NICKEL IMPREGNATED CALCIUM OXIDE AS A HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION FROM COTTON SEED OIL

A thesis submitted

in partial fulfilment of the requirement for the degree of

MASTER OF SCIENCE

IN

CHEMISTRY

Submitted By:

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Patiala

2014

CERTIFICATE

This is certify that the thesis entitled **"Nickel impregnated calcium oxide as a heterogeneous catalyst for biodiesel production from cotton seed oil "** being submitted in partial fulfilment of requirements for the award of degree of **Master of Science in Chemistry,** submitted in **the School of Chemistry and Biochemistry, Thapar University, Patiala** is a bonafide work carried out under the supervision of **Dr. Amjad Ali**, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and that no part of this project has been submitted for the award of any other degree.

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This is to certify that above statement made by the student concerned is correct and true to the best of my knowledge.

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CANDIDATE'S DECLARATION

I hereby declare that the work presented in the thesis entitled, **"Nickel impregnated calcium oxide as a heterogeneous catalyst for biodiesel production from cotton seed oil"** in partial fulfilment in the requirement for the award of Degree of **Master of Science in Chemistry**, submitted in the **School of Chemistry and Biochemistry, Thapar University, Patiala**, is an authentic record of my own work carried out under the supervision and guidance of **Dr. Amjad Ali**, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and refers other researcher's work which are duly listed in the reference section.

The matter embodied in this thesis has not formed the basis for the award of any other degree of this or any other university.

Date: July, 2014

Place: Patiala

(SIDHARTH SHARMA)

This is to certify that the above statement made by the student concerned is correct and true to the best of my knowledge.

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Life at Thapar University, Patiala has been enjoyable with friends like Gurpreet Singh. I thank them all for their great company.

In the end, I wish to express my deep sense of gratitude to my family, for supporting and encouraging me at every step of my work. It is power of their blessings, which has given me the courage, confidence and zeal for hard work.

Date: July, 2014

Regards,

Place: PATIALA

(SIDHARTH SHARMA)

INDEX

ABSTRACT

In present thesis, Ni impregnated CaO (Ni/CaO) was prepared in nano-crystalline form using a simple wet chemical impregnation method followed by calcination. The prepared catalyst was used for transesterification of triglycerides with methanol to yield Fatty acid methyl esters (FAME). The structural analysis of Ni/CaO was investigated by powder X-ray diffraction whereas the surface morphology was determined by scanning electron microscope study. The catalytic activity of prepared Ni/CaO catalyst towards the transesterification was found to be a function of its calcination temperature and basic strength. The catalyst prepared by impregnating 1.5-wt% Ni over CaO support followed by calcination at 600 ^{o}C was found to give > 99% FAME yield in 2.75 h under the optimized reaction condition of methanol to oil molar ratio of 12:1, 5 wt% catalyst, and at 65 ^{o}C reaction temperature. A pseudo first order kinetic model was applied to evaluate the kinetic parameters such as rate constant (k) and activation energy (E_a) for the transesterification of cotton seed oil.

Chapter 1

INTRODUCTION AND LITERTURE REVIEW

1.1 INTRODUCTION

Spiralling growth in consumption of petroleum oil throughout the world due to heavy industrialization has caused economic and environmental problems. Moreover, the fossil fuel sources are decreasing with a significant pace and we need to find a suitable substitute for the fossil based fuel. In this context, biodiesel (BD) has emerged as renewable and eco-friendly substitute for the fossil derived diesel fuel. There are four primary ways to produce biodiesel: direct use and blending of raw oils[1], micro-emulsions[2], thermal cracking[3] and transesterification. Chemically BD is a mixture of alkyl esters of fatty acids and at industrial scale it is derived from the transesterification of vegetable oils or animal fat (triglycerides) with short chain alcohols in presence of a catalyst as shown in Fig 1,

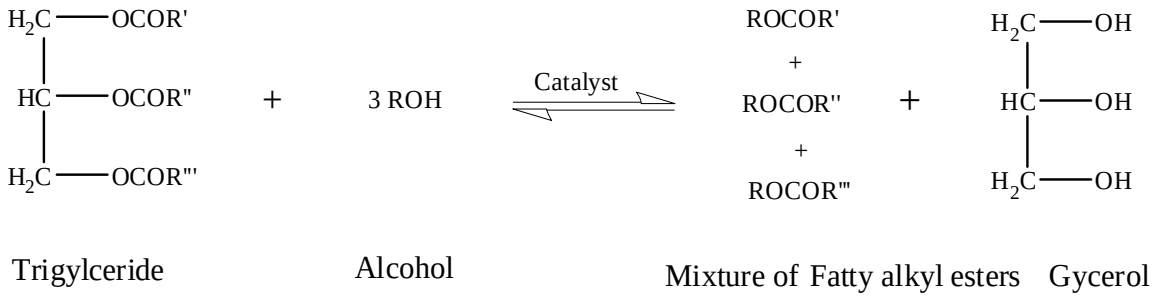

Fig.1. Transesterification of the vegetable oil.

Biodiesel has several advantages compared to petro-diesel fuel such as higher cetane numbers, higher flash point, better lubricating efficiency and ultra low sulfur concentration. Additionally, it is biodegradable and provides lower emissions of particulate matter, hydrocarbon and greenhouse gases such as CO, SO_x and CO_2 [4]. Biodiesel can be used either in pure form or in the form of blends with conventional diesel fuel in most modern diesel engines[5]. 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. Up to 20% (v/v) blend of biodiesel in conventional diesel fuel does not require any modification in present diesel engines.

1.2 LITERATURE REVIEW:

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[6] and required high temperature and pressure. The catalytic process may

involve biocatalysts (Lipase) and chemical catalysts. Usually, methanol is the preferred alcohol for producing biodiesel because of its low cost, ease of availability and high reactivity. The selection of the catalyst depends on the amount of free fatty acids (FFA) present in the oils. For oils having low FFA contents base catalysts (NaOH, KOH, $NaOCH_3$, $KOCH_3$, etc.) are preferred while for oils having higher FFA contents, acid catalysed (HCl, H_2SO_4, sulfonic acid, etc.) esterification followed by transesterification in presence of alkali catalyst is suitable.

1.2.1 HOMOGENEOUS CATALYST FOR TRANSESTERIFICATION

An industrial scale biodiesel production technology mainly utilizes homogenous alkali catalysts (NaOH, KOH, etc.,) for the transesterification reactions. The main advantage of using homogeneous alkali catalysts is their high activity even under ambient conditions, lower cost and readily availability. The mechanism of base-catalysed transesterification reaction is shown in Fig.2,

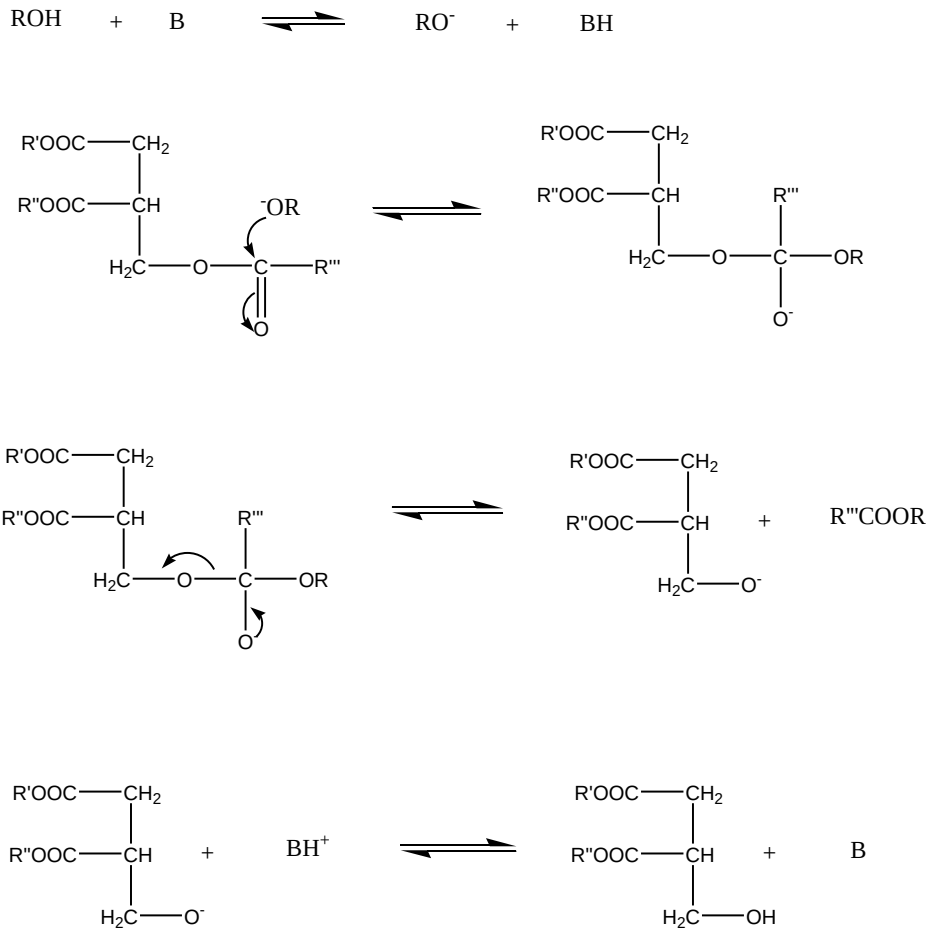

Fig.2. Mechanism of base-catalysed transesterification of vegetable oils.

However, these catalysts are highly sensitive to water (> 0.1 wt%) and/or FFA content (>0.6 wt%) present in feedstock. High water content leads to soap formation (Fig. 3), which reduces the ester yield and make the separation of glycerol from methyl ester difficult due to emulsion formation.

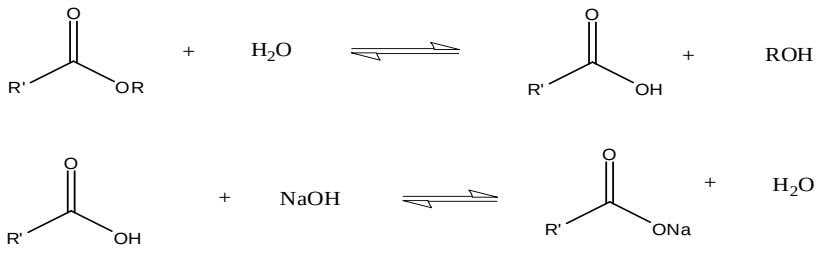

Fig.3. Saponification fatty acids in presence of alkali

The drawbacks of the homogenous alkali catalysts could be circumvented by using homogeneous acid catalysts like sulphuric acid, hydrochloric acid[7] . They generally require harsh conditions as compared to homogeneous base catalysts such as high reaction temperature, high methanol to oil molar ratio and longer reaction duration. Acid catalysts are mainly utilized if FFA contents in feedstock are present in relatively higher concentration. The mechanism[8] of acid catalysed transesterification reaction is shown in Fig.4.

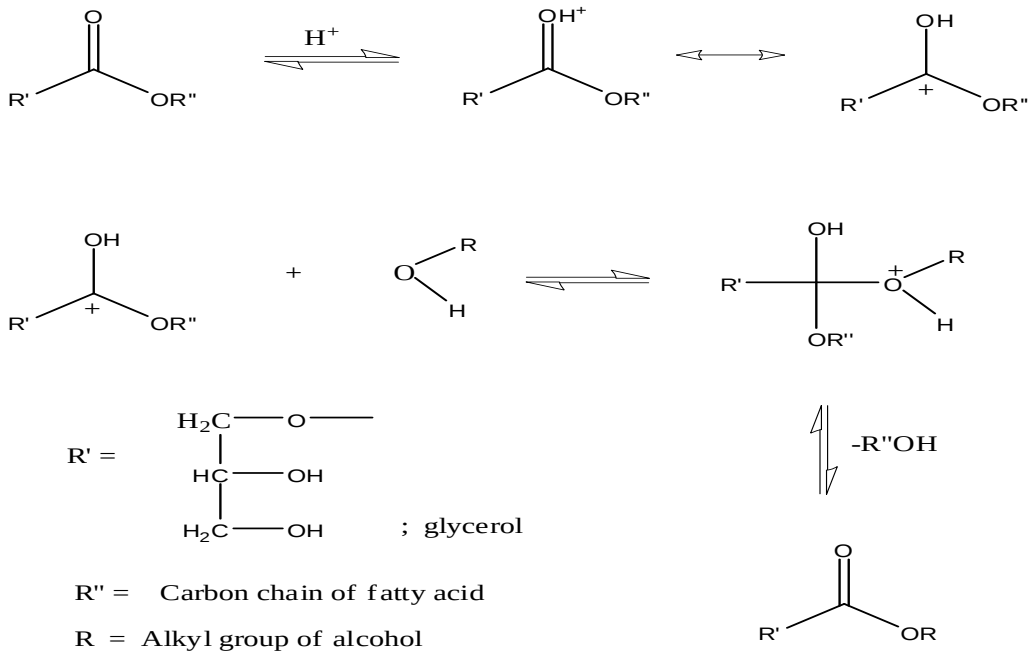

Fig.4. Mechanism of acid-catalysed transesterification of triglyceride.

The main problems with acids catalysts are their less reactivity and deactivation by the water, which is also a side product during the acid catalysed esterification reaction. Moreover, it causes the corrosion of the reactor and hence, costly acid resistance reaction vessel is required.

Both homogeneous acid and base catalysts must be neutralized after the completion of the reaction and removed from the products through water washing which generate huge amount of industrial effluents.

1.2.2 HETEROGENEOUS CATALYST FOR TRANSESTERIFICATION

In order to overcome the problems associated with homogeneous catalysts, research has been focused for the development of heterogeneous catalyst in recent past.

Heterogeneous catalysts have several advantages over homogeneous catalysts such as they could be recovered from the reaction mixture easily, reusable, and leads to the formation of non contaminated product and hence product washing id not necessary.

Several methods for the preparation of heterogeneous catalysts for the transesterification process are known. These methods include: calcination, hydrothermal synthesis, physical mixing, impregnation, and precipitation. To achieve high catalytic activity for transesterification reaction combination of these techniques has been used. But, the most commonly used combination for catalyst preparation for high catalytic activity of transesterification reaction is impregnation followed by calcination[41-43].

A variety of heterogeneous catalysts have been reported in literature for the transesterification reactions including calcium oxide[9], MgAZr[10], nano-magnetic KF/CaO-Fe_3O_4[11], modified CaO by trimethyl chlorosilane (TMCS)[12], and supported solid base catalyst such as Eu_2O_3/Al_2O_3[13], KI/Al_2O_3. Guo et al. investigated the use of sodium silicate as solid base catalysts for the transesterification to achieve 95% yield at optimum conditions of 3.0 wt% catalysts, 7.5:1 molar ratio of methanol to oil, 60 °C reaction temperature, 60 min reaction time, and 250 rpm mixing intensity.

French Institute of Petroleum (IFP) constructed a commercial biodiesel plant based on Esterfip-H technology which utilizes the mixed oxides of Zn and Al as a heterogeneous catalyst for the transesterification of triglycerides. This technology does not require catalyst recovery and biodiesel washing with water and yielded > 98% FAME yield. However, because of low catalytic activity under moderate reaction conditions, the catalyst demanded a high reaction temperature (200−250 °C) and high pressure to obtain high FAME yield.

Gryglewicz[14] reported that CaO is slightly soluble in methanol and form suspension in the reaction mixture due to its poor mechanical strength. The suspension causes the separation of catalyst from biodiesel, cumbersome. Therefore, supporting CaO onto carriers may improve the stability of CaO catalysts. ZnO and PbO are capable of catalyzing the simultaneous esterification and transesterification of high free fatty acid containing triglycerides. However, both the oxides may leach out in the reaction mixture. In recent works ZnO and PbO were immobilized over zeolite[15] support to use them as heterogeneous catalyst for transesterification of jatropha oil. Supported oxides yielded 93% conversion at 200^{o}C reaction temperature, using methanol to oil molar ratio of 30:1 in 1 h. These conditions are comparatively harsh than required by other solid basic catalysts. A comparison of transesterification activity of few literature reported heterogeneous catalysts is shown in Table 1.

Table.1. Different solid catalysts and their performances in biodiesel synthesis:

Catalyst	Vegetable oil	Reaction Temp (°C)	M:O	Catalyst amount (wt%)	Reaction Time (h)	FAME yield (%)	Ref
CaO	sunflower	252	41:1	5	0.25	99	16
MgO, MgO/Al_2O_3	soybean	180	12:1	5	1	92	17
Li/Al hydrotalcites	soybean	65	15:1	3	2	90	18
K_2CO_3/Al_2O_3	Triolein	65	25:1	6	1	94	19
KOH/sodium zeolite	soybean	65	10:1	3	8	85	20
basic ETS 10	soybean	100	6:1	10	3	92	20
Mg/MCM-41	soybean	220	8:1	5	5	96	21
KF/ZnO	soybean	65	10:1	5	9	87	22
PbO	soybean	215	7:1	-	2	89	23
La/zeolite	soybean	160	14.5:1	-	4	48.9	24
$CaTiO_3$, $CaMnO_3$	rapeseed	60	6:1	-	10	90	25
Zr/CaO	jatropha	65	15:1	5	-	99	26
Li/CaO	waste cottonseed	65	12:1	5	2.5	98	27
Zn/CaO	waste vegetable	65	9:1	5	0.75	99	28
K/CaO	waste cottonseed	65	12:1	7.5	-	98	29

M:O = Methanol to oil molar ratio; - = Not reported

The literature reported catalysts either required high methanol to oil ratio or high reaction temperatures and even long reaction durations. In order to develop a solid catalyst for the transesterification which could act under ambient conditions, following objectives were identified for the present project:

Objectives:

I. To prepare mixed metal oxide as heterogeneous catalyst for transesterification of triglyceride by chemical wet impregnation test.

II. To characterize the catalyst by SEM, XRD and Hammett indicators test.

III. To test the efficiency of the prepared catalyst for the transesterification reaction

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Materials

Cotton seed oil (CO) and Jatropha oil (JO) were purchased from local shops located in Patiala. Calcium oxide (CaO), $Ni(NO_3).6H_2O$, hexane, ethyl acetate and methanol (all chemicals are AR grade) were purchased from Merck, India and used without any further purification. Silica gel for thin layer chromatography (TLC) was obtained from Loba Chemie, India.

2.2 Methods

Powder X–ray diffraction (XRD) patterns were recorded on a PANalytical's X'Pert Pro using monochromatic Cu Kα radiation (λ=1.54060 Å) by scanning the samples over a 2θ range of 5–80°.

Field emission scanning electron microscopy coupled with energy dispersive X–ray spectrometry (FESEM–EDX) was performed on JEOL JSM 6510LV. Fourier transform–nuclear magnetic resonance (FT–NMR) spectra of FAAE and vegetable oils were recorded on a Bruker Avance–II (400 MHz) spectrophotometer.

The basic strength of the catalysts (pK_{BH+}) was obtained by using Hammett indicators. Approximately 25 mg of the catalyst was equilibrated with 5 mL Hammett indicators solution, prepared in methanol, for 2 hours. The Hammett indicators used were:

Neutral red (pK_{BH+}=6.8), bromthymol blue (pK_{BH+} =7.2), phenolphthalein (pK_{BH+}=9.3), Nile blue (pK_{BH+}=10.1), tropaeolin-O (pK_{BH+} =11.1), 2,4-dinitroaniline (pK_{BH+}15.0) and 4-nitroaniline (pK_{BH+} =18.4).

2.3 Catalyst preparation

The nanocrystalline Ni/CaO catalyst were prepared by wet chemical method. In a typical preparation, CaO (10 g) was suspended in 40 mL of deionized water. To this, 10 mL of an aqueous solution of nickel nitrate of a desired concentration was added. The concentration of the nickel nitrate was varied to obtain a 0.25 – 7 wt% Ni^{+2} concentrations in CaO. The slurry thus obtained was stirred for 3 h, then dried at 120°C for 12 hours in oven, and finally calcined in a muffle furnace in the temperature range of 150-950°C for 8 h. The catalyst thus prepared was labelled as x-Ni/CaO–T, where x and T represent the nickel concentration (wt%) and calcination temperature (°C), respectively.

2.4 Transesterification of Cotton seed oil

In a typical transesterification reaction, 100 mL of two-necked round bottom flask equipped with a water-cooled reflux condenser and oil bath was charged with 10 g oil, desired molar concentration of methanol and heated at a desired temperature. To monitor the progress of reaction, the sample from the reaction mixture was withdrawn after every 15 min with the help of a glass dropper and centrifuged to separate the catalyst from the supernatant. The liquid phase was diluted with hexane and subjected to TLC study using hexane/ethyl acetate (90:10, v/v) as mobile phase and silica gel as stationary phase. Biodiesel was identified by comparing its retention factor (R_f) with methyl oleate standard as shown in the Fig.1.

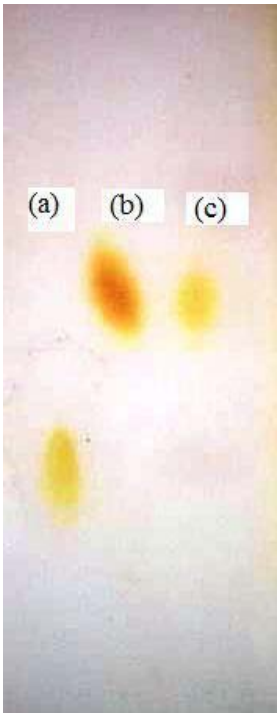

Fig.1. TLC analysis of (a) cotton seed oil (R_f = 0.4), (b) methyl oleate standard (R_f = 0.7) and (c) cotton seed oil derived FAME (R_f = 0.7).

Further, FAME was characterised and its yield was calculated by ^{1}H-NMR spectroscopy following the literature-reported[30] method as given below:

Percentage FAME yield (%) = $\{2I_{(methoxy)}/3I_{(methylene)}\} \times 100$

where $I_{(methoxy)}$ and $I_{(methylene)}$ are the area of methoxy (3.6 ppm) and methylene (2.33 ppm) protons respectively in ^{1}H-NMR spectra of FAMEs. An error of ±2% was observed when the FAME yield was quantified by this method.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Catalyst Characterization

3.1.1. Hammett indicator test

The basic strength (pK_{BH+}) of the pure CaO was found to be in the range of 9.8-10.1 and it was found to increase gradually from 9.8-10.1 to 11.1-15 as the concentration of Ni^{+2} in CaO was increased from 0.5 to 1.5 wt% (calcined at 600°C), as given in the table 2. A further increase in the Ni^{2+}concentration (up to 5 wt%) or calcination temperature (up to 800 °C) was not found to increase the basic strength of Ni/CaO. The enhancement of the catalyst basic strength is probably due to the formation of Lewis base sites (−O−) on the CaO surface upon Ni^{+2} doping followed by calcination. Table.1. shows the effect of Ni^{+2} concentration and calcinations temperature on the basic strength.

Table.1. Effect of the calcination temperature and Ni^{+2} concentration on the basic strength of Ni/CaO:

Catalyst type	Basic strength (pK_{BH+})
CaO	$9.8 < pK_{BH+} < 10.1$
1.5-Ni/CaO-350	$9.8 < pK_{BH+} < 10.1$
1.5-Ni/CaO-500	$9.8 < pK_{BH+} < 10.1$
1.5-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
1.5-Ni/CaO-700	$11.1 < pK_{BH+} < 15.0$
1.5-Ni/CaO-800	$11.1 < pK_{BH+} < 15.0$
0.5-Ni/CaO-600	$9.8 < pK_{BH+} < 10.1$
1.0-Ni/CaO-600	$9.8 < pK_{BH+} < 10.1$
1.5-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
2.0-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
2.5-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
3.0-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
3.5-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$
4.0-Ni/CaO-600	$11.1 < pK_{BH+} < 15.0$

3.1.2. X-Ray diffraction study (XRD)

Powder X-ray studies of Ni^{+2} impregnated (0.5-4%) CaO have been performed and comparisons of XRD patterns are given in the Fig.1. The CaO exhibited the characteristic

reflections of calcium oxide cubic form (JCPDS 821691). The XRD of Ni/CaO shows typical diffraction patterns of CaO in the cubic phase, and no distinct peak corresponding to the NiO phase was observed. This supports the formation of a homogenous solid solution of NiO in CaO.

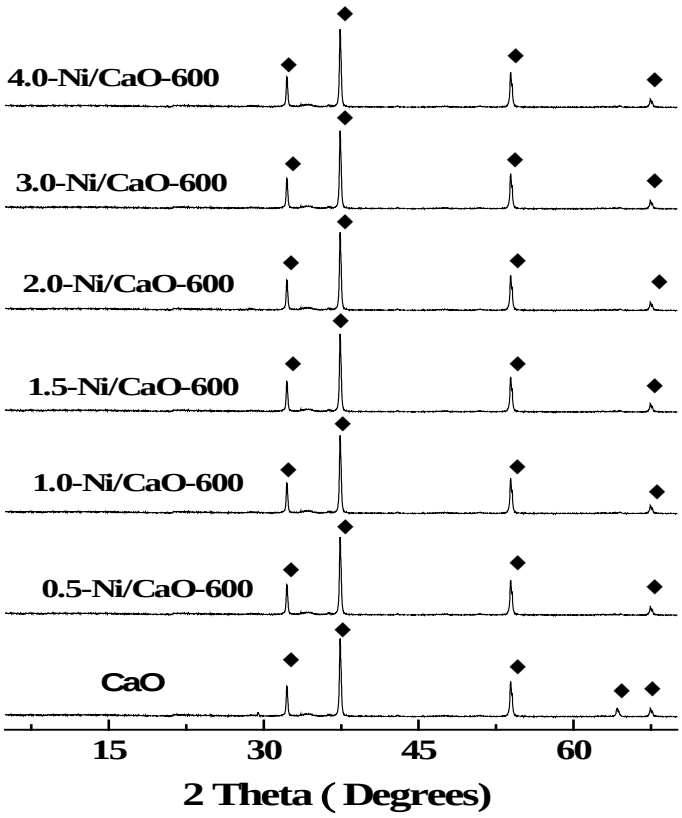

Fig.1. Comparative powder XRD patterns of CaO and Ni/CaO with a varying Ni^{2+} concentration (0.5−4 wt%)(♦ = calcium oxide)

To study the effect of the calcination temperature on the Ni/CaO structure, 1.5 wt% Ni^{2+}doped CaO has been calcined in the range of 350−800 °C temperature, and XRD patterns of the same are compared in Fig.2. The XRD patterns of Ni/CaO calcined up to 500 °C supported the formation of hexagonal $Ca(OH)_2$ as a major phase (JCPDS 841275) and CaO as a minor phase. A further increase in the calcinations temperature (≥ 600 °C) leads to the formation of a single CaO cubic phase (JCPDS 821691) due to the condensation of $Ca(OH)_2$. Similar XRD patterns were observed for Ni/CaO calcined up to 800 °C to indicate that an increase in the calcination temperature (from 600 to 800 °C) has not initiated any chemical or structural change in Ni/CaO.

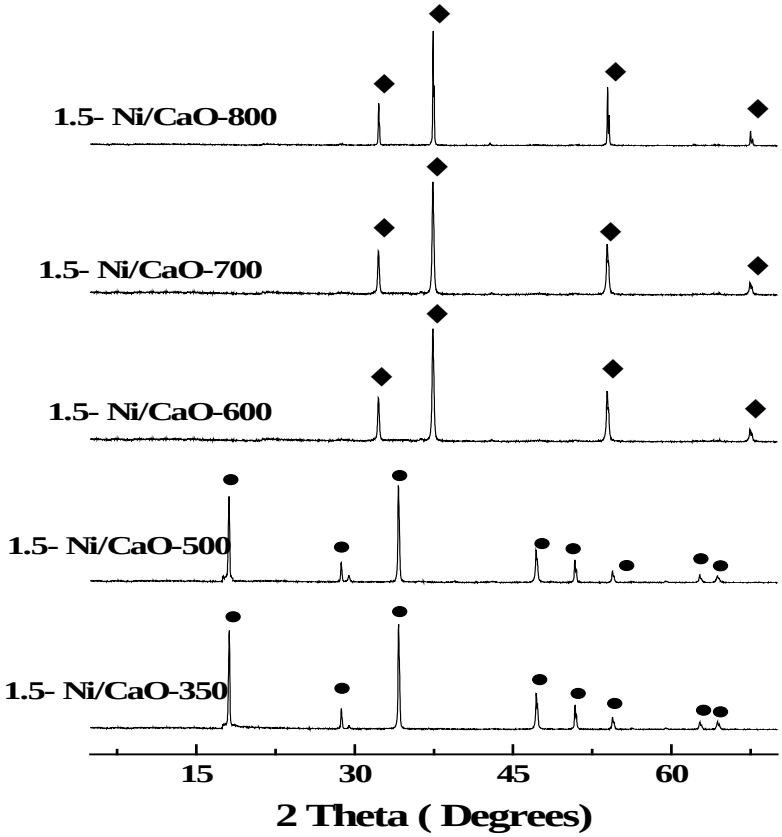

Fig.2. Powder XRD patterns of Ni/CaO, calcined in the temperature range of 350−800 °C.(•, calcium hydroxide ; ♦, calcium oxide).

3.1.3. SEM-EDS study:

The size, shape, and morphology of the Ni/CaO particles were observed by SEM, and the same study reveals that 1.5-Ni/CaO-600 exists as clusters of irregular-shaped particles of 2-5 μm size, as shown in Fig.3.

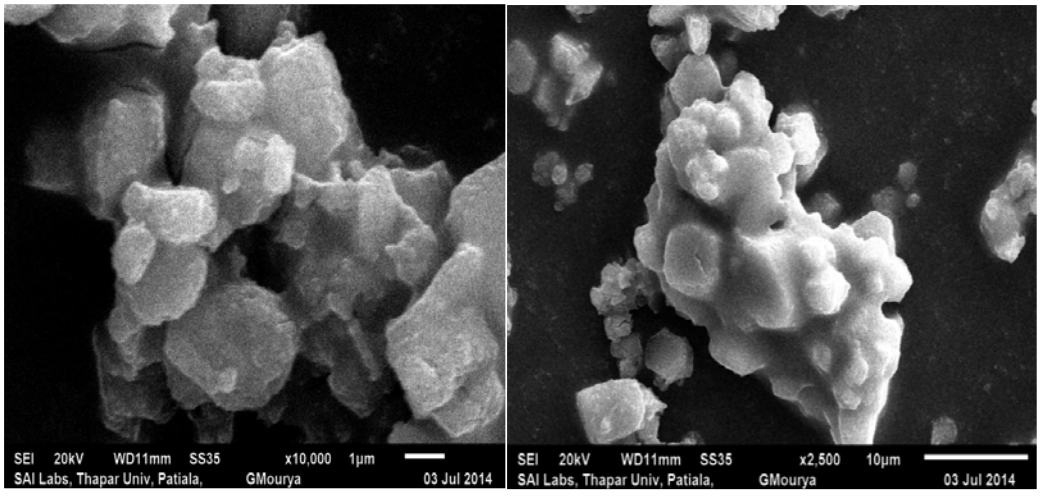

Fig.3. SEM images of 1.5-Ni/CaO-600.

Qualitative analysis of 1.5-Ni/CaO-600 by EDX study supports the presence of 1.2 wt% Ni^{+2} as shown in Fig.4.

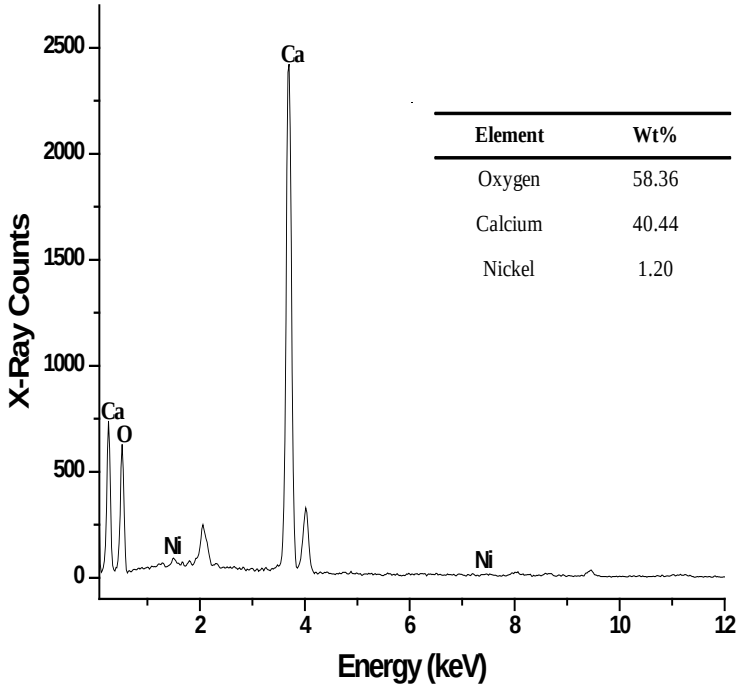

Fig.4. EDS image of 1.5-Ni/CaO-600.

3.2 Biodiesel Characterization:

Proton NMR technique is not only non-destructive but also did not require complicated derivatization and sample preparation procedure for the quantification of products. Moreover, this technique could also be used for the structural elucidation of the product molecule. Hence, in present work ^{1}H NMR technique is employed for the FAME quantification and characterization. The ^{1}H NMR spectrum of CO shows the characteristic glyceridic proton signals at 4.15–4.35 ppm, as shown in Fig.5. On transesterification, same peaks were no longer found in the proton NMR spectrum of FAME (Fig.5). Moreover, the formation of FAME was further supported due to the appearance of new peaks at 3.6 ppm (singlet).

In ^{13}C-NMR spectrum of CO, signals due to glyceridic carbon appear at 62.2 and 69.0 ppm, as shown in Fig. 6. The formation of FAME could also be supported due to the appearance of peaks at 51.4 due to -OCH_3 carbons. Further, peaks corresponding to the glyceridic carbons were no longer found in the ^{13}C NMR spectrum of FAME.

Fig.5. ^{1}H-NMR of (a) cotton seed oil and (b) cotton seed oil derived FAME.

Fig.6. ^{13}C-NMR of (a) cotton seed oil and (b) cotton seed oil derived FAME.

3.3 Catalytic Activity

To optimize the reaction conditions for the optimum catalytic activity, transesterification reactions have been carried out at a fixed stirring speed of 500 rpm by varying one parameter at a time out of the following: (i) Ni^{+2} concentration in CaO (ii) calcination temperature of the catalyst (iii) catalyst amount with respect to oil (iv) methanol/oil molar ratio (v) reaction temperature, and (vi) amount of FFA and moisture contents present in feedstock. The reusability of the catalyst was also studied.

3.3.1 Effect of the impregnated Ni^{+2} concentrations in CaO

To determine the optimum amount of nickel impregnation on CaO, a series of catalysts by varying the amount of nickel ion from 0.5 to 4.0 wt% in CaO were prepared. The transesterification of cotton seed oil was performed with methanol to oil molar ratio of 12:1 at 65°C in the presence of 5 wt% of the prepared catalysts and for reaction duration of 2.75 h. Fig.7.suggest that up to 1.5 wt% increase in the Ni^{+2} concentration was found to enhance the activity of the Ni/CaO catalyst. However, a further increase in the Ni^{+2} concentration has not influenced activity of Ni/CaO on transesterification of cotton seed oil.

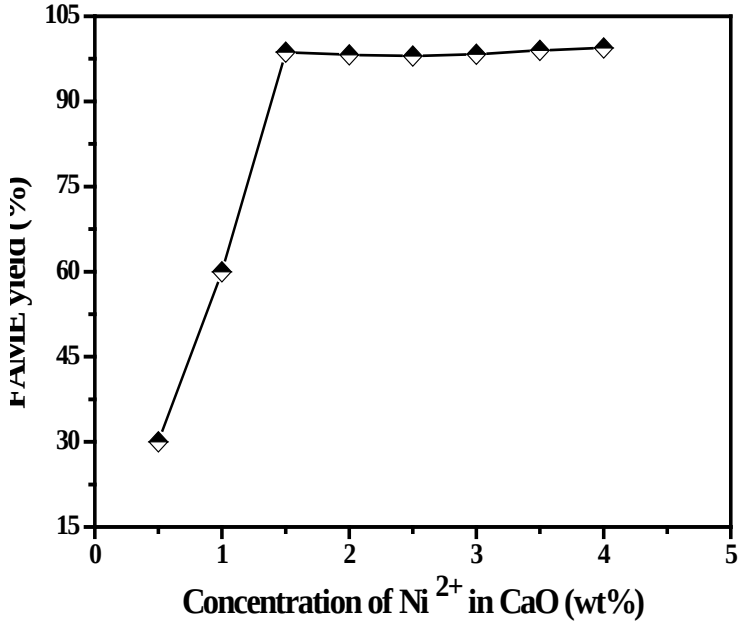

Fig.7. Effect of Ni^{+2} concentration in CaO on the FAME (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.3.2 Effect of the calcination temperature

To determine the optimum calcination temperature for the better catalytic activity, a series of catalysts was prepared by calcining 1.5 wt% Ni^{+2}-impregnated CaO in the temperature range of 200 – 800 °C. The transesterification reaction of cotton seed oil was carried out at 12:1 molar ratio of methanol to oil, 5 wt% catalyst amount and 65°C for reaction time of 2.75 hours. The FAME yield was found to increase from to 35% to 99% (±2%) as the calcination temperature of Ni/CaO was increased from 200 to 600°C. It reached maximum at 600°C and then decreases on further increasing the calcination temperature beyond 600°C as shown in Fig.8.

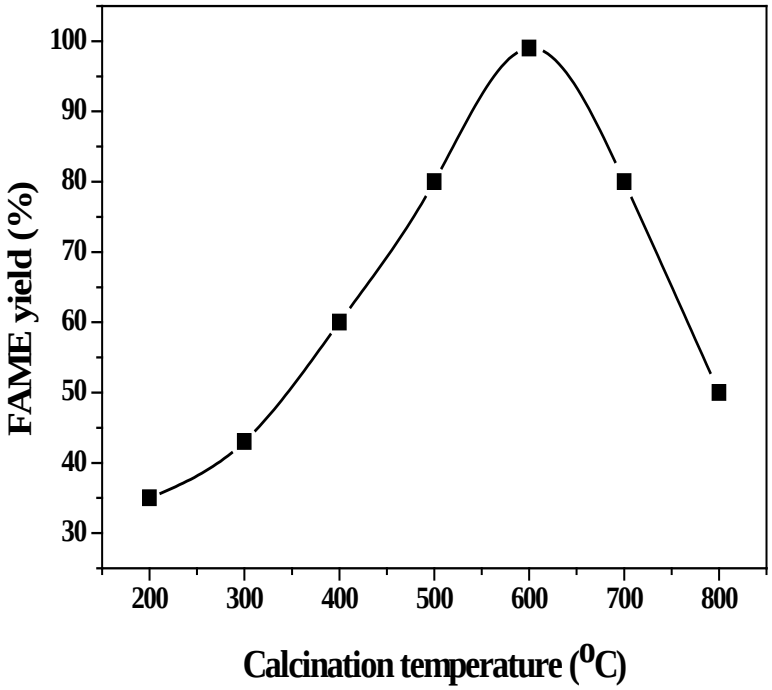

Fig.8. Effect of the calcination temperature on the FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.3.3. Effect of the Catalyst Amount

To find the optimum catalyst concentration, a series of transesterification reactions of Cotton seed oil (CO) with methanol (1:12 molar ratio) were performed in the presence of 1−10 wt% (with respect to oil) of 1.5-Ni/CaO-600 for 2.75 hours. The FAME yield was found to increase as the catalyst concentration was increased from 1 to 5 wt%. But, further increase in the catalyst loading (≥5 wt%) was not found to change the FAME yield significantly as

shown in Fig.9. This could be due to the fact that at higher catalyst loading reaction mixture becomes more viscous which could resist the mass transfer in the liquid–liquid–solid system[31].

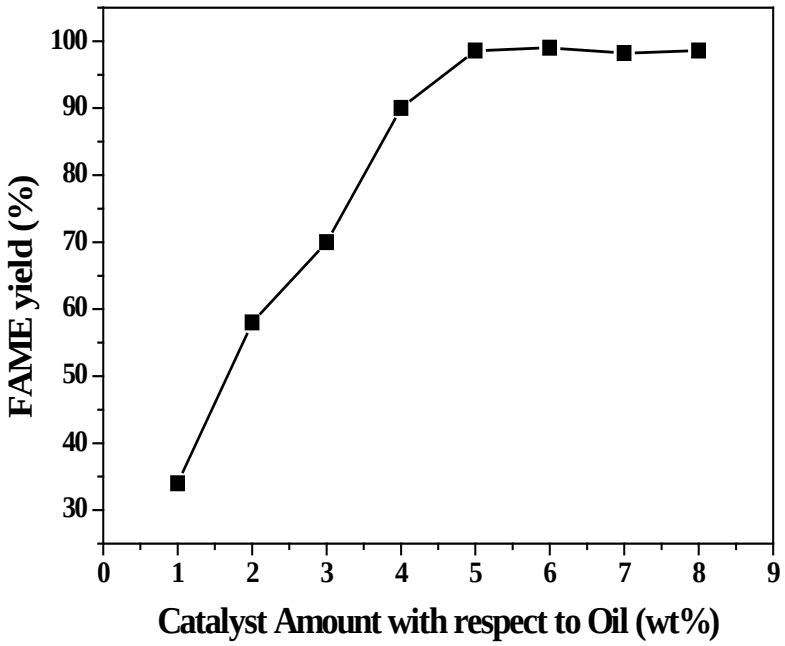

Fig.9. Effect of the catalyst amount with respect to oil on the FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.3.4. Effect of Methanol to Oil Molar Ratio

The effect of the methanol/oil molar ratio on the transesterification reaction is an important parameter which affects the FAME yield as well as cost of biodiesel production. The theoretical minimum methanol to oil molar ratio should be 3:1 for the complete conversion of oils to FAME. However, transesterification being a reversible reaction usually performed with excess of methanol to shift the equilibrium in forward direction to achieve maximum FAME yield[32]. Heterogeneous catalysts usually catalysed the transesterification reaction at a slower rate and required longer reaction duration for the completion of reaction. The use of higher molar ratios of methanol/oil (*viz*. 15:1, 40:1 and 275:1) in presence of heterogeneous catalysts to improve the FAME yield in less time have been reported frequently in the literature ZnO/zeolite and PbO/zeolite[15] catalyzed transesterification of jatropha oil using 30:1 alcohol to oil ratio at 200°C and 4 wt% catalyst to achieve 90% FAME yield. To

determine the optimum methanol/oil molar ratio for 1.5-Ni/CaO-600 catalyst, the reactions were performed by varying the methanol/oil molar ratio from 3:1 to 18:1 for 2.75 hours at 65°C. The FAME yield increases from 25 to 99% on increasing methanol/oil molar ratio from 3:1 to 12:1, and a further increase in molar ratio was not found to influence the FAME yield significantly as shown in Fig.10.

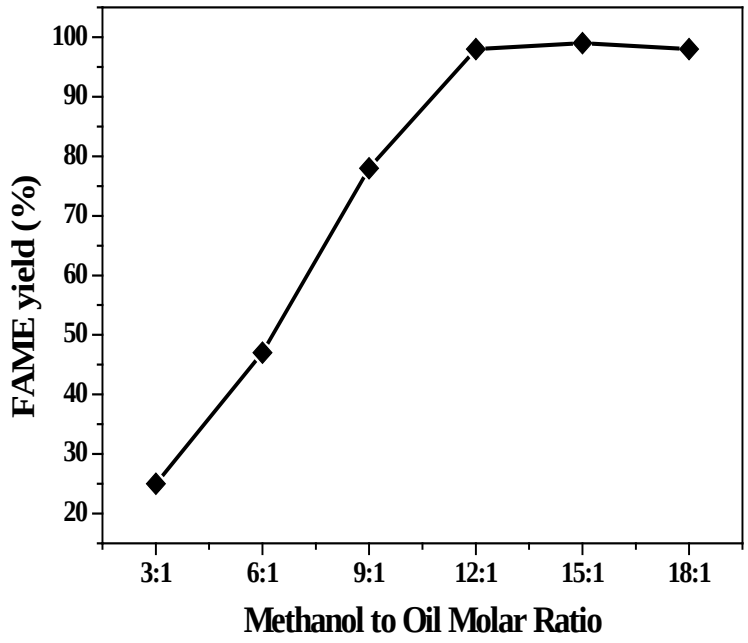

Fig.10. Effect of methanol to oil molar ratio on the FAME yield (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.3.5. Effect of reaction 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. To optimize the reaction temperature, the transesterification reaction of cotton seed oil with methanol to oil ratio of 12:1, 5 wt% of 1.5-Ni/CaO-600°C was carried out at different temperature. The FAME yield was found to increase regularly as the reaction temperature was increased from 35 to 65°C and a further increase in the reaction temperature was not found to influence the FAME yield significantly as shown in Fig.11. Although the catalyst was found to be more effective at 65°C, however, even at the room temperature (35 °C), > 98% conversion of CO into corresponding FAMEs was achieved in 6.5 h of reaction duration.

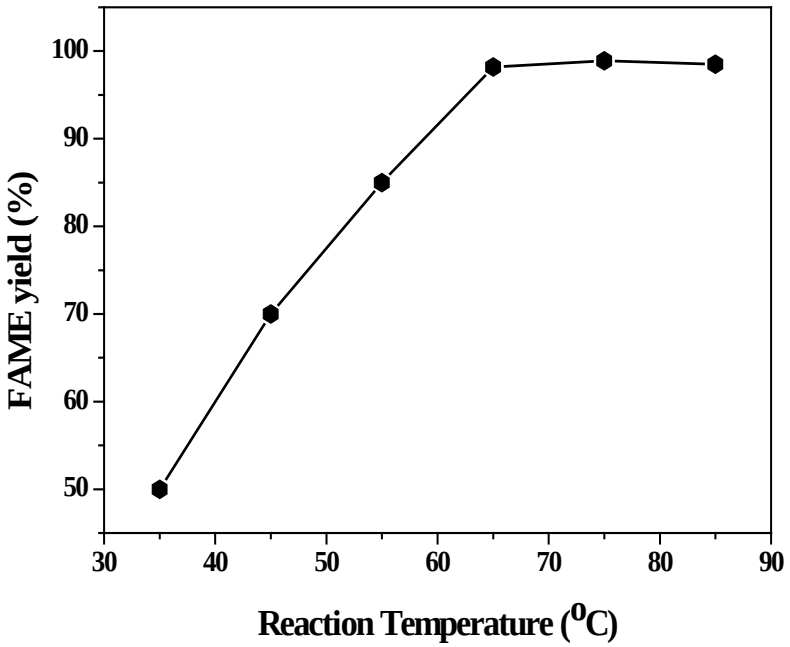

Fig.11. Effect of reaction temperature on FAME yield catalyst (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

Thus, a 12:1 methanol to oil molar ratio at 65 °C in the presence of 5 wt% catalyst (with respect to oil), was found to be an optimum condition for the 1.5-Ni/CaO-600 catalyzed transesterification of CO.

3.3.6. Effect of the Moisture and FFA Contents on the Catalytic Activity:

Presence of > 0.1 wt% moisture contents in reaction mixture was found to deactivate the homogeneous alkali and acid catalysts. Heterogeneous catalysts, due to immobilized active sites, are expected to demonstrate higher moisture resistance. To prove the moisture resistance of Ni/CaO catalyst, the transesterification reactions of CO were performed by adding up to 6 wt% (water/oil) water in the reaction mixture. As shown in Fig.12, the catalyst was found to be effective for the transesterification of CO, even in presence of 5 wt% moisture contents. A further increase in moisture contents (> 5 wt%) in the reaction mixture, results in a high degree of catalyst deactivation, which could be due to the reaction between water and catalyst support (CaO) to yield the conversion of stronger Lewis basic (-O-) sites into weaker Bronsted basic (-OH) sites[33].

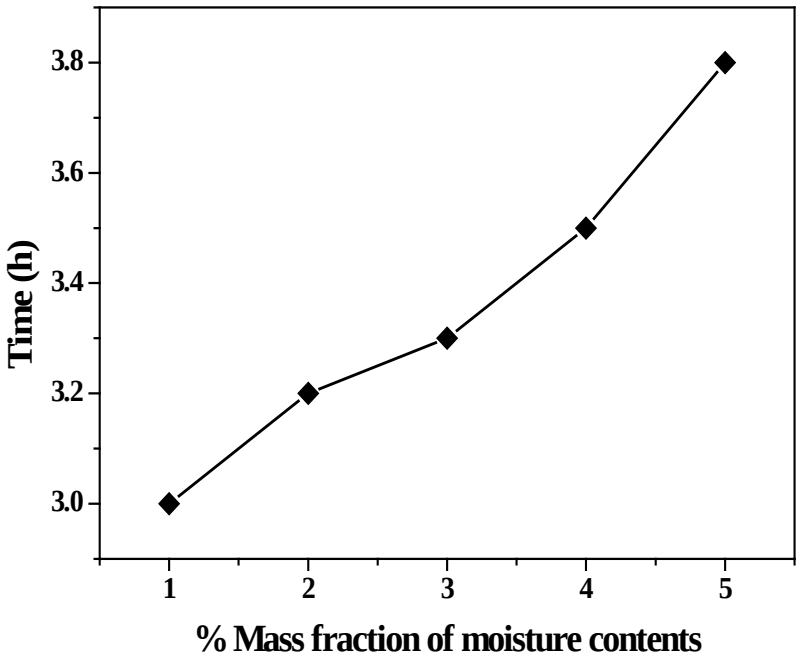

Fig.12. Effect of the moisture contents on the activity of Ni/CaO catalyst (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

Free fatty acids, present in feedstock, can deactivate the alkali catalyst by forming the soap. Hence, homogeneous alkali catalysts must require FFA free refined oil for the transesterification reaction. To determine the maximum FFA tolerance of Ni/CaO, transesterification reactions of CO, WO and JO (having 0.4−8 wt% FFA) were performed with methanol. Fig.13, shows that the catalyst was able to complete the transesterification of oil having up to 8 wt% FFA. Moreover, the catalyst activity was not found to be affected as long as the FFA concentration in feedstock remains below 1.8 wt%. An increase in FFA was found to reduce the catalytic activity, as depicted by the more time requirement for the complete conversion of KO to corresponding FAMEs.

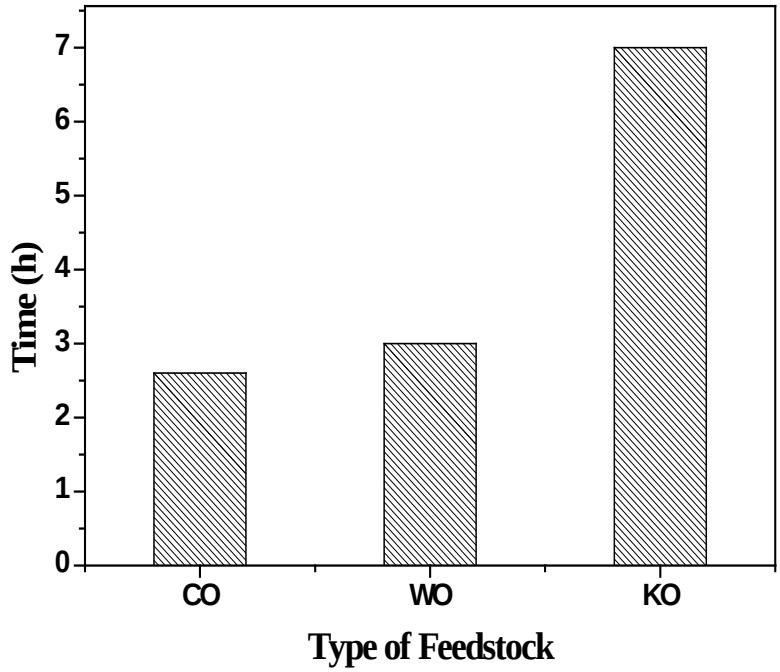

Fig.13. Effect of FFA on Ni/CaO catalyzed transesterification (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.3.7 Reusability Study:

The reusability of the heterogeneous catalyst is an important advantage over the homogeneous catalyst because it could reduce the overall processing cost of the reaction. To test the reusability of 1.5-Ni/CaO, transesterification of the CO was performed with methanol under optimized reaction conditions. After the completion of the reaction, Ni/CaO was recovered from the reaction mixture by filtration, washed with hexane, and calcined at 600 °C. The catalyst hence recovered and regenerated was employed for 5 successive catalytic cycles under the same experimental and regeneration methods. As shown in Fig.14. the reused catalyst was also found to yield > 99% FAME yield in four successive catalytic runs. However, after the fifth cycle, partial conversion was achieved even after 8 h of reaction period.

The gradual loss of the catalytic activity could be due to (i) the blockage of active sites because of the adsorbed organic molecule, and/or (ii) the partial leaching of the active species from the catalyst.

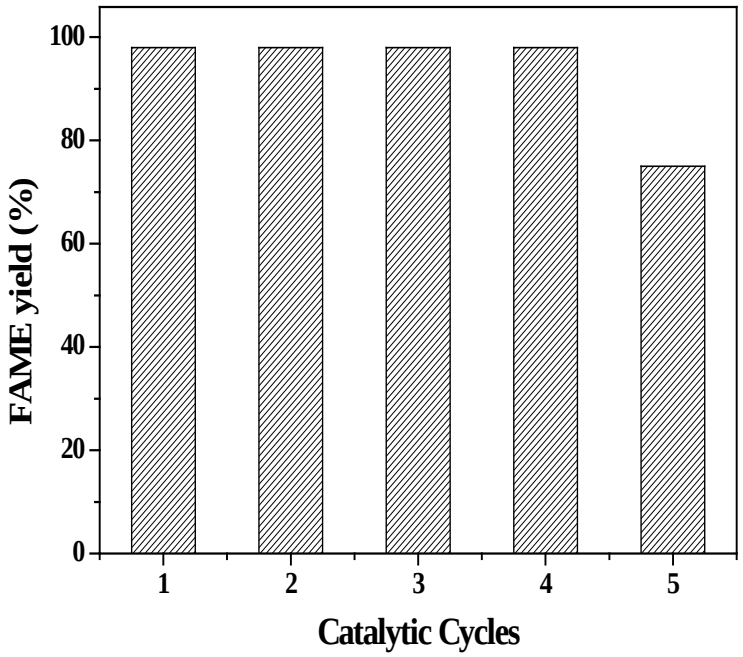

Fig.14 Reusability studies of 1.5‑Ni/CaO‑600 catalyst transesterification of CO (reaction conditions: methanol/CO molar ratio, 12:1; catalyst amount, 5 wt% of oil; temperature, 65 °C; and reaction duration, 2.75 hours).

3.4 Kinetic Study:

The transesterification of triglycerides in the presence of excess methanol has been reported to follow a pseudo-first-order kinetic model[34] as given in equation 1.

$$-\ln(1 - X_{me}) = kt \quad (1)$$

,where X_{me} is the fraction of FAME content at time t (min). The kinetics of the 1.5-Ni/CaO-600 catalyzed transesterification of CO has been studied at a 12:1 methanol/oil molar ratio in the temperature range of 35−65 °C. Fig.15, shows the linear nature of $-\ln(1 - X_{me})$ versus t(time) plots to maintain that the Ni/CaO-catalyzed reaction has followed pseudo-first-order kinetics.

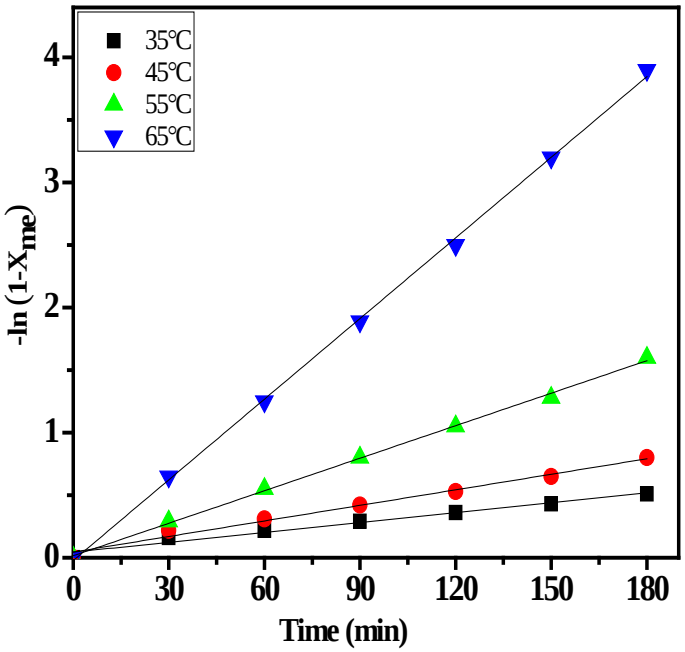

Fig.20. Plot of $-\ln(1-X_{me})$ versus kt at different reaction temperatures for the 1.5-Ni/CaO-6000-catalyzed transesterification of CO.

The rate constants were calculated from these plots and found to be 0.022, 0.087, 0.0041 and 0.00026 min^{-1} at 65, 55, 45, and 35°C, respectively. The Arrhenius model was employed to estimate the activation energy (E_a) and pre-exponential factor (A) by following the equation 2.

$$\ln k = -E_a/RT + \ln A \qquad (2)$$

where R is the gas constant (8.31 J $K^{-1}mol^{-1}$) and T is the reaction temperature in Kelvin.

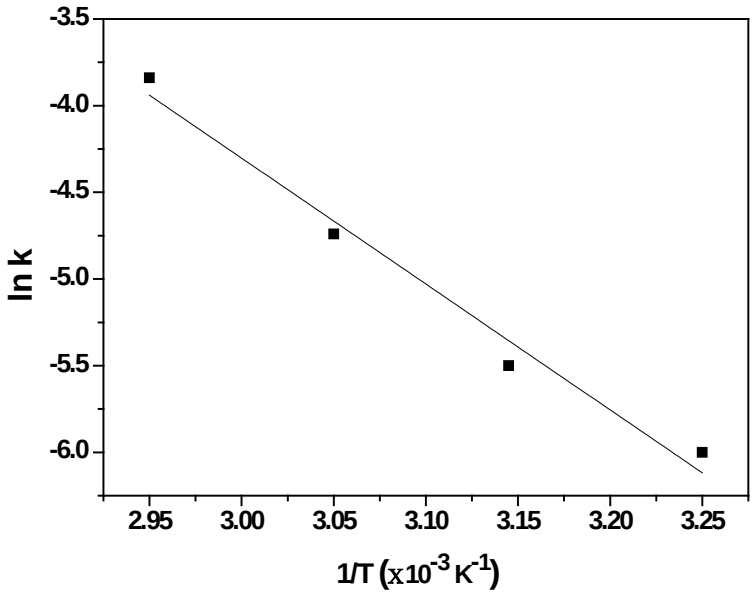

Fig.16. The Arrhenius plot for 1.5-Ni/CaO-600 catalyzed transesterification of cotton seed oil with methanol.

The values of E_a and A, calculated from 1/T versus ln k plot in Fig.16, were found to be 60.4 kJ $mol^{-1}$and 3.9 x $10^7 min^{-1}$, respectively. The calculated activation energy ($kJmol^{-1}$) for the CO transesterification was found within the range of reported values (26−84 $kJmol^{-1}$) for the transesterification of various vegetable oils[35-39].

CHAPTER 4

CONCLUSION

5. Conclusion:

The catalyst, 1.5-Ni/CaO-600, has been prepared by a wet chemical method in nanocrystalline form as revealed by TEM and powder XRD studies. The same catalyst was found to have the highest basic strength among the prepared catalysts, as supported by the Hammett indicator analysis. The Ni/CaO nanocatalyst was found to be efficient even at room temperature (35 °C) for complete transesterification reactions of triglycerides with methanol. The optimized conditions are methanol/oil molar ratio, 12:1; catalyst concentration, 5 wt%; reaction temperature, 65 ° C; and reaction duration of 2.75 hours. Under optimized reaction conditions, Ni/CaO catalyzed transesterification of CO was found to follow pseudo-first-order kinetics, and the apparent first-order rate constant and activation energy for the same reaction were found to be 0.0215min^{-1} (at 65 °C) and 60.4 kJ mol^{-1},respectively. Further, the catalyst could be employed for 4 catalytic cycles without significant loss in activity. The catalyst was found to be effective even for the transesterification of low quality feedstock having up to 5 wt% moisture and 8 wt% FFA contents.

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