Catalyst Supports for Renewable Diesel Production

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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. The application of the supported catalyst in increasing the selectivity and yield of renewable diesel is significant, in which the catalytic properties depend on the interaction between catalyst and catalyst support. The supported 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.

catalyst support renewable diesel recyclability stability enhancement

1. Introduction

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][2][3]. As renewable diesel is chemically identical to diesel, it contains no oxygen, 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 m^2 g^{-1}. For example, the specific areas of common supports such as active carbons, alumina, and silica can be up to 1000 m^2 g^{-1} or more for active carbons, and range from 200 to 300 m^2 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 [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].

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.

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) [11]. 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 [12]. 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 [13]. Hence, transesterification is applied to convert vegetable oil into biodiesel. Transesterification can be conducted with or without catalysts, where homogeneous catalysts are the traditionally used catalysts for industrial production [14]. 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. 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 [15][16][17]. Biocatalysts are studied as they are eco-friendly, generate minimal waste while consuming less energy, and function well under mild process conditions [17].

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 nitrogen-free 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 [18]. 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 of hydrogenation and the following by-product varies depending on the later reactions mentioned after hydrogenation. The catalysts commonly applied in hydrotreatment are transition metals, for example, Ni- and CO-based catalysts as good conversion can be achieved [19][20][21].

3. Catalyst Supports

3.1. Activated Carbon

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 [22]. 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 [23]. 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 1**.

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 [24][25]. 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. 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 loading of the active phase, Ni and Mo leads to a reduction of the specific surface area of the support, from 1800 m^2/g to 1500 m^2/g [26]. 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 favoured by high Ni/Mo molar ratio at a temperature below 400 °C. 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 [27]. 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 μmol/g) distributions as well as high basicity (2447.25 μmol/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 [27]. 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.

Table 1. 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	NiP	Ni: 5.14 wt% P: 2.23 wt%	Micropore: 739 m^2/g External: 15 m^2/g	Micro: 0.22 cm^3/g Total: 0.25 cm^3/g	Charcoals from Iwasaki kiln	[25]
AC	NiP	Ni: 4.66 wt% P: 2.24 wt%	Micropore: 851 m^2/g External: 16 m^2/g	Micro: 0.26 cm^3/g Total: 0.31 cm^3/g	Charcoals from tube furnace	[25]
AC	Ni_2P	-	BET: 612 m^2/g	-	Total acidity: 1.3 mmol/g	[31]
AC	Ni	O (on the surface): 9.4%	BET: 807.26 cm^2/g	Total: 0.185 cm^3/g	-	
AC	Mo_2C	Mo(II): 52% Mo(IV): 8% Mo(VI): 40%	Total: 417.02 m^2/g	Total: 0.22 cm^3/g	-	[32]
AC	Mo_2C	Mo_2C (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	-	[28]
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	[29]
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	[30]

References

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

3.2. Metal Oxides

Metal oxides are well known as catalyst supports for industrial catalysts, for example, alumina, zirconia and silica [33]. 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 [34]. The metallic elements also dominate their wide range of attractive physicochemical properties, from the aspects of morphological, electronic, textural, structural, and redox [35].

The catalyst support alumina (Al_2O_3), also known as the aluminium oxides, is often found compatible with a mixture of catalysts containing two or more types of catalysts. It was reported that the catalyst 4Pt-8Mo/Al_2O_3 (where M includes Ce, Mn and Re) has exhibited improved catalytic activity on hydrodeoxygenation compared to “neat” Pt supported on alumina [36]. These metal oxides impregnated with Pt have affected the electronic and textural properties of Pt, resulting in hydrodeoxygenation reaction rather than decarboxylation or decarbonylation reaction during deoxygenation. The metal oxides such as MoO_x and ReO_x have higher weak (100-200 ^oC) and moderate (200-350 ^oC) acid sites than “neat” Pt; while the SnO_x and WO_x have less weak acid sites and higher strong (>350 ^oC) acid sites than the “neat” Pt. The good compatibility of NiMo with Al_2O_3 was proved in another study as high product yield (80 wt%), with relatively stable activity if NiMo is supported even after 5 cycles of re-used [37]. Parameters such as reaction pressure and time possess a positive effect on the yield of the product while the negative effect was observed at temperature.

Silicon oxide known as silica (SiO_2), is utilized as catalyst support due to the uniform distribution of pores and pore sizes, their good chemical and thermal stability [39]. These features are important as catalyst support is utilised aiming to improve the catalytic activity of reactions [40]. It was reported that the high activity of Ir-ReO_x/SiO_2 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 [41]. The comparable catalytic activity was also observed for such combination after regenerated with calcination. Besides common metal catalyst, SiO_2 as support is suitable to be utilised with coal fly ash as a heterogeneous catalyst in renewable diesel production. As compared to pure coal fly ash, the reinforcement of SiO_2 as its support has enhanced the pore and micropore volume as well as BET surface area of coal fly ash [42]. As for the surface structure, the catalyst with SiO_2 reinforced was found to be having hexagonal-shaped particles, regular surface structure, as well as more pores, compared to the catalyst without SiO_2, representing the high amount of SiO_2 that benefits the catalysis efficiency. The combination showed good thermal stability as no further weight loss was observed at 700 ^oC 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 are potential to be utilized as they are widely used as part of the catalyst in other applications even biodiesel production. However, these metal oxides are often utilised with other types of components and act as catalyst support in a combination of two or more components.

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3.3. Zeolites

Zeolite has been outstanding support as it possessed high porosity, surface area, adsorption capacity as well as ease of reactant and product separation [43]. 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 zeolite. Each type of zeolite consists of a distinct structure and function when incorporate with catalysts.

3.3.1 Natural Zeolites

Natural zeolites are hydrated aluminosilicate minerals formed from volcanic rocks and volcanic ash with silicon, aluminium, and oxygen in their framework [44]. These porous aluminosilicate minerals have a variety of compositions and the catalytic properties are affected by the cations which replaced part of the silicon atoms. Hence, different types of zeolites are categorized depending on crystal structure, morphological characteristics, chemical composition and pore diameter etc. 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.

The upgradation of diesel to renewable diesel can be performed using zeolites supported catalysts. The study of 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 [45]. 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. Another study reported on the application of Fe/natural zeolite (NZ) showed enhancement in catalytic properties and selectivity towards hydrocarbons with straight-chain alkanes (C_{15}–C_{18}), and the presence of Fe did not change the morphology and crystal structure of zeolites supports [46]. 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 of Rostamizadeh et al. (2016) [46][47]. The mentioned study has 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.

3.3.2. Synthetic 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. The synthesis of synthetic zeolites can be completed using natural raw materials via microwave-assisted synthesis, dialysis, fusion method, ultrasonic method, molten salt method, alkali activation and hydrothermal synthesis [48][49][50]. However, the

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