

## Effect of Calcination Temperature on Catalytic Activity of Synthesis SrO/S-ZrO<sub>2</sub> by Solvent-free Method in Esterification of Oleic Acid

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Currently, the major concern in production of biodiesel fuel is to exploit new catalysts with the optimal conditions. In this study, the effect of calcination temperature on the synthesis of 20 mol % SrO/S-ZrO<sub>2</sub> was examined by solvent-free method. Moreover, the ability of the catalyst for esterification reaction of oleic acid with methanol was also assessed. To obtain this objective, X-ray diffraction and infra-red spectroscopy method was employed to characterize the structure of the catalysts. The results of this study reveal that the calcined strontium oxide promoted sulfated zirconia at 500 °C has the highest percentage of tetragonal phases of zirconia. It has also been demonstrated that owing to the high percentage of the tetragonal phases of zirconia and the acidity of the catalyst, conversion of oleic acid to fatty acids methyl esters (i.e., FAME) could be enhanced from 88.36 % to 91.13 %. Moreover, it has also been shown that 20 mol % SrO/S-ZrO<sub>2</sub> exhibits higher activity in comparison with S-ZrO<sub>2</sub> at 500 °C in esterification reaction due to the presence more sulfate ions and higher activity of strontium ions.

### Key words:

Solvent-free, strontium, sulfated zirconia, calcination temperature, esterification

## Introduction

In the last few years, biodiesel has emerged as one of the potential renewable energy sources and as an alternative to replace fuel oil due to environmental problems. Biodiesel is produced by transesterification of vegetable oil or animal fat with a short chain of alcohol in the presence of catalyst.<sup>1–2</sup> However, biodiesel production from crude vegetable oil will increase the final biodiesel production cost. Therefore, using low-cost oil such as waste cooking oil and inedible animal fats would decrease the biodiesel production cost. Nevertheless, the high concentration of free fatty acids (FFA) decreases biodiesel production from traditional homogeneous base catalysts such as NaOH and KOH. The reaction between FFA and the base catalysts produce soap and as a by-product needs to be separated from the biodiesel. Moreover, production of biodiesel from the transesterification reaction with homogeneous base catalysts needs to be washed with water. Thus, making a large amount of wastewater that causes environmental problems. In addition, the final biodiesel product must be neutralized and purified.<sup>3–6</sup> Prior to transesterification reaction and in order to reduce FFA to less than 1 percent, FFA

must be converted to ME (i.e., methyl esters) with esterification reaction.<sup>7</sup>

Esterification reactions conventionally are carried out with usual acid catalysts such as sulfuric and hydrochloric acid.<sup>8</sup> However, problems such as high temperature requirement, high molar ratio of alcohol to oil, separation of the catalyst, corrosion and environmental issues must also be taken into consideration for these catalysts.<sup>9</sup> Therefore, some researchers have suggested employing solid acid catalysts for biodiesel production. These catalysts have some advantages such as simple recovery with filtration, being environmentally friendly and waste free. These catalysts could be designed to have higher activity, selectivity and longer life. As a result, they could reduce the costs of biodiesel production.<sup>10–12</sup> Many researchers have employed these types of solid acid catalysts in the esterification reaction process;<sup>13–16</sup> however, modified zirconia has exhibited higher catalytic activity.<sup>17–21</sup> Amongst the modified zirconia, sulfated-zirconia exhibits high catalytic activity for isomerizing alkanes at relatively low temperature.<sup>22–24</sup> Nevertheless, it has some drawbacks such as deactivation after each reaction and is not easily regenerated by simple re-calcination in air.<sup>25</sup> Sejidov et al. reported that SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-SiO<sub>2</sub> has a higher catalytic activity, stability and surface area in comparison with

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$\text{SO}_4^{2-}/\text{ZrO}_2$  for the esterification of long chain fatty acids.<sup>8</sup> Wang et al. also reported that when sulfated zirconia is doped with CuO, it exhibits higher catalytic activity.<sup>26</sup> Researchers have also utilized different metal oxide to support the sulfated-zirconia for improving its properties.<sup>27–28</sup> However, the alkaline earth metal oxide has rarely been utilized as a modified sulfated zirconia.<sup>29–30</sup> Amongst the alkaline earth metal oxide, SrO has the highest activity after BaO (i.e.,  $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$ ).<sup>31–32</sup> Yoosuk et al. studied modified magnesia with strontium as a solid base catalyst in transesterification of palm olein and reported a yield 97.3 percent for ME.<sup>33</sup> Yang and co-workers reported that SrO with 10 wt.% CuO exhibits a high catalytic activity for transesterification of hempseed oil to biodiesel that yields as much as 96 %.<sup>34</sup> However, no comparative studies have yet been conducted on strontium oxide over sulfated zirconia.<sup>35</sup>

Many factors influence the activity of catalysts where catalyst preparation method is one of them, namely co-precipitation,<sup>26–36</sup> impregnation,<sup>34–37</sup> and solvent-free methods.<sup>38</sup> Ramu et al. investigated the effect of the catalyst preparation method of  $\text{WO}_3/\text{ZrO}_2$  in esterification of palmitic acid. They reported that both methods for preparation of catalyst approximately convert an equal amount of palmitic acid to its ME.<sup>39</sup> However, both Sun et al. and Garcia et al. demonstrated that solvent-free method exhibits better results in comparison with impregnation and co-precipitation methods.<sup>38</sup> On the other hand, it is a well-known fact that the calcination temperature is an important factor for catalyst synthesis.<sup>39–41</sup> Therefore, it is the aim of this work to obtain the optimal temperature for synthesis of SrO/S-ZrO<sub>2</sub>, adopting the solvent free method. To accomplish this task, the catalytic activity of synthesis SrO/S-ZrO<sub>2</sub> catalysts was assessed by RD, IR and NaOH titration methods. Furthermore, the percent conversion of oleic acid to biodiesel in esterification reaction has also been evaluated.

## Experimental procedure

### Catalysts preparation

In this work, SrO/S-ZrO<sub>2</sub> was prepared with solvent-free method. It was accomplished by pulverizing the  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in porcelain mortar with  $(\text{NH}_4)_2\text{SO}_4$  (molar ratio of 1:6) and  $\text{SrSO}_4$  (molar ratio of 1:0.20) for 20 min at room temperature. The mixture was kept at room temperature for 18 hours. Then, the oven was preheated to temperatures ranging from 400 to 900 °C and the samples were calcined for 5 hours.

### Catalyst characterization

Phase identification and crystallite size of modified sulfated-zirconia were determined by X-ray diffraction method employing the UNISANTIS/XMP 300 by means of Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 45 kV and 80 mA, over a  $2\theta$  range of 20–70° at a scanning speed of 10° min<sup>-1</sup>. The crystalline size of tetragonal and monoclinic phases was estimated from Scherrer's equation as shown below:<sup>42</sup>

$$D = K \lambda / \beta \cos \theta \quad (1)$$

Where  $K = 0.9$ ,  $D$  is the crystalline size in nm,  $\lambda$  is the radiation wavelength,  $\beta$  is the corrected half-width of the peak profile, and  $\theta$  is the corrected half-width of the diffraction peak angle.

The phases were identified using infrared (IR) spectra of the samples with Shimadzu spectrometer in the range of 600–4000 cm<sup>-1</sup>. A standard KBr technique was also employed for the sample preparation. The catalyst acidity was also estimated by titration of solution of 0.2 g of catalyst in 10 mL of deionized water using 0.1 mol L<sup>-1</sup> NaOH solution.<sup>40</sup>

### Catalytic testing

The esterification process was carried out in a stainless steel tank that was placed in a glycerol bath for controlling reaction temperature. 10.0 grams of oleic acid, 12.9 mL of methanol (molar ratio of 1:9) and 0.3 grams of catalyst (3 wt.% of oleic acid) were mixed and heated up to 90 °C with a magnetic stirrer set at 600 rpm for 30 min. The reaction time for the esterification process was then calculated when the temperature was at 90 °C. The reaction was not carried out in an optimal manner, however, it was near optimum conditions reported by Lucena et al.<sup>2</sup> Then, the catalyst was separated from the product with filtration process. Next, the biodiesel mixture product was separated from water with decanter and was heated in order to remove the excess methanol. Finally, the conversion percent of oleic acid to its ester was computed from the reduction of the acidity index of the product with respect to the initial oleic acid according to following equation where the acidity indexes were determined by titration with 0.1 mol L<sup>-1</sup> KOH-ethanol solution using phenolphthalein as an indicator.<sup>43–44</sup>

$$\begin{aligned} \text{Conversion (\%)} &= \\ &= 100 (AV_{\text{Oleic acid}} - AV_{\text{Methyl Ester}}) / AV_{\text{oleic acid}} \quad (2) \end{aligned}$$

where AV is the acid value (index).

## Results and discussion

### Effect of calcination temperature on the catalyst activity

The X-ray diffraction analysis

Fig. 1 demonstrates the XRD pattern of calcined 20 mol % SrO/S-ZrO<sub>2</sub> (0.2 SrO/S-ZrO<sub>2</sub>) at 400–900 °C. It shows that the catalyst calcined at 400 °C presents broad peaks at  $2\theta = 50^\circ - 70^\circ$ , indicating the presence of a slightly X-ray-amorphous structure and the existence of very small crystallites of tetragonal and monoclinic phases of zirconia. However, at other calcination temperatures tetragonal phase of zirconia (i.e., t-ZrO<sub>2</sub>) at  $2\theta = 30.2^\circ, 34.5^\circ, 35.4^\circ, 50.3^\circ, 59.6^\circ, 60.3^\circ$  and  $63.1^\circ$  were observed. Furthermore, the peaks at  $2\theta = 24.2^\circ, 28.2^\circ, 31.5^\circ, 33.5^\circ, 41.0^\circ, 49.5^\circ, 55.7^\circ$  and  $65.9^\circ$  also demonstrate the existence of monoclinic phase of ZrO<sub>2</sub> (i.e., m-ZrO<sub>2</sub>).<sup>45–47</sup>

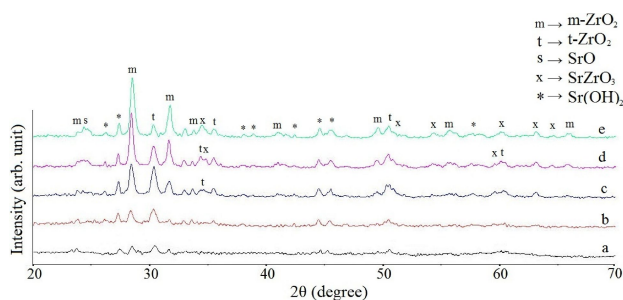


Fig. 1 – XRD pattern for 0.2 SrO/S-ZrO<sub>2</sub> calcined at a) 400 °C b) 500 °C c) 600 °C and d) 700 °C and e) 900 °C

For the 0.2 SrO/S-ZrO<sub>2</sub> at 500 °C there exists only one noticeable peak for monoclinic phase at  $2\theta = 28.2^\circ$ . It must be noted that monoclinic phases are also detected at  $2\theta = 31.5^\circ$  and  $33.5^\circ$ . However, as the calcination temperature increases from 500 °C to 600 °C, a new m-ZrO<sub>2</sub> peak at  $2\theta = 24.2^\circ$  and the t-ZrO<sub>2</sub> at  $2\theta = 34.5^\circ, 59.6^\circ, 60.3^\circ$  and  $63.1^\circ$  has also been observed. Moreover, a separation of phases occurred at  $2\theta \approx 50^\circ$  and  $60^\circ$  where the monoclinic completely separated from the tetragonal phase. Further increase of calcination temperature also led to the appearance of new peaks

of the monoclinic phases at  $2\theta = 41.2^\circ, 55.7^\circ$  and  $65.9^\circ$ .<sup>48</sup> Furthermore, as the calcination temperature rises, the monoclinic phase develops accordingly; on the other hand and in particular, the tetragonal phase drops at  $2\theta = 30.2^\circ$ . A further heat treatment to 900 °C would also accelerate the transition from the tetragonal phase to the monoclinic phase, which means some sulfate loss during this process. Therefore, 0.2 SrO/S-ZrO<sub>2</sub> under 600 °C could give a stronger acid, followed by a better catalyzing performance.<sup>49–50</sup> Furthermore, it also demonstrates that a reduction of the area of the tetragonal phases of zirconia is manifested with an increase of calcination temperature from 500 to 900 °C.

In addition to the zirconium peaks in XRD pattern, the SrO peak were also detected at  $2\theta = 24.6^\circ$  at 600 °C and it was more pronounced at higher calcination temperatures. The formation of strontium oxide would also extremely improve the activity of catalyst owing to its high activity.<sup>51</sup> It is also noteworthy that the enhancements of the calcination temperature caused the formation crystals of strontium and zirconium oxides and development of a new structure called SrZrO<sub>3</sub>. As shown in Fig. 2, the peaks of tetragonal phases vanish at  $2\theta \approx 35^\circ$  and  $60^\circ$  and completely transform to SrZrO<sub>3</sub> at 900 °C. Moreover, the SrZrO<sub>3</sub> structure for calcination temperatures at 700 and 900 °C also appears at  $2\theta = 51.5^\circ, 54.1^\circ$  and  $65.4^\circ$ .<sup>52</sup> Although, the crystal of SrZrO<sub>3</sub> forms with increasing calcination temperature, fraction of the tetragonal phases was reduced sharply; hence reducing the catalytic activity. Furthermore, the peaks at  $2\theta = 26.2^\circ, 27.3^\circ, 37.9^\circ, 38.9^\circ, 42.4^\circ, 44.5^\circ, 45.4^\circ$  and  $57.6^\circ$  indicate the presence of strontium hydroxide.<sup>33,53–54</sup> The strontium hydroxide could raise the basic sites of sulfated zirconia catalyst by OH<sup>-</sup> ions and improve the activity of catalyst.<sup>52</sup>

The percentage of the tetragonal phases for 25 mol % of SrO/S-ZrO<sub>2</sub> at different calcination temperatures are computed from the area underneath the curve using the following formula which has been exhibited in Table 1.<sup>55</sup>

$$f_t = A_t(101) / A_{\text{total}}(\text{ZrO}_2) \quad (3)$$

Table 1 – The properties of 0.2 SrO/S-ZrO<sub>2</sub> at different calcined temperatures

Calcination temperature (°C)	ZrO <sub>2</sub> phases	Tetragonal phase	Average crystalline size (nm)			Yield
			tetragonal phases	monoclinic phases	sample	
400	m, t	55	11.3	14.2	13.1	40.18
500	m, t	80	9.8	13.2	12.4	91.13
600	m, t	43	11.9	14.1	13.9	23.92
700	m, t	37	13.3	13.8	14.9	4.83
900	m, t	32	15.4	13.7	15.5	3.92



Where  $f_t$  is the fraction of tetragonal phase,  $A_t(101)$  is the peak area of (101) of tetragonal phases and  $A_{\text{total}}(\text{ZrO}_2)$  is the area of all tetragonal and monoclinic peaks in the pattern.

Table 1 shows a reduction of the percentage of the tetragonal phases with the enhancement of calcination temperature.

The activity of catalysts is roughly dependent on the percentage of the tetragonal phase. It means that there exists a reduction in catalytic activity of catalyst with increasing calcination temperature. The relationship between percentages of the tetragonal phases in the catalysts to their activity is shown in Fig. 2. The linear relationship shows the main effect of tetragonal phases on activities of the catalysts which agrees with the findings of other workers.<sup>39</sup> An important conclusion could be drawn from these results that the phase stability of the catalyst beyond 500 °C is not satisfactory in the esterification of oleic acid, owing to the formation of monoclinic phases. Moreover, increasing the calcination temperature causes the growth of crystal size of 0.2 SrO/S-ZrO<sub>2</sub>. Sun et al. reported that addition of the sulfated groups on the zirconia surface decreases the particle size and hence enhances the catalytic activity.<sup>38</sup> It is worth noting that according to the Sherrer's equation, as the temperatures increases from 500 to 900 °C, the particle size rises from about 12 to 16 nm. This could be caused due to the reduction of sulfate groups on the catalyst surfaces with the enhancement of calcination temperature and formation of monoclinic phases of zirconia. Furthermore, a reduction of the activity for the catalyst could also account for the crystalline size growth.<sup>38</sup>

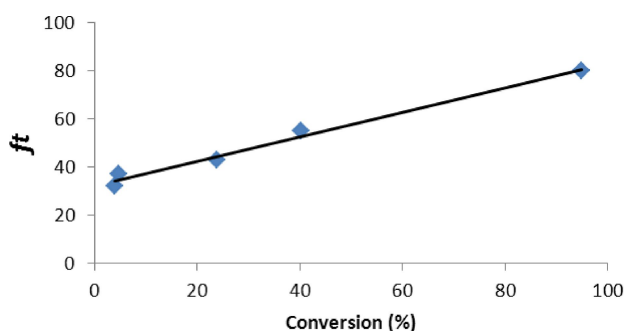


Fig. 2 – Variation of fraction of tetragonal phases of catalyst with conversion of oleic acid

#### Infrared spectroscopy analysis

Fig. 3 illustrates the IR spectroscopy of absorption bands of all the calcined 0.2 SrO/S-ZrO<sub>2</sub> nano catalysts at different temperatures. The bands at 1030, 1100 and 1380 cm<sup>-1</sup> were caused owing to the stretching vibration effect of sulfate ions (S = O). In

addition, the bands at 1151, and 1240 cm<sup>-1</sup> normally stand for chelating bidentate sulfate ions coordinated to the zirconium cation.<sup>56–58</sup> Increase in the calcination temperature led to decomposition of sulfated groups and formation the SO<sub>3</sub> species that occurs at higher calcination temperatures. A further enhancement of the calcination temperature fades away the weak peak of sulfate groups at 1100 cm<sup>-1</sup>, causing a reduction of sulfate ions on catalyst surface and decreasing of catalytic activity, consequently.<sup>59–60</sup> The band at 1070 cm<sup>-1</sup> also indicates the stretching vibration effect of Zr = O. Furthermore, Zr = O group could also have resulted from two stretching vibrations for two ZrO(OH)<sub>2</sub>.<sup>47</sup> Moreover, a broadband at 700 – 1000 cm<sup>-1</sup> exhibits the presence of Sr–O.<sup>53</sup> In addition to the Sr–O bands at 900 and 950 cm<sup>-1</sup>, a bending vibration of ZrO<sub>2</sub> exists for ZrO<sub>δ</sub>, for δ = 4 and 6, polyhedron. The peak of t-ZrO<sub>2</sub> has also been observed at 706 cm<sup>-1</sup> and the bending vibration band for ZrO<sub>2</sub> is related to m-ZrO<sub>2</sub>.<sup>61</sup> XRD images demonstrated that a new structure exists at higher calcination temperatures between SrO and ZrO<sub>2</sub>, namely SrZrO<sub>3</sub>. It was demonstrated by the IR spectra technique that the band in the region of 750–850 cm<sup>-1</sup> shifts to 800–900 cm<sup>-1</sup>. The bands at 1660 and 1640 cm<sup>-1</sup> could account for the bending mode of O–H. In addition, strong broadband exists t at 3000–3500 cm<sup>-1</sup>, which accounts for the water tension and has been caused due to the strong hygroscopicity of sulfated zirconia.<sup>62</sup> Furthermore, the bands at 1545 and 1455 cm<sup>-1</sup> could be allocated to Brønsted and Lewis acid sites, respectively, whereas the band at 1495 cm<sup>-1</sup> is normally assigned to a combination band associated with both Brønsted and Lewis acid sites.<sup>63–64</sup> Therefore, it could be concluded that all the calcined 0.2 SrO/S-ZrO<sub>2</sub> nano catalysts up to 400 °C, exhibit similar vibrational structures. In addition, small variation of frequencies or relative intensities occur for different Zr<sup>4+</sup> + distribution.<sup>47</sup>

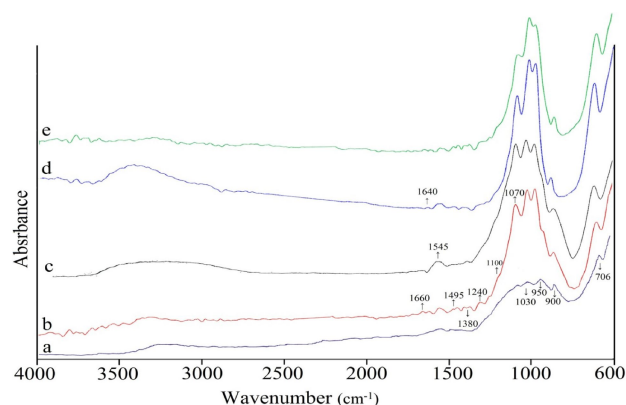


Fig. 3 – IR spectrum of 0.2 SrO/S-ZrO<sub>2</sub> calcined at a) 400 °C b) 500 °C c) 600 °C and d) 700 °C and e) 900 °C

### Catalyst acidity analysis

It has been demonstrated that the acidity of catalysts is an important index and a decisive factor for measuring the activity of catalysts in esterification reaction. Table 2 shows the acidity of the catalysts. It reveals that the acidity of catalysts significantly decreases with increasing calcination temperature due to the decomposition of the sulfate groups in the catalysts crystalline. Enhancement of sulfate groups on the catalyst surface could increase the catalytic activity in conversion of FFA to FAME, due to the generation of more Bronsted acid sites.<sup>28</sup> Therefore, the enrichment of sulfate ions on catalyst surface causes a reduction in the particles size and avoiding of the transformation of tetragonal to monoclinic phases of zirconia. Therefore, the acidity considerably enhances. It is worth mentioning that for the calcination temperature of about 900 °C, the acidity and activity is rather low due to the formation of SO<sub>3</sub> that have an adverse effect on the activity of the catalysts. Therefore, it could be concluded that the acidity of catalyst under and above 500 °C is inappropriate for the esterification of oleic acid.<sup>65</sup>

Table 2 – Acidity of 0.2 SrO/S-ZrO<sub>2</sub> syntheses at different calcination temperatures

Catalysts	Calcination temperature (°C)	Acidity (mmol NaOH/g cat.)
0.2 SrO/S-ZrO <sub>2</sub>	400	1.91
0.2 SrO/S-ZrO <sub>2</sub>	500	6.80
0.2 SrO/S-ZrO <sub>2</sub>	600	2.32
0.2 SrO/S-ZrO <sub>2</sub>	700	0.09
0.2 SrO/S-ZrO <sub>2</sub>	900	0.05

### Effect of the strontia loading on the sulfated zirconia

In this work, acidity and activity of S-ZrO<sub>2</sub> and 0.2 SrO/S-ZrO<sub>2</sub> were also compared as shown in Table 3. It demonstrates that the acidity and the activity of sulfated zirconia increase with strontium sulfate loading, as they contain two very active ions (SO<sub>4</sub><sup>2-</sup> and Sr<sup>2+</sup>). It is known that zirconium is an amphoteric; therefore, the sulfate and strontium ions increase acidic and basic sites of zirconium, respectively. Furthermore, strontia improves the reaction conditions for biodiesel production where the

Table 3 – Effect of strontia loading on sulfated zirconia

Catalysts	Calcination temperature (°C)	Acidity (mmol NaOH/g cat.)	Yield
S-ZrO <sub>2</sub>	500	4.5	88.36
0.2 SrO/S-ZrO <sub>2</sub>	500	6.8	91.13

rate of biodiesel production by basic catalysts is higher than acidic catalysts. Even though the esterification reaction with 0.2 SrO/S-ZrO<sub>2</sub> was not carried out in optimized conditions, it was however a good choice for biodiesel production reactions.

The findings of this work also revealed that a higher percentage conversion of oleic acid were obtained as compared to findings of Lopez et al. (around 99 % at 120 °C, of WZ, 9/1 molar ratio of methanol/Oleic acid and for 10 hrs),<sup>66</sup> Park et al. (94 % at 200 °C, 2 wt.% of WZ as catalyst, 9/1 molar ratio of methanol/Oleic acid),<sup>6</sup> Hu et al. (87.18 % at 200 °C, 1 g of SZ/0.1 mol of oleic acid, 2/1 molar ratio of methanol/Oleic acid and after 2 hrs),<sup>25</sup> and Chen et al. (89.2 % at 70 °C, 2 wt.% of SiO<sub>2</sub>-SZ, 10/1 molar ratio of methanol/Palmitic acid and for 6 hrs).<sup>67</sup>

Therefore, calcined 0.2 SrO/S-ZrO<sub>2</sub> at 500 °C has higher acidity and activity than S-ZrO<sub>2</sub> and hence a higher conversion of FFA to biodiesel.<sup>35</sup>

### Conclusion

In this work, the effect of calcination temperature was investigated on the esterification of oleic acid with methanol. The results reveal that the activity of catalysts is highly dependent upon the calcination temperature. It has also been demonstrated that an increase in the calcination temperature causes the formation of the stable monoclinic phase of zirconia. Furthermore, enhancing the percentage of the monoclinic phases of zirconia would lead to the reduction of the activity of the catalysts. Moreover, increase of calcination temperature influences the decomposition of sulfate ions on catalyst surfaces and causes a reduction of the catalysts acidity. Therefore, the catalyst Sr-promoted sulfated zirconia at 500 °C exhibits the highest acidity and fraction of the tetragonal phases of zirconia; therefore, it could convert 91.13 % of oleic acid to FAME in esterification reaction. Furthermore, the result of this study demonstrates that Sr-promoted sulfated zirconia has a higher activity than non-promoted sulfated zirconia at 500 °C.

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## Nomenclature

- A – volume, cm<sup>3</sup>  
 $A_t(101)$  – peak area of (101) of tetragonal phases  
 $A_{\text{total}}(\text{ZrO}_2)$  – area of all tetragonal and monoclinic peaks in the pattern  
 AV – acid value  
 D – crystalline size, nm  
 FAME – fatty acids methyl esters  
 FFA – free fatty acid  
 $f_t$  – fraction of tetragonal phase  
 IR – Infrared spectroscopy  
 XRD – X-ray diffraction method

## Greek letters

- $\beta$  – corrected half-width of the peak profile  
 $\lambda$  – radiation wavelength  
 $\theta$  – corrected half-width of the diffraction peak angle

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