential to ensure renewable diesel production in replacing petroleum diesel, enlightening environmental pollution severity, and fulfilling the energy demand worldwide.

7. Conclusions

In renewable diesel production, the catalyst has always been an essential component for increasing the rate of reaction, product yield, and selectivity of hydrocarbons in the diesel range. The properties of the catalysts are varied after synthesizing with catalyst support, depending on the type of catalyst and catalyst support used. The existence of catalyst support enables the increment of surface area and alters the acidity as well as basicity of the catalyst. The investigation of support produced from zeolites, metallic oxides, and activated carbon was discussed, along with the enhancement of these components through reducing the size of pores (nano-sized) and combining two (or more) types of supports as well as the coking issues, stability, and recyclability of catalyst. The catalytic performance of spent supported catalyst may reduce as more runs of experiments have been conducted due to the coking issues, leading to less active sites. Potential materials such as oil palm wastes, kaolin clay, and tin oxides in Malaysia could be utilized as catalyst support for renewable diesel production on a large scale due to their abundancy. These indigenous materials as catalyst support could lead to a greener energy industry in Malaysia by replacing conventional diesel with renewable diesel using a low-cost catalyst.

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