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BIODIESEL FORMING REACTIONS USING HETEROGENEOUS CATALYSIS

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BIODEISEL FORMING REACTIONS USING HETEROGNEOUS CATALYSIS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Yijun Liu
Aug 2007

Accepted by:
Dr. James G. Goodwin, Jr., Committee Chair
Dr. David A. Bruce
Dr. Richard W. Rice
Dr. Stephen Creager
ABSTRACT

Biodiesel synthesis from biomass provides a means for utilizing effectively renewable resources, a way to convert waste vegetable oils and animal fats to a useful product, a way to recycle carbon dioxide for a combustion fuel, and production of a fuel that is biodegradable, non-toxic, and has a lower emission profile than petroleum-diesel. Free fatty acid (FFA) esterification and triglyceride (TG) transesterification with low molecular weight alcohols constitute the synthetic routes to prepare biodiesel from lipid feedstocks. This project was aimed at developing a better understanding of important fundamental issues involved in heterogeneous catalyzed biodiesel forming reactions using mainly model compounds, representing part of on-going efforts to build up a rational base for assay, design, and performance optimization of solid acids/bases in biodiesel synthesis.

As FFA esterification proceeds, water is continuously formed as a byproduct and affects reaction rates in a negative manner. Using sulfuric acid (as a catalyst) and acetic acid (as a model compound for FFA), the impact of increasing concentrations of water on acid catalysis was investigated. The order of the water effect on reaction rate was determined to be -0.83. Sulfuric acid lost up to 90% activity as the amount of water present increased. The nature of the negative effect of water on esterification was found to go beyond the scope of reverse hydrolysis and was associated with the diminished acid strength of sulfuric acid as a result of the preferential solvation by water molecules of its catalytic protons. The results indicate that as esterification progresses and byproduct water is produced, deactivation of a Brønsted acid catalyst like H$_2$SO$_4$ occurs.
Using a solid composite acid (SAC-13) as an example of heterogeneous catalysts and sulfuric acid as a homogeneous reference, similar reaction inhibition by water was demonstrated for homogeneous and heterogeneous catalysis. This similarity together with other comparisons between the catalytic behaviors of liquid and solid acids suggests a common mode of operation of their Brønsted acid sites in carrying out esterification of a carboxylic acid with alcohol. The hypothesized Eley-Rideal type heterogeneous reaction mechanism involving a nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol as the rate-limiting step was found to fit well the experimental observations and successfully predict the esterification rate obtained with SAC-13 as reaction progresses. The SAC-13 catalysis assay was also extended to carboxylic acids of higher molecular weights. A set of carboxylic acids with various alkyl chain lengths was used to investigate the structural effect of reacting carboxylic acids on heterogeneous catalyzed esterification. It was found that the reactivity of carboxylic acids was controlled by steric factors as the alkyl chain linearly lengthened. Despite their increased hydrophobicity, large carboxylic acids hardly impacted the deactivating effect of water on Brønsted acid sites. However, catalyst reusability and regeneration showed significant dependency on the size of the carboxylic acid used. With the use of larger reacting carboxylic acids, SAC-13 underwent more significant activity loss in consecutive reaction cycles due to stronger adsorption of the larger organics in the polymeric domains of the Nafion resin.

In parallel to the research activity on acid catalyzed esterification, the use of strong solid bases with organic functionality (quaternary ammonium, QN⁺) was investigated from a fundamental perspective. Using triacetin as a model compound for TG molecules,
the effectiveness of this Brønsted base functionality in transesterification was demonstrated even at mild reaction conditions. But its catalytic behavior including catalyst selectivity and deactivation was significantly affected by the nature of the adopted support. A purposive design of the immobilizing matrix is expected to optimize the activity, selectivity, and stability of the QN\textsuperscript{+} groups, thus enhancing their applicability in practical biodiesel synthesis from lipid feedstocks. As the solid organic base-matrix composite catalyst remains to be better designed to fit the need of TG methanolysis, inorganic solid bases composed of metal oxides appear to be a more feasible choice given that their thermal robustness generally allows the achievement of sufficient activity by increasing reaction temperature and potentially permits a convenient regeneration by recalcination. A study dealing with the methanolysis of real lipid feedstock (poultry fat) was carried out using Mg-Al hydrotalcite derived catalysts. From a practical standpoint, the impact of a variety of operational variables on reaction, such as catalyst pretreatments, temperature, reactants molar ratio, and usage of co-solvent were addressed. As a result, biodiesel synthesis from poultry fat was successfully conducted by appropriately adjusting these variables. However, many underlying aspects associated with catalyst performance remain unexamined and unexplained.
DEDICATION

I would like to dedicate this dissertation to my loving father and mother for their devoted parenting, priceless support, and undoubted confidence in me. Particularly to my considerate and patient boyfriend, Chun (Jeffrey), whose love, inspiration, and support have accompanied me throughout the course of this work and will continuously do so forever.
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CHAPTER 1
INTRODUCTION

Biodiesel is made up of mono alkyl esters of long chain fatty acids produced from biomass. As an alternative fuel, the most reputed advantages of biodiesel are its renewability, cleaner emission of exhaust gas, biodegradability and null greenhouse effect given the photosynthetic origin of the lipid feedstocks (oils and fats). Fats and oils primarily consist of triglycerides (TGs) and low to moderate amounts of free fatty acids (FFAs) depending on the origin of the lipids. Transesterification of TGs with low molecular weight alcohols is the central reaction in biodiesel synthesis:

\[
\begin{align*}
R_1\text{COOCH}_2 \quad & \quad \text{Catalyst} \quad & \quad \text{HOCH}_2 \quad & \quad R_1\text{COOCH}_3 \\
R_2\text{COOCH} \quad + \quad 3 \text{CH}_3\text{OH} \quad & \quad \text{\Leftrightarrow} \quad & \quad \text{HOCH} \quad + \quad R_2\text{COOCH}_3 \\
R_3\text{COOCH}_2 \quad & \quad \quad \quad & \quad \text{HOCH}_2 \quad & \quad R_3\text{COOCH}_3 \\
\text{Triglyceride} \quad & \quad \quad \quad & \quad \text{Glycerol} \quad & \quad \text{Methyl esters (Biodiesel)}
\end{align*}
\]

**Figure 1.1** TGs Transesterification with methanol, \( R_{1,2,3} = \text{alkyl chain} \).

Esterification of FFAs with alcohol can constitute another crucial reaction type for low grade feedstocks (as for instance unrefined/degraded animal fats and waste cooking oils) containing high concentrations of FFAs:
Currently, most processes for biodiesel synthesis are less than desirable, where the use of expensive feedstocks and homogeneous base and acid catalysts are typically involved. Expensive raw materials, such as highly refined vegetable oils, constitute a large portion of the manufacturing cost of biodiesel (up to 80%), thus mainly accounting for biodiesel being less cost competitive with its petroleum-based counterpart. What is crucial to make biodiesel economically favorable is the successful use of the cheap alternative feedstock whereby FFA esterification using acid catalysis has to be carefully integrated into the process. In parallel, replacement of liquid homogeneous catalysts with solid heterogeneous catalysts (which are non-corrosive, separable and recyclable) would greatly solve problems such as expensive separation/purification protocols and neutralization steps encountered with the former and facilitate continuous operation, thus enabling the design of more economical continuous processes.

Despite the great importance of heterogeneous acid/base catalysis in biodiesel forming reactions, many relevant fundamental issues remain poorly understood which hampers the accurate adoption, efficient use and specific alteration of solid catalysts and process optimization. For instance, the effect that water produced from esterification may have on the acid catalysis is obscure even for homogenous acids. The correlations existing between solid and liquid catalysts and the impact of lengthening alkyl chains on esterification under acid catalysis are not yet conclusive. A great emphasis has been put

\[
\text{RCOOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{RCOOC}_3\text{H} + \text{H}_2\text{O}
\]

Figure 1.2 FFAs esterification with methanol, R = alkyl chain
on solid strong bases to replace NaOH whereas the truly heterogeneous substitution without signs of leaching is still under investigation. In general, the outlook for the application of solid catalysts for biodiesel synthesis is promising; however, studies regarding optimum reaction conditions to enhance catalyst activities are still required to ensure the maximum performance from solid catalysts in the synthesis of biodiesel from lipid feedstocks.

The main objective of this research has been to study the heterogeneous catalysis of biodiesel forming reactions. Using model compounds, important fundamental issues including water effect, esterification mechanism and the structural effect of carboxylic acids in acid catalysis have been studied. The mechanistic correlations between homogeneous and heterogeneous have been investigated and elaborately analyzed. Potential solid base catalysts have been compared, characterized and evaluated for TGs transesterification using model compound and poultry fat. Particular attentions have been paid to catalyst activity, selectivity, deactivation and reusability to better discern the suitability of solid catalysts for biodiesel forming reactions.
CHAPTER 2
BACKGROUND

Vegetable Oils and Animal Fats

Vegetable oils and animal fats belong to an ample family of chemicals called lipids. Lipids are produced from the metabolism of living organism and used for energy storage, serve as structural components of cell membranes, and constitute important signaling molecules. Most lipids are readily soluble in common nonpolar solvents whereas insoluble in water, indicating they are hydrophobic. If a lipid is liquid at 25°C, it is classified as an oil; otherwise, it is a fat. Typically, fats are produced by animals and oils by plants, but both are mainly made of triglyceride (TG) molecules, which are fatty acid-derived ligands attached to the glycerol backbone by ester linkages. A TG made of only one kind of fatty acid moiety is called a simple TG. Neither oils nor fats are simple TGs but contain different types of fatty acids as building blocks varying in carbon chain length (4~24 carbon) and the number of unsaturated bonds (1-3 C=C). Fats have more saturated fatty acids as compositional building blocks than oils, which gives rise to higher melting point and higher viscosity of the former.

In addition to TGs, oils and fats usually contain some fatty acids in their free form as a result of the spontaneous hydrolysis of the parent TG molecules. The free fatty acid contents vary among different lipid sources and also depend on the treatments and storage conditions. Other compounds, such as phospholipids, glycolipids, sterols, water,
long chain alcohols, carbohydrates and vitamins, can be found in oils and fats in minor concentrations [1].

**Biodiesel Technology**

Historically, the potential use of oils and fats as engine fuels has been envisaged long before (1910s) by the Rudolf Diesel who invented the diesel engine. The desirable characteristics of biomass as engine fuels include high heat content (80% of petrodiesel), ready availability and renewability. However, with the advent of cheap petroleum during the 1920s, appropriate crude oil fraction has been refined and successfully used for the diesel engine fuel. As a consequence, there was a near elimination of the biomass fuel production infrastructure. Vegetable oils were just used from time to time as emergency backups. Only recently, the escalating crude oil price, depletion of petroleum as well as increasing environmental concerns have stimulated a renewed focus on utilizing oils and fats to make biomass fuels.

The big differences in physicochemical properties of lipids compared to petroleum diesel, however, preclude their direct use to drive modern engines. For instance, the high viscosity and poor combustion property of lipidic compounds can give rise to significant carbon deposit, lubricating oil contamination, excessive engine wear thus dramatically decreasing engine durability [2]. Compared to fossil diesel, vegetable oils have low cetane numbers and low flash points which make cold weather starting infeasible and also cause engine knocking [2]. In addition, the polyunsaturated fatty acids contained in natural biomass feedstock are very susceptible to polymerization and gum formation by oxidation during storage or by complex oxidative at high temperature and pressure inside
combustion chamber, leading to plugging of filter, oil line and injector, and lubrication oil thickening [3]. Great efforts have been taken aiming to modify oils and fats to be engine usable. Thus far, blending (hydrocarbon dilution), pyrolysis, microemulsion have been attempted but with only partial success [4]. The most successful approach to obtain compounds with properties quite similar to normal diesel has been the transformation of triglycerides in lipid feedstocks to mono-alkyl fatty esters by transesterification with small alcohols [1, 4].

Research into blending of lipids with fossil fuel in various part ratios initially emerged in the early 1980s following the fast identification regarding the infeasibility of the direct use of food as a fuel. Blending oils and fats with petrodiesel was able to improve the physicochemical properties of the former as a fuel, such as lower viscosity, higher flash point and higher volatility [4]. For example, Strayer et al. [5] have reported that a 75/25 blend of canola oil and fossil fuel has a viscosity of 40 cSt at 10°C, lower than pure canola oil by 60 cSt and a 50/50 blend has even lower value, only 19 cSt. Other than petrodiesel, hydrocarbons such as ethanol have been also used for blending serving as dilution agent to lower viscosity and enhance volatility [5]. The blends in a wide range of proportions, from 5% of 90% petrodiesel, have been tested using both direct and indirect diesel engines [6, 7]. Despite some satisfactory results reported in short-term performance test [7, 8], the long-term use of blends of the oils leads to significant decrease in power output and thermal efficiency by carbon deposit and lubricating oil fouling [7-9]. As a result, the means of hydrocarbon dilution has generally been considered to be not practical in utilizing biomass as modern diesel engines [4].
Pyrolysis or thermal cracking refers to the chemical degradation of compounds by the application of heat in an oxygen-depleted atmosphere, which usually is involved with the aid of a catalyst. Pyrolysis of TGs has been investigated long before with the aim of obtaining products suitable as fuel [4, 10]. A variety of catalysts have been used for the catalytic cracking of TGs, including SiO$_2$/Al$_2$O$_3$ [11], NiMo/γ-Al$_2$O$_3$ [12], NiMo/γ-Al$_2$O$_3$ [13], Al$_2$O$_3$ [14], MgO [14], Al-MCM-41 [15, 16], composites of zeolites [17], etc.. The pyrolytic process cleaves the chemical bonds of TGs, producing hydrocarbons of lower molecular weights. Depending on the TG source and the pyrolytic method employed, alkanes, alkenes, aromatic compounds, esters, CO$_2$, CO, water and H$_2$, can be produced in different proportions [18]. In comparison to TG precursor, the resulting hydrocarbon mixture has decreased viscosity and improved cetane number, being chemically more similar to petroleum-derive gasoline and fossil fuel. Pyrolytic process, however, is associated with high equipment cost and vast energy consumption even for modest throughputs [4]. Oxygen removal from TG precursors is another downside of pyrolysis. It eliminates any environmentally benign edge over petroleum-derived fuel of using an oxygenated fuel [4]. Moreover, solid residues of ash and carbon can be created throughout thermal cracking, forcing to additional separation steps [10].

Microemulsion, technically defined, is optically isotropic, clear or translucent, and thermodynamically stable dispersions of two normally immiscible liquids and one or more ionic or non-ionic amphiphiles (as surfactants) [4, 10]. With the use of solvents such as methanol, ethanol, 1-butanol and 2-octanol, microemulsions have been prepared for vegetable oils as a means to solve their high viscosity [19-21]. With appropriate formulations, all emulsified oils using butanol, hexanol and octanol met the maximum
viscosity requirement for No. 2 diesel [21]. Microemulsion can also give rise to a better spray pattern of oils by explosive vaporization of the low boiling constituents in the micelles [19, 20]. Both ionic and non-ionic microemulsions of soybean oil were able to pass 200 h EMA (Engine Manufacturers Association) tests, showing no deteriorations in engine performance [22]. However, despite the success in short term performance test, heavy carbon deposits due to incomplete combustion have been found afterwards, which further led to injector needle blocking and in-take valve sticking [20, 22].

The transesterification process reacts TGs with low molecular weight alcohols to break the fatty acid ligands from the glycerin backbone while forming three long chain monoesters. Unlike the aforenamed pathways, transesterification (also called alcoholysis) can not only significantly reduce the viscosity of TGs but convert them to the derivatives (monoesters) which are fully compatible with current diesel fuels and can be directly used in today’s engines without modification. Nowadays, owing to their bio-origin and diesel-equivalence, mono alkyl esters of long chain fatty acid prepared from biological sources such as vegetable oils and animal fats, has been generally termed as biodiesel and recognized as a promising alternative energy source to fossil fuel. As a point of comparison, pure biodiesel (B100) releases about 90% of the energy that normal diesel does and gives nearly the same engine performance in terms of engine torque and horsepower. Furthermore, Table 2.1 shows that biodiesel matches well with diesel in a wide range of different characteristics but tops the latter by its renewability, high oxygen content, biodegradability and null greenhouse effect given the photosynthetic origin of the lipid feedstocks. Biodiesel even showed a higher lubricity than petrodiesel, which prolongs an engine’s lifetime and makes less frequent engine part replacement. Biodiesel
can be used in pure form (B100) as a substitute of petroleum diesel or more commonly blended with the latter at any concentration. For example, fuel containing 20% biodiesel is labeled B20. The second option is important because limited feedstock quantity for biodiesel production does not allow their massive utilization whereas in the blend, biodiesel (even used as minor component) act as oxygenate additive adding positive effect on the combustion of fuel mixture in the engine. As shown in Table 2.2, in comparison to fossil oil, both pure and blended biodiesel have much cleaner emission profiles with considerably less solid particles, polycyclic aromatic hydrocarbons, sulfates, etc.. Hence, biodiesel synthesis from biomass provides a way to effectively utilize renewable resources, to recycle carbon dioxide for a combustion fuel, to reduce environmental pollution, and to relief the crisis of crude oil.
### Table 2.1 ASTM standards for diesel and biodiesel

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>ASTM D975</td>
<td>ASTM D6751</td>
</tr>
<tr>
<td>Composition</td>
<td>HC\textsuperscript{a} (C10-C21)</td>
<td>FAME\textsuperscript{b} (C12-C22)</td>
</tr>
<tr>
<td>Kin. viscosity (mm\textsuperscript{2/s}) at 40 °C</td>
<td>1.9-4.1</td>
<td>1.9-6.0</td>
</tr>
<tr>
<td>Specific gravity (g/mL)</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>60-80</td>
<td>100-170</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>-15 to 5</td>
<td>-3 to 12</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-35 to -15</td>
<td>-15 to 16</td>
</tr>
<tr>
<td>Water, % vol.</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon, wt.%</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen, wt.%</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen, wt.%</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulfur, wt.%</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cetane number</td>
<td>40-55</td>
<td>48-60</td>
</tr>
<tr>
<td>HFRR\textsuperscript{c}, microns</td>
<td>685</td>
<td>314</td>
</tr>
<tr>
<td>BOCLE\textsuperscript{d} scuff, (g)</td>
<td>3,600</td>
<td>&gt; 7,000</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Hydrocarbons \textsuperscript{b}Fatty Acid Methyl Esters \textsuperscript{c}High Frequency Reciprocating Rig \textsuperscript{d}Ball-on-Cylinder Lubricity Evaluator

### Table 2.2 Average B100 and B20 emissions compared to normal diesel.

<table>
<thead>
<tr>
<th>Emission</th>
<th>B100</th>
<th>B20</th>
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<tbody>
<tr>
<td>Carbon monoxide</td>
<td>-48%</td>
<td>-12%</td>
</tr>
<tr>
<td>Total unburned hydrocarbons</td>
<td>-67%</td>
<td>-20%</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>-47%</td>
<td>-12%</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>+10%</td>
<td>+2%</td>
</tr>
<tr>
<td>Sulfates</td>
<td>-100%</td>
<td>-20%</td>
</tr>
<tr>
<td>Air toxics</td>
<td>-60% to -90%</td>
<td>-12% to -20%</td>
</tr>
<tr>
<td>Mutagenicity</td>
<td>-80% to -90%</td>
<td>-20.0%</td>
</tr>
</tbody>
</table>
**Biodiesel Feedstock**

Basically, any TG and FFA source such as vegetable oil, animal fat and waste restaurant grease can be used for biodiesel formation with small alcohols via the aid of base/acid catalysts. But from the standpoint of chemical reaction, the refined oil with low impurity and low fatty acid content is the desired feedstock for biodiesel production. In such case, homogeneous alkali catalyst can be used to provide considerable catalytic efficiency for lipid transformation. For instance, only a relatively short duration of 30~60 min is required to drive the conversion of triglycerides to completion at 60°C.

However, alkaline catalysis is very sensitive to the purity of reactants. It suffers from saponification and neutralization in the presence of free fatty acid or moisture. Thus, strict feedstock specification must be satisfied (as for instance, FFA <0.5 wt%; water<0.1~0.3 wt %) for base catalysis [4]. Otherwise, soap production would seriously hinder productivity and complicate product separation by formation of gel and increasing viscosity. Also, the alcohol and catalyst must be essentially anhydrous (0.1-0.3 wt% or less) complying with rigorous specifications. Such demanding feedstock specifications, consequently, translate into a high overall production cost of biodiesel because the high expense if refined oil has to be used. According to NREL (National Resource Energy Laboratory), the raw material contributes 60~70% of final manufacture cost for biodiesel made from refined soybean oil. The usage of expensive feedstocks has been attributed to be mainly responsible for the lack of economical competitioness of biodiesel as compared to fossil fuel and has consequently retarded its commercial expansion.

As a matter of fact, there is a large quantity of high FFAs and moisture-rich lipid materials readily available at low price in a wide variety of forms. For instance, in United
States alone, there are nearly 2.75 billion pounds of waste recyclable restaurant grease annually. Yellow grease is obtained from restaurant waste oil and sells for only $0.09-0.20/lb, averagely cheaper than refined vegetable oil by 50%. Brown grease which is mainly collected from traps installed in commercial, municipal or industrial sewage facilities, is another cheap feedstock priced at $0.01-0.07/lb. Other than the greases, inedible animal fats such as poultry fat (2.2 billion lb/yr), tallow (3.9 billion lb/yr) and lard (1.3 billion lb/yr), also constitute important sources of inexpensive feedstocks for biodiesel. The traditional use of inedible animal fats has been as an animal feed ingredient. This use, however, has been seriously challenged with emerging concerns that this practice facilitates the transmission of potential infectious diseases from one animal species to another. Thus, alternatively, the synthesis of biodiesel from inedible fat provides a way for using more efficiently and environmentally a renewable resource to convert a highly available derived co-product to an important value-added product. As can be expected, the ample and low cost feedstocks would significantly lower the production cost, making biodiesel more accessible in the coming future (Table 2.3).

**Table 2.3 Biodiesel Feedstock Pricing and Impact on Production Cost [23]**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Price per Pound</th>
<th>Estimated Pounds of Feedstock per Gallon of Biodiesel</th>
<th>Feedstock Cost per Gallon of Biodiesel Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refined Soybean Oil</td>
<td>$0.28</td>
<td>7.5</td>
<td>$2.11</td>
</tr>
<tr>
<td>Crude Soybean Oil</td>
<td>$0.25</td>
<td>7.5</td>
<td>$1.88</td>
</tr>
<tr>
<td>Tallow, Inedible</td>
<td>$0.18</td>
<td>7.5</td>
<td>$1.35</td>
</tr>
<tr>
<td>Yellow Grease (&lt;10% FFA)</td>
<td>$0.12</td>
<td>8</td>
<td>$0.96</td>
</tr>
<tr>
<td>Brown Grease (&gt;20% FFA)</td>
<td>$0.05</td>
<td>8</td>
<td>$0.40</td>
</tr>
</tbody>
</table>
Process Protocols

Despite low price, both waste greases and crude animal fats contain high concentrations of FFAs which makes them inappropriate for the conventional base catalyzed transesterification. The FFAs impurity has to be pre-esterified with alcohol using acid catalysis before the subsequent base catalyzed transesterification. Alternatively, FFAs esterification can be carried out simultaneously with the TGs transesterification in presence of acid catalysts [24].

Acid catalysis, however, results in a slower transesterification of TGs than base catalysis. For a given amount of catalyst, the alkali-catalyzed transesterification is about 3 orders of magnitude faster than the acid-catalyzed reaction [25]. Large alcohol excess and/or high reaction temperature are usually required to speed up acid catalysis [25, 26]. Using waste cooking oil with the acid value of 75.9 mg KOH/g oil, Wang et al. [27] have shown that a one-step process is less efficient in producing biodiesel than the integrated acidic pretreatment-alkali process. The advantage of the acid-base integrated process is that it limits the use of sulfuric acid to only the feedstock treatment step where acid-catalyzed esterification is practically effective. Recently, to more efficiently eliminate FFAs in used cooking oil, Canakci and Van Gerpen [28] have developed a 2-step sulfuric acid-catalyzed pre-esterification process. Water was removed in-between the steps. After short operation time (1 h for each step), FFA levels was able to be reduced to below 1 wt% which is amenable for the subsequent base-catalyzed transesterification.

The slow activity of acid catalysis, however, could be compensated by the decrease in process complexity, equipment pieces, and the amount of waste stream. For instance, for biodiesel production from feedstock containing 6% FFAs (acid value = 119.4 mg KOH/g
oil), Zhang et al. [26] recently have proposed the one-step acid-catalyzed system as a viable alternative, capable to economically compete with base-catalyzed processes. More recently, Zullaikah et al. [29] demonstrated the application of 2-step sulfuric acid-catalyzed esterification/transesterification to rice bran oils with FFA content as high as 24.5%. Water removal was demanded in-between the steps to ensure an efficient and high biodiesel production. Given the respective advantages and disadvantages of the two protocols against each other, the specific selection is probably a function of the particular characteristics of lipid feedstock and catalysts adopted.

**Homogeneous Catalysis**

**Base catalysis**

Transesterification can be catalyzed by acids, bases or enzymes. Among them, base catalysis is the most popular way and most often used commercially for biodiesel production owing to the high catalytic activity. Also, base catalysts are less corrosive than acidic compounds avoiding the necessity of expensive stainless steel as construction material [26]. Homogeneous base-catalyzed triglyceride transesterification has been thoroughly studied on the laboratory scale. For instance, it has been well documented that the reaction mechanism under alkaline conditions can be formulated into four steps as presented in Figure 2.1 [1, 4, 30]. The first step describes the reaction of the base catalysts with alcohol producing the catalytically active species, RO⁻. Second, the nucleophile RO⁻ attacks on a carbonyl carbon in the TG yielding a tetrahedral intermediate. Third, a fatty acid ester and a diglyceride anion form upon the decomposition of the tetrahedral intermediate. In the last step, proton transfer from
alcohol to diglyceride anion regenerate the nucleophile RO⁻. The above sequence is then repeated twice to yield monoglyceride and finally the glycerol with concomitant release of biodiesel.

The most common homogeneous basic catalysts used for lipids methanolysis include alkaline metal compounds, such as NaOH and KOH, CH₃ONa and CH₃OK, Na₂CO₃ and K₂CO₃. Alkaline metal alcoxides are the most effective catalysts for the transesterification reaction [31, 32]. As low as 0.5 wt% of catalyst (by the weight of oil) can allow more than 98% biodiesel yielded in very short times. However, in practice, alkaline hydroxides (NaOH and KOH) are more favored because of their cheaper price and easier handling with respect to alkaline alcoxides. Nevertheless, the use of hydroxides can be problematic considering the formation of water in the initial step of reaction (refer to Figure 2.1) [1, 30]. Water then hydrolyzes esters to FFAs and consequently causes saponification which in turn translates to catalyst deactivation and productivity loss. Alkaline carbonates can be an alternative choice in order to reduce saponification [1, 30] but their use is limited by the weaker base strength. 4–6x amount of carbonate catalyst against the hydroxides or alcoxides are necessitated to achieve yields comparable to those obtained with the latter ones.

Despite the high activity and rich abundance of alkaline catalysts, their use in biodiesel production is usually involved with complicated downstream workup such as glycerol purification and catalyst neutralization. In order to simplify manipulation and avoid soap formation, a great number of organic bases have been developed and investigated for transesterification of TGs with alcohols [30, 33, 34]. Schuchard et al. [34] studied the catalytic efficiency of a series of alkylguanidines in the methanolysis of
rapeseed oil. The catalytic activities of the guanidines were found to be directly related with their relative base strength and also factored by the steric hindrance presented in methanol proton transfer (activation). 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD) is the most active guanidine affording 90% oils after 1 h with the use of only 1 mol% catalyst [34]. As compared to the traditional alkaline catalysts, TBD showed slightly less activity than NaOH but outperformed the K₂CO₃ even at low molar concentrations [30]. In order to further increase the catalytic efficiency of the organic bases, a stronger polynitrogen base, highly N-substituted biguanide, were prepared through the addition of guanidines on carbodiimides [35, 36]. Biguanides are the vinylogs of guanidines. In comparison, the higher conjugation of protonated biguanide compound allow an extended delocalization of the positive charge making it intrinsically more basic. The greater basicity of biguanides translate to their higher activity in biodiesel synthesis, outperforming soluble guanidines by about thirtyfold [35, 36]. At the end of reaction, the guadino compounds which are mainly entrapped in glycerol phase can be either recycled by distillation or disintegrate into ammonia at elevated temperatures followed by sulfuric acid wash to originate ammonium sulfate as a valuable fertilizer [37].

The application of other basic amino-compounds in biodiesel synthesis, including amines and tetramethylammonium hydroxide (TMAH), have also been demonstrated by Cerce et al. [33]. Despite increasing the mutual solubility between methanol and rapeseed oils, the Lewis amines such as 4-methylpiperidine (4-MP) and N,N-dimethyltrimethylenediamine (DMTMD) showed only moderate activity in mediating TG transesterification. TMAH, on the other hand, was found to give sensational results. In presence of 3 wt% TMAH, all triglycerides were converted to methyl esters after only 15
min. Also, the organic base can allow a fast phase separation at the end of reaction and never arouse soap formation. Even better, methanol and catalyst can be simply recovered by distillation yielding high purity glycerol without the need of time-consuming water washing [33]. Accordingly, a pilot plant using TMAH has been designed with a capacity of approximately 1 ton/h [33].

What has been also the subject of extensive studies are the operational variables in base-catalyzed TG transesterification, such as reactant molar ratio, reaction temperature, mixing intensity and catalyst concentration. For instance, despite the fact that each mole TG requires 3 mole of alcohol stoichiometrically, an alcohol-to-oil molar ratio of 6:1 has been recommended as optimal to achieve high TG conversion while maintaining good glycerol separation [32, 38]. A reaction temperature near the boiling point of the alcohol adopted is generally used to carry out reaction at atmosphere pressure, e.g. 60°C for methanolysis. Owing to the poor miscibility between hydrophobic lipid compounds and polar methanol, a low operation temperature more likely gives rise to a diffusion-controlled reaction regime characterized by low reaction rate. Intense mechanical mixing is certainly a way to provide efficient mass-transfer among reactant phases. Alternatively, a scheme using THF as a co-solvent has been proposed to overcome the immiscibility problem thus allowing a fast transesterification at low temperature even in absence of stirring [31]. Other organic solvents such as toluene, benzene, and methyl tertiary butyl ether, have also been investigated showing similar success [39, 40]. In summary, Table 2.4 gives typical reaction conditions used for homogeneous base-catalyzed transesterification process in biodiesel production.
Figure 2.1 Alkaline-catalyzed reaction mechanism for triglyceride transesterification [1]
Table 2.4 Typical reaction conditions for biodiesel synthesis using homogeneous base catalysis [1, 4, 26]

<table>
<thead>
<tr>
<th>Homogeneous base-catalyzed biodiesel synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
</tr>
<tr>
<td>Highly refined lipid feedstock with low free fatty acid contents (&lt; 0.5%) and low moisture contents (&lt; 0.06 %) + anhydrous methanol</td>
</tr>
<tr>
<td>Alcohol to oil molar ratio</td>
</tr>
<tr>
<td>6:1</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>60–65 °C</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>1.4–4.1 bar</td>
</tr>
<tr>
<td>Mixing</td>
</tr>
<tr>
<td>&gt; 600rpm</td>
</tr>
<tr>
<td>Catalyst</td>
</tr>
<tr>
<td>NaOH (most common) at 0.5–2 wt% (by weight of lipid feedstock)</td>
</tr>
</tbody>
</table>

TG conversion of ≥ 95% can be expected after 1 h reaction

Acid catalysis

Strong liquid mineral acids, such as sulfuric acid, phosphoric acid, hydrochloric acid, and others, are effective for the esterification of FFAs with alcohol. They have also been used to catalyze transesterification of TGs to produce biodiesel. However, because of their much lower activity (by 3 orders of magnitude) [41] and much stronger corrosiveness than the base catalysts [26], the acid catalysts have never enjoyed the same popularity for biodiesel synthesis as its counterpart in both the academic and industrial sectors. Only recently, given the versatility of acid catalysis to deal with FFAs, has its use been proposed as an economically viable alternative to base catalysis for biodiesel formation form low cost feedstocks [26].

Esterification of FFAs
As the most common way to synthesize organic esters of enormous practical importance, esterification of carboxylic acids with alcohols, indeed, represents a well-known category of liquid-phase reactions of considerable industrial interest. The accepted mechanistic route for the homogeneous acid-catalyzed transesterification is illustrated in Figure 2.2 [42]. The sequence of steps can be summarized as following: in the first two steps, the catalysts essentially activate the carbonyl carbon on the carboxylic group by protonating the carbonyl oxygen; third, the activated carbonyl group undergoes the nucleophilic attack by an alcohol molecule to form a tetrahedral intermediate; forth, proton migration gives rise to a good leaving group; fifth, the carbonyl carbon-hydroxyl oxygen bond of the hemiacetal species (tetrahedral intermediate) cleaves yielding a protonated alkyl ester and a water molecule; finally, the catalyst regenerates by the deprotonation of the ester product.

Figure 2.2 Acid-catalyzed reaction mechanism for carboxylic acid esterification
Simple Brønsted acid catalysts such as H₂SO₄, HCl, H₃PO₄ and arylsulfonic acid, are generally known to be effective for the direct esterification. In a few cases involving substrates with either high sterical hindrance or aromatic moieties, several alternative Brønsted acids have been suggested such as a combination of sulfuric acid and H₃BO₃ and trifluorobenzeneboronic acid [43]. Recently, given their non-corrosiveness and reusability, acidic ionic liquids are proposed as catalysts to offer a new and environmental benign approach for alkyl ester synthesis. Ionic liquids have the potential as dual solvent-catalyst in organic synthesis. And enormous variety of precursors is available to further tune their versatility making them more adapted to a specific reaction. Available examples have shown that SO₃H- and R₃NH-functional Brønsted-acidic ionic liquids can efficiently carry out esterification for multiple cycles without a need of organic solvents or simultaneous removal of water [44, 45]. Ionic liquids, however, are generally less acidic than strong mineral acids, requiring either higher amounts of catalysts or reaction temperatures to achieve comparable ester yields as the latter. Even though this type of catalysts has some reusability owing to their limited solubility in apolar ester phases, the high synthetic cost and innegligible aquatic toxicity hinder their industrial applications. Currently, sulfuric acid still remains to be the catalyst of choice in the manufacturing industry.

Even if esterification is an old reaction with ample literature available concerning the performances of various catalysts and the kinetics of different ester syntheses, there is relatively limited information regarding acid-catalyzed esterification of long chain fatty acids in the presence of triglycerides as the situation requires in biodiesel synthesis. In
most cases, related studies focus on the impacts of reaction parameters on the final free acidity of lipid feedstock without paying much attention to the reaction kinetics.

Mainly using H$_2$SO$_4$ as catalyst, the pre-esterification of different lipid feedstocks with high FFA contents have been investigated. In accordance, oils with initial FFA contents up to 19% can be easily reduced to 1% or lower using 1-step reaction at 60°C after short reaction time, regardless the origins of oils. The specific efficiency of a process is adjustable by varying operation parameters. For instance, the use of larger amounts of catalysts speeds up esterification rate therefore substantially shortening the necessitated reaction time. Also, higher catalyst concentration appears to favor a deeper FFA conversion before a reaction platform reaches [46]. However, excessive amounts of acid were observed to darken the ester products by inducing side reactions [47]. Furthermore, the expedient range of H$_2$SO$_4$ can be interfered with by either the initial FFA content [48] or methanol-to-oil molar ratio [46]. Typically, catalyst concentration ranged between 1 and 2 wt% (with respect to oil) in academic studies using sulfuric acid. Likewise, within appropriate range, methanol amount and reaction temperature impose positive impacts on the pre-esterification of FFAs [48, 49]. When using methanol, the typical reaction temperature remains to be 60-70°C as that used in base catalyzed transesterification. The optimum methanol-to-oil molar ratio, on the other hand, has not been yet established and the adopted value widely ranges from 4 to 40:1 [28, 46, 50]. Alternatively, co-solvents such as THF and dioxane have been found to enhance FFA conversion efficiency by ca. 30% [51].

When dealing with cheap lipid feedstocks and their high FFA content, one has to consider that important amounts of water will be formed during pre-esterifying treatment.
or might directly originate within the feedstock. The presence of water is not tolerable in the subsequent base catalysis since the hydrolysis of TGs can cause saponification. However, more than this, substantial inhibition effects of water on acid catalyzed esterification have been reported by different researchers [52-55]. Since esterification reaction of FFAs is reversible in nature, the decrease in esterification kinetics in the presence of water has generally been ascribed to reverse hydrolysis [52, 53]. But a few researchers have tentatively suggested that the impaired acid strength of catalytic protons by water is a more important factor [54], whereas the deactivation mechanism still remains unexplored. Regardless, the negative effect of water is probably the reason that the highly acidic feedstock (FFA >30 wt%) fails to be sufficiently deacidified even over an extended period [51].

Simultaneous water removal as esterification proceeds can be realized in a variety of ways. When the alcohol is miscible with water, the easiest way is to add another solvent, removing water by azeotropic distillation [56]. For a process where the temperature windows for distillation and reaction coincide, reactive distillation is a more often applied technique for such purpose owing to its advantages in efficiency and energy management [57]. An alternative technique with larger flexibility than reactive distillation with regards to temperature and pressure is reactive stripping, whereby water is removed by means of a sweep gas [58, 59]. Other methods make use of vacuum distillation, membrane separation, and the addition of a dehydration agent.

However, few of the above techniques have been applied to biodiesel production. Instead of the simultaneous operation, a more common method has been using 2-step esterification with water removal conducted in-between steps by azeotropic distillation or
gravitational settling [28, 50, 60]. Despite its simplicity, this way is discontinuous and
time consuming thus being less advantageous in improving esterification efficiency. Only
recently have a handful researchers proposed a strategy fulfilling the continuous water
removal in pre-esterification of lipid feedstock [42, 61]. Instead of 60°C, FFA
esterification is carried out at high temperatures (100-120°C) but at ambient pressure
whereby the continuously fed methanol functions as reagent and also carrier flow to
consecutively strip water out. As a result, water-deficiency and high temperature
efficiently facilitate the reduction of free acidity in highly acidic feedstock.

*Transesterification of TGs*

In contrast to the base-catalyzed biodiesel synthesis, much fewer studies have dealt
with the use of acid catalysts in transesterification of lipid feedstocks. The slow reaction
rate has mainly been why it has fallen into disfavor. Indeed, the homogeneous acid-
catalyzed transesterification follows a similar mechanistic route as the acid-catalyzed
esterification, whereby the catalytic turnover is initiated by the activation of carbonyl
carbon followed by nucleophilic attack of alcohol to form a tetrahedral intermediate [1,
24, 30]. Disproportionation of this intermediate complex yields the alkyl monoester and
diglyceride. This sequence is repeated twice to transform a triglyceride molecule to three
alkyl monoesters and one glycerol as ultimate products. Lotero et al. [1] compared this
acid-catalyzed mechanism to the base-catalyzed and pointed out that there is a crucial
difference lying between them in the reaction initiation steps which mainly discriminate
the catalytic efficiency: the formation of a weak and lump electrophilic species (in acid
catalysis) vs. that of a strong and small nucleophile (in base catalysis).
Sulfuric acid is the most often used catalyst owing to its low price and wide availability. Using sulfuric acid as the catalyst, Freedman et al. [41] have examined the transesterification kinetics of soybean oil with butanol. This catalyst can give a high yield in alkyl monoesters, but the reaction proceeds slowly, typically requiring temperatures above 100°C and more than 3 h to achieve complete conversion. High temperatures can essentially improve phase miscibility minimizing mass transfer resistance and promote more energized molecular collisions thus resulting in improved reaction rates. In particular, at 240°C and 70 bar, using 1.7 wt% H₂SO₄, a tallow conversion greater than 90% could be obtained in only 15 min [62]. For alcoholsysis using large alcohols, the use of high temperature could also allow the continuous removal of water, facilitating the transformation of high FFA feedstock.

In addition, acid catalysis also demands a large excess of alcohol to achieve acceptable reaction rates. For instance, Crabbe et al. [63] investigated the effect of molar ratio within the range of 3:1 to 23:1 and accordingly concluded that the highest molar ratio required for complete transmethylation could be found between 35:1 and 45:1 by extrapolation. More recently, a pilot-scale biodiesel synthesis from waste cooking oil and methanol was carried out at 70°C using 1.5-3.5 mol% sulfuric acid (by total reaction mixture mass) [26]. As high as 50:1 methanol-to-oil molar ratio turned out to be necessitated to convert 97% oil within 240 min. However, an overwhelming amount of alcohol is known to complicate the downstream glycerol purification and alcohol recovery. Hence, the optimized value, should be determined not only based on ester formation rate but also accounting for separation efficiency and recovery cost [24, 30].
Homogeneous catalysis limitations

Homogeneous catalysts, although effective, carry with themselves several serious limitations. For instance, all process methodologies using homogeneous catalysts present problems of product purification and catalyst recovery. Even a minor amount of acid or base residual in the biodiesel could cause engine problem, as base catalysts can induce high levels of incombustible ash while acid ones corrode the metallic parts inside the engine. Hence, an extensive water wash is generally required to separate and clean the catalyst residuals from the products. This washing step produces a large amount of waste water which has to undergo neutralization treatment before being drained away. Homogeneous catalysts are essentially not recoverable thus not reusable. Each batch requires the preparation of a new catalytic solution. By distillation with methanol, organic liquid bases such as tetraalkylammonium hydroxide may be recovered and reused for another reaction cycle [33]. However, distillation process is associated with excessive energy consumption and also the organic basic compounds are generally susceptible to thermal decomposition at escalated temperatures. In addition, homogeneous base/acid catalysts, especially sulfuric acid, are strongly corrosive. As a result, expensive high quality material such as stainless steel is required to build reactors and containers in order to resist the tremendous corrosion.

In summary, homogeneous catalysis is not an environmental friendly means to conduct biodiesel synthesis. All of its drawbacks addressed above transit in high production cost in the end, making biodiesel less economically competitive than petroleum-based diesel fuel.
**Heterogeneous Catalysis**

Currently, biodiesel synthesis using homogeneous catalysis is less than desirable. To be environmentally friendly and to compete commercially with petrodiesel, the process for biodiesel synthesis needs to involve as few reaction steps as possible, to reduce separation and purification workout, and to minimize the production of waste stream. Evidently, the key to develop such process is to replace homogeneous catalysts with suitable heterogeneous ones. Heterogeneous catalysts which are not soluble in reaction mixture do not require costly catalyst neutralization and separation steps. Also, solid catalysts are not corrosive, avoiding the use of expensive construction materials and equipment maintenance. Better yet, the recovered catalysts can be potentially used for a long time and/or multiple reaction cycles. Moreover, heterogeneous catalysis readily allow for the implementation of continuous processes.

**Base catalyzed transesterification of TGs**

The scientific literature contains a good number of reports regarding the use of solid base in TG transesterification. Thus far, a variety of basic solids have been tested and shown some catalytic capability. These catalysts can be grouped into four major categories: ion-exchanged zeolites, alkaline earth oxides/hydroxides, supported metal salts/ions, and heterogenized organic bases.

Zeolite faujastite X is widely accepted as one of the most basic zeolites in the zeolite family. The basicity of as-synthesised NaX can be enhanced by ion-exchange with higher electropositive metals like K and Cs. A series of X-zeolite saturated with different alkali cations has been examined for the transesterification of soybean oil with methanol [64]. All of these catalysts, however, showed only moderate activity owing to the diffusion
resistance of bulky triglycerides molecules through the channels of faujasites [64]. For instance, with the catalyst loading of 0.03 g/0.375 ml and after 24 h of reaction time at 150°C, even the most active KX gave rise to methyl ester yield of only 31.5 wt%. According to Leclercq et al. [65], a high TG conversion of 70% can be achieved using CsX within a reasonable timescale but necessitates the use of a tremendous excess methanol (MeOH/rapeseed oil = 275:1).

ETS-10 is a newly developed inorganic titanium-containing zeolite material. It has a well-defined three-dimensional pore structure consisting of corner sharing octahedral titanium (TiO$_6^{8-}$) and tetrahedral silicon (SiO$_4^{2-}$). Like X-zeolites, EST-10 also has high ion-exchange capacity but superior to the former by exhibiting a much stronger basicity [66]. The high basicity of ETS-10 appears to be well correlated with its great catalytic activity. As reported by Suppes et al. [64] for the methanolysis of soybean oil, ETS-10 titanosilicate was able to considerably outperform X-zeolites in all cases regardless the type of the saturated alkali ion. In particular, under the reaction conditions typically used for homogeneous catalysis (MeOH/Oil = 6:1, 60°C), methyl ester yields obtained using ETS-10 catalysts after 24 h were 67-81 wt% vs. 6-11 wt% using X-zeolites. ETS-4, a titanosilicate with 2-dimensional pore network, has also been tested for biodiesel synthesis by Bayense et al.[67], showing an even higher activity than ETS-10. The ETS catalysts, however, are microporous solids with typical pore opening of 3-8 Å, no larger than that of X-zeolites. Taking into account the effective radius of TG molecules, the basic sites located inside the micropores should remain inaccessible and it is surprising that the ETS catalysis did not significantly suffer from site-accessibility but behave actively. Hence, the superior performance of ETS-10 has been suspected to result from
the leaching out alkali methoxide [1], which was later proven experimentally by Lopez et al. [68].

Considering the strong base characteristics of alkali earth oxides and hydroxides, they have also been used for transesterification of triglycerides with methanol to form biodiesel [65, 69, 70] or with glycerol to synthesize monoglycerides [71]. The basicity of alkali earth metal hydroxides increases as the electronegativity of metals decreases following the order Mg(OH)\(_2\) < Ca(OH)\(_2\) < Ba(OH)\(_2\). Using Ba(OH)\(_2\), both Gryglewicz [69] and Leclercq et al. [65] have demonstrated its high catalytic activity for the methanolysis of rapeseed oil. As reactions were carried out at conditions normally used for liquid alkali catalysts, high oil conversions (>80%) were achieved in only 1 h. In contrast, Ca(OH)\(_2\) did not give rise to any significant TG conversion when using identical reaction conditions [69]. Barium hydroxide, however, has strong ionic character owing to the extensively polarized HO-Ba-OH bonds and undergoes dissociation in polar media. Gryglewicz [69] determined the solubility of Ba(OH)\(_2\) in methanol to be 1.17% which is two orders of magnitude higher than that of the inactive Ca(OH)\(_2\). Hence, Ba(OH)\(_2\) is not an absolute heterogeneous catalyst and the dissolved portion working as homogeneous catalyst can be responsible for most of its activity. In addition, soluble barium compounds are highly toxic which further preclude its potential to serve as an environmentally friendly catalyst for biodiesel synthesis [69].

The oxides of alkaline earth metals are stronger bases than their corresponding hydroxides. Among them, calcium oxides appear to be one of the most promising candidates owing to its cheap price, readily availability, slight methanol solubility and low toxicity. In fact, CaO has been one of few heterogeneous alcohoysis catalysts that is
commonly use to synthesize monoglycerides at 200-220°C within reaction times of 1-4 h [72]. However, at high reaction temperature, the reaction mixture containing CaO forms a slurry owing to its increased solubility in alcohol phase and the residual basicity in the liquid phase has to be neutralized using phosphoric acid [72]. Therefore, one has to take caution against the use of CaO under strenuous conditions where a homogeneous rather heterogeneous catalysis could be occurring.

The alcoholysis activities of CaO has been tested for TGs as found in various lipid feedstocks [69, 70, 73] or their simple model substrates [74] under mild reaction conditions (25-65°C). The different researchers, however, reported contradictory results. For instance, using CaO and after several hours, Peterson and Scarrach [73] and Gryglewicz [69] have determined high biodiesel yields of more than 90%, comparable to those obtained using homogeneous catalysts such as NaCH₃O and Ca(CH₃O)₂. On the other hand, despite the use of a excessive amount of methanol, Watkins et al. [74] and Reddy et al. [70] observed only negligible activities of CaO in this type of reaction. The dilution effect of methanol on catalyst concentration in the latter cases might partially account for the reported inconsistencies, whereas the determination of Peterson and Scarrach was based on thin layer chromatography results which were valid only for qualitative evaluation [1]. Likewise, there is also no consensus about the catalytic capacity of magnesium oxide in transesterification reactions. Some researchers have reported very low or no activity using MgO in methanolysis of lipidic or model triglycerides [68, 69, 75], whereas Corma and co-workers have showed the success of this catalyst in promoting the glycerolysis of triolein [76] and polyglycolysis of methyl oleate [77].
Indeed, it is well known that the nature and number of basic sites in solid bases are especially susceptible to catalyst pretreatment [78]. Therefore, failing to calcine the oxides at optimum temperatures such that release any pre-fouled strong sites from acidic species and also give rise to reactive and ample ion pairs of low coordination numbers, would certainly discount their activities in base-catalyzed reactions. For instance, Leclercq et al. [65] have observed a strong dependence of MgO activity on calcination temperature: the catalyst calcined at 823K showed a much more appreciable activity than the one calcined at 723K in the methanolysis of rapeseed oil. Many related studies, unfortunately, either applied no thermal-treatment on catalysts [70, 74] or lacked clear address regarding this aspect [69]. More recently, Di Serio et al. [79] have pointed out that both structural texture and surface basicity of MgO catalysts are sensitive to the adopted precursor and preparation method. The physicochemical parameters of catalyst along with reaction operation variables further constitute a more complex function for its catalytic performance. For example, the basicity of the pure oxides is known to be not homogeneous but rather associated with the surface O$^{2-}$ anions in M$^{2+}$-O$^{2-}$ pairs of different coordination numbers which correspond to different basic strengths [78]. For MgO-catalyzed soybean oil methanolysis, it has been concluded that at low reaction temperatures (100°C or below), only the strongest sites are involved whereas a large portion of basic sites of medium strength requires an elevated temperatures (180°C or above) to be operative and thus contribute to total activity [79].

Nevertheless, low surface area [70], limited concentrations of edge and corner defect sites [70, 74] and insufficient basicity [74] have been attributed to cause the unsatisfactory performances of the alkali earth metal oxides under mild reaction
conditions. Accordingly, the means of alkali metal doping [74], crystal nanonization [70], dispersion on mesoporous support [71], and mixed oxides preparation by calcining clay materials [80, 81] have been proposed as solutions to create catalysts possessing larger surface area and/or more surface defects thus higher activity. Using LiNO\(_3\), Watkins et al. [74] have prepared a series of Li doped CaO by wet impregnation. An optimum Li loading of 1.23 wt% was found to provide a remarkable activity improvement over the unpromoted CaO, as a result of surface defects generation by isolated Li\(^+\) species in the submonolayer regime. Higher loadings of Li, associated with the formation of LiNO\(_3\) multilayer (bulk phase), led to a dramatic decrease in activity for tributyrin methanolysis. Reddy et al. [70] examined the potentials of nanocrystalline oxides to allow TG transesterification to efficiently occur at room temperature. According to the authors, nanocrystalline MgO, despite a high surface area of 600 m\(^2\)/g, remained as inactive as non-nanosize MgO and CaO. In contrast, all kinds of nanocrystalline CaO (NC-CaO) showed significant activity towards the formation of biodiesel, regardless of the particle shape and surface area. These NC-CaO catalysts differentiate themselves only in their reusabilities which are affected by polycrystallites aggregation occurring during reaction. The most sustainable sample was able to be recycled 8, 4, and 3 times for the methanolysis of refined soybean oil, virgin soybean oil and waste poultry fat, respectively, before any substantial deactivation was determined.

Supports, such as mesoporous MCM-41, have been used to disperse metal oxide particles in order to increase the availability and accessibility of the basic sites in catalysts. Moreover, in the reactions involving the formation of multiple species, the uniform pore network of MCM-41 support was also expected to improve the selectivity.
of desired products. However, comparing the studies conducted by Barrault and co-workers [71, 82], the prepared MgO/(Al)MCM-41 catalyst failed to show any activity enhancement over the bulk MgO in the glycerolysis of methyl stearate. As a matter of fact, the initial activity of the supported catalyst was determined to be only 0.64 mmol·h⁻¹·g⁻¹ or 1.99 mmol·h⁻¹·(g of MgO)⁻¹, which is about 10% of those unsupported MgO as reactions were carried out under identical reaction conditions (glycerol-to-ester molar ratio = 1:1 and 220°C). Unfortunately, the above comparisons were missed in their study [71] using MgO/(Al)MCM-41 and so were any associated rationalization. Nevertheless, the authors did demonstrate an improved monoglyceride yield induced by a shape selectivity as using a mesophase MCM41 of smaller pore size (d₁₀₀ = 3.43 nm) [71].

Anionic clay materials, especially hydrotalcites (Mg²⁺ₓAl³⁺ᵧ(OH)ₓ⁺ᵧ(CO₃)ₓ⁻ᵧmH₂O), represent an interesting class of catalytic materials or precursors [83]. Hydrotalcites (HTs) themselves generally behave as solid bases mainly owing to the structural hydroxyl anions. However, the basicity of HTs is less than sufficient to display any significant activity in TG transesterification [65, 81]. Through controlled thermal decomposition, HTs are converted to homogeneously interdispersed mixed Mg-Al oxides (CHTs). CHTs have strong surface basicity, much like the pure oxides, whereas usually a more desirable surface morphology of higher surface area and larger pore opening [75]. More importantly, the Al³⁺ cations incorporated in the MgO lattice favored the formation of smaller crystallites and thus a higher abundance of surface defects with respect to pure MgO [79, 80].

CHTs are considered as attractive candidates for biodiesel synthesis and some related studies can already be found in the literature. Inspired by the pioneer work devoted to the
application of CHT in TG glycerolysis by Corma and the co-workers [76], Leclerq et al. [65] first examined the catalytic efficiency of this type catalyst in biodiesel synthesis from rapeseed oil. Poor results were obtained by them, as only 34% oil was converted after 22 h at 60°C. In a subsequent study, Xie et al. [81] synthesized a series of hydrotalcites with compositions over the range Mg-to-Al molar ratio = 2 to 4 and calcined them at different temperatures from 300 to 800°C. The HT with the Mg/Al = 3 and calcined at 500°C has the highest basicity and accordantly, behaves most actively in soybean oil methanolysis. Using 7.5 wt% (by oil mass) the most active CHT and a MeOH/oil molar ratio of 15:1, a moderate oil conversion, 67%, was achieved after 9 h reaction at methanol reflux temperature. Only recently have the use of CHT catalyst at elevated temperatures given rise to outstanding biodiesel yields in short reaction times [79]. With 10 wt% catalyst and MeOH/oil ratios of 6, a biodiesel yield of ca. 58%, 92% and 96% can be reached after 1 h at the reaction temperature of 100, 180 and 200°C, respectively. In comparison, CHT outperformed all kinds of MgO prepared, especially at low temperature. Also, according to the authors [79], CHT and MgO catalysis appear not to be sensitive to the presence of water as the intentional addition into reaction mixture of 10000 ppm water did not impair the biodiesel yield to any extent, which would be a striking advantage over homogeneous alkali catalysis.

Simple metal salts have also been used for triglyceride transesterification reactions. For instance, with M₂CO₃ (M= K, Na) and MCO₃ (M = Zn, Mg, Ca), Suppes et al. [72] conducted soybean oil and beef tallow alcoholsysis at temperatures above 200°C. High TG yields (> 95%) were achieved after short times for all carbonate salts tested. However, it is not clear if such salts have to demand a high temperature to behave actively. After all,
for biodiesel synthesis, instead of using the bulk salts directly, most of researchers have loaded them on porous supports such as Al2O3, ZnO, ZrO2, Zeolites etc.[73, 84-87].

Using alkali metal salts and hydroxides, Ebiura et al. [84] have prepared a series of alumina-supported solid bases by impregnation followed by a prescribed thermal treatment, namely, drying at 120°C for 12 h and then evacuated at 550/400 °C for 2 h prior to reaction. Of these synthesized catalysts, alumina loaded with K2CO3 and KF are the most active catalyst for triolein methanolysis, affording a methyl oleate yield of 92% and 91%, respectively, after 1 h reaction at 60°C. Supported NaOH and KOH also showed high activity whereas alkali nitrates performed poorly with the exception of LiNO3. This activity trend exhibited by these catalysts for transesterification, however, did not correlate with that for the double-bond isomerization of 2,3-dimethyl-1-butene, a characteristic test reaction for base strength evaluation. The best isomerization catalyst KNO3/Al2O3, for example, is one of the worst bases for transesterification. Using a group of catalysts covering a wide range of base strengths, Climent et al. [77], by contrast, have been able to demonstrate an excellent correlation between an alcoholysis reaction and another basicity test reaction, the condensation between benzaldehyde and ethyl cyanoacetate. On the other hand, the low transesterification activity of KNO3/Al2O3 observed by Ebiura et al. [84] was probably due to the non-optimized KNO3 loading (2.6 mmol/g-Al2O3 = 20.8 wt%) and/or calcination temperature (400°C), as Xie et al. [86] have manifested a strong dependence of KNO3/Al2O3 activity with these two parameters. Accordingly, the catalyst with 35 wt% KNO3 loaded on Al2O3 and after calcined at 500°C showed the highest basicity and thus the best activity in the transesterification of soybean oil with methanol [86]. Besides optimizing preparation parameters, the co-
doping of alkali metal along with its salt on Al₂O₃ can yield a more basic composite catalyst. For instance, Na/NaOH/γ-Al₂O₃ was found to be highly active for the vegetable oil methanolysis conducted at conditions normally used to prepare biodiesel, giving a comparable performance as homogeneous NaOH [88].

Supports are well known to be capable to affect the activity of the supported active species. For instance, though the reason is not elucidated yet, Al₂O₃ has been shown to be unique for potassium amide (KNH₂), yielding a much more active catalyst for isomerization than other supports such as CHT, SiO₂, TiO₂, etc. [89]. Other than Al₂O₃, ZnO, ZrO₂ and zeolites have been used to prepare supported alkali salts for biodiesel synthesis. In a recent study, Xie and Huang [87] disclosed the use of KF/ZnO in the transesterification of soybean oil with methanol. KF loading of 15 wt% and calcination temperature of 600°C yielded the best catalyst. More recently, Jitputti et al. [85] have supported KNO₃ on ZrO₂ and KL zeolite, respectively, and used them for biodiesel production. However, probably due to the use of crude lipid feedstocks with high FFA (1.25-2.25 wt%) and water (0.09-0.17 wt%) contents, these two solid bases gave only moderate biodiesel yields, even less than those obtained with solid acids (SO₄²⁻/ZrO₂ and SO₄²⁻/SnO₂). If simply comparing the results reported in these related studies ([84-87]), Al₂O₃ seems to be a better support for both KNO₃ and KF than other solids. Nevertheless, the reaction conditions and feedstock properties used by these researchers are significantly different from each other making this argument hardly convincing. Only using KI, a comparison among different supports has been made directly in soybean oil methanolysis wherein Al₂O₃ were evidenced to be the best support in terms of both catalyst basicity and activity followed by ZrO₂, ZnO and zeolites in order [90].
Despite the appreciable activity of the supported alkali salts catalysts, the identity of the active sites is not definitive yet. For alumina-supported KNO₃ and KI, by means of IR and XRD, Xie and co-workers [86, 90] proposed as the active species the K₂O formed through potassium salts decomposition and the Al-O-K originated from K⁺ substitution for protons of the isolated hydroxyl groups. Corroborating the hypothesized importance of K₂O, as supported on Al₂O₃, more thermal stable salts, KBr and KCl, produced much less inactive bases than KI as well as KNO₃, K₂CO₃ and KOH [90]. While for KF/ZnO and KF/Al₂O₃, due to their higher activity than the corresponding K₂CO₃ and KOH supported solids, F⁻ ions have been suggested to be the catalytically active species against O²⁻ ions for the other two alkali salts [87, 89, 91]. Ando et al. [92] stressed the importance of coordinatively unsaturated F⁻ as the source of the strong basicity. On the other hand, Weistock et al. [93] ascribed the catalyst activity to surface hydroxyl groups and/or aluminates supported on Al₂O₃. To elucidate these controversial arguments, further study is certainly required to better understand the alkalis supported catalysts. However, for reaction conducted in polar medium and at high temperature, the potential lixiviation problem associated with this type of solid bases should not be overlooked. Climent et al. [77], for example, determined a significant leaching of F⁻ from KF/Al₂O₃ and Li⁺ from Li/Al₂O₃ occurring in the transesterification of methyl oleate with polyoxyethylglycols at 220°C, which eventually cause catalyst deactivation and product contamination. Also, the leaching out of potassium of K₂O/ZrO₂ was observed in the soybean oil methanolysis carried out at 250°C in a fixed-bed continuous flow reactor [94].

Organic bases such as guanidines and biguanides are superior to liquid alkali in biodiesel synthesis by avoiding heavy downstream workup and production of salts-
containing effluents. Coupled with the increasing emphasis on the development of greener biodiesel technology, the heterogenization of these organic bases is a desirable goal. In open literature, the first attempt at immobilizing organic bases and using them for triglyceride transesterification with alcohol was taken by Schuchardt et al. [95]. Guanidines were successfully grafted on gel-type polystyrene matrix by covalent bonding or by sequential syntheses on aminated polystyrenes [95]. As used for soybean oil methanolysis, basic polymers thus synthesized showed comparable activity to their homogeneous analogues, affording the same high oil conversions after only slightly prolonged reaction times. However, due to a nucleophilic attack of methoxide on benzylic CH₂ groups, the heterogenized guanidines slowly leached out from polymer during consecutive reaction cycles, in parallel to a continuous loss in catalytic activity. Introducing a linear spacer-arm between guanidine and polystyrene did not increase catalyst activity as supposed but caused additional deactivation by allowing the side reaction of the guanidine functionalities with vicinal unreacted haloalkyl subsituents to form inactive hexasubstituted guanidinium compounds. Therefore, in order to avoid/minimize the occurrence of this side reaction, a polymer containing a low loading of chloromethyl groups has been recommended for heterogenization. In a similar way to that used in [95], Gelbard and Vielfaure-Joly [35, 96] confined biguanides to polystyrene, yielding a more reactive solid base than the polymer-supported guanidines. More importantly, these heterogenized biguanides catalyst appeared to be more resistant to the methoxide anion attack, as their activities remained unaffected for at least 10 successive cycles [96]. Recently, guanidine functionalized polymers were also used for transesterification of methyl fatty ester with glycerol targeting the formation of
monoglycerides [97]. Despite the use of an elevated temperature, 110°C, good catalyst stability was reported as it was simply reused four times showing only a slight diminution in catalyst activity.

Alternatively, siliceous materials afford convenience to prepare hybrid porous solids by covalent anchoring of organic moieties onto the supporting mineral surface. Mesoporous ordered silica such as MCM-41 and MTS are popular choice for this purpose and have been used to entrap guanidines [98-100]. The mesoporous silica, however, is no better support than polystyrene, giving lower activity in TG transesterification and still entailing the issue of guanidine leaching [99]. The H-bonding interactions between basic sites and the proximal residual silanol groups are blamed for the decrease in activity by interfering with the site strength. Derrien et al. [100] demonstrated that the removal of residual silanol groups by silylation (so called endcapping) improved the activity of guanidine/silica catalyst in the ethyl propionate butanolysis. The beneficial of end-capping treatment, on the other hand, did not extend into the preclusion of active species leaching in the repeated reaction-regeneration cycles [100]. The encapsulation of guanidine in the supercage of Zeolite Y represents one of the ongoing efforts of the researchers to circumvent this intractable issue [98, 101]. The strategy of the encapsulation involves an in-situ local formation of a guanidine by reacting carbodiimide and amine inside the supercage of zeolite. The as-synthesized guanidine is of such proper size that is small enough to allow its accommodation, together with the substrates, in the supercage of 13 Å but large enough to be geometrically confined by the micro-dimensional channels of the zeolite [101]. Consequently, the use of spatial constraint instead of covalent bonding for guanidine immobilization, completely removed the
concern of leaching. However, as can be expected, the encapsulated guanidine in zeolite shown no practical activity in biodiesel synthesis due to the lack of diffusion of TG molecules through the micro channels [99].

Most recently, a creative way to take advantage of guanidine catalysis in biodiesel synthesis is making use of organic carbonates [37]. Guanidine reacts with carbonic acid forming crystalline carbonate salts. In the crystalline state, the salts are stable and permit the ease to handle like general solid catalysts. During boiling at methanol reflux, guanidine carbonates decompose releasing gaseous CO₂ while leaving basic guanidine in the liquid phase to carry out transmethylation of triglycerides. Despite not being addressed, the production of water should concur with the disintegration of guanidine carbonates. Nevertheless, owing to the homogeneous catalysis of liquid guanidine in nature and its strong basicity, the reaction proceeds rather fast. It takes only 45 min and 1 g organic carbonate for 100 ml of refined rapeseed oil to be completely transesterified and 90 min for 1.1 g catalyst for undeacidified oil with 1.0 wt% FFA [37]. It is worth noting that guanidine carbonates are insoluble in alcohols, oils, fats and esters of fatty acids [37]. Herein, in view of this fact, it seems to be possible to purge CO₂ and H₂O back to glycerol phase to precipitate guanidine, permitting a convenient catalyst recovery without the need of energy-consuming distillation. In this way, the organic carbonate may be accounted for in the scope of solid bases while its use is limited to batchwise operation.

In addition to guanidine compounds, other strong organic bases have been used to design heterogeneous catalysts including simple alkyl amines [102, 103] and tetraalkylammonium hydroxide [104-106]. However, the related research focusing on
their application in biodiesel formation is far less extensive than guanidino species with few examples available [107, 108].

**Acid catalyzed esterification of FFAs**

During the last decade, given the environmental and economical concerns, industrial processes for organic esters derivation from small carboxylic acid began to shift towards heterogeneous catalysis. Most of them use acidic resins functionalized with -HSO₃ group as solid catalyst [57]. However, due to their polymeric matrix, such resin catalysts have poor thermal stability (<140°C) and lack structural integrity at high pressures. These inherent drawbacks somewhat prohibit their application in biodiesel production, because the long chain FFAs are much less active than small carboxylic acids and require operations at higher temperatures. In addition, when using organic resins, their swelling capacity has to be concerned since it controls substrate accessibility to the acid sites. Unfortunately, neither TG nor FFA is a good swelling agent due to their lengthy alkyl tails of substantial hydrophobicity [109], further disfavoring the promise of organic resins as biodiesel catalysts. Limitations notwithstanding, a couple of very recent works furnished by Santacesaria and the co-workers [61, 110] have demonstrated the feasibility of polymeric resins in the deacidifying treatment of biodiesel feed. Both batchwise and continuous-mode operations have shown good results, completely refining the oil within 200-400 minutes. But a temperature above 100°C has to be used to ensure such efficiency in both cases and continuous water depletion by methanol vapor is required for the latter one. However, a long term test was missed in their reports obscuring the prospect of the lifetime length of these resin catalysts under the claimed conditions. Indeed, another recent study confirmed the poor stability of this type catalyst at 130°C, as both
Amberlyst-15 and Nafion-NR50 deactivated after only 2 and 4.5 h, respectively, in esterification of dodecanoic acid with 2-ethylhexanol [111].

Regardless of the limitations of polystyrene matrix, the effectiveness of the -SO$_3$H group in esterification is well recognized. More efforts were then taken to explore and apply desirable support substitutes. Due to a combination of high surface area, flexible pore sizes and well-defined mesostructure as well as high thermal and mechanical stability, MCM-41 and SBA-15, both belonging to the M41S family of molecular sieves, have been most extensively used to prepare sulfonic group assembled hybrid catalysts for FFA esterification [112-118]. Even better, the physicochemical properties of the composite solid acid can be tailored at molecular scale to meet application desired requirements. As shown in [115, 118], acid strength of -SO$_3$H can be manipulated by choice of organosulfonic precursors and/or spatial pre-arrangement of acid sites. Indeed, SBA-15 functionalized with benzenesulfonic acid groups integrated delicate mesostructure and high acid strength and showed sensational activity in catalyzing palmitic acid methanolysis in the presence of soybean oil, resembling homogeneous p-toluenesulfonic acid while far outperforming both Amberlyst-15 and Nafion [115].

Equally important, the surface hydrophobicity of mesoporous silica and thus the local surrounding of –SO$_3$H groups can be deliberately controlled by introducing alkyltrimethoxysilane agents [112, 117]. Expectably, hydrophobic decoration around acid sites showed much improved resistance against the deactivation effect of water on esterification [112, 117] and it also posed a positive impact on monoglyceride selectivity of fatty acid glycerolysis. Additionally, it was found that the activity of these hybrid mesoporous silicas was highly dependent on their texture properties [115, 119]. Hydroxyl
source and/or surfactant template have to be judiciously chosen to create appropriate pore dimension and arrangement to facilitate the reactant diffusion.

This organic-inorganic hybrid silica has been typically used at 85-120°C in FFA esterification. With a methanol-to-FFA molar ratio of 20:1 and a catalyst loading equivalent to 10 wt% FFA, SBA-15-SO$_3$H reduced the FFA content in acidic oil by 90% within 180 min at 85°C [115] and within 120 min at 120°C [116]. During at least two esterification cycles, the sulfonic group functionalized silica was shown to behave consistently in such deacidifying treatment, providing that the polar impurities in lipid feedstock had been pre-removed using porous adsorbents before reaction [116]. Nevertheless, in esterification of FFAs with glycerol, Diaz et al. [114] have determined a trival S leaching which is more pronounced at longer reaction times, particularly at high temperature. Accordingly, 9.9% S was leached out after 24 h as the oleic acid glycerolysis was carried out at 150°C. However, no further experiments were conducted to develop a mechanistic rationalization for the phenomena of sulfur leaching. After all, 150°C is far below the decomposing threshold of the sulfonic group, 460°C, as evidenced by DTA (differential thermogravimetric) analysis [118]. Indeed, the authors also hypothesized that the leached sulfur might result from nonacidic partially oxidized sulfur species rather than sulfonic groups [114]. However, regardless of its provenance, sulfur is a species subject to strict regulation in diesel fuel (< 15ppm). Hence, studies are desired to overcome this issue to improve the feasibility of silica-SO$_3$H hybrid solid in practical biodiesel production.

Despite their promise in terms of somewhat adequate activity and especially glorious flexibility, organosulfonic-mesosilica hybrids are criticized for the relatively high
synthetic cost [120]. Carbon material is considered as a readily available substitute at low cost to assemble sulfonic groups. Recently, sulfonated carbons derived by incomplete carbonization of simple cheap sugars were reported to show interesting activities in the esterification of carboxylic acids as well as FFA [121-123]. These so-called sugar catalysts were prepared using a two-step approach: first, a natural product such as sugar, starch or cellulose is pyrolyzed in N\textsubscript{2} at 300-450\textdegree{}C resulting in a rigid material composed of polycyclic aromatic carbon sheets in a 3-dimensional sp\textsuperscript{3}-bonded structure; second, the hydrocarbon precursor is sulfonated by heating in concentrated or fuming H\textsubscript{2}SO\textsubscript{4} to generate a solid functionalized with a high density of sulfonic acid sites (0.48-1.74 mmol/g).

As such prepared carbon-based acids are thermally stable up to ca. 230\textdegree{}C and chemically robust against a variety of both polar and apolar solvents even at their boiling points as well as long time exposure to hot steam [123]. Despite a low surface area (1-2 m\textsuperscript{2}/g) and amorphous structure, sugar catalyst possesses high acid strength (-11<pK\textsubscript{a}< -8) due to the highly electron-withdrawing polycyclic aromatic carbon rings and strong surface hydrophobicity, which make it highly effective in esterification of oleic acid with ethanol. In a benchmark assay, its activity was comparable to that of H\textsubscript{2}SO\textsubscript{4} even on a weight basis while considerably topped those of conventional solid acids such as Nafion NR50 and H-mordenite. The strong stability of this catalyst was able to be demonstrated again in five consecutive esterification cycles [122]. The above results, however, can not be extrapolated to any carbon material or hydrocarbon precursors. Many of them, owing to the lack of either flexibility (activated carbon, amorphous glassy carbon, carbon black,
etc.) or integrity (incompletely carbonized naphthalene) in polycyclic aromatic sheets, failed to assemble active and stable solid catalysts through sulfonation [123].

Due to their effective and stable performance, all of these aforementioned -SO$_3$H group functionalized solids constitute a major category in esterification viable catalysts. However, pure inorganic solid acids afford advantages over them by the allowance of further elevated reaction temperature and easy regeneration upon calcination. Zeolite, as a classic solid acid of the highest industrial importance, has been preliminary tested for FFA esterification [111, 124, 125]. Nevertheless, when using zeolites, mass transfer resistance becomes a critical issue due to their microporous nature. Generally speaking, zeolite catalysis of reactions involving large molecules such as FFA takes place at the external surface of the zeolite crystals. For this reason, zeolites catalyze rather slowly FFA esterification. Therefore, only large pore zeolites (unit cell of 24.43 Å) have shown some success in FFA esterifications conducted at high temperature and high pressure [126]. But their use appears to be more advantageous and reasonable for the case emphasizing product selectivity such as monoglyceride synthesis from FFA glycerolysis [126, 127].

Related to zeolites, but with amorphous pore walls, the aforementioned molecular sieves such as MCM-41 and SBA-15 generally lack sufficient acidity to catalyze esterification due to their pure silica structure. Partial replacement of Si with Al is a convenient way to introduce some Lewis acidity. However, neither can thus prepared alumina-silicates lead to adequate acid strength. For instance, in the esterification of oleic acid with glycerol, Al-MCM-41 was able to show marginal activity which was even lower than that of zeolite beta with a similar Si/Al ratio [112].
Alternatively, using impregnation or so-gel techniques, other stronger inorganic acidic species have been incorporated into silica matrix in order to take advantage of its mesoporous structure. In particular, heteropolyacids (HPA) and their salts are a class of highly acidic polyoxometalates compounds composed of heteropoly-anions having metal-oxygen octahedral as the basic structural unit. Their application, nevertheless, is limited by the significant solubility in polar media as well as low surface area. MCM-41-supported HPA has been reported to show good activity in esterification of acetic acid and 1-butanol, rivaling the pure HPA bulk as a result of a high dispersion of acid sites on silica surface [128]. However, during esterification, continuous water formation caused HPA migration from the MCM-41 pores to the outer surface, facilitating the sintering of HPA species. Consequently, the initial high dispersion of HPA units underwent substantial loss, in parallel to the significant deactivation with catalyst reuse [128]. Indeed, it was revealed that the segregation of HPA species can reach such an extent that induces the formation of bulk HPA and the subsequent leaching thereof (from the silica surface) [129]. The leaching occurred in the use of ZrO$_2$ supported HPA as such [129]. A hydrophobic matrix i.e. activated carbon (AC), on the other hand, was able to circumvent this issue by impeding the detrimental interaction of water with HPA species. Interestingly, in a recent study by Kulkarni et al. [130], HPA impregnated on hydrous zirconia was reported to effectively catalyze simultaneous esterification and transesterification of acidic Canola oil (10 wt% FFA) at 200\degree C and was able to be successfully reused with only negligible activity loss. The preserve of HPA units on spent catalyst was also manifested by elemental analysis.
Most of forenamed solid acids possess clear protonic character with the exception of zeolites and alumina-silicates. In FFA esterification, Lewis acids may be preferred over Brønsted acids for the sake of minimizing alcohol dehydration or racemization [43]. Owing to the electron deficiency of the transition center, a variety of transition metal complexes usually possess strong Lewis acidity. They either act as solid Lewis acids by themselves with/without a promoter or disperse on appropriate supports to generate composite catalysts. For instance, zinc ethanoates and acetates supported on silica matrix have been used for palmitic acid esterification with isopropanol [52, 131]. \(\text{ZiOCl}_2 \cdot 8\text{H}_2\text{O}_2\) were impregnated on MCM-41 assembling solid acids with \([\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}\) as active center [132]. All of these silica-supported Lewis acids showed appreciable activity in FFA esterification at 140-170°C and can be reused without the sign of deactivation.

Among Lewis acids, sulfated zirconia (\(\text{SO}_4/\text{ZrO}_2\), SZ) is one of catalysts which have received most attentions during the past decade. It is enjoying wide applications in paraffin isomerization, cracking and alkylation due to its high acid strength. Though still contentious, it is argued that the Zr cation acts as a Lewis center while sulfate group enhance its acidity by an inductive effect [133]. Recently, SZ has been applied for the preparation of 2-ethylhexyl dodecanoate from lauric acid and 2-ethyl hexanol. But it showed significant activity only at a high reaction temperature (\(>180^\circ\text{C}\)) [134]. As an example, in a batch-wise operation at 80°C, it took 100 h for 0.86 wt% SZ to reach equilibrium even with an alcohol-to-FFA molar ratio of 25:1. A much more successful use of SZ was then demonstrated in a reactive distillation system wherein the products separation speeded up the right-shift of reaction. Moreover, by removing water continuously, reactive distillation is also essential for a long-term use of SZ. Otherwise,
water promotes sulfate leaching as H$_2$SO$_4$ and HSO$_4^-$ by hydrolysis leading to permanent
catalyst deactivation [135]. Despite that the repeated use of SZ has been recently alleged
as successful within at least five consecutive cycles of lauric acid esterification with 1-
propanol [111], a leaching of sulfur occurring at a slow rate in the organic-rich phase can
not be excluded. Efforts have been taken to make sulfate overcome the susceptibility of
SZ to water through a new synthesis route, which involved the use of a chlorosulfonic
acid precursor dissolved in an organic solvent, instead of the conventional sulfuric acid
impregnation [136]. Accordingly, thus prepared SZ not only exhibited good retention of
its activity for successive acetic acid esterification cycles but withstood sulfur leaching
even in aqueous phase.

Sulfated tin oxide (SO$_4^{2-}$/SnO$_2$, STO), prepared from meta-stanate acid, is another
familiar sulfated oxide. It has shown superior acidity than SZ and consequently, higher
activity in esterification of n-octanoic acid with methanol [137]. In a flow reactor using
methanol-to-FFA molar ratio of 4.5:1, STO can afford nearly 100% yields of methyl
caprate after 20 h of time-to-stream at 100°C, whereas SZ can not do the same thing
until at 150°C. Unfortunately, the related report did not indicate whether or not a lower
susceptibility to water is also possessed by STO, which would further stress its
application prospect in FFA esterification. Nevertheless, the use of STO has been as
popular as SZ due to the difficulties and poor yields associated with its synthetic routes.

Tungstated zirconia (WZ) is well known to be a robust and stable solid acid. Even
though WZ has a lower activity than the counterpart SZ because of its weaker acid
strength, it has been considered as a good candidate as an alternative catalyst for alkane
isomerization because it does not deactivate as severely. Recently, the use of WZ in pre-
esterification of acidic oils was examined and compared with SZ [94, 125]. Surprisingly, WZ was able to function comparably to SZ while outperforming other solid acids including sulfated alumina, zeolites, as well as Cs-Heteropoly acid. In another study, both promoted with Al$_2$O$_3$, WZ and SZ also resembled each other in FFA esterification conducted in a flow reactor at 175-200°C [94]. The addition of Al$_2$O$_3$ helps stabilize the tetragonal phase of the ZrO$_2$ support and also prevents the growth of WO$_3$ particles. The percentage of tetragonal phase of the ZrO$_2$ support has been found to be associated with WZ acidity as well as its activity in palmitic acid esterification [138]. More interestingly, as used in transesterification of soybean oil with methanol, WZ-Al$_2$O$_3$ surpassed SZ-Al$_2$O$_3$ as well as SnO by a significant margin [94]. Together these facts indicate that the acid strength can never be an arbitrary criterion in catalyst activity estimation and the activity trend can not be simply extrapolated from one reaction to another.
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CHAPTER 3
PROJECT OBJECTIVES AND APPROACH

Despite increasing attempts towards finding and/or developing solid catalysts as well as reaction processes suitable for biodiesel forming reaction, most studies on the literature limit themselves by showing only TG/FFA conversion at a specific time. The important exploration of catalyst activation-deactivation, catalyst selectivity, reusability and regeneration is missing. Also missing from comprehensive research aiming to the development of solid catalysts is about how solid catalysts work in biodiesel forming reactions and how their catalytic performance could be effectively improved. Systematic research is necessary to explore the principles of catalyst activity in reaction medium as well as their integration with reaction conditions. Regarding these fundamental concerns, model reaction studies using low molecular weight model compounds of FFAs and TGs such as carboxylic acids and their glycerol esters allow a greater convenience and accuracy in reaction characterization and thus in kinetic measurement.

The objectives of this research were (1) to characterize, evaluate and compare the use of strong solid acid/basic catalysts for biodiesel forming reactions, e.g. transesterification of triglycerides and esterification of fatty acids, (2) to investigate the mechanistic aspects underlying catalyst activation and deactivation in transesterification and esterification, (3) to understand the most demanding traits required for practical solid catalysts in biodiesel synthesis, and (4) to investigate the structural effect of reacting molecules (such as increasing carbon chain length) on heterogeneous catalysis in an effort to justify the
rationality of the use of model compounds, and (5) to develop a better understanding of the relationship between the existing fundamental knowledge obtained using low molecular weight carboxylic acids/esters and the behavior of fatty acids/triglycerides in solid acid/base catalyzed esterification/transesterification.

Study started with an investigation into the impact of water for the acid catalyzed esterification using homogeneous catalyst, H$_2$SO$_4$. Acetic acid was used as model compound to simulate the behavior of fatty acid in acid catalyzed esterification with methanol. Controlled initial water addition along with initial kinetic measurements was used to increase the quantitative and conceptual understanding of the deactivating effect of water on acid catalyzed esterification.

In succession, the mechanistic aspects concerning the heterogeneous acid catalyzed esterification were investigated using a strong solid acid, Nafion supported on silica (SAC-13). The strong liquid acid, sulfuric acid, was used as the reference catalyst because it has similar acid site centers as those of SAC-13. The identical characteristic of having only protons as active sites suggests that the catalytic behavior of SAC-13 may resemble sulfuric acid. Thus, fundamental knowledge concerning the catalytic activity of sulfuric acid provides a good basis to probe and understand the catalytic behaviors of such solid acids.

A systematic kinetics study was made of the esterification of some FFA model compounds (Acetic acid, HAc; Propionic acid, HPr; Butyric acid, HBu; Hexanoic acid, HHx; Caprylic acid, HCp). This set of linear chain carboxylic acids was used in order to show the impact that increasing carbon chain length of the carboxylic acid has on acid catalysis for both homogeneous and heterogeneous catalyzed reactions. This study
permitted us to bridge the knowledge gap between reactions of small carboxylic acids and those of bulky FFAs such as can be found in a feedstock like poultry grease.

In parallel to the study of heterogeneous acid catalyzed esterification, the possibility in using strong solid bases with the basic functionality either being organic or inorganic for the effective catalyst for transesterification was also investigated fundamentally and practically with model compounds and poultry grease, respectively. Important assessing parameters such as catalytic activity, selectivity, deactivation and regeneration were emphasized.
CHAPTER 4

EFFECT OF WATER ON SULFURIC ACID CATALYZED ESTERIFICATION

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Abstract

This paper reports on an investigation into the impact of water on liquid phase sulfuric acid catalyzed esterification of acetic acid with methanol at 60°C. In order to diminish the effect of water on the catalysis as a result of the reverse reaction, initial reaction kinetics were measured using a low concentration of sulfuric acid (1x10^{-3} M) and different initial water concentrations. It was found that the catalytic activity of sulfuric acid was strongly inhibited by water. The catalysts lost up to 90% activity as the amount of water present increased. The order of water effect on reaction rate was determined to be -0.83. The deactivating effect of water also manifested itself by changes in the activation energy and the pre-exponential kinetic factor. The decreased activity of the catalytic protons is suggested to be caused by preferential solvation of them by water over methanol. A proposed model successfully predicts esterification rate as reaction progresses. The results indicate that, as esterification progresses and byproduct water is produced, deactivation of the sulfuric acid catalyst occurs. Autocatalysis, however, was found to be hardly impacted by the presence of water, probably due to compensation effects of water on the catalytic activity of acetic acid, a weak acid.
Introduction

Esterification of carboxylic acids with alcohols represents a well-known category of liquid-phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products. These ester products include environmentally friendly solvents, flavors, pharmaceuticals, plasticizers, polymerization monomers and emulsifiers in the food, cosmetic and chemical industries [1-3]. Recently, a growing interest in ester synthesis has been further stimulated due to the great promise shown by long chain mono alkyl esters as fuels for diesel engines [4, 5].

Esterification can take place without adding catalysts due to the weak acidity of carboxylic acids themselves. But the reaction is extremely slow and requires several days to reach equilibrium at typical reaction conditions. Either homogenous mineral acids, such as H₂SO₄, HCl or HI, or heterogeneous solid acids, such as various sulphonic resins, have been shown to be able to effectively catalyze the reaction. The catalysts essentially promote the protonation of the carbonyl oxygen on the carboxylic group, thereby activating nucleophilic attack by an alcohol to form a tetrahedral intermediate [5]. Disproportionation of this intermediate complex ultimately yields the ester (refer to Figure 4.1).

In spite of the long history of esterification and the large amount of literature concerning the performances of various catalysts and the kinetics of different ester syntheses, there are still many fundamental issues that remain poorly understood. For instance, an important subject that needs to be better understood is the effect that water
produced from esterification may have on the acid catalysis. Pronounced inhibition effects of water on homogenous acid catalyzed esterification have been reported by different researchers [4, 6-8]. For example, Aafaqi et al. [4] showed that, when esterification was carried out using homogenous p-TSA (para-toluene sulfonic acid) with an initial 15 vol% water, the conversion of carboxylic acids was decreased by around 40% (after 4h of reaction). Similarly, Hu et al. [7] found that homogenous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ lost about 30% of its catalytic activity when only 7.5 mol% water was introduced into the esterification of propionic acid with isobutyl alcohol at 70°C.

Few studies, however, have ever focused on how water actually affects reaction activity. The decrease in esterification kinetics in the presence of water has generally been attributed to reverse hydrolysis [4, 6]. The water retardation effect on ester formation, however, is not limited to esterification. Acid catalyzed transesterification has also been found to be inhibited in the presence of water [6, 7, 9, 10]. Moreover, when carried out in an alcoholic medium, acid catalyzed hydrolysis has been found to be faster than in an aqueous medium [11, 12]. Obviously, these observations suggest that the effect of water on esterification is more than just simple reverse hydrolysis. Smith [13], based on the assumption that the interaction between protonated methanol and carboxyl acid was the rate determining step, ascribed the effect of water on esterification to the competition for protons between water and methanol. More recently, it has been suggested that the hindered catalyst performance is due to the reduced acid strength of the catalyst caused by the coordination of water to protons [7].
Currently, knowledge regarding how water affects the efficiency of acid catalysts for esterification is quite limited and mostly qualitative. Thus, the focus of the present study was to increase the quantitative and conceptual understanding of the deactivating effect of water on acid catalyzed esterification. Here, the esterification of acetic acid with methanol using sulfuric acid was investigated with different initial water concentrations.

![Chemical reactions]

**Figure 4.1** Mechanistic route of acid catalyzed esterification.

**Experimental**

**Material**

Reagents including methanol (99.9%, Acros Organics), acetic acid (99.7 %, Aldrich) and water (HPLC, Acros Organics) were used without further purification. Because both methanol and acetic acid are hygroscopic, the moisture contents of the reagents were determined by Galbraith Laboratory using Karl Fischer titration. The analysis showed water contents of 160 ppm for methanol and 961 ppm for acetic acid. These moisture
contents were able to be ignored since they were very small compared to the amount of water produced during the initial reaction period.

**Reaction procedure**

Kinetic measurements were carried out in a Parr 4590 batch reactor that consisted of a stainless steel chamber of 50 ml, a three-blade impeller and a thermocouple. The temperature was maintained within +/- 0.5°C. Prior to reaction, a predetermined amount of reagent mixture was loaded into the reactor and heated to the desirable temperature while being stirred at 850 rpm. This mixing speed was determined to be sufficient to eliminate any mass transfer limitations. No change in reaction rate was detected when the stirrer speed was varied from 567 to 1417 rpm. The catalyst, concentrated sulfuric acid alone or diluted in a small amount of methanol, was charged into the reactor to initiate reaction. Although esterification occurs during the heating period due to autocatalysis, this starting method of reaction was the best way to ensure good control of temperature, which is particularly important for accurate determination of initial reaction kinetics (below 10% conversion of the limiting reagent). A microscale syringe was used for sampling at definite time intervals. A sample was always taken right before catalyst charging as the zero point for every run. Samples from the reaction mixture were immediately diluted in cold 2-propanol, and reaction stopped because of cooling and dilution.

A Hewlett-Packard 6890 gas chromatograph equipped with a DB-1 column (0.32mm
x 30m x 0.53µm) and a FID detector was used for sample analysis with toluene as an internal standard. The concentrations of all species (except water) were accurately quantified and found to obey well the stoichiometry of the reaction, which along with the nonappearance of unknown peaks as detected by GC analysis indicated the absence of side reactions under the experimental conditions used.

Experimental design

In order to better observe the effect of water on reaction and to minimize the contribution of reverse hydrolysis, a small amount of catalyst \((C_C = 1 \times 10^{-3} \text{ M})\) was used and attention was focused particularly on the initial period of reaction. A series of experiments with varying amounts of initial water addition were carried out at 60°C with a fixed catalyst concentration. Table 4.1 shows initial concentrations of reagents and the concentrations of water initially added. The initial water concentrations used corresponded to the amounts of water that could have been produced by esterification at different conversions. The idea behind this approach was to observe how catalyst activity is affected with increasing concentration of water, as occurs during esterification.

Because the molar ratio of methanol-to-acetic acid was kept constant and no solvent was used, kinetic comparisons are based on reaction constants instead of reaction rates. As mentioned earlier, esterification can be autocatalyzed by acetic acid itself. At 60°C, the rate of autocatalysis was about a seventh of the overall catalysis rate when only \(1 \times 10^{-3} \text{ M}\) sulfuric acid was employed. Therefore, esterification occurred as a combination
of two catalytic routes. As has been reported [14-18], homogenous acid catalyzed and auto-catalyzed esterification follows second order and third order kinetics, respectively. Thus, the overall esterification rate can be written as:

\[-\frac{dC_A}{dt} = (k_CC_c + k_{Auto}C_A)C_AC_M - (k_{-C}C_c + k_{-Auto}C_A)C_EC_W\]  \(1\)

Where \(k_C\) and \(k_{Auto}\) represent the observed acid catalyzed and auto-catalyzed esterification constants respectively, \(k_{-C}\) and \(k_{-Auto}\) are related to reverse hydrolysis; \(C_c, C_A, C_M, C_E\) and \(C_W\) denote the concentrations of sulfuric acid, acetic acid, methanol, methyl acetate ester and water, respectively. For initial kinetic measurements, because reverse hydrolysis is negligible and \(k_CC_c + k_{Auto}C_A \approx k_CC_c + k_{Auto}C_{A,0}\), equation (1) can be reduced, in terms of acetic acid conversion (\(x = \frac{C_{A,0} - C_A}{C_{A,0}}\)), to

\[\frac{dx}{dt} = [k_CC_cC_{A,0} + k_{Auto}C_{A,0}^2](1-x)(\frac{C_{M,0}}{C_{A,0}} - x)\]  \(2\)

Integrating equation (2) and letting \(k_i = k_CC_c + k_{Auto}C_{A,0}\), at \(C_{M,0}/C_{A,0}=2\), we have:

\[\ln\left(\frac{2-x_i}{1-x_i}\right) - \ln\left(\frac{2-x_0}{1-x_0}\right) = k_iC_{A,0}t\]  \(3\)
where \( x_0 \) and \( x_t \) represent the conversion of acetic acid at time=0 and time=\( t \), respectively. Thus, \( k_1 \) can be determined by applying equation (3) to experimental data. Typical plots of \( \ln[(2-x)/(1-x)] \) versus \( t \) are shown in Figure 4.2, and \( k_1 \) values were calculated from the slopes of these plots. In a similar way, the autocatalytic reaction constant \( k_{Auto} \) was able to be obtained using equation (2), setting \( C_C=0 \), and integrating:

\[
\left[ \frac{1}{1-x} - \ln\left(\frac{2-x}{1-x}\right) \right]_{x_0}^{x_t} = k_{Auto} C_{A,0}^2 t
\]

(4)

Note, reaction constants calculated this way are actually average values for the initial reaction period. Because water is produced by esterification, the water concentration used must account for both the initial water added and the average amount of water formed during the reaction period:

\[
C_W = C_{A,0}(w + \bar{x})
\]

(5)

where \( w \) is the molar ratio of water initially added to the acetic acid, \( C_{W,0}/C_{A,0} \) and \( \bar{x} \) is the average conversion of acetic acid from \( t=0 \) to \( t=t \).
Table 4.1 Concentrations of initial water added ($C_{W,0}$) and equivalent acetic acid conversion based on the initial acetic acid concentration ($C_{A,0}$) and the amount of water initially added.

<table>
<thead>
<tr>
<th>Initial water added (M)$^a$</th>
<th>0</th>
<th>0.5</th>
<th>1.3</th>
<th>2.6</th>
<th>9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{A,0}$ (M)$^a$</td>
<td>7.32</td>
<td>7.26</td>
<td>7.20</td>
<td>7.07</td>
<td>6.27</td>
</tr>
<tr>
<td>$C_{M,0}$ (M)$^a$</td>
<td>14.6</td>
<td>14.5</td>
<td>14.4</td>
<td>14.1</td>
<td>12.5</td>
</tr>
<tr>
<td>Equivalent acetic acid conversion based on $C_{A,0}$ and initial amount of water added</td>
<td>0.0%</td>
<td>6.3%</td>
<td>14.9%</td>
<td>27.0%</td>
<td>58.8%</td>
</tr>
</tbody>
</table>

$a.$ experimental error: +/-1%

Figure 4.2 Suitability of equation (3) to experimental data collected in initial period of reaction catalyzed by $1 \times 10^{-3}$M H$_2$SO$_4$. 

![Graph showing the logarithm of the reaction rate vs. time for different initial water concentrations. The graph shows a linear relationship with a slope that increases with the initial water concentration.](image-url)
Results and Discussion

The reaction constants for autocatalysis, $k_{\text{Auto}}$, at 60°C and at different initial water concentrations are summarized in Table 4.2. The autocatalytic activity was almost unchanged when water content varied from 0.4 to 9.3 M. The small fluctuation in $k_{\text{Auto}}$ can be ascribed to experimental errors. However, the multiple roles of water in autocatalysis could also account for some of this small variance. This will be discussed in more detail later. Since the water concentration range used covered the equivalent conversions of acetic acid from about 5% to 60%, it is clear that autocatalysis is hardly affected by the increasing concentration of water produced as esterification progresses. Hence, the $k_C$ can be determined by using the average $k_A$ value of $12.4 \times 10^{-6} \text{ (M}^2\cdot\text{min}^{-1})$, 

$$k_C = (k_i - 12.4 \times 10^{-6} C_{A,0}) / C_C.$$ 

By plotting $k_C$ versus $C_W$, the impact of water on sulfuric acid catalyzed esterification was able to be determined (Figure 4.3). In contrast to autocatalysis, the catalytic activity of sulfuric acid was significantly decreased by water; the greatest decrease was manifested at low water concentrations. The rate constant appeared to approach a limiting value as water concentration increased to above 6 M with the concentration of catalyst used in our experiments. Using a power law model, the effect of water concentration on the rate constant was found to be -0.83 order:

$$k_C = 0.38 C_W^{-0.83} \left( \frac{l}{\text{mol} \cdot \text{min} \cdot \text{Mcat}} \right)$$ (6)
Table 4.2 Dependence of autocatalytic reaction constant ($k_A$) on water content ($T=60^\circ$C, $C_{M,0}/C_{A,0}=2$).

<table>
<thead>
<tr>
<th>$C_W$ (M)$^{a,b}$</th>
<th>0.4</th>
<th>1.6</th>
<th>3.0</th>
<th>9.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{A,0}$ (M)$^c$</td>
<td>7.3</td>
<td>7.2</td>
<td>7.1</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Equivalent acetic acid conversion based on $C_{A,0}$ and initial amount of water added:

| $k_{Auto}$ ($1/M^2.min)x10^6$ | 13.7 | 11.2 | 11.6 | 13.0 |

$^{a}$ Water concentration includes both the initial amount of water added and the average amount formed during the initial period of esterification: $C_W = C_{A,0} (w + \bar{w})$, $w = C_{W,0}/C_{A,0}$

$^{b}$ Experimental error: +/-3%

$^{c}$ Experimental error: +/-1%

Figure 4.3 Dependence of $k_c$ on water concentration ($T=60^\circ$C, $C_{M,0}/C_{A,0}=2$). The dotted line represents the fitted power law model $k_C = 0.38C_w^{-0.83} (1/M.min.Mcat)$. 

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To confirm the absence of contributions from reverse hydrolysis even for very high initial water concentrations, a series of experiments with initial methyl acetate introduction instead of water were carried out and results are shown in Table 4.3. Interestingly, larger rate constants for product formation were observed with ester addition rather than being decreased by reverse hydrolysis. However, the addition of an inert (tetrahydrofuran, THF), yielded an identical kinetic enhancement. Here, it should be noted that the ester/THF introduction actually replaced a partial amount of reactants due to the absence of a solvent. Consequently, less water was able to be produced during the initial reaction period of acetic acid (<10% conversion). Therefore, the apparent positive effect exhibited by ester/THF was probably due to this decreased water concentration. This possibility was then confirmed by estimation of the respective reaction constant ($k_C$) from equation (6) (Table 4.3). The good agreement between estimated and experimental values supports the earlier hypothesis. The primary role of methyl acetate present during initial reaction period was then that of a dilution agent just like THF. Therefore, the variance of $k_C$ as determined in the present study is little affected by any contribution of reverse hydrolysis.

The impact of molar ratio on the inhibition effect of water on acid catalysis was also inspected by fixing the water concentration while varying the molar ratio of alcohol-to-carboxylic acid (Table 4.4). It was found that as the methanol-to-acetic acid molar ratio was increased from 2:1 to 20:1, the reaction rate constant remained unchanged at a fixed water concentration of 3.0 M. This result points to a conclusion that
the impact of water on the catalytic activity of sulfuric acid is not affected by the methanol or acetic acid concentration at the $C_W$ of 3.0 M.

**Table 4.3** Variation of $k_C$ with the ester concentration ($C_E$) and predicted $k_C,_{\text{calc}}$ from equation (6) ( $T=60^\circ\text{C}$, $C_{M,0}/C_{A,0}$=2)

<table>
<thead>
<tr>
<th>$C_E$ (M)$^{a,b}$</th>
<th>0.5</th>
<th>2.6</th>
<th>5.9</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{THF}}$ (M)$^c$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>$C_W$ (M)$^b$</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$k_C$ (l/M.min. Mcat.)$^d$</td>
<td>0.67</td>
<td>0.99</td>
<td>1.28</td>
<td>1.23</td>
</tr>
<tr>
<td>$k_C,_{\text{calc}}$ (1/M.min. MCat.)</td>
<td>0.71</td>
<td>0.99</td>
<td>1.30</td>
<td>1.30</td>
</tr>
</tbody>
</table>

*a. Ester concentration includes both the initial amount of ester added and the average amount formed during the initial period of esterification: $C_E = C_{A,0}(e + \bar{e})$, $e = C_{E,0}/C_{A,0}$
*b. Experimental error: +/-3%
*c. Experimental error: +/-1%
*d. Experimental error: +/-5%

**Table 4.4** Impact of initial molar ratio of methanol-to-acetic acid on the effect of water on sulfuric acid catalysis (T=60°C, $C_w$=3.0 M)

<table>
<thead>
<tr>
<th>$C_{M,0}/C_{A,0}$</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{M,0}$ (M)$^a$</td>
<td>14.6</td>
<td>18.5</td>
<td>20.8</td>
<td>22.0</td>
</tr>
<tr>
<td>$C_{A,0}$ (M)$^a$</td>
<td>7.3</td>
<td>3.7</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td>$k_C$ (1/M.min. MCat.)$^b$</td>
<td>0.15</td>
<td>0.14</td>
<td>0.15</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*a. Experimental error: +/-1%
*b. Experimental error: +/-5%

In addition to molar ratio, temperature is another crucial operational parameter. The sensitivity of acid catalysis to water was also examined at 40°C. The apparent order of
water effect on reaction rate was found to be almost identical to that at 60°C, as evidenced by the parallel lines in Figure 4.4. The apparent activation energies and pre-exponential factors were determined at different water concentrations using the **Arrhenius relationship** (Figure 4.5):

\[
\ln k = -\frac{\Delta E^\#}{R} \cdot \frac{1}{T} + \ln A
\]

Results are tabulated in Table 4.5. The increase in water concentration from 0.3 M to 2.9 M, resulted in a 15 kJ increase in \(\Delta E^\#\). However, the enhanced energy barrier was partially compensated for by a simultaneously increase in the pre-exponential factor of around 2 orders of magnitude. If compared to the “transition state theory” represented by the **Eyring equation**:

\[
\ln \frac{k}{T} = -\frac{\Delta H^\#}{R} \cdot \frac{1}{T} + \left(\frac{k_B}{h} + \frac{\Delta S^\#}{R}\right)
\]

where \(k\) is rate constant, \(\Delta H^\#\) is activation enthalpy, \(\Delta S^\#\) is activation entropy, \(k_B\) and \(h\) are Boltzmann and Planck constants respectively, our results actually indicate a rise in activation enthalpy and entropy caused by water. On the other hand, neither the enthalpy nor entropy term change linearly with water concentration. With a further even larger increase in water concentration from 2.9 M to 9.2 M, only very small changes
were found for in $E^s$ and A.

As shown by the initial kinetic measurements, water has a distinct inhibition effect on sulfuric acid catalysis. However, in many kinetic studies of esterification with either homogenous catalysts [1, 14] or pseudo-homogenous resin catalysts [19, 20], constant catalytic activity independent of reaction progress has been assumed. Few efforts have been made to address the deactivating effect of water on acid catalysis and elucidate the phenomena in a quantitative and conceptual way. In a kinetics study of sulfuric acid catalyzed esterification of palmitic acid by Goto et al. [8], the inhibition effect of water was included in their rate expression. However, their mechanistic scheme was based on the assumption that the protonation of carboxylic is the rate determining step. Nowadays, studies using modern techniques have shown that the protonation of carbonyl oxygen is fast and occurs in a quasi-equilibrium step in the presence of strong acids [21]. The accepted mechanism regards the formation of a tetrahedral intermediate from the nucleophilic attack of alcohol on the protonated carboxylic acid as the rate-limiting step [5, 15, 22] (refer to Figure 1). In an aqueous medium, sulfuric acid dissociates into hydronium ions and bisulfate ions. $\text{H}_3\text{O}^+$ ions are strong acidic species, so it is unlikely that the increasing amount of water could change the rate-limiting step. Otherwise, ester/ether hydrolysis would not have a symmetric/analogic mechanistic route as esterification as suggested by kinetic studies [21, 23-25].
Figure 4.4 Determination of apparent reaction order of water at different temperatures ($C_{M,0}/C_{A,0}=2$).

Figure 4.5 Arrhenius plots of esterification at different water concentrations ($T=30-60^\circ C$, $C_{M,0}/C_{A,0}=2$).
Table 4.5 Variation of apparent activation energy and pre-exponential constant at different concentrations of water (30–60°C)

<table>
<thead>
<tr>
<th>$C_w$ (M)$^a, b$</th>
<th>0.3</th>
<th>2.9</th>
<th>9.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E^#$ (kJ/mol)$^c$</td>
<td>46</td>
<td>61</td>
<td>61</td>
</tr>
<tr>
<td>$A \times 10^{-7}$</td>
<td>1.46</td>
<td>80.7</td>
<td>53.6</td>
</tr>
<tr>
<td>$\ln A$</td>
<td>16.5</td>
<td>20.5</td>
<td>20.1</td>
</tr>
</tbody>
</table>

a. $C_w = C_{A,0}(w + \bar{x})$, $w = C_{W,0}/C_{A,0}$

b. Experimental error: +/-3%
c. Experimental error: +/-5%

Two main possibilities exist for the deactivating effect of water on sulfuric acid catalysis: 1) decreased acid strength and/or 2) loss of catalyst accessibility. In terms of Bronsted acidity, Sadek et al. [11] have suggested that ROH$_2^+$ is more acidic than H$_3$O$^+$ to explain the enhanced ester hydrolysis in the presence of glycol and glycerol. Indeed, according to the solvation chemistry of protons, the strength of strong acids like sulfuric acid is determined by the solvation state of protons rather than the extent of dissociation. The more strongly solvated a proton is, the lower the chemical and catalytic activity of the proton [26]. If the acid strengths of methoxonium and hydroxonium ions are examined without accounting for the interactions among solvating molecules, such as comparing single MeOH$_2^+$ and H$_3$O$^+$ in vacuum, one would expect MeOH$_2^+$ to be a weaker acid than H$_3$O$^+$, given the greater inductive effect of the methyl group in methanol. This means that gaseous methanol molecules would have a higher proton affinity [26, 27]. Consequently, the higher intrinsic basicity of methanol with respect to
water would give rise to a weaker conjugated acid (MeOH_2^+). This is contrary to the suggestion by Sadek et al. [11] of more acidic ROH_2^+ with respect to H_3O^+.

On the other hand, in condensed phase where molecular interactions must be accounted for, the solvation state of protons is determined by the overall contributions of all solvating molecules. Multiple water molecules are known to form strong hydrogen bond networks through which a charged species can be delocalized and therefore stabilized [28]. Methanol, compared to water, with one hydrogen atom replaced by a -CH_3 group, has less ability to form hydrogen bonds [28]. As indicated by a higher Gutmann’s Donor Number (DN=33), water is a better electron pair donor and can establish a stronger interaction with cationic species, stabilizing them better than methanol (DN=19) [29, 30]. Therefore, in line with the higher electron donating capacity, a larger enthalpy release would be expected for the proton solvation process in water making the enthalpic state of the H_3O^+ less positive than MeOH_2^+. On the other hand, water can preferentially self-orient to oppose the external field created by cations due to its high polarity. In turn, water has been described as a proton “sponge” [31] where protons can be easily accommodated inside the “self-assemble” water network with an associated lower entropic state. Methanol molecules, however, having a smaller orientational polarizability than water and being less symmetric due to the -CH_3 group, can only accommodate protons in their hydrogen bond network in a less ordered way than water does.

Accordingly, in acid-base reactions with a given substrate,
the hydroxonium reaction would require more energy than its methoxonium counterpart. That is, \( 0 < \Delta H_{MS} < \Delta H_{WS} \), which translates to weaker acid strength for protons inside the solvation sphere of water. But deprotonation of hydroxonium has a larger entropic force due to its lower entropic state, \( 0 < \Delta S_{MS} < \Delta S_{WS} \). Thus, when the higher enthalpy demand in reaction (II) is not compensated for by its entropy gradient at temperature T, formation of \( \text{SH}^+ \) is more favorable via reaction (I) due to \( \Delta G_{MS} < \Delta G_{WS} \). In esterification, where S is the carboxylic acid and the reaction rate is determined by the nucleophilic attack of the alcohol on a protonated acetic acid molecule, lower concentrations of \( \text{CH}_3\text{COOH}^+ \) will certainly result in hindered kinetics. Thus, we conclude that the diminished catalytic activity observed as the concentration of water increases is likely a consequence of acid strength decline due to strong solvation of protons by water molecules.

As shown in Table 5, our measurements of reaction thermodynamics agree well with the above thermodynamic interpretation. Thus, as proton solvation by water takes over, higher energy is required for the protonation of the C=O moiety in acetic acid by \( \text{H}_3\text{O}^+ \) proton carriers. On the other hand, larger entropy release accompanying protonation of
substrates contributes more geometric configurations for the subsequent nucleophilic attack by alcohol and increases the collision efficiency. In addition, this variation of proton activity with water concentration (Figure 3) is in good agreement with other observations of proton-related characteristics, proton dissociation rate and acid-base equilibrium constant in water-organic mixtures [31]. Water was found to produce the greatest decrease in activity for esterification at low water concentrations ($C_W = 0\sim3M$) where it constituted 0-10% of the total amount of (H$_2$O+MeOH) present. This is almost identical to the results of Pines and Fleming [31] for the impact of water on proton dissociation lifetimes in a H$_2$O+MeOH mixture (Fig. 1, ref. [31]) and for the acid-base equilibrium constant of protonated aniline in a H$_2$O+MeOH mixture (Fig. 4, ref. [31]), where the greatest impact was seen for $C_W = 0\sim4.5M$ (also 0-10% of the total amount of (H$_2$O+MeOH) present). This narrow range has been explained in terms of the great preference of water as proton acceptor over methanol by Pines and Fleming [31]. Beyond this range, water seems to dominate the solvation sphere of protons, resulting in the protons behaving fairly constantly with increasing water concentration.

The strong correlation between the competitive proton solvation of water and methanol and the observed esterification kinetic and thermodynamic data can be accounted for by the following set of chemical equations describing a mechanistic path:

$$2H_2SO_4 + CH_3OH + H_2O \xrightarrow{fast} CH_3OH^+ + H_3O^+ + 2HSO_4^-$$

(M-1)
\[ \text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{OH} + \text{CH}_3\text{COOH}_2^+ \]  
\[ (\text{MH}^+) \quad (A) \quad (M) \quad (AH^+) \]  
\[ (\text{M-2}) \]

\[ \text{H}_3\text{O}^+ + \text{CH}_3\text{COOH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{COOH}_2^+ \]  
\[ (\text{WH}^+) \quad (A) \quad (W) \quad (AH^+) \]  
\[ (\text{M-3}) \]

\[ \text{CH}_3\text{OH} + \text{CH}_3\text{COOH}_2^+ \rightleftharpoons \text{CH}_3\text{COOCH}_3\text{H}^+ + \text{H}_2\text{O} \]  
\[ (M) \quad (AH^+) \quad (EH^+) \quad (W) \]  
\[ (\text{RDS} \text{ M-4}) \]

\[ \text{CH}_3\text{COOCH}_3\text{H}^+ + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{COOCH}_3 \]  
\[ (EH^+) \quad (M) \quad (MH^+) \quad (E) \]  
\[ (\text{M-5}) \]

\[ \text{CH}_3\text{COOCH}_3\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COOCH}_3 \]  
\[ (\text{M-6}) \]

First, let us consider what applies during the initial reaction period where reverse hydrolysis is not important. For (M-4) being the RDS, the forward rate expression can be written as:

\[ r = kC_{AH}C_M \]  
\[ (7) \]

With the assumption of fast protonation steps (M-2) and (M-3) occurring in quasi-equilibrium and the consideration of the charge balance in the reaction mixture...
while neglecting the contribution of AH\(^+\), EH\(^+\) and the second proton dissociation of sulfuric acid, the rate expression becomes:

\[
I = \frac{kC_C}{\frac{C_M}{K_M} + \frac{C_W}{K_W}} C_A C_M
\]  

(8)

As defined by reactions (M-2) and (M-3), \(K_M\) and \(K_W\) are the equilibrium constants for the protonation of acetic acid from methanol and water respectively. These constants represent the extent of proton exchange in reactions (M-2) and (M-3) and are related to the acid strength of MH\(^+\) and WH\(^+\). By subtracting reaction (M-3) from (M-2), \(K_M\) is connected to \(K_W\) by the proton exchange constant in methanol-water mixtures:

\[
CH_3OH_2^+ + H_2O \leftrightarrow K_{MW} \rightarrow CH_2OH + H_3O^+
\]  

(III)

\[
K_{MW} = \frac{K_M}{K_W} = \left(\frac{1}{K_W}\right) \left(\frac{1}{K_M}\right)
\]  

(9)

When the reaction mixture is anhydrous or the concentration of water is significantly low, equation (8) can be reduced to:
\[ r_l = \frac{k}{(C_l/K_l)} C_C C_A C_M \]  \quad (10)

\[ k_{C,l} = k K_{M}/C_M \]  \quad (11)

where \( r_l \) represents reaction rate of esterification at low \((l)\) water concentration and \( k_{C,l} \) is the reaction constant. Therefore, according to equation (11), the temperature dependency of \( k_{C,l} \) (apparent activation energy) is a result of the combination of the RDS and M-2 steps:

\[ \frac{\partial \ln k_{C,l}}{\partial (1/T)} = \frac{\partial \ln k}{\partial (1/T)} + \frac{\partial \ln K_M}{\partial (1/T)} \sim \frac{-\Delta E_l^\#}{R} \]  \quad (12)

where \( E_l^\# \) is the activation energy of esterification at low water concentrations.

On the other hand, as esterification proceeds, alcohol is consumed while water is produced. When the methanol term becomes less important and may be considered negligible at high water concentration, we have:

\[ r_h = \frac{k}{(C_w/K_w)} C_C C_A C_M \]  \quad (13)
\[
\frac{\partial \ln k_{c,h}}{\partial (1/T)} = \frac{\partial \ln k}{\partial (1/T)} + \frac{\partial \ln K_m}{\partial (1/T)} \sim -\frac{\Delta E_h^\#}{R}
\]  \hspace{1cm} (14)

where \(r_h, k_{c,h}\) and \(E_h^\#\) represent reaction rate, reaction constant and activation energy of esterification at the high (h) water concentrations, respectively. From equation (9), (12) and (14), the difference in apparent activation energy between low and high water concentrations can be expressed as:

\[
\frac{\Delta E_h^\# - \Delta E_i^\#}{R} \sim \frac{\partial (\ln K_{MW})}{\partial (1/T)}
\]  \hspace{1cm} (15)

Using the Van’t Hoff equation, the increase in apparent activation energy caused by an increase in \(C_W\) can be related to the reaction enthalpy of proton exchange between water and methanol:

\[
\frac{\Delta E_h^\# - \Delta E_i^\#}{R} = -\frac{\Delta H_{MW}}{R}
\]  \hspace{1cm} (16)

Similarly, the difference in pre-exponential factor at high and low water content regimes can be related to the entropy term of the same reaction:

\[
\ln A_h - \ln A_i = -\frac{\Delta S_{MW}}{R}
\]  \hspace{1cm} (17)
The thermodynamic characteristics of proton exchange between water and methanol have been studied at 25°C by Zhurenko et al.[32]. Since ΔS and ΔH are usually weakly dependent on temperature, the data from Zhurenko et al. may be used to check the validity of equation (16) and (17). From Table 5, the determined difference in ΔE° and lnA between high (C_W=2.9 M) and low (C_W=0.3 M) water concentrations are 15 kJ and 4.0 respectively. Both of these values are in fairly good agreement with Zhurenko, but somewhat higher: −ΔH_MW=9.1 kJ/mol, −ΔS_MW/R = 2.26. Although the difference may be partially accounted for by the differences in methodology for data acquisition and the deviation of components from ideality in our reaction mixtures, the possible reduced accessibility of acetic acids to protons due to a heavy hydrophilic hydration sphere may have also played a role. In addition, for nucleophilic substitution, the different sensitivities of transition state and ground state to the change in solvent medium may be another cause for the increase in apparent activation energy [33].

From equation (8), the sulfuric acid catalysis constant can be written as:

\[ k_c = \frac{k}{\frac{C_M}{K_M} + \frac{C_W}{K_W}} \]  

(18)

Comparing equation (18) to equation (6) (experimental correlation between C_W and k_c), the -0.83 apparent order, while not -1, can be explained by the presence of the methanol
term in the denominator of equation (18). Moreover, the comparison supports the predominant impact of water as previously shown, which almost covers the entire esterification process unless a large excess methanol is used. Equation (18) also agrees with the experimental determination of the apparent reaction order of alcohol being 1 at low alcohol-to-carboxylic acid molar ratios [14, 15] while 0 at high molar ratios with simultaneous water removal [34, 35].

It is worthwhile to recall that the acid strength of strong acids is determined by solvation state of protons, while for weak acids, the overall acidity depends on both proton dissociation extent and solvation energy [26]. During autocatalysis, esterification is catalyzed by acetic acid which is well known as a weak organic acid. In principle, both acetic acid molecules and dissociated protons can activate the C=O group, catalyzing esterification:

\[
CH_3COOH + CH_3COOH \rightleftharpoons CH_3COOH^+ + CH_3COO^-
\]

\[
H^+ + CH_3COOH \rightleftharpoons CH_3COOH^+
\]

but second order kinetics with respect to acetic acid indicates that undissociated acid protolysis dominates over the proton catalyzed route [16]. This is probably due to the low availability of protons from the weakly dissociated parent acid (pKa = 9.72, in pure methanol [36]). Water, on the other hand, is able to promote the dissociation extent of
weak acids due to its ability to stabilize carboxylate anions and protons electrostatically[28, 36, 37]. Thus, with increasing water content, more protons would be released to solution through acetic acid dissociation; however, the catalytic activity of these newly available protons would be diminished due to the same water characteristics that promote acetic acid dissociation. In addition, water is also believed to promote protolysis between carboxylic acid molecules by interacting with acetic acid molecules in such a way that provides a low-energy pathway for proton transfer [38]. Thus, the weak sensitivity of autocatalysis to water should be a result of these multiple balancing effects, higher acetic acid dissociation, inter-molecular proton transfer, and proton deactivation.

Finally, a mathematical model has been developed to account for the deactivating effect of water on acid catalysis during the course of esterification. Although equation (6) is relatively less general compared to equation (18) which is derived mechanistically, the absence of accurate determinations of $K_M$ and $K_W$ makes more difficult the application of equation (18). Therefore, using equation (6) and inserting it into equation (1), we obtain:

$$-\frac{dC_A}{dt} = C_c \cdot \left(0.38 \cdot \frac{C_A C_M - \frac{C_E C_W}{K}}{C^W_{0.83}}\right) + k_A C_A(C_A C_M - \frac{C_E C_W}{K})$$  \hspace{1cm} (19)

where $K$ is the equilibrium constant for esterification at reaction temperature ($K=6.22$ at $60^\circ$C). Autocatalysis can be neglected when using high catalyst concentrations, thus equation (19) reduces to
For a molar ratio of $C_{M,0}/C_{A,0} = 2$, when expressed in terms of acetic acid conversion, equation (20) becomes:

$$-rac{dC_A}{dt} = C_c \cdot \left( \frac{0.38}{C_w^{0.83}} \right) \cdot (C_A C_M - \frac{C_c C_w}{K})$$  \hspace{1cm} (20)$$

By using numerical integration (Runga-Kutta), the acetic acid conversion at a given time can be predicted from equation (21). To check the applicability of equation (21), experiments using higher catalyst concentrations, 0.5 wt% and 2 wt% ($C_c = 0.046$ M and 0.224 M), with and without initial water addition were conducted. As shown in Figure 4.6, experimental results are successfully predicted using equation (21) for all cases. The good agreement between predicted and experimental data further supports applicability of equation (6) and the validity of initial kinetic measurements as an approach to help build a practical reaction model.
Figure 4.6 Comparison of experimental data with values predicted by equation (21) for esterification of acetic acid with methanol at 60°C and $C_{M,0}/C_{A,0}=2$ (symbol is experimental data; dashed line is model prediction).

Summary

The effect of water on liquid phase sulfuric-acid-catalyzed esterification of acetic acid with methanol was studied by initial water addition. The decrease in initial reaction kinetics with increasing concentration of water indicated that catalysis is impaired as esterification proceeds and water is continuously produced from the condensation of carboxylic acids and alcohols. The negative impact of water on catalysis was found to be essentially independent of temperature or molar ratio of methanol-to-acetic acid under the experimental conditions used. The thermodynamic concordance between proton solvation in binary mixtures of methanol/water and esterification indicates a strong correlation between preferential proton solvation by water and the observed deactivating
effect of water. It would appear that the loss in acid strength of catalytic protons due to water solvation leads to a decrease in the concentration of protonated carboxylic acid, thus inhibiting the formation of esters. Not only esterification but also other reactions may also suffer such a deactivating effect of water when catalyzed by strong protonic acids. Thus, the simultaneous water removal during reaction should not only inhibit the reverse hydrolysis reaction, but also preserve high activity of the catalytic protons throughout reaction.
References


CHAPTER 5
A COMPARISON OF THE ESTERIFICATION OF ACETIC ACID WITH METHANOL USING HETEROGENEOUS VS. HOMOGENEOUS ACID CATALYSIS


Abstract

In order to investigate the similarities and differences between the heterogeneous and homogeneous catalyzed esterification, the kinetics of acetic acid esterification with methanol were investigated using a commercial Nafion/silica nanocomposite catalyst (SAC-13) and H₂SO₄, respectively. Reactions were carried out in an isothermal well-mixed batch reactor at 60°C. Organic base titration, TGA and elemental sulfur analysis were carried out to estimate the acid site density of SAC-13, permitting the assessment of its catalytic performance for esterification on a per site basis. It was found that SAC-13 has comparable site activity for acetic acid esterification as H₂SO₄. SAC-13 and H₂SO₄ also exhibited similar reaction inhibition due to the presence of water. The similar response to the presence of water and the results of pyridine poisoning experiments suggest that esterification with these catalysts occurs through a common reaction mechanism. Consistent with the hypothesized homogeneous-type reaction mechanism, reaction on SAC-13 appears to involve single-site catalysis with a probable rate-controlling Eley-Rideal surface reaction. A mechanistically derived kinetic model
successfully predicts the esterification rate of SAC-13 as reaction progresses. The dissimilarities existing between homogeneous and heterogeneous acid catalyzed esterification are also discussed.

**Introduction**

Organic esters are important fine chemicals widely used in the manufacture of flavors, pharmaceuticals, plasticizers and polymerization monomers. They are also used as emulsifiers in the food and cosmetic industries. There are several synthetic routes available to obtain organic esters and most have been briefly reviewed by Yadav and Mehta [1]. The most used methodology for ester synthesis is direct esterification of carboxylic acids with alcohols in the presence of acid catalysts.

Strong liquid mineral acids, such as H₂SO₄, HCl and HI, are effective for the esterification of carboxylic acids. These homogenous acid catalysts and others have been the subject of extensive studies. It has been well documented, for instance, that when using this type of catalysts the slow step of the reaction is the nucleophilic attack of the alcohol on the protonated carbonyl group of the carboxylic acid [2, 3]. This mechanistic route involves first the protonation of the carboxylic acid, which activates it for reaction with non-protonated methanol to yield a tetrahedral intermediate that by decomposition produces the products of reaction, ester and water.

On solid acid catalysts with mainly Brønsted acid sites, one might expect a similar esterification behavior with a homogeneous-like mechanism mediating the molecular transformation [4]. However, thus far, it appears there is no consensus about the reaction mechanism occurring on different (although similar) solid acid catalysts. In particular, the
literature has many contradictory reports about whether esterification occurs via a single site (Eley-Rideal, E-R) or a dual site mechanism. For instance, using kinetic correlations of experimental data, Teo and Saha [5] and Lee et al. [6] found that a dual site model fit better the behavior of acid resin catalysts used in the esterification of acetic acid with amyl alcohol. In contrast, for the esterification of hexanoic acid with 1-octanol using zeolite BEA and SAC-13, an E-R kinetic model yielded better results with 15% lower error in fitting the experimental reaction results [7]. Altiokka and Citak [8] proposed an E-R mechanism involving the reaction of isobutanol adsorbed on the acid sites of an Amberlyst catalyst with free acetic acid from the bulk solution as the primary route for esterification. However, just the opposite picture was proposed by Lilja et al. [9], where the rate determining reaction step was suggested to be the nucleophilic attack by the liquid alcohol on the adsorbed carboxylic acid on the Brønsted acid sites of Amberlyst-15.

The focus of the present study was to provide a fundamental insight into the similarities and differences existing between heterogeneous and homogeneous Brønsted acid catalyzed esterification. Here, esterification on a solid acid catalyst, SAC-13 (Nafion resin supported on a porous silica matrix), was compared to esterification in the presence of \( \text{H}_2\text{SO}_4 \). The resin/silica composite is strongly acidic, with highly accessible sites and robust enough to withstand reasonably high temperatures (~200°C) and attrition stress [10]. Having only protons as active acid sites similar to \( \text{H}_2\text{SO}_4 \), one might expect that SAC-13 would show a catalytic behavior resembling that of the homogeneous catalyst. Thus, the similarity between these two catalysts provided a good way to examine the effect of the heterogeneous catalyst surface on catalyst activity and mechanistic pathway.
Determination of reaction kinetic parameters together with the derivation of an analytical kinetic model able to satisfactorily explain our experimental observations led to some important insights. The derived kinetic model was also able to account for the apparent contradictory reports made by other authors on esterification catalyzed by solid acids.

**Experimental**

Methanol (MeOH: 99.9 wt%, Acros Organics), acetic acid (HAc: 99.7 wt%, Aldrich) and tetrahydrofuran (THF, 99.9 wt%, Aldrich) were used without further purification. Concentrated sulfuric acid was purchased from Fisher Scientific, and SAC-13 was obtained from Aldrich. SAC-13 was dehydrated at 80°C under vacuum and stored in a desiccator until use.

Using a Pyris 1 TGA (Perkin Elemer), thermogravimetric analysis was conducted to determine the loading of Nafion on the composite catalyst. Under a nitrogen atmosphere, the temperature was first stabilized at 25°C for 30 min and then ramped to 700°C at 10°C/min. The fraction of Nafion in the composite was calculated based on the weight loss observed in the range 280-500°C, corresponding to the decomposition window for Nafion-H domains [10]. Elemental sulfur analysis of SAC-13 was performed by Galbraith Laboratories. Pyridine adsorption experiments were carried out by saturating SAC-13 in a solution containing a known concentration of pyridine in THF. A GC was used to quantify the amount of pyridine adsorbed on the catalyst, calculated from the difference in pyridine concentration in solution before and after SAC-13 saturation.

Reactions were carried out in an isothermal well-stirred batch reactor as shown in reference [11]. In brief, prior to reaction, reagent mixtures (methanol and acetic acid in a
2:1 molar ratio as well as the solvent THF) were heated to the desired temperature while being continuously stirred. Once at the desired temperature, the esterification reaction was started by charging the catalyst.

For the pure resin catalyst (Nafion), swelling of the polymer network in polar solvent is known to occur. However, for SAC-13 (Nafion/silica), only negligible swelling has been reported [12] due to the high dispersion of the polymeric domain on the high surface area SiO₂. However, catalyst swelling even to a small degree could affect catalytic activity since during swelling additional acid sites can be exposed falsifying kinetic measurements. To assess if swelling played a role in catalyst activity, SAC-13 was pre-soaked in polar MeOH overnight prior to reaction, and esterification was then initiated by charging the acetic acid and THF which are known to have much less capability to swell the polymeric resin in SAC-13 than methanol [13]. Under these conditions, identical reaction profiles were obtained as in experiments using the catalyst charged last. This confirms that catalyst swelling due to methanol had a negligible effect on reaction rate.

A SAC-13 loading of 1.09 g/45 ml in its pellet form (1mm), as provided by the vendor, and a stirring rate of 1133 rpm were used in all reaction experiments. Diffusional limitations were ruled out by varying the particle size and stirring rate between 0.10~1 mm and 850~1700 rpm, respectively. No change in reaction rate was detected when using particles smaller than 1mm or stirring speeds greater than 850 rpm. A microscale syringe was used for sampling at definite time intervals. Sample analysis using a Hewlett-Packard 6890 gas chromatograph followed the same procedure as used in previous work [11].

Plots of acetic acid conversion (Xₐ) vs. reaction time (t) were linear at conversions
below 10% for both liquid and solid acid catalysts (Figure 5.1). Despite 2\textsuperscript{nd} order kinetics being well documented for H\textsubscript{2}SO\textsubscript{4}, this linearity observation is expected due to the use of a high substrate-to-catalyst ratio (>1200) [14]. This way, the concentration of protonated complex changed negligibly at low conversions (<10%). Thus, values for initial reaction rates were calculated as \( r = C_{A,0} \frac{dX_A}{dt} \) with \( C_{A,0} = \) initial concentration of the carboxylic acid and \( X_A = \) conversion of the carboxylic acid. In addition, despite the catalytic activity of acetic acid itself [11, 15], the autocatalysis was able to be ignored under the present experimental conditions because of its negligible contribution to the overall reaction rate.

**Figure 5.1** Initial reaction period for esterification of acetic acid with methanol at 60\degree C using H\textsubscript{2}SO\textsubscript{4} (0.011 g /45 ml) and SAC-13 (1.09 g/ 45 ml).
Results

Acid site density characterization

The maximum expected acid site density of SAC-13 can be estimated by TGA or sulfur element analysis [10, 16], since each sulfonic acid group constitutes a potential acid site. TGA analysis (not shown) yielded an average of 14.5 wt% Nafion loading on the silica matrix, corresponding to an acid site density of 0.129 mmol/g. This agrees well with the value of 0.131 mmol/g determined from elemental sulfur analysis carried out by Galbraith Laboratory using ICP. Liquid phase pyridine adsorption experiments can also be used for surface acid site density determination (Table 5.1). Nevertheless, organic base adsorption on the silanol groups of silica matrix must be excluded. Pyridine adsorption experiments with sodium-exchanged SAC-13 (NaO-SO2/SiO2), obtained using aqueous NaCl solution as the ion exchange reagent) showed that approximately 10% of the pyridine could be adsorbed on the silica matrix (Table 5.1). After adjustment, the acid site density of SAC-13 obtained from pyridine adsorption was about 0.129 mmol/g, conforming to the values calculated by TGA and elemental sulfur analysis.

Table 5.1 Pyridine adsorption on SAC-13 and Na+-SAC-13

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>T</th>
<th>Acid site density (mmol/g )&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC-13</td>
<td>THF</td>
<td>RT (25°C)</td>
<td>0.143</td>
</tr>
<tr>
<td>SAC-13</td>
<td>THF</td>
<td>50°C</td>
<td>0.145</td>
</tr>
<tr>
<td>Na+-SAC-13</td>
<td>THF</td>
<td>RT</td>
<td>0.016</td>
</tr>
</tbody>
</table>

<sup>a</sup> Experimental error: ±5%
Catalytic activity of H$_2$SO$_4$ and SAC-13

Figure 5.2 compares the reactivity of acetic acid esterification at 60°C catalyzed by sulfuric acid and SAC-13, respectively. On a per weight basis, the homogenous acid catalyst was more active than the heterogeneous catalyst. Using a very small amount of H$_2$SO$_4$, 0.011 g/45 ml, acetic acid conversion reached 82% after 11 h of reaction time at 60°C with 2x stoichiometric methanol. On the other hand, a hundredfold amount of SAC-13 (1.09 g/45 ml) was required to yield a similar reaction profile with 75% transformation of acetic acid after 11h. The better catalytic activity of H$_2$SO$_4$ can be attributed to its larger density of acid sites per gram. Calculation of turnover frequencies (TOFs) provides a comprehensive way to make catalyst comparisons on a per site basis. Using the acid site density of 0.13 mmol/g for SAC-13 and assuming 1 mol H$^+$/1 mol H$_2$SO$_4$ by neglecting the dissociation of the weak acid HSO$_4^-$, initial TOF values were calculated and are shown in Table 5.2. On a per site basis, the catalytic activity of H$_2$SO$_4$ was greater by a factor of only 3 than that of SAC-13.
Figure 5.2 Conversion vs. time for acetic acid esterification catalyzed by (a) H$_2$SO$_4$ (2.5 mM) and (b) SAC-13 (1.09 g/45 ml) at 60°C ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M, symbols represent the experimental data; dashed line represents the model prediction for SAC-13 catalysis).

Table 5.2 Initial kinetic parameter comparison for H$_2$SO$_4$ and SAC-13 catalyzed acetic acid esterification with MeOH at 60°C ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M$^a$).

<table>
<thead>
<tr>
<th>$C_{W,0}$ (M)$^a$</th>
<th>H$_2$SO$_4$$^b$</th>
<th>SAC-13$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOF$^c$ (min$^{-1}$)</td>
<td>$E_a$ (kJ)</td>
</tr>
<tr>
<td>0</td>
<td>22.76</td>
<td>52.7</td>
</tr>
<tr>
<td>2.85</td>
<td>3.07</td>
<td>63.8</td>
</tr>
</tbody>
</table>

$^a$ $C_{A,0}$, $C_{M,0}$ and $C_{W,0}$ represent the initial concentrations of acetic acid, methanol and water, respectively.

$^b$ Experimental error +/-6%

$^c$ 1 mol H$^+$/1 mol H$_2$SO$_4$ is assumed.

$^d$ The elemental analysis value for sulfur content of 0.131 mmol/g was used.

$^e$ The subscript h and l represent high initial water concentration ($C_{W,0} = 2.85$ M) and low initial water concentration ($C_{W,0} = 0$ M), respectively.
Effect of reactant composition on SAC-13 catalysis

Homogeneous acid-catalyzed esterification follows second order kinetics, first order with respect to each reagent [15, 17]. The calculation of kinetic parameters for heterogeneous acid catalysts is complicated due to the complexity associated with the catalyst surface-adsorbate interactions. As is typically done, apparent kinetic parameters such as reaction orders were determined by varying the concentration of one reactant while fixing that of the other at 2.0 M and measuring initial kinetics at 60°C. Results are shown in Table 5.3. Both the concentrations of the alcohol and the carboxylic acid had positive impacts on the reaction rate as reactant concentration was increased. Using a power law approximation, the apparent reaction orders were determined to be 0.59 and 0.74 for methanol and acetic acid, respectively, with a 0.99-1.00 correlation coefficient.

Table 5.3 Initial reaction rate data for the determination of apparent reaction orders of methanol and acetic acid in SAC-13 (1.09 g/45 ml) catalyzed esterification at 60°C.

<table>
<thead>
<tr>
<th>C_{M,0} (M)</th>
<th>r_0^a (M/min) x 10^3</th>
<th>C_{A,0} (M)</th>
<th>r_0^a (M/min) x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.05</td>
<td>2</td>
<td>8.05</td>
</tr>
<tr>
<td>4</td>
<td>13.3</td>
<td>4</td>
<td>13.9</td>
</tr>
<tr>
<td>6</td>
<td>17.0</td>
<td>5</td>
<td>15.7</td>
</tr>
<tr>
<td>14</td>
<td>25.6</td>
<td>6</td>
<td>18.4</td>
</tr>
<tr>
<td>C_{A,0} = 2 M</td>
<td>C_{M,0} = 2 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Experimental error +/-6%

Water sensitivity

In our previous work, the esterification by-product water was found to significantly inhibit H_2SO_4 catalysis [11]. The resistance of solid catalysts to water poisoning is an important characteristic in determining their applicability for commercial esterification
processes. The effect of water on acid-catalyzed esterification was studied using initial reaction kinetics (<10% conversion of the limiting reactant) with varying amounts of initially added water. This permits a better determination of the effect of water on the catalyst because the rate is little affected by the reverse reaction since only small amounts of the methyl ester are present [11]. The concentrations of acetic acid and methanol were fixed at 3.0 M and 6.0 M, respectively. Water addition experiments used THF (as a solvent) to keep the total reaction volume constant.

Figure 5.3 shows acetic acid conversion on SAC-13 vs. time at 60°C for experiments using different initial concentrations of water (C_{W,0}). The catalytic activity was significantly inhibited with increasing water concentration in the reaction mixture. After 1 h of reaction, a reaction mixture with 2.85 M initial water concentration had a conversion about 60% lower than that with no initial water added. Chen et al. [18] have shown that when esterification is carried out using Nafion-H in the presence of an initial water concentration of 4.3 M, the conversion of acrylic acid after 4 h decreases from 60% without water addition to 30.6% at 80°C. Hence, the response to water observed here for SAC-13 is consistent with what has been reported for the parent resin. Nevertheless, both SAC-13 and Nafion appear to be more resistant to water deactivation than other solid acids such as SO_4^{2-}/ZrO_2 and Amberlyst-15 [18]. In particular, SO_4^{2-}/ZrO_2 is well known to suffer from serious leaching in media containing water [15, 19].

In Figure 5.4, the water sensitivity of SAC-13 and H_2SO_4 are compared using initial reaction rates. Here, activity ratios were used in order to put the results for the two catalysts on the same scale. C_W, the concentration of water, includes both the amount added initially and the average amount formed during the initial reaction period [11].
Figure 5.4 reveals that the heterogeneous catalyst SAC-13 and the homogeneous catalyst H₂SO₄ exhibit a very similar response to water deactivation. Using the Arrhenius relationship, apparent activation energies were determined at initial water concentrations of 0 and 2.85 M for both catalysts (Figure 5.5), respectively. Results are included in Table 5.2. The liquid and solid acid catalysts showed almost identical apparent reaction energy barriers at each C₇₀₀₅, with greater values at the higher initial water concentration.

![Graph showing HAc conversion over time for different water concentrations](image)

**Figure 5.3** Water sensitivity of acetic acid esterification catalyzed by SAC-13 at 60°C.

**Discussion**

Thanks to the strong electron-withdrawing α-CF₂ polymer moiety, the Nafion resin is known to have a similar acid strength to H₂SO₄, as estimated by Hammett H₀ values (-H₀~12) [10]. Taking into account the almost unrestricted site accessibility of the highly dispersed nano-Nafion domains on the porous silica matrix in SAC-13, the smaller intrinsic activity shown by the heterogeneous catalyst may be due to the interaction of the
polymer with the silanol groups of the silica support resulting in a decreased activity of
the sulfonic acid group [20]. Alternatively, the lower observed site activity of SAC-13
might be due to the more restricted conformation of intermediate complexes adsorbed on
the solid surface compared to those moving freely in solution. A reduction in the number
of available energy levels of the transition state could give rise to a lower pre-exponential
factor (or activation entropy in terms of “transition state theory”) [21]. Nevertheless, the
apparent activation energy determined for the heterogeneous acid catalyzed esterification
is essentially identical to that for homogeneous catalysis (Figure 5.5, Table 5.2), pointing
to the possibility of the same rate-limiting step involved in SAC-13 and in H₂SO₄
catalyzed esterification.

![Graph](image)

**Figure 5.4** Water sensitivity of acetic acid esterification with methanol at 60°C (Cₐ₀ = 3
M, Cₘ₀ = 6 M) on SAC-13 compared to that on H₂SO₄.
Figure 5.5 Arrhenius plots for acetic acid esterification at different initial water concentrations using H2SO4 and SAC-13 (T=40-60°C, C_{M,0}/C_{A,0}=2).

One more similarity existing between H2SO4 and SAC-13 catalyzed esterification of acetic acid with methanol is the positive dependency of reaction rate on the concentrations of both reagents (Table 5.3). Our experimental data agree with those obtained by Altiokka and Citak [8] for the esterification of acetic acid and isobutanol catalyzed by Amberlite resins at 60°C. In contrast, Nijhuis et al. [7] reported that the SAC-13 catalyzed esterification of hexanoic acid in cumene at 150°C decreased with increasing concentration of n-octanol. Studies in our group of the gas phase esterification of acetic acid with methanol catalyzed by SAC-13 at 100-120°C have also shown negative reaction order for methanol [22]. These seemingly contradictory results, however, can be understood assuming a mechanistic pathway operating in a way similar to the accepted homogeneous mechanism for esterification. This will be discussed in
The effect of water on activity allows for a means to compare the similarity/difference between homogeneous and heterogeneous catalysis mechanism. The solid and liquid acid catalysts presented the same water deactivation profile (Figure 5.4), suggesting that: 1) water deactivates the active sites of the solid and liquid catalysts in probably the same way, and 2) the mechanistic route involved in SAC-13 esterification catalysis resembles that of H$_2$SO$_4$.

One might expect water deactivation of SAC-13 and of H$_2$SO$_4$ to be similar since both possess Brønsted-type acid sites for catalysis. Even though silica contains silanol groups, their contribution to the acid catalysis should be negligible due to their low acid strength [23]. We have found, for instance, that sodium-exchanged SAC-13 presents no activity for HAc esterification at 60°C. Using pure silica, Samantaray and Parida [24] have reported negligible activity for the esterification of acetic acid with butanol, as have Wang et al. [25] for transesterification of dimethyl oxalate with phenol and Mbaraka et al. for esterification of palmitic acid with methanol [26]. Consequently, the -CF$_2$SO$_3$H group in SAC-13 must be fully responsible for the catalytic activity. It, like HO-SO$_3$H (H$_2$SO$_4$), would be susceptible to solvation and proton transfer [27]. The common nature of the acid sites of both catalysts constitutes probably the most important basis for the similar water sensitivities of SAC-13 and H$_2$SO$_4$. Although the Brønsted acid sites are anchored to a solid surface in SAC-13, in condensed media containing polar molecules these sites can still be solvated giving rise to hydrogen-bonded clusters of polar molecules around them with proton transfer ability [28]. In fact, the IR spectrum of hydrated Nafion-H has been reported to resemble that of an aqueous solution of
concentrated H₂SO₄ [29]. Hybrid inorganic-organic silicas with immobilized sulfonic groups have also been found to behave in water essentially like homogeneous phase p-toluenesulfonic acid (p-TsOH) [30]. In our previous study of the esterification of acetic acid with methanol catalyzed by H₂SO₄, water deactivated the catalyst by decreasing its acid strength [11]. It was suggested that the deactivating effect of water was due to water solvation of the protons being favored over methanol solvation. The driving force for this behavior was probably the better ability of water to form hydrogen bonding networks that can delocalize “free” protons in solution [11]. Similar reports of loss of acid strength with water addition have been made for Nafion-H. Buzzoni et al. [29] reported a higher red shift for O-H stretching frequencies of Nafion-H contacted with water than for methanol contacted Nafion-H, indicating a lower acidic character for the water solvated resin. 

Using acid-base calorimetric titration, Koujout and Brown [30] demonstrated how the acid strengths of sulfonic acid silicas and p-TsOH (p-toluenesulfonic acid) were influenced by their chemical surroundings. These authors were able to show a clear trend of decreasing acid strength as the solvent varied from cyclobenzene to acetonitrile to water.

Despite all evidence pointing to water having a similar inhibiting effect on esterification for SAC-13 as it does for H₂SO₄, SAC-13 did exhibit slightly less deactivation by water than H₂SO₄ at high water concentrations (Figure 5.4). This observation supports the view of Nusterer et al. [31] that water solvation of solid acid sites is sterically hindered by the support matrix compared to the solvation of free protons in the liquid phase. In addition, the thermochemical comparisons of homogeneous p-TsOH and heterogeneous acid resin (Dowex 50W-X8) by Arnett et al. [13] showed that
the liquid acid underwent a more significant decay in the heat of ionization of pyridine (-\(\Delta H_i\)) as water concentration increased than the solid acid resin (Table VII and Fig. 3, ref. [13]). A loss of 13.6 kcal/mol in -\(\Delta H_i\) was determined for the former as water/acid ratio increased from 0 to 10.3, whereas a loss of only 8.7 kcal/mol was found for the latter as water/acid ratio increased from 0 to 11.4 [13]. This large difference in -\(\Delta H_i\), however, may not properly reflect the real difference in acid strength variation due to water solvation for solid and liquid acid catalysts. Given the significant swelling effect of water on Dowex 50W-X8 which could expose more acid sites, the loss in acid strength may be compensated for in part. For instance, acetic acid esterification catalyzed by SAC-13 shows only a slightly lower increase in energy barrier in the presence of water than does the case using H\(_2\)SO\(_4\), 10.4 vs 11.1 kJ/mol (Figure 5.5, Table 5.2). It should be noted, however, that the apparent activation energy determined in this work for H\(_2\)SO\(_4\) catalysis with THF as solvent is larger by about 7 kJ/mol than that reported in previous work [11] where no solvent was used. This difference suggests that probably changes in the polarity of the media due to the solvent THF (vs. only methanol) may affect the reaction. But still, this effect is minor compared to that of water, given the large quantity of solvent used.

In order to explore if the molecular pathway for esterification on SAC-13 resembles that of H\(_2\)SO\(_4\) (which is single site), a series of pyridine poisoning experiments were conducted to determine if the reaction followed a single site or a dual site mechanism. Prior to each run, the catalyst was first immersed in a mixture of methanol-THF containing a known amount of pyridine. This immersion last overnight to allow the complete equilibrated adsorption of the organic base on the acid sites of the catalyst.
Afterwards, the reactor was heated to 50°C (methanol and THF form an azeotrope at 60°C) and pre-heated HAc was charged into the reactor to initiate the reaction. As shown in Figure 5.6, the initial reaction rates decreased linearly with increasing amounts of pyridine, suggesting that the heterogeneous reaction involves a single-site mechanism. Moreover, if mono-molecular adsorption of pyridine per acid site is assumed, the acid site density of SAC-13 can be estimated by extrapolating to zero the esterification rate as a function of the pyridine concentration. The acid site density calculated this way was 0.148 mmol/g after subtraction of the 10% adsorption of pyridine on the silanol groups of the silica surface. Though somewhat higher, it agrees fairly well with the values obtained earlier (0.129 mmol/g) from elemental sulfur analysis and pyridine adsorption experiments, thus indicating that the reaction has complete accessibility to SAC-13 acid sites. The incomplete protonation of the organic base [14] may account for the slight overestimation. Nevertheless, the equilibrium constant for the protonation of pyridine is greater than $2 \times 10^4$ as estimated from reaction data (Figure 5.6), following the method given by Kogelbauer et al. [14] and using an acid site density of 0.131 mmol/g for SAC-13. Clearly, this large value indicates a very strong acid-base interaction between surface sulfonic acid groups and pyridine and, thus, an almost complete protonation.
Figure 5.6 Pyridine poisoning of SAC-13 catalyzed esterification of acetic acid with methanol at 50°C (C_{A,0}=3M, C_{M,0}=6M, C_{Py} = concentration of pyridine).

The existing strong correlations in observed esterification kinetics between SAC-13 and H\textsubscript{2}SO\textsubscript{4} point to similar mechanistic pathways. Thus, the evidence in terms of site activity, apparent activation energy, water deactivation behavior, and single site mechanism, strongly suggests that SAC-13 catalyzed esterification likely proceeds via a mechanism analogous to the homogeneous catalyzed one:

\[ k_i \]

\[ M + S \underset{k_i}{\overset{k_i}{\rightleftharpoons}} M \cdot S \quad (M-1) \]
where M represents methanol, S a vacant acid site on the catalyst surface, A acetic acid, E methyl acetate, and W water. M·S, A·S, E·S and W·S are molecules adsorbed on the catalytic acid sites, respectively. In the above mechanism, (M-2) to (M-4) orderly depict the activation of carbonyl oxygen of acetic acid, the nucleophilic attack of protonated acetic acid by methanol forming ester and water and the deprotonation of methyl acetate. Methanol being a strong nucleophile also competes for the catalyst acid sites with acetic acid and so does water once it is produced from reaction, as shown in (M-1) and (M-5) respectively.

Let us first consider what applies during the initial reaction period where reverse hydrolysis is not important. Using the pseudo-steady-state approximation for the protonated complexes (M·S and A·S) and solving for $C_{A\cdot S}$ with the site balance ($\rho C_C =$
\( C_{A_S} + C_{M_S} + C_S \) gives the rate expression,

\[
r = \frac{k_2 k_3 \rho C_{C} C_{M} C_A}{(k_{-2} + k_3 C_M)(1 + K_M C_M + \frac{k_2}{k_{-2} + k_3 C_M} C_A)}
\]  

(1)

where \( C_C, C_M \) and \( C_A \) are the concentrations of catalyst, methanol and acetic acid, respectively. \( \rho \) denotes the site density of the catalyst. \( K_M \) represents the adsorption equilibrium constant for methanol on the Brønsted acid sites. \( k_2 \) and \( k_{-2} \) are the acetic acid adsorption and desorption constants, respectively, and \( k_3 \) is the surface reaction constant.

If surface reaction (\( k_3 \)) is favored over the adsorption and desorption of the acid (\( k_2 \) and \( k_{-2} \)), then \( k_3 C_M >> k_2, k_{-2} \), equation (1) can be approximated by,

\[
r = \frac{k_2 \rho C_{C} C_A}{1 + K_M C_M}
\]  

(2)

If, on the other hand, the opposite is true with the adsorption and desorption process being faster than surface reaction, \( k_3 C_M << k_2, k_{-2} \), equation (1) reduces to,

\[
r = \frac{k_2 k_3 \rho C_{C} C_M C_A}{k_{-2} (1 + K_M C_M + \frac{k_2}{k_{-2}} C_A)}
\]  

(3)

Defining \( K_A = \frac{k_2}{k_{-2}} \) as the adsorption equilibrium constant of the carboxylic acid,
where $k$ is a lumped constant equivalent to $K_A k_3 \rho$. Note that although surface reaction, (M-3), occurs by an Eley-Rideal mechanism, equation (4) is not a typical E-R rate expression due to the competing adsorption of methanol on acid sites.

From the standpoint of the two extreme situations give above, inconsistencies among reports studying acid catalyzed esterifications using solid Brønsted acid catalysts can be explained by a shifting in the terms dominating the reaction kinetic behavior. If, for instance, as the temperature is raised, the kinetic behavior characterized by equation (4) evolves into behavior characterized by equation (2), one would expect that after a certain point the reaction order of methanol would transits from positive to negative. This may explain what has been reported for heterogeneous acid-catalyzed esterifications at 100°C and above in references [7] and [22]. Under the conditions used in this study, however, the positive reaction order determined for methanol suggests that equation (4) should apply.

Nonetheless, in order to further confirm our hypothesis ($k_3 C_M \ll k_2$, k -2) for the reaction at 60°C, experiments using catalyst samples pre-saturated with HAc prior to initiating the reaction by charging preheated methanol were carried out (not shown). The logic behind these experiments was that, if the adsorption/desorption of acetic acid was comparable to or slower than the surface reaction, then, an initial reaction rate different from that obtained when the catalyst was added last (no preadsorbed HAc) would be obtained given that acetic acid was already adsorbed on the catalyst surface ready for
attack by methanol. In particular, in a parallel study of our lab of the gas phase esterification of HAc with methanol on SAC-13 at 100°C, experiments using the pre-adsorption of HAc showed faster initial reaction rates, indicating that under these conditions the surface reaction of acetic acid was not the rate controlling step [22]. However, the results for liquid phase esterification at 60°C showed no improvement in initial reaction rates compared to experiments using the catalyst with no pre-adsorbed carboxylic acid. Hence, a fast reagent adsorption/desorption equilibrium with the rate limiting step being surface reaction is likely the case under our reaction conditions and, accordingly, equation (4) appears to be further confirmed to be the suitable kinetic model.

Using equation (4) and initial reaction rate \( r_0 \) measured at different initial reactant compositions, a mathematical model was developed to predict esterification rate as reaction progresses. Equation (4) can be rearranged to give

\[
\frac{1}{r_0} = \frac{K_M}{kC_A C_{A,0}} + \frac{1 + K_A C_{A,0}}{kC_A C_{A,0}} \left( \frac{1}{C_{M,0}} \right) \tag{5}
\]

or

\[
\frac{1}{r_0} = \frac{K_A}{kC_C C_{M,0}} + \frac{1 + K_M C_{M,0}}{kC_C C_{M,0}} \left( \frac{1}{C_{A,0}} \right) \tag{6}
\]

According to equation (5), when \( C_{A,0} \) is fixed at 2.0 M, a plot of \( 1/r_0 \) vs. \( 1/C_{M,0} \) yields a straight line with the ratio slope/intercept equal to \( (1 + 2K_A)/K_M \). Likewise, \( (2K_M + 1)/K_A \) can be determined from the plot of \( 1/r_0 \) vs. \( 1/C_{A,0} \). The plots based on equations (5) and (6)
are shown in Figures 5.7a and 5.7b, respectively. By this means, $K_M$ and $K_A$ were calculated to be 0.16 L/mol and 0.13 L/mol, respectively. The somewhat larger adsorption equilibrium constant for methanol than for acetic acid is consistent with its lower apparent reaction order indicating more extensive methanol coverage of the acid sites.

![Graph (a)](image)

![Graph (b)](image)
Figure 5.7 Determination of the adsorption constants for methanol, acetic acid and water at 60°C for SAC-13.

As was determined, water can seriously inhibit SAC-13 catalysis (Figure 5.5). Therefore, as water is continuously produced by the reaction, the adsorption term of water must be included in the kinetic expression. For initial kinetics measurements in the presence of added water, equation (4) should then be,

\[
W_{W}M_{A}A_{M} + C_{K}C_{A} + k_{r} = 0, 0, 0, 0, 0, 0, 1 \quad (7)
\]

Rearranging this equation, one get

\[
\frac{1}{r_0} = \frac{1 + K_{M}C_{M,0} + K_{A}C_{A,0}}{kC_{C}C_{M,0}C_{A,0}} + \frac{K_{W}C_{W}}{kC_{C}C_{M,0}C_{A,0}} (C_{W}) \quad (8)
\]
With the $K_A$ and $K_M$ values previously determined and fixing $C_{A,0}$ (3 M) and $C_{M,0}$ (6 M), the adsorption constant for water was able to obtained from plots of $1/r$ vs. $C_W$ (Figure 5.7c) to be 3.11 L/mol.

Furthermore, an expression for $k$ can be derived from equation (8) as

$$k = \frac{r_0 (1 + K_M C_{M,0} + K_A C_{A,0} + K_W C_W)}{C_C C_{M,0} C_{A,0}}$$  \hspace{1cm} (9)

By inserting calculated adsorption constants into equation (9) and employing the initial kinetic data, the lumped reaction constant for acetic acid was determined to be $1.50 \times 10^{-4}$ L$^2$/(g cat.· mol· min). Thus far, since the adsorption of solvent and ester are known to be negligible [7, 8], equation (7) can be expanded to include reverse reaction at high conversions,

$$-\frac{dC_A}{dt} = \frac{kC_C}{1 + K_M C_A + K_A C_A + K_W C_W} \left( C_M C_A - \frac{C_w C_E}{K_e} \right)$$  \hspace{1cm} (10)

where $K_e$ is the equilibrium constant for esterification ($K_e = 6.2$ at 60°C). For a molar ratio of $C_{M,0}/C_{A,0} = n$ and an initial water addition of $C_{W,0}/C_{A,0} = u$, equation (10) expressed in terms of acetic acid conversion becomes,

$$\frac{dx_A}{dt} = \frac{kC_C C_{A,0}}{1 + C_{A,0} [K_M (n - x_A) + K_A (1 - x_A) + K_W (x_A + u)]} \left[ (n - x_A)(1 - x_A) - \frac{(x_A + u)x_A}{K_e} \right]$$  \hspace{1cm} (11)
Using numerical integration (Runga-Kutta), carboxylic acid conversion at a given time can be predicted from equation (11). The dotted line in Figure 5.2 gives the prediction of reaction conversion based on equation (11). Thus, equation (11) satisfactorily represents the esterification of acetic acid with methanol on SAC-13.

As shown in Figure 5.8, the derived mathematical model successfully predicts reaction profiles for the esterification of HAc using different reaction conditions from those used originally to calculate it (i.e. double loading of catalysts and higher molar ratio of methanol-to-HAc). In addition, Figure 5.8 shows how the model can accurately assess reaction profiles for esterification in the presence of initial amounts of water, supporting the estimation made of the water inhibition effect on SAC-13 catalysis.

**Figure 5.8** Comparison of experimental data with values predicted by equation (11) for the esterification of acetic acid with methanol on SAC-13 under different reaction conditions (symbols represent the experimental data; dashed lines represent the model predictions).
Summary

The catalytic performance of the Nafion/silica nanocomposite SAC-13 has been evaluated for the esterification of acetic acid with methanol and compared to that of H$_2$SO$_4$. TOF values calculated for SAC-13 showed that the activity of the resin is comparable to that of H$_2$SO$_4$ on a per site basis. It was also determined that most acid sites on the Nafion nanodomains were available for reaction without the need for polymer swelling. Both SAC-13 and H$_2$SO$_4$ showed very similar reaction inhibition by water, suggesting a common reaction mode on their Brønsted acid sites. A typical Eley-Rideal type heterogeneous reaction mechanism involving a nucleophilic attack between adsorbed carboxylic acid and unadsorbed alcohol as the rate-limiting step fits well the experimental data obtained under our reaction conditions. A mathematical model was analytically derived from which it was possible to reproduce the kinetic profiles of acetic acid esterification under different experimental conditions.
References


CHAPTER 6
EFFECT OF CARBON CHAIN LENGTH ON ESTERIFICATION OF CARBOXYLIC ACIDS WITH METHANOL USING ACID CATALYSIS

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Abstract
This paper reports on an investigation into the impact of carboxylic acid chain length on the kinetics of liquid phase acid-catalyzed esterification. Using sulfuric acid and a commercial Nafion/silica composite solid acid catalyst (SAC-13), initial kinetics were measured for the reactions of a series of linear chain carboxylic acids (acetic, propionic, butyric, hexanoic and caprylic acid) with methanol at 60°C. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H₂SO₄ and SAC-13. This trend has been discussed in terms of the polar and steric effects of the alpha-substituent to the carboxylic group and evaluated by a Taft type correlation. Using a mechanistically based kinetic model, the reaction kinetic parameters of SAC-13 catalysis were determined and compared for different carboxylic acids. Moreover, important parameters such as water deactivation, catalyst reusability and regeneration were also affected by the size of the carboxylic acid used. SAC-13 underwent significantly more activity loss with subsequent reaction cycles as the size of the alkyl tail on the carboxylic acid increased. Characterization of the catalyst after reaction
suggested that the deactivation of SAC-13 is likely caused by the entrapment of bulky reaction intermediates in/on Nafion polymeric nano-domains blocking catalytic acid sites.

**Introduction**

Esterification of carboxylic acids with alcohols represents a well-known category of liquid-phase reactions of considerable industrial interest due to the enormous practical importance of organic ester products [1-3]. Recently, the acid-catalyzed esterification of long alkyl chain fatty acids has spurred a great deal of interest since long chain fatty acid alkyl esters can be used as a biofuel. The reaction is especially important in the synthesis of biodiesel from low cost feedstocks containing large amounts of free fatty acids [4-6]. Such free fatty acids have to undergo acid catalyzed esterification first before transesterification of the larger triglycerides is carried out using a base catalyst (usually NaOH) [7, 8].

Currently, the esterification of fatty acids with alcohols is commercially achieved using liquid acid catalysts, such as sulfuric acid, hydrochloric acid, and para-toluene sulfonic acid (p-TsOH). The scientific literature contains some reports about the use of heterogeneous acid catalysts for esterification. The most popular inorganic solids used to produce esters have been ion exchange organic resins such as Amberlyst-15 [9], zeolites [10] and silica-supported heteropoly acids (HPA/silica) [11, 12]. Nevertheless, they have been shown to exhibit limitations in applicability for catalyzing esterification due to either low thermal stability (Amberlyst-15, <140°C), mass transfer resistance (zeolites) [13, 14] or loss of active acid sites in the presence of a polar medium (HPA/silica) [12, 15].
SAC-13, a Nafion/silica nanocomposite [16], has been marketed as a new generation of supported resin catalyst. It has higher acid strength than conventional strong solid acids like H-ZSM-5, SO₄²⁻/ZrO₂ and SiO₂/Al₂O₃ [17], higher thermodynamic stability than the polystyrene-based resins (Amberlyst, Dowex), and highly accessible acid sites due to the porous silica matrix [18]. The porous structure of the silica support with adjustable pore openings at the nanometer scale [16] diminish the likelihood of mass diffusion limitations, making it favorable for bulky reactants. This eco-friendly solid acid could have great potential for esterification reactions of free fatty acids (FFAs) as found in lipid feedstocks used for biodiesel production.

While low molecular weight carboxylic acids have been widely used to address fundamental issues of esterification due to their simplicity, availability and ease of reaction analysis, good kinetic information regarding acid-catalyzed FFAs esterification, in general, is quite limited. Certainly, having correlations between chemical structure and chemical reactivity helps to understand differences in chemical behavior between low molecular weight carboxylic acids and their larger and bulkier counterparts, free fatty acids. Dating back to the 1950s, researchers have already conceptualized and quantified some of the effects that substituents can have on the chemical reactivity of alkyl esters in hydrolysis reaction [19]. The Hammett equation in aromatic systems and the Taft equation in aliphatic systems were the first proposed models that tried to quantify polar, resonance and steric effects of substituents in chemical reactivity [19]. These models have been followed by extensive efforts to improve [20], modify [21] and expand them to other reactions [22]. Although most studies have been limited to the use of homogeneous catalysts, the qualitative conception and quantitative correlations reported in them
provide a rational basis for understanding probable structural effects that large carboxylic acids may have on the activity of heterogeneous catalysts [23, 24].

On the other hand, in contrast to the extensive studies done of the structural effect of carboxylic acids on homogeneous catalyzed esterification, the parallel topic for heterogeneous catalysis has been scarcely explored. Only a couple of studies related to this topic can be found in the literature: Lilja et al. [24] using ion-exchanged resins and Mochida et al. [23] using sodium-poisoned silica-alumina. These two papers, however, have used only straight alkyl chain carboxylic acids no larger than butyric acid. In addition, no direct kinetic comparisons between homogenous and heterogeneous catalysis were done in either study. Thus, in an effort to develop a better understanding of the relationship between the existing fundamental knowledge obtained for esterification using low molecular weight carboxylic acids and the behavior of fatty acids in heterogeneous acid catalyzed esterification, a set of linear chain carboxylic acids (acetic acid, HAc; propionic acid, HPr; butyric acid, HBu; hexanoic acid, HHx; caprylic acid, HCp) were used in this work. H$_2$SO$_4$ was used as a reference liquid catalyst to carry out reaction studies under identical experimental conditions to the solid acid, SAC-13, allowing for a more precise rationalization of the results obtained with the heterogeneous catalyst SAC-13. In addition, for the solid catalyst, the impact of increasing the carboxylic carbon chain length acid on catalyst deactivation, reusability and regeneration was investigated.

**Experimental**

Reagents including methanol (99.9 wt%, Acros Organics), acetic acid (99.7 wt%,
Aldrich), propionic acid (99.0 wt%, Aldrich), butyric acid (99.0 wt%, Aldrich), hexanoic acid (99.5 wt%, Aldrich) and caprylic acid (99.0 wt%, MP Biomedicals) were used without further purification. Concentrated sulfuric acid was purchased from Fisher Scientific and SAC-13 was obtained from Aldrich.

The sulfur content of SAC-13 was determined by elemental analysis using ICP (Galbraith Laboratory, Knoxville, TN). BET surface area, pore diameter and BJH cumulative pore volume were obtained using N₂ adsorption at −196°C in a Micromeritics ASAP 2020. Prior to N₂ adsorption, the catalyst samples were outgassed for 3 h at 120°C. IR spectra were recorded using a Nicolet Avatar 360 FTIR spectrometer equipped with a nitrogen-purged chamber and DRIFT attachment. A Pyris 1 TGA (PerkinElmer) was used for thermogravimetric analysis (TGA) to characterize the used catalysts. Under a flow of nitrogen at 20 ml/min, the temperature was first stabilized at 25°C for 30 min and then ramped to 700°C at 10°C/min.

Reactions were carried out in an isothermal batch reactor (Parr 4590) following the procedures described elsewhere [25, 26]. Typically, a reaction temperature of 60°C was employed. A catalyst loading of 1.09 g and 0.022 g in the reaction mixture of 45 ml was used for SAC-13 and H₂SO₄ (5 mM), respectively. The absence of mass transfer limitations and catalyst swelling for SAC-13 was experimentally determined as before [26], thus ensuring the measurement of intrinsic reaction kinetics. THF was used as a solvent in order to fix the concentrations of carboxylic acids at 3 M and methanol at 6 M. In addition, the use of THF ensures the complete miscibility of all carboxylic acids/methanol reagent mixtures investigated.

At particular times of reaction, 30–60 µL reaction mixture samples were taken using a
microscale syringe. Samples from the reaction mixture were immediately chilled and diluted in cold 2-propanol to minimize any residual reaction. A Hewlett-Packard 6890 gas chromatograph equipped with an FID detector and a split/splitless inlet was used for sample analysis. A DB-1 column (0.32mm x 30m x 0.53μm) was used for analysis of the HAc and HPr reactions using ethanol as the internal standard. A CP-SIL 5CB column (0.25mm x 10m x 0.12μm) was used for the HBu, HHx and H Cp reaction analysis with methyl laurate as the internal standard.

Autocatalysis was negligible compared to SAC-13 or H2SO4 catalysis under the experimental conditions used; thus, it did not have to be accounted for in the rate determinations. In addition, kinetic measurements focused particularly on the initial period of reaction (<10%) in order to minimize the impact of reverse hydrolysis. The determination of initial reaction rate used the same methodology as described in ref. [26].

**Results and Discussion**

**Reactivity of carboxylic acids**

Figures 6.1a and 6.1b show the reactivity differences of the carboxylic acids for esterification with methanol at 60°C catalyzed by sulfuric acid and by SAC-13, respectively. On a per weight basis, the homogenous acid catalyst was much more active than the heterogeneous catalyst due to the lower acid site concentration of the latter. 10% carboxylic acid conversion was achieved within 3-8 min using 5 mM (0.022 g/45 ml) H2SO4 at 60°C with 2x stoichiometric methanol. However, it took 20-60 min for esterification to reach the same level of conversion when using 1.09 g SAC-13 as catalyst. Furthermore, HAc esterification using SAC-13 required several hundred minutes to
approach equilibrium conversions. An even longer time was required for the esterification of the bulkier HCp to do the same. Table 6.1 summarizes activity differences of the two catalysts in esterification at 60°C using turnover frequencies (TOFs) based on the assumption of 1M H⁺/1M H₂SO₄ and 0.13 mmol of acid sites /1g SAC-13 [26]. Thus, on a per site basis, the catalytic activities of H₂SO₄ and SAC-13 were much more comparable, with H₂SO₄ being only 2-to-5 times more active than SAC-13 for the set of carboxylic acids investigated.
Figure 6.1 Reactivity of different carboxylic acids in esterification catalyzed by (a) \( \text{H}_2\text{SO}_4 \) (5 mM) and (b) SAC-13 (1.09 g/45 ml) at 60\(^\circ\)C (\( C_{A,0} = 3 \) M, \( C_{M,0} = 6 \) M, symbols represent the experimental data; dotted lines represent the model prediction).

Table 6.1 TOF values calculated for sulfuric acid and SAC-13 catalyzed esterification of different carboxylic acids with methanol at 60\(^\circ\)C (\( C_{A,0} = 3 \) M, \( C_{M,0} = 6 \) M).

<table>
<thead>
<tr>
<th></th>
<th>HAc</th>
<th>HPr</th>
<th>HBu</th>
<th>HHx</th>
<th>HCp</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TOF (min(^{-1}))(^a)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>_\text{H}_2\text{SO}_4(^b)</td>
<td>22.76</td>
<td>12.12</td>
<td>7.42</td>
<td>7.98</td>
<td>8.46</td>
</tr>
<tr>
<td>_SAC-13(^c)</td>
<td>7.28</td>
<td>4.75</td>
<td>2.87</td>
<td>2.22</td>
<td>1.47</td>
</tr>
</tbody>
</table>

\[ \log r = \psi \nu + h \]

\(^a\) Experimental error +/-6%

\(^b\) 1 mol H\(^+\)/1 mol \( \text{H}_2\text{SO}_4 \) is assumed.

\(^c\) 0.131mmol H\(^+\)/g was used [26].
The decreasing trend in carboxylic acid reactivity with increasing alkyl chain length using acid catalysis is evident in both Table 6.1 and Figure 6.1. The reactivity loss per additional \(-\text{CH}_2\)- moiety was greatest for the small carboxylic acids from HAc to HBu for both liquid and solid catalysts. However, in the case of H\(_2\)SO\(_4\), the effect of chain length on reactivity became indiscernible for carboxylic acids larger than HBu. The observed reactivity trend for carboxylic acids can be conceptualized using the homogeneous catalysis mechanism model for esterification [28]. Initially, there are two components contributing to the diminished carboxylic acid reactivity with size: an inductive effect and a steric effect [19]. The inductive effect results from the increase in electron-releasing ability of the acid with lengthening alkyl chain. Although the inductive effect facilitates the protonation of the carbonyl oxygen, it also lowers the electrophilicity of the carbonyl carbon resulting in a more energy-hindered rate-limiting nucleophilic attack by the alcohol.

The steric component affecting carboxylic acid reactivity is perhaps the decisive factor for acid-catalyzed esterification [19, 21, 29]. Steric hindrance increases with molecular size inducing electronic repulsions between non-bonded atoms of reacting molecules. This repulsive hindrance lowers electron density in the intermolecular region and disturbs bonding interactions [29]. Thus, as the alkyl chain in the carboxylic acid increases in size its steric effect increases as well. However, steric constraints are not simply governed by the size of molecules, but also by their preferential conformations [30, 31]. This gives rise to the so-called “conformational leveling” effect [31]. Thus, the reactivity plateau exhibited by HBu, HHx and HCp for H\(_2\)SO\(_4\) catalysis (Table 6.1 and Figure 6.1) may be understood by using this established principle. More specifically, in
homogenous catalysis, large carboxylic acid molecules may be assuming conformations that minimize contributions to steric hindrance. The probable conformations for the reaction intermediates must be in a dynamic equilibrium probably favoring those allowing the reaction.

On the other hand, any conformational leveling effect in heterogeneous catalysis seems to be limited, as suggested by the reactivity gap observed for reactions using HBu, HHx and HCp (Table 6.1). The reduced conformational freedom of adsorbed alkyl groups on the SAC-13 catalyst is likely causing this. Additional interactions of the carboxylic acid, while bonded to the acid site, with polymer moieties of the Nafion nanodomains and/or surrounding silanol groups may also play a role here. As a result, it is more difficult for methanol molecules to reach the protonated carboxylic group when there is a large alkyl chain blocking access.

As the evidence suggests, steric considerations are less important for acid sites free in solution (homogeneous catalysis) than for acid sites fixed on a surface. Likewise, conformational constraints underwent by intermediates during heterogeneous catalysis should also account for the lower site activity of SAC-13 compared to H2SO4 (Table 6.1). Conformational restrictions, nevertheless, should weaken at high reaction temperatures. For instance, at 250°C, Mochida et al. [23] observed only small steric effects in the esterification of different carboxylic acids with a wide range of structures using sodium-doped silica-alumina. At high temperature, reaction intermediates on the solid surface have a shorter residence time due to fast adsorption/desorption dynamic equilibrium. Thus, conformational restrictions are compensated for in part by the fast exchange of absorbed and in-solution species.
On the basis of LFER (Linear Free-Energy Relationships), Taft quantitatively evaluated the steric effect caused by substituents in aliphatic systems using the correlation \( \log(r/r_0) = \delta E_S \) [19]. Here, \( r/r_0 \) stands for the reactivity ratio of a carboxylic acid having a given substituent vs. one with -CH\(_3\) (acetic acid), which is the reference group. \( E_S \) characterizes the steric hindrance associated with a substituent relative to that of –CH\(_3\). \( \delta \) serves as a measure of the susceptibility of a particular reaction series to the steric effects of substituents. Charton [21] further improved the Taft correlation by replacing the \( E_S \) constant with the van der Waals radii \( \nu \) associated with a given substituent and proposed the equation \( \log r = \psi \nu + h \), where \( \psi \) and \( h \) are constants.

\( \nu \) values for alkyl chains have been determined using homogeneously catalyzed esterification [27]. Using the results and the Charton equation to correlate the probable steric hindrance from low molecular weight carboxylic acids on H\(_2\)SO\(_4\) and SAC-13 resulted in linear plots with similar dependences on \( \nu \) (Figure 6.2). This suggests that steric effects indeed dominate catalyst activity in acid-catalyzed esterifications of small carboxylic acids (HAc to HBu) for both H\(_2\)SO\(_4\) and SAC-13 and the two catalysts share similar steric-reactivity responses for these small reactants.
Figure 6.2 Charton correlation for H$_2$SO$_4$ (HAc, HPr, HBu and HHx) and SAC-13 (HAc, HPr and HBu) catalysis.

**Kinetic parameters for the esterification of carboxylic acids in SAC-13 catalysis**

In a recent study [26], we showed that SAC-13 catalyzed esterification involves single-site catalysis similar to what takes place using a homogenous acid catalyst. The following kinetic model, which was derived using a hypothesized mechanism with strong parallels to the one proposed for homogeneous acid catalyzed esterification, was validated by its excellent representation of experimental data for acetic acid esterification on SAC-13 [26]:

\[
\frac{dC_A}{dt} = \frac{k_C C_{A,e} C_{A,0}}{1 + (K_M C_M + K_A C_A + K_{Ww} C_{Ww}) (C_M C_A - \frac{C_{Ww} C_{E}}{K_e})}
\]  

(1)
Here, \( k \) is the lumped reaction constant; \( C \) denotes concentrations and \( K \) represents adsorption equilibrium constants with the exception of \( K_e \), which represents the equilibrium constant for esterification. The subscript \( M \) stands for methanol, \( A \) for the carboxylic acid, \( W \) for water and \( E \) for the ester. From a mechanistic standpoint, equation (1) represents a rate-controlling surface reaction between adsorbed carboxylic acid and methanol free in the bulk phase. The terms for methanol and water in the denominator of equation (1) correspond to their competitive site occupation with carboxylic acid owing to their intrinsic larger proton affinities.

For a molar ratio of \( \frac{C_{M,0}}{C_{A,0}} = n \) and an initial water addition of \( \frac{C_{W,0}}{C_{A,0}} = u \), equation (1) expressed in terms of carboxylic acid conversion (\( x_A \)) becomes,

\[
\frac{dx_A}{dt} = \frac{kC_e C_{A,0}}{1 + C_{A,0}[K_M(n - x_A) + K_A(1 - x_A) + K_W(x_A + u)][(n - x_A)(1 - x_A) - \frac{(x_A + u)x_A}{K_e}]} \quad (2)
\]

Using the same methodology outlined in ref. [26], the kinetic and equilibrium adsorption parameters have also been determined for the esterification of HBu and HCp and are summarized in Table 6.2 together with those for HAc esterification.
Table 6.2 Adsorption equilibrium constants for methanol, carboxylic acids and water, reaction constant k for SAC-13 and reaction equilibrium constants for different carboxylic acid esterifications at 60°C.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>HAc</th>
<th>HBu</th>
<th>HCp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^a$ (L^2/g cata. mol. min) x10^4</td>
<td>1.50</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>$K_e^b$</td>
<td>6.2</td>
<td>5.7</td>
<td>5.5</td>
</tr>
<tr>
<td>$K_M^a$ (L/mol)</td>
<td>0.16</td>
<td>0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>$K_A^a$ (L/mol)</td>
<td>0.13</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>$K_W^a$ (L/mol)</td>
<td>3.11</td>
<td>2.12</td>
<td>1.78</td>
</tr>
<tr>
<td>$K_W/K_A$</td>
<td>24</td>
<td>30</td>
<td>18</td>
</tr>
</tbody>
</table>

$a$ Experimental error +/-5%  
$b$ Experimental error +/-6%

A rapid look at these constants shows that catalyst surface coverage of methanol and water decreases as the alkyl chain of the reacting carboxylic acid increases. Particularly, the adsorption of methanol on surface acid sites is noticeably affected by HCp. In fact, one might have expected a reverse trend given the polar and hydrophilic nature of methanol, which could have been expected to preferably bond to the Nafion domains on SAC-13 [18] while hampering the contact of other hydrophobic reactants with the catalyst surface. The decreased methanol adsorption on the catalyst, however, may suggest a longer residence time for the carboxylic acids on the Brønsted sites of SAC-13 as their alkyl chain length increases. It is probable, then, that adsorbed HCp is able to modify the catalyst surface affecting alcohol adsorption.

Using the kinetic and adsorption equilibrium parameters listed in Table 6.2 and numerical integration (Runga-Kutta), carboxylic acid conversion at a given time can be predicted from equation (2). The dotted lines in Figure 6.1b depict calculations of esterification progress from equation (2). Thus, equation (2) is able to satisfactorily
represent the evolution of esterification for small acids with methanol on SAC-13. However, the model somewhat overestimates the conversion profile for the bulkier HCp. So, given that equation (2) was derived from initial kinetics, there might be some unaccounted deactivating factors coming into play with reaction progress that become more important as the reacting acid increases its size. For instance, when the derived mathematical model is applied to the HCp esterification using twice the amount of catalyst ($C_C = 2.18$ g/45 ml) or a higher molar ratio of methanol to HCP ($n = C_{M,0}/C_{A,0} = 5$), the quantitative prediction precision of equation (2) is greatly improved as shown in Figure 6.3. However, the good agreement between predicted and experimental data suggests identical reaction mechanistic routes [26] in all cases under SAC-13 catalysis.

![Figure 6.3](image-url)  

**Figure 6.3** Comparison of experimental data with values predicted by equation (1) for esterification of HCp with methanol under different reaction conditions (symbols represent the experimental data; dotted lines represent the model prediction).
Catalyst deactivation in esterification of carboxylic acids

Water deactivation

The effect of water on reaction is important in esterification since \( \text{H}_2\text{O} \) is continuously produced as a byproduct. Certainly, the presence of water promotes the reverse reaction; however, water impact on catalyst activity is even more critical, as has been previously shown by us for \( \text{H}_2\text{SO}_4 \) [25] and SAC-13 [26] catalyzed esterification of acetic acid.

The hydrophobicity of the reacting carboxylic acid increases with increasing carbon chain length. Here, using different carboxylic acids, the impact of reactant hydrophobicity on the water inhibition effect was compared. The parallel lines shown in the logarithmic plots of initial reaction rate vs. water concentration (Figure 6.4) clearly indicate that the deactivating behavior of water is not a function of the hydrophobicity of the reacting acids in a wide range of water concentration (0.45-3 M) for both heterogeneous and homogeneous acid catalysts. As can be seen, only the most hydrophobic reactants showed some protection over acid sites in the low water concentration range (< 0.45 M) given the extreme large proton affinity of water [25]. Despite the somewhat decreased adsorption equilibrium constant of water on acid sites in HCp esterification (Table 6.2), the site affinity of water remained about 20 times as great as that of the carboxylic acids, as indicated by the ratio of \( K_{W}/K_{A} \) in Table 6.2. In this respect, the information obtained from this fundamental study using low molecular weight model compounds helps us to better understand the esterification of FFAs contained in lipid feedstocks such as vegetable oils and animal fats.
Figure 6.4 The impact of carboxylic acid hydrophobicity on the water inhibition effect using (a) SAC-13 and (b) H$_2$SO$_4$. 
Catalyst reusability and regeneration

The reusability of solid catalysts is one of their main advantages over liquid homogeneous catalysts. In order to inspect this characteristic for the SAC-13 catalyst, the esterification reactions of HAc, HBu and HCp at 60°C were investigated by running consecutive reaction cycles using the same reaction conditions as described earlier. Each reaction cycle took 11 h for HAc and HBu esterification and 24 h for HCp, so that the latter could reach a similar conversion level (60~75%) at the end of the first reaction cycle. After each cycle, reaction mixtures were decanted, the catalyst was recovered, and a new reaction cycle was started with fresh reactants. The relative initial catalytic activity for each cycle is plotted in Figure 6.5. Continuous activity loss of SAC-13 with each reaction cycle was observed for all carboxylic acids. Catalyst reusability was highest for HAc esterification with SAC-13 retaining about 75% of its original activity after three 11 h cycles. SAC-13 underwent more significant deactivation with reactions involving larger carboxylic acids. For instance, after three 11 h cycles the catalyst only retained 65% and 50% of its initial activity in the first cycle for HBu and HCp, respectively.

Water produced from esterification can be expected to have inhibited SAC-13 catalytic activity. When catalysts were recovered from reaction mixtures and reused with fresh reactants without any catalyst treatment, the amount of water chemically and physically bonded to the catalyst surface from the previous cycle may have been an important contributing factor to deactivation. However, the activity pattern shown in Figure 6.5 cannot be explained totally by catalyst deactivation due to water clustering around the acid sites. Otherwise, reaction involving HAc esterification should have shown the highest deactivation since this reaction had the highest conversion of
carboxylic acid, 75% after the first reaction cycle of 11 h vs. only 60% for HBu (11 h) and for HCp (24 h). Furthermore, according to Table 6.2, the acid sites of SAC-13 showed a higher site coverage and a larger water adsorption equilibrium constant for HAc esterification than for esterification involving the larger carboxylic acids. Thus, it is unlikely that residual water on the catalyst surface after each reaction cycle was the most significant factor for the observed differences in catalyst deactivation following multiple reaction cycles.

For reactions using HBu and HCp, an additional series of reaction cycles were carried out in an attempt to examine the possibility of catalyst regeneration by solvent washing. In these experiments, after the catalyst was recovered from each reaction cycle, it was washed extensively with THF and dried again under vacuum at 25°C for 4h before a new cycle was started with fresh reactants. Catalytic activity and conversion for each cycle are shown in Table 6.3. THF washing was able to improve catalyst reusability for the reaction of HBu. Catalyst activity decreased only 10% after two 11 h cycles and this activity was maintained during the next 2 cycles. A different situation, however, was observed for HCp. Despite some improvement, THF washing was not able to maintain catalyst activity. SAC-13 still showed continuous activity loss after each reaction cycle. The initial activity lost after three reaction cycles was about 30%. For the cycling series of 11 h, the catalyst showed an almost identical deactivation profile to that observed in the cycling series of 24 h, suggesting that catalyst deactivation takes place early during the reaction cycles. In addition, increasing the temperature of vacuum pretreatment from 25 to 80°C had little effect on catalyst reactivation (4th 24 h cycle of HCp, Table 6.3). Using alcohol washing of the spent catalyst, Alvaro et al. [32] have reported excellent
reusability for a “SAC-13 like” perfluoroalkylsulfonic acid modified MCM-41 silica in the esterification of HCp with ethanol. The possible in-situ washing ability of methanol could have been responsible for the better correlation of the derived mathematical model based on initial kinetics and experimental data when using a larger excess of methanol during reaction (Figure 6.3). However, we found that methanol washing between cycles was no better for SAC-13 catalyst reusability than THF washing (Table 6.3).

Sulfur leaching could have been a possible cause behind the catalyst deactivation during multiple reaction cycles as it is known to occur for SO₄²⁻/ZrO₂ [33, 34]. Elemental analysis, however, showed that the spent SAC-13 after four 11 h HCp esterification cycles maintained 96% of its original sulfur content.

Differences observed in catalyst reusability for reactions using different carboxylic acids suggest the entrapment of bulky reactants, intermediates, and products in the Nafion nanodomains as the most probable cause for the loss of catalyst activity. Supporting this hypothesis, the spent catalyst after 4 HCp esterification cycles (using THF washing between) showed decreased BET surface area and pore volume but increased average pore diameter (Table 6.4), thus suggesting the blockage of micropores in the catalyst. By contrast, the spent catalyst after 4 reaction cycles using HBu possessed similar physical properties as fresh SAC-13, which is consistent with its better reusability.
Table 6.3 SAC-13 deactivation following multiple reaction cycles of esterification of methanol and HBu/H Cp at 60°C with solvent washing and vacuum drying between cycles (CA,0 = 3 M, CM,0 = 6 M; catalyst loading = 1.09 g/45 ml.)

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>Cycling time (h)</th>
<th>Solvent</th>
<th>Parameter</th>
<th>Reaction cycles</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBu</td>
<td>11</td>
<td>THF</td>
<td>η&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>100%</td>
<td>94.3%</td>
<td>90.4%</td>
<td>91.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x&lt;sub&gt;A,f&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>0.59</td>
<td>0.57</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>HBu</td>
<td>24</td>
<td>THF</td>
<td>η&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>100%</td>
<td>89%</td>
<td>77%</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x&lt;sub&gt;A,f&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>0.58</td>
<td>0.54</td>
<td>0.51</td>
<td>0.47</td>
</tr>
<tr>
<td>HCp</td>
<td>11</td>
<td>THF</td>
<td>η&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>100%</td>
<td>88%</td>
<td>78%</td>
<td>68%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x&lt;sub&gt;A,f&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>0.39</td>
<td>0.35</td>
<td>0.33</td>
<td>0.31</td>
</tr>
<tr>
<td>HCp</td>
<td>11</td>
<td>MeOH&lt;sup&gt;d&lt;/sup&gt;</td>
<td>η&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>100%</td>
<td>88%</td>
<td>77%</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x&lt;sub&gt;A,f&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>0.40</td>
<td>0.37</td>
<td>0.33</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>a</sup> η = \( \frac{r_{0,f}}{r_{0,1}} \times 100\% \) is defined as the ratio of the initial reaction rate using the recycled catalyst to that using fresh catalyst.

<sup>b</sup> \( x_{A,f} = \frac{C_{A,0} - C_{A,f}}{C_{A,0}} \) is the conversion of carboxylic acid when each cycle ends.

<sup>c</sup> Catalyst was evacuated at 80°C for 4h after washing with THF at room temperature prior to the 4<sup>th</sup> cycle.

<sup>d</sup> Catalyst was washed in MeOH at 50°C for 4h followed by evacuation at 25°C for 4h.
Table 6.4 Physical properties of the fresh and used catalyst samples recovered after HBu and HCp esterification for four consecutive 11 h reaction cycles.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{BET}$ (m²/g)</th>
<th>Average pore diameter (Å)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh SAC-13</td>
<td>233.6 ± 5.6</td>
<td>101.0 ± 2.3</td>
<td>0.59 ± 0.01</td>
</tr>
<tr>
<td>Spent SAC-13 (HBu)$^a$</td>
<td>230.6 ± 4.8</td>
<td>103.7 ± 1.1</td>
<td>0.60 ± 0.01</td>
</tr>
<tr>
<td>Spent SAC-13 (HCp)$^a$</td>
<td>179.0 ± 0.2</td>
<td>120.6 ± 0.3</td>
<td>0.55 ± 0.01</td>
</tr>
</tbody>
</table>

$^a$ Spent catalysts were washed using THF and then evacuated at 25°C after each cycle.

Figure 6.5 SAC-13 deactivation following multiple reaction cycles of esterification of HAc, HBu, or HCp with methanol at 60°C without any treatment ($C_{A,0} = 3$ M, $C_{M,0} = 6$ M; catalyst loading=1.09 g/45 ml; The cycling time was 11 h for HAc and HBu and 24 h for HCp.)
FT-IR was used to characterize the catalyst before and after reaction cycling. Figure 6.6 shows IR spectra in the range of 1200-3200 cm\(^{-1}\), for both fresh and spent catalyst samples. The peaks centered at 2900 cm\(^{-1}\) and 1700 cm\(^{-1}\) that evolved for the used catalysts can be assigned to the stretching frequencies of -CH\(_2\)/-CH\(_3\) and C=O groups, respectively. Appearance of these signals together with the small band at 1460 cm\(^{-1}\) which may be ascribed to the bending and/or scissoring vibration of C-H provide evidence for the strong adsorption of carboxylic acids on the catalyst surface. Note that after multiple esterification cycles, the adsorption band at 1630 cm\(^{-1}\) due to the bending vibration of O-H bonds in water [35, 36] weakens more on the HCp spent catalyst. This suggests a higher hydrophobic character for the surface of this material conforming to the
hypothesis of greater hydrocarbon accumulation on the catalyst surface when HCp is used.

Since FT-IR is usually good only as a qualitative technique, TGA was carried out to make a further assessment of the hydrocarbon accumulation on the used SAC-13 catalysts. In the calculation, we assumed that the mass of silica matrix in the catalyst was unchanged by the reaction. Thus, the mass of the catalyst was normalized to the residual silica amounts at 700°C. TGA profiles re-plotted this way are shown in Figure 6.7. As can be seen, spent catalysts recovered from the esterification of HCp showed the greatest weight loss after 280°C. It is at this temperature that the decomposition of the -SO₃H moieties starts, marking the thermal degradation of Nafion nanodomains. Since at this temperature (280°C) any physisorbed or reversibly chemisorbed compounds should have already desorbed, it is reasonable to ascribe the extra loss in mass (in comparison to the fresh catalyst sample) to strongly adsorbed organic species on the catalyst surface. Strong adsorption of larger organic compounds may happen through a combination of two pathways: 1) irreversible adsorption on acid Bronsted sites; or 2) entanglement of long alkyl chains with the Nafion nanodomain polymeric chains in a “spaghetti-like” fashion.

In Figure 6.7, note how the spent catalyst sample recovered from the esterification of HBu showed a TGA profile after 280°C similar to that of a fresh catalyst sample, suggesting little accumulation of strongly bonded hydrocarbon species on the SAC-13 catalyst, in accordance with the catalyst reusability pattern observed for this reaction (Table 6.3). Note as well in Figure 6.7 that the thermal stability of the Nafion perfluorinated polymeric backbone was affected by the presence of hydrocarbon species.
from reaction. For instance, for the catalyst after HCp reaction, rapid degradation started at 375°C, about 60°C below the onset temperature for the degradation of a non-used catalyst sample. In contrast, the used catalyst from the HBu reaction was destabilized by only 20°C compared to fresh catalyst. The shift in thermal stability of the used catalyst samples was probably caused by the faster decomposition of hydrocarbons (compared to fluorinated polymers) which facilitated the production of OH and/or carbon-based radicals. Radical species are known to act as reaction initiators in the degradation of the Nafion polymeric perfluorinated resin [37].

Consequently, TGA data support the hypothesis of greater accumulation of hydrocarbons from the HCp reaction on the used catalyst. This is in agreement with the idea of acid site blockage by the large carboxylic acids, crowding access to active sites and inhibiting catalyst activity. In addition, the larger the carboxylic acid, the more difficult is its removal by solvent washing. However, it is possible that intensive catalyst washing with solvents [38] or techniques more apt to extract hydrocarbons such as supercritical fluid extraction [39] might in fact improve catalyst regeneration.
**Figure 6.7** Thermogravimetric analysis (TGA) of the fresh and the used catalyst samples recovered after HBu and HCp esterification for four consecutive 11 h reaction cycles (Used catalyst samples were washed using THF and then evacuated at 25°C after each cycle).

**Summary**

The impact of carboxylic acid carbon chain length on heterogeneous acid catalyzed esterification using silica supported Nafion (SAC-13) was studied and compared to the case using H2SO4. The reactivity of the carboxylic acids was controlled by steric factors as the alkyl chain linearly lengthened. The reactivity-structure response was similar for both liquid and solid acid catalysis for small carboxylic acids (HAc to HBu). For larger carboxylic acids (HBu to HCp), there was little if any additional impact of increasing chain length on reactivity for homogeneous catalysis. A contrasting trend, however, was observed for heterogeneous catalysis where there was a continuous inhibition effect on activity by the increasing chain length of the carboxylic acid. This difference was
probably due to the restricted conformational freedom of molecules as they adsorb on solid surfaces. Large carboxylic acids hardly impacted water deactivation of Brønsted acid sites for both the liquid and solid catalysts, despite the increased hydrophobicity. Nevertheless, alkyl chain length had an important effect on SAC-13 reusability. Using THF washing, the Nafion/SiO₂ nanocomposite catalyst showed good reusability in the esterification of low molecular weight acids. However, the catalyst underwent continuous activity loss in consecutive reaction cycles using the larger HCp. Catalyst deactivation was probably due to the accumulation of the carboxylic acid molecules/intermediates on/in the nanodomains of the Nafion resin. Such accumulation may have been caused by the irreversible adsorption of carboxylic acids on Brønsted sites and/or their entanglement with the polymeric chains of the Nafion nanoparticles. Effective regeneration is needed to improve the applicability of SAC-13 in the esterification of large free fatty acids.
References


CHAPTER 7
TRANSESTERIFICATION OF TRIACETIN USING SOLID BRØNSTED BASES

[As published in *Journal of Catalysis* 2007, 246, 428-433]

Abstract

This paper reports the results of an investigation into the use of solid Brønsted base catalysts as a potential alternative to homogeneous base catalysts in the transesterification of triacetin with small alcohols carried out under mild reaction conditions. Two catalysts having organic quaternary ammonium functionality (QN⁺OH⁻) were used for the transesterification of triacetin with methanol (a model reaction) and their performances were compared in detail. One was a resin (A26) and the other a functionalized silica gel (QN⁺OH⁻/SiO₂). Reactions were carried out in an isothermal well-mixed batch reactor at 60°C. Both solid bases showed appreciable catalytic activity for the transesterification of triacetin conforming to the base strength of the active centers. Although the polymeric organic catalyst showed lower site activity, it was more stable during multiple reaction cycles (i.e., showed less deactivation) than the silica-supported catalyst and exhibited a higher total selectivity for glycerol for a given triacetin conversion. The effect of the support on the Brønsted base catalyzed transesterification is discussed as well as probable routes for silica-supported catalyst deactivation.
Introduction

Transesterification of triglycerides (TGs) with low molecular weight alcohols is the central reaction in the synthesis of biodiesel from oils and fats. Commercially, this reaction is carried out using homogeneous base catalysts, which are corrosive and non-reusable but also produce neutralization waste causing increased cost and environmental concern. Replacement of liquid homogeneous catalysts with solid heterogeneous catalysts would greatly solve problems associated with expensive separation protocols involved with the former, yielding a cleaner product and greatly decreasing the cost of synthesis [1].

Great emphasis has been put on the possibility for solid strong bases to replace homogeneous bases such as NaOH. A variety of basic solids, such as alkali ion-exchanged zeolites [2-4], supported alkaline metal ions/oxides/salts [5], alkaline earth oxides [6], aluminum-magnesium mixed oxides derived from clay minerals such as hydrotalcite [7], anion exchange resins [8] and heterogenized alkylguanidines [9], have been tried and have shown some catalytic ability for TG transesterification. However, most of these solid bases reported in the literature are of the Lewis type. The problem for Lewis bases like MgO is that the polar species (i.e., methanol and glycerol) present during biodiesel synthesis can form Mg\(^{2+}\) methoxylate and glycerates, which end up leaching from the solid catalyst and acting as homogeneous catalysts in the solution media [1, 10]. In recent studies using ETS-10 (Na, K) [4] and alkylguanidines/resin [9], these Lewis bases have been found to leach out to the bulk solution even under mild conditions (60°C and 70°C), losing much of their activity after only a few reaction cycles and contaminating the products. Besides leaching, the nucleophilic attack on the carbonyl
carbon of esters is also a potential problem for some Lewis bases such as γ-aminopropylsilica leading to catalyst deactivation [11].

Here, the use of solid Brønsted bases having organic quaternary ammonium functional groups (QN⁺OH⁻) is reported for TG transesterification. One base was a polymeric resin with QN⁺OH⁻ terminated groups (A26, Rohm & Hass) and the other a QN⁺OH⁻ functionalized silica. The Brønsted base functionality in these materials should result in a reaction initiation step in transesterification of a triglyceride with methanol analogous to that for homogeneous bases. The first step is the formation of a methoxide ion, which is able to carry out a nucleophilic attack on the glycerol ester moieties of the glyceride species [1]. The positive counter ions (organic ammonium groups), being bonded directly to the support surface, electronically retain the catalytic anions on the solid surface, preventing base sites from being leached out. For instance, the rehydrated hydrotalcites of Brønsted type have been shown to undergo less deactivation than the Lewis type counterpart (calcined hydrotalcites) in fatty ester glycerolysis [12]. Moreover, heterogenized base catalysts with grafted QN⁺OH⁻ groups have been successfully applied in various fine chemical synthesis reactions showing high and sustained catalytic activity [13, 14] even under mild reaction conditions. The uses of the resin catalyst in organic synthesis have been reviewed in Chinese [15, 16].

In this work, triacetin (the acetic acid triester of glycerol) was used as a model compound for TGs in order to provide fundamental insight into TG transesterification catalyzed by catalysts with Brønsted base functionality. Triacetin, having the same chemical functionality of any triglyceride molecule, shares the same reactivity principles of triglycerides. Triacetin, however, differs from common TGs in terms of its size. Hence,
this study should be considered as an initial exploration of TG transesterification by solid Brønsted bases. Further studies are required to address issues relating to substrate size, polarity, alcohol miscibility, etc.

**Experimental**

Anhydrous methanol (Aldrich, 99.9 wt%) and triacetin (Fisher Scientific, 99 wt%) were used without further purification. A diacetin mixture (25 wt% triacetin, 45 wt% diacetin, 26 wt% monoacetin and 4 wt% glycerol) obtained from Fisher Scientific was used for GC calibration. A26 in the hydroxide form and 3-(trimethylammonium)-propyl-functionalized silica gel chloride form (QN⁺Cl⁻/SiO₂) were purchased from Aldrich. The as-received A26 contained large amounts of water owing to the high hydroscopic character of the OH⁻ function. Prior to reaction, the catalyst was thoroughly washed with methanol and then dried to constant weight at room temperature under vacuum. The activation of QN⁺Cl⁻/SiO₂ to QN⁺OH⁻/SiO₂ was carried out following the methodology used by Rodriguez et al. [13]. The solid was recovered by filtration and then extensively washed with methanol at room temperature in order to completely remove NMe₄OH residues physisorbed onto the porous silica matrix. Although the proton-transfer between methanol and OH⁻ taking place in methanol has been shown to have a low equilibrium constant (K<1) [17, 18], the extensive washing with methanol is still expected to push the reaction to the right given the large excess of methanol used and the limited concentration of OH⁻ groups on the catalyst. In addition, multiple methanol washing steps removes the byproduct water each time. However, since actual exchange of OH⁻ by MeO⁻ groups was not experimentally verified, in the following text, we will keep referring to these
materials as OH\(^{-}\) functionalized. After overnight vacuum drying, the catalyst samples were stored in a desiccator until use. The physicochemical properties of catalyst samples were characterized by elemental analysis (Galbraith Lab., Knoxville, TN) and isothermal N\(_2\) adsorption (Micromeritics ASAP 2002). The results are summarized in Table 7.1.

**Table 7.1** Physicochemical properties of the fresh catalysts

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A26</th>
<th>QN(^7)OH(^{-})/SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td>styrene-divinylbenzene</td>
<td>silica gel</td>
</tr>
<tr>
<td>Crosslink (% DVB)</td>
<td>11%</td>
<td>---</td>
</tr>
<tr>
<td>Functional group</td>
<td>-ph-CH(_2)N(CH(_3))(_3)(^+)</td>
<td>-pr-N(CH(_3))(_3)(^+)</td>
</tr>
<tr>
<td>Surface area</td>
<td>21.9 m(^2)/g</td>
<td>244 m(^2)/g</td>
</tr>
<tr>
<td>Pore size</td>
<td>59 nm</td>
<td>5.1 nm</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.33 cm(^3)/g</td>
<td>0.32 cm(^3)/g</td>
</tr>
<tr>
<td>Site density(^a)</td>
<td>2.94 mmol/g</td>
<td>0.61 mmol/g</td>
</tr>
<tr>
<td></td>
<td>0.13 mmol/m(^2)</td>
<td>2.52 x10(^{-3}) mmol/m(^2)</td>
</tr>
</tbody>
</table>

\(^a\) Based on nitrogen elemental analysis of the fresh catalyst after washing and drying.

Reaction experiments were carried out in an isothermal well-stirred batch reactor at 60°C under a nitrogen atmosphere. The presence of mass transfer limitations on reaction at these conditions was experimentally ruled out as before [19]. Prior to reaction, methanol and triacetin were mixed in a 6:1 molar ratio (total reaction volume of 30 ml) and heated. The compounds are completely miscible at the conditions used. Once at the desired temperature, the transesterification reaction was started by charging the catalyst. In one separate experiment, the resin catalyst A26 was pre-soaked in MeOH before initiating reaction by adding triacetin. Within experimental error, the reaction profiles obtained for the two different startups of A26 catalyzed transesterification were very close, indicating little effect on reaction kinetics of the swelling of the polymer-based
catalyst by methanol. Reaction progress was monitored by withdrawing aliquots of 30 µl at definite time intervals. A Hewlett-Packard 6890 gas chromatograph equipped with a DB-1 column (0.32mm x 30m x 0.53µm) and split/splitless inlet was used for sample analysis with ethanol as an internal standard.

**Results and Discussion**

Figure 7.1 shows the typical conversion profiles for triacetin transesterification in the presence of the solid Brønsted bases. As expected, the strong base character of the functionalized quaternary ammonium groups resulted in high catalytic activity. After 240 min, around 60% triacetin conversion was achieved using either base, which is very good considering the low concentration of catalyst used in these experiments (0.88 wt% relative to the total mass of the reaction mixture). Upon doubling the catalyst loading of A26 (to 1.67 wt%), 90% triacetin conversion was achieved after 240 min (data not shown). The catalytic activities exhibited by the solid Brønsted bases in triglyceride transesterification are still lower than that of the homogeneous base NaOH. For instance, when the same reaction was performed in the presence of only 4x10⁻³ wt% (1.2x10⁻³ g/30 ml) NaOH, 52% triacetin conversion was reached in 2 min. At 15 min, the triacetin conversion was 90%.
If the N content of A26 and QN⁺OH⁻/SiO₂ is used as an estimation of the maximum expected base site density (Table 7.1), a TOF calculation using initial kinetic data (conversion < 10%) allows a catalytic comparison on a site basis. As a result, TOF values during initial reaction were determined to be higher for QN⁺OH⁻/SiO₂ (56 x 10⁻³ s⁻¹) compared to A26 (11 x 10⁻³ s⁻¹), pointing to silica as a more efficient support for quarternary ammonium functionalities. There are three factors likely causing the discrepancy in apparent site activity between the two catalysts, site accessibility, dispersion and base site strength. For the silica catalyst, the location of active sites is restricted to the surface of the support, whereas for the organic resin, it is known that a portion of reactive groups are buried inside the nodules and/or gel microspheres, remaining unapproachable for large reactant molecules [20]. The fact that pre-swelling
A26 with methanol prior to reaction showed little effect on transesterification kinetics suggested a rapid access of methanol throughout the macroreticular resin [21]. This, however, does not necessarily guarantee that methanol swelling can make available for the TG reactants all the sites buried inside the gel microspheres. For instance, by comparing to a silica-supported Nafion (SAC-13) on a site basis (TOF), Lopez et al. found that the unsupported Nafion, even pre-swollen by methanol, had only 30–40% active sites exposed to the reactant molecules for triacetin transesterification (60°C) [22]. Secondly, the high dispersion of the basic species on SiO₂, 2.52x10⁻³ vs. 0.13 mmol/m² for A26, probably accounts in some part for the TOF difference. The macroreticular divinylbenzene polymer with low or medium crosslink level (<25% DVB) is known to have poor ability to disperse organic functional groups homogenously [20]. Short intervals among immobilized functionalities have been experimentally observed using phosphine displacement on tricarbonylnitrosylcobalt [20]. It is likely that some neighboring sites get too close to carry out reaction simultaneously owing to steric constraints. Moreover, the α-positioned benzene ring in A26 with electron-withdrawing properties can increase the positive character of the ammonium ion, thereby increasing the strength of the ionic bond with its counter ion and thus decreasing its basic strength.

For instance, the quaternary salts of bulkier and more electron-donating alkyl groups, having greater distances between cations and anions, are known to present higher activity in base catalyzed organic syntheses [23].

Triglyceride transesterification can be carried out using not only base but also acid catalysis. A variety of heterogeneous acid catalysts have been investigated for triacetin transesterification in a recent study carried out by our group [4]. By comparison, the solid
Brønsted bases of this study were able to show an obvious edge over the solid acids in catalytic efficiency. For example, even the most active catalyst among those used in ref. [4], Amberlyst 15 (A15) at a loading of 2 wt%, could only reach 80% triacetin conversion after 480 min when reaction was carried out under otherwise identical reaction conditions. Moreover, if compared on a site basis (using N content for the estimation of base sites and S content for that of acid sites), both A26 and QN⁺OH⁻/SiO₂ catalytically outperformed the sulphonic acid resin A15 with initial TOF values of 11 x 10⁻³ and 56 x 10⁻³ s⁻¹, respectively, versus 1.9 x 10⁻³ s⁻¹ for A15 [4]. This is consistent with the lower energy demanding mechanistic route involved in base catalyzed transesterification [1]. It should be noted, however, that homogenous alkali-catalyzed soybean oil transesterification has been estimated to be about 3 orders of magnitude faster than the acid-catalyzed reaction [24]. The smaller activity gap measured for heterogeneous catalysts, as given above, could be due to an effect of site immobilization and/or the complexity in estimating the number of “active” reaction sites. For instance, the base site density of A26 can vary from 2.94 to 1.6 to 0.33 mmol/g as the methodology employed for the assessment of base sites changes from N elemental analysis to aqueous HCl-NaOH back titration to phenol (in MeOH) adsorption at 60°C.

A26 drives triglyceride transesterification to completion to a larger extent than QN⁺OH⁻/SiO₂ does. For instance, for identical amounts of triacetin reacted, a greater methyl ester yield was obtained for A26 (Figure 7.2), and this was more obvious as reaction progressed. Figure 7.3 shows the observed selectivities of diacetin, monoacetin and glycerol at ca. 64% triacetin conversion using NaOH as a reference. Similar product distribution profiles were obtained for NaOH and QN⁺OH⁻/SiO₂, whereby diacetin and
monoacetin (intermediate products) were the predominant compounds with concentration levels double that of glycerol (the final product). By contrast, the opposite was observed for A26 where glycerol was significantly the main product.

Given that the active sites on both catalysts are essentially identical, the significant dissimilarities in selectivity between A26 and QN°OH/SiO₂ seem to be due to the distinct properties of the respective supports. Barrault and co-workers [25, 26] and Corma et al. [27] have noted that the basic strength of solid bases hardly impacts the selectivity of glycerolysis of either methyl stearate or triolein. Indeed, other polymeric matrix supported catalysts such as A15 and Nafion, despite operating through different catalytic functions (acidic sulphonic groups), show triacetin transesterification selectivities rather similar to that obtained with A26 under the same reaction conditions [4]. Moreover, the use of small reagent molecules with relatively little steric constraints helps to bring the focus onto the differences in support surface chemistry rather than morphology (product shape selectivity). The crosslinked styrene divinylbenzene copolymer is hydrophobic in nature favoring the adsorption of lipophilic species. Hence, the interaction of the non-polar matrix with the polar hydroxyl group in the glycerol backbone must be thermodynamically less favorable. This way, the ester branch(es) of tri/di/monoglycerides should have an elevated tendency to be exposed to methoxide anions within the vicinity of the active sites. In addition, glycerol is known to be a rather polar species that can form a strong solvation sphere around the ionic active center [28]. As the triacetin transesterification progresses and glycerol is continuously produced, the stepwise replacement of methoxy moieties by glycerate species at the reaction sites favors the reverse glycerolysis reaction. Thus, the high glycerol selectivity of A26 further suggests
that glycerate formation in this case is hindered probably due to the lower tendency of the polar glycerol molecule to remain around active sites. In line with the above explanation, we have found that the presence of a hydrophobic solvent, hexane, can make triglyceride transesterification using A26 more selective to glycerol even at a lower MeOH/TG ratio (data not shown). By contrast, the silanol groups on the silica matrix constitute a rather hydrophilic micro-environment around highly isolated active sites impacting product selectivity in an exactly opposite manner to the polymeric resin. In the case of NaOH, the mobile OH-/MeO⁻ species are favorably solvated by methanol molecules also establishing a hydrophilic sphere around the catalytic sites.

**Figure 7.2** Methyl acetate (MeAc) yield in A 26 or QN⁺OH⁻/SiO₂ catalyzed triacetin (TAc) transesterification as a function of TAc conversion (Open symbols and lines denote the behavior of fresh catalyst in the 1ˢᵗ cycle; the four labeled solid triangles represent the reaction data of QN⁺OH⁻/SiO₂ at the end of 1-4 consecutive 4h reaction cycles, respectively.)
Although highly active in the initial period, QN\(^+\)OH\(^-\)/SiO\(_2\) began to suffer significant activity decay after 50% triacetin conversion. At this point, QN\(^+\)OH\(^-\)/SiO\(_2\) was outperformed by A26 (reaction time of 4 h) (Figure 7.1), suggesting that the active sites on A26 are more stable. Catalyst reusability was examined by carrying out subsequent reaction cycles. The used catalyst was separated from the reaction mixture after 4 h and used again with fresh reactants in a second reaction cycle under the same reaction conditions as before. The same procedure was repeated twice more for a total of four reaction cycles. Results for all consecutive reaction cycles are given in Table 7.2. As can be seen, A26 was able to largely maintain its overall catalytic activity and selectivity for all reaction cycles. The small variation in reaction activity observed in the series of reaction cycles was probably due to experimental error or some hydrocarbon accumulation on the catalyst surface in the absence of any washing treatment between cycles. Different from our observations, deactivation of anionic resins used for biodiesel synthesis was observed by Shibasaki-Kitakawa et al. [8] to be due to neutralization of active sites by fatty acid molecules formed during reaction. Fatty acids formed via the reaction of active catalytic sites consisting of OH\(^-\) groups with ester species in the reaction media (glycerides and the biodiesel product). Indirectly, the results of these authors support our earlier hypothesis that methanol washing is able to exchange most OH\(^-\) groups in the resin by MeO\(^-\) groups that cannot give rise to the formation of carboxylic acid and, hence, preclude catalyst deactivation by this route.

The silica-supported catalyst, however, underwent continuous activity loss with consecutive reaction cycles. The triacetin conversion at 4 h quickly dropped from 58% to 14% after 3 cycles. The glycerol selectivity exhibited a sharp decrease as well. This latter
observation, however, was due to the decreased total triacetin conversion. For instance, when the methyl acetate yields were compared at the same level of conversion, no change was found for the used catalysts (Figure 7.2). The nitrogen elemental analysis for the fresh and the used QN⁺OH⁻/SiO₂ catalyst after 4 cycles showed a decreased N content from 0.86 wt% to 0.26 wt%, indicating a permanent loss of base sites accompanying the strong deactivation. To further confirm the presence and absence of site leaching for functionalized silica and polymeric resin, respectively, catalysts samples were soaked in methanol at 60°C for 4 h and the methanol then recovered by filtration and used for triacetin transesterification in the absence of the solid catalyst. As shown in Figure 7.4, appreciable transesterification activity was determined using the methanol from the QN⁺OH⁻/SiO₂ soak, but only negligible activity using the methanol from the A26 soak. This result provides further evidence for the different chemical stabilities of the two Brønsted solid bases and also indicates that the sites of the silica-supported catalyst were leached out in the form of basic species.
Figure 7.3 Selectivity to diacetin, monoacetin and glycerol of NaOH, A26 and QN$^+$OH$^-$/SiO$_2$ at triacetin conversion ($x_{TAc}$) of 64 \pm 5.5\% (T=60^\circ C).

Figure 7.4 Transesterification of triacetin using methanol that had been exposed to A26 or QN$^+$OH$^-$/SiO$_2$ at 60^\circ C overnight.
Table 7.2 Cycling experiments (4 h reaction) for triacetin transesterification (TAc) on A-26 and on QN⁰OH⁻/SiO₂.

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<tr>
<td><strong>TAc Conversion</strong></td>
<td>0.65</td>
<td>0.67</td>
<td>0.58</td>
<td>0.61</td>
</tr>
<tr>
<td>MeAc Yield&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.49</td>
<td>0.52</td>
<td>0.43</td>
<td>0.44</td>
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<tr>
<td>GL&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50.6</td>
<td>53.8</td>
<td>47.5</td>
<td>48.4</td>
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<tr>
<td><strong>A26 Selectivity&lt;sup&gt;c&lt;/sup&gt; (%)</strong></td>
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<tr>
<td>MA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>25.9</td>
<td>25.8</td>
<td>25.6</td>
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<td>DA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>23.4</td>
<td>20.5</td>
<td>26.9</td>
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<tr>
<td><strong>QN⁰OH⁻/SiO₂ Selectivity&lt;sup&gt;c&lt;/sup&gt; (%)</strong></td>
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<tr>
<td>MA&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>33.6</td>
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<td>DA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>48.2</td>
<td>51.4</td>
<td>70.6</td>
<td>87.9</td>
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<sup>a</sup> Methyl acetate (MeAc) Yield = CₓMeAc/ (3 x CₓTAc,0)

<sup>b</sup> GL, MA and DA denote glycerol, monoacetin and diacetin, respectively.

<sup>c</sup> Glycerol Selectivity, GL% = CₓGL/ (CₓGL + CₓMA + CₓDA) x 100%

Monoacetin Selectivity, MA% = CₓMA/ (CₓGL + CₓMA + CₓDA) x 100%

Diacetin Selectivity, DA% = CₓDA/ (CₓGL + CₓMA + CₓDA) x 100%

Site leaching for the QN⁰OH⁻/SiO₂ catalyst is probably taking place through bond cleavage of the methylene moiety alpha to the ammonium center. This way, active site leaching can occur in the form of a tertiary amine. In order to identify the leached species, fresh catalyst samples of QN⁰OH⁻/SiO₂ were put in contact with deuterated methanol (CD₃OD) at 60°C overnight. After catalyst separation, the residual methanol was analyzed using <sup>1</sup>H-NMR (JEOL ECX 300, 300.5 MHz). In the resulting spectrum, the proton peak at 2.14 ppm corresponding to trimethylamine [29] indicates the degradation of the quarternary ammonium sites via the cleavage of the CH₂⁻⁻N⁺(CH₃) bond. In contrast, this characteristic peak is absent from the <sup>1</sup>H-NMR spectrum of the residual
methanol separated from A26, coinciding with the high chemical stability of the functionalized polymer.

Leaching of quaternary ammonium ions could have taken place due to a nucleophilic attack of hydroxy and/or methoxy ions on the alpha carbon (Figure 7.5a), resembling the Hofmann thermal degradation of quaternary ammonium groups. However, one would imagine that this reaction scheme should have been more important for A26, which has a more labile methylene due to the adjacent benzene ring [30]. But, evidently, under our reaction conditions, this does not occur to any great extent for A26. Thus, a likely deactivation mechanism for the deactivation behavior of QN⁺OH⁻/SiO₂ may be associated with the silica support. For instance, nitroxide groups immobilized on a silica surface have been found to have much higher mobility, i.e. rotational motion, than those covalently attached to a polystyrene matrix [18]. The surface-solvent-substrate hydrogen-bonding interaction has been suggested to be an important factor influencing the rotational freedom of the silica-bound nitroxide function [18]. Likewise, it is reasonable to assume that the quaternary ammonium species grafted on silica are less rigid than those on a polystyrene-divinylbenzene matrix. Moreover, it can be expected that charge transfer is more favorable on a silica surface where a methanol solvation sphere may be more easily developed around ionic sites than on a polymeric matrix such as in A26. In this sense, the leaching route depicted in Figure 7.5a may be more favorable on functionalized silica where less steric hindrance is present. Alternatively, considering the weak acidity of surface silanol groups on silica, the other plausible route for active site leaching could take place through the nucleophilic attack of Si-O⁻ groups (formed in the vicinity of active sites) on the methylene group alpha-bonded to the ammonium ion.
moiety (Figure 7.5b). To date, the exact nature of the resulting deactivated sites have not been determined.

![Schematic representation of possible active site leaching mechanisms for QN\textsuperscript{+}OH\textsuperscript{-}/SiO\textsubscript{2}.](image)

**Figure 7.5** Schematic representation of possible active site leaching mechanisms for QN\textsuperscript{+}OH\textsuperscript{-}/SiO\textsubscript{2}.

**Summary**

The transesterification of triacetin with methanol was successfully carried out under mild reaction conditions using solid catalysts with Brønsted base functionality of organic ammonium quaternary ions bonded to either silica or a polymeric support. The support
played an important role in catalyst selectivity and deactivation behavior. Despite a
greater site activity, the basic groups grafted to silica were less selective to glycerol for a
given triacetin conversion and more prone to deactivation. The polymeric resin catalyst,
on the other hand, exhibited outstanding features, such as great capacity to drive the
series reaction of glycerides to completion and to sustain high activity through multiple
reaction cycles without signs of significant deactivation. This catalyst appears as an
interesting alternative to strong soluble inorganic bases for triglyceride transesterification.
Deactivation of the QN+OH-/SiO₂ catalyst was due to site leaching caused by the
cleavage of the CH₂–N⁺(CH₃) bond. Such deactivation routes may be precluded by
raising the steric hindrance for the nucleophilic attack using bulkier tetraalkylammonium
(e.g., tetrabutylammonium) groups as the active site and/or silanol group derivation of the
silica surface.


CHAPTER 8
TRANSESTERIFICATION OF POULTRY FAT WITH METHANOL USING MG-AL HYDROTALCITE DERIVED CATALYSTS

Abstract

The synthesis of biodiesel from poultry fats provides a way to convert the by-product of a renewable resource to a very important value-added biofuel. In this work, the use of heterogeneous base catalysts derived from Mg-Al hydrotalcite was investigated for the conversion of poultry lipid to biodiesel. This solid base showed high activity for triglyceride (TG) transesterification with methanol without signs of catalyst leaching. Catalytic performance was significantly affected by pretreatment and operating conditions. Calcination at optimum temperature was key in obtaining the highest catalyst activities. Rehydration of the calcined catalyst before reaction using wet nitrogen decreased catalytic activity for the transesterification of poultry fat, opposite to what has been reported for condensation reactions. Also, methanol had to be contacted with the catalyst before reaction; otherwise, catalyst activity was seriously impaired by the strong adsorption of triglycerides on active sites. Both temperature (60-120°C) and methanol-to-lipid molar ratio (6:1-60:1) affected the reaction rate in a positive manner. The use of a co-solvent (hexane, toluene, THF), however, gave rise to a decrease in TG conversion overall. The catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest base sites. Subsequent reaction cycles showed stable activity. By re-calcination in air, complete catalyst regeneration was achieved.
Introduction

According to the U.S. Department of Agriculture (2002), there are 2.2 billion pounds of inedible poultry fat rendered each year making for approximately 20% of the total U.S. production of animal fats and 6.7% of that of total lipids [1]. Traditionally, the primary use of poultry fat has been as an animal feed ingredient. This use, however, has been seriously challenged with emerging concerns that this practice facilitates the transmission of potential infectious diseases from one animal species to another. Thus, the exploration of alternative routes to process and use this type of animal co-product is of great significance from both environmental and economical perspectives. Recently, the synthesis of biodiesel from poultry lipid provides a way for using more efficiently a renewable resource to form an important value-added biofuel [2, 3].

The conventional production of biodiesel from lipid feedstocks involves the use of homogenous basic catalysts such as sodium or potassium hydroxides, or alkoxides, which are very active, but present problems of corrosion, separation, and waste streams. The substitution of homogeneous catalysts with heterogeneous ones is crucial to eliminate problems associated with homogenous catalysts. Moreover, solid catalysts can be potentially used for long periods of time allowing for a technology easy to adjust to continuous processing, improving the economics of biodiesel production.

Thus far, a variety of solid bases including basic zeolites, metal carbonates, supported alkali metal ions and alkali earth oxides, have been tested for biodiesel synthesis [3]. Of these, the base form of X-zeolites showed only moderate activity owing to the diffusion resistance of bulky triglycerides (TGs) through the channels of faujasites [4, 5]. By contrast, the base form of the titanosilicate ETS-10 with microporous structure presented
promising activity for the methanolysis of TGs even at low temperature [5, 6]. The high catalytic performance of ETS-10, however, is the result of alkali methoxide leaching [3, 6], giving rise to homogeneous catalysis. Similarly, reports regarding the catalytic activity of other base catalysts, such as metal carbonates that can dissolve in the presence of polar compounds [3-5] (especially at reaction conditions with $T > 200^\circ$C, as required for this type of catalysts to be active [7, 8]), should also be examined in light of the leaching ability of those materials. Another example of a material with strong basicity and high activity for biodiesel synthesis was shown by Kim et al., who carried out transesterification of soybean oil using Na/NaOH/$\gamma$-Al$_2$O$_3$ obtaining around 75% biodiesel yield after 2 h reaction at 60$^\circ$C [9]. These authors, however, did not carry out a catalyst reusability study nor address catalyst deactivation and leaching. Hence, the possibility of homogenous base catalysis in this case cannot be completely disregarded.

Given their strong base character, alkali earth oxides, such as MgO and CaO, were expected to show high activities for triglyceride transesterification with low molecular alcohols [10]. However, so far, reported catalytic activities for biodiesel synthesis using solid bases from this metal group have been disappointing [6, 11-13]. Low surface area [6, 13] and limited concentrations of edge and corner defect sites [12, 13] are most probably responsible for the poor catalytic performance observed from this type of materials. Several techniques such as alkali metal doping [12], crystal nanonization [13], and dispersion on mesoporous supports [14] have been proposed as potential solutions.

The calcination of hydrotalcites (HTs), Mg$_x$Al$_y$(OH)$_{2(x+y)}$(CO$_3$)$_{y/2}$·mH$_2$O, at high temperatures yields homogeneously interdispersed mixed Mg-Al oxides (CHTs). CHTs have strong surface basicity, much like the pure oxides, whereas potentially containing
more surface defects owing to the Al$^{3+}$ cations incorporated in the MgO lattice [15]. In addition, these materials show high surface areas and pore volumes developed during the thermal decomposition of the parent hydrotalcites. Being an inorganic base, CHTs have high thermal stability, thus affording the potential for easy regeneration by re-calcination. Furthermore, as shown by previous studies [15, 16], the surface chemistry of these materials can be tuned by the careful control of compositional and pretreatment parameters, such as carbonate content, Mg/Al ratio, and activation temperature. CHTs have been applied in a variety of based catalyzed organic transformations with success [10, 17, 18]. They are considered as attractive candidates for biodiesel synthesis and some preliminary studies can already be found in the literature [16, 19, 20]. In this work, we have investigated the use of calcined CHTs in the transesterification of poultry fat with methanol, showing that their effective use can be greatly affected by catalyst pretreatment conditions as well as operational variables. In addition, catalyst deactivation and regeneration were addressed in this study.

**Experimental**

**Materials**

Anhydrous methanol (99.9 wt%) was purchased from Aldrich. High grade poultry fat with an acid content of less than 0.2% and a water content of 0.05% was kindly provided by Fieldale Farms Corporation. Tripalmitin, dipalmitin, $\alpha$-monopalmitin, glycerol and methyl palmitate were purchased from Sigma and used as reference compounds for GC calibration. All analytical chemicals were chromatographically pure and used without further purification. Hexane and ethyl acetate of HPLC grade were obtained from Fisher
Scientific. They were mixed in a volume ratio of 1:1 and used as solvent for GC analysis. The hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$, was purchased from Aldrich. Noteworthy, despite the fact that the Mg/Al molar ratio based on the given molecular formula would be expected to be 3, the actual Mg/Al ratio was determined to be 2.3 based on the compositional analysis provided by the vendor. The latter was further confirmed by us using ICP and EDS. Under a continuous flow of dry $\text{N}_2$, calcinations were carried out at 400-800°C in a horizontal furnace to obtain the Mg-Al mixed oxides. The heating rate was 10°C/min and the final temperature was maintained for 8 h.

**Characterization**

Monochromatic powder x-ray diffraction spectra were recorded with an XDS 2000 (Scintag Inc.) diffractometer (Cu-Kα radiation, $\lambda = 1.54$ Å) over a 2Θ range of 5–70° (step size, 0.02°; time per step, 1.0 s). Mg and Al content were determined by ICP (Galbraith Laboratory, TN) and by SEM-EDS using a SEM-Hitachi S3500N. BET surface area, pore diameter and BJH cumulative pore volume were obtained using $\text{N}_2$ adsorption-desorption at –196°C in a Micromeritics ASAP 2020. Typically, a 0.2 g sample was used for measurements. Prior to $\text{N}_2$ adsorption, the sample was outgassed for 12 h at 400°C. $\text{CO}_2$ and $\text{NH}_3$ TPD were carried out using an Altamira Instrument to characterize the basicity and acidity of CHTs, respectively. First, 0.2 g of catalyst was re-calcined at its original calcination temperature for 1 h in 20 mL/min of $\text{He}$ to remove any adsorbed volatile matter. Next, the sample was cooled to 30°C and saturated for 1 h using 20 mL/min of the adsorbate, $\text{CO}_2$ or 10% $\text{NH}_3$/He. Physisorbed $\text{CO}_2$ and $\text{NH}_3$ were eliminated by flushing with $\text{He}$ for 1 h at 30°C and 4 h at 100°C, respectively. The temperature was then ramped up at 10°C/min to 500°C for all samples with the exception
of catalysts initially calcined at 400°C for which 400°C was used as the ending point. CO₂ or NH₃ evolution was monitored by a TCD detector.

**Reaction Study**

Transesterification of poultry fat with methanol was carried out at 120°C in a Parr 4590 batch reactor consisting of a stainless steel chamber, a glass liner, a three-blade impeller, and a thermocouple. A typical molar ratio of methanol to poultry lipid was 30:1. The catalyst concentration was 10 or 20 wt% based on the poultry lipid weight. A 0.15 mL sample was periodically extracted from the reaction mixture using a microscale syringe with a pressure-lock button. The reaction sample was immediately mixed with 0.8 mL solvent (hexane: ethyl acetate = 1:1 v/v) at room temperature followed by centrifuging to separate out catalyst particles. Forty µL of homogeneous liquid was then withdrawn and further diluted in 5 mL solvent containing a known amount of methyl laurate, an internal standard, followed by GC analysis. Note, trimethylsilylation of the free hydroxyl groups in glycerol, mono- and diglycerides was not carried out. The resolution of analytes and their quantification were successful due to the high chemical inertness of the column used in our GC analysis (BPX5, SGE).

The GC analysis was performed using a Hewlett-Packard 6890 gas chromatograph equipped with an automatic injector, an on-column inlet, a 15 m x 0.25 mm x 0.1 µm BPX5 column and an FID detector. Following the injection of 1 µL of analyte solution, the column temperature was initially held at 50°C for 1 min, then ramped up at 15°C/min to 370°C and maintained there for 4 min. UHP helium was used as the carrier gas flowing at a constant rate of 6.0 mL/min. The fatty acid profile of poultry fat was determined using GC analysis coupled with ¹H NMR analysis (JEOL ECX 300, 300.53MHz) in
CDCl₃. The proton chemical shift assignments and quantification method for NMR spectroscopy of triglycerides can be found elsewhere [21, 22]. With the fatty acid composition obtained (palmitic, 18.1 wt%; palmitoleic, 6.4 wt%; stearic, 3.6 wt%; oleic, 47.0 wt%; linoleic, 23.8 wt%; linolenic, 1.1 wt%), the average molecular weight of the poultry fat was calculated to be 863 g/mol.

**Results and Discussion**

**Catalyst treatment**

*Catalyst calcination*

In the absence of calcination, the crystalline layered double hydroxide (LDH) intercalate precursor, HT, showed no catalytic activity for the reaction (data not shown), in agreement with the results reported for soybean oil transesterification [16]. Controlled thermal pretreatment is essential to convert HTs through dehydration, dehydroxylation, and decarbonization to Mg-Al oxides having strong Lewis basic sites associated with the M⁺[O²⁻] acid-base pairs [23, 24].

The calcination temperature has been reported to be an important parameter affecting the surface basicity of the resulting Mg(Al)O solid solution (CHT), i.e., the site strength, as well as site concentration and accessibility. This has been extensively shown from a variety of physico-chemical characterizations of CHT materials [15, 16, 24, 25]. To determine the influence of the calcination temperature on catalytic activity, hydrotalcite samples were activated at different temperatures (400-800°C) and then used for poultry fat transesterification with methanol at 120°C. All CHT samples exhibited the typical features of Mg(Al)O mixed oxides as identified by the XRD spectra (2θ = 43 and 63°)
Their catalytic activities are compared in Figure 8.2. As the calcination temperature rose from 400°C to 800°C, the poultry fat conversion (at 2 h) increased proportionally up to the maximum of 75% for CHT calcined at 550°C (CHT550) and then decreased gradually upon further increase in calcination temperature. Correlating well with the catalytic performance, the surface area and basicity of calcined HTs conformed to the existence of a maximum as a function of calcination temperature (Table 8.1) with the maxima also for CHT550. The acid site concentration, on the other hand, did not follow the same trend but rather continuously increased as the calcination temperature increased (Table 8.1). Thus, even though acid sites are known to be catalytically active for transesterification [2, 3] and help stabilize dehydrogenated intermediates [15], our results suggest that triglyceride methanolysis is predominantly mediated by base sites whereas the contribution due to Lewis acid sites (meanly Al^{3+} centers), in comparison, is limited. This observation was further confirmed using pyridine (py) poisoning experiments where py was used to neutralize the catalyst Lewis acid sites. The py-poisoned CHT500 catalyst did not show any change in TG transesterification activity at 120°C (data not shown), suggesting that Lewis acid sites neither significantly contribute to TG transesterification nor help to stabilize dehydrogenated intermediates (namely, methoxy groups on the catalyst surface). Note that the organic base, py, was purposively used here, as it has the ability to poison the Lewis acid sites of the CHT catalyst while being a weak base (pK\textsubscript{a} of C\textsubscript{5}H\textsubscript{5}NH\textsuperscript{+} = 5.2), minimizing any possible catalytic contributions to the reaction from physic-adsorbed and/or unadsorbed residuals. In a blank run in absence of CHT and in presence of 10x stoichiometrical py (using TPD-NH\textsubscript{3} as an estimation of acidity), negligible TG conversion was determined over an 8 h
reaction course at 120°C.

The change in catalyst basicity with calcination temperature can be understood using the thermal decomposition mechanism of HTs elucidated by Rey and Fornes [23] and the phase transition model proposed by Shen et al. [24]. The calcination temperature has to be high enough to break down the ordered structure, remove the counterbalancing anions, and induce phase transitions within the oxide lattice. The calcination temperature, however, has to be low enough to avoid the formation of the spinel (MgAl₂O₄) and the segregation of the alumina phase. The fact that no bulk spinel phase was observed by XRD even for CHT calcined at 800°C (Figure 8.1) cannot necessarily exclude the existence of MgAl₂O₄ domains, since they may have been too small to be detectable [25].

Similar effects of calcination temperature on catalytic activity have already been reported in the literature for transesterification of soybean oil with methanol by Xie et al. [16]; however, with the optimum calcination temperature being 50°C lower. The small shift in optimum point was probably due to differences in the HT precursor preparation methods and/or in chemical compositions (e.g., Mg/Al molar ratio =3 in ref [16] vs. 2.3 in our study) that are known to be important in influencing the surface properties of HT-derived mixed oxides [15, 25, 26]. For instance, for the self-condensation of acetone, the best calcination temperature for HT materials was 500 and 550°C for samples with Mg/Al molar ratios of 4 and 3, respectively [26].
Figure 8.1 XRD spectra of CHT samples: (a): calcined at different temperatures; (b): after post-calcination rehydration.

Table 8.1 Characteristics of HT-derived MgAl mixed oxides obtained by calcination at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>BET Surface area (m²/g)a</th>
<th>Avg. Pore size (Å)a</th>
<th>Total pore volume (cm³/g)a</th>
<th>N_base (µmol/g)b</th>
<th>N_Acid (µmol/g)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHT400</td>
<td>234</td>
<td>27</td>
<td>0.15</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>CHT500</td>
<td>285</td>
<td>31</td>
<td>0.23</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>CHT550</td>
<td>288</td>
<td>30</td>
<td>0.25</td>
<td>96</td>
<td>43</td>
</tr>
<tr>
<td>CHT600</td>
<td>240</td>
<td>35</td>
<td>0.27</td>
<td>54</td>
<td>44</td>
</tr>
<tr>
<td>CHT800</td>
<td>186</td>
<td>47</td>
<td>0.26</td>
<td>38</td>
<td>48</td>
</tr>
</tbody>
</table>

a Experimental error +/- 3%
b Experimental error +/- 6%
Catalyst rehydration

Recently, CHTs modified by post calcination rehydration with wet nitrogen have shown significant improvements in activity for a variety of condensation reactions [17, 26-28] and other reactions such as Henry reaction [18] and alcohol cyanoethylation [29]. The positive impact of rehydration on CHT catalysts is has also been observed by Corma et al. [30] for the glycerolysis of methyl fatty esters. However, these authors observed only a relatively small activity gain over the original CHT samples. By contrast, Leclercq et al. [4] have reported that rehydrating calcined hydrotalcites gave rise to no improvement in catalyst activity for rapeseed oil transesterification with methanol. More recently, the aldol condensation between heptanal and acetaldehyde was found to proceed slower using rehydrated CHT [31].
To study the effect of post-rehydration of thermally activated CHT samples on poultry fat transesterification, CHT catalysts were rehydrated for 12 h at room temperature under a flow of He (UHP grade, 80 mL/min) saturated with water vapor. This process resulted in a water gain of 26 ± 2 wt% for the rehydrated CHT (RCHT) regardless of the original calcination temperature. After rehydration, the RCHTs originally calcined at lower temperatures (i.e., 400 and 550°C) exhibited partially restored lamellar structures similar to the parent hydrotalcite as shown by their XRD spectra (RCHT400 and RCHT550 in Figure 8.1), resembling the results previously reported for RCHT [30]. By contrast, the CHT initially calcined at 800°C showed no restoration of the original HT structure, retaining the periclase phase after rehydration as shown in Figure 8.1 (RCHT800). Indeed, Tichit and Coq [32] have pointed out that a calcination temperature below the threshold leading to the appearance of the spinel phase MgAl₂O₄ is essential to preserve the structure reversibility of HT-derived mixed oxides. BET measurements were conducted for the RCHTs following 12 h vacuum degassing at 120°C. As a result, all rehydrated samples presented a significant decrease in surface area as from 180-300 m²/g (CHTs) to a typical value of 10 m²/g. Platelet agglomeration due to high surface tension of water has been attributed to lead to the closure of micropores and small mesopores thereby giving rise to the substantial surface area loss [27, 33]. Notwithstanding, according to de Jong and co-workers [34, 35], the evolved hydroxyl ions are situated near the disordered edges of the reconstructed platelets of the lamellar structure, remaining highly accessible.

The amount of the RCHTs used for reaction took into account the water gain in order to keep the dry mass portion as 10 wt% of the lipid feedstock under identical reaction conditions as used for the CHT catalysts (2 h reaction at 120°C). The rehydration
procedure did not improve catalyst activity for any of the samples studied (Figure 8.2). In fact, the catalysts initially calcined at higher temperatures underwent a greater activity loss upon rehydration. For instance, after rehydration, the catalytic activity of CHT450 and CHT800 decreased by 18% and 64%, respectively (Figure 8.2).

The rehydration treatment of CHT is expected to restore the layered structure of HTs and introduce intercalated OH\(^-\) counter ions [17, 30]. The reaction takes place between O\(^2-\) anions on the solid surface and the weakly acidic H\(_2\)O leading to a transition from base sites of Lewis type to ones of Brønsted type. Despite the great decrease in surface basicity (in terms of both site strength and concentration) [17], the Lewis-to-Brønsted transformation gives rise to interesting activity enhancement for many reactions, a consequence which has been attributed to the optimal effect that mild strength Brønsted sites generated during the rehydration process have on those specific reactions [17, 18, 28, 29].

Our results show that rehydrated CHTs are less reactive than calcined CHTs, suggesting that the base catalyzed poultry fat transesterification with methanol has no specificity for Brønsted base sites. The mild base strength of the generated Brønsted sites may have also contributed to the observed decrease in activity, implying that only strong base sites are able to carry out successfully transesterication of triglycerides with low molecular alcohols. However, re-hydrated catalysts have been found to be much more active than CHT mixed oxides in cyanoethylation of methanol [29, 36], wherein the formation of methoxide anions is known to be necessary for the subsequent reaction cycle [36]. On the other hand, one may expect the presence of free water to be deleterious for catalyst activity since it can yield free fatty acids by hydrolysis of glyceride species.
and ester products. Free fatty acids can then react with base sites on the catalyst neutralizing them for further reaction. In addition, water itself may cluster around strong base sites and/or activated methanol thus limiting their contact with triglycerides through hydrophobic repulsion.

Given their higher catalytic activity, CHTs were used for the study of general reaction parameters. The calcination temperature of 500°C was chosen for the following detailed reaction study, since it is typically used in preparing CHTs and since it also exhibited high activity.

**Effect of reactant-catalyst pre-contact**

Figure 8.3a shows poultry fat conversion profiles for reactions when the catalyst was initially contacted with either methanol or the poultry fat before the other reactant. As can be seen, it is essential for optimum catalyst activity that the catalyst be contacted with methanol before it comes into contact with the lipid feedstock. Otherwise, the catalyst activity is affected. Given the low miscibility of methanol with poultry fat, one might assume that the obvious lag in reaction activity for the lipid pre-contacted reaction was probably due to mass diffusion. However, note that mass diffusion limitations should have also applied for the methanol-catalyst pre-contacting case, which were not observed, suggesting a different reason for the differences in catalyst activity. Despite the low fatty acid content of 0.2 wt%, other unknown impurities in the poultry fat could have been responsible for the activity lag. However, when the catalyst was precontacted with other lipid sources, such as highly refined olive oil (obtained from Aldrich), the same kinetic delay was observed (data not shown), indicating that catalyst deactivation is not related to unspecified lipid impurities.
On the other hand, the adsorption of triglycerides themselves on active sites could have been responsible for the activity differences in reagent-catalyst pre-adsorption experiments. For instance, triglyceride compounds in lipid feedstocks are made of large bulky molecules with linear saturated and unsaturated alkyl chains. To gain a fundamental understanding of what is behind the difference in catalytic activities of reagent pre-contacted CTHs, similar experiments were carried out with a model triglyceride compound, triacetin, a synthetic triglyceride-like molecule consisting of a glycerol backbone and three acetic acid ligands. Triacetin was used here because it shares the same transesterification-active functionality as any other triglyceride but with the advantages of its simplicity (homogeneous saturated structure), ready availability in pure form, and complete miscibility with methanol even at room temperature.

Using triacetin, the reactant-catalyst pre-contacting experiments were initially carried out at 120°C. In contrast to poultry lipid, different reagent-catalyst pre-contacting showed no impact on the conversion profile of triacetin. Interestingly, however, when the reaction temperature was lowered to 60°C, the activity gap due to different reagent-catalyst pre-contacting appeared (Figure 8.3b). Evidently, these results indicate the negative role of pre-adsorbed triglyceride molecules and its significant thermal dependency. Hence, a likely source of initial catalyst deactivation is associated with the strong adsorption of triglycerides on active sites. Adsorption processes are intrinsically exothermic and therefore less thermodynamically favored at higher temperatures. In this sense, the reaction profiles displayed in Figure 8.3 can be rationalized if 120°C is above the temperature threshold for the rapid reversible adsorption-desorption of reagents on the catalyst surface for the triacetin case, and below such a threshold for the poultry lipid...
Figure 8.3 The effect of reagent-catalyst mixing prior to reaction carried out at 120°C: (a) CHT + MeOH: the catalyst and methanol were mixed first. CHT + PF: the catalyst and poultry fat were mixed first. (b) The same reagent-catalyst pre-mixing experiments as in a) carried out with a model triglyceride compound, triacetin (TAc), at two reaction temperatures, 60 and 120°C.
case. In either case, the observations here seem to point to the essentiality of the adsorption of methanol on the active sites rather than that of triglycerides, analogous to the classic homogeneous base catalyzed mechanism [3].

**Parametric study**

*Reaction temperature*

Temperature is known to play an important role in biodiesel synthesis. Not only does increasing temperature lead to better reaction kinetics, also improves phase miscibility, important in potentially diffusion-limited process. The influence of reaction temperature on the transesterification reaction of poultry lipid with methanol was studied in the presence of CHT500 (10 wt%) with a MeOH/triglyceride molar ratio of 30:1. The effect of temperature on triglyceride conversion is illustrated in Figure 8.4a. As would be expected, reaction temperature positively impacted triglyceride transesterification. For instance, at 120°C, it took about 2 h to achieve 60% triglyceride conversion, whereas at 90°C more than 8 h was required. When the reaction was carried out at 60°C, a typical reaction temperature for biodiesel synthesis using homogeneous base catalysts, the lipid conversion barely reached 20% in 8 h. By contrast, at 120°C and 8 h the reaction conversion was 93%.

Accordingly, one can expect a faster kinetic process and shorter residence times for a batch operation upon increasing reaction temperature. However, the use of higher temperatures requires not only greater energy consumption, but also higher system pressure to keep methanol in the liquid phase, which leads to increased reactor costs. An increase from 120 to 170°C has been estimated to lead to a doubling in equipment costs [5]. In contrast, an increase in temperature from 60 to 120°C would result in an increase
of only ca. 30% in equipment cost [5] which can be compensated for by the gains resulting from shorter processing times (Figure 8.4a) and the convenience of allowing adiabatic flash separation of unreacted methanol [5].

The methyl fatty ester yield as a function of poultry fat conversion at different temperatures is displayed in Figure 8.4b. For a given conversion level of triglyceride, methyl fatty ester yield was not dependent on reaction temperature, reflecting a parallel thermal dependency of the three consecutive reactions that constitute the complete transesterification of triglycerides to biodiesel and glycerol. This result is similar to that reported by Corma et al. [10] for the glycerolysis of rapeseed oil catalyzed by MgO for the synthesis of monoglycerides.

Using the initial reaction rates determined at different temperatures, the apparent activation energy for triglyceride transesterification was estimated to be 56.8 kJ/mol which resembles the value (57.1 kJ/mol) determined by Noureddini and Zhu [37] for NaOH catalyzed soybean oil transesterification by using computational simulation. This result suggests similarities involved in the mechanistic routes of the homogeneous and heterogeneous catalysis and also corroborates the absence of mass transfer limitation. Moreover, the Arrhenius plot (Figure 8.5) is linear throughout the range 60-to-120°C, indicating an unchanged rate-determining step within this temperature region.
Figure 8.4 Influence of reaction temperature on transesterification of poultry fat with methanol at 120°C. (a) poultry fat conversion; (b) fatty methyl ester yield as a function of triglyceride conversion.
Figure 8.5 Arrhenius plot for the transesterification of triglycerides to diglycerides using CHT500 (temperature range: 60-120°C).

Reactant molar ratio

Other than reaction temperature, molar ratio of reactants is another important variable in the transesterification reaction. Stoichiometrically, three moles of alcohol are required per mole of triglyceride to produce three moles of mono-alkyl fatty esters and one mole of glycerol. But given that transesterification is a reversible reaction, the use of a large excess of alcohol should benefit the conversion of triglycerides from the standpoint of thermodynamics. However, high alcohol-to-lipid molar ratios have been reported to slow down the reaction owing to a diminution in catalyst concentration by the large excess of alcohol [38]. In order to separate the dilution effect from the assessment of the kinetic role of the excess methanol in the triglyceride transesterification, a fixed catalyst/total reaction volume of 0.04 g/mL was used while varying the methanol/poultry fat molar
ratio from 6 to 60. All reactions were carried out at 120°C in the presence of CHT500. The results are tabulated in Table 8.2.

Our results show that methanol impacts the reaction rate in a positive manner. For a given reaction time of 2 h, the poultry lipid conversion steadily increased from 23% to 75% as the molar ratio increased from 6 up to 60. Increased triglyceride conversion was concomitant with a 6-fold increase in the ester yield. With the methanol/poultry lipid molar ratio of 60, only 3 h was required to achieve 91% TG conversion. However, it took about threefold, fivefold and fifteenfold this reaction time to do the same when using molar ratios of 30, 15 and 6, respectively. Using a calcined MgAl hydrotalcite catalyst, Xie et al. [16] studied the transesterification of soybean oil with methanol at molar ratios between 2:1 and 20:1. In contrast to our observation, these authors found that the benefit was only marked in the region of low methanol excess but approached saturation after a molar ratio of 12:1. However, given that they used a fixed mass ratio of catalyst-to-triglyceride, the effect of catalyst dilution was unaccounted for, explaining the difference with our reaction results.

Besides its effect on activity, using a larger excess of methanol should also drive triglyceride transesterification to a greater completion from the standpoint of thermodynamics. As shown in Table 8.2, with 91% poultry lipids converted, the apparent biodiesel yield was 8% lower when using MeOH/TG = 6 vs. MeOH/TG = 60 (i.e., 76% vs. 84%, respectively). And, for MeOH/TG = 6, a large fraction of the di/monoglyceride intermediates (40% selectivity in total) still remained in the reaction mixture. For MeOH/TG =15 and 30, the selectivities to glycerol fell in between that of MeOH/TG = 6 and 60. However, it is worthy to mention that the use of a large excess of methanol may
not be the only or the most efficient way to increase glycerol selectivity. In a recent study [6, 39] using triacetin, we have pointed out that catalyst surface hydrophobicity may play a key factor governing product selectivity in triglyceride transesterification.

Despite the highest activity with 20x stoichiometric methanol (MeOH/TG = 60), one should bear in mind that economically, an optimal molar ratio must balance the cost associated with subsequent glycerol separation and alcohol recovery [3]. To compare the interference of alcohol excess with phase separation, the methanolysis was stopped at a TG conversion of ca. 93% and the reaction mixture was allowed to settle overnight to form two clear phases, one enriched with the ester products and the other with glycerol and methanol. Compositional analysis was then performed for each layer to determine the partition of biodiesel and glycerol between the two phases. As shown in Table 8.2, the largest methanol excess (MeOH/TG = 60) yielded the worst biodiesel partition with 71% biodiesel and 95% glycerol in one phase unseparated. On the other hand, the use of MeOH/TG = 15 gave rise to good glycerol-biodiesel separation with only a negligible amount of biodiesel (4%) in the glycerol phase. In the case of MeOH/TG = 30, 28% biodiesel was found in the polar glycerol phase.
Table 8.2 Influence of the MeOH/lipid molar ratio on transesterification using CHT500 as the catalyst (10 wt%) at 120°C

<table>
<thead>
<tr>
<th>MeOH / PF time (h)</th>
<th>TG Conv.</th>
<th>FAME&lt;sup&gt;a&lt;/sup&gt; Yield</th>
<th>Selectivity (%)</th>
<th>Phase separation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DG&lt;sup&gt;b&lt;/sup&gt;</td>
<td>MG&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>0.23</td>
<td>0.10</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>44</td>
<td>0.91</td>
<td>0.76</td>
<td>11</td>
<td>29</td>
</tr>
<tr>
<td>15</td>
<td>0.39</td>
<td>0.24</td>
<td>43</td>
<td>35</td>
</tr>
<tr>
<td>15</td>
<td>0.93</td>
<td>0.80</td>
<td>9</td>
<td>25</td>
</tr>
<tr>
<td>30</td>
<td>0.63</td>
<td>0.43</td>
<td>27</td>
<td>41</td>
</tr>
<tr>
<td>8</td>
<td>0.93</td>
<td>0.82</td>
<td>4</td>
<td>22</td>
</tr>
<tr>
<td>60</td>
<td>0.75</td>
<td>0.61</td>
<td>13</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>0.91</td>
<td>0.84</td>
<td>4</td>
<td>15</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fatty methyl ester (FAME) Yield = C<sub>MeFA</sub>/ (3 x C<sub>TG0</sub>)

<sup>b</sup> DG, MG and GL represent diglyceride, monoglyceride and glycerol, respectively.

- Diglyceride Selectivity, DG% = C<sub>DG</sub>/ (C<sub>GL</sub> + C<sub>MG</sub> + C<sub>DG</sub>) x 100%
- Monoglyceride Selectivity, MG% = C<sub>MG</sub>/ (C<sub>GL</sub> + C<sub>MG</sub> + C<sub>DG</sub>) x 100%
- Glycerol Selectivity, GL% = C<sub>GL</sub>/ (C<sub>GL</sub> + C<sub>MG</sub> + C<sub>DG</sub>) x 100%

<sup>c</sup> BD<sub>GL</sub> denotes the molar fraction of biodiesel (FAME) distributed in the glycerol phase at RT

<sup>d</sup> GL<sub>BD</sub> denotes the molar fraction of glycerol distributed in the biodiesel (FAME) phase at RT

Use of a Solvent

The use of co-solvents for the synthesis of biodiesel using homogeneous catalysts at low temperatures (30~60°C) has allowed the elimination of the initial induction period for reaction due to the low miscibility of the alcohol/oil phases, resulting in faster reaction rates [40, 41]. In our case, the higher temperature and mixing intensity used has enabled sufficient contact between reactants and catalyst such that phase separation has not been an issue. However, the introduction of a co-solvent can also impact reaction rate
by modifying substrate interaction with catalyst surface, reactant/intermediate conformations, etc.

The influence of several solvents was examined for poultry fat methanolysis using CHT500. Experiments were carried out at 120°C with a methanol/lipid molar ratio of 30. The solvents used were hexane, toluene and THF at a solvent/reactants ratio of 1 v/v. Reaction profiles of experiments using co-solvents are shown in Figure 8.6. A great difference of reactivity was observed for different solvents. In the early stage of reaction (0~40% poultry fat conversion), transesterification with hexane as solvent progressed at a somewhat faster rate than that without solvent especially considering the 50% dilution in reactant concentrations for the former. Reaction, however, slowed down dramatically after 1 h of reaction and ended up with only 70% triglyceride conversion after 8 h compared to 93% for the solvent-free run. Toluene impacted the methanolysis in a way resembling hexane with the reaction rate slowing down at an even earlier time (1/2 h) and an even lower fraction of triglyceride being converted after 8h (58%).

The early high activity and following deactivation of reactions using hexane and toluene as co-solvents may be related to the change in polarity that hexane and toluene introduce to the reaction media. These two co-solvents, being non-polar in nature, more easily dissolve/interact with the triglyceride reactant than they do with the polar methanol. Using ultrasonic velocity measurements, Gonzalez et al. [42] compared the intermolecular interactions between soybean oil and different organic solvents. The authors were able to show that triglyceride molecules have a more significant affinity with hexane than methanol. As a result, the presence of hexane should favor a more efficient interaction between the polar methanol and the anionic catalyst surface (Lewis
base sites), important for methanol activation. In addition, triglycerides, despite tending to adopt a tuning fork conformation with unfolded hydrocarbon chains [43, 44], can be greatly restricted upon solvation. For instance, in aqueous solution, the most stable solvated conformation of triacetin is a highly rigid system of three intramolecular ring-like arrangements around the glycerol backbone [45]. González et al. [42] have also demonstrated that hexane gives rise to a less rigid solvation arrangement than methanol. Thus, triglyceride molecules in the hexane solution may be allowed to assume conformations potentially favoring the reaction.

On the other hand, as the reaction progresses, triglycerides are converted to di- and mono-glycerides, and ultimately glycerol is produced. All these species possess increasing polarity with respect to the initial triglycerides. We suggest that as glycerol is produced those effects that initially favored the reaction also cause the later observed deactivation. For instance, glycerol should preferentially adsorb on the catalyst surface due to its high polarity and low miscibility in non-polar media, displacing methanol from the active sites. Hence, with less and less methanol activation, the reaction progress would be hindered giving rise to the activity plateau observed after 40% TG conversion. Moreover, di- and more importantly mono-glycerides with both polar hydroxyl groups and non-polar long alkyl chains are known to be strong surface active agents that ease the formation of emulsions. Hexane, for instance, has also been found to improve the emulsion characteristic of mono/diglycerides [46]. Thus, as glyceride intermediates are formed they themselves can contribute to the isolation of the active polar surface from triglycerides, affecting overall triglyceride conversion. All of these factors, combined with methanol depletion as the reaction progresses, may explain the observed reactivity.
differences for reaction using hexane and toluene as co-solvents.

THF has been portrayed as an ideal co-solvent for biodiesel synthesis using homogeneous catalysis owing to the good solubility of both methanol and lipid molecules in THF. In addition, THF has a boiling point similar to that of methanol, which means that methanol and THF separation and recycle can be carried out simultaneously. Our results, however, show that THF gives rise to much lower catalyst activity for the methanolysis of poultry fats using the solid base CHT500 (Figure 8.6). The use of THF as a co-solvent for biodiesel synthesis using vegetable oils and a solid base, Na/NaOH/γ-Al₂O₃, was also found to gave rise to low catalytic activities [9].

Using a similar approach to that used to explain the effect of hexane and toluene on triglyceride transesterification, one has to acknowledge that, unlike hexane and toluene, THF is a solvent of medium polarity. This means that even though THF dissolves efficiently poultry lipids, it also does the same with methanol, resulting in a more homogenous distribution of species between both the liquid media and the catalyst surface. We suggest it is the latter effect that allows greater competition by triglycerides for surface active sites giving rise to a higher degree of catalyst deactivation than what is observed for the reaction using no co-solvent. In any case, more research is needed to investigate the exact nature of catalyst activation-deactivation by the presence of co-solvents in the reaction media of biodiesel synthesis systems.
The reusability of solid catalysts is a key parameter in discerning their suitability for triglyceride transesterification in practical applications. Thus, the re-usability of hydrotalcite-derived mixed oxides was examined by carrying out subsequent reaction cycles. After each cycle, reaction mixtures were carefully withdrawn, the catalyst sediment was recovered, and a new reaction cycle was started with fresh reactants. During the whole process, care was taken to minimize the exposure time of the catalysts to the atmosphere, thus limiting possible site contamination by CO$_2$.

As shown in Figure 8.7, the catalyst sample underwent significant deactivation during the first reaction cycle. Catalyst deactivation, however, was not evident for subsequent reaction cycles whereby relatively constant catalytic activity was observed, taking into
account some inevitable catalyst loss during sampling and recovery steps. CHTs are known to have heterogeneous surface basicity with basic sites of low (OH$^{-}$ groups), medium (Mg-O pairs), and strong (O$^{2-}$ anions) basicity [15]. The deactivation pattern presented by CHT (Figure 8.7) may be associated with the heterogeneity of surface basicity: what deactivated during the first reaction cycle may have been the strong Lewis sites (O$^{2-}$), whereas sites of medium and low basicity may have remained stable and been responsible for the residual activity shown in the subsequent reactions cycles.

![Figure 8.7 CHT500 deactivation during multiple reaction cycles of poultry lipid methanolysis at 120°C with a catalyst loading of 10 wt%.

For basic oxides, metal ion leaching into solution is always a primary concern directly affecting catalyst deactivation characteristics [3, 6]. However, the elemental analysis of reaction residuals using atomic absorption spectroscopy (AAS) showed negligible catalyst leaching in either the methanol-glycerol phase or the biodiesel layer (Table 8.3).
In addition, both SEM-EDS and AAS showed very similar Mg/Al ratios for used catalyst samples vs. fresh CHT catalysts suggesting no preferential dissolution of ionic metal species, Mg\(^{2+}\) or Al\(^{3+}\), as would not be expected if catalyst leaching were taking place. Also, to further test our conclusion about catalyst leaching, catalyst samples were soaked in methanol overnight, and the methanol then was separated from the catalyst and used for reaction. No transesterification activity was observed for the residual methanol, further excluding leaching effects on catalyst activity.

Table 8.3 Elemental analysis

<table>
<thead>
<tr>
<th></th>
<th>Solid catalyst samples</th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>HT</td>
<td>CHTN500</td>
</tr>
<tr>
<td>Mg/Al (atomic ratio)</td>
<td>AAS</td>
<td>2.30(^{a})</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>EDS(^{b})</td>
<td>---</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Liquid residuals separated from CHT500 after reaction (AAS)

<table>
<thead>
<tr>
<th></th>
<th>Glycerol-rich layer</th>
<th>FAME-rich layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg content</td>
<td>&lt;74 ppm</td>
<td>&lt;59 ppm</td>
</tr>
<tr>
<td>Al content</td>
<td>&lt;74 ppm</td>
<td>&lt;59 ppm</td>
</tr>
</tbody>
</table>

\(^{a}\) Vendor information  
\(^{b}\) Average value of multiple spots

As mentioned earlier, the presence of water can cause the formation of fatty acids leading to permanent deactivation of base sites. Given the presence of a large excess of methanol and the Lewis acid sites of CHT, water produced from the secondary side reaction of alcohol condensation cannot be discarded as a possible deactivation source. Alcohol condensation, nevertheless, is an energy-demanding reaction requiring high reaction temperature and is unfavorable on base sites [15]. To estimate the significance of
this side reaction, in a separate run, methanol condensation was carried out at 120°C using CHT500 in the absence of TGs. After 8 h, the moisture content was determined using Karl-Fisher titration (Mettler Toledo DL31) as 0.41 ± 0.02 wt% which corresponded to a water amount of 2.16 mmol (38.9 mg) present in the reaction system. Thus, the water produced from methanol condensation was not that significant. However, considering that one water molecule may give rise to one free fatty acid (by hydrolyzing TGs) resulting in the neutralization of one base site, the water abundance would be enough to bring about the deactivation 37 times over the base sites in the quantity of CHT500 employed for reaction (using TPD-CO$_2$ for the estimation of base sites, see Table 8.1). Nevertheless, this result should be taken as a maximum limit and, under reaction conditions with poultry fat present, a lower amount of water should be formed.

Attempts to regenerate the activity of used catalyst samples were first made by re-calcination under N$_2$ after an extensive methanol wash. As a result, the used CHT was only able to recuperate part of its activity, but still presented lower activity than the fresh CHT (Figure 8.8a). On the other hand, re-calcination carried out in air completely restored catalyst activity (Figure 8.8a). Indirectly, these results indicate that the methanol wash cannot completely remove accumulated hydrocarbons on the catalyst surface which may form coke at high temperatures under nitrogen. Moreover, using air re-calcination, 4 regeneration cycles were carried out (Figure 8.8b). Constant catalytic activity throughout these cycles demonstrates once again no metal ion leaching of any kind and points to air re-calcination as a simple and reliable methodology to regenerate the catalyst.
Figure 8.8 Catalyst regeneration for poultry fat transesterification (120°C, MeOH/PF = 30:1, catalyst loading of 10 wt%): (a) effect of re-calcination in N₂ and air (b) regeneration cycling experiments using air re-calcination between each cycle.
Summary

The use of heterogeneous base catalysts derived from an Mg-Al hydrotalcite has been investigated for the transesterification of poultry fat with methanol. This solid base showed high activity for triglyceride transesterification with methanol without any sign of catalyst leaching. Catalytic performance was significantly affected by pretreatment and operating conditions. Calcination at 550°C gave rise to the most active catalyst. Rehydration of the calcined catalyst before reaction using wet nitrogen, however, decreased catalytic activity regardless of the calcination temperature originally used. The contact of catalyst with poultry lipids before methanol resulted in diminished catalyst activity owing to the strong adsorption (potentially irreversible) of the heavy lipid species under the reaction conditions employed. Within the investigated range, both temperature and a methanol/lipid molar ratio positively affect TG methanolysis in terms of reaction efficiency. Large excess methanol, however, complicates the post-separation of biodiesel from glycerol by increasing their mutual solubility. Solvent-free reaction turned out to be the most effective way to achieve the highest triglyceride conversion. The catalyst underwent significant deactivation during the first reaction cycle probably due to deactivation of the strongest most accessible base sites. Nevertheless, simple re-calcination in air afforded complete restoration of catalyst activity.
References


CHAPTER 9
CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Conclusions

This research has investigated the potential of heterogeneous catalysis in biodiesel synthesis while emphasizing the related fundamental aspects. Study concerning the effect of water on an acid Brønsted type catalyst like sulfuric acid has shown that water may seriously hamper catalyst activity as it is produced from esterification reactions. A negative reaction order of almost -1 has been estimated for water on the sulfuric acid catalyzed esterification of acetic acid with methanol. Reaction profiles built using this negative reaction order for water were able to successfully predict reaction profiles for esterification. Water may hinder esterification probably by forming more stable, more polar solvation spheres around protons, lowering their acid strength and limiting their accessibility to reagents. Simultaneous water removal and/or delicate surface hydrophobicity control of solid catalysts appear essential to preserve high conversion efficiency throughout the course of FFA esterification.

The catalytic performance of the Nafion/silica nanocomposite SAC-13 has been evaluated for esterification reactions of carboxylic acids and compared to that of sulfuric acid. TOF (turnover frequency) values calculated for SAC-13 showed that the activity of the resin is comparable to that of H₂SO₄ on a per site basis. The reactivity of carboxylic acids was controlled by steric factors as the alkyl chain linearly lengthened. The
reactivity-structure response was the same in both liquid and solid acid catalysis for small acids no larger than butyric acid. It, nevertheless, became larger for SAC-13 catalysis for reactions using larger acids. Both catalysts SAC-13 and H2SO4 showed very similar reaction inhibition by water, suggesting a common reaction modus operandi of their Brønsted acid sites. The Nafion/SiO2 nanocomposite catalyst showed good reusability in the esterification of low molecular acids but underwent continuous activity loss in consecutive reaction cycles using caprylic acid, probably due to a stronger adsorption/entanglement of the bulky organics in/on Nafion polymeric nano-domains blocking catalytic acid sites. In all, great potential has been shown by solid acid SAC-13 as the replacement of homogeneous catalyst in FFA esterification. This promise, nevertheless, can be further enhanced by better integrating the support nature, site strength and reaction design to match up reaction mechanism by favoring the competition of FFA with alcohol for the catalytic sites and to extend the sustainability of catalyst by increasing the adsorption reversibility.

Despite being strongly susceptible to any FFA impurity, base catalyst predominates over its acid counterpart in TG transesterification. This is ascribed to its overwhelming advantage in catalytic activity, which is intrinsically determined by the corresponding catalysis mechanisms. Immobilized Brønsted base functionality of tetraalkylammonium completely outperforms the heterogenized sulfonic acid group, allowing triacetin methanolysis to proceed efficiently even under mild reaction conditions. High surface hydrophobicity of the support surface is also desired in solid base configurations in order to increase the catalyst capacity to drive the series reaction of glycerides to completion. However, grafted strong Brønsted ammonium species potentially underwent attack of
strong nucleophiles like MeO⁻ on the organic linkage, which leads to active site leaching and eventually catalyst deactivation. Results from a comparison study suggested that an inert vicinity and increased electronic/steric hindrance against the nucleophilic attack are necessary to preclude the proposed catalyst deactivation route. Alternatively, inorganic solid bases such as Mg-Al mixed oxides derived from hydrotalcites, are able to show significant activity in managing TG transesterification without any sign of catalyst leaching, provided a moderate reaction temperature is used. Despite noticeable catalyst deactivation during the first reaction cycle probably due to the irreversible TG adsorption on the strongest most accessible base sites, the application of a very simple regeneration protocol afforded complete restoration of catalyst activity suggesting that this type of catalyst could be used for several reaction cycles before catalyst replacement is necessary.

**Recommendations for Future Work**

In order to further build up the scientific infrastructure for the application of heterogeneous catalysis to biodiesel synthesis, a few aspects missed in and some ideas derived from this research are suggested here for future research: (1) the effect of unsaturated FFAs and TGs on solid acid/base catalysis, in terms of both catalyst activity and deactivation; (2) the mechanistic exploration regarding heterogeneous base catalyzed TG transesterification wherein the role of methanol necessitates detailed elucidation to provide more information towards the designs of catalyst/reaction conditions/operation mode; (3) the sensitivity of FFA/TG alcoholysis to the characteristics of the catalyst sites, i.e., Brønsted and Lewis, respectively; (4) the correlation among acid/base site strength, catalyst activity and deactivation, and reaction conditions. Generally, higher site strength is assumed to correspond to higher catalytic activity. Nevertheless, as shown in this work,
active sites of higher acid/base strength are more susceptible to deactivation caused by the strong/irreversible adsorption of bulky FFA/TG molecules. The use of high reaction temperature is a probable means to circumvent this by enhancing the reversibility of adsorption of substrates. It, however, adversely promotes side reactions, likely causing additional catalyst deactivation by inducing coking and/or polymerization of unsaturated species. A final suggestion relates to (5) the surface hydrophobicity control in solid base catalysts used for TG transesterification. High surface hydrophobicity of solid base has been found to favorably drive TG conversion to completion. On the other hand, such an effect may be complicated by the necessity of methanol adsorption in base catalyzed transesterification, since the competitive edge of methanol adsorption on basic sites compared to that of TGs would be weakened by a hydrophobic surrounding, likely leading to a lower reaction rate.