

## Development of Ethanol Conversion Catalysts from Various Clays

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(Received on 14<sup>th</sup> April 2017, accepted in revised form 3<sup>rd</sup> September 2018)

**Summary:** Clay-based catalysts were synthesised from non-modified bentonite and kaolin by beneficiation, acid modification and hydrothermal treatment. The effects of beneficiation and acid modification on Si/Al, catalyst morphology, mineralogical composition of clay-based catalysts were investigated. Further on, the mineralogical phase identity of the produced clay-based zeolite was studied and compared to that of a commercial zeolite. The produced clay-based zeolite was found to consist dominantly of cuboidal crystals and fits in structural framework and phase of ZSM-5 by 86.92 %. Clay-based catalysts produced in turn showed high activity in the conversion of ethanol to valuable hydrocarbons; at 350 °C and reaction time 6 hours. Bentonite was the most active with 84.95 % conversion among several of raw clays, increasing to 87.3 % upon beneficiation and acid modification. Clay-based zeolite further resulted to highest activity of more than 95 % in ethanol conversion.

**Key words:** Clay; Ethanol; ZSM-5; Conversion; Beneficiation; Fuel.

### Introduction

Catalysts play a vital role in our day to day activities and are very powerful ingredients in chemical reaction processes. Due to specific requirements in terms of product selectivity, synthetic catalysts to a great extent dictate the prices of final products because of the expensive precursors they are usually synthesized from. The drive towards sustainable technologies has led researchers to focus on readily available raw materials that could do minimum damage to the environment; of which clays have been identified to be one of such materials. Clays are hydrous aluminosilicate materials that mainly contain cations in their crystalline structure [1]. Clays geologically occur as natural deposits, are numerous and differ in properties majorly as a result of their chemical compositions. Clays possess properties that have been identified to enhance their suitability as catalysts, these include generic high surface area and surface charge, acidic and ion exchange properties [2]. The industrial uses of clays as catalysts dates from the early 20th century, where they were used for the cracking of petroleum crude oil and encompassed about 40 % among the cracking catalysts [3, 4]. Clay catalysts to date are applicable mostly in the transformation of fossil fuels and fossil fuel-derivative to petrochemical fuels [4, 5]. Clays to a limited extent, have been applicable for the transformation of ethanol to hydrocarbons, precisely light olefins such as ethylene and diethyl ether [6, 7]. Bentonite and kaolin are the most common known clays used industrially for the manufacture of catalysts [4].

In recent years however, zeolites have been the predominant and prominent catalysts for the conversion of ethanol to hydrocarbons of relatively more value and in larger distribution than those obtained over clays [8, 9, 10]. These include straight chained and branched olefins,

paraffins and aromatic hydrocarbons such as benzene, toluene and xylene (BTX) [11, 10]. Clay materials possess promising catalytic properties and similar basic composition as those of zeolites [12, 7], including acidic and tuneable nature as zeolites with regard to catalytic applications [7].

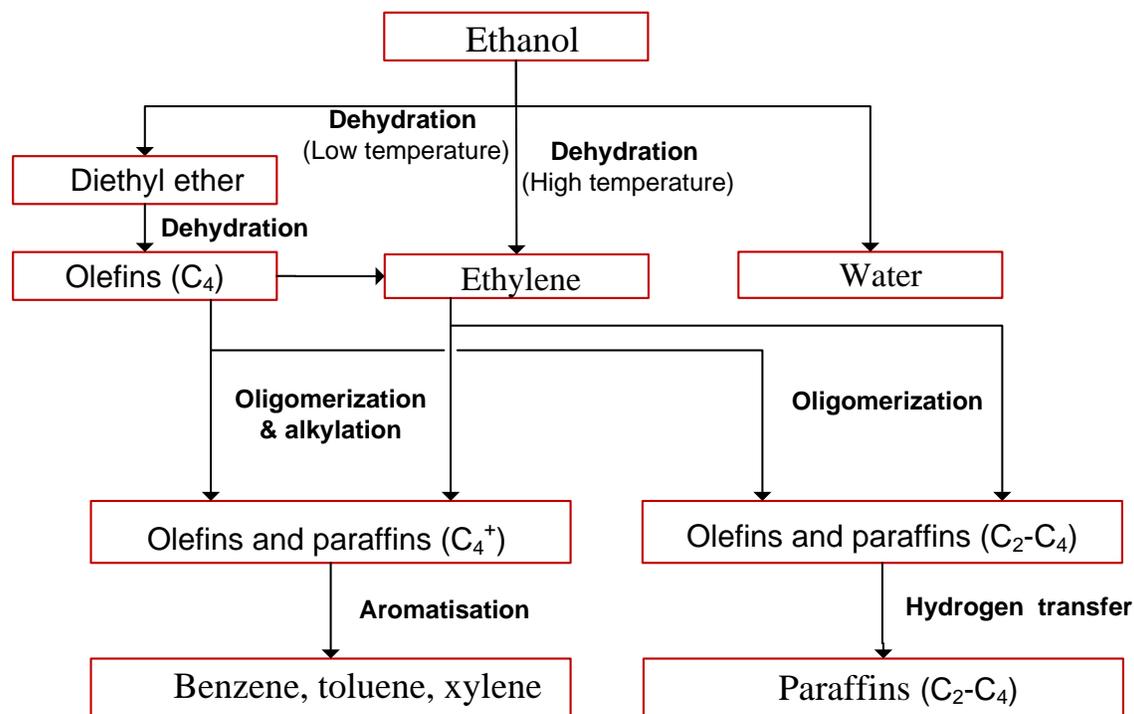
In works by Widjaya *et al.* [5], typical bentonite clay demonstrated comparable results to commercial H-ZSM-5 zeolite in the transformation of ethanol to gasoline-range hydrocarbons. Clays have also proven to be transformable to zeolites [4,12,13].

Zeolites have been conventionally produced mostly from commercial reagents, hence the use of clay materials as precursors would tackle the unavailability and high cost limitations imposed by other sources [12, 14]. Clay materials are abundant in nature and can therefore serve as cheap raw materials for the synthesis of potential and valuable catalysts such as zeolites required for the conversion of ethanol to petrochemicals [15, 5, 4]. Introducing clay as starting materials for zeolite synthesis could lead to about 5 times cheaper zeolites based on the average prices from major global suppliers of chemicals [12, 14, 16].

Ethanol is a fuel that does not meet the criteria of modern engine and is rather commonly used as a blending oxygenate agent to gasoline [9]. Further on, ethanol exhibits higher evaporative nature when blended with gasoline [11], which the basis of the above setbacks calls for the need of rather directly converting ethanol to gasoline range and other hydrocarbons to meet targeted needs. Various pathways and corresponding hydrocarbon products of ethanol transformation are presented in scheme 1.

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Scheme-1: Reaction pathways of ethanol transformation to hydrocarbons.

Research findings have prompted this work of synthesizing clay-based catalysts that could be active in the conversion of ethanol. In this paper, we report the development and evaluation of clay based catalysts. While noting some research work that has been done in application of clay materials, the novelty here lies in the assessment of various clays and relating their compositions to their suitability for ZSM-5 synthesis applicable in the transformation of ethanol to various hydrocarbons with no limits to a particular range of hydrocarbons

## Experimental

### Reagents and catalysts preparation

Kaolin, bentonite and talc clay obtained from Kankara in Nigeria, Cape bentonite mines in South Africa and Tati Nickel mine in Botswana respectively, were used as starting materials for the production of clay-based catalysts. High purity ethanol (96 %, v/v) and sulphuric acid (98 %) were purchased from Scienceworld; Sodium hydroxide pellet from Kimix chemicals, Tetrapropylammonium bromine (TPABr) was purchased from Sigma Aldrich and commercial zeolite from Zeolyst international. All chemicals used were of reagent grades.

Clay materials as obtained in their non-modified states were individually crushed and ground, followed by multiple screening for grit removal and recovery of clay fractions in the particle size range between 75-212  $\mu\text{m}$ . The resulting products were referred to as N.B, N.T and N.K<sub>2</sub> representing material obtained from bentonite, talc and kaolin respectively. Among these, the N.T showed the least activity in ethanol conversion during screening and this sample as a result, was not processed for further evaluation. Bentonite was further beneficiated to ensure a better concentration of silicon and aluminium ions. For beneficiation purposes, the obtained materials with particles less than 53  $\mu\text{m}$  were mixed with water in a separatory funnel. The obtained suspension was then gently agitated and let to settle over a period of 48 hours. After settling, the sediment (at the bottom of the funnel) was collected in a beaker and dried in the oven at 105°C. The beneficiated clay material (B.B) was then sent for characterisation.

Subsequently, the B.B sample was modified with 1M sulphuric acid solution; by mixing the sample with the prepared sulphuric acid in solid to liquid mass ratio of 1:3. The acid activation was carried out by heating the mixture suspension in a temperature controlled shaker at 98°C for 6 hours. The activated sample was filtered, and then the

precipitate was washed with deionized water. The resultant catalyst sample, B.B<sub>1M</sub>, was then dried overnight in the oven at 105°C. This was then let to cool before characterization.

Clay-based zeolite was synthesised by fusion of sodium hydroxide prior to hydrothermal synthesis. In this, an amount of kaolin (N.K<sub>2</sub>) was mixed with 4 M NaOH solution, under stirring for 24 hours in a temperature controlled shaker at 100°C. The mixture was then let to settle, after which the resultant NaOH fused kaolin cake (sediment) was dried at 105°C overnight. The dried sample was then calcined in a muffle furnace for 3 hours at 700°C, resulting in metastable phase of kaolin (metakaolin). To prepare the zeolite batch mixture, sodium silicate solution was then added and mixed onto the metakaolin under stirring for 2 hours at room temperature. Solutions of sodium hydroxide and Tetrapropylammonium bromine (TPABr) were separately added to the mixture, followed by addition of required amount of deionized water. The entire batch mixture was further stirred for one hour at room temperature, during which the pH of the mixture was adjusted to around 11 by dropwise addition of sulphuric acid. Drops of ethanol were then added to the resultant gel, which in turn was transferred into autoclaves. The Teflon autoclaves were put into an oven for hydrothermal synthesis at 175°C for 48 hours.

The resultant sample (recovered solid product) was cooled, filtered, washed with deionised water; and then let for drying at 105°C overnight. This was then calcined for 5 hours at 600°C. The calcined clay-based zeolite obtained, was further protonated with 1 M ammonium chloride solution (NH<sub>4</sub>Cl), under stirring for 6 hours at 100°C. Washing, filtering, drying followed by calcination, as done for the unpromoted zeolite was (as above) similarly applied to the resultant (recovered) solid protonated product, H-ZeoClay. The above protonation procedure was similarly repeated using a commercial zeolite catalyst (ZeoCOM), to obtain H-ZeoCOM.

#### Sample Characterization

All the clay-based materials produced using the mentioned procedures were then sent for Energy-dispersive spectroscopy (EDS), Scanning Electron Microscopy (SEM) and X-Ray diffraction (XRD) analyses. The EDS and SEM characterizations used to determine the elemental composition and morphology of clay samples; were performed on a FEI Nova NanoSEM 230, equipped with an Oxford

X-Max 20 mm<sup>2</sup> EDS detector, operating at an accelerated voltage of 5 KeV. The XRD carried out to determine the crystallinity and mineralogical phase of samples, was performed on a Bruker AXS operating with Cu-K $\alpha$  radiation ( $\lambda K\alpha_1 = 1.5406 \text{ \AA}$ ) and equipped with LynxEye detector. Origin (version 8.5) and XRD Match software (version 3.1) were used for the interpretation of XRD data.

#### Catalytic activity tests

The catalytic activity of the samples was evaluated in a fixed bed reactor with ethanol as feed. To evaluate catalyst performance, an appropriate amount of each individual catalyst produced was then loaded and evaluated for ethanol conversion in a stainless steel-tubular fixed-bed reactor at 350°C for 6 hours and at 2h<sup>-1</sup> weight hourly space velocity (WHSV).

In a typical evaluation test, ethanol was fed continuously into the reactor using a pump. The reactor was fitted with a thermocouple required for measuring and controlling reaction (furnace) temperature. The product leaving the reactor was cooled; the condensate liquid product was collected accumulatively in a flask and the gaseous product was collected using Tedlar bags. The reaction products were analysed using gas chromatography. The liquid product was analysed using a pre-calibrated Gas Chromatography-Flame Ionisation detector (GC-FID) equipped with a polar capillary column that detects for diethyl ether, C<sub>5</sub>-C<sub>8</sub> (mainly aromatics BTX) hydrocarbons in the sample. The gas product was analysed using a Gas chromatography-Mass Spectroscopy (GC-MS) equipped with a non-polar column that mainly detects for C<sub>1</sub> - C<sub>5</sub> hydrocarbons in the product.

Conversion of ethanol (EtOH conv.) was determined in terms of moles (N) by using the initial amount of ethanol in the feed relative to final amount of unreacted ethanol present in the product as shown below.

EtOH conv (%) =

$$\frac{N_{\text{Ethanol feed}} - N_{\text{Unreacted Ethanol in the product}}}{N_{\text{Ethanol feed}}} \times 100 \quad (1)$$

Selectivity of hydrocarbon product (C) was determined by accounting for the yield of C over the total product yield in mole (N<sub>total</sub>).

$$\text{Selectivity of C (mole \%)} = \frac{N_{\text{C in reaction product}}}{N_{\text{total of product}}} \times 100 \quad (2)$$

## Results and Discussion

### Catalyst characterization

#### Elemental composition of clay-based catalysts

EDS analysis from an average of three scans was used to determine the elemental composition of the various clays/minerals and their precursors. The results as shown in Fig. 1 implies that all the samples have relatively similar basic elemental composition, however they vary quantitatively as reported by many researchers [1, 17, 18]. The amount of Si and Al in the investigated samples is highest compared to other elements in the samples; however, oxygen is considered an exception considering that it serves as an elemental linkage in the clay structure. The major proportion of Si and Al in turn serve as evidence for the potentials of the considered samples to be used as aluminosilicate catalysts.

Modification of the non-modified bentonite (N.B) by beneficiation led to enrichment of the sample in Si content by 6.23%, and a decrease in percentage content of Al by 5.65 %, as seen in Fig. 1.

Beneficiation therefore increases the Si/Al ratio of the sample from 1.07 (N.B) to 2.83 (B.B).

Upon further modification of B.B with sulphuric acid (resulting to B.B<sub>1M</sub>), the Si content in the sample decreased (by 10.33 %) while the concentration of Aluminium (Al) further decreased by 3.56%. Acid modification, unlike clay beneficiation led to decrease in Si/Al ratio of the catalyst (2.83 to 2.75). It is suggested that the acid treatment led to a decrease of an aluminosilicate structure.

B.B<sub>1M</sub> (Acid modified bentonite) and N.K<sub>2</sub> (non-modified kaolin) were further used as precursors for the hydrothermal synthesis to obtain clay-based zeolites. During the ageing step, using B.B<sub>1M</sub> as a precursor resulted in a hard substance that was found unsuitable for zeolite synthesis. Hence only the sample produced using N.K<sub>2</sub> was further considered. The N.K<sub>2</sub> sample was successfully transformed to H-ZeoClay, which due to sodium silicate supplement to N.K<sub>2</sub>, resulted to Si/Al ratio of 23 as confirmed by EDS data. The protonated commercial zeolite on the other hand that was used as a standard catalyst had a Si/Al ratio of 50.

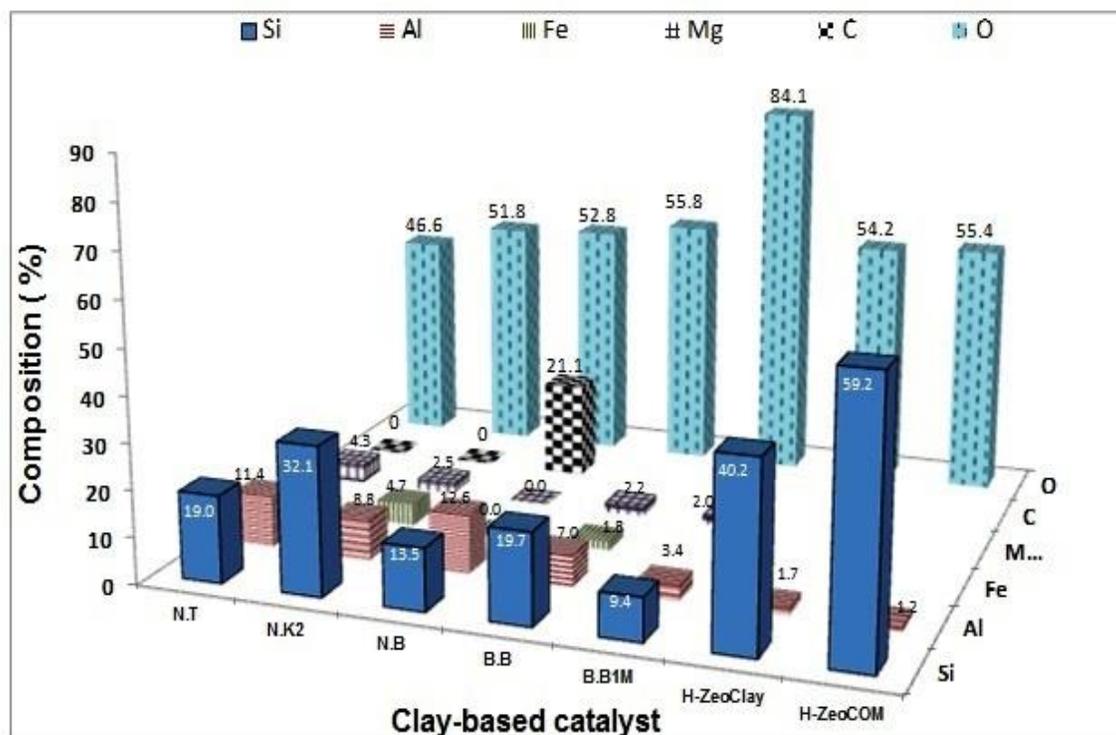


Fig. 1: Elemental composition of the various clay-based catalysts.

### Mineralogical composition of clay-based catalysts

The mineralogical composition of clay is among the properties found to have impact on their catalytic performance on ethanol conversion. Clay-based catalysts were found to contain numerous minerals, which could possibly be promoters or poisons towards ethanol conversion. The mineralogical composition of clays was determined through their XRD analyses

The core mineralogical content (phase) identified in bentonite catalyst (starting material) were montmorillonite, silica quartz and an aluminium-silicate based mineral phase. Fig. 2 shows that N.B (bentonite) catalyst contained 42.6% of montmollonite phase by mass; 48.8% silica quartz and 8.6% alumimium-silicate based mineral phase. The montmorillonite phase found in bentonite ascertains the identity of bentonite and often is referred to as the chief mineral content in bentonite [2].

Beneficiation carried out on the selected material (N.B), was intended to concentrate the sample in Si/Al ratio and also to reduce the non-clay mineralogical phases present in the sample. Beneficiation, followed by acid modification, was found not to have effect on the qualitative nature of the clay sample, however resulted to quantitative difference in mineralogical composition other than reduction in non-clay minerals as intended. Fig. 2 represents the various phases found in bentonite.

The natural bentonite fraction of particle size less than 53  $\mu\text{m}$ ; initially contained large amount of quartz about 48.8% and amorphous aluminosilicates phase about 42.6%. The proportion of these two mineralogical components ascertains that elemental silicon is found in large amounts in bentonite.

Beneficiation of bentonite clay sample as observed in Fig. 2, resulted to drastic increase in concentration of quartz (48.8 to 89.4 %), while decreasing the concentration proportion of montmorillonite phase in the sample (24.6 to 4.4 %). Further modification of the sample (B.B) with sulphuric acid, led to recovery in the concentration proportion of montmorillonite phase to 32.9% and drop in the concentration of the quartz component phase by 24.8 % (89.4 to 64.6 %). Reduction in particle size fraction below 53  $\mu\text{m}$  as a result of beneficiation, was the main cause of enrichment in the quartz content since quartz consist of very tiny particles that accumulated into the sample through screening. Minimization of both quartz and aluminium silicate phase by acid modification was due to leaching off effect of sulphuric acid on both minerals by the modification.

While beneficiation and acid modification resulted to sample's particle size fraction below 53  $\mu\text{m}$ , both modifications jointly led to increase in silica quartz content by 15.8 % (From 48.8 to 64.6 %), and slightly decrease in both montmorillonite and amorphous aluminium silicate by 9.7 % (42.6 to 32.9 %) and 6.1 % (8.6 to 2.5 %) respectively.

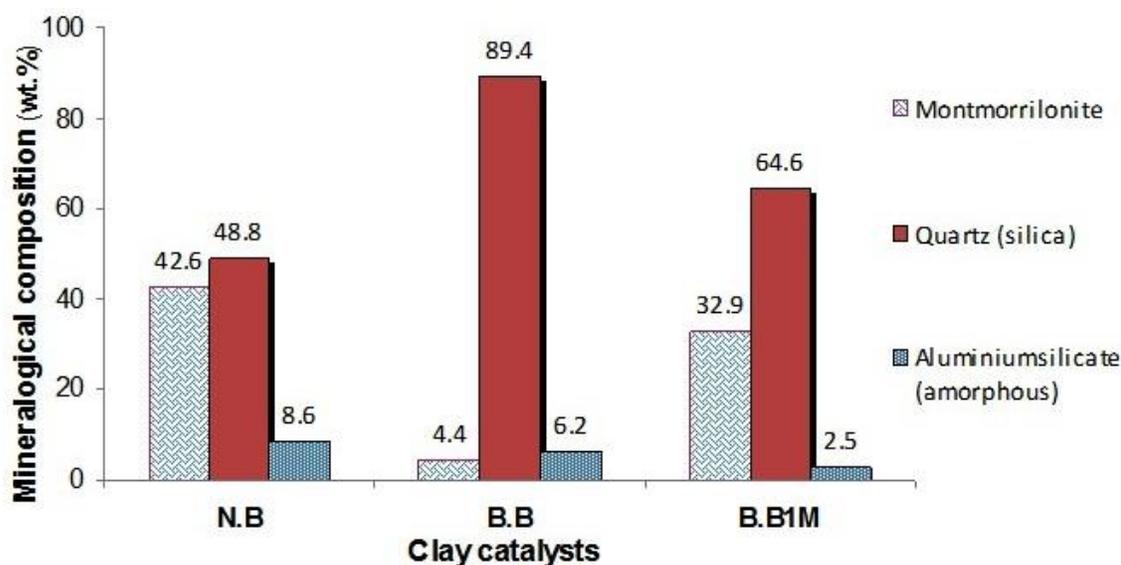


Fig. 2: Effect of beneficiation and acid modification catalyst mineralogical composition.

### Structural morphology and XRD correlation of clay-based catalysts

The morphology of the non-modified clay samples was investigated using scanning electron microscopy (SEM). Fig. 3 shows the micrographs of bentonite and modified bentonite samples, which appear not to have a distinct morphology and hence, beneficiation and acid modification were found not to have significant effect on morphology of clay sample.

The morphology of H-ZeoClay (Clay-based zeolite) derived from kaolin, is revealed through SEM in Fig. 4 (A1 and A2) to consist mostly of cuboidal and rectangular crystals, including a relatively small proportion of spheroidal crystal units. This morphology corresponds to the ones of ZSM-5 crystals reported in literature; such as work of Rownaghi *et al.* [8] who has similarly reported on the dominance of cuboidal and small proportion of spheroidal morphology of zeolite catalysts. The standard H-ZeoCOM (commercial zeolite) on the other hand, was also similarly revealed to consist dominantly of cuboidal particles (micrographs B2 and B3). This sample also consists of small fraction of rectangular and pyramidal crystals (micrograph B1). The dominance in cuboidal crystal morphology of both H-ZeoClay and H-ZeoCOM samples, was mostly observed with increase in magnification of the SEM micrograph (A2, B3). Similarity the morphological structure of H-ZeoClay, H-ZeoCOM and that of several zeolites in literature [8, 11], prove that the clay-based zeolite synthesised in this work

(H-ZeoClay), successfully correlates to actual zeolite structures.

The XRD data reported in Fig. 5 shows the diffraction pattern of H-ZeoClay and H-ZeoCOM. A doublet at  $6-10^\circ 2\theta$  and a triplet at  $22-25^\circ$  were observed along the diffraction pattern of H-ZeoClay and; these are the most significant peaks that correspond to that of ZSM-5 in literature [11, 19, 20]. This therefore proves that the clay-based zeolite produced in this work represents the structural framework of ZSM-5 zeolite. The interpretation of XRD data through Match software revealed that the H-ZeoClay sample correlates with the stipulated ZSM-5 XRD pattern by 86.92%. This high Fig of correlation or crystallinity proves an outstanding phase similarity between H-ZeoClay and conventional ZSM-5 zeolite catalyst.

Further on as observed in Fig. 5, the XRD pattern of H-ZeoClay was found to correlate with that of H-ZeoCOM (standard zeolite) in respect to almost all diffraction peaks. H-ZeoCOM as closely comparable to H-ZeoClay, was found to correlate to the stipulated ZSM-5 XRD pattern by 87.58 %. The ZSM-5 XRD pattern was obtained from database of zeolite structures built in XRD Match software (version 3.1) and supplied as data files interpreted through Origin XRD software (version 8.5). This further proves the similarity between the synthesised H-ZeoClay and the H-ZeoCOM and successful synthesis of ZSM-5 zeolite from clay.

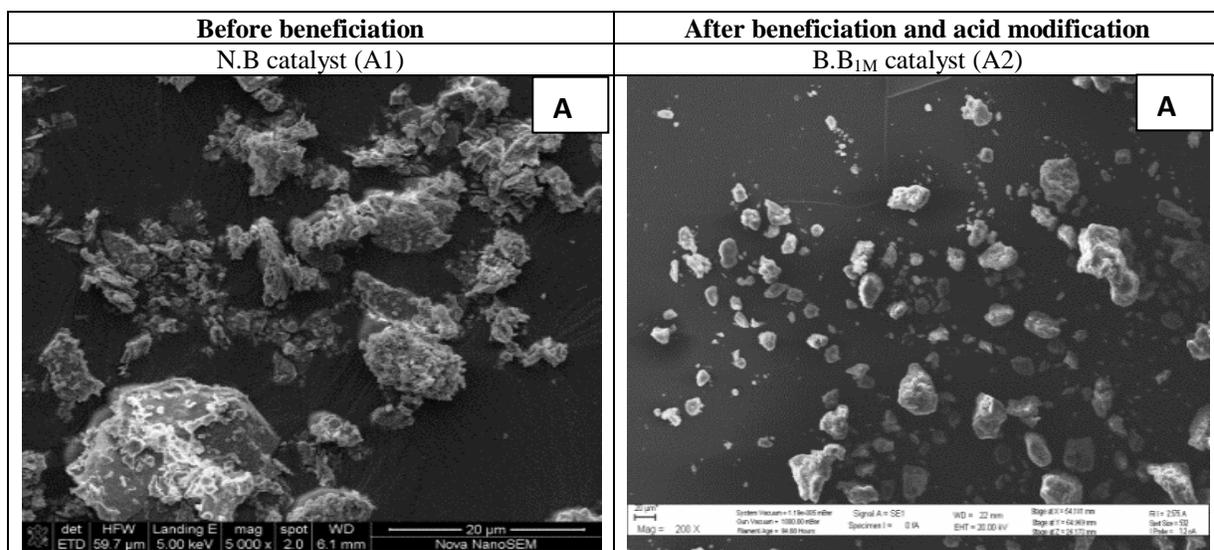


Fig. 3: SEM image of N.B (non-modified) and B.B<sub>1M</sub> (acid-modified) samples.

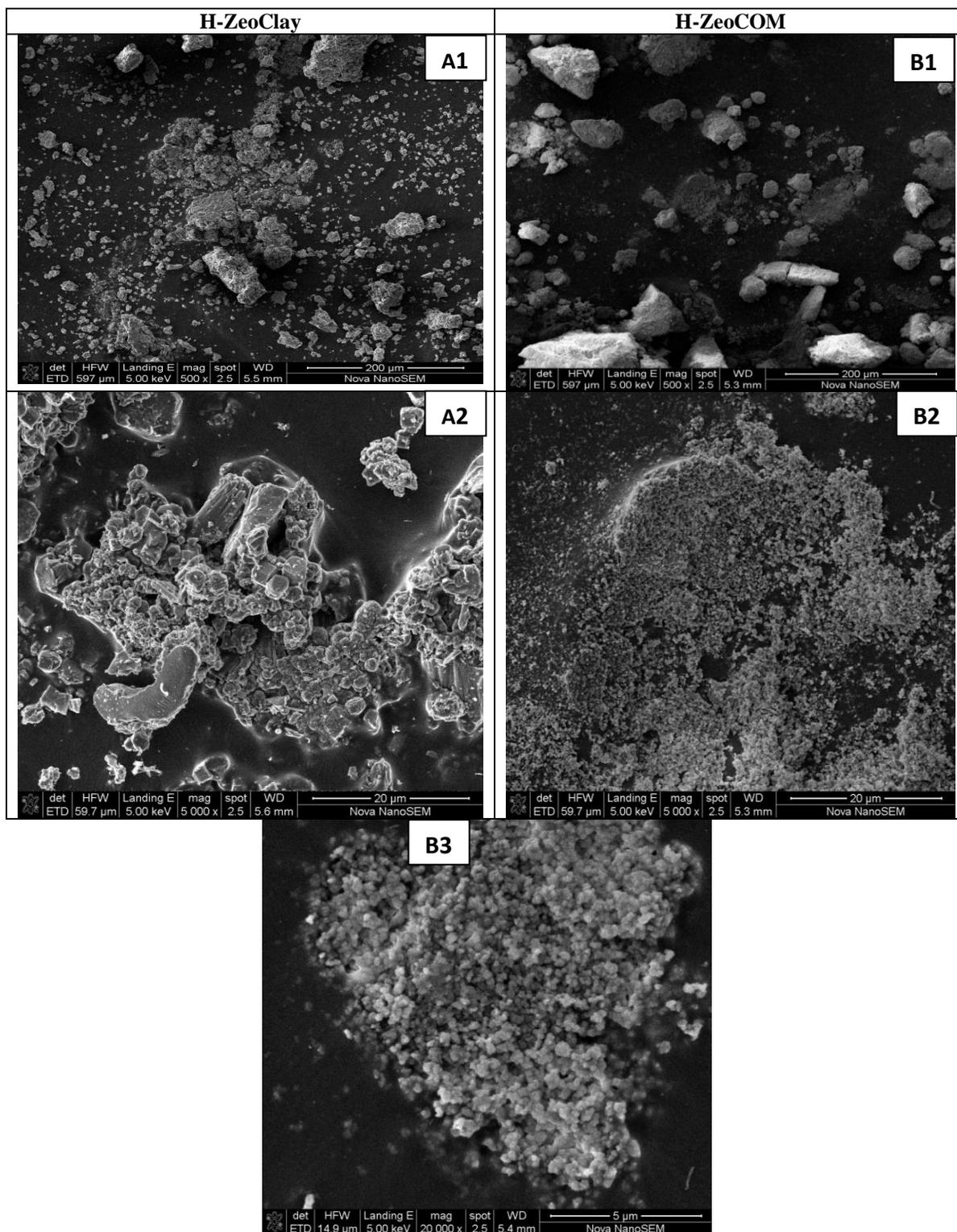


Fig. 4: SEM micrographs of H-ZeoClay (A2, A3) and H-ZeoCOM (B1-B3).

### Catalytic performance of clay-based catalysts on ethanol conversion

All the prepared clay-based catalysts evaluated in this work, were found active for catalytic conversion of ethanol to hydrocarbons (Fig. 6). This aligns to findings from work done on clays and zeolites by numerous researchers [9, 6, 7]. Among the non-modified clays, N.B resulted in highest activity of 84.95 % ethanol conversion. Beneficiation and acid modification of the N.B sample (i.e. NB to B.B<sub>1M</sub>) further resulted to increased activity of the catalyst in ethanol conversion of 87.3 %. This further increased to 99 % over H-ZeoClay.

Slight increase on ethanol conversion as a result of clay beneficiation and acid modification, may be accounted based on change in acidity as Si/Al ratio changed. The observed variation in catalyst morphology (from quadrilateral to pentagonal

crystals) as well as reduction in particle size due beneficiation and acid modification; are additional determinant factors that could have increased catalyst activity. It was also observed that the phase of silica quartz in clay, which slightly was enriched in the sample as a result of beneficiation and acid modification (Fig. 2), was jointly active with montmorillonite to have achieved the above increase in ethanol conversion. Variation in the concentration of mineralogical composition of clay however, as compared to other properties mentioned, in overall was found to have minor impact of the clay's performance on ethanol conversion.

Fig. 6 shows the activity of clay-based catalysts, accompanied by Table 1 which additionally reports on their corresponding product distribution and selectivity during ethanol conversion.

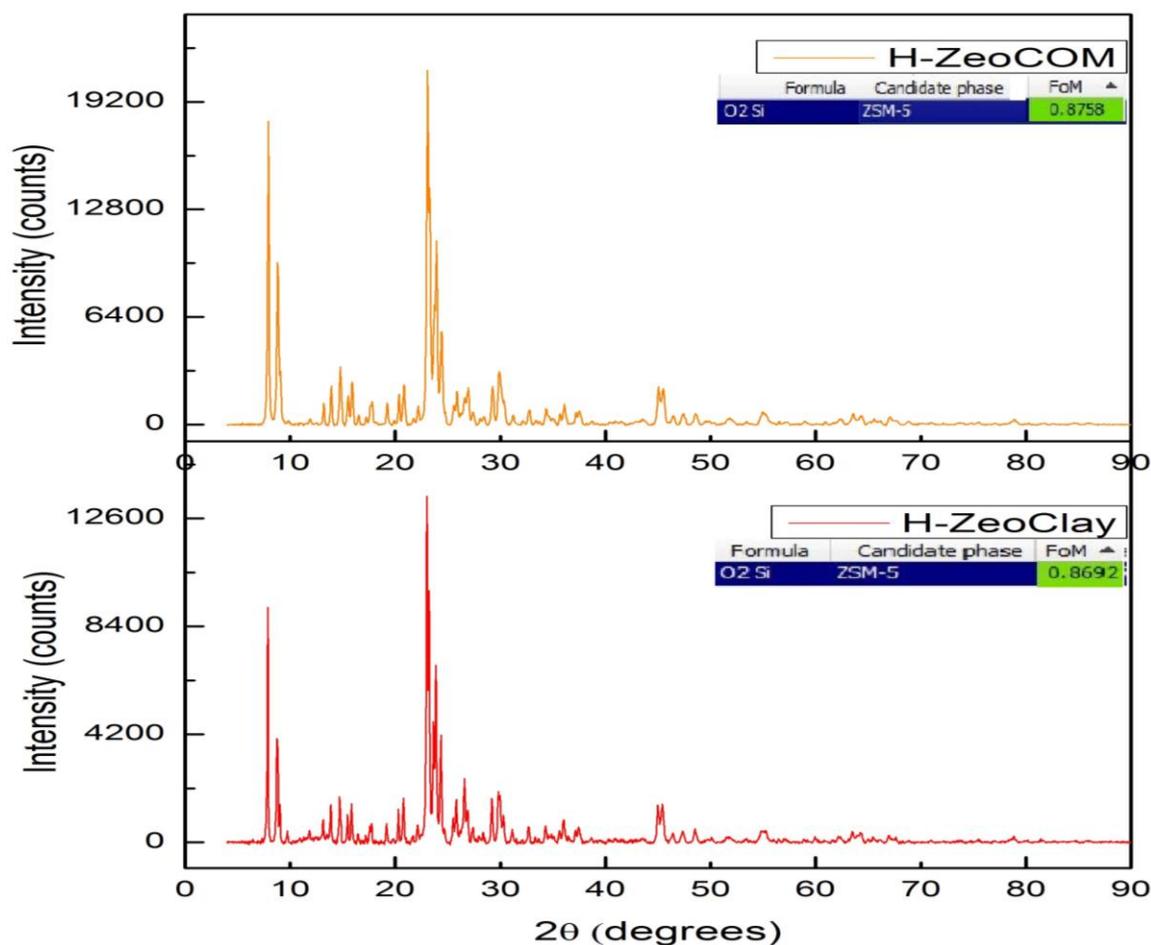
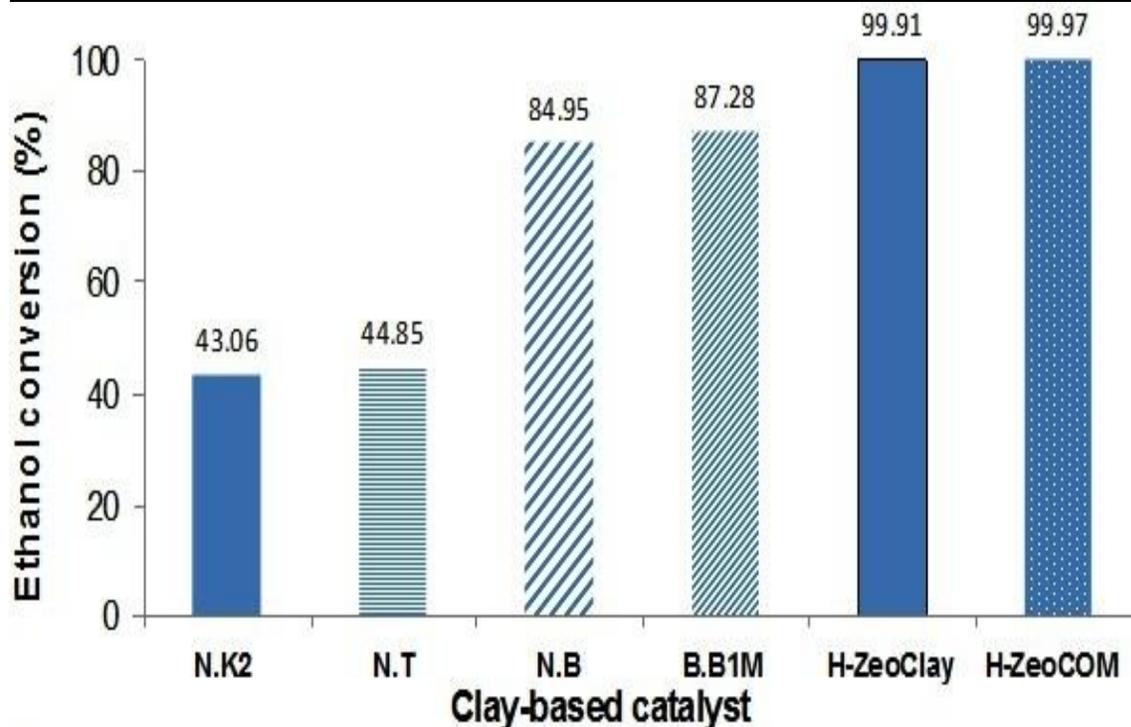


Fig. 5: XRD pattern of clay-based zeolite (H-ZeoClay) and commercial zeolite (H-ZeoCOM) with their respective Fig of Match (FoM) to ZSM-5.

Table-1: Product selectivity and distribution of some hydrocarbons over clay-based catalysts (T = 350 °C, WHSV = 2 h<sup>-1</sup>, TOS = 6 hour).

Clay-based catalysts	EtoH conv. (%)	Liquid and gaseous product selectivity (Mole %)									
		Alcohols			Diethyl ether		Olefins	Paraffins	Aromatics		
		EtOH	BuOH	MeOH	Liquid	Gas	(C <sub>3</sub> -C <sub>5</sub> )	(C <sub>3</sub> -C <sub>5</sub> )	Benzene	Toluene	Xylene
N.B	84.95	7.99	1.87	2.47	1.9	31.4	10.33	5.16	-	-	-
B.B	81.01	5.28	0.73	0.73	1.36	44.97	18.15	9.08	-	-	-
B.B <sub>1M</sub>	87.28	5.29	0.76	2.03	2.98	30.86	17.37	2.68	-	-	-
H-ZeoClay	99.91	0.035	-	-	7.51	-	37.89	21.73	2.11	3.135	2.41
H-ZeoCOM	99.97	0.017	1.8	-	1.9	-	22.71	14.64	7.13	16.12	9.38

Fig. 6: Activity of clay-based catalysts on ethanol conversion [T = 350 °C, WHSV = 2 h<sup>-1</sup>, Time-On-Stream (TOS) = 6 hour].

It is worth noting that kaolin (N.K2) which initially had an activity of less than 50 %; was transformed successfully to ZSM-5 catalyst with an activity of more than 99% (H-ZeoClay).

This activity resulted to be the highest among all clay-based catalysts at fixed given reaction conditions, and proved to be comparable to ethanol conversion activity obtained over H-ZeoCOM (commercial zeolite). The activity of H-ZeoClay unlike B.B<sub>1M</sub> or other non-zeolite clay-based catalysts is attributed to the sample's stronger acidity caused by its greater Si/Al ratio of 23; which is more than 10 times greater than this property in non-zeolite clay-based catalysts. The dominance of spheroidal particles in H-ZeoClay is an indication of the sample's larger surface area with regard to the higher activity as compared to non-zeolite clay-based

catalysts; which the latter rather consisted of pentagonal and relatively small surface area crystals.

H-ZeoClay and H-ZeoCOM were the only catalysts that had selectivity to BTX (Benzene, toluene and xylene) in the liquid product. N.B and B.B<sub>1M</sub> in comparison to zeolite (H-ZeoClay and H-ZeoCOM), were exclusively selective to both light alcohols and non-condensed diethyl ether collected at high temperature in the gas product. Water in the product obtained over clay-based catalysts (Table 1), represents the fraction of between 25 and 39 mole % (4 - 17 wt. %).

According to Wiswanadham *et al.* [11], gasoline fuel is stipulated mainly for aromatics and paraffins components; which surprisingly the H-ZeoClay was found to be exclusively selective to

BTX (Aromatics) and had the highest selectivity to paraffins and olefins among all clay-based catalysts. This coincidence or cohesion then makes H-ZeoClay the only clay-based catalyst suitable for gasoline production in this work (As comparable to H-ZeoCOM).

Moreover, H-ZeoClay had the highest selectivity to diethyl ether (7.51%) in the liquid product; whereas other than paraffins and olefins, were the most common hydrocarbon component obtained over both non-zeolite (N.B and B.B<sub>IM</sub>) and zeolite (H-ZeoClay) clay-based catalysts. The relatively high selectivity of H-ZeoClay to paraffins reveals the occurrence of hydrogen transfer (HT) reaction during ethanol conversion [11, 10] and this majorly was due to strong acidity of the sample. The HT reaction however was limited since the product obtained over H-ZeoClay was dominated with olefins more than paraffins; calling for the necessity to enhance the acidity of H-ZeoClay in order to obtain rather higher and the desired proportion of paraffins suitable for high quality gasoline.

#### *Effect of temperature on ethanol conversion and product selectivity*

Increase in temperature for ethanol conversion over H-ZeoClay was found to have insignificant impact on the activity of the catalyst

under fixed reaction conditions (2 h<sup>-1</sup> WHSV, 6 hour time-on-stream). This is observed in Fig. 7.

Aromatics, paraffins, olefins and diethyl ether were yielded over H-ZeoClay at both reaction conditions of 350 °C and 400 °C. Although similarity in product composition at both reaction temperatures still adhered to the stipulation of gasoline fuel, slight variation in proportions of respective hydrocarbon components in the product were observed as discussed below.

The slight increase in the yield of olefins and paraffins as shown in Fig. 8 is believed to have been prompted mainly by the endothermic nature of the reaction other than the performance of the catalyst during ethanol conversion. The drop in the yield or selectivity of aromatics (BTX) as observed might have been induced due to several reasons, of which one includes the observed reduction in the yield of diethyl ether (5.11 to 4.71 %). Diethyl ether as observed in the reaction path of ethanol in Scheme-1 is among the precursor hydrocarbons for the obtainment of aromatics. Decrease in selectivity of aromatics could have also been induced due to decrease in stability of H-ZeoClay caused by the sample's subjection to an elevated thermal reaction condition. This reveals the possibility of carbon deposit on the sample and reduction on its porosity during ethanol conversion.

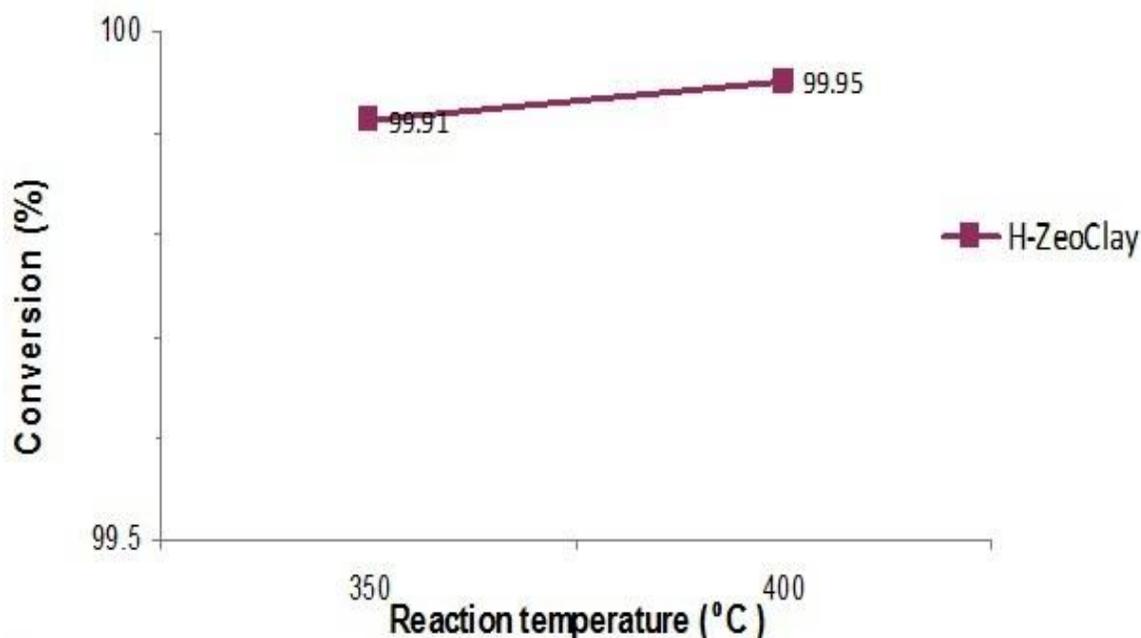


Fig. 7: Evaluation of ethanol conversion with increase in reaction temperature (T = 350 °C, WHSV = 2 h<sup>-1</sup>, TOS = 6 hour).

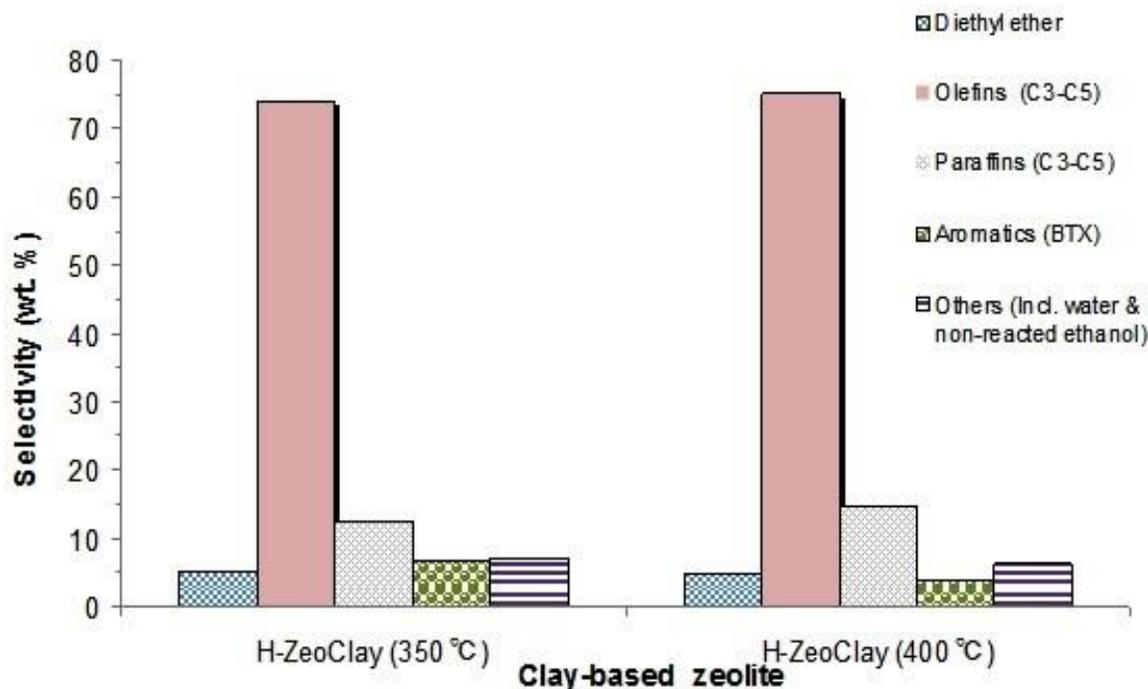


Fig. 7: Evaluation of product selectivity over H-ZeoClay with increase in reaction temperature (WHSV = 2 h<sup>-1</sup>, TOS = 6 hour).

## Conclusions

Different clay materials have been evaluated as potential candidates for production of zeolite and subsequent application in ethanol conversion. Si/Al ratio was successfully increased through clay beneficiation and acid modification and these modifications resulted to variation in the mineralogical composition of clay. EDS analysis revealed that zeolite catalyst of Si/Al ratio of 23 was successfully produced from clay material and the morphology of the sample consisted dominantly of cuboidal crystals. The XRD data confirmed that the clay-based zeolite sample resulted in the ZSM-5 phase by 86.92% and as closely comparable to the yardstick commercial zeolite by 87.58%. Clay-based catalysts produced showed high activity in the conversion of ethanol to petrochemicals, and over 100% boost in activity was observed for NK2 on transformation to H-ZeoClay. Clay-based zeolite in turn presented itself as a suitable and potential catalyst for the production of gasoline.

## Acknowledgments

The authors are grateful to Centre for Images and Analysis (CIA) at the University of Cape Town, Agrifood Station (Food Technology Department), Chemical Engineering Department at

the Cape Peninsula University of Technology, and iThemba Labs, South Africa and Directorate for Research and Postgraduate support, Durban University of Technology.

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