

Chapter 4

HETEROGENEOUS CATALYTIC PROCESS TO CONVERT VEGETABLE OIL INTO BIODIESEL

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ABSTRACT

In the existent process to produce biodiesel, alkali hydroxide dissolved in methanol catalyzes the transesterification of the feedstock oil consisting of triglycerides with methanol. The homogeneous base catalysis is very effective in enhancing the reaction efficiency, but it is necessary to wash the homogeneous base catalyst off the crude biodiesel with water after the reaction. A massive amount of wastewater originating in the purification mentioned above is one of the problems causing costly production of biodiesel. Also, the purification allows stable emulsion to be formed, which not only disturbs the process operation but also decreases the productivity. Therefore, many researchers took their interests in utilizing heterogeneous catalytic process for biodiesel production. In the present work, research papers studying the heterogeneous catalyst for the transesterification of triglycerides are reviewed.

INTRODUCTION

Most of the biodiesel factories employ alkali hydroxide dissolved in methanol for conversion of the feedstock oil consisting of triglycerides into fatty acid methyl esters (FAME), because the homogeneous base catalysis results in the reasonable converting efficiency [1]. According to a research paper by Freedman et al., the yield of FAME produced by transesterifying sunflower oil with methanol in the presence of 1 % sodium hydroxide at the temperature of 333 K was above 90 % for 0.1 h [2]. However, it is necessary to wash the

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homogeneous catalyst off the crude biodiesel with a massive amount of water. Not only the crude biodiesel but also the by-produced glycerol is contaminated with the homogeneous catalyst, and the contaminated glycerol is difficult to recycle for chemicals. Moreover, stable emulsion is formed by adding water into the crude biodiesel for its purification, which disturbs the process operation and leads to loss in the synthesized biodiesel. Due to a massive amount of the wastewater, the contamination of glycerol and the formation of stable emulsion, the current production of biodiesel seem to be costly [3].

For the purpose of solving the problems mentioned above, many researchers make great efforts at studying the novel process to transesterify triglycerides with methanol [4]. One of the solutions is to utilize the enzymatic process in which microbial cell producing lipase serves as the biocatalyst [5-6]. Lipase such as *Candida Antarctica* is an enzyme active in hydrolysis of triglycerides into fatty acids and glycerol, while the addition of alcohol into a mixture of lipase and triglycerides brings about its transesterification [7]. Long-chain alcohol and branched one provide the high transesterifying ratio over 90 %, whereas methanol is not proper for the enzymatic transesterification [8]. Lipase is markedly deactivated in the presence of methanol. The deactivation of lipase seems to be eased by using hexane as the solvent. Also, it was reported that the stepwise addition of methanol allowed the perfect conversion of vegetable oil into FAME to be achieved [9]. But, it took 40 hours to achieve the perfect conversion. For facilitating the handling of the biocatalyst, the use of lipase-producing microbial cells immobilized in porous material has been studying for the purpose of enhancing the lipase recovering efficiency [10].

On the other hand, Saka and Kusudiana proposed the catalyst-free process in which supercritical methanol reacts with vegetable oil [10-11]. Liquid methanol is a polar solvent and molecules of methanol are formed into cluster due to their hydrogen bond. The supercritical condition allows the hydrogen bond to be weakened, which causes a decrease in polarity of methanol. The decreased polarity enhances a solubility of triglyceride in methanol. Moreover, the ionic product increases markedly under the supercritical condition. With the help of the improved chemical property of methanol, biodiesel is produced with the very fast converting rate: it took only 4 minutes to achieve the perfect conversion of rapeseed oil into its methyl ester. As high temperature (523-673 K) and high pressure (35-60 MPa) was required for using supercritical critical, improvement of the catalyst-free process has been studying for reducing the reaction temperature and pressure [12]. The modified process is characterized by the two step reactions: the primary hydrolysis to convert triglyceride into fatty acids and the following esterification with methanol into fatty acid into its methyl ester. Both the primary hydrolysis and the following esterification were operated at 543 K under 10 MPa.

Also, utilization of the heterogeneous catalytic process is the promising way to improve the biodiesel production [13]. The reaction to produce biodiesel was initiated by nucleophilic attack of methanol to a carbonyl carbon in a molecule of triglyceride, and then the nucleophilic attack decomposes triglyceride into FAME and diglyceride [14]. By the further transesterification, triglyceride is finally converted into three molecules of FAME and a molecule of glycerol. For the transesterification, solid base catalytically acts on formation of methoxide anion that is the stronger nucleophile than methanol (Figure 1). Kabashima et al. indicated that the basic site allowed proton to be abstracted from methanol for its conjugated addition to unsaturated ketone [15], and there is a research paper showing that the same action of the basic site promoted transesterification of ethylacetate with methanol [16]. Not only

solid base but also solid acid is able to function as the heterogeneous catalyst. The Bronsted acidity results in donation of proton to triglyceride, which intensify the positive charge of the carbonyl carbon (Figure 2). Due to the intensified positive charge, the nucleophilic attack of methanol to triglyceride is promoted. The solid acid catalysis for the nucleophilic reaction was reviewed in the research paper by Lotero et al [17].

Recently, liquid hydrocarbon produced from triglycerides begins to attract notice as the alternative diesel fuel [18-19]. A procedure to convert into the liquid hydrocarbon is dehydrogenation based on the petroleum hydrotreatment technology, in which nickel-molybdenum sulfide loaded on alumina is used as the heterogeneous catalyst for hydrotreatment of the heavy distillate [20]. The liquid hydrocarbon has an advantage of the high oxidation stability and the good cold flow properties, in comparison to FAME. The conversion into the liquid hydrocarbon was operated at the high temperature (623-673 K) under the high hydrogen pressure (5MPa).

The present work focuses on the heterogeneous catalysts active in the transesterification, and the concerning research papers are reviewed. In the published articles studying solid acid catalysis for transesterification of triglyceride, sulfated metal oxides, cation-exchange resins and the other acid materials were tested. On the other hand, researchers who are interested in the solid base catalysis investigated the catalytic activities of alumina supported alkali metals, alkaline earth metal oxides, hydrotalcite and so on. For these heterogeneous catalysts active in the transesterification, the catalytic mechanism is described in the present review paper. Additionally, the catalytic performance for transesterifying triglycerides into FAME is appreciated on the basis of data shown in the reviewed research papers.

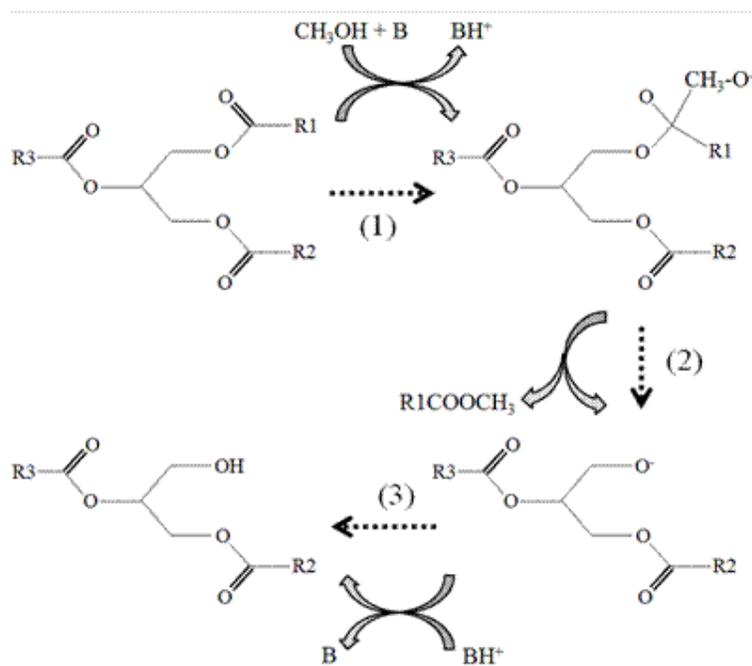


Figure 1. Mechanism on the base-catalyzed transesterification of triglyceride with methanol. (1) Attack of nucleophile generated from methanol, to triglyceride, (2) Dissociation of fatty acids methyl ester from anionic alkoxycarbonyl intermediate, (3) Addition of proton to diglyceride anion.

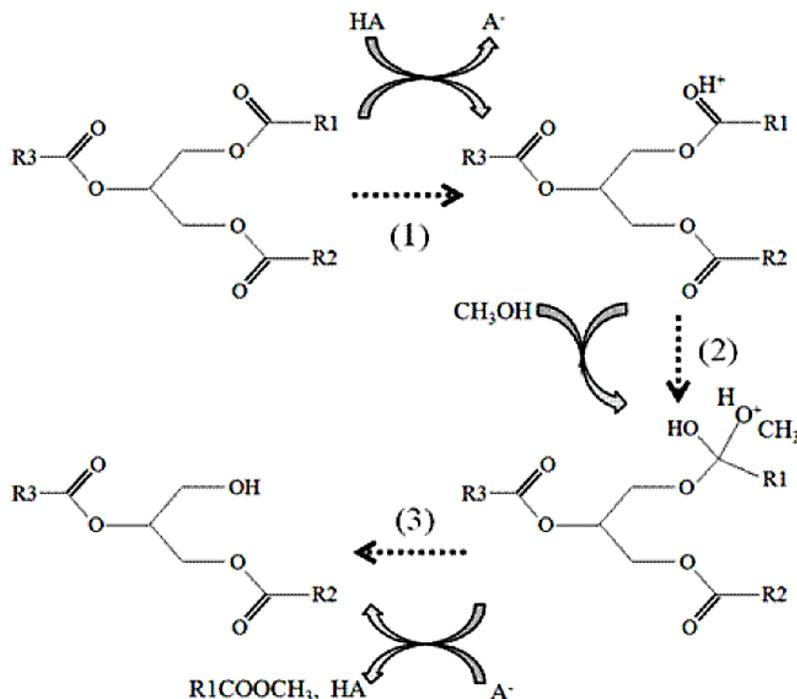


Figure 2. Mechanism on the acid-catalyzed transesterification of triglyceride with methanol. (1) Addition of proton to triglyceride, (2) Nucleophilic attack of methanol to triglyceride, (3) Dissociation of proton and fatty acids methyl ester from cationic alkoxy-carbonyl intermediate.

SOLID ACID CATALYSTS

Sulfated Metal Oxides

Sulfated metal oxides, which are prepared by bonding sulfuric anion onto surface of transition metal oxides, are interpreted as “Superacidic solids”, because the acidic strength of sulfated metal oxides is larger than that of pure sulfuric acid [21]. The acidity is strong enough to catalyze the isomerization of alkanes at room temperature. Among a variety of sulfated metal oxides, great attention is drawn to sulfated zirconia (SO_4/ZrO_2), due to its stronger acid property. Surface of SO_4/ZrO_2 is illustrated by giving Figure 3, and it is considered that the strong acidity originates in electron attracting force of sulfur-oxygen double bond [22-23].

Lopez et al. carried out transesterification of triacetin in the presence of SO_4/ZrO_2 for investigating its catalytic activity, on a stainless steel batch reactor [24]. At the temperature of 333 K with the methanol/triacetin molar ratio of 6, 20 % of triacetin was converted into methyl acetate after 2 hours. However, the catalytic activity of SO_4/ZrO_2 was reduced by reusing it. The catalytic deactivation resulted from leaching of the active sulfate group from the solid acid catalyst by hydrolysis [25]. Jitputti et al. used SO_4/ZrO_2 for the transesterification of coconut oil including 2.25 % fatty acid [26]. The test reaction was conducted at 473 K with the result that the yield of FAME produced after 2 hours was 86 %. Since the catalytic deactivation was appreciable, the authors regenerated the solid acid

catalyst by immersing it in 0.5 M sulfuric acid solution. As a result, the catalytic activity returned to the original level. When we tested SO_4/ZrO_2 at the temperature of 353 K, 16 % of FAME was yielded from soybean oil after 12 hours. Figure 4 shows the yield of FAME produced by transesterifying soybean oil with the methanol/oil molar ratio of 12 in the presence of SO_4/ZrO_2 .

For the purpose of preventing the active sulfate group from being leached away from SO_4/ZrO_2 , the catalytic modification has been studied. Yadav and Murkute prepared the solid acid catalyst tolerant to the leaching by their own procedure, in which chlorosulfonic acid dissolved in an organic solvent was used as a precursor of the active sulfate group [27]. Chen et al. investigated the solid acid catalysis of SO_4/ZrO_2 loaded on mesoporous silica SBA-15 [28]. Their experimental data indicated that tolerance to the leaching was enhanced for the prepared catalyst, and it was considered that the supporting material was effective in adsorbing water causing the hydrolysis.

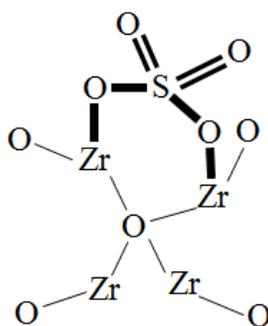


Figure 3. Surface chemical structure of sulfated Zirconia (SO_4/ZrO_2).

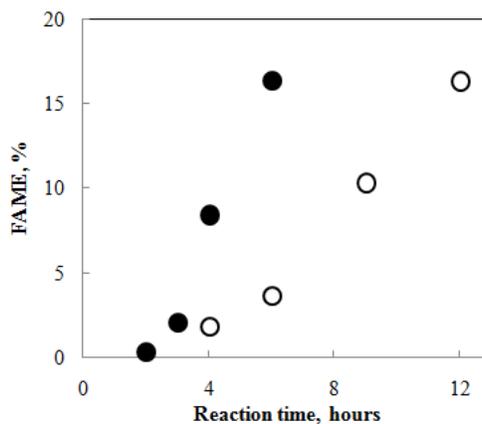


Figure 4. The yields of FAME produced by transesterifying soybean oil at 353 K in the presence of SO_4/ZrO_2 (○) and sulfonated polystyrene (●).

Furthermore, there was a research paper testing SO_4/ZrO_2 on a fixed bed continuous flow reactor unit [29]. The employed reactor unit has the advantage of simplified product separation, and is intrinsically appropriate for the heterogeneous catalytic reaction. Soybean

oil and methanol were pumped into the reactor at the flow rate of $3.0 \text{ g}\cdot\text{h}^{-1}$ and $4.4 \text{ g}\cdot\text{h}^{-1}$, respectively, which was corresponded to the methanol/oil molar ratio of 40. The test reaction was carried out at 523 K under atmospheric pressure with WHSV of 0.54 h^{-1} as a result and oil fraction in the product effluent contained 50 % of FAME. Although sulfated tin oxide (SO_4/SnO_2) is the stronger acid than SO_4/ZrO_2 , the catalytic activity was less for SO_4/SnO_2 in the research paper.

As well as SO_4/ZrO_2 , tungstated zirconia (WO_3/ZrO_2) was interpreted as the superacidic solid. WO_3/ZrO_2 was more active than SO_4/ZrO_2 in the soybean oil transesterification performed on a fixed bed continuous flow reactor unit [29], while WO_3/ZrO_2 was inferior to SO_4/ZrO_2 in catalyzing the transesterification of triacetin with methanol [24]. The former test was carried out at the higher temperature with the larger methanol/oil molar ratio than the latter one. Ramu et al conducted the esterification of palmitic acid with refluxing methanol for evaluating the catalytic activity of WO_3/ZrO_2 [30]. The solid acid catalyst calcined below 723 K was so active that 95 % of palmitic acid was converted into methyl palmitate. The crystalline structure of zirconia changed from tetragonal phase into monoclinic phase by calcining above 723 K, which was probably due to the esterifying activity of the solid acid catalyst.

Cation-Exchange Resins

Cation-exchange resin was divided into two classes: sulfonated polystyrene and perfluorinated resin sulfonic acid. They are commercially available: “Amberlyst” is one of the sulfonated polystyrenes, and “Nafion” is on the market as a perfluorinated resin sulfonic acid. For both of the classes, donation of proton from the sulfonic group is responsible for the solid acid catalysis. The solid acid catalysis of cation-exchange resin is industrially utilized for some chemical reactions: hydrolysis of ethylacetate, synthesis of bisphenol, methanolysis of methacrylic acid, alkylation of phenol and so on [31]. Therefore, cation-exchange resin is advantageous to the practical use, as compared to the other solid acids tested for the transesterifying activity.

A research work studying utilization of solid acid catalyst for biodiesel production elucidated that sulfonated polystyrene was more active than perfluorinated resin sulfonic acid [24]. The catalytic activity was measured by transesterifying triacetin with methanol at 333 K. At 2 hours of the reaction time, the yield of methyl acetate produced in the presence of sulfonated polystyrene and perfluorinated resin sulfonic acid were 35 % and 12 %, respectively. The order of the catalytic activity was correspondent with that of the acid site density. Experimental data shown by dos Reis et al. indicated that textile structure of sulfonated polystyrene affected its catalytic activity [32]. They employed various sulfonated polystyrenes differing in the textile structure for transesterification of Babassu coconut oil with methanol. When the test reaction was carried out at 333 K, the catalytic activity was larger for the macro-reticular polystyrene than for the gelatinous one. Furthermore, they found that triglyceride consisting of short-chain fatty acid brought about the large transesterifying rate. Accordingly, it was considered that penetration of the reactants into the polymer particle was crucial for the catalytic activity. The most active catalyst caused 80 % of the conversion into FAME, but the methanol/oil molar ratio was very large, above 300, in their experiment. Vicente et al. carried out transesterification of sunflower oil with the

methanol/oil molar ratio of 6 at 333 K in the presence of sulfonated macroporous polystyrene [33]. The yield of FAME did not reach 1 % even after 8 hours of the reaction. Although a great effort to control accessibility to the acid site by modifying the textile structure were made for enhancing the catalytic activity [34], it is certain that the higher temperature is required for achieving the reasonable conversion efficiency. However, at the reaction temperature above 413 K, the sulfonated polystyrene is thermally deteriorated [17].

The reasonable utilization of sulfonated polystyrene might be to catalyze esterification of the free fatty acids contaminating the feedstock oil, in advance of the base-catalyzed transesterification. Since the free fatty acids poisons active phase of the base catalyst seriously, the preliminary treatment is advantageous to the conversion of the low-quality oil into biodiesel by the base-catalyzed transesterification. Since esterification and transesterification share a common molecular pathway, it is no wonder that sulfonated polystyrene is active in the esterification of fatty acid with methanol. Ozbay et al appreciated that sulfonated polystyrene catalyzed the esterification of the free fatty acids contained in the waste cooking oil [35]. For their experiment, the waste cooking oil containing 0.5 % of the free fatty acid was employed. The esterification was carried out at 333 K under atmospheric pressure for 3 hours as a result and the conversion ratio ranged from 35 % to 46 %. Also, it was reported that an effect of internal mass transfer on the catalytic activity was small for the macroporous polystyrene [36]. Figure 5 shows the significant data to verify that the sulfonated polystyrene could be reused without the catalytic deactivation for the esterification of the free fatty acids. The waste cooking oil containing 2.5 % of the free fatty acids was mixed with methanol in the presence of sulfonated polystyrene with the macroreticular texture, and the test reaction was repeated three times without exchanging the catalyst. The conversion into FAME was over 90 % after 4 hours for the every runs.

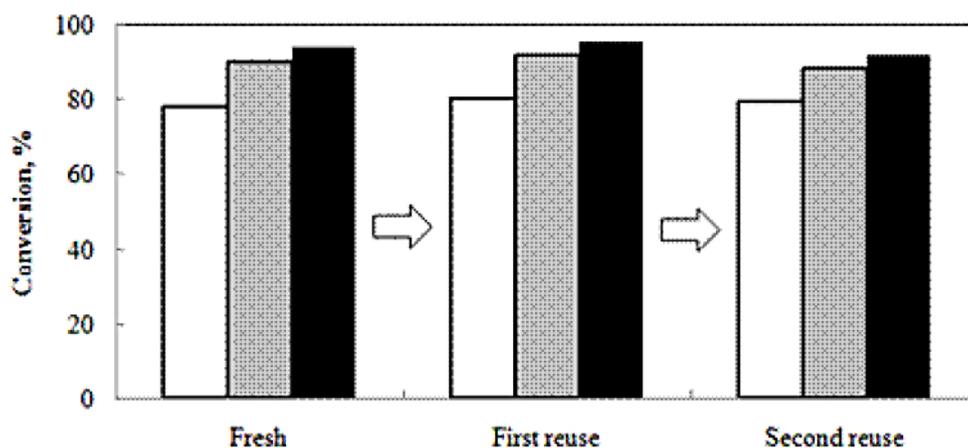


Figure 5. Conversions of the free fatty acid for three esterifying runs repeated with reusing sulfonated polystyrene catalyst. □; After 2 hours, ▨; After 4 hours, ■; After 5 hours. The esterification was carried out at 333 K.

Liu et al. carried out the acid-catalyzed esterification followed by the base-catalyzed transesterification for rapeseed oil deodorizer distillate containing 49 % of the free fatty acids [37]. The acid-catalyzed esterification in the presence of sulfonated polystyrene resulted in 90 % of the conversion of the free fatty acids after 4 hours, and the residual triglycerides was

transesterified into FAME in the presence of potassium hydroxide dissolved in methanol. Talukder et al proposed the novel process combining enzymatic hydrolysis of triglycerides with the following methanolysis of fatty acids for producing biodiesel [38]. The final product oil was measured up the standards of EN14214 and ASTM6751-03. The reaction kinetics on the esterification catalyzed by sulfonated polystyrene was investigated by Tesser et al. [39], and they showed that a pseudo-homogeneous second-order model agreed with the conversion of oleic acid mixed with soybean oil.

Perfluorinated resin sulfonic acid is characterized by the stronger acid property than sulfonated polystyrene [40]. However, the surface area is much smaller for perfluorinated resin sulfonic acid than for sulfonated polystyrene. With the view of enhancing the accessibility to the strong acid site, a new catalytic composite combining perfluorinated resin sulfonic acid with high surface silica was studied [41-42]. The solid acid composite was much more active than sulfonated polystyrene in the esterification of cyclopentadiene with acrylic acid: the product was obtained in 91 % yield for the solid acid composite and in < 5% yield for sulfonated polystyrene. Ni and Meunier studied utilization of the silica supported perfluorinated resin sulfonic acid for the preliminary treatment to catalytically convert the free fatty acid into FAME [43].

Other Solid Acids

Sulfonated carbon nano-graphite has the strong basic property combined with the enhanced durability to the thermal deterioration. Therefore, much attention has been attracted to sulfonated carbon nano-graphite as the solid acid catalyst appropriate for biodiesel production [44]. The superior catalytic properties originate in the carbon structure formed by incomplete carbonization of carbohydrates such as sugar and cellulose [45]. The small polycyclic aromatic carbon sheet in a three dimensional sp^3 -bonded structure brings about generation of many hydroxyl and carboxyl groups. The carboxyl groups are effective in intensifying the chemical bonding between sulfonic groups and polycyclic aromatic carbon in the nano-graphite, which enhances stability of the active sites. The enhanced stability resulted in the thermal durability of the catalyst. The hydroxyl groups are useful in penetrating the reactant into the catalyst particle, which promotes the access to the catalytic sites. Okumura et al. prepared the sulfonated carbon nano-graphite with fuming sulfuric acid [45]. When the carbon nano-graphite was obtained by calcining at 673 K, the prepared catalyst was more active than Nafion perfluorinated resin sulfonic acid in esterification of acetic acid with ethanol. Also, the catalytic activity of the sulfonated carbon nano-graphite was measured by transesterification of triolein with ethanol at 353 K [46]. With the ethanol/oil molar ratio of 30, the solid base catalyst resulted in 24 % of the conversion into fatty acid ethyl esters (FAEE) after 6 hours. Under the same reacting condition, the yield of FAEE produced in the presence of Amberlyst-15, Nafion NR50 and SAC-13 were 2 %, 3% and 14 %, respectively. The similar data was shown in the research paper by Lou et al [47]. Since the enhanced stability of the active phase led to the water tolerance in addition to the thermal durability, the sulfonated carbon nano-graphite is useful in catalyzing hydrolysis of cellulose, which is the primarily conversion to produce bioethanol and biochemicals [48].

Heteropolyacid such as 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) acts on the acid-catalyzed reaction, but is easy to dissolve in polar solvents. But, substitution of proton of $H_3PW_{12}O_{40}$

with large monovalent cation such as Cs^+ changes the soluble property to the insoluble one [49]. Furthermore, the cation exchange results in marked increase of the surface area, which enhances the surface acidity. Since the enhancement of the surface acidity shows a maximum for $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ compounds with $x=2.5$ [50], the heteropolyacids partially substituted with cesium-cation has been tested for the solid acid catalysis. Alsalmeh et al showed on the basis of data from transesterification of short-chain FAEEs with methanol that no substituted heteropolyacid functions as the homogeneous catalyst, and that $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was tolerant to the leaching in the methanol [51]. Pesaresi et al. investigated an effect of degree of the cation exchange on the solid acid catalysis of $\text{Cs}_x\text{H}_{4-x}\text{SiW}_{12}\text{O}_{40}$ for transesterification of triglycerides [52]. The substituted heteropolyacid acted as the solid acid catalyst, above 1.3 Cs^+ loading. On the other hand, the transesterification was catalyzed in the homogeneous manner, below 0.8 Cs^+ loading. Katada et al. found that $\text{H}_4\text{PNbW}_{11}\text{O}_{40}/\text{WO}_3\text{-Nb}_2\text{O}_5$ was the novel heteropolyacid catalyst insoluble in methanol [53]. They measured the catalytic activity by transesterifying triolein with ethanol at 373 K, on an autoclave reactor. The catalytic activity was dependent of the calcination temperature: the novel heteropolyacid calcined at 773 K was most active in the transesterification. The yield of FAEE produced after 8 hours in the presence of the most active catalyst was 45 %. Also, the insoluble property originated in the combination of the heteropolyacid with $\text{WO}_3\text{-Nb}_2\text{O}_5$.

The solid acid catalysis of zeolite was shown in the research paper by Brito et al [54]. They carried out transesterification of waste cooking oil with methanol at the temperature ranging from 473 K to 749 K. The conversion into FAME started above 573 K in the presence of Y-faujasite. Kiss et al. evaluated the catalytic activities of H-ZSM-5, Y and Beta by esterifying dodecanoic acid with 2-ethylhexanol at 403 K [55]. Regrettably, the conversion data indicated that all of the employed zeolites were catalytically inactive in the reaction.

Here, it should be noted that Esterfif-HTM is the process promising the utilization of solid acid catalyst for biodiesel production [13]. The promising process was developed by the French Institute of Petroleum and commercialized by Axens. Bournay et al. described a flow diagram of the “Esterfif-HTM” process including two fixed bed reactor [56]. The heterogeneous catalytic process is able to convert vegetable oil into biodiesel whose properties meets the European standard, with the help of solid acid catalysis of a spinel mixed oxide of zinc and aluminium, at the temperature of 483-523 K under 3-5 MPa. Additionally, by-production of highly pure glycerol is characteristic of the heterogeneous catalytic process.

SOLID BASE CATALYSTS

Supported Alkali Metals

Alumina supported sodium was used at the opening of the research on the solid base catalyst [57]. In this research, the solid base catalysis for migration of double bond in a molecule of olefin resulted from electron donating ability of sodium. With a view of investigating the base-catalyzed reaction useful for the organic synthesis to obtain fine chemicals and pharmaceuticals, alumina supported potassium was employed for Knoevenagel condensation, aldolization and Michael addition [58]. For these reactions, the Bronsted basicity allows proton of alpha position to be abstracted from carbonyl compounds.

In order to study the solid base catalyst for transesterification of triglycerides into biodiesel, Xie et al prepared alumina supported potassium by impregnating potassium nitrate onto alumina. The obtained catalytic precursor was calcined at 773 K in advance of the activity measurement [59]. The catalytic activity was measured by transesterifying soybean oil at reflux of methanol. With the methanol/oil molar ratio of 15, the yield of FAME produced after 7 hours was around 90 %. From IR spectrum and XRD pattern for the solid base catalyst, it was considered that potassium oxide produced by thermal decomposition of potassium nitrate and Al-O-K group were the catalytically active phase. The same catalyst was tested with jatropha oil by Vyas et al [60]. The catalytic activity corresponded to experimental data mentioned above. As shown in Figure 6, our experimental data also verified that alumina supported potassium prepared from potassium nitrate is very active in the transesterification of soybean oil. When the soybean oil transesterification was conducted at reflux of methanol with the methanol/oil molar ratio of 12, the perfect conversion into FAME was achieved for 1 hour. Ebiura et al impregnated potassium carbonate onto alumina in order to prepare the solid base catalyst for transesterification of triolein with methanol [61]. Their experimental data indicated that potassium carbonate was the source of the catalyst superior to potassium nitrate. Furthermore, the authors conducted double-bond isomerization of 2,3-dimethylbut-1-ene for evaluating the basic property and elucidated that the catalyst from potassium nitrate was the stronger base than that from potassium carbonate. Therefore, it was concluded that activation of carbonyl group in triolein was more important than the abstraction of proton from methanol to form nucleophile. There were research papers studying the supported potassium catalyst that was prepared with potassium iodide [62], potassium hydroxide [63] and potassium fluoride [64]. Regrettably, reuse of alumina supported potassium attended with its deactivation. According to a research paper by Alonso et al., the fresh catalyst led to the perfect conversion for 1 hour, whereas the yield of FAME decreased to 30 % by reusing the catalyst [65]. The catalytic deactivation was due to leaching of the active phase.

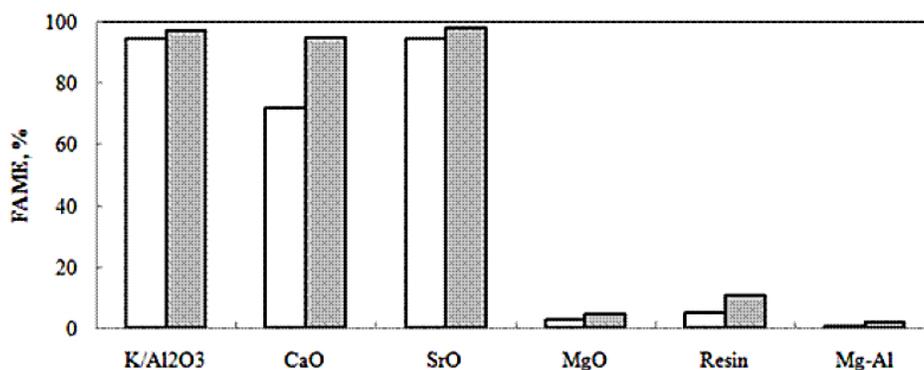


Figure 6. The yield of FAME produced by transesterifying soybean oil at reflux of methanol in the presence of alumina supported potassium (K/Al₂O₃), calcium oxide (CaO), strontium oxide (SrO), magnesium oxide (MgO), anion-exchange resin (Resin) and aluminum-magnesium mixed oxide from hydrocalcite (Mg-Al). □; After 0.5 hour, ■; After 1 hour.

Kim et al. prepared Na/NaOH/Al₂O₃ by impregnated melted sodium hydroxide and melted metal sodium onto alumina at the temperature of 593 K [66]. This catalyst is

interpreted as a “superbase solid”, because its basic strength is above $H_{-} = 37$ [67]. The prepared catalyst was employed for transesterification of soybean oil with methanol/oil molar ratio of 9. At the temperature of 333 K, the yield of FAME produced after 2 hours reached 90 %. The authors concluded that both the sodium aluminate generated by reaction of alumina with sodium hydroxide and the ionization of sodium generated served as the stronger basic site.

Alkaline Earth Metal Oxides

When alkaline earth metal oxides were employed for transesterification of soybean oil with refluxing methanol, as shown in Figure 6, the order of the catalytic activity was in the sequence of strontium oxide > calcium oxide > magnesium oxide [68]. This corresponded to the order of the basic property determined by temperature-programmed desorption of carbon dioxide [69]. From the economical point of view, calcium oxide is a candidate for the solid base catalyst.

The solid base catalysis of alkaline earth metal oxides originate in their ionic crystal structure [70]. Since Lewis acidity of the metal cation is very weak due to its small electronegativity, the conjugated oxygen anion is easy to attract acidic substance chemically. When the carbonyl compound comes into contact with surface of the metal oxide, the surface oxygen anion functioned as Bronsted base that abstracts proton of alpha position from the carbonyl compound. Therefore, alkaline earth metal oxides acted on the base-catalyzed reaction such as aldol reaction and Micheal addition [71-72]. In the case of transesterification of triglycerides with methanol, nucleophile attacking carbonyl carbon in a molecule of triglyceride was generated by abstracting proton from methanol. Basic property of the surface oxygen anion is dependent of its coordination number: the surface oxygen anion of low coordination number brings about the strong basic property, because ionic force bonding the oxygen anion with calcium cations becomes weak. However, the disordered surface abundant in the ion pairs of low coordination number is unstable. Therefore, calcination to prepare alkaline earth metal oxides should be carried out at as possible as low temperature. On the other hand, the high calcination temperature is required for complete elimination of carbon dioxide and water that interact with the strong basic sites.

Not only the calcination temperature but also handling after the calcination is very important for preparation of the active catalyst. Granados et al investigated properties of calcium oxide by some instrumental methods, XRD, IR EGA-MS, and XPS [73]. The characterization data indicated that surface of calcium oxide was rapidly hydrated and carbonated by exposing it to air. The exposed catalyst resulted in the slow transesterification, while evacuation at the high temperature was effective in activating the exposed catalyst. The catalytic activity was measured by transesterifying sunflower oil at 333 K with the methanol/oil molar ratio of 13, and the yield of FAME produced after 1.5 hours increased from 60% to 95 % by evacuating calcium oxide at 973 K. Additionally, they pointed out that the sunflower oil transesterification was catalyzed by not only surface of calcium oxide but also the soluble fraction leached away from calcium oxide. Also, the leaching of the catalyst was observed in our previous research paper [74]. The leached substance was concentrated in the glycerol phase after the transesterification: calcium contents of oil and glycerol phases were 139 ppm and 4602 ppm, respectively.

Reusability of calcium oxide was noted in the research papers by Liu et al. [75] and Ngamcharussrivichai et al [76]. Both of the articles elucidated that calcium oxide could be reused without the serious deactivation for the reactions repeated several times. In our research work to evaluate the reusability, the reused catalyst consisted of the other calcium compound [77]. Since the calcium compound was identified as calcium glyceroxide by measuring XRD, it was evident that calcium oxide was combined with glycerol of the by-product. The test reaction transesterifying soybean oil was performed at reflux of methanol with the methanol/oil molar ratio of 12, and the reused catalyst resulted in around 90 % of the conversion into FAME after 2 hours. Under the same reacting condition, the conversion of soybean oil in the presence of the fresh catalyst consisting of calcium oxide was approximately perfect. Interestingly, the catalytic deactivation by exposing to air was not obvious at all for calcium glyceroxide, as shown in Figure 7. Although it was deduced at that time that calcium glyceroxide functioned as the solid base catalyst, the deduction did not agree with data from our later work [78].

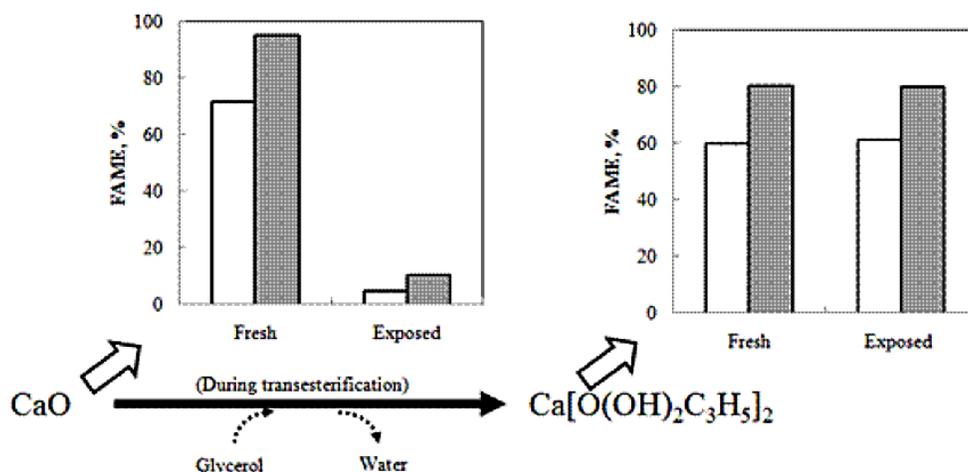


Figure 7. Enhancement of tolerance to air-exposure by transforming calcium oxide into calcium glyceroxide during the transesterification. Catalytic activity was measured by transesterifying soybean oil at reflux of methanol. □; FAME yield measured after 0.5 hour, ■; FAME yield measured after 1 hour.

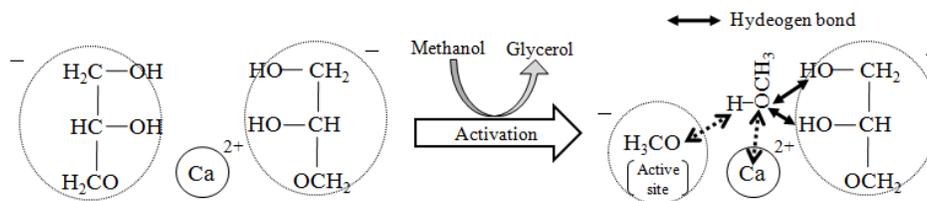


Figure 8. Catalytic mechanism of calcium glyceroxide for transesterification of triglycerides with methanol.

The later work provided data showing that calcium glyceroxide was activated by reacting with methanol under the transesterifying condition, and that chemical composition of the catalytically active phase was estimated at CH₃O-Ca-[O(OH)₂C₃H₅]: the methoxyl anion and

the glyceroxyl one were bonded with calcium cation. Possibly, the glyceroxyl OH groups attracted methanol with the help of hydrogen bond, which enhanced accessibility to the basic site. This catalytic mechanism is illustrated by giving Figure 8. Taking the experimental results from a series of our works into consideration, we prepared the practical catalyst from lime stone whose size distribution was regulated within the range of 1.0 mm to 2.0 mm [79]. On a batch reactor unit consisting of a circulating loop passing through a glass column reactor packed with the practical catalyst, rapeseed oil was transesterified at 333 K with the methanol/oil molar ratio of 20. After 2 hours of the transesterifying operation, the yield of FAME reached 97 %.

Since the heterogeneous catalytic process is not at all equal to the homogeneous catalytic process in the reaction rate, it is important to enhance the catalytic activity of calcium oxide. Watkins et al. doped lithium into calcium oxide for the purpose of intensifying the basic property, and reported that transesterification of glyceryl tributyrates to methyl butyrate was promoted by the intensified basic property [80]. The same doping effect was reported in the research paper by Alonso et al [81]. The doping effect is possibly due to the electron-deficient Li^+ by the exchange of lattice Ca^{2+} for Li^+ and/or to the evolution of surface hydroxyl groups at the defect sites resulting from a reaction lithium-salt with calcium oxide [82]. Also, loading fine particle of calcium oxide onto the proper supporting material is one of the ways to enhance the catalytic activity. Umdu et al prepared calcium oxide loaded on alumina from aluminum isopropoxide and calcium nitrate [83]. The catalytic precursor was calcined at 723 K, and then was employed for transesterification of *Nannochloropsis oculata* microalga's lipid with methanol. Albuquerque et al., who paid their attention to mesoporous materials, synthesized SBA-15 mesoporous silica as the supporting material [84]. Calcium oxide loaded on SBA-15 was tested by methanolysis of ethyl butyrate heated up to 333 K. In the presence of the catalyst including 14 wt% of calcium oxide, 50 % of ethyl butyrate was yielded after 2 hours. Also, increase in the amount of calcium oxide dispersed on the supporting material caused the increase in the conversion ratio. For loading a large amount of calcium oxide onto silica, Yamanaka et al applied the industrial technology to manufacture nano-sized calcium carbonate [85]. The catalytic precursor was prepared by reaction of calcium hydroxide in its aqueous suspension with carbon dioxide, in the presence of silica gel powder. An amount of the loaded calcium compound and the calcination temperature were crucial for the catalytic activity.

Additionally, the waste matters consisting of calcium carbonate could be used as the raw material of the catalyst. In the research paper by Nakatani et al., calcium oxide prepared from oyster shell was employed for transesterification of soybean oil [86]. The catalytic transesterification was carried out at 338 K with the methanol/oil molar ratio of 6, and the yield of FAME produced after 4 hours was 95 %. The similar results were shown in the research works that employed eggshell, Golden apple snail shell, Meretrix venus shell and Mud crab. [87-89]. It seemed that surface area was smaller for calcium oxides deriving from the waste matters than for that from lime stone. Therefore, a large amount of the catalyst was required for the reasonable converting efficiency.

Hydrotalcite

Hydrotalcites is a clay mineral having the unit cell formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. The structure of hydrotalcite is based upon the layered double hydroxides with brucite like $Mg(OH)_2$ hydroxide in which magnesium cations are octahedrally coordinated by hydroxyl anions, and the hydroxide layers are stacked with sharing their edges [90-91]. A part of magnesium cation is replaced with aluminum cation, which causes positive charge of the hydroxide layers. The positive charge is balanced with carbonate anion and water molecule, which are situated in the interlayer between the stacked brucite-like layers. By calcination at high temperature, hydrotalcite is transformed into a mixed magnesium-aluminum oxide that acts on the base-catalyzed reaction. The solid base catalysis of the calcined hydrotalcite originates in the isolated oxygen anion (strong basic site), the structural oxygen anion on the surface (medium basic site), and the surface hydroxyl group (weak basic site) [92]. Corma et al. studied the catalytic activity of the calcined hydrotalcite for the Knoevenagel condensation of benzaldehyde with activated methylenic compounds with different pKa values, and concluded that maximum strength of the basic sites was H_- up to 16.5 [93]. Moreover, the structural aluminum-oxygen pair gives moderate Lewis acidity to the calcined hydrotalcite [94]. It was reported that the acid-base property of the calcined hydrotalcite is effective in catalyzing cycloadditions of carbon dioxide to epoxides [95] and aldol condensations to form nonenal [96].

The catalytic activity of the calcined hydrotalcite for conversion of triglycerides into biodiesel was investigated in the research paper by Xie et al [97]. They prepared the catalytic precursor by adding sodium hydroxide and carbonate into an aqueous solution of magnesium nitrate and aluminium nitrate, and then calcined the catalytic precursor at 773 K. XRD measurement appreciated that the calcined hydrotalcite consisted of magnesia, alumina and their solid solution.

When soybean oil was transesterified at reflux of methanol with the methanol/oil molar ratio of 15, 7.5 % of the catalyst caused 65 % of the conversion into biodiesel after 9 hours. The catalytic activity of the calcined hydrotalcite was markedly intensified by combining it with potassium compound such as potassium fluoride [98]. Additionally, Helwani et al. studied the catalytic modification by incorporating trivalent cation such as Fe^{3+} into lattice of the calcined hydrotalcite [99].

There is a research paper pointing out that hydrotalcite prepared by the conventional procedure is contaminated with alkali used as the precipitant [100]. The alkali contamination for the catalyst causes the homogeneous catalytic reaction, which disturbs the evaluation of the solid base catalysis. With a view of solving this problem, Cantrell et al examined the alternative way to synthesis hydrotalcite [101].

In their way, hydrotalcite was precipitated with ammonium hydroxide and carbonate in the aqueous phase, and then calcined at 723 K. The catalytic activity of the calcined hydrotalcite was measured by transesterifying glycerol tributyrate at 333K for 3 hours. Also, the authors investigated the effect of an amount of trivalent aluminum cation on the basic property. An increase in the amount of trivalent aluminum cation weakened the basic property of the calcined hydrotalcites. Additionally, the order of the basic properties corresponded to that of the catalytic activity.

Other Solid Bases

Some organic bases such as guanidine are catalytically active in transesterification of triglycerides with methanol [102]. Schuchardt et al. prepared alkyl guanidines grafted onto polystyrene for investigating their catalytic activity. When transesterification of soybean oil was carried out at 343 K with the methanol/oil molar ratio of 27 in the presence of the prepared catalyst, the yield of FAME produced after 1 hour ranged from 60 % to 80 % [103]. However, the catalytic activity was reduced by reusing the organic solid base due to leaching of the grafted active phase. Feria et al. grafted tetramethylguanidine onto silica gel with 3-chloropropyltrithoxysilane [104]. After tetramethylguanidine was combined with 3-chloropropyltrithoxysilane, the synthesized silylant agent was attached to surface of silica gel. The catalytic activity of the organic base-silica gel composite was measured by transesterifying soybean oil with the methanol/oil molar ratio of 4 at 353 K.

Trimethylamine grafted on polystyrene is a commercially available solid organic base, which is termed as “anion-exchange resin”. Shibasaki-Kitakawa et al. investigated the catalytic activity of the anion-exchange resin by transesterifying triolein with ethanol at 323 K [105]. The anion-exchange resin characterized by a lower cross-linking density and a smaller particle size led to the fast transesterification. Although the oleic acid deriving from triolein deteriorated the catalytic site, the catalytic activity returned to the original level by washing with citric acid and alkali hydroxide solution.

Among a variety of zeolites, faujasite is transformed into a solid base catalyst by modifying with alkali metal cation. The origin of the basicity is considered to be the oxygen anion in the zeolite framework [106]. The basic strength of the alkali metal ion-exchanged zeolite increases with increasing electropositivity of the exchanged cation: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. XPS data showed that the binding energy of O1s core level of the alkali metal ion-exchanged zeolite was in the sequence of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+$ [107]. The order of the binding energy corresponds to increase in the electron density of the core level, which verified the order of the basic strength. Concerning the parent zeolite, X-faujasite provided the strong basic property than Y-faujasite. Leclercq et al. employed Cs-exchanged X-faujasites for the methanolysis of rapeseed oil [108]. The test reaction was conducted at reflux of methanol with the methanol/oil molar ratio of 275 for 22 hours with the result that the solid base catalyst gave 70 % of the conversion. Suppes et al. carried out the test reaction with the methanol/oil ratio of 6 at the temperature of 333 K [109]. The yield of FAME produced in the presence of the same catalyst after 24 hours was only 7 %. Under the same reacting condition, ETS-10 zeolite containing titanium resulted in 80 % of the conversion into FAME, due to the strong basic property.

CONCLUSION

For the purpose of solving the problems concerning the utilization of homogeneous base catalysis for current production of biodiesel, many researchers have made great efforts to study the heterogeneous catalytic process to transesterify triglycerides composing vegetable oil into FAME. The heterogeneous catalysts tested in the concerning research papers are classified into two types: solid acids and solid bases. Solid acids are less active than solid

base in catalyzing the transesterification, while the acid-catalyzed transesterification is advantageous to the conversion of the low-quality oil containing a large quantity of the free fatty acids. Since solid acids catalyze esterification of the free fatty acids with methanol, the two step heterogeneous acid-base reactions system is one of the promising ways to convert a variety of the feedstock oil into biodiesel under the mild operating condition. However, the heterogeneous catalytic reaction is slow as compared to homogeneous one utilized for the existent process. Moreover, soluble substance is leached away from the heterogeneous catalyst under the transesterifying condition. These are the major study assignments for the practical use of the heterogeneous catalytic process, and the further research works are necessary for understanding of the catalytic mechanism. Characterization of the active sites, study on the catalytic material and theoretical quantification of the reaction kinetics will provide the significant data not only to modify the heterogeneous catalyst but also to design the appropriate process.

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