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Kinetics and reusability of Zr/CaO as heterogeneous catalyst for the ethanolysis and methanolysis of *Jatropha crucas* oil

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ABSTRACT

Zirconium impregnated (5–20 wt.%) calcium oxide (Zr/CaO) was prepared by a simple wet chemical method followed by calcination up to 900 °C. The prepared Zr/CaO was employed as a heterogeneous catalyst for the transesterification of *Jatropha crucas* oil with ethanol and methanol for the production of fatty acid ethyl and methyl esters, respectively. The catalysts were characterized by powder X-ray diffraction, Fourier transform-infrared spectroscopy, Brunauer–Emmett–Teller surface area measurement, scanning electron microscopy, transmission electron microscopy techniques and basic strength of the catalyst were established by acid–base titration. The catalytic activity was found to be a function of basic sites which in turn depend on calcination temperature and zirconium concentration. The catalyst with 15 wt.% zirconium concentration and calcined at 700 °C, showed the highest catalytic activity among the prepared catalysts. A pseudo first order kinetic equation was applied to evaluate the kinetic parameters of Zr/CaO catalyzed transesterification. The activation energy (E_a) for the Zr/CaO catalyzed methanolysis and ethanolysis was found to be 29.8 kJ mol^{-1} and 42.5 kJ mol^{-1}, respectively. The Koras–Nowak test was performed to demonstrate that catalytic activity was independent from the mass transport phenomenon and follows the kinetic regime.

1. Introduction

Due to rapidly increasing crude oil price, diminishing fossil fuel resources, and increasing environment pollution because of fuel burning, the development of alternate, clean and renewable energy sources has become essential. In this context biodiesel has attracted the attention as a renewable and eco-friendly alternative to the conventional diesel fuel [1]. Biodiesel is chemically a mixture of fatty acid alkyl esters (FAAE) and prepared from triglycerides (vegetable oils or animal fat) *via* transesterification reaction [2]. At industrial scale biodiesel is generally produced by the transesterification of triglycerides with methanol in the presence of homogeneous base (*e.g.*, NaOH, KOH, NaOMe and KOMe) [3,4] or acid (*e.g.*, HCl and H_2SO_4) catalysts [5]. Although homogeneous base catalysts catalyze the reaction at faster rate, however, these catalysts required costly and refined vegetable oil as feedstock. Further, biodiesel thus produced must be washed with water to remove the catalyst and hence, huge amount of industrial effluents are generated.

In order to circumvent the problems associated with the use of homogeneous catalysts, research has been directed towards the development of heterogeneous catalysts for biodiesel production. Heterogeneous catalysts, although less effective in comparison to the homogeneous one, are easy to separate from the reaction mixture, reusable, and expected to produce biodiesel without catalyst contamination. The catalytic activity of solid alkali catalysts was found to be higher than respective acid catalysts and hence solid alkali catalysts have been extensively studied in literature [6].

Mixed oxides of zirconium such as Zr/Mg, WO_3/ZrO_2, Sr/ZrO_2, and SO_4^{2-}/ZrO_2 were also found to be promising solid catalysts [7–15] for the transesterification reaction. The reaction conditions for various types of literature reported zirconium containing catalysts have been compared in Table 1.

As could be seen from Table 1, most of the zirconium containing catalysts demand not only high reaction temperature and pressure but also a higher alcohol to oil molar ratio to achieve the significant FAAE yield.

The conventional method of biodiesel production utilizes methanol, a highly toxic chemical, for the transesterification reaction. Methanol is not only highly toxic but also a refinery residue and hence, fatty acid methyl ester (FAME) will not be completely carbon neutral. In this regard, application of ethanol could be advantageous as it is renewable and also considered as non toxic green chemical. However, due to the lesser reactivity in comparison to methanol, ethanol has not been frequently employed for the transesterification reaction in the presence of heterogeneous catalysts [16]. Li et al. [17] reported the application of Mg_2CoAl mixed oxide as a heterogeneous catalyst for the transesterification of rapeseed oil with ethanol at 200 °C and 25 atmospheric pressure to achieve a 97% conversion in 5 h. Soldi et al. [18] employed ion-exchange resin-sulfonated polystyrene for the ethanolysis of beef tallow (100:1 ethanol to fat ratio) to achieve 27% yield in 18 h. To the best of our knowledge, there is no reported work available in literature related with the application of Zr/CaO as heterogeneous catalyst for the ethanolysis of triglycerides.

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Table 1
Comparison of the transesterification activity of few literature reported zirconium containing catalysts.

Catalyst	Catalyst amount (wt%)	Reaction temperature (°C)	MeOH:oil molar ratio	Reaction duration (h)	FAME yield (wt%)	Reusability (number of cycles)	Oil	Reference
CaO–ZrO_2	10	65	30:1	2	92.1	NR	Waste cooking oil	[7]
Zr/Mg	10	65	53:1	1	100	4	Soybean, Rice bran, Jatropha, Sunflower oil	[8]
La_2O_3/ZrO_2	5	200	30:1	5	84.9	5	Sunflower oil	[9]
SO_4^{2-}/ZrO_2	3	200	6:1	4	90.3	1	Crude palm kernel oil	[10]
KNO_3/ZrO_2	3	200	6:1	4	65.5	NR	Crude coconut oil	[10]
WZ	1	250	24:1	0.17	94.1	5	Refined palm oil	[11]
SiO_2–ZrO_2	5	50	40:1	3	96.2	6	Soybean oil	[12]
TiO_2/ZrO_2	4	250	40:1	20	80	NR	Soybean oil	[13]
Al_2O_3/ZrO_2	4	250	40:1	20	82	NR	Soybean oil	[13]
WZA	4	250	40:1	20	90	NR	Soybean oil	[13]
SZA	8	150	8:1	3	78.2	NR	Jatropha oil	[14]
Sr/ZrO_2	2.7	115.5	29:1	2.8	79.7	NR	Waste cooking oil	[15]

FAME — Fatty acid methyl ester, WZ — tungstated zirconia, SZA — sulphated zirconia–aluminia, WZA — tungstated zirconia aluminia, NR — Not Reported.

Although, many reports are available regarding the development and application of the heterogeneous catalysts for the transesterification reaction, however, only few of them describe the kinetic study. The kinetics of K–CaO, KF/Mg–La, CaO, and CaO·ZnO catalyzed methanolysis of triglycerides have been studied by various research groups [2,19–21]. The alcohol to oil molar ratio in these reactions was usually employed in excess (>6:1) to the required amount of 3:1 and hence, (pseudo) first order kinetic equation was applied to study the kinetics. The activation energies of the catalysts were found to be in the range of 16–79 kJ/mol. Kinetic study of the ethanolysis reaction in the presence of heterogeneous catalyst is rare in literature. To the best of our knowledge, Mg_2CoAl mixed oxide is the only heterogeneous catalyst which has been employed [17] to study the kinetics of ethanolysis reaction. The activation energy for this reaction was found to be 60.5 kJ mol^{-1}, following the first order reaction kinetics.

In our work, Zr/CaO catalyst was prepared by wet impregnation method and employed for the ethanolysis as well as methanolysis of the jatropha oil. The reaction parameters have been optimized to achieve the optimal catalytic activity. The kinetics of the ethanolysis as well as methanolysis was studied under optimized reaction condition. Further, the effect of the free fatty acid and moisture contents on the catalytic activity and reusability of the catalyst was also examined. The Koras–Nowak criterion test was employed to demonstrate that catalytic activity was free from the mass transport phenomenon.

2. Experimental section

2.1. Materials and methods

Calcium oxide (CaO) and zirconium (IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) were obtained from Sigma Aldrich (USA). Hexane, methanol and ethanol (analytical grade purity), were obtained from Loba Chemie Ltd (India) and used as such without further purification. Jatropha (*Jatropha crucas*) oil (JO), karanja (*Pongamia piñata*) oil (KO), fresh cottonseed (*Gossypiun arboreum*) oil (CO) and waste cottonseed (WO) employed for the transesterification reactions were procured from the local shops situated in Patiala and their chemical analysis is provided in Table 2.

Powder X-ray diffraction (XRD) patterns of the prepared catalysts were recorded on a PANalytical's X'Pert Pro diffractometer, operating at 40 kV and using nickel-filtered Cu Kα radiation (λ = 1.54060 Å). The samples were scanned over a 2θ range of 5–80°. Fourier transform-infrared spectra (FTIR) of the samples were recorded in KBr on Perkin Elmer-Spectrum RX1 spectrophotometer, in the range of 400–4000 cm^{-1}.

Field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometry (FESEM-EDX) was performed on JEOL JSM 6510LV and transmission electron microscopy (TEM) pictures were recorded on HITACHI 7500 instrument.

The surface area of the catalysts was determined by using the adsorption desorption method at 77 K by the standard Brunauer–Emmett–Teller (BET) method using TriStar-Model 3000 equipment. Prior to the analysis, all samples were degassed at 473 K for 2 h under nitrogen atmosphere to remove the physisorbed moisture.

The basic strength of the catalysts ($H\_$) was measured by Hammett indicators [2] *viz.*, neutral red ($H\_ = 6.8$), bromothymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.3$), Nile blue ($H\_ = 10.1$), tropaeolin-O ($H\_ = 11.1$), 2, 4-dinitroaniline ($H\_ = 15.0$), and 4-nitroaniline ($H\_ = 18.4$).

Total basic sites (f_m) of the catalysts were evaluated by measuring the acidity of conjugate acid, by titration method. In a typical experiment, 25 mg Zr/CaO catalyst was dissolved in 25 mL of 0.1 M HCl and resulting mixture was stirred for an hour. The catalyst would neutralize HCl equivalent to its basicity. The resulted solution was titrated against standard NaOH solution to determine the exact concentration of excess HCl. Finally, the amount of HCl neutralized by the catalyst was determined [22–25] and represented as basicity of the catalyst as mmol of HCl/g of catalyst.

Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of FAAE and vegetable oils were recorded on a Bruker Avance-II (400 MHz) spectrophotometer, using tetramethoxysilane as an internal standard and $CDCl_3$ as a solvent.

2.2. Catalyst preparation

A series of zirconium impregnated CaO was prepared by the wet impregnation method. In a typical preparation, 10 g of CaO was suspended in 40 mL of deionized water, and to this 10 mL aqueous solution of $ZrOCl_2 \cdot 8H_2O$ of desired concentration was added. The resulted slurry was stirred for 4 h, then evaporated to dryness, and heated at 120 °C for 24 h. A series of Zr/CaO was prepared by varying zirconium concentration in the range of 5–20 wt.% and calcination temperature 300–900 °C. Prepared catalysts were labeled as *x*-Zr/CaO–T, where *x* and T represent the zirconium concentration (wt%) and calcination temperature (°C), respectively.

Table 2
The chemical analysis of the vegetable oils employed as feedstock in present study.

S. no.	Feedstock	Free fatty acid value (wt%)	Moisture content (wt%)	Saponification value (mg of KOH/g of sample)	Iodine value (mg of I_2/g of sample)
1	CO	1.2	0.23	180.5	87.1
2	WO	4.6	0.26	190.2	93.6
3	JO	7.5	0.35	185.3	97.2
4	KO	15.0	0.28	195.1	103.2

2.3. Transesterification reaction

Transesterification reactions of JO were carried out in a 50 mL two-neck round bottom flask, equipped with a water bath, magnetic stirrer and a water-cooled reflux condenser. In a typical reaction 10 g of JO was stirred (500 rpm) with desired molar concentration of methanol or ethanol and catalyst, and heated at desired temperature to achieve the complete (>99%) conversion of oil into corresponding FAAE. To monitor the progress of reaction, a sample (0.25 mL) from the reaction mixture was withdrawn after every 15 min with the help of glass dropper, centrifuged and subjected to proton NMR analysis to quantify the FAAE produced. After the course of the reaction, the solid catalyst was recovered through filtration and liquid phase was kept in a separating funnel for 12 h to separate the lower glycerol layer from the upper FAAE layer.

Fatty acid methyl esters (FAME) and ethyl esters (FAEE) thus obtained were characterized by ^1H NMR and ^{13}C NMR techniques.

Methyl esters of jatropha oil: ^1H 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, $=CH-CH_2-$), 1.29 (m, $-(CH_2)_n-$), 0.88 (m, $-CH_2-CH_3$); ^{13}C NMR ($CDCl_3$, δ ppm): 174.09 ($-CO-CH_2-$), 129.9 ($-CH{=}CH-$), 51.4 ($-OCH_3$), 34.1 ($-CO-CH_2-$), 31.9 (ω3 $-CH_2-$), 29.66–29.08 ($-CH{=}CH-CH_2-$, $-CH_2-$), 27.2 ($-CH{=}CH-CH_2-CH{=}CH-$), 25.6–24.80 ($-CO-CH_2-CH_2-$), 22.70, 22.47 (ω2 $-CH_2-$) and 14.16 (ω1 $-CH_3$).

Ethyl esters of jatropha oil: ^1H NMR ($CDCl_3$, δ ppm): 5.34 (m, $-CH{=}CH-$), 4.1–4.2 (q, $-OCH_2-$), 2.77 (m, $-CH{=}CH-CH_2-CH{=}CH-$), 2.3 (m, $-CH_2-CO-$), 2.03 (m, $=CH-CH_2-$), 1.29 (m, $-(CH_2)_n-$, $-CO-CH_2-CH_3$), 0.88 (m, $-CH_2-CH_3$); ^{13}C NMR ($CDCl_3$, δ ppm): 174.09 ($-CO-CH_2-$), 129.9 ($-CH{=}CH-$),60 ($-OCH_2-$), 34.1 ($-CO-CH_2-$), 31.9 (ω3 $-CH_2-$), 29.66–29.08 ($-CH{=}CH-CH_2-$, $-CH_2-$), 27.2 ($-CH{=}CH-CH_2-CH{=}CH-$), 25.6–24.80 ($-CO-CH_2-CH_2-$), 22.70, 22.47 (ω2 $-CH_2-$) and 14.16 (ω1 $-CH_3$, $-OCH_2-CH_3$).

^1H NMR technique was also employed to quantify the FAME or FAEE following the literature reported procedure [26,27] as given in Eqs. (1) and (2), respectively.

$$\%C_{ME} = 100 \times \frac{2 \times I_{OCH_3}}{3 \times I_{\alpha CH_2}} \tag{1}$$

$$\%C_{EE} = 100\left(\frac{4(I_{TAG+EE} - I_{TAG})}{4(I_{TAG+EE} - I_{TAG}) + 6(2I_{TAG})}\right) \tag{2}$$

where $\%C_{ME}$ and $\%C_{EE}$ are the fatty acid methyl and ethyl ester yield, respectively; I_{OCH3} and $I_{\alpha CH2}$ are the peak area of methoxy and methylene protons at 3.7 ppm and 2.3 ppm respectively; I_{TAG} is the peak area for glyceryl methylenic protons at 4.15–4.35 ppm; $I_{(TAG\,+\,EE)}$ is of glyceryl methylenic and $-OCH_2-$ of ethoxy hydrogens superimposed at 4.10–4.20 ppm.

2.4. Reaction kinetics

Transesterification is generally assumed to be a pseudo first order reaction as alcohols are usually employed in excess to the required stoichiometric molar ratio of 3:1 (alcohol to oil). To calculate the activation energy, reactions were carried out at five different temperatures, *viz.*, 35, 45, 55, 65, and 75 °C. The conversion of JO at different reaction times was obtained and apparent first order rate constants [20] and activation energy [28] were calculated by fitting the appropriate values in Eqs. (3) and (4), respectively.

$$-ln(1\text{-}X)=k\ \ t \tag{3}$$

$$k = A.\ \ e^{-Ea/RT} \tag{4}$$

where k is the apparent first order rate constant (min^{-1}), X is the conversion of oil into FAME or FAEE at time t, E_a is the activation energy ($kJ\ mol^{-1}$), A is the pre-exponential factor (min^{-1}), R is the gas constant (8.314×10^{-3} $kJ\ K^{-1}\ mol^{-1}$) and T is the reaction temperature (°K).

The turnover frequency (TOF) of the catalyst [19] is calculated from Eq. (5).

$$TOF = \frac{mol_{actual}}{f_m \times t} \tag{5}$$

where mol_{actual} is the moles of FAME or FAEE produced at time *t* and f_m is the total basic sites (mmol/g) of catalyst calculated by acid base titration.

3. Results and discussion

3.1. Characterization of fatty acid alkyl esters

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 ^1H NMR technique is employed for the FAAE quantification and characterization. The ^1H NMR spectrum of JO shows the characteristic glyceridic proton peaks at 4.15–4.35 ppm and 5.23 ppm, as shown in Fig. 1(a). On transesterification, same peaks were no longer found in the proton NMR spectrum of FAME or FAEE (Fig. 1a). Moreover, the formation of FAME and FAEE was further supported due to the appearance of new peaks at 3.6 ppm (singlet) and 4.1–4.2 ppm (quartet), respectively. In ^{13}C NMR spectrum of JO, signals due to glyceridic carbon appear at 62.2 and 69.0 ppm, as shown in Fig. 1(b). The formation of FAME and FAEE could also be supported due to the appearance of peaks at 51.4 and 60.0 ppm, due to $-OCH_3$ and $-OCH_2-$ carbons, respectively [29,30]. Further, peaks corresponding to the glyceridic carbons were no longer found in the ^{13}C NMR spectrum of FAME and FAEE (Fig. 1b).

Similar patterns were observed in ^1H and ^{13}C NMR spectrum of CO and KO and their corresponding FAME as shown in Figs. S1 and S2 (electronic supplementary information).

3.2. Catalyst characterization

3.2.1. X-ray diffraction

The catalyst structure and crystallite size were determined by powder XRD study. The effect of calcination temperature on structure was studied by calcining the prepared samples in the temperature range of 300–900 °C but maintaining a fix zirconium concentration of 15 wt.%. As could be seen from Fig. 2(a), up to 400 °C calcination temperature the zirconia phase remains absent due to the homogeneous solid solution formation of ZrO_2–$Ca(OH)_2$. The thermal decomposition of $Ca(OH)_2$ into *cubic*-CaO phase (JCPDS 82-1691) was initiated at 500 °C and completed at 600 °C, as supported by the absence of $Ca(OH)_2$ diffraction patterns. As a consequence of increasing calcination temperature, *tertragonal*-ZrO_2 (JCPDS 88-1007), m*onoclinic*-ZrO_2 (JCPDS 88-2390), and *perovskite*-$CaZrO_3$ (JCPDS 76-240) phases were also formed above 600 °C calcination temperature.

The effect of the calcination temperature on crystallite size of *tetragonal and monoclinic*-ZrO_2 phases was studied following the Debye–Scherrer method as given in Table 3. At 500 °C calcination temperature, only *tertragonal*-ZrO_2 phase exists with a crystallite size of ~36 nm and monoclinic phase remains absent. At 600 °C calcination temperature, besides tetragonal phase, *monoclinic*-ZrO_2 was also formed with crystallite size of ~27 nm. The formation of *monoclinic*-ZrO_2 was accompanied with the reduction in crystallite size of *tetragonal* phase to 16 nm. This observation

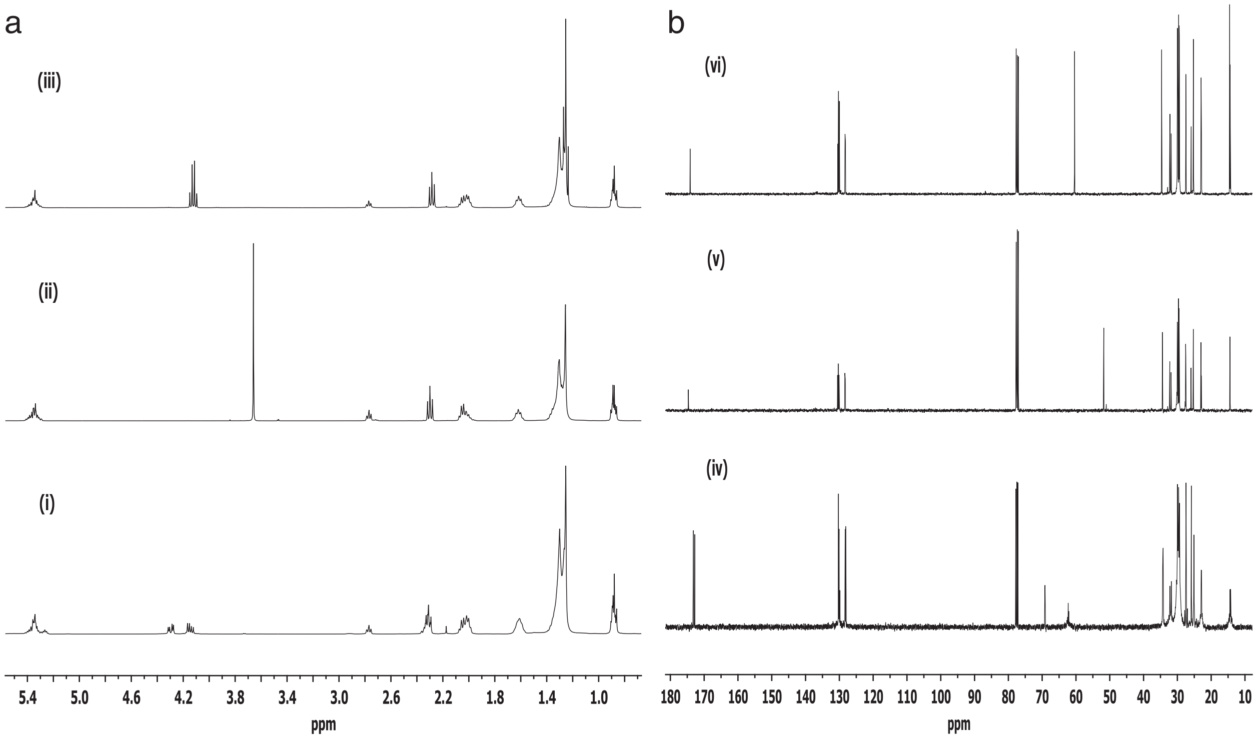

Fig. 1. Comparison of (a) ^{1}H NMR and (b) ^{13}C NMR spectra of jatropha oil (i and iv) with its methyl (ii and v) and ethyl esters (iii and vi).

supports that *monoclinic*-ZrO_2 might have formed from the existing *tetragonal* phase. A further increase in calcination temperature (≥700 °C) has neither initiated the formation of any new phase of ZrO_2, nor changed the crystallite size significantly.

The effect of the zirconium concentration (5–20 wt.%) on Zr/CaO structure was studied at a fixed calcination temperature of 700 °C. As could be seen from Fig. 2(b), a variation in zirconium concentration has not initiated any new phase formation in Zr/CaO. However, the ratio between tetragonal to monoclinic phases was found to decrease with an increase in zirconium concentration, as given in Table 3. This may be due to the formation of mainly *monoclinic*-ZrO_2 with increasing zirconium concentration in Zr/CaO at 700 °C calcination temperature.

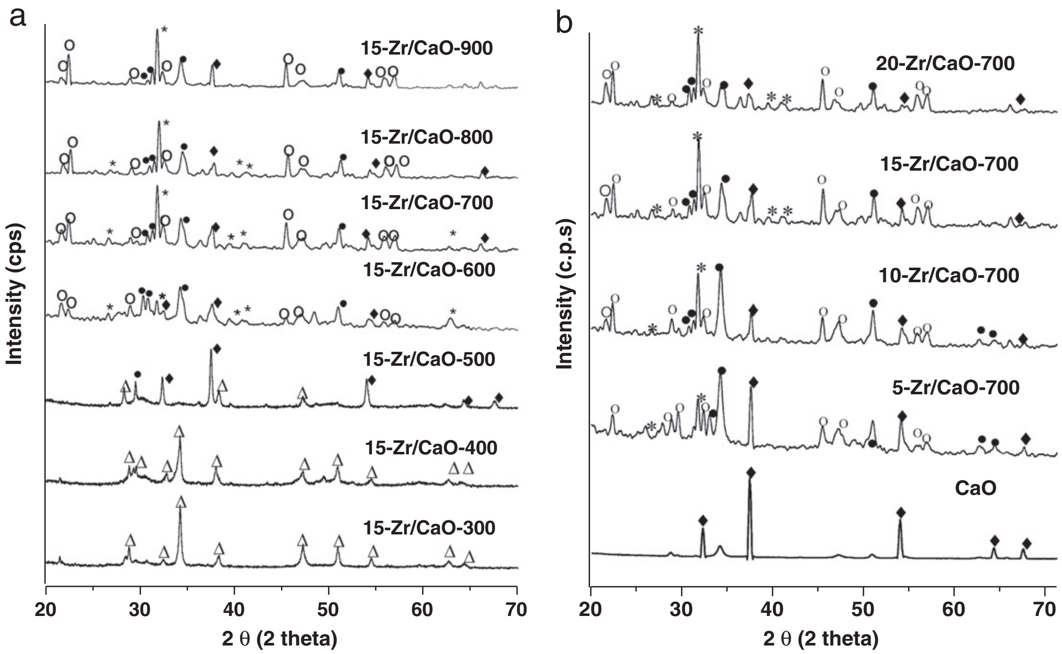

Fig. 2. Comparison of powder XRD patterns of (a) 15-Zr/CaO calcined in the temperature range of 300–900 °C and (b) Zr/CaO having zirconium concentration in the range of 0–20 wt.% (* = *monoclinic* ZrO_2, • = *tetragonal* ZrO_2, o = *perovskite* $CaZrO_3$, ◆ = *cubic* CaO, Δ = $Ca(OH)_2$).

Table 3
Effect of calcination temperature and Zr concentration on Zr/CaO structure and crystallite size.

Catalyst	Crystallite size[a] (nm)		Tetragonal phase[b] (%)	Ratio between tetragonal and monoclinic phase
	$(002)_{\text{tetragonal}}$ $(2\theta = 34.1)$	$(111)_{\text{monoclinic}}$ $(2\theta = 31.6)$		
Effect of calcination temperature				
15-Zr/CaO-300	Absence of phase	Absence of phase	–	–
15-Zr/CaO-400	Absence of phase	Absence of phase	–	–
15-Zr/CaO-500	35.77	Absence of phase	100	1:0
15-Zr/CaO-600	16.01	27.50	69	2.23:1
15-Zr/CaO-700	13.87	28.53	54	1.17:1
15-Zr/CaO-800	14.35	28.54	54	1.17:1
15-Zr/CaO-900	17.30	28.50	55	1.22:1
Effect of Zr concentration				
5-Zr/CaO-700	15.41	26.68	70	2.33:1
10-Zr/CaO-700	16.65	28.52	68	2.13:1
15-Zr/CaO-700	13.87	28.53	54	1.17:1
20-Zr/CaO-700	11.25	27.57	48	0.92:1

[a] Calculated by Debye–Sherrer method.
[b] Calculated by following the method as given in ref. [31].

3.2.2. Fourier transformation infrared spectroscopy (FTIR)

The formation of ZrO_2 phase in Zr/CaO is further supported by the FT-IR study as shown in Fig. 3. The appearance of the bands at 535 and 684 cm^{-1} due to Zr–O and $Zr-O_2-Zr$ vibrations, respectively [31,32], supports the formation of ZrO_2 species above 500 °C calcination temperature.

3.2.3. Scanning and transmission electron microscopic studies

The surface morphology and particle size of 15-Zr/CaO-700 were studied by SEM and TEM studies, respectively. As could be seen from FE-SEM image (Fig. 4a), Zr/CaO has formed in the form of 0.5–2 μm sized particles with irregular shape. Qualitative analysis by SEM-EDX study supported the presence of ~17 wt.% Zr in 15-Zr/CaO-700 as shown in Fig. S3 (electronic supplementary information).

TEM analysis reveals that Zr/CaO particles are actually the clusters of further smaller particles with an average size of ~30 nm in quasi-spherical shape as shown in Fig. 4(b). Thus powder XRD as well as TEM study supports the formation of nano structures of Zr/CaO.

3.2.4. BET surface area measurements

The specific surface area of Zr/CaO catalysts, prepared either by varying the zirconium concentration (10–20 wt.%) or calcination temperature (600–800 °C) is compared in Table 4. Minimum surface area (1.86 m^2/g) was observed in the case of Zr/CaO prepared with 15 wt.% zirconium at 700 °C calcination temperature. Interestingly, same catalyst was found to show the best activity among the prepared catalysts. Thus the activity of the catalyst was found to be a function of its basic strength rather than surface area. These results are in line with that of literature reports where the activity of the catalysts towards transesterification reaction was found to be a function of basic strength rather than surface area [22,33,34].

3.3. Catalytic activity of Zr/CaO

The number of product molecules produced in per unit time is known as rate of reaction. It is not reasonable to compare the efficiency of catalysts on the basis of reaction rate alone as it did not factor in the catalytic sites. On the other hand, turnover frequency (TOF) is defined as the number of product molecules formed per catalytic site in per unit time and it is one of the best ways to compare the efficiency of catalysts of similar type. However, TOFs for heterogeneous acid or base catalysts have not been reported frequently due to the difficulties associated with the evaluation of number of active sites [35]. In case of Zr/CaO catalyzed transesterification reaction, TOFs are calculated (at 50% conversion of JO) assuming that basic sites in catalyst were the active sites.

Calcium oxide used as support for the catalyst preparation, not only is non toxic and cost efficient but also possesses basic sites on its surface in the form of oxygen anions [36]. However, pure CaO found to show poor activity towards the transesterification reaction and hence, required relatively longer reaction duration (6–24 h) for the completion of the reaction [37,38]. In present work, in order to improve the activity, CaO has been impregnated with varying amounts of zirconium.

An increase in Lewis base sites was observed on increasing the zirconium concentration (from 5 to 15 wt.%) followed by an increase in calcination temperature (from 300 to 700 °C). At high calcination temperature (≥600 °C), due to the thermal decomposition of hydroxides into corresponding oxides, the strong Lewis basic sites were created in catalyst as given in Table 4. The maximum basic strength as well as basic sites were observed in 15 wt.% Zr impregnated CaO, prepared at 700 °C calcination temperature. On the basis of structural and activity analyses of Zr/CaO it was observed (Tables 3 and 4) that better activity (in terms of the reaction rate) is shown by the catalysts having tetragonal/monoclinic ratio close to unity (*e.g.* 15-Zr/CaO-700, 20-Zr/CaO-900, 15-Zr/CaO-800 and 15-Zr/CaO-900).

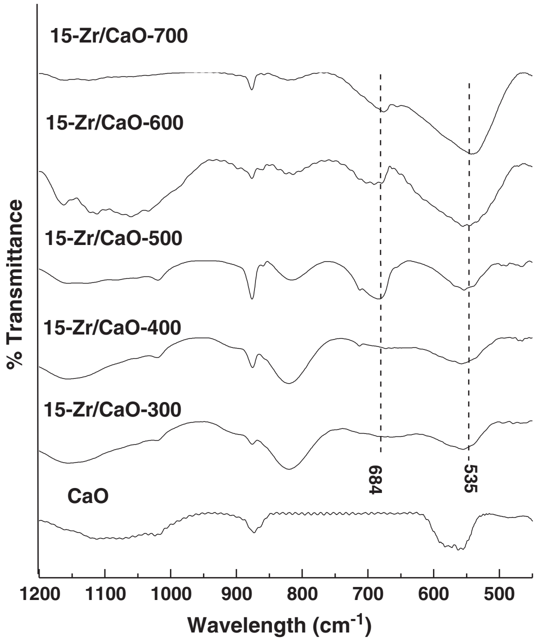

Fig. 3. Comparison of FTIR spectra of CaO and 15-Zr/CaO calcined at 300–700 °C.

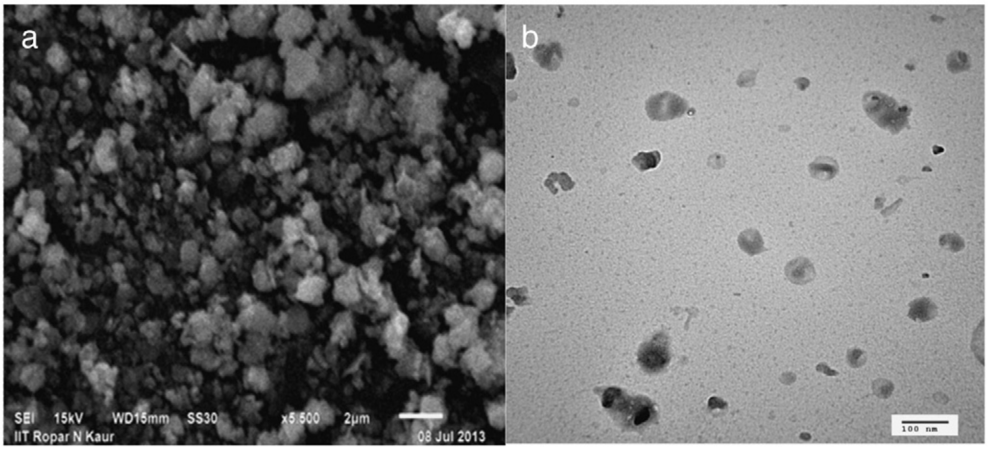

Fig. 4. (a) FE-SEM image and (b) TEM image of 15-Zr/CaO-700.

The efficacy of Zr/CaO catalysts towards the methanolysis and ethanolysis of JO was compared on the basis of reaction rate and TOF. The reaction rate is found to be a function of basic sites present in Zr/CaO. However, the increase in reaction rate did not follow the linear relationship with the basic sites, and hence, 15-Zr/CaO-700 catalyzed reaction exhibited maximum rate of reaction but not the highest TOF (Table 4). Since, 15-Zr/CaO-700 was found to enhance the reaction rate to the maximum extent; hence, it was selected to optimize various reaction parameters for the transesterification reaction. As evident from the Table 4, owing to higher mobility of methoxide nucleophile, due to its shorter carbon chain length, the rate of methanolysis was always found higher than that of ethanolysis [16].

To find out the reaction conditions for the optimum catalytic activity of 15-Zr/CaO-700, transesterification reactions were carried out by varying one parameter at a time out of the following: (i) catalyst amount with respect to oil, (ii) reaction temperature and (iii) alcohol to oil molar ratio. Further, transesterification reactions were also performed in the presence of varying amounts of moisture and FFA contents in order to evaluate the maximum tolerance of the catalyst towards them. Under optimized reaction conditions, reusability of the catalyst and kinetics of the Zr/CaO catalyzed transesterification were also studied.

3.3.1. Effect of catalyst amount with respect to oil

In order to optimize the catalyst concentration, a series of transesterification reactions of JO with methanol (15:1 molar ratio) and ethanol (21:1 molar ratio) were performed in the presence of 1–6 wt.% (with respect to oil) of 15-Zr/CaO-700. The FAME and FAEE yields were found to increase as the catalyst concentration was increased from 1 to 5 wt.% as shown in Fig. 5(a) and (b), respectively. A 5 wt.% catalyst concentration required 105 and 420 min for the complete conversion of JO into corresponding FAME and FAEE, respectively. However, a further increase in catalyst concentration (≥5 wt.%) was not found to change the conversion significantly. 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 [39].

3.3.2. Effect of reaction temperature

Heterogeneous catalysts, due to the phase difference from reagents, usually required high temperature and pressure and longer reaction period to yield the significant conversion. Such reaction conditions demand complicatedly designed costlier reactor which in turn may increase the biodiesel production cost [1].

The optimum reaction temperature for 15-Zr/CaO-700 was determined by performing the transesterification of JO in the temperature range of 35–85 °C. An increase in FAME and FAEE yields was observed with the increase in reaction temperature from 35 to 65 °C and 45 to 75 °C, respectively (Fig. 6a and b). A further increase in reaction temperature was not found to influence the FAME and FAEE yields significantly. Although the catalyst was found to be more effective at 65 °C, however, even at room temperature (35 °C) complete conversion of JO into corresponding FAME was achieved in 5 h of reaction period. High basic

Table 4
Comparison of basic strengths, basicity, BET surface areas, rate of reactions and TOFs for the Zr/CaO catalyzed transesterification reactions.

Catalyst	Basic strength	Basicity (mmoles of HCl/g of catalyst)	BET surface area (m^2/g)	Methanolysis		Ethanolysis	
				TOF ($\times 10^{-3}$ s^{-1})	Rate of reaction ($\times 10^{-6}$ mol s^{-1} g^{-1} of catalyst)	TOF ($\times 10^{-4}$ s^{-1})	Rate of reaction ($\times 10^{-7}$ mol s^{-1} g^{-1} of catalyst)
CaO	$9.8 < H\_ < 10.1$	9.48	3.90	0.33	0.80	1.29	3.22
5-Zr/CaO-700	$10.1 < H\_ < 11.1$	9.71	ND	0.79	1.93	1.65	4.02
10-Zr/CaO-700	$10.1 < H\_ < 11.1$	14.24	6.40	0.60	2.15	1.50	5.37
15-Zr/CaO-700	$11.1 < H\_ < 15.0$	20.21	1.86	0.54	2.76	1.37	6.90
20-Zr/CaO-700	$10.1 < H\_ < 11.1$	11.91	3.26	0.77	2.32	1.62	4.83
15-Zr/CaO-300	$10.1 < H\_ < 11.1$	6.01	ND	0.95	1.20	1.93	3.43
15-Zr/CaO-400	$10.1 < H\_ < 11.1$	6.23	ND	0.91	1.40	1.90	3.65
15-Zr/CaO-500	$10.1 < H\_ < 11.1$	7.36	ND	0.83	1.89	1.85	4.00
15-Zr/CaO-600	$10.1 < H\_ < 11.1$	9.94	4.99	0.80	2.00	1.77	4.39
15-Zr/CaO-800	$10.1 < H\_ < 11.1$	15.67	5.68	0.60	2.38	1.29	5.08
15-Zr/CaO-900	$10.1 < H\_ < 11.1$	14.44	ND	0.66	2.41	1.64	5.93

(Reaction conditions: *Methanolysis*: methanol to oil molar ratio of 15:1 at 65 °C reaction temperature; *Ethanolysis*: ethanol to oil molar ratio of 21:1 at 75 °C reaction temperature, and 5 wt.% of 15-Zr/CaO-700 with respect to oil in both the cases, ND — Not determined).

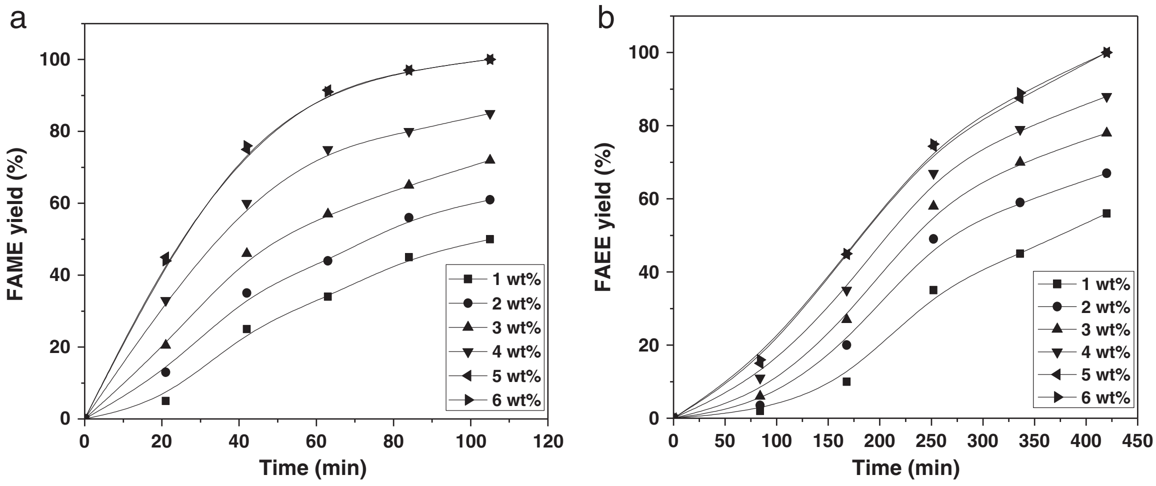

Fig. 5. Influence of catalyst concentration on 15-Zr/CaO-700 catalyzed transesterification of JO. Reaction conditions: (a) methanol to oil molar ratio of 15:1 at 65 °C reaction temperature and (b) ethanol to oil molar ratio of 21:1 at 75 °C reaction temperature.

strength and presence of more number of basic sites could be responsible behind the moderate activity of catalyst even at ambient temperature.

3.3.3. Effect of alcohol to oil molar ratio

The effect of alcohol/oil molar ratio on transesterification reaction is one of the important parameters which affects not only the alkyl ester yield but also the cost of biodiesel production. Stoichiometrically, a 3:1 alcohol to oil molar ratio is required for the complete transesterification of vegetable oil into corresponding alkyl esters. Transesterification, being a reversible reaction, is usually performed with an excess of alcohol to shift the equilibrium in forward direction and to achieve the maximum alkyl ester yield in relatively short reaction duration [40]. Excess alcohol not only promotes the transesterification rate but also removes product molecules from the catalyst surface to regenerate the active sites [41–43].

To determine the optimum alcohol/oil molar ratio for 15-Zr/CaO-700, the reactions were performed by varying the alcohol/oil molar ratio from 3:1 to 18:1 in case of methanolysis and 3:1 to 24:1 in case of ethanolysis. The FAME yield increases from 60 to 99% on increasing the methanol/oil molar ratio up to 15:1, as shown in Fig. 7(a). Similar trend was observed in case of ethanolysis (Fig. 7b) and 99% FAEE yield was observed with a 21:1 ethanol/oil molar ratio.

Thus a 15:1 methanol to oil molar ratio at 65 °C or 21:1 ethanol to oil molar ratio at 75 °C in the presence of 5 wt.% catalyst (with respect to oil), was found to be an optimum condition for the 15-Zr/CaO-700 catalyzed transesterification of JO.

3.3.4. Effect of moisture and FFA content

Homogeneous catalyst required costlier refined vegetable oil for the transesterification reactions as the presence of >0.3 wt.% moisture and/or >0.5 wt.% FFA contents in feedstock deactivates the catalyst due to the saponification [2]. In present study JO employed as feedstock was found to have 7.5 and 0.35 wt.% FFA and moisture contents, respectively. In order to demonstrate the advantage of developed Zr/CaO catalyst over homogeneous one, methanolysis of JO was also performed in the presence of NaOH. Although saponification of JO was observed in the presence of homogeneous catalyst, however, >99% FAME yield was observed in the presence of Zr/CaO catalyst. In

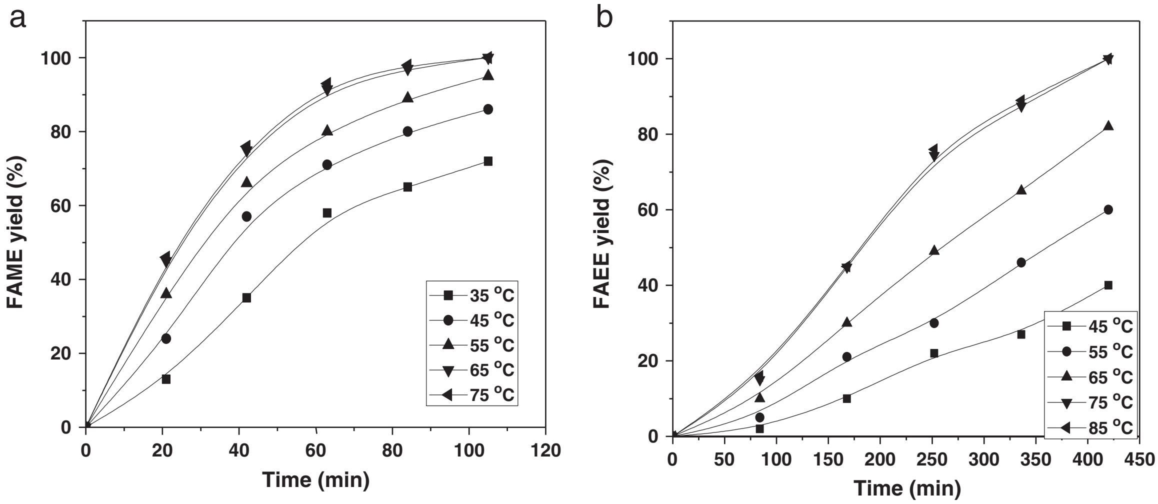

Fig. 6. Effect of reaction temperature on 15-Zr/CaO-700 catalyzed transesterification of JO. Reaction conditions: (a) methanol to oil molar ratio of 15:1 and (b) ethanol to oil molar ratio of 21:1 and 5 wt.% of 15-Zr/CaO-700 with respect to oil in both the cases.

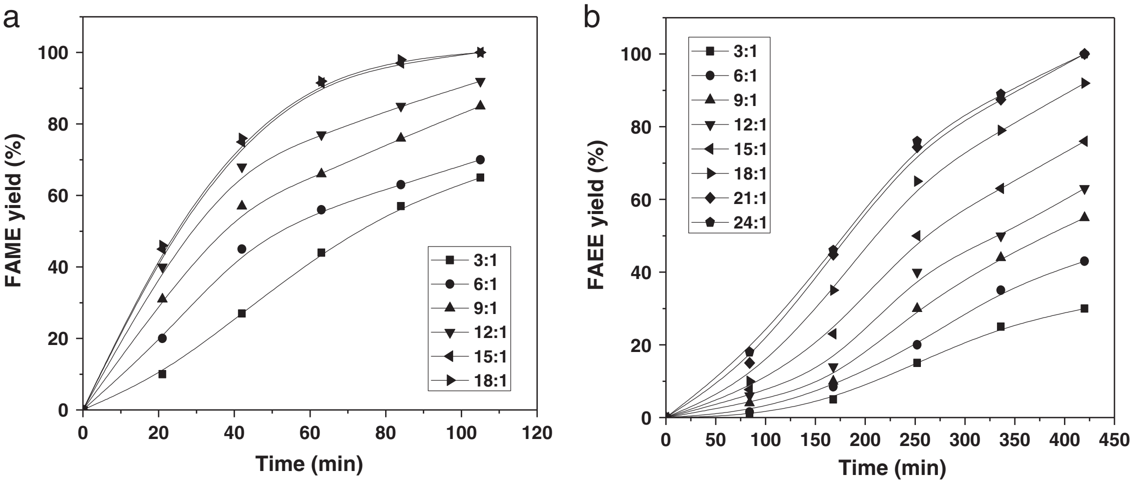

Fig. 7. Effect of alcohol:oil molar ratio on 15-Zr/CaO-700 catalyzed transesterification of JO. Reaction conditions: Reaction temperature (a) methanolysis at 65 °C and (b) ethanolysis at 75 °C, both reactions were performed in the presence of 5 wt.% of 15-Zr/CaO-700 with respect to oil.

order to determine the maximum moisture resistance of the developed catalyst, transesterification reactions of JO were performed by adding up to 6.0 wt.% of water (with respect to oil) in reaction mixture. The Zr/CaO activity was not found to be effected by the presence of up to 2 wt.% of moisture contents as shown in Fig. 8(a). Nevertheless, a further increase in moisture concentration (3–6 wt.%) was found to affect the catalytic activity adversely as more time was required by the catalyst for the complete methanolysis of oil. Lesser activity of Zr/CaO catalyst in the presence of high moisture concentration could be due to the reaction between water and catalyst support (CaO), which could convert the stronger Lewis basic (–O–) sites back into weaker Bronsted basic (–OH) sites [38]. A further increase in moisture content (>6 wt.%), results in high degree of deactivation of the catalyst and hence, only ~30% FAME yield was achieved.

In order to determine the maximum FFA tolerance of the prepared catalyst, transesterification reactions of CO, WO, JO and KO (having 1–15 wt.% FFA) were performed with methanol. As shown in Fig. 8(b), Zr/CaO catalyst was able to complete the transesterification of oil having up to 15 wt.% FFA. Increase in FFA content was also found to reduce the catalytic activity and hence, Zr/CaO catalyst required more time for the complete transesterification of oils having higher FFA concentration (Fig. 8b).

Thus, prepared Zr/CaO catalyst not only has demonstrated better moisture and FFA resistance but also was found to be effective for the transesterification of a variety of low quality feedstock in single step without any pre-treatment.

3.4. Reusability and homogeneous contribution of catalyst

The repeated use of a heterogeneous catalyst is expected to reduce the overall processing cost of a chemical reaction. To test the reusability of 15-Zr/CaO-700, transesterification of the JO was performed with methanol under optimized reaction conditions. After the completion of the reaction, Zr/CaO was recovered from the reaction mixture by filtration, washed with hexane and finally regenerated at 700 °C calcination temperature. The catalyst hence recovered and regenerated was employed for 4 successive catalytic cycles under the same experimental and regeneration methods. As shown in Fig. 9, the reused catalyst was also found to yield >99% FAME in second run. However, 80% and 40% FAME yields were achieved during the third and fourth runs,

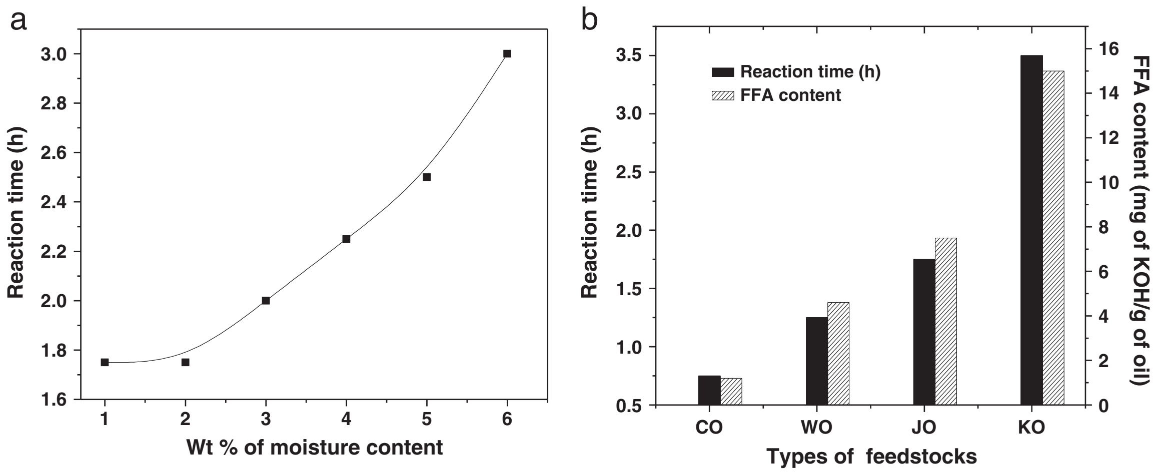

Fig. 8. Effect of (a) moisture content and (b) FFA contents on the 15-Zr/CaO-700 catalyzed transesterification of JO (reaction time is the time required for the completion of the reaction). Reaction conditions: Methanol to oil molar ratio of 15:1 at 65 °C reaction temperature in the presence of 5 wt.% (catalyst/oil) catalyst.

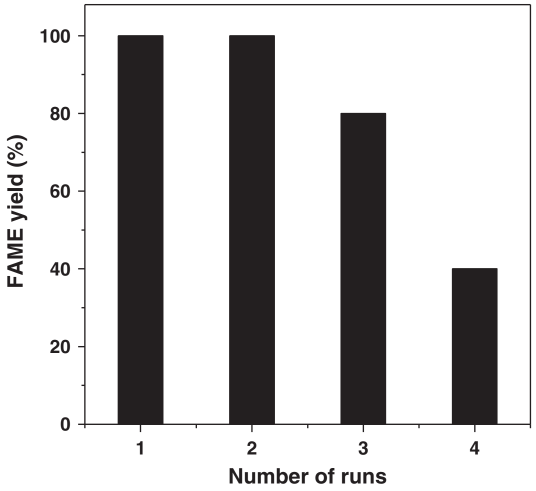

Fig. 9. Reusability study of 15-Zr/CaO-700. Reaction conditions: methanol to oil molar ratio of 15:1 at 65 °C reaction temperature in presence of 5 wt.% catalyst.

respectively. The gradual loss in catalytic activity may be due to, (i) the blockage of active sites either due to the adsorption of organic molecules or due to the contamination by atmospheric O_2, H_2O, and CO_2 (ii) the structural changes that occurred during catalytic and regeneration process and (iii) the partial leaching of active species from the catalyst.

In order to evaluate the structural changes that occurred in Zr/CaO, the XRD patterns of the fresh and regenerated Zr/CaO are compared in Fig. 10(a). In the XRD patterns of regenerated Zr/CaO, peaks corresponding to *cubic*-CaO phase, *tetragonal*-ZrO_2 phase and few peaks corresponding to *perovskite*-$CaZrO_3$ phase were no longer found. Further, the presence of a new diffraction peak at 2θ~30.06, in regenerated catalyst supports the formation of *orthorhombic*-ZrO_2 phase (JCPDS-87-2105) during the catalyst activation step.

The deposition of the adsorbed organic species on catalyst support could partially deactivate the catalyst due to the blockage of catalyst active sites [44]. The FTIR spectrum (Fig. 10b) of the regenerated catalyst did not show vibrations corresponding to any adsorbed organic molecules to indicate that FAME or glycerol has not been adsorbed on the surface of regenerated Zr/CaO.

The metal analysis supported the presence of Zr (120 ppm) and Ca (700 ppm) in FAME. Thus during the catalytic cycle metal is gradually lost and could also be another reason for the loss of catalytic activity. Hence, the gradual loss of the catalytic activity, upon repeated use, could be attributed to the (i) structural changes that occurred in catalyst, and (ii) partial loss of the Zr from Zr/CaO catalyst.

Metal ions, found in reaction mixture could catalyze the reaction similar to a homogeneous catalyst. To investigate whether the leached metal ions have catalyzed the reaction, 15-Zr/CaO-700 (500 mg) was stirred vigorously with refluxing methanol (13 mL) for 105 min. After the stipulated time, the catalyst was removed by filtration and recovered methanol was mixed with JO (15:1 molar ratio) and heated at 65 °C for another 105 min. Under mentioned reaction conditions, not more than 5% FAME yield was obtained. Thus it is safe to assume that leached metal ions have not catalyzed the reaction to the significant extent and heterogeneous Zr/CaO catalyst is mainly responsible for the catalytic activity.

3.5. Kinetic study

The transesterification of triglycerides in the presence of excess alcohol has been reported to follow pseudo-first order kinetics [45,46]. The kinetics of the 15-Zr/CaO-700 catalyzed methanolysis and ethanolysis of JO were studied at different temperatures and corresponding graphs between $-\ ln(1-X)$ *vs* t are shown in Fig. 11(a) and (b) respectively.

The linear nature of these plots supported that both reactions follow the (pseudo) first order rate law. The apparent first order rate constants from these plots were found to be 0.062 min^{-1} at 65 °C for the methanolysis and 0.0123 min^{-1} at 75 °C for the ethanolysis reaction.

The Arrhenius model was employed to estimate the activation energy (E_a) and pre-exponential factor (A) for both the reactions following the Eq. (4) [28]. A plot between lnk *vs* 1/T is shown in Fig. 12, and the values of E_a and A from this plot were found to be 29.8 kJ mol^{-1} and 1.8×10^3 min^{-1}, respectively for methanolysis and 42.5 kJ mol^{-1} and 2.2×10^4 min^{-1}, respectively for ethanolysis.

The literature reported activation energy for the methanolysis and ethanolysis in the presence of homogeneous and heterogeneous catalysts has been compared with that observed in present work as given in Table 5.

It is evident from the comparison, for heterogeneous catalysts, that the activation energy for methanolysis was observed within the range of reported values and for ethanolysis lower than the literature reported values.

3.6. Koras–Nowak criterion test

In order to study the kinetics of the reaction, the catalytic data should be independent from all transport influences. To prove that measured catalytic activity was independent of the influence of transport

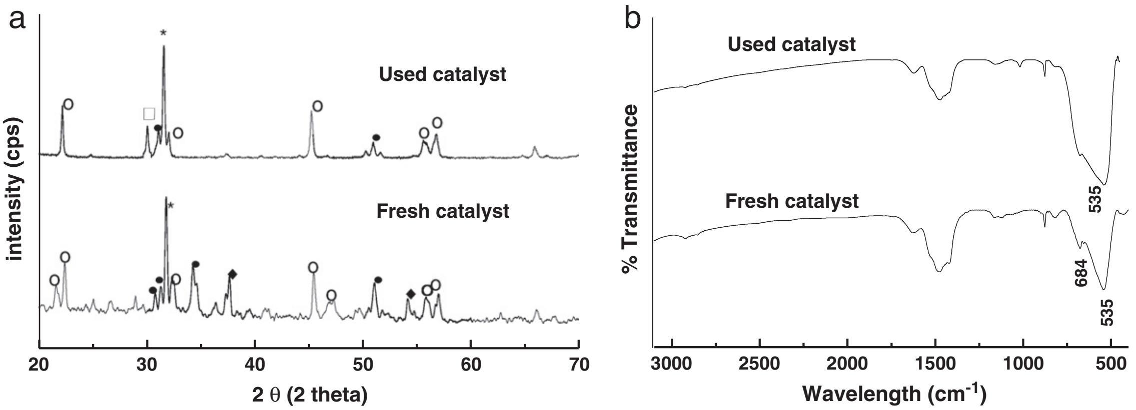

Fig. 10. Comparison of (a) XRD and (b) FT-IR of fresh and used catalyst. (* = *monoclinic* ZrO_2, • = *tetragonal* ZrO_2, o = *perovskite* $CaZrO_3$, ♦ = *cubic* CaO, □ = *Orthorhombic* zirconia).

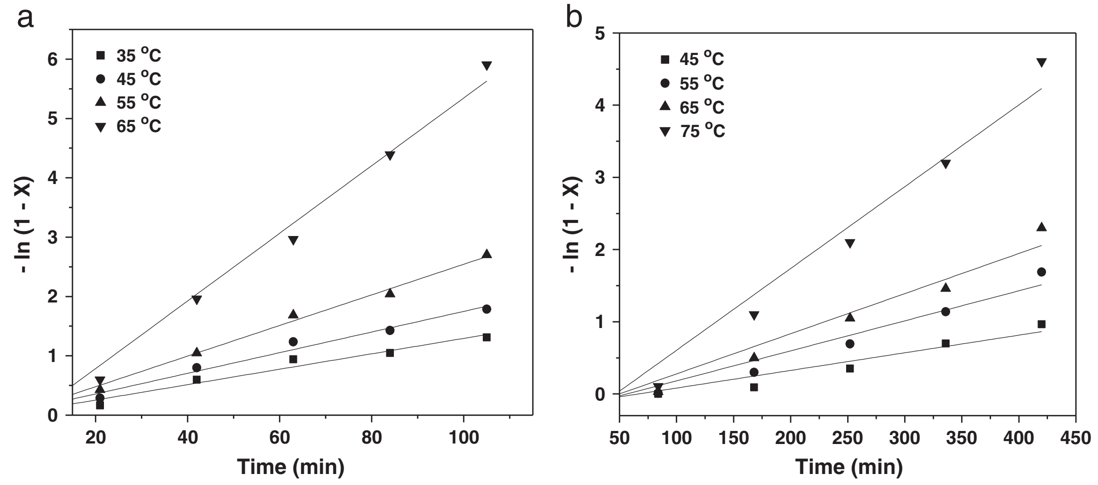

Fig. 11. Plots of −ln(1 − X) *vs* time at different temperatures. Reaction conditions: (a) methanol to oil molar ratio of 15:1 (b) ethanol to molar oil ratio of 21:1 and 5 wt.% of 15-Zr/CaO-700 with respect to oil in both the cases.

phenomena, the Koros–Nowak criterion test modified by Madon–Boudart was applied [55,56]. The reactions were carried out in the presence of two catalysts with similar fractional exposures of basic sites but having different Zr loadings. In present study, 5 wt.% of 15-Zr/CaO-700 or 7 wt.% of 10-Zr/CaO-700 catalyst dosages was employed with a methanol/oil ratio of 15:1 at 65 °C or ethanol/oil ratio of 21:1 at 75 °C as shown in Fig. 13. Alkyl esters formed during the course of reaction were quantified with a time gap of 15 min by ^{1}H NMR technique. The time required for the similar conversions of JO into alkyl esters was determined and a plot between TOF *vs* % conversion is drawn as shown in Fig. 13. The results as shown in Fig. 13 supported that TOFs were found to be almost similar for the identical conversions in the presence of catalyst having varying zirconium concentration. Hence, it could be concluded that the reaction obeyed the Koros–Nowak criterion and reaction rates were not masked by the rates of transport.

3.7. Physicochemical properties of FAME and FAEE

The fatty acid ethyl or methyl esters must meet certain standards *viz.*, ASTM D6751 or EN 14214, before they could be employed for the commercial application as biodiesel. To study the physicochemical properties, FAME and FAEE were prepared by the transesterification reactions of JO with methanol and ethanol, respectively, under optimized reaction conditions. Upon completion of the reaction, the catalyst was separated through filtration and liquid phase thus obtained was kept in a separating funnel for 12 h to separate the lower glycerol layer from upper FAME/FAEE layer. Excess alcohol from later was recovered with the help of rotary evaporator, and few physicochemical properties of the FAME/FAEE ware studied by following the standard test methods as given in Table 6. The values of the studied properties of the obtained fatty acid alkyl ester were found within the acceptable limits of European standards (EN-14214).

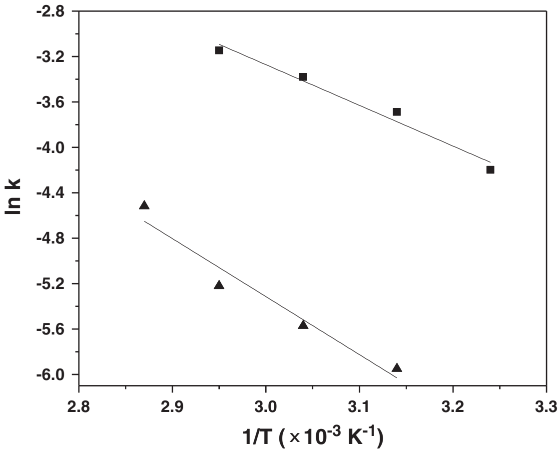

Fig. 12. Arrhenius plot for the transesterification of JO with methanol (■) and ethanol (▲) over 15-Zr/CaO-700 catalyst.

3.8. Conclusions

In summary, a series of the Zr/CaO was prepared by varying the calcination temperature and zirconium loading in CaO. The catalyst prepared with 15 wt.% zirconium in CaO at 700 °C calcination temperature (15-Zr/CaO-700), owing to higher basicity, has demonstrated better catalytic activity towards the methanolysis and ethanolysis of jatropha oil. The catalyst has shown high moisture and FFA tolerance and was found to be effective for the transesterification of feedstocks having up to 6 and 15 wt.% moisture and FFA contents, respectively. The optimum values of the parameters, to achieve >99% fatty acid alkyl ester yield, were: catalyst concentration of 5 wt.%, methanol/oil molar ratio of 15:1 at 65 °C and ethanol/oil molar ratio of 21:1 at 75 °C. Following the pseudo first order kinetic equation, activation energy for the methanolysis and ethanolysis of jatropha oil was found to be 29.8 and 42.5 kJ mol^{-1}, respectively. The catalyst was reusable and its catalyst activity was persistent for two catalytic runs. The lixiviation study supports the negligible homogeneous contribution in catalytic activity, and the Koros–Nowak test demonstrates that the activity is independent of the influence of transport phenomenon. Few physicochemical properties of the FAME and FAEE prepared from jatropha oil were studied, and observed values were found within the limits of EN 14214 specifications.

Acknowledgments

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Table 5
Activation energy comparison for the transesterification reaction catalyzed by homogeneous and heterogeneous catalysts.

Oil	Alcohol	Catalyst/quantity (wt% with respect to oil)	Alcohol:oil molar ratio	Reaction temperature (°C)	Order of reaction	Activation energy (kJ mol^{-1})	References
Homogeneous catalysts							
Palm	Methanol	KOH/1	6:1	55–65	Second-order	26.8–61.5	[47]
Soybean	Methanol	$NaOCH_3$/0.5	6:1	20–60	Second and forth order for consecutive and shunt reactions, respectively	56.8–83.8	[45]
Soybean	Methanol	NaOH/0.2	6:1	30–70	Second-order	21.7–83.1	[48]
Brassica carinata	Methanol	KOH/0.5–1.5	6:1	25–65	Second-order	12–104.8	[49]
Sunflower	Methanol	KOH/0.5–1.5	6:1	25–65	Second-order	6–41.6	[50]
Sunflower	Ethanol	NaOH/0.75–1.25	6:1,9:1 and 12:1	25–75	Irreversible pseudo second-order	3.4–43.9	[51]
Castor	Ethanol	C_2H_5ONa/1	16:1	30–70	First-order	70.6	[52]
Heterogeneous catalysts							
Soybean	Methanol	CaO·ZnO/2	10:1	60–96	Pseudo first-order	26.5	[21]
Used vegetable	Methanol	CaO·ZnO/2	10:1	60–96	Pseudo first-order	16.6	[21]
Soybean	Methanol	Zeolite Linde Type A/50	20:1	40–63	Pseudo first-order	14.09	[53]
Palm	Methanol	Zeolite Linde Type A/10	10:1	50–63	Pseudo first-order	48.87	[53]
Soybean	Methanol	SrO/2	12:1	40–65	Pseudo first-order	40.12	[54]
Soybean	Methanol	CaO/2	12:1	40–65	Pseudo first-order	81.09	[54]
Waste frying	Methanol	CaO/2	6.03:1	50–65	Pseudo first-order	79	[20]
Waste cottonseed	Methanol	K-CaO/7.5	12:1	35–65	Pseudo first-order	54	[2]
Jatropha	Methanol	Zr/CaO/5	15:1	35–65	Pseudo first-order	29.8	In our work
Rapeseed	Ethanol	Mg_2CoAl/2	16:1	140–200	Irreversible first order	60.5	[18]
Jatropha	Ethanol	Zr/CaO/5	21:1	45–75	Pseudo first-order	42.5	In our work

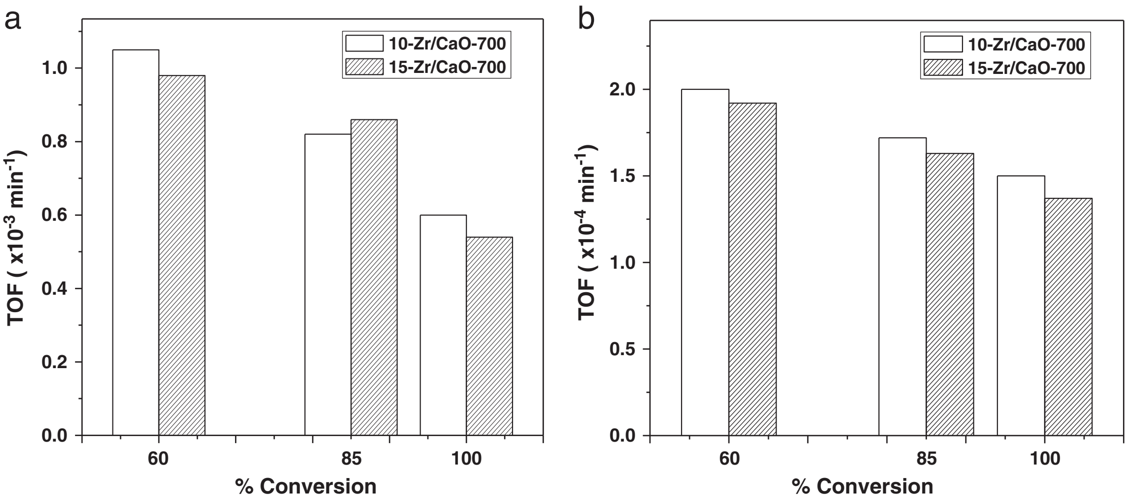

Fig. 13. A plot of TOF *vs* % conversion for the 10-Zr/CaO-700 and 15-Zr/CaO-700 catalyzed (a) methanolysis and (b) ethanolysis of JO. Reaction conditions: (a) methanol to oil molar ratio; 15:1 at 65 °C (b) ethanol to oil molar ratio; 21:1 at 75 °C and catalyst concentration; either 7 wt.% of 10-Zr/CaO-700 or 5 wt.% of 15-Zr/CaO-700 in both the cases.

Table 6
Physicochemical properties of the FAME and FAEE prepared from JO.

S. no.	Parameters	Units	FAME	FAEE	EN14214	Test method
1	Ester content	%	>99%	>99%	96.5	^{1}H NMR
2	Flash point	°C	110	120	100–170	ASTM D93
3	Pour point	°C	1	2	−5 to10	ASTM D2500
4	Kinematic viscosity at 40 °C	cSt	4.50	4.83	1.9–6.0	ASTM D445
5	Density at 31 °C	kg/mm^3	870	880	860–900	ISI448 P:32
6	Ash	%	NIL	0.01	0.02	ASTM D874
7	Iodine value	mg of I_2/g of sample	75.9	87.8	<120	^{1}H NMR[a]
8	Acid value	mg of KOH/g of sample	0.7	0.8	0.8	ASTM D664
9	Saponification value	mg of KOH/g of sample	180	182.32	–	ASTM D5558

[a] Following the method given in reference [57].

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2013.11.002.

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