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Development of Effective Composite Supports for Production of Biodiesel - A Detailed Review

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Abstract

Developing a renewable, eco-friendly and readily available fuel source that can be used in place of traditional fossil fuel is an important aspect of meeting increasing energy demands worldwide. Biodiesel has emerged as a promising option as a wide variety of waste oil sources can be utilized to manufacture this potentially useful fuel. Composites based on carbonaceous, calcareous, siliceous and mixed metal oxide spinel materials with different structures, assembly and porosity are being used for biodiesel production. Catalytically active entities such as Lewis acids or bases, lipase enzymes, metals or metal oxides are immobilized over the support material to generate heterogeneous solid catalysts. The recent advancement in heterogeneous catalysts with appropriate support materials for the production of biofuel is discussed in detail in this review.

Key words: Biodiesel, Composite Support, Heterogeneous Catalyst, Magnetically Active Supports

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1. Introduction

Biodiesel is a fuel derived from animal and plant fatty acid sources [1]. Chemically, it consists of long-chain mono alkyl esters. It provides a renewable, ecofriendly and biodegradable energy source that can be used in place of traditional fossil fuels thereby reducing the demand on non-renewable sources. Due to the prolonged increase in the world's population and hence energy requirements, biodiesel is a much-needed alternative resource of energy [2]. Biodiesel additionally provides various advantages over the conventional petro-diesel such as reduced pollutant forming on burning, high flash point and lubricity [3].

The European Union set a ten percent target for renewable energy use in transport for 2020, and raised the target to 14 percent by 2030. Taking double-counting into account, biofuels accounted for 7.1 percent of energy use in transport sector in Europe in 2018 making it a significant contributor. Importantly, the European Union agreed to a seven percent cap for food-based biofuels, which is forecast at 4.6 percent in 2019 [4].

Biodiesel production can be achieved from a large number of animal and plant fatty acid sources [5]. Feed stock can be distributed into three main categories: edible, non-edible, and waste oil. Edible feedstock comprises plants that can be used as a food source such as soy bean oil, palm oil, and olive oil. The first generation biodiesel was synthesized from edible oils and condemned due to food security resulting from competition between cultivation of crops for food or fuel preparation. Contrary to that, non-edible feedstocks are extracted from plant sources such as Pongamia and Jatropha, as well as seed sources from rapeseed, flax, hemp and apricot. Biodiesel from non-edible feedstock is preferred over edible feedstock as it does not impose direct competition with the food requirements of the world's population. Waste oils obtained from different sources such as fish, cooking oil, frying oil, and animal tallow are also commonly used to produce biodiesel [6]. The use of waste material not only makes the biodiesel cheaper and reduces competition for agricultural land but also helps reduce environmental pollution. Algal biomass is another potential candidate for biodiesel production due to high productive capacities which allows a cheaper, readily available feedstock for oil extraction [7]. However, thus far the challenge to make the process of oil extraction from algae economically viable has not been met.

Biodiesel is commonly produced from fatty acids by transesterification catalyzed by a homogeneous catalyst such as an acid, base or enzyme. Common acids include phosphoric acid, p-toluene-sulphonic acid, and sulphuric acid while common bases are potassium hydroxide, sodium

hydroxide, and sodium silicate The process converts triglycerides from the oil into alkyl esters in the presence of the catalyst and an alcohol (methanol or ethanol) and forms "glycerol" as a by-product [8]. Modern approaches include supercritical and superheated transesterification. The supercritical method involves the application of high temperature and pressure to assist conversion of the oil into biodiesel. This result in rapid formation of a high-quality product requiring low amounts of catalyst, however, at the expense of high energy consumption required to achieve high temperature and pressure making the entire process less effective.

The use of acids or bases as catalysts in the transesterification poses problems of corrosion of the reactor and engine. Moreover, a considerable amount of energy is required to remove the catalyst from the reaction mixture and saponification of free fatty acids is also a problem [9]. Therefore, to overcome these problems, functionalized heterogeneous catalysts are used for the transesterification reaction. Such heterogeneous catalyst are stable, effective, reusable and environment friendly and they improve the product purity, while producing less waste water and thus resulting in low environmental pollution. Heterogeneous catalysts include metal oxides, doped metals, mixed oxides, supported alkali metals, zeolites and minerals [10]. Enzymatic conversion of oils to biodiesel is an effective way that involves the use of lipase enzymes either as a free catalyst or functionalized over a support surface [11]. In spite of its effectiveness for catalyzing various feedstocks with larger free fatty acid ratios, the large manufacturing price of enzymes renders it difficult to use on an industrial scale.

A support material is a substance that is used to functionalize a catalytically active entity at its surface to perform the function of catalysis. It provides the larger concentration of reactant-catalyst contact sites compared to traditional heterogeneous catalysts, while maintaining the advantage of easy removal from the reaction mixture. The corrosive effects of pure acids or bases can be mitigated by the use of a support material [12]. A number of different support materials produced from different sources have been investigated. Waste biomass derived supports such as biochar, carbonaceous, calcium-based and mineral-based supports have been used effectively. Porous materials such as silica, alumina or carbon-based nanoparticles and different composites is another class of suitable supports [13]. Magnetically active specifically designed support materials are also being tested as their magnetic property allows the efficient removal and recycling of the catalyst. Amongst the waste derived supports, biochar is derived from plant wastes such husks and calcium-based supports are derived from sea animal shells, eggshell, waste marine barnacles or calcareous rocks [14]. Furthermore, different minerals which are porous in nature have been used as support material. These include dolomite, kaolinite, calcite and bauxite.

A support material that is made of two or more characteristically different components is referred to as a composite support material. A number of composite supports have been extensively investigated to evaluate their efficiency and feasibility. Carbonaceous composite supports include single walled carbon nanotubes (SWCNT), carbon nanohorns (CNHs) and multiwalled carbon nanotubes (MWNT), activated carbon and doped carbon-based composites [15]. Composite siliceous supports can be produced from meso, micro and nano-porous silica combined with metals, metal oxides and other inorganic materials. A very small number of calcareous composites have been reported to be used as support because mainly this class when used in pure form as CaO produced from calcination display considerably good catalytic properties [16]. A few studies evaluated the use of composite material membranes that have functionalized surfaces and are being used as heterogeneous catalysts. Simple metal composites are also being used as support for the catalyst for efficient production of biodiesel [17].

The research into fabrication of effective composite supports for biodiesel production is a relatively new field that has increased significantly over the past five years based on a search in the database Web-of-Science. In 2018 a review paper was published in the journal Catalyst which focused on biochar-based catalysts including composite supports [18]. This present review will give detailed description of a range of different types of composite supports and will also provide an overview of the effectiveness of these supports for biodiesel production.

2. Methods for Development of Composite Supports

Composite support materials can be synthesized by various methods. Table 1 gives an overview of the most common methods for their synthesis. The method of formation affects the size, structure, assembly and arrangement of molecules in the composite. Most composites are meso-porous or nano-porous and can be produced using co-precipitation, sol-gel and impregnation methods. The co-precipitation method is the most common and conventional method for the synthesis of nano-porous materials, in which reactants are co-precipitated in an inert solvent at relatively high temperature. Micro-emulsion is another promising method for nanocomposite support formation in which an aqueous system of surfactant and co-surfactant agents, are dispersed with fine oil droplets of 50 to 500 nm size range. Core shell structured composites have an inner core of a metal oxide over which an organic or inorganic layer is synthesized. Most core shelled composites are magnetically active such as ferromagnetic, for example, superparamagnetic iron oxide cores are common.

Table 1. Common methods for the preparation of composite supports

Method	Examples	References
Solvothermal	SiO_2-Fe_3O_4,	[19-20]
Co-precipitation	Hydroxyapatite -γ-Fe_2O_3 and MgO-ZrO_2	[21]
Mini-emulsion	PEGylated poly(urea-urethane)nanoparticles	[22]
Chemical Synthesis	Ca/Al/Fe_3O_4	[19]
Sol-gel Method	GPTMS functionalized SiO_2-Fe_3O_4	[23]
Impregnation	KF/CaO-Fe_3O_4 and diatomite/CaO-MgO	[24-25]

There is a variety of composite supports as outlined in Section 1. The relative number of reported studies for different types is shown in Fig. 1. The following sections of this review will describe these different types in detail.

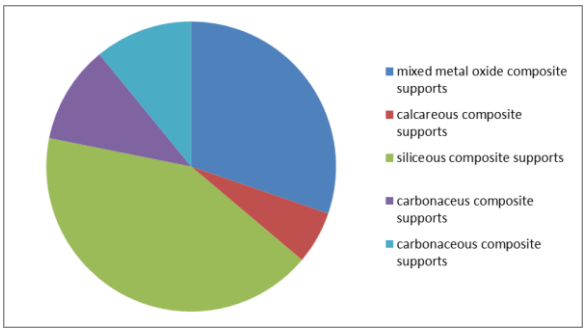

Fig.1 Ratio of composite supports reported in last 10 years

3. Carbon-Based Composite Supports

Carbon has proven to be an excellent contender as a heterogeneous catalyst or catalyst support. The chemical properties of electron conductivity and inertness makes it a reliable candidate in chemical and especially catalytic processes. Carbon derived from cheap environmental sources (e.g. tea waste), when used as a catalyst or catalytic support, makes the product cost effective. Moreover, it plays an important role in combating the increasing environmental pollution. When functionalized with catalytically active entities such as acidic or basic group containing moieties, metals, enzymes etc., carbon gives efficient, stable and remarkably reusable catalysts, which not only lower the price of biodiesel synthesis on an industrial scale but also improves the quality of the product. This is a major reason that much research is ongoing to invent better carbon-based heterogeneous catalysts or catalytic supports. A brief synopsis of the carbonaceous composite supports that have been used is given below. An overview of some key studies, are given in Table 2A.

3.1 Nano Structured Carbon Composite Supports

Nano-structured carbon materials such SWCNT, CNHs, MWNT and graphene have been frequently used as support materials to synthesize heterogenous catalysts. Carbon provides the benefit due to its inert nature and when in nanoparticle form, it gives large surface area, more efficient active sites for catalysis as well as better stability [26]. Nano-carbon supports can be functionalized with simple effective acidic or basic entities or these are combined with magnetically active metals. Magnetic removal of the catalyst simplifies the catalyst removal process and wastewater generation. A comparison between CaO dispersed CNHs and calcium ferrite supported over CNH was reported. Due to hybridization of basic sites of calcium ferrite with hydrophobic CNHs, the catalyst showed enhanced activity compared to the CaO-based catalyst. The hydrophilic glycerol produced is discarded due to the hydrophobic nature of the support. As a result, the active sites are available for the reactants to approach resulting in 97.1% yield of biodiesel [27].

Single walled carbon nano-horn (SWCNH) were sulfonated and mixed with iron nanoparticles Fe_2O_3 to produce a composite support for iron-based heterogeneous catalysis for the production of biodiesel from tributyrin which yielded a methyl-butyrate product. This study revealed that the use of magnetically active support attracted the reactants towards it so that the free fatty acids did not cause poisoning of the catalytic sites and did not affect the biodiesel yield [27].

3.2 Graphene Oxide (GO)-Based Composites

Because of its high surface area (up to 2600m^2/g), excellent adsorbing quality due to p-p interactions and high carrier mobility, graphene is good catalyst support. Metal oxide supported sulphonated carbon-based materials have proven to be more efficient, stable and readily available solid acid catalyst as opposed to conventional acid supported catalysts because of the presence of both Lewis and Brønsted acid sites. Due to low surface area and acidic leaching, some early carbonaceous acid catalysts were rejected. This lead to the development of novel sulphonated solid composite support such as graphene oxide with Fe_2O_3 (GO Fe_2O_3@SO_3H) which is magnetically active. This catalyst was used in the transesterification of oleic acid from waste cooking oil along with ethanol. The GO Fe_2O_3@SO_3H catalyst showed high catalytic activity as well as recyclability due to its magnetic properties. This support was found to be better than GO, GO-SO_3H and GO-Fe_2O_3. The maximum yield of biodiesel was obtained in 4 hours, at 100°C using 5 % by wt. of the catalyst. A single step conversion of waste cooking oil (WCO) to biodiesel could be achieved at 90°C in 6 h using 5wt % of the catalyst. The catalyst was recovered by applying external magnetic field and was able to be reused for 7 cycles [28].

3.2.1 Enzyme Modified Graphene Oxide Composites

Another solid GO-based catalyst involved functionalized GO with lipase enzyme immobilized on its surface to perform the catalytic activity. This nano-biocatalyst has a magnetically active iron oxide core that

makes it recyclable and it can be used in up to 5 consecutive cycles after applying a simple washing procedure at the end of use. The enzymes were immobilized by covalent crosslinks over the composite support in the form of aggregates (CLEAs-lip). GO provides a good coating material both for magnetic nano-particles and to functionalize the lipase enzyme due to reactive functional groups and high surface activity. A good biodiesel yield of 78% was achieved in 24 hours [29].

Another magnetically recyclable GO support is reported in which lipase from *Candida Rugosa* was immobilized over magnetic Fe_3O_4 nanoparticles encapsulated GO. The biodiesel was synthesized at 40°C by three step addition of methanol in a shaking water bath. Approximately, 92.8% conversion of soybean oil was obtained through transesterification. A recyclability of 5 times without considerable loss of activity was achieved by applying an external field [30].

3.3 Metal Doped Carbon Composite Supports

Metal doped carbonaceous catalysts have been used efficiently for biodiesel production e.g., iron doped activated carbon showed 96.3% conversion of rubber seed oil to biodiesel with minimal loss (0.8–1.2%) in catalytic activity after three cycles. The electron availability of the transition metal and high surface area of the activated carbon are the reasons for high catalytic activity shown by such types of catalysts. The catalyst without metal ions present showed a decreased % age yield even at high temperature of 100ºC in 6 hours reaction time [31]. A mixture of oxides of different metals including Ca, Mg, Fe, Al and K derived from waste slag was used as a heterogeneous basic catalyst. The results showed that much resistance resulted in lowering of active site accessibility and caused a low rate of reaction [32].

3.4 Metal Organic Frameworks

Another proposed structure to be used as a support is a metal organic framework over which any catalyzing entity could in theory be immobilized. A few such nano-porous carbonaceous supports have been investigated. Zhang et al. has reported a lipase immobilized support, which has a carbonized aluminum support. It proved to be an excellent catalyst as it gave 100% biodiesel yield with a recyclability of several times. The catalytic activity, however, was diminished to yield only 20% of biodiesel by the 9^{th} cycle. The pore morphology played a role in the high biodiesel yield as a result of the high surface area.

4. Calcareous Composite Supports

Calcium-based composites may be synthetic or naturally derived. Waste materials including eggshells, and marine-based structures such as shells and barnacles are rich sources of calcium carbonate ($CaCO_3$) which upon calcination is converted into CaO. This provides a cost effective, readily available support material. CaO can also be obtained from mineral sources such as dolomite. Table 2B detail a selection of studies.

CaO is not only a good basic catalyst for transesterification reactions but can also be used as a support material when combined with other metal oxides. A CaO/MgO composite was used as support material with diatom skeletons attached for the biodiesel production from waste cooking oil. This assembly provided a considerable opportunity for the synthesis of biodiesel at an industrial level using a novel, cost effective and easily available heterogenous catalyst. The Diatomite@CaO/MgO catalyst gave 96% oil conversion in 120 min at 90°C using 6 wt% catalyst and 1:15 oil:methanol ratio. The catalyst was also recyclable several times [25].

Hydroxyapatite-encapsulated γ-Fe_2O_3 nanoparticles served as another novel calcium-containing composite support over which bigunide was covalently attached to perform the function of a catalyst. The heterogenous catalyst was magnetically active and recyclable. It was used in the transesterification of soybean oil with methanol. A better catalytic activity was reported with 99.6% biodiesel yield in 3 hours reaction time and a methanol:oil molar ratio of 25:1 and a catalyst loading of 3 wt%. Simple magnetic separation of the catalyst as well as efficient recyclability of 5 consecutive cycles was also reported. Another calcium oxide and iron oxide composite (CaO/Fe_3O_4) was used as support for a potassium fluoride (KF) catalyst. The ferromagnetic catalyst could easily be recovered by application of an external magnetic field. Its characterization was done by vibrating sample magnetometer (VSM) to evaluate the magnetic susceptibility of this composite support. The porous catalyst produced a good biodiesel yield of 95% at optimal conditions [24].

Carbonated alumina doped by calcium oxide has also been studied for the transesterification reaction. The catalyst was synthesized by a microwave combustion method and used to convert canola oil to biodiesel. Almost 98.8% yield was obtained without loss in catalytic activity [33].

5. Silica-Based Composite Supports

Silica has been shown to be a versatile support material which can be produced in different particle sizes. These can be used with other materials to form a novel, efficient and cost effective composites support. Much research has reported silica-based composites used as support materials. Table 2C outlines some key studies for this group of composite supports. Magnetically active Fe_3O_4 composites with silica was functionalized with Ca to produce a nanocatalyst for biodiesel production; $Ca/Fe_3O_4@SiO_2$. The highest oil conversion was obtained at 15 to 1 methanol to oil ratio, at a temperature of 65°C after constant mechanical stirring for 5 hours. The characterization revealed that a more basic catalyst improved the biodiesel production and that the catalyst was

magnetically active and could be recycled for several times without appreciable loss in activity [34].

Another study reported calcium sulphate functionalized core shell nano-structures incorporated into mesoporous silica nanoparticles; $CaSO_4/Fe_2O_3$-SiO_2. The controllable nature of size, shape and surface properties allowed gauging the physical and chemical properties of the nanocatalyst. The catalysts showed a good yield of biodiesel of more than 94%. The magnetic properties of the core shell particles made the catalyst easily recoverable by simply applying an external magnetic field, which improved its reusability for several cycles (up to 9) without showing a diminished catalytic activity. The morphology, porosity and conjugated structure of the $CaSO_4/Fe_2O_3$-SiO_2 catalyst were evaluated systematically [20].

A series of magnetic $CsH_2PW_{12}O_{40}/Fe–SiO_2$ nano-catalysts were prepared via a combination of the sol–gel and impregnation methods. The effects of different $H_3PW_{12}O_{40}/(Fe–SiO_2)$ weight percentage, loading of Cesium (Cs) as a promoter and calcination conditions on the catalytic performance was studied. It was found that the catalyst with $H_3PW_{12}O_{40}/Fe–SiO_2$ = 4 wt.% and Cs = 2 wt.% was an optimal catalyst for biodiesel production. The activity of this catalyst was studied in different operational conditions and the best conditions were CH_3OH/oil = 12/1 at 60°C with mechanical stirring rate of 500 rpm. This resulted in a biodiesel yield of 81% in 4 hours [35].

A mesoporous silica-based iron oxide core-shell structure, Fe_3O_4/MCM-41, was prepared and functionalized with sodium silicate such that no structural damage to the magnetic support occurred. Epichlorohydrin was used as cross-linking agent to attach a basic catalyst on the magnetic composite support. This catalyst was shown to be efficient, stable and easily recyclable 5 times with oil conversion reaching up to 99.2% by using the methanol:oil molar ratio of 25:1 and a catalyst loading of 3 wt% at reflux of methanol over 8 hours of reaction [36].

A number of silica composites have been shown to be excellent substrates for immobilization of lipase with the use of a cross-linking [37]. Studies have compared the use of the immobilized enzyme to a free enzyme in solution used as the catalyst and results has shown a far better biodiesel production when using immobilized enzyme. A magnetically active mesoporous silica and iron oxide composite was reported to give 91% biodiesel yield at mediated reaction conditions. The analysis was made using response surface methodology (RSM) to predict the maximum FAME (fatty acid methyl esters) contents at the optimum condition. Moreover, the immobilized lipase could be used four times without considerable loss of the activity.

Minerals are a good source for production of composites. They can be coated with nano-porous and mesoporous silica to synthesize composite supports for heterogeneous catalysts. Enzyme immobilized silica coated magnetite was used as a novel biocatalyst for biodiesel production. A number of cross-linking agents can be used to attach the enzyme to the surface off the support, for example gluteraldehyde and aminosilane [38]. Synthesis of an enzyme immobilized ($Fe_3O_4@SiO_2$) catalyst in which (3-glycidoxypropyl)trimethoxylsilane (GPTMS) was functionalized to provide a matrix for the enzyme. Close to 100% conversion was obtained at optimum reaction conditions [23]. A superparamagnetic iron oxide core-shell silica support functionalized with aldehyde groups was manufactured by Karimi et al.. A 91% biodiesel yield was obtained when using waste cooking oil as feedstock at reaction conditions of methanol:oil molar ratio of 6:1, immobilized lipase concentration of 25 wt%, *n*-hexane content of 10 wt%, water content of 10 wt%, reaction temperature of 35°C, and reaction time of 35 hours [39]. Two more research studies reported aminosilane functionalized superparamagnetic iron oxide cored silica nanoparticles which were then immobilized with lipase enzyme. Both nanocomposites were prepared by co-precipitation method [39].

Both organic and inorganic catalytic entities can be attached to a support surface. Heteropolyacids was attach to magnetic nanoparticles to catalyse the transesterification palmitic acid which gave 90.4% oil conversion in 2 hours. The hybrid support had a central core of iron oxide over which a silica shell was formed to attach an amino-silane and to this, the heteropolyacids on the surface. The magnetic susceptibility allowed easy catalyst separation as well as recycling for 5 cycles [40]. Another Core–shell Fe_3O_4@silica magnetic nano-particle composite functionalized with triazabicyclodecene (TBD), was evaluated for is catalytic effect for the production of biodiesel from algal feedstock. An appreciable yield of 97.1% was obtained at optimum reaction conditions [40]. The silane agents 3-aminopropyltriethoxysilane (APTES) and 3-mercaptopropyltrimethoxysilane (MPTMS) were used as immobilization matrix. A Fe_3O_4 core with a silica shell was treated with dimethyl octadecyl [3-(trimethoxysilyl) propyl] ammonium chloride as an immobilization supporter. The *Burkholderia* lipase was immobilized to the synthesized nanoparticles to be used for production of biodiesel [41].

A novel magnetically separable nanocatalyst was fabricated by covalent bonding of 3-sulfopropyl-1-(3-propyltrimethoxysilane) imidazolium hydrogen sulfate ($[SO_3H$-PIM-TMSP$]HSO_4$) on mesoporous silica modified Fe_3O_4 nanoparticle. Approximately, 93.5% of oleic acid from different feed stock was converted into the final product even at mild reaction conditions such as 373 K reaction temperature and a reaction time of 4 hours. The magnetically active catalyst showed a high specific surface area, mesoporous channel and good catalytic activity [42].

6. Composite Membranes Used as Supports

A recent trend investigates the use of a composite catalytic membrane that acts as a support material for the attachment of a catalyst on its surface. A phosphotungstic acid (PWA)/poly(vinyl alcohol) (PVA) membrane was manufactured via electrospining on a substrate of non-woven fabric. The nano-fibrous PWA/PVA membrane had fiber diameters of 157 nm as characterized by SEM. Further evaluation using DSC and TGA showed good thermal stability for 10 days in the rage of 30°C to 600°C at a heating rate of 10°C/min and indicated interaction between PWA and PVA. The stability test of the nano-fiber membrane suggested that the conversion could remain stable for 10 days in a continuous flow-through reactor for biodiesel production [43].

A number of different GO/chitosan composite membranes have been evaluated for their ability to perform the function of support for catalyst in biodiesel production. A study reported esterification of acetic acid and pre-esterification of palmitic acid in the presence of alcohol. The reaction and separation could be carried out either simultaneously or separately. The outcome determining parameters were found to be methanol to oil ratio, temperature and the amount of embedded graphene oxide as these directly affect the kinetics of the reaction [44].

Membrane-immobilized enzymes have received increasing attention in a variety of fields such as biosensors, enzymatic reactors and membrane bioreactors. In one study, *Candida rugosa* lipase (CRL) was covalently immobilized on a nanocomposite membrane. Initially, the Fe_3O_4@SiO_2 nano-particles were dip-coated onto the ultrafiltration membrane surface through a low temperature hydrothermal (LTH) process, and then reacted with APTES. Glutaraldehyde was used as a coupling agent to covalently immobilize lipase on the nanocomposite membrane surface. The results showed that the immobilization process was successful in terms of enzyme activity and immobilization efficiency. It was found that the activated nanocomposite membrane greatly improved the relative activity and loading capacity in comparison to the unmodified membrane. An investigation of the kinetic parameters of the enzymatic reaction showed a decrease of K_m and v_{max} values due to the immobilization process, which represents an increasing in substrate affinity and decrease in catalytic activity of the immobilized enzyme. The higher thermal stability, long term storage and operational stability of immobilized enzyme make it a suitable candidate for bio-catalytic processes.

7. Mixed Metal Oxide Composites Used as Supports

Mixed metal oxides in composites have been used as support materials. Key examples of such composites are shown in Table 2D. One example is a study by Zhang et al. evaluating CaO/$ZnFe_2O_4$, CaO/$MnFe_2O_4$ and CaO/$CoFe_2O_4$. Although all of them proved to be good catalysts to carry out the transesterification reaction with soybean oil and alcohol, a comparison was made to evaluate the catalytic performance. It was found that CaO/$CoFe_2O_4$ had the best catalytic performance and this was attributed to its high wettability that resulted in good contact between the catalyst and the reactants [45].

In another paper by Zhang et al., ($MgFe_2O_4$@CaO) was fabricated by an alkali precipitation method and was utilized for biodiesel production from soybean oil and methanol. The catalytic efficiency was compared to a pure CaO catalyst. A good percentage yield of 98% was obtained with catalyst recyclability of 5 cycles. Optimal reaction conditions were a catalyst dosage 1.0 wt.%, methanol:soybean oil ratio of 12:1, reaction temperature of 70°C, and a reaction time of 3 hours. The $MgFe_2O_4$@CaO catalyst showed the higher activity, higher acid-resistance and the better water resistance compared with pure CaO [45].

An example of a metallic composite support based on tungsten supported TiO_2/SiO_2 as the mixed metal oxide was synthesized by the sol-gel method. It showed 98% fatty acid conversion at 65°C, 30:1 methanol to oil molar ratio and 5 wt% of catalyst loading in 4 hours and the catalyst was recyclable for 5 consecutive runs. Another metallic composite support with a mixed metal oxide (Mn@MgO-ZrO_2) provided 96.4% of biodiesel yield at 90°C, a catalyst loading of 3wt%, a methanol:oil ratio of 15:1 and reaction duration of 4 hours [21]. A MgO/$MgAl_2O_4$ mixed metal oxide composite was synthesized by a combustion method and used to prepare biodiesel at reaction conditions of 110°C, an alcohol:oil molar ratio of 12, a catalyst-to-feed concentration of 3 wt. % and a reaction time of 3 hours. The nanocatalyst showed a good percentage yield and a recyclability up to 6 cycles [46].

La doped $ZnAl_2O_4$ with spinel structure was used for the transesterification of soybean oil. The catalyst showed a good catalytic activity with 95% yield at 160°C, 2.0 MPa and 0.9 per hour. The characterization showed that the number of catalytic sites increased with the La content and reached a maximum at 18.5 wt% [47].

A study reported a magnetically active iron oxide zeolite composite, ZSM-5-Fe_3O_4, over which potassium hydroxide was supported to produce a mesoporous nano-crystalline solid base catalyst for the transesterification of canola oil. The nano structure provided high surface area, which enhanced physical contact to provide an oil conversion of 93.6% at optimum reaction conditions of 65°C, 3.3 hours reaction time, a molar ratio of alcohol to oil of 12 and 9% catalyst loading. The catalyst was removed after completion of the process by an external magnetic field and reused for five successive cycles [48].

Bauxite is an aluminium mineral containing oxides of iron. It was used in a composite with silver nanoparticles and used for the transesterification of sunflower oil with methanol. The highest oil conversion of 94% was obtained

at optimal conditions of 67°C, 9:1 alcohol:oil ratio, 0.3 wt% catalyst loading in a reaction time of 3 hours without the loss of catalytic activity for 7 consecutive cycles. The catalytic potential of this heterogeneous nanocomposite was studied through various characterization techniques including XRD, SEM, EDX, FT-IR and TG-DTA. The reaction conditions were optimized by central composite design of response surface methodology [49].

Chemically synthesized Fe_3O_4 nanoparticles were loaded with calcium aluminate to fabricate a heterogenous magnetic composite catalyst for biodiesel production. The catalyst was of good quality giving 98% oil conversion without the loss of catalytic activity after 5 cycles at reaction conditions of 600°C in 6 hours. The catalyst was also compared with the simple calcium aluminate catalyst and appeared to be more efficient [19].

The composite of iron, aluminum and titanium was functionalized with sulphate ions to prepare a new magnetic catalyst for the production of biodiesel from waste cooking oil. The catalyst was manufactured by functionalizing rutile/anatase mixed phase TiO_2 nanoparticles with alumina as a buffer layer. The Brønsted acid SO_4^{2-} was immobilized to impart catalytic entities. The catalyst achieved 96% fatty acid methyl ester (FAME) yield from waste cooking oil (WCO) after 2.5 hours of reaction at 90°C, using 3wt % of the catalyst, and a methanol:oil molar ratio of 10:1. The SO_4/Fe-Al-TiO_2 catalyst was also effective for feedstock containing up to 20wt% of free fatty acid and showed excellent stability for WCO (trans) esterification over 10 recycles [50].

Table 2: Summary of types of composite supports for biodiesel production as well as their efficiency

Feedstock	Composite support	Functionalized catalyst	Reaction time (h)	Methanol/ oil ratio	Reaction temp (°C)	Yield (%)	Recyclability	Characterization	Ref
Part A: Carbonaceous Composite Supports									
Tributyrin	Fe_2O_3-SWCNH	SO_3H-Fe	3-7	20:1	60	90	Several times	XRD, TEM, N_2 sorption	[27]
Oleic Acid	Fe_2O_3-GO	SO_3H	4	12:1	100	100	7	AFM, XPS, TGA, FTIR	[28]
R. communis oil	GO-CLEA's	Lipase	3	10:1	65	78	5	SEM, FTIR	[29]
Soybean Oil	Fe_2O_3-GO	Lipase	0.25		40	93	5	SEM, XRD, FTIR, XPS, VSM	[30]
Part B: Calcium-Based Composite Supports									
Stillingia Oil	CaO–Fe_3O_4	KF	3	12:1	65	95	Several times	TEM, TGA, FTIR	[24]
WCO	CaO/MgO	Diatomite	2	15:1	90	96	Several times	XRD, SEM, FTIR	[25]
Soybean Oil	HAp-γ-Fe_2O_3	Biguanide	3	25:1	-	99.6	5	TEM, EDX, XRD, VSM	[51]
Canola Oil	$Ca_{12}Al_{14}O_{33}$	KOH	0.5	15:1	-	98.8	3	EDX, FTIR, FESEM, TGA/DSC	[52]
Part C: Siliceous-Based Composite Supports									
Oleic Acid	Fe_3O_4@SiO_2	Ca	5	15:1	65	97	Several Times	XRD, VSM, SEM, TEM	[34]
Sunflower Oil	Fe–SiO_2	$CsH_2PW_{12}O_{40}$	4	12:1	60	81	Several Times	VSM, XRD, DSC, TGA	[35]
Jatropha Curcas	Fe_3O_4@SiO_2	$CaSO_4$	7	-	110	94	9	TG/DTA, FTIR	[20]
Soy Bean Oil	Fe_3O_4/MCM-41	Na_2SiO_3	8	25:1		99.2	5	FTIR, VSM	[36]
WCO	SiO_2/Fe_3O_4	Lipase Enzyme	6	6:1	35	91	4	TEM	[39]
Soybean Oil	Silica-Coated Magnetite	Lipase Enzyme	-	6:1	40	-	5	SEM, TEM, XRD, FTIR	[38]
Oleic Acid	SiO_2/Fe_3O_4	Hetero-polyacids	2	-	-	90	5	DRIFTS, PXRD	[40]
Algal	Fe_3O_4@SiO_2	Triazabicyclo-	-	-	-	97	Several	-	[52]

Feedstock	Composite support	Functiona-lized catalyst	Reac-tion time (h)	Methanol/ oil ratio	Reaction temp (°C)	Yield (%)	Recycla-bility	Charac-terization	Ref
Biomass		decene					Times		
Soybean Oil	Fe_3O_4@SiO_2	GPTMS attached Lipase	24	3:1		100	6	XRD, TEM, SEM	[23]
WCO	Fe_3O_4@SiO_2	Lipase	-	-		91	Several Times	XRD, SEM, TEM	[37]
Part D: Mixed Metal Oxide-Based Composite Supports									
Soybean Oil	$MgFe_2O_4$	CaO	3	3:1	70	98	5	SEM,VSM, TEM, XRD	[45]
Triglyceride Source	TiO_2/SiO_2	W	4	30:1	65	98	4	FESEM,TEM, XPS	[53]
P. dactylophera oil	MgO ZrO_2	Mn	3	15:1	142	96	-	SEM,TEM, VSM	[54]
Soybean Oil	$MgAl_2O_4$	MgO	3	12:1	110	95	6	FESEM, EDX, TGA	[46]
Soybean Oil	$ZnAl_2O_4$	La	0.9	-	160	95	-	CO_2-IR, N_2 ad/de-sorption, XRD	[55]
Soybean Oil	$CoFe_2O_4$	CaO	5	15:1	70	-	Several times	XRD, TGA	[45]
Canola Oil	ZSM-5-Fe_3O_4	KOH	3.3	12:3	65	94	5	FESEM, XRD, VSM	[48]
Sunflower Oil	Bauxite	Ag	3	9:1	67	94	7	SEM, TEM, XRD, EDX	[49]
WCO	Fe/Al/TiO_2	SO_4	2.5	10:1	90	-	10	FTIR, XRD, SEM, EDX	[50]

Conclusions

A vast variety of composite supports have been synthesized and been shown to be suitable, efficient, stable and reusable heterogenous acid, base or enzymatic catalysts for biodiesel production. Until now, composites based on carbonaceous, siliceous, calcareous and mixed metal oxide materials are widely used as heterogenous catalyst supports. The most frequently type of structure of these supports are core shell magnetically active composites, which have enhanced reusability due to the ease of recovery of the catalyst simply by applying an external magnetic field. Reaction conditions such as the reaction time, temperature and catalyst loading can be selected according to the catalyst chosen. Nano-porous composites are generally found to be more effective due to their large surface area, better reactant binding ability and more available catalytic sites for the transesterification reaction. Moreover, the collected catalyst can be used for many cycles. GO Fe_2O_3 nanoparticle composites functionalized with sulphonate groups provided the best results as compared to simple GO, GO-SO_3H and GO-Fe_2O_3 giving 100% oil conversion in less than 4 hours and a recyclability of 7 consecutive cycles. Lipase immobilized GO also showed appreciable biodiesel yield (92.8%) in just 15 minutes at 6000 rpm and 40°C. Another catalyst having carbonated alumina doped with calcium oxide provided so far the best results with 98.8% yield in 30 minutes but the recyclability was greatly reduced after the 3rd cycle. Very few calcium-based composites have been reported thus far. The KF functionalized CaO/Fe_3O_4 gave a good yield at relatively lower temperature. Waste biomass derived calcium oxide in composites with other common metal oxides can provide efficient and economical support materials. Magnetically active siliceous composites are the most frequently used composites with maximum recyclability and highest biodiesel yields at moderate conditions. The silica and iron oxide composites are equally suitable for functionalization with lipase and basic metal oxides for catalysis. Although such lipase immobilized catalysts gave better yield (almost 100%), a long reaction time (24 hours) and the expense of isolating the enzyme and immobilizing it on support results in an economical compromise. On the other hand, simple basic catalytic entities have no such restrictions and take much less time (i.e. 3 to 4 hours) providing above 90% yield. The use of composite membranes as support is a new concept, which not only takes part in catalysis but also aids in separation of the biodiesel at the end of the process as the membranes are porous in nature. Metal spinels are another common and efficient support for the synthesis of basic heterogenous catalysts for biodiesel production. Many of these materials are functionalized with metals such as Mn, W and Zn. A number of comparisons have been made amongst the metal

spinels including Co, Mn and Zn where Co spinels gave the highest oil conversion of 98.3% in just 3 hours at moderate temperature (65°C).

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