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Heterogeneous Base Catalysts for Transesterification in Biodiesel Synthesis

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Abstract The heterogeneous base-catalyzed transesterification for biodiesel synthesis has been studied intensively over the last decade. This review classifies the solid base catalysts for transesterification into the following six categories based on Hattori's classification: single metal oxides, mixed metal oxides, zeolites, supported alkali/alkaline earth metals, clay minerals (hydrotalcites), and non-oxides (organic solid bases). The catalysts in each category have acceptable catalytic activities overall, and follow specific catalyst design rules, although not completely systematically, thereby drawing the best activity from them. In parallel, each catalyst is not versatile and has some limitations specifically related to its catalytic structure and properties. This review focuses on the heterogeneous base-catalyzed transesterification in terms of catalyst development, based on the published research, especially over the last decade.

Keywords Renewable energy · Biodiesel synthesis · Transesterification · Alcoholysis of triglyceride · Heterogeneous base catalyst

1 Introduction

Biodiesel is one of the pioneering bioenergy technologies, with vegetable oil having first been proposed as an engine fuel by Rudolf Diesel about 100 years ago [1]. When Diesel presented the diesel engine, he used groundnut oil because there was no specific fuel to feed this engine until petroleum-derived diesel fuel appeared. With the maturation of technologies for petroleum refinery and application, suggestions for the utilization of vegetable oils have surfaced intermittently whenever a worldwide energy crisis has prevailed. Recently, as fossil fuels have been criticized for their environmental hazards and lack of sustainability, biofuels have become recognized as a renewable energy source and promising alternative energy.

As originally found by Diesel, vegetable oils can be used directly as a fuel for diesel engines. However, the high viscosity of vegetable oil renders its utilization practically unacceptable [2]. The chemical or physical modifications that have been attempted to overcome the problem include pyrolysis, microemulsification, dilution, and transesterification. The latter is the most common method to reduce the viscosity of vegetable oils, and the products are collectively termed 'biodiesel' because they can be used either neat or blended with the petrodiesel (petroleum diesel).

1.1 Biodiesel Synthesis: Transesterification of Triglyceride

Biodiesel synthesis is chemically described as the transesterification of triglycerides (oil sources) into alkyl esters using alcohol, typically progressed under an acid, base or enzyme catalyst. The resulting alkyl esters (i.e., fatty acid alkyl esters) with various alkyl groups are utilized as biodiesel in the industry. The general reaction formula is as follows:

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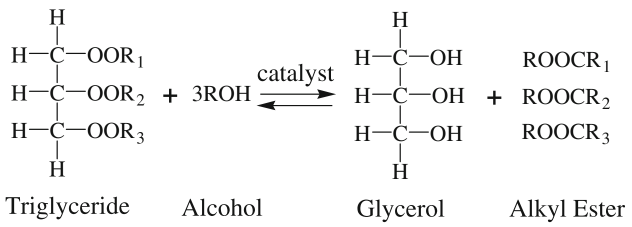


The stoichiometric ratio of triglyceride to alcohol is 3, and the reaction produces 3 mols of alkyl ester from 1 mol of triglyceride. Transesterification consists of a number of consecutive, reversible reactions, with diglycerides and monoglycerides placed as intermediates [3].

The sources of triglycerides are diverse, ranging from single fatty acids to waste oils, with edible soybean oil being the most frequently used research [4]. Other vegetable oils such as rapeseed, sunflower, palm kernel, and canola oils follow in terms of frequency of application [4]. Animal fats and waste edible oils are also studied, from the motivation to use cheap oil sources or meet the regional oil availability, but their irregular chemical composition makes application difficult. In chemical terms, each oil source has a specific composition of fatty acids, as shown in Table 1 [5–7]. The chemical features of fatty acid are collectively described by the carbon number and degree of unsaturation. These features affect the reactivity toward transesterification and, as a result, the properties of the produced biodiesel (alkyl ester). For instance, the fuel properties for biodiesels, such as cetane number, heat of combustion, melting point and viscosity, increase with increasing carbon number and unsaturation degree [4]. Therefore, the properties of biodiesel will probably be improved by genetic engineering of the parent oils, thereby enriching the fuel with specific fatty acids [8].

Alcohol provides the alkyl group that substitutes the fatty fraction of triglyceride. Methanol is most frequently used, mainly because the reaction rate is higher and the price is cheaper than any other commercial alcohols. The fuel qualities of alkyl esters have received varying evaluations in terms of alcohol used. Huber et al. [3] and Saraf and Thomas [9] commented that higher or branched alcohols can produce biodiesel with better fuel characteristics. In contrast, Tyson [10] reported that methyl ester and ethyl ester are similar in heat content, but that the former is slightly less viscous than the latter. Knoth [11] also concluded that methyl ester was better than ethyl ester from the standpoint of engine performance: higher power and torque were achieved from the engine when methyl ester was used as fuel. Narasimharao et al. [8] claimed that higher alkyl esters cause more injector clogging than methyl ester and that their industrial uses are hindered by some technological problems.

1.2 Acid and Base Catalysis for Biodiesel Synthesis

In the laboratorial synthesis, the production of biodiesel (methyl ester) is mainly affected by the type of catalyst (acid/base), oil to methanol molar ratio, reaction temperature and impurity contents (usually free fatty acids and water). Among these issues, the determination of catalyst is the first step for designing a transesterification system.

For acid catalysis, the transesterification process is usually progressed by a Brønsted acid. If the oil source has high free fatty acid (FFA) content, such as waste vegetable oil, acid-catalyzed transesterification is generally favored because the FFA is also converted to biodiesel [12–14]. Acid-catalyzed transesterification affords high yields in alkyl ester but suffers from a slow reaction rate when compared with base-catalyzed transesterification, resulting in a long process (and sometimes, high temperature) to reach complete conversion. The most common acid catalysis using H_2SO_4 requires more than 50 h to reach 100% conversion of soybean oil with a methanol/oil molar ratio of 30:1 at a reaction temperature of 65 °C. Due to this sluggish reaction rate, acid catalysis is usually studied with a high catalyst content (low pH) and large methanol/oil ratio (20–300:1) at a high reaction temperature of 150–250 °C.

Table 1 Examples of fatty acid compositions in the oil sources [5–7]

Soybean oil from [5]		Palm oil from [6]		Cottonseed oil from [7]	
Palmitic (C16:0)	11.0%	Lauric (C12:0)	0.1%	Palmitic (C16:0)	23.0%
Stearic (C18:0)	4.0%	Myristic (C14:0)	1.0%	Palmitoleic (C16:1)	0.9%
Oleic (C18:1)	23.0%	Palmitic (C16:0)	42.8%	Stearic (C18:0)	2.3%
Linoleic (C18:2)	54.0%	Stearic (C18:0)	4.5%	Oleic (C18:1)	16.8%
Linolenic (C18:3)	8.0%	Oleic (C18:1)	40.5%	Linoleic (C18:2)	0.1%
		Linoleic (C18:2)	10.1%	Linolenic (C18:3)	55.4%
		Linolenic (C18:3)	0.2%	Others	1.5%
		Others	0.8%		

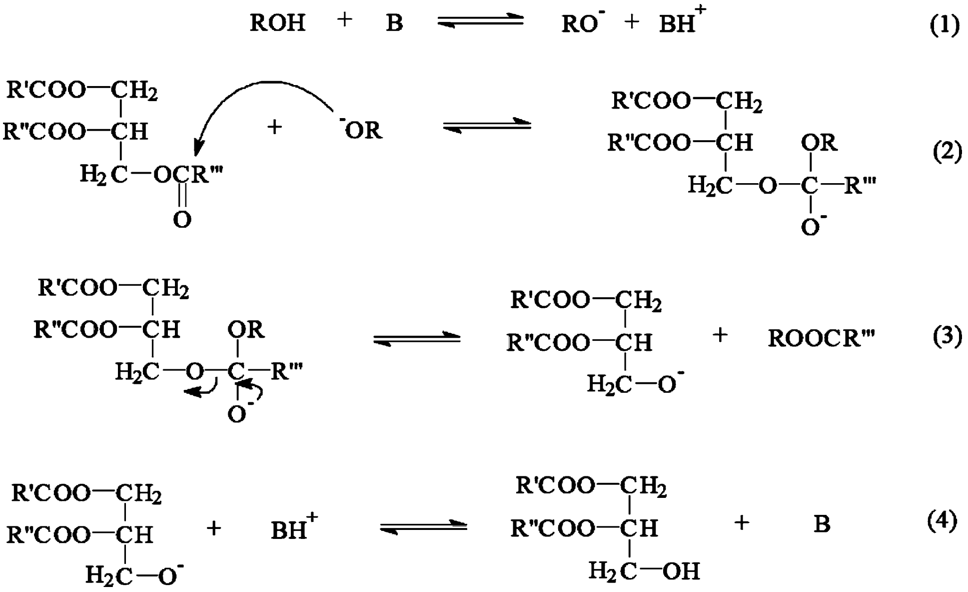
Numbers in parentheses (Cxx:y) signify the number of carbon atoms (xx) and the unsaturated centers (y)

Another disadvantage is that the reaction is very sensitive to water content in the reaction system. The mechanism of acid-catalyzed transesterification starts from protonation of the carbonyl group of triglyceride and generates a carbocation intermediate [15, 16], which is readily converted to carboxylic acids in the presence of water [8]. Since this depresses the biodiesel (alkyl ester) yield, the acid-catalyzed transesterification should be operated in the absence of water, in order to slow down the competitive parallel reaction to carboxylic acids.

On the other hand, base catalysis in homogeneous state is fast and needs less methanol (5–15:1 methanol/oil ratio) and a lower reaction temperature (60–75 °C, around the reflux temperature of methanol). Near complete conversion (>90%) is usually achieved within 2–6 h depending on the catalyst.

The reaction mechanism of base-catalyzed transesterification is summarized as follows [16–20]:

The first step is the generation of an alkoxide ion (RO$^-$) through proton abstraction from alcohol by base catalyst (B). Then the alkoxide ion attacks a carbonyl carbon of triglyceride molecule and forms a tetrahedral intermediate ion (step 2), which is rearranged to generate a diglyceride ion and alkyl ester molecule (step 3). Finally, the diglyceride ion reacts with the protonated base catalyst, which generates a diglyceride molecule and turns the base catalyst into the initial form (step 4). The resulting diglyceride is ready to react with another alcohol molecule, thereby starting the next catalytic cycle. Heterogeneous base catalysis also follows a similar mechanism. The alkoxide anion attaches to the basic site of the catalyst (for instance, the metallic elements of alkaline oxides) and reacts with triglycerides from the liquid phase [20–22].



The most common base catalysts are alkaline metal hydroxides (NaOH, KOH). Their use, even at small amounts of 1–2 mol%, completes the reaction within a few hours. However, the homogeneous catalysis of alkaline metal hydroxide can be disturbed by water arising as either a reagent impurity or via the formation by in situ reaction between hydroxide and methanol. Water reacts with alkyl esters to produce carboxylic acids, which rapidly react with alkaline metals to form 'soaps' such as RCOO$^-$Na$^+$. This soap formation makes the process inefficient by reducing alkyl ester yield and interrupting glycerol recovery [23].

1.3 Requirements of Heterogeneous Catalysis for Biodiesel Synthesis

In addition to this saponification issue, homogenously catalyzed transesterification, whether an acid or base catalyst is used, suffers some drawbacks in terms of process integrity. The first drawback is corrosion of the reactor and pipelines by dissolved acid/base species, which inevitably raises the material cost for process construction. The second is the impossibility of catalyst recovery from the reactant-product mixture. Catalyst separation can only be achieved by neutralizing the remaining catalysts and disposing of them at the end of the reaction, which raises problems with environmental pollution. A third drawback of homogenously catalyzed transesterification is the limitation in establishing a continuous process. For these reasons, the heterogeneously catalyzed process, especially using solid base catalysts, has been studied continuously for the last decade.

The most recognized problem with the heterogeneously catalyzed process is its slow reaction rate compared with the homogeneous process. For this reason, the reaction conditions of heterogeneous catalysis are intensified to enhance its sluggish reaction rates by increasing reaction temperature (100–250 °C), catalyst amount (3–10 wt%) and methanol/oil molar ratio (10:1–25:1). Another problem of the heterogeneous process is the dissolutions of active species into liquids, which makes the catalysis partly 'homogeneous' and then causes problems in biodiesel quality and limits the repeated utilization of catalyst. Many studies about the use of heterogeneous catalysts for transesterification treated anti-leaching performance as issue of equal importance to catalytic activities. The deactivation mechanism of heterogeneous catalysts towards transesterification can be classified into the leaching of active species and the adsorption of acidic hydrocarbons onto basic sites. The deactivation tests usually take the form of repeating the reaction cycle several times and measuring the catalytic activity in the interval between each cycle. If the deactivation of the catalyst is unavoidable, a method for regenerating its initial activity was suggested in most cases.

2 Case Study About Heterogeneous Base Catalysis: Na/NaOH/Al_2O_3

The history of heterogeneous base catalysis is shorter than that of heterogeneous acid catalysis. Although well-known acidic materials also possess basic characters, base catalyses by solid materials were not utilized in the early developmental period, because the basic sites are easily covered with atmospheric components such as CO_2, H_2O, and O_2, which generate carbonate, hydroxide and peroxide, respectively, and incapacitate the function of the basic sites. It was not recognized until the early 1970s that the basic sites could be resurfaced with thermal pretreatment at over 725 K, which removed the poisonous coverings [24].

The initial study by Pines and Eschinazi [25] reported in 1955 on heterogeneous base catalysis was sodium-catalyzed double bonds migration and dehydrogenation of cyclic alkenes. As previously stated, studies on solid base catalysts began burgeoning in the 1970s, and most dealt with basic single metal oxides such as alkaline oxides and rare-earth metal oxides (+3 valence state metal oxides such as La_2O_3). The studies were expanded to alkali metal exchanged zeolites, alkali metal ion-supported catalysts and clay minerals such as hydrotalcites. Table 2 categorizes the types of solid base catalyst that have attracted the most study and development so far, according to the classification suggested by Hattori [24].

Table 2 Types of heterogeneous basic catalyst [24]

Single component metal oxides	Alkali metal oxides
	Alkaline earth oxides
	Rare earth oxides
	ThO_2, ZrO_2, ZnO, TiO_2
Zeolites	Alkali ion-exchanged zeolite
	Alkali ion-supported zeolite
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
Clay minerals	Hydrotalcites
	Crysotile
	Sepiolite
Non-oxides	Alkaline alkoxide
	Alkaline carbonate
	Guanidine-containing catalysts

The demands of solid base catalysis were placed industrially in various hydrocarbon conversions such as double bond migration, isomerization, alkylation, dehydration and the theme of this present article, esterification/transesterification. All of these have been beautifully reviewed in other studies [5, 24–28].

Some seminal studies on the utilization of solid base catalyst for biodiesel synthesis were published in the literature in the late 1990s and the early 2000s, including our own study using Na/NaOH/Al_2O_3, which revealed some important facets of heterogeneous, base-catalyzed transesterification for biodiesel synthesis [29].

Na/NaOH/Al_2O_3 is a commercialized, 'super base' catalyst for the alkylation of cumene, isomerization of safrole, dimethyl butene and vinylbicyclo heptene [24]. The basic activity of Na/NaOH/Al_2O_3 can be explained with the Lewis acid-base concept, according to our previous interpretation of the O 1s XPS results shown in Fig. 1 [29]. The figure shows that the O 1s binding energy is shifted downward as Na and NaOH are impregnated on γ-Al_2O_3, which indicates the increase of electron donating ability with the progression of impregnation (γ-Al_2O_3 < NaOH/Al_2O_3 < Na/Al_2O_3 < Na/NaOH/Al_2O_3). We supposed that the loaded sodium was completely ionized and dispersed into the defect sites of the γ-Al_2O_3 structure, which increased the electron donating ability of the surface oxygen atom. CO_2-TPD studies presented the same results about the basic strength of the catalysts as the XPS results, but indicated a similar total base concentration for each catalyst.

The transesterification activities (yield of biodiesel from soybean oil) of the catalysts followed the order of basic strength precisely (Fig. 2). However, the activity of the heterogeneous catalyst (Na/NaOH/Al_2O_3) was inferior to

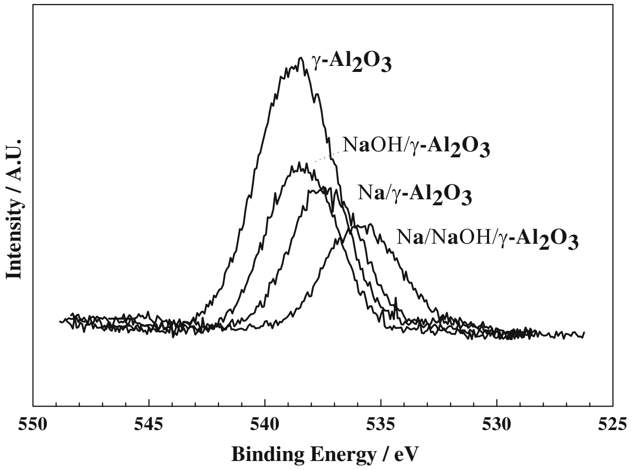


Fig. 1 XPS analysis of O 1s binding energies for γ-Al_2O_3, Na/Al_2O_3, NaOH/Al_2O_3, and Na/NaOH/Al_2O_3 [29]

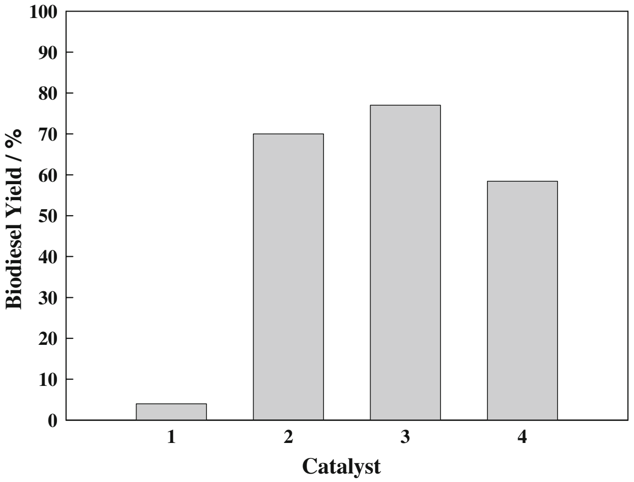


Fig. 2 Effect of basic strength on the biodiesel production yield: (*1*) γ-Al_2O_3, (*2*) Na/Al_2O_3, (*3*) Na/NaOH/Al_2O_3, and (*4*) NaOH/Al_2O_3; methanol/soybean oil molar ratio of 6:1, reaction temperature 60 °C, stirring speed 300 rpm, without co-solvent [29]

that of the homogeneous NaOH catalyst at the reaction condition optimized to the homogeneous system (Fig. 3). We claimed that the activity of the heterogeneous catalyst could be increased to that of the homogeneous catalyst by changing the following three reaction conditions:

(1) Improvement of oil-methanol miscibility by adding proper hydrocarbon co-solvent:

In the homogeneous system, the catalyst (NaOH) also acted as a miscibility enhancer between soybean oil and methanol. However, in the heterogeneous system, the reactants were separated into two phases, which seriously retarded the transesterification rate. This problem was effectively solved by the addition of an appropriate co-solvent. Among the hydrocarbons tested, *n*-hexane was the most effective co-solvent, which transformed the immiscible phases into a homogeneous state and increased the biodiesel yield by 10%. The optimum oil to *n*-hexane molar ratio was 5:1 in this study. Other schemes for improving oil-alcohol miscibility such as increasing the agitation speed were not as effective as the addition of co-solvent for increasing biodiesel yield. In other studies, the adoption of ultrasonic radiation was reported to be also effective for improving the miscibility between oil and alcohol [30–32].

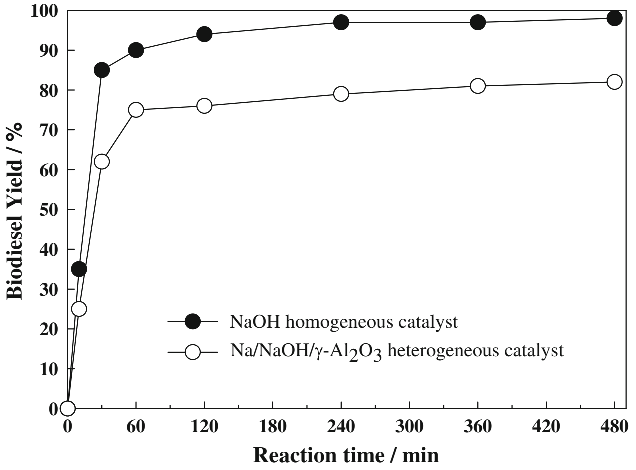


Fig. 3 Comparison of biodiesel production yield between heterogeneous (Na/NaOH/Al_2O_3) and homogeneous (NaOH) catalysts: methanol/soybean oil molar ratio of 6:1, reaction temperature 60 °C, stirring speed 300 rpm, without co-solvent [29]

(2) Feeding methanol in the over-stoichiometric amount:

For the transesterification of vegetable oil (triglycerides), the stoichiometric molar ratio of methanol to oil is theoretically 3:1. In the case of the kinetically limited mass transfer due to system heterogeneity, the apparent reaction rate can be elevated by introducing an excess amount of a reactant. In this study, an over-stoichiometric amount of methanol displaced the reaction equilibrium to the right-hand side, which increased the yield of transesterification. As represented in Fig. 4, the biodiesel production yield increased with increasing methanol/oil ratio and reached a plateau at a methanol/oil ratio of 9. However, feeding too much alcohol adversely affected the transesterification process by rendering the product separation difficult. Because glycerol, a co-product species of methyl ester, is highly soluble in methanol, the removal of glycerol becomes very difficult with an excessive amount of methanol, which reverses the transesterification progress according to Le Chatelier's principle [8]. The oil/methanol molar ratio is therefore a more important factor in the engineering transesterification process.

(3) Optimization of solid catalyst amount:

The amount of solid catalyst should be balanced between the reactivity and viscosity of the reaction system.

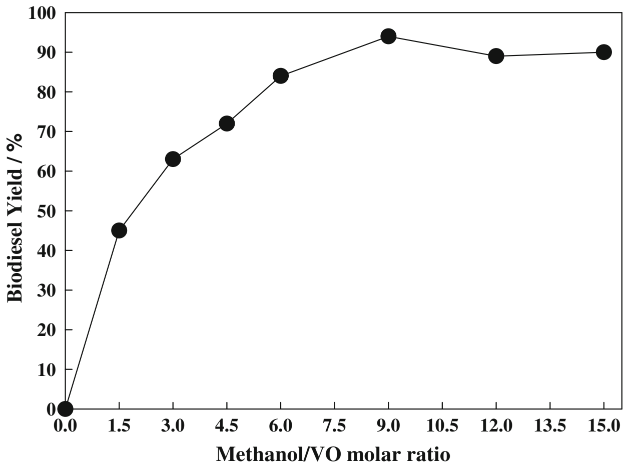


Fig. 4 Effect of methanol/soybean oil ratio on the biodiesel production yield: reaction temperature 60 °C, reaction time 2 h, stirring speed 300 rpm, co-solvent *n*-hexane 10 ml, and amount of catalyst 1 g [29]

Increasing catalyst amount did not guarantee a monotonous increase of production yield, because the fluid became heavily viscous at some point, which inevitably handicapped the system in terms of reaction efficiency.

After the optimization considering the above three points, the biodiesel production yield of the heterogeneous $Na/NaOH/Al_2O_3$ catalyst system was up to that level of the homogenous catalyst system. As shown in Fig. 4, the biodiesel production yield peaked at a maximum of 94%.

Over the last decade, several collective reviews have examined the catalytic conversions in biodiesel synthesis [2–4, 8, 9, 16–20, 33–35]. The remainder of this review will concentrate on the heterogeneous base-catalyzed transesterification from the standpoint of catalyst development. The catalysts are classified into six categories according to Hattori's classification about solid base catalysts (Table 2): single metal oxide, mixed metal oxides, zeolites, supported alkali/alkaline earth metals, hydrotalcites and organic base solids. Some of the content about each solid catalyst introduces the relationship between catalyst properties/structure and catalytic performance.

3 Developments of Heterogeneous Catalyst for Transesterification

3.1 Single Metal Oxides

The early studies on heterogeneously catalyzed transesterification were focused on the catalysis by single metal oxides.

Bancquart compared the base-catalyzed activities of single metal oxides, La_2O_3, MgO, CaO, and ZnO [36], for the transesterification of glycerol with fatty acid methyl esters (FAME) at 220 °C. The author concluded that the reaction rates by single metal oxides directly depend on the basicity of the oxide, especially of the strong basic sites. Therefore, the order of activity followed that of the intrinsic basicity of oxides: $La_2O_3 > MgO \gg ZnO \fallingdotseq CeO_2$. The reaction results collectively exhibited the tendency for the higher conversion of triglyceride to lead to a lower selectivity of mono alkyl ester.

Calcium oxide is the single metal oxide catalyst most frequently applied for biodiesel synthesis, probably due to its cheap price, minor toxicity and high availability. Gryglewicz [37] compared heterogeneous catalysis using CaO with typical homogeneous catalysis by alkaline-earth metal hydroxides and alkoxides for the transesterification of rapeseed oil by methanol at the boiling point of methanol. The order of activities of the tested catalysts followed the order of Lewis basicity: $Ca(OH_2) < CaO < Ca(CH_3O)_2$. The reaction rate over the heterogeneous catalysts, however, was much lower than that of the homogeneous catalysts such as NaOH. Demirbas [38] has reported the biodiesel production of sunflower oil in supercritical methanol using a CaO catalyst. The FAME yield by the CaO catalyst was heavily dependent on the reaction temperature and especially the methanol/oil molar ratio. The FAME yield increased from 65 to 99% as the methanol/oil molar ratio was increased from 6:1 to 41.1:1 at methanol supercritical condition with a catalyst amount of 3.3 wt% [38]. In the transesterification of soybean oil, a similar level of FAME yield (~97%) was obtained at 300 °C with a smaller amount of catalyst (0.58 wt%) only when a large amount of methanol (methanol/oil ratio ~39.3:1) was used [39]. Liu et al. [40] revealed that the rate of CaO catalysis is accelerated in the presence of water, because methoxide ions, which are the true catalytic agent for transesterification, are increased through the hydrolysis of monoglyceride molecules. However, if too much water (more than 2.8% by weight of soybean oil) is added to methanol, the FAME will hydrolyze under basic conditions to generate fatty acid, which can react with CaO to form soap. The catalysis by CaO sometimes produces a lower FAME yield than expected from its high triglyceride conversion, which is usually attributed to the formation of $Ca(OCH_3)_2$ on the CaO surface [37, 41]. Some careful handling is required in order to use CaO as a base catalyst, because its active surface is chemisorbed very easily by H_2O and CO_2 in the atmosphere. Therefore, the poisonous species must be removed at high temperature (more than 973 K) and exposure to the atmosphere should be strictly prevented before its use [42]. As a method to increase catalytic activity, Huaping et al. [43] attempted to increase the surface basicity of CaO by chemical treatment. The authors immersed CaO into ammonium carbonate solution and calcined the catalyst at high temperature of 900 °C, which turned CaO into a superbasic material. A FAME yield of 94% was obtained for the transesterification of jatropha curcas oil with a relatively lower methanol/oil ratio (9:1) and catalyst amount (1.5 wt%) at a reaction temperature of 70 °C [43].

3.2 Mixed Metal Oxides

The general motivation to use mixed metal oxides for transesterification is to change the basic strength of a single metal oxide or, intermittently, to give enhanced stability to a single metal oxide as in the general approaches of catalyst design.

Macedo et al. [44] prepared Al_2O_3–SnO and Al_2O_3–ZnO catalysts and examined their effectiveness. The catalysts achieved biodiesel yields of about 80% from soybean oil after 4 h at 60 °C using 5 wt% of catalyst (b/o oil wt). The yield noticeably decreased to 28.3% when the methanol was replaced by ethanol, and decreased to only a few percent as the chain length of alcohol was increased or branched alcohol was used. These results were attributed by the authors to the steric effects on the catalytic activities of these mixed catalysts.

Babu et al. [45] investigated the transesterification activities of coprecipitated Mg–La oxides obtained by precipitating both nitrate precursors with KOH/K_2CO_3, which contained MgO, La_2O_3, and La_2MgO_x phases. With increasing magnesium content in the mixed oxides, the basicity of the Mg–La oxides increased but the surface area decreased. The conversion of sunflower oil using Mg–La oxide (Mg/Al = 3 in weight) reached 100% within 2.2 h, even at room temperature, using 5 wt% catalyst (b/o oil wt) and a methanol/oil molar ratio of 20:1. The activities of the Mg–La oxides were compared with those of the CaO, SrO, Mg–Al, and Li–Al oxides, which demonstrated the superior activity of the Mg–La oxides. The catalysts showed tolerant activities even in the presence of FFAs and water, which the authors attributed to the superbasicity of the catalysts.

Kawashima et al. [46] studied A–B–O type metal oxides, where A is an alkaline-earth metal (Ca, Ba, Mg), alkaline metal, or rare earth metal (La) and B is a transition metal (Ti, Mn, Fe, Zr, Ce). The catalysts were prepared through high-temperature calcination of a ball-milled mixture of transition metal (B) oxide and alkaline metal (A) carbonate. The catalysts showed very small specific surface areas (0.7–4.9 m^2/g) due to the high-temperature calcination. In terms of Hammett basicity ($H\_$), the Ca series catalysts such as $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaCeO_3$ had the highest base strengths, ranging from 7.2 to 9.3, while the Ba, Mg, and La series catalysts showed the weakest base strengths (<6.8). These results correlated with the transesterification reaction, in which the Ca series catalysts showed high catalytic activities. Especially, $CaZrO_3$ and CaO–CeO_2 catalysts showed methyl ester yields >80% at 60 °C with a oil/methanol ratio ~6:1 in a persistent manner, and this activity was maintained after 5–7 reaction repetitions.

As stated in the previous section, the single metal oxides such as CaO possess moderate transesterification activities. However, in some applications, some of the CaO was changed into a form of suspensoid due to its poor mechanical strength, leading to problems in separating the catalyst from the biodiesel products. Yan et al. [47] tried to solve this problem by impregnating CaO on metal oxide carriers. Basic oxide MgO, neutral oxide SiO_2, acidic oxide Al_2O_3, and zeolite HY were used as support materials and the best result was obtained with CaO/MgO, in which case the conversion of rapeseed oil reached 92% at 64.5 °C. A noticeable drop of activity was observed after four reaction repetitions, which the authors attributed to the active site blockage by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerin, and the contamination by O_2, H_2O, and CO_2 in the air during the catalyst filtering process. The activity was recovered nearly to the initial value through high-temperature treatment, but an additional dosage of calcium precursor needed to be included in the procedure.

3.3 Zeolite

As generally recognized, the versatile catalysis ability of zeolites results from their chemical composition, pore size distribution and ion-exchange abilities. The acid-base properties of zeolites are controlled by the kinds and quantities of ion-exchanged cations, and by the Si/Al ratio of the main zeolite framework. To control the basicity of zeolite, two approaches are generally undertaken: ion-exchange with alkali metal ions and the impregnation of basic components on the inner surface of the zeolite pores [28, 48–52]. It has been reported that the former produces relatively weak basic sites, and the latter strong basic sites [28].

Among the zeolite family, zeolite-X, titanosilicates (esp. ETS-4 and 10) and mesoporous zeolites have attracted the most research attention for biodiesel synthesis. Zeolite X is generally accepted as one of the most basic zeolites, and the ion exchange of Na–X with larger monovalent cations such as K and Cs increases the basicity markedly [49]. According to a study by Suppes et al. [53], the ion exchange with K was more effective than that with Cs, in terms of the basicity and transesterification activity, because the large size of the Cs^+ ions limits the exchange capacity compared to that for the smaller K^+, which affects the basicity associated with the framework oxygen.

Leclercq et al. [54] came to the same conclusion about the steric constraints involved with Cs exchange, but the specific amount of partial Cs exchange positively affected the basicity and transesterification activity of the catalyst. The optimum Cs exchange rate of (Na, Cs)–X was 34% for rapeseed oil conversion. The leaching of Cs species from (Na, Cs)–X was not observed, but the glycerol produced by the reaction acted as a poison and a methanol/oil molar ratio over 30:1 was required to dissolve the glycerol from the catalyst surface.

In the aforementioned study by Suppes et al. [53], the incorporation of occluded NaO_x species in zeolite-X drastically increased the basic strength and concentration, which eventually enhanced the transesterification activity, and the yield of methyl ester from soybean oil increased from 22.7 to 94.2% when NaO_x/NaX replaced K–X as a catalyst. Although this result required a long operation time (24 h) and the reaction temperature was slightly higher (120 °C), it is noteworthy that such high yields were obtained at a methanol/oil molar ratio of 6:1, which is the lowest for heterogeneous biodiesel synthesis. Similar enhancement of activity was noticed when KOH was impregnated on the Na–X zeolites [55]. The methyl ester yield of 10 wt% KOH/Na–X reached ~85% at 65 °C after 8 h with a methanol/oil molar ratio of 8:1, but as the reaction was repeated, the catalytic activity declined as the KOH leached from the catalyst.

Engelhard titanosilicate structure (ETS) series zeolites have also gained recent attention due to their strong basic characters, high cation-exchange capacities and unique large pore structures, which give them advantages over other zeolites for liquid phase reactions [53–57]. The idea of using titanosilicate for biodiesel synthesis came from the requirement for fixation of titanium species into a solid lattice structure [58]. The soluble titanates are quite active for homogeneous base-catalyzed transesterification, but the problem is the existence of equilibrium between the monomeric and dimeric titanium species, the latter being prevalent but catalytically inactive at low temperature [59]. Many ideas for titanium fixation have been practiced (Ti-grafted SiO_2 [59], Ti supported on SiO_2 as an alkoxide [60, 61], Ti anchoring on polymers through various methods [62–64]) but supporting titanium species includes the inherent problem of titanium leaching. In this respect, fixing Ti into the zeolite framework is considered a viable idea.

ETS-10 is a microporous titanosilicate with a three-dimensional, 12-ring pore structure consisting of octahedral titanium (TiO_6^{8-}) and tetrahedral silicon (SiO_4^{4-}) building blocks [53, 56, 57]. ETS-10 has strong basicity: approximately four times more basic than Na–X [50, 53]. Suppes et al. [53] reported that ETS-10 gave better triglyceride conversions than Na–X and that its activity level was similar to NaOx/Na–X. Yields of methyl esters over 90% were achieved at temperatures of 120 and 150 °C and a methanol/oil molar ratio of 6:1 with residence times of 24 h. At 100 °C, the ETS-10 provided a better performance, reaching 92% conversion within 3 h. The authors compared the activity of ETS-10 with that of some heterogeneous catalysts (Fig. 5), to demonstrate that the activity of ETS-10 in this study was superior to the result from another study [65]. They claimed that thermal treating ETS-10 at 500 °C for 4 h was necessary to achieve such elevated activities.

López et al. [66] compared the transesterification activities of acid and base catalysts, and noted that ETS-10 in its acidic form [ETS-10 (H)] showed reasonable activities, along with other acid catalysts, but exhibited probable homogeneous catalysis as the alkali methoxide species were leached out in the case of neutralized ones [ETS-10 (Na, K)]. They also pointed out that the internal mass transfer limitation limited the performance of microporous catalysts such as ETS-10 and zeolite $H\beta$. Suppes et al. [53] similarly commented that the liquid phase transesterification benefits from larger pore structures but not as much from the high surface area created by the inner pore structures of zeolites. The emphasis on large pore structure naturally motivated the utilization of mesoporous zeolites such as SBA-15 and MCM-41 [58, 67, 68].

SBA-15 is a mesoporous silicate with uniform pore size (50–250 Å) having a thick wall and strong hydrothermal stability, greater than MCM-41 [69, 70]. The incorporation of another element to SBA-15 usually requires a post-synthesis procedure, because the main body of SBA-15 is synthesized at strong acidic conditions [70–73]. Li and Rudolph [68] introduced MgO into SBA-15 by

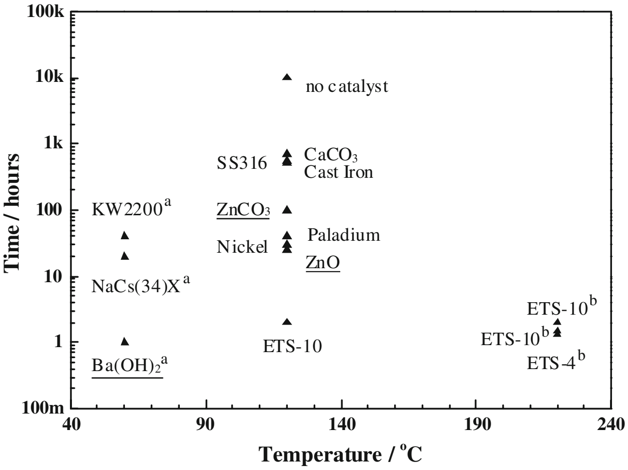


Fig. 5 Comparison of different catalyst systems to achieve 80% conversion to methyl esters [53]. '*a*' is from reference [54] and '*b*' from [65]. The underlined catalysts are believed to have a significant homogeneous component to their activity

impregnation and applied the catalyst to vegetable oil transesterification. The activity of the catalyst did not depend on any isolated determining factor such as basicity, surface area, porosity and surface MgO concentration, but was rather related to the combined effects of multiple attributes.

Albuquerque et al. [74] studied mesoporous silica (SBA-15 and MCM-41)-supported CaO and reported that SBA-15, as compared to MCM-41, proved to be thermally more resistant and to interact more strongly with supported calcium species. The strong interaction between CaO and SBA-15 effectively prevented the leaching of active calcium species. The authors estimated that the catalytic activity of CaO/SBA-15 was better than that of homogeneous NaOH when the catalytic activity was expressed per gram of active phase (CaO, NaOH). The most active catalyst, 14 wt% CaO/SBA-15, showed 95% conversion after 5 h for the transesterification of sunflower oil at 60 °C and a methanol/oil molar ratio of 12.

Saravanamurugan et al. synthesized amino-functionalized SBA-15 catalysts in three different ways: direct co-condensation, prehydrolysis of sodium metasilicate, and post synthetic-grafting methods. They studied the morphologies of catalysts and the molecular shapes of alcohols related to the different activities for the transesterification of diethyl manolates [75]. The conversion of diethyl manolates decreased as the reaction was repeated several times. The authors suggested that the deactivation was caused by the adsorption of organic molecules on the active sites, rather than by leaching of amine species.

3.4 Supported Alkali Metal/Metal Ion Catalysts

Alkali (or alkaline earth) metal is the most common source of superbasicity and is frequently selected as the active species of supported catalysts for biodiesel synthesis. Our study summarized in the previous Sect. 2 is the case utilizing superbasicity formed by introducing sodium and its hydroxide onto alumina support [29]. Na, K, Li, Ba, and Mg are frequently used in the metallic form or as various ionic forms of halide, carbonate, hydroxide and nitrate. The metal ion-supported catalysts are usually calcined at 400–600 °C before reaction to get rid of the adsorbed atmospheric chemicals. The catalysts generally exhibit the preferential dependence of activity on the surface basicity, rather than on the other properties such as specific surface area and pore volume. In terms of basicity and catalytic activity, the supported halide catalysts show the best results as usual. For instance, KF/Al_2O_3 and KI/Al_2O_3 catalysts generally showed higher transesterification activities than K_2CO_3/Al_2O_3, KOH/Al_2O_3, and KNO_3/Al_2O_3 [12, 76]. On the other side, results have varied regarding the best performance among nitrates, hydroxide and carbonates [12, 76, 77]. When comparing the results from two different studies [12, 76] examining KF-, K_2CO_3-, and KNO_3-supported Al_2O_3 catalysts, the different activity orders between the studies were mainly attributed to the difference in impregnated K amount. As shown in Table 3, the basicity and activity of KF/Al_2O_3 depended weakly on the loaded amount of K, while those of K_2CO_3/Al_2O_3 and KNO_3/Al_2O_3 showed relatively strong dependence on the K amount. As aforementioned, the calcination temperature is another key factor determining the surface basicity of alkali metal salt-supported catalysts, but the calcination condition was same at 500 °C and 3 h in both studies.

Xie and Li [76] explained the effect of salt form on the activity (and basicity) with the salt-support interaction. The K^+ ion could be inserted in the vacant sites of alumina, thereby accelerating the dissociative dispersion and decomposition of KI to form basic sites in the activation process. The differences in precursor-support interactions revealed the superior dispersion of K^+ from halide precursor compared to that from the nitrate precursor. For KI/Al_2O_3, the monolayer deposition of potassium was maintained until 35 wt% of KI was loaded [76], while KNO_3/Al_2O_3 maintained the monolayer deposition until 25 wt% of KNO_3 was loaded. The comparisons were allocated to the samples at a calcination temperature of 773 K in both studies [78]. For either case, the K_2O species formed by thermal decomposition of precursor and the surface Al–O–K groups by precursor–support interaction were revealed as the active species toward the transesterification reaction [76, 78].

The support for alkali metal species could be diversified from alumina to basic oxides such as CaO [41, 79, 80], ZnO [81, 82], BaO [83], and MgO [80, 84, 85]. Mehr et al.

Table 3 Differences of Hammett basicity and oil conversion for K salt-supported Al_2O_3 catalysts with different K amounts [12, 76]. The calcination condition for the catalyst was 500 °C and 3 h in both studies

Catalyst	0.35 g K-salt/g Al_2O_3 [12]			2.1 mmol K-salt/g Al_2O_3 [76]		
	K amount (wt%)	Hammett basicity (H_)	Oil conversion (%)	K amount (wt%)	Hammett basicity (H_)	Oil conversion (%)
KF/Al_2O_3	23.5	15.0–18.4	98	8.2	15.0–18.4	86
K_2CO_3/Al_2O_3	19.8	15.0–18.4	97	16.4	9.3–15.0	48
KNO_3/Al_2O_3	13.5	9.8–15.0	63	8.2	15.0–18.4	67

[79] reported that the transesterification performances of CaO-supported catalysts (Li/CaO, Na/CaO, K/CaO) were effective for the transesterification of vegetable oil in the presence of FFA. A methyl ester yield over 90.3% was obtained with 2 wt% Li/CaO in the presence of an FFA content up to 5.75% (8 h, 65 °C, methanol/oil = 12:1), although some metallic soap was formed through the reaction between FFA and CaO. The study targeted the utilization of nonedible Karanja oil from Indian origin, which contained FFAs and toxic chemicals, and showed that the methyl ester produced using (Li, Na or K)/CaO catalyst had a purity (98.6 wt%) and acid value (0.36 mg KOH/g) that satisfied the ASTM and European specifications for biodiesel. Macleod et al. [80] similarly reported that Li-supported on alkaline earth oxides showed the best catalytic performance for the transesterification of vegetable oil (not including FFA), but that MgO was more effective than CaO as an alkaline earth oxide support. In every case, supported alkali metals on alkaline earth oxides are partly dissolved into the liquid phase and the catalysis section invariably becomes homogeneous, regardless of whether the calcination step was included in the preparation procedure of the catalysts or not. The authors also tried to achieve a biodiesel product satisfying EU standard eN14214 using (Li, Na or K)/CaO catalysts at 65 °C within 3 h. The qualification was prohibited by the mass transfer barrier caused by the glycerol film which was coproduced with biodiesel, but the strategy of multi-stage catalytic reactors ensured that the production satisfied the standard rather than the common approaches such as increasing the catalyst amount or the methanol/oil ratio. Occasionally, the support materials (alkaline earth oxides) leached into the ester phase more than the impregnated metal species [79, 83], which was especially intense when BaO was used as a support [83].

3.5 Hydrotalcites

Hydrotalcite or layered double hydroxide (LDH) is an anionic clay material found naturally. The general formula of hydrotalcite is $[\mathrm{M}_x^{z+}\mathrm{M}_y^{\prime 3+}(\mathrm{OH})_{2(x+y)}]^{b+}\ [(\mathrm{A}^{n-})_{b/n}]\cdot m\mathrm{H_2O}$, where M is a monovalent (alkali metal) or divalent (alkaline earth metal) ion, M′ is a trivalent metal ion (usually Al^{3+}), and A^{n-} is an anion (usually $\mathrm{CO_3}^{2-}$) neutralizing the compound electrically. M is structured in a form of brucite-like "sheets" of $\mathrm{M(OH)_2}$, being formed by the edge sharing of $\mathrm{M(OH)_6}$ octahedra. The isomorphous substitution of M^{2+} (or M^{1+}) by trivalent cations of $\mathrm{M}^{\prime 3+}$ generates a positive charge while maintaining a brucite-like sheet structure. This leads to the formation of a layered structure with the charge neutralizing anions and water in the interlayer region [85, 86].

Hydrotalcites and their derivatives have attracted much attention recently, as a good example of catalyst design strategy for basic catalysis [86, 97], including catalytic transesterification [7, 88–103]. The main reason for this interest is that the basicity and surface area of the hydrotalcites can be tuned by modifying the chemical composition and preparation procedure. The calcined Mg–Al is prominently featured in the studies, because its catalytic activity for transesterification has been confirmed positively and consistently [88–91]. The Li–Al hydrotalcites being dehydrated in a proper way under $\mathrm{CO_2}$-free condition have been reported to have stronger Brönsted basicity than the Mg–Al hydrotalcites [90] and some seminal studies implied that Li–Al hydrotalcites are also very promising for biodiesel synthesis [90, 104], although more future research is required.

The determining factors for the base-catalyzed activities of hydrotalcites are the Mg/Al ratio and calcination temperature. For biodiesel synthesis, the Mg/Al molar ratio of hydrotalcites is usually set from 2 to 4, with the ratio 3 being chosen as the best in terms of basic activity by many authors [89, 91, 94, 105, 106]. The change of the Mg/Al ratio in Mg–Al hydrotalcite leads to the variation of the basic property that is induced by the redistribution of acid-base sites, change of structure and transformation of the cation (Mg^{2+} or Al^{3+}) environment [107]. Surface basic sites of calcined hydrotalcites consists of low (OH^- groups), medium (O^- in Mg–O pairs), and strong (O^{2-} anions with unsaturated coordination) basic sites [89, 107, 108]. The relative abundance of low and medium strength basic sites increased with increasing Al content. However, for the Mg–Al hydrotalcites featuring Al contents of $1 < \mathrm{Mg/Al} < 5$, the basic site density increased because the Al^{3+} cations within the MgO lattice created a defect in order to compensate for the positive charge generated, and the adjacent oxygen anions became coordinatively unsaturated [108].

By calcining hydrotalcite materials at high temperature, the interlayer water is lost first, followed by dehydroxylation and decomposition of interlayer carbonate to $\mathrm{CO_2}$, which generate a porous structure and specific surface area ranging from 150 to 300 $\mathrm{m^2/g}$ [87]. These effects combine to make the catalyst quite competitive as a heterogeneous basic catalyst. The calcined hydrotalcites also show a change of chemical structure from their origin, consisting of homogeneously dispersed, mixed Mg–Al oxides, which feature strong thermal stabilities and high basicities [93, 108].

Cantrall et al. [89] studied the structure-activity correlations of Mg–Al hydrotalcites for biodiesel synthesis, and showed that all the $[\mathrm{Mg}_{(1-x)}\mathrm{Al}_x(\mathrm{OH})_2]^{x+}(\mathrm{CO_3})^{2-}_{x/n}$ ($x = 0.25$–0.55) catalysts are quite effective for the methanolysis of glyceryl tributyrate. The activities of the catalysts were higher than that of MgO and the best activity was exhibited by $\mathrm{Mg_{2.93}Al}$. The increase of Mg decreased the specific surface area of the catalyst, but increased both the basal plane spacing and the intralayer electron density, of which the latter established a good correlation with catalytic activity toward tributyrate transesterification. Xie et al. [91] also found that the best activity of hydrotalcite appeared at Mg/Al ~ 3 ($Al/(Mg + Al) = 0.25$) for the transesterification of soybean oil at 60 °C . The basicity and transesterification activity were also dependent on the calcination temperature, exhibiting the best result at 500 °C. When the reaction was carried out at 60 °C with a methanol/soybean oil molar ratio of 15:1, reaction time of 9 h and catalyst amount of 7.5 wt%, the soybean oil conversion was 67%. Similar effects of calcination temperature were also found by Liu et al. [93], the best temperature being shifted slightly higher to 550 °C due to differences in the preparation method and Mg/Al ratio (2.3 in this study). This study asserted that the rehydration of calcined Mg–Al hydrotalcite was not effective for improving catalytic activities for poultry fat transesterification, because the rehydration only generates mild strength basic sites which are active with other condensation reactions [98–100] but are not active enough to trigger biodiesel synthesis. The weak effect of rehydrating Mg–Al hydrotalcite on the transesterification activity was also reported in another study [54]. The negligible metal ion leaching from calcined Mg–Al hydrotalcite was confirmed through various experiments [93], but was contradicted by Oku et al. [101] who found larger amounts of Mg (17,800 ppm) and Al (6,900 ppm) ions dissolved in the reaction product from the methanolysis of triolein. This difference was attributed to the differences of catalyst preparation, the structure and composition of oxides, reaction conditions and oil species, all issues that require further investigation. The authors commented that the deactivation of Mg–Al hydrotalcite was caused by the poisonous adsorption of hydrocarbons on the strongest basic site [93], which could be removed and the activity regenerated to the initial level by simple air calcination [7, 93].

The most attractive feature of Mg–Al hydrotalcite-catalyzed transesterification is that the catalyst shows relatively robust activity in the presence of water or FFA [7, 102, 103]. It was proved that Mg–Al hydrotalcites are very active up to 210 °C when feeds with high FFA and water content were processed [7]. For acidic cottonseed oil (FFA 9.5 wt%) and animal fat oil (water 45 wt%), 99% conversion of triglycerides to biodiesel was achieved within 3 h at 200 °C and a methanol/oil ratio of 6:1 using 1 wt% catalyst, while the FFA content decreased considerably to 1 wt% after reaction [7].

Wang et al. [95] investigated the basic strength and transesterification activity of MgO-rich $MgAl_2O_4$ spinel-type catalyst prepared from Mg–Al LDHs precursor. The study attempted to obtain high transesterification activity by utilizing a catalyst featuring both high surface area and basicity. Mesoporous $MgAl_2O_4$ with a high surface area was obtained by extracting an Al_2O_3 template from Mg–Al LDHs using caustic NaOH solution. Removal of acidic alumina in this way should afford a material with higher basicity than that of the original composite. The improved basic strength and textural properties (surface area and pore size) supported the superior performance of the MgO-rich $MgAl_2O_4$ compared to $MgO/MgAl_2O_4/\gamma\text{-}Al_2O_3$ in the methanolysis of soybean oil.

The introduction of other active metals into Mg–Al hydrotalcite increased the catalyst's activity toward transesterification [96, 97]. KF/Mg–Al hydrotalcite showed 88.7% FAME yield at the condition of methanol/palm oil ratio of 12:1, catalyst weight of 3 wt%, reaction temperature of 65 °C and reaction time of 5 h, while unimpregnated, calcined Mg–Al hydrotalcite showed a very low FAME yield of 44.7% [96]. Doping of ferric ion (Fe^{3+}) into Mg–Al hydrotalcite, where Fe^{3+} ions substitute for some Al^{3+} in the Mg–Al LDH lattices, was also effective in improving the catalytic activity [97]. Upon calcination, the Fe-doped hydrotalcites turned into amorphous porous metal oxides, which were demonstrated to be much stronger bases than calcined hydrotalcites. The activity of 10% Fe-doped Mg–Al hydrotalcites afforded a 100% conversion of triacetin within 40 min at an oil/methanol ratio of 6:1, reaction temperature of 60 °C and catalyst amount of 1 wt%. Under the same reaction conditions, the activity of undoped Mg–Al hydrotalcite was limited to <20% conversion within 90 min.

3.6 Organic Solid Bases

Guanidine $[C(NH)(NH_2)_2]$ is a crystalline compound of strong alkalinity with a p*K*a value similar to that of pyridine. Its alkylated molecules, alkylguanidines, are strong non-ionic organic bases with base strengths that are comparable to sodium hydroxide and the capability to catalyze liquid phase organic reactions such as methylation of phenol [109], Michael addition [110], alkylation of carboxylic acids [111] and transesterification [112–117]. Schuchardt and colleagues published several studies related to the application of alkylguanidine for the transesterification of triglyceride [112, 113, 116]. The most well-known commercial alkylguanidine, triazobicyclodecene (1,5,7-triazabicyclo[4.4.0]dec-5-ene or TBD) was very effective for catalyzing the methanolysis of rapeseed oil, which could produce a 90% yield of methyl ester within 1 h using only 1 mol% catalyst at 60 °C and a low methanol/oil molar ratio of 2.3:1 [112]. The outstanding advantage of organic bases such as alkylguanidine is that they allow the use of unrefined acidic oil and simplify the biodiesel-glycerol separation, because the guanidine-FFA complex is soluble in the reaction mixture and does not form soap or emulsions [112].

The efforts to heterogenize the guanidine were made by same authors, firstly bonding TBD on the substituted polystyrene [113]. The activity was slightly less than that of homogeneous system due to the hydrophobicity of the polymer support and the decreased symmetry of the alkylguanidinium cations, but the real issue was the leaching of active guanidine via nucleophilic attack of methoxide ion on the benzylic CH_2 group linking between the guanidine cation and polystyrene chain. The next strategies of heterogenizing alkylguanidine were encapsulation in the supercages of zeolite Y [114, 116], entrapment in SiO_2 sol–gel matrices [116] and anchoring onto MCM-41 [116]. For the methanolysis of soybean oil, the FAME yield by these catalysts approached that of homogeneous counterparts after prolonged reaction time. However, the leaching of guanidine (MCM-41), collapse of support matrix (SiO_2 sol–gel matrix) and strong diffusion resistance (Zeolite-Y) rendered those heterogeneous guanidine catalysts unacceptable, thereby necessitating further researches about heterogenization strategies [116].

Peter et al. [117] studied the biodiesel synthesis using metal salts of organic amino acids containing highly basic group and showed that Zn-arginate was the most active among the tested metal salts. Zn-arginate was insoluble to palm oil and methanol up to 150 °C, indicating the action of heterogeneous catalysis. The methyl ester yield of 69% was achieved within 3 h using an uncertain amount of catalyst at a methanol/palm oil ratio of 6:1 and a reaction temperature of 75 °C. The catalyst activity was lowered slightly in the presence of 0.8% FFA, but the leaching of metal species or soap formation was not reported.

Anion-exchange polymer resins are porous solid bases worthy of attention. In addition to their basicities and porosities, their cheap price and larger availability by large-scale production make them attractive as a biodiesel synthesis catalyst [118, 119]. Shibasaki-Kitakawa et al. [118] found Diaion® PA306s (Mitsubishi Chemical) was very effective for the ethanolysis of triolein. PA306s is a porous, anion-exchange resin with a structure consisting of a polystyrene chain containing quaternary ammonium groups. The ammonium cation terminals are bonded with chlorine anions and, for generating basic sites, the anions should be exchanged with hydroxyl ion using NaOH solution [118]. The yield of ethyl oleate by PA306s reached 80% within 1 h at an ethanol/oil ratio of 20:1, reaction temperature of 50 °C and catalyst amount of 2 g (about 40 wt% based on triolein weight, estimated from the authors' experimental data). The catalysis was free of saponification, but the hydroxyl groups of resin were reacted with oleic acid during reaction. Therefore, the regeneration of catalytic activities started with the removal of oleic acid (using 5 v/v% citric acid/ethanol in this study), followed by the regeneration of hydroxyl ions using NaOH solution [118]. Liu et al. [119] investigated the use of similar anion-exchange resin (A26 from Rohm & Haas, styrene-divinylbenzene co-polymer), featuring organic quaternary ammonium functionality (QN^+OH^-) toward transesterification, and compared its catalytic performance with commercially available, functionalized silica gel (QN^+OH^-/SiO_2). Both catalysts showed 60% triacetin conversion within 4 h at 60 °C and a methanol/triacetin molar ratio of 6:1 with a low catalyst concentration (0.88 wt% to the total reactant mixture: estimated to be $\sim$1.6 wt% to the weight of triacetin). However, the anionic polymer resin A26 drove the reaction to completion without signs of deactivation, while QN^+OH^-/SiO_2 was less selective to glycerol (and methyl ester, probably) and more prone to leaching of active species (QN^+OH^-). The leaching mechanism suggested by the authors was similar to that for the guanidine catalyst previously stated in this review, being initiated by the nucleophilic attack of methoxide anion on the alpha carbon [CH_2–$N^+(CH_3)$] of QN^+OH^- branch. The lower leaching feature of A26 was explained by the relatively lower rotational freedom of the N^+–OH^- bond. The deactivation incurred by the neutralization of OH^- groups by fatty acids, as reported by Shibasaki-Kitakawa [118], was also precluded. The authors explained that the methanol washing prior to transesterification led to the exchange of most of the OH^- groups of the resin by MeO^- groups, which prohibited the formation of fatty acids.

4 Summary and Future Perspectives

Heterogeneous base catalysis is the most viable process for the transesterification of triglyceride into biodiesel. The heterogeneous catalysis features lower corrosiveness, environmental friendliness, easy catalyst recovery and high process integrity, all at levels superior to those of homogeneous catalysis. Some seminal studies proved the possibility of heterogeneous base catalysts for transesterification during the late 1990s and early 2000s. Our early study about $Na/NaOH/Al_2O_3$ was exemplified for the introduction of the methodologies to evaluate heterogeneous transesterification catalysts.

The research and development on heterogeneous base catalysis for biodiesel synthesis have focused mainly on improving its slow reaction rate up to the level of its homogeneous counterpart. The reaction performances were usually evaluated in the following respects: what level of FAME yield can be achieved within a given time frame, how low the reaction temperature is and how the methanol/oil molar ratio and catalyst amount can be reduced. Generally, a higher reaction temperature (100–250 °C) and/or methanol amount are required for the performance of the heterogeneous process to equal that of its homogeneous counterparts, as evidenced in the commercialized Esterfip-H process [20].

The selectivity of the reaction product is also important. The reaction should produce as much FAME as possible while minimizing production of mono- or di-glycerides. The deactivation of the catalyst is the second hottest issue. Typically, the leaching of base active species is very important, due to its considerable influence on the recyclability of the catalyst and degree of purity for biodiesel and glycerol application. The deactivation by acidic hydrocarbons is sometimes observed. The regeneration method for this type of poisoning usually requires a specific washing procedure. The reaction tests in the presence of FFA and/or water are regarded as crucial in examining the potential for commercialization, because the utilization of waste cooking oil is a key issue for process profitability and most waste oils contain FFA and water as impurities. The decrease of activity and metallic soap formation should be avoided to qualify the tests.

This review classified the heterogeneous base catalysts into six categories according to Hattori's classification system: single metal oxides, mixed metal oxides, zeolite, supported alkali/alkaline earth metals, hydrotalcites and organic solid bases. First, the single metal oxide for transesterification can be represented by CaO. It generally required a high methanol/oil ratio ($\sim$40:1) to achieve near complete FAME yield. Its good performance at an inexpensive price is a definite advantage for CaO, but the leaching of surface CaO into $Ca(OCH_3)_2$ is a barrier toward future success. The basicity of the solid oxide is a determining factor for their transesterification activity and one of the proper methods for tuning this basic property is the making of mixed metal oxides. The mixed metal oxides sometimes introduce a third lattice structure that enhances the catalyst durability. The first commercialized heterogeneous catalyst used for the Esterfip-H process is also a mixed oxide consisting of Zn and Al [120, 121]. This catalyst was reported to have a high basicity and transesterification activity without catalyst loss or leaching [120]. Zeolite is also one of the catalyst materials frequently studied for transesterification. Zeolite-X, titanosilicate and mesoporous silicates are three such representative materials. Cation exchanges by Cs and K and inclusions of alkali oxides into pore cavity have been adopted to increase the basicity of zeolite. The conventional zeolites suffer mass transfer limitation due to their microporous structures, which motivated the utilization of mesoporous zeolites such as MCM-41 or more preferentially, SBA-15. Supported alkali/alkaline earth metal catalyst is the most classical approach for application of base catalyst. The choice of precursor for the alkali/alkaline earth metal is important for the basic activity of the catalyst. The halide precursors are usually favored due to their strong precursor-support interaction generating highly dispersed, specific active species. However, the leaching of impregnated metal is especially critical for this type of catalyst. Calcined Mg–Al hydrotalcite is an attractive base catalyst with catalytic properties that can be controlled by modifying the chemical composition and preparation procedure. Mg/Al at a molar ratio of 3 is generally chosen in order to maximize the basic activity, and most calcined hydrotalcites have a medium porosity and surface area due to the decomposition of interlayer carbonates and water. Despite not having a prominent activity, hydrotalcites offer the significant advantage of maintaining their activity in the presence of FFA and water. The incorporation of other active species into the hydrotalcite lattice is expected to hold promise if the activity increases while maintaining the resistivity against FFA and water. Organic base materials were also studied from the standpoint that their catalyses are free of soap and emulsions, which are advantageous at the separation stage. Guanidine catalysts were reported to be very active for transesterification in the homogeneous state but a proper heterogenization method has not yet been developed. The use of quaternary ammonium cation-grafted polymer resin also showed good catalytic performances. This type of catalyst exhibited deactivation by adsorption of fatty acids, requiring the regeneration of –OH species by washing the deactivated catalysts with NaOH solution.

The development of the catalytic process for biodiesel synthesis can be diversified according to the overall process requirements. Basically, base catalysis is a better choice than acid catalysis in terms of the reaction rate and biodiesel productivity. If the process needs to be heterogeneous, the reaction rate will inevitably be decreased and the process requires a high reaction temperature, methanol amount and catalyst amount to maintain the productivity. This leads to a complex process and high process costs. For example, the high temperature and large methanol amount incur a high-pressure condition that negatively affects the process installation and operation. Excess methanol causes problems in the gravity separation of glycerol and increases the cost of methanol separation [9]. Therefore, the future development of heterogeneous base catalysts for biodiesel synthesis should be more focused on the low temperature activity and use of smaller amounts of methanol and catalyst. In addition, the adverse effects on the activity by water and FFA must be overcome before any developed catalyst can claim to possess robust activity for base-catalyzed biodiesel synthesis. On the other hand, the process cost for biodiesel synthesis is heavily dependent on the feedstock cost. Although the use of waste cooking oil is a natural choice for this issue, the base catalyst cannot be used alone in this case because the used oil contains FFA, which necessitates the addition of a precedent FFA removal unit using acid-catalyzed esterification. Even though a base catalyst can maintain its activity against FFA and does not cause any side reaction, FFA must be removed afterward to satisfy the biodiesel quality standard. Therefore, future research will concentrate on the development of an acid-base bifunctional catalytic reactor either by dual bed formulation combining acid and base catalysts or bifunctional single body catalyst [8]. For the use of pure oil sources, the transesterification activity of a base catalyst is varied according to the type of oil source used as a feedstock [45, 47]. However, little research has investigated the correlation between the chemical structure of the oil source and catalytic activity; systematic study on this issue is critical in the future. The durability of the catalyst is the key issue for heterogeneous base catalysts. As previously stated, the commercialization of heterogeneous base catalysts will require prevention of any leaching. For some catalysts such as hydrotalcites, contradictory reports exist regarding the presence of the leaching phenomenon, indicating the need for correlative explanations regarding preparation procedure and catalyst structure. We consider that the fixation of active species into a specific lattice structure is more effective as an anti-leaching catalyst design, rather than anchoring metallic species on the porous support through impregnation or ion exchange. As a final comment, the realization of a continuous fixed bed process is the ultimate objective of heterogeneous catalysis. As can be observed in the Hesterfip-H process, the commercialized process takes the form of multi-staged, continuous, fixed bed reactors [120, 121]. More active research on a continuous process should be progressed based on the process design principles, with the anticipation of increasing pilot-scale studies in the future.

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