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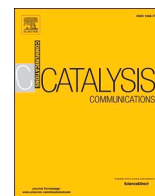
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The role of textural properties and surface chemistry of activated carbon support in catalytic deoxygenation of triglycerides into renewable diesel

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ABSTRACT

The textural properties and surface chemistry of activated carbon support are commonly known to have influence on the catalytic performance of catalysts. Many authors have assessed the effect of textural properties and surface chemistry of activated carbon support in the deoxygenation of triglycerides. This review focuses on reconciling literature on the role/relevance of textural properties and surface chemistry of activated carbon support in deoxygenation of triglycerides into diesel-like hydrocarbons. It is revealed that different activated carbon (AC) exhibit distinct effects on the catalytic behaviors of the supported catalyst. The degree of influence of both textural properties and surface chemistry of AC support varies with the nature of the supported catalyst.

1. Introduction

Researches have established that fossil fuel emissions are the dominant cause of enhanced global warming. The phenomenon is believed to be the culprit behind climate change, and is threatening the global ecosystem. Global warming is projected to worsen with time for as long as burning fossil fuels for energy continues. The International Energy Agency report shows that CO₂ emission from energy and industry has increased by 60% since the United Nations Framework Convention on Climate was signed in 1992 [1]. The Organization calls for net zero emissions by 2050 Scenario. Current assessments reveal that petroleum-based fuels continue to be the leading source of energy, dominating the transportation sector while playing a significant role in electric power and industrial sectors.

The rising environmental concerns, the projected inevitable fossil oil depletion and the global geopolitics (due to uneven spatial global distribution) have motivated intensified research on renewable biofuels over the last two decades to replace petroleum-based fuels. More effort has been directed towards converting biomass into biofuels.

Biomass feedstock include dedicated energy crops, agricultural crop residues, forestry residues, algae, wood processing residues, municipal waste, and wet waste. Biomass contains organics including lignocellulose, starch, fats and oils, and sugars, which are converted into biomass-derived fuels in various processes [2]. The use of waste and by-products as feedstock is being emphasized as it has the potential to increase atom

efficiency and minimize energy consumption. Processes to convert biomass into biofuel include pyrolysis, hydrothermal liquefaction, gasification, fermentation, transesterification, cracking and catalytic deoxygenation.

Although some of these processes have reached industrial piloting stages, they are yet to provide a practical and economically competitive alternative energy source to replace fossil fuels, calling for further researches. One of the challenges facing biomass-derived fuels industry is lack of effective yet environmentally friendly catalyst, which has high selectivity for desired products, to mediate the conversion and upgrading of the products to on-specification fuels.

It remains an irrefutable fact that fats and oils are one of the most promising candidate feedstocks for the synthesis hydrocarbon liquid fuels owing to possession of low oxygen content and long carbon chain moieties [3,4]. They are also chemically suitable for use as precursors in the synthesis of many petroleum-based products currently in use [5]. The widely used method for conversion of oils and fats (triglycerides) into biofuel is transesterification, but the method yields biodiesel with high oxygen content and unsaturated hydrocarbon chains, which render the fuel viscous and susceptible to undergoing rancidity/oxidation. Oxidized biodiesel not only further increases viscosity but also corrodes the engine block, limiting the direct application of the fuel in combustion engines. The synthesis of deoxygenated diesel using triglycerides as feedstock, catalytic deoxygenation, seems attractive. Various studies have been carried to deoxygenate triglycerides but there is still lack of

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ineffective, yet environmentally friendly catalyst. One of the materials studied in this regard is carbon; activated carbon, carbon black and nanostructured carbon. Carbon is being studied as both a catalyst and a catalyst support. Its attractiveness stems in the possession of high surface area, tunable surface and its local availability [6]. Since carbon black and nanostructured carbon are primarily prepared from nonrenewable sources, activated carbon continues to attract substantial research attention, as it can be prepared sustainably from biomass agricultural wastes.

It is generally known that catalytic performance of a heterogeneous catalyst is determined by factors such as nature of active phase and support materials, feedstock/reactants and operation conditions. Activated carbon has been studied as a catalyst support in various catalysis works, some of which have demonstrated that the material alters the catalytic activity, stability and selectivity of the support catalyst. Various studies have focused on role of textural properties (surface area, pore size distribution, pore volume) and surface chemistry of catalyst support materials in catalysis. The studies are justified by the fact that understanding the role of textural properties and surface chemistry of carbon support, like other catalyst supports, has the potential to provide a basis for rational design of a superior carbon-based catalyst.

In view of the fact that nature of substrate and operation conditions can influence the catalytic behavior of catalyst/catalyst support combination, some researchers have studied the effect of textural properties and surface chemistry of activated carbon support specifically on deoxygenation of triglycerides. Some of the studies have reported interesting results including limited influence of textural parameters of carbon support on the catalytic activity, selectivity of product and durability, seemingly contradicting the general and widely accepted literature [7,8]. This calls for a review dedicated to reconciling the effect of texture and surface chemistry of activated carbon specifically on deoxygenation of triglycerides and fatty acids into diesel like hydrocarbons.

Many previous reviews on catalyst support discuss the role texture and surface chemistry in catalysis [9–17]. The reviews establish a generic view of the role textural and chemical properties of carbon support materials on the catalytic activity, selectivity and stability of carbon-based catalysts [18].

Therefore, this review will focus on the role of textural parameters and surface chemistry of activated carbon in the catalytic conversion of triglycerides into renewable diesel. Although the focus is on activated carbon, selected nitrogen and oxygen-doped carbons will be included to facilitate understanding the effect of surface chemistry.

2. Conversion of triglycerides into biofuels

Methods for production of biofuel with reduced oxygen content (or for the removal of oxygen from biodiesel) using triglycerides as feedstock include cracking and catalytic deoxygenation carried out at high temperature (300–500 °C) and pressure. Cracking/pyrolysis is one of the methods that can be employed to convert or upgrade triglycerides, fatty acids and FAME into renewable diesel. Pyrolysis can be carried out in the presence or absence of a catalyst, procedures referred to as catalytic cracking or thermal cracking, respectively. Pyrolysis yields three product: solids, liquids, and gases. The relative fractional abundances of the products are a function of the operational conditions, feedstock composition and type of catalyst [19–21]. In addition, different catalysts also yields distinct product composition [22,23]. The liquid fraction, bio-crude or bio-oil, is a complex mixture of olefins, paraffins, oxygenated compounds and some, aromatics. It can be upgraded and fractionated (by distillation) into a wide range of renewable fuels. The gaseous fraction is composed mainly of H₂, CH₄, CO₂, CO, and light hydrocarbons in the range of C₂-C₄ [23,24]. These products can be used in turbines and boilers, engines and as precursors for various chemicals. The solid fraction (char) can be used as an alternative fuel. Usually pyrolysis is optimized to minimize the char production and to increase

liquid fuel production. However, the pyrolysis method is unappealing due to high yields of light hydrocarbons (C₁-C₄) and short-chain alkanes (C₅-C₁₅) which have low energy densities [25–27]. Commercial zeolites, silicaalumina, and fluid catalytic cracking catalysts are typically used for this type of reactions [26]).

Deoxygenation involves removal of oxygen from the feedstock, in this case triglycerides, to produce diesel-like hydrocarbons. Three key processes for deoxygenating bio-based oils have been explored so far. In this method, catalysts (especially noble metals) supported on SiO₂, carbon and Al₂O₃ are used to achieve selective deoxygenation under inert atmospheres [28–30]. Deoxygenation reaction in this method occurs primarily through cracking of triglycerides, and some decarboxylation (DCO₂) and decarbonylation (DCO) pathways, collectively abbreviated as deCO_x, where x = 1 or 2. Decarboxylation (DCO₂) refers to the removal of carboxyl group from the triglyceride/fatty acid carbon chain, as carbon dioxide [25,31]. Decarbonylation (DCO) reaction, on the other hand, refers to the removal of carbonyl group in carbon monoxide (CO). Both decarboxylation (DCO₂) and decarbonylation (DCO) yield a product with one carbon lesser than the original fatty acid [31]. Although the method yields diesel-like hydrocarbons (comparable to petrol diesel), several issues including rapid deactivation of catalyst due to coking, limited deoxygenation, and poor selectivity for the desired product are limiting development of this method into a full flagged commercial production [28].

The second type of deoxygenation is one carried out under high H₂ partial pressures between 4 and 15 MPa and is referred to as hydroprocessing [32]. Deoxygenation in this method occurs primarily through hydrodeoxygenation (HDO) pathway, although decarboxylation (DCO₂) and decarbonylation (DCO) reactions may also occur [29,33–36]. Hydrodeoxygenation (HDO) involves removal of oxygen in the presence of high hydrogen pressure without reducing the carbon chain of the fatty acid involved. Deoxygenation in hydrogen environment hinders undesired reactions such as aromatization, cracking, oligomerization, coking and cyclization [31,32,37] associated with inert deoxygenation. The feedstock composition, reaction conditions, and nature of catalyst determines which reaction route, either DCO or HDO, dominates.

It has been established that conventional hydrotreating catalysts exhibit higher selectivity for HDO than DCO. On the contrary, supported noble metal catalysts prefer DCO to HDO in hydrogen environment [31,37]. Comparatively, deoxygenation processes in the absence of hydrogen (hydrotreatment) is found to be superior to inert atmosphere processes. Even when Pd/C catalysts (initially believed to work identical under Ar/He and H₂ environments) are used, hydrogen has been found beneficial [31,37]. Furthermore, hydrogen saturates double bonds on triglycerides chains which otherwise compromise the stability of the end product by being rendered susceptible to autoxidation. However, deoxygenation in the presence of hydrogen too suffers drawbacks including the requirement to use precious metals catalysts and the high hydrogen inputs. These drawbacks have rendered the products unable to compete commercially with fossil diesel. Possible solutions include use of alternative deoxygenation routes such as decarboxylation/decarbonylation [25] and hydrothermal deoxygenation [38] which do not require the use of high hydrogen inputs.

The third deoxygenation process is hydrothermal deoxygenation [39–43]. The process is achieved in the presence of sub- or super-critical water (300–400 °C and 50–220 bar), over a suitable catalyst. Pt, Pd, Ni, and Cu catalysts supported on hydrothermally stable supports like activated ZrO₂ and carbon have been reported to effectively mediate hydrothermal decarboxylation [5,38,44,45]. Activated carbon has also been reported to be effective catalyst at 380–400 °C under supercritical conditions (220 bar) [46,47]. The process has also been demonstrated to be efficient with in situ generated hydrogen (catalytic transfer hydrogenation) for production of diesel-like hydrocarbons from fats and oils [48,49].

Literature establishes that catalytic deoxygenation of oils and fats

produces diesel, referred to as renewable diesel, which has quality properties that can even surpass fossil diesel [31]. Moreover, the quality of renewable diesel is so profound that it is not even assigned upper limit in diesel engines, and can be further isomerized to meet specific prescribed standards [25,31]. However, the methods for the synthesis of renewable diesel suffer undesirable side reactions (including cracking, isomerization), the requirement for high pressure, specialized and expensive equipment, use of precious metal catalysts and high hydrogen inputs. To circumvent the use of high hydrogen inputs and precious metal-based catalysts, researchers are focusing on developing catalysts to mediate reaction routes that do not require the materials, DeCOx being more preferred. Some of the materials studied in this regard are the mixed oxides and non-precious metals supported on activated carbon. Carbon as a support material has been reported to play an important role in catalysis either as a passive entity that is catalytically inactive or as a catalysts modifying material.

2.1. Carbon basics

Carbon atoms join covalently in various ways through orbital hybridization allowing formation of different allotropes, e.g., amorphous carbon, graphite, diamond, carbon nanotube and fullerenes [50]. The ability of carbon atoms to combine s and p orbitals to form up to four hybridized orbitals that are equal in energy, sp^1 , sp^2 , and sp^3 , offers the element the ability to form extensive networks of covalent bonds with both itself and other elements. Considering monoatomic bonding, each carbon atom can combine with up to four atoms of its kind. The type of hybridization formed determines the physical, electrical and chemical properties of the resulting carbon material. When the hybridization is sp^2 (three energy-leveled sp orbitals), two-dimensional hexagonal or honeycomb planar sheets containing double bonds form, resulting in graphene or graphite [50]. On the other hand, sp^3 hybridization leads into a three-dimensional network of diamond structure. For sp^1 , in theory, a carbon strand with alternating triple bonds material forms. The different ways in which carbon atoms bond leads to various materials with distinctive chemical, structural, physical, mechanical, electrical and properties, which make it appropriate for a wide range of respective applications [50]. The resulting type of hybridization formed through the chemical bonding is responsible for the various characteristics, physical and chemical properties for each class of allotrope.

The attractiveness of carbon stems in the fact that the substance exhibits high porosity, large specific surface area, high electron conductivity, and relative chemical stability. The material can be physically and/or chemically functionalized to either impart or enhance its catalytic function. Literature has demonstrated that carbon-based catalysts are resistant towards coke formation and have high chemical stability with high product selectivity. Porous carbons, including biochar [51], carbon nanotubes [52,53] and activated carbons [54] have been investigated as catalyst support materials. According to the studies, porous carbons are some of the most promising support materials for deoxygenation catalysts [51–53].

Although some porous oxides (TiO_2 , $\gamma-Al_2O_3$, and mesoporous silica hydroxalcite) can offer catalytic capabilities of carbon, the oxides are unstable at the high reaction temperature and pressure [50]. The structural disintegration of the oxide supports results in compromised catalytic performance, leaching metals causing product contamination and non-recovery of catalyst material.

Many review publications have identified some of the catalytically relevant features of carbon materials to be [18,50];

1. Resistance to acidic or basic media.
2. Tailored pore size distribution for specific reactions.
3. Amphoteric character due to the presence of various oxygenated functional groups which enhances metal adsorption and catalyst dispersion.

4. The structure is stable at high temperatures (even above 1000 K); except in the presence of oxygen >500 K and for hydrogenation reactions >700 K.
5. Less expensive compared to alumina and silica supports. Porous carbons can be prepared in different physical forms (granules, extrudates, pellets, fibers, cloths, etc.).
6. Hydrophobic carbon can be modified to increase the hydrophilicity.
7. Active phase can be recovered by eliminating the support through burning away the carbon.

2.2. Carbon materials used in catalysis

Amorphous carbon, carbon fibers, activated carbon, ordered mesoporous carbon, graphene oxide, carbon black, carbon nanotubes, and carbon nanodots are just a few examples of the carbon-based materials that present new opportunities for the development of numerous catalytic supports and catalytic performances [50]. Most often, graphitic or porous carbons are used in sorption, sensors, and catalysis. In addition, the regulated pore structure of carbons and the surface chemistry of carbons (surface oxygen, other heteroatoms, amphoteric character, and hydrophobicity) are crucial for catalysis applications [55].

The commonly used carbon materials to function as either catalysis or catalyst support are activated carbon and carbon black [50]. The high surface area they present and the relatively less costly preparation account for their suitability. Advanced science and engineering paves the way for the synthesis of various nanostructured carbon materials: (i) zero dimension (nanoparticles); (ii) one dimension (carbon nanotubes); (iii) two dimensions (graphene sheets); and (iv) three dimensions (mesoporous carbons). Although these carbon materials show promising results in various applications, including as catalyst support materials, their synthesis is hindered by high energy usage, tangling of products and prohibitively high cost of production [55]. Most of the available methods for the synthesis of carbon nanostructured materials are designed to use non-renewable petroleum feedstock, and recently edible biomass (sugars and oils), known to cause environmental issues. The exclusive use of non-renewable sources is largely caused by the difficulty with which to manipulate biomass (lignocellulose being the most prominent) directly into carbon nanostructured materials using the currently applied methods. Currently, there are only a few available pioneering studies that have dealt with the conversion of biomass into nanostructured materials [56–58] where the preparation methods have proven to be prohibitively costly and to have scalability issues. These methods are only applicable on a narrow range or a specific type of biomass such as some type of grass, some leaves, oils, soluble sugars and grinded biochar. Universal protocols that cover a wide range of biomass feedstocks are yet to be developed.

2.3. Carbon black

Carbon black is an amorphous carbon prepared by the pyrolysis of organic polymers or hydrocarbon precursors at ~ 1500 °C [55]. Since the preparation of carbon black involves the use of petroleum derivatives as precursor materials, its application contributes to carbon dioxide emissions proving to be environmentally unfriendly [55]. In this regard, activated carbon seems to be a better option for the preparation of carbon-supported catalysts, as it is synthesizable from biomass-derived carbon materials, including agricultural wastes, and requires low temperature to prepare.

2.4. Activated carbon

Activated carbon is prepared by physical or chemical activation of carbonized carbonaceous materials. With physical activation, carbonized materials are oxidized in oxidizing atmospheres (steam or oxygen) at 600–1200 °C [50]. On the other hand, the carbonized materials are impregnated with a strong base, an acid, or a salt (usually zinc

chloride or calcium chloride or), followed by carbonization at 450–900 °C to activate the material. The activation of carbon material improves surface area determining and reactivity factors including high porosity, pore volume, active sites, structures and particle size [50,59]. Therefore, activation is not only a tool to increase surface area/porosity but also manipulate and optimize nature of active sites and selectivity. The reader is advised to reach out to the excellent review work of [50] which gives some insights on carbon precursor selection and carbonization methods.

Different natural carbon precursors yield distinct carbon materials depending on composition and structure, and the preparation method [50]. More research attention is currently being focused on using biomass derived activated carbon owing to the renewability of biomass feedstock. The proper precursor should yield carbon materials that give not only high surface area but also large pore volume and optimum pore diameter [60]. The synthesis of biomass derived activated carbon for a specific application requires proper identification of biomass. For instance, biomass containing proportionally large lignin content, will give rise to less porous carbon materials [60].

3. Activated carbon as a catalyst support

In deoxygenation reactions, catalysts are usually prepared by a method consisting of a catalyst on high surface area materials, referred to as support materials. Different support materials have different effects on the catalytic activity and route/product selectivity [61]. Differences in textural properties (surface area, pore volume, pore size distribution) and surface chemistry (acid/base characteristics, presence of heteroatoms functional groups and hydrophobicity) lead to differences in product distribution and the overall deoxygenation activity [62]. Other properties of the support material include mechanical strength, chemical and thermal stability. Some catalyst supports are inert/passive while others are inactive. Those that are inactive may engage in stabilizing materials to prevent the agglomeration.

Several support materials, particularly porous materials including active carbon, carbon nanotube [54,63], zeolites (e.g., HY, HZSM-5, HZSM-22) [52] and mesoporous SiO₂ (e.g., MCM-41, SBA-15) have been investigated to establish their effects on the catalytic activity of various catalysts. The catalyst supports having high acidity (high density and strength of acidic sites), such as zeolites, can influence the catalyst to incline towards favoring deoxygenative activity, accompanied by high cracking and isomerization activities. According to literature, the acidic sites play a major role in catalyzing C–O and C–C bond cleavages, and selectivity of HDO products. However, excessively high acidic supports enhance the acidity of hybrid catalysts (support-catalyst system) which causes coke formation and the consequential catalyst deactivation or carbon deposition (a coke precursor). In addition, cracking c-c bond leads to formation of light weight hydrocarbons which reduces the selectivity for the desired long-chain hydrocarbons selectivity [64]. Basic sites with acid sites are known to suppress coke formation, with retained deoxygenation activity. Another method to avoid the negative effect of excessive acidity/basicity properties is the use of mild acid supports, such as porous carbons, TiO₂, and ZrO₂ [64].

The inertness of carbon plays a great role in catalysis. Unlike acidic supports such as alumina and silica, which promote cracking leading to catalyst deactivation through coking (by pore clogging and/or active site poisoning), carbon inertness in catalysis offers much lower coking propensity. In contrast to alumina and silica, carbon exhibits weak chemical carbon-active phase interaction, thus the behavior of the catalyst is largely determined by the physicochemical nature of the active phase. Furthermore, the weak interaction between the catalyst precursor and carbon support facilitates reduction of the metallic catalyst precursor into active phase [65]. The oxide support materials have been reported to interact with the active phase so strongly that, for some metal ions, reduction of the precursor oxide is hindered, leaving the materials in a catalytically inactive state/phase. For instance, iron

cations strongly interact with the alumina support surface, which renders the in-situ formed oxide precursor hard to reduce to iron zero-valent state. The inertness of carbon also facilitates easy formation of alloy phases during preparation of multi-element catalyst. The role of surface chemistry of carbon support gets complicated by findings that some metal catalysts [10] for sulfided afford higher catalytic activity when supported on activated carbon (less inert surface) than carbon black (more inert surface). It is also further reported that the type and amount of surface groups and impurities in the carbon support significant influence on catalyst activity and selectivity [10]. Activated carbon, particularly biomass derived, seems more promising, owing to environmentally friendliness and low cost of production.

4. Effect of activated carbon supported catalysts on catalytic performance

Catalysts supported on activated carbon have been found to exhibit superior catalytic activity, higher conversion rate and higher selectivity for diesel range hydrocarbons. Table 1 provides a summary of studies on deoxygenation of triglycerides into diesel-like hydrocarbons using carbon supported catalysts. Han et al [66] studied the conversion of various vegetable oils (olive, soya bean, rapeseed and maize oil) on Mo₂C supported on activated carbon (surface area 1189 m²/g) under hydrogen atmosphere. The study was motivated by the need to replace prohibitively expensive precious metals in the conversion of fatty acids into diesel. In the study, unsupported Mo₂C catalyst was used on model compounds to compare its performance with the supported catalyst. The supported Mo₂C was highly effective in converting the model compounds, and the vegetable oils, to diesel-range hydrocarbons. The unsupported Mo₂C catalyst exhibited low kinetics and poor yields of hydrocarbons. While Mo₂C/AC reached 65% conversion after just an hour, the unsupported Mo₂C afforded similar conversion (67%) after 5 h. The two catalysts led to the formation of paraffins primarily via HDO. with a selectivity of 42% versus 69% for Mo₂C and Mo₂C/AC, respectively. The yield of hydrocarbon ranged between 76% and 88%. Mo₂C/AC was found to be active and stable over sixteen runs with olive oil as feedstock. The authors speculated that the higher performance of the carbon supported catalyst (Mo₂C/AC) was due to molybdenum carbide dispersion on activated carbon that increased accessibility to catalytically active sites. The speculation was based on the fact that the supported catalyst (Mo₂C/AC) exhibited higher surface area that of the unsupported one (Mo₂C). Here the activated carbon was regarded as a surface for catalyst attachment alone, playing insignificant chemical role in both catalytic activity and product/ route selectivity. The pore size distribution, acid-base profile and surface chemistry of the activated carbon were not reported.

Hui et al. [67] prepared activated carbon-supported nickel phosphide catalysts via wet impregnation and tested them on the deoxygenation of palmitic acid for high-grade diesel production. They found that the activated carbon supported Ni_xP (X = molar ratio N/P) has higher selectivity decarboxylation/decarbonylation than one which was supported on zeolite H-ZSM-22 in their previous study [68]. H-ZSM-22 exhibited high cracking and isomerization activities of palmitic acid leading to a high gaseous product fraction. The pore diameter of the catalyst in the previous publication (HZSM-22 zeolites) were microporous range (approximately 0.46 × 0.57 nm) whereas in the later it was mesoporous range (10–40 nm). Moreover, the zeolite is characterized by strong acidic sites while activated carbon is dominated by weak acid-base sites. In the two studies, the catalyst, Ni_xP (that form Ni₁₂P₅ and Ni₂P as the active phases), was found to favor decarboxylation and decarbonylation. The HZSM-22 support was also found to participate in the reaction by presenting Brønsted acid sites, suggested to be mainly responsible for the isomerization reactions, and Lewis acid sites known to cause cracking reactions. On the other hand, activated carbon was assigned the role of inert support materials, whose sole purpose is to increase surface area for greater catalyst dispersion to expose its active

Table 1

Summary of studies on deoxygenation of triglycerides into diesel-like hydrocarbons using carbon supported catalysts.

Catalyst Support	Support	Reaction condition	Reaction	Feedstock	Hydrocarbon yield (%)	deCOx Selectivity (%)	References
Ag ₂ O ₃ -La ₂ O ₃ / AC _{nano}	Walnut shell	Temperature = 350 °C, time = 120 min, Catalysts' loading = 1 wt%, under inert N ₂ flow	DO	Waste cooking oil	89	93 (n-C15 + C17)	[71]
Ni ₅ -Ag ₅ /AC	Coconut meat residue	Temperature = 350 °C, time = 60 min, Catalysts' loading = 5 wt%, under inert N ₂ flow	DO	Waste cooking oil	80	83 (n-C15 + C17)	[74]
Co(10 wt%)-Ag(10 wt %)/AC	Coconut shell waste	Temperature = 350 °C, time = 120 min, Catalysts' loading = 1 wt%, under inert N ₂ flow	DO	Palm Fatty Acid Distillate	92	95 (n-C15 + C17)	[75]
CoP/Porous carbon		340–420 °C, 50 bar, LHSV = 1 h – 1 (continuous reactor)	DO	Palm olein oil	100		[61]
Co ₃ O ₄ (20%)- La ₂ O ₃ (20%)/ AC _{nano}	Walnut shell	Catalyst loading: 1 wt% Temperature: 330 °C Time: 1 h and 5% of water content	DO	Waste cooking oil	96	93 (n-C15 + C17) 8	[72]
CaO-La ₂ O ₃ /AC	Walnut shell	Semi-batch reactor, temp.330 °C, time 60 min Temp. 350 °C, Pressure1 bar, continuous reactor	DO	Waste cooking oil	72%	>80 n-C15	[53]
NiP/AC			DO	Palmitic acid	86.2–100		[67]

sites. For Ni_xP/AC (X = molar ratio of N/P), the main products were C15 (the desired), and the minor ones were C11–C14 alkanes and alkenes. The high selectivity for C15, and the absence of C₁₆ in the products, lead to the conclusion that Ni_xP/AC active sites mediates the conversion of palmitic acid high grade diesel through decarboxylation and decarbonylation (DCOx) pathways which required lower H₂ consumption.

The poor performance of the Ni_xP/H-ZSM-22 is attributed to the acidic nature of the support material, H-ZSM-22, while the relatively better performance of Ni_xP/AC was credited to the inertness of activated carbon. While the inertness of carbon (absence strong acidic sites) may account for the better performance of the carbon supported, the role of parameters, pore size, pore size distribution and surface chemistry on both activity and selectivity requires scrutiny.

Couman & Hensen [69] compared the catalytic effectiveness of sulfide NiMo supported on activated carbon, mesoporous alumina, and amorphous silica-alumina on the hydrodeoxygenation of methyl oleate. From the results, the activated carbon-supported NiMo catalyst exhibited the highest MoS₂ dispersion and stacking degree than the oxide supports. The carbon support was able to stabilize the very small MoS₂ slabs efficiently and that active phase exhibited a pronounced type II NiMoS phase character. The catalytic performance of the NiMo sulfides on activated carbon in the hydrodeoxygenation (HDO) reaction was found to be 2× more active than the other oxide supports and remaining active over a prolonged on-stream reaction. Activated carbon has the potential to enhance the dispersion of catalytic active metal sulphides due to the weak interaction of the carbon support with a metal sulfide.

Kaewtrakulchai et al [61] used cobalt phosphide (CoP) nanoparticles supported on porous activated carbon derived from palm male flowers (PMFs) for the conversion of palm oil into diesel-like hydrocarbons. The PC, carbonized at 400 °C was found to contain micropores and significant amount of mesopores. The BET surface area of the obtained PC is approximately 964.0 m²/g with total pore volume (V_T) of 0.57 cm³/g. The phosphide (CoP) nanoparticles supported on PMF-derived PC was prepared by simple wet-impregnation with subsequent thermal treatment (600–900 °C). The catalyst thermally treated at 600 °C, the least acidic of the tested catalysts containing predominantly Co₂P as opposed to CoP, exhibited 100% triglyceride conversion and the highest yield of liquid hydrocarbon product (C9–C18) of 77%. The superior catalytic performance of the catalyst pyrolyzed at 600 °C was credited to the greatest particle dispersion on carbon support, while higher temperatures resulted in aggregation and formation of the more acidic phase CoP that intensifies cracking. Though not so discussed by the authors, it the results suggest that at temperatures above 600 °C, the basic/weak acid groups on AC responsible for anchorage decompose [10,13,14] leaving the active phase (Co₂P) to aggregate and transform into CoP, a more

acidic phase. It was concluded that the catalyst mediates palm oil conversion into hydrocarbon fuels through both decarbonylation/decarboxylation (deCOx) and cracking reactions, as evidenced by the release of CO/CO₂ and light hydrocarbons such as CH₄, C₂H₆, C₃H₈. The authors emphasized that yield and selectivity of the desired hydrocarbon products were profoundly a function of the operating parameters and acidity of the cobalt phosphide/PC.

It has been observed that basic metallic catalysts are potential candidates for deoxygenation catalysis due to their high thermal stability and less susceptibility to deactivation due to coke deposition [70]. However, the basic catalysts have a tendency to have poor deCOx activity, requiring hydrogen in puts, which is undesirable as hydrogen synthesis is usually environmentally unfriendly. In attempts to resolve this problem, Alsultan et al. [53] has worked on the possibility of using carbon-based catalysts that can provide both acidic and basic metallic properties. The authors studied CaO-La₂O₃/AC materials for the DO of waste cooking oil into hydrocarbons in hydrogen free environment. It was concluded that CaO-La₂O₃/AC mediated the conversion of cooking oil through decarboxylation/decarbonylation route (hydrocarbon yield 72% with n-C15 selectivity >80%), accompanied with mild cracking. However, when the oxides (CaO/AC and La₂O₃/AC) were used individually, cracking dominated, signifying the importance of the influence of the supported oxides. In addition, CaO-La₂O₃/AC showed high catalytic stability and reusability up to 6 cycles with >73% of yield and selectivity to n-C15 of >82%. The catalyst showed an excellent coke inhibitor with <2 wt% of coke under TGA analysis. The authors attributed the impressive reactivity of CaO-La₂O₃/AC nanocatalyst to synergic effect between active acidic promoter (Ca–La) and high surface area of carbon support, regarding carbon support as being catalytically inactive. However, unsupported CaO-La₂O₃ was not included in the study to confirm the role of carbon. The development of high n-C15 formation over n-C17 in the deoxygenation (DO) of WCO is due to mild cracking of the deCOx product (n-C17) and fatty acid intermediates.

In another publication, Alsultan and coworkers investigated the conversion of waste cooking oil (WCO) into renewable diesel using nano-sized Ag₂O₃-La₂O₃ supported on walnut-derived activated carbon (Ag₂O₃-La₂O₃/AC_{nano}) under hydrogen-free environment [71]. The authors aimed to avoid coke problems and to improve selectivity for decarboxylation/decarbonylation (deCOx). The results revealed that the Ag₂O₃(10%)-La₂O₃(20%)/AC_{nano} formulation resulted in a higher yield (~89%) of liquid hydrocarbons with majority of diesel fractions selectivity (n-(C15 + C17) at ~93%. The high stability of the Ag₂O₃(10%)-La₂O₃(20%)/AC_{nano} catalyst was proven by maintain six continuous runs with constant yield (>80%) of hydrocarbons and (>93%) selectivity of n-(C15 + C17) under mild reaction conditions. Approximately

~89% of hydrocarbon yield and excellent *n*-(C15 + C17) selectivity (93%) was obtained under optimum conditions of 1 wt% of loading of catalyst, 350 °C of temperature of reaction, and 120 min time of reaction. The hybrid catalysts afforded high yield and selectivity for diesel range hydrocarbons despite low specific surface area of about 372–299 m²/g. The paper demonstrated, among other things, that Ag₂O₃(10%)–La₂O₃(20%) supported on activated carbon is resistant to coke formation which is accused of rendering the catalyst-support combination catalytically ineffective.

Elsewhere, untreated waste cooking oil (WCO) containing 38.4 wt% FFA and 5% water was deoxygenated over Co₃O₄–La₂O₃/AC_{nano} catalysts to produce green diesel under flow of N₂ in a micro-batch closed system [72]. The idea was to suppress decarbonylation exhibited by Co₃O₄, and enhance decarboxylation, by combining it with La₂O₃ rich in basic sites on activated carbon. The catalyst containing 20% of each of the oxides (Co₃O₄(20%)–La₂O₃(20%)/AC_{nano}) was observed to have the maximum catalytic activity. Catalyst loading of 1 wt% yielded 96% hydrocarbons with 93% *n*-(C15 + C17) selectivity within 60 min at 330 °C, though higher catalyst loading (3 wt%) resulted in poor performance, even at higher temperature of 350 °C within 180 min. The catalyst exhibits high stability as it could be reused up to eight times with insignificant loss of its catalytic activity. The higher performance of the Co₃O₄(20%)–La₂O₃(20%)/AC_{nano} was attributed to the superior acid and base profile distribution of the support-catalyst.

Kaewtrakulchai et al [73] investigated activated biochar derived from palm fiber waste as a support material for nickel phosphide (Ni–P) and iron phosphide (Fe–P) catalysts to be applied in palm oil conversion into green diesel by catalytic deoxygenation (DO). The synthesis of the activated biochar-supported Ni–P and Fe–P catalysts was carried out by wetness impregnation method followed by thermal treatment (pyrolysis) at 500 °C. The choice of pyrolysis temperature was probably informed by their previous work [61] also reviewed in this work. The palm fiber activated biochar (PFAC) support used in the study exhibited high porosity (*S*_{BET} of 1039.64 m² g^{−1} and *V*_T of 0.572 cm³/g, micropore volume 70%, mesopore volume 28%, volume average diameter of 1.8 nm) which promoted the metal phosphide nanoparticle dispersion. The DO of palm oil was tested in a trickle bed down flow reactor under hydrogen atmosphere. The catalytic deoxygenation of the activated carbon supported Ni–P and Fe–P catalysts afforded liquid hydrocarbon yield between 63.37 and 79.65%, with the highest green diesel selectivity of 62.64%. The major conversion routes were found to be decarbonylation (DCO) and decarboxylation (DCO₂), with significant hydrocracking due to acidic nature of the metal phosphides. The use of activated biochar support enhanced metal phosphide dispersion resulted in higher catalytic performance.

Elsewhere, some research findings have indicated that different types of carbon materials exhibit distinct catalytic activities and product selectivity [10,60]. The physico-chemical properties of activated carbon are a function of preparation methods and the nature of the precursor, making it feasible to tune the material for a particular application.

5. The role of textural parameters

Literature shows that textural properties of support materials (specific surface area, pore size, or pore size distribution, pore volume) can affect the size, dispersion, and reducibility of active phase, which in turn determines the product selectivity and catalytic performance [15,62]. It is generally accepted that large surface area and wide pore size are important for greater active phase dispersion, which in turn results in increased catalyst performance [15]. Various researchers have demonstrated, using materials other than carbon (e.g. porous silica materials), the existence of a correlation between pore diameter and catalytic activity, where an optimum pore width has to be empirically determined to improve both catalytic activity and product selectivity. The researchers document that increasing pore size of support materials leads to increase in crystallite size of the catalyst and the consequential poor

catalyst dispersion, resulting in altered product selectivity and reduced catalytic effectiveness [16,17,76]. However, this is still not clearly resolved in reactions involving conversion of triglycerides into hydrocarbons over carbon-supported catalysts.

It is also established that micropores are prone to blockage or further narrowing by the particles of the supported catalyst (the active phase), leading to restricted access to active sites. Restricted access to active sites results in low catalytic performance even when the support exhibits high surface area and greater degree of catalyst dispersion. Micropores are also susceptible to clogging by the coke formed as the reaction being mediated progresses [15].

However, this widely accepted conception is threatened by some recent publications which suggest that textural properties of carbon support have limited influence in the triglyceride deoxygenation reaction, implying an exception to the general establishment [15]. This section attempts to harmonize literature on influence of the textural properties of activated carbon supports on catalytic activity, product selectivity and stability during deoxygenation of triglycerides for diesel-range hydrocarbons.

Asikin-Mijan et al [74] investigated the effect of various types of carbon on the catalytic activity of the mixed oxide NiO–Fe₂O₃. The mixed oxide was mounted on multi-wall activated carbon nano-tubes (MWCNT), walnut shell activated carbon (AC_{walnut shell}) and commercial activated carbon (AC_{commercial}). The NiO–Fe₂O₃/MWCNT exhibited higher catalytic activity and selectivity for diesel-like hydrocarbons, proving superiority of MWCNT as a carbon support materials. The BET surface area, pore size, pore size distribution and degree of dispersion on catalytic activity and selectivity are presented in Table 2. NiO–Fe₂O₃/MWCNT catalyst consistently gave the highest hydrocarbon yield (89%) and *n*-(C15 + C17) selectivity (79%), despite having, by far, the lowest degree of dispersion and BET SSA. The higher performance of NiO–Fe₂O₃/MWCNT is possibly due to a combination of the MWCNT-inspired surface chemistry (as discussed in the next section) and mesoporosity of the catalyst. Generally, the data does not present general trends to depict the influence of textural properties of carbon support on the activity, stability and reaction route selectivity of the resultant catalyst. From the data, higher BET specific surface area (SSA) and greater degree of dispersion did not make Fe₂O₃/AC_{commercial} to have better catalytic activity than NiO–Fe₂O₃/MWCNT, which exhibited 5 and 3 times lower SSA and dispersion, respectively. Quick approximations would conclude that surface area and degree of dispersion of activated carbon used as a catalyst support have no effect on catalytic performance of the catalyst. The low pore volume of Fe₂O₃/AC_{commercial}, partly due to narrow pore size could partially explain the poor performance of the catalyst by despite its relatively higher surface area. Mechanistically, this occurs by access restriction of the reacting substances to active sites. The explanation for the poor performance of NiO–Fe₂O₃/AC_{walnut shell} relative to that of NiO–Fe₂O₃/MWCNT is attributable to the agglomeration of the oxide active phase, possibly resulting from loss of anchoring groups from carbon or over deposition. Therefore, the lack of trends in the data in Table 2 should not be mis-interpreted to lead to a conclusion that textural properties have no influence catalytic activity. A plausible general explanation may be existence of a complex interplay of the physico-chemical properties of both the support and the supported catalyst to determine catalytic performance, selectivity and possibly durability/stability.

Just recently, Konwar et al [7] reported that textural properties of carbon support have limited effect on the catalytic activity and stability of carbon supported Pd, Pt and Ru during hydrothermal deoxygenation of tristearin, a triglyceride model, in the presence of subcritical water [7]. The authors investigated the effect of textural and surface properties of carbon support on the activity, selectivity and durability (stability) of the metal catalysts during hydrothermal decarboxylation/decarbonylation of tristearin. They found no correlation between textural parameters and deoxygenation activity. The finding undermines the generally accepted conception that pore size and surface area govern

Table 2

Physicochemical properties of NiO-Fe₂O₃ supported on Multiwall carbon nanotubes (MWCNT), activated carbon from walnut shell (AC_{walnut shell}) and commercial activated carbon (AC_{commercial}) [74].

Catalyst	Surface area (m ² /g)	Pore Diameter nm	Pore volume (cm g ⁻³)	Dispersion (%)	Weak + medium	Strong	Weak + medium	Strong
NiO-Fe ₂ O ₃ /MWCNT	85	38	0.75	18	177.52	2914.58	–	1177.4
NiO-Fe ₂ O ₃ /AC _{walnut shell}	88	31	0.67	44	–	5651.71	–	840.72
NiO-Fe ₂ O ₃ /AC _{commercial}	433	2.5	0.39	62	–	5820.53	285.41	1572.87

diffusion, dispersion and crystallite size of the supported catalyst, which in turn influences catalytic activity and product selectivity [15]. However, in the study the pore sizes of the carbon supports were in the range of 2.7–5.24 nm (mesopores), which is significantly larger than the kinetic diameter of hydrolyzed intermediates of steric acid and glycerol. The large pore size (mesopores) is possibly behind the insignificant influence of the pore size on the catalytic performance and stability of the metal catalysts supported on carbon in the hydrothermal deoxygenation of triglycerides. Many authors have also reported similar findings in the past (prior to this publication) [12].

Contrary to the findings of Konwar et al [7], Huo [77] observed that it is harder to convert triglycerides into hydrocarbons by hydrodeoxygenation, at 350 °C and 30 bar H₂ using W₂C supported on small pore size and low acidity AC. In their study, W₂C supported on larger pore size and higher acidity carbon nanofibers (CNF), and carbon-covered alumina (CCA) exhibited better activity than W₂C/AC characterized by smaller pore size and low acidity. In the study, the W₂C supported on activated carbon yielded the highest amount of oxygenates. The authors were able to deduce that pore size had a significant influence on product selectivity.

Ruangudomsakul et al [78] studied the properties of AC (hydrophobicity and acidity) influencing catalytic performance of Ni₂P in hydrodeoxygenation of palm oil. The differential hydrophobicity of the two carbon materials was derived from the conditions under which the carbonization was conducted. The more hydrophobic was prepared under limited air supply in Waisaki kiln while the other was prepared under nitrogen in a laboratory tube furnace. The higher catalytic performance of Ni₂P/hydrophobic AC, despite lower BET specific surface area, was attributed to easy accessibility of active sites as the active phase was found outside micropores. In substance, the authors observed that: 1) For hydrophobic AC, Ni₂P was dispersed mainly on the outside micropores (Ni₂P/hydrophobic AC) while for the relatively less hydrophobic (more hydrophilic) carbon dispersion was predominately inside micropores, 2) The catalytic activity of Ni₂P/hydrophobic AC, which exhibited greater degree of dispersion of the active phase outside micropores (Ni₂P), was higher than Ni₂P/hydrophilic AC with predominantly microporous dispersion.

The low catalytic performance of (Ni₂P/hydrophilic AC), despite its Ni₂P high dispersion, is attributable to restricted intra-particle diffusion of the large reacting species due to small pore size of the support materials (microporosity). This conclusion is in sharp contradiction with that of Konwar & Mikkola [7] which suggested that textural properties of support materials have limited influence on the catalysis of the supported catalyst. It is important to note that Konwar & Mikkola [7] worked with mesoporous carbon materials (pore size 2.7–5.24 nm) while Ruangudomsakul et al [78] used microporous carbon materials. The pore size of the carbon supports used by [7] was significantly larger than the kinetic diameter of hydrolyzed intermediates of steric acid and glycerol. It is therefore logical to presume that the pore size in the study of Konwar & Mikkola [7] was within the range of optimum pore size, accounting for the seemingly limited influence of the of the carbon support pore size. Considering the two publications, it is logical to conclude that the traditionally accepted role of textural properties still holds even with deoxygenation of triglyceride reactions. It seems increase in pore size translates into higher catalytic performance, but a maximum size is reached where catalytic performance improvement

stops. The conclusion in this work is in line with the well-established fact that microporosity, being narrow, restricts reacting species entry and products exit, and are prone to blockage and active phase deposition narrowing, leading to poor catalytic performance [15,79]. It is therefore safe to state that for large molecules, micropores are detrimental to catalysis, though more work is required to establish the optimum pore size window for triglyceride deoxygenation mediation. Although the authors attributed the low activity of Ni₂P/hydrophilic AC to restricted access to the active phase dispersed inside micropores, it remains unclear why the active phase was not just as distributed outside micropores as inside to cause the same catalytic activity as the Ni₂P/hydrophobic AC.

More studies are required to establish the interplay of textural properties of carbon in relation to their role in catalytic deoxygenation of triglycerides. It can be speculated that within certain boundaries, increase in mesoporosity (as well as other textural parameters) of the carbon support results in higher catalytic performance, though a maximum point should be reached where catalytic performance improvement stops [10].

6. Effect of surface chemistry

In the mid-1970s researchers realized that support textural properties could not sufficiently account for the many catalytically relevant properties of carbon supported catalysts [15]. In the late 1980s, the long neglected importance of carbon surface chemistry begun to attract attention, following which it was analyzed in depth for its influence on catalysis. It is well documented that while carbon is inert material relative to other catalyst supports such as silica and alumina, its surface contains unsaturated vacancies at the defects and edges of the graphitic hexagonal crystallites (graphene layers which are characterized by delocalized π -electrons) [15]. More importantly, the presence of heteroatoms (mainly oxygen, nitrogen and sulfur) introduces active sites in the carbon matrix which renders the surface chemically more active. When carbon is activated, chemically or physically, the surface becomes even more active by incorporating more heteroatoms, creating more defects and increasing surface area. Since heteroatoms affect the surface chemistry of carbon surfaces, this section will include a discussion on the effect of O and N on activated carbon surfaces, emphasizing on how they cause increased durability and catalytic performance of the supported catalysts. The justification for the choosing O and N is the previous dominates activated carbon while the latter has been reported to increase durability and catalytic performance of supported catalysts.

Great interest has been focused on oxygen, possibly due to its importance in the preparation of carbon-supported catalysts. The amount and type of oxygen functionality determines the hydrophilicity, acid-base properties and active phase attachment sites, necessary for the active phase dispersion in common methods. Some of the oxygen groups on the carbon surface are acidic while others are basic or neutral [10,80]. Acidic groups include carboxylic acids and anhydrides, lactones or lactones, and phenols (Fig. 1). On the other hand, carbonyl and other oxygen containing groups can be neutral or may form basic moieties including pyrone, chromene and quinone groups (Fig. 1).

The more acidic groups reduce hydrophobicity of the carbon thus making the surface more accessible to the aqueous solution of the metal precursor during impregnation. Oxidation of the carbon increases the

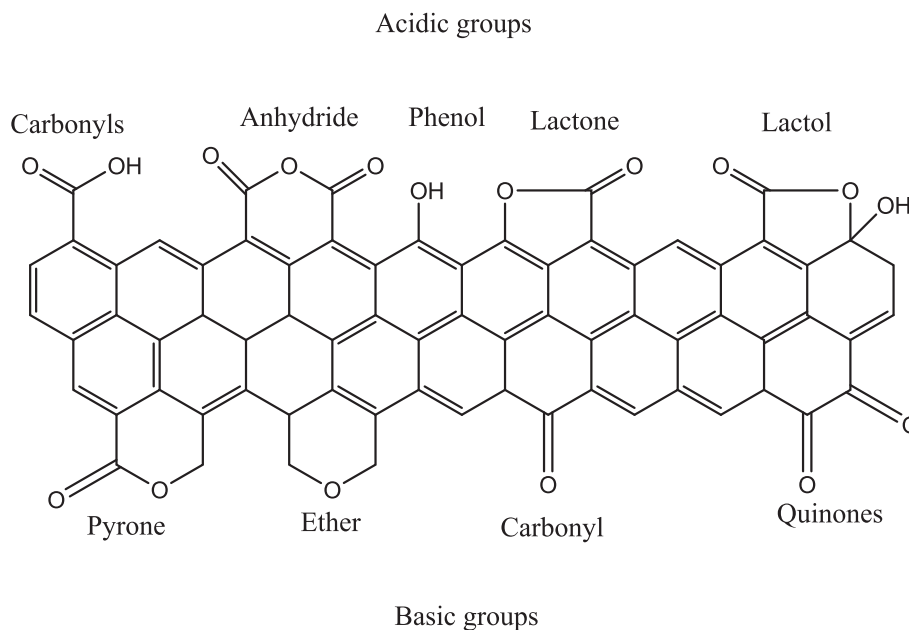


Fig. 1. Oxygen functional groups.

acidity of the carbon surface, consequently making the surface negatively charged over a wide range of pH; this in turn maximizes catalyst dispersion [10,14,81]. Unfortunately, more acidic groups have low thermal stability, hence susceptible to destruction by elevated temperatures during reduction of the catalyst precursor into active forms. Upon destruction of the acidic groups holding the catalyst precursor materials, the forming active phase coalesce to form aggregates and sinter, compromising not only the textural properties of the catalyst particles but also its dispersion [14,81]. Although acidic groups are thermally unstable, they are still important as they render the surface hydrophilic to facilitate dispersion of the precursor ions to the surface. The less acidic groups such as C=O are more stable and act as anchoring centers for the active phase to promote dispersion of the active phase, which in turn hinders agglomeration and sintering of the supported catalyst [10,13,14,80,81]. Since oxygen groups on the carbon surface have different thermal stabilities, selective removal of some of the oxygen containing groups formed can be achieved by thermal treatments at increasing temperatures, which should lead to higher basicity/hydrophobicity.

In addition to the basic functional groups, the pi electron system of the basal planes contributes to the carbon basicity. Increasing the basic C sites on the basal plane surface of oxygen-free carbon increase the electrostatic attraction with the anionic complexes [10,11,13,14,81]. The delocalized π -electrons on the condensed polyaromatic basal plane sheets act as electron-rich Lewis base sites capable of forming cation- π complexes.

Although carbon support materials offer many advantages, such as high thermal stability and resistance extreme pH levels and low cost, weak interactions between the carbon and the supported active phase renders the catalyst susceptible to aggregation, sintering and leaching. The surface oxygen groups imparted on carbon materials during activation to obtain activated carbon (AC) seem not adequately resolve the problem. Adding other heteroatoms, especially nitrogen, to the carbon matrix have shown promising results in improving not only dispersion and stability of the active phase but also catalytic activity and selectivity of the catalyst [10]. It is for this reason that N doped carbon (naturally or artificially doped) will be discussed in this section alongside oxygen.

Nitrogen atoms associated with carbon-catalyst interaction include pyridinic N, pyrrolic N, quaternary N and pyridine N-oxide. Reportedly, pyrrolic and pyridinic N play a dominant role in anchoring active sites

and enhancing their dispersion [82,83] (Fig. 2).

Studies have shown that the largest effect of N-doping on the surface of carbon materials is that it disrupts the delocalized double typical of graphene systems. N activates the neighboring carbon atoms disrupting the double bond delocalization and increasing the binding energy between carbon atoms and the supported active phase [84,85]. The high binding energy of the activated carbon atoms and the supported phase, due to the influence of the neighboring nitrogen, stabilizes leading to mitigating aggregation and leaching issues normally encountered in catalysts mounted on conventional activated carbons [86].

Mechanistically, N atoms attract electrons from their neighboring C atoms towards themselves and increase local dipole moment of N—C bond [84,86]. The magnitude of the induced dipole moment depends on the degree of doping, and renders the neighboring carbons partially positively charged (dipole moments), disrupting the double bond delocalization. The activated C atoms interact more strongly with the supported active phase (increased binding energy) than if the material is not doped with N. Fig. 3 presents a schematic diagram depicting how pyridinic N affects the surface of carbon support, activating carbon matrix and increasing binding energy between carbon and the supported phase. Fig. 4 shows the probable active sites where deoxygenation of fatty acids may occur, as speculated by the authors of this review. Fatty acids may adsorb on these regions (electron rich and electron deficient areas) lowering activation energy for some elementary steps during deoxygenation reaction. It has also been demonstrated that the activated carbon atoms, to which the supported phase attaches, attract more electrons from active phase, strengthening the bond and reducing the neutrality of the metal active phase (Fig. 3). It appears that the high electronegativity of N affects the electronic distribution in the carbon structure (graphene), not only activating the carbon atoms for firm active phase attachment but also influences the catalytic properties of the active phase. Using density functional theory, Groves et al [84] observed increased electron density in the valence band of the Pt, increase in total electron density in the bonds between the Pt and C atoms and a decrease in natural charge on the Pt, a phenomena whose magnitude decreases as N—N distance decreases. It has been suggested that graphitic N (Ng) and pyrrolic N (Nl) avoid direct interaction with Pt active phase. due to Coulomb repulsion between electron-rich Pt (single atoms or nanoparticles) and the Pz orbital of the N species, necessitating attachment on the neighbourig activated carbon atoms [114]. On the

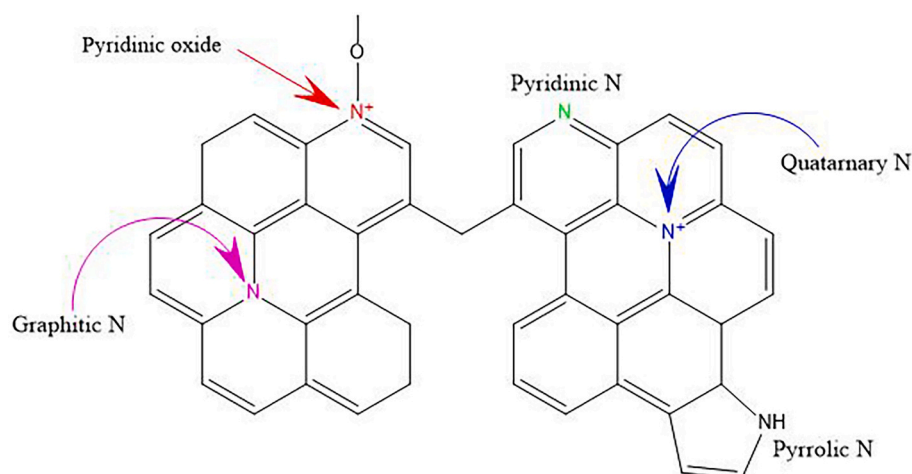


Fig. 2. Carbon/graphene showing Nitrogen functional groups commonly reported to important in catalysis.

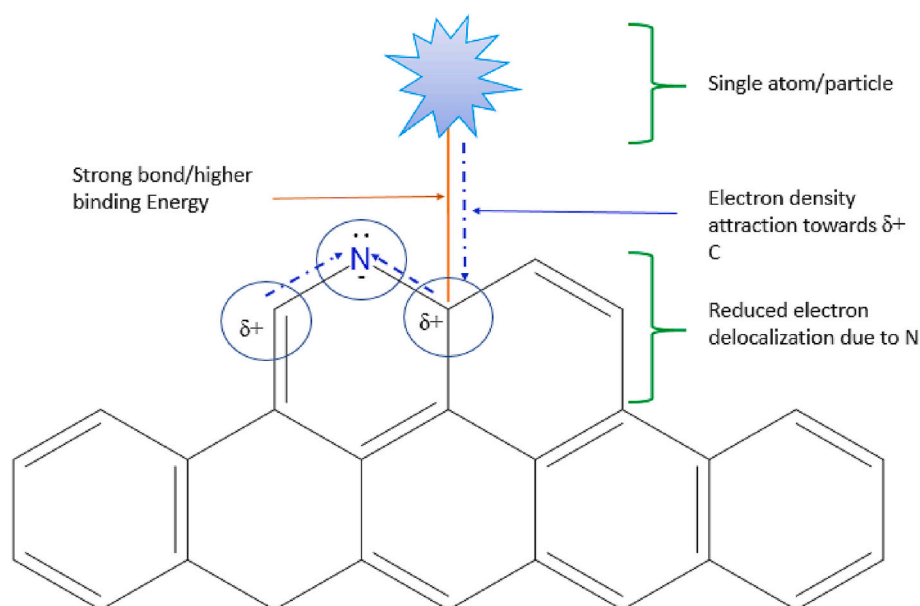


Fig. 3. Schematic diagram of carbon depicting how pyridinic N affects the surface of carbon support. The dotted lines represents the electron density pulling. M represents the supported phase (single atom or particle) [84,87]. Note that the particle can be held in position with many bonds.

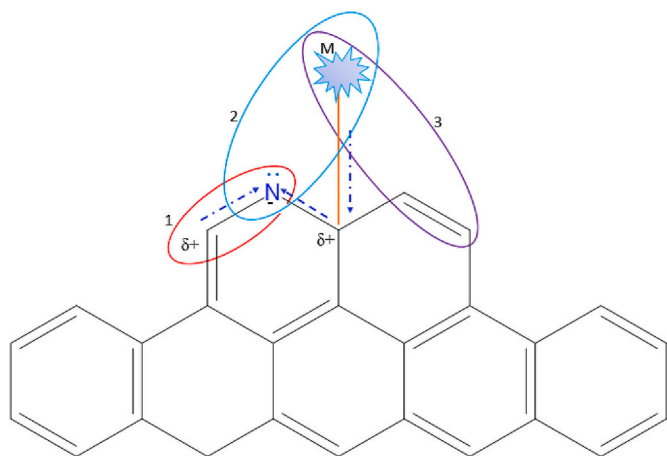


Fig. 4. N-Carbon/graphene showing speculated active sites (circled regions) where deoxygenation of fatty acids may occur.

other hand, the bonding between NPs and pyridinic N (Np) is not so restricted due to the electron withdrawing propensity of Np, possibly allowing attachment on both N and Carbon atoms.

Nitrogen incorporated in the carbon structure have been suggested to act as electron-rich sites that attracts electron deficient species. Jin et al. [87] have suggested that the N-carbon supported catalyst is altered to favor interaction with electrophilic groups such as carbonyls, thus boosting the DeCOx route over the HDO pathway during hydro-treatment of triglycerides/fatty acids. The authors view N in the carbon lattice structure as electron-rich sites that adsorbs electrophilic groups resulting in higher selectivity for DeCOx. Jiang et al. [88] also proposes that N atoms in the carbon structure alters the electronic density of the sp^2 carbon, which in turn alters the electronic distribution of the catalyst in manner that lowers the dissociation energy of H_2 hydro-treatment.

Nitrogen doping also enhances acid/base properties of carbon supports, which alters the catalytic properties of the catalyst including selectivity and durability [89]. The incorporation of nitrogen into the pyridine-like position is known to cause formation of carbon vacancy,

thereby increasing defectiveness [90,91] and is usually associated with structural disordering [82].

Apart from activating carbon, N atoms can also act as anchoring sites for the attachment of the active phase [92,93]. This complicates the understanding of the role of the heteroatom in catalysis.

Nitrogen species is formed not only on the edges of graphite sheets but also in the graphite layers where N-coordinated metals with porphyrin-type coordination, M–N₄, are dominant in single-atom catalysts [82,94].

There are several methods for incorporation of N into carbon materials. Detailed discussion of these methods fall out of the scope of this work.

From this background, it is evident that the suitability of carbon materials as catalyst support is not only determined textual properties but also surface chemistry. Several publications have reviewed the effect of surface chemistry of carbon materials on the catalytic performance of various catalysts. However, the reviews provide general and non-specific analysis of the role of surface chemistry of carbon. For instance are no reviews available focusing on the role of surface chemistry of carbon on the conversion of triglycerides into diesel-like hydrocarbon. This section focuses specifically on the influence of surface chemistry of activated carbon as support materials in the catalytic deoxygenation of triglycerides. Emphasis is on the influence of carbon support surface chemistry on the reaction catalytic activity, route selectivity and the support-catalyst stability.

Asikin-Mijan et al [74] found that different carbon support materials have distinct influence on the catalytic activity, selectivity and stability of the catalyst. The authors supported NiO catalyst on the three different carbon materials (NiO–Fe₂O₃/AC_{MWCNT}, NiO–Fe₂O₃/AC_{commercial} and NiO–Fe₂O₃/AC_{walnut shell}) exhibited distinct acid/base properties. Of the three support-catalyst combinations, only NiO–Fe₂O₃/MWCNT exhibited a noticeable number of weak + medium acid sites (177.52 mol g⁻¹), in comparison with the other catalysts, NiO–Fe₂O₃/MWCNT exhibited the highest density of both strong basic and acidic sites, though basic sites were four times higher than acid sites. The authors credited the higher selectivity for decarboxylation/decarbonylation (deCO_x) reaction exhibited by NiO–Fe₂O₃/MWCNT partially to the possession of large density of weak + medium acid sites and strong basic sites, with strong acid sites causing undesirable cracking. Both NiO–Fe₂O₃/AC_{commercial} and NiO–Fe₂O₃/AC_{walnut shell} were found to contain a larger number of strong acid sites (>5651.71–5820.53 mol g⁻¹) than NiO–Fe₂O₃/MWCNT (2914.58 mol g⁻¹), which accounts for the higher selectivity for cracking products observed on the two catalysts.

Nevertheless, the message that comes out clear is that different carbon materials exert distinct effects on the acid-base properties of catalysts, changing their catalytic behavior, just as it can be done using multiple phases/ mixed oxides [53,61,67,71,72,74,75]. Since different carbon materials exert distinct effects on the supported phase, it is therefore feasible to tailor the surface chemistry of carbon materials to be used to manipulate the catalytic behavior of the supported phase. A molecular level understanding of how acid-base properties of a catalyst are altered upon contact with activated carbon would help to design carbon-based catalysts with optimized catalytic activity. In an attempt to explain the differences in acid-base properties of NiO–Fe₂O₃ when supported on the three activated carbon materials tested (AC_{MWCNT}, AC_{commercial} and AC_{walnut shell}), the authors (Asikin-Mijan et al) [74] suggested formation of a new set of active sites whose properties depend on the type of the carbon materials. There is, however, a need for a mechanistic account of how acid-base properties of carbon support-catalyst vary with carbon. It is worth noting that acid-base properties of the carbon alone was not determined. The acid-base property would have contributed to understanding the impact of surface chemistry of carbon supports on the catalytic behavior of the catalyst-support combination.

Konwar & Mikkola [7] also studied the effect of surface chemistry of carbon support on the catalytic performance (activity, selectivity and

stability) of metal active phase in hydrothermal deoxygenation of triglycerides. The authors used commercial and in-house prepared carbon. Except for the commercial carbon which was only washed, otherwise used as purchased (contained oxygen and phosphorus functional groups, ACP_{comm}), all other carbons were synthesized from chitin flakes. The authors prepared activated carbon (containing oxygen and phosphorus, NAC) and un-activated carbon NC, both nitrogen-self-doped, to obtain acidic and basic carbon support respectively. Activated carbon without N was prepared by oxygen-doping (KOH activation) and removing nitrogen functionality by treating it with acid to obtain a neutral carbon support AC. Based on the NH₃-TPD, the carbon materials exhibited distinct acid-base properties, with the order acidity being ACP_{comm} > NAC > AC > NC, while the CO₂-basicity in a decreased order of NAC > NC > AC > ACP_{comm}. The results indicate that the surface chemistry (acid-base properties) of carbon supports strongly influence the activity, selectivity, and stability of catalysts during hydrothermal deoxygenation of triglycerides under subcritical water. Pt and Pd supported on nitrogen doped carbon, containing abundant basic surface defects (such as pyrrolic, pyridinic and quaternary N) was found to promote deoxygenation activity. The decarboxylation products increased linearly with increase in CO₂ basicity, which is in line with the work of Asikin-Mijan et al [74], but decreased with increase in NH₃ acidity (moderated Brønsted acidic phosphate sites). The presence of moderate Brønsted acid sites (phosphates) on the carbon support was detrimental to activity deoxygenation/decarboxylation activity, even when present in small quantities, causing up to 6-fold reduction in the activity. In contrast to Pt and Pd, support surface basicity caused no influence on the catalytic activity and selectivity Ru-based, with higher acidity worsening the dominant cracking and isomerization activity. From the work of Asikin-Mijan *et al* [74] and Konwar et al [7], it can be deduced that the effect of acid-base properties of carbon support on the catalytic behavior of the resultant catalyst during triglyceride deoxygenation is also dependent on the nature of the active phase, with some catalysts being impacted more than others. Theoretically, it implies that different catalysts supported on the same carbon materials may catalytically behave differently under the reaction conditions.

The presence of surface basic sites on the carbon support stabilized the metals (Ru, Pd and Pt) nanoparticles, reducing nanoparticle leaching, coking and side reactions, thereby improving catalyst stability. It was, however, observed that at temperatures >300 °C significant leaching begins, with susceptibility to leaching decreasing in the order Pd > Pt > Ru. The temperature-induced leaching was attributed to loss of various surface defects (oxygen and nitrogen) responsible for stabilizing the metal nanoparticles from the surface. Hydrothermal stability has also been reported in other reactions using water as a solvent [80].

Liu et al [95] investigated the effect of nitrogen in carbon support materials during the deoxygenation of saturated and unsaturated fatty acids under hydrogen (hydrotreatment). The introduction of N into the carbon structure was meant to increase the basicity of the carbon support. To achieve this, the authors comparatively studied the catalytic activity of Pt supported on three carbon materials; nitrogen-free mesoporous carbon (Pt/MC), nitrogen-rich mesoporous carbon (Pt/NMC) and the activated carbon (Pt/AC). NMC exhibited lower BET specific surface area (1152 m²/g vs 1473 16 m²/g), MC smaller average mesopore size (4.3 nm vs. 4.7 nm) and lower total pore volume (1.15 cm³/g vs. 2.24 cm³/g). It was observed that Pt/NMC exhibited the highest catalytic performance, with the saturated fatty acids yielding over 97% of alkanes while the unsaturated fatty acids showing yields of between 44.0% and 63.6% at 330 °C for 3 h. The turnover frequencies of Pt/NMC were estimated as 335–522 h⁻¹ in the decarboxylation of saturated acids, which were almost 3-fold higher than Pt/AC and 2-fold higher than Pt/MC. The authors attributed the outstanding performance of the Pt/NMC catalyst to N species, which provided not only anchoring sites for Pt nanoparticles, as evidenced by higher the degree of dispersion that the catalyst exhibited, but also alkaline sites onto which carboxyl group in fatty acids adsorbs in the course of reaction. The authors suggested

that the role of the basic sites in the Pt/NMC catalyst is expediting the adsorption of acidic substrates to the vicinity of metal particles where the actual decarboxylation reaction takes place. The low performance of AC-supported Pt can be attributed to microporosity nature of the support and lack of basic sites.

Wang et al [89] prepared nitrogen doped mesoporous carbon (NMC) by situ polymerization of aniline and used it to support molybdenum carbide catalyst for hydrotreatment of fatty acids. The nitrogen doping significantly improved the catalytic performance of Mo₂C/N_{1.0}MC-700, with 92.7% conversion and 86.7% selectivity for hydrocarbons, compared to 84.8% and 70.1% achieved on Mo₂C/MC. Although both Mo₂C/MC and Mo₂C/N_{1.0}MC-700 mediated the conversion of the fatty acid predominantly through hydrodeoxygenation, significant deCOx (decarboxylation and decarbonylation) was observed. The ratio of HDO to deCOx products increased with increase in the amount of nitrogen doped, indicating that the nitrogen favors hydrodeoxygenation to deCOx. It was deduced that the nitrogen doping reduced apparent activation energy, favoring hydrodeoxygenation. The authors attributed high catalytic activity and stability of Mo₂C/NMC to pyridinic N and pyrrolic N in NMC, which improved the degree of dispersion of Mo and decreased in the particle size of the catalyst. The results also indicated that saturated fatty acids and ester group are more easily convertible into hydrocarbons. The nitrogen-doped catalyst showed decent stability, with the conversion and selectivity over Mo₂C/N_{1.0}MC (thermally treated at 700 °C) decreasing only by 4.4% and 6.9% respectively, after recycling three times. The hydrotreatment conditions of oleic acid were studied, and the optimal reaction conditions were as follows: reaction temperature, 350 °C; initial H₂ pressure, 3.0 MPa; n-hexane as solvent.

Jin et al [87] developed a novel Pt-based catalyst supported on N-doped activated carbon (Pt/N-AC) prepared from polypyrrole as the nitrogen source. The catalyst was used to mediate the conversion of palm oil into bio-hydrogenated diesel (BHD) via hydrotreatment in a fixed bed reactor system. Pt/N-AC catalyst achieved a conversion rate of >90%, which was significantly higher than 76% attained over N-free catalyst Pt/AC. The N-doped carbon supported catalyst (Pt/N-AC) preferentially mediated the deoxygenation of the palm oil triglycerides through deCOx routes (76%), though some HDO products of about 7% were obtained. The authors attributed the preference for deCOx over HDO exhibited by Pt/N-AC catalyst on the N atoms in the carbon support that alters the electronic density of the catalyst to favor the interaction with electrophilic groups such as carbonyls. Deoxygenation was carried out at optimized reaction conditions: $T = 300$ °C, 30 bar of H₂, and LHSV = 1.5 h⁻¹. Additionally, the Pt/N-AC catalyst was found to be highly stable, showing no signs of deactivation via sintering or carbon deposition during the reaction in the deoxygenation reaction.

Wang et al [96] compared the ultrafine MoC nanoparticles supported on nitrogen-rich carbon (MoC/CN) with one on nitrogen free mesoporous carbon in their activity for the hydrotreatment of oleic acid. They reported that MoC/CN catalyst exhibited significantly higher activity (94.3% conversion and 90.3% selectivity at 310 °C) than those of the Mo₂C/MC (84.8% and 70.1%, respectively). The higher performance of MoC/CN was attributed to the presence of large amounts of pyrrolic N and pyridinic N in nitrogen-rich carbon, which not only provided anchoring sites for the molybdenum, leading to a uniform dispersion, but also higher catalytic activity. Based on density functional theory (DFT) calculations, the authors suggested that MoC/CN serves to expedite dissociative adsorption of hydrogen, which results in the increased activity in the hydro treatment reaction.

Jin and Choi [97] investigated the impact of oxygen surface density of carbon support on the catalytic activity of PtRe catalyst in hydrothermal deoxygenation. To achieve this, the authors used four different carbons; carbon nanotubes (CNT), oxidized carbon nanotubes (oCNT), activated carbon (AC) and oxidized activated carbon (oAC), as support materials for the catalyst (PtRe). The oxidation of the carbons was done using nitric acid. Oxygen content of the carbons increased in the order PtRe/CNT (0.8%) > PtRe/oCNT (3.3%) > PtRe/AC (10.8%) > PtRe/oAC

(16.2%). They observed that PtRe catalyst supported on carbon with low oxygen content exhibited higher deoxygenation activity than those on oxygen-rich carbons (i.e., PtRe/oAC < PtRe/AC < PtRe/oCNT < PtRe/CNT). PtRe/CNT exhibited the best deoxygenation performance, yielding 72 wt% n-paraffin using palm oil feedstock (theoretical: 79 wt %) with up to 5 times cycles of application without significant loss of activity. The authors attributed the higher catalytic activity of PtRe supported on carbon with low oxygen content to superior alloy formation and greater degree of dispersion, while oxygen-rich carbon surfaces caused segregation of Re which compromised performance [98]. The authors, therefore, suggest that high oxygen intensity/density on carbon surface, regardless of the functional groups to which they belong, is the problem behind Re segregation and the consequential poor catalytic performance. However, it is known that acidic groups on carbon have low thermal stability and when they decompose the supported phase lose anchoring centers, [99] and coalesce to form aggregates, facile leading to low catalytic activity [10,14,81,100]. Acidic functional groups on carbon surface, being negatively charged upon dissociating, can repel negatively charged reactants and intermediates, which results in low catalytic activity, while basic groups enhances adsorption and improves catalytic performance [101]. Therefore based on previous literature, it appears also valid to argue that the segregation of Re could have been caused by decomposition of the thermally unstable acidic functional groups (loss of anchoring centers) during thermal reduction of the catalyst precursors into the catalysts/active phases. Another possible explanation of the low catalytic activity exhibited by the catalysts supported on oxygen-rich carbon supports is inhibition of electron transfer between the supported active phase and the carbon structure by the negative charge on oxygen [102]. The negative charges on the carbon surface, due to acid group dissociation, may also exert its effect by hindering deposition of anionic carrier/precursor which leads to poor dispersion and hence the consequential low catalytic activity [98,101,103–107]. It is therefore critical that future work on deoxygenation of triglycerides should consider the effect of surface oxygen, type of oxygen group and electron transfer inhibition. It will be noted that oxygen rich carbon supports may also increase carbon polarity, rendering it unsuitable for reactions using nonpolar solvents. High surface oxygen group concentration of carbon supports have been reported to enhance catalytic activity and durability of supported catalysts in various reactions such as oxygen reduction, deoxygenation of pyrolysis bio-oil, Fischer–Tropsch process [108–113].

This section shows that different activated carbon materials exert distinct effects on the catalytically active phase, altering activity and selectivity. The surface chemistry of carbon/activated carbon support influences the activity, selectivity and stability of the catalyst in decarboxylation of triglycerides. It also appears that the degree of influence of the surface chemistry of AC support on the catalytic activity of the catalyst (support-catalyst system) is also dependent on the nature of the active phase, with some materials showing insignificant catalytic behavior change. The differences in the effect of carbon surface on the active phase may be partially explained in terms of the differences in the functional groups/heteroatoms they possess and the nature of the active phase. The effects include withdrawal of electrons towards itself (electronegativity or resonance), donating electrons, or promote or inhibit electron transfer between the carbon lattice and the supported phase, all of which have the potential to alter catalytic behavior of the catalyst. It is therefore important to identify the role of the functional groups on carbon and the supported phase.

The functional groups on the surface of carbon do not only serve as anchoring sites for the active phase but also act as carbon atoms activating agents potentially improving dispersion, stability and the consequential catalytic activity of the catalyst. In addition, they act as electron rich sites on which reactions can take place.

The higher electronegativity of the heteroatoms is responsible for the C activation as the functional groups pull electrons towards themselves, leaving neighbouring carbon atoms more positively charged and with

greater binding energy. For N doped carbon, pyridinic N (Np), pyrrolic N (Nl) and, to some degree, graphitic N (Ng) have been reported to activate neighboring carbon atoms resulting in improved binding energy of the activated neighboring carbon atoms. It is also established that the N-activated carbon atoms, being highly positive, have a tendency to draw electrons from the supported phase, reducing electron density on the supported phase. Except for Np, direct attachment on N is restricted. The N incorporated in the carbon lattice can also act as electron-rich sites on which electrophilic groups such as carbonyls adsorb to facilitate reaction progression and improving selectivity for DeCOx [87]. However, for oxygen doped carbon, little is known about the effect oxygen functional groups on carbon support in relation to deoxygenation of triglycerides despite the fact that oxygen is dominantly found on activated carbon surfaces. The few available studies show that the presence of high concentration oxygen functional groups is detrimental to triglyceride deoxygenation reaction despite that oxygen is more electronegative than N and has two lone pairs to donate. Since heteroatoms may behave differently depending on the functional group to which it belongs, there is a need to carry out studies aimed at understanding how various oxygen functional groups on activated carbon affect the catalytic behaviors of the active phase. The understanding of how these heteroatoms affect the carbon and the supported catalyst in relation to catalytic behavior could help in guiding rational designing of catalysts. This work also finds that there is limited literature covering the effect that heteroatoms/functional groups have on each other in relation to their effect on the catalytic properties of activated carbon-supported catalysts in triglyceride deoxygenation. Fig. 5 shows a schematic diagram of activated carbon containing various functional groups supporting various active phases and their effects on carbon and the supported phase. It is meant to depict a generalized deliberation from this review that:

1. Different carbon materials exhibit distinct effects on the catalytic behaviors of the supported catalyst
2. Differences in the nature and abundance of functional groups are responsible for the distinct effects that different activated carbon supports have on a particular active phase
3. Some functional groups can hinder the electron transfer between the carbon lattice structure and the supported catalyst, altering the catalytic performance of the catalyst
4. Some functional groups activate the parent carbon materials, affecting the adsorption of carbon and catalytic properties of the catalyst
5. The functional groups and the active phase supported on carbon may work together as an active site for a single or a series of elementary steps

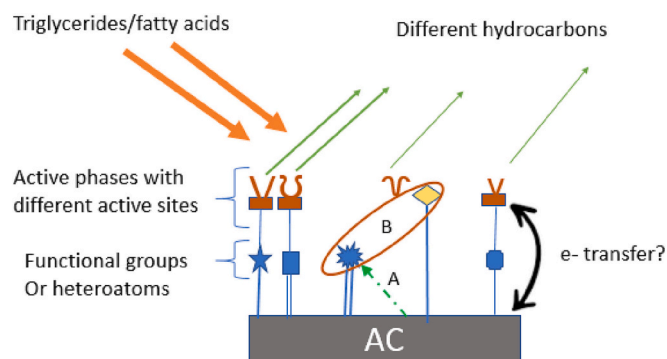


Fig. 5. A schematic diagram of activated carbon containing various functional groups supporting various active phases. The arrow labelled A shows activation of C atoms by functional group which increases the binding energy of carbon. The circle B shows that functional group/heteroatom and supported phase can together form a catalytic site.

It is further indicated in this section that in H₂ free environment, high density of 'weak + medium acid sites' and strong basic sites, a combination of high density strong acid sites and basic sites or high density of strong basic sites exhibit high selectivity for deCOx reaction. High acidic sites with limited basicity selectively favors cracking reaction that forms undesirable light weight hydrocarbons and causing catalyst deactivation due to coking. Therefore, activated carbon support should be engineered to enhance the properties in the resultant support-catalyst combination.

This review reveals that both the textural properties and surface chemistry of activated carbon support can alter catalytic properties of the supported active phase towards mediation of triglyceride deoxygenation reaction. However, the degree to which activated carbon materials influence catalytic properties (catalyst stability, activity and selectivity) varies with not only their differences in textural properties and surface chemistry but also the nature of the supported phase. It has to be emphasized that literature has a limited number of publications dedicated to the influence of textural parameters (specific surface area, pore volume, pore size and pore size distribution) and surface chemistry (various functional groups) of activated carbons in relation to catalytic deoxygenation of triglycerides for diesel-like hydrocarbons. There is a need for comparative experimental studies seeking to correlate various physicochemical features of carbon materials with their performance as catalyst support in the mediation of deoxygenation reaction of triglycerides. Despite the abundance of oxygen on activated carbon, there is still limited studies on the influence of individual oxygen functional groups on the catalytic behavior of the supported phase. It is not clear which oxygen functional groups would alter the catalytic properties of supported phase to favor deoxygenation of triglycerides/fatty acids to engineer activated carbon accordingly. The influence of oxygen functional groups on functional groups of other heteroatoms also requires some attention.

7. Recommendations for future research

Modification of the surface chemistry of a catalyst using tuned carbon support is an attractive research area with a potential to revolutionize catalysis including the mediation of the conversion of triglycerides into green diesel. Making the surface chemistry of carbon support to have high strength basic sites seems promising in tailoring supported catalysts to favor deCOx reaction. The role of different oxygen-containing groups, acidic and basic, still requires some attention.

Currently there are only a few studies that have been carried out to modify the surface chemistry, and hence the catalytic activity of a catalyst towards deoxygenation of triglycerides using tuned carbon support. Most studies have relied on the use of other metals or oxides (hybrid catalysts) to control the surface chemistry and morphology of catalysts. More work is still required to understand why some catalysts are affected by the surface chemistry of activated or heteroatom doped-carbon support while others are not. Although N and O containing functional groups are known to influence or act as anchorage sites, their electronic role in altering the catalytic performance catalysts in triglyceride deoxygenation reactions is not yet settled and requires some attention. The results should guide the synthesis of a superior activated carbon for mediating this particular reaction. The available publications lack consensus on the effect of textural parameters on the catalytic performance of carbon support materials in the catalytic deoxygenation of triglycerides and fatty acids.

8. Conclusion

This review investigated the influence of textural parameters (specific surface area, pore volume, pore size and pore size distribution) and surface chemistry of activated carbon support in deoxygenation of triglycerides into green/renewable diesel. The review maintains that the interplay between the different aspects of the textural properties and

surface chemistry of carbon (activated carbon) determines the catalytic behavior of a catalyst in the mediation a particular reaction, including deoxygenation of triglycerides. While microporosity of carbon support continues to be detrimental to large molecule catalysis, increase in mesoporosity (small and medium pores) is found to enhance deoxygenation activity. The reported limited influence of textual parameters of carbon support on the catalytic performance of carbon-based metal catalysts in deoxygenation of triglycerides requires being qualified with boundaries for proper interpretation.

On the other hand, many studies seem to agree that different carbon materials exert distinct effect on the catalytically active phase, altering its catalytic activity, selectivity and enhancing stability of triglyceride deoxygenation. During deoxygenative upgrading of triglycerides, carbon support minimizes cracking and catalyst deactivation caused coke formation. It is still not settled why N groups perform better than oxygen groups in catalyzing decarboxylation reactions despite that oxygen is even more electronegative than Nitrogen. Moreover, there is limited literature covering the effect that heteroatoms (such as N and O) have on each other in relation to their effect on the catalytic properties of activated carbon-supported catalysts in triglyceride deoxygenation. Nevertheless, the ability of activated carbon to alter the catalytic behavior of supported phase presents potential opportunity to tune activated carbon-based catalysts for a particular reaction. The unleashing of the potential however still requires deep understanding the effect of various function groups found on activated carbon.

CRedit authorship contribution statement

Wilson L. Mahene: Conceptualization, Investigation, Writing – review & editing, Writing – original draft. **Thomas Kivevele:** Supervision, Writing – review & editing. **Revocatus Machunda:** Supervision, Writing – review & editing.

Declaration of Competing Interest

None.

Data availability

Data will be made available on request.

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