DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR FORMATION OF BIODIESEL

A Thesis submitted in the partial fulfillment of the requirement for the Degree of

Doctor of Philosophy

by

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Thesis Approval Sheet

Thesis entitled "**DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR FORMATION OF BIODIESEL**", being submitted by Mr. Vishal, to the School of Chemistry and Biochemistry, Thapar University, Patiala is approved for the degree of Doctor of Philosophy.

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This is to certify that thesis entitled "**DEVELOPMENT OF HETEROGENEOUS CATALYSTS FOR FORMATION OF BIODIESEL**", being submitted by Mr. Vishal, to the School of Chemistry and Biochemistry, Thapar University, Patiala for the award of degree of DOCTOR OF PHILOSOPHY, is a record of bonafide research work carried out by him. Mr. Vishal Mutreja has worked under our guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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List of Abbreviations

ASTM	American Society for Testing and Materials
BET	Brunauer- Emmett-Teller
BJH	Barret-Joyner-Halenda
FAMEs	Fatty Acid Methyl Esters
FEG-SEM	Field emission Gun-Scanning Electron Microscope
FFAs	Free Fatty Acids
FT-IR	Fourier Transform Infra red
FT-NMR	Fourier Transform Nuclear magnetic Resonance
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
mg	Milligram
TEM	Transmission Electron Microscope
TLC	Thin Layer Chromatography
wt.%	Weight Percentage
XRD	X-ray Diffraction
mL	Milliliters
min	Minute
mol	Mole
mmol	Millimoles
nm	Nanometre
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis
MCM	Mobil composition of matter
SBA-15	Acronym for Santa Barbara
kW	Kilowatt
ppm	Parts per million

List of Symbols

Å	Angstrom
Α	Alpha
H_	Basic Site Strength
°	Degree
K	Kelvin
%	percentage
Μ	Micro
Θ	Theta
Rf	Retention factor
T	Time
%T	% Transmittance
N	Frequency
G	Gram
M	Metre
h	Hour
% C	Percentage Conversion
δ	Delta

ABSTRACT

In present thesis, heterogeneous catalysts for the transesterification of triglycerides have been developed. Four types of catalysts were prepared viz.; (i) KOH impregnated MgO (ii) potassium impregnated mixed oxides of La and Mg (iii) potassium impregnated SiO_2 (iv) KNO_3 and MgO modified mesoporous SBA-15. These catalysts were characterized by powder XRD, TEM, SEM-EDX, TGA/DTA, FT-IR, Hammett indicators and soluble basicity measurements. In addition to this work, commercially available sodium aluminate has also been evaluated for the transesterification.

Potassium hydroxide (5-20 wt.%) impregnated MgO catalysts were prepared by wet-impregnation followed by drying and calcination. Powder XRD and DTA studies support the formation of heterogeneised potassium species over MgO during calcination at 550^{o}C. TEM studies supported that size of these particles are in the range 20-45 nm. Prepared catalysts were used for the transesterification of mutton fat and optimized reaction parameters were the 4 wt.% of MgO-KOH-20 (MgO impregnated with 20 wt.% of KOH), 1:22 molar ratio of fat to methanol, 65^{o}C reaction temperature and 20 min of reaction duration.

Potassium impregnated mixed oxides of La and Mg in 1: 1 to 1: 5 atomic ratios were prepared by co-precipitation method. TEM studies of these oxides supported the formation of polygonal, square and hexagonal shaped particles. The catalyst prepared by using 1: 3 atomic ratio of La to Mg was found to have stronger basic sites and better activity towards the transesterification reaction of used cotton seed oil. Under optimized reaction conditions of 1: 54 molar ratio of oil to methanol and 5 wt.% of the catalyst (prepared with La to Mg atomic ratio of 1:3 at pH 10) at 65^{o}C reaction temperature, 96% FAME yield was obtained in 20 min. Concentration of potassium ions leached out from catalyst into biodiesel was found within permissible limit of ASTM

Potassium impregnated SiO_2 having 1:1 to 1:6 atomic ratios of Si to K were prepared by sol gel method and evaluated as heterogeneous catalysts for the transesterification of jatropha and karanja oil with methanol. TEM studies of the catalyst having Si and K in 1:6 atomic ratio reveals that catalyst has uniform impregnation of 1-5 nm sized potassium nanoparticles over 15-40 nm sized spherical silica nanoparticles. Same catalyst was found to be efficient for the transesterification of jatropha and karanja oil in 0.3 h and 0.75 h respectively at 65°C.

Mesoporous SBA-15 wrapped with MgO was prepared by one pot synthesis. It was further coated with the third layer of KNO_3 (10-30 wt.%) via grinding in the presence of water followed calcination at 600°C under nitrogen atmosphere for 4 h. Coating of MgO prevents the destruction of SBA-15 from potassium as MgO acts as a obstruction and prevents the direct contact between potassium and SBA-15. The BET surface area and pore volume of SBA-15 modified with 20 wt.% of MgO and 25 wt.% of KNO_3 was found to be 183 m^2/g and 0.39 cm^3/g respectively. These values are less than that observed for SBA-15 wrapped with MgO to indicate that potassium species have been incorporated inside the mesoporous sieves. The material showed super basic nature and was used as a catalyst for the transesterification of used cotton seed oil with methanol to produced biodiesel with > 98% conversion.

Sodium aluminate and its calcined forms have been evaluated as basic catalysts for the transesterification of waste mutton fat with methanol. The decrease in catalytic activity has been observed with calcined sodium aluminate. Fat and methanol in 1:29 molar ratio with 1.5 wt.% of sodium aluminate under reflux resulted in 97 % conversion to biodiesel in 1h 20 min. The catalyst was found to effective even in the presence of 1 wt.% of moisture.

Chapter 1: Introduction and Literature Review

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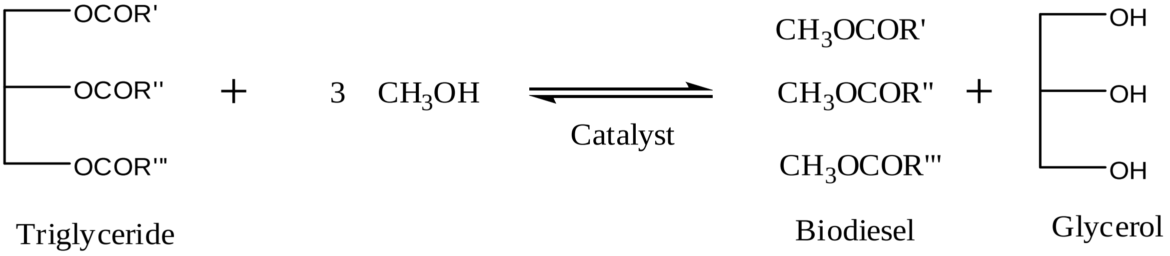
ABSTRACT

This chapter includes introduction, historical background about the biodiesel and earlier work done in the field of catalysis for biodiesel preparation. Detailed account of each type of catalyst; homogeneous viz., KOH, NaOH etc and heterogeneous catalyst viz., alkaline earth metal oxides, impregnated mixed metal oxide etc is included. Basic idea about research problem and transesterification is given in this chapter.

1.1. Introduction

The majority of world energy needs are supplied from fossil fuels like crude oil, coal and natural gas. These sources are finite and non renewable and will be consumed shortly at current usage rates. Increasing world population and industrial development have led to serious energy crisis and global warming. The rate of the global primary energy demand is estimated to increase 1.7% annually. This is expected to reach a value of 16,487 Million Tons of Oil Equivalent (Mtoe) by 2030 (Pandey et al., 2012). The interest in energy self sufficiency and periodic petroleum shortage has increased the research interest into vegetable oil as a petroleum diesel substitute. Peanut oil was used initially as fuel in the diesel engine invented by Rudolph Diesel on August 10, 1893 at Augsburg, Germany. To acknowledge this contribution, August 10 has been declared "International Biodiesel Day". So, the idea of using vegetable oil as fuel for diesel engines was over a century old. Later on, vegetable oils were again investigated as diesel fuel substitutes during the energy crisis of the 1970–1980s and were also used as emergency fuels during World War II. However, their direct use has not been found satisfactory because of high viscosity and poor ignition quality.

First patent on biodiesel entitled “Procedure for the transformation of vegetable oils for their uses as fuels” was granted to G. Chavanne from University of Brussels (Belgium) on August 31, 1937 (Knothe et al., 2001). This patent described the transesterification of vegetable oils with short chain alcohol to yield fatty acid methyl esters (FAMEs) commonly known as biodiesel and byproduct glycerol (Scheme 1.1).



Scheme 1.1. Reaction of triglyceride with methanol to form biodiesel.

Biodiesel derived from fats and oils offers several advantages compared to petro-diesel fuel such as higher cetane numbers, higher flash point, better lubricating efficiency and ultra low sulfur concentration (Goodrum et al., 2005; Kiss et al., 2006). Additionally, it is biodegradable and provides lower emissions of particulate matter, hydrocarbon and greenhouse gases such as CO, SOx and CO_2 (Dorado et al., 2003; Nabi et al., 2006; Demirbas et al., 2009). In United States, the driving force for research on biodiesel fuel is primarily related with the environmental concerns (Piazza et al., 2001). Recent studies showed that the use of biodiesel can decrease 95% of cancers, 90% of air toxicity and also provide clean environment (Huang et al., 2010; Mandjiny et al., 2011)

Biodiesel can be used either in pure form or in the form of blends with conventional diesel fuel in most modern diesel engines (Szybist et al., 2007). Blends of biodiesel and petroleum diesel are designated by “B” followed by the vol % of biodiesel e.g. B5 and B20, consisting of 5 and 20% biodiesel respectively in petroleum diesel. Upto 20% (v/v) blend of biodiesel in conventional diesel fuel does not require any modification in present diesel engines.

1.2. Catalysts for transesterification

Transesterification reaction can be carried out either via catalytic or non-catalytic approach. In case of non-catalytic process, there is a need of supercritical conditions which is an energy intensive process (Helwani et al., 2009) and required high temperature and pressure. The catalytic process may involve biocatalysts and chemical catalysts. Biocatalysts such as lipases are costly and contaminate the product with residual enzyme (Lam et al., 2010). There are mainly two categories of chemical catalysts; (1) homogeneous and (2) heterogeneous. These are being described in following sections:

1.2.1. Homogeneous Catalysts

If the catalyst is present in the same phase as that of reactants, it is called a homogeneous catalyst. At present, the biodiesel industry is dominated by application of homogeneous catalysts due to their simple usage and less time required for conversion of oils to their respective esters. Mainly strong acids viz., sulphuric acid and strong base viz., sodium hydroxide, potassium hydroxide have been used as homogenous catalysts and work regarding this type of catalysts for the biodiesel preparation is shown in Table 1.1.

Table 1.1. Homogeneous catalysts for transesterification

Catalyst	**Feedstock (oil)**	**Reaction Conditions**				**Conversion (C) / Yield (Y)**	**Reference**
		Temp. (^oC)	**Time (h)**	**Oil to Methanol molar ratio**	**Catalyst amount (wt.%)**		
H_2SO_4	Soybean	65	50	1: 30	1	$\geq$ 99 (C)	Narasimharao et al., 2007
H_2SO_4	Soybean	120	1	1: 6	3	$\geq$ 95(C)	Wahlen et al., 2008
H_2SO_4	Soybean	100	8	1: 9	0.5	99(C)	Goff Michael et al., 2004
H_2SO_4	Waste cooking	95	10	1 : 20	4	$\geq$ 90 (C)	Wang et al., 2006
KOH	Rapeseed	65	2	1:6	1	96 (Y)	Rashid et al., 2008
KOH	Karanja	65	2	1:6	1	98 (Y)	Meher et al., 2006
KOH	Pongamia pinnata	60	1.5	1:10	1	92 (C)	Karmee et al., 2005
KOH	Sunflower	25	60	1: 6	1.3	98.4 (Y)	Warabi et al., 2004
NaOH	Sunflower	60	2	1:6	1	97.1 (Y)	Rashid et al., 2008
NaOH	Waste cooking	70	0.5	1: 7.5	1.1	85.3 (Y)	Leung et al., 2006
NaOH	Soybean	45	0.1 - 0.3	1: 6	0.3	100 (Y)	Ji et al., 2006

As can be seen in Table 1.1, acid catalyzed reactions require comparatively higher reaction time, therefore these are less popular. On the other side, base catalyzed reaction was found to be 4000 times faster (Vyas et al., 2010) than acid catalyzed reaction. This is because of their mechanistic pathways which they follow as shown in Figure 1.1 and Figure 1.2 (Mbaraka et al., 2006). The first step in the base catalyzed reaction was the formation of an alkoxide ion due to the reaction between NaOH and alcohol (Figure 1.1). This alkoxide ion act as nucleophile and attacks on the carbonyl carbon of triglyceride to form the tetrahedral intermediate. This intermediate rearranges to give one molecule of ester and diglyceride. Diglyceride molecule further reacts with more molecules of alcohol to yield two more molecules of esters and glycerol as a by-product.

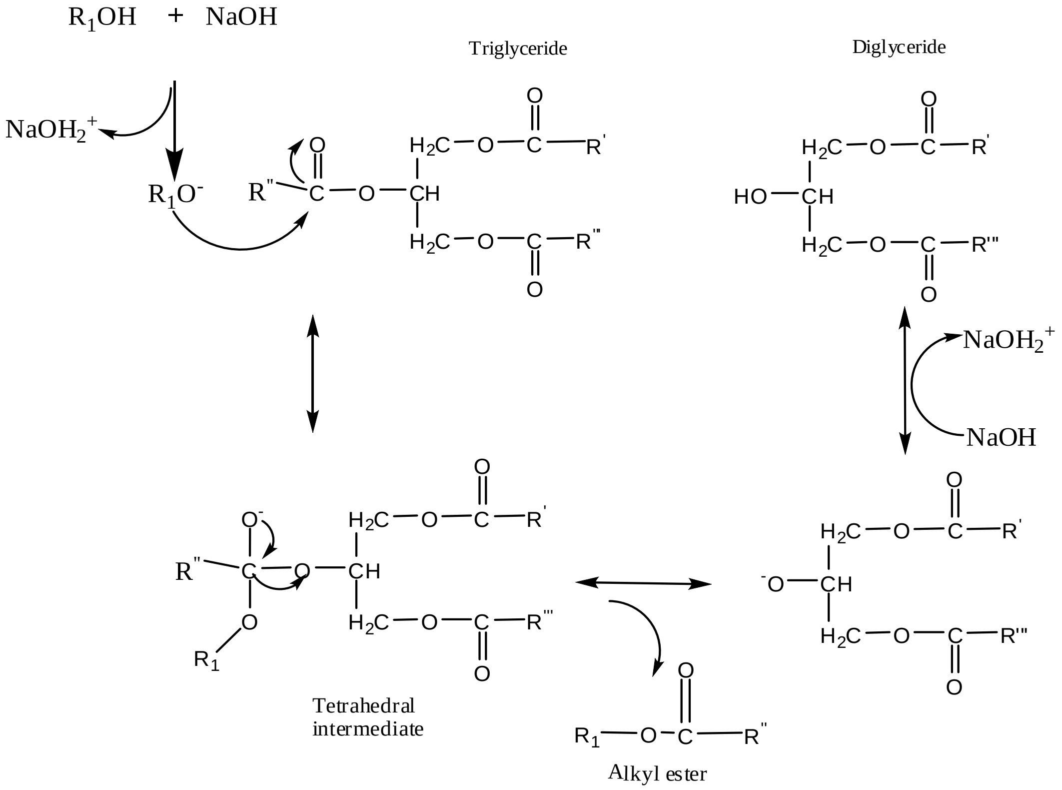


Figure 1.1. Mechanistic pathways of homogeneous base catalysed transesterification.

In contrast, the first step in the acid-catalyzed transesterification reaction was the protonation of carbonyl oxygen of the triglyceride molecule (Figure 1.2). The protonation of the oxygen make the carbonyl carbon susceptible to nucleophilic attack from alcohol. The main difference between the two reaction mechanisms is the strength of the nucleophile attack on the carbonyl carbon of the triglycerides. The nucleophile generated in the base catalyzed reaction (alkoxide ion) was found to be significantly stronger than the alcohol acting as nucleophile, in acid catalyzed reaction.

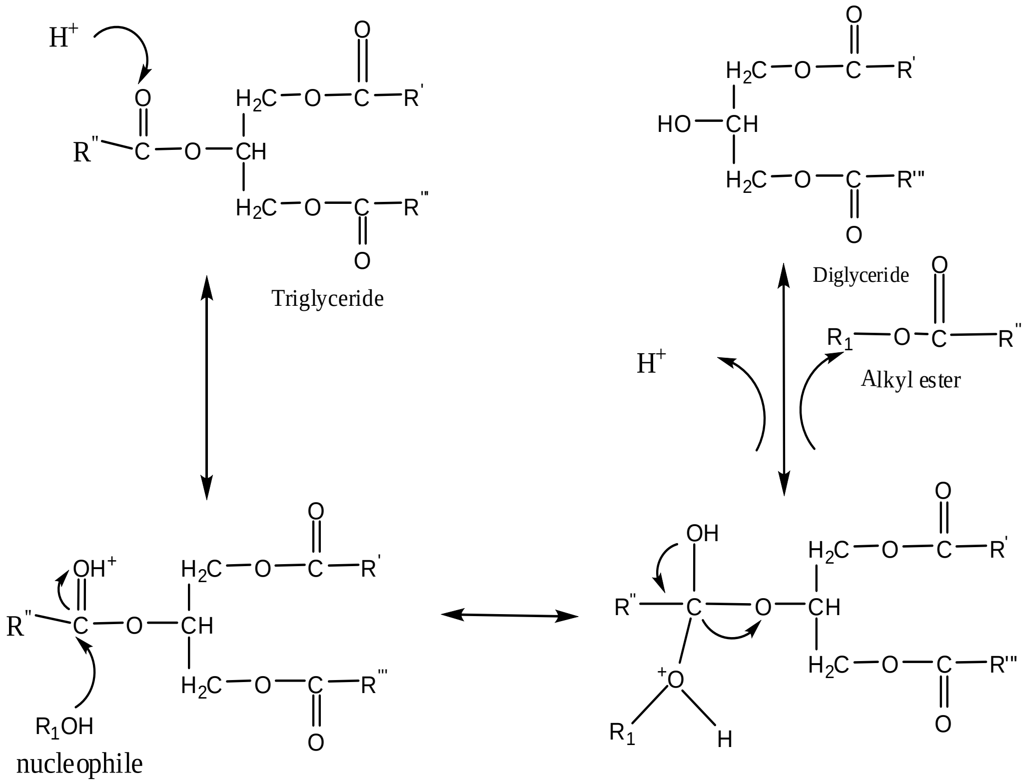
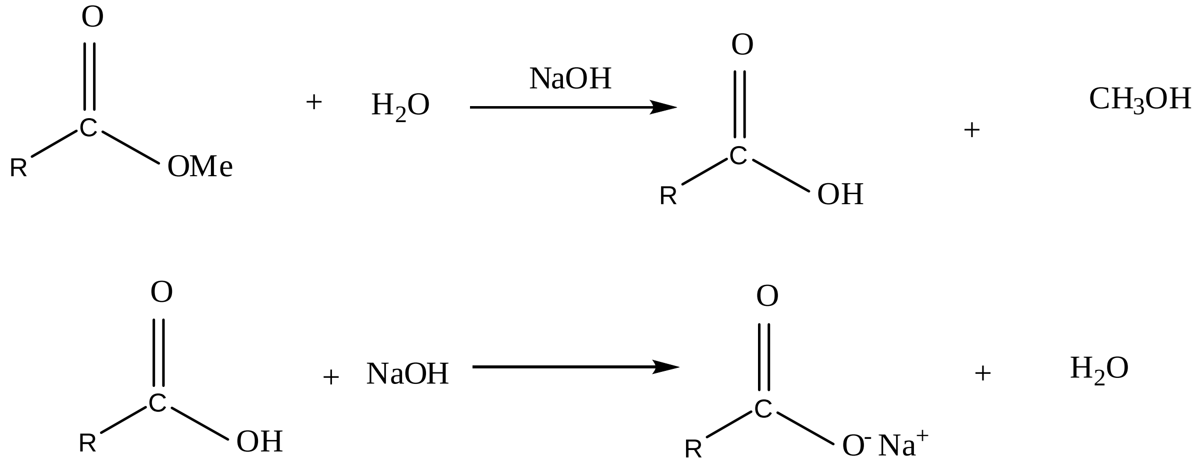


Figure 1.2. Mechanistic pathways of homogeneous acid catalysed transesterification.

Nevertheless, homogeneous base catalyzed transesterification needs a high purity feedstock. Triglycerides and alcohol must be anhydrous in order to prevent undesirable saponification reactions (Scheme 1.2). Furthermore, triglycerides should have low free fatty acids (< 0.5%) content as they can react with the alkaline catalyst resulting in soap formation (Scheme 1.2).



Scheme 1.2. Effect of water and FFA over homogenously catalysed reaction.

The soap formation consumes the catalyst, prevents glycerol separation from biodiesel and decreases the ester yields. When the acid value of oil is high (> 0.5 wt.%), acid catalysts such as H_2SO_4 and HCl are used since these catalysts could catalyze the esterification of FFA and transesterification of triglyceride simultaneously. However, this process requires a high molar ratio of alcohol to oil, higher reaction temperature and longer reaction time (Freedman et al., 1984). Besides, during acid catalyzed reactions, all parts of the reactor must be acid resistant to prevent the corrosion (Canakci et al., 1999).

Although homogeneous catalysts provide high biodiesel yield (Table 1.1), yet their use is not satisfactory as they cannot be reused or regenerated. They are consumed in the reaction and separation of catalyst from products is difficult and requires thorough washing and neutralization (Ma and Hanna., 1999). Besides, the process is not environment friendly as large amount of water is consumed to remove the catalyst and biodiesel thus obtained must needs to be dried (Vicente et al., 2007).

1.2.2. Heterogeneous catalyst

The high consumption of energy and costly separation of the homogeneous catalyst from the reaction mixture, have motivated the intense research on heterogeneously catalyzed transesterification. Benefits of using heterogeneous catalysts include ease of separation and purification of the reaction products, easy reuse of the catalyst in the reactor, reduced corrosion problems and low sensitivity towards FFAs and moisture contents (Meher et al., 2006).

Various types of heterogeneous catalysts which have been reported for the transesterification of vegetable oils/animal fat are; (1) alkaline earth metal oxides, (2) active metal supported metal oxides (3) hydrotalcites and (4) mixed oxides and (5) mesoporous based catalysts. These are discussed in detail in the following sections.

1.2.2.1 Alkaline earth metal oxides

The basic strength of the group II oxides and hydroxides increases in the order Mg < Ca < Sr < Ba. These have been used as heterogeneous basic catalysts for the transesterification of triglycerides as summarized in Table 1.2. In methanolysis of oils, they provide sites for methanol adsorption, in which O–H bonds readily break into methoxide anion (which act as nucleophile) and hydrogen cations (Zabeti et al., 2009).

Among alkaline earth metal oxides, calcium oxide has been extensively used for transesterification reactions as it possesses relatively high basic strength, non-toxic and cost effective (Table 1.2).Further, it can be prepared from cheap sources like limestone and calcium hydroxide. Its catalytic performance increases in the presence of small amount of water, as O^{2-} ion on the surface of the catalyst extracts H^+ from water molecules to form OH^-

ion which subsequently extracts H^+ of methanol and generate methoxide anons which act as stronger nucleophile (Liu et al., 2008).

Table 1.2. Alkaline earth metal oxides as catalysts for transesterification.

Catalyst	Feedstock	Reaction Conditions				Conversion (C) / Yield (Y)	Reference
		Temp (°C)	Time (h)	Oil to Methanol molar ratio	Catalyst amount (wt.%)		
CaO	Sunflower	60	1.66	1:13	3	94% (C)	Granados et al., 2007
CaO	Sunflower	80	5.5	1:6	1	91% (Y)	Verziu et al., 2011
CaO	Sunflower	75	0.75	1:4	1.2	80% (C)	Vujicic et al., 2010
CaO	Soybean	65	3	1:12	8	95% (C)	Liu et al., 2008
CaO	Jatropha	70	2.5	1:9		93% (Y)	Huaping et al., 2006
CaO	Palm	60	1	1:15	7	93.9% (Y)	Yoosuk et al., 2010
CaO from waste shell of mollusk	Palm	60	2	1: 18	10	90% (Y)	Viriya-empikul et al., 2010
CaO from eggshells	Palm	65	2	1:12	1.5	98% (C)	Cho et al., 2010
CaO from natural calcites	Palm olein	60	0.75	1:15	7	95.7% (Y)	Yoosuk et al., 2010
BaO	Palm	65	1	1:9	3	95.2 (Y)	Mootabadi et al. (2010)
Nano MgO	Soybean	250	0.16	1:36	3	99% (C)	Wang et al., 2007
SrO	Soybean	65	0.5	1:12	3	95% (C)	Liu et al., 2007

There is a report showing as high as 98% FAME yield during first catalytic run using CaO (Veljkovic et al., 2009), however, the catalyst was not reusable. Gryglewicz et al. (1999) indentified calcium diglyceroxide from the reaction of CaO with glycerol during transesterification of soybean oil with methanol. Granados et al. (2007) investigated the role of water and carbon dioxide on the deterioration of the catalytic performance of CaO upon contact with air for different period of time. This study suggests that the active sites of CaO were poisoned due to chemisorption of carbon dioxide and water on the surface sites to form carbonates and hydroxyl groups respectively. However, the catalytic activity of CaO could be regenerated by removing poisoning species (the carbonate groups) from the surface by heat treatment at 700°C. However, leaching of the catalyst was observed in the transesterification reaction even prior thermal treatment was employed.

Calcium oxide was also investigated as heterogeneous catalyst for the transesterification of refined sunflower oil by Vujicic et al. (2010). The catalyst activation in air at 900^{o}C leads to the formation of strong basic sites. However, coalescence of catalyst particles takes place during the reaction, giving a gumlike structure, and resulted in a significant catalyst deactivation. Yoosuk et al. (2010) studied the hydration–dehydration approach for the preparation of CaO from natural calcites. They demonstrated the effect of water on properties and activity of CaO prepared by hydration and subsequent thermal decomposition method of calcined calcite. The CaO formed by hydration followed by thermal decomposition was found to have higher surface area and more number of basic sites than CaO generated from the decomposition of calcite. Hai-xin et al. (2009) prepared porous CaO microspheres by calcining spherical $CaCO_3$ precursor. The prepared CaO microsphere was used as catalyst for the transesterification reaction of soybean oil and showed excellent FAME yield of 98.72%.

Recently, research interest has grown in the production of biodiesel using waste mollusk shells and eggs shells as catalysts. Pioneering work done by Wei et al. (2009) has suggested a green way of catalyst preparation from egg shell for the transesterification of vegetable oil. Based on this study, different researchers have proposed the utility of industrial waste shells as catalyst for biodiesel production and in other fields of catalysis. Shrimp shells (Yang et al., 2009), shells of golden apple snail and meretrix venus (Viriya-empikul et al.,

2010) are some of the examples which have been successfully used as heterogeneous catalysts for biodiesel production. The shell material is composed of 95–99% crystalline calcite or aragonite (a form of calcium carbonate) and protein film which is used as the binder in varying amount from 0.1% to 5% by weight (Kaplan et al., 1998). Engin et al. (2006) studied the chicken egg shell after heat treatment in the temperature range of 25–900^{o}C by X-ray diffraction (XRD), infra-red (IR), thermogravimetric analysis (TGA) and electron spin resonance (ESR) studies. Their study confirmed that the egg shells were mainly composed of calcites and upon heating at higher temperature it converted to CaO.

Di Serio et al. (2008) observed 92% yield of methyl esters using 5 wt.% of MgO catalyst and 12:1 molar ratio of methanol to oil. Tateno and Sasaki (2004) investigated that MgO showed 91% of FAME yield under supercritical conditions using methanol to oil molar ratio of 40:1.

Mootabadi et al. (2010) studied the ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts (CaO, SrO and BaO). Their catalytic activity was in the sequence of CaO < SrO < BaO and found to be a function of their basic strength. Barium oxide underwent more severe drop in the activity due to the leaching of the catalyst.

Zabeti et al. (2009) mentioned the suitability of SrO as heterogeneous catalyst for transesterification. Liu et al. (2008) observed that SrO has high basicity and insolubility in methanol, vegetable oil and methyl esters and could be a suitable heterogeneous catalyst.

Although there are satisfactory results with metal oxides in terms of conversion/yield as can be seen in Table 1.2 yet, their leaching problem limits their application as heterogeneous catalyst. Problem of leaching was more frequent in the presence of polar substances such as methanol, water and FFA. Therefore, these types of catalysts are recommended only for the transesterification of refined oil.

1.2.2.2. Active metal supported metal oxides

With a view to improve the basic site strength and catalytic efficiency of metal oxides (e.g. MgO, CaO, Al_2O_3) they were impregnated with various active metals viz., Li, K, Na (Dinesh et al., 2010; Mandeep et al., 2011). These efforts were made by various researchers to prepare strong solid base catalysts for the transesterification reaction. Work regarding the application of such catalysts for bio-diesel preparation from various feedstocks is complied and shown in Table 1.3. Generally, these catalysts are prepared by wet-impregnation followed by drying and calcinations.

Table 1.3. Alkali impregnated metal oxides as catalysts for transesterification

Catalyst	Feedstock (oil)	Reaction conditions				Conversion (C) / Yield (Y)	Reference
		Temp. (^{o}C)	Time (h)	Oil to methanol molar ratio	Catalyst amount (wt.%)		
KF/ZnO	Soybean	65	9	1: 10	3	87% (C)	Xie et al., 2006
KI/Al_2O_3	Soybean		8	1: 15	2.5	96% (Y)	Furuta et al., 2006
KNO_3/Al_2O_3	Soybean		7	1: 15	6.5	87% (Y)	Xie et al., 2006
KF/Eu_2O_3	Rapeseed	65	1	1: 12		92.5% (C)	Sun et al., 2008
KF/CaO	Chinese tallow seed	65	2.5	1: 12	4	96.8% (Y)	Wen et al., 2010
KNO_3/CaO	Rape	65	3	1: 6	1	98% (C)	Encimar et al, 2010
KOH/MgO	Mutton fat	65	0.33	1: 22	4	>98% (C)	Mutreja et al., 2011
Li/MgO	Soybean	60	2	1: 12	9	93.9% (Y)	Wen et al., 2010
Li- ZnO	Soybean	65	3	1: 12		96.3 (C)	Xie et al., 2007
Al_2O_3/Na/ NaOH	Soybean	60	2	1: 9	1 g	83% (Y)	Kim et al., 2004
Na/SiO_2	Jatropha	65	45	1:15		99 %(C)	Akbar et al., 2009

Mainly lithium, potassium and sodium have been used for impregnation as they increase the basic site strength of supports (e.g. CaO, MgO and ZnO etc.) which inturn increase the catalytic activity (Dinesh et al., 2010; Mandeep et al., 2011). As could be seen from Table 1.3, impregnation of sodium over SiO_2 resulted in highest conversion (99%) of triglycerides into methyl esters. Although these catalysts have shown good results in term of FAME yields, yet they have not attracted attention of biodiesel industry due to the leaching of active metal species and poor reusability.

1.2.2.3 Hydrotalcites /Layered Double Hydroxides

Hydrotalcites (HTs) or Layered Double Hydroxides (LDHs) are anionic and basic clays found in nature with the general formula $[M_{(1-x)}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}\ (A^{n-})_{x/n}.yH_2O$ where M^{2+} and M^{3+} are divalent and trivalent cations and A^{n-} is the interlayer anion (Bejoy et al., 2001). Schematic representation of a typical HT is shown in Figure 1.3.

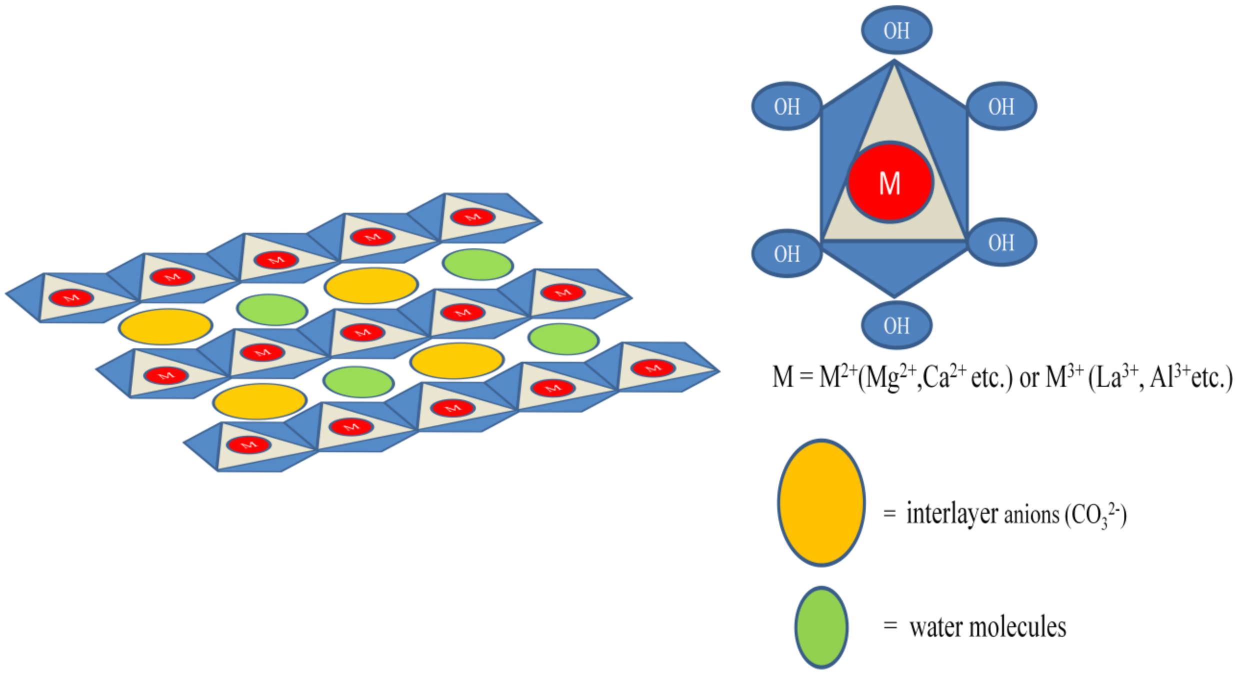


Figure 1.3. Schematic representation of a typical hydrotalcite.

The most commonly studied HT is $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. It presents a positively charged brucite-like layers ($Mg(OH)_2$) in which some of Mg^{2+} are replaced by Al^{3+} in the octahedral sites of hydroxide sheets. Interstitial layers formed by CO_3^{2-} anions and water molecules compensate the positive charge resulting from this substitution (Helwani et al., 2009; Reyes-Labarta et al., 2009).

They form an important group of catalysts as their acid and basic properties can be controlled by varying their composition. A wide range of HTs, containing various combinations of Group (II), Group (III) and different anions A^{n-} have been synthesized (Carja et al., 2001). Conventionally, HTs are synthesized by co-precipitation method wherein metal nitrates and precipitants are added slowly and simultaneously at a fixed pH under stirring, followed by ageing (about 1 day) and/or hydrothermal treatment in order to improve the crystallinity. A particular chemical composition and the method of synthesis, i.e., temperature, solution pH, and ageing time of the gels, have a strong influence on the final basicity and structure of HTs (Schulze et al. 2001; Morato et al., 2001).

Pioneering work on HTs as catalysts for the synthesis of biodiesel have been provided by Helwani et al. (2009) and Zabeti et al. (2009). Since then a variety of HTs have been used as catalyst as well as support for exogenous catalytic species for transesterification reaction of different feedstocks (vegetable oil/fat) and work regarding this type of catalysts is summarized in Table 1.4. These catalysts without any modification required comparatively higher reaction temperature. But they can also work under ambient conditions when impregnated/doped by some co-catalyst like potassium or any other alkali metal. Co-catalyst supported over LDH, may be at the surface or between the LDH structure layers.

Table 1.4. Hydrotalcites as heterogeneous catalysts for transesterification.

Catalyst	Feedstock (oil)	Reaction conditions				Conversion (C) / Yield (Y)	Reference
		Temp. (^{o}C)	Time (h)	Oil to methanol molar ratio	Catalyst amount (wt.%)		
Mg-Al	Sunflower	140	6	1: 24	6	100 (C)	Brito et al., 2009
Mg-Al commercial	Sunflower	60	24	1: 12	2	50 (C)	Navajas et al., 2010
Mg-Al	Soybean	230	1	1: 13	5	90 (C)	Silva et al., 2010
Mg-Al	Jatropha	45	1.5	1: 4	1	95.2 (Y)	Deng et al., 2011
Mg–Al–CO3	Cotton seed /animal fat	180–200	3	1:6	1	99 (C)	Barakos et al., 2008
K/Mg–Al	Palm	100	6	1:30	7	96.9 (C) / 86.6 (Y)	Trakarnpruk et al., 2008
KF/Mg-Al	Palm	65	5	1: 12	3	92 (Y)	Gao et al., 2008
KF/Ca–Al	Palm	65	3	1: 12	5	99.7 (Y)	Gao et al., 2010

Siano et al. (2006) patented the application of Mg–Al hydrotalcite for biodiesel production from soybean oil and found that the activity of the catalyst was affected by the ratio of Mg/Al and the most active catalyst was obtained with Mg/Al ratio of 3 to 8.

Di Serio et al. (2006) reported four types of basic sites in Mg–Al HTs. These include weak basic sites related to OH^- surface groups; medium basic sites corresponding to oxygen in MgO and Al_2O_3; and strong basic sites and super-basic sites belonging to O_2^-. These HTs also possess large pore size which resulted in their high catalytic activity in comparison to pure MgO. Their decomposition yields a high surface area Mg–Al mixed oxide. The reconstruction of decomposed Mg–Al HT by rehydration at room temperature was found to enhance the catalytic activity (Xi et al., 2008). During the rehydration, the brucite-like structure reformed and the charge-compensating carbonate anions were replaced by hydroxyl anions, thus forming Bronsted base sites. The decomposed–rehydrated Mg–Al HT with Bronsted base sites exhibited higher catalytic activity than the decomposed Mg–Al HT with

Lewis base sites. Georgogianni et al. (2009) compared the catalytic activities of Mg–Al HT and MgO supported on MCM-41 for transesterification of soybean frying oil with methanol. Under similar operating conditions, conversion of 97 and 85 % was observed in 24 h of reaction duration with Mg–Al HT and MgO/MCM-41 catalysts respectively. The greater activity of the hydrotalcite was correlated to its higher basicity although the specific surface area of Mg-MCM-41 (1289 m^2/g) was much higher than the specific surface area of Mg–Al hydrotalcite (82 m^2/g).

1.2.2.4. Mixed oxides

Mixed metal oxides i.e. the oxides containing two or more different kinds of metal cations, represent an interesting class of heterogeneous catalysts and catalyst supports for alkali, rare-earth and noble metals. These can be prepared by calcinations of HTs type materials of respective elements which can be prepared by hydrothermal treatment, sol-gel method and wet-impregnation methods. Some of the mixed metal oxides are better in terms of their catalytic activity than corresponding pure oxides in various reactions. It could be due to increase in active acidic or basic sites and increase in surface area whiles the formation of mixed oxide. Work regarding these catalysts is compiled and shown in Table 1.5. As can be seen from Table 1.5, these catalysts require either longer reaction time or higher methanol to oil molar ratio for the yield > 97% FAME. An alternative to increase their performance was impregnation/doping of alkali metals on these oxides. However, such catalyst suffers from leaching of active species in reaction mixture during their usage.

Table 1.5. Mixed metal oxides as heterogeneous catalysts for transesterification.

Catalyst	Feedstock (oil)	Reaction conditions				Conversion (C) / Yield (Y)	Reference
		Temp. (^{o}C)	Time	Oil to methanol molar ratio	Catalyst amount (wt.%)		
Mg–Ca	Sunflower	60	-	1: 12	2.5	92	Albuquerque et al., 2008
Mg-La	Sunflower	65	0.5	1: 53	5	100	Babu et al., 2008
Ca-La	Soybean	58	1	1: 20	5	94.3	Yan et al., 2009
Al_2O_3–SnO, Al_2O_3–ZnO	Soybean	60	4		5	80	Macedo et al., 2006
$CaZrO_3$, CaO–CeO_2	Rapeseed	60	10	1: 6	10	79-92	Kawashima et al., 2008
1.5% K over Mg–Al	Palm	100	9	1: 45	8	96	Tittabut et al., 2008
CaMgO, CaZnO	Jatropha	65	6	1: 15	4	>80% (C)	Taufiq-Yap et al., 2011
CaO.ZnO	Palm kernel	60	1	1: 30	10	94.2 (C)	Ngamcharussrivichai et al., 2008

First commercial heterogeneous catalyst based on mixed oxides for biodiesel production was developed by French Institute of Petroleum (IFP) (Bloch et al., 2008). A patent (Stern et al., 1999) awarded to IFP describe that is a mixed oxide of spinel type (AB_2O_4) having composition of $ZnAl_2O_4$, xZnO, yAl_2O_3 (with x and y being in the range of 0–2). Another subsequent IFP patent (Bournay et al., 2005) states that the catalyst is sensitive to water and hence water concentration should be below 1000 ppm which implies that only refined feedstock could be used with this catalyst.

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1.2.2.5. Mesoporous based catalysts

The discovery of molecular sieve family (M41S) has provided the platform for designing the heterogeneous catalyst supports with the control of textural features in addition to the high surface area (Kresge et al., 1992) The M41S family had three members, namely

MCM-41	(hexagonal, one-dimensional pore structure)
MCM-48	(three-dimensional, cubic pore structure)
MCM-50	(unstable lamellar structurre)

These materials have following advantages which make them efficient catalytic support:

1. Large accessible surface area (up to 1200m^2/g).
2. Tunable pore size and pore volume which facilitate the entry of the desired molecule inside the catalyst cavities to achieve better selectivity of targeted product.
3. These can be manipulated with acidic, basic and hydrophobic moieties.
4. These can be made selective for a particular reaction.
5. These could be fabricated with homogenously dispersed active catalytic species in nano particle form.

In spite of the amazing features of catalytic support in mesoporous materials, there are only few reports (Li et al. 2008; Melero et al., 2009) available regarding the preparation of mesoporous materials modified with any alkali/alkaline metals and their use for the transesterification reaction under ambient conditions. Li et al. (2008) investigated different mesoporous silicas (MCM-41, KIT-6, and SBA-15) loaded with MgO as solid base catalysts for the transesterification of a blended vegetable oil. Highest activity with a conversion of 96% in 5 h was observed with SBA-15 coated with MgO. Same study also suggested minor or no effects of the precursor salt (magnesium acetate and nitrate) on the performance of the catalyst. In contrast, the catalytic activity was affected by the type of silica support and by the loading method viz., impregnation and in situ coating.

Melero et al., (2009) reported FAME yield of over 95 % using sulfonic acid-modified mesostructured catalyst (6 wt % with respect to oil) and methanol/oil molar ratio of 10 at 180° C.

1.3. Lacunae

At present biodiesel is not cost competitive with conventional diesel fuel owing to its high production cost which could be attributed to high feedstock cost and high energy consumption during the transesterification and purification process. In order to decrease the cost of biodiesel production, cheap feedstocks viz., waste cooking oils, animal fat, greases and non-edible oils could be employed as feedstock into biodiesel. However, such feedstock usually possess high moisture and FFA contents and hence, homogeneous catalyst could not be employed for their transesterification. From literature review discussed above following lacunae were indentified:

1. Production of biodiesel from low quality oils (having high FFA and moisture content) using efficient and economical catalyst processes
2. A heterogeneous catalyst that works under ambient conditions for the transesterification is not commercially available.
3. Fewer reports regarding the preparation of biodiesel from waste animal fat.
4. Fewer reports available regarding the evaluation of mesoporous material as catalytic support for the transesterification

1.4. Objectives

By considering the lacunae, following objectives were undertaken:

1. To develop heterogeneous (Mesoporous and Group II metal based) catalysts for the formation of biodiesel
2. Use of heterogeneous catalysts for the conversion of triglycerides into biodiesel and optimization of reaction conditions
3. To study recyclability of developed catalysts for the formation of biodiesel

In order to achieve first objective, four different types of heterogeneous catalysts were synthesized; (1) KOH impregnated MgO (2) Potassium impregnated mixed oxides of magnesium and lanthanum, (3) Potassium impregnated SiO_2, (4) MgO and KNO_3 coated messporous SBA-15. These were used for the transesterification of triglycerides and their reusability and various catalytic parameters were evaluated to cover the 2nd the 3rd objective. Additionally, commercially available sodium aluminate and its calcined forms have also been evaluated as basic catalysts for the transesterification of waste mutton fat. Entire work accomplished under these objectives is given in the following chapters.

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Chapter 2: Materials and Methods

ABSTRACT

This chapter is about various chemicals and materials which have been used in the research work. In this chapter detailed description of methods viz., site strength measurement by Hammett indicators and monitoring of reaction by thin layer chromatography (TLC) and ^1H NMR and, other analytical tools and techniques viz., Powder XRD, TGA/DTA, TEM and SEM-EDX is given.

This chapter includes the list of various chemicals and materials, and detailed description of methods and analytical techniques which have been used in the research work. These are given below:

2.1. Chemicals

Tetraethylorthosilicate (TEOS), Pluronic P123, sodium aluminate, magnesium nitrate and lanthanum nitrate of 99.9% purity were purchased from Sigma Aldrich. Ethanol, magnesium acetate, magnesium oxides, potassium hydroxide, potassium carbonate, potassium nitrate, hydrochloric acid, sodium hydroxide, silica gel, hexane, ethyl acetate, neutral red, bromothymol blue, phenolphthalein, alizarin, 2,4-dinitroaniline and 4-nitroaniline of GR grade were obtained from Loba Chemicals Pvt. Ltd and used as such without further purification. Methanol (>99%) was obtained from MERK, India.

2.2. Feedstocks

Jatropha and karanja oil was purchased from Medors Biotech Pvt. Ltd. New Delhi (India). Waste mutton fat was purchased from meat shop located in Patiala (Punjab) India. Cotton seed oil was purchased from a local departmental store located in Patiala (Punjab) India. It was heated at 170-180 ^{o}C for 60 min and frying of food materials was carried out three times. Physicochemical properties viz., FFA, saponification and iodine values of the feedstocks were determined by the reported methods (Plummer, 1988; Virmani, 1995). Moisture content of these feedstocks was determined by Karl Fisher method using AF7LC Orion Coulometric autotitrator. These are given in Table 2.1.

Table 2.1. Physiochemical properties of feedstocks.

Feedstock	Free fatty acid content (wt. %)	Iodine value	Saponification value (mg KOH/g)	Moisture content (wt.%)
Jatropha oil	5.62	101.5	192.5	0.26
Karanja oil	11.28	96.8	187.6	0.33
Virgin cottonseed oil	0.2%	90.6	188.7	0.12
Used cotton seed oil	0.8%	91.23	200.4	0.19
Mutton fat	0.258 for fresh fat 2.49 for six month old fat	46.1	192.4	0.02

2.3. Method and analytical equipments used for characterization of prepared catalytic samples are given below:

2.3.1. Powder X-ray diffraction (XRD)

Powder XRD were carried on PANalytical X'pert using Ni-filtered Cu Kα radiation in steps of 0.0130° with a scan step time of 13.7 s in the 2θ range of 5–80°. Low angle measurements were recorded in case of mesoporous materials from 0.1 to 5°. Identification of the crystalline phases was made with the help of Joint Committee on Powder Diffraction Standard (JCPDS).

2.3.2. Field emission gun-scanning electron microscope (FEG-SEM-EDX)

SEM images of samples were taken after gold coating on Jeol (JSM-7600F) from Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology (IIT), Bombay.

2.3.3. Transmission electron microscopes (TEM)

TEM images were recorded on Hitachi (H-7500) 120 kW from SAIF, Panjab University, Chandigarh.

2.3.4. Fourier transform infra red (FT-IR) spectroscopy

Infra red spectra were recorded in KBr matrix on Nicolet FT-IR spectrometer (iS10, Thermo Scientific) in the range of 400-4000 cm^{-1}.

2.3.5. Thermogravimeteric analysis (TGA)

TGA of samples were recorded on Perkin Elmer Diamond TGA/DTA under nitrogen atmosphere with a heating rate of 10 ^{o}C/min upto 1000 ^{o}C.

2.3.6. Brunauer-Emmett-Teller (BET) surface area

BET surface area of catalytic samples was recorded on single point (29.74% nitrogen and 70.26% Helium) using Smart Sorb 92/93. All samples were degassed at appropriate temperature under nitrogen atmosphere to remove the adsorbed gases and moisture.

2.3.7. Measurement of basic site strength

Site strength is the relative tendency of an acid or base to donate or accept a proton. It was determined by shaking 200 mg of catalyst in 10 ml methanolic solution of each Hammett indicator (0.02 M) viz., neutral red ($H\_ = 6.8$), bromthymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.3$), alizarin ($H\_ = 11$), 2,4-dinitroaniline ($H\_ = 15.0$) and 4- nitroaniline ($H\_ = 18.4$). It was predicted by observing the colour change of respective Hammett indicators (Mutreja et al., 2012).

2.3.8. Measurement of soluble basicity

Soluble basicity of the prepared catalysts was determined by acid-base titrations (Singh et al., 2008). For the determination of soluble basicity, catalyst was mixed with excess amount of HCl of known concentration. The residual HCl concentration was determined by titration with standard NaOH in presence of phenolphthalein indicator and the amount of HCl consumed by the catalyst was then determined and soluble basicity was referred as mmol HCl/g of catalyst.

2.4. Method and analytical equipment used to monitor the progress of transesterification are following:

2.4.1. Thin layer Chromatography (TLC)

It is easy, rapid and cost effective technique for preliminary investigation of the progress of the reaction. In order to monitor the progress of reaction, aliquots of the sample were taken from the reaction mixture after appropriate time intervals. These were analyzed by TLC using silica gel G as stationary phase, and a mixture of hexane and ethyl acetate (24:1, v/v) as mobile phase (Mutreja et al., 2011).

2.4.2. Proton Nuclear Magnetic resonance (^{1}H NMR)

After preliminary investigation by TLC, formation of fatty acid methyl esters (FAMEs) under different reaction conditions during transesterification reaction was studied by ^{1}H NMR spectroscopy (Bruker, 400 MHz FT-NMR Cryo Spectrometer Bruker) from SAIF, Panjab University, Chandigarh. The appearance of a peak at 3.6 ppm due to the formation of $–OCH_3$ and the disappearance of glyceridic protons present in triglycerides at 4.1 and 5.2 ppm indicate the formation of FAMEs.

Quantification of biodiesel from ^{1}H NMR spectra was carried out as per reported method (Knothe et al., 2001) using following formula:

$$\% \mathrm{C} = \frac{100 \times 2 \times \mathrm{I}_{-\mathrm{OCH3}}}{3 \times \mathrm{I}_{\alpha-\mathrm{CH2}-}}$$

% C is conversion of triglycerides into FAMEs and L_{OCH3} and $L_{\alpha\text{-}CH2\text{-}}$ are the integration values of the signals corresponding to methoxy protons (3.6 ppm) and methylene protons (2.3 ppm) respectively in FAMEs.

2.5. Ash method and analytical equipment used to determine the leaching of active metal species:

In this method, biodiesel (0.5 g) was heated at 250 ^{o}C in silica crucible for 1 h followed by slow increase in temperature up to 600^{o}C and further maintaining the temperature for 4 h. The resulting ash was dissolved in dilute nitric acid and analyzed for leached K^{+} ions (Oliveira et al., 2009) on flame photometer (Esico 1382 E).

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Chapter 3: Nanocrystalline potassium impregnated silicon dioxide as heterogeneous catalysts for the transesterification of karanja and jatropha oil

Contents Page

ABSTRACT

Potassium impregnated SiO_2 having 1:1 to 1:6 atomic ratio of Si to K were prepared by sol gel method and evaluated as heterogeneous catalysts for the transesterification of jatropha and karanja oil with methanol. These catalysts are characterized by powder XRD, TEM, SEM-EDX, Hammett indicators, soluble basicity and FT-IR studies. TEM study of the catalyst having Si and K in 1:6 atomic ratio reveals that catalyst has uniform impregnation of 1-5 nm sized potassium nanoparticles over 15-40 nm sized spherical silica nanoparticles. Prepared catalyst was found to be efficient for the transesterification of jatropha and karanja oil in 0.3 h and 0.75 h.

3.1. Introduction

One of major hurdle faced by biodiesel industries is the use of edible oils as feedstock which could leads to the global food problem, deforestation and ecological imbalance while changing the virgin forests and arable lands to large scale biofuel production. On the other hand, the potential of non-edible oil or waste cooking oil or animal fat has been less explored in comparison to edible oil, which may be due to the lack of efficient catalytic system (Endalew et al., 2011). There are several non-edible oil species in India such as karanja (*Pongamia pinnata*), jatropha (*Jatropha curcas*), Neem (*Azadirachta indica*), Mahua (*Madhuca indica*), Simarouba (*Simarouba indica*) etc., which can be cultivated for the production of non-edible oil. Among these, karanja is grown in certain parts of India and Australia. Its seed kernels contain 27-39 percent of oil and annual production of karanja oil in India is 200 million tonnes, of which only 6% is being used in the soap and leather tanning industries (Biswas et al., 2002). Jatropha oil is also equally potent feedstock for biodiesel production having ~34.4% oil content in the seeds (Achten et al., 2008). Fuel properties of biodiesel obtained from both jatropha and karanja oil are quite comparable to those of ASTM biodiesel standards (Patil et al., 2009).

The scheme for the production of biodiesel form karanja oil at industrial scale was proposed by Vivek et al. (2004). This scheme involves the neutralization of FFA content of oil prior to its transesterification. Meher et al. (2006) also reported the neutralization of karanja oil with appropriate amount of potassium hydroxide followed by filtration before transesterification. Recently, Patil et al. (2009) has reported the preparation of biodiesel from jatropha and karanja oils via two steps; esterification of free fatty acids (FFA) followed by the alkali catalyzed transesterification using KOH as homogeneous catalyst. Thus it is evident from the literature review that biodiesel production from non-edible oil demand two step process involving (i) neutralization of free fatty acid either via esterification in the presence of acid catalyst or by KOH treatment (ii) after neutralization of acid, transesterification in presence of alkali catalyst. This procedure also required washing of the biodiesel with water to remove excess acid and alkali catalyst form the reaction mixture, and hence, generated huge amount of effluents. In order to simplify the process, we report the preparation of biodiesel in a single step from the non-edible oils (jatropha and karanja) using the developed potassium impregnated silica as heterogeneous catalyst.

3.2. Experimental section

3.2.1. Catalyst Preparation

Silicon dioxide impregnated with potassium having Si: K in 1:1, 1:2, 1:3, 1:4, 1:5, 1:6 atomic ratio was prepared by sol-gel method and designated as Si: K-X (X being the atomic ratio of Si to K). In a typical method of impregnation, calculated amount of KOH was dissolved in mixture of 20 ml of ethanol and 20 ml of deionized water followed by the addition of 10 g of Pluronic P123. After stirring for 2h, 10 g of TEOS was added drop wise and the mixture was stirred for another 2 h. Gel, so obtained was dried at 80^{o}C for 48 h followed by calcination at 550^{o}C for 6 h with a heating rate of 0.25 ^{o}C/min.

3.2.2. Catalytic activity

All the prepared catalysts were tested for transesterification of karanja and jatropha oil with methanol for optimizing the Si: K ratio for the efficient catalytic activity. For jatropha oil, oil and methanol in 1:60 molar ratio respectively and 6 wt.% of the catalyst amount (with respect to oil) were stirred at 65°C. For karanja oil, oil and methanol in 1:80 molar ratio respectively and 8 wt.% of the catalyst amount (with respect to oil) were used. Progress of the reaction was monitored on TLC and ^{1}H NMR as explained in chapter 2.

Various reaction parameters viz., catalyst amount, oil to methanol molar ratio and reaction temperature were optimized. Catalytic activity was also investigated in the presence of additional 1 wt.% moisture.

3.3. Results and discussion

3.3.1. Catalyst Characterization

3.3.1.1. Powder XRD

Powder XRD patterns of Si: K-X (X=1-6) are shown in Figure 3.1. In Si: K-1, no sharp peak was observed to support the amorphous nature of silica. There is formation of coesite (a polymorph of silicon dioxide having monoclinic crystal symmetry, JCPDF 73-1748) supported by the appearance of peaks at 25.8^{o} and 28.7^{o} in all the other prepared catalysts. In Si: K-2, peaks at 29.8^{o}, 30.3^{o}, 34.3^{o}, 37.0^{o} and 43.8^{o} were observed to support the formation of $K_2Si_2O_5$ (JCPDS: 49-0163) as major phase observed. Other peaks at 31.6^{o}, 32.1^{o}, 34.21^{o} and 43.4^{o} also support the presence of $K_6Si_3O_9$ (JCPDS: 84-0366). Similar diffraction patterns were observed for the other catalysts (Si: K-X, X=3-6) to support the formation of $K_6Si_3O_9$ (JCPDS: 84-0366) as major phase and $K_2Si_2O_5$ (JCPDS: 49-0163) as minor phase.

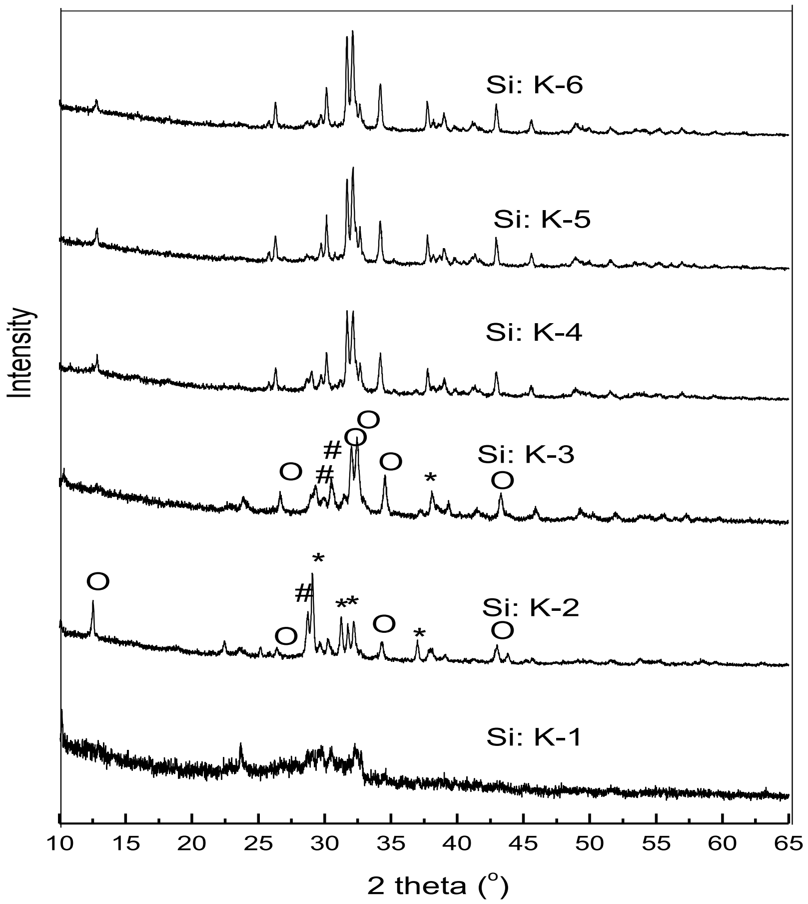


Figure 3.1. Powder XRD pattern of Si: K-X (X = 1-6) (*, $K_2Si_2O_5$; O, $K_6Si_3O_9$; #, SiO_2).

3.3.1.2. Basic site strength and Soluble Basicity

Pure silicon dioxide is amphoteric in nature (Ryan et al. 2011) and its basic site strength was found in the range of $6.8 < H\_ < 7.2$. The basic site strength of all potassium impregnated silicon dioxide catalysts (Si:K-X, X=1-6) was found to be same that is $9.8 < H\_ < 15.0$.

Soluble basicity (total basic sites) of Si: K-X (X=1-6) was determined by acid-titration method as explained in chapter 2 and was found to be 6.4, 7.4, 8.2, 10.1, 15.6 and 19 mmol of HCl/g of catalyst for Si: K-1, Si: K-2, Si: K-3, Si: K-4, Si: K-5, and Si: K-6, respectively. Thus increase in total basic sites was found to be a function of potassium concentration, present in the catalyst.

3.3.1.3. TEM Study

TEM images of Si: K-6 are shown in Figure 3.2a and Figure 3.3a. These images support the formation of spherical silica nanoparticles of 15 to 40 nm. Histogram for the diameters of these particles is shown in Figure 3.2b and average particle size obtained from Gaussian fitting was found to be 28.5 nm.

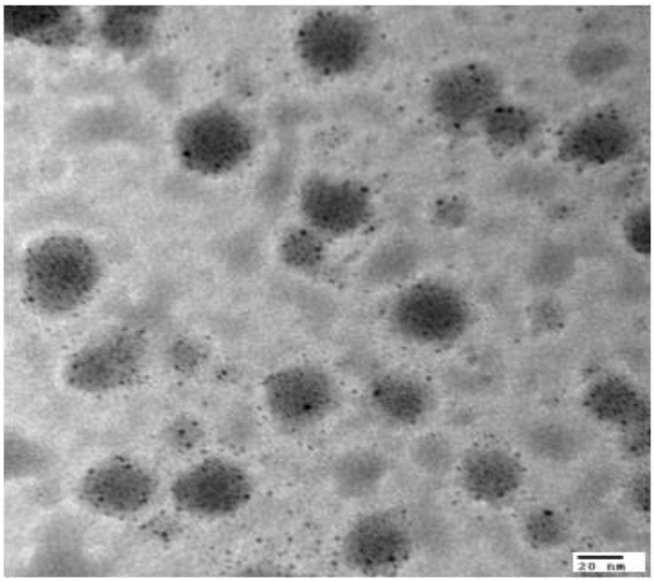


Figure 3.2a TEM image of Si: K-6.

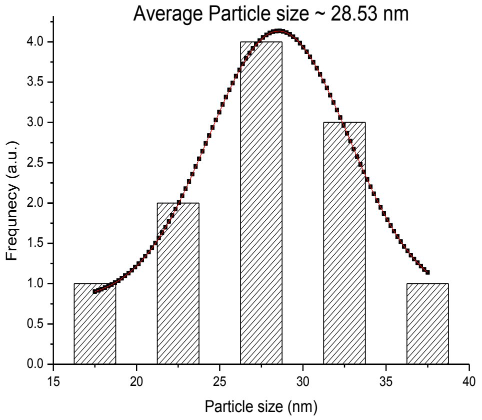


Figure.3.2b Histogram for the particle size distribution of SiO_2 in Si: K-6.

Further Magnification (Figure 3.3a) of these particles support the impregnation of potassium over silica nanoparticles. Appearance of dark dot like spheres of 1-5 nm size could be the potassium particles over silica nanoparticles. Histogram for the diameters of these species is shown in Figure 3.3b and it showed average particle size of 2.9 nm.

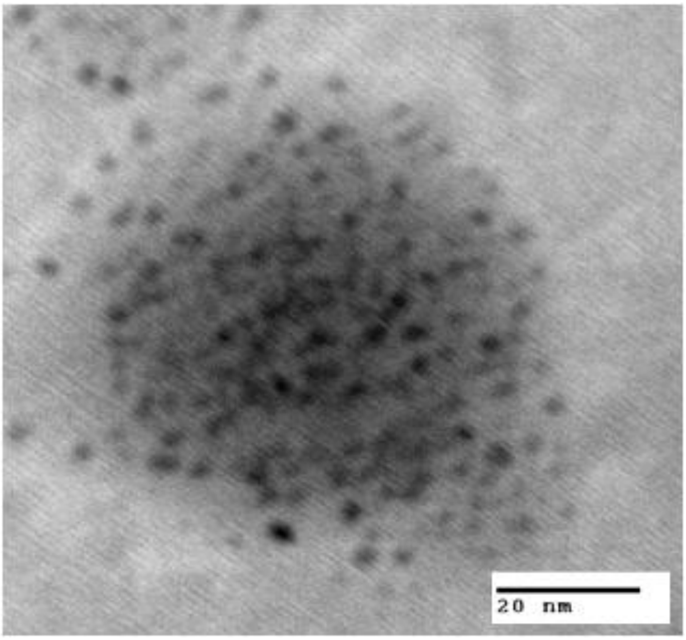


Figure 3.3a. TEM image of Si: K-6 (enlarged view)

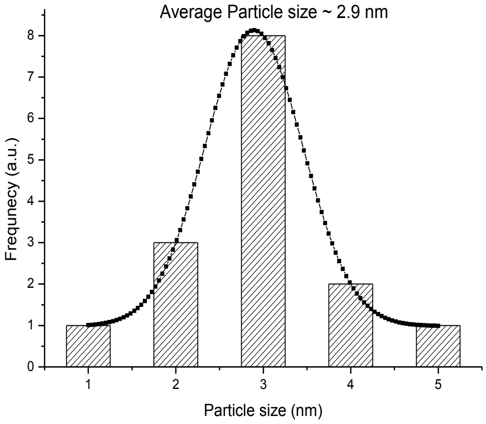
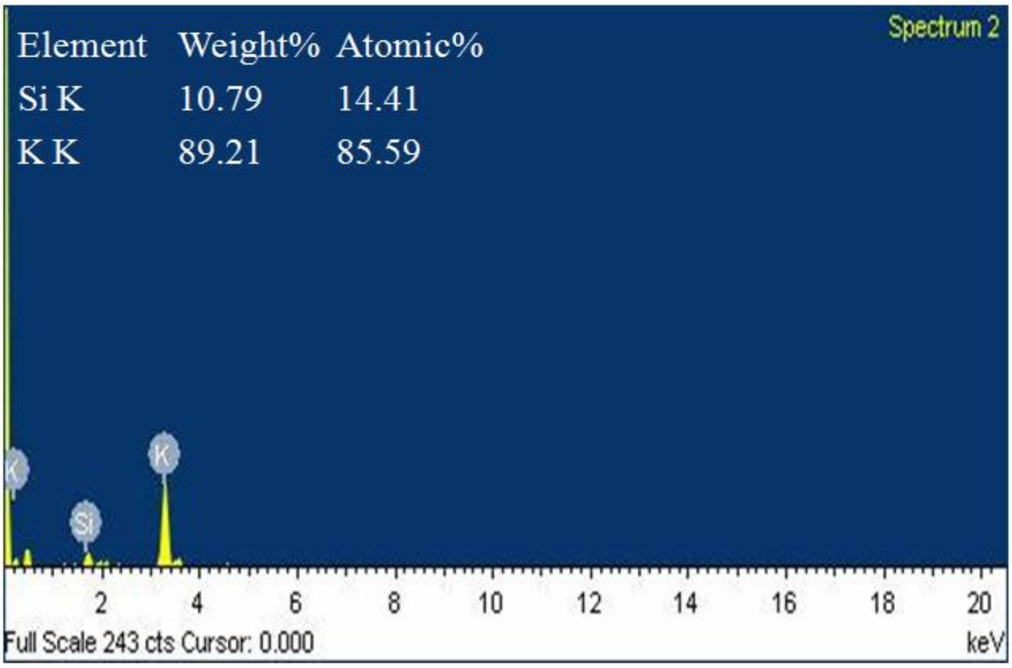


Figure.3.3b Histogram for the diameters of impregnated species in Si: K-6.

To support the potassium impregnation, SEM-EDX of the same catalyst has been performed and shown in Figure 3.4. EDX of Si: K-6 demonstrates the presence of 85.59 % (atomic percentage) of potassium and 14.41% (atomic percentage) of silicon. These amounts correspond to the expected atomic ratio 1:6 of Si and K respectively.



Element	Weight%	Atomic%
Si K	10.79	14.41
K K	89.21	85.59

Figure 3.4. SEM-EDX measurement of Si: K-6.

3.3.1.4. FT-IR

FT-IR spectra of Si: K-X, (X=2-6) are compared in Figure 3.5. Bands at 3200-3600 and 1630 cm^{-1} are due to the vibrations of OH and Si-O respectively. Innocenzi et al (2003) mentioned that the position of OH groups is due to strong hydrogen bonding, otherwise isolated or partially bonded OH groups appears at 3650-3800 cm^{-1}. Vibration observed at 1100 cm^{-1} is due to the Si-O stretching within the tetrahedral. Band at 960 cm^{-1} represents the non bridging Si-O terminal stretching. The weak band at 800 $cm^{-1}$and peak at 465 cm^{-1} can be assigned to the symmetric stretching and bending vibration respectively of Si–O–Si network. Similar spectrum for silica has been reported by Nassar et al (1999) and Mustafa et al (2010).

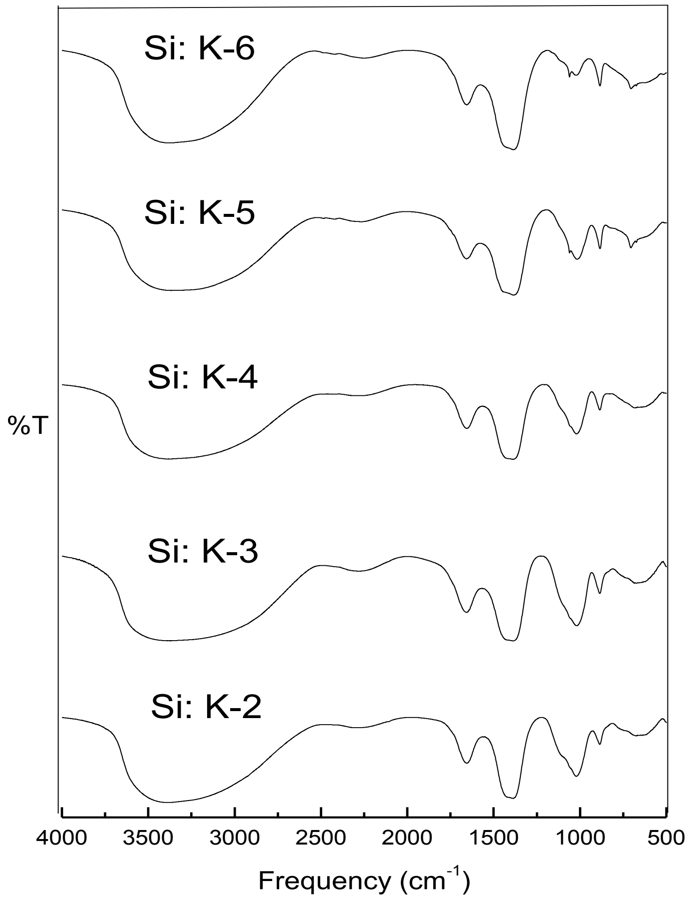


Figure 3.5. FT-IR spectra of Si: K-X, (X = 2-6).

3.3.2. Transesterification reaction, biodiesel characterization and quantification.

Transesterification reactions of jatropha and karanja oil with methanol were performed in the presence of prepared catalysts at 65°C. Prepared catalysts were used to carry out the transesterification reactions of jatropha and karanja oil in order to determine the least reaction time for the completion of the transesterification reaction. During the course of study, the following parameters have been varied (i) silicon to potassium atomic ratio (ii) catalyst concentration, (iii) reaction temperature, (iv) oil to methanol molar ratio, (v) moisture content. Biodiesel produced in the transesterification reactions was characterized by ^{1}H NMR spectroscopy. The proton NMR spectrum (Figure 3.6a) of Jatropha oil shows a multiplet at 4.1 and 5.2 ppm due to the presence of glyceridic protons along with other hydrocarbon-proton peaks at their normal positions. The appearance of a new peak at 3.6 ppm due to -OCH_3 protons and disappearance of the glyceridic protons support the formation of biodiesel as shown in Figure 3.6b. The proton NMR spectra have also been used to confirm the completion of the reaction (>97% conversion of Jatropha oil to biodiesel) by using the following formula as given below:

$$\% \mathrm{C} = \frac{100 \times 2 \times \mathrm{I}_{-\mathrm{OCH3}}}{3\ \times \mathrm{I}_{\alpha-\mathrm{CH2}-}}$$

% C is conversion of triglycerides into FAMEs and L_{OCH3} and $L_{\alpha\text{-}CH2\text{-}}$ are the integration values of the signals corresponding to methoxy protons (3.6 ppm) and methylene protons (2.3 ppm) respectively in FAMEs

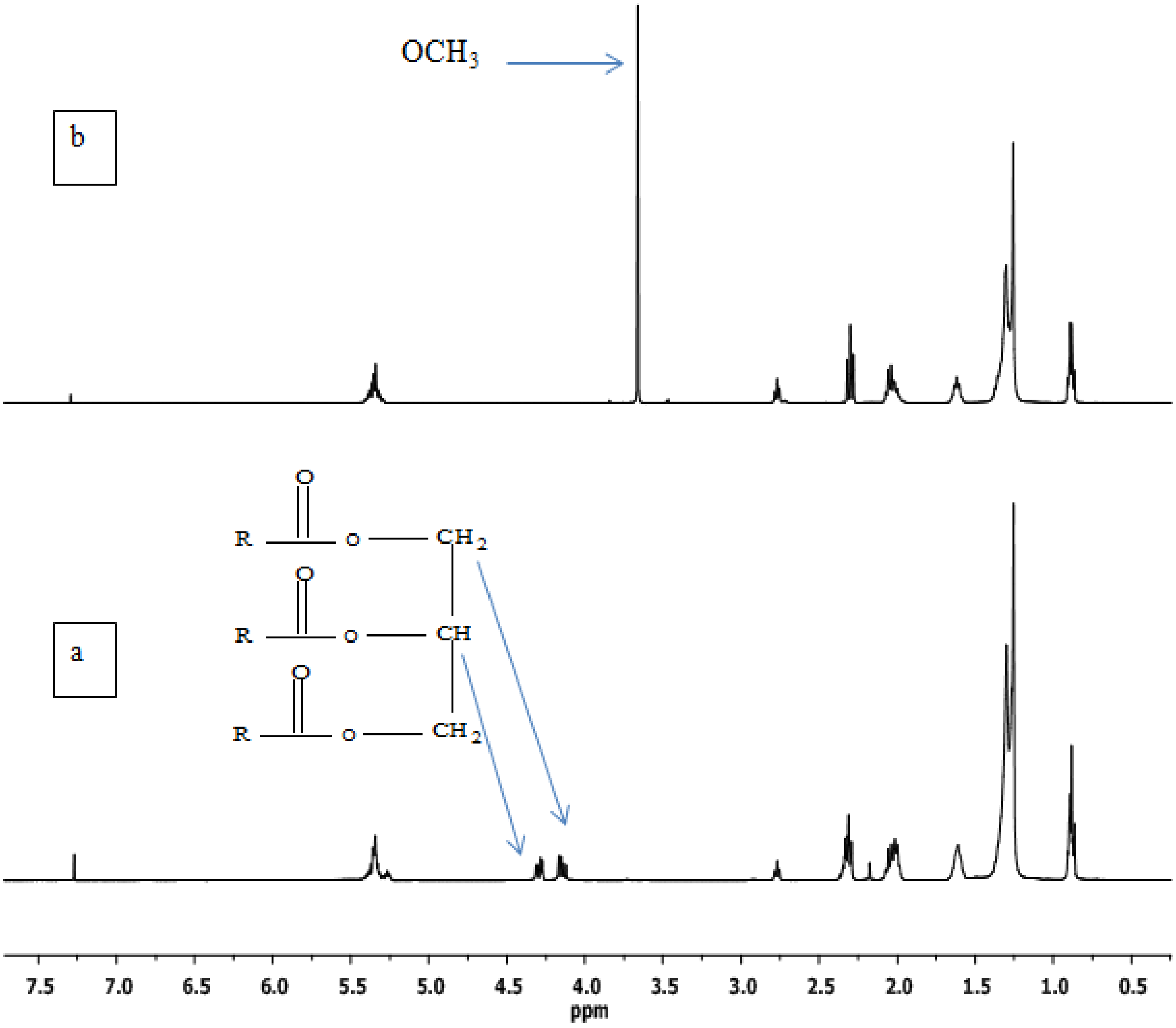


Figure 3.6. ^{1}H NMR spectra (a) Jatropha oil and (b) Methyl esters obtained from Jatropha oil.

^{1}*H-NMR of methyl esters (CDCl3, δ ppm): 5.33 (m, -C**H**=C**H**-), 3.61 (s, -OC**H3**), 2.77 (m, -CH=CH-C**H2**-CH=CH-), 2.3 (m, -C**H2**-CO-), 2.02 (m, -C**H**2-(CH2)n-), 1.61-1.25 (m, -(C**H2**)n-), 0.89 (m, -CH2-C**H3**)*

3.3.3. Catalytic activity

To optimize the Si:K atomic ratio for the optimum catalytic activity, a series of transesterification reactions of karanja oil were performed using 8 wt.% of Si: K-X, (X = 1-6) catalyst and 1:80 molar ratio of oil to methanol at 65°C and results are shown in Table 3.1. Similar reaction has been employed for the transesterification of jatropha oil but using 1: 60 molar ratio of oil to methanol and 6 wt.%. of the catalyst at 65°C, and results are shown in Table 3.1.

Table.3.1. Comparison of soluble basicity and time period for conversion of jatropha and karanja oil into biodiesel by using Si: K-X, (X = 1-6) catalysts.

Catalyst	Soluble basicity (mmol HCl/g catalyst)	Time period (h) for conversion of jatropha oil into biodiesel	Time period (h) for the conversion of karanja oil into biodiesel
Si: K-1	6.4	NC	NC
Si: K-2	7.4	1.25	NC
Si: K-3	8.2	1	NC
Si: K-4	10.1	0.66	3.75
Si: K-5	15.6	0.5	1.0
Si: K-6	19	0.3	0.75

NC, Not Completed; *reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; catalyst amount, 6 wt % of oil; and temperature, 65 °C; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; catalyst amount, 8 wt % of oil; and temperature, 65 °C.*

As evident from the comparison shown in Table 3.1, the catalyst Si: K-6 has demonstrated best performance, among the prepared catalysts. The activity of the catalysts increases with the increase in total basicity of the catalysts. The basicity in the catalysts increase with the increase of potassium concentration which could be attributed to the formation of $K_6Si_3O_9$ as major phase. Both TEM and SEM-EDX studies also confirm more and uniform impregnation of potassium nanospecies in this catalyst.

The Si: K-6 catalyst required the least time period of 20 min and 45 min for the complete conversion (yield > 97%) of jatropha and karanja oil into biodiesel respectively. Large time period for the karanja oil may be due to its higher FFA's content. The use of KOH as homogeneous catalyst resulted in saponification instead of biodiesel when used with oil having FFA content > 0.5 wt.% (e.g. karanja, jatropha). However, Si:K-6 catalyst catalyzed transesterification of jatropha and karanja oil having 5.62 and 11.28 wt.% of FFA respectively, yielded > 97% conversion into fatty acid methyl esters.

Other silicate based catalytic systems are also reported in the literature. Wang et al., (2012) reported lithium orthosilicate (Li_4SiO_4) for the 98.1% conversion of soybean oil to biodiesel after 2 h of reaction using 6 wt.% of catalyst at 65^oC. Guo et al., (2010) studied the effect of calcination temperature on basicity and catalytic activity of sodium silicate for the transesterification of soybean oil and identified Na_2SiO_3 as major phase for the activity.

3.3.3.1. Effect of catalyst amount

Transesterification reactions were carried out by using different amount of catalyst (Si: K-6) with 1:60 and 1:80 molar ratios of oil to methanol (jatropha and karanja respectively) at 65°C and results are shown in Figure 3.7. The time period for the completion of reaction for the jatropha oil was found to decrease from 1.75 to 0.3 h as the catalyst conc. was increased from 3 to 6 wt.% A further increase (upto 7 wt.%) was not found to reduce the reaction time significantly. Hence, 6 wt.% catalyst was used as a optimized catalyst amount for the transesterification. For the karnaja oil, with 8 wt.% catalyst, a minimum reaction duration of

0.75 h was observed and hence for karanja oil, further experiment were performed with 8 wt.% catalyst.

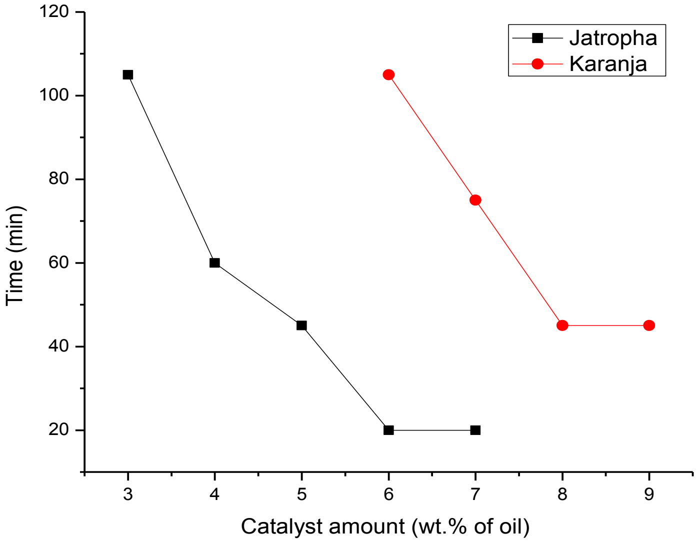


Figure 3.7. Effect of catalyst amount *(reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; and temperature, 65 °C; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; and temperature, 65 °C).*

3.3.3.2. Effect of methanol to oil molar ratio

Transesterification reactions were performed by varying the methanol to oil molar ratios from 20:1 to 90:1 for karanja oil and from 20:1 to 70:1 for jatropha oil at 65°C till the completion of reaction and results are shown in Figure 3.8.

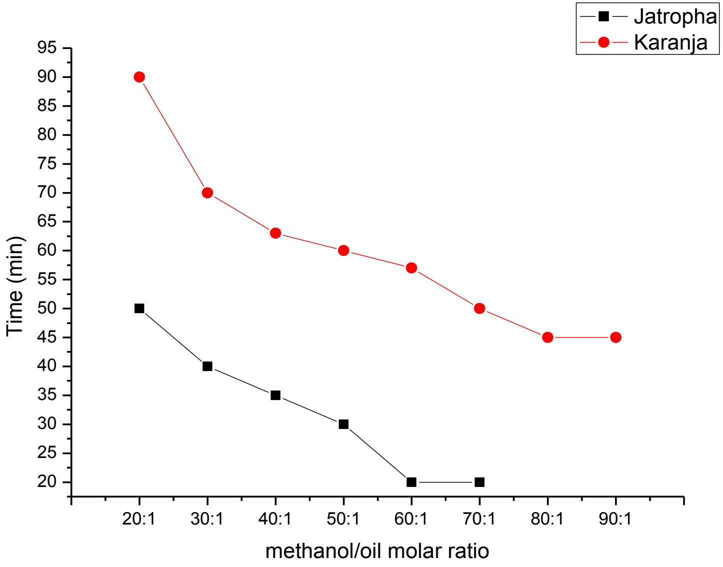


Figure 3.8. Effect of methanol to oil molar ratio *(reaction conditions for jatropha oil: catalyst amount, 6 wt % of oil; and temperature, 65°C; reaction conditions for karanja oil: catalyst amount, 8 wt % of oil; and temperature, 65°C).*

For jatropha oil, time period for the completion of reaction was found to decrease from 0.83 h to 0.3 h with the increase in molar ratio of methanol/oil from 20:1 to 60:1 and further increase in the amount of methanol (methanol and oil in 70:1 ratio) did not showed any marked reduction in reaction time of completion. For karanja oil also, variation in the reaction time of completion from 1.5 h to 0.75 h was observed with the increase in molar ratio of methanol/oil from 20:1 to 80:1 molar ratios respectively. Molar ratio of higher than 80:1, did not reduces the reaction time of completion of 0.75 h. Hence, 80: 1 and 60: 1 molar ratios of methanol to oil were selected for karanja and jatropha oil respectively for the other optimization studies.

3.3.3.3. Effect of Temperature

Transesterification of karanja and jatropha oil was not found to complete at temperature lower than 50 and 45°C respectively. For jatropha oil, reaction time of completion decreases from 2.25 h to 0.3 h with the increase in temperature from 45 to 65^{o}C and for karanja oil, time period decreases from 5 h to 0.75 h by varying the temperature from 50 to 65^{o}C (Figure 3.9).

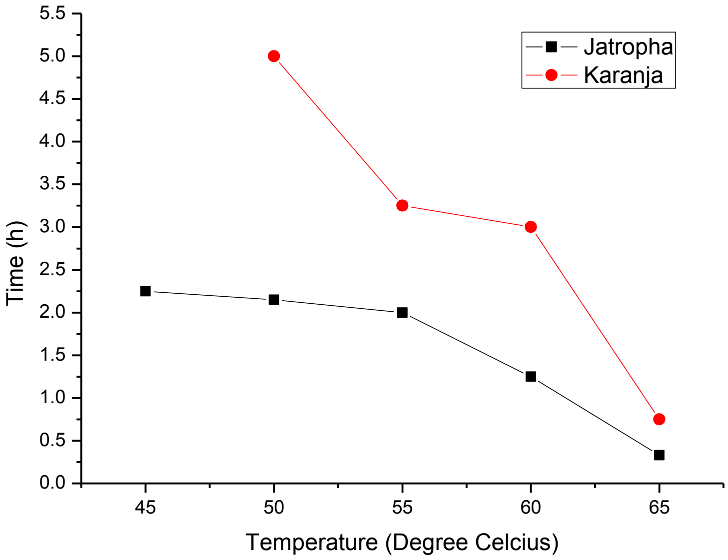


Figure 3.9. Effect of Temperature *(reaction conditions for jatropha oil: oil/methanol molar ratio, 1: 60; catalyst amount, 6 wt % of oil; reaction conditions for karanja oil: oil/methanol molar ratio, 1: 80; catalyst amount, 8 wt % of oil).*

Least time period of 0.3 h and 0.75 h was observed with jatropha and karanja oil respectively at 65^{o}C. This is because higher reaction temperature speeds up rate of reaction and improves the miscibility of the alcoholic polar media into a non-polar oily phase.

On the basis of the above-mentioned experiments, a 1:60 molar ratio of oil to methanol, 6 wt.% of catalyst amount, 65°C reaction temperature and 0.3 h of reaction duration has been established as optimum reaction conditions for jatropha oil, and a 1:80 molar ratio of oil to methanol, 8 wt.% of catalyst amount, 65°C reaction temperature and 0.75 h of reaction duration has been established as optimum reaction conditions for karanja oil.

3.3.3.4. Effect of moisture on catalytic activity

In order to establish the moisture resistance of the catalyst (Si:K-6), transesterification of jatropha oil with methanol was performed in the presence of additional water content. Complete conversion of oil into FAME was achieved even in the presence of 1 wt.% moisture content. Homogeneous KOH and NaOH catalysts used for the transesterification of triglycerides in the presence of moisture > 0.06 wt.% produce soap instead of desired methyl esters where as Si: K-6 catalyst produces methyl esters even in the presence of 1 wt.% of moisture. Potassium species are in the impregnated/heterogeneised form in the Si: K-6 catalyst and due to this it remain insensitive to moisture present in reaction mixture and resulted the formation of methyl esters instead of soap.

3.3.4. Reusability

Reusability experiments were performed using Si: K-6 catalyst with jatropha oil under optimized reaction conditions. The catalyst was separated from the product by filtration, washed with methanol, dried and activated at 550°C before reuse for the next run. It showed 42% and 30% conversion during first two recycles respectively. Powder XRD and soluble basicity of Si: K-6 catalyst was also measured after both catalytic runs. Powder XRD diffraction of reused catalysts (Figure 3.10) showed the diffraction patterns corresponding to $K_6Si_3O_9$ (JCPDS: 84-0366) as major phase and $K_2Si_2O_5$ (JCPDS: 49-0163) as minor phase. Both the phases were also present in fresh catalyst and hence, upon repeated use the catalysts structure has not been changed to significant extent. The soluble basicity of reused catalyst (after 2nd recycle) was found to decrease from 19 to 6.8 mmol of HCl/g of catalyst may be due to neutralization of basic sites with higher FFA (5.62 wt.%) content of jatropha oil.

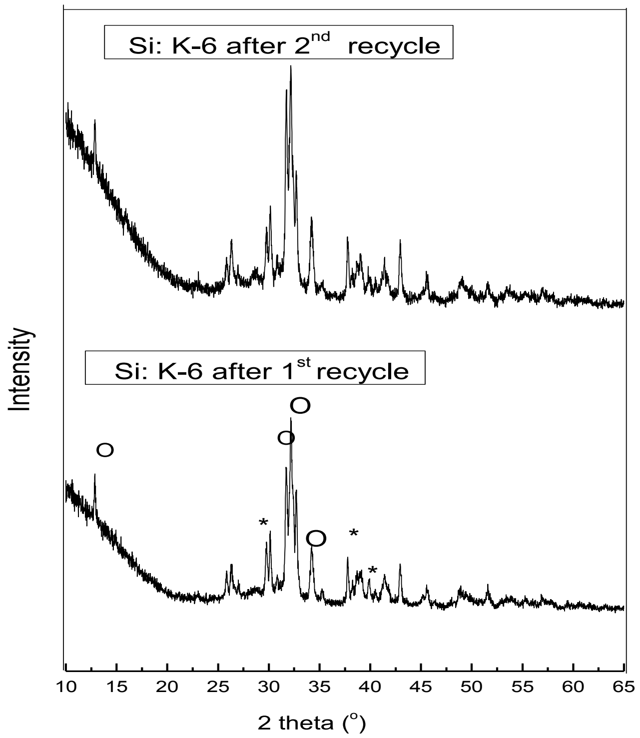


Figure 3.10. Powder XRD pattern of reused Si: K-X-6 catalysts (*,$K_2Si_2O_5$; O, $K_6Si_3O_9$).

The catalyst reusability was also tested with cotton seed oil having 0.2 wt.% FFA contents. The catalyst demonstrated 95%, 92.5% and 92% conversion during 1st three recycles showing better reusability compared to that found in jatropha oil. Thus, catalyst reusability was negatively affected by the presence of FFAs content in the triglyceride.

3.4. Conclusion

Potassium has been heterogeneised over SiO_2 by sol-gel method to prepare the Si: K-X (X= 1-6) catalysts. TEM and SEM-EDX study confirm the presence of impregnated potassium nanospecies over silica particles. These species generate basic sites over silica nanoparticles.

Transesterification of jatropha and karanja oil with methanol using Si: K-6 catalyst resulted in conversion of more than 97 % biodiesel in 0.3 h and 0.75 h respectively at 65^{o}C. The Si: K-6 catalyst also showed the formation of biodiesel in presence of additional 1 wt.% of the moisture in jatropha oil. The same catalyst also demonstrated reusability with cotton seed oil.

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Chapter 4: Potassium impregnated nanocrystalline mixed oxides of La and Mg as heterogeneous catalysts for transesterification

Contents Page

ABSTRACT

Potassium impregnated mixed oxides of lanthanum and magnesium in 1: 1 to 1: 5 atomic ratios were prepared by co-precipitation at a constant pH. These were characterized by FEG-SEM-EDX, TEM, Powder XRD, Hammett indicators and acid/base titration and, were evaluated as heterogeneous catalysts for transesterification of used cotton seed oil with methanol. The optimized reaction conditions for the catalyst, prepared at pH 10 using 1:3 atomic ratio of lanthanum and magnesium, were the use of 1: 54 molar ratio of oil to methanol and 5 wt.% of the catalyst at 65°C that resulted into 96% conversion to biodiesel within 20 min. The catalyst showed tolerance of 1 wt.% of moisture. Concentration of potassium ions leached out form catalyst into biodiesel was within permissible limit of ASTM.

4.1. Introduction

Nowadays, rare earth elements are neither ra nor restricted to laboratory scale research. In fact, quite the reverse is true (Russbueldt et al., 2010). The rare earth elements belong to the long lasting commodity reserves due to the large known ore deposits in Inner Mongolia, China. Therefore, many applications had opened up and a high future potential is expected. Recently, rare earth oxide containing catalysts like $Eu_2O_3/\gamma\text{-}Al_2O_3$ (Li et al., 2007), KF/EuO_3 (Sun et al., 2008) and ZnO/La_2O_3 (Yan et al., 2009) have been reported for the transesterification. Russbueldt et al. (2010) explored the potential of rare earth oxides, their supported and mixed oxides as heterogeneous catalysts for transesterification. Among oxides, activity was found to decrease from La to Sm as expected due to decrease in ionic radius and basicity, leading to the excellent activity for La_2O_3 which showed the best result with 50% methanol at 200^{o}C. Desmartin-Chomel et al. (2010) determined the strong basic sites over mixed oxides MgLaO and MgAlLaO by microcalorimetry and their catalytic activity for transesterification was comparable to strong bases after several hours of reaction. Yan et al. (2009) studied the CaO modified with La for transesterification of soyabean oil and reported 94.3% yield of the reaction. There is a report (Babu et al.,2008) for the preparation of mixed oxides of La (lanthanum) and Mg in 1: 1 to 1: 3 (wt./wt.%) and study of the physiochemical properties by BET surface area, X-ray diffraction and temperature-programmed desorption of CO_2. In the present study, we are reporting the preparation of potassium (K) impregnated mixed oxides of La and Mg in 1: 1 to 1: 5 atomic ratios and their catalytic activity for the transesterification of used cotton seed oil.

4.2. Experimental section

4.2.1. Preparation of the catalysts

Potassium impregnated mixed oxides of La and Mg having 1: 1 to 1: 5 atomic ratio were prepared by co-precipitation at pH = 10 using K species. In a typical preparation, required amounts of $Mg(NO_3)_2.6H_2O$ and $La(NO_3)_3.6H_2O$ were dissolved in appropriate amount of water to make the total metal concentration 1 M and co-precipitated at pH 10 using alkali solution having 2M KOH and 1M K_2CO_3. Precipitates were filtered through G-3, dried at 120^{o}C for 24 h and calcined at 550^{o}C for 4 h and, were grounded to fine powder. The catalysts having 1: 3 ratio of La to Mg were also prepared by precipitation at pH 8 and 12 by similar procedure. These catalysts have been designated as LaMg-X@Y (X being atomic ratio of La to Mg and Y being the pH at which precipitation was carried out).

4.2.2. Catalytic activity

All the prepared catalysts were tested for transesterification of used cotton seed oil with methanol for optimizing La to Mg atomic ratio and the amount of impregnation of K for efficient catalytic activity. In a typical procedure, oil and methanol in 1: 54 molar ratio were stirred (1500 rpm) in a two neck round bottom flask with 3/5 wt.% (catalyst to oil) of catalyst under reflux conditions (65°C) using double walled glass condenser. Aliquots of the sample were taken after appropriate time intervals and progress of the reaction was monitored on thin layer chromatography. After the completion of reaction/stipulated time period, methyl esters in the product were quantified by ^{1}H NMR as explained in chapter 2 and chapter 3.

Various reaction parameters viz., catalyst amount, oil to methanol molar ratio and reaction temperature were also optimized. Catalytic activity was also studied with optimized catalyst and reaction conditions in the presence of additional moisture (upto 2 wt.%) / 0.5 wt.% FFA contents.

Concentration of K^+ in the sample of biodiesel prepared under optimized conditions was determined by Ash method.

4.2.3. Reusability

The selected catalyst with efficient activity was separated from the product by filtration, washed with methanol, dried and activated at 550°C before reuse for the next run. All the reusability experiments were performed using the optimized reaction parameters viz., 5 wt.% of the catalyst amount, 1: 54 molar ratio of oil to methanol at 65°C.

4.3. Results and Discussion

4.3.1. Catalyst Characterization

4.3.1.1 Powder XRD analysis

Powder XRD patterns of LaMg-X@10 (X = 1-5), LaMg-3@8 and LaMg-3@12 are shown in Figure 4.1. Crystalline phases corresponding to the La_2O_3, La_2MgO_x, $La_2O_2(CO_3)$ and K_2O were present in LaMg-X@10 (X = 1-5). Peaks at 26.1°, 29.1°, 29.9°, 46.0°, 52.1°, 55.4°, 55.9° and 62.2° correspond to the diffraction pattern of La_2O_3 (JCPDS: 71-4953). Formation of La_2MgO_x has been confirmed by the appearance of peaks at 15.6°, 27.3°, and 28.0° (JCPDS: 42-0339). Peak at 42.9° showed the presence of $La_2O_2(CO_3)$ (JCPDS: 70-5539). Peaks at 29.3°, 39.5° and 41.9° confirm the presence of K_2O (JCPDS: 77-2151; 47-1701; 77-2176). The formation of MgO (JCPDS: 75-1525) along with La_2O_3, La_2MgO_x during precipitation of La and Mg in 1: 3 wt.% (equivalent to 1: 17 atomic ratio) from their aqueous solution of corresponding nitrates has also been reported (Babu et al.,2008).

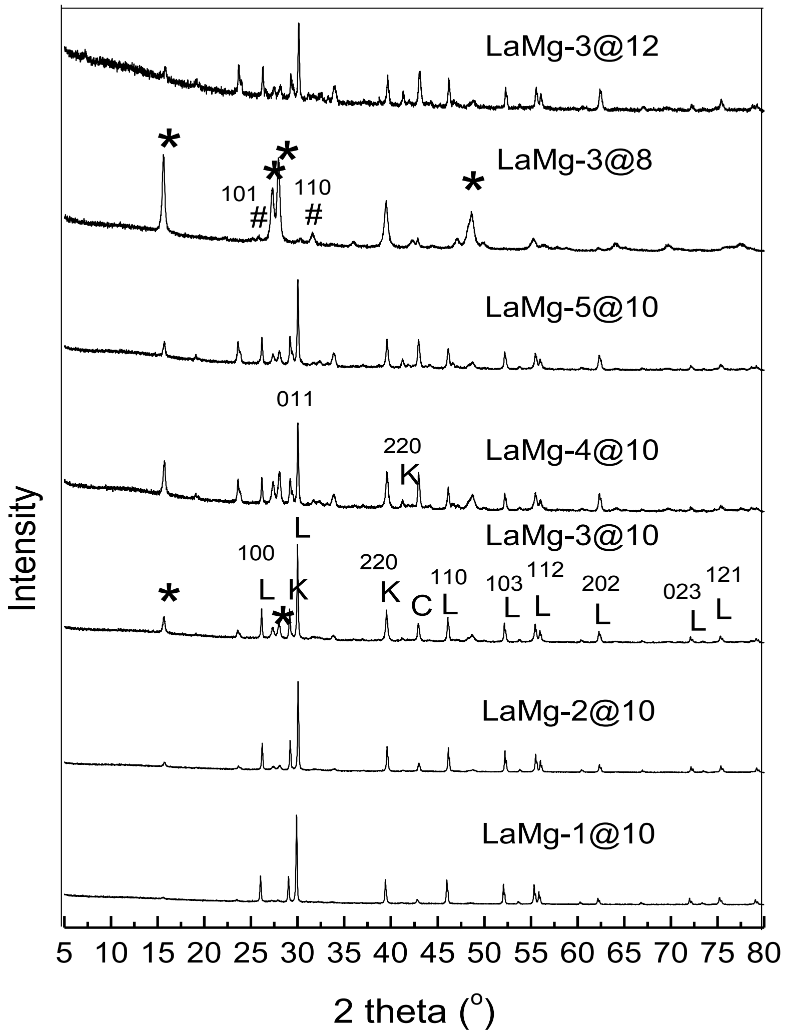

Figure 4.1. Powder XRD pattern of LaMg-X@10 (X = 1-5), LaMg-3@8 and LaMg-3@12. (L, La_2O_3; C, $La_2O_2(CO_3)$; K, K_2O; *, La_2MgO_x ; #, KO_2)

Decrease in d-spacing (Table 4.1) corresponding to all major reflections of La_2O_3 and La_2MgO_x was observed with the increase in X from 1 to 5 in LaMg-X@10 catalysts. This was found to be 0.68, 2.41 and 0.44% corresponding to peaks 26.1^o, 29.1^o and 29.9^o of La_2O_3 respectively and 0.7% corresponding to the peaks 27.3^o and 28.0^o of La_2MgO_x. This indicates reduction in impregnation of K species with the increase in Mg content.

Table 4.1
d-spacing corresponding to the major reflections of La_2O_3 and La_2MgOx phases in prepared catalysts

Catalyst	La_2O_3			La_2MgO_x	
	d-spacing corresponding to 26.1^o	d-spacing corresponding to 29.1^o	d-spacing corresponding to 29.9^o	d-spacing corresponding to 27.3^o	d-spacing corresponding to 28.0^o
LaMg-1@10	3.42359	3.07641	2.99042	3.27532	3.19696
LaMg-2@10	3.41163	3.06894	2.97427	3.25797	3.17801
LaMg-3@10	3.41035	3.06583	2.98064	3.26268	3.17619
LaMg-4@10	3.40645	3.05980	2.97745	3.26018	3.17216
LaMg-5@10	3.40009	3.00216	2.97700	3.25227	3.17234
LaMg-3@8	Absent	Absent	absent	3.36235	3.19619
LaMg-3@12	3.48984	3.05260	2.99783	3.24662	3.16965

LaMg-3@12 showed similar diffraction pattern as that of LaMg-3@10. However, diffraction peaks are much sharper in the former case indicating increased particle size. LaMg-3@8 showed diffraction pattern similar to La_2MgO_x (JCPDS: 42-0339) in addition to the peaks at 25.7^o, 31.3^o corresponding to KO_2 (JCPDS: 77-0211). As La_2O_3 was absent in LaMg-3@8, so K species probably occupy the interplanar positions in La_2MgO_x. With the increase in pH from 8 to 10 during preparation of LaMg-3@Y (Y = pH), d-spacing corresponding to peaks 27.3^o and 28.0^o of La_2MgO_x decreases to 2.96% and 0.62% respectively and peaks corresponding to the La_2O_3 evolved. With further increase in pH to 12 during their preparation, d-spacing corresponding to peaks 27.3^o and 28.0^o of La_2MgO_x again decreases to 0.49% and 0.2% respectively and those corresponding to 26.1^o and 29.9^o of La_2O_3 increases to 2.33% and 0.57% respectively suggesting that K species leave the interplanar positions of La_2MgO_x and occupy that of La_2O_3.

4.3.1.2. FEG-SEM-EDX and TEM

TEM image of LaMg-1@10 is shown in Figure 4.2a. LaMg-1@10 catalyst showed polygonal nanospheres of size between 30 to 40 nm. Histogram (Figure 4.2b) of particle size distribution for this catalyst showed the average particle size of 35 nm.

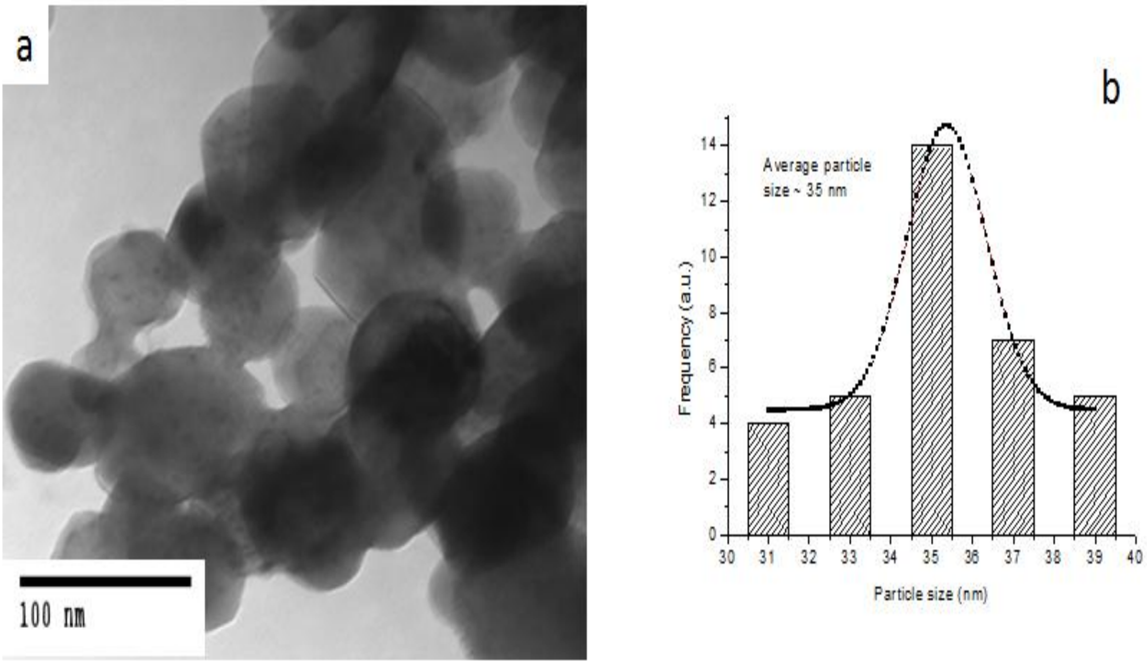

Figure 4.2: (a) TEM image; (b) histogram for particle size distribution of LaMg-1@10.

SEM and TEM images of LaMg-3@10 are shown in Figure 4.3a-b and 4.3c respectively. LaMg-3@10 catalyst showed ice-cube like structures (Figure 4.3a,; 3-D view in the marked area) with size distribution in the range of 55-60 nm. Histogram for particle size distribution of this catalyst is shown as Figure 4.3d and it showed the average particle size of 57.5 nm.

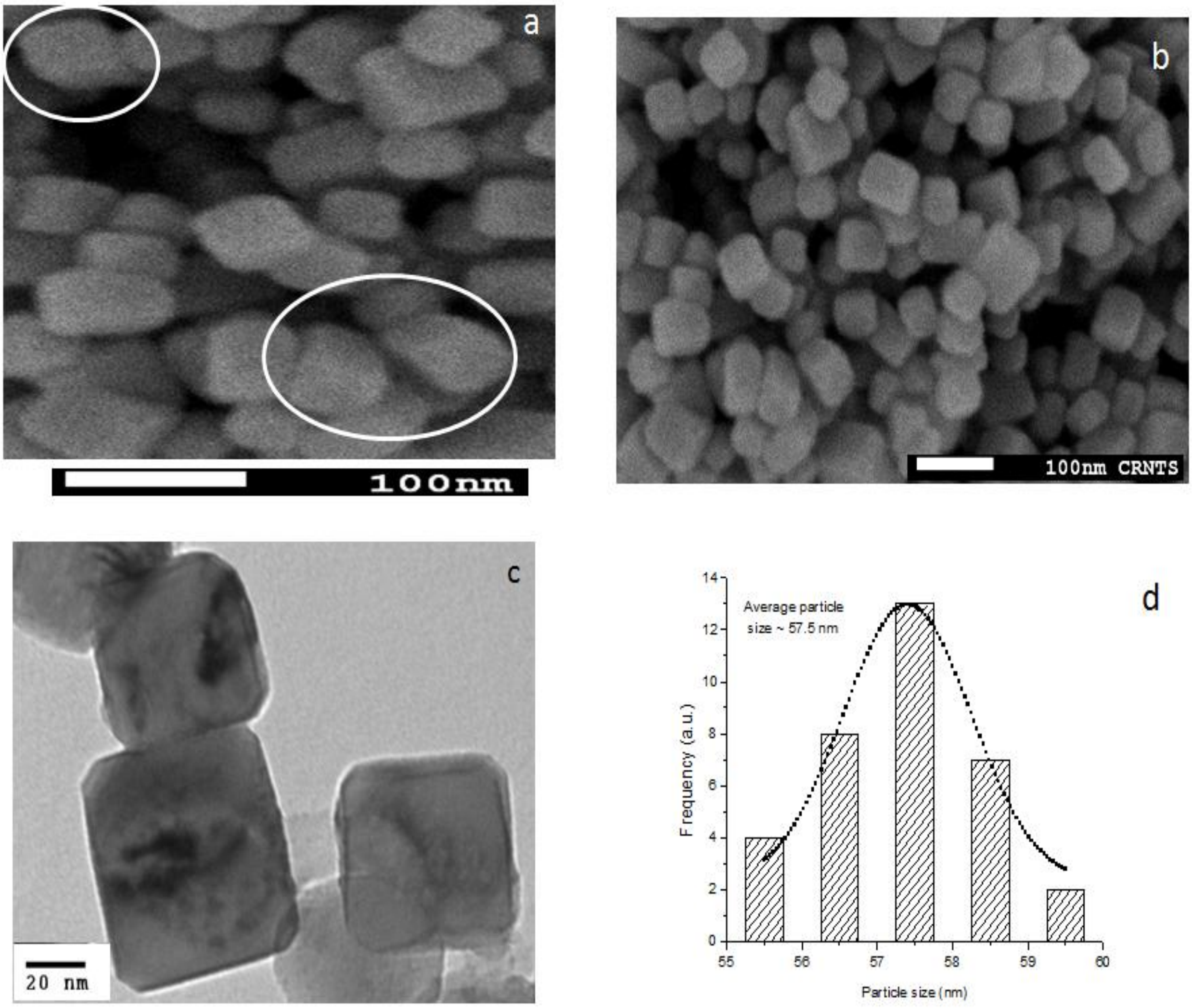

Figure 4.3: (a, b) SEM images; (c) TEM image; (d) histogram for particle size distribution of LaMg-3@10.

SEM and TEM images of LaMg-5@10 are shown in Figure 4.4a-b-c and 4.4d respectively. Histogram for particle size distribution of this catalyst is shown in Figure 4.4e. LaMg-5@10 showed hexagonal shapes with size distribution in the range 55-120 nm. Their average particle size was found to be 110 nm. Increase in the amount of Mg from X= 1 to 5 in LaMg-X@10 catalysts, resulted in the distortion of crystal lattice from polygonal spheres to hexagonal shapes and increase in average particle size from 35 nm to 110 nm

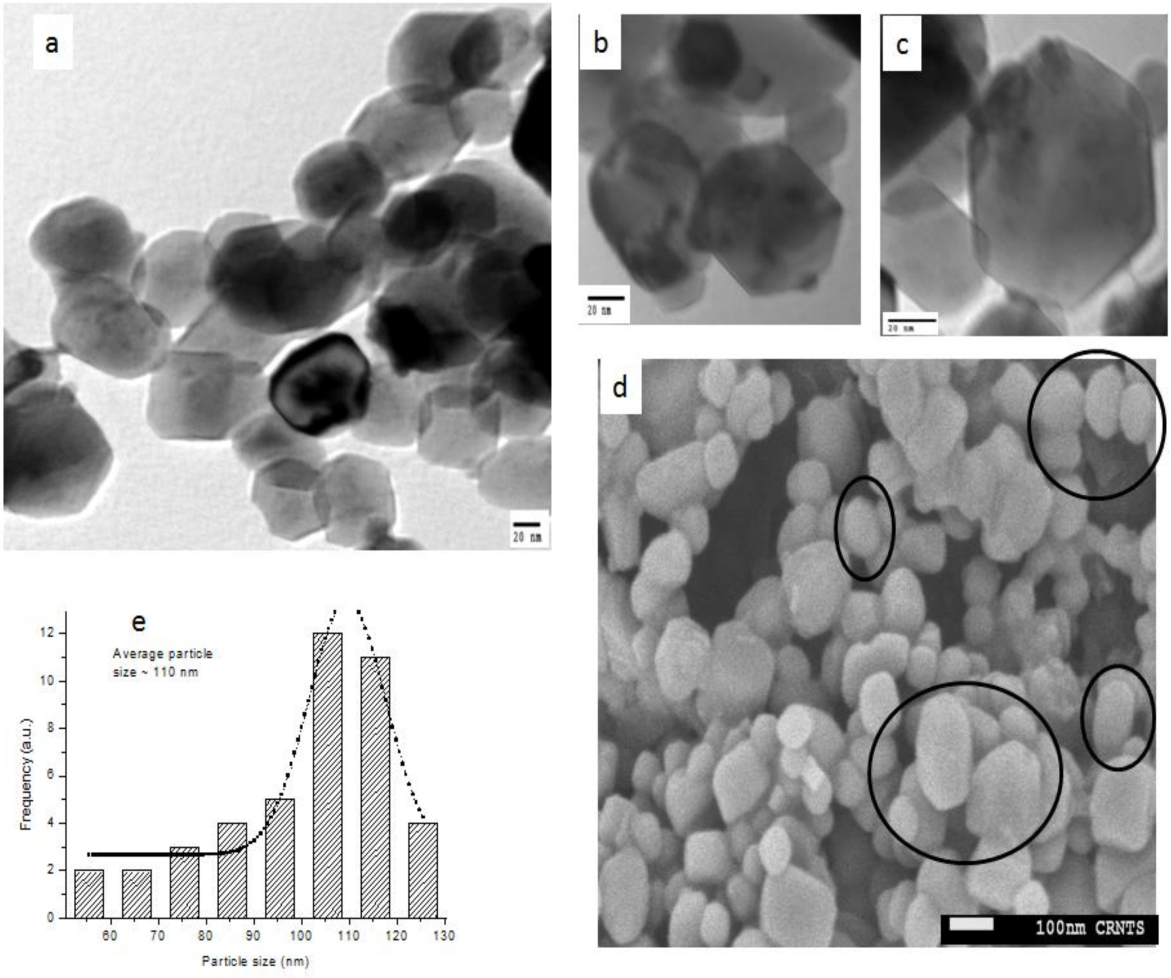

Figure 4.4: (a,b,c,) TEM images; (d) SEM image; (e) histogram for particle size distribution of LaMg-5@10.

Impregnated K species were determined from EDX (Table 4.2). These can be seen on the corners as well as on the surface of particles (Figures 4.2a, 4.3c and 4.4b-c). Their amount was found to decrease with the increase in Mg content.

Table 4.2
EDX measurement for the LaMg-X@10 (X = 3, 5) and LaMg-3@8.

Catalyst	Mg (Atomic %)	K (Atomic %)	La (Atomic %)
LaMg-3@10	49.65	34.51	15.84
LaMg-5@10	57.28	27.22	15.50
LaMg-3@8	31.84	6.09	62.07

4.3.1.3 FT-IR

FT-IR Spectra of LaMg-X@10 (X = 1-5), LaMg-3@8, LaMg-3@12 and used LaMg-3@10 catalyst (after washing and drying) were recorded to examine the characteristic vibrations of carbonate and metal oxides (Mg-O/La-O) and are shown in Figure 4.5. In all the spectra, sharp peak at 3610 cm^{-1} correspond to the stretching vibration of free OH group. Broad band at 3400-3435 cm^{-1} correspond to the bound OH group. The ν2 and ν3 peaks of carbonate appear at 1384 cm^{-1} and 826-828 cm^{-1}. Similar findings are reported elsewhere (Zeng et al., 2008). In the low energy range of spectra, peaks at 643 and 510 cm^{-1} correspond to characteristic vibration of metal oxides (Mg-O/La-O). In addition to all these absorptions, used LaMg-3@10 catalyst also showed band at 1445 cm^{-1} due to surface carbonates probably due to the absorption of CO_2 during usage/storage.

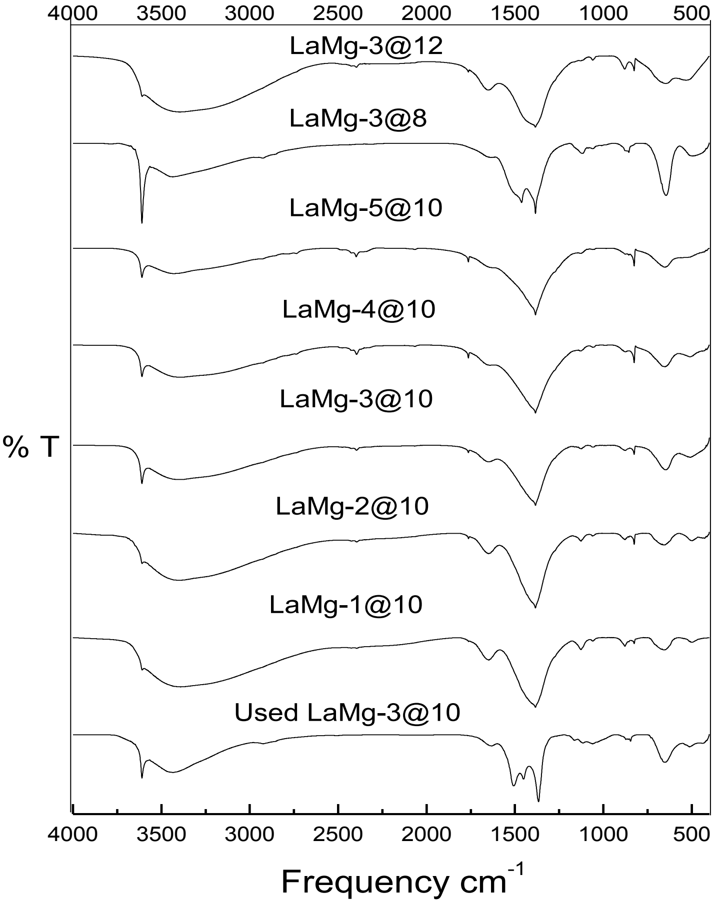

Figure 4.5. FT-IR spectra of LaMg-X@10 (X = 1-5), LaMg-3@8 and LaMg-3@12.

4.3.1.4. TGA

TGA of freshly prepared and used LaMg-3@10 catalyst (after washing and drying) is shown in Figure 4.6. There is a gradual weight loss between 600-780^{o}C that can be due to decomposition of carbonate salts. Additionally, used catalyst showed weight loss between 300-400^{o}C probably due to loss of physically adsorbed CO_2 and decomposition of hydroxyl groups $La(OH)_3$ and $Mg(OH)_2$.

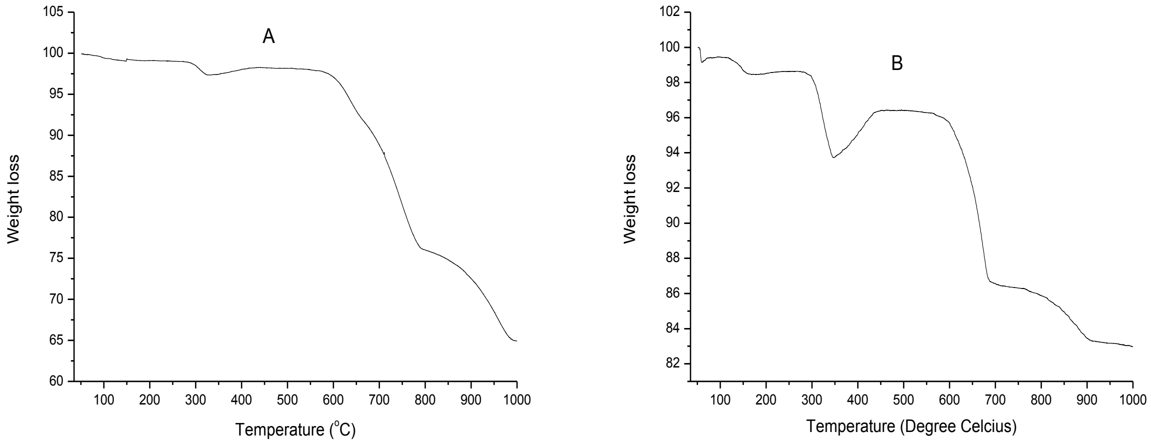

Figure 4.6. TGA of (A) LaMg-3@10 and (B) used LaMg-3@10.

4.3.1.5. Basic site strength and soluble basicity

Basic site strength and soluble basicity of LaMg-X@10 (X=1-5), LaMg-3@8 and LaMg-3@12 are shown in Table 4.3. LaMg-X@10 (X = 1-3) and LaMg-3@12 showed change in colour of 2,4-dinitroaniline solution confirming the presence of basic sites of strength (H_) >15. LaMg-3@8, LaMg-4@10 and LaMg-5@10 showed change in colour with alizarin instead of 2,4-dinitroaniline, showing reduced basic site strength (11< H_ < 15).

Soluble basicity of LaMg-X@10 (X = 1-3) and LaMg-3@12 was also found to be comparatively higher (15.5±1 mmol of HCl/g). Other catalysts showed reduced basicity in the range of 6.5 to 13.8 mmol of HCl/g.

Table 4.3
Basic site strength and soluble basicity of the catalysts.

Catalyst	Hammett indicator with higher basic strength showing colour change	Site strength (H_)	Soluble basicity (mmol of HCl /g of catalyst)
LaMg-1@10	2,4-Dinitroaniline	15 < H_ < 18	15.2
LaMg-2@10	2,4-Dinitroaniline	15 < H_ < 18	16.2
LaMg-3@10	2,4-Dinitroaniline	15 < H_ < 18	15.7
LaMg-4@10	Alizarin	11 < H_ < 15	13.8
LaMg-5@10	Alizarin	11 < H_ < 15	11.7
LaMg-3@8	Alizarin	11 < H_ < 15	6.5
LaMg-3@12	2,4-Dinitroaniline	15 < H_ < 18	16.4

4.3.2. Catalytic activity

Transesterification reactions of used cotton seed oil with methanol (1: 54 molar ratio of oil to methanol) were performed with 3 wt.% of LaMg-X@10 (X=1-5), LaMg-3@8 and LaMg-3@12. LaMg-X@10 (X = 1-3) showed completion of the reaction in 40 min where as time period for completion of reaction with LaMg-4@10 and LaMg-5@10 was 1 h and 3 h 30 min respectively. The decline in the catalytic activity from LaMg-3@10 to LaMg-5@10 may be due to the distortion of crystal lattice and increase in particle size resulting in the reduction of percentage of surface active atoms. Powder XRD studies also showed comparatively reduced impregnation of K species in LaMg-4@10 and LaMg-5@10 catalysts resulting in reduced basic site strength and decline in catalytic activity. LaMg-3@12 and LaMg-3@8 catalysts showed the completion of reactions in 40 min and in 2h 45min respectively. The reduction in catalytic activity of LaMg-3@8 can be ascribed due to the absence of K_2O and La_2O_3 resulting in less impregnation, reduced site strength and basicity. The activity of the catalysts was independent the concentration of precipitating agents and the use of nitrogen/ air during calcination.

However, LaMg-3@10 was selected from LaMg-X@Y catalysts (X = 1-5; Y = 8, 10 or 12) for optimizing other reaction parameters as it showed better catalytic activity, contained less expensive Mg in the bulk and lesser K species, and hence reduced probability for its leaching.

4.3.2.1. Effect of catalyst amount

Transesterification reactions were carried out using different amount of the catalyst (LaMg-3@10) with 1: 54 molar ratio of oil to methanol at 65^{o}C. Conversion (%) with 3-6 wt.% of the catalyst in a stipulated time period of 20 min is shown in Figure 4.7. With the increase in amount of the catalyst from 3 to 5 wt.% there was an increase in conversion from 54.6 to 96%. Lower amount of catalyst gives low conversion that may be due to the lesser number of catalytic sites available for the reactants. With further increase in amount of the catalyst from 5 to 6 wt.%, only marginal increase in conversion from 96 to 96.7% was observed, hence 5 wt.% of the catalyst amount was selected for optimizing other reaction parameters. These results are better than those reported for transesterification of palm oil using 8 wt.% of similar type of the catalyst (1.5% K over Mg–Al oxides) and 1: 45 molar ratio of oil to methanol at 100^{o}C for 9 h resulting in 96% conversion (Tittabut et al., 2008).

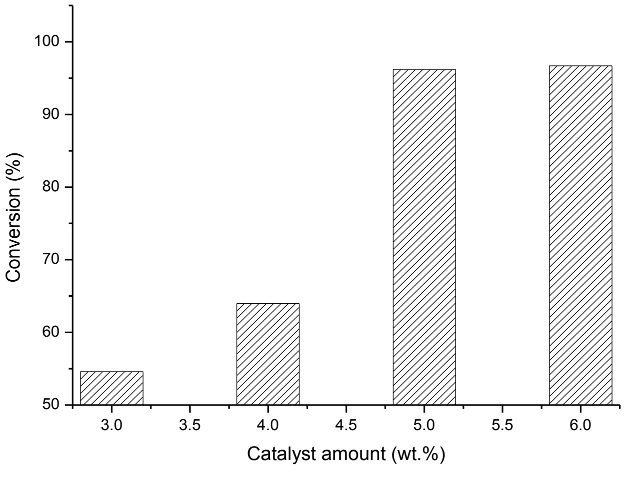

Figure 4.7. Effect of catalyst amount (*reaction conditions: oil/methanol molar ratio, 1:54; and temperature, 65 °C).*

4.3.2.2. Effect of oil to methanol molar ratio

Transesterification reactions were performed by varying the oil to methanol molar ratio from 1: 10 to 1: 54 with 5 wt.% of catalyst (LaMg-3@10) at 65°C for a stipulated time period of 20 min and results are as shown in Figure 4.8. Oil and methanol in 1: 54 molar ratio resulted in the highest conversion of 96% and was used for optimizing other parameters.

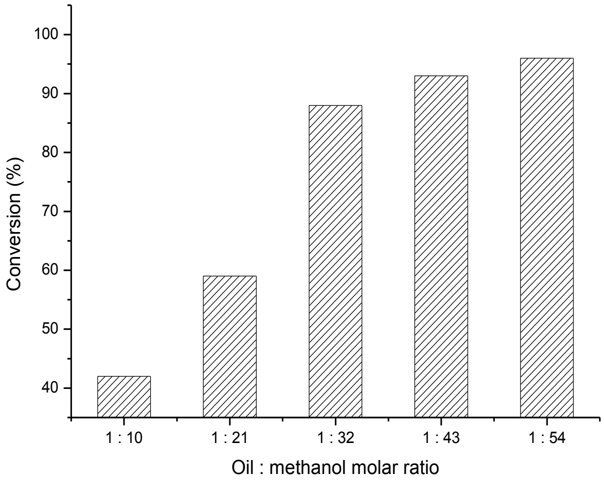

Figure 4.8. Effect of oil to methanol molar ratio (*reaction conditions: catalyst amount, 5 wt. % of oil; and temperature, 65 °C).*

4.3.2.3. Effect of Temperature

A series of transesterification reactions were carried out at 35-65°C for a fixed time period of 20 min using 5 wt.% of LaMg-3@10 with 1: 54 molar ratio of oil to methanol and the results are shown in Figure 4.9. Highest conversion of 96% was obtained at 65°C. Higher reaction temperature, in this case, not only speeds up the rate of the reaction, but also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in faster reactions and higher conversion. Brito et al. (2009) reported reaction temperature of 140°C and time period of 6 h for the transesterification of sunflower oil using 6 wt.% of Mg–Al hydrotalcite catalyst.

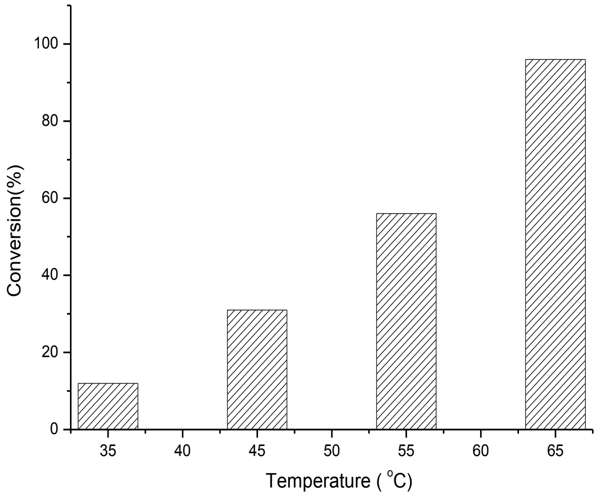

Figure 4.9. Effect of reaction temperature (*reaction conditions: oil/methanol molar ratio, 1: 54; and catalyst amount, 5 wt. % of oil).*

4.3.2.4. Effect of additional moisture and FFA content

Transesterification of virgin cotton seed oil (FFA: 0.2 % and moisture content: 0.12 wt.%) with methanol using optimized reaction conditions resulted into 97.6% methyl esters in reaction time of 15 min. Under similar conditions, the used cotton seed oil (FFA; 0.8 % and moisture content; 0.19 wt.%) showed 96 % conversion to methyl esters in 20 min. With the addition of FFA content of 0.5 wt.% of palmitic acid/oleic acid in used cotton seed oil, reduction in conversion from 96% to 55 and 60% respectively was observed. However, 95% methyl esters were formed in 30 min with the use of additional 1 wt.% of moisture in used oil. With further increase in the moisture content to 2 wt.%, conversion was reduced to 90%. These findings are far better than those reported with homogeneous KOH/NaOH catalysts showing tolerance of < 0.06 wt.% of moisture in feedstock for biodiesel preparation (Ma et al., 1998).

4.3.3. Potassium ions analysis in biodiesel

Leaching of K^+ in the sample of biodiesel prepared by using optimized conditions viz., 5 wt.% of LaMg-3@10 catalyst in 1: 54 molar ratio of oil to methanol at 65°C was determined by ash method. This was found to be 4.5 ± 0.2 ppm which is lesser than 5 ppm, the permissible limit of ASTM (Monteiro et al., 2008) .

4.3.4. Reusability

The LaMg-3@10 catalyst was checked for reusability and it showed conversion of 94, 90 and 87% during first three recycles respectively. The decline in catalytic activity may be due to poisoning of catalytic sites by CO_2 and the leaching of active K species. Adsorption of CO_2 during usage/drying/ storage has been supported by the TGA of the used catalyst. Therefore, used catalyst was calcined at 550°C before its use for the next run to remove adsorbed CO_2 and to regenerate the catalytic sites.

4.4. Conclusion

In concluding remarks, LaMg-X@Y (X =1-5; Y = 8, 10 or 12) act as both catalysts and catalyst supports, and impregnated K as co-catalyst. For atomic ratios X = 1-3, comparatively more impregnation of K species was observed, resulting in the generation of more catalytic sites with strong basic strength. Further enrichment of Mg in the catalysts (X = 4, 5) resulted in the distortion of crystal lattice and increase in the average particle size. Generally, with the increase in the particle size, there is a decrease in the percentage of surface active atoms. Hence, there was reduction in catalytic activity due to reduction in percentage of surface active atoms and less impregnation / lesser basic site strength. LaMg-3@10 from all the prepared LaMg-X@Y (X =1-5; Y = 8, 10 or 12) catalysts was found to be most suitable as it involves less expensive Mg in the bulk, lesser K species and efficient catalytic activity.

Transesterification of used cotton seed oil with methanol at 65^{o}C resulted in 96% conversion in 20 min with 5 wt.% of LaMg-3@10. The catalyst was effective even in the presence of additional 1 wt% of water and showed its effectiveness during its reuse.

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Chapter 5: Transesterification of used cotton seed oil using superbasic mesoporous SBA-15

Contents Page

ABSTRACT

Mesoporous SBA-15 wrapped with MgO was prepared by one pot synthesis and was mixed with 5-30 wt.% of KNO3 in the presence of water, grinded and calcined at 600oC under atmosphere of nitrogen for 4 h. These materials were characterized by powder XRD, TEM, Hammett indicators and BET surface area analysis. During preparation, MgO coating over SBA-15, has prevented the direct interaction between potassium and SBA-15. Due to this the structure of SBA-15 has not been destructed. BET surface area studies of SBA-15 wrapped with MgO and 25 wt.% of KNO3 indicated surface area and pore volume to be 183 m2/g and 0.39 cm3/g respectively. These values are less than that observed for SBA-15 wrapped with MgO. The material showed super basic nature and was used as a catalyst for the transesterification of used cotton seed oil with methanol to biodiesel with >98% conversion.

5.1. Introduction

The use of basic zeolites and related crystalline molecular sieves as catalysts has limited activity for transesterification of triglycerides because of small pore openings which restrict the bulky molecules and prevent them to reach at catalytic sites (Hattori et al., 1995). On the other way, use of mesoporous materials instead of zeolite as catalytic support may be advantageous due to long range ordered structure, comparatively higher surface area, pore diameter and pore volume (Soler-Illia et al., 2002). Among the mesostructure materials, mesoporous silica's (MCM-41, MCM-48 and SBA-15) seem to be the cheapest catalytic support, and introducing basic guests or their precursors inside these sieves may be useful strategy for the preparation of strong solid basic catalyst for the transesterification. There are some reports regarding the preparation of organic bases grafted mesoporous materials such as aminopropyl-modified HMS (Macquarrie et al. 2001) and aminopropyl-functionalized SBA-15 (Wang et al., 2004; Wang et al., 2005) using silanizing agents. However, these organic-inorganic composites need to be used in mild conditions viz., low temperature and pressure etc.

There are also some reports regarding the incorporation of inorganic salts/oxides over mesoprous materials. Zhu et al., (1999) prepared a superbasic material by incorporating cesium acetate over mesoporous MCM-41. However, this material did not show good thermal and chemical stability because the cesium oxides could corrode and damage the host siliceous framework at high temperature. There are also few reports regarding alkaline earth metal oxides CaO, and MgO supported over mesoporous materials. Albuquerque et al. (2008) investigated CaO supported over SBA-15 and MCM-41 and reported the superior thermal stability and catalytic activity of SBA- 15, as compared to MCM-41. The strong interaction between CaO and SBA-15 effectively prevented the leaching of active calcium species. This catalyst (14 wt% CaO/SBA-15) resulted 95% conversion after 5 h of reaction period at 60^oC

using oil to methanol (sunflower) molar ratio of 1 to 12. In spite of amazing features of catalytic supports in mesoporous materials, these do not work for transesterification under ambient conditions. This is because of lack of superbasic sites under normal conditions over these materials. Current status in the study of basic materials is findings new ways to prepare solid mesoporous superbase becomes a challenge. This is because synthesis of mesoporous SBA-15 required acid condition and incorporation of basic species during in-situ condition results the failure of structure formation.

Present work demonstrates the preparation of super basic meosoporous SBA-15 materials by slight modification in method reported by Wu et al., (2006) and their use as heterogeneous catalysts for the transesterification of used cotton seed oil.

5.2. Experimental Section

5.2.1. Catalyst preparation

SBA-15 coated with 20 wt.% of MgO and different amounts of potassium nitrate were prepared. First, MgO coated SBA-15 was prepared in situ condition by dissolving 2 g of triblock copolymer P123 and 1.862 g of magnesium acetate in 75 g of 1.6 M HCl followed by addition of 4.25 g of tetraethyl orthosilicate under stirring at 40^{o}C. The mixture was stirred for 24 h at 40^{o}C and heated at 100^{o}C for another 24 h under static conditions and finally liquid was evaporated by stirring at 80^{o}C. The solid obtained was dried at 80^{o}C and calcined at 550^{o}C for 6 h to remove the surfactant. Potassium salt coating was carried out by grinding different amount (5-30 wt.%) of KNO_3 with the prepared material (2 g) in the presence of small amount of water (1 ml) followed by drying at 100^{o}C and calcinations under an atmosphere of nitrogen at 600^{o}C. Prepared catalysts were designated as SBA-15/MgO/X (Where X being the wt.% of KNO_3)

5.2.2. Transesterification of used cotton seed oil

All the prepared materials were tested for transesterification of used cotton seed oil with methanol for optimizing the amount of potassium coating for the efficient catalytic activity. In a typical procedure, oil and methanol in 1: 54 molar ratio were stirred (1500 rpm) in a two neck round bottom flask with 5 wt.% of SBA-15/MgO/X (X = 5-30) catalyst under reflux conditions (65°C) using double walled glass condenser. Progress of reaction was monitored by TLC and ^{I}H NMR as described in chapter 2.

Various reaction parameters viz., catalyst amount, oil to methanol molar ratio and reaction temperature were also optimized.

5.3. Results and Discussion

5.3.1. Catalyst characterization

5.3.1.1. Powder XRD

Powder XRD pattern of SBA-15/MgO and SBA-15/MgO/25 are shown in Figure 5.1. A prominent peak at 0.9° and two weak peaks at 1.6° and 1.9° corresponding to (100), (110) and (200) planes matches with standard powder XRD pattern of SBA-15. It has been observed that mesoporous structure is retained and it does not undergo destruction due to MgO coating followed by KNO_3 coating. However, direct coating of KNO_3 over SBA-15 causes destruction of its structure. It seems that the formation of MgO layer on the surface of SBA-15 obstructed the contact and interaction of potassium species with the silica framework.

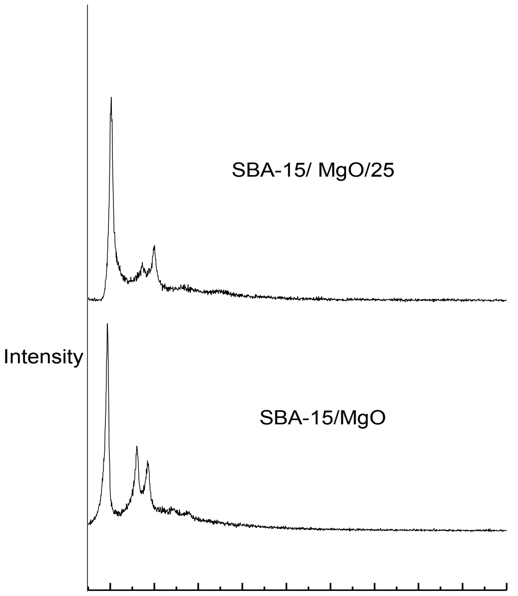

Figure 5.1. Powder XRD pattern of SBA-15/ MgO and SBA-15/MgO/25.

Structural parameters viz., *d*-spacing, unit cell parameter and wall thickness corresponding to plane (100) of SBA-15, SBA-15/MgO and SBA-15/MgO/25 are shown in Table 5.1. These parameters were found to be higher for the SBA-15/MgO in comparison to SBA-15 due to the strain developed upon MgO incorporation inside the mesoporous sieves.

Table 5.1. Structural parameters of SBA-15, SBA-15/MgO and SBA-15/MgO/25

Sample	d-spacing, d_{100} (nm)	Unit cell parameter, a_o (nm)[a]	Wall thickness, d_w (nm)[b]
SBA-15	8.99	**10.39**	**1.4**
SBA-15/ MgO	9.42	**10.89**	**1.47**
SBA-15/MgO/25	9.11	**10.53**	**1.42**

[a] $a_o = 2/3^{1/2}\, d_{100}$; [b] $d_w = a_o - d_{100}$

5.3.1.2. BET surface area, pore volume, basic site strength and soluble basicity

BET surface areas and pore volumes of the prepared catalysts are shown in Table 5.2. SBA-15 showed highest surface area. The decrease in surface area upon coating with MgO and further with potassium species clearly indicated that interior pores were decorated with MgO and then with potassium species. Pore volumes showed the same trend upon coating with MgO and then with potassium species.

Basic site strength of all the prepared materials is shown in Table 5.2. SBA-15 showed the change in colure of bromothymol blue ($H\_ = 7.2$) solution and do not showed the change in colure of next Hammett indicator with higher basic site strength that is phenolphthalein ($H\_ = 9.3$), therefore having basic site strength $7.2 < H\_ < 9.3$. SBA-15/MgO indicated the colure change with alizarin ($H\_ = 11$) which showed the increase in site strength ($11 < H\_ < 15$) upon coating with MgO. All other materials showed colure change with 4-nitroaniline ($H\_ = 18.4$) indicating increased basic strength ($H\_$) > 18.4. The increase in basic site strength may be due to the potassium coating, Therefore these materials were expecting to show catalytic activity for transesterification.

Soluble basicity of the prepared materials is compared in Table 5.2. Bare SBA-15 did not show any soluble basicity, while for SBA-15/MgO the soluble basicity was observed as 5.4 mmol HCl/g of material. A regular increase in soluble basicity was obtained on increasing the potassium concentration in SBA-15/MgO and a maximum value (8.2 mmol HCl/g of catalyst) was observed with 30 wt.% KNO_3 coating.

Table 5.2. Surface area, pore volume, basic site strength and soluble basicity of the prepared materials.

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Basic site strength	Soluble bascity mmol of HCl/g
SBA-15	613	1.1	$7.2 < H\_ <9.3$	NF
SBA-15/ MgO	367	0.83	$11 < H\_ < 15$	5.4
SBA-15/MgO/5	ND	0.86	$18.4 < H\_$	5.9
SBA-15/MgO/10	304	0.6	$18.4 < H\_$	6.1
SBA-15/MgO/15	272	0.58	$18.4 < H\_$	6.2
SBA-15/MgO/20	221	0.42	$18.4 < H\_$	6.9
SBA-15/MgO/25	183	0.39	$18.4 < H\_$	7.4
SBA-15/MgO/30	175	0.28	$18.4 < H\_$	8.2

Not found (NF); ND (Not determined)

5.3.1.3. TEM

TEM images of SBA-15, SBA-15/MgO and SBA-15/ MgO/ 25 are shown as 5.2a, 5.2b, and 5.2c respectively. Hexagonal mesostructures can be seen in all the images. SBA-15/ MgO/ 25 showed unharmed mesostructures which indicate due to MgO coating, SBA-15 structure remains intact even after potassium incorporation. Presence of comparatively denser and narrow channels in this material indicates that interior pores and channels has been impregnated with MgO and potassium species.

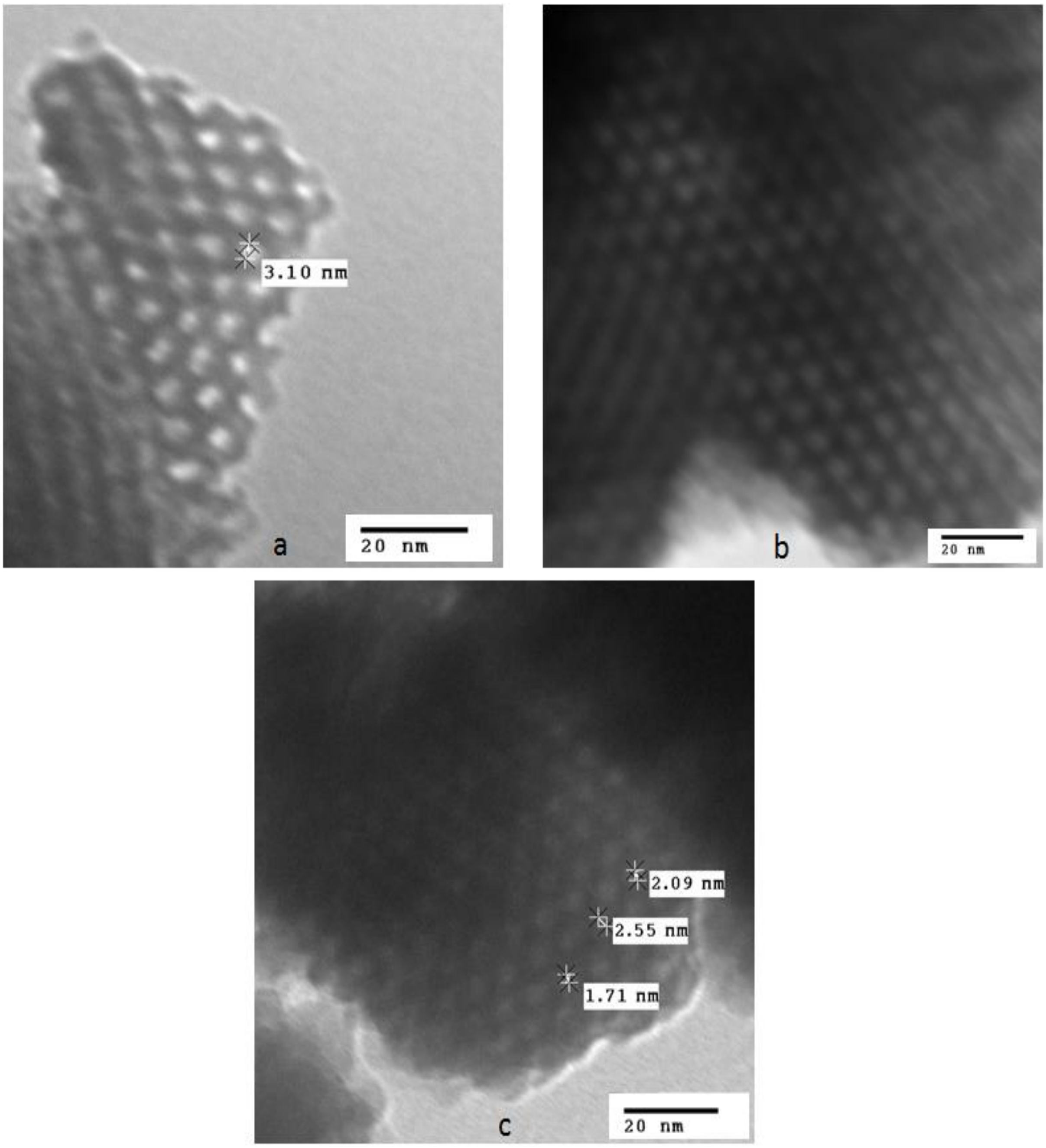

Figure 5.2. TEM image of (a) SBA-15, (b) SBA-15/MgO and (c) SBA-15/MgO/ 25.

5.3.2. Catalytic activity

In order to evaluate the catalytic activity of prepared materials for transesterification of used cotton seed oil, a series of reactions were performed by using 1: 54 molar ratio of oil to methanol with 5 wt.% of SBA-15/MgO/X (X = 5-30 wt.% of potassium) catalyst under reflux conditions (65°C).

The increase in d-spacing (***d*$_{100}$**) in SBA-15/MgO, support the incorporation of MgO inside the mesoporous sieves of SBA-15 during in-situ conditions. Further, lower surface area of SBA-15/MgO in comparison to the SBA-15 also support the incorporation of MgO with SBA-15. However, only MgO coated SBA-15 was not found to show the significant catalytic activity towards the transesterification of used oil. In order to enhance the catalytic activity, it was further coated with varying amount of potassium (5-30 wt.%). An increase in basic strength was observed with the increase in potassium concentration in SBA-15/MgO. Even after 12 h of reaction time, presence of up to 15 wt.% of potassium coating over SBA-15/MgO resulted in incomplete conversion (conversion < 97.5%). A further increase in potassium concentration (20 and 25 wt.%) resulted the complete transesterification of oil in 4 h and 2.5 h, respectively. Further, increase in potassium concentration (30 wt.%) was not found to reduce the reaction time significantly. Therefore, SBA-15/MgO/25 catalyst was used for the optimization of other reaction parameters and reusability experiments.

Quantification of biodiesel samples obtained with SBA-15/MgO/X (X = 20-25) catalysts was carried out as per reported method as described in chapter 2 and chapter 3 and was found to be more that 98 %.

5.3.2.1. Effect of catalyst amount

Transesterification reactions of oil with methanol (1:54 molar ratio) were carried out at 65°C with varying amount of SBA-15/MgO/25 catalyst and results are shown in Figure 5.3. The increase in amount of the catalyst from 1 to 5 wt.%, was found to decrease the time required for the completion of reaction (4.5 to 2.5 h). A further increase in catalyst concentration was not found to reduce the reaction time significantly. This could be due to fact that at a higher catalyst loading, reaction mixture becomes more viscous which could resist the mass transfer in the liquid-liquid-solid system. Hence, other parameters were studied by using 5 wt.% of catalyst as this catalyst amount showed nominal reaction time.

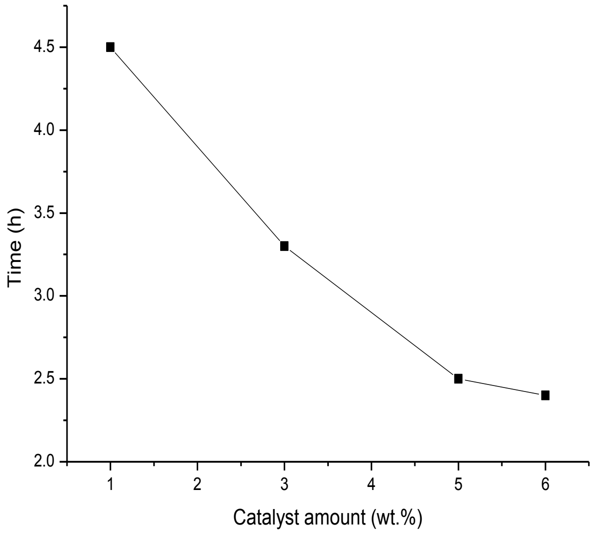

Figure 5.3. Effect of amount of catalyst (*reaction conditions: oil/methanol molar ratio, 1: 54; and temperature, 65 °C.)*

5.3.2.2. Effect of methanol/oil molar ratio

The effect of the methanol/oil molar ratio on the transesterification reaction is one of the important parameters that affect the methyl ester yield as well as the cost of biodiesel production. The use of higher molar ratios of methanol/oil in the case of heterogeneous catalysts was found to improve the methyl esters yield because excess alcohol not only promotes the transesterification rate but also removes product molecules from the catalyst surface and thus regenerates the catalytic sites. To determine the optimum molar ratio of methanol and oil, a series of transesterification reactions were performed by varying the methanol to oil molar ratio from 46:1 to 58:1 with 5 wt.% of SBA-15/MgO/25 at 65°C (Figure 5.4). The reaction was found to complete in 2.5 h with 54:1 molar ratio of methanol to oil and any further increase in methanol amount showed marginal decrease in completion time. Hence, other reaction parameter has been optimized at 54:1 molar ratio of methanol to oil.

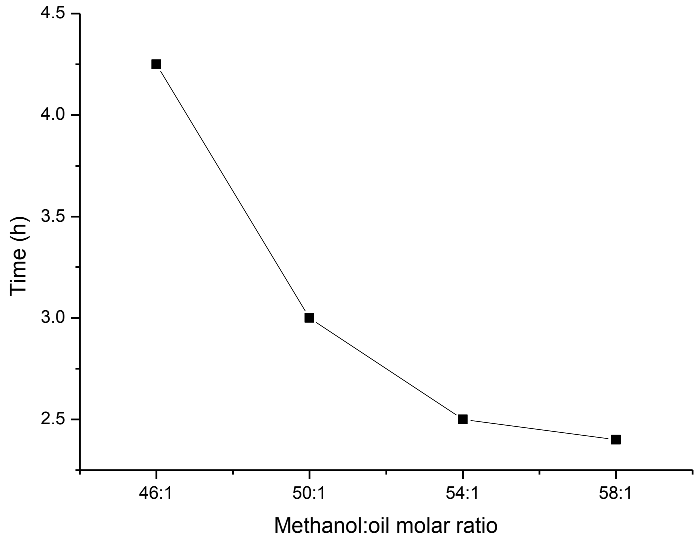

Figure 5.4. Effect of methanol to oil molar ratio (*reaction conditions: catalyst amount, 5 wt. % of oil; and temperature, 65 °C).*

5.3.2.3. Effect of temperature

Heterogeneous catalysts, because of the phase difference from reagents, usually required a high temperature and pressure and longer reaction period to yield the significant conversion. The same reaction conditions demand costlier and complicated reactor design, which lead to an increase in the biodiesel production cost (Huber et al., 2006). To study the effect of temperature, transesterification reactions of used oil with methanol (1:54 molar ratio) were carried out in the presence of 5 wt.% SBA-15/MgO/25 at different temperatures from 45-65°C. The time period for completion of the reaction decreases with the increase in temperature (Figure 5.5) and at 65°C, minimum time (2.5 h) was required for the completion of reaction.

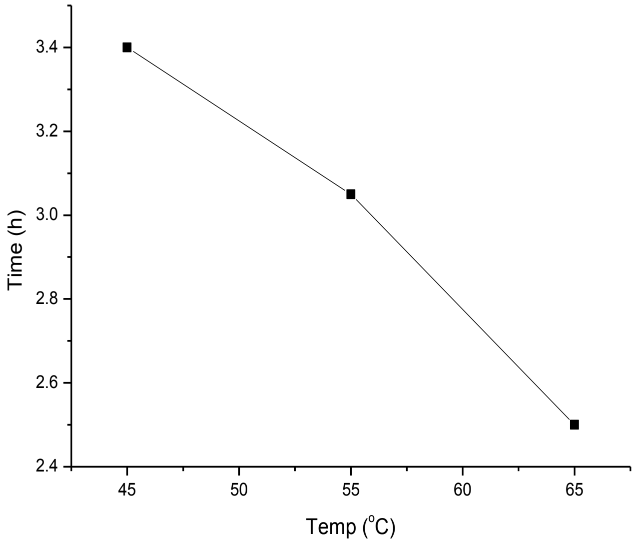

Figure 5.5. Effect of temperature (*reaction conditions: oil/methanol molar ratio, 1: 54; and catalyst amount, 5 wt. % of oil).*

On the basis of the above-mentioned experiments, a 1:54 molar ratio of oil to methanol, 5 wt.% of catalyst amount, 65°C reaction temperature and 2.5 h of reaction duration has been established as optimum reaction conditions for used cotton seed oil.

5.3.3. Reusability

Reusability experiments were performed using SBA-15/MgO/25 catalyst under optimized reaction conditions. After the completion of reaction, catalyst was filtered, washed with methanol and calcined at 550^{o}C before successive reuse. The reused catalyst showed 65%, 52% and 35% conversion during first three cycles respectively. Decline in the catalytic activity may be due to modifications in surface and blocking of pores of catalyst due to successive reuse and recalcination. BET surface area of used SBA-15/MgO/25 catalyst (after 3rd catalytic run) was found to decrease from 183 to 169 m^2/g suggesting lesser number of surface active sites available for catalyzing the reaction. Similarly, basic strength of the reused catalysts was also decrease to $15 < H\_ < 18.4$ from $18.4 < H\_$ showing reduced activity.

5.4. Conclusion

Mesostructure having basic nature was prepared by the incorporation of MgO inside the SBA-15. In order to further increase the basic strength, SBA-15/MgO was coated with potassium and basic strength of the resulted material was found to be a function of potassium concentration. Even upon potassium coating, mesostructure silica of SBA-15/MgO retained as such due to prevention of destruction and corrosion of framework by the presence of MgO protective layer. The catalyst with 25 wt.% of potassium loading (SBA-15/MgO/25) was employed for the transesterification of used cotton seed oil. The BET surface area and pore volume was found to decrease upon MgO and KNO_3 coating. However, due to the formation of strong basic sites, at the same time, it catalyzes the transesterification of used cotton seed oil with methanol at 65°C with more than 98 % FAMEs yield.

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Chapter 6: Transesterification of mutton fat using KOH impregnated MgO as heterogeneous catalysts

ABSTRACT

The use of MgO impregnated with KOH as heterogeneous catalysts for the transesterification of mutton fat with methanol has been evaluated. The mutton fat (fat) with methanol (1:22 molar ratio) at 65°C showed > 98 % conversion to biodiesel with 4 wt% of MgO-KOH-20 (MgO impregnated with 20 wt% of KOH) in 20 min. The reaction conditions optimized were; the amount of KOH impregnation (5-20 wt%), the amount of catalyst (1.5 – 4 wt%, catalyst/fat), the reaction temperature (45 – 65°C), fat to methanol molar ratio (1:11 – 1:22) and the effect of addition of water/ oleic acid/ palmitic acid (upto 1 wt%). Although, transesterification of fresh fat (moisture content 0.02 wt% and free fatty acids 0.002 wt%) with methanol in the presence of KOH (homogenous catalyst) resulted in the complete conversion to biodiesel, but in the presence of additional 1 wt% of either free fatty acid or moisture content, formation of soap was observed. The MgO-KOH-20 catalyst was found to tolerate additional 1 wt% of either the moisture or FFAs in the fat.

6.1. Introduction

In literature significant reports are available which deals with conversion of fat into biodiesel using homogeneous or heterogeneous catalysts. Ma et al. (1998) used 0.3 and 0.5 wt.% of NaOH and $NaOCH_3$ respectively for the transesterification of beef tallow and maximum conversion was obtained within 15 min of reaction time. Potassium hydroxide as catalyst has been reported for biodiesel production (Moraes et al., 2008) from bovine and beef fat (Bhatti et al., 2008) as feedstock. Mixtures of vegetable oils (virgin and waste) and lard in different compositions have also been reported for the biodiesel production using NaOH as catalyst (Dias et al., 2008). A report by Ngo et al. (2008) have shown the preparation of biodiesel from greases in two steps by using a series of diarylammonium catalysts as homogeneous catalyst as well as heterogeneous (immobilized on polymer support) catalyst, for the esterification of the FFA (12–40 wt.%) present in greases. Resulting ester-glyceride mixtures were completely converted to esters by base-catalyzed transesterification. Canoira et al. (2008) investigated the production of biodiesel from the different mixtures of animal fat and soybean oil in two steps. In first step, esterification was carried out with p-toluenesulfonic acid and then transesterification of the same was performed with methanol using sodium methoxide as catalyst. Nanocrystalline CaO were reported by Reddy et al. (2006) as heterogeneous catalysts for the transesterification of poultry fat at room temperature with fat to methanol ratio 3:10 (v/v) and requires 6 h for the maximum conversion of fat. Liu. et al. (2007) used the heterogeneous base catalysts derived from Mg–Al hydrotalcite for the transesterification of poultry lipids into biodiesel in the temperature range of 60–120 °C and varying methanol to lipid molar ratios from 6:1 to 60:1. High temperature (120°C), high methanol to fat ratio (60:1) and use of co- solvent (hexane, toluene, THF) were found to show the positive effect for the same reaction.

It is manifested from the literature review, that most of the heterogeneous catalysts require high fat to methanol ratio, high reaction temperature, higher pressure and in most cases, their use requires longer time and addition of co-solvents during reaction for the maximum conversion of fat to biodiesel. All these factors directly or indirectly are expected to increase the production cost of biodiesel, which is a major hurdle for the commercialization of the biodiesel. In order to develop a heterogeneous catalyst that could catalyze the transesterification of fat under ambient conditions, here we report the preparation, characterization and use of KOH impregnated MgO catalysts for the transesterification of mutton fat.

6.2. Experimental Section

6.2.1. Catalyst preparation

KOH impregnated MgO catalysts were prepared by wet impregnation method (Ilgen et al., 2009). In a typical preparation, MgO (10g) was suspended in 100 ml of deionized water followed by addition of 10 ml aqueous solution of KOH of appropriate concentration. The slurry was stirred for 2 h, heated to 120°C for 16 h followed by calcination at 550°C for 5.5 h. MgO was impregnated with 5 – 20 wt.% of KOH and designated as MgO-KOH-X (X being the wt.% of KOH impregnated over MgO). Catalysts were characterized by FT-IR, powder XRD, TEM and DTA. Basic strengths of the catalysts were measured by Hammett indicators.

6.2.2. Transesterification of fat

In a typical transesterification reaction, fat and methanol (1:22 molar ratio) and 4 wt.% of the catalyst (catalyst/fat) were stirred at 65°C till the completion of the reaction. Progress of the reaction and quantification of methyl esters was carried out by TLC and ^{1}H NMR as described earlier in chapter 3.

The reaction conditions were optimized by varying: the amount of KOH impregnation, amount of the catalyst, reaction temperature, fat/methanol molar ratio, moisture content and the FFAs (addition of oleic acid and palmitic acid). Pure MgO (4 wt.%) and KOH (0.8 wt.%, an equivalent amount of KOH present in 4 wt.% of MgO-KOH-20) were also used as catalysts for transesterification to compare the results obtained with MgO-KOH-20.

Concentrations of potassium ions in samples of biodiesel (obtained from KOH and MgO-KOH-20) were determined by ash method as described earlier in chapter 2. Biodiesel samples (5 g) from both homogenous and heterogeneous catalyzed reactions were stirred with 25 ml of deionized water for half an hour to study pH and the leaching behavior of K^+ ions from the catalysts into biodiesel.

6.3. Results & Discussion

6.3.1. Catalyst characterization

6.3.1.1. Basic Site Strength

Basic site strength of prepared catalysts was determined by Hammett Indicators and shown in Table 6.1. Basic strengths of MgO was found to be $9.8 < H\_ < 11$. Increase in the site strength in the range of $11 < H\_ < 15$ was observed upon impregnation with 5 to 15 wt.% of KOH. MgO-KOH-20 was found to have highest basic strength ($15 < H\_ < 18.4$) among all the prepared catalysts.

Table 6.1 Basic strengths of KOH impregnated MgO.

Catalyst	Hammett Indicator with Higher Basic Strength Showing Colour Change	Basic strength
MgO*	Phenolphthalein ($H\_ = 9.8$)	$9.8 < H\_ < 11$
MgO-KOH-05	Alizarin ($H\_ = 11$)	$11 < H\_ < 15$
MgO-KOH-10	Alizarin ($H\_ = 11$)	$11 < H\_ < 15$
MgO-KOH-15	Alizarin ($H\_ = 11$)	$11 < H\_ < 15$
MgO-KOH-20	2,4-Dinitroaniline ($H\_= 15.0$)	$15 < H\_ < 18.4$

*Without impregnation with KOH

6.3.1.2. FT-IR

FT-IR spectra of MgO-KOH-X (X = 5-20) are shown in Figure 6.1. MgO-KOH-20 showed a weak and broad band at ~ 3400 cm^{-1} due to the presence of -OH group. Another peak at 1430 cm^{-1} indicated the presence of CO_3^{2-} (Tatzber et al., 2007; Sutter et al., 2005) probably formed during calcination.

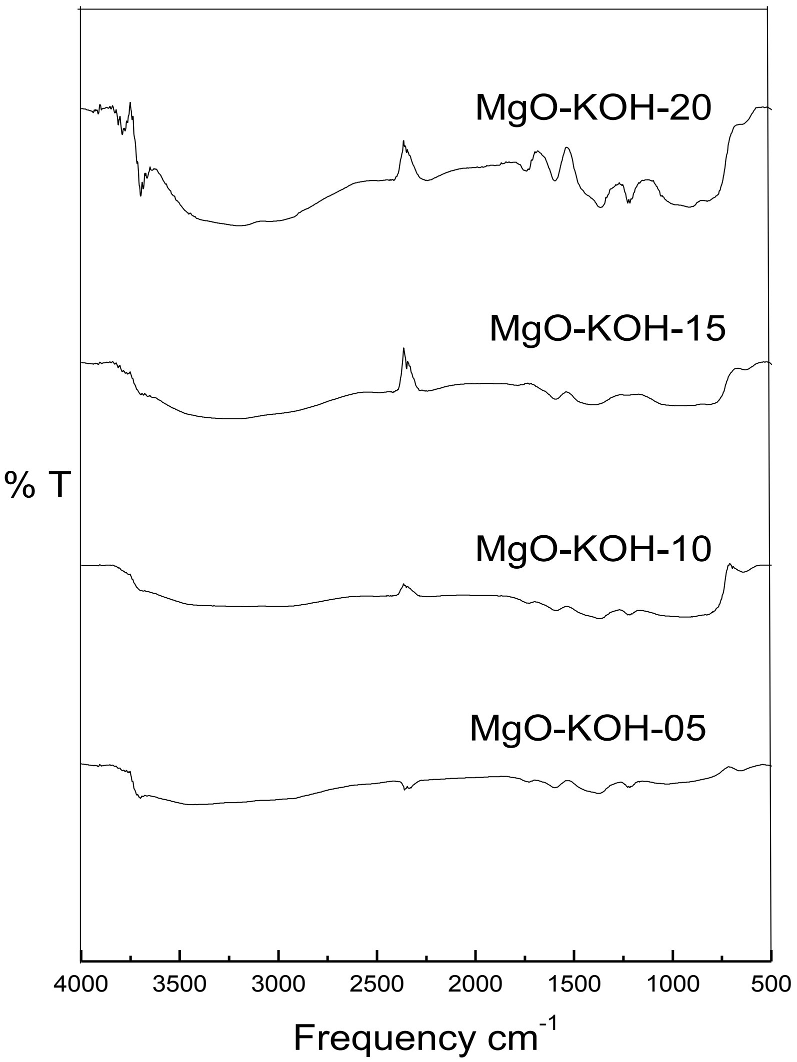

Figure 6.1. FT-IR spectra of MgO-KOH-X (X = 5-20)

6.3.1.3. Powder XRD

Powdered XRD patterns of calcined MgO and MgO-KOH-X (X = 5-20) are shown in Figure 6.2. The impregnated catalysts showed peaks at 37.0°, 43.0° and 62.3° due to the presence of MgO crystalline phases (PDF 78-0430). Another peak at 31.3° due to monoclinic K_2CO_3 has been observed (PDF 70-0292), probably due to the reaction of KOH with O^{2-} species of MgO and CO_2 during calcination. Similar finding has been reported elsewhere (Ilgen et al., 2009). In MgO-KOH-20, an additional peak at 32.3° showed the presence of KOH (PDF 78 - 0190). The effect of temperature during calcinations for MgO-KOH-20 has been shown in Figure 6.3. Formation of K_2CO_3 was observed during calcinations at 350-850°C and it disappeared at 950°C possibly due to its decomposition.

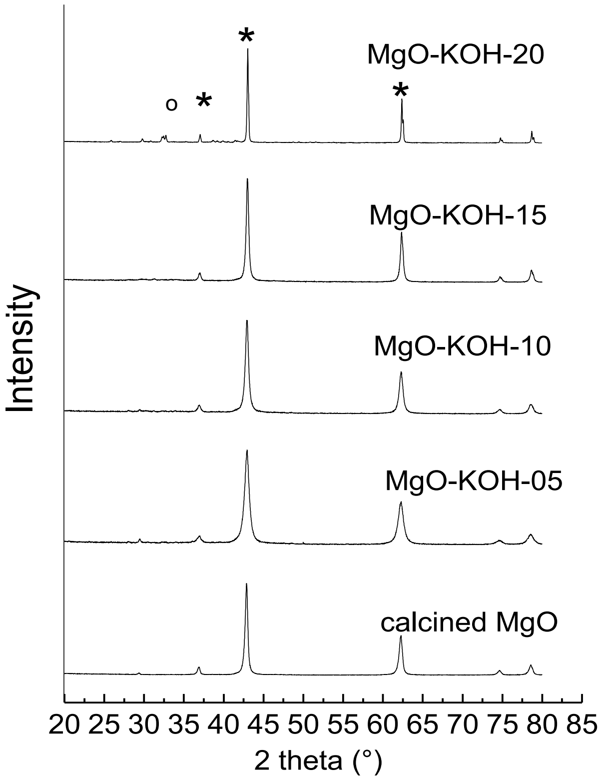

Figure 6.2. Powder XRD of MgO and MgO-KOH-X (X = 5-20) (*, MgO; o, K_2CO_3; x, $Mg(OH)_2$)

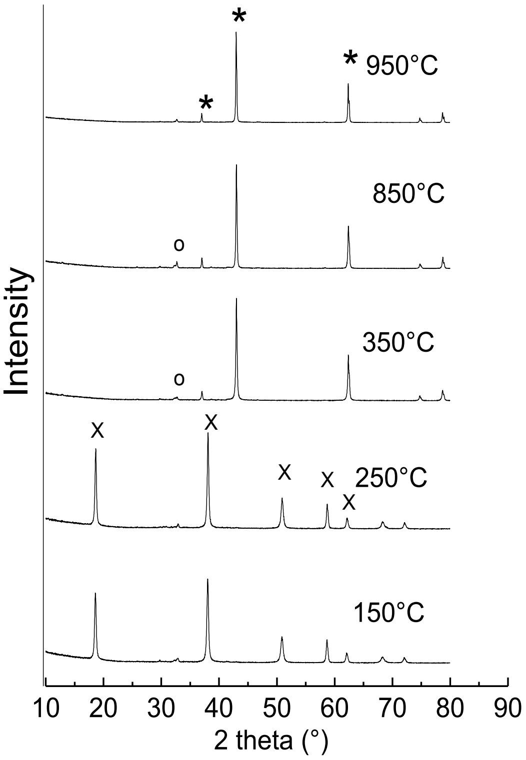

Figure 6.3. Powder XRD of MgO-KOH-20 at different calcinations temperature (150-950°C) (*, MgO; o, K_2CO_3; x, $Mg(OH)_2$).

6.3.1.4. DTA

DTA study of MgO-KOH-20 (Figure 6.4) showed an endothermic peak at 955°C corresponding to decomposition temperature (Lehman et al., 1998) of potassium carbonate. This further supports the presence of potassium carbonate which was formed during calcination.

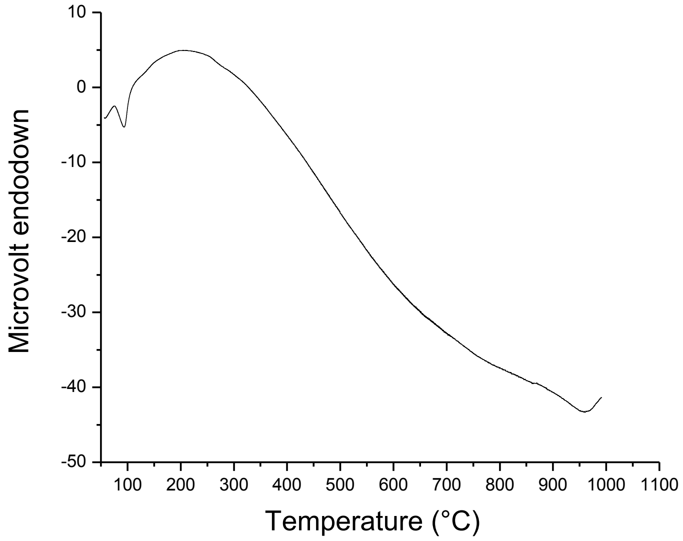

Figure 6.2. DTA of MgO-KOH-20

6.3.1.5. TEM

TEM of MgO and MgO-KOH-20 has been shown in Figure 6.5 (a, b and c). There are separate non aggregate capsule shaped particles in the range of 34-74 nm (Figure 6.5a). Impregnation of MgO with KOH followed by calcination at 550°C showed an increase in the particle size and change in the shape (Figure 6.5b). There seems agglomeration of MgO particles in cell like structure of KOH (5b, marked area). Agglomeration of MgO particles may be due to the change in surface charge properties and surface morphology after KOH impregnation.

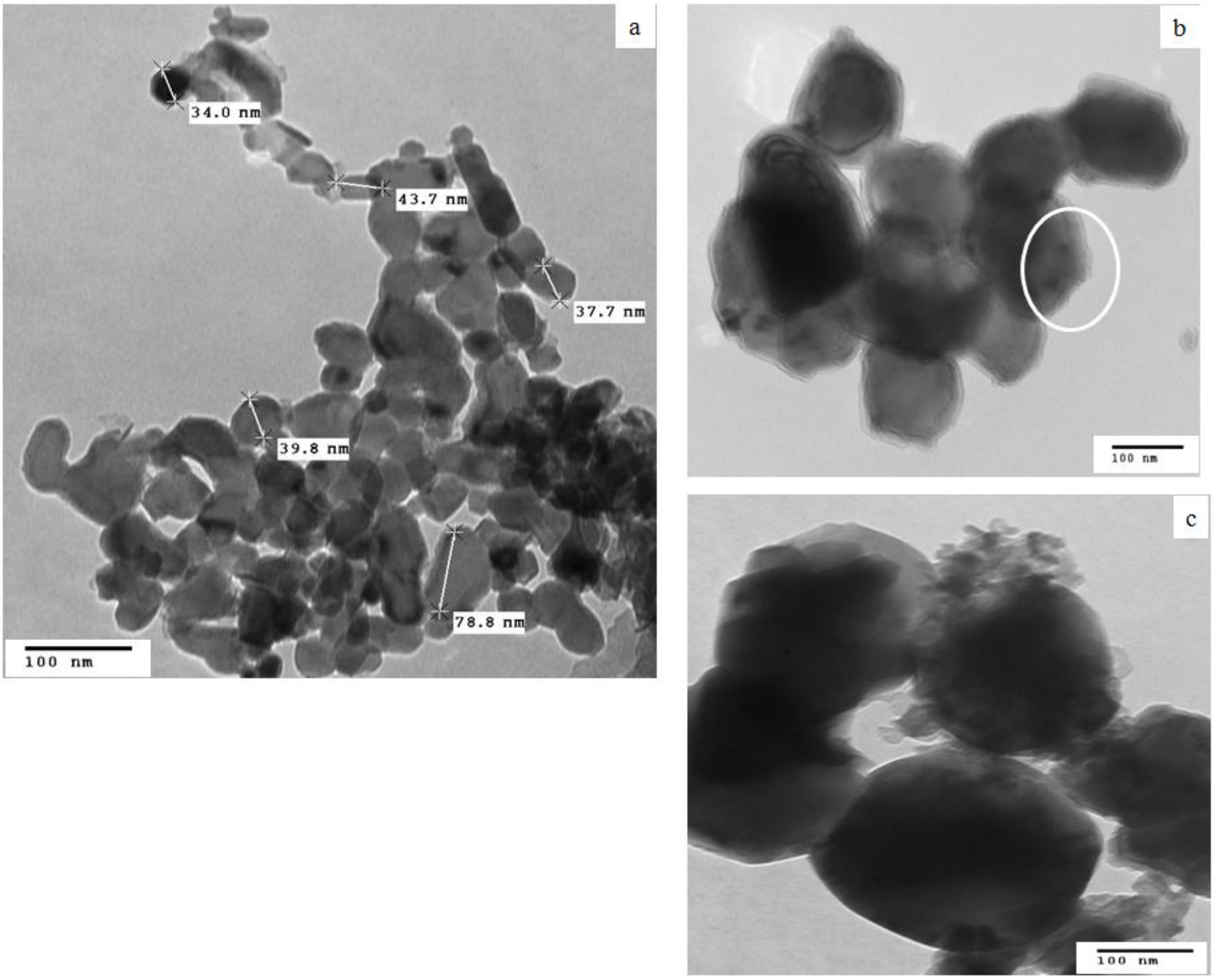

Figure 6.5. (a):TEM image of MgO, (b) and (c):TEM images of MgO-KOH-20

6.3.2. Catalytic activity

Transesterification reactions of fat with methanol (1:22 molar ratio) at 65°C were carried out in the presence of 4 wt.% of MgO-KOH-X (X = 5-20 wt.%). The reaction could not be completed with MgO catalyst even after 12 h. However, MgO-KOH-20 resulted in the completion of the reaction (> 98 % by ^{1}H NMR) in 20 min. With the decrease in wt.% of impregnation from X =15 to 5, the reaction time increases from 0.6 to 4.5 h. These results are shown in Figure 6.6. Least time period with MgO-KOH-20 catalyst may be due to the increased site strength and formation of heterogeneised potassium species as confirmed by powder XRD and DTA studies. Hence, MgO-KOH-20 was used for optimizing other reaction parameters.

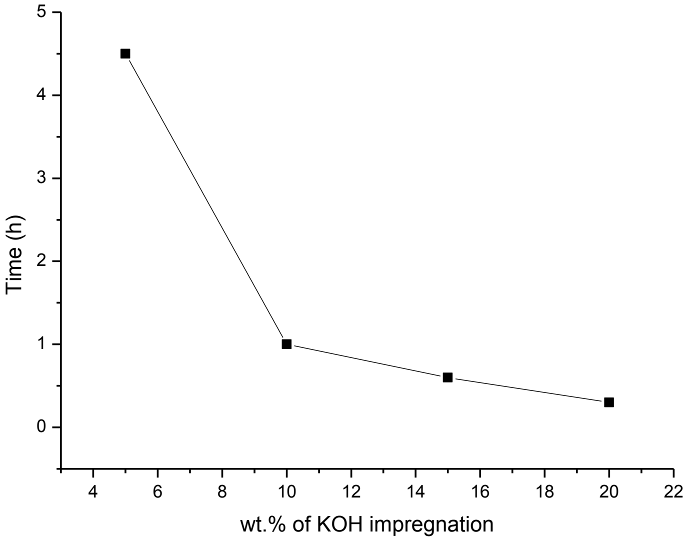

Figure 6.6. Effect of KOH impregnation over MgO on the completion of reaction (*reaction conditions: fat/methanol molar ratio, 1:22; temperature, 65 °C; and catalyst amount, 4 wt.% of fat).*

6.3.2.1. Effect of amount of catalyst on transesterification of fat

Transesterification reactions of fat with methanol (1:22 molar ratio) at 65°C were carried out with varying amount of MgO-KOH-20 and results are shown in Figure 6.7. The reaction was complete within 20 min by the use of 4 or higher wt.% of the catalyst. The decrease in amount of the catalyst from 3.5 to 1.5 wt.% showed an increase in time for completion of reaction (0.5 to 7 h). Hence, other parameters were studied by using 4 wt.% of catalyst.

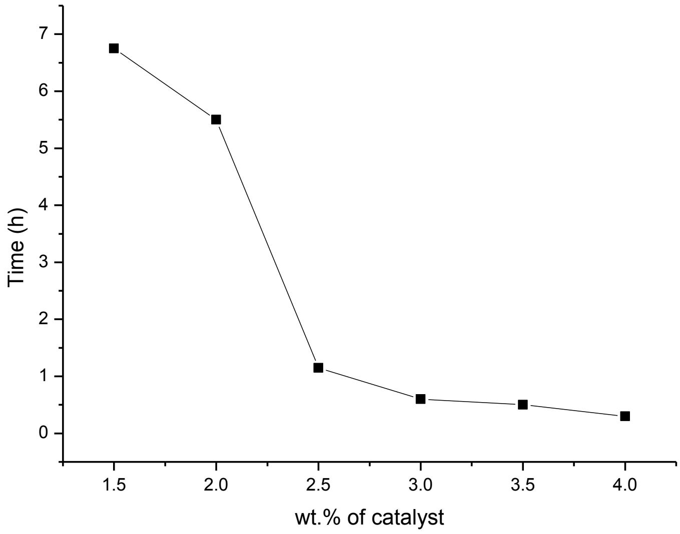

Figure 6.7. Effect of amount of MgO-KOH-20 on the completion of reaction (*reaction conditions: fat/methanol molar ratio, 1:22; and temperature, 65 °C).*

6.3.2.2. Effect of fat/methanol molar ratio on transesterification of fat

Transesterification reaction being reversible usually requires higher molar ratio of fat: methanol than stoichiometry of 1:3. A series of transesterification reactions were performed by using fat/methanol molar ratio of 1:11, 1:14, 1:16, 1:19, and 1: 22 with 4 wt.% of MgO-KOH-20 at 65°C (Figure 6.8). The reaction was complete in 20 min with 1: 22 molar ratio of fat to methanol and any further increase in methanol amount did not affect the reaction time.

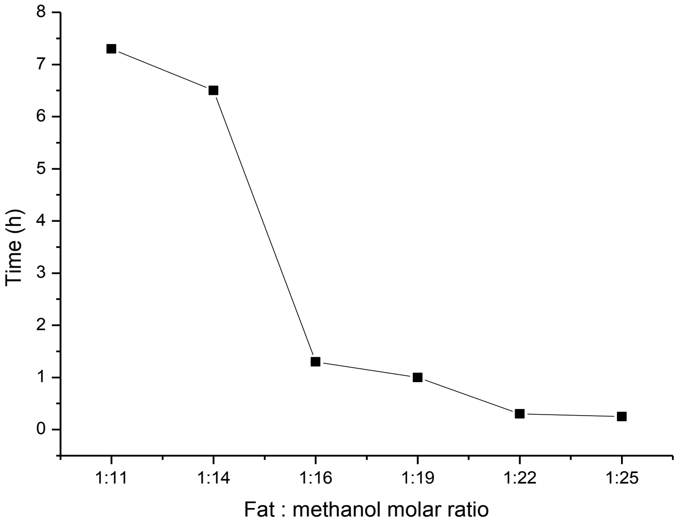

Figure 6.8. Effect of fat/methanol molar ratio on the completion of reaction (*reaction conditions: catalyst amount, 4 wt.% of fat; and temperature, 65 °C).*

6.3.2.3. Effect of temperature on transesterification of fat

Transesterification reactions of fat with methanol (1:22 molar ratio) in the presence of 4 wt.% MgO-KOH-20 were carried out at different temperatures from 45-65°C. The time period for completion of the reaction decreases with rise in temperature (Figure 6.9). At temperature < 45°C, reaction could not be completed.

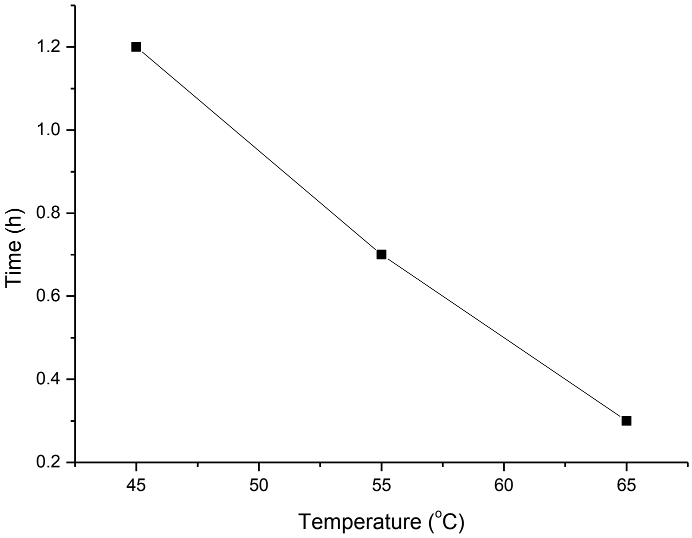

Figure 6.9. Effect of temperature on the completion of reaction (*reaction conditions: fat/methanol molar ratio, 1: 22; and catalyst amount, 4 wt.% of fat).*

6.3.2.4. Effect of moisture on transesterification of fat

Fresh fat (0.02 wt.% moisture) showed complete transesterification with methanol (1:22 molar ratio of fat/methanol) in presence of 4 wt.% of MgO-KOH-20 at 65^{o}C in 20 min. However, with additional 1.0 wt.% of the moisture, reaction time increases to 1 h (Figure 6.10). Similar reaction of fat (fresh) with KOH (homogeneous) catalyst showed the formation of soap with additional 1 wt.% of moisture. In case of Beef tallow, NaOH as homogenous catalyst for biodiesel production, Ma et al. (1998) reported the tolerance of < 0.06 wt.% of the water. However, MgO-KOH-20 was found to be effective and tolerant to additional 1wt.% of water content.

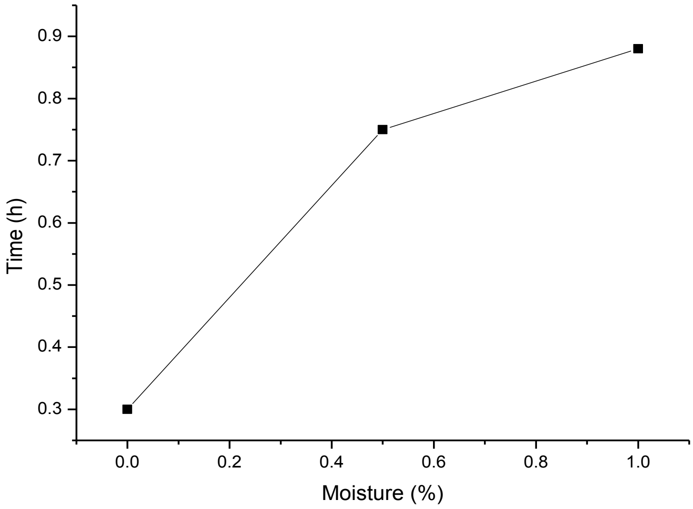

Figure 6.10. Effect of moisture on the completion of reaction (*reaction conditions: fat/methanol molar ratio, 1:22; temperature, 65 °C; and catalyst amount, 4 wt.% of fat).*

6.3.2.5. Effect of FFAs on transesterification of fat

Transesterification of fat (fresh; 0.002% FFAs) with methanol (1:22 molar ratio of fat/methanol) in the presence of 4 wt.% of MgO-KOH-20 was complete in 20 min at 65°C. However, increase in reaction time was observed from 20 min to 6.5 h with the addition of 1 wt.% of palmitic/ oleic acid (Figure 6.11). Similar reaction of fat with homogenous KOH catalyst and additional 1 wt.% FFAs, leads to soap formation

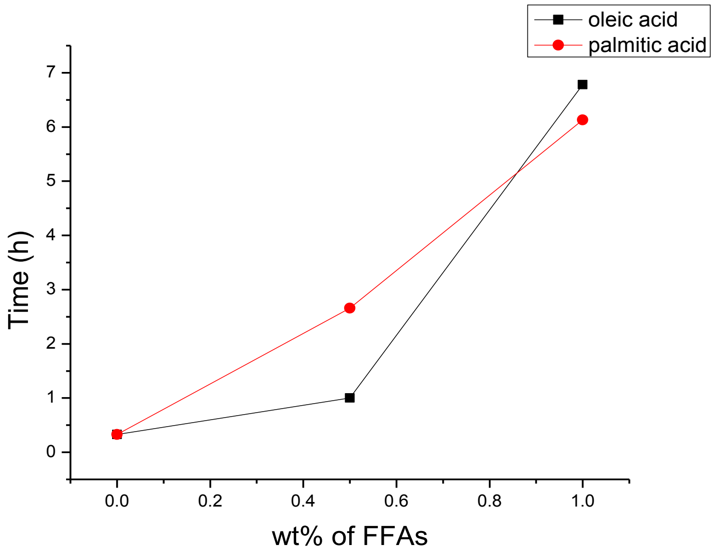

Figure 6.11. Effect of addition of palmitic acid/oleic acid on the completion of reaction *(reaction conditions: fat/methanol molar ratio, 1:22; temperature, 65 °C; and catalyst amount, 4 wt.% of fat).*

6.3.3. Quantification of biodiesel

Formation of biodiesel under different reaction conditions during transesterification were studied by ^{1}H NMR as explained in chapter 2. The appearance of a peak at δ 3.6 due to the formation of –OCH_3 and the disappearance of glyceridic protons present in fat at δ 4.1 and δ 5.2 supports the formation of biodiesel (Figure 6. 12 a, b). Quantification of biodiesel from ^{1}H NMR spectra was carried out as per reported method and was found to be 98.2 ± 2%.

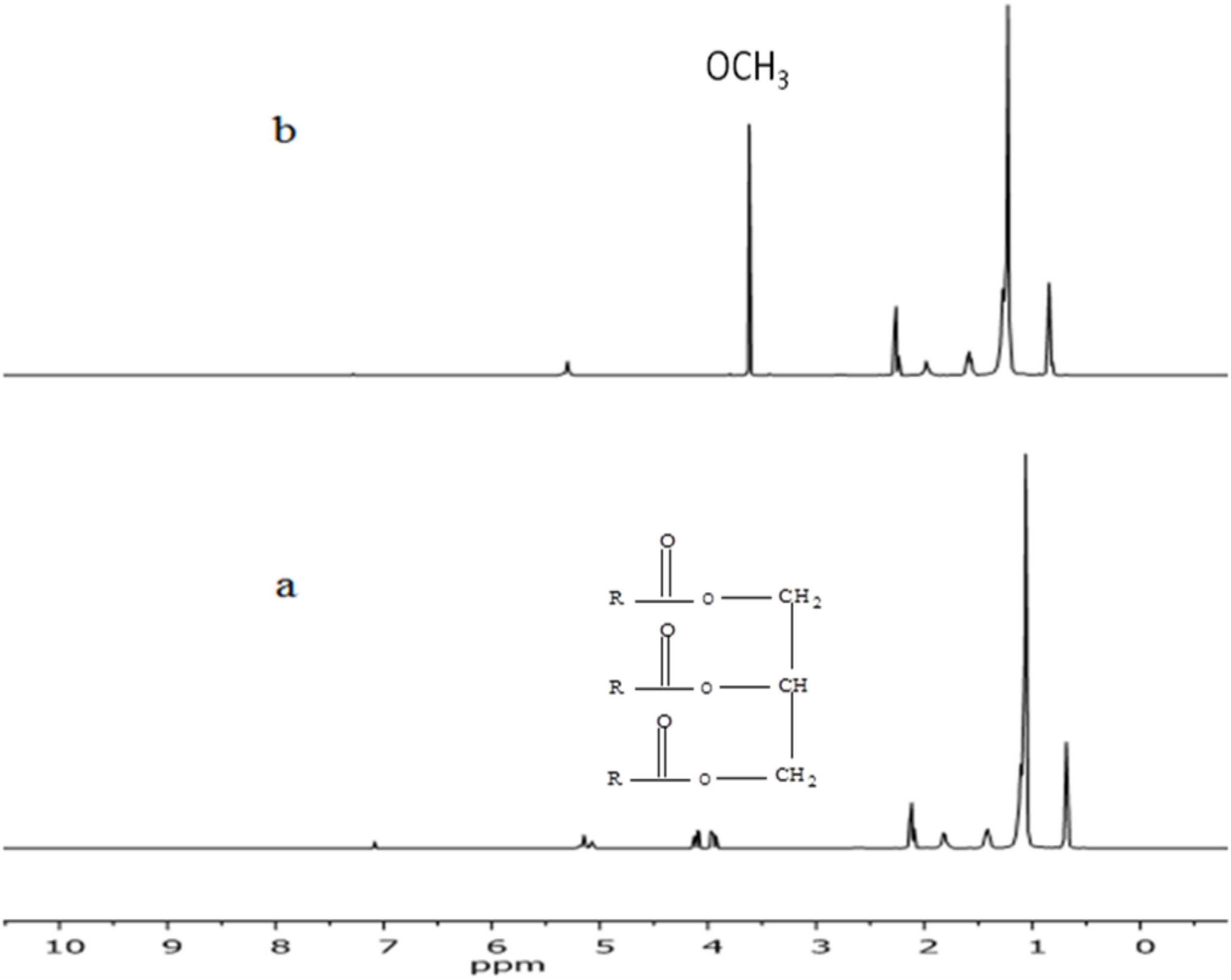

Figure 6.12. ^{1}H NMR spectrum of (a) mutton fat; (b) biodiesel

^{1}H-NMR of methyl esters of mutton fat (solvent, $CDCl_3$; δ, ppm): 5.34 (m, -C**H**=C**H**-), 3.6 (s, -OC**H3**), 2.3 (m, -C**H2**-CO-), 2.0 (m, -C**H**2-(CH2)n-), 1.61-1.25 (m, -(C**H2**)n-), 0.88 (m, -CH2-C**H3**).

6.3.4. Potassium ion analysis in biodiesel

Potassium ion concentration in biodiesel obtained from transesterification with MgO-KOH-20 (4 wt.%) was found to be one third (31 ppm) than obtained by homogenous KOH catalyst (0.08%, catalyst/fat). Further, pH of aqueous layers obtained from washings of biodiesel was found to be 7.55 for the former and 9.55 for the latter. These results indicated the presence of lesser amount of K^+ ions in the biodiesel obtained from MgO-KOH-20.

6.3.5. Reusability

Reusability experiments were performed using MgO-KOH-20 catalyst under optimized reaction parameters viz., 4 wt.% of catalyst and 1:22 molar ratio of fat and methanol at 65°C. Conversion of 62%, 59%, 58% was obtained during first three recycles. Heat treatment after every reuse in order to activate catalytic sites and remove CO_2 poisoning was not found to improve the catalytic activity. However, powder XRD study of the reused catalyst (after 3rd catalytic run, Figure 6.13) showed the same structure as that of fresh catalyst, so decrease in the catalytic activity may be due to the decrease in site strength from $15 < H\_ < 18.4$ to $11 < H\_ < 15$.

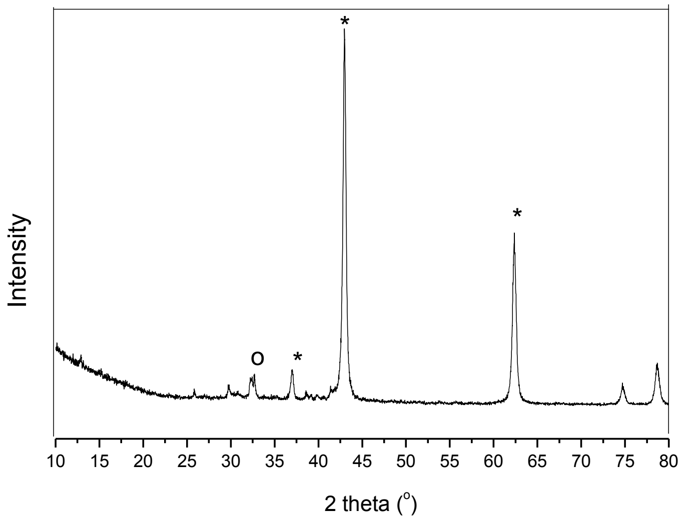

Figure 6.13. Powder XRD of used MgO-KOH-20 (*, MgO; o, K_2CO_3).

6.4. Conclusion

Potassium hydroxide impregnated MgO has been prepared as heterogeneous catalyst for the transesterification of mutton fat. Impregnation with 20 wt.% KOH increases the basic strength of MgO. Transesterification of mutton fat with methanol in 1:22 molar ratio in the presence of MgO-KOH-20 catalyst at 65°C resulted in the conversion of > 98% of biodiesel in 20 min. The catalyst was effective even in the presence of additional 1wt.% of the added FFA (Palmitic acid / oleic acid) or the moisture content.

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Chapter 7: Sodium aluminate as catalyst for transesterification of waste mutton fat

ABSTRACT

Sodium aluminate and its calcined forms have been evaluated as basic catalysts for the transesterification of waste mutton fat with methanol. The decrease in catalytic activity has been observed with calcined sodium aluminate. Fat and methanol in 1:29 molar ratio with 1.5 wt.% of sodium aluminate under reflux resulted in 97 % conversion to biodiesel in 1h 20 min. The reaction showed tolerance of additional moisture content of 1 wt.%.

7.1. Introduction

Use of edible oil as a raw material for biodiesel production leads to global food problem, deforestation and ecological imbalance while changing the virgin forests and arable lands to large scale biofuel production. It is also costing about 88% of the total estimated production cost of biodiesel (Haas et al., 2006). So their use is not recommended from ecological and economical point of view. There should be a focussed entirely on the non-edible oil viz., jatropha, karanja and waste animal greases. There are comparatively fewer reports (Liu. et al., 2007; Canoira et al., 2008; Reddy et al., 2006 ; Ngo et al., 2008) for the production of biodiesel from beef tallow, poultry fat and grease and work regarding them has been discussed already in chapter 6.

Mutton fat being waste by-product of meat industry seems to be an excellent feedstock for biodiesel production. There seems no report regarding the preparation of biodiesel from fat using sodium aluminate. Sodium aluminate is an important inorganic compound which is basic in nature. We are reporting the catalytic activity of sodium aluminate and its calcined forms (250-850^{o}C) for the transesterification of waste mutton fat (fat) and moisture tolerance of the catalyst under optimized conditions.

7.2. Experimental Section

7.2.1. Catalysts and their characterization

Commercially available sodium aluminate and its calcined forms at different temperatures (250^{o}C-850^{o}C) were characterized by powder XRD, TGA, BET surface area. Variation in basic site strengths with calcinations was measured by Hammett indicators. These were used as catalysts for the transesterification of waste mutton fat

7.2.2. Transesterification

In order to study the effect of calcination temperatures on the catalytic activity of sodium aluminate, all calcined samples were used for the transesterification of waste mutton fat. In a typical reaction, 10 g each of fat and methanol (in 1: 27 molar ratio) were stirred with 1.5 wt.% of the catalyst at the reflux/selected temperature in a round bottom flask. Aliquots of the sample were taken after appropriate time intervals and progress of the reaction was monitored by TLC and ^{1}H NMR as described in chapter 2.

Other reaction conditions optimized were: the amount of catalyst, reaction temperature, fat/ methanol molar ratio, moisture content and the FFAs content (addition of oleic/ palmitic acid).

7.2.3. Leaching of sodium ion from catalyst

Sodium ion concentration in unwashed biodiesel obtained by using 1.5 wt.% of sodium aluminate and its calcined form at 250 and 350^{o}C and 1.5 wt.% of sodium hydroxide (homogeneous) was determined by ash method as described in chapter 2.

7.3. Results and Discussion

7.3.1. Catalyst characterization

7.3.1.1 Basic site strength

The basic site strength of sodium aluminate and its calcined forms at different temperatures (250-850°C) was studied with Hammett indicators. Sodium aluminate with no thermal treatment showed the highest basic strength $H\_= 18.4$, as 4-nitroaniline changes colure from yellow to orange. The decrease in site strength to $H\_= 15$ was observed for calcined sodium aluminate in the temperature range 250 to 650^{o}C (at an interval of 100^{o}C) as colure change was observed in case of 2,4-dinitroaniline instead of 4-nitroaniline. Further decrease in site strength to $H\_= 11.0$ was observed for sodium aluminate calcined at 750 and 850^{o}C as colour change was observed with alizarin from orange to brown.

7.3.1.2. TGA/DTA

TGA/ DTA study of sodium aluminate is shown in Figure 7.1. There is a weight loss of 5.7% in the temperature region 100-150^{o}C that may be due to loss of water and desorption of CO_2 from the basic sites. There is a phase transition at 320 ^{o}C in the DTA study (Figure 7.1b). Finne et al. (1994) has also reported irreversible phase transition on the basis of IR emission spectra of calcined forms of sodium aluminate.

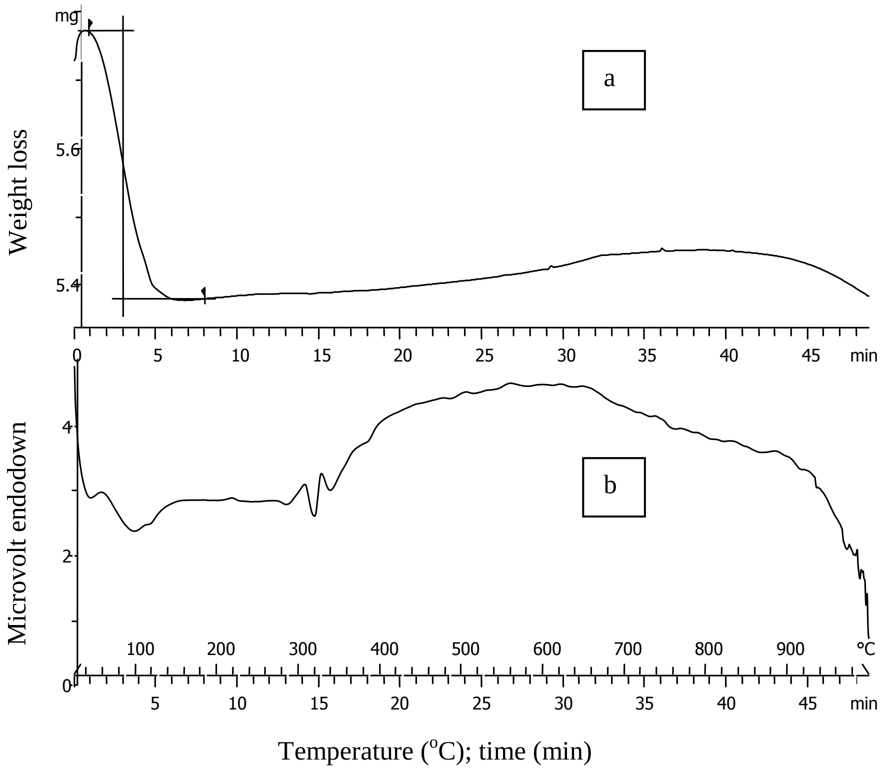

Figure 7.1. (a) TGA of sodium aluminate (b) DTA of sodium aluminate.

7.3.1.3. Powder XRD analysis

Powder XRD patterns of sodium aluminate calcined in temperature range 250-850^{o}C are shown in Figure 7.2. Any additional crystalline phase was not observed on heating sodium aluminate at different temperatures. However, crystallite size by Scherrer's formula (Cullity et al., 2001) depicted variation along with some shifting and broadening of peaks. Crystallite size of sodium aluminate, its calcined forms at 250, 350, 450 and 550-850^{o}C were found to be 97, 52, 34, 37 and 113 $\underline{+}$ 2 nm respectively. Variation in crystallite size upon calcination upto 450^{o}C may be due to phase transition. Moreover, when the grain is subjected to the tensile strain at right angles to the diffraction planes, their spacing become larger resulting in the shifting of corresponding diffraction lines to lower angles (Cullity et al., 2001). Similar shifts has been observed towards low diffraction angles for the samples calcined at 250 - 450^{o}C indicating the development of the strain resulting from disordering which may be due to evolution of CO_2 and H_2O. The peak positions showed shift towards higher angle at 550^{o}C and then appear at almost same positions upto 850°C, thereby signifying the reduced strain and ordered structure. The lattice parameters of sodium aluminate have been reported to decrease slightly with increasing dehydration temperature and the reduction of strain with heating at higher temperature (Kaduk et al., 1995).

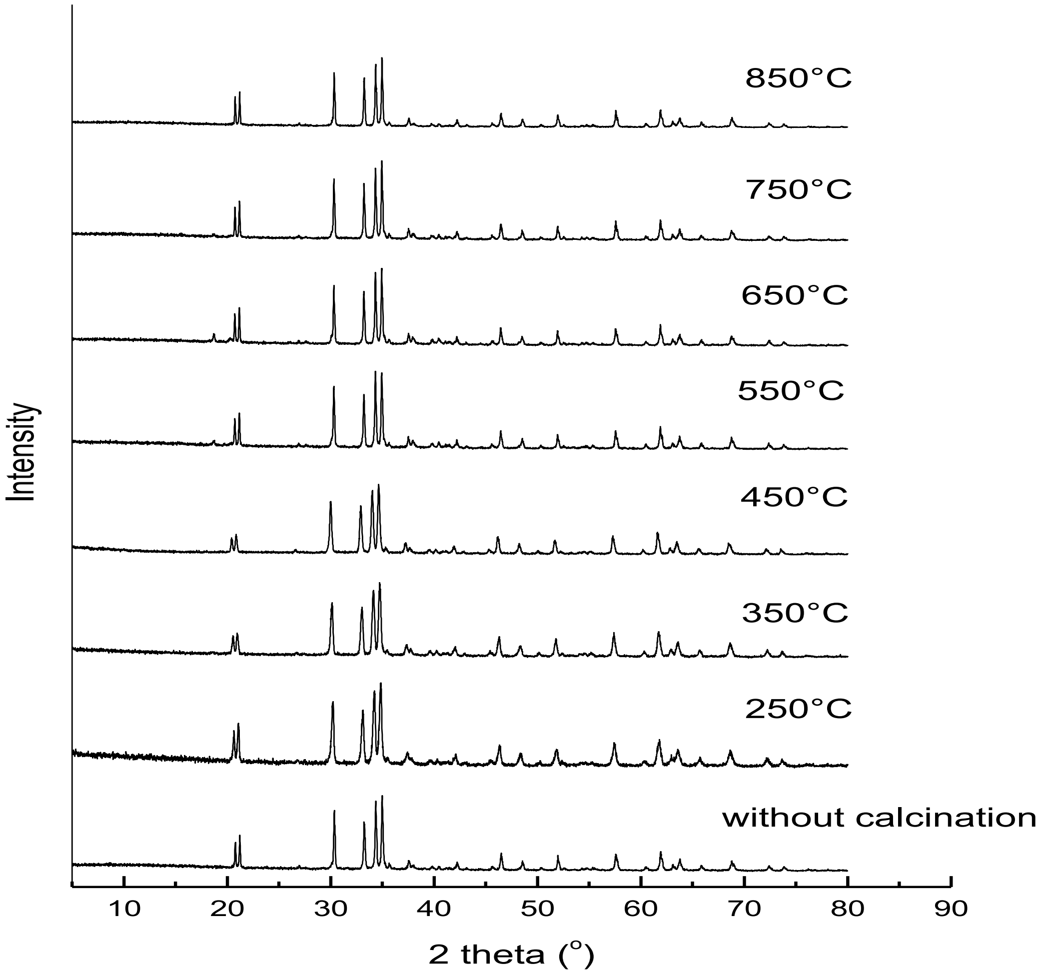

Figure 7.2. Powder XRD pattern of sodium aluminate calcined at different temperatures.

7.3.1.4. BET surface area

BET surface area of sodium aluminate and its calcined forms at 250-850°C is shown in Table 1. Sodium aluminate calcined at 350°C exhibited the highest surface area (7.7 m^2/g), where as 0.5 m^2/g was the minimum value in case of uncalcined form. These results can be rationalized with crystallite size predicted by powder XRD study which showed smallest crystallite size, and hence largest surface area for the sodium aluminate calcined at 350°C and lesser surface area for bigger crystallites of uncalcined form.

Table. 7.1. BET surface area of sodium aluminate at various calcination temperatures

Calcination temperature (°C)	BET surface area (m^2/g)
Without calcination	0.5
250	7.1
350	7.7
450	6.1
550	3.2
650	2.9
750	2.1
850	1.8

7.3.2. Catalytic activity

Transesterification reactions were carried out using 1:27 molar ratio of fat to methanol and 1.5 wt.% of the different catalysts under reflux conditions. Sodium aluminate (without calcination) and calcined at 250 °C and at 350°C showed the completion of reaction (97 % conversion obtained from ^{1}H NMR) in 3h 10 min, 7 h and 15 h, respectively. However, the reaction carried out by the use of sodium aluminate calcined at 450-850°C did not go to completion. These results can be rationalized on the basis of TGA/DTA study of sodium aluminate which showed the phase transition near to 400°C. Powder XRD study showed the increase in crystallite size on calcination. These factors may be responsible for the increase in time of completion of reaction. Hence, uncalcined sodium aluminate was used for optimizing other reaction parameters.

7.3.2.1. Effect of fat to methanol molar ratio

Transesterification being reversible usually requires higher molar ratio of methanol than the stoichiometric amount. For optimum reactant ratio, fat to methanol molar ratio was varied from 1:27 to 1:35 in the presence of 1.5 wt.% of the catalyst under reflux. Reaction time of completion increases from 1h 5 min to 3h 10 min when fat to methanol molar ratio varied from 1:35 to 1:27 as shown in Figure 7.3. Fat to methanol ratio of 1: 29 was found to be optimum as further increase in the amount of methanol, did not showed any marked reduction in the reaction time of 1h 20 min. These parameters are better than reported for preparation of biodiesel from poultry lipids using using 1:60 fat to methanol molar ratio along with co-solvents at 120°C using Mg–Al hydrotalcite catalyst (Liu et al., 2007)

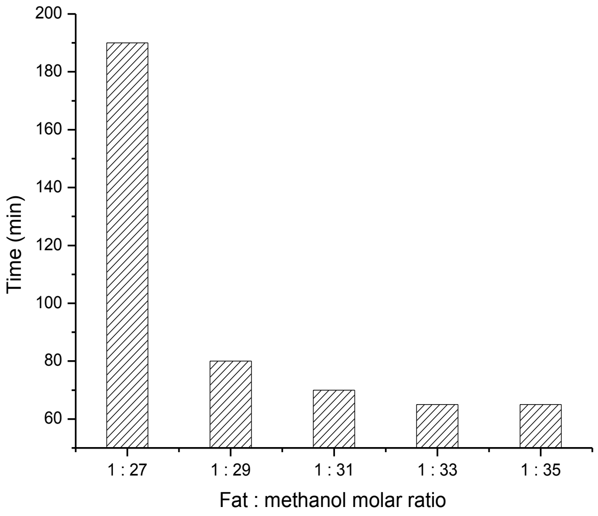

Figure 7.3. Effect of fat to methanol molar ratio (*reaction conditions: catalyst amount, 1.5 wt. % of fat; and temperature, 65 °C).*

7.3.2.2. Effect of amount of catalyst

Transesterification reactions were carried out by using different amount of sodium aluminate (with fat and methanol in 1:29 molar ratio) under reflux conditions. With 0.75, 1, 1.5, 2 and 2.5 wt.% of catalyst, the time period for completion of reaction was 7 h 15 min, 4 h, 1h 20min, 1h 10 min and 1h respectively. Reasonable amount of catalyst was 1.5 wt.% as further increase did not showed any marked reduction in time period for the completion of reaction, therefore, other parameters were optimized with 1.5 wt.% of catalyst. Optimized reaction parameters for the transesterification of mutton fat using MgO impregnated with KOH catalyst (Mutreja et al., 2011) were; 4 wt.% of catalyst (MgO impregnated with 20% KOH) and 1:22 molar ratio of fat to methanol under reflux. As sodium aluminate and MgO impregnated with KOH catalysts resulted in 97% and 98% conversion respectively, hence both are efficient catalysts for transesterification. However, use of sodium aluminate seems to be economical in comparison to activated nanopowder of MgO, which further required KOH impregnation.

7.3.2.3. Effect of reaction temperature

Transesterification reaction did not proceed to completion by using 1:29 fat to methanol molar ratio at 45^{o}C. Although, molar ratio of fat to methanol of 1:29 is higher than stochiometry of reaction, but was not sufficient for the completion of reaction. However, by increasing amount of methanol (1:54 fat to methanol molar ratio) reaction showed completion at 45^{o}C. The results with 1:54 molar ratio of fat to methanol at 45-65^{o}C are shown in Figure 7.4. At 65^{o}C, lowest time period of 1h 5 min was observed for the completion of reaction.

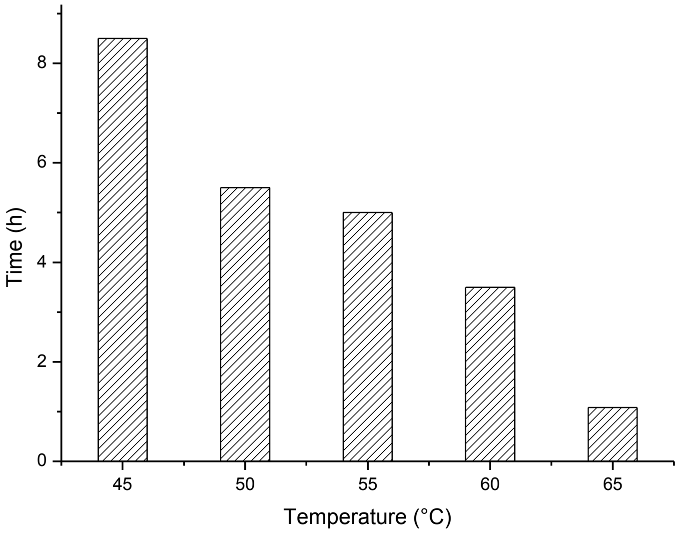

Figure 7.4. Effect of reaction temperature (*reaction conditions: fat/methanol molar ratio, 1: 54; and catalyst amount, 1.5 wt. % of fat).*

7.3.2.4. Effect of added moisture

Moisture tolerance of the catalyst was studied by performing transesterification in the presence of added moisture. Higher fat to methanol molar ratio was found to have a positive effect on transesterification reaction performed in the presence of added moisture, hence 1:54 molar ratio was selected for studying the effect of added moisture with 1.5 wt.% of the catalyst under reflux condition. Transesterification of fat with methanol in the presence of 1 wt.% of moisture also resulted in 97% conversion. These findings are far better than production of biodiesel from beef tallow by the use of homogenous catalyst showing tolerance of < 0.06 wt.% of moisture (Ma et al., 1998). Higher moisture tolerance of sodium aluminate can be due to formation of $NaAlO_2.xH_2O$ (PDF: 41-638).

7.3.2.5. Effect of free fatty acid

Transesterification did not go to completion in the presence of additional amount of free fatty acid by using optimized fat to methanol ratio. However, higher molar ratio of fat to methanol (1:54) showed positive effect for the reaction in presence of additional amount of added free fatty acid, hence was selected for studying the effect of free fatty acid. Reaction time of completion (97 % conversion) increases from 1h 5 min to 3 h 15 min and 3 h 40 min respectively with the addition of 0.5 wt.% of either palmitic acid or oleic acid respectively.

7.3.3. Leaching sodium ions from catalyst.

Sodium ion concentration in unwashed biodiesel obtained by using 1.5 wt.% of sodium aluminate, calcined form at 250 and at 350°C was found to be 5.6, 4.8 and 3.8 ppm respectively. However, reaction performed with 1.5 wt.% of NaOH catalyst resulted in much higher concentration of sodium ions (173 ppm) in biodiesel.

7.4. Conclusion

Sodium aluminate (1.5 wt.%) as catalyst was found to complete the transesterification of fat with methanol (1:29 molar ratio) within 1h 20 min under reflux. Leaching of sodium ions was found to be near to the ASTM permissible limit. Higher fat: methanol molar ratio increases the tolerance of the catalyst towards both FFA and moisture. However, calcination of sodium aluminate resulted in the reduction of catalytic activity probably due to phase transition, increase in crystallite size, and desorption of carbon dioxide and water from its surface. So, sodium aluminate can be better alternative in comparison to homogenous NaOH catalyst.

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Chapter 8: Conclusion, Future Perspective and Scope

ABSTRACT

This chapter involves summary of all the major findings, co-relations and comparison between results with all the evaluated catalysts. Future prospective and further scope of the work is also given in this chapter.

This chapter have two sections; the first section includes the summary of major findings, conclusions, comparison and correlation between the results obtained with all prepared and evaluated catalysts and the second section involves the future prospective and further scope in this field.

8.1. Conclusion, Co-relation and comparison

In the present thesis, work was carried out for the preparation and development of strong solid base catalysts for the transesterification of triglycerides (vegetable oil and animal fat). There was an approach for the complete heterogeneisation of alkali metal species over some support. So, with this aim, impregnation of potassium over MgO, mixed oxides of La and Mg, SiO_2 and SBA-15 was carried out by wet impregnation, co-precipitation, sol-gel and coating-grinding methods respectively. The major findings with these catalysts are given below:

Wet-Impregnation of KOH (5-20 wt.%) over MgO followed by drying and calcinations leads to the formation of heterogeneised K_2CO_3 using oxygen of MgO lattice. These catalysts were found to catalyze the transesterification of mutton fat with methanol completely (> 98%). The catalyst prepared with 20 wt.% of KOH impregnation over MgO was found to tolerate additional 1 wt.% of either the moisture or FFAs content present in the reaction mixture.

Potassium impregnated mixed oxides of La and Mg were prepared by co-precipitation method. TEM studies of these catalysts supported the formation of polygonal, square and hexagonal shaped particles. Potassium impregnation resulted in the generation of strong basic sites when atomic ratio of La to Mg varied from 1: 1 to 1: 3 respectively.

Potassium impregnated SiO_2 having Si and K atomic ratios of 1:1 to 1:6 respectively were prepared by so-gel method. TEM studies of the catalyst having Si and K in 1:6 atomic ratio reveals the uniform impregnation of 1-5 nm sized potassium nanoparticles over 15-40 nm sized spherical silica nanoparticles. The same catalyst was found to be suitable for the transesterification of jatropha and karanja oil, having high FFAs content of 5.62 and 11.28 wt.% of respectively.

Mesoporous material SBA-15 also seems to be efficient catalyst for transesterification after modification with MgO and KNO_3. Mesoporous SBA-15 wrapped with MgO was prepared by one pot synthesis and further modified by 5-30 wt.% of KNO_3 via grinding in presence of water, followed by calcination at 600^oC under nitrogen atmosphere for 4 h. Coating of MgO act as protective sheath and prevent the damage and corrosion by potassium species to mesostructure silica frameworks. Increase in the potassium content upto 30 wt.% resulted in the increase in basicity of mesoporous materials. The catalyst with 25 wt.% potassium loading (SBA-15/MgO/25) was employed for the transesterification of used cotton seed oil. The BET surface area and pore volume was found to decrease upon MgO and KNO_3 coating. However, due to the formation of strong basic sites, at the same time, SBA-15/MgO/25 catalyzes the transesterification of used cotton seed oil with methanol at 65^oC with more than 98 % FAMEs yield.

Additionally, commercially available sodium aluminate and its calcined forms have been evaluated as basic catalysts for the transesterification of waste mutton fat with methanol. Sodium aluminate seems to be an efficient catalyst as it is economical, commercially available and found to be effective even in the presence of additional 1 wt.% of moisture due to the formation of $NaAlO_2.xH_2O$.

Under optimized reaction conditions, KOH impregnated MgO and sodium aluminate catalysts show leaching of potassium and sodium ions higher than 5 ppm i.e., permissible limit of ASTM into biodiesel. Blank experiments did not showed any observable transesterification of triglycerides, although leached ions might have some homogenous contribution.

Among all the prepared catalysts, LaMg-3@10 catalyst (La and Mg in 1: 3 atomic ratio co-precipitated at pH 10 using K_2CO_3 and KOH) demonstrated better performance and reusability. Leaching of potassium ions from this catalyst was also found to be within the permissible limit of 5 ppm of ASTM.

Various optimized reaction parameters with different catalysts are given in Table 8.1.

Table 8.1. Optimized reaction parameters with all the prepared and evaluated catalysts.

Catalyst	Feedstock	Catalyst amount	Temp.	TG to methanol molar ratio	Tolerance to total FFAs*	Tolerance to additional moisture content	Reusability during 1st two successive runs
Potassium impregnated SiO_2	Jatropha oil, Karanja oil	6 wt.% -j oil 8 wt.%- k oil	65°C	1: 60-j oil 1:80-k oil	11. 28 wt.%	1 wt.%	42 and 30% (95 and 92.5%)[#]
Potassium impregnated mixed oxides of La and Mg	Used cotton seed oil	5 wt.%	65°C	1: 54	NF	0.5 wt.%	94 and 90%
Potassium and MgO coated SBA-15	Used cotton seed oil	5 wt.%	65°C	1: 54	ND	ND	65 and 52%
MgO impregnated with KOH	Waste mutton fat	4 wt.%	65°C	1: 22	1.25 wt.%	1 wt.%	62%, 59%,
Sodium aluminate	Waste mutton fat	1.5 wt.%	65°C	1: 29	0.75 wt.%	1 wt.%	NF

ND (Not determined); NF (Not found); Temp. (Temperature); TG (Triglyceride)

* Total FFA content = FFAs content of feedstock + externally added FFA (Palmitic or oleic acid)

[#] Reusability with 95 and 92.5% Yield was observed with cotton seed oil

8.2. Future Perspective and Scope

In the work accomplished for this thesis, efforts were made for the preparation and development of a reusable strong solid base catalyst for the transesterification. Although there are satisfactory results and findings in the work carried out, yet there is further scope in the same field. There is need for the development of heterogeneous catalyst that could catalyze transesterification reaction without any leaching. Such catalysts may be prepared by modifying the catalyst preparation techniques as suggested below

1. The mixed oxides of transition metals and rare earth may be used as support for the impregnation of alkali metals.
2. Lithium is strongly basic in nature and due to it small atomic size it may be doped/supported/impregnated at interstitial/lattice/surface sites. Some defects may be created by doping alkali metal to generate super basic sites over suitable metallic support.
3. Mesoporous based materials may be further evaluated as these are efficient supports due to higher surface area, long range ordered structure and tuneable pore diameter.

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