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

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A B S T R A C T

Cesium modified sodium zirconate (Cs-Na_2ZrO_3) was prepared by ionic exchange from sodium zirconate (Na_2ZrO_3), which was synthesized via a solid state reaction. Both ceramics, i.e., pristine Na_2ZrO_3 and the Cs-Na_2ZrO_3, 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 Na_2ZrO_3. The results showed that Cs-Na_2ZrO_3 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 Na_2ZrO_3 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

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, $Cs-Na_2ZrO_3$) 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 sublimate. Cesium impregnated sodium zirconate ($Cs-Na_2ZrO_3$) 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 $Cs-Na_2ZrO_3$ 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 $Cs-Na_2ZrO_3$ 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 $Cs-Na_2ZrO_3$ 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.
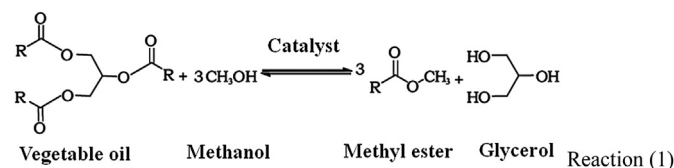
Reaction (1)

Transesterification reactions catalysed by Na_2ZrO_3 and by $Cs-Na_2ZrO_3$ 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 (^{1}H 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

purchased from Sigma–Aldrich (GLC-10-1891-1AMP). This standard was used to identify the methyl ester composition in the biodiesel. All analyses were performed at room temperature and with analytical grade ethanol (Sigma–Aldrich, HPLC purity) as the solvent. The ethanol retention time, as a mobile phase, was observed to be 1.7 min. Several ^{1}H NMR analyses were performed using a Bruker Avance 400 Ultrashield spectrometer (9.3T). The NMR probe was BBI 400 MHz 5 mm SB with z-gradients, using 5 mm diameter tubes. Top Spin 2.1 was used as the software package. The NMR samples were prepared with deuterated chloroform (CDCl$_3$, Sigma–Aldrich, 99.8%) as a solvent at a ratio of 1:1 by volume. The chemical shifts were referred indirectly to the TMS signal ($\delta = 0.0$ ppm).

The biodiesel yields were calculated using Eq. (1):

$$Biodiesel\ yield = \frac{weight\ of\ biodiesel}{weight\ of\ oil\ sample} \times 100\% \qquad (1)$$

Finally, the biodiesel density was estimated according to the ASTM-D1298 norm. Excluding the biodiesel yield or density, all of the reports are direct measurements. The uncertainties reported in those cases include the specified tolerance of the measurement and the system calibration. The biodiesel yield uncertainties (ΔBY) were calculated using the relative uncertainties as expressed in Eq. (2):

$$\Delta BY = \left[\frac{\Delta(weight\ of\ biodiesel)}{weight\ of\ biodiesel} + \frac{\Delta(weight\ of\ oil\ sample)}{weight\ of\ oil\ sample} \right] \times Biodiesel\ yield \qquad (2)$$

A similar equation was used for calculating the density uncertainties. All of the calculated uncertainties are reported in Table 1. Table 1 shows the biodiesel yields for all samples obtained with Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ from soybean and Jatropha oils. To standardize the uncertainty values, the larger values of the uncertainties calculated are presented in each column.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction (XRD) measurements of Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ samples, which confirmed the purity of both samples. The diffraction patterns of both samples were fitted to the JCPDS file 35-0770, which corresponded to Na$_2$ZrO$_3$ with a monoclinic structure. Additionally, it was also possible to identify two other phases: ZrO$_2$ (JCPDS file 37-1484) and Na$_2$CO$_3$ (JCPDS file 37-0451). Both phases were mainly found in the Cs-Na$_2$ZrO$_3$ sample and in particular the Na$_2$CO$_3$ phase. The presence of these phases (ZrO$_2$ and Na$_2$CO$_3$) on both zirconate samples was due to the carbonation process. Because it is well known that Na$_2$ZrO$_3$ is able to capture CO$_2$ at room temperature, this result is consistent with
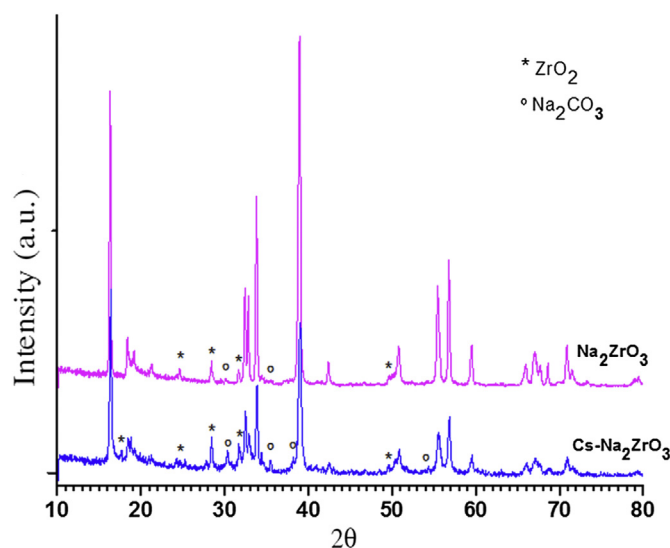

Fig. 1. XRD patterns of Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ samples.

Table 1
Reaction parameters and biodiesel yields for samples obtained with Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ as catalyst from (a) soybean and (b) Jatropha oil.

(a) Biodiesel from soybean oil						
Catalyst	Catalyst (%w/w)	Time (min)	Methanol:oil molar ratio	Temperature (°C)	Density (g/mL)	Gravimetric yield (%)
Na$_2$ZrO$_3$	0.5	60	15:01	65	0.84	39.2
Na$_2$ZrO$_3$	1	60	15:01	65	0.86	43.2
Na$_2$ZrO$_3$	1.5	60	15:01	65	0.86	38.2
Na$_2$ZrO$_3$	3	60	15:01	65	0.86	34.7
Na$_2$ZrO$_3$	1	60	15:01	65	0.86	43.2
Na$_2$ZrO$_3$	1	90	15:01	65	0.86	36
Na$_2$ZrO$_3$	1	120	15:01	65	0.86	30.9
Na$_2$ZrO$_3$	1	60	30:01	65	0.86	96
Cs-Na$_2$ZrO$_3$	1	15	15:01	65	0.86	43.5
Cs-Na$_2$ZrO$_3$	1	30	15:01	65	0.86	39.6
Cs-Na$_2$ZrO$_3$	1	15	30:01	65	0.86	98.8

(b) Biodiesel from Jatropha oil						
Catalyst	Catalyst (%w/w)	Time (min)	Molar ratio methanol:oil	Temperature (°C)	Density (g/mL)	Gravimetric yield (%)
Na$_2$ZrO$_3$	1	60	30:01	65	–	–
Na$_2$ZrO$_3$	2	60	30:01	65	0.83	98.3
Na$_2$ZrO$_3$	3	60	30:01	65	0.86	99
Na$_2$ZrO$_3$	3	180	30:01	65	0.86	87.3
Na$_2$ZrO$_3$	3	60	15:01	65	0.85	67.8
Na$_2$ZrO$_3$	3	120	15:01	65	0.88	90.7
Na$_2$ZrO$_3$	3	180	15:01	65	0.88	87.5
Cs-Na$_2$ZrO$_3$	3	30	15:01	65	0.85	67.4
Cs-Na$_2$ZrO$_3$	3	60	15:01	65	0.88	90.8
Cs-Na$_2$ZrO$_3$	3	120	15:01	65	0.88	89.7
Cs-Na$_2$ZrO$_3$	3	120	15:01	45	0.88	88.8
Cs-Na$_2$ZrO$_3$	3	120	15:01	85	0.88	87.9

previous reports [40–42]. According to the diffraction pattern for the Cs-Na$_2$ZrO$_3$ sample (Fig. 1), it was possible to ensure that the amount of Cs employed did not change the structure of Na$_2$ZrO$_3$, within the XRD detection level (~5%).

To evaluate the microstructural characteristics of the Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ samples, SEM and N$_2$ adsorption-desorption measurements were carried out. Thus, the morphological particle sizes of Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ were analysed by SEM (Fig. 2). There was not a significant morphological difference between the Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ samples. These particles showed a dense polyhedral morphology and large agglomerates with sizes greater than 30 μm for Na$_2$ZrO$_3$ and 15 μm for Cs-Na$_2$ZrO$_3$ (Fig. 2a and c, respectively). The average particle size for Na$_2$ZrO$_3$ was approximately 1 μm, whereas it was ~0.5 μm for Cs-Na$_2$ZrO$_3$ (see Fig. 2c and d). Additionally, to evaluate the Cs distribution over the Na$_2$ZrO$_3$ particles, a chemical map analysis was obtained by X-ray dispersion (Fig. 3), showing a highly homogeneous distribution. The experimental atomic percentage of Cs was 3.6%.

The dense morphology of both catalysts was corroborated by N$_2$ adsorption measurements. According to the IUPAC classification, both samples (Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$) showed typical type II isotherms (non-porous material) [38,39]. Additionally, Cs-Na$_2$ZrO$_3$ presented a narrow H3 hysteresis loop, which may be produced by a partial particle sintering process during the Cs addition and thermal treatment (data not shown). The BET surface areas for Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ from the N$_2$ isotherm data were found to be (1.65 ± 0.01) m^2/g and (2.22 ± 0.01) m^2/g, respectively. The introduction of Cs to the catalyst increased the surface area, which was in agreement with the particle size shown in the SEM images (Fig. 2).

After the characterization of both materials (Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$), they were used as catalysts in the transesterification reaction of soybean and Jatropha oils with methanol, using similar experimental conditions as that reported in Ref. [37]. Thus, in the present work, we tested a molar ratio of 15:1 between methanol

and the oil, and the catalyst was varied between 0.5 and 3 wt% (catalyst/soybean oil weight ratio) using a reaction temperature of 65 °C for 1 h. The FAME conversion varied from 34.7 to 43.2%, showing the best conversion ratio for the 1 wt% catalyst. Once the amount of catalyst was established at 1 wt%, the reaction was carried out at the same conditions but at longer reaction times. Additionally, after running the reaction for 1.5 h, the FAME conversion was 36.0%, while for 2 h, the conversion was 30.9%. Although the conversion was reduced with longer reaction times, the purity of the biodiesel was unchanged. These FAME samples were analysed by ATR-FTIR (data not shown), which were in very good agreement with previous reports [43–46]. Then, the Cs-Na$_2$ZrO$_3$ catalyst was employed in the reaction of soybean oil and methanol at the same previous conditions (1 wt% catalyst, 15:1 methanol/oil, 65 °C, and 1 h). After just 15 min of the reaction, the FAME conversion reached 43.5%, and after 30 min, the conversion went down to 39.6%; therefore, the reaction was stopped. Fig. 4 shows the comparative ATR-FTIR spectra of the reference soybean oil and the samples from the best conditions of the samples from the best conditions of the Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ catalyst with a 15:1 methanol/oil ratio. It is important to note the reduction in the reaction time. The Na$_2$ZrO$_3$ reaction time was 60 min, while for the Cs-Na$_2$ZrO$_3$ catalyst, the reaction time was 15 min to obtain ~43% conversion. At approximately 3330 cm^{-1}, there was a vibration band associated with the O–H bond that corresponded to the presence of methanol. The three well-defined vibration bands located at ~3004, 2926 and 2853 cm^{-1} corresponded to carboxylic acid compounds. There were some specific vibration bands that identified biodiesel production at 2972, 1741, 1188 and 1050 cm^{-1}. The presence of a strong C=O double bond band at approximately 1748 cm^{-1} corresponded to the ester group, which corroborated the transesterification of the oil [45,46]. Other vibration bands were observed between 1480 and 1100 cm^{-1}, which corresponded to the –CH$_2$ scissor and –CH$_3$ antisymmetric vibrations. The band located at ~1050 cm^{-1} can be attributed to the symmetric angular
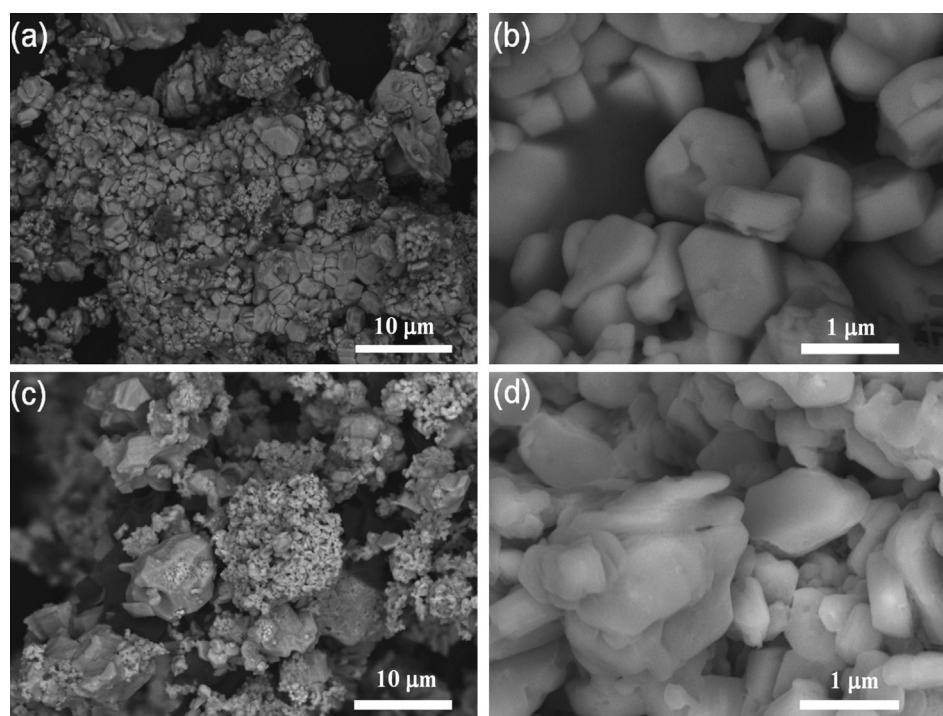

Fig. 2. SEM images of Na$_2$ZrO$_3$ (a and b) and Cs-Na$_2$ZrO$_3$ (c and d) samples.
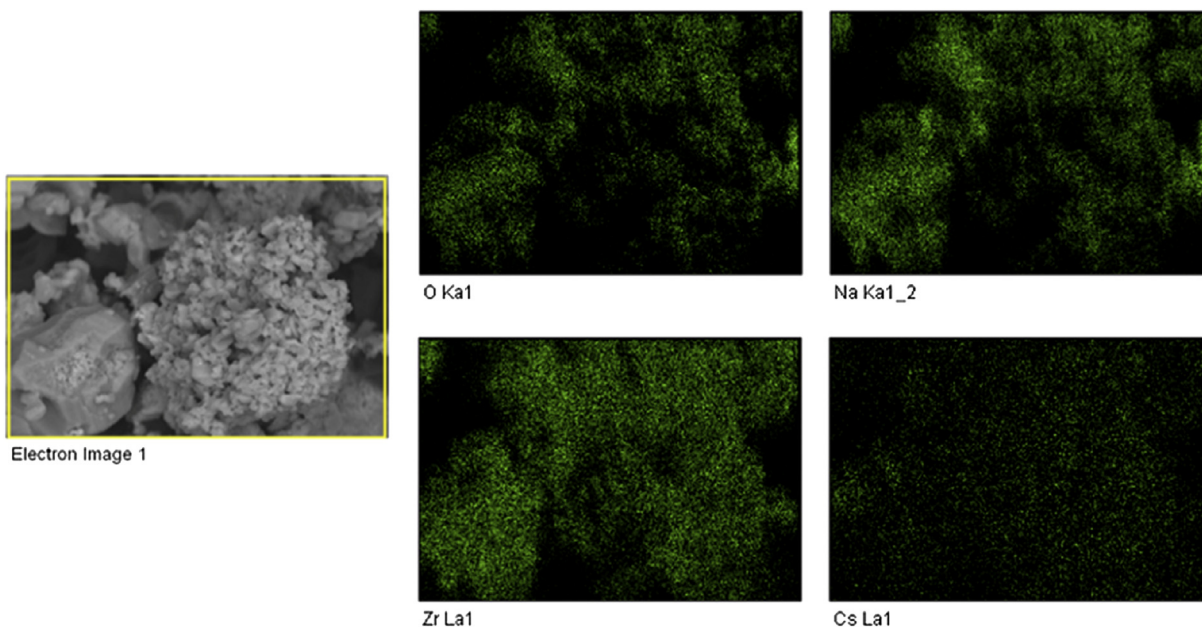
Fig. 3. Chemical map distribution of Cs, Na, Zr, and O over the Cs-Na$_2$ZrO$_3$ catalyst.
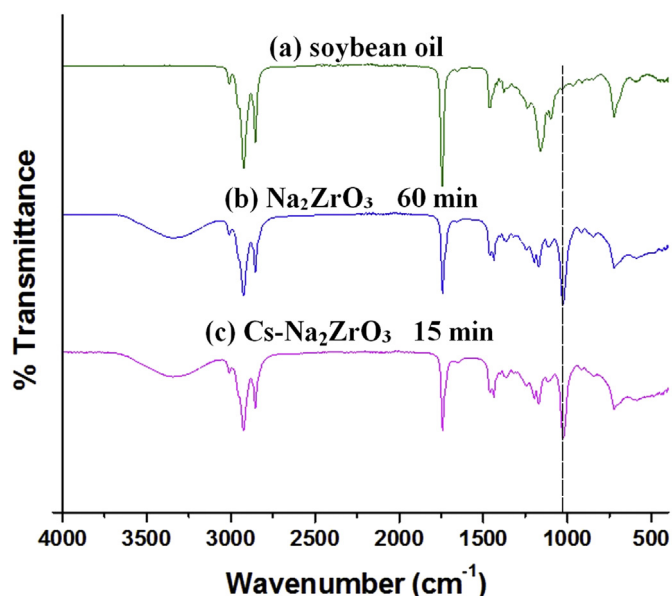

Fig. 4. ATR-FTIR spectra of (a) soybean oil, (b) biodiesel sample from soybean oil with 1 wt% Na$_2$ZrO$_3$ as catalyst at 65 °C for 60 min and (c) biodiesel sample from soybean oil with 1 wt% Cs-Na$_2$ZrO$_3$ as catalyst at 65 °C for 15 min.

deformation of the C−H bond of olefins. These spectra also showed a particular vibration band at ~720 cm^{-1}, corresponding to the *cis* isomers of −CH. Clearly, the impregnation with Cs of the sodium zirconate catalyst improved the kinetics of the TG reaction, affording the same conversion as the catalyst without doping in just 15 min. The reduction in the reaction time and catalyst concentration can be related to the presence of cesium in the material, even when a slightly higher surface area was obtained after Cs impregnation. The ATR-FTIR spectra confirmed that after 15 and 30 min, the purity of the biodiesel was about the same, in which both spectra showed a vibration band associated with O−H at ~3330 cm^{-1} characteristic of residual methanol.

Motivated by achieving an improvement in the FAME conversion, another variable was changed. Here, we modified the molar ratio between methanol and oil. A ratio of 30:1 was utilized, which afforded a much better FAME conversion for both catalysts. In the case of the Na$_2$ZrO$_3$ catalyst (1 wt%, 30:1 methanol/oil, 65 °C, and 1 h), the conversion reached was 96.0%. For the Cs-Na$_2$ZrO$_3$ catalyst (1 wt%, 30:1 methanol/oil, 65 °C, and 15 min), the maximum conversion observed was 98.8%. The ATR-FTIR spectra of both catalysts exhibited residual methanol.

To evaluate the reusability performance of the Cs-Na$_2$ZrO$_3$ catalyst, which represented its capacity to perform the same catalytic activity, this catalyst was evaluated by conducting several more experimental runs after the first test at the optimum FAME yield conditions. The transesterification reaction was repeated nine times (cycles) in the same flask using the same catalyst without any treatment. We chose the Cs impregnated catalyst because it showed the best FAME conversion (98.8%) at the following conditions: 1 wt%, 30:1 methanol/oil, 65 °C, and 15 min of reaction. The FAME conversion was slightly diminished as a function of the cycle number, from 98.8% in the first cycle to 95.0% in the ninth cycle. This suggested a relatively small decrease in the efficiency of the catalyst, which could be solved by a simple re-activation of the catalyst. The reason for the activity loss in the catalyst was possibly due to the presence of glycerol which covered the surface of the catalyst. After evaluating the catalytic activity of Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ in the transesterification reaction of soybean oil, the impact of introducing Cs into the sodium zirconate catalyst was clear in that the kinetics of the reaction were improved considerably as observed by the reduction of the reaction time from 1 h to just 15 min with a FAME conversion of 98.8%.

Subsequently, as one of the main objectives of this work, the reaction of Jatropha oil was carried out using both catalysts, i.e., Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$. First, the amount of the Na$_2$ZrO$_3$ catalyst was varied between 1 and 3 wt% (catalyst/Jatropha oil weight ratio). A molar ratio of 30:1 between methanol and oil and a reaction temperature of 65 °C for 1 h were used. The FAME conversion varied from 92.5 to 99.0%, with the best conversion ratio at 3 wt% of the catalyst. These FAME samples were analysed by ATR-FTIR (Fig. 5), which were in good agreement with previous reports
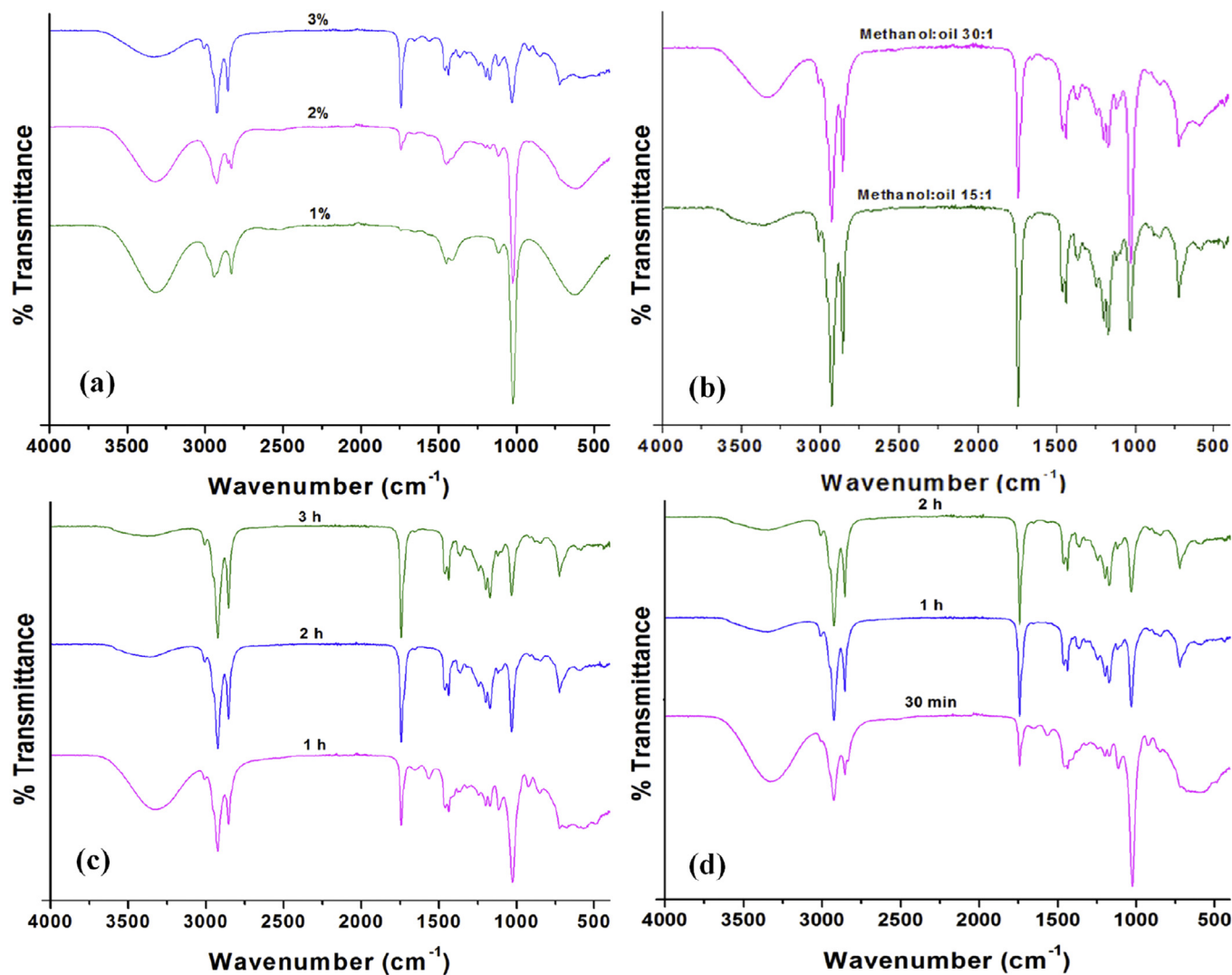
Fig. 5. ATR-FTIR spectra of biodiesel samples obtained at (a) different catalyst percentages (1, 2 and 3 wt%) of Na$_2$ZrO$_3$, (b) different methanol:oil molar ratios with 3 wt% of Na$_2$ZrO$_3$ as the catalyst, (c) different reaction times with 3 wt% of Na$_2$ZrO$_3$ as the catalyst, and (d) different reaction times with 3 wt% of Cs-Na$_2$ZrO$_3$ as the catalyst.

[37,43–46]. Fig. 5a shows the ATR-FTIR spectra of biodiesel with varying percentage of the Na$_2$ZrO$_3$ catalyst (1, 2, and 3 wt%) at 1 h. The characteristic vibration band associated with O−H (residual presence of methanol) at approximately 3330 cm^{-1} clearly decreased in intensity when the amount of catalyst was increased. Thus, at 3 wt%, the purity was much better than at 1 or 2 wt%, although there was still some residual methanol. To obtain better purity of the biodiesel produced, the reaction time was increased to 3 h, and 3 wt% of the catalyst (with a molar ratio of 30:1 at 65 °C) was used. The FAME conversion was lower at 87.3%, but the purity of the biodiesel did not improve after running the reaction for a longer time. Thus, we decided to modify the ratio of methanol:oil from 30:1 to 15:1, while keeping the other parameters unchanged (3 wt% catalyst at 65 °C for 3 h) as in the previous experiment. It was then found that the FAME conversion was about the same as the previous test (87.5%), but the purity of the biodiesel was significantly better, the increase of intensity of peak located at 1050 cm^{-1} (associated to biodiesel) and the decrease of 3330 cm^{-1} bands associated to the presence of methanol in the ATR-FTIR spectrum (Fig. 5b). Fig. 5b shows a clear reduction of the characteristic band for residual methanol (3330 cm^{-1}). Once the ratio of methanol:oil was adjusted, we varied the reaction time from 1 to

3 h and found that running the transesterification reaction for just 2 h led to a FAME conversion of 90.7%. The ATR-FTIR spectra (Fig. 5c) confirmed the good purity of the biodiesel produced with Na$_2$ZrO$_3$. Then, the Cs-Na$_2$ZrO$_3$ catalyst was tested in the transesterification reaction using 3 wt% of the catalyst at a 15:1 ratio of methanol:oil at 65 °C and for different reaction times from 30 min to 2 h. The AFT-FTIR spectra of the biodiesel samples (Fig. 5d) showed that the best reaction time (on the basis of purity) was 1 h, which was in agreement with the results of the FAME conversion (90.8%). In particular, the band located at ~1050 cm^{-1} can be attributed to the symmetric angular deformation of the C−H bond of olefins that was not observed in both oils (soybean and Jatropha oils) and methanol precursors. Thus, the presence of this band clearly indicated the success of biodiesel production.

To elucidate more precisely the chemical composition of the biodiesel samples generated by both catalysts (Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$) from soybean and Jatropha oils, the biodiesel samples were characterized by GC−MS. Fig. 6 shows typical chromatograms obtained from a mixture of biodiesel esters catalysed by Na$_2$ZrO$_3$ and Cs-Na$_2$ZrO$_3$ from soybean oil (Fig. 6a) and Jatropha oil (Fig. 6b). All biodiesels produced at different conditions presented similar chromatograms with similar retention times, which were
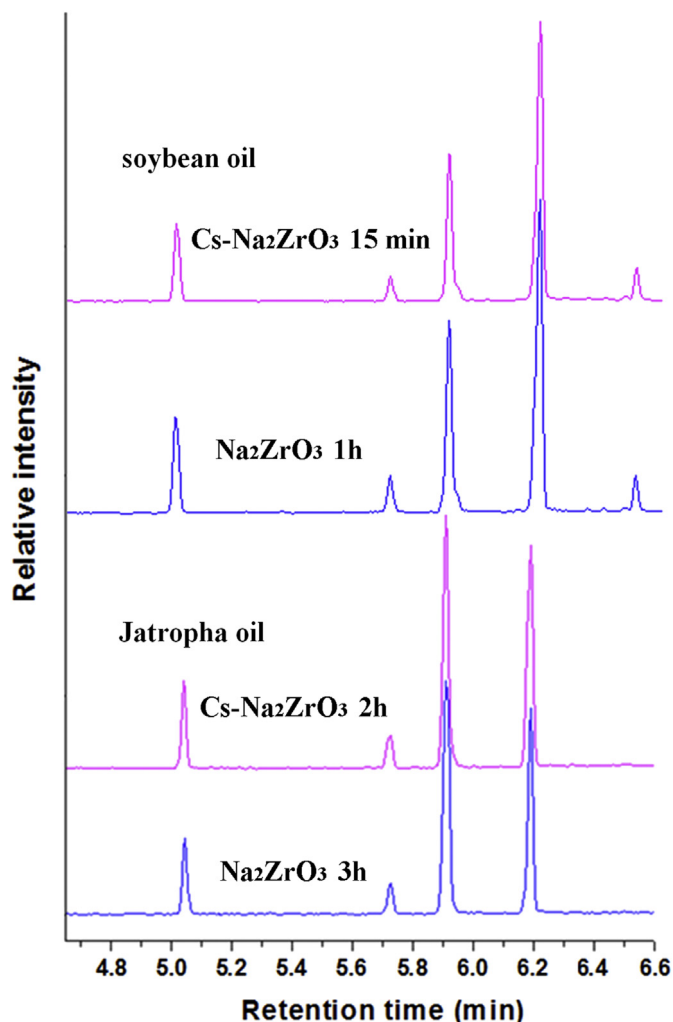
Fig. 6. Representative GC—MS chromatograms obtained from biodiesel samples produced from soybean oil (1 wt% of catalyst, 30:1 methanol/oil, 65 °C and 15 min reaction time) and from Jatropha oil (3% of catalyst, 15:1 methanol/oil, 65 °C and 1 h reaction time).

consecutively identified by mass spectroscopy. The first peak (5.0 min) was associated with hexadecanoic acid methyl ester ($CH_3-O-CO-(CH_2)_{14}-CH_3$, from palmitic fatty acid); the second peak (5.7 min) corresponded to octadecanoic acid methyl ester ($CH_3-O-CO-(CH_2)_{16}-CH_3$ from stearate acid); the third peak (5.9 min) corresponded to cis-9-octadecenoic acid methyl ester ($CH_3-O-CO-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$, from oleic acid); and the fourth peak (6.2 min) was associated with cis-9-,12-, octadecadienoic acid methyl ester ($CH_3-O-CO-(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$, from linoleic acid). Additionally, a fifth peak (6.5 min) in Fig. 6b of the soybean biodiesel was determined to be cis-octadeca-9,12,15-trienoic acid methyl ester ($CH_3-O-CO-(CH_2)_4-CH=CH-CH_2-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$, methyl linolenate). The mass values corresponded to 270, 298, 296, and 294 (from Jatropha oil) and 292 *m/z* (from Soybean oil) for the respective methyl esters and their retention times, according to the FAME standard. No significant differences were observed with respect to the intensities of the chromatographic peaks, which indicated that the maximum conversion was achieved (~90%). These results were consistent with the results of infrared spectra and the mass of the biodiesel obtained, as the product quality was similar. Lara-García et al. [43]

reported similar biodiesel characterization results using ZrO_2 as a catalyst. ZrO_2 was synthesized with sodium hydroxide and different cationic, nonionic, and anionic surfactants.

In addition, the biodiesel samples were obtained at different temperatures, i.e., 45 and 85 °C. Reactions under the optimal conditions for both temperatures were performed, i.e., 3 wt% of Cs-Na_2ZrO_3 with a 15:1 methanol:oil ratio and 2 h of reaction time (Table 1). It is important to note that it was possible to carry out the reaction even at 45 °C, obtaining good yields of pure biodiesel, which meant less energy and reduced cost of the operation. Overall, Table 1 discloses the biodiesel yields for all samples obtained with Na_2ZrO_3 and Cs-Na_2ZrO_3 from soybean and Jatropha oils. According to ASTM D1298 ($0.875 \leq \rho \leq 0.900$ g/mL), the product density was within the acceptable range.

Finally, aliquots of the biodiesel products were characterized by ^{1}H NMR. Fig. 7 shows the ^{1}H NMR spectra of the biodiesel obtained from Jatropha oil by using both Na_2ZrO_3 and Cs-Na_2ZrO_3 catalysts. Both spectra were characteristic of a mixture of biodiesel esters. It can be noted that the signal at 7.2 ppm corresponded to the deuterated chloroform ($CDCl_3$) that was used to obtain the spectra. It must be mentioned that glycerol was insoluble in $CDCl_3$; therefore, it was not detected. Table 2 displays the proton identification for the different chemical groups present in the biodiesel. It is important to note the absence of a signal at ~3.42 ppm, corresponding to the methylenic $-CH_3$ protons, i.e., protons of unreacted methanol. The absence of this signal is an indication of a high FAME conversion [37]. Additionally, some specific differences were observed among the spectra. The 3 wt% spectrum showed three very small peaks located at 0.9, 4.1, and 4.2 ppm. These peaks were observed in the spectrum for the Jatropha oil and corresponded to the $-CH_2$ and $-CH_3$ protons of the hexadecanoic acid methyl ester and octadecadienoic acid methyl ester chains. The total conversion to biodiesel occurred because the signals corresponding to the Jatropha oil at 4.1 and 4.3 ppm were not observed. These signals can be associated with the protons attached to the triglyceride carbons of the Jatropha oil [47]. The signal at 3.6 ppm belonged to the methyl ester protons that were increased (Fig. 7). A completed transesterification reaction should yield only methyl esters and glycerol, whereas an incomplete transesterification would yield monoglycerides, diglycerides, or other related intermediate products and any unreacted triglyceride. No intermediate products were observed here.
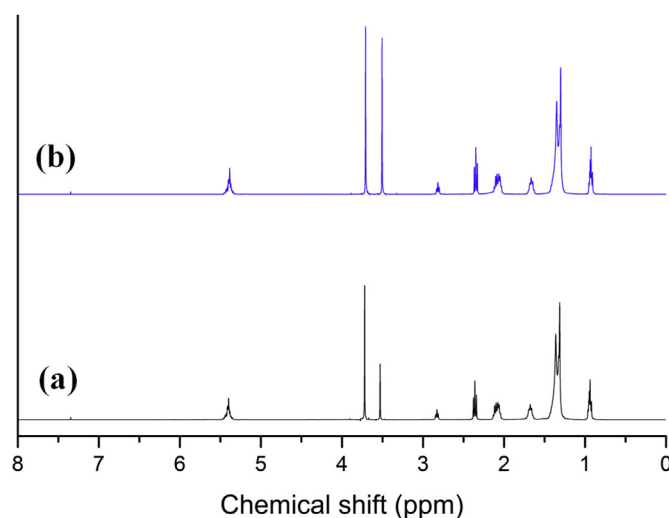

Fig. 7. ^{1}H NMR spectra of the (a) biodiesel sample produced with Na_2ZrO_3 and (b) Cs-Na_2ZrO_3 catalysts.

Table 2
^{1}H NMR biodiesel chemical groups identification.

Chemical shift (ppm)	Proton type	Chemical compound(s)
0.81—0.86	$CH_3-(CH_2)_n-R-COO-CH_3$	Four FAME
1.21—1.25	$CH_3-(CH_2)_n-R-CH_2-CH_2-COO-CH_3$	Four FAME
1.53—1.61	$CH_3-(CH_2)_n-R-CH_2-CH_2-COO-CH_3$	Four FAME
1.94—2.03	$CH_3-(CH_2)_n-CH_2-(CH=CH)-CH_2-(CH_2)_n-COO-CH_3$	Methyl oleate and methyl linoleate
2.23—2.27	$CH_3-(CH_2)_n-R-CH_2-CH_2-COO-CH_3$	Four FAME
2.70—2.74	$CH_3-(CH_2)_n-(CH=CH)-CH_2-(CH=CH)-(CH_2)_n-COO-CH_3$	Methyl linoleate
3.42	CH_3-OH	Methanol
3.61	$CH_3-(CH_2)_n-R-COO-CH_3$	Four FAME
5.26—5.34	$CH_3-(CH_2)_n-R-(CH=CH)-(CH_2)_n-COO-CH_3$	Methyl oleate and methyl linoleate
7.24	$CHCl_3$	Chloroform

4. Conclusions

Sodium zirconate (Na_2ZrO_3) and its modified form (Cs-impregnated sodium zirconate, Cs-Na_2ZrO_3) were synthesized, characterized, and tested as solid basic heterogeneous catalysts for biodiesel production. The biodiesel produced by the transesterification reaction between soybean or Jatropha oil and methanol was characterized. Both materials exhibited excellent catalytic activities and good stabilities due to their basic characters. In particular, Cs-Na_2ZrO_3 showed a remarkable catalytic performance in comparison to Na_2ZrO_3 by shortening the reaction time considerably and improving the efficiency. For the case of the transesterification reaction of soybean oil and methanol, Cs-Na_2ZrO_3 showed an optimal reaction time of just 15 min (instead of 1 h for Na_2ZrO_3), and the efficiency increased from 96.0% (Na_2ZrO_3) to 98.8%. The transesterification reaction of Jatropha oil and methanol with both Na_2ZrO_3 and Cs-Na_2ZrO_3 catalysts afforded very similar efficiencies, i.e., 90.7% and 90.8%, respectively, but the Cs-Na_2ZrO_3 provided a purer product (biodiesel) and performed the reaction in a shorter time (1 h). In addition, the re-utilization of Cs-Na_2ZrO_3 was exceptionally good and thus is a very desirable candidate for biodiesel production in an industrial setting. The results revealed that the introduction of Cs enhanced the reaction kinetics for obtaining biodiesel and reduced the reaction time in comparison with pristine Na_2ZrO_3. Thus, the Cs containing sample (element that confers a higher basic property) represents a very exciting alternative heterogeneous base catalyst for biodiesel production.

Acknowledgements

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