



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



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ABSTRACT

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

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1. Introduction

Due to rapidly increasing crude oil price, diminishing fossil fuel resources, and increasing environment pollution because of fuel burning, the development of alternate, clean and renewable energy sources has become essential. In this context biodiesel has attracted the attention as a renewable and eco-friendly alternative to the conventional diesel fuel [1]. Biodiesel is chemically a mixture of fatty acid alkyl esters (FAAE) and prepared from triglycerides (vegetable oils or animal fat) via transesterification reaction [2]. At industrial scale biodiesel is generally produced by the transesterification of triglycerides with methanol in the presence of homogeneous base (e.g., NaOH, KOH, NaOMe and KOMe) [3,4] or acid (e.g., HCl and H₂SO₄) catalysts [5]. Although homogeneous base catalysts catalyze the reaction at faster rate, however, these catalysts required costly and refined vegetable oil as feedstock. Further, biodiesel thus produced must be washed with water to remove the catalyst and hence, huge amount of industrial effluents are generated.

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

acid catalysts and hence solid alkali catalysts have been extensively studied in literature [6].

Mixed oxides of zirconium such as Zr/Mg, WO₃/ZrO₂, Sr/ZrO₂, and SO₄²⁻/ZrO₂ were also found to be promising solid catalysts [7–15] for the transesterification reaction. The reaction conditions for various types of literature reported zirconium containing catalysts have been compared in Table 1.

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

The conventional method of biodiesel production utilizes methanol, a highly toxic chemical, for the transesterification reaction. Methanol is not only highly toxic but also a refinery residue and hence, fatty acid methyl ester (FAME) will not be completely carbon neutral. In this regard, application of ethanol could be advantageous as it is renewable and also considered as non toxic green chemical. However, due to the lesser reactivity in comparison to methanol, ethanol has not been frequently employed for the transesterification reaction in the presence of heterogeneous catalysts [16]. Li et al. [17] reported the application of Mg₂CoAl mixed oxide as a heterogeneous catalyst for the transesterification of rapeseed oil with ethanol at 200 °C and 25 atmospheric pressure to achieve a 97% conversion in 5 h. Soldi et al. [18] employed ion-exchange resin-sulfonated polystyrene for the ethanolsis of beef tallow (100:1 ethanol to fat ratio) to achieve 27% yield in 18 h. To the best of our knowledge, there is no reported work available in literature related with the application of Zr/CaO as heterogeneous catalyst for the ethanolsis of triglycerides.

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

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

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

Although, many reports are available regarding the development and application of the heterogeneous catalysts for the transesterification reaction, however, only few of them describe the kinetic study. The kinetics of K–CaO, KF/Mg–La, CaO, and CaO–ZnO catalyzed methanolysis of triglycerides have been studied by various research groups [2,19–21]. The alcohol to oil molar ratio in these reactions was usually employed in excess (>6:1) to the required amount of 3:1 and hence, (pseudo) first order kinetic equation was applied to study the kinetics. The activation energies of the catalysts were found to be in the range of 16–79 kJ/mol. Kinetic study of the ethanolysis reaction in the presence of heterogeneous catalyst is rare in literature. To the best of our knowledge, Mg₂CoAl mixed oxide is the only heterogeneous catalyst which has been employed [17] to study the kinetics of ethanolysis reaction. The activation energy for this reaction was found to be 60.5 kJ mol⁻¹, following the first order reaction kinetics.

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

2. Experimental section

2.1. Materials and methods

Calcium oxide (CaO) and zirconium (IV) oxychloride octahydrate (ZrOCl₂·8H₂O) were obtained from Sigma Aldrich (USA). Hexane, methanol and ethanol (analytical grade purity), were obtained from Loba Chemie Ltd (India) and used as such without further purification. Jatropha (*Jatropha curcas*) oil (JO), karanja (*Pongamia pinnata*) oil (KO), fresh cottonseed (*Gossypium arboreum*) oil (CO) and waste cottonseed (WO) employed for the transesterification reactions were procured from the local shops situated in Patiala and their chemical analysis is provided in Table 2.

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

Field emission scanning electron microscopy coupled with energy dispersive X-ray spectrometry (FESEM-EDX) was performed on JEOL

JSM 6510LV and transmission electron microscopy (TEM) pictures were recorded on HITACHI 7500 instrument.

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

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

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

Fourier transform-nuclear magnetic resonance (FT-NMR) spectra of FFAE and vegetable oils were recorded on a Bruker Avance-II (400 MHz) spectrophotometer, using tetramethoxysilane as an internal standard and CDCl₃ as a solvent.

2.2. Catalyst preparation

A series of zirconium impregnated CaO was prepared by the wet impregnation method. In a typical preparation, 10 g of CaO was suspended in 40 mL of deionized water, and to this 10 mL aqueous solution of ZrOCl₂·8H₂O of desired concentration was added. The resulted slurry was stirred for 4 h, then evaporated to dryness, and heated at 120 °C for 24 h. A series of Zr/CaO was prepared by varying zirconium concentration in the range of 5–20 wt.% and calcination temperature 300–900 °C. Prepared catalysts were labeled as x-Zr/CaO–T, where x and T represent the zirconium concentration (wt%) and calcination temperature (°C), respectively.

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

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

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