Appraisal of heterogeneous solid acid-base catalysts for trans-esterification

Abstract

The studies on biodiesel production are mainly focused on the following aspects: (i) Examining the appropriate fuel source (ii) Establishing the adequate alcohol to oil molar ratio (iii) Evaluating the available solid acid and base catalysts. Though homogenous catalysts are superior in terms of reaction rate compared to heterogeneous catalysts, the focus of research on possible heterogeneous catalysts is directed from the points of view economics, easy process and possible adoption for large scale manufacture. The scope of this presentation is to examine these aspects in detail and to provide a comprehensive outlook on the aspects mentioned.

Keywords*- biodiesel, heterogeneous catalyst, solid acid, solid base, zeolite, hydrotalcite*

Contents

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9   **1. Introduction**

10   The world has been confronted with an environmental and energy crisis due to

11   depletion of resources and increased population as well as environmental pollution. Other

12   than hydroelectricity and nuclear power, energy production from other fuels has been

13   increased world wide for transportation purposes.   It is important to search for an

14   alternate fuel for every day usage, which should be sustainable and also friendly to the

15   environment. Conventional fuels like petrol and diesel cause major air pollution all over

16   the world. Many efforts have been underway to develop clean fuel in many countries.

17   Among the many possible sources, biodiesel derived from vegetable oil (VOs) attracts

18   attention as a promising one for substitution or blending with conventional diesel based

19   fuels. If pure or blend biodiesel is used as fuel, the net production of carbon dioxide can

20   be suppressed. Sharmer et al. [1] have estimated that in the case of 1.0 Kg of pure

21   biodiesel instead of fossil fuel, 3.2 Kg of CO_2 production could be reduced. Diesel fuel is

22   largely utilized in the transport, agriculture, commercial, domestic and industrial sectors.

23   In view of the increase in crude oil prices, limited resources of fossil oil and

24   environmental concerns, there has been a renewed focus on vegetable oils and animal fats

25   to make them as alternate fuel. Adoption of alternate fuel like biodiesel will control the

26   pollution and it may also help to facilitate the economic growth of the nations. In the past

27   decades, many researchers adopted the biodiesel as an alternate fuel due to easy

28   availability from vegetable oils/animal fats and also its techno-economic competitiveness.

29   The vegetable oil (VO) is renewable, non-toxic and is widely available from a variety of
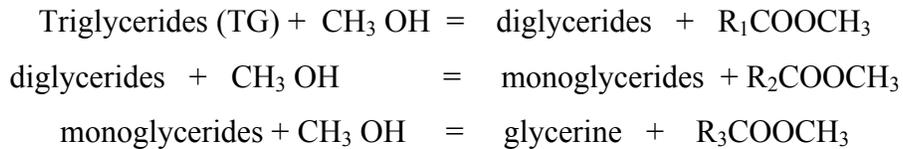
sources and has low sulphur contents close to zero. The vegetable oils (VOs), such as palm, soybean, sunflower, peanut and olive oils are used as alternative fuels for diesel engine. Depending upon the climate and environmental conditions, different countries are looking for different source of vegetable oils as substitutes for diesel fuels. For example soybean oil in the US, rapeseed and sunflower oils in Europe, palm oil in south-east Asia and coconut oil in the Philippines are being considered. The production of oil seeds, percentage of recovery and their cost have been detailed elsewhere [2]. Fats and oils are primarily water insoluble, hydrophobic substances in the plants and animals that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (TG) [3]. Fatty acids vary in carbon chain length and in the number of unsaturated bonds. In beef tallow, the saturated fatty acid component accounts for almost 50 % of the total fatty acids. The higher stearic and palmitic acid contents give beef tallow the unique properties of high melting point and high viscosity [4]. Natural vegetable oils and animal fats are extracted to obtain crude oil or fat.   It usually contains free fatty acids (FFAs), phospholipids, sterols, water, odorants and other impurities. The FFAs and water contents have significant effects on the trans-esterification of glycerides with alcohols using acid or base catalysts. They also interfere with the separation of fatty acid esters and glycerol. Considerable research has been carried out on vegetable oils as a possible alternate. The palm, soybean, sunflower, coconut, rapeseed, tung oils and animal fats have been considered for this conversion.. Oil from algae, bacterial and fungi has also been studied [5].

2. Trans-esterification process

Trans-esterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the trans-esterification process is called alcoholysis. The trans-esterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (acid or base) could accelerate and control the equilibrium, to achieve a high yield of the ester, however the alcohol has to be used in excess. The overall process is a sequence of three consecutive and reversible reactions, in which di and mono-glycerides

1   are formed as intermediates. The stoichiometric reaction requires 1 mol of a TG and 3

2   mols of the alcohol. However, an excess of the alcohol is used to increase the yield of the

3   alkyl esters and to allow its physical separation from the glycerol formed. Many aspects

4   determine the extent of the reaction such as type of catalyst (acid or base), alcohol to

5   vegetable oil molar ratio, temperature, purity of the reactants and free fatty acid content.

6   Methyl esters of fatty acids are produced by alcoholysis (trans-esterification) of TG with

7   methanol in the presence of an acid or base catalyst as illustrated by reaction. Complete

8   conversion of the TG involves three consecutive reactions with monoglyceride and

9   diglyceride intermediates. The equations of the reaction sequence is given as:

10

11   Triglycerides (TG) + CH_3OH = diglycerides + R_1COOCH_3

12   diglycerides + CH_3OH = monoglycerides + R_2COOCH_3

13   monoglycerides + CH_3OH = glycerine + R_3COOCH_3

14

15

16   Conventional synthesis techniques rely on soluble sodium and potassium hydroxide

17   catalysts; however, removal of these catalysts is technically difficult and brings extra cost

18   to the final product. The flow and combustion properties of biodiesel are similar to

19   petroleum-based diesel and thus, it can act as a substitute for diesel fuel or more

20   commonly for blending with fuels. Pure biodiesel carries about 90 % of the energy

21   content of the normal diesel and hence it can be expected that the engine performance can

22   be nearly the same. Biodiesel has higher flash point than normal diesel. In addition,

23   biodiesel increases lubricity, which prolongs engine life and reduces the frequency of

24   engine part replacement. Another significant advantage of biodiesel is that it has low

25   emission profile and its oxygen content is 10-11%. A brief comparison of the ASTM

26   standards for diesel and biodiesel is given in Table.1. [6a]. Trans-esterification needs a

27   catalyst in order to obtain reasonable conversion rates. The nature of the catalyst is

28   fundamental since it determines the compositional limits of the feedstock, reaction

29   conditions and the post separation steps. The preparation method of catalyst also plays a

30   role in catalytic conversion of organic substrates [6b]. Most biodiesel is prepared using

31   alkaline catalysts, such as sodium and potassium methoxides and hydroxides. In

industries, NaOH and KOH are preferred due to their wide availability and low cost, but from the chemical point of view the active species with both type of catalyst is methoxide ions. Methoxide ion is formed either by dissociation of methoxide salts or when methanol reacts with hydroxyl ions from added alkaline hydroxides. Methoxide ions are strong nucleophiles and attack the carbonyl moiety in glyceride molecules to produce the alkyl esters. Overall base catalyzed process suffers from serious limitations that translate into high production cost for biodiesel, even though it is a more active catalyst for biodiesel production. The Scope of this presentation is to review the differences in the catalytic activity of various solid acid and base catalysts and to evaluate the potential heterogeneous catalysts for transesterfication process for biodiesel production. Among the available solid acid/base catalysts, zeolites, sulfated metal oxides, hydrotalcites and alkali metal loaded metal oxides are effective and exhibit interesting results for the conversion of TG to biodiesel. Another important aspect of this conversion is the effect of the mole ratio of alcohol to TG. The effect of methanol to tryglycerides mole ratio has also been discussed in the presence of solid acid and base catalysts.

3. Biodiesel production from different oils

3.1 Canola oil

Katikaneni et al. [7] used a number of catalysts, including Al-PILC (aluminum pillared clay catalyst), to convert canola oil to fuel using a fixed bed reactor. They examined the performance of each catalyst with respect to yield of organic liquid product (OLP), selectivity and the extent of coke formation. They found that HZSM-5 (proton exchanged zeolite type acid catalyst) gave the highest yield of OLP (63 mass %). The OLP obtained with PILC catalyst contained more aliphatic hydrocarbons and least amount of aromatic hydrocarbons as compared to OLP obtained with other catalysts. Their studies showed that the increase of the pore size of the catalyst increased the conversion of canola oil, coke formation and the selectivity for aliphatic compounds, while the yield of hydrocarbons and the selectivity for aromatics decreased. This led them to the conclusion that the medium pore size of the catalysts would enhance the initial cracking and deoxygenation reactions needed for an optimum fuel yield. A further study by these authors showed that the co-feeding with steam during the reaction helps to

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increase the olefin formation as well as increase the catalyst life by decreasing the coke formation [8]. The effect of acidity, basicity and shape selectivity of the catalyst on the conversion of canola oil was also examined by Idem et al. [9]. A comparative evaluation of the activity of the catalyst systems such as HZSM-5, silica-alumina and γ-alumina has been made. Product distribution obtained for runs using silica-alumina and γ-alumina as catalysts is similar to what was obtained without the catalyst. The realized product selectivity and the increased OLP yield obtained using HZSM-5 have to be associated with the ZSM's shape selectivity and not with its acidity. The studies have been extended using calcium and magnesium oxide as catalysts to examine how the basicity of the catalyst affected the product yield. The results showed that the presence of basic centers inhibited the secondary cracking and produced large amounts of residual oil.

3.2. Palm oil

Leng et al. [10] used a fixed-bed reactor to crack palm oil over HZSM-5 catalyst. The maximum formation of gasoline range hydrocarbons was achieved at 673 K with a low space velocity. The conversion of palm oil was low (40-70%) as compared to canola oil where conversions up to 100 % was achieved [9]. This was attributed to the fact that palm oil contains more saturated fatty acids (palmitic acids) than canola oil and these saturated compounds have a greater stability than unsaturated fatty acids. Twaiq et al. [11] have also studied the palm oil conversion using HZSM-5, Zeolite-β and ultra stable Y zeolites. Conversions of up to 99 wt% with gasoline yields of 28% were achieved. They concluded that the HZSM-5 was the best catalyst from the points of view of conversion of the substrate, gasoline yield, selectivity for aromatics and lower coke formation.

3.3. Sunflower oil

Dandik et al. [12] examined the products of the conversion of used sunflower oil with HZSM-5 using a special fractionating pyrolysis reactor. A conversion of 96.6% was achieved at 693 K with an OLP yield of 33%. The length of the fractionating column of the reactor had an effect on the OLP content with increase in length giving a significant increase in n-alkene content.

4. Homogeneous acid catalyzed reactions and the effect of oil to alcohol mole ratio

The liquid phase acid-catalyzed trans-esterification process does not progress like base-catalyzed process, due to the sluggishness of the process. In fact the homogeneous acid-catalyzed reaction is about 4000 times slower than that of homogeneous base-catalyzed reaction [13a]. However, this is not true for all vegetable oil, for instance cottoned seed oil, which has similar composition like vegetable oil can be esterified in a facile and effective manner in the presence of base catalysts [13b]. One of the advantages of acid-catalyzed trans-esterification is that it is not strongly affected by the presence of FFAs in the feedstock. One of the superiority of the acid catalysis is that it can simultaneously catalyze both esterification and trans-esterification. Recently few studies have shown that the acid-catalyzed biodiesel production can be economically compete with respect to base-catalyzed processes using virgin oils, especially when the former uses the low-cost feedstocks [14, 15]. The data on the content of FFAs in common oil sources and crude beef tallow are given in Tables 2 and 3. As already mentioned, the trans-esterification of TGs, catalyzed by either bases or acids, consists of three consecutive and reversible reactions. The trans-esterification chemical pathway for an acid-catalyzed reaction indicates how the catalyst-substrate interaction is the key step for the protonation of the carbonyl oxygen [6]. Thus, this protonation in turn, increases the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack. In contrast, base catalysis takes on a more direct route and forming first an alkoxide ion, which directly acts as a strong nucleophile, giving rise to a different chemical pathway for the reaction. The main difference is that the formation of a more electrophilic species (acid catalysis) versus that of a stronger nucleophile (base catalysis), which is ultimately responsible for the observed differences in activity. For acid-catalyzed systems, sulfuric acid has been the most investigated catalyst, but other acids, such as HCl, BF_3, H_3PO_4, and organic sulfonic acids, have also been used by different researchers [16]. Freedman et al. [17] examined the trans-esterification kinetics of soybean oil with butanol, using sulfuric acid as the catalyst. They found that the rate-limiting step varied over time and that there are three regimes, in accordance with the observed reaction rate. Initially, the reaction was characterized by a mass-transfer controlled regime that resulted from the low miscibility of the catalyst and reagents (oil

phase). These two were separated from the polar alcohol-acid phase. As the reaction progressed, ester products act as an emulsifiers, a second-rate regime emerged, which is kinetically controlled and characterized by a sudden surge in product formation. Finally, the third regime was reached once equilibrium was approached near reaction completion. They have also established that the large molar ratio of alcohol-to-oil, 30:1, was needed to have acceptable reaction rates. In this way, for the trans-esterification reaction, the forward reactions follow the pseudo-first-order kinetics, while the reverse reactions exhibited second-order kinetics. In a continuing effort to decrease the cost of biodiesel production, researchers have attempted to ascertain what optimum ratio of alcohol-to-TG should be used. Two factors must be considered during this optimization process. First, increasing the molar ratio between alcohol and TG and the second, acid-catalyzed trans-esterification achieves greater and faster conversions at high alcohol concentration. Canakci and Van Gerpen [18] studied how the reagent molar ratio affected reaction rates and product yield of soybean oil trans-esterification process by sulfuric acid. Five different molar ratios, from 3.3:1 to 30:1, were studied. Their results indicated that the ester formation increased with increasing the molar ratio, reaching its highest value, 98.4%, at the highest molar ratio used,i.e., 30:1. In a related study, Crabbe et al. [19] also determined the effect of molar ratio within the range of 3:1-23:1 and concluded that the highest molar ratio required for complete transmethylation can be between 35:1 and 45:1 a result obtained by extrapolation. Alcohols used in acid-catalyzed trans-esterification include C_1 - C_5 alcohol. Methanol and ethanol are used most frequently in both laboratory research and in biodiesel industry [20, 21]. But the low cost of methanol makes it the first choice for the trans-esterification reaction. Ethanol, however, is derived from agriculture products (renewable sources) and biologically less objectionable to the environment than methanol; thus, ethanol is the ideal candidate for the synthesis of a fully biogenerated fuel [20]. Nonetheless, working with higher molecular weight alcohols, such as butanol, brings about interesting advantages. For instance, butanol has better miscibility with the lipid feedstock than lighter alcohols, contributing to a less pronounced initial mass-transfer-controlled regime. Additionally, the elevated boiling points of larger alcohols enable the liquid reaction system to be operated at higher temperatures while maintaining moderate pressures. This is an important issue in the

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1 acid-catalyzed trans-esterification since higher reaction temperatures are often required to

2 achieve faster reaction rates. However, only a limited number of papers have actually

3 addressed the subject of the alcohol characteristics. Nye et al. [22] compared the series of

4 linear alcohols from methanol to butanol to find the most suitable alcohol for the trans-

5 esterification of waste frying oil. All reactions were carried out using 0.1% sulfuric acid

6 at reflux temperatures with all other conditions remaining the same. Butanol yielded the

7 highest reaction rates and conversion followed by 1-propanol and then ethanol. Even

8 though acid-catalyzed reactions carried out with methanol proved to be the slowest, the

9 reverse was true for the base-catalyzed process. These results suggest that the initial

10 reagent phase miscibility was more critical in acid catalysis than in base catalysis. Two

11 factors could have affected phase miscibility: (i) increased hydrophobicity associated

12 with larger alcohols, and (ii) the higher reaction temperatures that were applied as the

13 alcohol molecular weight is increased. Thus, temperature plays an important role in the

14 acid-catalyzed synthesis of biodiesel [16]. However, side reactions such as alcohol

15 etherification can also be observed under such harsh reaction conditions. Reaction rates in

16 acid-catalyzed processes may also be increased by the use of larger amounts of catalyst.

17 Abreu et al, recently reported that tin compounds are active for multi-phasic catalytic

18 system. They studied the effect of tin pyrone complexes for the alcoholysis of vegetable

19 oil; unfortunately it was not possible to reuse the tin complexes due to anchoring of the

20 complex with ionic liquid or solid phase [23]. Abreu et al. [23] have also studied the use

21 of different anchored metal complexes for transesterification of vegetable oil with linear

22 and branched chain alcohol, with   alcohol/vegetable oil/catalyst mole ratio being

23 (400:100:1). Tin and lead pyrone complexes were active at all reaction conditions and the

24 catalytic activities are higher when vegetable oil with short chain fatty acids or with high-

25 unsaturated degree and short and linear chain alcohols are used [24].

26

27 **5. Heterogeneous acid catalyzed reactions**

28   Homogeneous catalysts though effective, lead to serious contamination problems that

29 make essential the implementation of good separation and product purification protocols,

30 thus contributing to increased production cost. To be economically viable and to compete

31 commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel

need to involve continuous processing in a flow system, should have as few reaction steps as possible, limit the number of separation processes, and ideally use the robust heterogeneous (solid) catalyst. The appropriate solid catalysts can be easily incorporated into a packed bed continuous flow reactor, simplifying product separation and purification and reducing waste generation. Research on the direct trans-esterification of lipid feedstocks into biodiesel by solid acid catalysts has not been examined extensively. Actually, less than a handful of studies have explored this topic, without any decisive conclusions on the potential of the process. In one of the few published studies dealing with trans-esterification of TG feedstocks using solid acid catalysts, Mittelbach et al. [25] compared the activities of a series of layered aluminosilicates with sulfuric acid for the trans-esterification of rapeseed oil. These researchers used an initial molar ratio of 30:1 alcohol-to-oil and 5 wt% of the catalyst. Among the catalysts tested, sulfuric acid showed the highest activity. The solid catalysts showed varied activities depending on reaction conditions. The most active catalyst was the impregnated system. For instance, activated montmorillonite showed a 100% conversion after 4 h of reaction at 493 K and 52 bar. However, leaching of sulfate species restricted the reusability of the catalyst. It is also likely that some degree of homogeneous reaction was concurrently taking place due to sulfuric acid leaching. Attempts to prepare other solid acid catalysts with high activities for trans-esterification have been reported, as well. In particular, Kaita et al. [26] designed aluminum phosphate catalysts with various metal-to phosphoric acid molar ratio (1:3-1:0.01) and used these materials for the trans-esterification of kernel oil with methanol. According to the above authors, durable and thermostable catalysts showed good reactivity and selectivity to methyl esters. However, the use of these materials still needed high temperatures (473 K) and high methanol-to-oil molar ratio (60:1) for effective process. In a related study, Waghoo et al. [27] reported on the trans-esterification of ethyl acetate with several alcohols over hydrous tin oxide. Linear and aromatic alcohols were tested in a temperature range of 443-483 K. All reactions were selective for trans-esterification. In particular, this catalyst presented an appreciable activity for reactions involving *n*-butyl alcohol, n-octyl alcohol, and benzyl alcohol. Amberlyst-15 has also been studied for trans-esterification reaction. However, mild reaction conditions are necessary to avoid degradation of the catalyst. At a relatively low

temperature (333 K), the conversion of sunflower oil was reported to be only 0.7%, when the reaction was carried out at atmospheric pressure and a 6:1 methanol-to-oil molar ratio was employed [28]. On a related study, Brønsted solid acids have also been proposed for the trans-esterification of α-ketoesters to produce precursors for other natural products [29]. The catalysts normally used include Amberlyst-15 [30], Envirocat EPZG [31], natural kaolinite clay [32], B_2O_3/ZrO_2 [33], sulfated SnO_2 [34], and zeolites [35]. Even though α-ketoesters usually show a higher reactivity than simple esters for trans-esterification, under the optimized reaction conditions, solid catalysts have also been active for the trans-esterification of α-ketoesters.

5.1. Zeolite type solid acid catalyst

Inorganic acid catalysts are generally more suitable for bio diesel process instead of ion exchange resins due to poor thermal stability and swelling behavior except for a few commercial high cost ion exchange resins like Nafion and Amberlyst-15 [36]. Hence inorganic acid catalysts are generally more suitable. Among the different types of inorganic solids that have been used to produce esters, the most popular one is zeolites. Different characteristics make zeolites as the excellent catalyst for organic syntheses. For instance, zeolites can be synthesized with different crystal structures, pore sizes, framework Si/Al ratio, and proton-exchange levels. These characteristics permit tailoring important catalytic properties, especially the acid strength. In zeolites, the acid strength can be adjusted such that it fits the reaction requirement. The reaction may not proceed at a reasonable rate under the chosen conditions with least acidic catalysts [35a]. Too high acidity causes the deactivation of the catalyst by coking or undesirable byproducts, which might be formed requiring additional and expensive separation procedures. For esterification, however, optimum acidity has yet to be established. In addition, zeolites provide the possibility to choose among different pore structures and surface hydrophobicity, according to the substrate's size and polarity. Multi-functionalization of mesoporous silica with both organosulfonic acid and hydrophobic organic groups was shown to be effective in esterifying the free fatty acid while excluding water, which is an undesired reaction product, from the proximity of the active sites. Both post synthesis grafting and one-step co-condensation techniques were used to introduce the hydrophobic organic groups, preferentially to modify the external and internal surfaces, respectively. It

1 was shown that the technique of incorporating the hydrophobic organic group into the

2 mesoporous silica and knowledge of the reaction mixture are important for effecting the

3 enhancement of the performance of the catalysts [35b].

4 *5.2. Heteropoly acid loaded MCM-41 catalyst*

5   In general, reactions with large molecules take place on the external surface of

6 zeolite crystals. Zeolites are active catalysts for the esterification of large carboxylic

7 acids, but they catalyze the reaction rather slowly. Thus, only large-pore zeolites have

8 been used with any success in fatty acid esterification [37]. But even in those successful

9 cases, the reaction always gives a variety of undesired byproducts due to the high reaction

10 temperatures. In general, the catalytic activity of zeolites for the esterification of fatty

11 acids increases with increasing Si/Al ratio, indicating that the reactivity is influenced by

12 acid site strength as well as surface hydrophobicity. Pore size, dimensionality of the

13 channel system (related to the diffusion of reagents and products) and aluminum content

14 of the zeolite framework strongly affect the catalytic activity of zeolites for esterification.

15 Related to zeolites, but with amorphous pore walls, silica molecular sieves, such as

16 MCM-41 mesoporous materials, are generally not sufficiently acidic enough to catalyze

17 esterification reaction. Introducing aluminum, zirconium, titanium or tin ions into the

18 silica matrix of these solids can significantly improve their acid properties. However,

19 metal-doped materials behave more like weak acids and can only be used for reactions

20 that do not require a strong acid catalyst. For instance, the catalytic activity of Al-MCM-

21 41 in the esterification of oleic acid with glycerol was found to be significantly lower

22 than that of zeolite beta with a similar Si/Al molar ratio [38]. To enhance the catalytic

23 activity while keeping the benefits of large pore diameters, strong acid species have been

24 introduced to the pore interior of MCM-like solids. In particular, MCM-41-supported

25 heteropoly acids (HPAs) have been used as catalysts in the gas-phase esterification of

26 acetic acid and 1-butanol [39]. These catalysts showed good activity at 383 K (95%

27 conversion of 1-butanol). As expected, MCM-41-supported HPA was more active than

28 pure HPA. The enhanced activity could be ascribed to a high dispersion of the HPA on

29 the MCM-41 internal surface, giving rise to a higher population of available acid sites

30 than in pure HPA. However, the supported catalyst is considerably more hydrophilic than

31 the original HPA. Water formation caused HPA migration from MCM-41 pores to the

1   outer surface thus facilitating the sintering of HPA species. This was verified by

2   measuring the activity of the spent catalyst, which decreased with catalyst reuse. Other

3   composite catalysts, made using silica mesoporous materials modified with sulfonic

4   groups, were used in the pre-esterification of mixtures of FFAs and soybean oil. Mbaraka

5   et al. [40] found that the activity of these hybrid mesoporous silicas was highly dependent

6   on their pore dimensions and probably on their hydrophobic character as well. Pore

7   dimensions strongly affected reagent diffusion.

8   *5.3.Sulfated zirconia and tin oxide type solid acid catalyst*

9   Acid strength of the catalysts has an important role in these reactions. For instance,

10 catalysts prepared from a stronger acid precursor containing benzene sulfonic acid groups

11 are more active than those containing only propylsulfonic acid groups. Indeed, catalysts

12 with a medium pore diameter of 50 Å and benzene sulfonic acid groups showed activities

13 comparable to that of sulfuric acid. Recently, sulfated zirconia (SO_4/ZrO_2) has been

14 shown to be active for several acid-catalyzed reactions [41]. For esterification, SO_4/ZrO_2

15 has shown some promise as an active catalyst due to its high acid strength; however,

16 SO_4/ZrO_2 deactivates due to leaching of sulfate enhanced by hydrolysis [42]. Sulfate

17 groups can leach out as H_2SO_4 and HSO_4^-, which in turn can give rise to homogeneous

18 acid catalysis, interfering with measurements of the heterogeneous catalytic activity. To

19 overcome the susceptibility of SO_4/ZrO_2 to water and to improve its general

20 characteristics, new preparations of SO_4/ZrO_2 have recently been proposed. For instance,

21 Yadav and Murkute [43] published a route to preparing SO_4/ZrO_2 with higher sulfate

22 loadings and resistant to leaching of sulfate by hydrolysis. This catalyst was prepared by

23 using a chloro sulfonic acid precursor dissolved in an organic solvent, instead of the

24 conventional impregnation of sulfuric acid. The prepared SO_4/ZrO_2 exhibited higher

25 catalytic activity for esterification than the conventionally prepared SO_4/ZrO_2 and no

26 leaching of sulfate was observed. Additionally, the catalyst demonstrated good retention

27 of its activity for subsequent experiments. Sulfated tin oxide (SO_4^{2-}/SnO_2), prepared from

28 meta-stannic acid, has shown activity superior to that of SO_4^{2-}/ZrO_2 for the esterification

29 of n-octanoic acid with methanol at temperatures below 423 K due to its superior acid

30 strength [44]. However, a more widespread testing of SO_4^{2-}/SnO_2 has not been carried out

31 due to inadequacies in the preparation method. New synthetic routes for preparing SO_4^{2-}

1   /SnO$_2$ are evolving and additional studies are expected with this material soon [45]. The

2   catalytic activities of hafnium and zirconium salts have been investigated for the

3   esterification of carboxylic acids with primary and secondary alcohol in equimolar ratios.

4   In general, for esterification of an equimolar ratio of reactants is preferred instead of

5   excess alcohol. Equimolar ratios can reduce waste and simplify the product separation

6   protocols, leading to the environmental and economic benefits. In particular, hydrous

7   zirconium oxide showed good activity and selectivity for esterification. The low acid

8   strength of this catalyst helps to avoid undesirable side reactions, such as alcohol

9   dehydration. In addition, the hydrated oxide is not sensitive to water. Thus, esterification

10 does not require water-free conditions.

11   Furuta et al. [46] carried out the biodiesel production over solid super acid catalysts in

12 fixed bed reactor under atmospheric pressure. Solid superacid catalysts, such as sulfated

13 tin and zirconium oxides and tungstated zirconia are prepared by solid state method and

14 they were evaluated for trans-esterification of soybean oil with methanol at 473-573 K

15 and the esterification of n-octanoic acid with methanol at 458-473 K. Tungsten contining

16 zirconia–alumina is a promising solid acid catalyst for the production of biodiesel from

17 soybean oil because of its high performance (conversions were in the range of 90%). The

18 trans-esterification of soybean oil with methanol to fatty acid ester was carried out over

19 WZA (tungstated zirconia), SZA (sulfated zirconia), and STO (sulfated tin oxide) at 473-

20 573 K; the conversions of soybean oil after 20 h of time on stream show that the WZA

21 catalyst is quite effective for the reaction, the conversions being more than 90% at

22 temperatures over 523 K. This high activity was maintained up to 100 h of time on

23 stream, but a little amount of by-products were detected by the gel permeation

24 chromatographic (GPC) analysis. The formation of glycerin was confirmed by GC–MS

25 analysis, but the other two by-products were not detected due to their high boiling point

26 and that were identified to be mono- and di-glyceride from their molecular weight

27 analysis by GPC. The esterification of n-octanoic acid with methanol to give methyl n-

28 octanoate was carried out in the same manner as that of the trans-esterification of soybean

29 oil; the yields of ester after 20 h and the catalysts such as WZA, STO, and SZA showed

30 quite high activities close to 100% yield at temperatures above 448 K. No by-products

31 were detected. Therefore, high performance of the WZA catalyst for trans-esterification

1 is also based on its high activity for the esterification of the liberated free-fatty acids.

2 STO showed especially high activities for the esterification of n-octanoic acid. This is

3 due to its strong acidity. Very recently, the catalytic action of STO in comparison with

4 that of SZA has been reported, along with temperature programmed desorption (TPD)

5 measurements using ammonia and pyridine as probes [47]. The fact that the acid strength

6 of STO is higher than those of SZA and WZA was confirmed by the adsorption heat of

7 Ar, calculated from a temperature dependence of amount of Ar adsorption around room

8 temperature, it has been reported that Ar is more suitable than ammonia for a probe

9 molecule of acid sites [48, 49]. The values of heat of adsorption were 20.7, 31.0, and

10 24.3 kJ mol^{-1} for WZA, STO, and SZA, respectively. It appears that the acid strength of

11 WZA is suitable for both of the esterifications, though the acidity of WZA has not been

12 determined in detail yet. In summary, three types of solid super acid catalysts were

13 prepared and evaluated in the trans-esterification of soybean oil with methanol and the

14 esterification of n-octanoic acid with methanol. Tungstated zirconia–alumina is a

15 promising catalyst for the production of biodiesel because of its activity for the trans-

16 esterification as well as the esterification.

17 *5.4. Tungsten trioxide loaded zirconia type solid acid catalyst*

18 Ramu et al. [50] studied the esterification of palmitic acid with methanol over

19 tungsten oxide supported on zirconia solid acid catalyst, prepared by both impregnation

20 and co-precipitation methods; the extent of tungsten loading and calcination temperature

21 were varied. They characterized the catalysts by X-ray diffraction (XRD) for structural

22 elucidation and by temperature-programmed desorption (TPD) of ammonia for surface

23 acidity. The impregnated catalysts exhibited both tetragonal and monoclinic phases of

24 zirconia, at calcination temperatures beyond 773 K and their co-precipitated analogues

25 showed stability towards the tetragonal phase. The formation of monoclinic phases of

26 zirconia and crystalline tungsten oxide phase decreased the esterification activity, as a

27 consequence of decreased surface acidity. Coexistence of tetragonal zirconia with the

28 amorphous tungsten oxide offered maximum esterification activity.

29 A series of WO$_3$/ZrO$_2$ catalysts were prepared by the impregnation technique with

30 tungsten concentration ranging from 2.5 to 25 wt%. These systems were used for the

31 liquid phase esterification of palmitic acid with methanol. This reaction was carried out at

1   two different reaction times: 3 and 6 h. It is seen that the esterification activity of the

2   catalysts increased with WO_3 loading up to 5% and thereafter the activity showed a

3   decreasing trend. They tested two sets of catalysts with two different loadings of WO_3,

4   namely 5 and 15 wt% prepared by the co-precipitation method, two dried masses were

5   subjected to calcination at the same temperature. The 15 wt% catalyst was selected based

6   on the literature evidence that the co-precipitated catalysts containing 10–15% WO_3 in

7   ZrO_2 stabilizes the tetragonal phase [51]. The 5 wt% WO_3/ZrO_2 exhibited the

8   transformation of tetragonal to monoclinic phase of zirconia with increase in calcination

9   temperature from 773 to 1173 K. However, the 15 wt% WO_3/ZrO_2 catalyst showed the

10   presence of tetragonal phase predominantly, irrespective of the calcination temperature.

11   These catalysts were evaluated for their esterification activity and the results are shown

12   in Table 4. With increase in calcination temperature, the activity of the catalysts

13   decreased drastically. An interesting observation in this case is that, even though the

14   catalyst calcined at 1173 K showed the presence of tetragonal phase of zirconia

15   exclusively, but its activity is found to be negligible. This implies that the presence of

16   tetragonal phase alone is not sufficient for exhibiting the required activity. This catalyst

17   has also shown the presence of crystalline WO_3 phase. The 5 wt% WO_3/ZrO_2 catalyst

18   also showed a decrease in activity with increase in calcination temperature. The high

19   temperature calcined catalyst displayed lower activity even in the absence of crystalline

20   WO_3.

21   It can be concluded from these studies that the presence of zirconia in tetragonal

22   phase is not the only criterion but the co-existence of amorphous WO_3 is also required for

23   obtaining considerable activity. The presence of monoclinic phase of zirconia and

24   crystalline WO_3 had detrimental effects on the esterification of palmitic acid. Literature

25   data also support the presence of such species for obtaining high efficiency from the

26   tungstated zirconia super acid catalysts. Furuta et al. [52], Larson and Petkovic [53]

27   concluded that the active sites of tungsten oxide supported on zirconia are generated by

28   the interaction of amorphous tungsten trioxide and the crystalline zirconium oxide. Such

29   an active species exists in the case of 5 wt.% WO_3/ZrO_2 catalyst, prepared by

30   impregnation and it showed the maximum esterification activity.

In order to understand the exact nature of the active species of the catalyst correlations are essential between the catalyst preparation method and their physioco-chemical properties like structure and surface acidity and their reactivity in the esterification process. A comparison is made by taking 5 wt% WO_3/ZrO_2 catalysts prepared by both impregnation and co-precipitation method. These catalysts were calcined at low and high temperatures (i.e., 773 and 1173 K), respectively. The relevant data are given in Table 5. The 5 wt% WO_3/ZrO_2 catalyst prepared by both impregnation and co-precipitation and subjected to calcinations at 773 K, exhibited the presence of tetragonal phase of zirconia and amorphous tungsten oxide. They showed high activity and they also possessed the high acidity. The method of preparation seems to influence the nature of active phase. Monoclinic phase of ZrO_2 dominates in the impregnated catalyst, while the tetragonal phase is predominant in the catalyst obtained by co-precipitation. These observations show that the WO_3/ZrO_2 catalyst requires tetragonal phase of ZrO_2 and amorphous WO_3 for better activity in esterification of palmitic acid. The effect of reaction time on the esterification of palmitic acid was also studied using the active 5 wt% of WO_3/ZrO_2 catalyst. With the increase in reaction time the esterification activity is increased and it showed considerable conversion even with a reaction time of 1 h. This high activity at low reaction time shows that the heterogeneous catalyst is comparable with the homogenous catalyst system, where the reaction proceeds rapidly.

6. Heterogeneous base catalysts for the production of biodiesel

Kim et al. [54] studied the trans-esterifaction of soyabean oil, using heterogeneous base catalyst such as sodium and sodium hydroxide loaded γ-alumina, correlating the catalytic activity of trans-esterification process with respect to basic strength of the catalyst. They also studied the role of co-solvent in the trans-esterification process in the presence of base catalyst. Optimum amount of n-hexane was found to be 5:1 for vegetable oil (VO) to n-hexane molar ratio. When n-hexane was added, the immiscible two-phase system was changed to the homogeneous emulsion state. The optimum molar ratio of methanol to VO was found to be 9:1, the excessively added methanol had no significant effect on the production yield. The maximum biodiesel production yield

1 reached 94%, which was almost the same value as compared to the conventional

2 homogenous NaOH system [55]. Both the sodium aluminate formed by loading sodium

3 hydroxide on γ-alumina, and the ionization of sodium are responsible for the strong basic

4 sites of the catalysts. The activities of the heterogeneous base catalysts correlated with

5 their base strengths. The reaction conditions for the system were optimized to maximize

6 the biodiesel production and the utilization of a co-solvent was found to be inevitable for

7 the trans-esterification of VOs to biodiesel. Among the co-solvents tested, n-hexane was

8 the most effective with the amount of of n-hexane is 5:1 with respect to VO to n-hexane.

9 *6.1. Zeolite*

10 The base strength of the alkali ion-exchanged zeolites increases with increasing

11 electropositive nature of the exchanged cation. The occlusion of alkali-metal oxide

12 clusters in zeolite cages via decomposition of impregnated alkali metal salts results in

13 increase in the basicity of these materials. The zeolites faujasite NaX and titanosilicate

14 structure-10 (ETS-10) were used for the alcoholysis of soybean oil with methanol. These

15 catalysts are predominantly alkali-cation-exchanged zeolite type materials. The basicity

16 of zeolites NaX and ETS-10 were enhanced by ion exchange with higher electropositive

17 metals like K and Cs using conventional techniques. Sodium oxide clusters in the

18 faujasite zeolites were occluded in zeolite cages via decomposition of impregnated

19 sodium acetate or sodium azide to further increase their basicity. ETS-10 is a new type of

20 microporous inorganic titanium containing zeolite that has a three-dimensional 12-ring

21 pore structure consisting of interlocking chains of octahedral titanium (TiO_6^{8-}) and

22 tetrahedral silicon (SiO_4^{4-}) atoms [56, 57]. Owing to the high framework charge

23 associated with the octahedral Ti, ETS-10 also exhibits a very high cation-exchange

24 capacity (CEC). Its unique large pore structure, novel chemical composition, and strong

25 basic character are the factors responsible for the performance advantages over other

26 zeolites for liquid phase reactions. Potassium and cesium exchanged ETS-10 type

27 catalysts were prepared by partial ion exchanging of 15 g of ETS-10 zeolite using 0.5 M

28 aqueous solutions of potassium hydroxide and cesium chloride at 333K (30 mL g^{-1}),

29 respectively [58]. NaX faujasites have an aluminosilicate framework structure. The rigid

30 framework structure was remarkably stable having the largest void space of any known

31 zeolite and amounts to about 50 vol.% of the dehydrated crystal. Zeolite NaX was triply

ion-exchanged with K and Cs by contacting the zeolite in 1.0 M solutions of potassium acetate and cesium chloride, respectively, for 2 h at room temperature. Zeolite catalysts with nominal loadings of 0.25, 1 and 3, excess Na per super cage were prepared for each of the two types of sodium precursors investigated. Each supported catalyst was then dried overnight at 373 K and stored in desiccators for future use. Decomposition of the supported precursor was carried out immediately prior to reaction or micro calorimetric investigation. Zeolites absorb water and carbon dioxide upon exposure to the ambient atmosphere hence they were pretreated in order to expose the oxide surfaces before its use as a catalyst. The nature of basic sites depend upon the severity of the pretreatment, therefore the catalytic activity is a function of pretreatment temperature. Molecules with weak surface interaction require low pretreatment temperatures and the others require pretreatment at high temperature. Pre-treatment of the catalyst varied according to what kind of alkali species was to be formed. The sodium acetate supported catalysts were heated in flowing air while heating at $1^{\circ}C$ min^{-1} to 773 K and held at that temperature for 4 h to form the occluded sodium oxide species in the cages of the NaX. Nickel showed particularly high activity, and it or similar valance metals could be effective catalysts for alcoholysis especially if they are dispersed on high surface area supports. Zinc oxide and zinc carbonate were also effective, however, the propensity for them to go into solution, especially at high concentrations of free fatty acids, diminishes their potential. Due to the impact of metals on the reaction, studies on the catalytic activity of zeolites towards this reaction were conducted in glass capillary tubes or glass vials. In spite of the higher surface areas of these catalysts, they were not as effective as nickel and palladium. Due to their low conversions the reactions were repeated with the zeolite catalysts pretreated at 773K for 4 h. The conversions over the pretreated catalysts at 333,393, and 423 K are studied. These systems provided greater conversions, and several catalysts exhibiting conversions greater than 90%. The increase in activity is attributed to the removal of water and carbon dioxide from the catalyst surface by pretreatment. Conversions at 24 h decreased with decreasing temperature**.** At 333 K low conversions and high intermediate concentrations was observed at 24 h indicate that 333 K is marginally viable commercial temperature for these catalysts. The one solid acid catalyst (NaY) evaluated at 423 K did not perform well, with a 33% conversion to methyl esters at 24 h. The ETS-10 catalyst

19

provided a 32% conversion to methyl esters at room temperature for 24 h, this was the only study conducted at room temperature. The conversion to methyl ester over the NaX faujasite zeolites that were ion exchanged with more electropositive cations was higher than over the parent zeolites with the exception of cesium. Fig. 1 graphically illustrates this where the intermediate electronegativity of the solid is correlated with yield of methyl ester. The intermediate electronegativity was calculated based on the principle of electronegativity equalization proposed by Sanderson [59], which states that when two or more atoms initially different in electronegativity combine chemically they adjust to have the same intermediate electronegativity within the compound. This intermediate electronegativity is given by the geometric mean of the individual electronegativities of the component atoms. After 24 h the conversion of soybean oil to methyl ester is 15.4% for NaX, 22.5% for KX and 18.7% for CsX. The decreased conversion for CsX compared to that of KX is unexpected and relates to the degree of ion exchange of these solids. The large size of cesium cations limits the exchange capacity compared to that for the smaller potassium, which affects the basicity associated with the framework oxygen. Similar phenomenon was observed (Fig. 1) in the case of the ETS-10 zeolites as well. The parent ETS-10 catalyst is reported to be approximately four times more basic than NaX [60]. The more basic sites produced remarkably higher conversions to methyl esters in the case of ETS-10 compared to NaX zeolite on an identical mass basis. The ETS-10 catalyst generally had the greatest reactivity. Incorporation of occluded sodium oxide species results in an increase in the base strength and number of basic sites over the parent zeolite. This approach was used in an attempt to increase the activity of NaX faujasites toward the alcoholysis reaction. Increasing the number of occluded species resulted in an increase in the number of basic sites present, but did not increase the strength of the sites formed. The sites obtained are non-uniform in strength, which indicates that the occluded species do not decompose to create the same type of basic site. The increased incorporation of excess sodium oxide per supercage was found to be proportional to the conversion for the trans-esterification reaction, indicating that the reaction is enhanced by the incorporation of additional basicity in the zeolite cages. The strength of the basic sites formed via the decomposition and oxidation of sodium azide was higher than that obtained for occluded sodium species in NaX of similar loading prepared via the

1   decomposition of sodium acetate. This explains why the yield of methyl esters for the

2   NaO_x/NaX^* catalysts was higher than that of the NaO_x/NaX catalysts at identical catalyst

3   masses. However, the total CO_2 uptake for similarly loaded catalysts prepared via the two

4   precursors are comparable, indicating that similar loadings of sodium azide-based

5   catalysts create a similar number of basic sites as the sodium acetate, but of higher base

6   strength. The effect of sodium occlusion on methyl ester yield is more pronounced at

7   loadings lower than those of three sodium atoms per supercage. Further increase in the

8   basicity of ETS-10 can be achieved by impregnating the porous solids with sodium

9   acetate or sodium azide to form extra framework basic sites. ETS-10 catalyst has an

10 activity to a level comparable to the occluded NaX zeolite, which had undergone a

11 number of chemical treatments in order to reach that level of activity. Fig. 2 compares the

12 performance of ETS-10 zeolites and occluded faujasite NaX zeolites to other

13 heterogeneous catalysts reported in the literature. A first-order linear regression model

14 was used to obtain a least-squares rate constant. This rate constant was then used to

15 calculate the time necessary to achieve 80% conversion to methyl esters. The ETS-10

16 zeolites and occluded faujasite NaX zeolites have activities greater than any other

17 heterogeneous catalyst, that are reported in the literature. The few solid catalysts reported

18 to have higher activities are likely to follow a homogeneous mechanism [61]. For

19 example, barium hydroxide is known to have useful solubility in water and polyols [62],

20 it will have a non-negligible solubility in fats and oils. In fact, the better of these catalysts

21 provide similar conversions at temperatures about 323 K lower than the best reported

22 alternatives.

23 *6.2. Hydrotalcite*

24 Cantrell et al. [63] studied the alkali free co-precipitate route synthesized magnisum-

25 aluminum hydrotalcite materials, which has a composition of $[Mg_{(1-}$

26 $_{x)}Al_x(OH)_2]^{x+}(CO_3)_{x/n}^{2-}$ over the range x = 0.25–0.55. Hydrotalcite is another interesting

27 class of solid bases whose acid/basic properties can be easily controlled by varying with

28 their composition. The structure of hydrotalcites is based on layered double hydroxides

29 with brucite like $(Mg(OH)_2)$ hydroxide layers containing octahedrally coordinated M^{2+}

30 and M^{3+} cations A^{n-} as the counter anion. Variations in the Al content (x) are known to

31 modify the basic properties of the material, with stable pure hydrotalcite structures

reported to form for compositions over the range of $0.25 < x < 0.44$. The basic sites in the alkali earth oxides can originate from O^{2-} (strong basicity), O^- species near hydroxyl groups (medium strength) and OH groups (weak). The addition of Al^{3+} alters the acid-base site distribution through the introduction of $Al^{3+}–O^{2-}$ sites which are of moderate Lewis acidity and only medium basicity.

Mg content progressively reduce the surface area of the resulting hydrotalcites, their total area remaining in excess of 90 m^2/ g even for the Mg:Al = 3:1 sample (Table 6). This gradual loss of surface area has been previously observed and attributed to the effect of carbonate decomposition on the resulting morphology of the material [64]. Al-rich hydrotalcites tend to have higher carbonate contents, which favor porous open networks following thermal processing. Therefore, they exhibit larger pores than Al_2O_3 or MgO, which have a broad pore size distribution in the range of 20 nm. The reduced porosity of the calcined Al_2O_3 reference sample can be attributed to structural collapse at 473 K upon thermal decomposition of CO_3^{2-} containing bayerite like precursor.

The catalytic trans-esterification of glyceryl tributyrate with methanol to form methyl butanoate was investigated using the series of Mg/Al hydrotalcites. Triglyceride conversion to the methyl ester occurred immediately without an induction period with concomitant formation of the diglyceride. The yield of these primary products rose linearly with triglyceride consumption over the first 15 min of reaction, after which secondary trans-esterification of the diglyceride to monoglyceride initiated. This continued to boost the methyl butanoate yield, while the yield of diglyceride intermediately reached a plateau, before slowly declining concomitant with monoglyceride production. The rate of tributyrate conversion and associated methyl butanoate and diglyceride formation were both 1st-order in triglyceride concentration during the initial stage of reaction (< 20 min). The surface area normalizes the initial rates for glyceryl tributyrate trans-esterification and it increased continuously with Mg content across the hydrotalcite, while pure Al_2O_3 was completely inactive. The activities of the higher loaded 21 and 24 wt% Mg hydrotalcites are comparable to those reported for the best alternative Li-doped CaO solid base catalysts of 2.5 mmol min^{-1} g $(cat)^{-1}$ [65]. Pure MgO shows a lower activity and selectivity, which may be attributed to a reduced number of accessible basic sites associated with its low porosity compared to the hydrotalcite

materials. The catalytic activities of these hydrotalcites show a striking correlation with their corresponding intralayer charge densities towards tributyrate trans-esterification. This increased intralayer electron density of the Mg rich hydrotalcites would be expected to correlate with an increase of the basicity of these materials. All hydrotalcite materials are effective catalysts for the trans-esterification of glyceryl tributyrate with methanol. The rate of tributyrate conversion and associated methyl butanoate and diglyceride formation was 1st-order respect to triglyceride concentration. The rate increases steadily with Mg content with the most active $Mg_{2.93}Al$ catalyst was 10 times more active than MgO while pure Al_2O_3 was completely inactive. They have also correlated the rate of reaction with intralayer electron density, which can be associated with increased basicity [64a]. Serio et al, recently reported the comparative catalytic activity of calcined hydrotalcite and MgO prepared by a different method, which showed efficient catalytic activity for transesterification of soybean oil than MgO prepared nomally [64b].

6.3. Lithium–calcium oxide (Li-CaO)

Watkins et al. [65] studied the Li-CaO solid base catalyst for trans-esterification reaction. They chose the glyceryl tributyrate as model substrate for testing the catalytic activity in presence of various amount of lithium doped calcium oxide material. A series of $LiNO_3$ impregnated CaO catalysts were prepared by wet impregnation with theoretical Li contents in the range of 1–20 wt % [65]. Alkali earth oxides are potential as solid bases for use in tri-glyceride trans-esterification [66]. The origin of basic sites in alkali earth oxides has been debated, and it is generally believed that they are generated by the presence of $M^{2+}- O_2^-$ ion pairs in different coordination environments [67]. The basic strength of the group 2 oxides and hydroxides increased in the order Mg < Ca < Sr < Ba. Of these Ca-derived bases are the most promising as they are inexpensive, and exhibit low methanol solubilities and they are also the least toxic [66]. The conversion of glyceryl tributyrate is shown in Fig. 3 as a function of Li loading. CaO exhibited poor activity in trans-esterification, with only 2.5% conversion being observed after 20 min of reaction. In contrast, catalysts with as little as 0.23 and 1.23 wt% Li loadings showed activity with 83 and 100% conversion respectively after the same reaction time. Further increase in Li content proved detrimental to activity of the catalyst with the 4 wt% Li sample giving only 37% conversion. Negligible leaching of $LiNO_3$ occurred during

1 reaction; catalysts were successfully filtered and recycled with minimal (10%) loss of

2 activity. Pure $LiNO_3$ was inactive for trans-esterification; hence the influence of trace

3 homogeneous Li^+ species can be discounted. In conclusion, an optimum Li content of

4 1.23 wt% gave maximum activity for formation of methyl butanoate. Lithium

5 incorporation is shown to increase the base strength of CaO. XPS and DRIFTS

6 measurements show that this optimum loading correlates with the formation of an

7 electron deficient Li^+ species and the evolution of –OH species at defect sites on the

8 support [65].

9 *6.4. Alkali metal salt load with alumina*

10 Ebiura et al. [68] studied the selective trans-esterification of triolein with methanol

11 to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid base

12 catalyst. The trans-esterification of triolein with methanol proceeded over a solid-base

13 catalyst at a lower reaction temperature than 473 K, at which the conversion of triolein

14 was 3% without a catalyst. Reaction at 300 K using the alkali metal salt-loaded alumina

15 gave the methyl oleate and glycerol yield. Non-loaded alumina did not yield methyl

16 oleate or glycerol within 1 h, and yielded only 7% methyl oleate over 12 h at 473 K

17 without the production of glycerol. Thus, the catalytic activity of this material is

18 generated by loading the alumina with alkali metal salts followed by evacuation of the

19 samples at 673 or 823 K [68]. Among the catalysts, alumina loaded with K_2CO_3, KF,

20 $LiNO_3$ and NaOH gave methyl oleate and glycerol in high yield over 1 h at 333 K. For

21 example, K_2CO_3/Al_2O_3 shows 93% yield of methyl oleate and 87% yield of glycerol.

22 However, KOH/Al_2O_3 exhibited low catalytic activity. To compare the catalytic activity

23 of K_2CO_3/Al_2O_3 with that of KOH as a heterogeneous catalyst, trans-esterification at 273

24 K for 1 h, K_2CO_3/Al_2O_3 (0.05 g, K_2CO_3 loading of 0.13 mmol) exhibited nearly the same

25 catalytic activity as 0.023 mmol of KOH. Since the trans-esterification is a reversible

26 reaction, the effect of the molar ratio of methanol to triolein on the yields of esters such

27 as methyl oleate and glycerol was examined by varying the amount of methanol in

28 reactions at 333 K. The initial amount of triolein was set at 1.0 mmol, and 5.0 mL of tetra

29 hydra furan (THF) used as a solvent. The conversion of triolein and the yields of methyl

30 oleate increased with increasing addition of methanol. The yield of methyl oleate

31 reached (ca. 100%) when more than 25 mmol of methanol was present (methanol/triolein

> 25). These results confirm that the trans-esterification of triolein with methanol in the presence of heterogeneous solid base catalyst proceeds effectively at 333 K at atmospheric pressure. It may be the convenient route for biodiesel and glycerol production. Xie et al. [69] recently reported the use of KF loaded ZnO instead of typical alkali loaded alumina type solid base. The KF loaded on ZnO is an active and promising heterogeneous catalyst for the production of biodiesel from soybean oil. Both the active KF species formed by the reaction of KF and ZnO and surface hydroxyls, are responsible for the strong basic sites of the catalyst. The catalyst with 15 wt.% KF loaded on ZnO and after calcined at 873 K for 5 h was found to be the optimum catalyst, which exhibited the highest basicity and the best catalytic activity for the transesterification reaction. Transesterification was carried out with methanol, with a molar ratio of methanol to soybean oil of 10:1, and the reaction time is 9 h, and the catalyst amount was 3%, the corresponding conversion of soybean oil was observed over 87% at the above reaction conditions. The catalytic activities showed a correlation with the corresponding basic properties towards soybean oil transesterification [69]. Macedo et al. [70] recently reported $(Al_2O_3)_4(SnO)$ and $(Al_2O_3)_4(ZnO)$ type heterogeneous solid oxide catalyst for transesterification of vegetable oil using different chain length alcohol, highest yield of 84% was observed with methanol at the 4 h reaction time. Differences were observed for the reaction yield of soybean methanolysis assisted by solid catalyst $(Al_2O_3)_4(SnO)$ and $(Al_2O_3)_4(ZnO)$, it is probably due to the fact that solids possessed similar surface structures, independent of the presence of tin or zinc in the final composition of the solid catalyst. These heterogeneous solid catalyst shows high activity with short and linear alcohol (methanol) for transtestrification of vegetable oil.

7. Conclusion

. Transesterification is basically a sequential reaction. The monoglycerides are finally reduced to fatty acid esters. The order of the reaction changes with the reaction conditions. The main factor affecting transesterification is the molar ratio of alcohol to glycerides. The optimum ratio is 6:1. From the commercial point of view, solid base catalysts are more effective than acid catalysts and enzymes. Solid acid catalysts have the capacity to replace strong liquid acids.These systems eliminate the corrosion

1 problems and the production of environmentally waste pollutants. However, research

2 studies dealing with the use of solid acid catalysts for biodiesel production have been

3 limited due to the expectations on reaction rates and unfavorable side reactions. An ideal

4 or a model of solid acid catalyst should possess interconnected large porous texture with

5 moderate to high concentration of acid sites and a hydrophobic surface. Large

6 interconnected pores would minimize diffusion problems of molecules having long alkyl

7 chains and strong acid sites are needed for the reaction to proceed at an acceptable rate.

8 Hydrophobic surface is essential to promote preferential adsorption of oily hydrophobic

9 species on the catalyst surface and to avoid possible deactivation of catalytic sites by the

10 strong adsorption of polar byproducts such as water and glycerol.

11 Many metals and zeolites are efficient catalytic materials for transesterification

12 process. The most significant implication of the catalysis by iron, palladium and nickel is

13 that the reactor surfaces containing these metals can catalyze alcholysis in the absence of

14 catalysts for the non-catalytic transesterification process. Faujasite NaX and

15 Titanosilicate structure-10 (ETS-10) zeolites have shown higher conversion, nearly 92 %

16 for transesterifcation process compared to other zeolite materials. Ion exchanging the

17 parent zeolite with electropositive metals imparts stronger basicity to zeolites and it leads

18 to enhancement of the transesterfication process. Some solid base supported oxide

19 catalysts have also shown efficient conversion for transesterfication process such as

20 Na/NaOH/γ-Al_2O_3. Solid base catalyst Na/NaOH/ γ-Al_2O_3 shows almost same

21 conversion of vegetable oil under optimized conditions in presence of co-solvent (n-

22 hexane) compared to the conventional homogeneous NaOH catalyst. In conclusion,

23 adopting suitable reaction conditions such as optimized methanol to oil mole ratio and

24 identification of potential heterogeneous base catalysts with specific porous structure and

25 hydrophobic property can facilitate the efficient transesterification process for biodiesel

26 production in the coming decades.

27

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9

1   **Table 1.** Values for the American Society for Testing and Materials (ASTM)
2   standard of maximum allowed quantities and average emissions in diesel
3   (normal diesel B100) and biodiesel [6]

Property	Diesel	Biodiesel
Standard	ASTM D975	ASTM D6751
Composition	HC[a] (C10-C21)	FAME[b] (C12-C22)
Kin. Viscosity (mm^2/s) at 40°C	1.9-4.1	1.9-6.0
Specific gravity (g/mL)	0.85	0.88
Flash point (^{o}C)	60-80	100-170
Cloud poin (^{o}C)	-15 to 0.1	-3 to 16
Pour point (^{o}C)	-35 to -15	-15 to 16
Water (vol %)	0.05	0.05
Carbon (wt %)	87	77
Hydrogen (wt %)	13	12
Oxygen (wt %)	0	11
Sulfur (wt %)	0.05	0.05
Cetane number	40-55	48-60
EMISSILONS (%)	B100 (pure diesel)	B20
Carbon monoxide	-48	-12
Total unburned	-67	-20
hydrocarbons	-47	-12
Nitrogen oxides	+10	+2
Sulfates	-100	-20
Air toxics	-60 to –90	-12 to -20
mutagenicity	-80 to –90	-20.0

4   B20 which consists of 20 % biodiesel and 80 % diesel.
5   [a]- hydrocarbon [b]- fatty acid methyl ester

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2 **Table 2.** Typical fatty acid composition-common oil source
3

Fatty acid	Soybean (wt %)	Cottonseed (wt %)	Palm (wt %)	Lard (wt %)	Coconut (wt %)
Lauric	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	19.2
palmitic	10.2	20.1	42.8	23.6	9.8
stearic	3.7	2.6	4.5	14.2	3.0
oleic	22.8	19.2	40.5	44.2	6.9
linoleic	53.7	55.2	10.1	10.7	2.2
linolenic	8.6	0.6	0.2	0.4	0.0

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6 **Table 3.** Fatty acid composition of crude beef tallow
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Fatty acid composition (wt %)	Myristic (wt %)	Palmitic (wt %)	Stearic (wt %)	Oleic (wt %)	Linoleic (wt %)
	2-8	24-37	14-29	40-50	1-5

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2 **Table 4.** Effect of the calcination temperature on the esterification activity
3 over the catalysts prepared by co-precipitation
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Sample number	Calcination temperature (^{o}C)	Conversion (%)	
		5 wt % WO_3/ZrO_2	15 wt % WO_3/ZrO_2
1	400	93	78
2	500	95	81
3	600	10	20
4	700	5	25
5	900	5	17

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7 **Table 5.** Correlation between preparation method of the catalysts and structural
8 effect for esterification of palmitic acid on 5 wt.% WO_3/ZrO_2 catalysts
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| Calcination temperature (^{o}C)	Impregnation		Co-precipitation	
	Conversion (%)	XRD phase	Conversion (%)	XRD phase
500	98	Tetragonal ZrO_2	95	Tetragonal ZrO_2
900	8	Monoclinic ZrO_2/ WO_3	17	Monoclinic ZrO_2/ WO_3

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11 **Table 6.** Surface area of hydrotalcite (HY) samples
12 as a function of Mg contents
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Bulk Mg content (wt %)	Surface area (m^2/g)	Glyceryl tributyrate conversion (%)
$Mg_{13.4 \text{ (in HY)}}$	166	42.2
$Mg_{17.9 \text{ (in HY)}}$	121	49.2
$Mg_{20.5 \text{(in HY)}}$	92	55.3
$Mg_{24.0 \text{ (in HY)}}$	104	74.8
MgO	18	11.0

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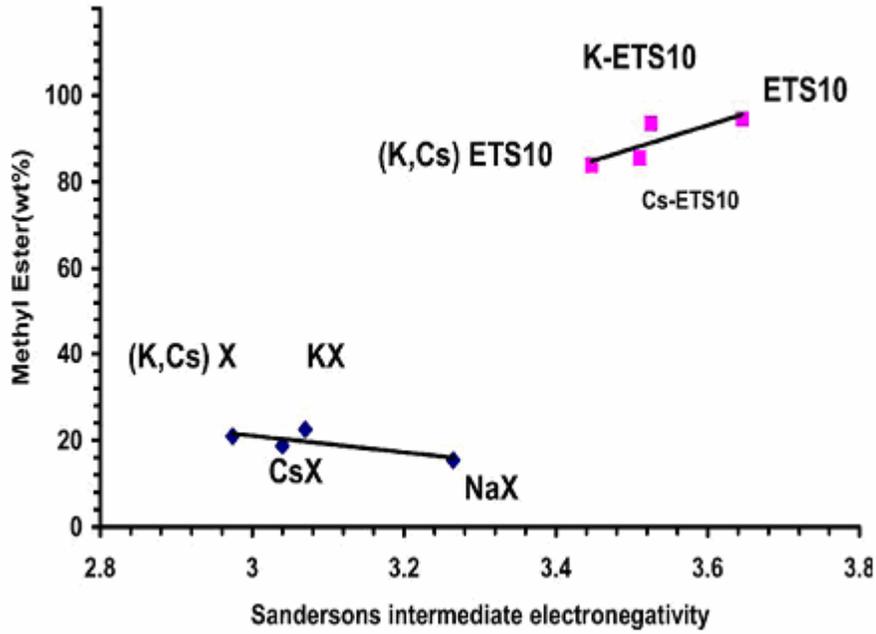
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Fig. 1. Methyl ester (wt.%) at 120°C as a function of intermediate electronegativity calculated from Sanderson intermediate rule at 120°C. Sixty percent ion exchange assumed for cesium to calculate electronegativity. Ninety-five percent ion exchange assumed for potassium to calculate electronegativity. [Reproduced from ref. 60].
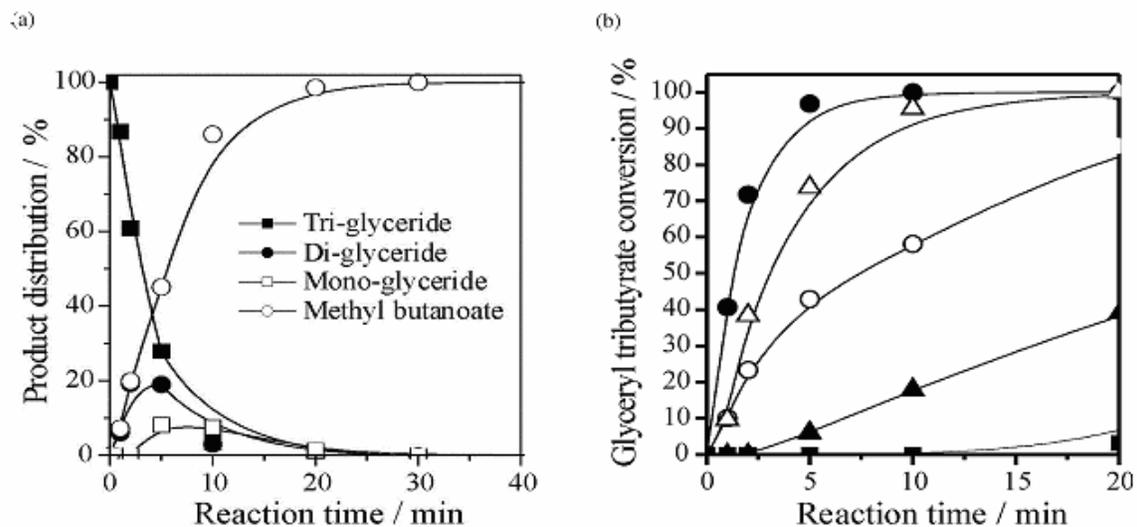
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4 **Fig. 2.** Comparison of different catalysts for achieve 80% conversion to methyl esters.
5 'a' and b are reference catalyst. The catalysts that have been underlined are believed to
6 have a significant homogeneous component to their activity [reproduced from ref. 61].
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10 **Fig. 3.** (a) Reaction profile for the trans-esterification of glyceryl tributyrate with methanol using
11 a 2.4 wt% Li/CaO catalyst. (b) Conversion of glyceryl tributyrate observed for the series of
12 Li/CaO catalysts: ▪ = CaO; ○= 0.25 wt% Li/CaO; ● = 1.23 wt% Li/CaO;Δ = 2.4 wt% Li/CaO; ▲
13 = 4.0 wt% Li/CaO. [reproduced from ref. 65].
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