Heterogeneous Basic Catalysts For Transesterification Of Vegetable Oils: A Review

A. Kumar, Simon O. Osembo, Saul S. Namango, Kirimi H Kiriamiti

Abstract— Biodiesels are biofuels made from renewable sources such as vegetable oils originating from plants and animal fats. Transesterification reaction is carried out by reacting triglycerides in oil/fat with an alcohol in presence of a catalyst. Important process variables are reaction temperature, time, reactant concentration and the catalyst. Catalysts can be homogeneous or heterogeneous. Homogeneous catalysts are liquid phase ionic acid and base, enzymes, and non-ionic organic base compounds. Heterogeneous catalysts are acid and base type. Examples of acid heterogeneous catalysts are ion-exchange resins, tungstated and sulphated zirconia, metal complexes and zeolite. Base heterogeneous catalysts consist of metal oxides in pure form or over support, zeolites, clays and non-oxides. Paper gives a brief introduction of catalytic transesterification process and a detailed review of solid basic catalysts. It is found that these catalysts are selective to feed and preparation method. Acid solid catalysts are suitable for high free fatty acid feed. Basic solid catalyst give a better yield compared to acid solid catalysts but lead to soap formation if feed has high free fatty acid.

Keywords— Biodiesel, heterogeneous catalysis, solid base catalyst, transesterification.

I. INTRODUCTION

Biofuels are fuels from renewable sources and are recognized to be an alternative to petroleum derived fuels. As per International Energy Statistics for the year 2010, the Africa and the World produced a total of 990 barrels and 1.9 million barrels of biofuel; and consumed 3.4 and 85.7 million barrels of petroleum fuel respectively (1 barrel = 0.159 m^3). It is also speculated that the present rate of consumption of the petroleum fuel is 2.7% of the reserves, and the petroleum stocks may deplete within the next 50 years or so [1], [2]. Liquid biofuels consist of biodiesel and bio-gasoline. Unlike petroleum hydrocarbons, these fuels do not add to net carbon dioxide; and also do not lead to air pollution, being free of nitrogen and sulphur. Biofuels consist of mainly C, H and O, the oxygen percentage ranging from 10 to 45%, whereas petroleum diesel is mainly C and H with no oxygen. This makes the chemical properties of the two fuels very different [3].

Bio-gasoline is a blend of ethanol, obtained from renewable plant sources, and petroleum gasoline. Biodiesel fuel can be a blend of biodiesel obtained from renewable sources and petro-diesel, or pure biodiesel. Studies using pure and blended biodiesels show that this biofuel can be used in diesel engine without any modification [4]. Historically pure vegetable oil (groundnut oil) was successfully used as engine fuel by Rudolf Diesel in 1900 [5]. Pure vegetable oils have a higher viscosity and problems of cold weather starting, plugging and gumming of filters, engine knocking, coking and carbon deposits, poor lubrication due to oil polymerization [6]. Biodiesel produced through transesterification of vegetable oils has a lower viscosity and properties close to petro-diesel. Biodiesel is the mono-alkyl ester of long chain fatty acids from vegetable oils and animal fats. Transesterification, also called alcoholysis, is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. If methanol is used for the reaction, then the products are fatty acid methyl esters (FAME) and glycerol. FAME constitutes biodiesel [7].

II. TRANSESTERIFICATION REACTION MECHANISM

The overall reaction between a triglyceride and an alcohol is given by,

$$\text{Triglyceride} + 3\,\text{ROH} \leftrightarrow \text{Glycerol} + 3\ \text{alkyl ester} \quad \text{(i)}$$

Reaction (i) is supposed to take place in three consecutive and reversible steps,

$$\text{Triglyceride} + \text{ROH} \leftrightarrow \text{Diglyceride} + \text{alkyl ester} \quad \text{(ii)}$$
$$\text{Diglyceride} + \text{ROH} \leftrightarrow \text{Monoglyceride} + \text{alkyl ester} \quad \text{(iii)}$$
$$\text{Monoglyceride} + \text{ROH} \leftrightarrow \text{Glycerol} + \text{alkyl ester} \quad \text{(iv)}$$

In the above, ROH represents an alcohol [8]-[11]. Above reactions require heat and a catalyst to increase the reaction rate. From stoichiometry, 3 moles of alcohols are required for each mole of triglyceride to produce 3 moles of alkyl ester (biodiesel). However, due to the reversible nature of the reaction an excess of alcohol is always employed for reactions to proceed in the forward direction. An alcohol to oil ratio of 6:1 is normally used in industrial processes to obtain high alkyl ester yields. A higher ratio of alcohol to oil interferes with the separation of glycerol, and therefore not used [12].

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Since alcohol and oils (triglyceride) form two phase, mixing is also needed to reduce mass transfer resistance. It is observed that initially the reaction rate is slow and the mixing effect is most significant. In the later stages, the two phases are almost merged and the effect of mixing becomes insignificant, and the reaction temperature controls the rate [13]. Reaction rates increase with the increase of temperature. However, the highest reaction temperature is somehow dictated by the saturation temperature of the alcohol. For example, for methanol the highest reaction temperature is about 70°C, at atmospheric conditions. To increase the yield, reactions can be carried out at pressures higher than atmospheric leading to high reaction temperatures [11], [14]. Microwave irradiation and ultrasonic mixing leads to faster reactions and lower reaction time [15]-[17]. Reactions under supercritical conditions usually do not require a catalyst, but because of high equipment cost such studies have so far been limited to laboratory scale only [18], [19].

III FEED STOCKS

Methanol and ethanol are common alcohols for transesterification reaction. Methanol has advantage of lower cost, and therefore more common in use. Ethanol has advantage of being produced from renewable sources (bio-ethanol) but the commercial grade contains water, which adversely affects reaction rate. Most of the commercial production of biodiesel employs methanol producing FAME [20]. Higher alcohol butanol has also been used but the studies still limited to lab scale [21].

Vegetable oils used by commercial plants in US are mostly soybean and used frying oils, whereas European plants use rapeseed oil and used frying oils. Other oils used mostly in Eastern countries are palm, jatropha, *pongomia pinnata* (karanj) [20], [22]. Oils used in the developing countries are essentially non-edible so they do not compete with food.

IV CATALYSTS FOR TRANSESTERIFICATION

Catalysts for transesterification can be categorized into homogeneous and heterogeneous. Another way to classify is, as alkali, acid, or biocatalysts such as enzyme. The conventional homogenous catalysts are alkali or acid catalysts such as sodium hydroxide, alkali metal alkoxides (such as sodium methoxide), potassium hydroxide, sulphuric acid, phosphoric acid. Alkali catalyzed transesterification is much faster than acid catalyzed [23]. The alkaline catalyst concentration in the range of 0.5-1% (w/w) leads to 94-99% conversion [24]. However for oils with higher free fatty acid and moisture, acid catalysts are better suited. Enzymes, lipases catalyze the transesterification in both aqueous and non-aqueous system. Biocatalysts eliminate the disadvantages of downstream process of product purification. A recent study involving use of soluble lipases from genetically modified *Asp. oryzae/Asp. niger* organism as catalyst and acid oil gave a biodiesel yield of 88.7 wt% [25]. Homogeneous catalysts require elaborate downstream treatment involving neutralization, washing and drying. They are not easy to separate as they dissolve fully in the glycerol layer and partially in the biodiesel [26]. Separation process is expensive involving operations such as distillation. This makes the separation process uneconomical and often not attempted. With increasing environmental regulations and emphasis on clean technology such catalysts have distinct disadvantage. A number of organic bases have been used as catalysts for transesterification. Examples are, amines (e.g., triethylamine, piperidine, pentamethylpiperidine, pyridine, butylpyridine, dimethyl aminopyridine) and various amidines. Reference [24] gives an account of non-ionic base catalysts, their molecular structure, and their relative activities.

Heterogeneous solid catalysts are noncorrosive with no adverse environmental effect. They can be easily separated and recycled and are suited for continuous production. Heterogeneous catalysts are highly selective and their activity depends upon their surface properties [27]. Solid catalysts are acid type and base type. Solid acid catalysts are suited to oils with high free fatty acid contents (eg., waste cooking oils) since these catalyze both esterification and transesterification reactions [28], [29]. Acid ion exchange resins have been successfully used to produce ethyl oleate biodiesel from triolein. In a study, the anion-exchange resins exhibited much higher catalytic activity as compared to cation-exchange resins, and the resin could be recycled without loss of activity [30]. In another study, commercial Nafion® acid resin was used to transesterify triacetin with methanol [31]. Reaction rate with these resins was found to be slower compared to basic catalysts and require higher temperatures [32]. Sulphated and tungstated zirconia, and sulphated tin oxide are another type of acid catalysts. They have been tested for the transesterification of soybean oil giving yield close to 100% and a long activity period [33],[34]. Metal complexes containing tungsten, silica, caesium, zinc have been used as acid catalysts for rapeseed oil, yellow horn oil and oleic acid. Conversion is reported to be high, ranging from 88% to 100% [35]- [38]. Zeolites are another group of solids used as acid catalysts. Zeolites are microporous crystalline solids with well defined structures containing silicon, aluminium, and oxygen in their framework and cations [39]. The acid strength in zeolites can be adjusted such that it fits the reaction requirements [40]. Zeolite catalysts require elaborate preparation procedure as reported for transesterification of methyl octanoate and soybean oil added with oleic acid. For methyl octanoate, a reaction temperature of 500°C and a time of 20 min, gave a 100% conversion; whereas for soybean oil-oleic acid mixture, reaction temperature was 60°C and time 1 min, to get a 80% conversion [41], [42]. In general, acid catalysts require a long reaction time and a high temperature, and show weak catalytic activity [43]. Another major drawback for acid catalysts, which arises from reaction mechanism, is its sensitivity to presence of water. Any presence of water slows down the main reaction giving rise to unwanted side reactions [44]. Basic heterogeneous catalysts consist of single component metal oxides, zeolites, supported alkali metals, clays and non-oxides.

V. HETEROGENEOUS BASIC CATALYSTS

Basic catalysts give a higher reaction rate as compared to acidic catalysts, whether they are homogeneous or heterogeneous [45]. The higher activity is explained by the generation of highly active alkoxide ion (RO^-) when the alcohol reacts with the base catalyst. Fig 1 gives the mechanism of alkali-catalyzed transesterification of triglycerides with alcohol. Equation (1) is a ‘pre-step’ leading to the formation of alkoxide ion, where B is the base catalyst and R is the short alkyl group belonging to alcohol [46]. Reaction (2) gives the ‘first step’ of the reaction in which alkoxide ion reacts with the carbonyl carbon of triglyceride molecule forming a tetrahedral intermediate ion, where R’, R’’ and R’’’ are the long chain alkyl groups. In the ‘second step’, the intermediate ion rearranges to give a diglyceride and alkyl ester molecule, given by reaction (3). Reaction (4), gives the ‘third step’ where the diglyceride ion reacts with the protonated base catalyst, generating a diglyceride molecule and the original base is recovered [47].

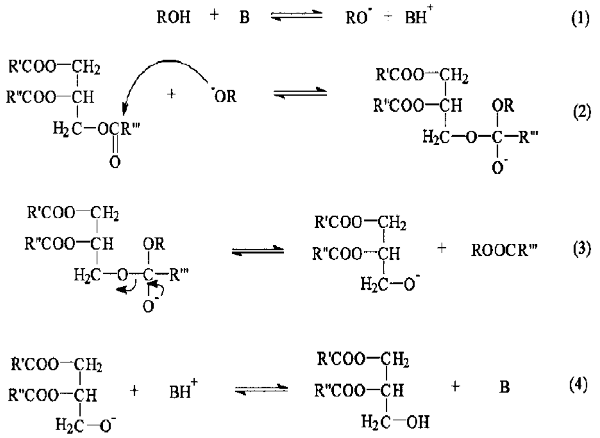

Fig 1: Mechanism of alkali-catalyzed transesterification of triglycerides with alcohol

Heterogeneous basic catalysts are sensitive to free fatty acids (FFA) in the feedstock. Soap formation decreases the biodiesel yield if the FFA content in oil exceeds 2% by mass [48]. Water is another component which adversely affects the biodiesel yield. Water reacts with alkyl esters to produce carboxylic acids, which react with alkaline metals to form sodium or potassium salts similar to a soap, reducing alkyl ester yield and making glycerol recovery difficult [45]. Zeolite and silica gel have been used in the catalyst to absorb water to offset the adverse effect of water [49], [50].

VI. CLASSIFICATION OF HETEROGENEOUS BASIC CATALYSTS

Hideshi Hattori [51] studied a wide spectrum of solid basic catalysts. His work included pre-treatment methods, and their relative reactivity for ten typical organic reactions, including transesterification of ethyl acetate. Hattori classified heterogeneous basic catalysts into five types as given in Table 1.

Homogenous catalysts are of uniform structure and composition, and have the advantage of reproducibility. Heterogeneous catalysts, on the other hand, are solids on non-uniform structure. Structure and surface properties depend on the method of preparation and pre-treatment prior to use. Surface properties including surface defects, are responsible for the active sites, where reaction takes place. Prolong use, poisoning, blocks the active sites making the catalyst inactive [52].

Table 1: Types of heterogeneous basis catalysts [51]

SN	Type	Material
1	Single component metal oxides	Alkali metal oxides Alkaline earth oxides Rare earth oxides ThO_2, ZrO_2, ZnO, TiO_2
2	Zeolites	Alkali ion-exchanged zeolite Alkali ion-supported zeolite
3	Supported alkali metal (or alkaline earth metal)	Alkali metal ions on alumina Alkali metal ions on silica Alkali metal on alkaline earth oxides Alkali metals and alkali metal hydroxides on alumina
4	Clay minerals	Hydrotalcites Crysolite Sepiolite
5	Non-oxides	Alkaline alkoxide Alkaline carbonate Guanidine-containing catalysts

VII. SINGLE COMPONENT METAL OXIDE CATALYSTS AND THEIR COMPOUNDS

For most basic materials, the surfaces are covered with water and carbon dioxide in air, and do not exhibit their intrinsic catalytic activities. Removal of the adsorbed species from the surface is essential to reveal oxide surfaces. SrO and BaO easily form peroxides on contact with oxygen, so removal of oxygen is also required to reveal the surface basic sites [51]. A pre-treatment at high temperature is required to remove the adsorbed species, and to decompose hydroxides, carbonates and peroxides. The nature of surface basic sites varies with the severity of the of pre-treatment conditions [53]. Calcium oxide is one of the most studied heterogeneous base catalyst for transesterification reaction. Producing biodiesel using CaO as a solid base catalyst has many advantages, such as higher activity, mild reaction conditions, reusability, easy availability and low cost. Pretreatment temperatures for removal of adsorbed water and carbon dioxide from CaO surface are 700K and 1000K respectively [54]. Transesterification of soybean oil and methanol was carried out using CaO as a solid base catalyst. One interesting feature of CaO catalyst is the effect of water in the reaction system. While the presence of water has adverse affect on yield of FAME for most catalyst systems, CaO performs better in the presence of small amount of water. In the presence of a little water in methanol, CaO reacts to generate methoxide ion, which is highly active and is the real catalyst. A reaction mechanism for transesterification over CaO catalyst in presence of little water is given in Fig 2 [55].

As a basic site of CaO catalyst, surface O^{2-} extracts H^+ from H_2O from surface OH^- (Eq. 1), which is easily extracted by reactants in chemical reactions. Then, the OH^- extracts H^+ from methanol to generate methoxide anion and H_2O (Eq. 2).

Also, O^{2-} can also extract H^{+} from hydroxyl group of methanol to form surface methoxide anions (Eq. 3). However, if too much water (exceeding 2.8 wt% of soybean oil) is added to methanol, the FAME is hydrolyzed to generate fatty acid and methanol.

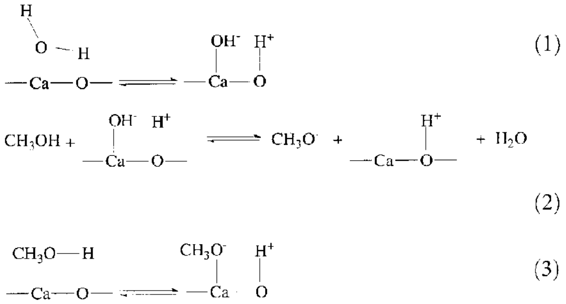

Fig 2: Reaction mechanism for transesterification over CaO catalyst in presence of little water

In the study a 12:1 molar ratio of methanol to oil, 8 wt% CaO catalyst, temperature of 65°C, reaction time of 1.5 h, gave the maximum yield of 95% [55]. Transesterification of soybean oil using nanopowder CaO and microwave irradiation gave 96.6% conversion, at methanol to oil ratio 6:1, 338K temperature, reaction time 60 min, and 3 wt% catalyst [56]. In a study involving transesterification of Jatropha oil, CaO was dipped in ammonium carbonate solution and calcined to get a super-base catalyst, of base strength of more than 26.5. For optimum conditions, calcinations temperature was 900°C, reaction temperature 70°C, reaction time 2.5 h, catalyst concentration 1.5 wt%, methanol to oil ratio 9:1, and the conversion 93% [57]. Another study, using a similarly prepared super-base CaO catalyst, for transesterification of Jatropha oil gave a maximum yield of 95% for a 12:1 molar ratio of methanol to oil, 1.5 wt% of catalyst, temperature 70°C, time 2 h, and water 2 wt%. Under supercritical conditions (200°C and 24bar), the reaction time was reduced to 1 h, and yield increased to 96% in presence of super-base CaO catalyst [58]. This is in contrast to some other transesterification studies under supercritical conditions where the catalyst was not employed and very high conversions obtained[14], [59[-[61]. Transesterification of *Camelina sativa* oil was studied using BaO, SrO, MgO, and CaO catalyst under conventional and microwave irradiation. The result of comparative experiments using conventional heating showed that the most effective catalyst was 1 wt% BaO, which showed >80% yield of camelina to biodiesel conversion in 3 h at 100°C. The FAME yield for BaO, SrO, CaO and MgO was 83%, 80%, 30% and 22%, respectively. The relative order of effectiveness of the catalysts was BaO > SrO > CaO > MgO [62], [63]. Under microwave irradiation, the FAME yield for BaO and SrO was 94% and 80% respectively. It was noted that microwave irradiation reduced the amount of methanol required, reduced the reaction time, but increased the catalyst amount [64], and SrO at 2 wt% gave a higher yield as compared to BaO at 1.5 wt%, although BaO has higher relative activity [65]. The relative activities of alkaline earth oxides compare well, with exception of CaO and MgO, as reported elsewhere, which gives the relative activities for transesterification of ethyl acetate with methanol as BaO > SrO > MgO > CaO [51]. In a study on transesterification of ethyl acetate with methanol, magnesium oxide has been identified as a good alternative to homogeneous catalysts for biodiesel production [66]. A simulation study indicated that a continuous production of 100,000 tonnes of biodiesel per year can be achieved at 323K in a continuous stirred reactor of 25 m^3 containing 5700 kg of MgO catalyst [67]. Performances of MgO, CaO, BaO, PbO, and MnO_2 for transesterification of soybean oil at high pressure and temperature were studied. A maximum biodiesel yield of 85% was obtained by BaO in 14 min, whereas PbO, MnO_2, CaO, and MgO gave maximum yields of 84%, 80%, 78%, and 66%, respectively at 215°C [68]. A similar high temperature, high pressure transesterification study of soybean oil involved seven metal oxide catalysts, PbO, ZnO, CaO, MgO, PbO_2, Tl_2O_3, and Pb_3O_4. Lead oxide catalysts were found to be most favourable towards the transesterification and gave yield >89%. MgO and Pb_3O_4 showed an increasing FAME yield trend from 75° to 225°C. MgO had the highest surface area, highest basicity, and relatively low leaching [69]. Transition metal oxides, zirconium oxide, titanium and zinc oxide have been tested as catalyst due to their strong acidic properties[70]. Transition metal solid base catalysts are moderately active and are of limited interest for transesterification reaction[71]. However, metal oxides prepared with calcium show strong basic character, and have been tested for transesterification reaction. The calcium-containing catalysts, $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaO–CeO_2$, showed high activities and approximately 90% yields of FAME from rapeseed oil. In a catalytic durability tests it was found that $CaZrO_3$ and $CaO–CeO_2$ show high durability and have the potential to be used in biodiesel production processes as heterogeneous base catalysts [72]. Mesoporous Li/ZrO_2, Na/ZrO_2, K/ZrO_2, Mg/ZrO_2, and Ca/ZrO_2 were synthesized and tested for soybean oil transesterification. Mg/ZrO_2, and Ca/ZrO_2 showed no activity, Na/ZrO_2 showed little activity, and Li/ZrO_2, K/ZrO_2 gave FAME yield of 98% at temperature 650-750°C [73]. A study of metals in homogeneous form showed the catalytic activity decrease in the order: $Sn^{+2} \geqslant Zn^{+2} > Pb^{+2} \cong Hg^{+2}$ [74]. Inspired by the high activity of Sn^{+2}, a solid SnO was used as a base catalyst for soybean oil. The yield of FAME was 56.5 to 94.7% for reaction time of 1 to 5 h. The catalyst was recycled up to four times without any loss of activity [75]. Magnesium methoxide was used as a solid base catalyst for transesterification of soybean oil. The reaction temperature varied from 50-65°C, keeping methanol to oil ratio at 9:1, and catalyst concentration of 8 wt% [76]. Transesterification of rapeseed oil was studied using alkaline earth metal compounds: calcium oxide, calcium methoxide and barium hydroxide. Tetrahydrofuran was used as a cosolvent to increase the solubility of methanol in oil. The results showed that barium hydroxide was most active, giving a conversion of 75% in 30 min, and >90% in 1.5 h; calcium methoxide was medially active, giving a conversion of 55% in 30 min, and

80% in 1 h, and 93% at equilibrium; solid CaO had the slowest rate, but the equilibrium conversion reached after 2.5 h had similar conversion. Magnesium oxide and calcium hydroxide showed no catalytic activity for rapeseed oil transesterification [77].

VIII. ZEOLITE HETEROGENEOUS CATALYSTS

Zeolites are microporous, aluminosilicate minerals having a porous structure that can accommodate a wide variety of cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+} and others [78]. They are available both in natural and synthetic form. The transesterification of soybean oil with methanol to methyl esters was carried out using NaX zeolites loaded with KOH as a solid base catalyst. The NaX zeolite did not present any particular catalytic activity, most likely due to the lack of strong basic sites on which the transesterification reaction could occur. However, loading of KOH onto the NaX zeolite produced a dramatic increment of basic strengths on the KOH/NaX catalyst. Best result was obtained with NaX zeolite loaded with 10% KOH, followed by heating at 393 K for 3 h. When the transesterification reaction was carried out at reflux of methanol (338 K), with a 10:1 molar ratio of methanol to soybean oil, a reaction time of 8 h and a catalyst amount of 3 wt%, the conversion of soybean oil was 85.6% [79]. Transesterification of soybean oil was studied using two types of zeolite, Nax faujasite zeolite and ETS-10 zeolite as catalyst at temperatures of 60, 120 and 150°C. Stock zeolites were exchanged with K and Ce; NaX containing occluded sodium oxide (NaO_x/NaX) and occluded sodium azide (NaO_x/NaX). The catalysts were calcined at 500 °C prior to use in order to increase activity. The ETS-10 catalysts provided higher conversions than the Zeolite-X type catalysts. The increased conversions were attributed to the higher basicity of ETS-10 zeolites and larger pore structures that improved intra-particle diffusion. Methyl ester yield increased with an increase in temperature from 60 to 150 °C [80]. Soybean oil was transesterified with methanol using Mg MCM-41 zeolite, Mg-Al hydrocalcite, and K impregnated zirconia. Mg-Al hydrocalcite showed the highest activity, giving 97% conversion. For the K impregnated zirconia, the activity increased as K increased indicating the higher basicity increased activity [81]. In another study of soybean oil transesterification with methanol using modified zeolites such as Y, A, and clinoptilolite as natural zeolite catalyst; it was revealed that modified zeolite Y gave a higher conversion of 98.4% as compared to the natural zeolite clinoptilolite which gave 86.9% conversion [82]. Transesterification of *Jatropha curcas* seed oil with methanol was studied using artificial zeolites loaded with potassium acetate as a catalyst. After calcinations for 5 h at 823K, the catalyst loaded with 47 wt% potassium acetate exhibited the highest efficiency. Optimum conditions were at oil to methanol ratio 1:10, catalyst 2 wt%, reaction time 4 h, at reflux temperature [83]. Transesterification of sunflower oil was studied using NaX zeolite (Si/Al = 1.23) as a carrier for nano CaO particles. CaO mass percent ranged from 5-25%. Reactions were carried out at atmospheric conditions and at reflux temperature of methanol, at methanol to sunflower oil ratio of 6:1, for 6 hr. Highest yield for methyl ester was 93.5%, obtained at 16 wt% of CaO [84]. Zeolite Y with different Al_2O_3 content was tested as a catalyst to produce biodiesel from used vegetable oil and methanol. The methanol to oil ratio was 6:1 and the reactions were carried out at atmospheric pressure. The temperature varied from 200 – 476°C. Product obtained had lower viscosity. Higher temperature gave viscosity close to biodiesel [85]. Activity of zeolite as a catalyst was tested as compared to alkali metal and alkaline earth catalysts, CaO, MgO, $Ba(OH)_2$, Li/CaO, for transesterification of vegetable oil. $Ba(OH)_2$ gave the highest activity among all the catalysts [86].

IX. SUPPORTED ALKALI/ALKALINE EARTH METALS

Alkali and alkaline earth metal Na, K, Ba, Ca, Mg, and their carbonates, hydroxides, halides and nitrates can be supported on alumina and silica [87]. Potassium hydroxide supported on alumina was prepared by mixing alumina and the alkali, and separating and drying the solid. Some examples of supported alkali/alkaline earth metals are given in previous section [80], [84]. Catalytic activities of alumina loaded potassium compounds, KI, KF, K_2CO_3 and KNO_3 with 35 wt% loading, were tested for the transesterification of canola oil with methanol and ethanol. Synthesized KF/Al_2O_3 catalyst showed the highest activity in the transesterification of canola oil with methanol and gave much stabler methyl ester content during the reaction with the highest yield of 99.6% at the end of the 8 h reaction time at 60° C, with a methanol to oil ratio of 15:1 and a catalyst amount of 3 wt% [88]. Castor oil was transesterified with methanol using Al_2O_3/50% KOH catalyst. More than 90% conversion was obtained at 60°C, in 1 h, using conventional heating, at methanol to oil ratio of 6:1, and catalyst 10 wt%. The same reaction carried out using microwave irradiation (40W) give a 95% conversion in 5 min at similar conditions [89]. Transesterification of soybean oil with methanol was studied using alumina loaded with potassium iodide as a solid base catalyst. After loading KI of 35 wt% on alumina followed by calcination at 773 K for 3 h, the catalyst gave the highest basicity and the best catalytic activity with a conversion of 96% under the optimum reaction conditions [90]. Transesterification of soybean oil over KF loaded onto γ-Al_2O_3 heterogeneous basic catalyst was carried out. The best reaction conditions were at a load ratio of KF 72.68 wt%, methanol to oil ratio 12:1, temperature 338 K, mass of catalyst 2 wt%, reaction time 3 h, and the yield of biodiesel exceeded 99% [91].

The transesterification of palm oil to FAME was studied using KOH loaded on Al_2O_3 and NaY zeolite supports as heterogeneous catalysts. The 25 wt% KOH/Al_2O_3 and 10 wt% KOH/NaY catalysts are suggested here to be the best formula due to their biodiesel yield of 91.07% at temperatures below 70° C within 2–3 h at a 1:15 molar ratio of palm oil to methanol and a catalyst amount of 3–6 wt%. The leaching of potassium species in both spent catalysts was observed [92]. Mesoporous γ-alumina was used as a support for sodium azide, NaN_3, to yield a superbasic catalyst that showed high activity for soybean oil transesterification [93]. Transesterification of palm kernel oil with methanol over mixed oxides of Ca and Zn, CaO·ZnO catalysts was studied. The mixed oxides had a relatively small particle sizes and high surface areas, compared to pure CaO and ZnO. At 60 °C (catalyst amount = 10 wt%, methanol/oil molar ratio = 30, reaction time = 1 h), the FAME content of >94% could be achieved over CaO·ZnO catalyst with the Ca/Zn ratio of 0.25 [94]. Transesterification of palm oil was carried out using CaO/Al_2O_3 composite catalyst. It was shown that both the calcination temperature and the amount of calcium oxide loaded on the support had significant positive effects on the biodiesel yield. The maximum basicity and biodiesel yield obtained were about 194 mmol/g and 94%, respectively, and the catalyst showed high performance at moderate operating conditions and its activity was maintained after two cycles [95]. Transesterification of palm kernel oil and coconut oil with methanol was investigated using various Al_2O_3-supported alkali and alkali earth metal oxides, $LiNO_3/Al_2O_3$, $NaNO_3/Al_2O_3$ and KNO_3/Al_2O_3 . Effect of calcinations temperature on catalyst activity was studied. $Ca(NO_3)_2/Al_2O_3$ calcined at 450 °C yielded the FAME content as high as 94%, and calcined $Mg(NO_3)_2/Al_2O_3$ catalyst possessed an inactive magnesium-aluminate phase, resulting in very low FAME formation [96]. In another major study novel mesoporous Al_2O_3-, SiO_2-supported solid base catalysts containing Ca, K as active elements were synthesized by a single-step sol-gel method. The synthesized catalysts possess a large BET surface area in the range of 180-400m^2/g and a mesoporous pore size in the range of 60-120Å. A 100% yield was obtained in 30min when 1wt% K/Al-0.6 or Ca/Al-4.0 catalyst was used. Ca-loaded catalysts exhibited a higher stability than K-loaded catalysts. The amount of Ca leaching was reduced significantly with the Ca/Al or Si molar ratio [97].

X. CLAY MINERALS

Classic clay mineral used as heterogeneous catalyst is hydrotalcite. Hydrotalcite is a layered double hydroxide of general formula ($Mg_6Al_2(CO_3)(OH)_{16}{\cdot}4(H_2O)$). It is dimorphous and has anion exchange capabilities [98]. Hydrotalcites of Mg and Al (Mg/Al ratio 3) modified with Zn, Sn, Ba, Mn, Ce, and Ca with 5 wt% catalyst were used for transesterification of soy oil with methanol, at 70°C, time 3 h, and methanol to oil ratio 9:1. Good results regarding biodiesel yield and product quality were obtained [99]. Transesterification of canola oil with methanol was studied using Mg-Al hydrotalcites as solid base catalysts. The highest triglyceride conversion rate of 71.9% was achieved after 9 h of reaction at 60° C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt% catalyst with 125-150 μm particles. Hydrotalcites were prepared by the co-precipitation method using ($Mg(NO_3)_2$), ($Al(NO_3)_3$), and Na_2CO_3 [100]. Transesterification of palm was studied using KF/hydrotalcite solid base catalysts. At 338 K, with palm oil/methanol molar ratio of 12:1, reaction time of 3 h, and catalyst amount of 3 wt %, the yield of FAME reached 85%; and when the reaction time prolonged to 5 h, the yield became 92% [101]. Transesterification of soybean oil to biodiesel was carried out using Mg-Al hydrotalcite as heterogeneous catalyst. The Mg-Al hydrotalcite with Mg/Al molar ratio of 3.0 was synthesized by co-precipitation method. The best conditions for hydrotalcite preparation and transesterification reactions were as follows: calcination temperature 550°C, molar ratio of soybean oil to methanol of 6:1, reaction time 360 min, and catalyst dosage 5%, the yield of FAME 78% [102]. In another study on transesterification of soybean oil, new solid base catalysts were prepared by substituting Fe^{3+} ions substitute for a fraction of the Al^{3+} ions in the Mg/Al layered double hydroxide lattices of hydrotalcites and calcining to give porous metal oxides. These iron-doped porous metal oxides are much stronger bases than those derived from undoped or Ga^{3+} doped hydrotalcites and are effective catalysts for the methanol transesterification of triacetin (glycerol triacetate) and of soybean oil [103]. Heterogeneous base catalyst derived from Mg–Al hydrotalcite was investigated for the conversion of poultry lipids to biodiesel. This solid base showed high activity for triglyceride transesterification with methanol without signs of catalyst leaching. Both temperature (60–120° C) and methanol-to-lipid molar ratio (6:1–60:1) affected the reaction rate in a positive manner. The use of a co-solvent (hexane, toluene, tetrahydrofuran), however, gave rise to a change in triglyceride conversion profile which cannot be explained solely by a dilution effect. By re-calcination in air, complete catalyst regeneration was achieved [104]. In another study, vegetable and used frying oil were transesterified using pure hydrotalcite and hydrotalcite modified for increasing its alkali behavior and reactivity. Effect of temperature, mixing speed, reaction time, catalyst pretreatment, catalyst concentration, alcohol to feed-stock ratio, and percent hydrotalcite modification through introduction of sodium to structure, were investigated [105]. Production of biodiesel via transesterification of castor oil using metal oxides as solid catalysts was investigated using hydrotalcite derived Mg-Al mixed oxide as a heterogeneous catalyst and the effect of reaction parameters in transesterification reaction were observed [106]. Activities of hydrotalcite, Cs-sepiolite and Cs-MCM-41 have been compared as a heterogeneous catalyst for transesterification of triglycerides, at 240° C for 5 h, and the activities were found to be in the order: hydrotalcite (92% conversion) > Cs-sepiolite (45% conversion) > Cs-MCM-41 (26% conversion) [107].

XI. NON-OXIDES

Some studies involving metal halides, hydroxides, carbonates and their combinations have already been given in previous sections. A major category of non-oxide catalysts are non-metallic organic compounds, mainly guanidine containing catalysts. Guanidines are a group of organic compounds sharing a common functional group with the general structure $(R^1R^2N)(R^3R^4N)C{=}N{-}R^5$. The central bond within this group is that of an imine, and the group is related structurally to amidines and ureas [108]. A new catalyst based on amines (guanidine carbonate) for transesterification of vegetable oils was tested and it was found that conversions of >95% could be reached within one reaction step in less than one hour. Particularly in transesterification of oils containing free fatty acids, guanidine carbonate showed significant advantages as no soap formation was observed. The process is applied in an industrial pilot plant with a capacity of approx. 1t/h [109]. In another work to develop polymeric catalysts, three polycationic systems were studied, composed of poly(hexamethylene biguanide) (PHMBG, pKa in water ~11), branched polyethyleneimine (PEI, pKa, 9.7), and poly(N-vinylguanidine) (PVG, pKa ~13). Comparison of the methanolysis rates in anhydrous conditions revealed that uncross-linked PHMBG was a remarkably efficient catalyst, enabling 100% triglyceride conversion within 0.5 h at 70°C. The PHMBG-based networks also demonstrated 100% conversion, but the kinetics were 1.5- to 2.4-fold lower than those with uncross-linked PHMBG (which is soluble in methanol) due to the less efficient heterogeneous catalysis by the cross-linked networks [110]. For transesterification of soybean oil, guanidines were successfully grafted on gel-type polystyrene matrix by covalent bonding and the catalyst gave high conversion, but the reaction time was prolonged. However, the heterogenized guanidines slowly leached out from polymer resulting in a continuous loss in catalytic activity [111]. To contain the loss of activity due to side reactions, the biguanides were confined to polystyrene, yielding a more reactive solid base than the polymer-supported guanidines, and with a reactivity which was stable for at least 10 cycles [112], [113]. In another work, guanidine functionalized polymers were also used for transesterification of methyl fatty ester with glycerol targeting the formation of monoglycerides [114].

XII. CONCLUSION

Homogeneous acid and base catalysts are easily available, have a low initial cost, have a fast reaction rate with a predictable performance, and are therefore advantageous for lab or small scale batch production. For a large scale use these catalysts, are corrosive, cannot be recycled, are not suitable for a continuous process, have downstream processing problems leading to environmental concerns. Due to these disadvantages researchers are busy working on heterogeneous alternatives that are recyclable and environmentally benign. Solid acid catalysts are good for high free fatty acid feeds, as they do not form soaps. However, they are known to have low reaction rates. Most studied heterogeneous base catalysts are alkali metal and alkaline earth oxides and other salts, either in pure form, or on a suitable carrier. They are relatively inexpensive and give a reasonably fast reaction rate. Since the activity of these catalyst is due to active sites on surface, the specific surface area and pore size distribution plays a key role in determining the activity. Preparation and pre-treatment procedure thus becomes very important, and presence of water, carbon dioxide and free fatty acids poisons the catalyst. Alkali and alkaline earth metals are deposited over zeolites since zeolites alone are not very effective as catalyst. Clays and organic solids have also been developed as catalysts, but all these are still in the laboratory scale. One problem with the solid heterogeneous catalyst is their poor recyclability. Their activity usually drops after the first use as they leach into the reaction media. The loss of activity after the first use due to leaching of alkali metal, for example, dropped the activity to more-than-half of the original activity [115], [116]. This makes the catalyst unsuitable for a continuous use, and a solid catalyst soluble in the biodiesel would bring problems of standardization, and may not be acceptable. Challenges to design of an acceptable heterogeneous catalyst include a simple reproducible preparation method, low production cost, stability and recyclability, and above all, a high activity for economic biodiesel production.

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