



# Lithium zirconate as solid catalyst for simultaneous esterification and transesterification of low quality triglycerides



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## ABSTRACT

Alkali metal (Li, Na and K) doped zirconium oxide was prepared (Li/ZrO<sub>2</sub>, Na/ZrO<sub>2</sub> and K/ZrO<sub>2</sub>) by wet chemical route and used as active heterogeneous catalyst for the transesterification of waste cottonseed oil with ethanol and methanol to produce fatty acid ethyl and methyl esters, respectively. The catalyst characterization supports the formation of lithium zirconate single phase in the case of Li/ZrO<sub>2</sub> and it was able to catalyze simultaneous esterification and transesterification of high free fatty acid containing vegetable oils (VOs). The reaction conditions, such as catalyst concentration, reaction temperature, the molar ratio of alcohol/oil and stirring speed, were optimized in the presence of Li/ZrO<sub>2</sub> catalyst. The catalyst activity was found to be a function of its basic sites which in turn depends on calcination temperature and lithium content of the catalyst. A pseudo first order kinetic equation was applied to evaluate the kinetic parameters for the transesterification of waste cottonseed oil with methanol and ethanol. The activation energy ( $E_a$ ) for the Li/ZrO<sub>2</sub> catalyzed methanolysis and ethanolysis was found to be 40.8 and 43.1 kJ mol<sup>-1</sup>, respectively. The catalyst could be reused up to nine cycles without significant loss of performance as >90% fatty acid alkyl ester yield was maintained.

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## 1. Introduction

Conventional non-renewable fossil fuel resources, which are supplying the majority of the energy needs of the world presently, are expected to be exhausted shortly. Consequently, search of alternative and renewable fuels has attracted considerable attention in recent years [1]. Biodiesel (BD) has emerged as a green, non-toxic, renewable and biodegradable substitute for the conventional diesel fuel. Chemically BD is a mixture of fatty acid alkyl esters (FAAE) which could be obtained from the transesterification of triglycerides with short chain alcohol in the presence of catalysts [2]. Homogeneous base catalysts such as KOH or NaOH, owing to their high activity, are conventionally used under relatively mild reaction conditions for industrial scale biodiesel production [3]. However, these catalysts get deactivated via saponification if >0.5 wt% free fatty acid (FFA) contents and/or >0.3 wt% moisture contents are present in VOs. Thus biodiesel from high FFA containing VOs is produced in a two-step method which involves acid catalyzed esterification followed by alkali catalyzed transesterification. Highly corrosive strong acid and base catalysts must be

neutralized and resulted salt formed must be washed away from the biodiesel to generate significant amount of effluents. In this context application of solid catalyst would be advantageous from a commercial as well as an environmental point of view for biodiesel production from cheap feedstock, such as unrefined or waste VO via simultaneous esterification and transesterification reaction.

In literature solid acid/base catalysts have been reported for the simultaneous esterification and transesterification of high FFA containing triglycerides. The strategy involved in the preparation of such catalysts is the use of a support (e.g. ZrO<sub>2</sub>, CaO and MgO) on which catalytically active species are impregnated. Among these supports, ZrO<sub>2</sub> possesses both acidic and basic properties; hence, it is successfully employed for catalyzing simultaneous esterification and transesterification of high fatty acid containing VO [4].

The use of zirconia as support material results in distinctive interaction between the active metal and support materials which may yield enhanced activity and selectivity of the prepared catalysts [5]. Omar and Amin [6] reported that Sr/ZrO<sub>2</sub> catalyst has balanced active sites which facilitated simultaneous transesterification and esterification of waste cooking oil having 2.5 wt% FFA content. The main drawback of the prepared catalysts was the lower biodiesel yield of 40%. Kulkarni *et al.* [7] reported the use of tungstophosphoric acid supported hydrous zirconia as solid catalyst for the simultaneous esterification and transesterification of

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low quantity canola oil with 20 wt% FFA at 200 °C reaction temperature to obtain 90% ester yield. Yan *et al.* [8] used ZnO–La<sub>2</sub>O<sub>3</sub> catalyst to achieve 96% fatty acid methyl ester (FAME) yield from waste oil with 5.4 wt% FFA, at 170–200 °C reaction temperature. Addition of up to 5.1 wt% moisture content in oil was found to increase the reaction duration from 60 to 150 min. Sreepasanth *et al.* [9] 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 FAME into FFA due to hydrolytic activity of catalyst. Rattanaphra *et al.* [10] employed sulfated zirconia for the transesterification of rapeseed oil having 10 wt% FFA content to achieve 86% FAME yield. However, leaching of sulfate group in reaction mixture remains an issue for the catalyst. Mg–Al–CO<sub>3</sub> catalyst has shown 99% FAME yield at 200 °C reaction temperature for the transesterification of cotton seed oil having 43 wt% FFA and 3.5 wt% moisture contents [11]. Thus most of the zirconia based catalysts require high temperature and pressure conditions for the biodiesel production from low quality feedstock having high FFA and moisture contents.

Another issue related with the current biodiesel production technology is the use of methanol which is a toxic and non-renewable chemical as it is mainly produced from the crude oil refining [12]. Ethanol, being non-toxic and renewable (as it is mainly produced by the fermentation of biomass), could be a better alternative as alcohol for biodiesel production. Additionally, fatty acid ethyl esters (FAEE) have a slightly higher heat content and cetane number, and lower cloud and pour points than corresponding methyl esters [13]. Due to the lesser reactivity in comparison to methanol, and separation problem of ethyl ester from glycerol, ethanol has not been frequently employed for the transesterification of VOs. Mg<sub>2</sub>CoAl as a heterogeneous catalyst required 200 °C temperature and 25 atm pressure for the transesterification of rapeseed oil with ethanol to achieve 97% conversion level [14]. Garcia *et al.* [15] employed sulfated zirconia for the ethanolysis of soybean oil in Parr batch reactor at 120 °C reaction temperature to achieve 92% yield in 1 h. Kim *et al.* [16] reported CaO–La<sub>2</sub>O<sub>3</sub> catalyst for the ethanolysis of soybean oil using 8 wt% catalyst amount at 65 °C reaction temperature to obtain 71.6% conversion in 6 h. To the best of our knowledge, there is no reported work available in literature related to the application of alkali metal doped ZrO<sub>2</sub> as heterogeneous catalyst for the ethanolysis of triglycerides.

Alkali zirconates have been widely studied as an adsorbent for carbon dioxide, but, so far, it has received little attention as a catalyst for the transesterification of triglycerides [17]. In this study, alkali doped ZrO<sub>2</sub> was prepared via wet impregnation method and employed for the ethanolysis as well as methanolysis of the waste cotton seed oil. The kinetics of the Li/ZrO<sub>2</sub> catalyzed ethanolysis as well as methanolysis of waste cotton seed oil was studied under optimized reaction conditions. The catalyst, Li/ZrO<sub>2</sub>, was able to perform simultaneous esterification as well as transesterification of vegetable oil having free fatty acid content as high as 18.1 wt%.

## 2. Experimental section

### 2.1. Reagents and materials

Zirconium oxide (ZrO<sub>2</sub>) was obtained from Sigma Aldrich (USA) and lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O), sodium nitrate (NaNO<sub>3</sub>), potassium nitrate (KNO<sub>3</sub>), oleic acid, hexane, ethyl acetate, acetic acid, methanol, ethanol (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

Alkali doped zirconia was prepared via wet impregnation method. In a typical preparation 30 ml aqueous solutions of lithium hydroxide, or sodium nitrate, or potassium nitrate of desired concentrations was mixed with 10 g of zirconium oxide, which was suspended in 50 ml of deionized water. The resulted mixture was stirred for 4 h, initially dried at 120 °C for 12 h and finally calcined at desired temperature (300–800 °C) for 4 h.

Prepared M/ZrO<sub>2</sub> were labeled as *x*-M/ZrO<sub>2</sub>-*T*, where *M*, *x* and *T* represent the type of alkali dopant, its content (wt%) and calcination temperature (°C), respectively.

### 2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical's X'Pert Pro using monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) and scanning the samples over a  $2\theta$  range of 5–80°. The XRD diffraction patterns were compared with patterns in Joint Committee on Powder Diffraction Standards (JCPDS). Fourier transform-infrared spectra (FTIR) of the samples were recorded in KBr on Perkin Elmer-Spectrum 400 spectrophotometer, in the range of 400–4000 cm<sup>-1</sup>.

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. 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<sub>3</sub> solvent using tetramethyl silane (TMS) as internal reference.

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

In a typical experiment of CO<sub>2</sub>-TPD, 0.1 g of catalyst was loaded in a quartz reactor between two quartz plugs. Prior to CO<sub>2</sub> adsorption, the catalyst was pretreated with He gas at 300 °C for 2 h and then cooled to room temperature. The adsorption of CO<sub>2</sub> was carried out by passing a mixture of 10% CO<sub>2</sub>-balanced He gas over the catalyst for 1 h. Before the TPD run, the He gas was flushed over catalyst surface at 100 °C for 2 h to remove the physisorbed CO<sub>2</sub>. TPD of the catalyst was carried out in a He gas flow at a flow rate of 30 ml/min with a temperature ramp of 10 °C/min. The CO<sub>2</sub> desorption was monitored using the thermal conductivity detector (TCD) of a gas chromatograph (Varian, 8301).

The basic strength (*H*) and basicity of the catalysts (*f<sub>m</sub>*) was measured by Hammett indicators-benzene-carboxylic acid titration method [18,19] using 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) 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

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