



Biodiesel production from soybean and Jatropha oils using cesium impregnated sodium zirconate as a heterogeneous base catalyst



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ABSTRACT

Cesium modified sodium zirconate (Cs-Na₂ZrO₃) was prepared by ionic exchange from sodium zirconate (Na₂ZrO₃), which was synthesized via a solid state reaction. Both ceramics, i.e., pristine Na₂ZrO₃ and the Cs-Na₂ZrO₃, were used as basic heterogeneous catalysts in biodiesel production. Soybean and Jatropha oils were used as triglyceride sources for transesterification reactions. Parameters, such as catalyst concentration (between 0.5 and 3 wt%), reaction time, different methanol/vegetable oil molar ratios, and temperature of the reaction, were evaluated. The cesium cation influence was evaluated from the basic transesterification reactivity. The results showed that the introduction of cesium significantly modified the catalytic activity in biodiesel production. Cs enhanced the reaction kinetics in obtaining biodiesel and reduced the reaction time in comparison with pristine Na₂ZrO₃. The results showed that Cs-Na₂ZrO₃ as a basic heterogeneous catalyst exhibited the best fatty acid methyl esters (FAME) conversion for soybean oil (98.8%) at 1 wt%, 30:1 methanol/oil ratio, 65 °C, and 15 min. The best conditions for Jatropha oil (90.8%) were 3 wt%, 15:1 methanol/oil ratio, 65 °C, and 1 h. The impregnation of Na₂ZrO₃ with cesium represents a very exciting alternative heterogeneous base catalyst for biodiesel production.

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1. Introduction

Global energy requirements are expanding quickly due to rapid world population growth, the increase in the standard of living, and the development of technologies [1], in which the demand has doubled over the last three decades [2]. Fossil fuels currently produce 81% of the world's energy [3]. The use of fossil fuels as a principal energy source cannot continue indefinitely because they are non-renewable sources [4,5]. The supply of these fossil fuels will not be sufficient for the future [5] because the reserves are predicted to last less than 60 years for natural gas and 40 years for petroleum [6]. Thus, due to the declining fossil fuel stocks and global climate changes caused by increased atmospheric greenhouse gas emissions from fossil fuel burning, bioenergy production has emerged as one of the most promising solutions.

Among the bioenergy alternatives, biodiesel has been highly

investigated currently [7–37]. Biodiesel is a sulphur-free, biodegradable, and non-toxic diesel fuel substitute that can be used in unmodified diesel engines [7,8]. It possesses a considerable added value over petroleum-based diesel. The emissions from prototype vehicles using biodiesel contain 94% less carcinogenic agents than petroleum-based diesel emissions [10,11], thus reducing air pollution. In addition, biodiesel degrades about four times faster than petroleum-based diesel fuel and is easy to handle, transport, and store [11]. Typically, biodiesel is produced via triglyceride (TG) transesterification from vegetable oils and animal fats with short-chain alcohols and homogeneous acid or base catalyst to yield fatty acid methyl esters (FAMES), fatty acid ethyl esters (FAEEs), and glycerol (glycerine) as a by-product [10,12,13]. The most common method for the transesterification of TG is carried out in batch plants using homogeneous basic catalysts (e.g., NaOH, KOH and alkali metal alkoxides), which can lead to high biodiesel yields in short reaction times [14]. However, these homogeneous catalysts are unrecyclable after the reaction has been completed, and there exists several separation issues. Additionally, it causes an alkaline

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wastewater stream, which produces high corrosion on the equipment and results in high operation prices. Thus, the development of heterogeneous catalysts exhibiting high recyclability, simple recovery, easy separation, lower energy consumption, and cleaner operation conditions is crucial for biodiesel production [8,13–16]. In this regard, there is a considerable number of studies on heterogeneous catalysts for the transesterification of TG [8,10,13–17], mainly based on alkaline earth metal oxides, such as MgO, CaO, SrO, etc. [8,17,22], lithium based ceramics (Li_4SiO_4 and Li_2SiO_3 [18,19]), Na_2SiO_3 [20], transition metal oxides (ZnO, PbO_x , ZrO_2 , etc. [21–23]), basic ion-exchange resins [24,25], layered double hydroxides [26–28], supported bases [29,30], salts impregnated on Al_2O_3 and ZnO [31–33], and zeolites [34]. Among the oxides employed as catalysts, CaO holds a privileged position in biodiesel production due to its high reaction yield (c.a. 98%) after just the first cycle [33]. In addition, modifications of CaO or ZnO with lanthanum [35] and lithium [36] have drawn considerable attention for the production of biodiesel because these modifications have shown high basicity, low solubility, and low preparation cost [8,11,33].

The alteration in the chemical composition of the existing catalytic system is considered as a possible option to increase the number of active basic sites and improve the yield of reaction. Recently, it was shown that sodium zirconate (Na_2ZrO_3) exhibited interesting catalytic properties as a basic heterogeneous catalyst for the production of biodiesel via a soybean oil transesterification reaction [37], which led to good purity, as well as composition and unsaturation degree of the produced biodiesel comparable to previous reports [37]. Thus, motivated by these encouraging results, we present herein a modified zirconate (cesium impregnated sodium zirconate, $\text{Cs-Na}_2\text{ZrO}_3$) as a heterogeneous catalyst for the basic transesterification reaction between soybean oil or Jatropha oil and methanol for biodiesel production. Cesium was incorporated to the Na_2ZrO_3 catalyst by a simple impregnation method due to its basic character. The percentage of this catalyst, vegetable oil/alcohol ratio, reaction time, and temperature are varied in this study. Moreover, the main interest in using Jatropha oil for biodiesel production is because this oil is not suitable for human consumption, and therefore, its production does not interfere with the food industry or harvesting lands [7,12]. Additionally, the influence of cesium on the reactivity of the transesterification reaction and its re-utilization reaction is evaluated.

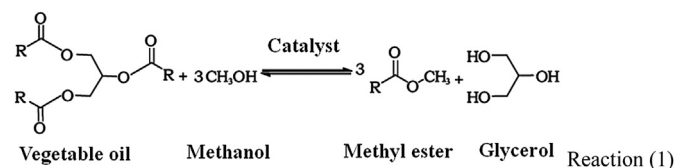
2. Materials and methods

Sodium zirconate (Na_2ZrO_3) was prepared via a solid state reaction. Zirconium oxide (ZrO_2 , Sigma–Aldrich México 99.9%) and sodium carbonate (Na_2CO_3 , Caledon México 99.5%) were mixed and heat-treated at 850 °C for 6 h. An excess of 10 wt% of Na_2CO_3 was used due to the tendency of sodium to sublime. Cesium impregnated sodium zirconate ($\text{Cs-Na}_2\text{ZrO}_3$) was prepared from the pure compound (Na_2ZrO_3), where a partial ionic exchange was attempted to form a solid solution. A portion of Na_2ZrO_3 was placed in an alumina crucible; subsequently, the amount corresponding to 10 wt% of cesium carbonate (Cs_2CO_3 , Sigma–Aldrich 99.9%) was dissolved in a minimum amount of water and added, drop by drop, to the Na_2ZrO_3 . The mixture was heat-treated at 650 °C for 5 h.

The Na_2ZrO_3 and $\text{Cs-Na}_2\text{ZrO}_3$ samples were then characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and nitrogen adsorption-desorption. X-ray diffraction patterns were obtained on a Bruker AXS D8 Advance diffractometer coupled to a copper anode X-ray tube. The resulting compounds were identified according to their corresponding JCPDS files (Joint Committee Powder Diffraction Standards). The microstructural characteristics of Na_2ZrO_3 and $\text{Cs-Na}_2\text{ZrO}_3$ were determined via N_2 adsorption-desorption and scanning electron microscopy (SEM)

measurements. BET and BJH models were estimated for the textural characterization [38,39]. For the N_2 adsorption-desorption experiments, isotherms were acquired on a Bel-Japan Minisorp II at 77 K using the multi-point technique. The samples were degassed at room temperature for 24 h under vacuum before analysis. The SEM experiments were performed on a JEOL JMS-7600F SEM.

Subsequently, Na_2ZrO_3 and $\text{Cs-Na}_2\text{ZrO}_3$ were tested as basic solid catalysts for biodiesel production. Reaction (1) shows the transesterification of a triglyceride (vegetable oil) using an alcohol in the presence of a catalyst to produce biodiesel.



Transesterification reactions catalysed by Na_2ZrO_3 and by $\text{Cs-Na}_2\text{ZrO}_3$ were performed in a 25 mL three-neck round-bottomed glass flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. Once the biodiesel was produced, the sample was centrifuged for 15 min to separate the solid catalyst from glycerol and the biodiesel immiscible phases. The top liquid layer was the FAME phase, whereas the bottom liquid phase was glycerol. The batch reactions were performed with different stoichiometric methanol/vegetable oil (soybean or Jatropha) molar ratios. Analytical grade anhydrous methanol (Sigma–Aldrich, 99.9% purity) was used along with pure soybean oil (Nutrioli brand NOM-051-SCFI-SSA12010, which was purchased from a local food store in México, D.F.), and with industrial Jatropha oil (from Jatropha México Company) to perform the biodiesel production. Various catalyst concentrations between 0.5 and 3 wt% under vigorous magnetic stirring at 65 °C were considered. The progress of the transesterification reaction was monitored at various reaction times between 0.25 and 3 h. Additional experiments were performed at different temperatures (45, 65 and 85 °C). After the corresponding reaction times, the samples were immediately quenched in an ice bath (−4 °C) to control the conversion rate, and the different phases were separated for analysis. The top liquid layer was the FAME phase, whereas the bottom liquid phase was glycerol. Both liquid layers were separated, and the catalyst was recovered.

Components of the FAME samples, as well as the purity of the biodiesel product, were determined using infrared spectroscopy (ATR-FTIR), gas chromatography coupled with mass spectrometry (GC–MS), and proton nuclear magnetic resonance (^1H NMR). For ATR-FTIR spectroscopy measurements, the samples were analysed using a Bruker FTIR ALPHA-Platinum spectrometer. Spectra were normalized for comparison purposes. For the GC–MS measurements, the samples were analysed using a Shimadzu GCMS-QP2010 instrument. A fused-silica capillary Rtx-2330 column, (30 m × 0.25 mm, biscyanopropyl cyanopropylphenyl polysiloxane) was used to evaluate the conversion and selectivity of the product in the transesterification reactions. The mobile phase was helium, and the final flow rate was 0.9 mL/min. The sample injection volume was 1 μL . The temperature of the injection port was 270 °C, and the temperature of the detector was 275 °C. The ion source was 200 °C, and the temperature analyses were initially performed from 100 to 250 °C at a rate of 10 °C/min. Mass selective detector was programmed for detecting ions with mass/charge ratios (m/z) between 150 and 350. The AART (Automatic Adjustment of Retention Time) function can estimate the retention times of target components from retention indices and the retention times of a standard biodiesel mix. The FAME standard was

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