



# Magnetic solid catalysts for sustainable and cleaner biodiesel production: A comprehensive review

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## ABSTRACT

Biodiesel has attracted widespread attention as a potential alternative energy source to fossil-derived fuels. The application of heterogeneous catalysts for biodiesel production can offer an environmentally-friendly more attractive process for sustainable and cleaner production requirement. Small-sized heterogeneous catalysts generally show better activities due to their higher surface area and less mass transfer limitation. However, the separation of these solid catalysts is particularly difficult; and the serious mass loss during the separation process together with more time- and energy-consumption precludes their practical utilization especially for high viscosity reaction mixtures. Magnetic solid catalysts have recently become the research hotspot for the transesterification and esterifications for biodiesel production, because of their easy separation with minimal mass loss by an external magnetic field. In this review, various magnetic solid catalysts, including magnetic solid acid, alkali, enzyme and acidic-basic bi-functional catalysts were introduced. The catalyst preparation, catalytic performances, reaction mechanism, and recyclability of the catalysts and their influential parameters with some justifications are discussed from previous literatures to the field of interest, mainly focusing on the influence of active species, surface properties and their synergisms on the catalytic performances. For achieving the goal of good progress in efficient biodiesel production, the evaluation of the present research state, the challenge faced by the magnetic catalysts and future development trend are put forward. Possible reaction mechanisms for different types of the catalysts are also presented, giving some critical guidance in the design of magnetic solid catalysts. Finally, the key influential parameters on the catalytic performances as well as current challenges and future perspectives are provided for further improvement.

## 1. Introduction

In recent decades, the exploration of alternative sustainable fuels has become a significant research hotspot mainly due to the depletion of fossil fuel reserves and aggravated environmental pollution. Among the proposed energy alternatives, biofuel has attracted extensive attention because it is biodegradable, renewable, non-toxic, and suitable for use in an automotive engine [1]. Biodiesel, chemically constituting of mono-alkyl esters of long-chain fatty acids and as renewable liquid biofuels, can be derived by the transesterification and esterification of vegetable oils, animal fats and long-chain fatty acids with low molecular weight alcohol (usually methanol) [2]. To a certain extent, the utilization of biodiesel can reduce fossil-derived fuel consumption and flatten out the price of crude oil, with the reduction in ever-growing environmental pollution issues caused by the combustion of petroleum-based fuels. The favorable combustion emission profile of biodiesel has the

less harmful gas emissions such as carbon monoxide, sulfur dioxide and aromatic hydrocarbon than petroleum fossil fuel, as well as the decreased emissions of polluting particulate matters [3,4].

The chemical methods used for biodiesel production principally include supercritical method [5], catalytic esterification and transesterification approaches [6–10]. The supercritical method is difficult to be popularized in industry due to the restrictions of harsh reaction conditions (high pressure and temperature) on the high energy consumption [11]. As illustrated in Fig. 1, the catalytic transesterification and esterification methods are widely utilized for the biodiesel production in academic studies and industrial applications. Generally, the transesterification reaction for the biodiesel production refers to the alcoholysis reaction of animal or vegetable oils, that is, in the presence of chemical or enzymatic catalyst, the transesterification of triglycerides with methanol produces fatty acid methyl esters (FAMES) that are well-known as biodiesel [3]. Since methanol is derived from fossil

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resources, the thus-produced biodiesel cannot be termed as fully renewable. Hence, to a certain extent, ethanol is applied for producing biodiesel due to the readily availability from fermentative processes using biomass feedstocks, which renders that the ethanol biodiesel production is fully independent of fossil-based energy and renewable. However, ethanol has lower reactivity for the transesterification and esterifications than methanol. Therefore, methanol is actually the most preferred low-carbon alcohols for the biodiesel production [2,5].

Both basic and acidic catalysts are effective for the transesterification reaction, and the base catalysts always show higher activities towards the reaction. However, even though having lower activities towards the transesterification reaction, the acid catalyst can catalyze the transesterification of triglycerides and esterification of free fatty acids (FFAs) simultaneously, thus achieving one step conversion of low-quality acidic oils (usually with high amounts of FFAs) to biodiesel [12]. In comparison with the chemical catalysts, lipase (triacylglycerol hydrolases, EC 3.1.1.3) has several advantages such as milder reaction conditions, little or no side reaction, environmentally friendly character and lower susceptibility to the FFAs and moisture generally present in the oil feedstocks. However, the lipase-mediated transesterifications of vegetable oils are handicapped owing to the difficult recovery of enzyme and relatively high cost.

Commonly, the traditional catalysts used for the oil transesterification reactions are homogeneous strong acids, strong bases and free enzymes, such as KOH, NaOH, concentrated  $H_2SO_4$ , benzenesulfonic acid,  $CH_3ONa$ , organic amines, and microbial lipases, etc [13]. Although these homogeneous catalysts have many metrics such as high catalytic activity, short reaction time, low-cost and easy control, they are inclined to corrode the equipment in the catalytic process, difficult to be separated from the product, and unable to recycle and reuse [14]. In an attempt to address these hitches, the use of heterogeneous catalysis processes has appeared to be the noteworthy development trend and has greatly attracted the research interest. Thus, heterogeneous solid catalysts have been widely applied in modern industrial production due to the need of green and cleaner production in today's society [15].

As compared with homogeneous catalysts, heterogeneous catalysts, where their active sites are in the different phases from the reactants, are reportedly non-corrosive, environmentally-friendly and recoverable, rendering the catalyst separation facilely, thereof cutting down the disposal stages and greatly improving the technological and economical feasibility [16]. But, the tedious filtration or centrifugation methods are generally used for the recovery of the solid catalysts and their inevitable mass loss is not avoided.

Up to date, as far as the catalyst used for the biodiesel production, heterogeneous catalysts are generally classified into four kinds of solid catalysts: acidic, alkali, acid-alkali and enzymatic solid catalysts. High

specific surface area of the solid catalysts can ensure the uniform dispersion of active species and better access of active sites, affording the high catalytic performances. As an example, Sulaiman et al. investigated the heterogeneous catalyst of Cr/Ca (10:90)/ $\gamma-Al_2O_3$  with larger surface area ( $164.32\text{ m}^2/\text{g}$ ) and higher basicity ( $3.38\text{ mmol/g}$ ) for the transesterification reaction of low-quality cooking oil, and the biodiesel yield of 93.1% was attained over this solid catalyst [17]. As for the heterogeneously catalytic processes, filtration and centrifugation methods are often-utilized for the separation of the solid catalysts from the reaction mixture. Generally, the small-sized solid catalysts exhibited better catalytic efficiency, because of their better exposure of active sites to oil feedstocks as well as less mass diffusion limitations. However, in most cases, the recycle of the solid catalysts with small sizes is invariably difficult by using filtration and centrifugation methods particularly for the high viscosity reaction mixture, facilitating these conventional separation methods to be highly time-consuming and inefficient, and additionally requiring energy-intensive steps [6,10].

Recently, magnetic materials have reportedly gained particular interest as potent catalyst supports, since their magnetic response features can endow the simple and easy separation of solid catalysts with minimal mass loss by applying an external magnetic field even for the high viscosity reaction mixture. This magnetic separation method, as an attractive alternative approach, can not only avoid tedious separation and recovery procedures, but also effectively reduce the loss of solid catalyst in the separation process. According to current research reports [18], the main magnetic materials used for the preparation of solid catalysts are conventional monodisperse nanocrystals (such as  $Fe_3O_4$  and  $\gamma-Fe_2O_3$ ) and ferrite microspheres (such as  $MFe_2O_4$ ,  $M = Mn, Co, Zn$  and  $Ni$ ) due to their facile preparation, inherent insolubility, and strong magnetic properties. The methods of synthesizing magnetic nano-materials include coprecipitation, thermal decomposition, microemulsion-based synthetic methods, hydrothermal and solvothermal synthetic methods [18]. Among these methods, co-precipitation method is simple and more suitable for synthesizing magnetic nanoparticles on a large scale; and hydrothermal or solvothermal synthetic methods can form the magnetic nano-materials with excellent crystallite structure [19].

Magnetic carrier materials are generally categorized into two types: monodisperse magnetic nanoparticles and magnetic nanocomposites. As compared with magnetic nanocomposites, monodisperse ones modified with small organic molecules as an efficient carrier for the preparation of the solid catalyst, can endow stronger magnetism and simpler recycle procedures to the heterogeneous catalysis. However, magnetic nanoparticles usually tend to aggregate into large clusters, which lead to the loss of their monodisperse state owing to their high surface energy and magnetic dipole attractions. In particular, this agglomeration

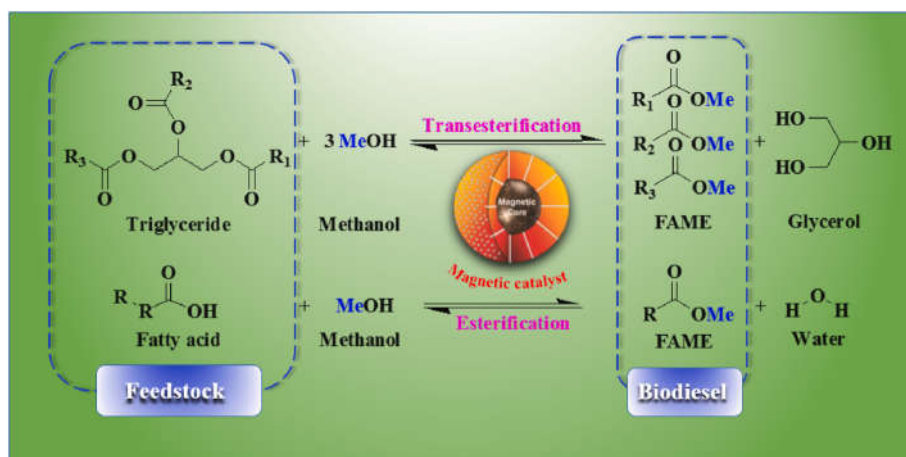


Fig. 1. Schematic illustration of the transesterification and esterification reactions for biodiesel production by using the magnetic solid catalyst.

phenomenon will hinder the homogeneous dispersion of the proposed magnetic catalyst in the reaction mixture, concealing some available active sites, resulting in their poor contact with the reactants, and therefore greatly reducing the catalytic performance [20]. As a viable solution to this problem, a protective layer deposited on the magnetic nanoparticles can effectively prevent the magnetic agglomeration and also improve their chemical stability [21,22]. Moreover, the tunable protective layer would provide some active groups that can be further functionalized through post-synthetic method for loading catalytically active components, and the thus-formed core-shell structured solid catalysts not only improve the specific surface area of the solid catalyst, but also protect the magnetic cores from erosion. As ideal carriers for the synthesis of solid catalysts, these magnetic nanocomposites possess the advantages of larger surface area and smaller mass transfer resistance [23,24]. So far, various materials, including carbonaceous materials, silicon materials, polymer, and metal-organic frameworks (MOFs), have been reported as satisfactory protective layer of magnetic nanoparticles, aiming to prepare the magnetic solid catalysts for the biodiesel production [25,26]. According to the property, magnetic solid catalysts can be classified as magnetic solid acid, base, lipase, and acid-base bifunctional catalysts. Further, these solid catalysts are subdivided into different classes based on their catalytic species, as shown in Fig. 2.

Availability and types of the oil feedstock, catalyst and operation cost are responsible for the overall cost of biodiesel production. Various oil feedstocks can be utilized to generate biodiesel, including vegetable oil, animal fats, microalga oil and waste oils [27]. Recently, low-quality oils, such as non-edible oil and waste-cooking oil, have been hailed as a promising feedstock for the biodiesel production mainly due to their cost-effective, providing stable availability and reliable feedstock supply and significantly reducing the biodiesel production cost. Unfortunately, these oils often contain a high content of FFAs and water, which can make the catalyst to be greatly deactivated, particularly for alkali catalysts [28]. Magnetic solid acid catalyst is reportedly suited for low-quality feedstocks with high FFA contents without additional pre-purification steps during the catalysis process, and more interestingly, it can catalyze the transesterification of triglycerides and esterification of FFAs simultaneously, thus achieving one-pot transformation of low-quality oils to biodiesel and minimizing the complex and tedious separation process [29].

In comparison with magnetic acid catalysts, magnetic base catalysts need lower reaction temperature and shorter reaction time to achieve a

satisfactory oil conversion rate [30]. However, the utilization of magnetic base catalyst would bring about saponification issues under the reaction conditions, which prevents glycerol separation from the biodiesel product and leads to a decreased biodiesel yield [30,31]. As compared to magnetic chemical catalysts, magnetic lipase biocatalysts have the merit of milder conditions, cleaner products, and less waste generation in the catalytic process of biodiesel production [32]. The main dilemma of magnetic lipase solid catalyst, when employed for the biodiesel production, is its high cost and poor operational stability [33]. Moreover, the newly developed solid acid-base catalysts have also been utilized for the biodiesel production, since they show better FFA- and water tolerance capacity and can concurrently convert the triglycerides and FFAs to biodiesel product.

To our knowledge, some excellent reviews have well documented on the solid catalysts used for the biodiesel production in the published literatures [15,29,30,32,34–36]. Comparatively, magnetic solid catalysts and their catalyzed-biodiesel production technologies have been seldom reviewed. The present review mainly focus on the current state of art and related knowledge for the magnetic solid catalysts in the biodiesel production through esterification and/or transesterification reactions. Herein, this paper branched into understanding magnetic solid catalysts from the active center of catalysts, and the key point is to accomplish the recent advancements in the mushroom growth of magnetic solid catalyst for the biodiesel production. Besides that, the synthesis method and the characterization of the magnetic solid catalysts which affects their catalytic performances are particularly highlighted. Additionally, optimal reaction conditions investigated in bibliography for the magnetic catalysts are also presented. Some guidance in the evaluation of the present state of the magnetic solid catalyst for the cleaner biodiesel production is clearly given in this contribution.

## 2. Magnetic solid acid catalysts

With the aims to produce cost-effective biodiesel, investigations on addressing the technical challenges have long been carried out. Magnetic solid acid catalyst has been broadly investigated as a potential catalyst for the biodiesel production under suitable reaction conditions, since they can render higher endurance to high water and FFA contents especially for cheaper and readily available oil feedstocks, thus improving the biodiesel production process to fulfill the requirement of green chemistry and sustainable development. However, for the

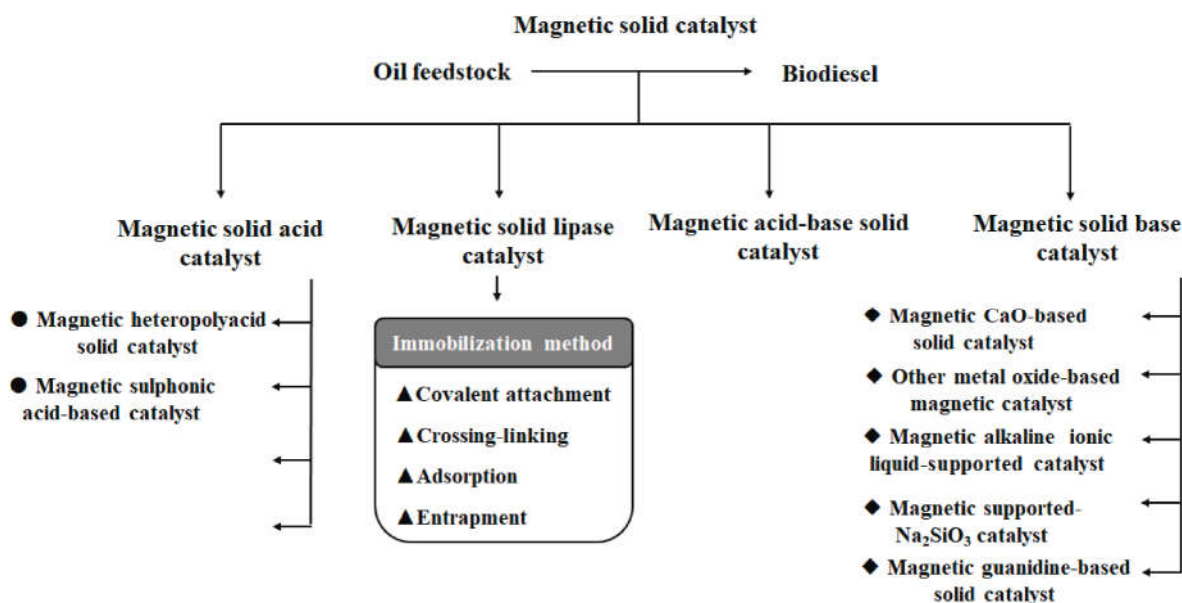


Fig. 2. Different types of magnetic solid catalysts used for the conversion to biodiesel.

magnetic solid acid catalyst, the higher reaction temperature and longer reaction time are often needed for the transesterification reaction to achieve a high oil conversion rate [29].

Recently, tremendous efforts have been dedicated to develop efficient approaches for modifying or creating acidic species in the magnetic solid catalysts for the biodiesel production. There are two major methods, including in-situ synthesis and post-synthesis treatment, to functionalize the magnetic support materials and so as to enhance the catalytic activity of the resulting magnetic solid catalyst. The in-situ synthesis can homogeneously introduce acidic species on the magnetic supports, improving the surface acidity by enhancing the number of both Lewis and Brønsted acid sites. The post-synthesis method creates the catalytic components through immobilizing acidic species on the magnetic support [36]. The surface acidity, surface area and pore size distribution are the main influential parameters to take into consideration as the magnetic solid catalysts are used as a catalyst for the biodiesel production. With regards to these respects, large pore size can efficiently induce the mass diffusion of the large triglyceride molecules and thus is suitable for the oil transesterification reaction. Moreover, the catalyst surface had better hydrophobic property favoring the adsorption of oily hydrophobic species on the catalyst, and also reduces deactivation caused by polar species, such as water.

### 2.1. Magnetic heteropolyacid (HPA) solid catalyst

In the past years, polyoxometalate (POM) acids with primary Keggin-type anion structure, such as  $H_3PW_{12}O_{40}$ ,  $H_3PMo_{12}O_{40}$ ,  $H_4PW_{11}VO_{40}$ , and  $H_4SiW_{12}O_{40}$ , have attracted considerable interest in catalysis for its well-defined structure, strong Brønsted acid sites and low corrosiveness [37]. The main shortcoming of such heteropolyacids (HPAs) as employed as a catalyst lies in their high solubility in particular in the polar reaction mixture and low specific surface area (less than  $5\text{ m}^2/\text{g}$ ), which make HPAs to be a homogeneous acid catalyst with serious separation and recycling problems [36,38]. To overcome the weakness, two strategies are proposed for the heterogenization of HPAs. In one method, researchers tried to seek for porous support materials to immobilize HPAs in order to improve its surface area, heterogeneity, and catalytic performance in the esterification and transesterification reactions [39]. In another method, the replacement of the protons in HPAs partially or completely with larger univalent cations (such as  $Cs^+$ ,  $NH_4^+$ ,  $Ag^+$ ) could also enhance their heterogeneity through the formation of the insoluble solid salts of HPAs [40]. As an example, doping cesium ions into HPAs (e.g. forming  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ) can greatly improve their insolubility in the reaction system, thereby resulting in heterogeneous catalysis nature [41].

Phosphotungstic acid ( $H_3PW_{12}O_{40}$ , HPW) is the widely used catalyst to produce the biodiesel via esterification and transesterification reactions owing to its stronger Brønsted acidity as compared with

conventional acid catalysts [40,42]. In an attempt to improve its reusability, HPW could be loaded on magnetic supports to prepare magnetic solid HPAs catalysts. Some selected magnetic HPA-based solid catalysts are summarized in Table 1.

In recent studies, the Cs-doped HPW was immobilized on magnetic composites ( $Fe-SiO_2$ ) through sol-gel and impregnation method to develop magnetic nanocatalyst  $CsH_2PW_{12}O_{40}/Fe-SiO_2$  for the biodiesel production [43]. In this study, the influence of various weight ratio  $H_3PW_{12}O_{40}/Fe-SiO_2$ ,  $Cs/H_3PW_{12}O_{40}$ , and different calcination temperatures on the catalytic performance of this magnetic nanocatalyst was systematically tested. The results showed that the magnetic catalyst with  $Cs = 2\text{ wt\%}$  and  $H_3PW_{12}O_{40}/Fe-SiO_2 = 4\text{ wt\%}$  is an optimal catalyst for the biodiesel production, giving 81% of the biodiesel yield after 4 h of reaction at  $60\text{ }^\circ\text{C}$  with oil/methanol molar ratio of 1:12. This catalyst can be facilely recovered with the help of an external magnet in a very short time ( $<20\text{ s}$ ).

The higher catalytic activity is an important nature for the solid catalyst to achieve the efficient production of biodiesel. As a promising oil feedstock, highly-acidic non-edible oil from *Pistacia chinensis* seed was used as raw material for the biodiesel production through transesterification reactions [44,45]. For this aim, Fu et al. [44] immobilized HPW on the magnetic cellulose microsphere (MCM) modified with triethylene tetramine (TETA) to prepare the magnetic cellulose-based catalyst MCM-HPW, as graphically shown in Fig. 3. Using highly-acidic tree born oil as oil feedstocks, the highest conversion to biodiesel (93.1%) was obtained at methanol/oil ratio of 10:1 (v:v), reaction temperature of  $60\text{ }^\circ\text{C}$  and reaction time of 80 min. Over this magnetic acid catalyst, the oil conversion to biodiesel was slightly decreased to 80.7% even after five cycles of reuse, revealing a satisfactory reusability of the solid catalyst. In this scenario, the good reusability of the catalyst was mainly due to the strong interactions between the MCM support and the Keggin heteropolyanions. More interestingly, this catalyst can simultaneously catalyze the transesterification of *Pistacia chinensis* seed oil and esterification of FFAs, thus rendering the one-step transformation of the low-quality oils to biodiesel without the pre-treatment of oil feedstocks.

A possible mechanism of the catalytic reaction is schematically illustrated in Fig. 4. Four steps are involved in this acid-catalyzed reaction: firstly, a carbocation is generated by the interaction of the carbonyl oxygen of triglycerides (TGs) or FFAs with the proton of MCM-HPW catalyst; subsequently, methanol molecules as the nucleophilic reagent attack the carbocation so as to form tetrahedral intermediates; then, this unstable intermediate is decomposed into one diglyceride (DG) and one FAME; and finally, the circulatory reaction is consecutively carried out by the same reaction mechanism with the aid of MCM-HPW to produce the other two FAME molecules. Moreover, the esterification of FFAs could also be conducted simultaneously through the similar reaction mechanism of the transesterification, thus achieving the

**Table 1**  
Magnetic heteropolyacid solid catalysts for the biodiesel production.

Catalyst	saturation magnetization	Feedstock	Optimum reaction conditions	Biodiesel yield	Refs.
$CsH_2PW_{12}O_{40}/Fe-SiO_2$	$\sim 12\text{ emu/g}$	Sunflower oil	$60\text{ }^\circ\text{C}$ ; 4 h; methanol/oil molar ratio 12:1; catalyst amount 4 wt%	81%	43
MCM-HPW	–	<i>Pistacia chinensis</i> seed oil	$60\text{ }^\circ\text{C}$ ; 80 min; methanol/oil molar ratio 10:1; catalyst amount 10 wt%	93.1%	44
GO/CM- $NH_2@Fe_3O_4$ -HPW	–	<i>Pistacia chinensis</i> seed oil	$80\text{ }^\circ\text{C}$ ; 8 h; methanol/oil molar ratio 12:1; catalyst amount 15 wt%	94%	45
HPW-PGMA-MNPs	$14.4\text{ emu/g}$	Waste grease	$122\text{ }^\circ\text{C}$ ; 24 h; methanol/oil molar ratio 33:1; catalyst amount 4 wt%	98%	46
Rubber- $Fe_3O_4@SiO_2@H_3PMo_{12}O_{40}$	$49\text{ emu/g}$	sunflower oil	$69\text{ }^\circ\text{C}$ ; 3 h; methanol/oil molar ratio 12:1; catalyst amount 3 wt%	94.5%	47
Clinoptilolite- $Fe_3O_4-H_3PW_{12}O_{40}$	$10.57\text{ emu/g}$	<i>Salvia mirzayanii</i> oil	$75\text{ }^\circ\text{C}$ ; 8 h; methanol/oil molar ratio 12:1; catalyst amount 0.5 wt%	80%	48
$Fe_3O_4-ZIF-8-H_6PV_3MoW_8O_{40}$	$8.9\text{ emu/g}$	Soybean oil	$160\text{ }^\circ\text{C}$ ; 10 h; methanol/oil molar ratio 30:1; catalyst amount 6 wt%	92.6%	49

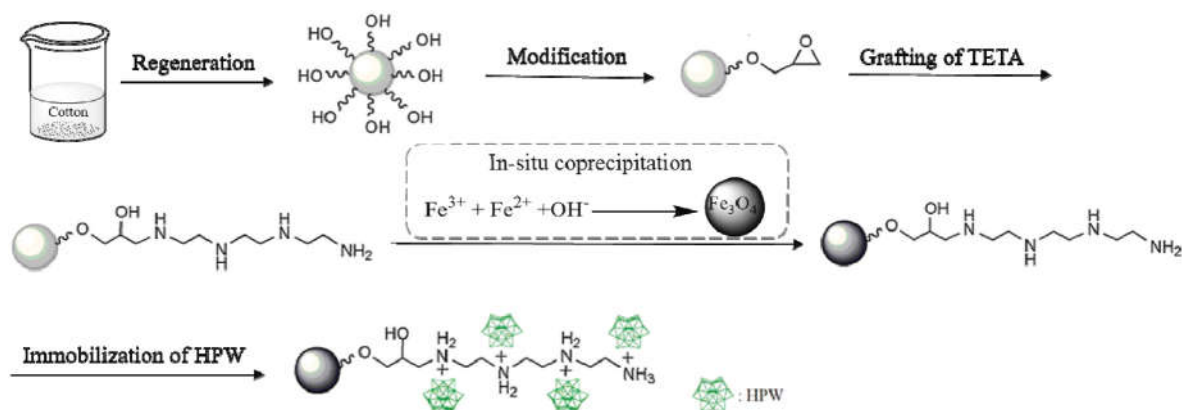


Fig. 3. Synthesis procedure of the MCM-HPW catalyst [Reproduced from ref. 44].

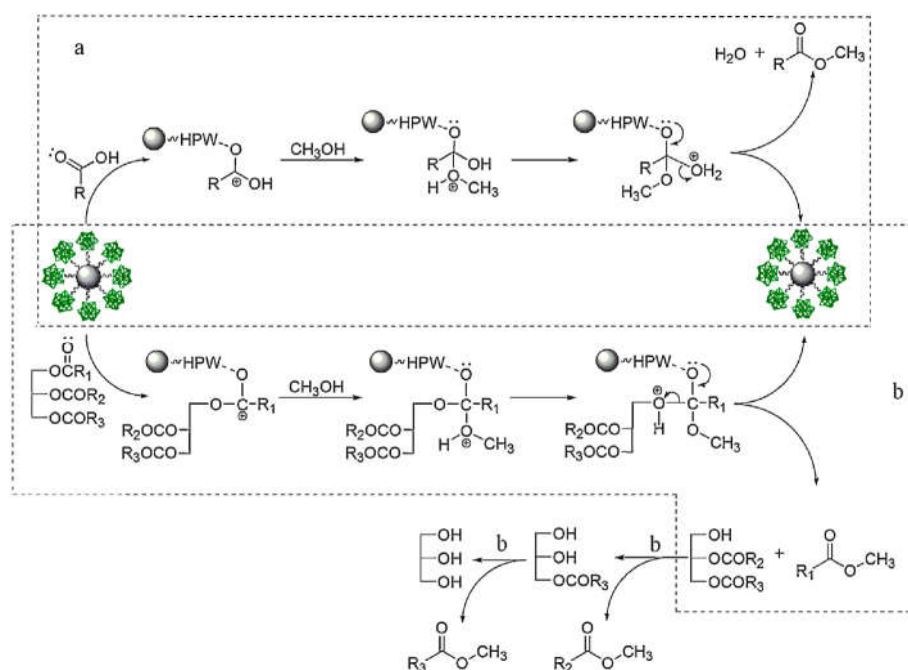


Fig. 4. The mechanism of the reaction catalyzed by MCM-HPW: (a) free fatty acid and (b) triglyceride [Reproduced from ref. 44].

TAGs and FFAs to be simultaneously transformed to biodiesel in a one-pot manner. In reality, the acidity of the solid acid catalyst plays a significant role in the biodiesel production process; and hence higher biodiesel yield is obtainable with strong solid acid-catalyzed reactions.

Similarly, magnetic graphene oxide/cellulose (GO/CM-NH<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>) microspheres were also prepared for the encapsulation of HPW into this magnetic composite, forming the magnetic GO/CM-NH<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>-HPW catalyst [45]. Under the optimized reaction conditions, the biodiesel yield of 94% was achieved over this magnetic catalyst, and 85% of biodiesel yield was maintained even after six reuse cycles. This catalyst is more stable and easier to be separated by using an external magnet than the MCM-HPW catalyst; however the latter requires shorter reaction time to obtain the maximum oil conversion rate. As a kind of bio-char, biomass cellulose as a catalyst support material seems to be more suitable from green chemistry point of view and can cause no additional pollution.

Li et al. [46] developed a novel magnetic nanoparticle PGMA-MNPs with core of iron oxide (MNP) and shell of poly (glycidyl methacrylate) (PGMA) with the aims to immobilize the HPW on the surface of the magnetic composite. In this research, the core-shell structured magnetic

catalysts were conveniently prepared from PGMA-MNPs via phosphonation with Na<sub>2</sub>HPO<sub>4</sub> and subsequent treatment with Na<sub>2</sub>WO<sub>4</sub> under acidic conditions, allowing for in-situ formation of HPW on the composite surface with a high acidity of 1.13 mmol/g. The thus-prepared catalyst showed the high activity to simultaneously catalyze esterification and transesterification reactions for converting waste grease into biodiesel in a one-pot transformation manner, reaching 98% of biodiesel yield under the optimum conditions: the molar ratio of methanol to oil of 33:1, catalyst amount of 4 wt%, reaction temperature of 122 °C and reaction time of 24 h. Moreover, the good reusability was shown for this solid catalyst, maintaining 95% productivity even after ten reuse cycles. This catalyst displayed better performances for the one-pot transformation of waste grease to biodiesel than commercially available solid acid catalysts such as Amberlyst 15, Purolite CT-275, and zeolite regarding their catalytic activity and recyclability, being useful for the green and economic production of biodiesel from waste grease.

Very recently, Ghasemzadeh et al. carried out a study on the preparation of HPA catalyst supported with magnetic rubber-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composites for the catalytic biodiesel production [47]. Herein, the rubber powder was used due to its existence of an inert and porous

structure. Initially, the magnetic rubber powders with high dispersibility and porosity were synthesized by co-precipitation method and covered by silica shell via the hydrolysis of tetraethyl orthosilicate (TEOS) to form rubber-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. Thereafter, the rubber-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> catalyst was obtained through immobilizing phosphomolybdic acid on the magnetic support via an impregnation method. The utilization of the synthesized catalyst in the transesterification of sunflower oil was optimized using response surface methodology with a central composite design. Over this nanostructured catalyst, the biodiesel yield could reach to 94.5% under the optimal conditions of 3 wt% catalyst dosage, 3 h of reaction duration, 12:1 of methanol/oil molar ratio and 69 °C of reaction temperature. During the reaction, no agglomeration of the catalyst particles occurred and this catalyst could be recycled and reused up to 5 runs with 78.8% of biodiesel conversion.

As stated earlier, in an attempt to efficiently prevent the magnetic agglomeration, magnetic nanoparticles can be coated with inert phases for the preparation of magnetic solid catalyst. In a study performed by Helmi et al. [48], the clinoptilolite-Fe<sub>3</sub>O<sub>4</sub> composite was fabricated by coating magnetite with clinoptilolite, which was then used as a magnetic composite support to form the clinoptilolite-Fe<sub>3</sub>O<sub>4</sub>-supported phosphomolybdic acid catalyst by impregnation of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>. By applying this magnetic catalyst for the transesterification of *Salvia mirzayanii* oil with methanol, the biodiesel yield of 80% could be attained at operating conditions of 0.5 wt% catalyst, methanol/oil ratio of 12:1, and temperature of 75 °C at 8 h. Moreover, in our previous research [49], the magnetic Fe<sub>3</sub>O<sub>4</sub>/ZIF-8 composites were prepared by incorporating ZIF-8 MOF into magnetite nanoparticles through in-situ approach, and then a vanadium-substituted HPA, H<sub>6</sub>PV<sub>3</sub>MoW<sub>8</sub>O<sub>40</sub>, was encapsulated in the magnetic support to afford the solid acid catalyst. This catalyst had good magnetic responsiveness, and could catalyze the transesterification of soybean oil and esterification of FFAs simultaneously, thus allowing to achieve the biodiesel production by one-pot transformation of triglycerides and FFAs to biodiesel from the low-grade oils in a heterogeneous manner. The good reusability of this catalyst was shown with slight decrease of catalytic activity over five reaction cycles, mainly due to the strong interactions of the Keggin structure of the HPAs with the imidazole groups in the ZIF-8 components.

## 2.2. Magnetic sulphonic acid based-solid catalysts

Sulphonic acid based-solid catalysts are considered as another kind of solid acid catalysts in the production of biodiesel thanks to their

existence of strong Brønsted acid sites [50]. Different magnetic sulfonated-based solid acids for the biodiesel production are listed in Table 2.

Recently, carbonaceous materials have extensively studied in the field of heterogeneous catalysis since they are cheaper and more environment-friendly. Generally, magnetic sulfonated carbon-based solid catalysts are prepared through sulfonation of magnetic carbon composites [31,36]. The usage of glucose as a carbon source was reported to fabricate the magnetic mesoporous carbon composites [51, 52]. In a recent study by Zhang et al. for example, magnetic sulfonated carbonaceous solid acid catalyst (AC-600-SO<sub>3</sub>H@Fe/C) with a high acid density (2.79 mmol/g) and strong magnetic responsiveness (Ms = 14.4 Am<sup>2</sup>/kg) was synthesized, and subsequently used as a solid catalyst to produce biodiesel using crude *Jatropha* oil with the acid value of 17.2 mg KOH/g as raw material [51]. To prepare this magnetic acid catalyst, magnetic carrier was initially synthesized from glucose and iron chloride through a novel method of double hydrothermal precipitation and pyrolysis, followed by the sulfonation of the magnetic carrier with concentrated sulfuric acid. It was confirmed that this solid catalyst (AC-600-SO<sub>3</sub>H@Fe/C) carbonized at 600 °C could afford 91.8% of biodiesel yield at reaction temperature of 200 °C. However, the high reaction temperature could result in the leakage of the active group in the reaction mixture, and also could bring about high energy-consumption in the biodiesel production processes. To alleviate this drawback, hollow magnetic carbon was used as support materials to synthesize the sulfonated Fe/C-SO<sub>3</sub>H fiber catalyst via the sol-gel process and sulfonation reaction [52]. The remarkable hollow pore structure of this catalyst provides large surface area and rough surface, rendering the active sites to be in better available contact with the oil feedstocks and thus ensuring the conversion of biodiesel more than 90% under the optimized reaction conditions. Further, this solid catalyst demonstrated excellent magnetic properties (Ms = 22.06 emu/g), advantageously remaining about 80% of its catalytic efficiency after the recycle for 10 times with the help of an extra magnetic field and posing potential industrial application perspective.

In another study, Chang et al. [53] prepared magnetic mesoporous carbon spheres from the carbon source of resorcinol and formaldehyde solution using triblock copolymer Pluronic F127 (EO<sub>106</sub>PO<sub>20</sub>EO<sub>106</sub>) as template agent, and then was sulfonated with organic sulfonic acid to obtain magnetic mesoporous carbon sphere solid catalyst (MMCS-SO<sub>3</sub>H). This MMCS-SO<sub>3</sub>H catalyst had high surface area (S<sub>BET</sub> = 275.9 m<sup>2</sup>/g) and SO<sub>3</sub>H density of 1.08 mmol/g, affording the biodiesel yield of 95% with excellent stability and recycling property. Graphene,

**Table 2**  
Magnetic sulphonic acid based-solid catalysts for the biodiesel production.

Catalyst	Saturation magnetization (emu/g)	Feedstock	Optimum reaction conditions				Biodiesel yield	Refs.
			Temperature (°C)	Reaction time	Catalyst loading (wt%)	Substrate molar ratio		
AC-600-SO <sub>3</sub> H@Fe/C	14.4	<i>Jatropha</i> oil	200	10 h	10	24 : 1	91.8%	51
Fe/C-SO <sub>3</sub> H	22.06	Oleic acid	70	4 h	10	18 : 1	97%	52
MMCS-SO <sub>3</sub> H	-	Oleic acid	100	6 h	5	30 : 1	95%	53
Graphene oxide -Fe <sub>2</sub> O <sub>3</sub> -SO <sub>3</sub> H	-	Waste cooking oil	100	4 h	5	12 : 1	~100%	54
MPC-0.8-SO <sub>3</sub> H	13.07	Oleic acid	80	8 h	3	33 : 1	94%	57
AC-Fe (10)-SO <sub>3</sub> Cl	7.67	Palm fatty acid distillate	100	3 h	4	16 : 1	98.6%	58
nM-CP-SO <sub>3</sub> H	11.163	<i>Milletia pinnata</i> seed oil	65	45min	3	11 : 1	98.7%	59
FCHC-SO <sub>3</sub> H	18.9	Oleic acid	80	3 h	4	15 : 1	96.7%	60
Fe <sub>3</sub> O <sub>4</sub> -SBA-15-SO <sub>3</sub> H	12.1	Oleic acid	60	6 h	3	10:1	75%	63
Sulfonic acid functionalized silica coated Fe/Fe <sub>3</sub> O <sub>4</sub>	-	Oleic acid	70	4 h	5	12:1	~100%	64
sulfonated cellulose-magnetite nanocomposite	0.0405	Oleic acid.	80	5 h	0.75	2 : 1	96%	66
Zr-CMC-SO <sub>3</sub> H@3Fe-C <sub>400</sub>	3.08	Oleic acid	90	4 h	9	12 : 1	97.39%	67
		Soybean oil	160	8 h	7	15:1	93.07%	
ZrFe-SA-SO <sub>3</sub> H	3.7	Oleic acid	90	5 h	9	12 : 1	99.5%	68

as known to have high surface area of about 2600 m<sup>2</sup>/g, can be incorporated into magnetic nanoparticles so as to enhance the specific surface of magnetic composite support. In this vein, D'Souza et al. [54] prepared magnetic graphene solid catalyst (GO-Fe<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>H) through sulfonation reaction, and then employed as a solid acid catalyst for the biodiesel production. The satisfactory catalytic property was obtained mostly owing to a combination of large surface of the catalyst with the highly accessible sulfonic acid sites presented on the solid acid catalyst.

Biomass, identified as the most abundant renewable resource, has been acknowledged as a potential and sustainable carbon source to develop advanced carbonaceous materials [55,56]. Magnetic biomass-based materials for preparing green solid catalysts are becoming a key research focus, since they can avoid the use of toxic substrates and the yield of more harmful wastes. Some investigators have reported the usage of waste pericarp as a low-cost potential feedstock to form the magnetic biochar-based catalyst used in the biodiesel production [57–60].

Waste banana peel (BP) with multi-functional groups could be utilized as a precursor to prepare porous carbons and easily coordinated with Fe (III) [57]. In this respect, magnetic porous carbons (MPCs) were successfully prepared by fast pyrolysis of waste banana peel (BP) with Fe (III)-based complexes. Through vapor-phase sulfonation, magnetic carbonaceous solid acid catalyst (MCSAs) was readily synthesized for the heterogeneous production of biodiesel. The effect of the Fe (III) ratio on the catalytic activity was tested to optimize the catalyst preparation process. Results showed that MPC-0.8-SO<sub>3</sub>H had the better catalytic activity and water-tolerant than Amberlyst-15 due to its high surface area (933.8 m<sup>2</sup>/g) and good hydrophobicity. Similarly, Ibrahim and coworkers [58] made use of empty fruit bunch (EFB) as raw material to synthesize the magnetic solid catalyst AC-Fe(x)-SO<sub>3</sub>Cl (with x = 2, 5, 10 and 15%) through a chemical activation-doping-sulfonation process for the biodiesel production from palm fatty acid distillate (PFAD). The prepared magnetic catalyst possessed a higher surface area (20.42 m<sup>2</sup>/g), high acidity (29.520 μmol/g), and high magnetic responsiveness. Over the formed AC-Fe (10)-SO<sub>3</sub>Cl catalyst, the highest biodiesel conversion of 98.6% was obtained with high durability for six continuous reuse cycles of the solid catalyst. Quit recently, Chellappan et al. [59] utilized cassava peel as carbon sources to prepare biochar *via* slow pyrolysis, and then the sulfonated biochar was obtained by sulfonation with concentrated H<sub>2</sub>SO<sub>4</sub>. The magnetized sulfonated biochar catalyst (nM-CP-SO<sub>3</sub>H) was developed by coprecipitation method through the ultrasonically assisted incorporation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the sulfonated biochar. Three functional acidic sites, including weak (-OH) and strong (-COOH and -SO<sub>3</sub>H) acidic groups, are presented in the solid catalyst. This sulfonated acid catalyst with high surface area of 423.89 m<sup>2</sup>/g displayed high catalytic performances mainly because of its high total acid density (3.2 mmol/g), thereby achieving the biodiesel yield of 98.7% from *Milletia pinnata* seed oil after 45 min of reaction at a reaction temperature of 65 °C with oil to methanol ratio of 11:1. Moreover, the good reusability of the catalyst was found for five reuse cycles thanks to the strong ionic interactions between the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and sulfonated biochar.

Chitosan (CS) derived from biomass was employed to fabricate magnetic chitosan composite with double shell structure, and the magnetic composite material was further served as non-toxic, non-corrosive and eco-friendly support materials for preparing sulfonated solid acid catalyst [60]. In this work, the hollow double-shell magnetic catalyst Fe<sub>3</sub>O<sub>4</sub>@Chitosan-Hollow-Chitosan-SO<sub>3</sub>H (FCHC-SO<sub>3</sub>H) was developed for the biodiesel production from the esterification of oleic acid with methanol, as depicted in Fig. 5. The unique structure of the hollow double-shell catalyst, not only increases the surface area of the solid catalyst, but also protects the magnetic core (Ms = 18.9 emu/g) from corrosion. By using the FCHC-SO<sub>3</sub>H catalyst, the biodiesel yield of 96.7% was attained under the reaction conditions of 4 wt% catalyst dosage, methanol/oleic acid ratio of 15:1 at 80 °C for 3 h. However, only 75% of biodiesel yield was achieved with the single shell catalyst

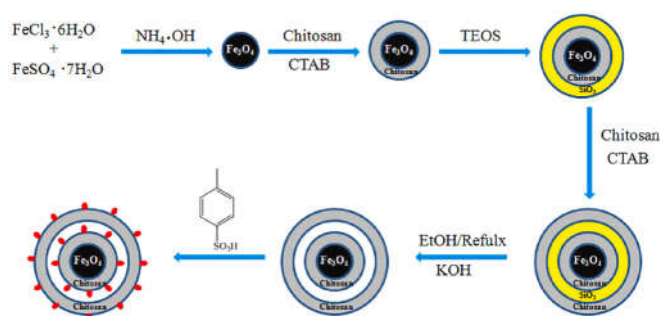


Fig. 5. Schematic illustration for the synthesis of the mesoporous magnetic biomass-based acidic catalyst FCHC-SO<sub>3</sub>H [Reproduced from ref.60].

Fe<sub>3</sub>O<sub>4</sub>@Chitosan-SO<sub>3</sub>H. Notably, the -SO<sub>3</sub>H and -NH<sub>3</sub><sup>+</sup> groups of the FCHC-SO<sub>3</sub>H catalyst can allow the solid catalyst to have enough active acid sites available to the reactants, which gives the catalyst with high total acid density (1.20 mmol/g). Additionally, the magnetic feature could make the catalyst easy to be separated from the product and have good reusability, thus showing a good prospect in the field of cleaner biodiesel production.

Besides, the magnetic sulphonated carbon-based catalysts prepared from biodegradable waste pericarp were also utilized as robust solid catalyst for the catalytic conversion of biomass into a variety of commodity chemicals [61]. In this respect, such magnetic biochar-based sulphonic acid catalysts possessed the excellent properties of high surface areas, good catalytic activity and high reusability, which can enhance the feasibility for the heterogeneous biodiesel production.

Reportedly, ordered mesoporous silicas as utilized as solid catalyst support possess several advantages of large surface area, tunable porosity, uniform pore size distribution, high thermal stability and easy-functionalization properties [62]. In this vein, Erdem et al. [63] successfully prepared magnetic Fe<sub>3</sub>O<sub>4</sub>-SBA-15-SO<sub>3</sub>H catalyst through oxidation of Fe<sub>3</sub>O<sub>4</sub>-SBA-SH with hydrogen peroxide. Over this Fe<sub>3</sub>O<sub>4</sub>-SBA-15-SO<sub>3</sub>H catalyst, the biodiesel conversion of 75% was attained with good reusability for four continuous runs of reactions. Moreover, this magnetic acid catalyst could catalyze both the transesterification of TAGs and esterification of FFAs, being potential for biodiesel production especially from low-quality feedstocks containing high level of FFAs. A similar investigation was also carried out by Wang and co-workers [64]. The magnetic crystalline Fe/Fe<sub>3</sub>O<sub>4</sub> was initially coated with SiO<sub>2</sub> to form core-shell magnetic nanoparticles (MNPs), and then was modified with sulfamic acid and sulfonic acid, respectively, so as to manufacture two magnetic solid acid catalysts. The two so-synthesized solid catalysts could give the conversion of almost 100% within 4 h of reaction at 70 °C in the esterification reaction. Furthermore, the sulfamic acid-functionalized MNPs maintained more than 95% of biodiesel yield for five reaction cycles. The catalytic activity of sulfamic acid-functionalized MNPs in the transesterification of glyceryl trioleate was better than that of sulfonic acid-functional MNPs owing to the higher acid loading and better dispersion on the surface of the MNPs.

As a matter of fact, the catalytic activities of solid acid catalysts are significantly dependent on their surface acid contents. Aiming to increasing the surface acid sites available for the reactions, magnetic sulphonic acid solid catalysts with both Lewis and Brønsted acid sites were also synthesized, and displayed high catalytic performances in the heterogeneous biodiesel production processes [65]. Cellulose is the most abundant natural polymer used by many researchers in establishing various applications because of its biocompatibility, biodegradability, and low toxicity. In this sense, magnetic cellulose nanocomposites were fabricated *via* the adsorption of magnetite onto the surface of functionalized nanocellulose, and subsequently were modified by acetic anhydride, succinic acid anhydride, phosphoric acid, and chlorosulfonic acid [66]. The sulfonated cellulose-magnetite nanocomposite (MSNC)

had good catalytic activities thanks to the presence of both Brønsted and Lewis acidities, affording 96% of biodiesel yield under the optimum reaction conditions. In the structure of the solid acid catalyst, the impregnated magnetite exhibited the Lewis acid sites, and the presented Brønsted acid sites were originated from the highly dispersed sulphonic acid groups on the surface of the nanocellulose. Interestingly, this MSNC catalyst showed excellent reusability and maintained about 95% productivity even after five reuse cycles.

Besides, the sodium carboxymethylcellulose and sodium alginate were also used as biomass materials to prepare the sulfonated magnetic solid acid catalysts, respectively. The thus-formed two magnetic acid catalysts had both Lewis and Brønsted acid sites, posing high catalytic performances for the transesterification of *Jatropha* oil and esterification of long-chain fatty acids for the biodiesel production [31,36]. In another study, the carbon-based magnetic solid acid catalyst (Zr-CMC-SO<sub>3</sub>H@3Fe-C<sub>400</sub>; CMC, carboxymethylcellulose) with high acid density (8.84 mmol/g) was synthesized by using CMC as biomass materials, and was found to possess both Lewis (CMC-COOZr or CMC-COOFe) and Brønsted (-SO<sub>3</sub>H) acid sites [67], as shown in Fig. 6. By applying this solid catalyst, the esterification of oleic acid in 97% of FAME yield and the transesterification of high acid value (AV) soybean oil in 93% of FAME yield were achieved in a heterogeneous manner. The excellent catalytic performance (i.e. higher than 90% of biodiesel yield) could be retained after ten consecutive cycles by facile magnetic separation, confirming that this catalyst possessed good reusability in the biodiesel production processes. Also, Wang et al. [68] reported similar magnetic solid acid catalysts (ZrFe-SA-SO<sub>3</sub>H and ZrFe-CMC-SO<sub>3</sub>H; SA: sodium alginate, CMC: carboxymethylcellulose) with both Brønsted and Lewis sites, and then further investigated the influence of the concentrations of Zr<sup>4+</sup> and Fe<sup>3+</sup> ions during the catalyst preparation process on the catalytic performance. In the structure of the synthesized solid catalyst, the -(COO)<sub>3</sub>Fe and -(COO)<sub>4</sub>Zr species display the Lewis acid sites, and the -SO<sub>3</sub>H groups exhibit the Brønsted acid sites. High yield of biodiesel (92.7–99.5%) was attained over this solid catalyst in a heterogeneous manner. The Zr<sub>1.0</sub>Fe<sub>1.0</sub>-SA-SO<sub>3</sub>H owned higher saturation magnetization (Ms = 3.7 Am<sup>2</sup>/kg) than the Zr-CMC-SO<sub>3</sub>H@3Fe-C<sub>400</sub> (Ms = 3.08 Am<sup>2</sup>/kg). On the contrary, the Zr-CMC-SO<sub>3</sub>H@3Fe-C<sub>400</sub> catalyst exhibited better recyclability than the Zr<sub>1.0</sub>Fe<sub>1.0</sub>-SA-SO<sub>3</sub>H catalyst.

Among the developed preparation methods, direct sulfonation of magnetic composites is deemed as a simple and facile approach to introduce active centers (-SO<sub>3</sub>H) to the solid catalyst [29]. The general sulfonation reagent used is chlorosulfonic acid, which is more efficient than sulfuric acid. The formed magnetic sulphonic acid-based solid catalysts commonly show excellent activities (generally affording above 90% biodiesel yield) and satisfactory recyclability for sustainable biodiesel production via the heterogeneous esterification and/or

transesterification reactions.

### 2.3. Magnetic acidic ionic liquids (ILs)-based solid catalysts

Acidic ionic liquids (ILs) are identified as a promising homogeneous catalyst in the processes of biodiesel production due to their high acidity, powerful solubility capability and high thermal stability [69]. However, owing to their homogeneous characters, they cannot be recycled easily and reused, leading to the catalyst loss and difficulty in the product purification. In order to improve the reusability of the acidic ILs and endow the heterogeneity, acidic ILs with Lewis and/or Brønsted acid sites were successfully immobilized on magnetic composites (including magnetic ordered mesoporous silica and magnetic metal-organic frameworks (MOFs)) to develop magnetic acidic IL-based solid acid catalysts [70–76]. The literature summary on such type solid acid catalysts for the biodiesel production is given in Table 3.

Sulfonic group (-SO<sub>3</sub>H) functionalized Brønsted acidic ILs are commonly utilized as active centers to fabricate magnetic solid acid catalyst for the biodiesel production. Magnetic silicas presenting a typical core-shell structure, are considered as an attractive support for loading acidic ILs, making the resultant solid catalysts to be easily separated from the product and have good mechanical strength. In one study, 1-(propyl-3-sulfonate) imidazolium hydrogen sulfate [SO<sub>3</sub>H-(CH<sub>2</sub>)<sub>3</sub>-HIM][HSO<sub>4</sub>] was loaded on core-shell structured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composites through covalent bonds using 3-chloropropyltrimethoxysilane as a linking reagent, thus forming the IL-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> catalyst with strong magnetic responsiveness [70]. The so-prepared catalyst could disperse uniformly in the reaction mixture and showed good catalytic activities in the esterification of long-chain fatty acids with methanol and transesterification of soybean oil for the biodiesel production. Moreover, the IL-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> catalyst not only was isolated facilely with an external magnetic force with no obvious weight loss, and but also maintained satisfactory catalytic activity after being reused for eight times. Inspired by this excellent research, magnetic double-shell mesoporous material Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub> (FSS) was successfully prepared so as to immobilize Brønsted acidic IL 3-sulfopropyl-1-(3-propyltrimethoxysilane) imidazole bisulfate ([SO<sub>3</sub>H-PIM-TMSP]HSO<sub>4</sub>) for preparing the magnetic solid catalyst FSS-IL [71], as illustrated in Fig. 7. The central silica layer of FSS can efficiently avoid the leakage and corrosion of the magnetite core and the outside silica shell can provide functional groups to covalently bind the acidic ILs via silane chemistry. Thus, the active sites of the FSS-IL catalysts were fully exposed to the reactants due to their high surface area (S<sub>BET</sub> = 175 m<sup>2</sup>/g). This solid catalyst could reach 93.5% of biodiesel yield, and could be reused for several runs via magnetic separation without significantly losing its catalytic activity, thereof corroborating the environmental and economic viability. The mechanism of esterification reaction catalyzed by this FSS-IL catalyst was schematically illustrated in Fig. 8. In another work, the magnetic acidic ILs solid catalyst (FS-B-L-IL) was investigated, presenting the Brønsted (-SO<sub>3</sub>H) and Lewis (Fe<sub>2</sub>Cl<sub>7</sub><sup>-</sup>) acidic sites [72]. By using non-edible *Koeleria integrifoliola* (*K. integrifoliola*) oil with high acid value (4.66 mg KOH/g) as raw material, this FS-B-L-IL catalyst could achieve 93.7% of biodiesel yield through simultaneously catalytic transesterification and esterification of the crude *K. integrifoliola* seed oil in one-pot process. The activation energy for the reaction was calculated to be 62.6 kJ/mol. Main fuel properties of the resulting biodiesel could satisfy the standards of ASTM D6751 and EN 14,214 through comparing their physical and chemical properties.

Magnetic metal-organic framework (MOF) materials are also investigated as novel support materials for synthesizing the solid acid catalyst for the biodiesel production. For example, magnetic amino-functionalized MOF carrier Fe<sub>3</sub>O<sub>4</sub>@NH<sub>2</sub>-MIL-88B(Fe) was prepared by solvothermal method, and subsequently Brønsted sulfonic IL 1,4-butanediyl-3,3'-bis(3-sulfopropyl) imidazolium dihydrogensulfate (DAIL) was immobilized onto the Fe<sub>3</sub>O<sub>4</sub>@NH<sub>2</sub>-MIL-88B(Fe) support through the ion bonding action between the -SO<sub>3</sub>H groups in the DAIL with -NH<sub>2</sub>

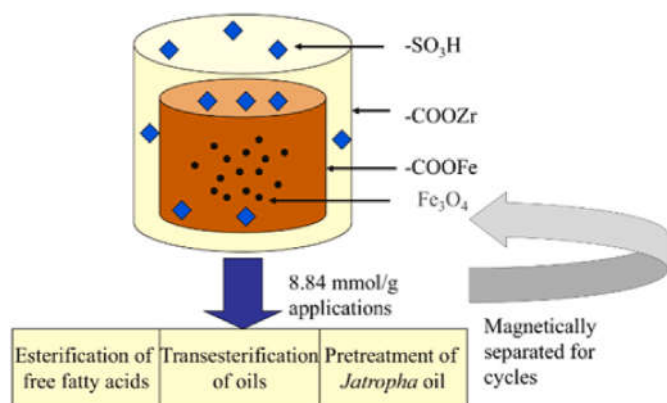


Fig. 6. Mesoporous magnetic biomass-based acidic catalyst for the biodiesel production [Reproduced from ref.67].



**Table 3**  
Magnetic solid acidic ionic liquids (ILs) catalysts for the biodiesel production.

Catalyst	Magnetic component	saturation magnetization	Feedstock	Optimum reaction conditions	Biodiesel yield	Refs.
IL-Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	26.1 emu/g	Oleic acid	110 °C; 4 h , ethanol/oil molar ratio 6:1; catalyst amount 10.8 wt%	92.9%	70
FSS-IL	Fe <sub>3</sub> O <sub>4</sub>	13.2emu/g	Oleic acid	110 °C; 4 h , ethanol/oil molar ratio 6:1; catalyst amount 10.06 wt%	93.5%	71
FS-B-L-IL	Fe <sub>3</sub> O <sub>4</sub>	22.1emu/g	Integrifoliola oil	160 °C , 10 h , ethanol/oil molar ratio 40:1; catalyst amount 10 wt%	93.7%	72
DAIL-Fe <sub>3</sub> O <sub>4</sub> @NH <sub>2</sub> -MIL-88B (Fe)	Fe <sub>3</sub> O <sub>4</sub>	7.2emu/g	Oleic acid	90 °C; 4 h , ethanol/oil molar ratio 10.5:1; catalyst amount 8.5 wt%	93.2%	73
CoFe <sub>2</sub> O <sub>4</sub> /MIL-88B(Fe)-NH <sub>2</sub> /(Py-Ps)PMo	CoFe <sub>2</sub> O <sub>4</sub>	18.5emu/g	Soybean oil	140 °C; 8 h , ethanol/oil molar ratio 30:1; catalyst amount 8 wt%	95.6%	74
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -PIL	Fe <sub>3</sub> O <sub>4</sub>	20.2emu/g	High FFA low-cost oils	120 °C; 6 h , ethanol/oil molar ratio 35:1; catalyst amount 9 wt%	93.3%	76
FnmS-PIL	Fe <sub>3</sub> O <sub>4</sub>	12.4emu/g	Oleic acid	120 °C; 6 h , ethanol/oil molar ratio 18:1; catalyst amount 5 wt%	91.7%	77

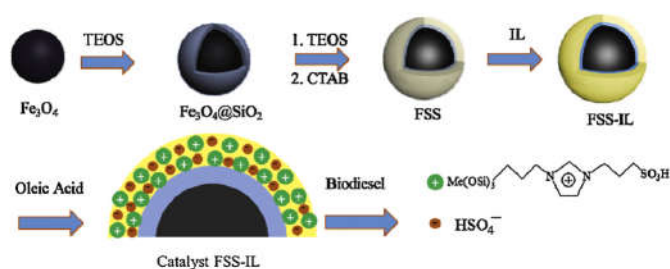


Fig. 7. Synthesis procedure of the FSS-IL catalyst [Reproduced from ref.71].

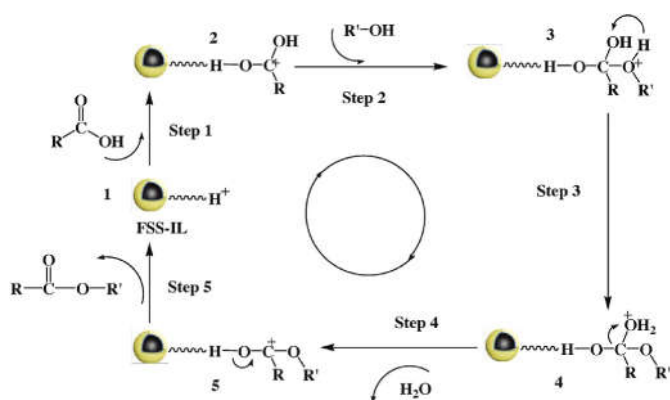


Fig. 8. The catalytic mechanism of esterification reaction catalyzed by FSS-IL catalyst [Reproduced from ref. 71].

groups on the surface of this magnetic solid support [73]. Satisfyingly, the formed magnetic DAIL-Fe<sub>3</sub>O<sub>4</sub>@NH<sub>2</sub>-MIL-88B(Fe) catalyst with high acidity (1.76 mmol/g) could give 93.2% of biodiesel yield and maintained more than 80% of biodiesel yield after six consecutive reuse cycles.

Similarly, polyoxometalate (POM)-based sulfonated ILs with Brønsted-Lewis acid sites, namely (Py-Ps)PMo, were also prepared by reaction of pyridine with 1,3-propanesultone, followed by anion exchange with phosphomolybdic acid (HPMo). Thereafter, the prepared acidic ILs were immobilized on the magnetic CoFe<sub>2</sub>O<sub>4</sub>/MIL-88B(Fe)-NH<sub>2</sub> support with the formation of the CoFe<sub>2</sub>O<sub>4</sub>/MIL-88B(Fe)-NH<sub>2</sub>/(Py-Ps)PMo catalyst, as visualized in Fig. 9 [74]. Compared to the DAIL-Fe<sub>3</sub>O<sub>4</sub>@NH<sub>2</sub>-MIL-88B(Fe) catalyst (DAIL: 1,4-butanediyl-3,3'-bis(3-sulfopropyl)), the so-synthesized solid catalyst owned better magnetic properties (*M<sub>s</sub>* = 18.5 emu/g) and higher catalytic performance by introducing the Lewis acid sites. Of particular interest, this catalyst could achieve the oil conversion of 95.6% through transesterification

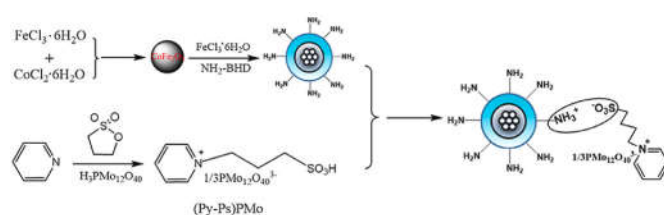
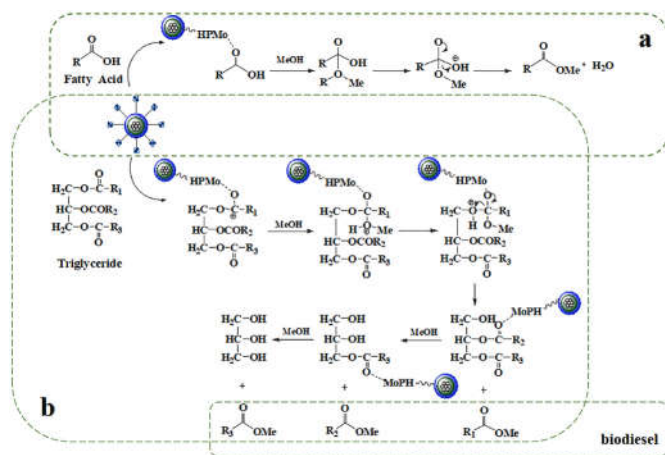


Fig. 9. Schematic illustration for the preparation of CoFe<sub>2</sub>O<sub>4</sub>/MIL-88B(Fe)-NH<sub>2</sub>/(Py-Ps)PMo catalyst. [Reproduced from ref.74].

reaction of triglycerides with methanol. The effect of FFAs and water present in oil feedstocks on the transesterification reaction was further investigated and the results confirmed that this catalyst had a better FFAs and water tolerant for the catalytic reaction. Moreover, the developed catalyst could be potential applicable for one-pot production of biodiesel from low-quality acidic oils through the transesterification of soybean oil and esterification of FFAs simultaneously. The easy catalyst recovery owing to its magnetic property is another significant advantage for this solid catalyst. In the structure of the solid catalyst, the loaded ILs could form some films on the catalyst surface, offering a homogeneous microenvironment to the rapid reaction. The surface acidic species could provide more easily accessible of catalytic sites available to the reactants, and hence the catalytic activity was substantially improved due to the loading of the ILs. Moreover, the pyridinium cation of the ILs was firmly bound to the POM anions by the ion exchange effect, efficiently preventing the active species from leaching from the magnetic support and thereof enhancing the reusability of the solid catalyst.

The mechanism for the magnetic solid acid-catalyzed reaction is proposed in Fig. 10 [74]. Firstly, the magnetic solid acid interacts with the carbonyl group of triglycerides or FFAs, and a carbocation is formed. Then, the nucleophilic reagent (mainly methanol) attacks the carbocation to generate the tetrahedral intermediate. Ultimately, the chemical bonds of the tetrahedral intermediates are readily broken with the production of one FAME and one diglyceride (DG) for the transesterification reaction, and one FAME and one water for the esterification reaction; meanwhile the solid catalyst is regenerated. In particular, for the transesterification reaction, this reaction mechanism could be repeated for the DG and monoglyceride, and 1 mol of FAME molecule was produced in each step.

Acidic ILs can be polymerized by themselves or copolymerized together with the formation of polymerized ILs (PILs) [75]. In the formed PILs, the acidic groups of each monomer IL are incorporated into the polymer chains, giving rise to affluent acidic groups in the polymeric materials through repeating chain unit. For instance, Xie et al. [76] immobilized the acidic ILs 1-vinyl-3-(3-sulfopropyl)imidazolium



**Fig. 10.** The proposed mechanism of the reaction catalyzed by  $\text{CoFe}_2\text{O}_4/\text{MIL-88B}(\text{Fe})\text{-NH}_2/(\text{Py-Ps})\text{PMo}$  catalyst: (a) free fatty acid and (b) triglyceride. [Reproduced from ref. 74].

hydrogen sulfate on the magnetic  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  composites by a graft-copolymerization approach to form the magnetic responsive  $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-PIL}$  catalyst. For the preparation of the magnetic core-shell structured support, the silica-coating procedure takes place on the magnetic nanoparticles *via* sol-gel approach with the hydrolyzation of tetramethyl orthosilicate (TEOS), which can enhance the chemical stability by protecting magnetic nanoparticles from aggregation, and moreover can introduce functional groups for further copolymerization reaction with azodiisobutyronitrile (AIBN) as an initiator. Notably, the combination of polymeric acidic IL with magnetic porous nanoparticles increases the catalytic activity and favors the easy and complete separation of the solid catalyst with an external magnet. Over this magnetic solid catalyst, the oil conversion of 93.3% and full conversion of FFAs could be attained for the simultaneous transesterification and esterification reactions of low-quality oils with high FFA content. The high acid density (3.65 mmol  $\text{H}^+$ /g) and high loading amount of the PILs (1.89 mmol/g) ensure this solid catalyst to display excellent catalytic performance, and the firm covalent binding of the acidic ILs with the solid support renders the catalyst to retain 84.5% of oil conversion after five reuse cycles. The influence of FFA and water in oil feedstocks on the transesterification reaction was investigated. It was indicated that this catalyst had good FFA- and water-tolerant capacity, retaining 76.8% of oil conversion as the water content was 5%, and maintaining 75.6% of oil conversion when the FFA content was 18%. In particular, this polymeric acidic ILs solid catalyst showed better catalytic activities for the esterification reaction of FFAs than the transesterification of soybean oil.

In another example [77], to improve the water-tolerant capacity of magnetic solid acidic PILs catalyst, a series of magnetic solid acidic PILs catalysts (FnmS-PILs) with varying hydrophobicity and controllable acidity was prepared by the copolymerization method using 2,2'-azobis (2-methylpropionitrile) as an initiator. Various anions ( $\text{CF}_3\text{SO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{Cl}^-$ , and  $\text{PW}_{12}\text{O}_{40}^{3-}$ ) were used as active sites to control the surface acidity of magnetic solid acid catalysts. Through introducing the different hydrophobic alkyl chain groups, the developed solid catalyst exhibited stronger hydrophobicity (water contact angle,  $115.4^\circ$ ). It was shown that the catalyst bearing  $\text{CF}_3\text{SO}_3^-$  anion and C8 alkyl chain possessed large surface area ( $S_{\text{BET}} = 128.1 \text{ m}^2/\text{g}$ ), strong magnetism (12.4 emu/g) and high loading amount of acidic PILs (2.14 mmol/g), thus displaying the best catalytic performance. Over this solid catalyst, the biodiesel yield of 95.3% was obtained under the mild reaction conditions:  $75^\circ\text{C}$  for 4 h with 17/1 methanol/oleic acid molar ratio and 4 wt% catalyst dosage. By using the crude *Euphorbia* oil with water content of 6% as oil feedstocks, this solid catalyst could afford above 90% of biodiesel yield, highlighting its excellent anti-water ability. The stronger hydrophobicity can obviously enhance the anti-deactivation

capacity of acidic sites caused by water, thereof exhibiting satisfactory reusability with biodiesel yield of 87.5% even after five reaction cycles. The obtained *Euphorbia lathyris* L. biodiesel properties were shown to meet the EN 14212 and ASTM D6751 standards.

#### 2.4. Magnetic mixed metal oxides

Mixed metal oxides are the traditional solid acid catalysts with high catalyst recovery rate and good reusability in organic transformations. In general, the density of Brønsted and Lewis acid sites together with the hydrophobicity in the mixed metal oxides can vary with the different ratios of individual metal oxide, which has a significant impact on their catalytic performance [29]. To improve their catalytic activity and reusability, various mixed metal oxides have fabricated in recent years for their practical biodiesel production applications. The sulfated zirconia owning both Lewis (anions) and Brønsted (cations) acid sites is identified as a robust solid acid catalyst for the biodiesel production mainly due to its strong acidic sites. For example, Wu et al. [78] successfully synthesized the magnetic solid acid catalyst  $\text{S}_2\text{O}_8^{2-}/\text{ZrO}_2\text{-TiO}_2\text{-Fe}_3\text{O}_4$  by co-precipitation and impregnation method for the biodiesel production from cottonseeds oils. In this contribution, the influence of Zr/Ti molar ratio and calcination temperature on the catalytic performance of this solid catalyst was extensively explored. The results showed that the solid catalyst calcined at  $550^\circ\text{C}$  with Zr/Ti = 3/1 (molar ratio) had the best catalytic activity, attaining the maximum biodiesel conversion of 98.5% under the optimum conditions (reaction time 10.8 h, reaction temperature  $50^\circ\text{C}$ , catalyst dosage 21.3 wt%). It is important to highlight that, after 14 recycle runs, this catalyst still remained above 85% productivity, revealing its excellent reusability and posing a high potential application in the heterogeneous biodiesel production.

Likewise, Bayat et al. [79] reported the preparation of  $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$  as an efficient nanocatalyst for use in the biodiesel production, which inherently owned the acidic sites confirmed by TPD of  $\text{NH}_3$ . The solid catalyst with  $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3 = 0.5$  (mass ratio) displayed the best activity for the transesterification of waste cooking oil to biodiesel, achieving the highest oil conversion about 99.1% by using this catalyst under the optimum reaction conditions of  $99.8^\circ\text{C}$ , methanol/oil ratio of 32.1, and a reaction time of 2.95 h. Also, the transesterification kinetics and thermodynamic studies were investigated; and it was indicated that the rate constants ranged from 0.059 to  $0.94 \text{ min}^{-1}$  and the activation energy was 55.48 kJ/mol. Besides, Dantas and coworkers [80] successfully developed the magnetic solid nanoparticles of  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  by a combustion method. This solid catalyst with abundant acidic sites showed highly catalytic efficiency in the biodiesel production, favoring more than 99% biodiesel yield *via* esterification reaction. By using this solid catalyst, 98% of biodiesel yield was remained after three recycle runs with the aid of an external magnet.

From the above presented works it can be concluded that the magnetic Brønsted-Lewis bifunctional solid acid catalyst is more attractive in the biodiesel production especially from the low-quality oil feedstocks through simultaneous transesterification of triglycerides and esterification of FFAs. Seemingly, Brønsted acidic sites show higher activities toward the esterification reaction, while Lewis acidic sites are more active toward the transesterification reaction. Therefore, the cooperatively loading of both Brønsted and Lewis acidic sites on the porous support, can efficiently enhance the catalytic performance of the thus-formed Brønsted-Lewis solid acid catalyst due to the favorable synergistic effect.

### 3. Magnetic solid base catalysts

One of the challenges for the solid acid catalyzed-biodiesel production is the low activity of the acid catalyst, and high reaction temperature often-required for the transesterification reaction. On the contrary, solid base catalysts have been widely applied in the transesterification of

triglycerides for the biodiesel production because of their higher transesterification activities in comparison with solid acid catalysts [81]. Generally, magnetic solid base catalysts could reach a satisfactory biodiesel yield with lower reaction temperatures and shorter reaction duration. However, for the oil feedstocks with high FFA and water contents, the base catalyst is not suitable, since FFA could react with the active species of solid base catalysts leading to undesirable soap formation, which could greatly deactivate the base catalyst, and impede the downstream separation and purification processes [82]. Therefore, the FFA and water contents in oil feedstocks should be reduced to a certain extent so as for the alkali-catalyzed transesterification reactions. In this section, the focus lies on the applicability of magnetic base catalysts for the biodiesel production.

### 3.1. Magnetic CaO-based solid catalyst

Calcium oxides formed through thermal decomposition of calcium carbonate by mean of calcinations at high temperature, can be utilized as a solid base catalyst thanks to its high basic strength. Some CaO catalysts are prepared from natural sources, mostly from different waste shells, for example waste eggshell, due to their readily available and renewable [15]. However, the application of CaO as a catalyst in a standalone form has serious drawbacks such as low surface and easy corrosion by moisture. Moreover, the solubility of CaO in methanol can be evidenced by performing in-situ filtration test and in-situ conductivity measurements [83]. Due to these reasons, the magnetic CaO-based solid catalysts have attracted considerable interest as a solid base catalyst as they commonly possess many benefits such as high activity, good stability and moderate reaction conditions [20]. In general, they can be fabricated by combining metal oxides with magnetic materials. Different magnetic nanoparticles as magnetic core for developing magnetic CaO-based catalysts were investigated, as listed in Table 4.

The magnetic monodisperse nanocrystals  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be used as magnetic core to prepare magnetic CaO-based catalysts. In a recent study by Ullah et al. for example [84], magnetic CaO-based catalyst (CaO- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was prepared from Ca(OH)<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> by a in-situ co-precipitation method, and as a promising solid catalyst for the biodiesel production, could be reused for more than four times without significant deterioration in its activity. This magnetic nanocatalyst possessed good magnetic property with high saturation magnetism (M<sub>s</sub> = 45.6 emu/g), advantageously showing high catalytic activities towards the biodiesel production from hemp oil. Herein, 92.16% of biodiesel yield was obtained under the reaction conditions of methanol/oil molar ratio of 6:1, reaction temperature of 60 °C, reaction duration of 2

h and catalyst loading of 2.25 wt%. Likewise, a similar CaO@  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst was successfully prepared by Shi and coworkers [85], and then was applied for the catalytic transesterification of soybean oil, palm oil and castor oil into biodiesel. In this study, two different Fe<sub>2</sub>O<sub>3</sub> crystals were prepared with and without KNO<sub>3</sub> for being employed as magnetic cores for loading CaO. The KNO<sub>3</sub> addition had a significant impact on the crystal type of Fe<sub>2</sub>O<sub>3</sub>, and the formed CaO@  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> showed higher catalytic activity than CaO@hematite Fe<sub>2</sub>O<sub>3</sub> mainly due to the stronger basicity. During the catalyst preparation procedure, the formation of Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> was beneficial for the composite catalyst to display good performance for the biodiesel production. Over this CaO@  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst, the biodiesel yield could be remained about 95% even as the acid value of oil feedstocks was 4 mg KOH/g, posing a good acid-resistance capacity.

Besides, to address the Ca<sup>2+</sup> leaching from the catalyst surface, MIL-100(Fe) metal organic framework and calcium acetate were used as precursors to synthesize the magnetic CaO-based CAM750 catalyst [86]. This magnetic solid catalyst demonstrated excellent catalytic efficiency and strong magnetism (112 emu/g), giving 95.09% conversion of palm oil to biodiesel with catalyst amount of 4 wt% and molar ratio of methanol to oil of 9:1 at 65 °C for 2 h. The formed crystallines of Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> and CaFe<sub>3</sub>O<sub>5</sub> are the predominant active sites for this catalyst. In the catalytic biodiesel production process, Ca<sup>2+</sup> leaching was almost prohibited during the repeated cycle, in which the leached Ca<sup>2+</sup> in biodiesel at the fourth cycle (1.4 mg/kg) was much less than the limit of EN 14214 standard. Lately, as an effort to improve the catalytic performance, Ibrahim et al. [87] employed activated carbon (AC) with high surface porosity to support the magnetic CaO-based catalyst for increasing the catalyst surface area. In this research, the CaO-Fe<sub>2</sub>O<sub>3</sub>/AC catalyst was synthesized via wet impregnation method and was then utilized for catalytic transesterification of waste cooking oil (WCO). The so-prepared catalyst possessed a high surface area of 106.28 m<sup>2</sup>/g, thus endowing the higher availability of catalytic sites. By using this solid catalyst, the oil conversion of 98.3% was achieved at 3 wt % catalyst loading, 18:1 methanol to oil molar ratio, 65 °C temperature, and 3 h reaction duration. Moreover, this catalyst had high recovery rates from the reaction mixture by magnetic decantation, with high catalytic stability (oil conversion >80%) for at least six consecutive cycles.

Other monodisperse ferrite nanocrystals used as the magnetic core, including CoFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub> and MnFe<sub>2</sub>O<sub>4</sub>, are also synthesized by hydrothermal method for preparing the magnetic catalysts. For example, Zhang et al. [88] prepared a series of magnetic solid base catalyst by hydrothermal method, such as CaO/CoFe<sub>2</sub>O<sub>4</sub>, CaO/ZnFe<sub>2</sub>O<sub>4</sub>, and CaO/MnFe<sub>2</sub>O<sub>4</sub>. Among these CaO-based catalysts, the CaO/CoFe<sub>2</sub>O<sub>4</sub>

**Table 4**  
Magnetic CaO-based solid catalysts for the biodiesel production.

Catalyst	Magnetic component	Saturation magnetization	Feedstock	Optimum reaction condition				Biodiesel yield	Refs
				Temperature (°C)	Reaction time	Catalyst loading (wt%)	Substrate molar ratio		
CaO- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	45.6 emu/g	Hemp oil	60	2 h	2.25	6 : 1	92.16%	84
CaO@ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	4 emu/g	Soybean oil	70	3 h	2	15 : 1	98.8%	85
			Palm oil					95.8%	
			Castor oil					90.9%	
Magnetic CaO-based CAM750	CaFe <sub>3</sub> O <sub>5</sub>	112 emu/g	Palm oil	65	2 h	4	9 : 1	95.09%	86
CaO-Fe <sub>2</sub> O <sub>3</sub> /AC	Fe <sub>2</sub> O <sub>3</sub>	7.59 emu/g	Cooking oil	65	3 h	3	18 : 1	98.3%	87
CaO/CoFe <sub>2</sub> O <sub>4</sub>	CoFe <sub>2</sub> O <sub>4</sub>	45 emu/g	Soybean oil	70	5 h	1	15 : 1	87.4%	88
MgFe <sub>2</sub> O <sub>4</sub> @CaO	MgFe <sub>2</sub> O <sub>4</sub>	39.3 emu/g	Soybean oil	70	3 h	1	12 : 1	98.3%	89
CaO@ (Sr <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub> -Fe <sub>2</sub> O <sub>3</sub> )	Fe <sub>2</sub> O <sub>3</sub>	11.09 emu/g	Soybean oil	70	2 h	0.5	12 : 1	94.9%	90
KF/CaO-Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	8.16 emu/g	Stillingia oil	65	3 h	4	12 : 1	>95%	92
KF/eggshell-Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	-	Crude neem oil	65	2 h	6	15 : 1	97%	93
Ca/Al/Fe <sub>3</sub> O <sub>4</sub>	Fe <sub>3</sub> O <sub>4</sub>	6.34 emu/g	Rapeseed oil	65	3 h	6	15 : 1	98.7%	94
CaO/Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	11 emu/g	Waste sunflower oil	65	5 h	6	15 : 1	97%	96

**Table 5**  
Covalent attachment immobilization of lipase on magnetic nanocomposites for the biodiesel production.

Lipase	Carrier	Oil feedstock	Optimum reaction conditions	Biodiesel yield	Refs.
Candida antarctica lipase B	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -epoxy	waste cooking oil	50 °C; 72 h; methanol/oil molar ratio 3:1	48%	126
<i>Pseudomonas cepacia</i> lipase	polymer-coated Fe <sub>3</sub> O <sub>4</sub> cluster@SiO <sub>2</sub> nanocomposite particles	soybean oil	50 °C; 24 h; methanol/oil molar ratio 3:1; three steps; 200 rpm	73.1%	127
Rhizomucor miehei lipase (RML)	<i>m</i> -MWCNTs-PAMAM matrix	waste vegetable oil	50 °C; 10 h; methanol/oil molar ratio 4:1; biocatalyst amount 6 wt%; three steps	94%	128
Candida rugosa lipase	Fe <sub>3</sub> O <sub>4</sub> /poly magnetic microsphere	soybean oil	35 °C; 24 h; methanol/oil molar ratio 4:1; biocatalyst amount 50 wt%; three steps	86%	129
Candida rugosa lipase	magnetic chitosan microspheres	soybean oil	35 °C; 30 h; methanol/oil molar ratio 4:1; biocatalyst amount 40 wt%; three steps	87%	131
<i>Pseudomonas fluorescens</i> lipase	magnetic chitosan microspheres	coconut oil	30 °C; 80 min; ethanol/oil molar ratio 11.25:1; biocatalyst amount 9.6 wt %	97.8%	132
<i>G.stearothermophilus</i> (GSlip-CBD) lipase	magnetic cellulose nanospheres	palm oil	55 °C; 6 h; methanol/oil molar ratio 3.5:1 biocatalyst loading 15 U	98%	133
Candida rugosa lipase	graphene oxides-Fe <sub>3</sub> O <sub>4</sub> nanocomposite	soybean oil	40 °C; 60 h; methanol/oil molar ratio 4:1 biocatalyst amount 25 wt %	93.2%	134
Candida rugosa lipase	Fe <sub>3</sub> O <sub>4</sub> @MIL-100(Fe) composite		40 °C; 60 h; methanol/oil molar ratio 4:1; biocatalyst 25 wt %; three steps	92.1%	135

catalyst exhibited higher catalytic activity, stronger wettability and weaker hydroscopicity with the saturation magnetism ( $M_s = 45 \text{ emu/g}$ ), reaching the best catalytic activity with 87.4% of biodiesel yield. It was shown that the catalytic performance was associated with both basicity of the catalyst and the full contact between the catalyst and the reactants. After reuse of this catalyst for five cycles, the biodiesel yield could still remain at 80%. In another study, the magnetic nanoparticle ( $\text{MgFe}_2\text{O}_4$ ) was coated by CaO using the alkali precipitation approach with the presence of sodium dodecylbenzenesulfonate (SDBS) [89], and the formed  $\text{MgFe}_2\text{O}_4@CaO$  catalyst with core-shell structure had highly catalytic efficiency for the soybean oil transesterification with methanol due to the synergism between calcium and magnesium. The 98.3% of biodiesel yield could be obtained by using this solid base catalyst under the reaction conditions of catalyst dosage of 1.0 wt%, methanol/soybean oil ratio of 12:1, reaction temperature of 70 °C, reaction time of 3 h. As compared with the CaO catalyst, the  $\text{MgFe}_2\text{O}_4@CaO$  catalyst had higher catalytic activity, better acid-resistance and stronger water-resistance in the catalytic process of biodiesel production.

Using SrO as co-catalyst could improve the catalytic performance of the magnetic CaO-based catalyst [90]. For this aim, Sr doping magnetic ferrite ( $\text{Sr}_2\text{Fe}_2\text{O}_5\text{-Fe}_2\text{O}_3$ ) coated with CaO was synthesized by co-precipitation method for the biodiesel production (Fig. 11). As compared with pure CaO, the formed  $\text{CaO}@(Sr_2Fe_2O_5\text{-Fe}_2O_3)$  catalyst showed better catalytic activity, higher FFA-resistance and better water-resistance in the transesterification process, giving 94.9% of biodiesel yield and being highly stable even after five repeated runs.

The incorporation of alkaline metallic elements into the CaO-based solid catalysts is reported as a viable tactic to increase their catalytic performances [91]. Incipient wetness technique is generally used to load

alkaline metal elements with metal salts as precursor compounds. In one work, Hu et al. [92] prepared a series of magnetic KF-doping CaO-based catalyst by impregnation and calcination method, including  $\text{KF/CaO-Fe}_3\text{O}_4$ ,  $\text{KF/MgO-Fe}_3\text{O}_4$  and  $\text{KF/SrO-Fe}_3\text{O}_4$  catalyst. The experimental results indicated that  $\text{KF/CaO-Fe}_3\text{O}_4$  catalyst, on one hand, owned the highest catalytic activity with the achieved biodiesel yield of 95% as KF loading was 25 wt%; on the other hand, this solid catalyst could maintain about 85% of biodiesel yield even after being reused for 14 times. Notably, during the catalyst preparation procedure,  $\text{KCaF}_3$  species were presented, which could greatly improve the catalytic activity and stability of the  $\text{KF/CaO-Fe}_3\text{O}_4$  catalyst. In another work by Oladipo et al. [93], to reduce the preparation cost, they utilized the waste eggshells as raw materials to synthesize a magnetically recyclable eggshell-based solid catalyst (MKEC,  $\text{KF/eggshell-Fe}_3\text{O}_4$ ) via co-precipitation method. In this work, the biodiesel conversion of 97% was obtained using neem oil with 4.2% of FFAs as feedstocks, and the conversion to biodiesel also reached 94.5% by using waste cooking oil as feedstocks. The obtained solid catalyst functionalized with alkaline metallic element (KF) had high catalytic activity and high acid-resistance for the reaction, advantageously with no noticeable deterioration in its catalytic activity even after five reaction cycles. Accordingly, the incorporation of alkaline metals can strengthen the basic properties of the solid catalysts, producing more Brønsted base sites.

Inspired by the works mentioned above, by changing the load of different basic sites on the catalyst surface, the catalytic performance is significantly improved accordingly [20]. In the literature [94], calcium aluminate metals were incorporated into  $\text{Fe}_3\text{O}_4$  nanoparticles to prepare magnetic  $\text{Ca/Al/Fe}_3\text{O}_4$  catalyst. The highest biodiesel yield of 98.7% for

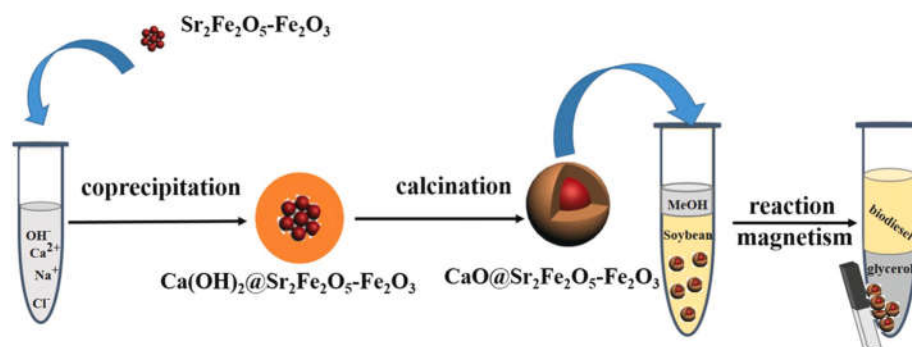


Fig. 11. Diagrammatic representation for the preparation of  $\text{CaO}@(Sr_2Fe_2O_5\text{-Fe}_2O_3)$  catalyst [Reproduced from ref.90].

the transesterification of rapeseed oil was obtainable over the magnetic composite catalyst. It is more convenient and thorough to separate the magnetic calcium aluminate catalyst from the reaction mixture with an external magnet. The catalytic activity and recovery rate of the magnetic catalysts were much better than those of the pure calcium aluminate catalyst.

Magnetic nanoparticles tend to inter-particle aggregations due to their higher surface energy and magnetic dipole-dipole attractions, thereof affecting their uniform dispersion in the reaction mixture [95]. The encapsulation of magnetic particles with porous materials is a viable strategy to effectively alleviate the magnetic aggregations. In a study by Feyzi et al. [96], the magnetic core-shell  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  composites were initially prepared, and then CaO was loaded onto the magnetic composite, so as to form  $\text{CaO}/\text{Fe}_3\text{O}_4/\text{SiO}_2$  catalysts via sol-gel and incipient wetness impregnation methods. The thus-prepared catalyst possessed a high surface area ( $189.2 \text{ m}^2/\text{g}$ ), affording the transesterification conversion of waste sunflower oil of 97%. This solid catalyst could be recovered simply by using an external magnetic field and the oil conversion still reached above 90% after five transesterification recycles. Interestingly, this catalyst could be facilely dispersed in the reaction mixture by shaking without evidence for agglomerations, thus leading to a uniform dispersion solution.

### 3.2. Other metal oxides-based magnetic catalyst

In addition to the magnetic CaO-based solid catalyst, other metal oxides are also utilized as active centers to prepare magnetic solid base catalysts suitable for the biodiesel production.

Magnesium oxide is introduced as a favorable catalytic species for the biodiesel production. Even though MgO does not have as strong of basic sites as CaO, it is not sensitive to the moisture present in the reactants, showing more stability and reusability of the solid catalyst. Lately, a study had been performed by Alaei et al. [97] to prepare magnetic  $\text{MgO}/\text{MgFe}_2\text{O}_4$  nanocatalysts via combustion method. The obtained solid catalyst with large pore ( $>10 \text{ nm}$ ) and high surface area ( $97.8 \text{ m}^2/\text{g}$ ), displayed high catalytic activity for the transesterification of sunflower oil, affording the biodiesel yield of 91.2% under the reaction conditions of temperature  $110 \text{ }^\circ\text{C}$ , methanol-to-oil molar ratio 12:1, catalyst dosage 4 wt% and reaction time 4 h. After five consecutive transesterification runs, the biodiesel yield of 82.4% was still achieved. This solid catalyst has many merits such as easy magnetic separation, high purity of final product, reusable, no need to further wash the final product. In another study done by Rahimi et al. [98],  $\text{MgO}/\text{Fe}_2\text{O}_3\text{-SiO}_2$  core-shell magnetic nanocatalyst was prepared by precipitation method for the biodiesel production from the transesterification of camelina seed oil with methanol. A high biodiesel yield of 99% over this magnetic base catalyst was obtained under optimized transesterification conditions (methanol to oil molar ratio 12:1, catalyst amount 4.9%, reaction temperature  $70 \text{ }^\circ\text{C}$  and reaction time 4.1 h). Moreover, this  $\text{MgO}/\text{Fe}_2\text{O}_3\text{-SiO}_2$  nanocatalyst could be removed facilely from the reaction mixture by a magnet and the catalytic activity still well-maintained for four reused cycles. The obtainable camelina biodiesel property values were within the specified value of EN142 14 standards.

By grinding and calcining the mixture of iron oxide ( $\text{Fe}_2\text{O}_3$ ) and  $\text{Li}_2\text{CO}_3$ , the catalyst of magnetic  $\text{LiFe}_5\text{O}_8\text{-LiFeO}_2$  was synthesized through a simple solid state reaction [99]. The components of the prepared solid catalysts were determined as lithium-iron oxides, namely  $\text{LiFe}_5\text{O}_8\text{-LiFeO}_2$ , with the basic strength of  $9.8 < \text{H}^- < 15.0$ . This catalyst could give the highest biodiesel yield of 96.5% by the transesterification of soybean oil and maintained the biodiesel yield of 94% even after five catalytic reaction runs. Besides, bimetallic Fe(III) doped ZnO (FZO) nanoparticles (NPs) were also reported to be employed as heterogeneous nano-catalysts for the biodiesel production [100]. This solid catalyst (FZO) had good activities for soybean oil transesterification, and could be recovered by an external magnetic field and reused with no significant decline in its activity. In order to enhance the magnetism and

simplify the synthesis method, Salimi et al. [101] successfully prepared new magnetic core  $\text{BiFeO}_3$  by a simple co-precipitation method, which could be used to manufacture the magnetic  $\text{ZnO}/\text{BiFeO}_3$  catalyst. This solid catalyst possessed super-paramagnetic behavior with satisfactory magnetization ( $M_s = 13.65 \text{ emu/g}$ ), reaching the maximum oil conversion of 95.43% from canola oil through the transesterification reaction under the reaction conditions: methanol/canola oil molar ratio of 15:1, a reaction temperature of  $65 \text{ }^\circ\text{C}$  and a catalyst amount of 4 wt%. The catalyst characterization results showed that the incorporation of ZnO into  $\text{BiFeO}_3$  could promote the surface basicity of the solid catalyst, resulting in the enhancement of the catalyst activity for the transesterification reaction. By recycling this solid catalyst with an external magnetic field, the good reusability was verified with more than 90% oil conversion after reuse of this catalyst for five times.

The incorporation of the strong alkaline site (for instance,  $\text{K}_2\text{O}$  species) into the solid base catalyst can greatly improve its catalytic performance in the biodiesel production. For example, the magnetic bamboo charcoal  $\text{BC-Fe}_2\text{O}_3$  composite was prepared by an in-situ method, and subsequently was treated through impregnating  $\text{KNO}_3$  solution [102]. After high-temperature calcinations at  $500 \text{ }^\circ\text{C}$ , the magnetic nanoparticles were presented as  $\gamma\text{-Fe}_2\text{O}_3$ , finely fixing to the carbon skeleton of the bamboo charcoal. The obtained  $\text{K}/\text{BC-Fe}_2\text{O}_3$  catalyst was used for the transesterification of soybean oil to biodiesel. In this contribution, the formation of the active site ( $\text{K}_2\text{O}$ ) was confirmed by suitable characterization techniques, and the possible formation mechanism was proposed. For the magnetically responsive catalysts, huge average pore diameter ( $14.5 \text{ nm}$ ) could ensure enough alkaline active sites to be loaded; meanwhile the saturation magnetization value approached  $35.4 \text{ emu/g}$ . By using this magnetic catalyst, the biodiesel yield of 98.0% was achieved. Through re-activation of the recovered catalyst at  $500 \text{ }^\circ\text{C}$ , the biodiesel yield retained 94.0% after the catalyst was reused for four times. Similarly, magnetic zeolite mesoporous material  $\text{ZSM-5-Fe}_3\text{O}_4$  was also investigated as carrier for loading  $\text{K}_2\text{O}$  owing to its high specific surface area and huge porosity [103]. The effect of KOH loading amount on the catalytic performance and the kinetics of this catalytic reaction were also explored. Both solid catalysts ( $\text{K}/\text{BC-Fe}_2\text{O}_3$  and  $\text{KOH}/\text{ZSM-5-Fe}_3\text{O}_4$ ) with  $\text{K}_2\text{O}$  active sites possessed excellent paramagnetism ( $M_s = 25 \text{ emu/g}$ ) and satisfactory catalytic performance for the transesterification of canola oil to produce biodiesel. Using these solid catalysts, the biodiesel yield of 93.65% was attained with 12.3 M ratio of methanol to oil and 9.03% catalyst loading at a reaction temperature of  $65 \text{ }^\circ\text{C}$  for 3.26 h of reaction time. Especially, the transesterification reaction kinetics was investigated, suggesting that the catalytic process obeys the behavior of pseudo-first order reactions with the activation energy of  $122.7 \text{ kJ/mol}$ .

### 3.3. Alkaline ionic liquids-supported magnetic catalyst

As compared to magnetic acidic ILs solid catalysts, alkaline ILs-based solid catalysts for the biodiesel production were less reported mostly due to their low thermal stability [104]. Some functional alkaline ILs were prepared through ion exchange methods, and then were loaded on magnetic porous supports so as to synthesize magnetic ILs-based alkali catalysts. Generally, alkaline ILs are mainly imidazolium-based ILs, and the prepared magnetic basic ILs-based solid catalysts have been used for the biodiesel production.

In a study of Zhang and co-workers [105], 1-allyl-dodecylimidazolium hydroxide ( $[\text{ADIm}][\text{OH}]$ ) basic ILs were immobilized on the magnetic mesoporous  $\text{SiO}_2/\text{CoFe}_2\text{O}_4$  nanoparticles (SCF) and magnetic  $\text{CoFe}_2\text{O}_4$  nanoparticles (CF) to synthesize the  $[\text{ADIm}][\text{OH}]/\text{SCF}$  and  $[\text{ADIm}][\text{OH}]/\text{CF}$  catalysts. The SCF carrier consisted of mesoporous silica and uniformly dispersed  $\text{CoFe}_2\text{O}_4$  nanoparticles, while the CF carriers were nanosized  $\text{CoFe}_2\text{O}_4$  particles with a mean size of  $15 \text{ nm}$ . The two magnetic catalysts showed better catalytic activities for the transesterification reaction as compared to NaOH, and moreover had excellent paramagnetism. The influence of pore diffusion on the

catalytic performance was extensively tested. Due to the effect of pore diffusion, for one thing [ADIm][OH]/SCF presented a lower catalytic activity at the beginning of the reaction but a higher catalytic activity as reaction time was long enough; for another thing the recycled [ADIm][OH]/SCF owned better catalytic stability.

In another example [106], as illustrated in Fig. 12, a novel magnetic mesoporous carrier ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-15}$ ) was initially prepared, and was then used to support basic polymeric ILs (PILs), with the formation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-15}$ -PILs catalyst. Herein, the basic PILs were formed through the facile radical polymerization and anion exchange methods. The synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-15}$ -PILs catalyst possessed uniform core-shell structure, high surface area ( $153.2 \text{ m}^2/\text{g}$ ), strong magnetism ( $13.6 \text{ emu/g}$ ) and relatively high basicity ( $2.3 \text{ mmol/g}$ ), thus exhibiting good catalytic activity to the transesterification of non-food *Firmiana platanifolia* Lf. oil with 92.8% of biodiesel yield. This catalyst could be facilely recovered by magnetic separation, still remaining above 90% of biodiesel yield even after five consecutive cycles. The activation energy ( $E_a$ ) for the transesterification reaction was measured by kinetics analysis to be  $51.6 \text{ kJ/mol}$  along with a determined pseudo first order model. The obtainable biodiesel properties were within the acceptable specifications of EN 14212 and ASTM D6751.

In our previous work [107], the amino-functionalized basic IL (ABIL-Im) was successfully immobilized on magnetic metal-organic framework composites  $\text{Fe}_3\text{O}_4@\text{HKUST-1}$  by coordination effect to synthesize the magnetic solid base catalyst ( $\text{Fe}_3\text{O}_4@\text{HKUST-1-ABILs}$ ) (Fig. 13). The  $\text{Fe}_3\text{O}_4@\text{HKUST-1-ABILs}$  catalyst displayed a superparamagnetic behavior and was easily separated by an external magnetic field. As this magnetic catalyst was used for soybean oil transesterification reaction with methanol, 92.3% of biodiesel yield was achieved. Furthermore, this catalyst could be reused for five times without significant degradation of its catalytic activity.

### 3.4. Magnetic supported $\text{Na}_2\text{SiO}_3$ catalyst

Very recently, sodium silicate ( $\text{Na}_2\text{SiO}_3$ )-based solid catalyst is emerged to be a promising heterogeneous base catalyst for the biodiesel production because it has strong alkalinity and excellent catalytic activity in the transesterification reaction [108,109].

Zhang et al. developed two magnetic carbonaceous composites  $\text{Fe}_3\text{O}_4/\text{C}$  [110] and Ni/JRC [111] as magnetic carriers to immobilize sodium silicate for the production of biodiesel. The formed magnetic solid catalysts were then utilized for the transesterification reaction, by using crude Jatropha oil with different acid values (AV) as raw materials to investigate the catalyst resistance to FFAs. Under ultrasonic irradiation assistant and optimal reaction conditions, the  $\text{Na}_2\text{SiO}_3@\text{Fe}_3\text{O}_4/\text{C}$

catalyst with  $\text{Fe}_3\text{O}_4$  core and active carbon material shell could achieve the biodiesel yield of 93.2% using Jatropha oil with AV of  $4.8 \text{ mg KOH/g}$  as raw materials [110]. The biodiesel yield rate could be attained above 80% over this magnetic solid catalyst using Jatropha oil with high AV of  $7.3 \text{ mg KOH/g}$  as oil feedstocks. Besides, by applying nickel oxide as magnetic core and Jatropha residue carbon as carbon source, the magnetic Ni/JRC composite was prepared so as to support sodium silicate, thus forming the  $\text{Na}_2\text{SiO}_3/\text{Ni/JRC}$  catalyst with the saturation magnetism of  $15.0 \text{ emu/g}$  and the base site density of  $3.24 \text{ mmol/g}$  [111]. The so-prepared  $\text{Na}_2\text{SiO}_3/\text{Ni/JRC}$  catalyst was utilized in the biodiesel production with FFA-containing oil feedstocks through a two-step transformation method. Firstly, the esterification of crude Jatropha oil with AV of  $17.2 \text{ mg KOH/g}$  was carried out by using the magnetic  $\text{C-SO}_3\text{H}/\text{Fe}/\text{JHC}$  acid catalyst, so that the high AV of Jatropha oil was decreased to  $1.3 \text{ mg KOH/g}$ . And then, the  $\text{Na}_2\text{SiO}_3/\text{Ni/JRC}$  was employed to catalyze the subsequent transesterification reaction and the biodiesel yield of 96.7% was reached. The two magnetic heterogeneous catalysts were magnetically recycled for several times with good reusability without significant loss of the catalytic performance.

Also, our research group [112] successfully prepared a magnetic  $\text{Fe}_3\text{O}_4/\text{MCM-41}$  composites with core-shell structure, and then sodium silicate was covalently tethered on the magnetic materials by using epichlorohydrin as a cross-linking reagent. The solid base catalyst exhibited a strong magnetic response ( $M_s = 31.8 \text{ emu/g}$ ) and displayed extraordinary catalytic activities in the transesterification of soybean oil for the production of biodiesel. This solid catalyst could give 99.2% of biodiesel yield under the transesterification conditions of the methanol/oil molar ratio of 25:1 and catalyst loading of 3 wt% after 8 h of reaction. After magnetically recycled for five cycles by an external permanent magnet, this magnetic catalyst remained high residual activity, achieving 83.6% of biodiesel yield.

### 3.5. Magnetic guanidine-based solid catalysts

Several types of organic bases have already been immobilized on porous supports with the aim to prepare the solid base catalyst. Especially, the organic guanidine base, known as a strong organic base, is loaded on magnetic composites, and these formed organic-inorganic hybrid materials are acted as a new generation of heterogeneous base catalyst for the biodiesel production [113].

One of the examples of the use of magnetic guanidine-based catalyst in the biodiesel production was carried out by Chiang et al. [114], who grafted triazabicyclodecene (TBD) on magnetic core-shell structured  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  MNPs via a covalent binding of nucleophilic pyrimido-nitrogen of TBD by using the epoxy-containing silane

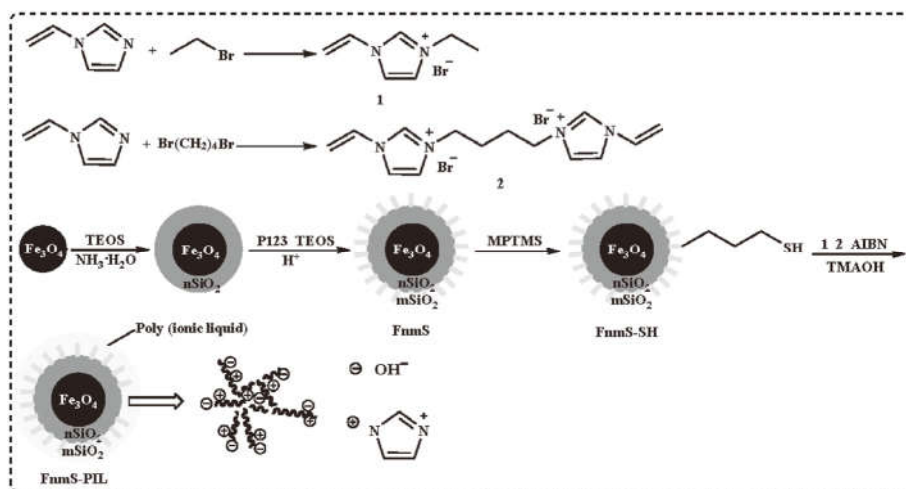


Fig. 12. Synthesis procedure of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-15}$ -PILs catalyst [Reproduced from ref.106].

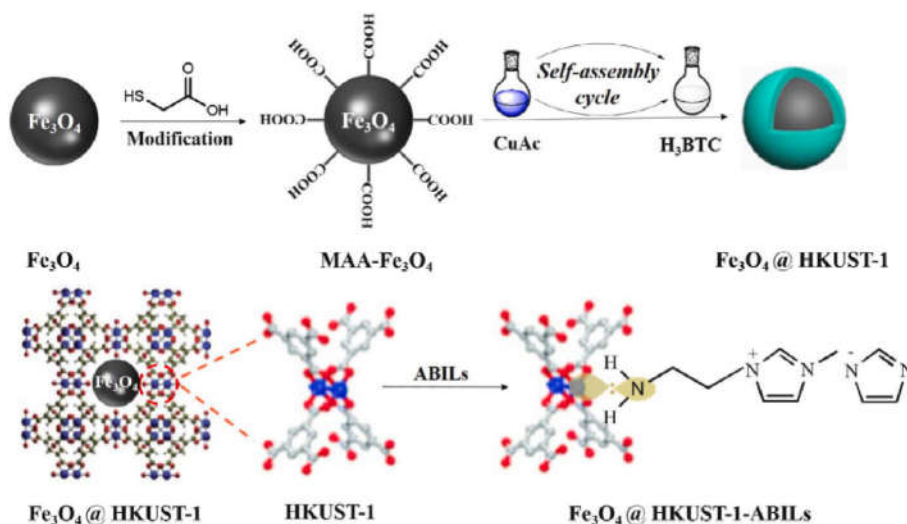


Fig. 13. Synthesis procedure of the  $\text{Fe}_3\text{O}_4$ @HKUST-1-ABILs catalyst [Reproduced from ref.107].

(trimethoxysilylpropoxymethyloxirane) as a linkage agent. This approach of functionalizing the magnetic silica composite with the covalent binding of TBD is dependent on the easily grafting of the epoxysilane on the silica surface by the reaction with the surface silanol groups. This enables the epoxy group of bonded silanes to be accessibly opened for further surface functionalization. The TBD- $\text{Fe}_3\text{O}_4$ @silica composites with the specific surface area of  $103.4 \text{ m}^2/\text{g}$  could efficiently transform algae oils into biodiesel in a heterogeneous manner with a highest conversion of 97.1%.

Another example was reported by Tang et al. [115], in which 1,1,3,3-tetramethylguanidine (TMG) was successfully loaded onto the magnetic  $\text{Fe}_3\text{O}_4$ @Chloromethyl PS nanohybrids and then employed as solid catalysts for improving the efficiency of biodiesel production, as shown in Fig. 14. For the transesterification of soybean oil, this  $\text{Fe}_3\text{O}_4$ @PS-TMG catalyst with amphiphilic surface could stabilize soybean oil-in-methanol Pickering emulsion, thus providing large interfacial area as well as surface enrichment of reactants, and resulting in a significant increment of oil transesterification rate. The Pickering emulsion was expected as dispersed microreactors, which possessed more interface areas and shorter molecule distances. This organic base solid catalyst was paramagnetic with the saturation magnetism of  $5.3 \text{ emug/g}$ , rendering magnetic responsiveness controllable and easy separation of the solid catalysts. After five reuse cycles in the transesterification reaction, the oil conversion still achieved 97.2%, representing the excellent reusability of this magnetic solid catalyst.

As an extension work in developing efficient and environmental

benign processes for the biodiesel production, our group [116] covalently anchored 1,1-dimethylbiguanide onto the hydroxyapatite-encapsulated  $\gamma\text{-Fe}_2\text{O}_3$  magnetic nanoparticles using 3-chloropropyltrimethoxysilane as a cross-linking reagent (Fig. 15), and the obtained magnetic responsive composites were then utilized to catalyze the transesterification of soybean oil with methanol. Through encapsulation of magnetic nanoparticles with the hydroxyapatite layer, the magnetic aggregation of the nanoparticles was efficiently prevented, and the stability of the formed magnetic nano-catalysts was accordingly improved. The maximum oil conversion of 99.6% was achieved over this magnetic nano-catalyst, due to its strong basic strength ( $\text{H}_\text{L}$ ) of 9.8–15.0 and relatively high BET surface area of  $83 \text{ m}^2/\text{g}$ . Further, even after reuse for five cycles, the oil conversion was still attained above 90% over the magnetic nano-catalyst, which highlighted the satisfactory reusability of the solid catalyst.

Although there has been much progress in the development of magnetic solid base catalyst for the biodiesel production, the catalytic performance, in particular the catalytic stability to the FFAs and water, should be further improved. In order to enhance the mass diffusion of bulky triglycerides on the catalyst surface, the hierarchically porous support with excellent surface diffusion nature seems to be promising catalyst supports for synthesis of the magnetic solid base catalysts. Therefore, more innovative researches should be dedicated to designing porous solid base catalysts with multi-functionality for the efficient biodiesel production.

#### 4. Magnetic solid lipase catalyst

In comparison with the chemical catalyst, lipase catalyst used for the biodiesel production has several benefits, including milder reaction conditions, minimal or no side reaction, environmentally-friendly character and low sensitivity to FFAs [117]. Among the lipases employed for the oil transesterification, microbial lipases, for example, the lipase from *Candida Antarctica* or *Rhizopus oryzae* (Lipozyme), are widely utilized as biocatalysts for the transesterification reaction, since they generally showed good stability at relatively high reaction temperature at a wide pH range. However, it still remains challenging for the implementation of lipase-catalyzed biodiesel production in industrial scale to reduce the high cost of the lipase and to efficiently recover the enzyme. The immobilization of lipase onto the porous support is a promising tactic to confer the lipase recovery and improve the lipase reusability.

Lipase has a peculiar catalytic mechanism, since it possesses two conformations: a closed form in which the active sites are secluded from

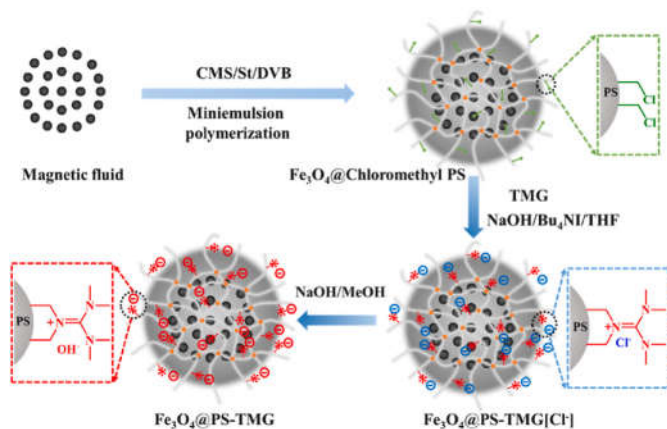


Fig. 14. Synthesis of the  $\text{Fe}_3\text{O}_4$ @PS-TMG catalyst [Reproduced from ref.115].

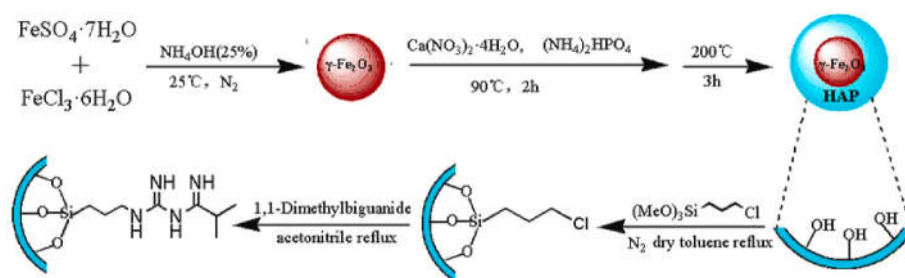


Fig. 15. Synthesis procedure of the biguanide-functionalized HAP- $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst [Reproduced from ref.116].

the reaction medium, and an open form in which the active sites are exposed to the reaction medium. Therefore, the activation of lipase is needed to display the better catalytic activity [118]. In the presence of hydrophobic surface, the open form of the lipase becomes adsorbed through the hydrophobic pocket around the active sites and thus the open form is stabilized, which is known as the interfacial activation of lipases. Therefore, the utilization of hydrophobic support for the lipase immobilization can render the immobilized lipase to be stabilized in its open form by the interfacial activation mechanism, enabling the solid biocatalyst to efficiently catalyze the transesterification reaction [119].

For the transesterification of vegetable oils, excess methanol is generally used to shift the reaction equilibrium to the biodiesel formation. However, the excess methanol has a serious inhibitory effect on the lipase activity. This phenomenon is mainly due to the low solubility of methanol in oils, forming droplets that encapsulate the lipase, and thereof causing the serious deactivation of lipase [117]. Accordingly, stepwise methanol addition method, by which methanol can retain at a low concentration in the reaction mixture, is often-utilized in the enzymatic biodiesel production.

The immobilization techniques of lipase on the magnetic support for the biodiesel production can include covalent attachment, adsorption, cross-linking, and entrapment methods [120].

#### 4.1. Covalent attachment immobilization

Covalent attachment immobilization method refers to the immobilization lipase technique in which the terminal group of the lipase molecule is tethered with the functional group on the magnetic carrier through covalent bonds [120,121]. With this approach, the firm covalent bonds can guarantee the operational stability of the immobilized enzyme with no or negligible lipase leakage into the reaction mixture during the biodiesel production processes. Besides, this method also improves the half-lives and thermal stability of lipases. However, the main disadvantage lies in the high-cost of the porous support and the loss of enzymatic activity after the chemical treatment. In general, the covalent attachment immobilization method is used by a two-step process, in which the initial step is the activation of the carrier surface by multifunctional reagents, such as carbodiimide and glutaraldehyde; and in the next step, the modified carrier is served as a linker for the covalent coupling of the lipase. The carbodiimide activation is commonly employed to improve the immobilization efficiency of lipase owing to its high efficiency and simplicity. Magnetic nanoparticles as used as carriers for enzyme immobilization have a high specific surface area, good biocompatibility and controllable particle size. As an example, our groups performed an investigation on the immobilization of lipase from *Thermomyces lanuginosa* onto magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles using 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDAC) as activator [122]. In this work, the lipase immobilization efficiency of 90.4% was reached with the activity recovery of 70.8%. In comparison to free lipase, better resistance to temperature and pH inactivation was shown for the immobilized lipase. By using three-stepwise methanol addition manner, the oil conversion to biodiesel of 94% was achieved over this bound lipase under the optimum transesterification conditions.

Actually, it is difficult for monodisperse magnetic nanoparticles to directly bind the lipase due to the lack of affluent reactive groups. Therefore, surface functionalization modification is necessitated for the easy binding of the lipase so as to improve the enzyme-carrying capacity of magnetic nanoparticles. Amino silanes such as (3-aminopropyl)triethoxysilane (APTES) are the most commonly used amino-functional reagents for the magnetic nanoparticle modification by the silane chemistry. In our study [123], APTES-modified magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were employed to immobilize *Thermomyces lanuginosa* lipase by using glutaraldehyde as a coupling agent. The glutaraldehyde with two terminal aldehyde groups is a bifunctional reactive compound capable of reacting with the amino-functionalized nanoparticles and amine groups of enzyme by a Schiff base linkage. The thus-immobilized lipase showed good pH tolerance and thermostability, being able to catalyze the soybean oil transesterification of methanol with the oil conversion of over 90%. Likewise, Miao et al. [124] loaded *Candida antarctica* lipase B (CALB) onto APTES-modified magnetic nanoparticles to produce biodiesel from rapeseed oil. Differently, superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Ms = 81.35 emu/g) were prepared by co-precipitation method using ionic liquid of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF<sub>4</sub>) as templates. The maximum conversion rate to biodiesel could reach 89.4% under the optimized transesterification conditions.

The functionalization of the magnetic support and covalent attachment to lipase have a significant influence on the density of binding sites on the support with the lipase and the stability of the bridges between the lipase and the support, which in turn greatly affect the enzymatic activity and operational stability of the immobilized lipase. In a previous investigation, by using different activating or coupling reagents, including EDAC, glutaraldehyde, and EDAC + N-hydroxysuccinimide (NHS), different immobilized lipases were synthesized by Raita et al. in four different forms with variation in covalent linkages and protein crosslinking [125]. It was indicated that the immobilized *Thermomyces lanuginosus* lipase on Fe<sub>3</sub>O<sub>4</sub> carrier modified by APTES and covalently linked by using EDAC and NHS coupling reagents, naming Fe<sub>3</sub>O<sub>4</sub>-A-P-EN-Lipase, showed the highest catalytic activity to the transesterification of palm oil with the oil conversion of 97.2%. The utilization of EDAC and NHS reagents for the lipase immobilization is known to be able to reduce the hydrolysis of active ester (*o*-acylisourea) from EDC activation in aqueous solution, thus resulting in the increased efficiency of the EDC-mediated coupling reaction and the improvement of the immobilization efficiency. Moreover, it was shown that appropriate amount of co-solvent tert-butanol could alleviate the toxic influence of methanol on the enzymatic activity of the immobilized lipase. The magnetic biocatalyst could be easily recovered by magnetic separation, and reutilized for five consecutive runs still with remaining 80% of the initial catalytic activity.

Some recent works on the covalently bound lipases used for the biodiesel production are summarized in Table 5. As afore-mentioned, the use of bare Fe<sub>3</sub>O<sub>4</sub> nanoparticles as carrier materials is easy to agglomerate and difficult to disperse uniformly in the reaction system, which affects the catalytic activity of the magnetic biocatalyst. The encapsulation of other porous materials, so as to form magnetic



nanocomposites, can reduce agglomeration of the magnetic biocatalyst, offering high specific surface area and accessible active functional groups. In this vein, magnetic silica nanocomposites have been widely used as enzyme immobilization carriers due to their low cost, non-toxicity, good biocompatibility, easy modification, large specific surface area, and controllable pore size. For example, Mehra et al. [126] successfully prepared a magnetic immobilized lipase through the covalent immobilization of *Candida antarctica* (CALB) lipase on epoxy-functionalized magnetic silica nanocomposites  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . For the covalently binding of lipase, the core-shell magnetic nanocomposites ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ) were firstly synthesized by coating  $\text{Fe}_3\text{O}_4$  core with silica shell, followed by functionalizing with (3-glycidioxypropyl)trimethoxysilane (GPTMS) as a linkage of the lipase. With this preparation procedure, the lipase immobilization efficiency could reach 84%, keeping 97% of initial activity of the free enzyme. The immobilized lipase was used for the biodiesel production by enzymatic transesterification of waste cooking oil with methanol. Furthermore, the effects of tert-butanol and water adsorbent on the yield of biodiesel were investigated. It was indicated that the application of molecular sieve as water absorbent in the reaction medium and addition of tert-butanol as co-solvent could obviously improve the biodiesel yield.

The hydrophilic/hydrophobic properties of magnetic supports seem to be a significant factor affecting the catalytic activity of the immobilized lipase. The magnetic supports with hydrophobic character are promising candidates for the lipase immobilization, since the accessibility of hydrophobic oil would be increased around the bonded lipase, and meanwhile the absorption of the hydrophilic methanol to the active sites would be decreased, causing the declined deactivation of the immobilized lipase by methanol. For this purpose, the coating of organic hydrophobic polymer on the magnetic nanoparticles can increase the mass transfer rate by enhancing the absorption capacity for the oil molecules and limiting the absorption capacity for the water and methanol molecules. Esmailnejad-Ahranjani et al. [127] developed  $\text{Fe}_3\text{O}_4$  cluster@ $\text{SiO}_2$  nanocomposite particles coated with the polyethylenimine (PEI) or polyacrylic acid (PAA) as the magnetic carrier for the immobilization of lipase from *Pseudomonas cepacia*. The immobilized lipase on the PEI-coated magnetic particles exhibited the best catalytic performance to the enzymatic transesterification of soybean oil for the production of biodiesel. In this work, a relationship between the transesterification activity of the immobilized lipases and the hydrophobic properties of the magnetic nanocomposites had been established, providing an insight into the enhanced production of biodiesel with the immobilized lipase by varying the hydrophobic properties of the magnetic support used for the enzyme immobilization.

In an investigation by Fan et al. [128], a polyamidoamine (PAMAM) dendrimer was grafted onto magnetic multi-walled carbon nanotubes (mMWCNTs) with the aim to prepare dendrimer-functionalized magnetic carbon nanotube (mMWCNTs-PAMAM) with a large surface that was functionalized with amino groups for the immobilization of *Rhizomucor miehei* lipase (RML). The attachments of the lipase by covalent bond formations between amine groups of the magnetic support and carboxyl groups of the lipase could be achieved by EDAC activation strategy. The esterification activity of thus-obtained magnetic solid lipase was 27-fold higher than that of the free enzyme. This immobilized enzyme was employed to catalyze the transesterification of waste vegetable oil with methanol for the biodiesel production in a tert-butanol solvent system. Biodiesel yield of 94% was achieved under the optimal reaction conditions, and no remarkable decrease in the biodiesel yield was observed on this magnetic biocatalyst even after 10 cycles of reuse. Besides, poly (styrene-methacrylic acid) with functional carboxyl groups [129], and poly (glycidyl methacrylate-co-methacrylic acid) with epoxy and carboxyl groups [130], have also been used as synthetic polymers to fabricate magnetic copolymer composites, followed by the binding of lipase using EDAC or EDAC/NHS as an activation reagent. The so-obtainable solid biocatalyst had good enzymatic activity and reusability for the biodiesel production through the

heterogeneous transesterification reaction.

In addition to synthetic polymers, organic biopolymers, such as chitosan and cellulose, have also become attractive to incorporate into magnetic nanoparticles for forming the magnetic polymer composites used for the lipase immobilization, mainly due to their characteristics of nontoxicity, physiological inertness, hydrophilicity and biocompatibility. Our group [131] prepared magnetic chitosan microspheres that were used as magnetic carrier for the immobilization of *Candida rugosa* lipase, in which the chitosan could be easily reacted with terminal groups of lipase. Thereafter, the magnetic responsive biocatalyst was applied in the biodiesel production through the soybean oil transesterification. Results showed that the FFAs generally present in the oil feedstocks did not significantly decrease the enzymatic activity of the immobilized lipase. Using this magnetic biocatalyst, the conversion to biodiesel from soybean oil achieved 87% under the reaction conditions of methanol/oil molar ratio of 4:1 at a reaction temperature of 35 °C for 30 h. The immobilized lipase showed good durability in the repeated use of five times after being recovered by magnetic separations.

Encouraged by the above results, Cubides-Roman et al. [132] successfully immobilized the lipase of *Pseudomonas fluorescens* on chitosan-coated  $\text{Fe}_3\text{O}_4$  nanoparticles, and the bound lipase was used to catalyze the transesterification of coconut oil with ethanol to biodiesel in a magnetically stabilized fluidized bed bioreactor assisted through electromagnetic field in a solvent-free medium. Such developed lipase-catalyzed biodiesel production in bioreactors assisted by a electromagnetic field would lead to a better distribution of the catalyst bed in the bioreactor and a significant increase in the oil conversion. The highest yield of biodiesel (97.8%) was attained on this bioreactor at ethanol-to-oil ratio of 11.25:1, reaction temperature of 30 °C, and reaction duration of 80 min.

To overcome the issue of low efficiency of enzyme binding to the carrier, in a study performed by Bandikari et al. [133], the magnetic cellulose nanosphere (MCNS) was initially prepared by coating of  $\text{Fe}_3\text{O}_4$  with nanocellulose, and then was further functionalized by 3-aminopropyltriethoxysilane (APTES) to confer the amino groups on the magnetic carrier. Thereafter, the lipase from *Gsteaerothermophilus* (GSlip-CBD) was efficiently immobilized onto the APTES-treated MCNS using glutaraldehyde as a linking agent to form the solid biocatalyst (GSlip-CBD-MCNS). The GSlip-CBD-MCNS exhibited high catalytic activity, good thermal stability and high resistant capacity to methanol, affording the biodiesel yield of 98% after 4 h incubation in one step addition of methanol. Moreover, this magnetic biocatalyst could be reused up to 8th and 19th cycles with 94 and 45% of biodiesel yield.

The utilization of hydrophobic carrier graphene oxide can render the lipase immobilization to follow the interfacial activation mechanism and make the active center of the lipase more expose to the reaction media. For this aim, as illustrated in Fig. 16, the magnetic graphene oxide nanocomposites were prepared by encapsulation of  $\text{Fe}_3\text{O}_4$  in graphene oxides (GO), and then employed as a magnetic carrier for the immobilization of *Candida rugosa* lipase with EDC/NHS as an activating agent, in terms of the interfacial activation of enzyme on hydrophobic support surface [134]. Over this magnetic immobilized lipase, the biodiesel yield of 92.8% could be achieved at a temperature of 40 °C by three-step addition of methanol, allowing for easily magnetic recycling of the biocatalyst for five times without significant loss of its enzymatic activity.

Very recently, metal organic frameworks (MOFs) have witnessed much attention as lipase supports because of their favorable characteristics such as highly ordered crystal structure, adjustable porosity and large surface area. For the immobilization of lipase, the core-shell structured  $\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$  composites with high regular porosity and strong magnetism were prepared by coating  $\text{Fe}_3\text{O}_4$  magnetite with porous MIL-100(Fe) MOF material [135]. By using the EDAC/NHS activation strategy, the lipase from *Candida rugosa* was covalently bound onto the  $\text{Fe}_3\text{O}_4@\text{MIL-100}(\text{Fe})$  composites through amide linkages, with the lipase immobilization efficiency of 83.1% and activity recovery of

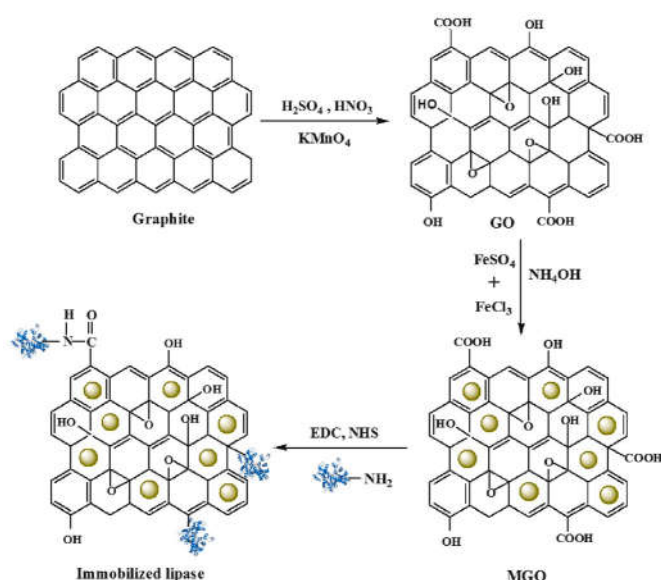


Fig. 16. Synthesis of graphene oxide  $\text{Fe}_3\text{O}_4$  nanocomposites and subsequent immobilization of lipase onto the magnetic support [Reproduced from ref. [134].

63.5%. With this magnetic biocatalyst, the maximum biodiesel conversion could attain 92.3%. The biocatalyst prepared in this study was recovered easily by magnetic separation without significant mass loss, and displayed 83.6% of its initial activity as it was reused for five runs, allowing its potential application for the cleaner production of biodiesel [135].

#### 4.2. Crossing-linking immobilization

Cross-linking enzyme aggregate (CLEA) is a carrier-free immobilization method that involves precipitation from aqueous buffer, followed by interconnection of lipase molecules by the bi-functional or multi-functional cross-linking agents, such as glutaraldehyde and dextran polyaldehyde. Taking the glutaraldehyde as an example, two aldehyde residues of one glutaraldehyde molecule can react with two reactive amino residues from different lipase molecules by Schiff-base linkages, making the enzyme cross-linking aggregations (without matrices). Herein, Asp and Glu amino acid residues bearing active groups  $\epsilon$ -amino,  $\alpha$ -amino, and guanidiny, play an important role in the cross-linker formation. With increasing the size of CLEAs clusters, the problem of high mass transfer limitations and difficult to separate should be carefully considered. Hence, the cross-linking aggregation method can be combined with other lipase immobilization approaches in an attempt to maximize the merits of cross-linking processes. As such, the CLEAs are immobilized onto magnetic carriers to prepare magnetic cross-linking lipase aggregates (mCLEAs) biocatalyst via covalent bonds. The mCLEAs could provide highly concentrated lipase activity in the biocatalyst and high catalytic stability, concurrently ensuring the easy separation of the solid biocatalyst from the reaction media.

Cruz-Izquierdo et al. [136] immobilized the insolubilized *Candida antarctica* lipase B (CALB)-CLEAs onto APTES-modified  $\text{Fe}_3\text{O}_4$  to prepare the CALB-mCLEAs biocatalyst using glutaraldehyde as cross-linking agents. This novel solid biocatalyst could combine the featured properties of CLEAs such as great stability, feasibility for the reutilization, and the magnetic character. Such advantages make the CALB-mCLEAs to be paramagnetic particles of a robust biocatalyst which is more stable than the free enzyme, easily recoverable from the reaction medium, and reusable for next catalytic cycles. For enzymatic biodiesel production from waste frying oils and non-edible vegetable oils, by using this magnetic biocatalyst, the oil conversion to biodiesel of 80% was achieved after 24 h, and after 72 h this oil conversion increased to 92%.

After ten reuse cycles of this biocatalyst, the residual activity still could give the oil conversion of 88%. Likewise, Badoei-dalfard et al. [137] prepared magnetic cross-linking enzyme aggregates by covalently binding of cross-linked enzyme aggregates (CLEAs) of Km12 lipases on the APTES-modified  $\text{Fe}_3\text{O}_4$  nanoparticles, as depicted in Fig. 17. In comparison with free lipase, the biodiesel production from waste cooking oils (WCOs) could increase approximately 20% by using this resulting Km12 lipases-mCLEAs biocatalyst.

In the literature [138], the lipids (containing oils and FFAs) are extracted using n-hexane as solvents from nitrogen-starved cells of *Chlorella vulgaris* var L3 as raw materials with the aim to produce biodiesel. Magnetic cross-linked enzyme aggregates (mCLEAs) of CALB (CALB-mCLEAs) were prepared using ammonium sulfate and glutaraldehyde as precipitating and cross-linking reagents, respectively. The conversion to biodiesel could reach above 90% in 10 consecutive catalytic cycles under mild reaction conditions, and the magnetic property permitted the solid biocatalyst to be recovered and reused easily. It was indicated that the self cross-linking among molecules of CALB and magnetic nanoparticles did not affect the catalytic properties of the immobilized lipase. Also, Badoei-dalfard et al. [139] immobilized cross-linking enzyme aggregates of *Enterobacter* lipase MG10 on magnetic amino-functionalized graphene oxide (maGO-CLEA-lip) nanocomposite to prepare an efficient solid nanobiocatalyst for the biodiesel production via glutaraldehyde as a linkage reagent, as shown in Fig. 18. This magnetic nanobiocatalyst displayed 3.0 folds higher activity to the transesterification reaction than free lipase, affording the biodiesel yield of 78% from *R. communis* oil after 24 h and retaining about 75% of its original activity after 30 days of incubation at 45 °C.

As a whole, the crossing-linking aggregates for the lipase immobilization on magnetic nanoparticles could greatly improve the lipase stability in the process of enzymatic biodiesel production, rendering the immobilized lipase to be easy to recover and reuse. In particular, with this immobilization strategy, the enzyme leakage from aggregates into reaction media after long time reaction can be efficiently avoided, being capable of as a robust biocatalyst for the effective production of biodiesel.

#### 4.3. Adsorption and entrapment immobilization

Adsorption method refers to the immobilization of lipase on the surface of the carrier by the adsorption forces, such as van der Waals force, hydrogen bond, hydrophobic interaction, and electron affinity. This method has the advantages of simple operation, high enzymatic activity and mild reaction conditions [140]. However, due to the weak interactions between the lipase and the carrier, the obvious enzyme leakage into reaction mixture due to the loose attachment on the carrier, is generally encountered during the reaction processes, hence leading to the lower catalytic stabilities. For this lipase adsorption strategy, a great challenge to the practical use is to increase the affinity of lipase to the carrier and thus to improve the enzymatic stability of the immobilized lipase.

Mukherjee et al. [141] precipitated *Thermomyces lanuginosus* lipase onto the clusters of  $\text{Fe}_3\text{O}_4$  nanoparticles via physical adsorption for the production of biodiesel. The formed solid biocatalyst could afford high biodiesel conversion of 96% under mild reaction conditions of oil/ethanol (w/w) of 1:4 at 40 °C after 7 h of reaction. In this work, the reusability of the immobilized lipase is not reported. In a study conducted by Wan et al. [142], a series of hollow magnetic mesoporous polydopamine (HM-MPDA) was firstly synthesized by a novel interface-directed co-assembly strategy, and then *Candida rugosa* lipase was successfully immobilized on the HM-MPDA nanoflowers via physical adsorption for the biodiesel production through oleic acid esterification with methanol. The HM-MPDA nanospheres possessed excellent thermal stability, high saturation magnetization ( $M_s = 82.2 \text{ emu/g}$ ), large tunable pore size (11.53–49.53 nm), and controllable shell (23–178 nm). By adjusting the weight ratio of the two soft organic

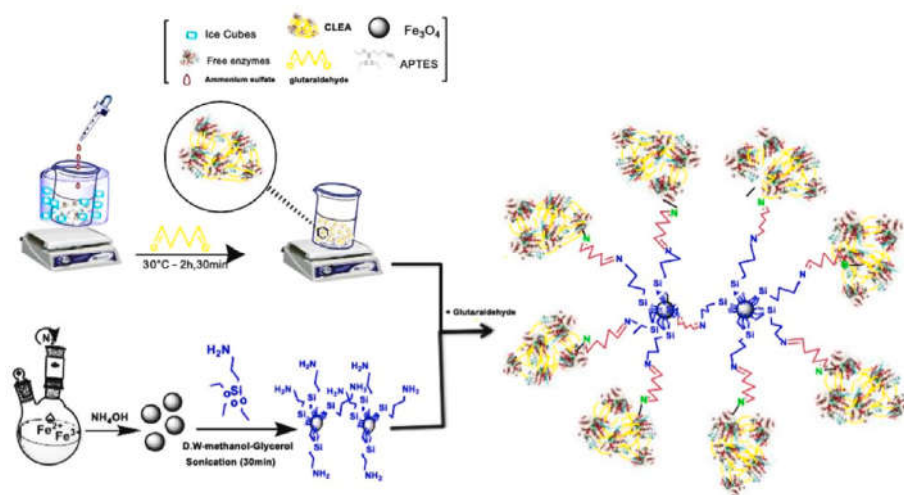


Fig. 17. Schematic representation for preparation of magnetic cross-linked enzyme aggregates (mCLEAs) of *Bacillus licheniformis* Km12 lipase (mCLEA-lip). [Reproduced from ref.137].

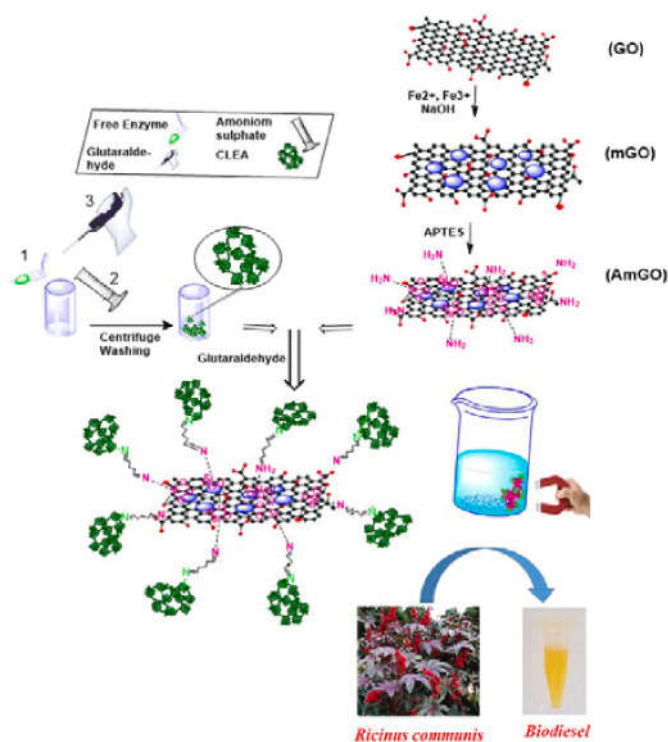


Fig. 18. Schematic illustration of the preparation of magnetic cross-linked enzyme aggregates (mCLEAs) of *Entrobacter* lipase MG10 (mCLEA-lip). [Reproduced from ref. [139]].

templates, the shell thickness and pore size could be regulated according to this immobilization strategy. The influence of lipase loading and pore structure on the enzymatic activity was investigated in this research. Under the optimized esterification conditions (oleic acid/methanol molar ratio 1:6, amount of CRL@HM-MPDA 35 mg, reaction temperature 40 °C), the conversion to biodiesel could reach up to 87.9% and still exceed 71% even after six times of recycling runs.

Gold nanoparticles have been considered capable to absorb enzymes and maintain their catalytic activity. In the presence of oleic acid and citric acid, the lipase from *Thermomyces lanuginosus* was immobilized on snowman-like Fe<sub>3</sub>O<sub>4</sub>/Au nanoparticles by physical interactions including hydrogen bond and interfacial interactions, as presented in

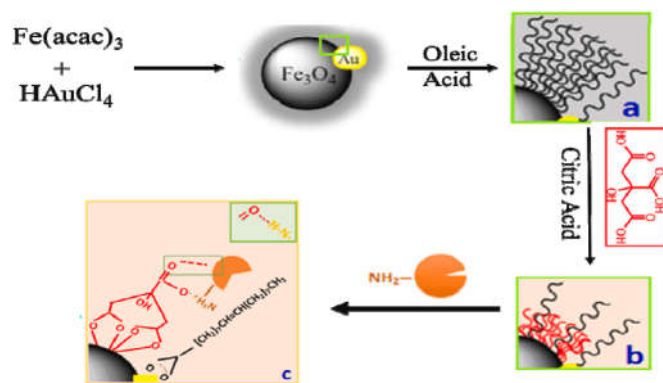


Fig. 19. Schematic representation of the lipase immobilization on the surface of snowman-like Fe<sub>3</sub>O<sub>4</sub>/Au nanoparticles [Reproduced from ref.143].

Fig. 19 [143]. In this research, Fe<sub>3</sub>O<sub>4</sub>/Au was formed through the growth of nano-sized gold particles on the surface of the magnetic nanoparticles. Interfacial activation originates from the residual oleic acid chains on the surface of Fe<sub>3</sub>O<sub>4</sub>/Au and improves the transesterification conversion rate of tomato seed oil to biodiesel (97.4%). It is worth noting that, the anchored lipase on the snowman-like Fe<sub>3</sub>O<sub>4</sub>/Au nanoparticles displayed more active than on magnetite alone for the transesterification reactions. Interestingly, Au was found as co-catalyst to promote electron conduction, helping lipases to assume a favorable orientation. This immobilized lipase showed a good reusability, due to the stabilizing effect of Au, still staying above 84% of its original reactivity after three reuse cycles.

Inspired by the excellent works mentioned above, Vahidi et al. [144] developed an efficient method for the immobilization of extracellular lipase without pre-purification by using core-shell structured magnetic nanoparticles containing long-armed nickel-nitilotriacetic acid surface groups (Ni-NTA-MNPs). To simultaneously purify and immobilize target His-tagged lipase from cell culture supernatant, the extracellular lipase in the supernatant was directly adsorbed onto the magnetic Ni-NTA-MNPs composites by affinity attachment, achieving the high specific enzyme loading (62 mg/g MNPs) and high enzyme loading efficiency (85%). With this prepared nanobiocatalyst, the one-pot transformation of waste grease (containing 24 wt% FFAs) with methanol could afford the biodiesel yield of 94%. This magnetic nanobiocatalyst was easily recovered under an external magnetic field and exhibited good recyclability, still retaining 97% of productivity in the seventh

cycle of biodiesel production run.

Entrapment immobilization method is also used for the immobilization of lipase, which refers to embedding of lipase in the carrier by using the gap in the carrier structure. Herein, there is no chemical reaction involved in the whole immobilization process. Notably, this approach is able to minimize the leakage and aggregation of the lipase, so as to boost the catalytic activity and stability, and to keep the lipase to be better stable than other physically adsorbed lipase. In general, in comparison with other immobilization methods, the immobilized lipase prepared by the entrapment method prevents the lipase from efficient contact with the substrate, and the high mass transfer resistance also impedes the enzymatic activity. For this reason, the use of entrapment or encapsulation method for the lipase immobilization is scarcely reported for the biodiesel production.

Recently, Chen et al. [145] directly synthesized magnetic whole-cell biocatalysts (MWCBs) by immobilizing *Pseudomonas mendocina* cells onto  $\text{Fe}_3\text{O}_4$ -chitosan microspheres. In this study, the whole-cell was entrapped onto the magnetic chitosan microspheres by using glutaraldehyde as a cross-linking agent to establish a connection between the chitosan and the whole-cell. The highest biodiesel yield of 87.32% over this MWCBs was achieved under the optimum reaction conditions (water content of 10 wt%, MWCBs concentration of 10 wt%, reaction temperature of 35 °C, methanol to oil molar ratio of 4:1). The kinetic data followed Michaelis-Menten model ( $r_{\text{max}}$ , 2.1801 mg/min;  $K_m$ , 0.4272 mg/mL;  $K_i$ , 0.2308 mg/mL) with competitive inhibition by methanol. Moreover, the MWCBs possessed excellent reusability that maintained a biodiesel yield of 83.57% after being reused for ten times, which was better than the  $\text{Fe}_3\text{O}_4$ -uncontained biocatalyst.

Overall, the magnetic solid biocatalyst can be employed for the biodiesel production in more moderate reaction conditions with better FFA- and water-tolerant capacity. However, the critical challenges are still the high operational cost and long reaction duration for the magnetic biocatalyst. Much further efforts would be focused on the development of novel magnetic composite support for the immobilization of lipase.

## 5. Magnetic acid-base solid catalyst

The low-quality oils, such as non-edible oils and waste cooking oils, have emerged as a potential feedstock for the biodiesel production, which can significantly reduce the cost of biodiesel production. However, these oil feedstocks always have a large amount of FFAs and water, showing a great harmful effect on the catalytic activity, particularly for alkali catalysts. As such, for the low-quality oils, a pre-esterification of FFAs to biodiesel using acidic catalysts is frequently required, followed by the alkali-catalyzed transesterification of triglycerides into biodiesel. In this regard, the heterogeneous catalysts with acidic and basic sites seem to exhibit better FFA- and water-tolerant capacity as compared to alkali catalysts, and perhaps they can catalyze the transesterification of triglycerides and esterification of FFAs simultaneously into the biodiesel product, thereby minimizing the processing steps, and achieving one-pot transformation of low-quality oils into biodiesel. Although the combination of acid and bases in a homogeneous solution will lead to rapid neutralization due to their chemical incompatibilities, this neutralization effect can be prevented through fixing the acid and base sites on porous supports and engineering tailoring spatial segregation between the chemically antagonistic sites.

Based on the above considerations, the excellent investigations on the development of magnetic acid-base solid catalysts for the biodiesel production have been conducted. In a research by Xue et al. [146], magnetic solid catalyst  $\text{CaFe}_2\text{O}_4$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$ - $\text{Fe}_2\text{O}_3$  with both acidity and basicity was prepared by coprecipitation and calcinations procedure. The so-prepared catalyst of  $\text{CaFe}_2\text{O}_4$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$ - $\text{Fe}_2\text{O}_3$  with weaker magnetism showed good catalytic activity to the transesterification of soybean and *Jatropha* oils with methanol to biodiesel. The highest biodiesel yield of 85.4% was achieved under the optimized conditions of

100 °C for 30 min, 15:1 methanol to oil molar ratio and 4 wt% catalyst loading. In this study, the  $\text{CaFe}_2\text{O}_4$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$ - $\text{Fe}_2\text{O}_3$  catalyst was reduced to  $\text{CaFe}_2\text{O}_4$ - $\text{Ca}_2\text{Fe}_2\text{O}_5$ - $\text{Fe}_3\text{O}_4$ -Fe catalyst under  $\text{H}_2$  atmosphere, and the latter displayed the improved magnetism. Moreover, the reduced magnetic catalyst could be easily separated by a permanent magnet, and still had good catalytic activity to the transesterification reaction. However, due to the leaching of active species, the catalyst stability was relatively poor and the catalyst was only reused for three transesterification cycles.

In 2018, Wang et al. [147] investigated the novel magnetic acid-base amphoteric nanoparticles  $\text{Zn}_8/\text{Fe}-\text{C}_{400}$ , which was employed as a novel solid catalyst for one-pot esterification and transesterification of high AV *Jatropha* oils without pretreatment. This  $\text{Zn}_8/\text{Fe}-\text{C}_{400}$  catalyst possessed high acidity (2.74 mmol/g), high basicity (3.16 mmol/g), and strong magnetism (12.3  $\text{Am}^2/\text{kg}$ ) due to the coexistence of the acidic -COOFe, basic oxides ( $\text{ZnFe}_2\text{O}_4$ , ferrite, and zincate), and magnetite components, thus endowing it to resist FFAs and to achieve full *Jatropha* oil conversion to biodiesel at AV of 6.3 mg KOH/g, and being reused for at least 10 times with biodiesel yield >94.3%. Notably, no obvious saponification phenomenon was observed during the biodiesel production processes.

In a recent study, porous core-shell magnetic bi-functional catalyst  $\text{CaSO}_4/\text{Fe}_2\text{O}_3\text{-SiO}_2$  with both Lewis acid and base sites was prepared in ethanol/ $\text{H}_2\text{O}$  media using  $\text{NaNO}_3$  as the etchant to construct the covalent bond in  $\text{Fe}_2\text{O}_3$  framework (Fig. 20), in which the  $\text{CH}_3\text{COONa}$  was an electrostatic supporter and subordinate reducing agent under solvothermal conditions [148]. The distinctive core-shell structure of this magnetic catalyst with controllable morphology was shown and ensured this catalyst to have high specific surface area (391  $\text{m}^2/\text{g}$ ) and large pore diameter (90 nm). Herein, the Lewis acid-base active sites were originated from calcium metal species and  $\text{SiO}_2$  components, respectively, and the porous core-shell structure could improve structural stability of the magnetic catalyst. The maximum biodiesel yield of 94% over this magnetic catalyst was obtainable using crude *Jatropha curcas* oil as raw material, and the biodiesel yield of above 80% was achieved after being recycled for nine cycle runs. This  $\text{CaSO}_4/\text{Fe}_2\text{O}_3\text{-SiO}_2$  catalyst with core-shell structure was easily dispersed in the reaction mixture, and was quickly separated from the biodiesel products by using a permanent magnet, hence being practicable for the biodiesel production from crude *Jatropha curcas* oil through the synergistic effect of Lewis acid and base active sites.

Besides, the biomass-based magnetic bifunctional catalyst, namely  $\text{CaO}-\text{Fe}_2\text{O}_3/\text{AC}$ , was prepared via wet impregnation method [149]. This prepared acid-base solid catalyst, with a high surface area of 106.28  $\text{m}^2/\text{g}$  and a saturation magnetization of 7.59 emu/g, was utilized for

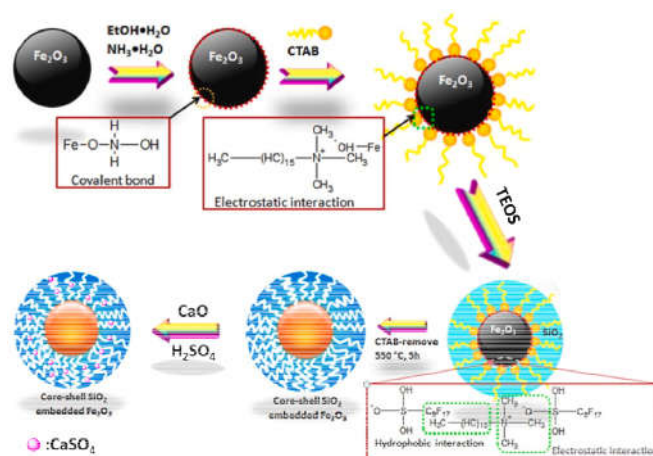


Fig. 20. Schematic illustration of the preparation for the  $\text{CaSO}_4/\text{Fe}_2\text{O}_3\text{-SiO}_2$  catalyst [Reproduced from ref. [148].

producing biodiesel from low-quality oils with high FFA content through a one-pot simultaneous transesterification and esterification procedure. The excellent catalytic performance was ascribed to the high amount of acidic (1852  $\mu\text{mol/g}$ ) and basic (2653  $\mu\text{mol/g}$ ) active sites on the catalyst surface. Moreover, the binary metal oxides exhibited better properties than individual oxide in terms of acidity and basicity, which was important for improving the transesterification and esterification reaction. By applying this solid catalyst, the biodiesel conversion of 98.3% was obtained with 3 wt % catalyst loading, 18:1 methanol to oil molar ratio, 65 °C temperature, and 3 h reaction time. This catalyst could be reused six times with biodiesel conversions above 70%. Similarly, in another research, a magnetic acid-base catalyst CaO-ZSM-5 zeolite/ $\text{Fe}_3\text{O}_4$ , was successfully synthesized by Lani et al. [150], from waste chicken eggshell and rice husk via an impregnation method. In the structure of the catalyst, the presence of ZSM-5 zeolite support and CaO component is advantageous in enlarging the surface area, and providing an acidity–basicity characteristic of the solid catalyst. However, the presence of the  $\text{CaSiO}_3$  species in this catalyst proved the strong interactions between CaO and zeolite during the catalyst preparation process. The CaO-ZSM-5 zeolite/ $\text{Fe}_3\text{O}_4$  showed good performance to catalyze the transesterification of used cooking oil to biodiesel, affording a high biodiesel yield of 91% with low leached  $\text{Ca}^{2+}$  concentration of 3.87 ppm. The surface area, saturation magnetization value, acidity and basicity of this catalyst were recorded to be 135.31  $\text{m}^2/\text{g}$ , 31.759  $\text{emu/g}$ , 1.4340  $\text{mmol/g}$ , and 1.8789  $\text{mmol/g}$ , respectively. Further, this magnetic catalyst showed a remarkable recyclability up to four consecutive cycles with biodiesel yield over 85%, making it to have the potential of cleaner and efficient production of biodiesel particularly from the low-quality oils.

Even though some efforts are made to fabricate magnetic acid-base solid catalysts for the biodiesel production because of their potential for the use of low-quality oils as feedstocks, the big challenge lies in the randomly distributed acid-base active sites throughout the solid catalyst, leading to negative interactions (such as neutralization) between the antagonistic catalytic species. However, such a type of solid catalysts can present compelling metrics in terms of good catalytic activity, waste and cost reduction, and step-saving, since the basic sites can catalyze the transesterification of triglycerides more efficiently than the acidic sites and moreover the acidic sites can catalyze the esterification of FFAs. By using the well-designed magnetic acid-base solid catalysts, the concurrent esterification and transesterification can be achieved via one-pot reaction process, and the catalytic activity and stability are also greatly improved, posing great potential for green and economic production of biodiesel especially from the low-quality oil feedstocks.

## 6. Conclusion and future perspectives

The utilization of biodiesel as an alternative renewable energy can alleviate the dramatic energy crisis, and the favorable combustion emission profile of biodiesel perfectly adapts to environmentally-friendly strategy and sustainable development. Heterogeneously catalyzed-transesterification and/or esterifications offers an environmentally more attractive option for the biodiesel production as compared to the homogeneously catalyzed-processes. Since the solid catalysts especially for the small-size ones might need high time- and energy-consuming filtration and centrifugation set-up to separate them from the biodiesel product, the usage of magnetic solid catalysts can greatly improve the catalyst separation efficiency, attaining the high recovery rate of the magnetic solid catalysts. For these solid catalysts, the catalytically active species, including acidic, basic and enzymatic active sites, play a crucial role in their catalytic performance; and the nature of magnetic supports such as specific surface area, pore distribution, and hydrophobicity, also has a great impact on the catalytic activity of the solid catalyst. Although the basic sites on the solid catalysts are more active for the oil transesterification reactions, they are easily deactivated by the impurities in the feedstocks (mainly FFAs and

water). By using solid acid catalysts for the oil transesterification for the biodiesel production, the higher reaction temperature and longer reaction time are often needed due to the lower activity of the acid catalyst. In this case, the ultrasound irradiation can be used as a viable process intensification method to accelerate the transesterification reaction. As for the immobilized lipase-catalyzed transesterification process, the higher cost and lower catalytic efficiency are the main defects, however posing several advantages such as milder operation conditions, no or little side reactions and environmentally friendly character. As another type of the solid catalysts, magnetic acid-base solid catalysts have seldom reported in the disclosed literatures, suffering from the mutual interference or deactivation issues between the hostile acidic and basic active centers, thus their catalytic performance is not very satisfying and needs to be further improved.

The low catalytic activity and the often-encountered leaching of active species are the future challenge for the magnetic solid catalysts to improve their catalytic performance and reusability. From these published literatures, even though the magnetic solid catalysts are easily recycled with the aid of a permanent magnet, their stability and durability are needed to be substantially enhanced in view of their practical use interest. Therefore, the development of novel magnetic solid catalyst with highly catalytic activity and stability is essential to enable the heterogeneous biodiesel production more economically and environmentally preferable.

As highlighted in this review, the feasibility of commercial biodiesel production is mainly affected by the cost of oil materials as well as the specific catalytic process for the biodiesel production. The oil feedstock accounts for approximately 70–80% of total estimated production cost of biodiesel. In terms of economic reason, cheap waste oil and non-edible oil seem to be an attractive raw material for the industrial biodiesel production. However, the FFAs and water generally presented in the low-quality oils can cause the serious deactivation and even leaching of catalytically active species, subsequently impeding their recyclability and reusability of the solid catalysts. Therefore, another great challenge for the magnetic solid catalysts is to improve their FFA- and water-tolerant capacity. For the magnetic solid acid catalyst, the transesterification of triglycerides and esterification of FFAs can be achieved simultaneously into the biodiesel product in one-pot reaction process, having economic and environmental beneficial for the industrial utilization. Even though potential progress has been obtained in the magnetic solid catalysts for the biodiesel production, more cutting-edge researches on advanced composite catalysts and clean synthesis routes are still required for improving the usage of these magnetic catalysts for durable biodiesel production with the aims to realize the commercial application of these solid catalysts.

As compared to the general organic feedstock, the triglyceride feedstocks have higher viscosities, and thus their diffuse and mass transfers on the catalyst surface are at a lower rate. In the future, to increase the mass transfer efficiency, the ordered hierarchically porous and yolk-shell structured materials would be employed as the potential support, so as to prepare the efficient solid catalysts for the transesterification reactions of triglycerides. The control of the reactant diffusion on the catalyst surface and accordingly strengthening the reaction process can be realized by means of the design and construction of hollow structure, macroporous/mesoporous and yolk-shell structure in the solid catalysts. Moreover, excellent multifunctional catalytic performances would be shown through the compounding and hybridization of organic and inorganic catalytic components, the ordered assembly and synergy of multiple active sites (such as acid-base sites, Brønsted and Lewis acid sites).

In particular, the magnetic antagonistic acid-base catalysts are expected to be fabricated by spatially segregating acidic and basic sites that are known to be chemically incompatible catalytic sites, so as to preclude their mutual interference or deactivation. In line with this, such type acid-base solid catalyst should be carefully constructed by engineering locating acid-base active species in different spatial parts or

regions of the solid catalysts, but operating independently their catalytic activity. Therefore, as a smart nanoreactor with this acid-base solid catalyst, the control of the reaction sequence wherein the triglyceride and FFAs would interact with the individual active species, can be realized. Very interestingly, these innovative design strategies as well as carefully tunable acid/base property can efficiently avoid the deactivation of basic sites by FFAs, optimize and integrate the cooperative catalysis between acid and base active sites, finally maximizing the catalytic performance of these solid acid-base catalysts.

Besides, the design principle for the magnetic solid catalyst used for the sustainable biodiesel production is still lacked. The studies on the structures of support materials, characteristics of pore and channels, modulations of surface properties, interaction mechanisms between active centers and supports, and synergistic mechanisms of multiple active sites would be expected to be performed, thus providing the theoretical guidance for the preparation of the magnetic solid catalysts with high-efficiency in the biodiesel production processes. And, more efforts are also required to optimize structure-performance features of the magnetic catalysts to attain breakthrough catalytic results in the biodiesel production.

### Credit author statement

Wenlei Xie: Conceptualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Jianguo Li: Writing - Investigation; Writing - original draft.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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