RSC Advances

REVIEW

Cite this: *RSC Adv.*, 2016, **6**, 78351

Efficient biodiesel production *via* solid superacid catalysis: a critical review on recent breakthrough

Peter Adeniyi Alaba,*[a] Yahaya Muhammad Sani[b] and Wan Mohd Ashri Wan Daud*[a]

Biodiesel produced from triglycerides and/or free fatty acids (FFAs) by transesterification and esterification has attracted immense attention during the past decades as a biodegradable, renewable and sustainable fuel. Currently, the use of solid superacid catalysts has proved a more efficient and "green" approach due to avoidance of environmental and corrosion problems and reduced product purification procedures. However, it is less viable economically because the reusability is low due to the lack of a hydrophilic/hydrophobic balance in the reactions that involve the use of inedible feedstock with a high water content. Therefore, this study gives a critical review on recent strategies towards efficient and "green" production of biodiesel *via* solid superacid catalysis. The strategies discussed include alkyl-bridged organosilica moieties functionalized hybrid catalysis to improve the hydrothermal stability of superacid catalysts, pre- and *in situ* water removal, and process intensification *via* temperature profile reduction. The strategies enabled well-defined porosity and an excellent hydrophobicity/hydrophilicity balance, which suppressed deactivation by water and glycerol.

Received 1st April 2016
Accepted 2nd August 2016

DOI: 10.1039/c6ra08399d

www.rsc.org/advances

1. Introduction

There is urgent need for alternative sources of energy due to the unrenewability, unsustainability and environmental threat posed by fossil diesel. Some studies have revealed that biodiesel has become the most interesting alternative.[1–3] The two major precursors of biodiesel are triglycerides and free fatty acids (FFAs), which are obtained from edible oil, nonedible oil,[4,5] animal fats and used vegetable oils.[6] Previously, the most popular biodiesel produced was from edible oil. However, this is quite not economically viable due to the high cost of feedstock. Currently, nonedible oil has gained immense popularity in production of second generation biodiesel because of high

Peter Adeniyi Alaba was born and raised in Kwara State, Nigeria. He did his undergraduate study in Chemical Engineering at the Federal University of Technology, Minna. He received his MEngSc by research in Chemical Engineering from the University of Malaya under the supervision of Prof. Wan Mohd Ashri Wan Daud. He was appointed as a research assistant at the University of Malaya in 2013 till date. His research interests lie in rational design of tailored solid acid catalysts for efficient green energy production CFD, computational chemistry and environmental engineering. He has published more than 9 papers in reputed journals and has been serving as a reviewer for reputable journals since 2015.

Professor Wan Mohd Ashri Wan Daud received his bachelor degree in Chemical Engineering at Leeds University, Leeds, UK in 1991 and his master's degree in Chemical Engineering at the University of Sheffield, Sheffield, UK in 1993. He received his PhD degree in Chemical Engineering at the University of Sheffield in 1996. After nine years as an academic and scientist at the Faculty of Engineering, in 2005, he became Professor of Chemical Engineering. Since 2005 until now, he has worked as a Professor of Chemical Engineering at the University of Malaya, Malaysia. His research fields include energy, biomass conversion to bio-fuel, catalyst synthesis, polymerization and separation processes, and hydrogen storage. He has more than 131 publications in Web Science journals.

---

[a] Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia. E-mail: adeniyipee@live.com; ashri@um.edu.my; Fax: +60 3796 75319; Tel: +60 1 116329054; +60 3796 75297

[b] Department of Chemical Engineering, Ahmadu Bello University, 870001 Nigeria

biodiesel yield and low feedstock price.[7,8] However, inedible oils are characterized with trace salts, water and high FFAs. Biodiesel comprises a C_{12}–C_{22} fatty acid monoalkyl esters (FAMEs) mixture, which has gained wide acceptability as "green" diesel due to its non-toxicity, biodegradability and sustainability. The remarkable properties of biodiesel also include higher lubricity, fewer emissions of carcinogenic particulate matter[9,10] and ease of handling, storage and transport compared to petrol-diesel.[11,12] Biodiesel is normally produced using homogeneous basic catalysts such as KOH, NaOH and other hydroxides.[13] The preference for homogeneous basic catalysts to their acidic counterparts is basically due to their better activity, particularly for triglycerides with low FFA content.[14,15] Likewise, homogeneous acids such as H_2SO_4 and HCl are more suitable for triglycerides from inedible oil due to the presence of Brønsted acidity, which promotes electrolytic activation of substrates.[16] However, the use of homogeneous catalysts is faced with the problem of long transesterification reaction times, corrosion, soap formation and separation of glycerol and water quenching, which requires large amounts of water. These generates large amount of wastewater.[17–20] The most common setback is separation cost, which covers more than half of the entire investment on the fuel industry and specialty chemical equipment.[21,22] In fact, separation cost majorly determines the economic viability of a process.[23]

Heterogeneous catalysts are suitable eco-friendly alternatives because of their ease of separation from the reaction medium, corrosion reduction and reusability.[22,24] Their development could aid process design for continuous production of biodiesel to minimize purification costs. However, they give rather lower biodiesel yields due to drawbacks such as leaching of the active sites and mass transfer limitations.[13,17,25,26] The FFA content of the feedstock also affects the performance of heterogeneous basic catalysts because they form soap, which consumes the catalyst and blocks the pore, thereby poisoning it.[23]

For better performance in the biodiesel production process, an efficient heterogeneous catalyst needs mesopores to minimize steric hindrance, higher acid strength and density as well as thermal and hydrothermal stability to minimize poisoning and leaching. Superacids are promising catalysts for biodiesel production because they simultaneously support both transesterification and esterification, thereby circumventing the threat posed by FFAs. Chemists synthesized them in both solid and liquid forms, and their amazing acid strength makes it easier to conduct problematic reactions under satisfactory experimental conditions. For instance, Misono and Okuhara[27] reported that activation of alkanes proceeds at low temperatures over a superacid catalyst. Conventional superacids such as liquid HF and $AlCl_3$ have been cited as hazardous to the environment; however, solid superacids are more attractive for industrial utilization. Solid superacid catalysts are indeed more environmentally benign in numerous industrial processes.[27–29]

Recently, several authors tested heteropoly acids, inorganic metal oxides as well as sulfonic and sulfuric acid based resins as solid superacid catalysts for transesterification of triglycerides and esterification of FFAs.[24,30–32] Sulfated inorganic metal oxides exhibit stronger super acidity compared to 100% sulfuric acid ($H_0 \leq -12$).[33] This is because metal oxides are chemically stable, environmentally benign, and possess remarkable acid–base and redox properties.[16] One of the most popular sulfated metal oxide catalysts is sulfated zirconia (SZ). SZ has been proved as an efficient superacid for both esterification and transesterification.[34–36] Kiss *et al.*[37] performed a comparative study on various solid acids, including ion exchange resins, zeolites and inorganic metal oxides for lauric acid esterification using different alcohols. They reported that SZ exhibited the best performance because zeolites are limited, being microporous, whereas low thermal stability is the bane of ion exchange resins. SZ is a promising catalyst for several industrial processes of commercial importance due to its super acid strength.[38–40] Saravanan *et al.*[40,41] also reported the outstanding performance of SZ in esterification of caprylic acid and myristic acid at mild temperatures and low catalyst loading.

Other sulfated metal oxides with remarkable performances include titania, silica and a combination of both. Recently, several authors have investigated the use of sulfated silicas as catalysts for esterification and transesterification.[24,42,43] The report of Ropero-Vega *et al.*[44] shows that sulfate ion addition to titania by incipient impregnation of ammonium sulfate inculcated super-acidity to titania. This engenders remarkable activity when used to esterify fatty acids.

Ordered mesoporous silicas and aluminosilicates such as MCM-41, HMS, SBA-15 and USY zeolite are viable supports due to their high specific surface area (SSA) and hierarchical mesoporosity.[43,45–48] The major problems attributed to such materials are hydrophobicity and lower catalytic activity as compared to microporous zeolites.[49] However, functional groups that are more reactive are added to improve the surface hydrophobicity as well as reactivity. Testa *et al.*[42] comparatively studied glycerol acetylation over different solid acid catalysts. They reported that mesoporous sulfated silica showed superior performance with respect to reactivity.

However, the use of solid superacid catalysts for biodiesel production can be affected by the presence of a substantial amount of water due to the robust interaction between acid sites and water molecules, which promotes hydrolysis reactions. This condition is typical of inedible raw materials, which are the most appropriate raw materials for 2nd generation biodiesel. Most of the non-edible raw materials such as sewage sludge[50] and rendered animal fats[51] consist of up to 50% FFA and water. Several attempts have been made towards the synthesis of a better solid superacid catalyst that could overcome this drawback. One of them is an organosulfonic acid-functionalized solid catalyst. The studies of Melero *et al.*[52–54] reveal that this type of functionalized solid acid exhibit high catalytic activity and stability during biodiesel production. They further used bi-dimensional NMR (solid-state) spectroscopic analysis to study the sulfonic acid sites interaction with water in hydrophobic reaction media to reveal their robust hydrophilic nature. Consequently, this jeopardized their catalytic activity in reactions that are water sensitive.

Several authors have reviewed the application of solid superacid catalysts for biodiesel production, focusing on the mechanism of solid acid catalysts, kinetics for transesterification and esterification reactions and the most effective parameters for the catalyst.[25,55–58] However, this study gives a review on the improvement of solid superacid catalysts in biodiesel production, which includes the detailed solid superacid catalyst synthesis, the super acidity characterization and functionalization with alkyl-bridged organosilica moieties as an improvement strategy. Furthermore, the biodiesel production process intensification was discussed towards a more careful control of hydrolysis–esterification–transesterification reaction mechanism.

2. Kinetics and mechanism of biodiesel production with solid superacid catalysts

Solid super acids support both esterification and transesterification reactions. Transesterification reactions in the presence of an alcohol proceed in three consecutive reversible reaction steps. The first is transformation of triglycerides to diglycerides, followed by formation of monoglycerides. Monoglycerides are then converted to glycerol. Each step yields one molecule of methyl ester from glycerides, as shown in Fig. 1. The reaction stoichiometry shows that a mole of triglyceride requires 3 mol of methanol to form a mole of glycerol and 3 mol of methyl ester.[36] However, for a reasonable conversion, the methanol/oil ratio should be more than 3. Therefore, the typical reaction condition employs a methanol/oil molar ratio of ≥5 at a temperature range of 60 to about 200 °C over a catalyst loading of ≥0.5 wt% for about an hour or more.

Several authors investigated the kinetics of transesterification of triglycerides with alcohol.[40,59,60] López *et al.*[59] investigated solid superacid catalyzed transesterification of triacetin with methanol, comparing the activity of sulfated zirconia (SZ) with H_2SO_4 as catalysts on a rational basis. The turnover frequency of the two catalysts was found to be similar, which indicates that both SZ and H_2SO_4 follow a similar reaction pathway. This is probably because they possess a similar acid strength.

Similarly, the esterification reaction is reversible. It occurs between the FFA and alcohol over an acid catalyst to produce water and ester:[61]

$$R_4\text{–OH} + R\text{–COOH} \Leftrightarrow R\text{–COO–}R_4 + H_2O \tag{1}$$

Peters *et al.*[61] studied the kinetics of esterification of acetic acid with butanol over solid acid catalysts. The kinetics

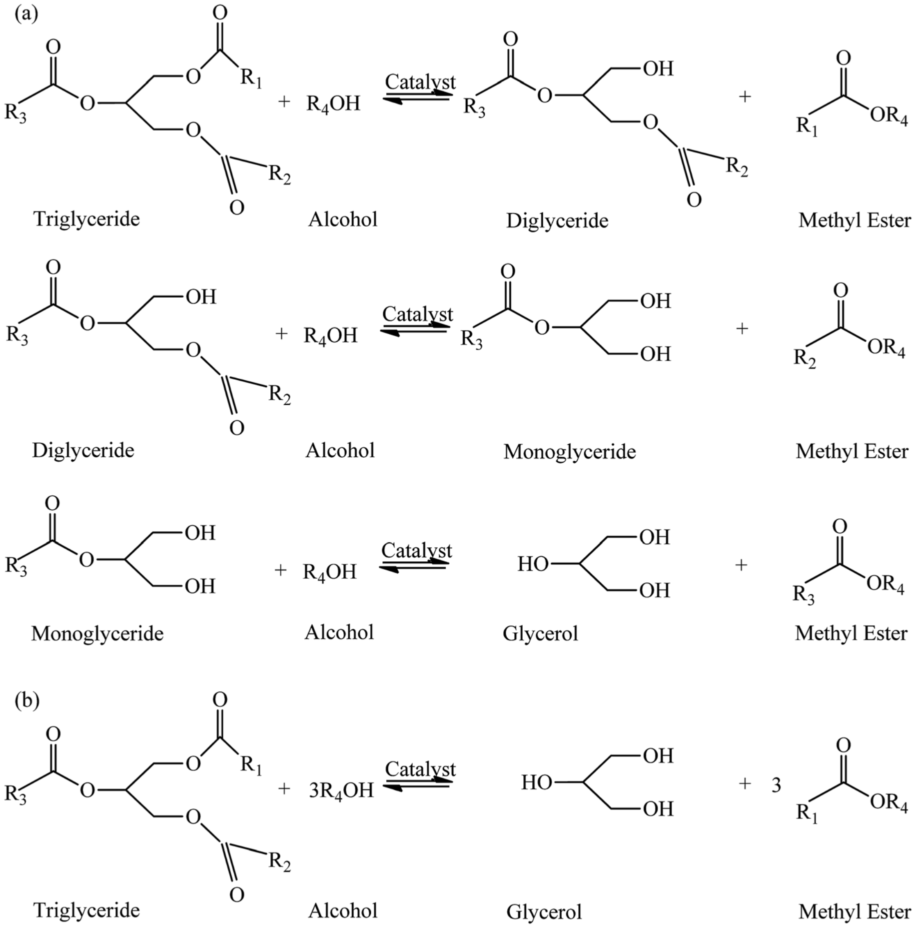

Fig. 1 Triglyceride transesterification with alcohol (a) of fatty acids and R_4 represents the alcohol alkyl group. (b) Overall reaction.

parameters were evaluated using the quasi-homogeneous model based on a first order reaction. They reported that the activity of solid acid catalysts per proton depends on their hydrophobicity, porosity and Brønsted acidity. This report corroborates with the investigation of Wilson and Lee.[62] Functionalization with sulfate ions enhance both the Lewis and Brønsted acidity.[63] Effective distribution of covalently bonded sulfur complexes (S═O), which act as electron-withdrawing species, increase the strength of the Lewis acid. Therefore, increase in the sulfate content leads to an increase in catalytic activity.

Both the Lewis and Brønsted acid sites promote esterification and transesterification of trigycerides.[57,63–65] However, Lewis sites are more active promoters of transesterification reactions in the absence of water. Water tends to poison the Lewis sites. The mechanism starts from absorption of substrate over both Lewis and Brønsted acid sites of the catalyst to form a protonated reactant intermediate, as illustrated in Fig. 2 and 3. The Brønsted sites acts as an H^+ donor, whereas the Lewis sites accept the electron pair. The intermediate reacts with alcohol in the bulk (nucleophilic attack) to form a tetrahedral intermediate. This is followed by proton migration and breakage of the tetrahedral intermediate.[57]

3. Solid superacids

3.1. Functionalized heterogeneous catalysts

Functionalization of heterogeneous catalysts, such as clays, carbons, zeolites, mesoporous silica and metal oxides, to form a solid superacid has become an active research area over several decades due to their interesting catalytic performance.[66–69] Functionalization is aimed at incorporating superacidity into the reference material for enhanced catalytic activity. Although metal oxides themselves possess both Lewis and Brønsted sites that are capable of biodiesel production, their Brønsted acidity could be enhanced by functionalization

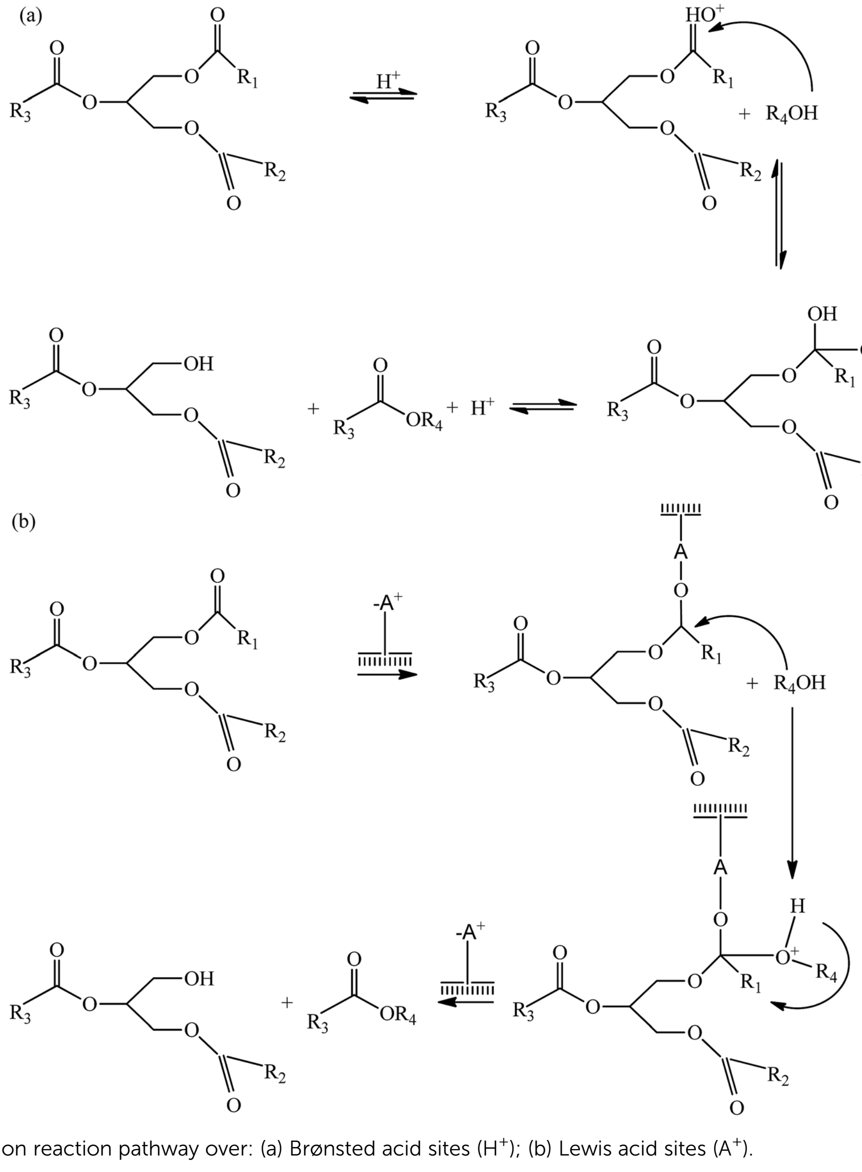

Fig. 2 Transesterification reaction pathway over: (a) Brønsted acid sites (H^+); (b) Lewis acid sites (A^+).

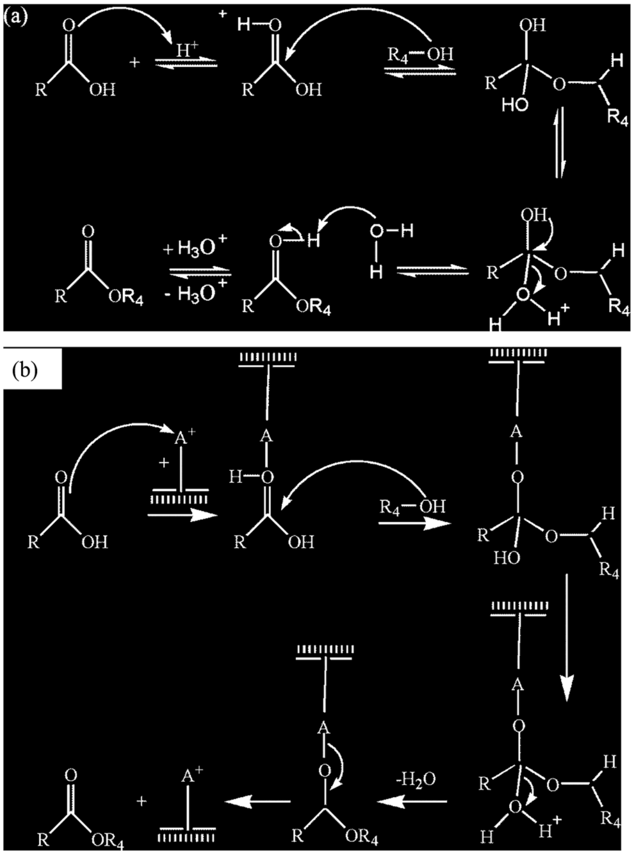

Fig. 3 Esterification reaction pathway over (a) Brønsted acid sites (H^+); (b) Lewis acid sites (A^+).

with proton-donating inorganic compounds.[70] These inorganic compounds include a sulfonic group, sulfuric acid, ammonium sulfate, an aqueous ammonium metatungstate solution and tungstophosphoric acid.[44,67,71,72] Prominent among these are the sulfate precursors because of the superacid attributes of sulfate ions, which are capable of inducing polarization in nearby OH groups. This sulfate structure shows that each sulfur atom is bonded to two tri-coordinated oxygen atoms in a special scheme.[73] This exhibits C_{2v} symmetry, which forms a bridge and chelate structure (Fig. 4).[44]

The S–O–M bonds show the presence of Brønsted acid sites due to cleavage with water in the chelate structure, whereas the bridge structure ($(M–O)_2S(=O)–OH$) indicates that S(v) is the oxidation level of sulfur.[33]

Metal oxide such as TiO_2,[24] SiO_2,[43] Nb_2O_5,[61] ZrO_2,[61] SnO_2,[74] Al_2O_3; mixed oxides such as $SnO_2–Al_2O_3$,[75] $TiO_2–SiO_2$,[33] $ZrO_2–Al_2O_3$;[33] hybrid silica such as amorphous, HMS, SBA-15, MCM-41,[45] and aluminosilicates have been functionalized successfully with sulfate groups. These have shown remarkable performance in production of biodiesel and specialty chemicals. Testa *et al.*[43] studied the catalytic performance of sulfated hybrid silicas for acetic acid esterification with butanol. The report shows that the samples produced exhibited splendid catalytic activity and are remarkably stable despite a decrease of sulfate ion concentration upon recycling. The catalytic performance of sulfated metal oxides is a major function of quantity of sulfate ions deposited onto the surface of the oxide. Increase in the sulfate ion content leads to an increase in the acid strength. Factors such as sulfate ion precursor, amount, calcination temperature and preparation method can influence the deposition of sulfate ions on a metal oxide.

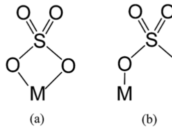

Fig. 4 Sulfate structures: (a) coordinated with C_{2v} chelate and (b) C_{2v} bridge.[44]

de Almeida *et al.*[24] investigated the effect of sulfate concentration used in the preparation of sulfated titania on its catalytic performance. They reported that an increase in sulfate concentration enhanced the textural properties such as pore volume and average pore diameter, specific surface area and the sulfate ion incorporation. Fig. 5 displays the Fourier transmission infrared (FTIR) spectra of sulfated titania prepared with different concentrations of sulfuric acid. This reveals the direct proportionality of sulfate ion concentration to the band intensities of the sulfate vibration between 980 cm^{-1} and 1300 cm^{-1}.

Ropero-Vega *et al.*[44] comparatively studied the synthesis of sulfated titania using ammonium sulfate and sulfuric acid as sulfate precursors and evaluated their performance in the esterification of oleic acid. Their report showed that larger amounts of sulfate ions were linked to the surface of the titania with ammonium sulfate than with sulfuric acid. This is because sulfation with ammonium sulfate ($[TiO_2/SO_4^{2-}–(NH_4)_2SO_4\text{-I}]$) incorporated both Lewis and Brønsted acid sites, whereas sulfuric acid treatment ($[TiO_2/SO_4^{2-}–H_2SO_4\text{-IS}]$) deposited only Lewis sites. Consequently, sulfation with ammonium sulfate gives superior catalytic performance. Fig. 6 presents the model for development of Lewis and Brønsted acid sites on sulfated titania. The inductive effect on S=O bonds could remarkably

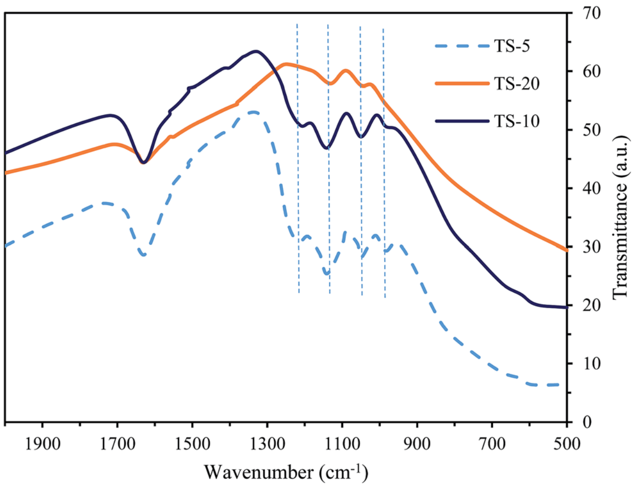

Fig. 5 FTIR spectra for catalysts TS-5, TS-10 and TS-20. Where TS is sulfated titania and TS-10 means $TiO_2/H_2SO_4 = 10$.[24]

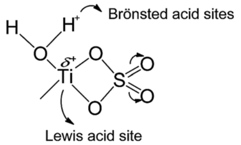

Fig. 6 Schematic of the Brønsted and Lewis acid sites present in the sulfated titania in chelate form.[44]

increase the acid strength. Although [TiO_2/SO_4^{2-}–H_2SO_4-IS] exhibits a higher porosity (0.278 cm^3 g^{-1} and 5.7 nm) relative to [TiO_2/SO_4^{2-}–$(NH_4)_2SO_4$-I] (0.188 cm^3 g^{-1} and 4.2 nm), the later shows a better catalytic performance compared to the former. This is attributed to the higher acidity of [TiO_2/SO_4^{2-}–$(NH_4)_2SO_4$-I] (1.1 mmol SO_4 g^{-1}) compared to [TiO_2/SO_4^{2-}–H_2SO_4-IS] (0.1 mmol SO_4 g^{-1}).

Usai *et al.*[47] compared the effect of two different organic sulfate precursors (propyl-sulfonic acid and phenyl-sulfonic acid) on mesoporous silica (SBA-15) for interesterification of a vegetable oil. They observed that phenyl-sulfonic acid functionalized SBA-15 showed outstanding catalytic performance due to its remarkably higher acidity compared to propyl-sulfonic acid. This report corroborates with previous findings.[76]

Calcination temperature is of vital importance in synthesis of sulfated oxides because calcination stabilizes the properties and produces the active sites of the materials. The optimum calcination temperature varies from one metal oxide to another. Khder *et al.*[63] studied the effect of calcination temperature on the formation of sulfated tin oxide for acetic acid esterification with amyl alcohol. Their report showed that an increase in calcination temperature up to 550 °C leads to an increase in sulfate content and corresponding increase in acidity, which culminated in an increased catalytic activity. However, a further increase in calcination temperature up to 750 °C resulted in decreased catalytic performance due to a decrease in acidity. This could be attributed to the removal of Brønsted acid sites and addition of Lewis acid sites at temperature above the optimum since better activity is essentially promoted by Brønsted acid sites. Moreover, Yang *et al.*[33] reported 450 °C as the optimum calcination temperature for sulfated titanium–silicon for acetic acid conversion. This is attributed to the highest number of acid sites and specific surface area produced at the said optimum temperature.

Similarly, acid strength of the sulfated metal oxide depends on the electronegativity of the metal element. Proton release is more facile for metal element with a lower electronegativity. Considering Zr, Ta, Ti and Nb, their electronegativities are 1.33, 1.50, 1.54 and 1.6, respectively. This corroborates with the report of Li *et al.*,[77] which shows that the order of the Brønsted acidity of the metal oxides as $SO_4^{2-}/ZrO_2 > SO_4^{2-}/Ta_2O_5 > SO_4^{2-}/Nb_2O_5 > SO_4^{2-}/TiO_2$. Furuta *et al.*[74] investigated the efficiency of sulfated tin oxide and zirconia for *n*-octanoic acid esterification with methanol. They reported that the acid strength of sulfated zirconia is lower than that of sulfated tin oxide, which enables better catalytic activities for sulfated tin oxide. This report is concomitant with previous findings.[74,78,79] Table 1 presents more reports on the activities of sulfated metal oxides.[34,52,80–91]

Mesoporous silica could also serve as a support for superacid catalysts because its mesostructure is adjustable and the hydrophobic/hydrophilic balance can be improved by functionalizing with diverse groups of sulfonic acid[54,92] to enhance their reusability.

In general, solid superacids are hydrothermally stable but they become less stable when used with low quality feedstock, which consist of large amounts of FFAs and water. The reusability can be enhanced by the method discussed below (Section 3.3).

3.2. Sulfonated carbon-based catalyst

Sulfonated carbon-based materials such as biomass have enjoyed wide application in biodiesel production because of their ability to absorb large quantities of hydrophilic functional groups such as $-SO_3H$, –OH and –COOH.[93,94] Incorporation of SO_3H onto a flexible carbon fiber of processed biomass materials gives the materials easy access to the SO_3H containing acid sites. Despite the small surface area reported for sulfated carbon-based catalysts (<30 m^2 g^{-1}), they exhibit a remarkable catalytic performance. For instance, in our recent study,[29] we prepared sulfonated carbon-based materials using palm fronds and spikelet powder as the carbon precursors and sulfuric acid as the sulfate source. The synthesized materials exhibited a better catalytic performance for esterification of used frying oil than some earlier reported solid acid catalysts (Table 2). The use of a sulfonated carbon-based catalyst leads to a more economical process because it requires mild reaction conditions such as a low temperature (100 °C), low catalyst amount (2 wt%) and a methanol-to-oil ratio of 5 : 1, which gives a FFA conversion of 98%.

Dawodu *et al.* also reported an outstanding performance for the sulfonated carbon-based catalyst prepared from *C. inophyllum* cake, which gives a *C. inophyllum* oil conversion of 96.6%. However, this is less economical when compared with our work because of the methanol-to-oil ratio of 30 : 1 and 7.5 wt% catalyst amount at 180 °C for 5 h. Table 2 shows more recent studies on the utilization of carbon-based materials as solid acid catalysts for biodiesel production.[95–102] The remarkable performance is due to the incorporation of large amounts of sulfate groups to the bulk of the carbon material by strong hydrogen bonds.[29,103,104] After regeneration by decantation, washing, and drying, the catalyst still maintained its performance after 8 cycles without significant leaching of its strong acid sites. This shows that sulfonated carbon-based catalysts show remarkable stability.

However, there is need for improvement in reusability in water and FFA rich reaction media.

3.3. Alkyl-bridged organosilica moieties functionalized hybrid catalysts

For rational design of efficient catalysts for biodiesel production, it is essential to consider improving the acid sites' environment such as hydrophobicity,[61,105] alleviating mass transfer limitations as well as increasing the density and access to acid sites on the catalyst surface. Hydrophobicity promotes preferential adsorption of hydrophobic reacting species on the catalyst surface and prevents strong adsorption of hydrophilic

Table 1 Some recent sulfated metal oxide for biodiesel production

Catalyst	Feedstock	Reaction conditions	Activity	Recycling	Ref.
SO_4^{2-}/Zr	Used frying oil (esterification)	Methanol-to-oil molar ratio = 5 : 1; 200 °C; 5 h; catalyst loading 2 wt%	Conv. (%) = 85	About 25% loss of activity after 5 successive cycles	61
TiO_2/SO_4^{2-}–$(NH_4)_2SO_4$, TiO_2/SO_4^{2-}–$(NH)SO_4$-IS	Oleic acid (esterification)	Methanol-to-acid molar ratio = 10 : 1; 80 °C; catalyst loading 2 wt%	Conv. (%) = 58.7–1 h; conv. (%) = 29.7–1.5 h	—	27
$ZrSO_4$–SiO_2		Methanol-to-oil molar ratio = 1.2 : 1; 110–120 °C; 1 h; catalyst loading 5 wt%	Conv. (%) = ∼80		62
ZS (sulfated zirconia)	Oleic acid (esterification)	Methanol-to-acid molar ratio = 40 : 1; 60 °C; 12 h; 0.5 g catalyst	Yield (%) = 90		63
Chlorosulfonic zirconia	Oleic acid (esterification)	Methanol-to-acid molar ratio = 8 : 1; 100 °C; 12 h; catalyst loading 3 wt%	Yield (%) = 100		57
Sulfated LaO/HZSM-5, sulfated LaO, HZSM-5	Oleic acid (esterification)	Methanol-to-acid molar ratio = 5 : 1; 100 °C; 7 h; catalyst loading 10 wt%	Conv. (%) = 100, conv. (%) = 96, conv. (%) = 80 with methanol-to-acid ratio = 20 : 1;		64
$Fe(HSO_4)_3$	Waste oil (esterification)	Methanol-to-oil molar ratio = 15 : 1; 205 °C; 4 h; catalyst loading 1 wt%	Yield (%) = 94		65
SO_2/ZrO–TiO/La^{3+}	Acid oil (esterification)	Methanol-to-oil molar ratio = 15 : 1; 200 °C; 2 h; catalyst loading 5 wt%	Yield (%) = 96.24		66
SZ	Caprylic acid (esterification)	Methanol-to-acid molar ratio = 1 : 2; 75 °C; 2 h; catalyst loading 0.08 g ml^{-1}	Conv. (%) = 60	Lost activity by 50% after 6 cycle	67
SZ	Soybean oil	Methanol-to-oil molar ratio = 20 : 1; 150 °C; 2 h; catalyst loading 5 wt%	Conv. (%) = 99.8	Not stable	68
SZ, STO (sulfated tin oxide)	*n*-Octanoic acid (esterification)	Methanol-to-acid molar ratio = 4.5 : 1; 134 °C; 20 h; catalyst loading 4 g	Conv. (%) = 100, conv. (%) = 95	—	46
SZ, STO	*n*-Octanoic acid (esterification)	Methanol-to-acid molar ratio = 4.5 : 1; 175 °C; 20 h; catalyst loading 4 g	Conv. (%) = 99, conv. (%) = 100	—	16
STO		Methanol-to-acid molar ratio = 12 : 1; 230 °C; 8 h; catalyst loading 2 wt%	Conv. (%) = 90		69
STO		Methanol-to-acid molar ratio = 6 : 1; 200 °C; catalyst loading 3 wt%	Conv. (%) = 80		70
SZ		Methanol-to-acid molar ratio = 20 : 1; 120 °C; catalyst loading 5 wt%	Conv. (%) = 98		71
STO	Acetic acid (esterification)	Methanol-to-acid molar ratio = 2 : 1; 250 °C	Conv. (%) = 92.5	—	36
SZ	Myristic acid (esterification)	Methanol-to-acid molar ratio = 10 : 1; 60 °C; 7 h; catalyst loading 0.5 wt%	Conv. (%) > 98	No significant decrease after 5 cycles	23
15SA-SBA-15-p	Carboxylic acids (esterification)	Methanol-to-acid molar ratio = 5 : 1; 50 °C; 5 h; catalyst loading 3 wt%	Conv. (%) = 50	No significant decrease after 5 cycles	72
SZ	Triacetin (transesterification)	Methanol-to-acid molar ratio = 6 : 1; 60 °C; 6.5 h; catalyst loading 2 wt%	Conv. (%) = 50	—	32
TiO_2/SO_4	Soybean oil, castor oil (transesterification)	Methanol-to-oil molar ratio = 6 : 1; 120 °C; 1 h; catalyst loading 1 wt%	Conv. (%) = 40, conv. (%) = 25		11
TiO_2/SO_4^{2-}	Oleic acid (esterification)	Methanol-to-oil molar ratio = 6 : 1; 80 °C; 3 h; catalyst loading 1 wt%	Conv. (%) = 82.2		27

Table 2 Some recent sulfonated carbon-based catalyst for biodiesel production

Catalyst	Preparation method	Feedstocks	Reaction conditions	Activity	Recycling	Ref.
Sulfonated vegetable oil asphalt and petroleum asphalt derived solid acids	Sulfonation of an incompletely carbonized vegetable oil asphalt and petroleum asphalt	Waste oil containing 50 wt% of oleic acid and 50 wt% of cottonseed oil (esterification and transesterification)	Methanol-to-waste oil molar ratio = 20.9 : 1; catalysts loading 0.3 wt% (related to waste oil)	Waste oil conv. (%) = 95 (only having the reaction proceeded at 220 °C; 5 h); waste oil conv. (%) = 98 (coupling reaction and separation; 3 h; 140 and 220 °C for the first and second step)	Recoverable	78
SO_3H-organic matter	Sulfonation of incompletely carbonized microcrystalline cellulose powder	Oleic acid, triolein (esterification and transesterification)	Methanol-to-acid molar ratio = 26 : 1; 95 °C; 4 h; catalyst loading 4 wt% (esterification); methanol-to-triolein molar ratio = 62 : 1; 130 °C; 700 kPa; 5 h; catalyst loading 7.3 wt% (transesterification)	Esterification yield (%) = 100, transesterification yield (%) = 98	Esterification and transesterification can be reused 10 and 5 times without decrease in activity	79
$OMC–H_2O_2–SO_3H$	Sulfonation of H_2O_2-treated OMC	Palmitic acid, oleic acid, stearic acid (esterification)	Methanol-to-acid molar ratio = 20 : 1; 80 °C; 2 h	Conv. (%) = 80	No obvious activity loss after 5 successive cycles	80
Sulfonated D-glucose derived sugar catalyst	Sulfonation of incompletely carbonized D-glucose	Palmitic acid, oleic acid, stearic acid, (esterification)	Methanol-to-acid molar ratio = 10 : 1; 65 °C; 5 h; catalyst loading 5 wt%	Yield (%) > 95	Stable after fifty cycles of successive re-use	81
Sulfonated palm fond, sulfonated palm spinket	Sulfonation of incompletely carbonized palm residues	Used frying oil (esterification)	Methanol-to-oil molar ratio = 5 : 1; 150 °C; 6 h; catalyst loading 1 wt%	Conv. (%) = 78, conv. (%) = 91	About 5% loss of activity after 8 successive cycles	77
Sulfonated *C. inophyllum* seed cake	Sulfonation of incompletely carbonized *C. inophyllum* seed cake	*C. inophyllum* seed oil (esterification and transesterification)	Methanol-to-oil molar ratio = 30 : 1; 180 °C; 6 h; catalyst loading 7.5 wt%	Conv. (%) = 99	Catalyst regeneration is achievable	82
Sulfonated carbon nanohorn	Sulfonation of incompletely carbonized carbon nanohorn	Palmitic acid (esterification)	Methanol-to-oil molar ratio = 33 : 1; 64 °C; 6 h; catalyst loading 3 wt%	Yield (%) = 93	The active sites were not deactivated after 3 cycles	82
Sulfonated corn straw	Sulfonation of incompletely carbonized corn straw	Oleic acid (esterification)	Methanol-to-acid molar ratio = 7 : 1; 60 °C; 4 h; catalyst loading 7 wt%	Yield (%) = 98	—	84
Sulfonated starch, cellulose, sucrose, D-glucose	Sulfonation of incompletely carbonized	Waste cooking oil (esterification and transesterification)	Methanol-to-oil molar ratio = 30 : 1; 80 °C; 8 h; catalyst loading 10 wt%	Yield (%) = 95, yield (%) = 88, yield (%) = 80, yield (%) = 76	Very stable. Only about 7% loss of activity after 50 cycles	85

products such as water and glycerol, thereby reducing the deactivation propensity of the active sites.[93,106] Furthermore, enhanced surface area as well as pore size and volume helps to alleviate mass transfer limitations and increase the density and access to acid sites.[67,72,93] These design specifications are simultaneously obtainable by functionalizing solid acids with alkyl-bridged organosilica moieties to form an organic–inorganic hybrid catalyst.[62,67,93,107] Alkyl bridged silica moieties are obtained by *in situ* incorporation of organosulfonic acid groups throughout the silica framework with bridging alkyl groups.

These polymer-oxides and moieties are hydrophobic in nature and are capable of incorporating excellent porosity and removal of the surface hydroxyl groups to maintain the hydrophobic/hydrophilic balance of the catalyst.[93,108] Organic–inorganic hybrid catalysts include $H_3PW_{12}O_{40}$–Ta_2O_5/Si(Et/Ph)Si, $H_3PW_{12}O_{40}$–ZrO_2/Si(Et/Ph)Si, $H_3PW_{12}O_{40}$/Ta_2O_5–Si(Me/Ph), $H_3PW_{12}O_{40}$/ZrO_2–Si(Me/Ph) and SO_4^{2-}/ZrO_2–SiO_2 (Et/Ph).[93] These hybrid catalysts are remarkably stable and easy to regenerate using dichloromethane to wash rather than employing thermal treatments as usual, thereby preserving the organic functionalities, Keggin unit and structural integrity of the catalysts.[93]

To successfully achieve a well-designed superhydrophobic hybrid catalyst of this type with a 2D hexagonal *p*6*mm*, 3D interconnected wormhole-like pore morphologies and 3D cubic *Im*3*m*, it is imperative to vary parameters such as preparation conditions, surfactant type, Si/Zr molar ratio, and organic silica precursor.[93,109] High organic content hybrid materials could be synthesized by co-condensation, a periodically ordered mesoporous organosilica (PMO) approach, using a special sol–gel and by a one-step templated sol–gel condensation.[93,107,110] All the approaches, except the one-step template sol–gel condensation, lead to a reduction in surface area and pore volume because of poor loading control, loss homogeneity and acid site leaching associated with a post-grafting approach.[111] The one-step template sol–gel condensation approach incorporates the hydrophobic functionalities *in situ* to produce mesoporous hybrid materials with better homogeneity of active species, which preserves the active phase from leaching, thereby improving the catalyst stability.[112–114] The catalytic activity of these materials is discussed in Section 5.1.

4. Super acidity characterization

Solid superacids are characterized by various techniques such as ammonia temperature program desorption (NH_3-TPD), infrared spectroscopy (FTIR) and pyridine adsorption. Moreover, a titration method with a probe using Hammett indicators and potentiometric titration is used.[44]

The titration method with a probe using Hammett indicators also determines the acid strength distribution and surface acidity of heterogeneous catalysts. Hammett indicators are uncharged bases that are converted to conjugate acids by proton transfer. The probe reagents for the titration include water, pyridine, ethyl alcohol and *n*-butylamine. While *n*-butylamine ($pK_a \leq +10.6$) and pyridine ($pK_a \leq +5.3$) are easily absorbed onto the active sites, ethyl alcohol ($pK_a \leq -2$) and water ($pK_a \leq -1.7$) are scarcely absorbed.[115] The most popularly used of these probe reagents is *n*-butylamine because it possesses the highest pK_a value. The degree of hydration and exchangeable cations of a sample strongly determines its surface acidity. Touillaux *et al.*[116] discovered that water molecules absorbed on montmorillonite dissociate 10^7 times faster than ordinary water. This is traceable to the acidic nature of the exchangeable cation in the absorbed water, which donates a proton as follows:[117]

$$M^n(H_2O) \rightarrow (M\text{–}OH)^{n-1} + H^+.$$

The ability of a solid sample to donate a proton (pK_a) is expressed by Hammett and Deyrup as

$$H_0 = pK_a + \frac{\log[B]}{\left[BH^+\right]}$$

where pK_a represents the activity of the hydrogen ion from the surface acid; $[BH^+]$ and [B] are the activity coefficients of the acidic and basic sites formed by the indicator, respectively.[118] If the reaction proceeds by the transfer of an electron pair to the surface, then the activity function is given by

$$H_0 = pK_a + \frac{\log[B]}{[AB]}$$

where [AB] represents the neutral base concentration that reacted with the electron pair acceptor, A or Lewis acid.

Prior to the titration, the sample is prepared by heating at 200 °C for 1 h under vacuum condition according to Yang *et al.*[33] Ropero-Vega *et al.*[44] proposed preparation by dispersing the sample in dry benzene. After preparation, the sample is titrated with a probe prior to addition of the Hammett indicators vapor. The color change of the indicators with their respective pK_a's is presented in Table 3.[119] The amount of acid sites for both Lewis and Brønsted sites are determined by the mole of the sites per gram of sample after the validation of acid strength. The acid strengths for solid acids are in from $H_0 = 6.8$ to as low as -8.2. Samples with an acid strength estimated greater than $H_0 = -11.93$ are said to be superacids. This corresponds to the strength of H_2SO_4 (100%). However, titration using Hammett indicators is not suitable for dark or colored samples due to the difficulty in observing a color change.

On the other hand, FTIR-pyridine adsorption is said to be more reliable in classifying and quantifying the acidity properties of solid acids because of it is has good resolution, sensitivity and ability to determine chemical species.[118,120] It classified the acid sites into Brønsted and/or Lewis and also classifies the acids based on acid strength. The samples are prepared by annealing and pressing them into a thin self-supporting wafer. This is followed by evacuation at 400 °C for 2 h in vacuum to purge the species that are strongly bonded to the sample and activate it prior to absorption. Furthermore, pyridine adsorption takes place at room temperature for about 10 min, after which the sample is desorbed at 200, 300, 400 and 700 °C. The desorption temperatures correspond to weak, mild,

Table 3 Basic indicators used for the measurement of acid strength[101]

	Color	Color		
Indicator	Base form	Acid form	pK_a	[H_2SO_4]%
Neutral red	Yellow	Red	6.8	8×10^{-8}
Methyl red	Yellow	Red	4.8	—
Phenylazonaphthylamine	Yellow	Red	4	5×10^{-5}
p-Dimethylaminoazobenzene	Yellow	Red	3.3	3×10^{-4}
2-Amino-5-azotoluene	Yellow	Red	2	5×10^{-3}
Benzeneazodiphylamine	Yellow	Purple	1.5	2×10^{-2}
Crystal violet	Blue	Yellow	0.8	0.1
p-Nitrobenzeneazo-(*p*′-nitro-diphenylamine)	Orange	Purple	0.43	—
Dicinnamalacetone	Yellow	Red	−3	48
Benzalacetophenone	Colorless	Yellow	−5.6	71
Anthraquinone	Colorless	Yellow	−8.2	90
2,4,6-Trinitroaniline	Colorless	Yellow	−10.1	98
p-Nitrotoluene	Colorless	Yellow	−11.35	[a]
m-Nitrotoluene	Colorless	Yellow	−11.99	[a]
p-Nitrofluorobenzene	Colorless	Yellow	−12.44	[a]
p-Nitrochlorobenzene	Colorless	Yellow	−12.7	[a]
m-Nitrochlorobenzene	Colorless	Yellow	−13.16	[a]
2,4-Dinitrotoluene	Colorless	Yellow	−13.75	[a]
2,4-Dinitrofluorobenzene	Colorless	Yellow	−14.52	[a]
1,3,5-Trinitrotoluene	Colorless	Yellow	−16.04	[a]

[a] The indicator is liquid at room temperature and acid strength corresponding to the indicator is higher than the acid strength of 100 percent H_2SO_4.

strong and super acidity. The band intensities at 1450 cm^{-1}, 1540 cm^{-1} and 1438 cm^{-1}, which correspond to Lewis and Brønsted acid sites and surface hydroxyl determine the concentration of each site.[33,121,122] Furthermore, the band at 1488 cm^{-1} represents a mixture of Lewis and Brønsted acid sites.[40]

NH_3-TPD determines the acid strength distribution and amount of acid sites in the solid acid samples. In comparison with other analytical methods available, NH_3-TPD is becoming increasingly used to probe the surface acidity of solid acid samples.[123] However, the technique is somewhat tedious and time consuming towards repeated operation for more sample analysis. Moreover, Wang *et al.*[124] developed a high throughput strategy using a multistream mass spectrometer screening (MSMSS) procedure. This technique shows an outstanding improvement over the conventional method because it can be used to analyze up to 10 samples in around 6 h. Gorgulho *et al.*[123] comparatively studied the effectiveness of titration and TPD techniques. They reported that both methods give closely related results; however, the quantitative results of TPD are closer to that of the elemental analysis. The titration method is less effective in quantifying weak acid sites.

5. Biodiesel production *via* solid superacid catalysis: more efficient strategies

Owing to the fact that biodiesel production could also involve water as a reactant, solid superacid catalysts produced by functionalization with sulfate ions are prone to deactivation due to the leaching of active sites (sulfate ions). Therefore, it is expedient to decipher a more effective way of preventing or reducing the side effects (leaching of active sites) of the moisture content of the feedstock or/and of the product. The following section discussed in detail the recent advances towards the more efficient biodiesel production from highly acidic feedstocks.

5.1. Alkyl-bridged organosilica moieties functionalized hybrid catalysis

Alkyl-bridged organosilica moieties are highly valued water tolerant materials for hydrophobization of sulfated mesoporous silica catalyst[54,111] to improve the chemical stability of the catalyst towards efficient biodiesel production.

Xu *et al.*[125–127] investigated the catalytic activity of hybrid catalysts synthesized by functionalizing Ta_2O_5 with both a Keggin-type heteropolyacid and alkyl-bridged organosilica moieties. The $H_3PW_{12}O_{40}$ loading was varied from 3.6% to 20.1% in a one-step sol–gel hydrothermal route using a triblock copolymer as the surfactant. The catalyst showed a remarkable performance in the transesterification of soybean oil and tripalmitin and in the esterification of myristic acid and lauric acid. The catalyst is also proficient towards simultaneous transesterification and esterification under mild operating conditions. The report also shows that incorporating both hydrophobic and superacid functionalities within the Ta_2O_5 surface enhances the catalytic performance. Lastly, the hybrid catalysts were said to be reusable after three runs of catalytic reaction. Melero *et al.*[54,111] also studied the superhydrophobicity

Table 4 Some recent sulfonic acid modified mesoporous organo-silica for biodiesel production

Catalyst	Preparation method	Feedstocks	Reaction conditions	Activity	Recycling	Ref.
Pr SO_3H-MM-SBA-15	Post-synthesis	Palmitic acid, glyceryl trioctanoate (esterification and transesterification)	Methanol-to-palmitic acid, molar ratio = 4 : 1; methanol-to-glyceryl, trioctanoate molar ratio = 30 : 1; 60 °C; 6 h; catalyst, loading 0.3 wt%	Conv. (%) of, palmitic acid = 55; conv. (%) of glyceryl trioctanoate = 2.5	No data about, deactivation, behaviour	110
Propyl-SO_3H SBA-15, Me/Arene-SO_3H SBA-15, arene-SO_3H SBA-15	Co-condensation, post-synthesis, co-condensation	Soybean oil containing, 20 wt% of oleic acid (esterification and transesterification)	Microwave irradiation; 1-butanol-to-oil molar ratio = 6 : 1; 190 °C; 15 min; catalyst, loading 5 wt%	Yield (%) = 38, yield (%) = 58, yield (%) = 56	The activity level of the 2nd run was 85–90% of the fresh catalyst activity	111
SBA-15-SO_3H, SBA-15-SO_3H-R, R/SBA-15-SO_3H (R = Me, Et or Ph)	Co-condensation, co-condensation, post-synthesis	Palmitic acid in soybean oil (esterification)	Methanol-to-palmitic, acid molar ratio = 20 : 1; 85 °C; 2 h; catalyst, loading 10 wt%	Conv. (%) = 88, conv. (%) = 84, conv. (%) = 70	No data about, deactivation, behaviour	112
Propyl-SO_3H-KIT-6 (5.2 nm), propyl-SO_3H-KIT-6 (6.2 nm), propyl-SO_3H-KIT-6 (7.0 nm)	Post-synthesis	Palmitic acid (esterification)	Methanol-to-palmitic, acid molar ratio = 30 : 1; 60 °C; 6 h; catalyst, loading 0.4 wt%	Conv. (%) = 14, conv. (%) = 28, conv. (%) = 39	Stable under the, mild operating, conditions, employed	113
Arene-SO_3H-SBA-15	Co-condensation		Methanol-to-oil, acid molar ratio = 30 : 1; 160 °C; 8 h; catalyst, loading 8 wt%	Yield (%) = 82		94
Propyl-SO_3H-SBA-15 arene-SO3H-SBA-15 arene-SOH-SBA-15 (capped)	Co-condensation	Crude palm oil	Methanol-to-oil, acid molar ratio = 20 : 1; 140 °C; 2 h; catalyst, loading 6 wt%	Yield (%) = ∼72, yield (%) = ∼78, yield (%) = ∼90		73
SiO_2-propyl-SO_3H	Co-condensation	Acetic acid (esterification)	Methanol-to-oil, acid molar ratio = 1 : 1; 110 °C; catalyst loading 25 mg	Conv. (%) = 86	The activity decreased by 5% after 5 cycles	26
SBA15-propyl-SO_3H SBA-15-phenyl-SOH	Co-condensation	Interesterification of extra virgin olive oil with ethyl acetate	Methanol-to-oil, acid molar ratio = 20 : 1; 130 °C; 6 h; catalyst loading 13 wt%	Conv. (%) = 6, conv. (%) = 20	—	30
Propyl-sulfonic SBA-15	Co-condensation	Ethyl hexanoate (transesterification)	Methanol-to-oil, acid molar ratio = 4 : 1; 60 °C; 4 h; catalyst loading 200 mg	Conv. (%) = 63	No significant decrease after 4 cycles	28

of a SBA-15-based hybrid catalyst obtained from SBA-15 modification with both arene-sulfonic acid and trimethyltrimethoxysilane (TMS) for biodiesel production from acidic crude palm oil. They reported that the alkyl-free sulfonated hybrid catalyst demonstrated low hydrophobicity when 1 wt% water was added to the reaction medium, leading to a vivid reduction in biodiesel yield. This weakens the active site environment, making it vulnerable to attack by glycerol, which is a polar by-product, thereby hindering the hydrophobic substrates from accessing the active sites. Furthermore, addition of more water up to 10 wt% leads to acid catalyzed hydrolysis, thus increasing the FFA content of the produced diesel, which makes it substandard. However, further modification with TMS alleviates blockage of active sites, so the catalytic performance improved remarkably.

To better manage water in biodiesel production, the study of Long *et al.*[105] dwells extensively on the synthesis of a polymer-oxide hybrid catalyst based on sulfate nonporous silica for hydrolysis of esters. The catalyst was synthesized by the formation of a polymer brush and subsequent functionalization with sulfonic acid. This gives a well-designed hybrid material with remarkable hydrolytic stability as well as access to the active site. They reported that the catalyst is as active as *p*-toluenesulfonic acid and more active than Amberlyst 15 in the hydrolysis of ethyl lactate. However, the major obstacle to its recyclability is that the polymer chains gradually detach from the oxide support and exclusion of SO_3H from the catalyst surface. Table 4 presents more reports on the activities of alkyl-bridged organosilica moieties.[128–131]

5.2. Pre- and *in situ* water removal

Apart from alkyl modification of the catalyst, several methods are employed to salvage catalyst deactivation in biodiesel production in the presence of water. These include introduction of molecular sieves into the reacting media to scavenge water, feedstock and catalyst pretreatment, and reduction of the temperature profile of the system by initially promoting transesterification at a high temperature and the subsequent temperature reduction to minimize hydrolysis of FAME.[111] The first method entails drying of the catalyst at 80 °C and the feedstock at 100 °C and 70 mbar for 12 h prior to the reaction[111] or drying by adding a dehydrating agent such as molecular sieves.[132,133] Li *et al.*[132] investigated this pretreatment strategy towards methanolysis of waste oil over a lipase catalyst. They reported that the pretreated waste oil was effectively converted to biodiesel with a higher yield of methyl ester than untreated waste oil. The yield from the treated waste oil is comparable with the yield from refined oil. Alternatively, the second method involves *in situ* water removal from the system by addition of dehydrating molecular sieve such as zeolite LTA using a catalyst/zeolite mass ratio of 10.[111,133] Prior to the reaction, the molecular sieve must degassed at about 110 mbar and 180 °C for about 12 h in an oven.[111] Molecular sieves are appropriate for dehydrating organic solvents. In the reaction media, both water and the products are strongly adsorbed on the surface of the molecular sieve, but the pores are only permeable by water molecules.[133] This facilitates in the effective removal of water molecule from the reaction media. Melero *et al.*[111] performed a comparative study of two of these strategies. They compared pretreatment of feedstock and catalyst with *in situ* water removal from the reaction media over arene-SO_3H-SBA-15. Fig. 7 shows the comparative yield of FAME as a function of time for the strategies. The pretreatment method gave a better FAME yield compared to the untreated catalyst and feedstock (about 5% difference). The most effective strategy is *in situ* water removal. This is mainly because the *in situ* water removal strategy scavenged the *in situ* generated water from the FFA esterification process. Therefore, it is tenable to say that water formation is more paramount to the catalytic process than the initial water content of the feedstock and the catalyst because of its preferential interaction with the active sites due to proximity.

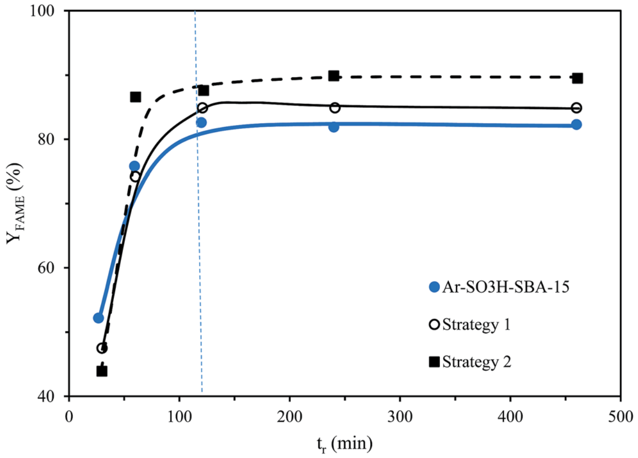

Fig. 7 Evolution of yield to FAME from crude palm oil over arene-SO_3H-SBA-15 catalyst with the different strategies. Strategy 1: pretreatment of feedstock and catalyst. Strategy 2: *in situ* water removal from the reaction media. Reaction conditions: 160 °C; 30 : 1 methanol : oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.[111]

5.3. Process intensification: temperature profile reduction

FAME production does not only proceed through transesterification of triglycerides and esterification of FFAs as discussed above. The presence of water molecules engenders hydrolysis of triglycerides to produce FFAs and subsequent esterification of the FFAs (Fig. 8). The major parameters that influence these reactions are water content and operating temperature.[111]

Temperature profile reduction helps to intensify the processes by minimizing FFA yield and maximizing FAME yield simultaneously. This strategy comprises two steps: the first step promotes transesterification and triglyceride hydrolysis of FFA at high temperature (160–180 °C).[105,134–140] The second step promotes esterification of FFA, both the ones inherent in the feedstock and the ones produced from the first step, thereby minimizing hydrolysis of FAME at low temperatures (80–100 °C).[111,136,141] Melero *et al.*[111] comprehensively investigated the effect of temperature profile reduction at various upper and

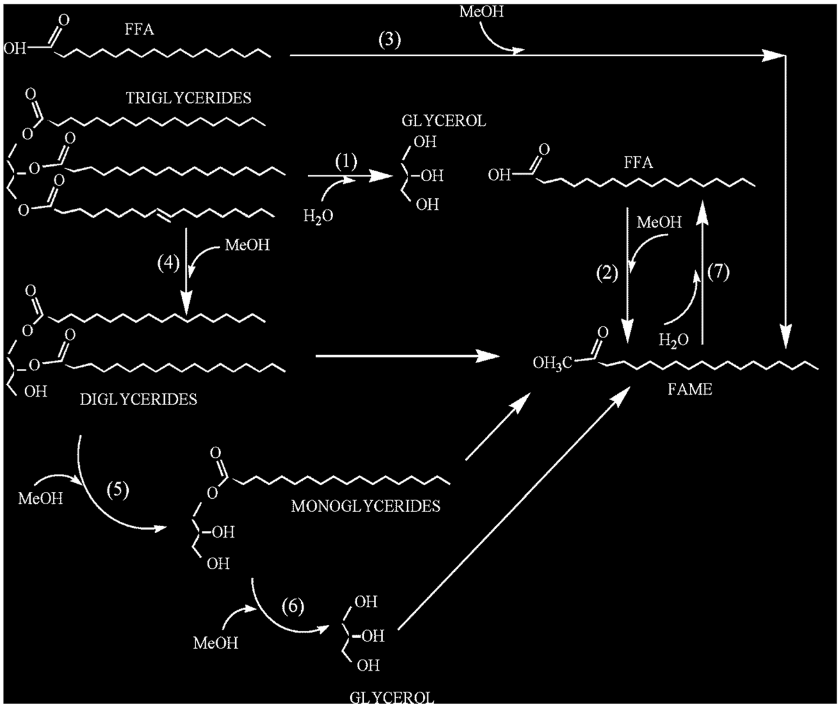

Fig. 8 Simplified reaction pathway for FAME production from highly acidic feedstock over solid superacid catalyst. Reaction (1), (4), (5) and (6), transesterification routes; (2) and (3) are FFA esterification routes; while (7) is a FAME hydrolysis route.[111]

lower temperature settings (Fig. 9). To reduce the transition period, they used a water–ice bath to step down the lower limit. This strategy remarkably reduced the acid value of the produced diesel (from 20 mg KOH per g to less than 5 mg KOH per g). It was also reported that the FAME yield increases with an increase in the higher limit temperature and a decrease in that of the lower limit. The optimal temperature profile reduction was 160–100 °C, which gave an acid value of 0.4 mg KOH per g and FAME yield of 96%.

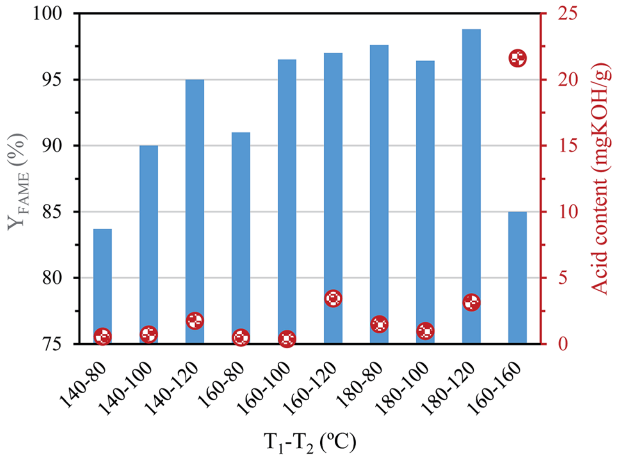

Fig. 9 Yield to FAME from crude palm oil over arene-SO_3H-SBA-15 using a decreasing temperature profile. Reaction conditions: 2 h at temperature T_1 followed by 2 h at temperature T_2; 30 : 1 methanol : oil molar ratio; 8 wt% catalyst loading; 2000 rpm stirring rate.[111]

6. Conclusion

Heterogeneous superacid catalysts are more effective in biodiesel production from low-grade/cost feedstock compared to their homogeneous counterparts because of their remarkable activity and reusability. This is made possible by their rational design, which ensures well-defined mesoporosity and an excellent hydrophobicity/hydrophilicity balance. A well designed solid superacid helps to minimize the mass transfer limitation and suppress deactivation by water and glycerol.

Zeolites are among the diverse possible known solid acids are, which are very popular in various industrial processes. However, zeolites being microporous are marred with stearic hindrance due to their micropore size preventing the diffusion of bulky molecules. Therefore, sulfated metal oxides become very popular. They are solid superacids with remarkable catalytic performance in biodiesel production from low-quality feedstock. However, the reusability still needs improvement due to leaching of sulfate groups into the reaction medium particularly in a reaction medium marred with moisture. Therefore, several strategies are employed to enhance the reusability of solid superacids such as functionalized heterogeneous catalysts and sulfonated carbon-based catalysts.

One of the strategies is hydrophobization with alkyl-bridge organosilica moieties for improved hydrothermal stability. The outstanding catalytic performance of hybrid catalysts is mainly due to their inherent Brønsted acidity, enhanced hydrophobic/hydrophilic balance and well-defined mesoporosity, which is traceable to the alkyl-bridged organosilica moieties incorporation. In addition, hybrid catalysts exhibit remarkable reusability because the incorporated moieties suppressed the sulfate groups leaching into the reaction medium.

The second visible strategy involves water removal either pre or *in situ*. The former involves feedstock and catalyst heat pretreatment, whereas the later involves introduction of molecular sieves to the reacting media as water scavengers. The later proved to be more effective because water formation is more paramount in the catalytic process than the initial water content of the feedstock and the catalyst due to proximity to the active sites, which engenders preferential interaction.

The third strategy is aimed at intensifying the process by reduction of the temperature profile, which aids in the simultaneous minimization of the FFA yield and maximization of the FAME yield. This helps to reduce the acid value towards producing high-quality biodiesel.

The second and the third strategies can be used over all the solid superacids discussed in Section 3 such as functionalized heterogeneous catalysts, sulfonated carbon-based catalysts and alkyl-bridged organosilica moieties functionalized hybrids.

Acknowledgements

We gratefully acknowledge the High Impact Research (HIR) Grant from the University of Malaya for fully funding this study through Project No. "D000011-16001". We also appreciate the support of Chemical Engineering Department with RP015-2012D Grant.

References

1 M. J. Ramos, A. Casas, L. Rodríguez, R. Romero and Á. Pérez, Transesterification of sunflower oil over zeolites using different metal loading: a case of leaching and agglomeration studies, *Appl. Catal., A*, 2008, **346**, 79–85.

2 M. Habibullah, H. Masjuki, M. Kalam, I. R. Fattah, A. Ashraful and H. Mobarak, Biodiesel production and performance evaluation of coconut, palm and their combined blend with diesel in a single-cylinder diesel engine, *Energy Convers. Manage.*, 2014, **87**, 250–257.

3 A. Abbaszaadeh, B. Ghobadian, M. R. Omidkhah and G. Najafi, Current biodiesel production technologies: a comparative review, *Energy Convers. Manage.*, 2012, **63**, 138–148.

4 S. Imtenan, H. Masjuki, M. Varman, I. R. Fattah, H. Sajjad and M. Arbab, Effect of *n*-butanol and diethyl ether as oxygenated additives on combustion–emission-performance characteristics of a multiple cylinder diesel engine fuelled with diesel–jatropha biodiesel blend, *Energy Convers. Manage.*, 2015, **94**, 84–94.

5 A. M. Ashraful, H. Masjuki, M. Kalam, I. R. Fattah, S. Imtenan, S. Shahir and H. Mobarak, Production and comparison of fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils: a review, *Energy Convers. Manage.*, 2014, **80**, 202–228.

6 M. Mosarof, M. Kalam, H. Masjuki, A. Ashraful, M. Rashed, H. Imdadul and I. Monirul, Implementation of palm biodiesel based on economic aspects, performance, emission, and wear characteristics, *Energy Convers. Manage.*, 2015, **105**, 617–629.

7 S. E. Onoji, S. E. Iyuke, A. I. Igbafe and D. B. Nkazi, Rubber seed oil: a potential renewable source of biodiesel for sustainable development in sub-saharan africa, *Energy Convers. Manage.*, 2016, **110**, 125–134.

8 Y. M. Sani, W. M. A. W. Daud and A. A. Aziz, Solid acid-catalyzed biodiesel production from microalgal oil—the dual advantage, *J. Environ. Chem. Eng.*, 2013, **1**, 113–121.

9 A. K. Agarwal, T. Gupta, P. C. Shukla and A. Dhar, Particulate emissions from biodiesel fuelled CI engines, *Energy Convers. Manage.*, 2015, **94**, 311–330.

10 S. Palash, H. Masjuki, M. Kalam, B. Masum, A. Sanjid and M. Abedin, State of the art of NO_x mitigation technologies and their effect on the performance and emission characteristics of biodiesel-fueled compression ignition engines, *Energy Convers. Manage.*, 2013, **76**, 400–420.

11 R. Luque, J. C. Lovett, B. Datta, J. Clancy, J. M. Campelo and A. A. Romero, Biodiesel as feasible petrol fuel replacement: a multidisciplinary overview, *Energy Environ. Sci.*, 2010, **3**, 1706–1721.

12 A. Demirbas and M. F. Demirbas, Importance of algae oil as a source of biodiesel, *Energy Convers. Manage.*, 2011, **52**, 163–170.

13 A. Carrero, G. Vicente, R. Rodríguez, M. Linares and G. Del Peso, Hierarchical zeolites as catalysts for biodiesel production from nannochloropsis microalga oil, *Catal. Today*, 2011, **167**, 148–153.

14 H. Farag, A. El-Maghraby and N. A. Taha, Transesterification of esterified mixed oil for biodiesel production, *Int. J. Chem. Biochem. Sci.*, 2012, **2**, 105–114.

15 N. Yusuf, S. K. Kamarudin and Z. Yaakub, Overview on the current trends in biodiesel production, *Energy Convers. Manage.*, 2011, **52**, 2741–2751.

16 M. Kour and S. Paul, Sulfonated carbon/nano-metal oxide composites: a novel and recyclable solid acid catalyst for organic synthesis in benign reaction media, *New J. Chem.*, 2015, **39**, 6338–6350.

17 D. Reinoso, D. Damiani and G. Tonetto, Synthesis of biodiesel from soybean oil using zinc layered hydroxide salts as heterogeneous catalysts, *Catal. Sci. Technol.*, 2014, **4**, 1803–1812.

18 W. Xie, H. Peng and L. Chen, Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst, *Appl. Catal., A*, 2006, **300**, 67–74.

19 P. Intarapong, A. Luengnaruemitchai and S. Jai-In, Transesterification of palm oil over KOH/NaY zeolite in a packed-bed reactor, *Int. J. Renew. Energy Res*, 2012, **1**, 271–280.

20 P. A. Suarez, S. M. P. Meneghetti, M. R. Meneghetti and C. R. Wolf, Transformação de triglicerídeos em combustíveis, materiais poliméricos e insumos químicos: Algumas aplicações da catálise na oleoquímica, *Quim. Nova*, 2007, **30**, 667–676.

21 C. J. King, Separation processes, introduction, *Ullmann's Encyclopedia of Industrial Chemistry*, 2000.

22 M. Balat, Potential alternatives to edible oils for biodiesel production – a review of current work, *Energy Convers. Manage.*, 2011, **52**, 1479–1492.

23 M. Besson and P. Gallezot, Deactivation of metal catalysts in liquid phase organic reactions, *Catal. Today*, 2003, **81**, 547–559.

24 R. M. de Almeida, L. K. Noda, N. S. Gonçalves, S. M. Meneghetti and M. R. Meneghetti, Transesterification reaction of vegetable oils, using superacid sulfated TiO_2-base catalysts, *Appl. Catal., A*, 2008, **347**, 100–105.

25 M. Zabeti, W. M. A. W. Daud and M. K. Aroua, Activity of solid catalysts for biodiesel production: a review, *Fuel Process. Technol.*, 2009, **90**, 770–777.

26 Z. Helwani, M. Othman, N. Aziz, J. Kim and W. Fernando, Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review, *Appl. Catal., A*, 2009, **363**, 1–10.

27 M. Misono and T. Okuhara, Solid superacid catalysts, *CHEMTECH*, 1993, 23.

28 Y. M. Sani, W. M. A. W. Daud and A. A. Aziz, Activity of solid acid catalysts for biodiesel production: a critical review, *Appl. Catal., A*, 2014, **470**, 140–161.

29 Y. M. Sani, A. O. Raji-Yahya, P. A. Alaba and W. M. A. W. D. ARA Aziz, Palm frond and spikelet as environmentally benign alternative solid acid catalysts for biodiesel production, *BioResources*, 2015, **10**, 3393–3408.

30 S. Furuta, H. Matsuhashi and K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, *Catal. Commun.*, 2004, **5**, 721–723.

31 S. Furuta, H. Matsuhashi and K. Arata, Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor, *Biomass Bioenergy*, 2006, **30**, 870–873.

32 J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho and P. Jenvanitpanjakul, Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts, *Chem. Eng. J.*, 2006, **116**, 61–66.

33 H. Yang, R. Lu and L. Wang, Study of preparation and properties on solid superacid sulfated titania–silica nanomaterials, *Mater. Lett.*, 2003, **57**, 1190–1196.

34 Y. M. Sani, P. A. Alaba, A. O. Raji-Yahya, A. A. Aziz and W. M. A. W. Daud, Acidity and catalytic performance of Yb-doped/Zr in comparison with/Zr catalysts synthesized *via* different preparatory conditions for biodiesel production, *J. Taiwan Inst. Chem. Eng.*, 2016, **59**, 195–204.

35 Y. M. Sani, P. A. Alaba, A. O. Raji-Yahya, A. A. Aziz and W. M. A. W. Daud, Facile synthesis of sulfated mesoporous Zr/ZSm-5 with improved Brønsted acidity and superior activity over SZr/Ag, SZr/Ti, and SZr/W in transforming UFO into biodiesel, *J. Taiwan Inst. Chem. Eng.*, 2016, **60**, 247–257.

36 P. A. Alaba, Y. M. Sani, I. Y. Mohammed, Y. A. Abakr and W. M. A. W. Daud, Synthesis and application of hierarchical mesoporous HZSM-5 for biodiesel production from shea butter, *J. Taiwan Inst. Chem. Eng.*, 2016, **59**, 405–412.

37 A. A. Kiss, A. C. Dimian and G. Rothenberg, Solid acid catalysts for biodiesel production-towards sustainable energy, *Adv. Synth. Catal.*, 2006, **348**, 75–81.

38 B. M. Reddy and M. K. Patil, Organic syntheses and transformations catalyzed by sulfated zirconia, *Chem. Rev.*, 2009, **109**, 2185–2208.

39 G. D. Yadav and J. J. Nair, Sulfated zirconia and its modified versions as promising catalysts for industrial processes, *Microporous Mesoporous Mater.*, 1999, **33**, 1–48.

40 K. Saravanan, B. Tyagi and H. Bajaj, Sulfated zirconia: an efficient solid acid catalyst for esterification of myristic acid with short chain alcohols, *Catal. Sci. Technol.*, 2012, **2**, 2512–2520.

41 K. Saravanan, B. Tyagi and H. Bajaj, Esterification of caprylic acid with alcohol over nano-crystalline sulfated zirconia, *J. Sol–Gel Sci. Technol.*, 2012, **62**, 13–17.

42 M. L. Testa, V. La Parola, L. F. Liotta and A. M. Venezia, Screening of different solid acid catalysts for glycerol acetylation, *J. Mol. Catal. A: Chem.*, 2013, **367**, 69–76.

43 M. L. Testa, V. La Parola and A. M. Venezia, Esterification of acetic acid with butanol over sulfonic acid-functionalized hybrid silicas, *Catal. Today*, 2010, **158**, 109–113.

44 J. Ropero-Vega, A. Aldana-Pérez, R. Gómez and M. Niño-Gómez, Sulfated titania [TiO_2/SO_4^{2-}]: a very active solid acid catalyst for the esterification of free fatty acids with ethanol, *Appl. Catal., A*, 2010, **379**, 24–29.

45 M. L. Testa, V. La Parola and A. M. Venezia, Transesterification of short chain esters using sulfonic acid-functionalized hybrid silicas: effect of silica morphology, *Catal. Today*, 2014, **223**, 115–121.

46 A. Venezia, G. Di Carlo, L. Liotta, G. Pantaleo and M. Kantcheva, Effect of Ti(IV) loading on CH_4 oxidation activity and SO_2 tolerance of Pd catalysts supported on silica SBA-15 and HMS, *Appl. Catal., B*, 2011, **106**, 529–539.

47 E. M. Usai, M. F. Sini, D. Meloni, V. Solinas and A. Salis, Sulfonic acid-functionalized mesoporous silicas: microcalorimetric characterization and catalytic performance toward biodiesel synthesis, *Microporous Mesoporous Mater.*, 2013, **179**, 54–62.

48 P. A. Alaba, Y. M. Sani and W. M. A. W. Daud, Kaolinite properties and advances for solid acid and basic catalyst synthesis, *RSC Adv.*, 2015, **5**, 101127–101147.

49 R. Ryoo, S. H. Joo and S. Jun, Synthesis of highly ordered carbon molecular sieves *via* template-mediated structural transformation, *J. Phys. Chem. B*, 1999, **103**, 7743–7746.

50 D. M. Kargbo, Biodiesel production from municipal sewage sludges, *Energy Fuels*, 2010, **24**, 2791–2794.

51 J. Encinar, N. Sánchez, G. Martínez and L. García, Study of biodiesel production from animal fats with high free fatty acid content, *Bioresour. Technol.*, 2011, **102**, 10907–10914.

52 J. A. Melero, L. F. Bautista, J. Iglesias, G. Morales, R. Sánchez-Vázquez and I. Suárez-Marcos, Biodiesel production over arenesulfonic acid-modified mesostructured catalysts: optimization of reaction parameters using response surface methodology, *Top. Catal.*, 2010, **53**, 795–804.

53 J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias and D. Briones, Biodiesel production with heterogeneous sulfonic acid-functionalized mesostructured catalysts, *Energy Fuels*, 2008, **23**, 539–547.

54 J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias and R. Sánchez-Vázquez, Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts, *Chem. Eng. J.*, 2010, **161**, 323–331.

55 A. S. Chouhan and A. Sarma, Modern heterogeneous catalysts for biodiesel production: a comprehensive review, *Renewable Sustainable Energy Rev.*, 2011, **15**, 4378–4399.

56 M. Borges and L. Díaz, Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: a review, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2839–2849.

57 E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce and J. G. Goodwin, Synthesis of biodiesel *via* acid catalysis, *Ind. Eng. Chem. Res.*, 2005, **44**, 5353–5363.

58 M. Di Serio, R. Tesser, L. Pengmei and E. Santacesaria, Heterogeneous catalysts for biodiesel production, *Energy Fuels*, 2007, **22**, 207–217.

59 D. E. López, J. G. Goodwin, D. A. Bruce and E. Lotero, Transesterification of triacetin with methanol on solid acid and base catalysts, *Appl. Catal., A*, 2005, **295**, 97–105.

60 H. Fukuda, A. Kondo and H. Noda, Biodiesel fuel production by transesterification of oils, *J. Biosci. Bioeng.*, 2001, **92**, 405–416.

61 T. A. Peters, N. E. Benes, A. Holmen and J. T. Keurentjes, Comparison of commercial solid acid catalysts for the esterification of acetic acid with butanol, *Appl. Catal., A*, 2006, **297**, 182–188.

62 K. Wilson and A. F. Lee, Rational design of heterogeneous catalysts for biodiesel synthesis, *Catal. Sci. Technol.*, 2012, **2**, 884–897.

63 A. Khder, E. El-Sharkawy, S. El-Hakam and A. Ahmed, Surface characterization and catalytic activity of sulfated tin oxide catalyst, *Catal. Commun.*, 2008, **9**, 769–777.

64 N. U. Soriano, R. Venditti and D. S. Argyropoulos, Biodiesel synthesis *via* homogeneous Lewis acid-catalyzed transesterification, *Fuel*, 2009, **88**, 560–565.

65 M. G. Kulkarni, R. Gopinath, L. C. Meher and A. K. Dalai, Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification, *Green Chem.*, 2006, **8**, 1056–1062.

66 M. Hino and K. Arata, Reaction of butane to isobutane catalyzed by iron oxide treated with sulfate ion. Solid superacid catalyst, *Chem. Lett.*, 1979, **8**, 1259–1260.

67 N. Narkhede, S. Singh and A. Patel, Recent progress on supported polyoxometalates for biodiesel synthesis *via* esterification and transesterification, *Green Chem.*, 2015, **17**, 89–107.

68 P. A. Alaba, Y. M. Sani, I. Y. Mohammed, W. Daud and W. M. Ashri, Insight into catalyst deactivation mechanism and suppression techniques in thermocatalytic deoxygenation of bio-oil over zeolites, *Rev. Chem. Eng.*, 2016, **32**, 71–91.

69 P. A. Alaba, Y. M. Sani and W. M. A. W. Daud, Synthesis and characterization of hierarchical nanoporous HY zeolites from acid-activated kaolin, *Chin. J. Catal.*, 2015, **36**, 1846–1851.

70 T. Jin, T. Yamaguchi and K. Tanabe, Mechanism of acidity generation on sulfur-promoted metal oxides, *J. Phys. Chem.*, 1986, **90**, 4794–4796.

71 K. Srilatha, C. R. Kumar, B. P. Devi, R. Prasad, P. S. Prasad and N. Lingaiah, Efficient solid acid catalysts for esterification of free fatty acids with methanol for the production of biodiesel, *Catal. Sci. Technol.*, 2011, **1**, 662–668.

72 A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, Heterogeneous catalysis for sustainable biodiesel production *via* esterification and transesterification, *Chem. Soc. Rev.*, 2014, **43**, 7887–7916.

73 T. Yamaguchi, T. Jin and K. Tanabe, Structure of acid sites on sulfur-promoted iron oxide, *J. Phys. Chem.*, 1986, **90**, 3148–3152.

74 S. Furuta, H. Matsuhashi and K. Arata, Catalytic action of sulfated tin oxide for etherification and esterification in comparison with sulfated zirconia, *Appl. Catal., A*, 2004, **269**, 187–191.

75 H.-F. Guo, P. Yan, X.-Y. Hao and Z.-Z. W., Influences of introducing Al on the solid super acid SO_4^{2-}/SnO_2, *Mater. Chem. Phys.*, 2008, **112**, 1065–1068.

76 J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, Direct syntheses of ordered SBA-15 mesoporous materials containing arenesulfonic acid groups, *J. Mater. Chem.*, 2002, **12**, 1664–1670.

77 W. Li, F. Ma, F. Su, L. Ma, S. Zhang and Y. Guo, One-step preparation of efficient and reusable SO_4^{2-}/ZrO_2-based hybrid solid catalysts functionalized by alkyl-bridged organosilica moieties for biodiesel production, *ChemSusChem*, 2011, **4**, 744–756.

78 T. Tatsumi, H. Matsuhashi and K. Arata, A study of the preparation procedures of sulfated zirconia prepared from zirconia gel. The effect of the pH of the mother solution on the isomerization activity of *n*-pentane, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1191–1194.

79 H. Matsuhashi, H. Miyazaki, Y. Kawamura, H. Nakamura and K. Arata, Preparation of a solid superacid of sulfated tin oxide with acidity higher than that of sulfated zirconia and its applications to aldol condensation and benzoylation, *Chem. Mater.*, 2001, **13**, 3038–3042.

80 J. C. Juan, J. Zhang and M. A. Yarmo, Structure and reactivity of silica-supported zirconium sulfate for esterification of fatty acid under solvent-free condition, *Appl. Catal., A*, 2007, **332**, 209–215.

81 A. Patel, V. Brahmkhatri and N. Singh, Biodiesel production by esterification of free fatty acid over sulfated zirconia, *Renewable Energy*, 2013, **51**, 227–233.

82 Y. Zhang, W.-T. Wong and K.-F. Yung, Biodiesel production *via* esterification of oleic acid catalyzed by chlorosulfonic acid modified zirconia, *Appl. Energy*, 2014, **116**, 191–198.

83 S. S. Vieira, Z. M. Magriotis, N. A. Santos, A. A. Saczk, C. E. Hori and P. A. Arroyo, Biodiesel production by free

fatty acid esterification using lanthanum (La^{3+}) and HZSM-5 based catalysts, *Bioresour. Technol.*, 2013, **133**, 248–255.

84 F. H. Alhassan, R. Yunus, U. Rashid, K. Sirat, A. Islam, H. Lee and Y. H. Taufiq-Yap, Production of biodiesel from mixed waste vegetable oils using ferric hydrogen sulphate as an effective reusable heterogeneous solid acid catalyst, *Appl. Catal., A*, 2013, **456**, 182–187.

85 Y. Li, X.-D. Zhang, L. Sun, M. Xu, W.-G. Zhou and X.-H. Liang, Solid superacid catalyzed fatty acid methyl esters production from acid oil, *Appl. Energy*, 2010, **87**, 2369–2373.

86 D. E. Lopez, J. G. Goodwin, D. A. Bruce and S. Furuta, Esterification and transesterification using modified-zirconia catalysts, *Appl. Catal., A*, 2008, **339**, 76–83.

87 C. M. Garcia, S. Teixeira, L. L. Marciniuk and U. Schuchardt, Transesterification of soybean oil catalyzed by sulfated zirconia, *Bioresour. Technol.*, 2008, **99**, 6608–6613.

88 H. Chen, B. Peng, D. Wang and J. Wang, Biodiesel production by the transesterification of cottonseed oil by solid acid catalysts, *Front. Chem. Eng. China*, 2007, **1**, 11–15.

89 S. H. Shuit, Y. T. Ong, K. T. Lee, B. Subhash and S. H. Tan, Membrane technology as a promising alternative in biodiesel production: a review, *Biotechnol. Adv.*, 2012, **30**, 1364–1380.

90 B. Fu, L. Gao, L. Niu, R. Wei and G. Xiao, Biodiesel from waste cooking oil *via* heterogeneous superacid catalyst SO_4^{2-}/ZrO_2, *Energy Fuels*, 2008, **23**, 569–572.

91 S.-Y. Chen, T. Yokoi, C.-Y. Tang, L.-Y. Jang, T. Tatsumi, J. C. Chan and S. Cheng, Sulfonic acid-functionalized platelet SBA-15 materials as efficient catalysts for biodiesel synthesis, *Green Chem.*, 2011, **13**, 2920–2930.

92 M. Avhad and J. Marchetti, A review on recent advancement in catalytic materials for biodiesel production, *Renewable Sustainable Energy Rev.*, 2015, **50**, 696–718.

93 F. Su and Y. Guo, Advancements in solid acid catalysts for biodiesel production, *Green Chem.*, 2014, **16**, 2934–2957.

94 J. A. Maciá-Agulló, M. Sevilla, M. A. Diez and A. B. Fuertes, Synthesis of carbon-based solid acid microspheres and their application to the production of biodiesel, *ChemSusChem*, 2010, **3**, 1352–1354.

95 Q. Shu, Z. Nawaz, J. Gao, Y. Liao, Q. Zhang, D. Wang and J. Wang, Synthesis of biodiesel from a model waste oil feedstock using a carbon-based solid acid catalyst: reaction and separation, *Bioresour. Technol.*, 2010, **101**, 5374–5384.

96 K. Nakajima and M. Hara, Amorphous carbon with SO_3H groups as a solid Brønsted acid catalyst, *ACS Catal.*, 2012, **2**, 1296–1304.

97 B. Chang, J. Fu, Y. Tian and X. Dong, Multifunctionalized ordered mesoporous carbon as an efficient and stable solid acid catalyst for biodiesel preparation, *J. Phys. Chem. C*, 2013, **117**, 6252–6258.

98 M.-H. Zong, Z.-Q. Duan, W.-Y. Lou, T. J. Smith and H. Wu, Preparation of a sugar catalyst and its use for highly efficient production of biodiesel, *Green Chem.*, 2007, **9**, 434–437.

99 F. A. Dawodu, O. Ayodele, J. Xin, S. Zhang and D. Yan, Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst, *Appl. Energy*, 2014, **114**, 819–826.

100 C. Poonjarernsilp, N. Sano and H. Tamon, Hydrothermally sulfonated single-walled carbon nanohorns for use as solid catalysts in biodiesel production by esterification of palmitic acid, *Appl. Catal., B*, 2014, **147**, 726–732.

101 T. Liu, Z. Li, W. Li, C. Shi and Y. Wang, Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol, *Bioresour. Technol.*, 2013, **133**, 618–621.

102 W.-Y. Lou, M.-H. Zong and Z.-Q. Duan, Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts, *Bioresour. Technol.*, 2008, **99**, 8752–8758.

103 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato and S. Hayashi, Hydrolysis of cellulose by amorphous carbon bearing SO_3H, COOH, and OH groups, *J. Am. Chem. Soc.*, 2008, **130**, 12787–12793.

104 M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi and M. Hara, Adsorption-enhanced hydrolysis of β-1, 4-glucan on graphene-based amorphous carbon bearing SO_3H, COOH, and OH groups, *Langmuir*, 2009, **25**, 5068–5075.

105 W. Long and C. W. Jones, Hybrid sulfonic acid catalysts based on silica-supported poly (styrene sulfonic acid) brush materials and their application in ester hydrolysis, *ACS Catal.*, 2011, **1**, 674–681.

106 D. M. Alonso, M. L. Granados, R. Mariscal and A. Douhal, Polarity of the acid chain of esters and transesterification activity of acid catalysts, *J. Catal.*, 2009, **262**, 18–26.

107 W. Li, Z. Jiang, F. Ma, F. Su, L. Chen, S. Zhang and Y. Guo, Design of mesoporous $SO_4^{2-}/ZrO_2–SiO_2$(Et) hybrid material as an efficient and reusable heterogeneous acid catalyst for biodiesel production, *Green Chem.*, 2010, **12**, 2135–2138.

108 K. Wilson, A. Renson and J. Clark, Novel heterogeneous zinc triflate catalysts for the rearrangement of α-pinene oxide, *Catal. Lett.*, 1999, **61**, 51–55.

109 Z. Kalemba-Jaje, A. Drelinkiewicz, E. Lalik, E. Konyushenko and J. Stejskal, Bio-esters formation in transesterification and esterification reactions on carbon and silica supported organo-sulfonic acids-polyaniline solid catalysts, *Fuel*, 2014, **135**, 130–145.

110 J. Peng, Y. Yao, X. Zhang, C. Li and Q. Yang, Superhydrophobic mesoporous silica nanospheres achieved *via* a high level of organo-functionalization, *Chem. Commun.*, 2014, **50**, 10830–10833.

111 J. A. Melero, L. F. Bautista, G. Morales, J. Iglesias and R. Sánchez-Vázquez, Acid-catalyzed production of biodiesel over arenesulfonic SBA-15: insights into the role of water in the reaction network, *Renewable Energy*, 2015, **75**, 425–432.

112 G. S. Armatas, A. P. Katsoulidis, D. E. Petrakis and P. J. Pomonis, Synthesis and acidic catalytic properties of ordered mesoporous alumina–tungstophosphoric acid composites, *J. Mater. Chem.*, 2010, **20**, 8631–8638.

113 E. Serrano, N. Linares, J. Garcia-Martinez and J. Berenguer, Sol–gel coordination chemistry: building catalysts from the bottom-up, *ChemCatChem*, 2013, **5**, 844–860.

114 A. Bail, V. C. dos Santos, M. R. de Freitas, L. P. Ramos, W. H. Schreiner, G. P. Ricci, K. J. Ciuffi and S. Nakagaki, Investigation of a molybdenum-containing silica catalyst synthesized by the sol–gel process in heterogeneous catalytic esterification reactions using methanol and ethanol, *Appl. Catal., B*, 2013, **130**, 314–324.

115 I. Matsuzaki, M. Nitta and K. Tanabe, Application of Hammett indicators to estimating coverages of acid sites of silica-alumina by nitrogen, ethylene, water, ethyl alcohol, pyridine and *n*-butylamine, *J. Res. Inst. Catal., Hokkaido Univ.*, 1969, **17**, 46–53.

116 R. Touillaux, P. Salvador, C. Vandermeersche and J. Fripiat, Study of water layers adsorbed on Na-and Ca-montmorillonite by the pulsed nuclear magnetic resonance technique, *Isr. J. Chem.*, 1968, **6**, 337–348.

117 M. Frenkel, Surface acidity of montmorillonites, *Clays Clay Miner.*, 1974, **22**, 435–441.

118 M. Yurdakoc, M. Akcay, Y. Tonbul and K. Yurdakoc, Acidity of silica-alumina catalysts by amine titration using Hammett indicators and FT-IR study of pyridine adsorption, *Turk. J. Chem.*, 1999, **23**, 319–328.

119 K. Tanabe, M. Misono, H. Hattori and Y. Ono, *New solid acids and bases: Their catalytic properties*, Elsevier, 1990.

120 X. Wang, C. Y. Jimmy, P. Liu, X. Wang, W. Su and X. Fu, Probing of photocatalytic surface sites on SO_4^{2-}/TiO_2 solid acids by in situ FT-IR spectroscopy and pyridine adsorption, *J. Photochem. Photobiol., A*, 2006, **179**, 339–347.

121 J. Li, X. Li, G. Zhou, W. Wang, C. Wang, S. Komarneni and Y. Wang, Catalytic fast pyrolysis of biomass with mesoporous ZSM-5 zeolites prepared by desilication with NaOH solutions, *Appl. Catal., A*, 2014, **470**, 115–122.

122 N. Cardona-Martínez and J. Dumesic, Acid strength of silica-alumina and silica studied by microcalorimetric measurements of pyridine adsorption, *J. Catal.*, 1990, **125**, 427–444.

123 H. F. Gorgulho, J. P. Mesquita, F. Gonçalves, M. F. R. Pereira and J. L. Figueiredo, Characterization of the surface chemistry of carbon materials by potentiometric titrations and temperature-programmed desorption, *Carbon*, 2008, **46**, 1544–1555.

124 H. Wang, Z. Liu, J. Shen and H. Liu, High-throughput characterization of heterogeneous catalysts by temperature-programmed analysis method, *Catal. Commun.*, 2004, **5**, 55–58.

125 L. Xu, Y. Wang, X. Yang, J. Hu, W. Li and Y. Guo, Simultaneous esterification and transesterification of soybean oil with methanol catalyzed by mesoporous Ta_2O_5/SiO_2-$[H_3PW_{12}O_{40}/R]$ (R = Me or Ph) hybrid catalysts, *Green Chem.*, 2009, **11**, 314–317.

126 L. Xu, W. Li, J. Hu, X. Yang and Y. Guo, Biodiesel production from soybean oil catalyzed by multifunctionalized Ta_2O_5/SiO_2-$[H_3PW_{12}O_{40}/R]$ (R = Me or Ph) hybrid catalyst, *Appl. Catal., B*, 2009, **90**, 587–594.

127 L. Xu, W. Li, J. Hu, K. Li, X. Yang, F. Ma, Y. Guo, X. Yu and Y. Guo, Transesterification of soybean oil to biodiesel catalyzed by mesostructured Ta_2O_5-based hybrid catalysts functionalized by both alkyl-bridged organosilica moieties and Keggin-type heteropoly acid, *J. Mater. Chem.*, 2009, **19**, 8571–8579.

128 J. Dhainaut, J.-P. Dacquin, A. F. Lee and K. Wilson, Hierarchical macroporous–mesoporous SBA-15 sulfonic acid catalysts for biodiesel synthesis, *Green Chem.*, 2010, **12**, 296–303.

129 I. K. Mbaraka and B. H. Shanks, Design of multifunctionalized mesoporous silicas for esterification of fatty acid, *J. Catal.*, 2005, **229**, 365–373.

130 D. Zuo, J. Lane, D. Culy, M. Schultz, A. Pullar and M. Waxman, Sulfonic acid functionalized mesoporous SBA-15 catalysts for biodiesel production, *Appl. Catal., B*, 2013, **129**, 342–350.

131 C. Pirez, J.-M. Caderon, J.-P. Dacquin, A. F. Lee and K. Wilson, Tunable KIT-6 mesoporous sulfonic acid catalysts for fatty acid esterification, *ACS Catal.*, 2012, **2**, 1607–1614.

132 L. Li, W. Du, D. Liu, L. Wang and Z. Li, Lipase-catalyzed transesterification of rapeseed oils for biodiesel production with a novel organic solvent as the reaction medium, *J. Mol. Catal. B: Enzym.*, 2006, **43**, 58–62.

133 D. B. G. Williams and M. Lawton, Drying of organic solvents: quantitative evaluation of the efficiency of several desiccants, *J. Org. Chem.*, 2010, **75**, 8351–8354.

134 K. Ngaosuwan, E. Lotero, K. Suwannakarn, J. G. Goodwin Jr and P. Praserthdam, Hydrolysis of triglycerides using solid acid catalysts, *Ind. Eng. Chem. Res.*, 2009, **48**, 4757–4767.

135 H. Luo, K. Xue, W. Fan, C. Li, G. Nan and Z. Li, Hydrolysis of vegetable oils to fatty acids using Brønsted acidic ionic liquids as catalysts, *Ind. Eng. Chem. Res.*, 2014, **53**, 11653–11658.

136 Y. Román-Leshkov and M. E. Davis, Activation of carbonyl-containing molecules with solid Lewis acids in aqueous media, *ACS Catal.*, 2011, **1**, 1566–1580.

137 R. Jothiramalingam and M. K. Wang, Review of recent developments in solid acid, base, and enzyme catalysts (heterogeneous) for biodiesel production *via* transesterification, *Ind. Eng. Chem. Res.*, 2009, **48**, 6162–6172.

138 K. Suwannakarn, E. Lotero, K. Ngaosuwan and J. G. Goodwin Jr, Simultaneous free fatty acid esterification and triglyceride transesterification using a solid acid catalyst with in situ removal of water and unreacted methanol, *Ind. Eng. Chem. Res.*, 2009, **48**, 2810–2818.

139 X. Liang, Novel efficient procedure for biodiesel synthesis from waste oils using solid acidic ionic liquid polymer as the catalyst, *Ind. Eng. Chem. Res.*, 2013, **52**, 6894–6900.

140 W. Xie and J. Chen, Heterogeneous interesterification of triacylglycerols catalyzed by using potassium-doped alumina as a solid catalyst, *J. Agric. Food Chem.*, 2014, **62**, 10414–10421.

141 V. Brahmkhatri and A. Patel, Biodiesel production by esterification of free fatty acids over 12-tungstophosphoric acid anchored to MCM-41, *Ind. Eng. Chem. Res.*, 2011, **50**, 6620–6628.