Sodium doped zirconia drenched SBA-15 as a reusable solid catalyst for concurrent esterification and transesterification of low-quality oils

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Solid catalyst for biofuel production

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Abstract

Sodium doped zirconia impregnated SBA-15 has been prepared without using hydrothermal treatment trailing the wet impregnation route. The prepared catalyst has been characterized by employing various techniques viz., BET for surface area analysis, SEM for morphological study, XPS for element oxidation state determination. It was found that catalyst seized both acidic and basic sites therefore, successfully employed for one-pot or concurrent esterification and transesterification of virgin cottonseed oil and high FFA containing vegetable oils. Under optimum reaction conditions of catalyst concentration of 10 wt% with respect to weight of oil, MeOH/oil molar ratio of 30:1 and at 65 °C reaction temperature, the catalyst could confer > 98 % fatty acid methyl ester yield within 3 h of reaction duration. Regeneration study advocated that the catalyst may well be recycled for 5 successive cycles

Regeneration study advocated that the catalyst may well be recycled for 5 successive cycles without any significant trouncing of activity and even yielded 86% fatty acid methyl esters during 6^{th} cycle.

Keywords: Heterogeneous catalysts, mesoporous, basicity, acidity, transesterification, thermodynamic parameters

Introduction

Hasty global population growth, diminution of non-renewable fossil fuel and anxiety and apprehension over ecological problems like global warming, fear of exhaustion of fossil fuels have led the world to search substitute for typical diesel fuel. The condition is further worsened by simultaneous raised global energy demands, for regular human activities such as transportation, health issues related to the conventional fuel exhaust which have paved the way to exploration for alternative renewable energy sources as substitutes for conventional fuels [1]. Statistics depict that apart from nuclear power, coal, and natural gas, more than 90% dependency of transportation sector relies on fossil fuels [2]. Biodiesel (BD), which has emerged as a promising and convincing replacement of typical diesel fuel, is an alternative source of energy which is renewable, eco-friendly, biodegradable, sulphur free and non-toxic. Biodiesel holds most of the characteristics, viz., high cetane number and high flash point, density and kinematic viscosity comparable to that of conventional diesel fuel [3]. Biodiesel (BD) synthesis requires the conversion of the triglycerides to methyl esters of fatty acids, commonly called as fatty acid methyl esters (FAMEs). Even after having above mentioned environmental benefits, BD haven't been gained the desired commercial success in India primarily owing to soaring production cost and limited availability of the feedstock. The feedstock availability could be addressed by producing the 2nd generation BD from used cooking oil, animal fat, and inedible oils. Although, such feedstock often hold high contents of free fatty acid (FFA) which limited their application in homogeneous alkali catalyzed transesterification reactions. With an aim to win over the issues linked to the homogeneous catalysts, BD production using heterogeneous catalysts has attracted significant attention in the gone decade. In case of heterogeneous catalysis, the reactants (oil and methanol) and the catalyst are present in different phases to facilitate the easy removal of the solid catalyst from the reaction mixture which could be recycled again in next reaction cycle. Moreover, in case of solid catalysts, neutralization of catalyst with acid and salt removal via washing is not required [4].

In order to prepare the solid catalysts for the BD production, ordered mesoporous materials have attracted considerable attention due to their adjustable pore size, lofty thermal stability,

inert nature, simplicity in surface modification and towering surface area [5]. According to a recent report, mesoporous sulphated zirconia was employed for transesterification of soyabean oil. However, the catalyst demanded high temperature of 120 °C and could yield 94% FAMEs within 4 h and employing 4 wt% catalyst to oil ratio [6]. In another report, mesoporous Ca/Al was employed for BD synthesis from sunflower oil. However, the catalyst yielded only 84.2% FAMEs utilising 10 wt% catalyst to oil ratio at a temperature of 70 °C [7]. An assessment of reaction conditions for few more literature reported mesoporous silica based catalysts explored for transesterification is presented in Table 1. As apparent from the details presented in Table 1, catalysts either required high reaction temperature, and/or exhibited meagre reusability.

Typically, biodiesel from VOs with high FFA content is produced by two step method involving acid- catalyzed esterification trailed by base-catalyzed transesterification.

Extremely acerbic acid and base catalysts necessitate to be initially neutralized and salt thus formed then has to be rinsed out from the BD product which generates considerable amount of effluents [12].

In this context, relevance of stable solid catalyst would be surely profitable and gainful from commercial and environmental aspect for biodiesel production using cheap quality high FFA containing feedstock or inedible oils. Solid catalysts cut down the production expenses and detrimental effluent generation, making the BD production more eco-friendly process. Literature reports the use of SnSO₄ for concurrent esterification and transesterification of high FFA holding soyabean oil. The catalyst yielded 92% FAMEs at a temperature of 100 °C using 5 wt% of catalyst [13]. Another report presents the use of 20-CeO₂/Li₂O/SBA-15 as catalyst for concurrent esterification and transesterification of waste cottonseed oil. The catalyst catalysed absolute transesterification within 4 h of reaction time by employing MeOH/oil molar ratio of 40:1 at 65 °C reaction temperature and even could be recycled for 5 successive runs [14]. Another report employed Sr:Zr as solid catalyst could catalyse complete transesterification by employing alcohol/molar ratio of 12:1 at 75 °C reaction temperature and 5 wt% of catalyst [15].

In this work, sodium metal doped zirconia (Na/ZrO₂) species was impregnated over mesoporous silica support and employed for one-pot esterification and transesterification of high FFA carrying non-edible oils. The prepared catalyst contained both acidic as well as basic sites liable to perform esterification as well as transesterification in concurrent manner. Alkali metal doped zirconates can be well explored in the field of biofuel generation. The reaction conditions were optimised and reusability, tolerance to FFA and kinetic study was also performed.

Catalyst	Triglyceride source	Temp (°C)	Time (h)	MeOH/oil molar ratio	catalyst mass(wt%)	Reusability (cycles)	Yield (%)	Ref.
Ca/Ce/SB A-15	Palm	65	50	50:1	5	15	96	[5]
CaO/MoO ₃ /SBA-15	Soyabean	65	50	36:1	6	Not reported	83.2	[8]
Ti/SBA-15	Jatropha	200	3	27:1	15	3	90	[9]
Al-SBA-15	Jatropha	180	24	12:1	Not reported	Not reported	99	[10]
мg0/SBA- 15	Jatropha	200	4	36:1	6	2	81.4	[11]

Table 1. A Comparison of activity of few literature reported mesoporous catalysts.

2. Experimental section

2.1. Materials and Methods

Virgin cottonseed oil (VCO) was obtained from local shops and waste Soyabean oil (WSO) was obtained from local restaurants in Patiala. Cotton seed oil price is reasonably low in comparison to other edible oils in India, and also is less preferred for edible purposes. Jatropha oil (JO) was procured from Medors Biotech Pvt. Ltd. New Delhi (India). Their FFA content found to be 0.4, 3.9, 9.7 wt%, saponification value were determined to be 189.3, 178, 188.5 g/kg respectively. The FFA and saponification values were determined by employing literature reported method [16]. Methanol (99.8%) was purchased from Merck (India) Ltd. Tetraethyl orthosilicate (TEOS) silica precursor and Pluronic 123, P123 (EO₂₀-PO₇₀-EO₂₀), surfactant copolymer were obtained from Sigma–Aldrich (USA). Oleic acid (99.9%) used in esterification reaction was procured from Loba Chemie, (India). Trichloroacetic acid and *n*–butylamine used for Hammett indicator study, and toluene (HPLC grade) were acquired from Spectrochem (India) Ltd. All other chemicals were purchased from Loba Chemie, (India) Ltd. and utilised without any further purification.

Powder X-Ray diffraction (XRD) was performed on Panalytical X'pert Pro diffractometer with Cu K α radiation (0.154 nm) in 2 θ range of 0.5-5° and 5–60°. SEM-EDS analysis was performed to study the morphology of the prepared catalyst on JEOL JSM 6510 LV equipment, (Japan). To perform the analysis, the sample was firstly sonicated in ethanol for 2h. Then, on a sample holder, a drop of suspension was mounted using a carbon tape. The test sample was then encrusted with gold and visually analysed with the instrument to study the morphology of the particles. The high resolution transmission electron microscopy (HR-TEM) study was executed on FEI Tecnai G2 F-20 transmission electron microscope instrument. X-ray photoelectron spectroscopy (XPS) study was carried out in order to determine the elemental state of the elements present in the prepared catalyst on KRATOS-AXIS DLD spectrometer with monochromatic Al K α radiation operating at 10 kV.

Surface area of samples was estimated on (Brunauer–Emmett–Teller) surface area analyser using Microtec Belsorp Miniell equipment. Prior to analysis, 0.1 g of sample was pre- treated at 150 °C under N_2 atmosphere for 3 h.

The amount of surface acidic and basic sites of the prepared catalysts was determined by employing Hammett indicator titration method.

The metal ion concentration was determined using ESICO microprocessor model 1382 E Flame Photometer, India. For the analysis, 0.5 g of recovered reaction sample was digested in 5 mL of HNO_3 (16 M) in order to eliminate the organic matter. The solution was then filtered and the volume was made upto 50 mL in a volumetric flask with water.

To characterise fatty acid methyl esters (FAMEs) produced during transesterification reactions, H^1 NMR spectra was recorded on Bruker Avance–II (400 MHz) spectrophotometer using CDCl₃ as solvent. Chemical shifts were expressed as parts per million (ppm) employing tetramethylsilane (TMS) as an internal standard. The FAMEs yield was quantified by putting the appropriate values in equation (1) as reported in literature [17].

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

(1)

where, $I_{(methoxy)}$ and $I_{(methylene)}$ are the integration values of methoxy (3.6 ppm) and methylene (2.3 ppm) protons, respectively in proton NMR spectrum of fatty acid methyl ester.

The turnover frequency (TOF) was calculated from equation (2) using the literature reported method [18].

 $TOF = (mol \ actual/f_m \times m_{cat} \ \times t)$

(2)

where mol_{actual} is the number of moles of FAMEs ; m_{cat} is the mass of catalyst; t is the reaction time and f_m is active basic sites of catalyst (in mmol g⁻¹) calculated by Hammett indicator benzene–carboxylic acid titration.

2.2. Synthesis of SBA-15

In the characteristic synthesis, 8 g of Pluronic 123 was suspended in 60 mL of distilled water and stirred for 1h. Further, 240 ml of 2M hydrochloric acid was added and stirring was continued for additional 2 h. In next step, 17 mL of TEOS was added and resulting solution was stirred at normal room temperature (38 °C) for 24 h. The mixture was then aged at 90 °C for 48 h without stirring. The solid product so formed was recuperated by filtration, dried and finally calcined at 600 °C for 5 h.

2.3. Synthesis of Na/ZrO₂

Sodium metal was impregnated over zirconia by wet impregnation method. 5 g of ZrO_2 was suspended in 20 ml of distilled water. To the suspension, 20 mL Na₂CO₃ solution containing 2.3 g of salt (1.05 M) was added to obtain 20 wt% loading of Na over zirconia. The slurry was agitated for 20 h at room temperature (38 °C), dried at 110 °C for 24 h and finally calcined at 900 °C for 5 h. The resulting product was designated as Na/ZrO₂.

2.4. Synthesis of sodium zirconate impregnated mesoporous silica

In order to impregnate Na/ZrO₂ over SBA-15, 1 g of SBA-15 was suspended in 40 ml of distilled water and to this 10 mL suspension of 20-Na/ZrO₂ of desired concentration (15-35 wt%) was added. The resulted slurry was agitated for 22 h at room temperature (38 °C), dried at 110 °C for 24 h and calcined in muffle furnace at 600 °C for 6 h. The catalysts so formed were designated as x-Na/ZrO₂/SBA-15, x is the wt% of Na/ZrO₂.

2.5. Transesterification of triglycerides

All reactions were carried out in a 100 mL, two-necked round bottom flask furnished with an oil bath, water-cooled reflux condenser, magnetic protester and a thermometer. In a typical reaction, the flask was indicted with 10 g of vegetable oil (VO) and desired molar concentration of methanol varying from 6:1 upto 36:1 as well as catalyst dosage varying from 7 wt% to 11 wt%. The flask contents were roused at a specific temperature for definite reaction duration. The reaction mixture so obtained was set aside in a separating funnel for 10 h in order to part the upper BD and the lower glycerol layer. The FAMEs thus produced were quantified with ¹H-NMR technique.

3. Results and discussion3.1 Catalyst characterisation3.1.1 Powder XRD study

Small angle XRD patterns (Fig. 1a) of as synthesised SBA-15, shows distinctive peak at $2\theta \sim 0.90^\circ$, which could be indexed to (100) plane. This peak is typical feature of *p6mm* hexagonal symmetry and 2D hexagonal structure of SBA-15. Small angle XRD patterns of Na/ZrO₂ impregnated SBA-15 shows the like kind of diffraction patterns. This demonstrates the preservation of long range mesoscopic order of SBA-15 even on functionalisation with active species. Though, after doping with active metallic species, reflection consequent to (100) plane was found to reallocate to a little higher angle from 0.90 to 1.1°. This may be accredited to small change in the wall properties and contraction in the lattice framework of mesoporous silica due to partial jamming of mesopores by active metallic species [19, 20].

Fig. 1b depicts the XRD pattern of as synthesised Na/ZrO₂ material which depicts the formation of monoclinic sodium zirconate and monoclinic zirconia. The wide angle powder XRD patterns of Na/ZrO₂ impregnated mesoporous silica are depicted in the Fig. 6.1b. The patterns show peak at $2\theta = 23.5^{\circ}$ which can be ascribed to the amorphous walls of siliceous SBA-15. The peaks at $2\theta = 17.1$, 31.1° , 34.2° , 35.5° , 38.8° , 40.9° , 50.5° 55.4° are due to subsistence of crystalline monoclinic sodium zirconate (JCPDS file no. 35-0770). Diffraction peaks of monoclinic zirconia at $2\theta = 49.1^{\circ}$, 54.2° , 28.2° were also observed (JCPDS file no. 88-2390). The observations clearly indicate that there was retention of crystalline phases of monoclinic sodium zirconate and monoclinic zirconia even after the impregnation of Na/ZrO₂ over mesoporous silica. Similar observation has been mentioned in literature while the native structure of phosphotungstic acid (HPW) and WO₃ were retained even after impregnating them over mesoporous siliceous support [21].



Fig. 1. (a) Low angle XRD patterns of SBA-15 and x-Na/ZrO₂/SBA-15 (b) XRD pattern of Na/ZrO₂ (\clubsuit = monoclinic Na₂ZrO₃, \blacklozenge = monoclinic ZrO₂) (c) wide angle XRD patterns of SBA-15 and x-Na/ZrO₂/SBA-15 catalysts (• =amorphous SBA-15, \heartsuit = monoclinic Na₂ZrO₃, \clubsuit = monoclinic ZrO₂).

3.1.2. Study of textural properties

To study the textural attributes of catalysts prepared, nitrogen sorption isotherms were assessed. Nitrogen adsorption-desorption isotherms for SBA-15 and Na/ZrO₂ loaded SBA-15 have been depicted in Fig. 2a. It is visible that all isotherms are type IV in nature with H1 hysterisis loop which is typical of mesoporous materials according to IUPAC categorization. This indicates that mesoporous nature is preserved even when active species is laden over the SBA-15 template. As the Na/ZrO₂ concentration was raised, the shift in P/P_0 to higher relative pressure was seen owing to a raise in pore diameter However, in case of 35-Na/ZrO₂/SBA-15, the hysteresis, transformed from H₁ to H₄. This transformation in the hysteresis could be endorsed to tapering and tightening of pores of SBA-15 on impregnation with high amount of Na/ZrO₂. Similar observation has been reported in a recent report in which 5-Na/ZnO was incorporated over mesoporous silica and the hysteresis was found to shift from H1 type to H4 type when the impregnation level was raised [22]. Table 2 represents demur in surface area, and average pore volume with the rise in Na/ZrO₂ concentration over SBA-15. This decline in surface area and pore volume upon incorporation of active species has also been reported earlier in literature where Au particles were incorporated over SBA-15 material and surface area declined from 664 m²g⁻¹ for bare SBA-15 to 292.6 m²g⁻¹ for Au loaded SBA-15 [23]. This decrease in surface area and pore volume can be backed to the dispersal of Na/ZrO₂ species into the pore channels of SBA-15. Inclusion of the active species over the support although led to the reduction in surface area, however, increase in number of active sites, at the same time, was found to enhance the catalyst activity.

Sample name	Surface area (m ² g ⁻¹)	Average pore	Average pore
		volume (cm ³ g ⁻¹)	diameter (nm)
SBA-15	441.8	0.56	5.09
15- Na/ZrO ₂ /SBA-15	255.8	0.39	6.14
30- Na/ZrO ₂ /SBA-15	78.3	0.15	7.95
35- Na/ZrO ₂ /SBA-15	23.9	0.10	16.9

Table 2. Surface area, average pore size and average pore volume of the synthesised catalysts.

Barrett-Joyner-Halenda (BJH) method was engaged to calculate pore size distribution (PSD) from adsorption branch of N_2 - adsorption-desorption isotherms (Fig. 2b) which depicted narrow PSD of prepared materials confirmative of uniformity of pores. The increase in pore

size can be credited to the anchorage of Na/ZrO₂ species to exterior silanol groups present on the outer area of pore walls. Hence, pores of SBA-15 might have inflated, either owing to ingress of active species into the pores or the attachment of Na/ZrO₂ outside the walls causing a stretch. The pore volume was found to reduce to support the jamming of mesochannels of siliceous support on permeation and infusion of Na/ZrO₂ particles. Similar observations have been reported earlier elsewhere when Al metal was infused over SBA-15 and a rise in pore diameter from 8 nm (bare SBA-15) to 12.7 nm (Al-SBA-15) was observed with the rise in Al metal content [24].



Fig. 2. (a) N₂ adsorption–desorption isotherms and (b) pore size distribution of SBA-15 and x-Na/ZrO₂/SBA-15 catalysts.

3.1.3. SEM-EDS study

Both SBA-15 support as well as $30-Na/ZrO_2/SBA-15$ catalyst were typified by SEM technique to scrutinize the morphological facets. The SEM analysis (Fig. 3a) of SBA-15 portrayed the clusters of hexagonal and few irregular units or particles with smooth surface. The particles tend to dwell in aggregated manner. Fig. 3b depicts the SEM image of $30-Na/ZrO_2/SBA-15$ which showed the almost rectangular shaped catalyst particles of an average length and width of 0.9 µm and 0.4 µm respectively. The SEM analysis clearly is indicative of transformation from hexagonal and irregular particles of stripped SBA-15 to rectangular shaped catalyst particles after impregnation of active species. The EDS of SBA-15 confirms the presence of only Si and O species indicating the purity of prepared material while EDS spectra of active catalyst demonstrates the presence of Na, Zr, Si, O species again

pointing towards no contamination in prepared catalyst. The elemental mapping or chemical map analysis (Fig. S1. ESI) of the catalyst also confirmed the loading of Na and Zr in the matrix of SBA-15 and uniform and consistent allocation of Na and Zr metallic species in the siliceous framework. The incidence of different elements in catalyst has been shown with different colours.



Fig. 3. SEM images of (a) bare SBA-15 support (b) 30-Na/ZrO₂/SBA-15.

3.1.4. HRTEM study

HRTEM analysis of Na/ZrO₂ functionalised mesoporous silica is portrayed in Fig 4. The investigation of the prepared catalyst by HRTEM technique revealed that the smooth clusters of catalyst particles are made up of rhombus and rectangular shaped units (Fig. 4a). The micrographs also displayed the well defined channels arranged in 2D hexagonal fashion, a typical feature of SBA-15 (Fig. 4b) and highly dispersed Na/ZrO₂ particles are present over the mesopore channels of SBA-15. Presence of Na/ZrO₂ particles over SBA-15 surface are evidently visible against the lighter backdrop of SBA-15 matrix (Fig. 4b). Moreover, it is further evident from HRTEM study that functionalisation and inclusion of SBA-15.

Presence of Na and Zr in the EDS analysis of prepared catalyst further sustain the Na/ZrO₂ inclusion over the SBA-15. The SAED pattern (Fig. 4c) of the catalyst depicts the polycrystalline nature of catalyst owing to the incidence of bright diffraction spots, arranged in multiple rings corresponding to planes of sodium zirconate crystal also consistent with aforementioned XRD analysis of the same catalyst. The minutely diffused character in the multiple rings is attributed to the non-crystalline nature of SBA-15 material present in the catalyst.



Fig. 4. HR-TEM images of a) rhombus and rectangular units of catalyst particles, b) dark spots signify the loading of Na/ZrO₂ over SBA-15, and c) SAED pattern of 30-Na/ZrO₂/SBA-15 catalyst.

3.1.5. XPS study

To establish the oxidation state of the elements present in 30-Na/ZrO₂/SBA-15, XPS study was utilized. As depicted in Fig. 5a, the peak detected at 105.1 eV supports the occurrence of Si 2p of amorphous silica in +4 oxidation state. A report observed similar value (103 eV) of binding energy (B.E.) for Si present in amorphous silica wherein ceria-silica composite was synthesised [25]. The peak at 105.6 eV is due to the presence of Si⁴⁺ in surface Si-O-Si bonds. In literature [26] presence of surface Si-O-Si bonding with Si⁴⁺ state was reported at B.E. of 103.7 eV. The peak consequent to the O 1s, could be deconvoluted into three peaks (Fig. 5b) viz., at 535 eV, 531.5 eV and 533 eV. The strong peak appeared at 535 eV can be ascribed to oxygen of amorphous SBA-15 material while remaining two peaks at 531.5 eV and 533 eV can be respectively pointed to O²⁻ species of lattice oxygen of active species and feebly bonded oxygen of physisorbed water molecule. Similar spectra for O 1s was obtained with 3 convoluted Gaussian peaks in a report where Ca ans Mo metals were impregnated over SBA-15 with peaks appearing at 533.1 eV, 529.8 eV and 531eV [8]. The peak at 1073.5 eV (Fig. 5c) refers to Na 1s state also supported by recent report [27] where Na 1s spectra was obtained at 1071.6 eV. Zr 3d spectrum (Fig. 5d) is a doublet corresponding to Zr^{4+} 3d_{5/2}-Zr 3d_{3/2} spin-orbit splitting corresponding to the B.E. positioned at 183.6 and 186.7 eV, respectively. Similar spectra and peak positions was obtained in another report [28] in which Zr was present in $Zr^{4+} 3d_{5/2}$ -Zr $3d_{3/2}$ spin states show the B.E. positions at 182.2 eV and 184.6 eV, respectively. It is to be noted that spectral lines of all elements in present catalyst show a general shift ~ 2 eV with regard to the reference lines (O 1s of SBA ~ 532.9 eV and Zr 3d_{5/2} at 182 eV). This slight reallocation is due to accumulation of excessive electrical charge on sample surface while irradiation of photons. Similar observation has been reported in the literature where a similar shift in XPS spectral lines has been observed [29].



Fig.5. XPS spectra of (a) Si (b) O (c) Na and (d) Zr present in 30-Na/ZrO₂/SBA-15.

3.1.6. Hammett indicator study

In order to compute the amount of basic and acidic sites, Hammett indicator test was executed. Trichloroacetic acid and n-butylamine were employed as titrants to enumerate the basic and acidic sites of the synthesised catalysts. Na/ZrO₂ impregnation boosted the Lewis basic and acidic sites that are liable to commence transesterification of the triglyceride (Table 3). Literature reports that presence of Lewis acid sites promotes esterification whereas existence of Lewis basic sites in the catalyst is responsible for transesterification [13]. A

catalyst which seizes both type of sites can bring about esterification and transesterification concurrently. The bare SBA-15 template, even though acquires some intrinsic acidity as well as basicity, but, not sturdy enough to commence and kick off the transesterification or esterification reactions under ambient conditions. As the impregnation amount amplified, the basicity and therefore activity of catalyst too simultaneously augmented up (from 4.19 mmol/g to 4.65 mmol/g). However, utmost catalytic action and highest catalyst bustle was observed with 30 wt% impregnation of Na/ZrO₂ over SBA-15 and therefore, it became the choice as most favourable catalyst for the further studies.

Table 3. Comparison of acidic and	basic strengths, a	and TOFs for t	the x-Na/ZrO ₂ /SBA-15
catalyzed transesterification.			

		I	Acidity	Basicity					Total acidity	Total basicity	TOF $(\times 10^{-3} h^{-1})$
Catalyst	(H₀≤+4.8)	(H₀≤+6.8)	(H₀≤+7.2)	(H₀≤+7.2)	(H₀≤+9.3)	(H₀≤+10.1)	(H₀≤+11.1)	(H₀≤+15)	(mmol g ⁻¹)	(mmol g ⁻¹)	
SBA-15	NCC	0.16	NCC	0.59	NCC	NCC	NCC	NCC	0.16	0.59	-
15- Na/ZrO ₂ /SBA-15	0.12	0.18	0.22	0.63	0.69	0.74	0.72	1.41	0.52	4.19	3.9
20- Na/ZrO ₂ /SBA-15	0.25	0.25	0.28	0.63	0.68	0.75	0.81	1.45	0.78	4.32	5
25- Na/ZrO ₂ /SBA-15	0.28	0.31	0.31	0.64	0.70	0.73	0.80	1.48	0.9	4.35	9.9
30- Na/ZrO ₂ /SBA-15	0.34	0.37	0.39	0.65	0.69	0.73	0.81	1.67	1.1	4.55	16.6
35-Na/ZrO ₂ /SBA-15	0.33	0.37	0.40	0.64	0.69	0.74	0.82	1.76	1.1	4.65	16.3

*NCC stands for No colour change.

*TOF is calculated at 50% conversion level on the basis of basic sites; Reaction conditions = methanol to oil molar ratio of 30 : 1 at 65 °C reaction temperature, in the presence of 10 wt% of catalyst with respect to oil at 600 rpm stirring speed. *Indicators used: methyl red (H0 \leq 4.8), neutral red (H0 \leq 6.8), bromothymol blue (H0 \leq 7.2), phenolphthalein (H0 \leq 9.3), Nile blue (H0 \leq 10.1), tropaeolin (H0 \leq 11.1), 2, 4-dinitroaniline (H0 \leq 15.0)

3.2. Catalytic activity

The catalytic activity of the prepared catalysts was tested for methanolysis of virgin cottonseed oil (VCO). The reaction parameters were optimised for transesterification activity with a goal to accomplish highest yield of FAMEs in minimum possible time. One factor at a time of the following was altered to attain the optimised reaction conditions: (i) impregnated Na/ZrO₂ concentration, (ii) catalyst amount (iii) molar ratio of MeOH/oil and (iv) reaction temperature.

3.2.1. Effect of Na/ZrO₂ concentration on catalytic action

SBA-15 on its own has very meagre inherent basicity/acidity as well maintained by Hammett indicator study (Table 3). Thus, it demands sufficiently high temperature and pressure conditions to catalyze any reaction on its own. The catalytic action of the SBA-15 could be raised by loading it with the appropriate active catalytic species ($20-Na/ZrO_2$ in present study).

To conclude the most favourable amount of Na/ZrO₂ over SBA-15, a sequence of catalysts were synthesised by varying Na/ZrO₂ concentration from 15-35 wt%. At 65 °C, using a 30:1 MeOH/oil molar ratio and 10 wt% (catalyst/oil) of catalyst, the reactions were performed. Entire transesterification of VCO into BD was achieved in 3 h when Na/ZrO₂ impregnation was increased from 15 to 35 wt% (Fig. 6a). This boost in rate of reaction with mounting Na/ZrO₂ amount is expected as there will be consequential rise in number of active sites in the catalyst as depicted in Table 3. An auxiliary increase in Na/ZrO₂ amount (from 30 to 35 wt %) could not reduce the duration of reaction significantly. Hence, 30 wt% of Na/ZrO₂ on SBA-15 was elected as the finest amount of active catalytic species. In the present study, maximum amount of active basic sites observed were with 35 wt% loading of active moiety. However, catalysts with highest Na/ZrO₂ loading amounts (30 and 35 wt%) depicted almost similar TOFs. Hence, 30 wt% of Na/ZrO₂ loading was optimised for loading on mesoporous silica. The observations are in quite in queue with those reported in literature, where any additional raise in the impregnation level of active species beyond a certain amount could not help upshot the reaction rate. As clearly mentioned in Hammett indicator study, the acidity/basicity of the catalyst improves with the increment in amount of impregnated active species [30]. Impregnation of active species (20-Na/ZrO₂) gives rise to the acidic/basic sites in catalyst which are liable to instigate the transesterification.

3.2.2. Effect of amount of the catalyst

For any chemical procedure, the amount of catalyst is vital and has noteworthy effect on the production cost. To assess the optimal catalyst concentration, transesterification reactions were carried out with 30-Na/ZrO_2 /SBA-15 using 30:1 MeOH/oil molar ratio at 65 °C. Amount of catalyst was stippled from 6 to 11 wt% (catalyst/oil). The FAMEs yield showed an augmentation as the catalyst amount was raised from 6 to 10 wt% as shown in Fig. 6b. Any more addition to catalyst amount (10 to 11 wt%) was not found to sway the reaction rate to any remarkable level. Therefore, all reactions were carried out using 10 wt% of catalyst at 65 °C.

Excess amount of solid catalyst heaves up the viscosity of reaction mixture which ultimately leads to ineffectual of the reactants. As a consequence, there is lesser contact between the oil and MeOH, making the BD synthesis sluggish and reduces FAMEs yield. Addition of excess concentration of solid catalyst causes emulsion formation which further obstructs the severance of glycerol and waning the apparent FAMEs yield [31]. In a report [32], the immobilisation of tetramethylguanidine as active catalytic moiety to prepare solid base catalyst was performed and utilised for production of BD. The oil conversion went up to 91.7% when catalyst amount was raised upto 5 wt%. However, with the further raise in the catalyst dose upto 7 wt%, the oil conversion diminished owing to inefficient mixing of reactants and hike in the viscosity of reaction mixture.

3.2.3. Effect of methanol to oil molar ratio

As discussed in previous chapters also, idyllically, for the transesterification to reach completion, the stoichiometric molar ratio compulsory, is 3:1 (methanol/triglyceride).

However, as the reaction is reversible, it is often performed by utilising superfluous amount of alcohol with an intension to smooth the progress of forward reaction and avert the back reaction.

To settle on the most advantageous methanol/oil molar ratio, a succession of methanolysis reactions were carried out with 30-Na/ZrO₂/SBA-15 at 65 °C and altering the MeOH/oil molar ratio from 10:1 to 30:1. The reaction rate amplified as the MeOH/oil molar ratio was raised from 9:1 to 24:1. The reaction went to completion within 3 h when 30:1 MeOH/oil ratio was employed. Any more addition in the MeOH/oil molar ratio did not influence the reaction rate to any momentous extent (Fig. 6c). Therefore, 30:1 MeOH/oil molar ratio was chosen to be optimum to achieve complete transesterification of VCO. If MeOH/oil molar ratio greater than 30:1 is utilised, it will lead to intrusion of excess MeOH in glycerol severance from BD due to superior solubility of glycerol. Furthermore, if glycerol stays in solution, it urges the reaction equilibrium towards the reactant direction, decreasing the BD yield [33]. In a report, WO₃/AlPO₄, was explored for transesterification [34] and it was observed that, the conversion levels rose up with hike in MeOH/oil molar ratio upto 30:1. However, beyond this ratio, there was no significant rise in the FAMEs yield.

3.2.4. Effect of reaction temperature

30-Na/ZrO₂/SBA-15 catalyzed transesterification was executed at different temperatures with a view to assess the effect of reaction temperature on pace of reaction by employing 30:1 MeOH/oil molar ratio and 10 wt% of catalyst.

The rate of methanolyis was found to boost up as the reaction temperature was raised from 35 to 65 °C as shown in Fig. 6d. Further raise in reaction temperature was not found to affect the FAMEs yield or reaction rate significantly.

This observation can be owed to the MeOH vapours formation leading to its subsequent loss from the reaction mixture. The vaporized methanol will lose its contact with reactants for sufficient time to not helping improving biodiesel yield [35] any further on rising the reaction temperature beyond 65 °C. The present work tales more than 98% FAMEs yield at easily attainable 65 °C and one atmosphere pressure conditions to imply the catalyst efficacy. Maintaining very high temperature during the reaction demands very high energy and complex reactor design to uphold the high pressure generated during the reaction. Similar observations have also been reported earlier in literature, *e.g.*, in a latest research report, mesoporous calcium titanate has been employed as catalyst for BD synthesis [36] and favourable reaction temperature was 65 °C and any auxiliary raise could not promote the reaction rate further. The transesterification at temperatures even upto 200 °C have been reported under high pressure conditions. Ti/SBA-15 catalyst has been explored for transesterification [9] of jatropha oil and 90% FAMEs yield within 3 h of reaction time. To sustain such high temperature requires high energy and also complicatedly designed reactors which will incur more input costs and hence not beneficial commercially.



Fig. 6. Effect of (a) Na/ZrO₂ concentration on SBA-15, (b) catalyst concentration, (c) methanol/oil molar ratio on methanolysis of VCO and (d) reaction temperature

3.3. Effect of FFA on catalytic activity

Non-edible or ravaged cooking oils generally contain usually FFA contents in fairly elevated amount. Traditionally, the transesterification of such elevated levels of FFA-holding oils is executed in two-steps involving firstly, acid-catalyzed pre-esterification with an acid catalyst and subsequent transesterification using an alkali catalyst. The 30-Na/ZrO₂/SBA-15 catalyst was found exhibit both esterification plus transesterification action. To express the simultaneous esterification and transesterification action of the catalyst in one-pot, system, transesterification reactions of waste soyabean oil (WSO) and jatropha oil (JO) (containing 3.9 and 9.7 wt% FFA respectively) were carried out with methanol. It was concluded that although the present catalyst was efficient for the transesterification of FFA rich feedstock,

dwindle in TOF was observed as the levels rose. The duration of reaction entailed to achieve absolute conversion raised to 5.5 h and 8.5 h for WSO and JO respectively (Fig. S2. ESI). This drop in TOF of catalyst can be endorsed to partial blocking of the active sites of catalyst due to the interaction of basic sites with free fatty acids in the feedstock to consequent the partial trouncing of catalyst action.

To establish the esterification activity of 30-Na/ZrO₂/SBA-15 catalyst, in a different reaction oleic acid was reacted with MeOH under the optimised conditions. Within 3 h of reaction duration 68% yield of methyl oleate was achieved to validate that the catalyst could catalyze esterification of fatty acids as well.

This is a clear advantage of present catalyst since cumbersome 2-step procedure first get rid of high FFA content in low-quality feedstock and then carrying out transesterification can be evaded to successfully bring about both esterification and transesterification in one-pot system.

3.4. Reusability and homogeneous contribution

Reusability and recycling of heterogeneous catalyst is a very imperative and gainful characteristic. Recycling of solid catalyst helps in their simpler separation procedure and simultaneously cutting down the cost and labour required during post production process. To assess the reusability and crumble in activity of present catalyst, transesterification reaction with 30-Na/ZrO₂/SBA-15 was executed under optimised conditions. The worn catalyst was then convalesced through filtration, subjected to washing with hexane and methanol to remove both polar as well as non polar contaminants, dried at 120 °C and then calcined at 600 °C. The revived catalyst was utilised for transesterification for 6 succeeding runs using parallel experimental clauses and revival method. It was found that the revived catalyst yielded complete conversion of feedstock into FAMEs for 5 subsequent runs. The action of the catalyst was found to show a noticeable demur in the 6th run when it yielded 86% FAMEs yield. The TOF of catalyst decreased following the 5th cycle (Fig. 7). Therefore, it may be construed that SBA-15 mesoporous support makes the catalyst consistent and stable and facilitates in convalescing the recyclability which stands as a benefit of the prepared catalyst under study.

Percolation of the active catalytic species in the catalyst is a recurrently faced issue in case of heterogeneous catalysts. The amount of Na metal was quantified in FAMEs layers in 6th cycle with Flame photometry technique and was determined to be 485 ppm. All through early runs, it can be supposed that no active metal would have oozed out into the reaction concoction since 30-Na/ZrO₂/SBA-15 was proficient of upholding its action and yielded complete conversion of VCO into BD. Hence, it can be construed that SBA-15 support was able to craft the catalyst into a sensibly and convincingly stable one simultaneously averting the leaking out of any active metal into reaction medium. Active species when seized over mesoporous silica evidently becomes a lucrative selection over unsupported catalyst, in view of the fact that it may well hang on to its venture over following cycles with no credible leaching of otherwise seepable alkali metals.

Additionally, surface area of reused catalyst were also calculated and was found to be 5.14 m² g⁻¹ which was significantly lesser than the surface area of fresh catalyst (78.3 m² g⁻¹). Thus, decline in activity can be clarified by combined percolation and reduction in surface area of reused catalyst showing the way to lower catalytic activity. Moreover, the basicity test of reused catalyst was also carried out to ascertain the basis for reduced catalytic action. The basicity of regenerated catalyst was found to be 4.27 mmol g⁻¹ (basicity of fresh catalyst = 4.55 mmol g⁻¹) to support the oozing of active metals into reaction mixture and consequential decline in catalytic flurry.

Percolation of active metallic species causes the fall in activity of catalyst and it is possible that leached species may catalyse the reaction like homogeneous catalysts. Hence, it becomes imperative to find the homogeneous contribution of the catalyst, if any. For quantification of the contribution of dissolved catalyst in overall activity, and validate the heterogeneous manner of activity of the prepared catalyst, hot filtration test was performed under optimal reaction conditions. The VCO transesterification was carried out under the optimized conditions for 1 h, after that catalyst was separated *via* filtration method and reaction was allowed to continue for more 2 h. As it could be clearly seen from the Fig. (S3. ESI), that no increment in FAMEs yield was observed when the reaction was continued in absence of catalyst to support that (i) the mode of action of the prepared catalyst is heterogeneous and (ii) the leached metal ions have no significant contribution in catalytic activity.



Fig. 7. Reusability of 30-Na/ZrO₂/SBA-15 catalyst (Reaction conditions: MeOH/oil molar ratio = 30:1; Catalyst amount = 10 wt% of oil; Temperature = 65 °C

4. Conclusions

Present work embodies the synthesis and investigation of $30-Na/ZrO_2/SBA-15$ as solid and revivable catalyst for BD production from virgin cotton seed oil. Under optimised reaction conditions of 10 wt% catalyst, 65 °C reaction temperature and MeOH/oil molar ratio of 30:1, > 98% FAMEs yield was attained within 3 h. The catalyst confiscated both acidic and basic sites and hence victoriously employed for concurrent esterification and transesterification of waste cooking oil as well. The catalyst paraded very fine recyclability for it was able to uphold its activity (98% FAMEs yield) for 6 catalytic runs. 86% FAMEs yield was achieved in 6th cycle. From commercial perspective, retention of activity, due to stable and locked siliceous matrix is considerable observation in present chapter. The catalyst followed heterogeneous mode of action and no homogeneous contribution was found.

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