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One pot transesterification and esterification of waste cooking oil *via* ethanolysis using Sr:Zr mixed oxide as solid catalyst

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Abstract: Mixed oxide of Sr and Zr has been prepared by co-precipitation method and examined as heterogeneous catalyst for one pot esterification and transesterification of waste cooking oil with ethanol for the production of fatty acid ethyl esters (FAEE). Mixed oxide of Sr:Zr with 2:1 atomic ratio and calcined at 650 ºC showed the optimum activity among the prepared catalysts. The catalyst possesses both acidic and basic sites, and hence was able to perform simultaneous esterification and transesterification of free fatty acid containing vegetable oils. The transesterification activity was found to be a function of basic sites of catalyst which in turn depends on calcination temperature and Sr:Zr atomic ratio. A pseudo first order kinetic equation was applied to evaluate the kinetics of the 2Sr:Zr-650 catalyzed ethanolysis of waste cottonseed oil and activation energy (E_a) for the reaction was observed as 48.17 kJ mol^{-1}. Thermodynamic activation parameters of the reaction was evaluated from Eyring-Polanyi equation and the values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be 88.23 kJ mol^{-1}, 45.97 kJ mol^{-1} and -121.37 J $mol^{-1}K^{-1}$, respectively. These values suggest that 2Sr:Zr-650 catalyzed reaction is endothermic, unspontaneous and following the associative kind of mechanism. The catalyst was recovered by simple filtration from the reaction mixture and reused in 4 cycles without any significant loss in activity as well as metal from catalyst in reaction mixture.

1. Introduction

The use of biodiesel as a substitute of fossil fuels is becoming gradually more popular nowadays due to global energy crisis and environmental reasons. Biodiesel (BD), defined as fatty acid alkyl esters (FAAEs), being renewable, biodegradable and non-toxic has become an ecofriendly substitute for the fossil based diesel fuel.[1] Additionally, BD burning causes lesser emissions of SO_x, CO, un-burnt hydro-carbons and particulate matter, which make it an ecofriendly fuel. Biodiesel is conventionally produced by the transesterification of edible or non-edible oils and animal fats with short chain alcohols in the presence of homogeneous acid or base catalyst.[2,3] Due to the limited supply, the application of the edible vegetable oil is prohibited for BD production in India. Nonedible oils (*e.g.* jatropha and karanja oils) and waste cooking oil could be an alternative feedstock, and may also provide solution for their disposal. However, such feedstock usually possess high concentration of free fatty acid (FFA) and moisture and hence, homogeneous alkali catalyst could not be employed for their transesterification. Conventionally high FFA containing vegetable oils (VO) are transesterified in two step process involving (i) homogeneous acid (e.g., H_2SO_4, HCl, etc.,) catalyzed pre-esterification followed by (ii) alkali (e.g., NaOH, KOH, etc.,) catalyzed transesterification.[4] The major drawbacks of this method are the subsequent neutralization, separation, and purification steps which are time consuming and generate huge quantity of industrial effluents. Thus a heterogeneous catalyst capable of catalyzing simultaneous esterification as well as transesterification of high FFA containing feedstock could avoid the problems linked with the use of homogeneous catalysts.

Omar and Amin[5] reported Sr/ZrO_2 catalyst which possesses both acidic and basic sites and capable of catalyzing simultaneous transesterification and esterification of waste cooking oil having 2.5 wt% FFA content. The main drawback of Sr/ZrO_2 catalyst was the lower biodiesel yield (79.7%) even at high reaction temperature (115.5 ºC) that using a too higher methanol to oil molar ratio (29:1). Yan *et al.*[4] used ZnO-La_2O_3 catalyst to achieve 96% FAAE yield from waste oil with 5.4 wt% FFA, at 170-200 ºC reaction temperature. Rattanaphra *et al.*[6] employed SO_4^{2-}/ZrO_2 for the transesterification of rapeseed oil having 10 wt% FFA content to achieve 86 % yield but leaching of sulfate group in reaction mixture remains an issue. Sreeprasanth *et al.*[7] prepared Fe-Zn double metal cyanide for the esterification and transesterification reaction but a decrease in biodiesel yield was observed due to the conversion of ester into FFA due to hydrolytic activity of catalyst. Kulkarni *et al.*[8] reported tungstophosphoric acid supported on hydrous zirconia for the simultaneous esterification and transesterification of low quantity canola oil with 20 wt% FFA to achieve 90 % ester yield at high reaction temperature (200 ºC). Thus most of the catalysts required high temperature and pressure conditions for the biodiesel production from low quality feedstock having high FFA contents. Such operational condition required complicated and costly reactors which eventually lead to increase the biodiesel production cost.

Another issue related with the current biodiesel production technology is the application of methanol which is a highly toxic chemical and itself a refinery residue.[9] On the other hand, ethanol is not only nontoxic but also renewable as produced mainly by the fermentation of biomass. However, due to low reactivity and difficulty in separation of FAEE from glycerol it could not be explored extensively for BD production in literature as well as at commercial level. SO_4^{2-}/ZrO_2, CaO, Zr/CaO, MgO/SBA-15, Mg_2CoAl, CaO-La_2O_3, $Ca(OCH_2CH_3)$ and calcium zincate are few examples of literature reported heterogeneous catalysts for the ethanolysis of VOs in batch reactors.[10-17] The major problems with the use of these catalysts are the requirement of high pressure and high temperature condition, and/or low conversion levels and poor reusability. To the best of our knowledge, no report is available in literature for the simultaneous esterification and transesterification of VOs ***with ethanol*** in presence of heterogeneous catalyst.

In present study, mixed oxides of alkaline earth metals and Zr was prepared *via* co-precipitation method and employed for the ethanolysis of the waste cotton seed oil. The activity of the catalysts were compared and 2Sr:Zr-650 catalyst was found to show better activity among them. The kinetics of the ethanolysis of waste cotton seed oil was studied under optimized reaction condition. The catalyst 2Sr:Zr-650 was able to perform simultaneous esterification and transesterification of vegetable oil having free fatty acid content as high as 18.1 wt%.

2. Experimental Section

2.1. Materials

Zirconium oxychloride octahydrate was obtained from Sigma Aldrich and strontium nitrate, barium nitrate, calcium nitrate, magnesium nitrate, hexane, ethyl acetate, acetic acid, methanol, ethanol, ammonia (all chemicals of analytical grade purity), and silica gel (TLC grade) were obtained from Loba Chemie Ltd. (India) and used as such without further purification. *n*–Butylamine, trichloroacetic acid and benzene (HPLC grade) used for Hammett indicator titration, were obtained from Spectrochem Pvt. Ltd. (India).

Waste cottonseed oil (WO), fresh cottonseed oil (CO), Karanja oil (KO) and Jatropha oil (JO) used for the transesterification reactions were procured from the local shops located in Patiala and their chemical analysis is provided in Table S1 (ESI).

2.2. Catalyst preparation

The mixed oxide of strontium and zirconium with atomic ratio 2:1 was prepared by co-precipitation method. In a typical preparation, 5 g of $ZrOCl_2.8H_2O$ and appropriate amount of $Sr(NO_3)_2$ was mixed in 50 ml distilled water. To this 25 wt% ammonia solution was added until the pH of mixture reached ~ 10. The resulted mixture was stirred for 4 h, and then filtered to obtain white precipitates which were washed with distilled water to make it pH neutral. The white solid, thus obtained, was dried at 120 °C for 24 h and finally calcined at 650 °C for 5 h. Mixed oxide of magnesium, calcium and barium with zirconium were also prepared following the same experimental procedure but using appropriate metal precursors in place of $Sr(NO)_3$. Prepared catalysts were labelled as xM:Zr-T, where x, M and T represents the M/Zr atomic ratio, alkaline metal and calcination temperature (ºC), respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical's X'Pert Pro using monochromatic Cu Kα radiation (λ=1.54060 Å) and scanning the samples over a 2θ range of 5–80°. Thermo-gravimetric–Diffrential Scanning Calorimetry analysis (TG-DSC) was recorded on Netzsch STA 449F3 instrument. The programmed heating ranged from 25 to 800 °C at a heating rate of 10 °C min^{-1} under normal atmosphere. Fourier transform-infrared spectra (FTIR) of the samples were recorded in KBr matrix on Perkin Elmer-Spectrum 400 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) was performed on HITACHI 7500 instruments.

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 Micromeritics TriStar - 3000 surface area analyzer. All samples were degassed at 473 K for 2 h under a nitrogen atmosphere to remove the physisorbed moisture from the catalysts.

Gas chromatography-Mass spectroscopy (GC-MS) of FAEE was performed on Bruker GC-45X coupled with Scion MS system. Gas chromatography of FAEE samples were performed on a 15 m × 0.25 mm × 0.25 mm (RTX -5MS sil) capillary column. One µL sample solution, prepared in hexane, was injected (injection temperature 250 °C) in GC for analysis in split/splitless mode (split ratio 1:20 for 0.01 s). The flow rate of carrier gas (helium) was maintained 1 ml/min. The column oven temperature was increased up to 300 °C with the heating rate of 10 °C/min. The output from the GC column entered into the ionization chamber of the mass spectrometer *via* a transfer line maintained at 260 °C. MS (EI 70 eV, ion source temperature 280°C, solvent delay 2.5 min) was scanned in the m/z range of 50-800. The National Institute of Standard and Test (NIST) library match software was used to identify the FAEE. Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of biodiesel and vegetable oils were recorded on a JEOL ECS-400 (400 MHz) spectrophotometer in $CDCl_3$ solvent using tertramethyl silane (TMS) as internal reference.

The metal ion concentration in FAEE and glycerol was estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on Spectro ARCOS instrument.

The basic strengths of the catalysts (H_) were measured by Hammett indicator benzene-carboxylic acid titration method[18] using the indicators 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). The acidic strength of the catalysts was measured by Hammett indicator benzene-amine titration method[18] using methyl red (H_= 4.8) and methyl orange (H_= 3.3) indicators.

2.4. Transesterification reaction and product analysis

Transesterification reactions of WO 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 transesterification reaction 10 g of waste cottonseed oil was mixed with desired molar concentrations of ethanol, and catalyst and stirred at with a constant speed at desired temperature. To monitor the progress of reaction, the samples (0.25 mL) from the reaction mixture have been withdrawn after every 15 min with the help of glass dropper, centrifuged and subjected to proton NMR and GC-MS analysis to quantify the FAEE by following the literature reported procedure.[19,20] ^{1}H and ^{13}C-NMR spectrum of corresponding oil and FAEE are shown in Fig. S1.

FFA conversion into FAEE was calculated[21] from eq. 1.

$$\text{Conversion of FFA (\%)} = \left(\frac{\text{A.V}_{\text{initial}} - \text{A.V}_{\text{final}}}{\text{A.V}_{\text{initial}}}\right) \times 100 \qquad (1)$$

where A.V is acid value of VO.

The turnover frequency (TOF) was calculated[22] from eq. 2.

$$\text{TOF} = \frac{\text{mol}_{\text{actual}}}{\text{f}_{\text{m}} \times \text{m}_{\text{cat}} \times \text{t}} \qquad (2)$$

where $\text{mol}_{\text{actual}}$ is the moles of FAEE; m_{cat} is the mass of catalyst; *t* is the reaction time and f_{m} is basic sites (active sites) of catalyst (in mmol) calculated by Hammett indicator benzene-carboxylic acid titration.

3. Results and Discussion

3.1. Catalyst characterization

3.1.1. X-ray diffraction (XRD). The XRD patterns of Sr:Zr with varying atomic ratio (0.5-3) are shown in Fig 1(a). At low Sr:Zr atomic ratio (0.3-1.0) the diffraction patterns supported the presence of three species *viz., monoclinic* zirconia (*m*-ZrO_2; JCPDS 88-2390), *cubic* strontium oxide (*c*-SrO; JCPDS 75-0263) and *tetragonal* strontium zirconate (*t*-$SrZrO_3$; JCPDS 70-0694). A further increase in Sr concentration (Sr/Zr = 2) leads to the formation of *t*-$SrZrO_3$ as major phase and a further increase in Sr/Zr atomic ratio was not found to initiate any new phase formation. Thus an atomic ratio of 2 (Sr/Zr) was considered as optimum ratio for the catalyst preparation.

Comparison of the XRD patterns of 2Sr:Zr at varying calcination temperature (350-750 °C) is shown in Fig 1(b). At lower calcination temperature (350-550 °C), strontium nitrate phase ($Sr(NO_3)_2$; JCPDS 87-0557) is the major phase along with *m*-ZrO_2, *t*-$SrZrO_3$ and *c*-SrO as minor phases. At 650 °C, due to the solid state reaction between $Sr(NO_3)_2$ and ZrO_2, diffraction patterns supported the formation of *t*-$SrZrO_3$ as major phase and a further increase in calcination temperature was not found to initiate any major structural changes in catalyst structure. Thus 650 °C was considered as optimum temperature for the catalyst preparation.

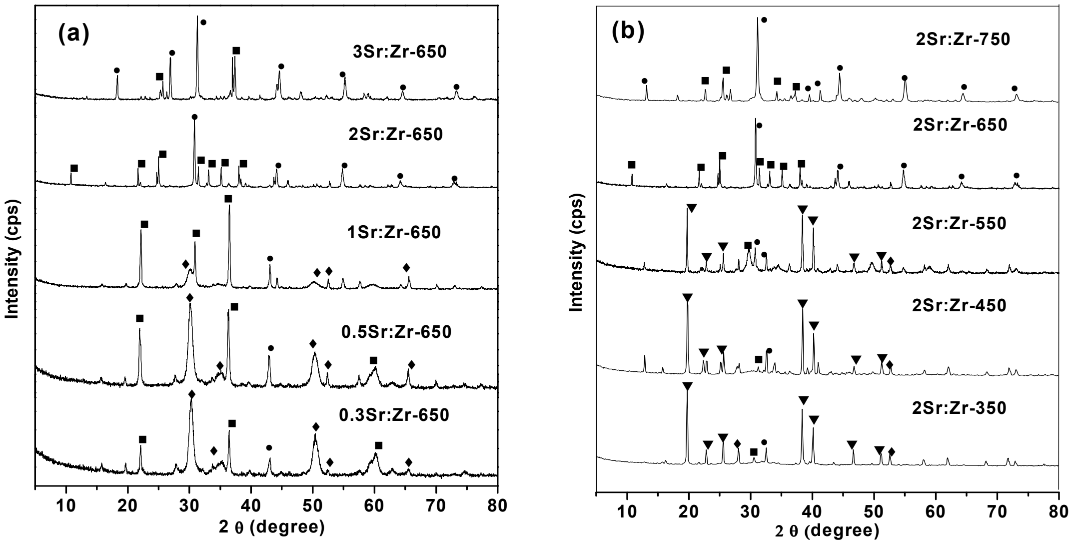

Fig. 1. XRD pattern of (a) varying Sr:Zr atomic ratio and (b) calcination temperature (• = *t*-$SrZrO_3$, ■ = *c*-SrO, ♦ = *m*-ZrO_2, ▼ = $Sr(NO_3)_2$).

As shown in Table 1, an increase in Sr/Zr ratio was also found to increase the crystallite size of the catalyst may be due to large ionic radii of Sr (1.27 Å) than Zr (0.76 Å). An increase in calcination temperature (350-650 °C) was found to increase the crystallite size due to the sintering of the catalyst particles at high calcination temperature.

3.1.2. Thermogravimetric and Differential scanning calorimetry analysis (TG-DSC). TG and DSC curves of the uncalcined catalyst are illustrated in Fig. S2 (ESI), which shows three endothermic weight loss regions existing in the temperature ranges of 25-200 °C, 200-350°C and 550–650 °C. The first weight loss of 7 wt% in 25-100 °C region may be ascribed to the loss of physically adsorbed water molecules over catalyst surface. The second weight loss of 23 wt% in 200-350 °C region corresponds to the loss of water molecule due to the decomposition of hydroxides of Sr and Zr. In third step, at 550-650 °C (endothermic), a weight loss of 21 wt% was observed due to the decomposition of $Sr(NO_3)_2$ into SrO and formation of $SrZrO_3$ phase. No significant weight loss or phase change in 2Sr:Zr was observed beyond 650 °C and hence the catalyst was prepared at 650 °C calcination temperature.

3.1.3. Electron Microscopic studies (SEM and TEM). The surface morphology and particle size of catalysts have been studied by SEM and TEM studies, respectively. As could be seen from SEM image (Fig. 2(a)), 2Sr:Zr-650 particles are either cubic or irregular shaped geometry within the range of 2-3 µm. TEM picture (Fig. 2(b)) of these particles reveal these are the clusters of smaller particles of ~25-30 nm size with few large relatively large sized particles of ~130 nm. Thus a powder XRD as well as TEM study supports the formation of nano structures of 2Sr:Zr-650 particles. As shown in Fig.S3 (ESI), EDX analysis supported the Sr:Zr atomic ratio of 1.7:1 which is close to the theoretical value of 2:1.

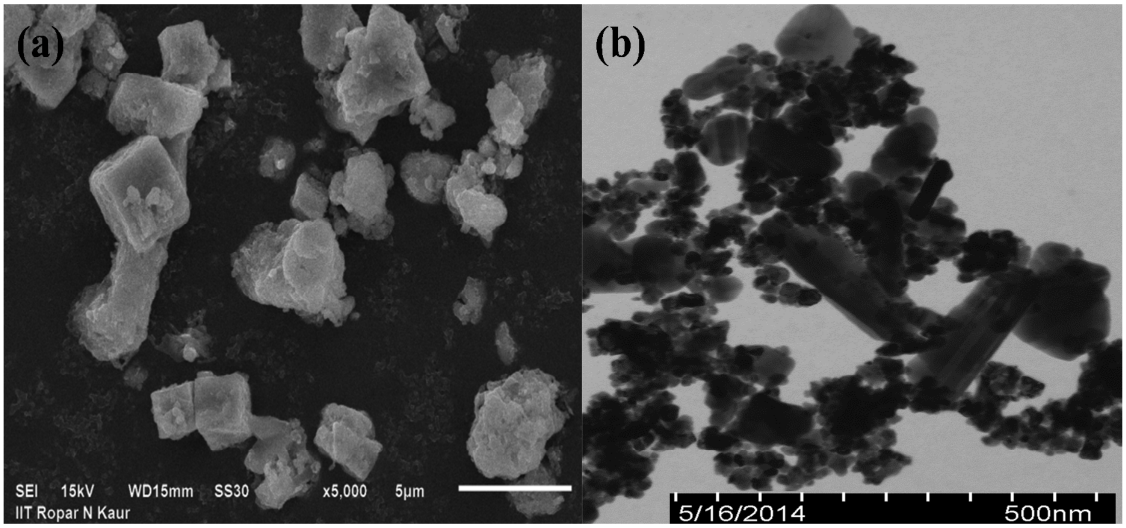

Fig. 2. (a) SEM and (b) TEM image of 2Sr:Zr-650 catalyst.

3.1.4. BET Surface area and porosity measurements. The surface properties of the catalysts at different calcination temperature were measured as shown in Table S2 (ESI). The surface area and pore volume of the catalyst were observed higher at low calcination temperature, although no regular trend of surface properties with calcination temperature was obtained. The 2Sr:Zr-650 catalyst has low surface area and low pore volume, however, same catalyst was found to show the best activity among the prepared catalysts owing to highest basic strength (Table 1) . 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 as well as with our previous work[12,23,24] where the activity of the catalysts towards transesterification reaction was found to be a function of basic strength rather than surface area.

The nitrogen adsorption-desorption isotherms (Fig. S4(a); ESI) indicate a type IV isotherm profile for 2Sr:Zr catalysts at different calcination temperature with hysteresis loop H3, at relative pressure of about 0.7-1.0; characteristic to mesoporous materials. The Non Localized Density Functional Theory (NLDFT) and Grand Canonical Monte Carlo (GCMC) method was used to calculate the pore size distribution. Despite the smaller surface area of the catalysts has a larger pore diameter in accordance with Table S2.The catalyst at low calcination temperature (350 °C) show narrow pore size distribution with ~ 9 nm pore diameter. On increasing the calcination temperature (450-550 °C), the pore diameter increases to ~ 24 nm (Fig. S4(b)) and at 650 °C it reached to the maximum value of ~32 nm. At low calcination temperature $Zr(OH)_4$ might be occupying the pores of $Sr(NO_3)_2/SrO$ to reduce the pore size of 2Sr:Zr. At high calcination temperature (650 °C) due to the solid state chemical reaction of ZrO_2 with $Sr(NO_3)_2/SrO$, the pores might have been vacated to form the material of relatively large pore sizes.

3.2. Structure-activity relation of catalysts

The activities of the various catalysts were compared on the basis of their total basic sites, and TOFs of WO ethanolysis. The catalyst prepared using Mg or Ba show very less activity while the catalyst having Ca was found to be lesser active in comparison to the Sr/Zr catalyst. There could be two reasons behind the activity difference viz., (i) difference in catalyst basic strength and (ii) difference in catalyst structure. It is evident from Table 1, basic strength of 2Sr:Zr-650 was found to be 22.7 mmol/g which is much higher in comparison to the 2Mg:Zr-650, 2Ca:Zr-650 and 2Ba:Zr-650 catalysts (9.7-17.8 mmol/g).

To compare the catalyst structure, 2Mg:Zr-650, 2Ca:Zr-650, 2Ba:Zr-650 and 2Sr/Zr-650 were prepared under the same experimental conditions and their powder XRD diffraction patterns were compared. As could be seen from Fig. S5 (ESI) in case of Mg:Zr catalyst, diffraction patterns supported the formation of a single MgO phase, while in case of Ba:Zr, pure $BaZrO_3$ phase formation was observed. On the other hand in case of Ca:Zr, and Sr:Zr catalysts, XRD diffraction patterns supported the formation of mixed phases of $CaO/CaZrO_3$ and $SrO/SrZrO_3$, respectively. This structural disparity might also be responsible for the variation in catalytic activity of the material prepared with different alkaline earth metals. Nevertheless, Sr/Zr being highest in activity has been studied in detail in present manuscript. As shown in Table 1, the basic sites of the catalysts increases gradually on increasing the Sr/Zr ratio and calcination temperature. The optimum atomic ratio of 2 (Sr/Zr) and calcination temperature of 650 °C was able to yield the catalyst with maximum basic sites. The increase in basicity may be due to the presence of *t*-$SrZrO_3$ as major phase at this ratio (Sr/Zr = 2) which is reported to be an active species for transesterification reaction.[25] A further increase in strontium to zirconium ratio (≥ 3) was not found to increase the activity of the catalyst to significant extent as the total basic site remains almost similar to the catalyst having Sr/Zr ratio of 2.

Similarly, on increasing the calcination temperature, the basic site as well as activity of the catalyst was found to increase and a maximum activity was observed at 650 °C. At low calcination temperature (350-550 ºC), the lesser activity could be due to the presence of strontium nitrate which decomposed into SrO and reacted with ZrO_2 at 650 ºC to form the $SrZrO_3$. Since, 2Sr:Zr-650 catalyst was found to catalyze the reaction rate to the maximum extent, hence it was selected for optimizing the other reaction parameters for the transesterification reaction.

Table 1. Comparison of basic strengths, basicity and TOFs for the 2M:Zr-T catalyzed transesterification.

Catalyst	Crystallite size (nm)	Basic strength	Neutral red pK_{BH+}=6.8	Bromothy mol blue pK_{BH+}=7.2	Phenolphth -alein pK_{BH+}= 9.3	Nile blue pK_{BH+} =10.1	Trapeolin pK_{BH+}=11.1	Total basicity (mmol/g of catalyst)	TOF[a] (h^{-1})
0.3Sr:Zr-650	8.74	9.3<H_<10.1	2.0	2.6	3.8	4.0	2.4	14.8	0.30
0.5Sr:Zr-650	9.88	9.3<H_<10.1	2.2	2.9	4.1	4.3	3.2	16.7	0.35
1Sr:Zr-650	24.8	10.1<H_<11.1	2.5	3.3	4.3	4.7	3.8	18.9	0.48
2Sr:Zr-650	27.1	11.1<H_<15.0	3.6	4.3	5.0	5.5	4.3	22.7	0.71
3Sr:Zr-650	26.1	11.1<H_<15.0	3.4	4.3	4.9	5.4	4.1	22.1	0.68
2Sr:Zr-350	22.8	7.2<H_<9.3	1.2	1.5	2.3	2.8	1.8	9.60	0.28
2Sr:Zr-450	24.9	9.3<H_<10.1	1.9	2.0	2.8	3.4	2.2	12.3	0.35
2Sr:Zr-550	26.8	10.1<H_<11.1	2.4	2.7	3.2	3.7	3.0	15.0	0.47
2Sr:Zr-750	24.7	11.1<H_<15.0	3.3	3.8	4.7	5.2	4.1	21.1	0.65
2Mg:Zr-650	21.8	9.3<H_<10.1	2.2	3.0	3.6	2.5	1.8	13.1	NC
2Ca:Zr-650	22.4	10.1<H_<11.1	2.7	3.6	3.9	4.2	3.4	17.8	0.24
2Ba:Zr-650	32.3	7.2<H_<9.3	1.4	1.6	2.4	2.7	1.6	9.70	NC

[a] TOF is calculated at 25% conversion level; NC = negligible conversion. **Reaction conditions** = ethanol to oil molar ratio of 12:1 at 75 ºC reaction temperature, in presence of 5 wt% of catalyst with respect to oil with 400 rpm stirring speed.

Usually catalysts with both acidic as well as basic sites were found to show simultaneous esterification and transesterification activity.[4] The catalyst, 2Sr:Zr-650, was also found to have moderate acidic sites (3.9 mmol/g of catalyst; Acidic strength 3.3<H_<4.8) which can catalyze the fatty acid esterification. In order to show the esterification activity of 2Sr:Zr-650 catalyst, esterification of oleic acid with ethanol (1:12 molar ratio) was performed at 75 ºC. As could be seen from Fig. S6 (ESI), in 3.5 h of reaction duration 70.6 % ethyl oleate yield was obtained, to prove the esterification activity of the catalyst. Moreover, biodiesel prepared from high FFA (up to 18 wt%) containing oil was found to show significantly lesser acid value (0.4 mg KOH/g) to further support the esterification of FFA present in triglyceride. To best of our knowledge this is the first report for the simultaneous esterification and transesterification of high FFA containing triglycerides ***with ethanol*** in presence of heterogeneous catalyst.

3.3. Optimization of the reaction parameters

In order to optimize the reaction parameters to achieve better catalytic performance following reaction parameters have been studied (Fig.S7; ESI): (i) stirring speed (100-700 rpm), (ii) catalyst concentration (1-6 wt%), (iii) ethanol/oil molar ratio (3-15), and (iv) reaction temperature (35-85 ^{o}C). On the basis of this study a 12:1 ethanol to oil molar ratio at 75 ºC in presence of 5 wt% catalyst (with respect to oil) at stirring speed of 400 rpm were found to be optimum conditions for the 2Sr:Zr-650 catalyzed transesterification of WO.

A comparison between ethanolysis activity of 2Sr:Zr-650 catalyst with few literature reported one is given in Table 2. As could be seen from the comparison the use of present catalyst for the vegetable oil ethanolysis is beneficial as it not only requires the lesser alcohol to oil molar ratio, lesser reaction temperature but also demonstrated moderate stability and reusability.

Table 2. Comparison of reaction conditions of literature reported heterogeneous catalysts used for ethanolysis with our catalyst.

Catalyst	Oil	C.A (wt%)	R.T (°C)	E:O	Reaction time (h)	FAAE yield(%)	Reusability (FAEE yield after last run)	Ref.
SO_4^{2-}/ZrO_2[a]	Soybean oil	5	120	20:1	1	92	4 (15)	10
CaO	Sunflower oil	20	75	18:1	6	100	N.R	11
Zr/CaO	Jatropha oil	5	75	21:1	7	> 99	N.R.	12
MgO/SBA-15[a]	Edible oil	2	220	6:1	5	96	N.R	13
Mg_2CoAl[a]	Rapessed oil	2	200	16:1	18	97	7 (97)	14
$CaO-La_2O_3$	Soybean oil	8	65	10:1	6	71.6	N.R	15
$Ca(OCH_2CH_3)$	Soybean oil	3	75	12:1	3	91.8	N.R	16
Calcium zincate	Sunflower oil	6	78	20:1	3	≈90	3 (40)	17
2Sr:Zr	Waste cotton seed oil	5	75	12:1	7	> 99	4 (98)	In present study

SPS- sulphonated polystyrene; C.A- Catalyst amount; R.T- Reaction temperature; E:O- Ethanol to oil molar ratio; N.R – Not reported; a – under high pressure in parr batch reactor.

3.4. Effect of moisture and FFA

Homogeneous catalyst required costlier refined feedstock for the transesterification reactions as presence of > 0.3 wt% moisture and/or > 0.5 wt% FFA contents in feedstock leads to the formation of soap instead of biodiesel.[4] In present study WO employed as feedstock was found to have 4.7 and 0.27 wt% FFA and moisture contents, respectively. When transesterification of the same oil in presence of homogeneous base catalyst (NaOH) was performed, catalyst deactivation occurred due to the soap formation. However, > 99 % FAEE yield was obtained in 2Sr:Zr-650 catalyzed transesterification of WO. In order to determine the maximum moisture resistance of the catalyst, the transesterification reactions of WO were performed by adding up to 4.5 wt% (water/oil) of water in reaction mixture. The 2Sr:Zr-650 was found to be effective for the transesterification of WO having up to 2.0 wt% of moisture contents as shown in Fig 3(a). However, a further increase in water concentration (2.0-4.5 wt%) was found to decrease the catalyst efficiency. This could be attributed to the change of Lewis basic sites (–O–) into Bronsted basic sites (–OH) due to the reaction of water with catalyst. The Bronsted basic sites were found to be less active towards the transesterification than corresponding Lewis basic sites.[4,12] The conversion of oxides into respective hydroxides is also evident from the comparison of XRD of neat and moisture exposed catalyst as shown in Fig 3(b).

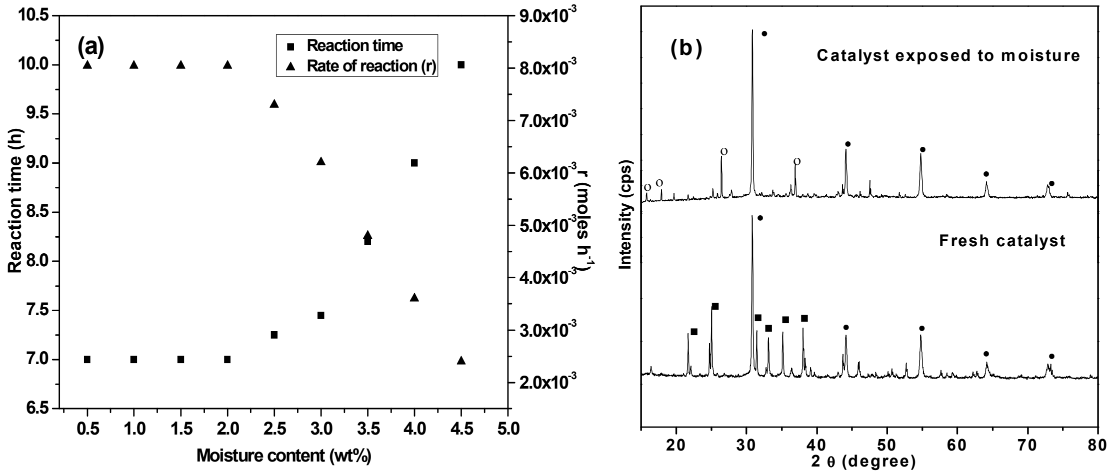

Fig. 3. (a) Effect of moisture content on the 2Sr:Zr-650 catalyzed transesterification of WO (reaction time is the time required to achieve > 99% FAEE yield) (b) Comparison of XRD spectra of fresh catalyst and catalyst exposed to water (● = $SrZrO_3$, o = $Sr(OH)_2$).

Non-edible or waste cooking oils, usually found to have FFA contents in relatively higher amount (4.6–18.1 wt% in present study). Conventionally transesterification of high FFA containing vegetable oils is performed in two step process involving acid-catalyzed pre esterification step in the presence of an acid catalyst followed by transesterification in presence of alkali catalyst.[4] The 2Sr:Zr-650 catalyst was found to show the esterification as well as transesterification activity as discussed in previous section. In order to demonstrate the simultaneous esterification as well as transesterification activity of the catalyst in one pot, transesterification reactions of CO, WO, JO and KO (having 1–18.1 wt% FFA) were performed with ethanol as shown in Fig. 4. Although catalyst was found to be effective for the transesterification of high FFA containing VOs, however, a decrease in TOF was observed with the increase in FFA contents. This may be due to the strong interactions of highly polar acetate (-COO$^-$) functional group with catalyst (Sr^{2+}/Zr^{4+}) to result in the partial blocking of the active sites.

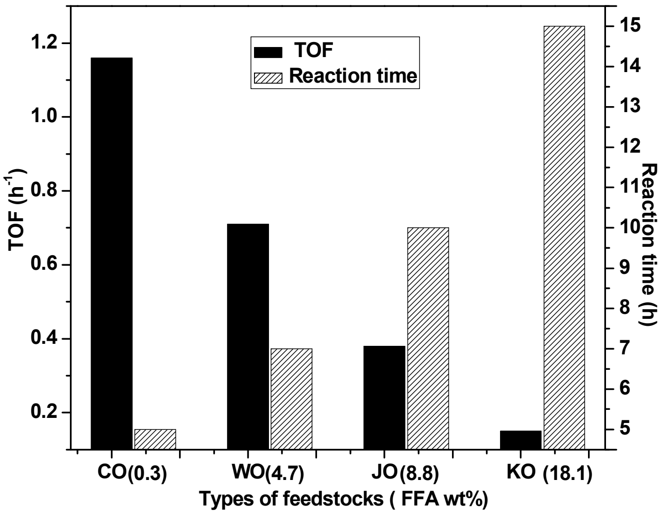

Fig. 4. Effect of FFA contents on the 2Sr:Zr-650 catalyzed transesterification of different feed stocks (reaction time is the time required to achieve > 99% FAEE yield). **Reaction conditions:**-Ethanol to oil molar ratio of 12:1 at 75 ºC reaction temperature in presence of 5 wt% (catalyst/oil) catalyst.

3.5. Reusability

Commercial success of BD production technologies depends on its production cost. Catalyst reusability could reduce the BD production cost to significant extent. In order to study the stability and reusability of catalyst, it was separated from the reaction mixture by centrifugation, washed with hexane and finally regenerated at 650 °C calcination temperature. The regenerated catalyst was employed in 5 successive catalytic cycles under the same experimental and regeneration methods. As could be seen from Fig. 5, no significant loss in catalytic activity was observed during first four runs, however, a partial decrease in activity was observed in fifth cycle.

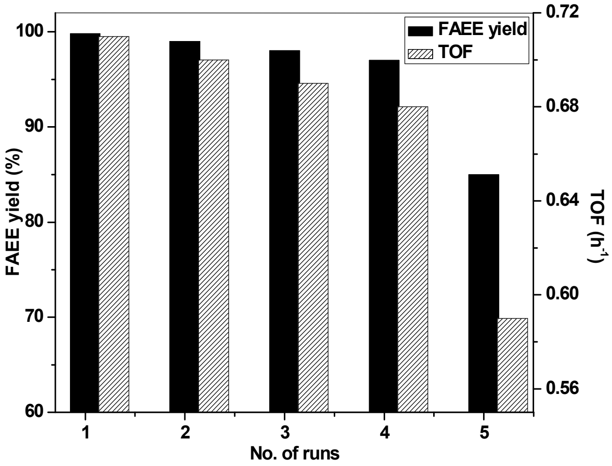

Fig. 5. Reusability study of catalyst.

The structural changes and/or leaching of the active catalysts ingredient or blockage/poisoning of active sites could be the reasons behind the activity loss of heterogeneous catalysts.[26] To identify the structural changes, XRD patterns of fresh and regenerated 2Sr:Zr-650 catalysts are compared in Fig. 6(a). In the XRD pattern of regenerated 2Sr:Zr-650 catalyst, diffraction peaks due to SrO were no longer found. The crystallite size of regenerated catalyst was found to be bigger (30.2 nm) than fresh catalyst (27.1 nm) to support partial agglomeration of catalyst during re-calcination process.

As shown from Fig. 6(b), in FTIR spectrum of fresh catalyst the stretching vibrations associated with Sr—O and Zr—O bonds appear at 550 and 648 cm^{-1}, respectively.[25] The bands appeared at 1453 and 1638 cm^{-1} supported the presence of hydroxide and water molecule due to catalyst surface hydration. In regenerated catalyst new bands appeared at 909 and 974 cm^{-1} , in addition to the original bands, to support the changes in catalyst structure which is also consistent with the XRD analysis of the reused catalyst. The spectrum of the regenerated catalyst didn't show vibrations corresponding to any adsorbed organic molecules to indicate that FAEE or glycerol have not been accumulated on the surface of regenerated catalyst.

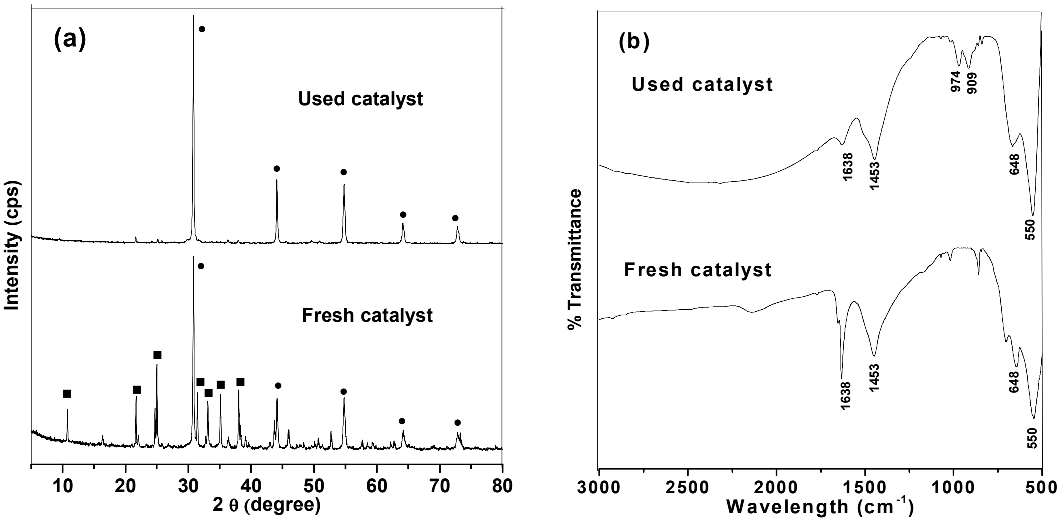

Fig. 6. Comparison of (a) XRD and (b) FT-IR of fresh and used catalyst. (■ = SrO; ● = $SrZrO_3$).

The metal analysis supported the presence of metal in FAEE (Sr =1.6 ppm and Zr = 0.8 ppm) as well as in glycerol (Sr = 4.6 ppm and Zr = 3.9 ppm). Thus metal is gradually lost during the catalytic run and could be another reason for the loss of activity. To ensure the heterogeneous nature of the catalyst, and to prove that leached metal ion has not acted like a homogeneous catalyst, a hot filtration test was performed under optimized reaction conditions. After 1.5 h of reaction duration the catalyst was removed by filtration and reactants were heated again for additional 3.5 h. As could be seen from Fig. 7, no significant gain in FAEE yield was obtained after the catalyst removal to prove (i) a truly heterogeneous mode of action of Sr:Zr catalyst and (ii) that leached metal has no contribution in catalytic activity.

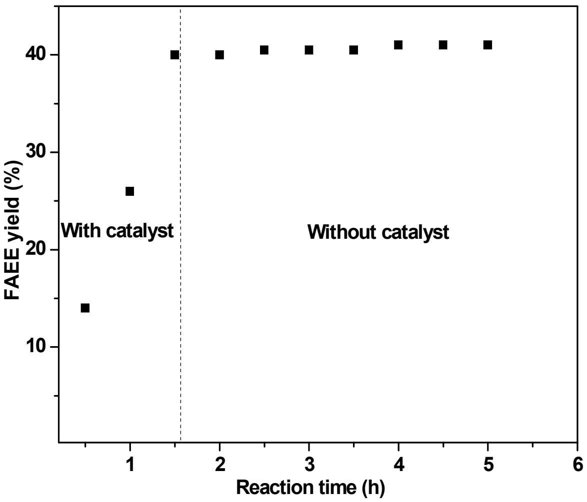

Fig. 7. Hot filtration test for 2Sr:Zr-650 catalyzed transesterification.

Therefore, the gradual loss of the catalytic activity could be attributed to the (i) structural changes occurred in catalyst structure and (ii) partial loss of the Sr and Zr from 2Sr:Zr-650 upon repeated use.

3.6. Koros–Nowak Criterion test

The absence of internal transfer limitations was demonstrated with the Koros–Nowak criterion test.[27,28] In present study the reactions were carried out in presence of two catalysts *viz.*, 5 wt% of 2Sr:Zr-650 or 6 wt% of 1Sr:Zr-650 catalyst dosages to maintain same fractional exposures of active (basic) sites. At similar conversion levels the TOF of both the catalysts were found to be almost similar as shown in Fig. S8 (ESI). Thus Sr:Zr catalyzed reaction is free from mass diffusion limitations and is a chemically controlled reaction.

3.7. Kinetics and thermodynamic study

Transesterification is generally assumed to follow pseudo-first-order kinetics as alcohol in such reactions are employed in excess to the required stoichiometric amount of 3:1 alcohol to oil molar ratio.[27] In present work also optimized alcohol to VO molar ratio was 12:1 and hence, the kinetics of 2Sr:Zr-650 catalyzed ethanolysis has been studied by following (pseudo) first order eq. 3:

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

where k is the first order rate constant, X is the conversion of oil into FAEE.

The linear nature of the plot between $-\ ln(1-X)$ *vs* t plot supported that the reaction has followed the (pseudo) first order rate law (Fig. 8(a)). The apparent first order rate constant form the plot was found to be 0.648 h^{-1} at 75 ºC.

To calculate the activation energy, reactions were carried out in temperatures range of 35-75 ºC. The Arrhenius equation was employed to estimate the activation energy (E_a) and pre–exponential factor (A) following[29] the eq. 4:

$$ln\ k = ln\ A\ - E_a/RT \tag{4}$$

where E_a is the activation energy (kJ mol^{-1}), A is the pre-exponential factor (h^{-1}), R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}) and T is the reaction temperature (°K).

A plot between ln k *vs* 1/T is shown in Fig.8(b), and the values of E_a and A from the plot was found to be 48.17 kJ mol^{-1} and 6.83×10^6 h^{-1}. The observed E_a value in present study (48.17 kJ mol^{-1}) was found within the range of the reported values (26-82 kJ mol^{-1}) for transesterification reaction catalyzed by heterogeneous catalysts.[12]

A value of $E_a > 25$ kJ mol^{-1} also supported that 2Sr:Zr-650 catalyzed transesterification is a chemically controlled reaction and not controlled by mass transfer limitations.[30]

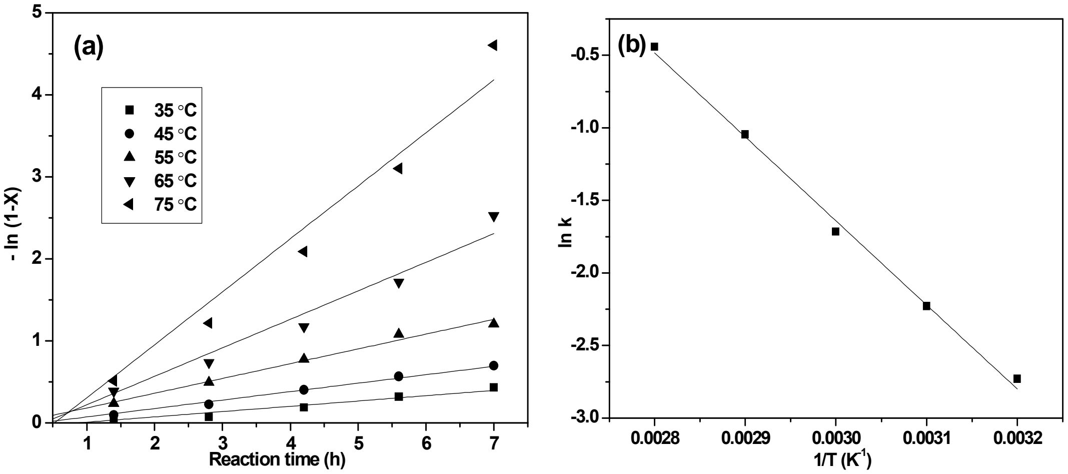

Fig. 8. Kinetic study of transesterification of WO with ethanol over 2Sr:Zr-650 catalyst. (a) Plots of $-ln(1-X)$ *vs* time at different temperatures (b) Arrhenius plot of ln k *vs* 1/T. **Reaction conditions:** ethanol to oil molar ratio of 12:1 and 5 wt% of 2Sr:Zr-650 with respect to oil.

Thermodynamic analysis was addressed for evaluating the enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and the Gibb's free energy of activation ($\Delta G^{\ddagger}$), which are the important features for interpreting the behaviour of transesterification reactions. In this regard activation complex theory, developed by Eyring, was applied to evaluate thermodynamic parameters from temperature-dependent rate constants. These parameters are calculated[31] from Eyring-Polanyi eq. 5 which is analogue to Arrhenius equation:

$$k = \frac{k_B \mathrm{T}}{h} \exp\left(-\frac{\Delta \mathrm{G}^{\ddagger}}{\mathrm{RT}}\right) \tag{5}$$

Taking the natural logarithm of eq. 5 and substituting the value of $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, eq. 6 is obtained:

$$\ln\left(\frac{k}{\mathrm{T}}\right) = -\frac{\Delta \mathrm{H}^{\ddagger}}{R}\left(\frac{1}{T}\right) + \left[\ln\left(\frac{k_B}{h}\right) + \frac{\Delta \mathrm{S}^{\ddagger}}{R}\right] \tag{6}$$

k_B and h are the Boltzmann (1.38×10^{-23} J K^{-1}) and Planck (6.63×10^{-34} Js) constants, respectively. Eq. (6) resembles van't Hoff's equation describing the mathematical relation between enthalpy and entropy of activation with rate constant. The slope and intercept of 1/T *vs* ln (k/T) plot would be equals to $-\Delta H^{\ddagger}/R$ and $\ln(k_B/h) + \Delta S^{\ddagger}/R$, respectively.

Fig. 9 depicts the Eyring plot of transesterification and the value of $\Delta H^{\ddagger}$ was found to be 45.97 kJ mol^{-1} indicating that energy input (heat) from external source is required to raise the energy level and transform the reactants to transition state. The value of $\Delta S^{\ddagger}$ was found to be -121.37 J $mol^{-1}K^{-1}$ and a negative value suggests associative mechanism in which reactant species have joined together to form a more ordered transition state. The $\Delta G^{\ddagger}$ value was found to be 88.23 kJ mol^{-1}, to indicate unspontaneous nature of the reaction having higher energy level of transition state than reactant species.

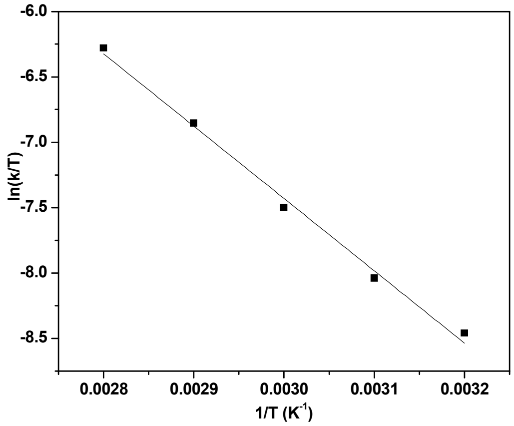

Fig. 9. The Eyring plot of 2Sr:Zr-650 catalyzed transesterification of WO.

3.8. GC/MS analysis of FAEE

Physicochemical properties such as viscosity, freezing point, cold flow properties of BD depends upon its chemical composition. GC/MS analysis was performed to quantify the FAEE yield as well as FAEE chemical composition. Seven peaks were observed in GC chromatogram (Fig. S9) of FAEE prepared from WO. Each peak corresponds to a fatty acid ethyl ester which was identified on the basis of MS pattern from the library match software (NIST) and the component corresponding to individual peak is listed in Table 3. The total FAEE contents obtained through area normalization method was found 99.61 wt%. Out of which total saturated and unsaturated fatty acid alkyl ester content was found to be 31.32 and 68.29 wt%, respectively. A higher unsaturated fatty acid alkyl ester contents reflects the better cold flow properties of BD even at low temperature.[32]

Table 3. Analysis of compositions of FAEE.

S.No.	Retention time (min)	Composition; Molecular formula	Corresponding acid (Cx:y)	Wt %
1	7.66	Myristic acid ethyl ester; $C_{16}H_{32}O_2$	Myristic acid (C14:0)	0.86
2	8.57	Palmitoleic acid ethyl ester; $C_{18}H_{34}O_2$	Palmitoleic acid (C16:1)	0.62
3	8.68	Palmitic acid ethyl ester; $C_{18}H_{36}O_2$	Palmitic acid (C16:0)	26.64
4	9.46	Linoleic acid ethyl ester; $C_{20}H_{36}O_2$	Linoleic acid (C18:2)	37.77
5	9.49	Oleic acid ethyl ester; $C_{20}H_{38}O_2$	Oleic acid (C18:1)	29.90
6	9.61	Stearic acid ethyl ester; $C_{20}H_{40}O_2$	Stearic acid (C18:0)	3.44
7	9.90	Eicosanoic acid ethyl ester;$C_{22}H_{44}O_2$	Eicosanoic acid (C20:0)	0.38

Cx:y = x is number of carbon atom, y is number of double bonds.

3.9. Physicochemical properties of FAEE

The fatty acid alkyl esters must satisfy ASTM D6751 or EN 14214 specifications, before they could be employed for the commercial applications as biodiesel. To study the physicochemical properties, FAEE were prepared by the transesterification of WO with ethanol, under optimized reaction conditions. After the completion of the reaction, the catalyst was separated through filtration and liquid phase thus obtained was kept in a separating funnel for 24 h to separate the lower glycerol layer from upper FAEE layer. Excess alcohol from ester layer was recovered with the help of rotary evaporator. Few physicochemical properties of prepared FAEE have been studied by following the standard test methods and compared with EN 14214 specifications. As could be seen from Table 4, the observed values of the studied properties were found within the acceptable limits of European standards. Specifically, total metal concentration in crude FAEE was found to be less than the acceptable limit and hence, biodiesel washing with water would not be required to avoid the generation of huge amount of industrial effluents which is inevitable in case of homogeneous catalytic process.

Table 4. Physicochemical properties of the FAEE prepared from WO.

S.No.	Parameters	Units	FAEE	EN 14214	Test method
1	Ester content	%	> 99 %	≥ 96.5	^{1}H–NMR,GC-MS
2	Flash point	ºC	120	100–170	ASTM D93
3	Pour point	ºC	3	–5 to10	ASTM D2500
4	Water content	%	0.25	≤ 0.5	ASTM D2709
5	Kinematic viscosity at 40 ºC	cSt	4.63	1.9–6.0	ASTM D445
6	Density at 31 ºC	kg/mm^3	875	860–900	ISI448 P:32
7	Ash	%	0.01	0.02	ASTM D874
8	Iodine value	mg of I_2/g of sample	88.4	≤ 120	^{1}H–NMR[33]
9	Acid value	mg of KOH/g of sample	0.4	0.8	ASTM D664
10	Saponification value	mg of KOH/g of sample	181.23	–	ASTM D5558
11	Sr/Zr	ppm	1.6/0.8	≤5 (Total metal)	ICP-AES

4. Conclusions

In present work, 2Sr:Zr-650 catalyst has been prepared as ~ 25-30 nm sized particles as revealed by powder XRD and TEM techniques. The catalyst was found to be effective for the one pot esterification and transesterification of a variety of feedstock having up to 2.0 and 18 wt% of moisture and FFA contents, respectively. Under optimized reaction conditions (catalyst concentration 5 wt%, ethanol to oil molar ratio of 12:1 at 75 °C and 400 rpm) the transesterification of the waste cottonseed oil was found to follow (pseudo) first order rate law. Activation and Gibbs free energy for the ethanolysis of waste cottonseed oil was found to be 48.17 and 88.23 kJ mol^{-1}, respectively. The catalyst has been recovered and recycled without any significant loss in activity during first four catalytic cycles. The leaching test supports the negligible homogeneous contribution in catalytic activity, and KN test demonstrated that the activity is free from transport phenomenon. Few physicochemical properties of the FAEE prepared from waste cottonseed oil have also been studied, and observed values were found within the limits of EN 14214 specifications.

Acknowledgements

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One pot transesterification and esterification of waste cooking oil *via* ethanolysis using Sr:Zr mixed oxide as solid catalyst

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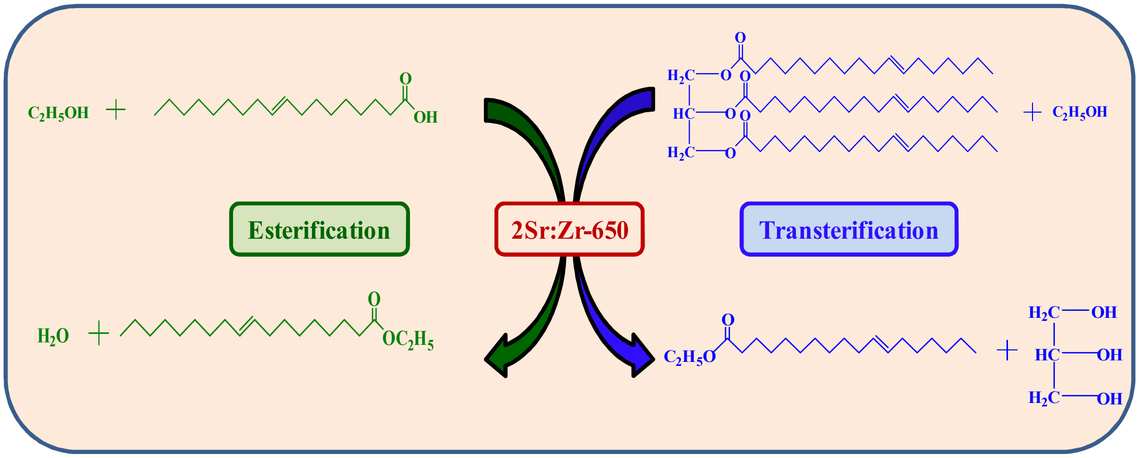
Graphical Abstract:



Textual Abstract:

Prepared 2Sr:Zr-650 possesses both acidic and basic sites, and hence was able to catalyze simultaneous esterification and transesterification of free fatty acid containing vegetable oils.