The effect of Calcination Temperature of Sulfated Zirconia Catalyst for Simultaneous Reactions in Biodiesel Production

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Abstract

The activity of sulfated zirconia catalyst for simultaneous esterification of free fatty acid and transesterification of triglyceride was studied. Oleic acid (free fatty acid) and tributyrin (triglyceride) were used as model compounds respectively. Mixtures of free fatty acids and triglycerides are typical biodiesel feedstock in low grade oils such as animal fats and used cooking oils. The effect of calcination temperature of synthesized sulfated zirconia catalyst XZO-01 on its activity was investigated. The activity of the synthesized sulfated zirconia XZO-01 and commercial sulfated zirconia XZO-1720 was compared. The optimum calcination temperature for the sulfated zirconia XZO-01 was found to be 600°C for both reactions.

The results reveal that the synthesized sulfated zirconia catalyzes both esterification and transesterification reactions simultaneously. This catalyst is promising used as solid acid catalyst for biodiesel production using low grade oils as starting material. The simultaneous reactions were performed in pressurized reactor at 120 °C. Characterization by X-ray diffraction and total BET surface area allowed to correlate the crystal structure and surface area was changes with calcination temperature and the effect on its activity.

Keywords: Solid acid, sulfated zirconia, calcination, simultaneous reaction, biodiesel.

Introduction

The current situation urgently needs the solution for long term sources of energy in sustainable way. The renewable energy includes biofuel such as ethanol and biodiesel which is one of alternatives to solve the problem. Biodiesel is made from renewable resources such as animal fats and vegetable oils[1]. Vegetable oils and fats are converted to biodiesel through either esterification or transesterification reaction with low molecular weight alcohols such as methanol or ethanol. This biodiesel synthesis is generally catalysed by homogeneous alkali catalysts such as NaOH, KOH and $NaOCH_3$.

However, those homogeneous catalysts have many drawbacks such as producing large amount of waste and only suitable for feedstock containing low concentration of free fatty acids and water. The other problems with homogeneous catalyst are low quality glycerol produced and the catalyst cannot be recycled.

In contrast, the use of heterogeneous catalyst has motivated many researchers due to ease to catalyst separation, purity of the product and also simple in operation. Some reviews of heterogeneous catalysts have been widely reported for refining biodiesel from vegetable oil using acidic, basic and enzyme catalysts. The esterification and transesterification reactions for replacing mineral acids were reported: Amberlyst-15[15] and sulfated zirconia[15-18], The activity of solid acids catalyst towards esterification of carboxylic acids has been applied effectively, however the use of the catalyst for transesterification of triglycerides is still a challenge.

Sulfated zirconia has shown catalytic activity in reactions such as isomerisation, alkylation, acylation, etherification, esterification, condensation, nitration etc[2]. Sulfated zirconia is classified as a “superacid”, which is defined as being stronger than 100% sulphuric acid[3-4]. The catalytic properties of sulfated zirconia are also related to the crystal structure. Zirconia crystalizes in three different polymorphs, with tetragonal, monoclinic and cubic symmetry. Out of these three structures, only the tetragonal structures show catalytic properties[5-6]. However, synthesis of the pure tetragonal structure is difficult. It requires control of various parameters, especially the calcination temperature.

The use of sulfated zirconia for biodiesel production has been reported by Furuta et al[7], who compared the activity of sulfated zirconia (SZ), tungstated zirconia (WZ) and sulfated tin oxide (STO) in the transesterification of soybean oil and in the esterification reaction of octanoic acid with methanol. The transesterification was conducted at 200-300°C and the esterification at 170-200°C. Lopez et al[8] studied the activities of sulfated and tungstated zirconia and titania/zirconia for the transesterification of triglycerides and the esterification of carboxylic acids with ethanol. The use of sulfated zirconia for the esterification of dodecanoic acid with 2-ethyl hexanol was reported by Kiss et al[9]. Study of the activity and stability of commercial sulfated zirconia catalyst (SZ) in transesterification has been reported by Suwannakarn et al.[10]

The purpose of this research is to study the effect of calcination temperature of sulfated zirconia (XZO-01) on the catalytic activity towards transesterification reaction and simultaneous esterification-transesterification reactions with methanol in biodiesel production. The simultaneous reaction used tributyrin as model compound for triglycerides and oleic acid as free fatty acids (FFAs). Commercial sulfated zirconia XZO-1720 (MEL International, Manchester, UK) was used for comparison purposes.

Material and Methods

Materials: Precursor zirconium hydroxide (hydrated zirconia) and zirconia XZO-1720 were provided by MEL International, UK. in powder form. Tributyrin was purchased from Acros organics at 98% purity. Oleic acid (analytical grade-99%) was purchased from Fluka. Anhydrous methanol 99.99% was supplied by Fisher Scientific.

Catalyst preparation and characterization: The synthesized sulfated zirconia (XZO-01) was prepared by the method of Miao and Gao[11]. Sulfated zirconia samples were characterized using powder X-ray diffraction on a Bruker D8 diffractometer. FT-IR measurements were performed on a Nicolet 380 spectrometer. The spectrum was measured in the range 4000 to 400 cm^{-1}. Nitrogen adsorption/desorption isotherm analysis to determine surface areas was performed on a ASAP 2020 Micrometrics instrument. The acid concentration or ion exchange capacities (IEC) of the catalysts was measured by acid-base titration. The procedure was described by Tsai et al.[12] The catalyst was calcined at temperature of 400 to 900°C with temperature ramping rate of 5°C/min. The hypothesis is that the calcination temperature will affect the acid properties, crystal structure and surface morphology. These properties may correlate to the catalyst reactivity.

The catalyst test: The transesterification and simultaneous reactions were performed in the same reactor, used tributyrin and methanol for transesterification and a mixture of the oleic acid and tributyrin for simultaneous reactions. The oleic acid content was set to 10% by weight of tributyrin and the catalyst used was 5% w/w of the oleic acid. The temperature of reaction was set to 120°C. The reaction was stopped after 2 h. The amount of oleic acid conversion was determined using acid base titration. Tributyrin concentration was analyzed using gas chromatography.

Results and Discussion

Catalyst characterization: Table 1 shows the properties of the commercial and the synthesized sulfated zirconia's studied following calcination at temperatures 400-900°C. The table shows that the increasing the calcination temperature from 400°C to 900°C decreases the surface area from 220 to around 6 m^2/g, both for the synthesized catalyst and the commercial XZO-1720.

XRD analysis: Figure 1 shows the influence of calcination temperature on the concentration of active sites on the catalysts. The two samples show broadly similar behavior, acid concentration increasing with calcination temperature up to 600°C and then decreasing dramatically on calcination at higher temperature. At high calcination temperatures, at 800°C and 900°C the acidity drops almost to zero. It is thought that above 700°C the catalyst loses the sulfate group due to decomposition and this may be responsible for the loss of acidity. Table 1 lists the dominant phases present after calcination at each temperature. These phases were identified through the powder XRD patterns of the calcined samples.

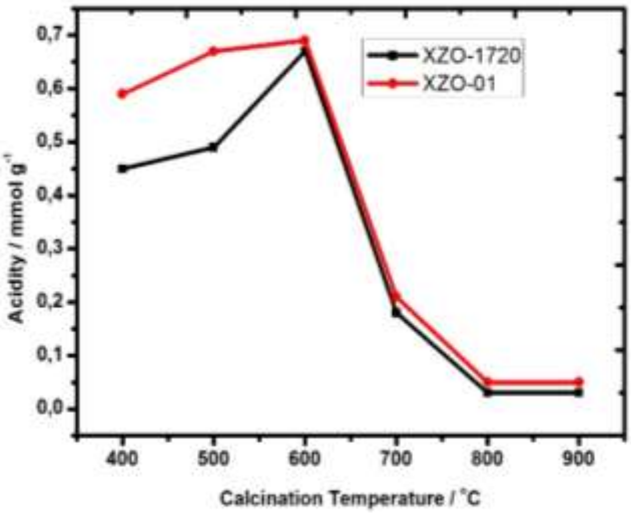

Figure 1: Effect of calcination temperature on acidities of sulfated zirconia catalysts.

Figure 2 and figure 3 show powder XRD patterns for sulfated zirconia XZO-01 and XZO-1720 calcined at 400 – 900°C. The powder XRD patterns of the two catalysts are similar. Calcination at 400°C gives an amorphous (to XRD) zirconia structure. This can be seen from the broad peaks at 2θ =20°–40° and 2θ =40°-70°. When the temperature is increased to 500°C for the XZO-01, the tetragonal phase characterized by strong reflectance at 2θ = 30° starts to develop. In contrast, the commercial sample XZO-1720 remains in the amorphous form as signaled by the broad peak at 2θ = 20° – 40°. On calcination at 600°C and 700°C the tetragonal structure for both catalysts becomes dominant as indicated by reflections at 2θ = 30, 35 and 50°. On further increase in temperature to 800°C, the peaks associated with the tetragonal phase of ZrO_2 are still detected but with some associated with monoclinic ZrO_2 appearing at 2θ = 28° and 31.5° in both catalysts.

On calcination at 900°C, more monoclinic phase is seen and the intensities are higher at 2θ = 28° and 31.5°. The strong peak at 2θ = 30° due to the tetragonal phase decreases. On heating to 900°C, the diffraction pattern for the sulfated zirconia sample is characteristic of the monoclinic zirconia structure with very little tetragonal material present. The pattern is very similar to that exhibited by zirconia (un-sulfated) on calcination at 600°C as seen at the top of fig. 2. Evidently, the presence of sulfate ions in zirconia changes the crystal structure from a mixture of the monoclinic and tetragonal phases to only tetragonal on 600°C and 700°C calcination.

The sulfate ions tend to inhibit the formation of the monoclinic structure, stabilizing the tetragonal phase up to 800°C. On further increase to 900°C, the sulfate ions decompose to form SO_2 as explained by Yadav and Nair[2]. Following decomposition, the material behaves like the original zirconia, converting to the monoclinic structure.

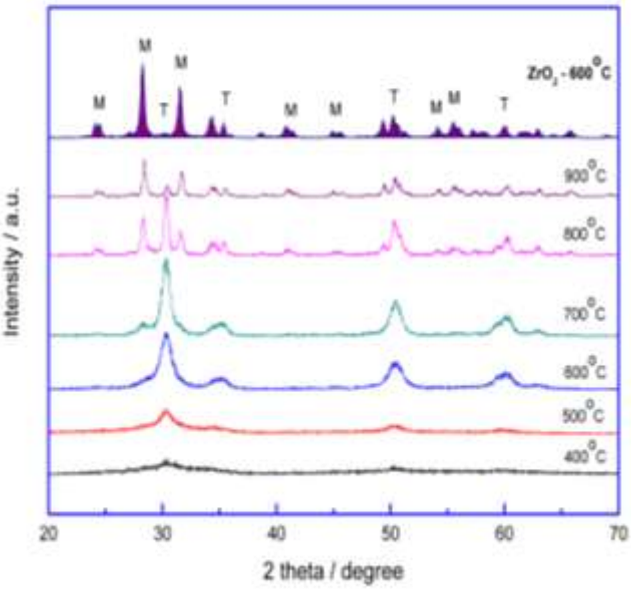

Figure 2: Powder XRD patterns of sulfated zirconia (XZO-01) calcined at 400-900°C and zirconia ZrO_2 at 600 °C. T = Tertagonal and M=Monoclinic.

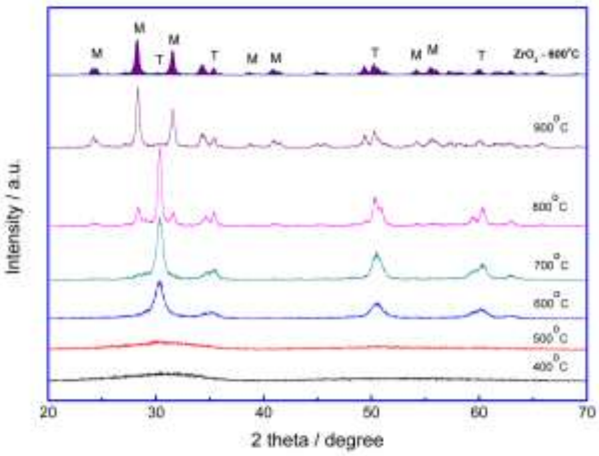

Figure 3: Powder XRD patterns of sulfated zirconia (XZO-1720) calcined at 400-900°C and zirconia ZrO_2 at 600 °C. T = Tertagonal and M=Monoclinic

FTIR analysis: The changes in the Infrared spectra caused by heating the catalyst to 400-900°C for XZO-1720 and XZO-01 are shown in figure 4 concentrating on the band associated with S=O vibration. The bands between 1000-1100 cm^{-1} are typical of sulfate ions coordinated to zirconium cations as suggested by Garcia et al[13] and Sun et al.[14] The detection of these bands verifies the effective sulfation of the zirconia substrate. The intensities of the bands for the two samples, while not quantified, are broadly similar, suggesting that the extent of sulfation on the XZO-01 sample was broadly similar to that of the commercial sample XZO-1720.

With both samples, the intensity of the coordinated sulfate bands remains almost constant through calcination to 500-600°C. Above this temperature the bands get smaller, effectively disappearing by 900°C. This is consistent with the idea that sulfate ions decompose and are lost from the solid over this temperature range. As the calcination temperature is increased, the band at 1000-1100 cm^{-1} becomes sharper and the peak maximum shifts in frequency, unpredictably for the two samples. It is not clear what gives rise to this behavior.

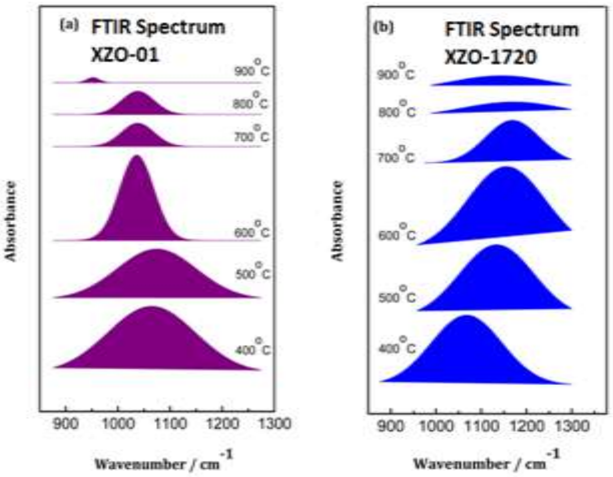

Figure 4: FTIR spectra of sulfated zirconia (a) XZO-1720 and (b) XZO-01 as function of calcination temperature.

Catalytic activities

Transesterification reaction: Figure 5 shows the conversion/time profiles for both catalysts XZO-01 and XZO-1720 in the transesterification reaction of tributyrin with methanol at 120°C in the 50 mL autoclave reactor. The catalyst was previously calcined at the optimum calcination temperature of 600°C. Figure 6 shows that XZO-01 exhibits 80% conversion after 2 h, compared to 65% with XZO-1720. This general level of activity is similar to that reported by Lopez et al[10] who reported the transesterification of tricaprylin (TCP) with methanol using the same amount of sulfated zirconia catalyst gave 84% yield after 2 h.

The rate constants of the two catalysts were calculated assuming pseudo-first order kinetics, since the amount of methanol used was in excess by plotting ln [tributyrin] vs time (h) as shown in figure 6. The rate constant for XZO-01 is 0.63 h^{-1} and for XZO-1720 it is only 0.49 h^{-1}.

Effect of calcination temperature on catalytic activity: The calcination temperature affects the catalyst surface area and acidity as shown previously (figure 1). In figures 7 and 8 the activity of sulfated zirconia XZO-01 and XZO-1720, expressed as the % conversion of tributyrin after 2 h reaction time, is plotted against calcination temperature. On the same graph, the acid site concentration is plotted against calcination temperature (data from table 1).

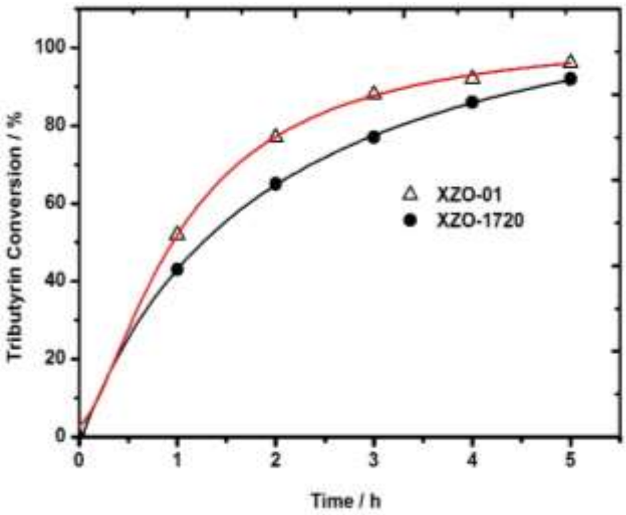

Figure 5: Catalytic activity comparisons of XZO-01 and XZO-1720 in the transesterification of tributyrin at 120°C.

Table 1
Properties of the sulfated catalyst following calcination at 400-900°C.

Calcination Temp. °C	BET surface area (m^2/g)		Acidity (mmol/g)		XRD phases
	XZ-1720	XZO-01	XZ-1720	XZO-01	
400	220	232	0.45	0.59	Amorphous
500	207	212	0.49	0.67	Amorphous
600	119	116	0.67	0.69	t-ZrO_2
700	68	85	0.18	0.21	t-ZrO_2
800	11	22	0.03	0.05	m, t-ZrO_2
900	6.0	6.0	0.03	0.05	m, t-ZrO_2

m=monoclinic, t=tetragonal

There is an excellent correlation between surface acidity and catalytic activity and both figures show very pronounced maxima on calcination at 600°C. Both acidity and activity fall at higher calcination temperature. This decrease occurs in significant loss in SO_4^{2-} from XRD and IR results and is thought to occur at 800-900°C. Our conclusion is that the maximum acidity and maximum activity correspond to the optimum temperature for the formation of the tetragonal zirconia structure as opposed to the amorphous phase and the monoclinic phase.

Simultaneous esterification and transesterification reactions: Table 2 shows the catalytic activity results for all the catalysts studied in the simultaneous esterification of oleic acid and the transesterification of tributyrin. It has already been shown that the transesterification reaction follows simple first order kinetics for reaction over 4-5 h. This justifies the use here of reactant conversion at a single reaction time of 2 h as a measure of catalytic activity. Experimentally, this was very much simpler than collecting data for full conversion/time plots. We found that the oleic acid (free fatty acid) esterification reaction also followed first order kinetics (not shown), so activities in this reaction are also expressed as a single % conversion of reactant at a reaction time of 2 h.

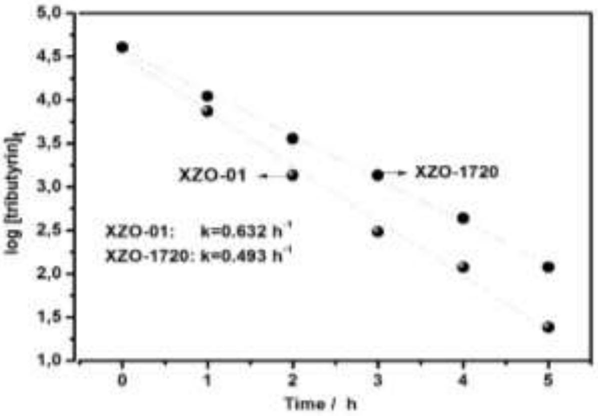

Figure 6: First order plot for XZO-01 and XZO-1720 catalysts in the transesterification reaction of tributyrin.

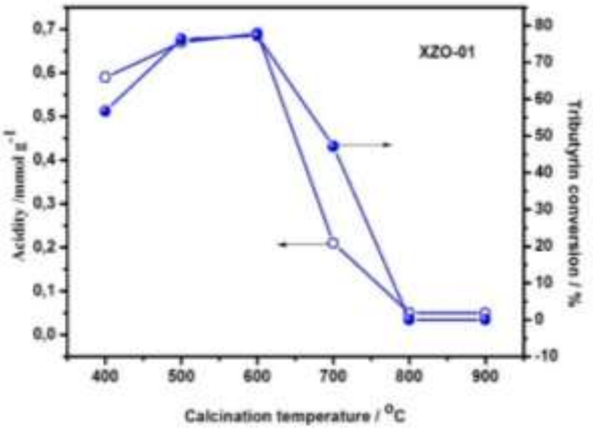

Figure 7: The effect of calcination temperature on acidity and catalyst activity for XZO-01.

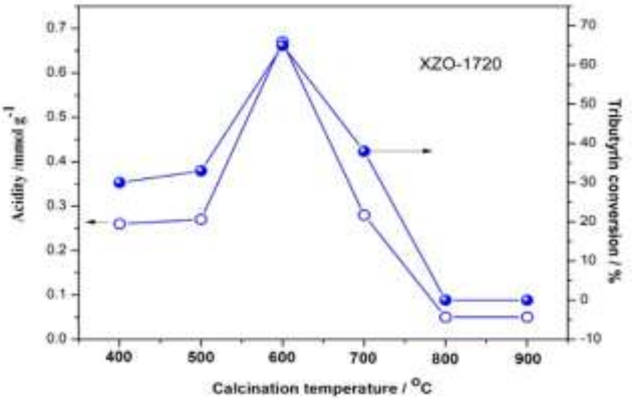

Figure 8: The effect of calcination temperature on acidity and catalyst activity for XZO-1720.

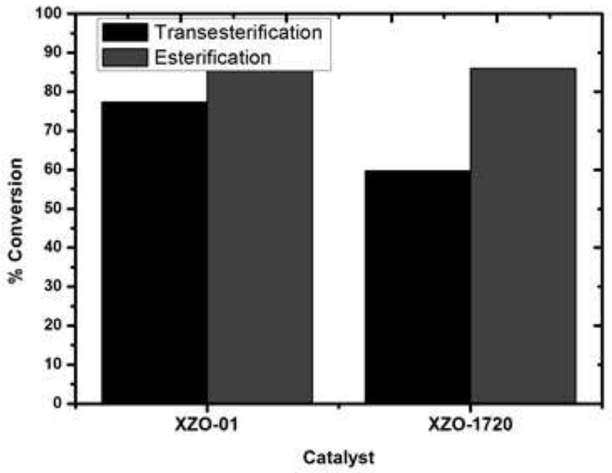

Figure 9: Catalytic activities of solid acid catalysts in simultaneous esterification and transesterification reactions at 120°C expressed as reactant conversion after 2h.

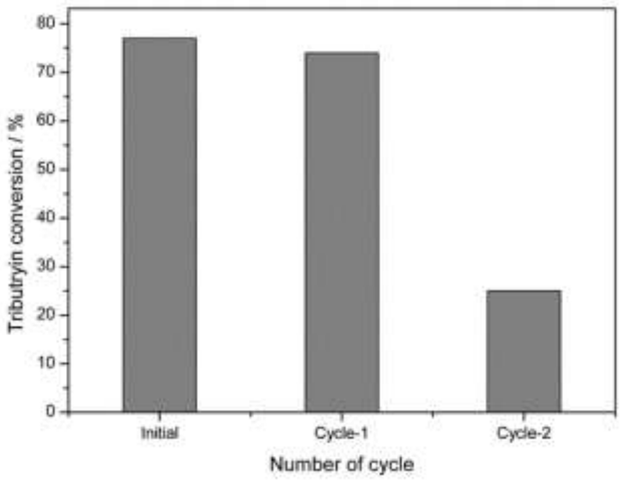

Figure 10: Reusability test on XZO-01 in transesterification of tributyrin at 120°C.

Figure 9 shows the esterification and transesterification results as a bar chart. In these simultaneous reactions, for the transesterification reactions, sulfated zirconia catalyst XZO-01 exhibit higher activities than XZO-1720.

Catalyst reusability: Catalyst reusability was tested in the transesterification reaction. The reusability test was conducted under the same conditions as described earlier and activity is expressed as conversion after 2 h. After each reaction, the catalyst was washed with methanol and re-calcined at 600°C before re-use.

Figure 10 shows the results for XZO-01 after two consecutive additional cycles. Activity is reduced significantly after two cycles. There are several possible explanations. One is that pores in the sulfated zirconia become blocked by triglyceride and that calcination forms carbon which reduces access to the active sites. Another is that water in the oil and methanol could bring about deactivation.

In theory, water could react with sulfate ion in the catalyst to form H_2SO_4, resulting in leaching[18]. However, Kiss at al[18] suggested that deactivation of sulfated zirconia is not affected by water in small quantities. Unfortunately, we did not measure sulphur leaching in this study.

Conclusion

The investigation of the effect of calcination temperature on the catalytic activity of SO_4^{2-}/ ZrO_2 shows that the optimum temperature for both XZO-01 and XZO-1720 is 600°C. Evaluation in the transesterification reaction of tributyrin with methanol showed that XZO-01 is more active than XZO-1720. Despite the reasonable catalytic activities of sulfated zirconia in the transesterification reaction, reusability is poor, suggesting that this type of catalyst may not be a practical alternative to homogeneous caustic catalysts.

It seems quite likely that the deactivation of sulfated zirconia could be due to SO_4^{2-} leaching since re-calcination did not help to recover the activity as might have been expected if pore blocking was responsible. The dependence of sulfated zirconia activity on calcination temperature suggests that it is the tetragonal phase of sulfated zirconia that is most active.

Acknowledgement

The author would like to thanks to the Politeknik Negeri Bandung, Indonesia, The University of Huddersfield, UK and MEL International, UK for their great supports.

Table 2
Catalyst activities in transesterification and esterification reactions.

Catalyst	BET Surface area ($m^2 g^{-1}$)	Acidity ($mmol g^{-1}$)	Transesterification[a] Conversion (%)	Esterification[a] Conversion (%)
XZO-01	116	0.69	77.3	86
XZO-1720	119	0.67	59.3	86

[a] The reaction was run for 2 h

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