

Synthesis and application of hierarchical mesoporous HZSM-5 for biodiesel production from shea butter

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ABSTRACT

Here, we report the upgrading of shea butter to biodiesel with hierarchical mesoporous ZSM-5 zeolites (HMZeol). Shea butter is a triglyceride (mainly oleic and steric acid) extracted from African shea tree nut. The catalysts synthesis was by desilication of conventional ZSM-5 with an aqueous solution of NaOH (0.3 and 0.4 M). XRF, XRD, NH₃-TPD and N₂ adsorption unveiled the effect of desilication of the parent zeolite. The study investigated the effect of NaOH concentration on matrix area, pore size, mesopore volume and Si/Al ratio. HMZeol showed superior activity on biodiesel yield when compared with the parent ZSM-5 zeolite. The catalytic material treated with 0.4 M NaOH (0.4HMZeol) gave 74% biodiesel yield at 5:1 methanol/oil molar ratio, 1 wt% catalyst, and 200 °C for 3 h reaction time while ZSM-5 gave 46.05% yield under the same reaction conditions. Further increase in the reaction time to 12 h for 0.4HMZeol, 0.3HMZeol and ZSM-5 gave 82.12, 79.21, and 72.13% biodiesel yield respectively. These results showed that hierarchical mesoporous HZSM-5 is a promising solid acid catalyst for biodiesel production via methanolysis.

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1. Introduction

Depleting global petroleum reserves, greenhouse gas (GHG) emissions, and health-related issues are increasing the demand for alternative energy resources. Incidentally, the benign nature, renewability and economic prospects of biodiesel is gaining attention [1]. This makes biodiesel more advantageous than fossil-diesel. Moreover, it exhibits superior lubricating property, flash point and cetane number thereby, prolonging engine life [2,3]. Biodiesel is obtained from lipid feedstock derived long chain fatty acid mono alkyl ester such as algae-derived oil, animal fats and vegetable fats and oils. One of such source is shea butter. Shea butter is an ivory colored fat extracted from shea nut of sub-Saharan African shea tree (*Vitellaria paradoxa*) with high free fatty acid (FFA) content [4]. The FFA contents are majorly of oleic acid and steric acid. Shea butter enjoyed wide utilization in confectionery and cosmetic industry. This leads to rapid growth in shea market, about 350,000 tons of shea export in the past decade

[5], the cost of which is close to that of palm oil (as low as USD 720 per tons) [6]. Table 1 presents the properties of crude shea butter.

There are four strategies for biodiesel production; these include transesterification, thermal cracking, micro-emulsions, and hydrodeoxygenation. The most popular of these strategies is transesterification [2]. Generally, transesterification proceeds with the aid of homogeneous basic catalysts such as KOH, NaOH and other hydroxides [8]. The preference of homogeneous basic catalysts to their acidic counterparts is basically due to their better activity especially for triglycerides with low free fatty acid (FFA) content [2]. However, transesterification with homogeneous catalysts have various drawbacks. These include catalyst separation to purify the biodiesel, soap formation and separation of glycerol and water quenching which requires a large amount of water. These generates large amount of wastewater [3,9,10]. Solid acid catalyzed transesterification is a promising route that could overcome these shortcomings because of ease of separation. However, some authors reported the limitations of solid acid catalysts such as leaching and diffusion limitations [3,11–13]. Consequently, synthesis of mesoporous stable solid acid catalysts is necessary to avoid leaching of the active sites, which leads to catalyst deactivation.

Zeolites are crystalline microporous aluminosilicate minerals, which exhibit remarkable attributes such as high surface area and

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Table 1
Properties of crude shea butter [7].

Properties	Values
Density (kg m^{-3}) at 25 °C	0.91
Viscosity ($\text{mm}^2 \text{s}^{-1}$) at 38 °C	39.98
Acid value	3.62
Iodine value ($\text{I}_2 \text{ g } 100 \text{ g}^{-1}$)	59.5
Saponification value (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

selectivity strong acidity. This engenders their wide range of utilization in process industries [14,15]. Moreover, ZSM-5 zeolites possess suitable pore structure for biomass conversion and bio-oil valorization into biodiesel because it has internal pore space and controlled pore openings that reduce deactivation [16,17]. Nevertheless, because ZSM-5 zeolites exhibit steric hindrance, they are less suitable for conversion of bulky reactants. Conversion of bulky molecules can only occur at the zeolite matrix, which constitutes a smaller percentage of ZSM-5 zeolite. Further, the matrix lacks enough active sites for effective conversion of bulky molecules [16]. Hierarchical ZSM-5 zeolite (HMZeol) is a choice catalyst that could enhance conversion of bulky reactants and simultaneously produce a high yield of aromatics [18,19]. While the auxiliary mesoporosity helps to enhance conversion, the microporosity provides the active site [16]. Therefore, it is imperative to investigate a suitable method for synthesis of mesoporous zeolite. This study explored the use of HMZeol synthesized by desilication of conventional ZSM-5 for biodiesel production from shea butter, a triglyceride with a high value of FFA.

2. Experimental

2.1. Materials

R&M Chemicals Sdn. Bhd., Malaysia supplied the NaOH pellets, NH_4NO_3 (99.0%), MeOH (99.9%) and ZSM-5 zeolite. Crude shea butter was purchased from Lagos, Nigeria. The study utilized the materials without further purification.

2.2. Methods

Initially, 30 g of reference ZSM-5 was mixed with 300 mL aqueous solutions of NaOH for 2 h at 70 °C. the mixture was filtered under vacuum, washed with deionized water and dried overnight at 100 °C. The sample was further transformed to hydronium form with 0.2 M NH_4NO_3 solution at 80 °C for 24 h before drying overnight at 100 °C and calcination at 550 °C for 5 h. The synthesized samples were designated nHMZeol, where n is the molar concentration of aqueous NaOH solution. For instance, sample treated with 0.3 M NaOH solution is 0.3HMZeol.

2.3. Catalyst characterization

The Si/Al ratio of the samples were determined by x-ray fluorescence (XRF). X-ray diffractometer (Seifert X-ray Diffractometer JSO 2002) recorded XRD pattern for all the samples the using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.544 \text{ \AA}$) ranging from 5.018 to 69.966° (2 θ) with a step size of 0.026°. The Nitrogen adsorption/desorption analysis was carried out using surface area and porosity analyzer (Micrometrics ASAP 2020) under analysis bath Temperature of 77.350 K.

SEM images were obtained with an SEM, FEI Quanta 400 FE-SEM microscope, using an accelerating voltage of 20 kV and 20 mA current. All the samples were coated with 5 nm Pt prior to the analysis to enhance the electrical conductivity. Further, the strength and number of acid sites of the samples were determined by ammonia temperature programmed desorption (TPD) analysis using Chemosorp 2720 apparatus.

2.4. Valorization of shea butter

Valorization of shea butter proceeded over the synthesized HMZeol by transesterification. The reaction occurred in excess methanol in airtight stainless steel autoclave reactor. The catalyst concentration, temperature, and methanol/oil molar ratio were varied to optimize the process. The reaction proceeded at 150 °C and 200 °C, 600 rpm with methanol/oil molar ratio of 5:1 to 20:1 and the catalyst amount was from 1 to 3 wt%. On completion, the glycerol was removed using separating funnel and vacuum pump. The samples are designated nHMZeol-m_x_t where t is the reaction time, m is the methanol/oil ratio and x is the catalyst amount (wt%). Further, the samples were analyzed with thermogravimetric analysis (TGA) using TGA Q500 to determine the shea butter conversion. TGA is a cheap and fast method for quantitative analysis of a mixture of materials [2,20]. Biodiesel conversion with TGA is comparable with GC method [2]. Chand et al. [20] investigated the suitability of TGA compared to proton NMR, HPLC, and GC method for determination of biodiesel composition in transesterification reaction mixtures. They reported that the TGA results are comparable to those of proton NMR, HPLC and GC. The effectiveness of TGA method relative to ^1H NMR method is within $\pm 1.5\%$. The TGA analysis of shea butter and the synthesized biodiesels was done by filling the crucible with a specific sample amount. The operating temperature was set to 50–500 °C with heating rate of 20 °C/min in the presence of nitrogen. Fourier transform infrared spectroscopy (FTIR) analysis of the samples was carried out using a Bruker Tensor 27 FT-IR in the range of 700–4000 cm^{-1} at 4 cm^{-1} resolution. Determination of higher heating value (HHV) was done using an oxygen bomb calorimeter (Parr 6100) according to ASTM M240 (2009). Anton Paar density meter (DMA 4500 M USA) and Brookfield (USA) DV-E viscometer were used in the measurement of sample density and viscosity respectively. Further, determination of elemental composition was done with the aid of Perkin Elmer 2400 Series II CHNS analyzer (Perkin Elmer Sdn Bhd, Selangor, Malaysia).

2.5. Influence transport phenomena on the catalysts

Investigation of transport influence in heterogeneous catalysis is of vital importance especially in a system that involve transfer of bulky molecules. This is investigated by using turnover frequency (TOF) value to comparatively check the activity of the catalyst. TOF is defined as the moles reacted per second per surface mole of the active species [21]. It quantifies the activity of the active center for catalytic reaction under a specific reaction condition by the number of molecules converted per unit time [22].

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

Where M_{actual} is the amount in moles of biodiesel produced; t is the reaction time; f_m is the amount of acid sites on the surface and m_{cat} is the mass of catalyst.

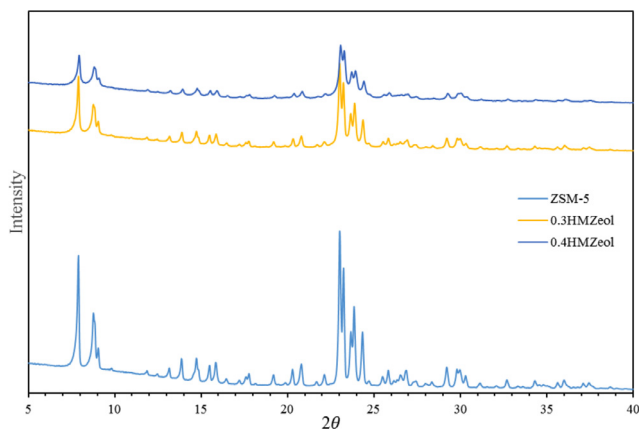
3. Results and discussion

3.1. Catalysts characterization

Table 2 presents the chemical compositions and Si/Al molar ratio of ZSM-5 and that of the synthesized HMZeol from XRF

Table 2
Catalyst composition.

Sample	Si	Al	Si/Al	Na (wt%)
ZSM-5	31.76	1.47	20.76	0.00
0.3HMZeol	27.45	1.90	12.51	0.78
0.4HMZeol	31.12	2.95	10.13	1.55

**Fig. 1.** XRD pattern of the starting ZSM-5 and the synthesized HMZeol.

analysis. Fig. 1 shows the XRD patterns of the synthesized catalysts with standard XRD peak positions. The entire samples spectrum showed a slight decrease in intensity of the characteristic peaks ($\sim 8^\circ$ and $23\text{--}25^\circ$) of ZSM-5. This is an indication that the MFI framework of ZSM-5 is intact. However, the decrease in intensity shows decrease in crystallinity. The crystallinity decreases with increase in the concentration of NaOH used for the desilication.

The acidity of the samples was measured by ammonia TPD analysis and the results are presented in Table 3. Generally, both acid density and strength decreased after desilication. This is evident in 0.3HMZeol and 0.4HMZeol samples with 2.96 mmol/g and 2.75 mmol/g, respectively. The strong acid strength exhibited by the parent zeolite around 435°C disappeared after desilication. Both HMZeol samples exhibited shoulder around 300°C . This shows that synthesized products possessed mild acidity, which is capable of suppressing deactivation.

Table 3 also presents the results of the surface area and porosity analysis from N_2 adsorption/desorption analysis. BET model gives the specific surface area (SSA) and the pore size distribution of the samples (Fig. 2). The result shows that desilication with 0.3 M NaOH slightly decreases the surface area but increases the external surface area (ESA), pore volume and pore size of the zeolite. Further increase in desilication leads to significant decrease in SSA but with subsequent increase in pore volume and pore size. This is due to collapse in the mesopore walls, which increases mesoporosity. Moreover, the reference ZSM-5 experienced a noticeable increase in ESA upon desilication. In fact, the hierarchical mesoporous ZSM-5 had almost 37% of the total SSA as ESA.

The SEM images in Fig. 3 shows the morphology of the reference ZSM-5 and the modified zeolite samples. The modified samples maintain the same surface structure as the reference ZSM-5. However, the surface of the modified samples crystals are somewhat rough and void.

3.2. Thermogravimetric analysis of shea butter

Fig. 4 shows the TGA of shea butter. The plot presents weight percent as a function of sample temperature. Shea butter exhibited small weight loss between 170 and 220°C , which corresponds to breaking down of an unsaturated bond. Further, remaining shea butter starts to decompose from 300 and ends at 470°C .

3.3. Catalytic activity

To identify the most promising of these heterogeneous catalysts, all the catalytic materials were screened under the same reaction conditions. The optimal catalyst was selected based on biodiesel yield. Table 4 presents the experimental results. From the table it is obvious that the parent ZSM-5 showed the lowest catalytic activity with biodiesel yield of 72.13% after 12 h reaction with methanol/oil molar ratio of 5:1 and 1% catalyst loading at 200°C . However, the synthesized hierarchical mesoporous zeolites (HMZeol) showed superior biodiesel yield due to their mesopore advantage. For instance, at methanol/oil molar ratio of 5:1 and 1% catalyst loading over 0.3HMZeol, a biodiesel yield of 79.21% was obtained, and a yield of 82.12% was attained with 0.4HMZeol catalyst after 12 h. Based on the above results, HMZeol catalysts showed greater potential for biodiesel production. Therefore, we studied the effect of reaction parameters on biodiesel yield.

3.4. Effect of reaction parameters on biodiesel yield

The 0.3HMZeol catalyst was tested for biodiesel yield at 10:1 methanol/oil molar ratio, 1 wt% catalyst varying temperature from 160 to 200°C . The obtained result showed that the biodiesel yield was less than 20% at 160°C . However, the yield increased rapidly to 51.15% upon increase to 200°C (Fig. 5). The increase in yield with increase in reaction temperature was due to increase in reaction rate as well as increase in the solubility of methanol in shea butter [23].

Stoichiometrically, the ratio of methanol to oil required for transesterification is 3:1. However, the use of excess methanol is essential to shift equilibrium of the reaction to favor the desired product. The influence of methanol/oil molar ratio was studied over 0.3HMZeol catalyst. Ratio 5:1 gave 41.84% biodiesel yield after 3 h with 1 wt% catalyst, on increasing the ratio to 10:1 the yield increased to 51.15%. The excess methanol were separated from the product by distillation, and glycerol was separated using centrifuge and follow by decantation.

The effect of catalyst loading was studied for both 0.3HMZeol and 0.4HMZeol. Methanol/oil molar ratio of 5:1 and 3 h reaction time at 200°C was used varying the catalyst loading from 0.5 to 2 wt%. Fig. 6 presents the effect of catalyst loading on biodiesel yield. For 0.3HMZeol, biodiesel yield increased from 38.48 to 54.41% as the catalyst loading increases from 0.5 to 2 wt%. This is attributed to an

Table 3
Textural parameters of ZSM-5 and the synthesized HMZeol.

Sample	S_{BET} m^2/g	S_{micro}^a m^2/g	S_{meso}^a m^2/g	V_{total}^a cm^3/g	V_{mic}^a cm^3/g	D_{meso} (nm)	Tpeak $^\circ\text{C}$	Acidity mmol/g
ZSM-5	385.20	356.54	28.66	0.1540	0.1383	1.60	219.7, 435.0	3.8085
0.3HMZeol	374.88	240.23	134.65	0.367	0.1114	3.92	210.0	2.9635
0.4HMZeol	340.36	215.01	125.35	0.3938	0.0998	4.63	200.0	2.7539

^a Calculated from the t-plot curve.

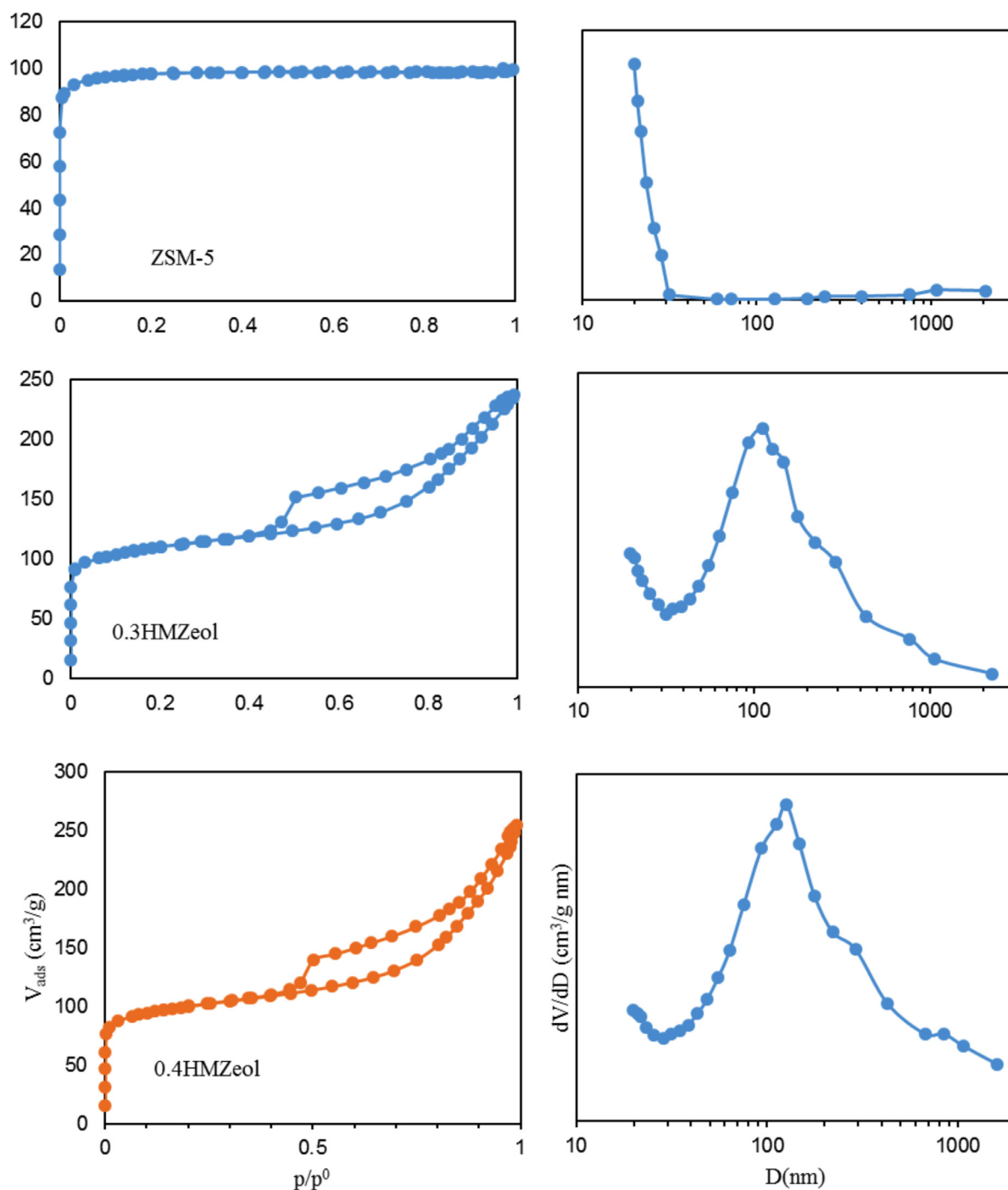


Fig. 2. Isotherms of nitrogen adsorption and pore size distribution of parent and modified zeolites.

increase in contact area between the reactants and the catalyst active sites. However, the optimum loading of 0.4HMZeol is 1 wt%. Increasing the loading from 1 to 2 wt% leads to decrease in biodiesel yield from 74 to 45.55%. Presumably, the decrease in the biodiesel yield at 2 wt% catalyst loading results from higher Na loading (1.55 wt%) compared to that of 0.3HMZeol (0.78 wt%). This is because the basicity of the catalyst increases as the Na loading increases, which is detrimental to shea butter conversion due to its high free fatty acids (FFA) content (2.279%). Naik et al. [24] reported that basic catalysts show inferior catalytic activity when the FFA content of the oil is beyond 2%. The excess FFA could react with the alkaline content of the catalyst to form soap and water rather than methyl ester

once the process exceeds the neutralization limit [25,26]. This also facilitates formation of gel/emulsion-like product thereby hindering glycerol separation. Therefore, the optimal loading of 0.4HMZeol catalyst was maintained at 1 wt%.

Fig. 7 presents the effect of reaction time on biodiesel yield. The parent ZSM-5 and the synthesized HMZeol catalysts were tested varying the reaction time from 3 to 18 h using 1 wt% catalyst loading, methanol/oil ratio of 5:1 at 200 °C. For the parent ZSM-5, the result showed that biodiesel yield increased rapidly with an increase in reaction time to optimal time of 18 h. The reaction rate was constantly high from 6 to 18 h as the biodiesel yield increased from 57.49 to 86.17%. The lower activity at the reaction time of 3 h was due to

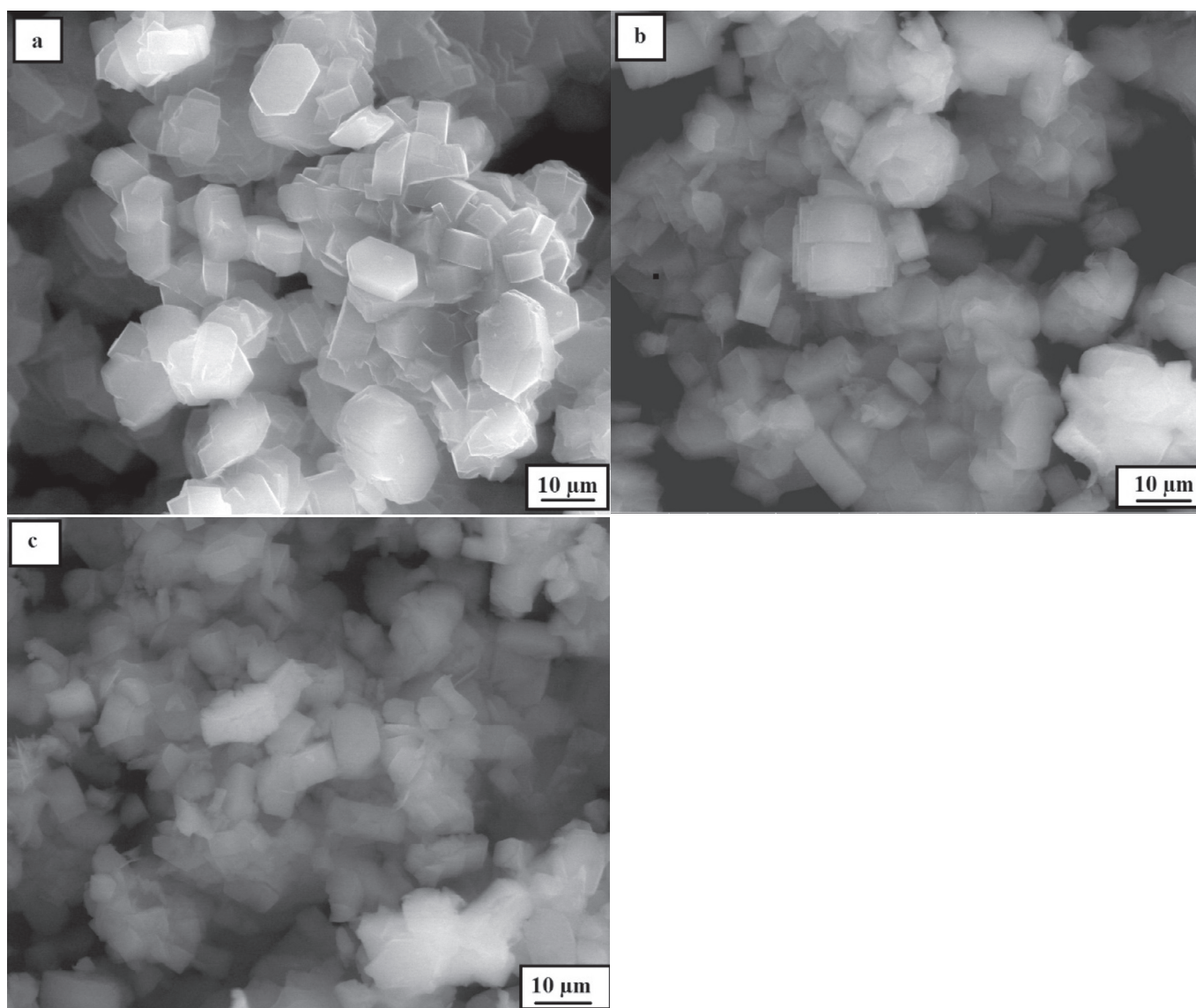


Fig. 3. SEM images of parent (a) and modified zeolites ((b) 0.3HMZeol and (c) 0.4HMZeol).

diffusion limitation, which slows the reaction rate. However, the parent ZSM-5 took advantage of its strong acid strength at higher reaction time to give high biodiesel yield over the same period. The biodiesel yield also increased rapidly with increase in reaction time for 0.3HMZeol catalyst until 12 h (79.21%). Further increase to 18 h resulted in small increase in the yield to 82.82%. Therefore, the suitable reaction time for shea butter methanolysis over 0.3HMZeol is ca. 14 h. Similarly, 0.4HMZeol catalyst showed the highest yield of 74.17% at 3 h reaction time, which increased to 78.45% when the reaction time was extended to 6 h. The reaction rate reduced as the reaction time increased from 6 to 12 h and there was no significant increase in the biodiesel yield when the reaction time was extended from 12 to 18 h. The outstanding performance of the 0.4HMZeol catalyst is ascribed to its large BET pore size (4.63 nm).

Biodiesel yield increases with the increase in methanol/oil molar ratio and catalyst loading for 0.3HMZeol. The maximum yield was obtained with 0.3HMZeol using 10:1 methanol/oil molar ratio, 2 wt% catalyst at 200 °C while ZSM-5 gave the least at the same condition. However, 0.4HMZeol gave the overall maximum conversion (74.01%) at 5:1 molar ratio, 200 °C and 1 wt% catalyst loading. Further increase in these parameters for 0.4HMZeol leads to decrease in conversion. The abnormal behavior exhibited by 0.4HMZeol is probably because

Table 4

Effect of operating parameters on shea butter conversion to biodiesel.

Catalyst	Catal. w.%	Temp. (°C)	MeOH/oil	Time (h)	Yield (%)
ZSM-5	1	200	5	3	46.05
ZSM-5	1	200	5	6	57.49
ZSM-5	1	200	5	12	72.13
ZSM-5	1	200	5	18	86.17
ZSM-5	2	200	5	3	32.09
0.4HMZeol	1	200	5	3	74.17
0.4HMZeol	1	200	5	6	78.45
0.4HMZeol	1	200	5	12	82.12
0.3HMZeol	1	200	5	3	41.84
0.3HMZeol	1	200	5	6	56.1
0.3HMZeol	1	200	5	12	79.21
0.3HMZeol	2	200	5	3	54.41
0.3HMZeol	2	200	10	3	35.51
0.3HMZeol	1	160	10	3	14.34
0.3HMZeol	0.5	200	5	3	38.48
0.3HMZeol	1	200	10	3	51.15
0.4HMZeol	0.5	200	5	3	41.29
0.4HMZeol	2	200	5	3	45.55
0.3HMZeol	1	200	5	18	82.82
0.4HMZeol	1	200	5	18	83.36
0.3HMZeol	1	180	10	3	31.68

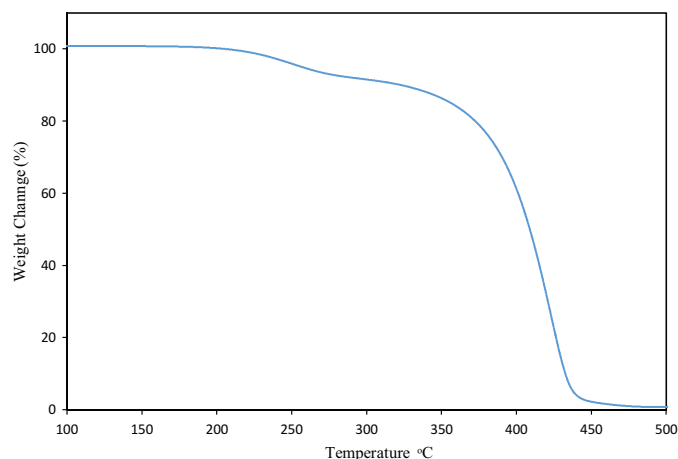


Fig. 4. TGA curve of the shea sample.

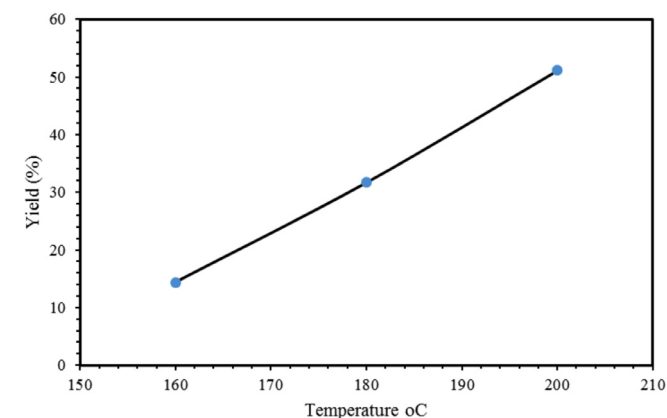


Fig. 5. Effect of reaction temperature on biodiesel yield over 0.3HMZeol catalyst. Reaction conditions: catalyst loading, 1 wt%; reaction time 3 h; methanol/oil molar ratio, 5:1.

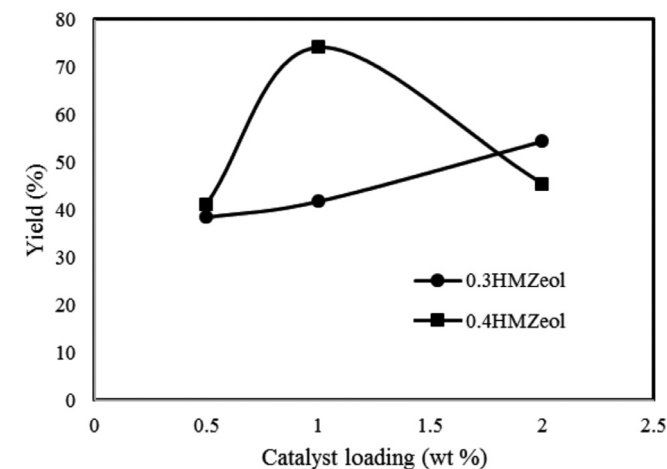


Fig. 6. Effect of catalyst loading on biodiesel yield over HMZeol catalysts. Reaction conditions: reaction temperature, 200 °C; reaction time 3 h; methanol/oil molar ratio, 5:1.

of the severe desilication of the parent material. This is because desilication leads to decrease in Si/Al molar ratio, which culminate in a severe reduction of the catalyst acidity thereby increasing its basicity. This result is corroborated by the report of Ma et al. [26] that basic catalysts require lower methanol to oil ratio than acid catalyst. Moreover, higher methanol/oil molar ratio could increase the glycerol solubility thereby making it difficult to separate from the methyl

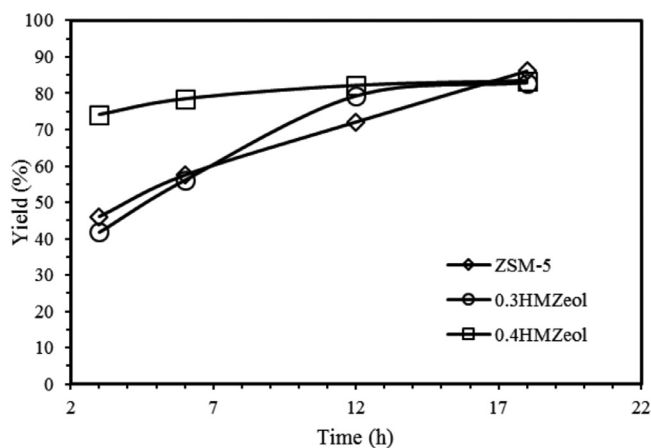


Fig. 7. Effect of catalyst loading on biodiesel yield over the parent ZSM-5 and HMZeol catalysts. Reaction conditions: reaction temperature, 200 °C; catalyst loading, 1 wt%; methanol/oil molar ratio, 5:1.

Table 5

TOF showing the activity of ZSM-5 and the synthesized HMZeol.

Catalyst	ZSM-5	0.3HMZeol	0.4HMZeol
TOF (s ⁻¹)	0.0041	0.0048	0.0091

ester. This explains the observed trend of methanol/oil molar ratio beyond 5:1 over 0.4HMZeol at 200 °C for 5 h, which leads to decrease in biodiesel yield.

Edgar et al. [27] reported that there is a significant decrease in conversion when the FFA content is beyond 2% for basic catalysts. The excess FFA could react with the alkaline content of the catalyst to form soap rather than methyl ester once the process exceeds the neutralization limit [28]. This facilitates formation of gel/emulsion-like product, which hinders glycerol separation. This becomes clear why increasing the catalyst amount to 3 wt% of 0.4HMZeol leads to decrease in conversion.

3.5. Influence of transport phenomena on the catalysts

Table 5 shows the activity with respect to TOF for the parent ZSM-5 and the desilicated samples. The optimal activity was observed with sample 0.4HMZeol followed by 0.3HMZeol. This attributed to their mesoporosity. The shows that sample 0.4HMZeol exhibits little or no mass transfer limitation as compared to other samples. Apart from mesoporosity, the outstanding performance of 0.4HMZeol could also be attributed to Na (wt%) loading due to desilication.

3.6. Biodiesel confirmation

FTIR techniques confirmed biodiesel yield fingerprint. Fig. 8 presents the spectrum of shea butter and those of biodiesel from the two HMZeol catalysts at varying parameters. The spectrum exhibits strongly stretched alkane groups at 2914.68 cm⁻¹ and strong vibration stretching of carboxylic at 1731.63 cm⁻¹. Then C-O joined with carboxylic group at 1239.32 and 1174.60 cm⁻¹. Further, strongly stretch alkane groups were observed at 2914.68, 2848.80 and 1470.85 cm⁻¹. The HMZeol spectrum exhibited symmetric and asymmetric carboxylic group strong vibration stretching from 3000 to 2500 cm⁻¹ as well as alcohol bonded with hydroxyl (broad O-H stretching) between 3500 and 3300 cm⁻¹ including phenols and alcohol group. Further, the spectrum also shows ketones, aldehyde along with carboxylic group and strongly stretch ester group between

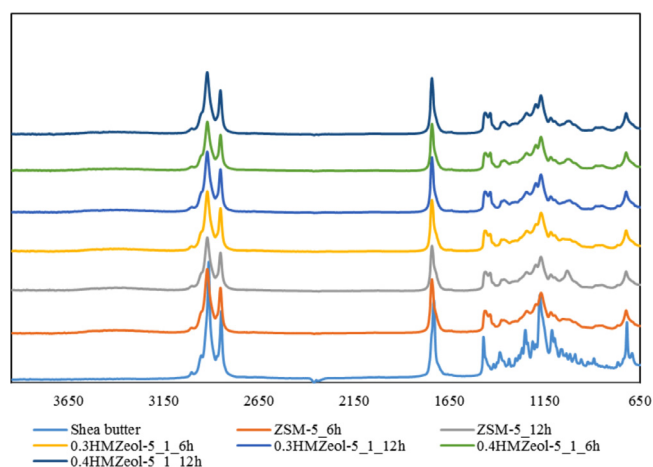


Fig. 8. FTIR spectrums comparison between shea butter and synthesized biodiesel samples using methanol/ oil ratio of 5:1 and catalyst loading of 1 wt% at 200 °C for 6–12 h.

Table 6
Properties of biodiesel sample produced with 0.4HMZeol.

Properties	Values
Weight of shea butter fed (g)	21.14
Weight of methanol fed (g)	12.02
Weight of biodiesel produced (g)	17.36
Biodiesel Yield (%)	82.12
Density (kg m^{-3}) at 25 °C	0.86
Viscosity ($\text{mm}^2 \text{s}^{-1}$) at 38 °C	3.38
HHV (MJkg^{-1})	40.01
Carbon	77.33
Hydrogen	12.82
Oxygen	9.76

1470 and 1744 cm^{-1} band. Then C–O joined with the carboxylic group and strongly stretch ester group appeared around 1029–1245 cm^{-1} . Further, strongly stretch alkane groups also appeared around 1363–1463.12 cm^{-1} .

The broad O–H stretching between 3500 and 3300 cm^{-1} could be ascribed to the strength and density of Bronsted acid sites on the catalysts. The reference ZSM-5 possesses strong Bronsted acid sites, which became weak upon desilication. The figure shows that transesterification over ZSM-5 shows the highest intensity between 3500 and 3300 cm^{-1} . Furthermore, the increase in catalyst amount also increases the intensity. This corroborates with the reports of Farag et al. [29] and Ndana et al. [30].

The properties of the sample produced over 1 wt% 0.4HMZeol with MeOH/oil ratio of 5 at 200 °C for 12 h in Table 6 shows that shea butter is a viable feedstock for high-quality biodiesel. The sample possesses higher HHV and lower oxygen content compared to the report of Hoekman et al. [31] and Fukuda et al., [32]. Although, the cost of shear butter is relatively higher than most reported feedstock like palm oil and jathrophia oil, the higher unsaponifiable fraction of shea butter as well as higher product quality, gives it an edge. Further, high biodiesel yield was attained with low molecular weight of alcohol and a small amount of catalyst, thereby reducing the cost of production.

3.7. Catalyst reusability

Reusability of 0.4HMZeol was studied to ascertain its durability and economic viability. Spent 0.4HMZeol sample was regenerated by rinsing with n-hexane to remove off the remaining product on it. The washed sample was dried overnight to remove physically absorbed

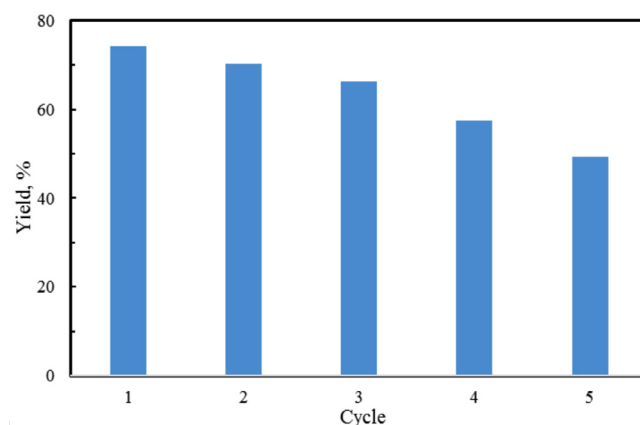


Fig. 9. Reusability of hierarchical mesoporous ZSM-5 on transesterification of shea butter.

water. The regenerated sample was reused for the next 4 cycles of reaction (Fig. 9).

4. Conclusion

Desilicating conventional ZSM-5 with an aqueous solution of NaOH produced mesoporous HMZeol. The technique enhances the matrix area, pore size, and mesopore volume of the zeolite. These ensure the suitability of the synthesized hierarchical material for conversion of large molecules of shea butter into biodiesel. A comparative study showed that HMZeol exhibits higher catalytic activity than the parent ZSM-5. The optimum operating condition within the parameters investigated is 5:1 methanol/oil molar ratio, 1.0 wt% catalyst, 12 h reaction time at 200 °C over 0.4HZSM-5. This gave biodiesel yield of 82.12%. This is a clear evidence that hierarchical mesoporous HMZeol prepared by desilication of conventional ZSM-5 zeolite is a promising catalyst for biodiesel production from shea butter.

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