NJC

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

One step synthesis of fatty acid diethanolamides and methyl esters from triglycerides using sodium doped calcium hydroxide as nanocrystalline heterogeneous catalyst

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Here, we report the preparation of a series of Na+ doped Ca(OH)2 in nanocrystalline form using very simple method, and investigation of their catalytic activities towards one step aminolysis and transesterification of used cottonseed oil. The catalyst prepared by doping 3.5 wt% Na in Ca(OH)2 was found to exist in nanocrystalline form (particle size = 25-30 nm) as suggested by TEM and powder XRD studies and found to have the basic strength of 15.0<H_<18.4 as supported by Hammett indicators test. Na/Ca(OH)2 was used as solid catalyst towards the aminolysis and transesterification of used cotton seed oil with diethanolamine and methanol, respectively. The catalyst was found to complete the aminolysis and transesterification of variety of feedstocks even at room temperature and show excellent reusability.

Introduction

In the development of viable green chemistry, renewable raw materials are going to play a significant role. In chemical industry renewable raw materials viz., vegetable oils and fat share the great proportion of the current consumption[1]. Vegetable oil derivatives have numerous benefits viz.; they are atoxic, biodegradable and environment friendly. These derivatives have potential industrial applications such as the fatty acid methyl esters commonly known as biodiesel, is a nontoxic, biodegradable, eco-friendly and renewable substitute for conventional fossil fuel[2] and fatty acid amides attract attention due to their biological activities and industrial application in surfactants, lubricants, cosmetics, shampoos, foam control agents, fungicides, corrosion inhibitors, water repellents, detergents and anti–blocking agents in the plastics processing industry.[3-5] Owing to their low reactivity and thermal properties they are used for the preparation of anti-slip and anti-block additives in polyethylene films and as flow improvers.[6] Fatty acid amides also enhance the ignition quality and characteristics of the fuel. The amide biodiesel should be considered as a good candidate to incorporate to the conventional fuels as it increases the cetane number of the fuel.[7, 8]

On the other hand due to their industrial applications, fatty acid amides produced in thousands of metric tons a year from fatty acids by reaction with anhydrous ammonia at approximately 200 °C and 345–690 kPa.[9] Fatty amides can be synthesized from fatty acids or their esters through treatments with amine compounds.[10, 11] Enzyme catalyzed synthesis of amides from the fatty acids or their esters has also been reported.[9, 12-14] Triglycerides can be converted into their fatty amides via amidation using ammonia or amine compounds.[15, 16] The fatty acid amides were synthesized from palm oil using sodium ethoxide as a homogeneous catalyst in the presence of ethanol at 78 °C for 8 h.[17] The aminolysis of *n*-butylamine and methyl stearate was performed using sodium methoxide as homogeneous catalyst.[18] Another method of preparation of fatty acid amides is based on the reaction of fatty acid with ethylenediamine at 180-185 °C under nitrogen and with continuous removal of water. However, high temperature causes self-condensation of diethylamine that results to form *N*,*N*'-bis(2-hydroxyethyl) piperazine or morpholine instead of amide derivative.[19, 20]

The preparation processes for fatty amides utilize the high temperature and pressure or homogeneous catalysts which contaminate the product and required to be washed out from the product. Thus, the whole process become tedious, lengthy and requires large amounts of water and energy. So, the heterogeneous catalyst could be the attractive alternative for such type of reactions due to reusability and easy separation from reaction mixture by simple filtration.

Low cost, ease of availability and non–toxicity made calcium oxide as desired choice for preparation of heterogeneous catalyst.[21, 22] Our research group has previously reported calcium oxide based heterogeneous catalysts for transesterification reaction of vegetable oils.[23, 24] But the application of heterogeneous catalysts in the aminolysis reaction of triglycerides has not been explored yet significantly. There are very rare reports available in literature using heterogeneous catalysts for the aminolysis of vegetable oils. Recently, $ZnO.La_2CO_5.LaOOH$ was reported as heterogeneous catalyst for complete aminolysis (100% conversion) of triglycerides using ethanolamides though need long time duration (8 hrs) for the completion of reaction.[25]

Thus, objective of the present work is to prepare a reusable heterogeneous catalyst that could be effective for the single step aminolysis of low quality triglycerides with short reaction time. Present work demonstrated preparation of Na^+ doped $Ca(OH)_2$ in nano-particle form using very simple chemical method and used as heterogeneous catalyst for the aminolysis and transesterification of used cotton seed oil with diethanolamine (DEA) and methanol, respectively. To the best of our knowledge, there is no reported work available in literature dealing with the preparation of Na doped $Ca(OH)_2$ as heterogeneous catalyst for the aminolysis of triglycerides.

Experimental Section

Materials and methods

Sodium nitrate, calcium oxide, methanol (99.8%) and diethanolamine (99.8%) used in the present study was obtained from Merck, India. The mutton fat, virgin cotton seed, soybean, castor, karanja and jatropha oil were procured from the local shops located at Patiala. Used cotton seed oil was collected from the restaurants located at Patiala. Methyl laurate (>98%) was purchased from Sigma-Aldrich, USA.

The free fatty acids (FFAs) value, saponification, and the iodine value of the mutton fat, soybean, virgin cotton seed, used cottonseed seed, castor, karanja and jatropha oil were determined by following the methods as reported in literature[24] and the moisture content was determined by the Karl Fisher titrimetric method (Table 1).

Table 1 The chemical analysis of vegetable oils used as feedstock in present study.

S. No.	Feedstock	Free fatty acid value (wt%)	Moisture content (wt%)	Saponification value (mg KOH/g)	Iodine value
1.	Used cotton seed oil	1.8	0.36	190.3	101.3
2.	Karanja oil	4.2	0.35	184	96.6
3.	Jatropha oil	8.4	0.38	195.2	101.3
4.	Virgin cotton seed oil	0.1	0.31	188.4	102.4
5.	Soybean oil	0.2	0.27	189.6	125.1
6.	Mutton fat	0.9	0.32	192.1	46.3
7.	Castor oil	2.0	0.34	180.2	90.5

Sodium ion concentrations in $Ca(OH)_2$ were determined by Systronics mediflame 127 flame photometer. The structural analysis was performed by X-ray diffraction (Rigaku D/MAX 2500 Tokyo, Japan). The surface areas of the catalyst were determined by using the adsorption/desorption method at 77 K by the standard Brunauer-Emmett-Teller (BET) method using Micromerities ASAP 2100 equipment. All samples were degassed at 473 K for 90 min under nitrogen atmosphere to remove the physisorbed moisture from the catalysts. The basic strengths of the catalysts (H_) were determined by Hammett indicators [24]. FTIR spectra of triglycerides, biodiesel and corresponding amide derivative have been recorded on Jasco FTIR-4200 spectrophotometer. Field emission scanning electron microscopy (FE-SEM) was performed on Hitachi SU-70 and transmission electron microscopy (TEM) were performed on H-7650, Hitachi to record TEM images. Particle size distribution of CaO and sodium doped $Ca(OH)_2$ were obtained with particle size analyzer (90-Plus, Brookhaven Instruments Corporation, USA). Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of biodiesel and vegetable oil were recorded on a Bruker Avance-II (400 MHz) spectrophotometer. Mass spectra of methyl laurate and amide derivative of methyl laurate were recorded on a Waters Micromass Q-ToF Micro mass spectrophotometer equipped with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APcI) sources having mass range of 4000 amu in quadruple and 20000 amu in ToF.

Preparation of catalyst

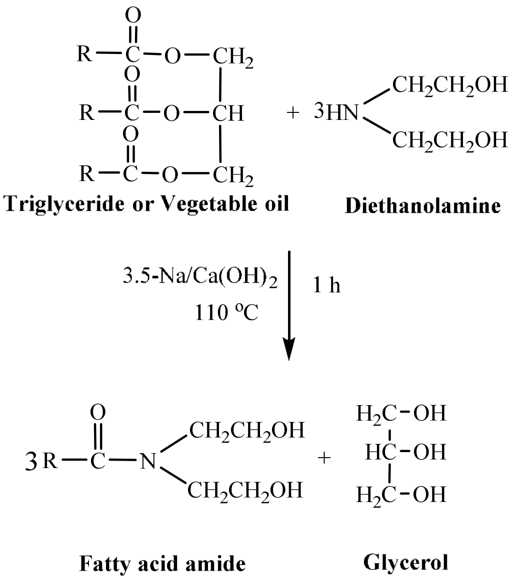
The nanocrystalline sodium metal ion doped calcium hydroxide was prepared by the chemical method. In a typical preparation, CaO (10 g) was suspended in 40 mL ethanol and to this 10 mL alcoholic solution of sodium nitrate of desired concentration was added. The concentrations of the sodium nitrate were varied to obtain Na^+ loading in the range of 1.5-5.5 wt% in CaO. The slurry was stirred for 3 h, then evaporated to dryness and heated at 200 °C for 24 h. The solid thus obtained was characterized by flame photometer, powder XRD, BET surface area measurement, Hammett indicator test, FE-SEM, DLS and TEM techniques.

The prepared catalysts were designated as *xx*-Na/Ca$(OH)_2$, where *xx* represents the sodium concentration (wt %) in Ca$(OH)_2$, e.g. 3.5-Na/Ca$(OH)_2$ represent the catalyst prepared by doping 3.5 wt% of Na^+ (using $NaNO_3$) in Ca$(OH)_2$.

Aminolysis reactions

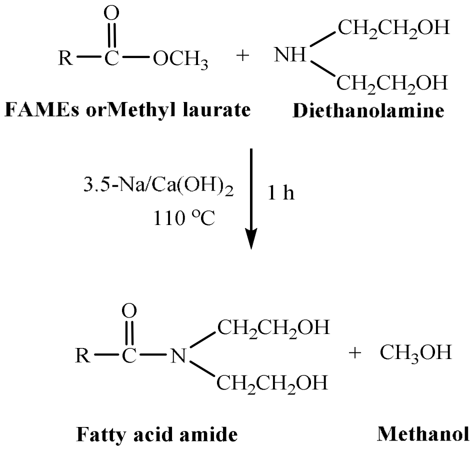
Aminolysis reactions of used cotton seed oil, virgin cotton seed oil, mutton fat, methyl laurate, FAMEs derived from used cotton seed oil, and FAMEs derived from mutton fat have been performed with diethanolamine in the presence of 3.5-Na/Ca$(OH)_2$ catalyst as shown in scheme 1 and 2, respectively. All aminolysis reactions were performed in a 100 mL, two neck round bottom flask equipped with a water-cooled condenser, oil bath and a magnetic stirrer. In a typical aminolysis reaction 10 g of vegetable oil was mixed with diethanolamine (DEA) to maintain the DEA to oil molar ratio of 6:1, in the presence of 5 wt% of 3.5-Na/Ca$(OH)_2$ at 110 °C as shown in scheme 1. Aminolysis reactions have been carried out by varying one parameter at a time in order to establish the best suited reaction conditions for the complete aminolysis of substrate. After the completion of the reaction, the reaction mixture was filtered through ordinary filter paper and was dissolved in 60 mL hexane and placed in a separatory funnel. The upper hexane layer was separated from the lower glycerol layer, washed with water, dried over sodium sulfate and the hexane was rotary-evaporated to yield the pure fatty acid amide derivative.

To monitor the progress of the reaction, the samples from the reaction mixture have been withdrawn after every 20 min with the help of glass dropper, and subjected to FTIR analysis.



Scheme 1 Aminolysis of cotton seed oil in the presence of 3.5-Na/Ca$(OH)_2$ catalyst.

In order to test the efficiency of 3.5-Na/Ca$(OH)_2$ catalyst with other substrates, same catalyst has also been employed for catalyzing the aminolysis reactions of used cotton seed oil derived biodiesel (as prepared in section 2.4) and commercially available methyl laurate using diethanolamine to FAMEs molar ratio of 4:1 in the presence of 5 wt% of 3.5-Na/Ca$(OH)_2$ at 110 °C as shown in scheme 2.



Scheme 2 Aminolysis of used cotton seed oil derived FAMEs or methyl laurate in the presence of 3.5-Na/Ca$(OH)_2$ catalyst.

After the completion of the reaction the reaction mixture was filtered through ordinary filter paper, washed with water and organic layer was dried over sodium sulphate. The amide product so obtained was further characterized by FTIR (Figure S3, supporting information) and ^{1}H-NMR (Figure S4, supporting information) techniques. The amide product obtained from the aminolysis of the methyl laurate was also characterized by mass spectrometry (Figure S5, supporting information) besides FTIR and proton NMR studies. The FTIR technique has also been used to monitor the progress of the reaction and quantify the amide products formed by following the literature reported procedure [7].

Fatty acid amide derivative of used cotton seed oil: Yield > 99%. FTIR (cm^{-1}): 3397 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -CH=CH-), 3.77 (m, $-CH_2OH$), 3.46 (m, $-NCH_2-$), 2.7 (m, $-CH=CH-CH_2-CH=CH-$), 2.31 (m, $-CH_2-CO-$), 2.0 (m, $-CH_2-(CH_2)_n-CH-$), 1.6-1.25 (m, $-(CH_2)_n-$), 0.95 (m, $-CH=CH-CH_3$)0.87 (m, $-CH_2-CH_3$).

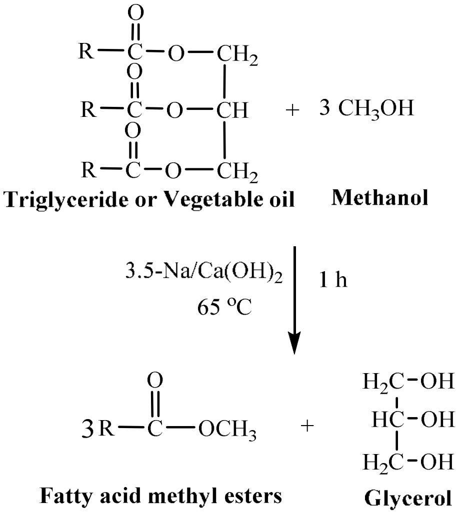
Fatty acid amide derivative of used cotton seed oil derived FAMEs: Yield > 99%. FTIR (cm^{-1}): 3398 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -CH=CH-), 3.78 (m, $-CH_2OH$), 3.48 (m, $-NCH_2-$), 2.7 (m, $-CH=CH-CH_2-CH=CH-$), 2.3 (m, $-CH_2-CO-$), 2.0 (m, $-CH_2-(CH_2)_n-$), 1.6-1.25 (m, $-(CH_2)_n-$), 0.95 (m, $-CH=CH-CH_3$), 0.87 (m, $-CH_2-CH_3$).

Fatty acid amide derivative of mutton fat derived FAMEs: Yield > 99%. FTIR (cm^{-1}): 3398 (ν_{OH}), 1615 ($\nu_{C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 5.3 (m, -CH=CH-), 3.75 (m, $-CH_2OH$), 3.47 (m, $-NCH_2-$), 2.3 (m, $-CH_2-CO-$), 2.0 (m, $-CH_2-(CH_2)_n-$), 1.6-1.25 (m, $-(CH_2)_n-$), 0.87 (m, $-CH_2-CH_3$).

Fatty acid amide derivative of methyl laurate: Yield > 99%. FTIR (cm^{-1}): 3397 (ν_{OH}), 1615 ($\nu_{amide\text{-}C=O}$); ^{1}H-NMR ($CDCl_3$, δ ppm): 3.8 (m, $-CH_2OH$), 3.5 (m, $-NCH_2-$), 2.3 (m, $-CH_2-CO-$), 1.6-1.25 (m, $-(CH_2)_n-$), 0.87 (m, $-CH_2-CH_3$); EI-MS (m/z) (Intensity (%), fragment): 287.2 (3, M), 270.3 (100, M-H_2O), 227.22 (10, M-$CH_3(CH_2)_3$), 175.2 (10, M-$CH_3(CH_2)_7$), 132.2 (12, M-$CH_3(CH_2)_{10}$), 114.2 (5, M-$CH_3(CH_2)_{10}OH$).

Transesterification reaction

In order to show the efficiency of the 3.5-Na/Ca(OH)$_2$ for catalyzing the reactions other than aminolysis, same catalyst has also been used for the transesterification of variety of triglycerides (virgin cotton seed oil, used cotton seed oil, soybean oil, castor oil, karanja oil, jatropha oil and mutton fat) with methanol as shown in Scheme 3. All transesterification reactions were performed in a 100 mL, two neck round bottom flask equipped with a water-cooled condenser, oil bath and a magnetic stirrer. In a typical transesterification reaction, triglyceride was mixed in 12:1 molar ratio of methanol with 5 wt% (with respect to triglyceride) 3.5-Na/Ca(OH)$_2$ and heated at 65 °C, till the completion of reaction.



Scheme 3 Transesterification of triglyceride (vegetable oil) in the presence of 3.5-Na/Ca(OH)$_2$ catalyst

After the completion of the reaction, the reaction mixture was filtered to remove the catalyst, rotary evaporated to recover the excess methanol and finally kept in separating funnel for 12 h to separate the lower glycerol layer from upper biodiesel layer. Fatty acid methyl esters (FAMEs), thus obtained, were further characterized and quantified by ^{1}H-NMR (Figure S6, supporting information) by following the literature reported procedure[24] as given below:

$\text{Yield} = \{2I_{(\text{methoxy})}/3I_{(\text{methylene})}\}100$

where $I_{(\text{methoxy})}$ and $I_{(\text{methylene})}$ are the areas of the methoxy and methylene protons, respectively, in ^{1}H NMR spectra of biodiesel.

Used cotton seed oil derived FAMEs: H-NMR (CDCl$_3$, δ ppm): 5.3 (m, -CH=CH-), 3.6 (s, -OCH$_3$), 2.7 (m, -CH=CH-CH$_2$-CH=CH-), 2.3 (m, -CH$_2$-CO-), 2.0 (m, -CH$_2$-CH=CH-), 1.6-1.25 (m, -(CH$_2$)$_n$-), 0.95 (m, -CH=CH-CH$_3$), 0.87 (m, -CH$_2$-CH$_3$).

Karanja oil derived FAMEs: ^{1}H-NMR (CDCl$_3$, δ ppm): 5.34 (m, -CH=CH-), 3.6 (s, -OCH$_3$), 2.75 (m, -CH=CH-CH$_2$-CH=CH-), 2.3 (m, -CH$_2$-CO-), 2.03 (m, -CH$_2$-(CH$_2$)$_n$-), 1.61-1.25 (m, -(CH$_2$)$_n$-), 0.97 (m, -CH=CH-CH$_3$), 0.88 (m, -CH$_2$-CH$_3$).

Jatropha oil derived FAMEs: ^{1}H-NMR (CDCl$_3$, δ ppm): 5.33 (m, -CH=CH-), 3.61 (s, -OCH$_3$), 2.77 (m, -CH=CH-CH$_2$-CH=CH-), 2.3 (m, -CH$_2$-CO-), 2.02 (m, -CH$_2$-(CH$_2$)$_n$-), 1.61-1.25 (m, -(CH$_2$)$_n$-), 0.96 (m, -CH=CH-CH$_3$), 0.89 (m, -CH$_2$-CH$_3$).

Soybean oil derived FAMEs: ^{1}H-NMR (CDCl$_3$, δ ppm): 5.34 (m, -CH=CH-), 3.6 (s, -OCH$_3$), 2.77 (m, -CH=CH-CH$_2$-CH=CH-), 2.3 (m, -CH$_2$-CO-), 2.03 (m, -CH$_2$-(CH$_2$)$_n$-), 1.6-1.25 (m, -(CH$_2$)$_n$-), 0.95 (m, -CH=CH-CH$_3$), 0.88 (m, -CH$_2$-CH$_3$).

Castor oil derived FAMEs: ^{1}H-NMR (CDCl$_3$, δ ppm): 6.5 (-OH) 5.51 (m, -CH$_2$-CH=CH-), 5.39 (m, -CH=CH-), 3.6 (s, -OCH$_3$), 3.61 (m, -CH-OH), 2.3 (m, -CH$_2$-CO-), 2.20 (m, -CH$_2$-CH=CH-), 2.03 (m, -CH$_2$-(CH$_2$)$_n$-), 1.61-1.30 (m, -(CH$_2$)$_n$-), 0.97 (m, -CH=CH-CH$_3$), 0.88 (m, -CH$_2$-CH$_3$).

Mutton fat derived FAMEs: ^{1}H-NMR (CDCl$_3$, δ ppm): 5.34 (m, -CH=CH-), 3.6 (s, -OCH$_3$), 2.3 (m, -CH$_2$-CO-), 2.0 (m, -CH$_2$-(CH$_2$)$_n$-), 1.61-1.25 (m, -(CH$_2$)$_n$-), 0.88 (m, -CH$_2$-CH$_3$).

Results and Discussion

Catalyst preparation and characterization

BET SURFACE AREA AND HAMMETT INDICATOR TEST

In present study CaO being less toxic and less expensive have been selected as support for the preparation of the catalyst. The activity of such catalyst was found to depend on the basic strength and surface area of the catalyst [26] and same has been tuned by doping calcium oxide with 1.5-5.5 wt% sodium. The basic strength (H_) of the pure CaO was found to be in the range of 9.8-10.1. Basic strength was further increased from 10.1-11.1 to 15.1-18.4 as the doping percentage of sodium ion was increased from 1.5 to 3.5 wt% as given in Table 2. A further increase in sodium ion concentration was not found to increase the basic strength of Na/Ca(OH)$_2$ material. The surface area of pure calcium oxide and Na/Ca(OH)$_2$ was measured by BET method and the same was found to be increased evidently from 3.7 to 9.6 m^2/g after 3.5 wt% doping of sodium as shown in Table 2. Also, the metal doping increase (from 1.5 wt% – 5.5 wt%) has insignificant effect on surface area.

Table 2 Comparison of BET and single point surface area of CaO with Na/Ca(OH)$_2$.

S. No.	Catalyst type	BET surface area (m²/g)	Basic strength (H_)
1.	CaO	3.7	9.8<H_<10.1
2.	1.5-Na/Ca(OH)$_2$	9.5	10.1<H_<11.1
3.	2.5-Na/Ca(OH)$_2$	9.6	11.1<H_<15.0
4.	3.5-Na/Ca(OH)$_2$	9.6	15.0<H_<18.4
5.	4.5-Na/Ca(OH)$_2$	9.2	15.0<H_<18.4
6.	5.5-Na/Ca(OH)$_2$	9.3	15.0<H_<18.4

POWDER XRD STUDIES

The comparisons of the powder XRD patterns of commercially available CaO with 1.5–5.5 wt% sodium doped Ca(OH)$_2$ are shown in Fig. 1A. The CaO shows peaks at 2θ values of 37.37°, 53.89° and 32.18° due to the presence of calcium oxide in cubic form (JCPDS card no. 821691) , as shown in Fig. 1A(a). The presence of low intensity peaks at 29.4° and at 64.4° reveals the presence of minor amount of calcium carbonate as calcite in the CaO used as a support (JCPDS 881811). The powder XRD patterns of Na doped (1.5-5.5 wt%) $Ca(OH)_2$ shows the peaks at 2θ values of 34.07, 18.07 and 47.19° to support the conversion of cubic CaO to hexagonal $Ca(OH)_2$ form as shown in Fig. 1A(c)-1A(g). The absence of the diffraction patterns of Na even after 5.5 wt% doping could be due to its high degree of dispersion on the $Ca(OH)_2$ surface. There was conversion of CaO to $Ca(OH)_2$ after chemical treatment, as suggested by XRD analysis, which played important role in basic strength enhancement.

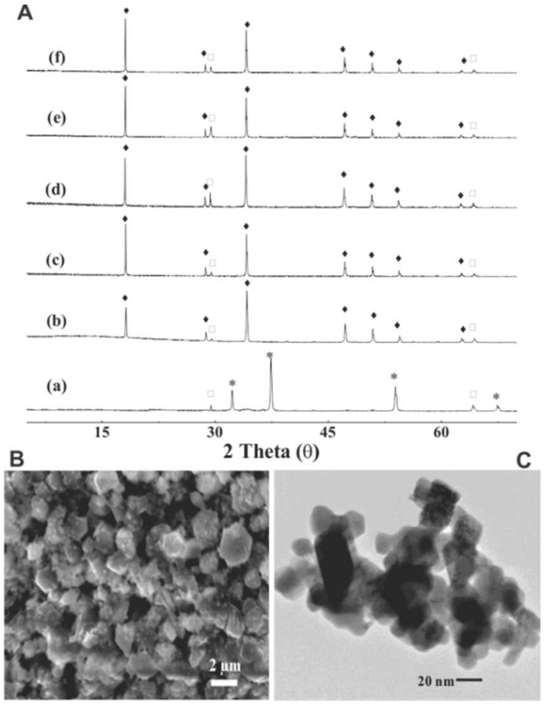


Fig. 1 (A) Comparative powder XRD patterns of (a) commercial CaO with (b) 1.5-$Na/Ca(OH)_2$, (c) 2.5-$Na/Ca(OH)_2$, (d) 3.5-$Na/Ca(OH)_2$, (e) 4.5-$Na/Ca(OH)_2$ and (f) 5.5-$Na/Ca(OH)_2$. Where *, ♦ and □ represents peaks of calcium oxide, calcium hydroxide and calcium carbonate respectively. **(B)** FE-SEM and **(C)** TEM images of 3.5-$Na/Ca(OH)_2$.

SURFACE MORPHOLOGY AND PARTICLE SIZE ANALYSIS

The surface morphology of 3.5-$Na/Ca(OH)_2$ was analyzed by FE-SEM studies and the images shows that it has mainly hexagonal shaped 2-4 µm sized particles as shown in Fig. 1B. Particle size distribution analysis (Dynamic light scattering analysis, DLS) of CaO and 3.5-$Na/Ca(OH)_2$ suggested that they have average particle size of 112 nm and 28 nm, respectively (Fig. S1, supporting information). The TEM analysis of the same particles also shows that particles of 3.5-$Na/Ca(OH)_2$ are the clusters of smaller hexagonal and irregular shaped particles with particle size in the range of 25-30 nm as shown in Fig. 1C. Both DLS and TEM analysis indicated the sharp decrease in particle size of $Ca(OH)_2$ after chemical treatment with sodium doping.

The characterization studies of 3.5-$Na/Ca(OH)_2$ reveals that it not only exist in nano particle form but also possesses higher basic strength and higher surface area than pure CaO and hence, expected to show higher activity than pure CaO towards the aminolysis and transesterification reaction.

AMINOLYSIS REACTION OF VARIETY OF TRIGLYCERIDES

The prepared catalysts have been used as catalyst for the aminolysis of a variety of feedstocks (cotton seed oil, used cotton seed oil, mutton fat, methyl laurate, and FAMEs derived from used cotton seed oil and mutton fat) with diethanolamine. However, used cotton seed oil (1.8 wt% FFAs) has been selected for optimizing the parameters to achieve the complete aminolysis. However, as suggested by literature,[27] it's difficult to catalyze direct aminolysis of carboxylic acids by using these kind of catalyst.

The aminolysis reactions of used cottonseed oil have been performed by varying one parameter at a time out of the following parameters (i) sodium ion concentration in $Ca(OH)_2$ (ii) catalyst concentration, (iii) reaction temperature and (iv) diethanolamine/oil molar ratio. Besides these parameters the reusability of the selected catalyst and its homogeneous contribution in the catalyst activity has also been studied.

OPTIMIZATION OF REACTION PARAMETERS FOR AMINOLYSIS

To determine the optimum sodium ion concentration in $Ca(OH)_2$ to achieve the best catalytic activity, a series of $Na/Ca(OH)_2$ catalysts were prepared by varying the amount of sodium from 0-5.5 wt%. The aminolysis reaction of used cottonseed oil was performed with diethanolamine (diethanolamine/oil = 6:1; m/m) at 110 ºC in the presence of 5 wt% catalyst.

Rate of aminolysis was found to increase as the amount of sodium ion in $Ca(OH)_2$ were increased from 1.5 to 3.5 wt%. However, further increase in Na^+ ion concentration does not have an impact on the reaction rate as shown in Fig. 2A and hence, 3.5-$Na/Ca(OH)_2$ catalyst was selected for optimizing the other parameters to achieve the minimum time for the complete aminolysis of used cotton seed oil. The aminolysis reaction of used cotton seed oil at same reaction conditions was also carried out with $Ca(OH)_2$, prepared without Na metal doping, and found the incomplete conversion even after 4 h of reaction period.

A series of aminolysis reactions of used cottonseed oil with diethanolamine (1:6, m/m) at 110 °C were performed in the presence of 3.5-$Na/Ca(OH)_2$ by varying its concentration from 1 to 8 wt% (catalyst/oil) in order to find the optimum catalyst concentration. The rate of reaction increases as catalyst concentration was increased from 2 to 5 wt%. A further increase in catalyst concentration does not change the reaction rate significantly as shown in Fig. 2B and hence, the aminolysis reactions were studied with 5 wt% catalyst concentration for optimization the other parameters. Though the complete aminolysis (<99% conversion) was possible with 1 wt% of prepared catalyst but required long reaction duration (4 h).

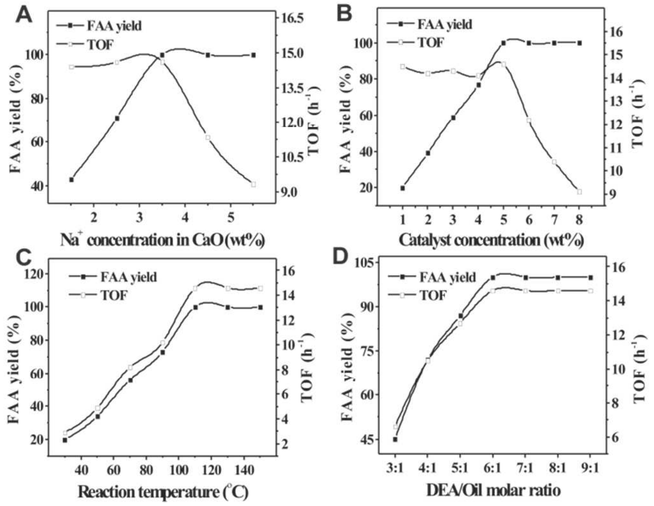


Fig. 2 Effect of **(A)** sodium ion concentration in $Ca(OH)_2$, **(B)** catalyst concentration, **(C)** reaction temperature, and **(D)** DEA/Oil molar ratio on the fatty acid amide (FAA) yield and turn over frequency (TOF). (Reaction time = 1 h).

*TOF: turn over frequency – moles of substrate converted per mole of metal (in the solid catalyst) per hour.

A series of aminolysis reactions were conducted in the presence of 5 wt%, (catalyst/used cottonseed oil) 3.5-$Na/Ca(OH)_2$ catalyst to find the optimum temperature for aminolysis reaction. The fatty acid amide yield increases as temperature of the reaction was increased from 35 °C to 110 °C. Further increase in reaction temperature was not found to influence the fatty acid amide yield significantly as shown in Fig. 2C and hence, all aminolysis reactions have been performed at 110 °C. Also, the complete aminolysis (100 % m/m) of used cotton seed oil has been possible at 35 °C though needed longer reaction duration (~ 4 h).

To determine the optimum diethanolamine/used cotton seed oil molar ratio, the reactions were performed with 3:1 to 9:1 molar ratios at 110 °C using 5 wt% of 3.5-$Na/Ca(OH)_2$ catalyst. The fatty acid amide yield increases as diethanolamine/oil molar ratio was increased from 3:1 to 6:1. Further increase in diethanolamine/oil molar ratio does not affect the fatty acid amide yield significantly as shown in Fig. 2D. The same reaction with low diethanolamine/oil molar ratio (3:1), which is also minimum ratio required for aminolysis, was also yielded the maximum conversion but in 3 h of reaction duration.

The necessity of high amount of diethanolamine has been described well by Talvik's hypothesis,[28] which stated that the possibility of formation of six-membered ring and the importance of an additional molecule of the amine demands the use of at least two equivalents of diethanolamine to achieve high yields of amide.

EFFECT OF FEEDSTOCK USED

In order to determine the effectiveness of the prepared $Na/Ca(OH)_2$ catalyst towards the aminolysis of other substrates than used cotton seed oil, same reaction has been performed using methyl laurate (ML), mutton fat (MF), virgin cotton seed oil (CSO), soybean oil (SO), FAMEs of MF, and FAMEs of UCSO. The catalyst was found to be effective for the complete aminolysis of the feedstocks used and in order to compare the efficiency of the catalyst, the turnover frequency (TOF) has been calculated and compared (Table 3). When fatty acid methyl esters were used as feedstock of aminolysis reaction the TOF was found ~ 3 times higher than the TOF obtained in case of triglycerides as given in Table 3. Also, in this case less amount of diethanolamine was required and the side product was methanol which was easy to separate. The chemical structure of FAMEs is quite small as compared to triglycerides and this could be the reason behind the higher TOF value or lesser requirement of diethanolamine.

Table 3 Comparison of effect of feedstocks on amount of diethanolamine and turnover frequency (TOF) of 3.5-$Na/Ca(OH)_2$ catalyst for the complete aminolysis. (Reaction conditions; catalyst amount = 5 wt% of feedstock, temperature = 110 °C, reaction time = 1 h).

S. No.	Type of feedstock	DEA:feedstock molar ratio	TOF (h^{-1})
1.	CSO	6:1	14.6
2.	SO	6:1	14.6
3.	MF	6:1	15.2
4.	FAMEs (UCSO)	4:1	43.8
5.	FAMEs (MF)	4:1	44.6
6.	ML	4:1	45.3

REUSABILITY AND HOMOGENEOUS CONTRIBUTION OF THE CATALYST

Reusability is one of the most important features of a solid catalyst for its commercialization. To test the reusability of 3.5-$Na/Ca(OH)_2$, it was recovered from the reaction mixture by filtration, washed with hexane and dried at 100 °C. The catalyst thus recovered was used for the six catalytic runs under the same experimental condition and regeneration method. The catalyst was able to complete (100 %, m/m) the aminolysis of used cotton seed oil for six successive cycles as shown in Fig. 3A. However, the reaction time increases gradually after every successive run, indicating there is a gradual loss of the activity. The decrease in catalytic activity after every cycle could be due to the partial leaching of sodium from the calcium oxide support or due to the partial deactivation of the catalytic sites.

The catalyst reusability study shows the gradual loss of the catalytic activity and same could be due to the partial leaching of the active species from the catalyst support. In order to quantify the homogeneous contribution involved in the catalyst activity, the catalyst, 3.5-$Na/Ca(OH)_2$ catalyst (500 mg, equivalent to 5 wt% of oil used later for the aminolysis), has been refluxed with diethanolamine for 1 h at 110 °C and then catalyst was separated from diethanolamine by filtration. Diethanolamine thus obtained was mixed with used cotton seed oil to maintain amine/oil molar ratio of 6:1, and reaction mixture was stirred at 110 °C for 1 h. Under these experimental conditions no conversion of oil to fatty acid amide has been achieved. Also, the concentration of Na^+ in first and after six catalytic cycles was analyzed using flame photometry and very little change, from 3.45 wt% to 3.34 wt%, was found. Evidently, these experiments ruled out the possibility of aminolysis due to any leached species, and also supports that solid catalyst is stable and responsible for the entire catalytic activity.

KINETIC STUDY

To monitor the progress of the reaction and calculate the rate, aminolysis of UCSO with diethanolamine have been performed under the optimized reaction conditions viz., using diethanolamine to oil molar ratio of 6:1 in the presence of 5 wt% catalyst (3.5-$Na/Ca(OH)_2$) at 110 °C. The samples from the reaction mixture have been withdrawn after every 20 min, centrifuged and rotary evaporated to remove the solid catalyst and excess diethanolamine, respectively and subjected to FTIR studies to calculate the fatty acid amide yield in the reaction mixture.

The aminolysis reaction of UCSO in the presence of 3.5-$Na/Ca(OH)_2$ was found to follow the pseudo first-order kinetics and the rate constant (k) for the same reaction could be given as:

$$k = -\ln\{(1-y)/t\} \qquad \text{(i)}$$

where y is the fatty acid amide yield at time t.

The kinetics of the $Na/Ca(OH)_2$ catalyzed aminolysis of UCSO has been studied at a 6:1 diethanolamine to oil molar ratio at two different temperatures of 35 ºC and 110 ºC.

The linear nature of $-\ln(1-y)$ *vs* t (time) plots (Fig. 3B) supported that $Na/Ca(OH)_2$ catalyzed reaction follow pseudo first order kinetics. The rate constants were obtained from Fig. 3B and found to be 0.077, 0.029, 0.013 and 0.004 min^{-1} at 110, 95, 65 and 35 °C, respectively.

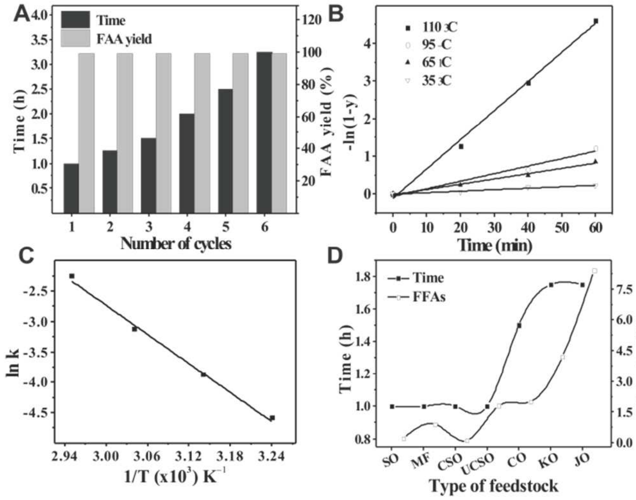


Fig. 3 **(A)** Reusability studies of the 3.5-$Na/Ca(OH)_2$ catalyst towards the aminolysis of used cotton seed oil. **(B)** Plot of $-\ln(1-y)$ *vs* time at two different reaction temperatures for the 3.5– $Na/Ca(OH)_2$ catalyzed aminolysis of UCSO. **(C)** The Eyring plot and the thermodynamics parameters for the aminolysis of waste cotton seed oil. **(D)** Effect of change of feedstock on the catalytic activity of 3.5-$Na/Ca(OH)_2$ catalyst for transesterification reaction, Reaction conditions; methanol: feedstock molar ratio = 12:1, catalyst amount = 5 wt% of feedstock, temperature = 65 °C.

The Arrhenius model[29] was employed to estimate the activation energy (E_a) and pre-exponential factor (A) for the same reaction as given in equation (ii).

$$\ln k = -Ea/RT + \ln A \qquad \text{(ii)}$$

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

A plot between 1/T and ln k is shown in Fig. 3C, and the values of E_a and A from the same graph was found to be 54.8 kJ mol^{-1} and 1.8 X 10^9 min^{-1}, respectively. The calculated activation energy (54.8 kJ mol^{-1}) for the UCSO aminolysis was found within the range (33‑84 kJ mol^{-1}), reported for the heterogeneous catalysis [30].

TRANSESTERIFICATION OF VARIETY OF FEEDSTOCKS

In order to show the versatile application of catalyst, it was used for the transesterification of variety of feedstocks viz., soybean oil (SO), mutton fat (MF), cotton seed oil (CSO), used cotton seed oil (UCSO), castor oil (CO), karanja oil (KO) and jatropha oil (JO). Transesterification reactions were performed in the presence of 5 wt% 3.5-$Na/Ca(OH)_2$ catalyst using methanol to triglyceride molar ratio of 12:1. Different kinds of triglycerides were converted completely into corresponding FAMEs at different time intervals. Mutton fat, soybean, cotton seed and used cotton seed oil required 1 h, castor and karanja oil required 1.5 h and jatropha oil needs 1.75 h for complete conversion as shown in Fig. 3D. Relatively lower catalytic activity of the selected catalyst towards the transesterification of karanja and jatropha oil could be due to the partial deactivation of the catalyst by the higher concentration of FFAs present in these oils.

COMPARISON OF ACTIVITY WITH FEW LITERATURE REPORTED CATALYSTS

In order to show the efficacy and advantages of 3.5–$Na/Ca(OH)_2$ catalyst over literature reported similar catalysts, a comparison has been made as shown in Table 4. As evident from the comparison, the catalyst 3.5–$Na/Ca(OH)_2$, and reaction conditions optimized in present study are clearly advantageous than the literature reported counter parts as former (i) yielded higher FAA yield (> 99%) than even homogeneous catalyst, (ii) needed shorter reaction duration (1 h) at 110 °C , (iii) effective (FAA yield > 99%) even at room temperature (35 °C), (iv) reusable (upto 6 catalytic runs), (v) effective for the aminolysis of a variety of triglycerides, and (vi) equally effective for the transesterification a variety of triglycerides.

Table 4 Comparative study of Na/Ca(OH)$_2$ activity towards aminolysis reaction with few literature reported catalysts.

Catalyst	Novozym 435	Novozym 435	Sodium methoxide*	ZnO.La$_2$CO$_5$.LaOOH	CdO$^{\#}$	Na/Ca(OH)$_2$
Substrate	caffeic acid methyl ester	Oleic acid	Soybean oil	Passiflora edulis oil	MO, OA, FA, BA	WO,SO,CO, KO, JO, MF/ methyl laurate
Amine	PEA	EA	NME	EA	Pyrrolidine	DEA
Catalyst amount (wt% of oil)	4	30	1	2.3	5	5
Reaction time	24 h	3 h	NR	8 h	24 h for MO, 3 h for OA, FA, BA	1 h
Reaction temperature (°C)	70	65	60	100	135	110
Amine:feedstock molar ratio	40:1	10:1	3:1	3:1	2:1	6:1/4:1
FAA yield (% m/m)	25.5	96.6	90	100	99 for MO, 95 for OA, 97 for FA, 82 for BA	> 99
Reusability of catalyst	5	NR	NR	2	8	7
Reference	14	31	15	25	32	PR

*homogeneous catalyst, #used ionic liquids as support, PEA = (R, S)-α-phenylethylamine, NME = N-methyl ethanolamine, EA=ethanolamine, DEA=diethanolamine, NR=not reported, MO=methyl oleate, OA=oleic acid, FA=fatty acids, BA=benzoic acid, PR=present report.

Conclusions

A simple method for preparation of Na$^+$ doped Ca(OH)$_2$ catalysts in nanocrystalline form was employed and its application as solid catalyst towards aminolysis and transesterification reactions of a variety of feedstocks has been demonstrated. Na/Ca(OH)$_2$ catalyst was found to yield the complete aminolysis of used cotton seed oil with diethanolamine in 1 h at 110 °C. The reaction rate and activation energy were found to be 0.07 min^{-1} and 54.8 kJ mol^{-1}, respectively, at 110 °C. Prepared catalyst was also found to complete the transesterification of used cotton seed oil with methanol in 1 h of reaction period at 65 °C. The catalyst was found to be equally effective to catalyze transesterification with other feedstocks (viz., mutton fat, soybean, virgin cotton seed, castor, karanja, and jatropha oil) and aminolysis of mutton fat, soybean, virgin cotton seed, used cotton seed oil, methyl laurate, fatty acid methyl esters derived from used cotton seed oil, and fatty acid methyl esters derived from mutton fat. Room temperature conversion of triglyceride to fatty acid amides or fatty acid methyl esters was also feasible though need extended reaction duration. Also, the catalyst was recyclable and catalyzed six successive catalytic cycles for the aminolysis of used cotton seed oil.

Acknowledgements

We are thankful to Center for University-Wide Research Facilities, Chonbuk National University, Jeonju, South Korea for powder XRD, FE-SEM, TEM and DLS analysis.

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Electronic Supplementary Information (ESI) available: [Spectrum (FT-IR, Mass and ^{1}H-NMR), Figures. S1–S6]. See DOI: 10.1039/b000000x/

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