



# Synthesis and characterization of sulfated hierarchical nanoporous faujasite zeolite for efficient transesterification of shea butter

Peter Adeniyi Alaba<sup>a,\*</sup>, Yahaya Muhammad Sani<sup>b</sup>, Isah Yakub Mohammed<sup>c</sup>,  
Yousif Abdalla Abakr<sup>d</sup>, Wan Mohd Ashri Wan Daud<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, University of Malaya, 50603, Kuala Lumpur, Malaysia

<sup>b</sup> Department of Chemical Engineering, Ahmadu Bello University, 870001, Nigeria

<sup>c</sup> Department of Chemical and Environmental Engineering, School of Engineering, The University of Nottingham Malaysia Campus, Jalan Broga, 43500, Semenyih, Selangor Darul Ehsan, Malaysia

<sup>d</sup> Department of Mechanical, Manufacturing and Material Engineering, School of Engineering, The University of Nottingham Malaysia Campus, Jalan Broga, 43500, Semenyih, Selangor Darul Ehsan, Malaysia

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## ABSTRACT

In this work, the transesterification of shea butter with MeOH over sulfated hierarchical nanoporous Faujasite zeolite catalysts to produce biodiesel was studied. The sulfated faujasite zeolite was prepared from kaolin as the zeolite precursor and sulfuric acid as sulfate precursor. Fourier transform infrared spectroscopy and energy-dispersive X-ray spectroscopy show the successful anchoring of sulfate ions onto the faujasite zeolite. There was a remarkable improvement in the porosity and acid strength of the faujasite zeolite upon sulfation, though with a small reduction in density due to dealumination, which enhanced the stability. The synthesized sulfated zeolite is efficient for transesterification of shea butter and gives biodiesel yield of 96.89% at 200 °C, 5:1 MeOH/oil, and 5 wt% catalyst for 3 h. The sulfated zeolite is stable after four consecutive cycle for a reaction that proceeds at 200 °C, 5:1 MeOH/oil, 5 wt% catalyst for 3 h and gave 90.76 wt% in the first cycle while unsulfated zeolite gave a yield of 72.42% at the same condition due to diffusion limitation, crystal size and lower acid strength. This indicates that both pore structure and acid strength decide the activity of solid acids catalysts in biodiesel production.

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## 1. Introduction

The use of animal fats or vegetable oils/fats, with short-chain alcohols for production of biodiesel is emerging as a smart alternative to fossil diesel to proffer solution to petroleum shortage, greenhouse gas emission and increasing energy demand (Alaba et al., 2017; Mohammed et al., 2016a). Biodiesel is normally produced over of homogeneous base catalysts for example NaOH, KOH, and other hydroxide (Carrero et al., 2011). However, the choice of acid catalysts rather than the base catalysts is mainly because of their better performance particularly for triglycerides that possess high percentage of free fatty acid (FFA) (Farag et al., 2012). Likewise, homogeneous acids like H<sub>2</sub>SO<sub>4</sub> and HCl are more suitable for samples with high FFA content. However, the use of homogeneous catalysts is challenged in catalyst separation, corrosion, formation

of soap and need to separate glycerol (Alaba et al., 2016a). Heterogeneous catalysts are suitable alternatives due to their ease of separation from the reaction stream, corrosion reduction and reusability (de Almeida et al., 2008). Their development could aid process design for continuous production of biodiesel to minimize purification costs. However, they give rather lower biodiesel yield due to drawbacks such as leaching and diffusion limitations (Sani et al., 2016a).

For better performance in transesterification process, an efficient heterogeneous catalyst needs mesopores to minimize steric hindrance, higher acid strength and density as well as thermal and hydrothermal stability to minimize poisoning and leaching. Conventional superacids such as liquid HF and AlCl<sub>3</sub> [sub 3] are hazardous to the environment contrary to solid superacids which are more attractive for industrial utilization (Sani et al., 2015). Solid superacids are promising catalysts for transesterification process to produce biodiesel because they are more environmentally benign in many industrial processes (Sani et al., 2016b). Further, their amazing acid strength makes it easier to carry out difficult reactions

\* Corresponding author.

E-mail address: [adeniyipee@live.com](mailto:adeniyipee@live.com) (P.A. Alaba).

under satisfactory experimental conditions.

Recently, several authors have tested sulfated metal oxide as solid superacid catalysts in transesterifying triglycerides and esterifying FFA (Lopez et al., 2007). Ordered mesoporous silicas and aluminosilicates such as Mobil Composition of Matter No. 41 (MCM-41), hexagonal mesoporous silica (HMS), stable mesoporous silicate (SBA-15) and ultra-stable Y (USY) zeolite are viable support because of high specific surface area (SSA) and hierarchical mesoporosity (Alaba et al., 2016b; Mohammed et al., 2016a,b). The major problems attributed to such materials are hydrophobicity and lower catalytic activity as compared to microporous zeolites (Alaba et al., 2016c). However, functional groups that are more reactive are added to improve their surface hydrophobicity as well as reactivity. Similarly, several authors have investigated the use of sulfated silicas as catalysts for esterification and transesterification (Cano-Serrano et al., 2003). Testa et al. (2013, 2014) comparatively studied glycerol acetylation over different solid acid catalysts. They reported that mesoporous sulfated silica showed superior performance with respect to reactivity.

There is presently no literature that describes the use of sulfated hierarchical nanoporous HY zeolites from kaolin as a superacid catalyst for effective transesterification of shea butter (SB). SB is a colored (mainly ivory) fat, which contains a high free fatty acid (FFA) composition. It originates from sub-Saharan African shea tree shea nut (*Vitellaria paradoxa*) (Glew and Lovett, 2014). Steric acid and oleic acid are the major FFA contents of SB. SB are widely utilized in cosmetic and confectionery industry. This result in speedy advancement of shea market to the tune of about 350,000 tons of export SB from sub-Saharan Africa in the past decade (Alaba et al., 2016d). The catalytic activity of the sulfated HY zeolite was investigated under varying experimental conditions.

Kaolin is a solid mineral with kaolinite ( $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_5$ ) content that range from 10% to 95%, and components such as mica, quartz and metal oxides ( $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{MnO}$ , and  $\text{P}_2\text{O}_5$ ) as impurities. Kaolin has found popular application as a precursor in synthesis of heterogeneous catalyst, which is an invention for quite a few industrial developments such as petrol chemistry and processes that need solid acid as a catalysts or a catalyst support, for a positive impact on the environment and economy (Alaba et al., 2015a). Therefore, this report is aimed to study the synthesis and characterization of sulfated HY zeolite (SHY) synthesized from kaolin and the influence of sulfation. The effect of sulfation was investigated on methanolysis of SB. The preference of HY zeolite in this work is because of its adjustable pore structure, acido-basicity and ion exchange properties, which engendered its wide utilization for several reactions in refinery and petrochemical industry. In addition, kaolin being the precursor is cheap and readily available.

## 2. Experimental

### 2.1. Materials

The kaolin, NaOH and  $\text{H}_2\text{SO}_4$  (95–98% pure) used in this study was purchased from R&M Chemicals Sdn. Bhd., Malaysia. The SB was obtained from Ikotun, Lagos, Nigeria and was heated in oven at 110 °C to get rid of the moisture therein. Table 1 presents the properties of crude SB as determined by (Enweremadu and Alamu, 2010):

- Fatty acid composition by a Varian GC (model No. CP3400);
- Acid value (as oleic acid), by standard titrimetry (ISO 660, 1996);
- Viscosity at 40 °C;
- Density at 15 °C;
- Iodine value, using Wijs reagent (ISO 3961, 1996);

**Table 1**

Properties of crude shea butter (Enweremadu and Alamu, 2010).

Properties	Values
Density ( $\text{kg m}^{-3}$ ) at 25 °C	0.91
Viscosity ( $\text{mm}^2 \text{s}^{-1}$ ) at 38 °C	39.98
Acid value ( $\text{mg KOH g}^{-1}$ )	3.62
Iodine value ( $\text{I}_2 \text{ g } 100 \text{ g}^{-1}$ )	59.5
Saponification value ( $\text{mg KOH g}^{-1}$ )	190
Peroxide value ( $\text{meq O}_2 \text{ kg}^{-1}$ )	12.15
Water content (wt%)	0.037
Fatty acid composition (%)	
Palmitic (C16:0)	5.4
Stearic (C18:0)	35.7
Oleic (C18:1)	49.6
Linoleic (C18:2)	7.8
Arachidic (C20:0)	1.3

- Saponification value (ISO 36,557, 2002);
- Peroxide value (ISO 3961, 1998);
- Water content (ISO 662, 1998).

### 2.2. Experimental techniques

#### 2.2.1. Synthesis of reference HY zeolite (HY)

The synthesis of HY zeolites precursor was carried out by thermal activation of the kaolin at 850 °C for 2 h to produce metakaolin, and subsequent activation with 6 M  $\text{H}_2\text{SO}_4$  at 90 °C for 2 h to form an amorphous aluminosilicate solution. The amorphous aluminosilicate solution was dried overnight at 110 °C and then processed in furnace at 550 °C for 2 h. The resulting amorphous aluminosilicate was mixed with an aqueous NaOH (14%) at ratio 1:6. The samples were aged for 36 h at room temperature and afterward crystallized for 24 h at 100 °C. Further, the gels was washed and filtered with deionized water with the aid of vacuum pump until the pH of 9–10. The resulting mixture was dried overnight at 110 °C, and subsequently soaked with a solution saturated with NaCl to their equilibrium water content (Alaba et al., 2015b). Further, the resulting samples was transferred to a fume cupboard to remove excess water and ensure adequate drying. The samples were transformed into hydronium form by treating with 1 M  $\text{NH}_4\text{NO}_3$  solution for 24 h. The samples were filtered and dried at 110 °C overnight and then treated in furnace for 2 h at 550 °C.

#### 2.2.2. Sulfated HY zeolite (SHY)

The sulfated HY zeolite was synthesized by incipient impregnation of sulfuric acid into the prepared HY zeolite. The impregnation was done by addition of sulfuric acid solution (1 M) to 10 g of HY in accordance to the work of (Yang et al., 2003). The mixture was left for 1 h at room temperature. Afterward, the samples was kept inside fume cupboard to reduce the moisture content before transferring to the oven for 24 h drying. The dried sample was treated in a furnace for 3 h at 450 °C.

### 2.3. Characterization of the catalysts

The Sulfur content and Si/Al molar ratio were analyzed using X-ray fluorescence (XRF) (Benchtop XRF Analyser - X-Supreme 8000). The XRF sample was prepared by pelletizing the sample mixed with binder (spectro blend) using a set of dies and a press machine. The X-ray powder diffraction (XRD) analysis was carried out with XRD (Seifert X-ray Diffractometer JSO, 2002) with Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.544 \text{ \AA}$ ) and  $2\theta$  between 5.018 and 69.966° with 0.026° the step size. The Nitrogen sorption experiment was performed with Micromeritics ASAP 2020 at 77.350 K analysis bath temperature. The catalysts were degassed for 3 h at 180 °C before

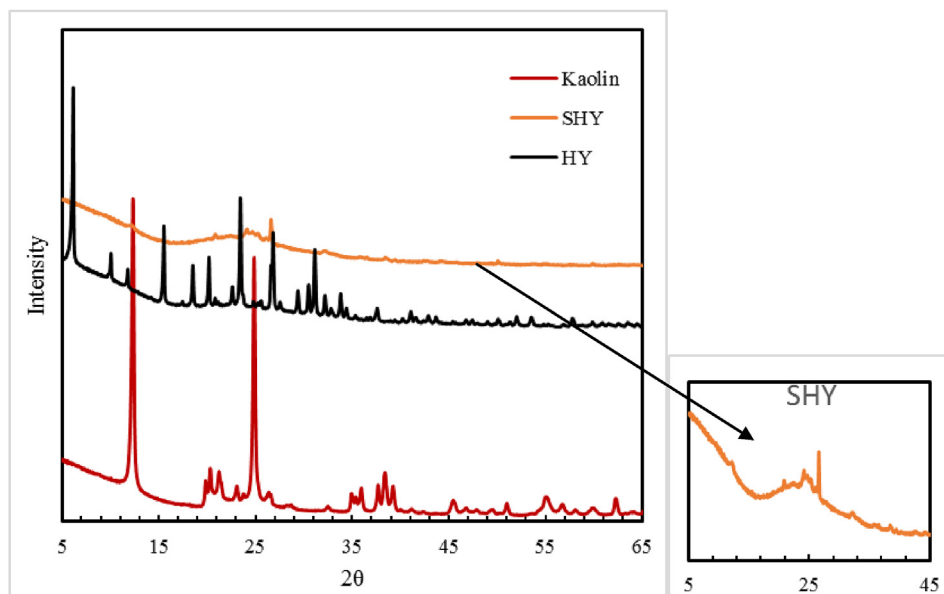


Fig. 1. X-ray diffraction patterns of the kaolin, HY and SHY.

measurement. FTIR measurements of the catalysts were performed with a Bruker Tensor 27 FT-IR. The acidities of the catalysts were obtained from  $\text{NH}_3$ -temperature program desorption (TPD) analysis from Micromeritics Chemosorp 2720. 50 mg of the sample was first heated at 600 °C for 1 h in the presence of Helium at the rate of 20 ml/min and cooled to 120 °C. Then, the adsorption was conducted by exposing the sample to 10% ammonia in helium for 1 h. The physically absorbed ammonia were flushed out and the  $\text{NH}_3$ -TPD was carried out from 100 °C to 1200 °C at 10 °C/min in the presence of helium and the signal was monitored with a thermal conductivity detector.

The morphology of the synthesized HY and SHY zeolites were visualized by scanning electron microscope (SEM), FEI Quanta 400 FE-SEM using 20 kV as the accelerating voltage. The samples were coated with gold, before the examination to improve the electrical conductivity.

#### 2.4. Methanolysis of SB

The SB was processed over SHY catalyst in a 50 ml stainless steel high-pressure reactor. The reaction proceeded in excess MeOH under air tight condition. The MeOH/oil ratio, temperature, and catalyst loading were varied to obtain the best catalytic performance, at the same time considering economic viability. The reaction parameters are: 1 atm, 150 °C and 200 °C, MeOH/oil of 5:1–30:1. The SHY quantity of 1–5 wt%. The reaction temperature was monitored with a K-type thermocouple. At the end of the reaction, the system was allowed to cool to room temperature, and

the product was discharged through a downward delivery. Afterward, the methanol was separated by evaporation at 70 °C for 4 h while the glycerol was separated using separating funnel and centrifuge. The produced biodiesel was analyzed with thermogravimetric (TG) using TGA Q500 to estimate the yield. TG is an inexpensive and faster technique to quantify the components in a material mixture (Yang et al., 2003). Quantification of biodiesel with TG can be compared with GC technique (Farag et al., 2012). Chand et al., 2009 studied the appropriateness of TG with respect to gas chromatography (GC), high-performance liquid chromatography (HPLC) and proton nuclear magnetic resonance (NMR) spectroscopy for biodiesel yield estimation of a transesterified product. They stated that the TG measurements could be compared with those of GC, HPLC, and proton NMR. The efficacy of thermogravimetric technique comparative to  $^1\text{H}$ NMR technique is about  $\pm 1.5\%$ . The TG quantification of the samples were performed with a particular quantity of the catalyst placed in the crucible. The measurement was taking at a temperature range of 50–500 °C at 20 °C/min heating rate in nitrogen atmosphere.

#### 2.5. Effect of mass transfer on the catalysts

The study of mass transfer in solid catalysts is highly significant particularly in a system that has to do with bulky molecules transfer. The influence was determined via turnover frequency (TOF) computation to examine the activities of the catalysts comparatively. In this context, TOF is the moles of the SB converted per second per surface mole of the acid sites of the catalysts (Madon

**Table 2**  
Characterization of sulfated HY zeolite and reference zeolite.

Catalyst	Crystallite size (nm)	Sulfur (wt%)	Si/Al	SBET ( $\text{m}^2 \text{g}^{-1}$ )	Pore vol. ( $\text{cm}^3 \text{g}^{-1}$ )	Pore size (nm)	Temp. (°C)	Acidity ( $\text{mmol g}^{-1}$ )	Total acidity ( $\text{mmol g}^{-1}$ )
HY	30.41	-	1.67	443	0.23	2.07	248.7	1.41	2.26
							694.1	0.24	
							761.0	0.43	
							992.7	0.19	
SHY	14.95	5.78	2.89	65	0.06	3.84	729.2	0.12	2.05
							749.4	1.93	

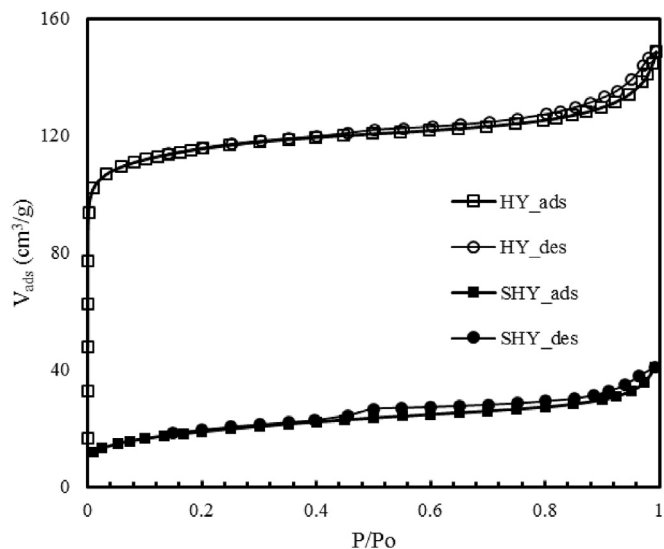


Fig. 2. Isotherms of nitrogen adsorption/desorption of HY and SHY.

where  $M_{actual}$  is the quantity of biodiesel yield in moles;  $m_{cat}$  is the mass of catalyst;  $f_m$  is the acid sites density and  $t$  is residence time.

### 3. Results and discussion

#### 3.1. Characterization of the catalysts

The XRD pattern in Fig. 1 showed the transformation from kaolin to SHY after series of treatment steps. The crystalline peaks of kaolin gave way to emergence of characteristic peaks of Y zeolite (at  $2\theta = 18.5, 20.2, 23.5$  and  $26.8$ ) after hydrothermal crystallization. Upon sulfation, the crystallinity of the zeolite dropped from 90.37 to 12.38%. This is evident in sharp decrease in intensity and disappearance of some of the zeolite peaks and decrease in crystallite size from 30.41 to 14.95 nm (Table 2). The loss of crystallinity was due to the sulfuric acid attack, which leads to severe dealumination, increasing the Si/Al ratio, thereby reducing the hydrophilicity for enhanced stability. The relative crystallinity (RC) is calculated by comparing the intensities of the Y zeolite characteristic peak of the sample with that of the conventional Y zeolite, and is given by:

$$RC(\%) = \frac{\text{Sum of the Y zeolite characteristic peak intensity of the sample}}{\text{Sum of the characteristic peak intensity of conventional Y zeolite}} \times 100$$

and Boudart, 1982). It estimates the performance of the catalyst acid center in a catalytic reaction under a particular reaction condition with the amount of transformed molecules per unit time (Alaba et al., 2016b).

$$TOF = \frac{M_{actual}}{t \times f_m \times m_{cat}} \quad (1)$$

Table 2 shows large decreased in the pore volume and the BET specific surface area (SSA) upon sulfation of the HY zeolite. However, SHY exhibited enhanced pore size because the sulfuric acid leaching culminated in collapse of the pore walls. Further, the pore walls collapse and severe pore blockage of the micropores of the samples by the acid attack is responsible for the decreased SSA and pore volume. The nitrogen adsorption isotherms in Fig. 2 revealed the enhancement in pore size. The result reveals that sulfation with

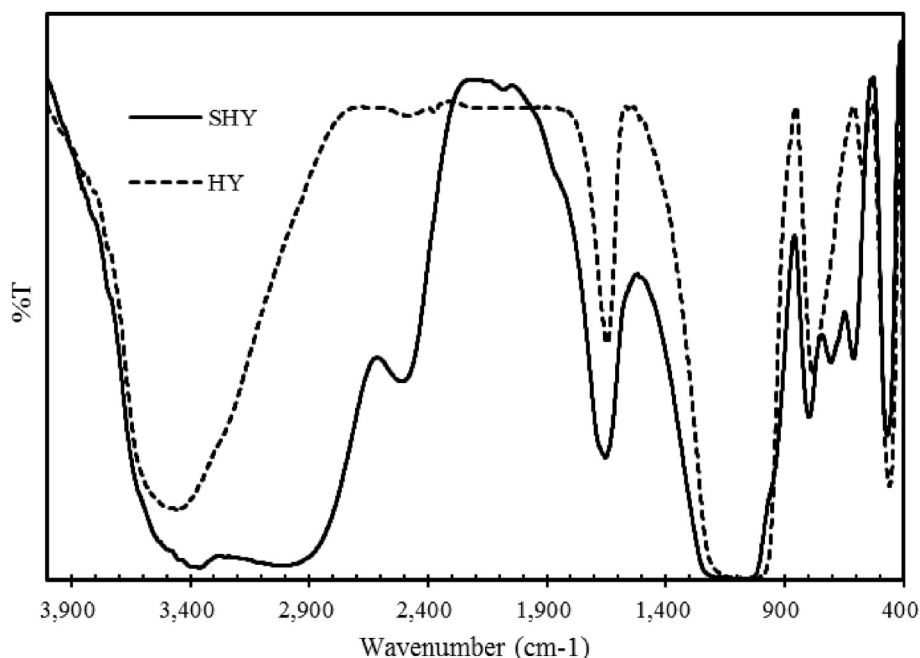


Fig. 3. FTIR spectra for catalyst HY and SHY.



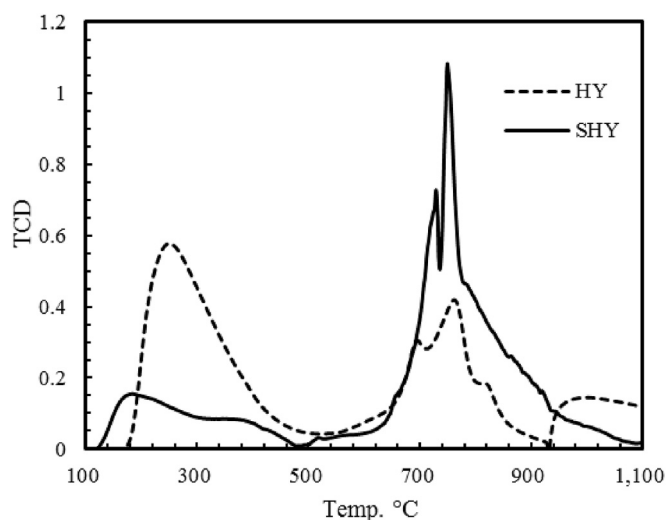


Fig. 4. TPD–NH<sub>3</sub> profiles of the HY and SHY catalysts.

1 M H<sub>2</sub>SO<sub>4</sub> considerably reduced the surface area but enhanced the mesoporosity as evident by the change in the hysteresis loop as well as reduction in the adsorbed volume ( $V_{ads}$ ).

The FTIR spectra in Fig. 3 revealed the presence of sulfate groups in SHY. The bands located at 704.96 cm<sup>-1</sup> and 796.36 cm<sup>-1</sup> are associated with stretching of S–O bond. The broad band that extends from 1064.73 cm<sup>-1</sup> to 1170 cm<sup>-1</sup> is linked to symmetric and asymmetric stretching vibration of and S=O bonds being sulfate of inorganic chelating bidentate (Saravanan et al., 2012). However, the broad band that covers 1064.73 cm<sup>-1</sup> to 1170 cm<sup>-1</sup> overlapped the HY band at 1032.75 cm<sup>-1</sup> associated with Si–O–Si stretching. The incorporated S=O bond increased the Bronsted acid sites of the zeolite due to its partial ionic nature. The results showed that sulfate groups were successfully embedded on the surface of HY to form SHY.

The NH<sub>3</sub>-TPD spectra shown in Fig. 4 confirms the super acidity of SHY with two intense peaks related to SO<sub>3</sub>H groups at 729.2 and 749.4 °C, which shows higher density of acid site as compared with that of HY at approximately the same temperature. This revealed that SHY has higher acid strength compared to HY. However, the amount of acid site in HY is slightly higher than that of SHY due to the effect of dealumination via acid activation. Moreover, the SO<sub>3</sub> content of SHY determined by EDX is 5.78%, which was greater than that of HY (Table 2). This suggests that the SO<sub>3</sub>H groups were

successfully grafted on HY.

SEM was used to observe the morphology of synthesized HY and SHY zeolites as shown in Fig. 5. The two samples show both the octahedral morphology ascribed to conventional Y zeolite, and globular particles with rugged surfaces, which confirms the mesoporosity of the samples. However, SHY appeared to be more amorphous texturally due to loss of crystallinity of the parent HY ascribed to the acid attack (Qin et al., 2013).

### 3.2. Catalytic activity

The catalytic activity of SHY was studied in methanolysis of SB to obtain the best reaction conditions such as temperature, MeOH/oil ratio and catalyst loading to attain the best yield of biodiesel. The activity of SHY was also compared with that of HY.

### 3.3. Influence of reaction condition on biodiesel yield

The reaction was initially investigated at different temperatures from 100 to 200 °C over SHY quantity of 1 wt% for 3 h at 5:1 MeOH/oil ratio. The result obtained revealed that the biodiesel produced was less than 8.37% yield at 100 °C. Meanwhile, there was rapid increase in yield to 74.77% upon increasing the temperature to 200 °C as illustrated in Fig. 6a. The yield improved as the reaction temperature increases because the reaction rate as well as MeOH solubility in SB increase with increase in temperature (Xie et al., 2011).

Theoretically, the requisite MeOH/oil ratio for transesterification process is 3:1. Nevertheless, there is equilibrium shift in the reaction to enhance the preferred product in excess MeOH. The effects of MeOH/oil ratio was investigated over 1 wt% SHY catalyst for 3 h at 200 °C. MeOH/oil, 5:1 gives biodiesel yield of 74.77% after 3 h at 200 °C using 1 wt% catalyst, when the MeOH/oil was increased to 30:1 the biodiesel yield improved to 90.76% (Fig. 6b). This confirmed that increase in MeOH/oil ratio favors biodiesel yield. Fig. 6c presents the effect of SHY quantity on the biodiesel yield. The MeOH/oil ratio of 5:1 was used with different the catalyst content from 1 to 3 wt% for 3 h at 200 °C. The results shows that yield of biodiesel improved from 74.77 to 92.77% with increase in the catalyst amount from 1 to 3 wt %. This is because increase in catalyst loading enhanced the accessibility of active sites, which improves the approachability of additional reactant molecules to the active center thereby favoring biodiesel yield. This is an indication that the best activity was obtained at 3 wt% catalyst loading because further increase to 5 wt% yield no significant increase.

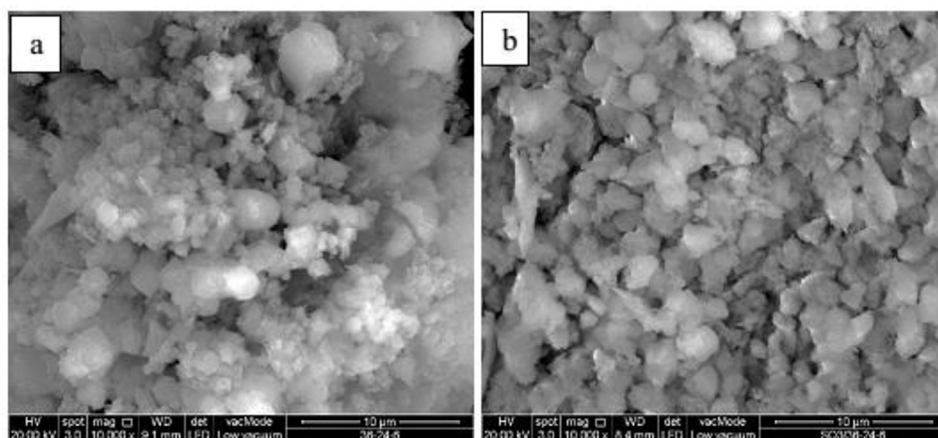
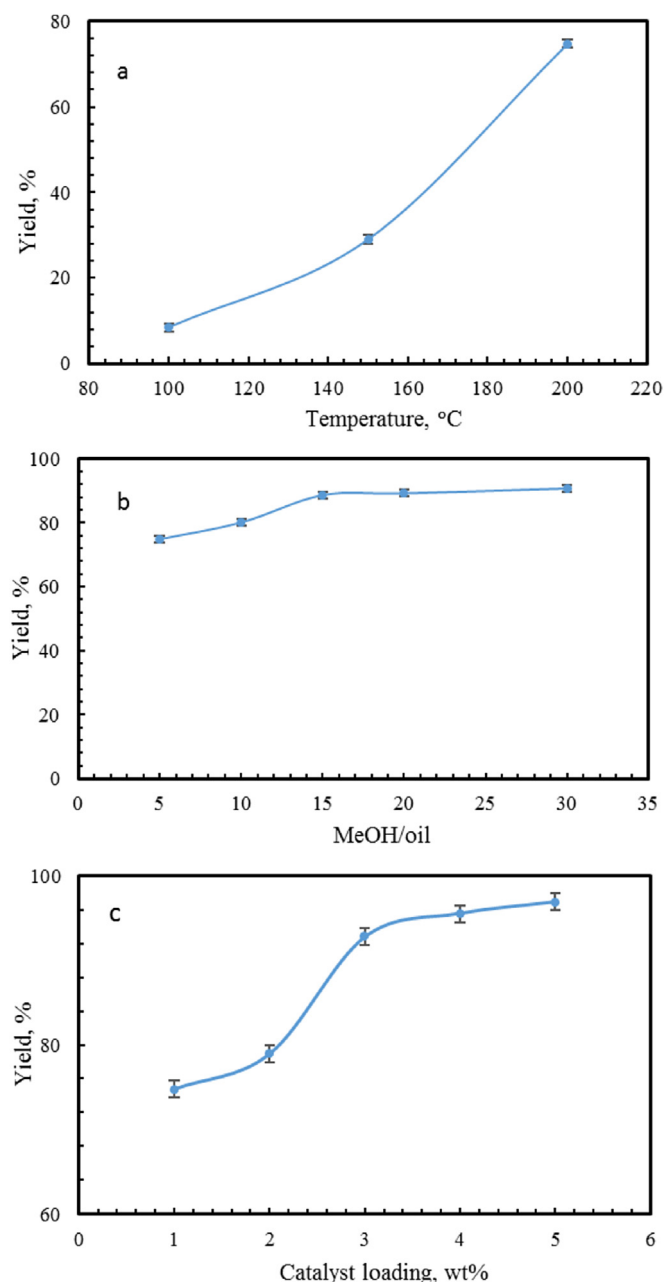


Figure 5. SEM image for catalyst HY (a) and SHY (b).



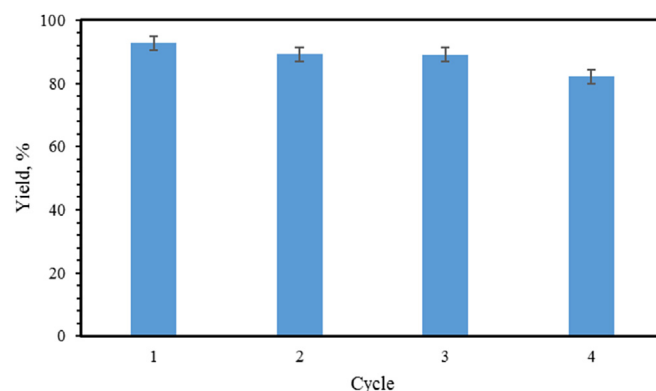
**Fig. 6.** Effect of operating parameters on biodiesel yield over SHY catalyst for 3 h, (a) 5:1 MeOH/oil; (b) 1 wt% Catalyst loading; (c) 5:1 MeOH/oil.

In comparison to HY, SHY showed outstanding performance in methanolysis of SB. Both catalysts were tested at 200 °C, for 6 h and 5:1 MeOH/oil ratio. The results showed biodiesel yield of 72.42 and 90.76% for HY and SHY. This was attributed to the fact that SHY possesses stronger acid strength and larger pore size compared to HY. The pore diameter of HY is approximately 2 nm (Table 2), which shows that it is microporous, and therefore suffers mass transfer limitation. Similarly, Table 3 shows the catalytic activity of SHY with respect to TOF for all the experimental runs. The value of TOF increases significantly with increase in MeOH/oil ratio. Although, increase in MeOH/oil ratio leads to significant increase in production cost due to the need for a larger reactor both the transesterification and MeOH separation. The catalytic activity with increase in catalyst loading. This was ascribed to improvement in the surface interaction between the reactants and the acid sites of SHY.

**Table 3**

Catalytic performance with TOF.

Catalyst	Temp. (°C)	Cat wt%	MeOH/oil	Time (h)	Yield (%)	TOF
SHY	100	1	5	3	8.37	0.0014
SHY	150	1	5	3	28.99	0.0048
SHY	200	1	5	3	74.77	0.0124
SHY	200	2	5	3	78.96	0.0131
SHY	200	3	5	3	92.77	0.0153
SHY	200	1	5	6	90.76	0.0075
SHY	200	1	10	3	80.06	0.0147
SHY	200	1	15	3	88.68	0.0132
SHY	200	3	15	3	96.36	0.0163
HY	200	1	5	6	72.42	0.0054
SHY	200	1	20	3	89.23	0.0443
SHY	200	1	30	3	90.76	0.0451
SHY	200	4	5	3	95.53	0.004
SHY	200	5	5	3	96.89	0.0032



**Fig. 7.** Reusability of SHY catalyst on transesterification of shea butter at 5:1 MeOH/oil, 1 wt% Catalyst loading for 3 h.

### 3.4. Catalyst reusability

Reusability of the catalyst is of vital importance in any industrial application. For this reason, the recyclability of SHY was examined in repeated cycle at 200 °C, 5:1 MeOH/oil ratio, and 3 wt% SHY for 3 h. After the first cycle, the spent SHY sample was renewed by washing in n-hexane to get rid of the residual product. This is followed by overnight drying to eliminate physically absorbed water and the calcined at 300 °C. The renewed sample was reused for the next reaction cycle and the results revealed a small decline in the activity (about 10.55%) of SHY after four cycle (Fig. 7). The decrease in the catalytic activity is due to leaching of the incorporated sulfate group, which reduced the sulfur content from 5.78 to 4.42% and corresponding reduction in amount of acid sites. The reusability trend corroborates with the report of (Zhou et al., 2013) on hydrolysis of hemicellulose over sulfated mesoporous USY zeolite. Further (Khder et al., 2008), also reported similar reusability, which is attributed to large quantity of Bronsted acid sites of the catalyst.

## 4. Conclusion

Sulfated hierarchical nanoporous HY zeolite was successfully prepared by incipient impregnation with sulfuric acid. The sulfation remarkably improved the acid strength and the porosity of the sample, which efficiently catalyzed methanolysis of SB. The sulfated zeolite showed better catalytic activity in biodiesel production in comparison with the reference zeolite. Despite the sharp decrease in the SSA from 444 to 66 m<sup>2</sup> g<sup>-1</sup> as well as porosity from 0.23 to 0.06 cm<sup>3</sup> g<sup>-1</sup>. The sulfated zeolite took advantage of the enhanced pore size, which enhance the fatty acid methyl ester (FAME)

diffusion, acid strength and hydrothermal stability to give a better performance. The best operating condition from the studied factors is 5:1 MeOH/oil ratio, SHY of 3.0 wt%, for 3 h reaction period at 200 °C. At this condition, a biodiesel yield of 92.77% was obtained, indicating that the sulfated zeolite is an efficient catalyst for biodiesel production from SB.

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