



Stability Assessment of Na-Doped Mesoporous Gamma Alumina Catalyst in Transesterification Reaction

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ABSTRACT

The leaching of active species was reported to have been the major problem among alkali doped heterogeneous catalysts. Modifying the structure and texture of catalyst support can improve the catalyst's stability and its activity. In this study, mesoporous gamma alumina, with excellent textural properties, was modified using different amount of NaOH by wet impregnation method, and the catalyst's stability evaluated. The catalysts were characterized using Fourier Transform Infra-Red (FTIR) spectroscopy, N₂-sorption (BET), Basic Back Titration, Field Emission Scanning Electron Microscopy (FESEM), and X-Ray Fluorescence (XRF) spectroscopy. There was increased in the number of basic sites and decreased in surface area with increased in the amount of NaOH doping. The FESEM image indicated the incorporation of Na into the alumina after modification. The catalysts were employed in the methanolysis of corn oil, and the biodiesel product analyzed using Proton Nuclear Magnetic Resonance (¹H NMR) and Fourier Transform Infra-Red/Attenuated Total Reflection (FTIR-ATR) analyses. The reaction conditions for the methanolysis were catalyst loading (5 wt%), oil:methanol molar ratio (1:15), temperature (65 °C) and reaction time (3 h). Highest biodiesel yield of 98.9% was obtained in the present of 15% Na/Al₂O₃ catalyst. From the leaching test, the catalyst was found to be relatively stable, as only 0.7% of Na₂O was leached out. The lixiviation study further buttresses this assertion, with only about 13.5% yield, ruling out any considerable homogeneous contribution in catalytic activity.

Keywords: Leaching, Lixiviation, Methanolysis, Na-Modified, Stable

INTRODUCTION

The 1970s oil crises initiated the quest for biofuels production so as to restrain price hike, over dependent and harmful effects of fossil fuel. Biodiesel is a methyl or ethyl esters of long chain fatty acids obtained from triglycerides by alcoholysis with low molecular weight alcohols. Methanol is more frequently used in biodiesel production compared to ethanol, due to its low cost, higher reactivity, coupled with ease of separation of methyl ester from glycerol (Kaur and Ali, 2015b). Biodiesel blended with petro-diesel fuel in different proportions will have energy density and kinematic viscosity similar to petro-diesel, hence can be used directly in the existing engines without extensive modifications. Due to these benefits, the development of biodiesel worldwide is rapidly growing annually (Ong *et al.*, 2013).

Heterogeneous catalysts are developed to overcome the problems of homogeneous catalysts. Heterogeneous catalyst can eliminate the corrosion problem and consequent environmental hazards

posed by homogeneous catalyst (Bello *et al.*, 2015). Solid heterogeneous catalysts have the advantage of reusability which makes continuous fixed-bed operation possible. Such continuous process can reduce costs for biodiesel separation and purification, which in turn makes it cheaper, as such can compete with commercial petroleum-based diesel fuel (Stoytcheva and Montero, 2011). Furthermore, heterogeneous catalyst can be designed to give high activity, selectivity and long catalyst life time (Atadashi *et al.*, 2013).

Supports should be modified during preparation of catalysts to anchor catalytic species and obtain reusability. MgO, CaO, ZnO and Al₂O₃ are used as supports. Alumina is the most widely used support in catalysis processes owing to its extremely thermal and mechanical stability, high specific surface area, large pore size and pore volume. Furthermore, Al₂O₃ possesses transition crystalline phases that exist in a wide temperature range (Stoytcheva and Montero, 2011; Sepehri *et al.*, 2016).

Sodium hydroxide is an excellent catalyst commonly used for transesterification reaction with high biodiesel yield, yet it suffered from problems associated with homogeneous catalysts that include high energy consumption, corrosion and costly separation of catalyst and glycerol. To address these problems, studies were reported using alumina as catalyst support for NaOH (Taufiq-Yap *et al.*, 2011; Kim *et al.*, 2004; Arzamendi *et al.*, 2007). However, the aforementioned literatures utilized commercial alumina as support, hence, little is known on the catalytic activity and stability of NaOH modified mesoporous alumina in transesterification reaction.

The leaching of the active species was reported to have been the major problem among the alkali doped heterogeneous catalysts, hence it is necessary to study the stability as well as leaching of Na from the alumina support (Patel and Brahmkhatri, 2013; Kaur and Ali, 2015a). The ease of separation and recycling of heterogeneous catalyst is an important benefit from economic as well as environmental point of view. The present study evaluates the activity of Na modified mesoporous gamma alumina catalyst to assess its stability in relation to the structural and textural properties of the alumina support.

EXPERIMENTAL

Materials

Mesoporous γ -alumina was synthesized from Kano kaolin, as reported elsewhere (Yacob *et al.*, 2016). Corn oil was purchased from Giant supermarket, Skudai, Johor, Malaysia. Hydrochloric acid (HCl) with 37% purity, sodium hydroxide (NaOH) and methanol purity > 99% were supplied by QR&CTM, while 99.8% deuterated chloroform used for NMR analysis was obtained from Merck, Germany. All chemicals were of analytical grade and used without further purification.

Wet Impregnation

The catalysts were prepared by doping NaOH on mesoporous γ -alumina to obtain 5, 10, 15, 20 and 25% Na/Al₂O₃, as reported elsewhere (Bello *et al.*, 2015).

Transesterification Reaction

Corn oil (11 mL) was transferred to a 250 mL two neck round bottom flask and preheated at 65 °C in a paraffin oil bath. Then 5 wt% catalyst (based on oil) was mixed with 7 mL of methanol (oil:methanol, 1:15 molar ratio), and the mixture added to the preheated oil with continuous stirring maintained at 65 °C under reflux for 3 h. At the end of the reaction the products were allowed to settle overnight and centrifuged at 3000 rpm for 15 min. Three layers were observed; the small upper layer of excess methanol was distilled, while the middle layer of biodiesel and the lower layer which

contained glycerol and settled catalyst were separated (Bello *et al.*, 2015).

Catalyst Recyclability

To test the recyclability of the catalyst, after completion of the transesterification reaction, the catalyst was recovered from the reaction mixture by filtration, washed with methanol and regenerated at 500 °C. The regenerated catalyst was employed for successive catalytic cycles under the same experimental and regeneration methods.

Catalyst Characterization

Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analysis of samples in the range of 4000 cm⁻¹ to 400 cm⁻¹. Micromeritics Pulse ChemiSorb 2705 (USA) was used to determine the surface area based on the principle of nitrogen gas adsorption-desorption on porous surfaces of the sample. 10 mg of each sample was placed in a tube and degassed for 1 h at 473 K under nitrogen gas flow condition. The tube containing the sample was then evacuated to 10⁻² Torr and immersed in liquid nitrogen. The basic strength of the catalysts was determined using basic back titration method. The morphology was determined by the field emission scanning electron microscope (FESEM) (SupraTM 35 VP operating at 10kV) (Germany). The chemical composition was determined using energy dispersive X-ray fluorescence spectrometer NEXCG (USA).

Characterization of Biodiesel

The NMR spectra of biodiesel samples were acquired using Bruker 400 (USA) to determine the percentage yield of the biodiesel. Perkin Elmer 1650 FTIR (USA) Spectrometer-Frontier fitted with universal attenuated total reflection (ATR) sampling accessory was used for the confirmation of the biodiesel yield in the wave number range of 4000 cm⁻¹ to 600 cm⁻¹. The spectra were obtained using 16 scans at spectral resolution of 2 cm⁻¹ (Pan *et al.*, 2013).

RESULTS AND DISCUSSION

Fourier Transform Infra-Red (FTIR)

Figure 1 depicts the FTIR spectra of the Na-modified Al₂O₃, all peaks present in the as-synthesized alumina are retained in the modified one. New peak is observed around 1394 cm⁻¹ after modification, it become more and more intense and shift to higher wavelength with increasing amount of NaOH loading. This peak is associated with the anti-symmetric vibration of carbonate (Wan *et al.*, 2008; Li and Wang, 2011; Liu *et al.*, 2013). This indicated the generation of basic sites and its increased with increasing amount of NaOH loading. The phenomenon can be explained by the fact that formation of surface carbonate is associated with adsorption of a molecule of CO₂ by oxide anion. Chemisorption of CO₂, an acidic

probe molecule, is one of the procedures to assess

the basic sites of a compound.

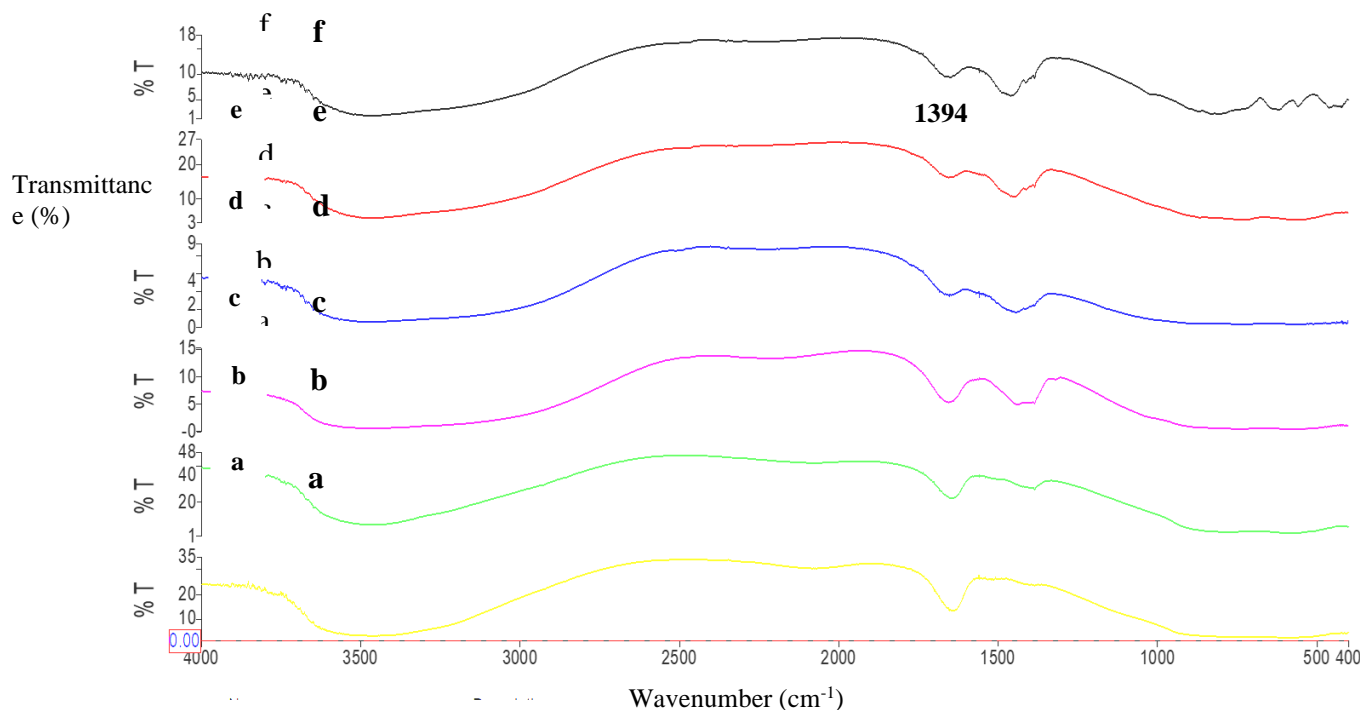


Figure 1: FTIR spectra of (a) 0% Na/Al₂O₃, (b) 5% Na/Al₂O₃, (c) 10% Na/Al₂O₃, (d) 15% Na/Al₂O₃, (e) 20% Na/Al₂O₃ and (f) 25% Na/Al₂O₃

BET Surface Area

The surface areas were found to be 273.8, 264.5, 250.5, 191.2, 125.4 and 97.5 m²/g, respectively for 0, 5, 10, 15, 20 and 25% Na/Al₂O₃, respectively. This decrease in surface area with increasing amount of NaOH doping can be ascribed to the coverage of the surface and pores of the Al₂O₃ by the sodium (Boz and Kara, 2009; Taufiq-Yap *et al.*, 2011; Asri *et al.*, 2012). Additionally, the decrease in the average pore volume and surface area may be due to the coverage of the mesoporous channels by some NaOH species (Patel and Brahmkhatri, 2013).

Basic Back Titration Analysis

The basic sites increased with increasing amount of NaOH loading and was found to be 0.67,

1.27, 4.53, 5.60, 7.40 and 7.93 for 0, 5, 10, 15, 20 and 25% Na/Al₂O₃ catalysts, respectively. This result concurred with the FTIR result that also point to the same trend in basicity with increasing NaOH loading.

FESEM Analysis of Catalysts

The FESEM images of the different catalysts are shown in Figure 2. The flaky like morphology of the unmodified alumina particles have changed into a worm like structure after modification and show particles agglomeration. The particles aggregation increased with increasing amount of NaOH addition, indicating incorporation of NaOH into the alumina support. This result further confirmed the results of FTIR analysis.

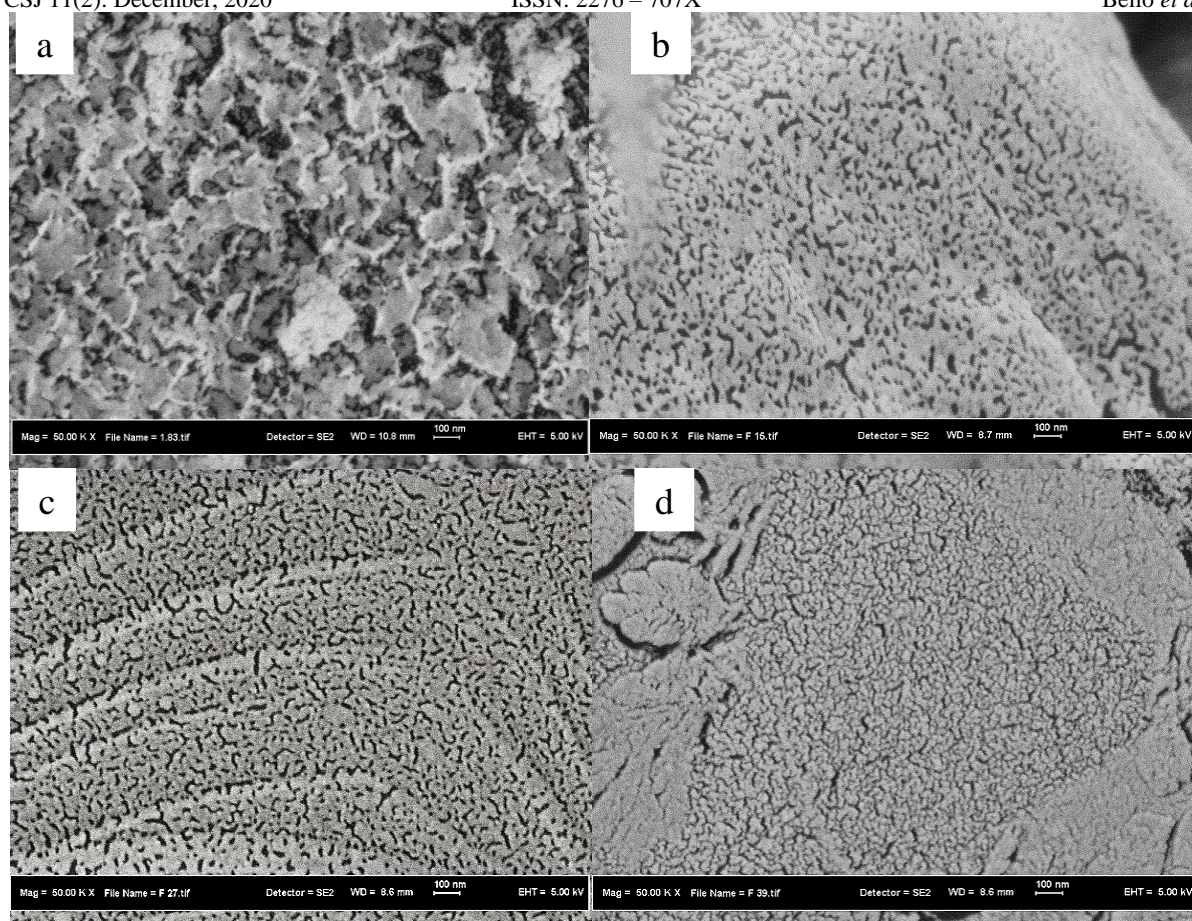


Figure 2: FESEM image of (a) 0% Na/Al₂O₃, (b) 10% Na/Al₂O₃, (c) 15% Na/Al₂O₃ and (d) 20% Na/Al₂O₃

BIODIESEL ANALYSIS

Nuclear Magnetic Resonance Spectroscopy (NMR)

The percentage yield of the biodiesel was calculated by comparing the peak area of the methoxy protons from methyl esters (singlet) at 3.7 ppm with that of α -carbonyl methylene groups from fatty ester at 2.3 ppm (triplet), using Equation 1.

$$\% \text{ Yield} = \frac{2A_1}{3A_2} \times 100 \quad (1)$$

Where, A_1 and A_2 are the peak areas of the methoxy and the methylene protons, respectively (Gelbard *et al.*, 1995; Kaur and Ali, 2015b).

The results for the biodiesel yields using different catalysts are presented in Table 1, the yield was observed to increase with increasing amount of NaOH doping. The decline in conversion with 25% NaOH loading may be attributed to the lower surface area as a result of excess Na on the surface of the alumina. This is likely since catalytic activity depends on both basic sites and surface area.

Table 1: Percentage yields of biodiesel

Catalyst	Reaction Time (h)	Catalyst Loading (%)	Oil:Methanol (Molar ratio)	Yield (%)
0% Na/Al ₂ O ₃	3	5	1:15	4.1
5% Na/Al ₂ O ₃	„	„	„	50.7
10% Na/Al ₂ O ₃	„	„	„	86.5
15% Na/Al ₂ O ₃	„	„	„	98.9
20% Na/Al ₂ O ₃	„	„	„	96.1
25% Na/Al ₂ O ₃	„	„	„	75.4

Fourier Transform Infra-Red Analysis/Attenuated Total Reflection (FTIR-ATR)

The corn oil and biodiesel spectra are compared in Figure 3. From the FTIR spectrum of the oil only peaks at 1100 cm⁻¹ and 1378 cm⁻¹,

characteristic of C-CH₂-O in TG and terminal CH₃ and OCH₂ in glycerol, are observed. For biodiesel produced with 5% Na/Al₂O₃ catalyst these peaks are retained, however with reduced intensity. In addition to that, small peak assigned to O-CH₃ stretching vibration in methyl ester at 1200 cm⁻¹ was observed, indicating low yield. For biodiesel

obtained using 15% Na/Al₂O₃ catalyst, this peak at 1200 cm⁻¹ became pronounced, whereas the other

two peaks at 1100 cm⁻¹ and 1378 cm⁻¹ disappeared, implying very high biodiesel yield.

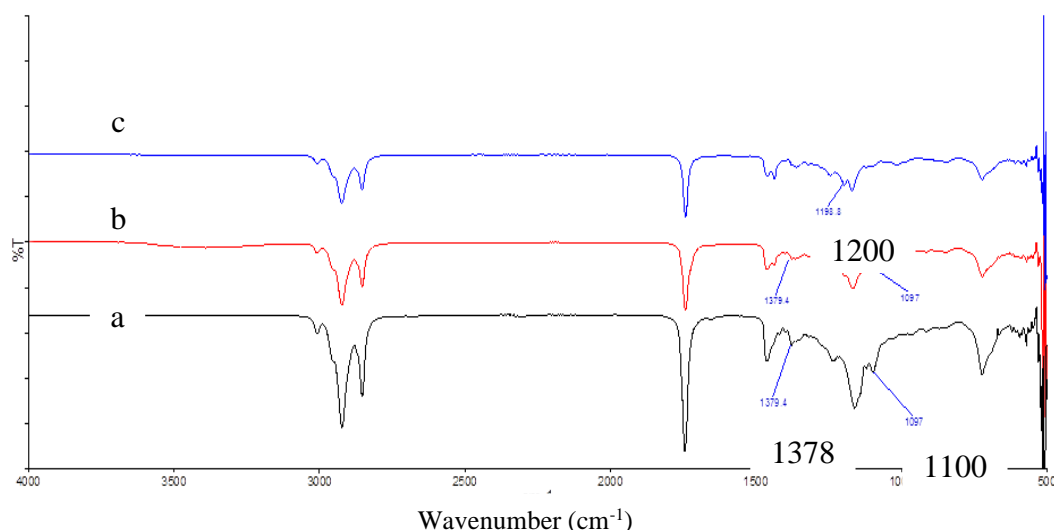


Figure 3: FTIR-ATR spectra of a) corn oil, b) 5% Na/Al₂O₃ and c) 15% Na/Al₂O₃

Recyclability Test

The 15% Na/Al₂O₃ catalyst was selected and recycled two times, with respective yields of 98.9, 92.1 and 46.4%. It is clear after the 2nd recycle the catalyst became deactivated, which may be due to; (i) the active sites blockage as a result of adsorption of organic molecules or contamination by atmospheric O₂, H₂O, and CO₂, (ii) the structural changes arising during catalytic and regeneration process, or (iii) the leaching of the catalyst active species (Kaur and Ali, 2014). To establish the factor(s) responsible for the loss in catalytic activity, XRF, FTIR and FESEM analyses were conducted.

Leaching and Heterogeneity Test

XRF analysis was performed on the raw Al₂O₃, as well as fresh and regenerated 15% Na/Al₂O₃ catalysts to evaluate the leaching of the active sites. The percentage of Na₂O in the raw alumina is found to be 60.4%, after modification the percentage in the fresh 15% Na/Al₂O₃ catalyst is 71.1%. When the catalyst is used for three successive catalytic cycles of corn oil methanolysis the percentage of Na₂O dropped to 70.4%. This implies that only 0.7% Na₂O was leached out, which can be considered as low.

To establish whether the leached Na ions from the catalyst have contributed considerably to the catalytic activity or not, hot filtration test was carried out (lixiviation study). Rigorous proof of heterogeneity can be obtained only by filtering the catalysts at the reaction temperature before completion of the reaction and testing the filtrate for activity (Patel and Brahmkhatri, 2013). The reaction was performed under optimized conditions in the presence of 15% Na/Al₂O₃ catalyst for 2 h without addition of oil then the catalyst removed by

filtration. Corn oil was then added to the filtered methanol and the reaction continued under the same condition for another 2 h.

About 13.5% of FAME yield was obtained from the lixiviation study suggesting no significant gain in FAME yield. This rule out any considerable homogeneous contribution in catalytic activity. Thus, the reaction is mainly catalyzed by solid catalyst and the leached metal ions did not contribute to the transesterification activity. Hence, the gradual loss of the catalytic activity upon repeated use may be due to the change in catalyst structure or adsorption of organic molecules (Kaur and Ali, 2015b). Song *et al.*, (2011), performed lixiviation study on catalyst synthesized by supporting KF on Mg doped La₂O₃ and obtained 20.0% FAME yield, yet considered the leached active site as not contributing to the transesterification of cottonseed oil and concluded that the catalyst is heterogeneous in nature.

FTIR of the Used Catalyst

The FTIR spectra of the fresh and recycled catalysts are depicted in Figure 4. From the spectrum of the regenerated catalyst no new band due to adsorbed organic molecules can be observed, indicating that FAME or glycerol has not accumulated on the surface of the regenerated catalyst. This rule out the possibility of catalyst deactivation by organic molecules, as the deposition of the adsorbed organic species on catalyst support may also partially deactivate the catalyst due to the blockage of catalyst active sites (Kaur and Ali, 2015b). Nevertheless, the peak around 1394 cm⁻¹ attributed to the basic sites of the catalyst was observed to decrease in intensity. This can be due to the small leaching observed from the XRF analysis.

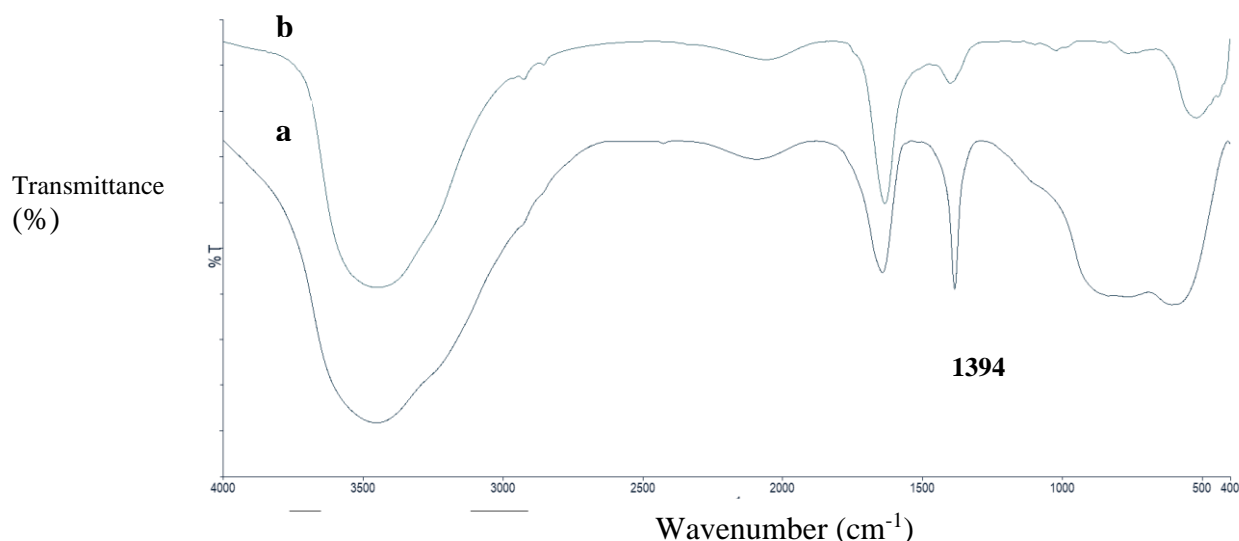


Figure 4: FTIR spectra of a) fresh catalyst and b) recycled catalyst

FESEM Analysis of Recycled Catalyst

The FESEM images of the fresh and regenerated 15% Na/Al₂O₃ catalysts are portrayed in Figure 5. The morphology of the regenerated catalyst differs from the fresh one, the particles become compacted after recycle. This may be the main reason for the deactivation of the catalyst

since from the leaching test only small amount of Na₂O was observed to be leached out. Likewise, from the FTIR analysis there was no formation of new band due to adsorbed organic molecules that may deactivate the catalyst as a result of the blockage of catalyst active sites.

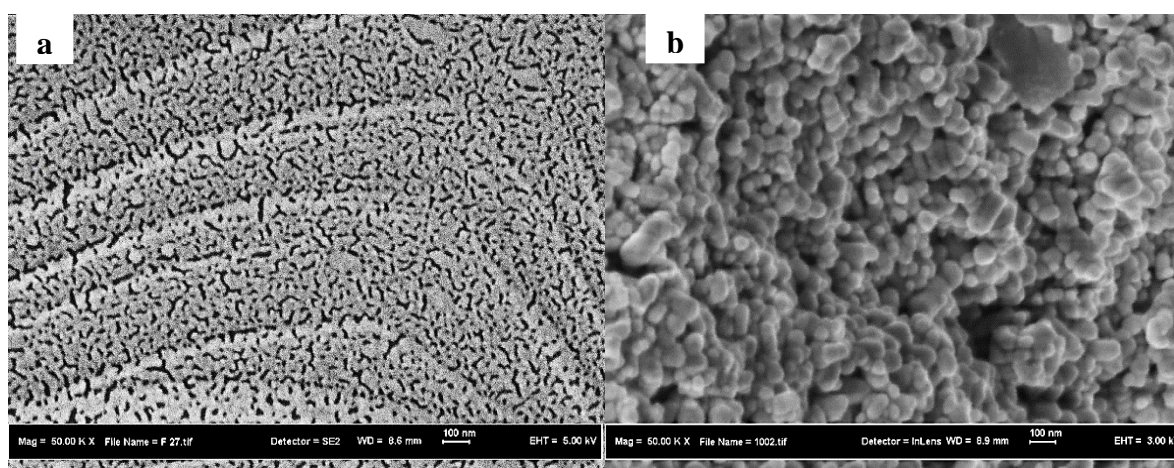


Figure 5: FESEM image of (a) fresh catalyst and (b) recycled catalyst

CONCLUSION

Different amounts of NaOH were supported on mesoporous gamma alumina by wet impregnation method. The number of basic sites were found to increase and the surface area decreased with increased amount of NaOH doping. The FESEM image indicated the incorporation of Na into the alumina after modification. The activity of the prepared catalysts was established by methanolysis of corn oil, and the biodiesel product was analyzed using NMR and FTIR-ATR analyses. The stability of 15% Na/Al₂O₃ catalyst was evaluated and was found to be relatively stable. This was established by the

leaching test that proved only a small amount of Na₂O (0.7%) was leached out. This is further buttressed by the lixiviation study, in which only 13.5% of FAME yield was obtained, indicating that the leached active sites do not contribute majorly to the catalytic activity. The recyclability and leaching tests of the catalyst revealed that the deactivation of the catalyst is mainly due to the loss of porosity as indicated by the FESEM image.

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