

On The Synthesis of Zeolite Y/ZSM-5 Composite via Novel Technique

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Abstract This work focused on the development of Zeolite Y/ZSM-5 Composite via a novel synthesis strategy and thereafter determine its structure, chemical composition, morphology, surface area and pore size. Zeolite Y/ZSM-5 was developed via a novel two step crystallization process, under static hydrothermal conditions. Microporous precursor gel containing the nucleus of zeolite Y was first developed and used in the development of zeolite Y/ZSM-5 composite in the second step. The XRD analysis of the synthesized composite showed high crystallinity of approximately 71 %. It also possessed a DR pore diameter of $3.2 \times 10^{-2} \mu\text{m}$, Lewis to Bronsted acid site ratio of 0.287, particle size of $0.816 \mu\text{m}$, Si to Al ratio of 42, pore volume of 0.089cc/g and BET surface area of $277.3 \text{ m}^2/\text{g}$. The characterization result for the composite showed that both zeolite Y and ZSM-5 were present in the composite. Hence, the synthesized zeolite Y/ZSM-5 possesses good acid site, surface area, pore volume, particle size, high silica to alumina ratio and crystallinity, and it is potentially suitable for use as a fluid catalytic cracking catalyst.

Keywords: composite zeolite, novel, hydrothermal, pore size, two step crystallization

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1. Introduction

Crude oil is a complex mixture of hydrocarbons and some sulfur, nitrogen and oxygen containing organic compounds, however Nigeria crude oil is low in its sulfur content hence 'sweet' therefore easy to process. One of the basic challenges faced by the Nigeria refineries is the ineffective conversion of the residue from atmospheric and vacuum distillation column (often referred to as heavy molecular weight hydrocarbon such as heavy gas oil and vacuum gas oil) into more valuable product (primarily high octane gasoline), these is the basic function of the fluid catalytic cracking (FCC) unit of the refinery [1]. The profit maximization of the refinery is dependent on the extent to which this refining step is effective. Hence, the need to focus research on these area, to help solve these challenge. Zeolite is the basic catalyst used in the fluid catalytic cracking unit of the refinery, for its molecular sieve property, high acidic nature, high thermal stability and high selectivity for gasoline yield [2]. Zeolite Y is the primary zeolitic component in FCC catalyst [3]. Common modifications carried out on zeolite Y to improve its catalytic performance includes the development of ultra-stable zeolite Y (USY) and rear earth metal ultra-stable zeolite Y (REUSY), where USY is formed via the dealumination of zeolite Y and REUSY is gotten when a rear earth metal is add to USY [4]. Furthermore, zeolite Y can also be modified by acid complex, hydrothermal treatment, with phosphoric or citric acid, ion exchange with ammonia, post synthesis using $(\text{NH}_4)\text{SiF}_6$ [5]. Zeolite

ZSM-5 is useful in various applications such as Fluid Catalytic Cracking (FCC), alkylation of aromatics, xylene isomerization and the disproportionation of toluene [6], for its unique shape and selectivity. Zeolite ZSM-5 can as well be modified via the incorporation of alkali earth metal, rare earth metal, and transition metals into the material as well as by post-synthesis modification through chemical vapour deposition (CVD) of silicon alkoxides, such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) [7]. Also calcination with different protocols, proper selection of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, steaming, treatment with acids or base can be used in modifying ZSM-5 [8]. The modifications listed for ZSM-5 are however aimed at controlling subsequent reactions from happening on the surface, also to stop the transmission of unwanted products from the zeolite pore [9]. However many more modifications for the both zeolite Y and ZSM-5 are possible.

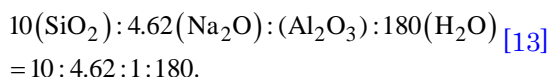
Nevertheless, most industrial processes such as FCC reaction are complex, hence the use of a single zeolite type catalyst may not serve effectively in meeting the requirement for elevated performance which could include high activity, notable selectivity as well as suitable resistance to deactivation, therefore the need to focus more research on the synthesis of composite zeolite catalyst [10]. Composite zeolite are made up of two or more zeolite-zeolite or zeolite-non zeolite phase [11]. Recent advance in FCC catalyst has been tailored towards the modification of zeolite Y. Research has shown that zeolite ZSM-5 is a suitable additive to zeolite Y [12]. The shape selectivity of ZSM-5 provides the refiner certain

benefits which includes; increase in gasoline octane number without change in conversion, increase in coke or dry gas yield, also ZSM-5 provides the refiner with a less rigid procedure, also with a very orderly addition of ZSM-5 the refiner can easily modify gasoline octane number and LPG olefin yield, these less rigid strategy helps to enhance increased profit, this strategy can also be used to reduce change in octane number with change in feed quality [13]. Till date the Nigeria refinery rely on the importation of zeolite catalyst, hence the need for local researchers to focus on the synthesis of these catalyst. This paper focuses on the development of zeolite Y/ZSM-5 composite via novel synthesis strategy and this is intended to afford the refinery operation of benefiting the synergistic effect of the two important zeolites.

2. Materials and Methods

The materials used in this synthesis were; diamines as structure directing template agent, sodium hydroxide as the alkaline medium (98% purity), aluminum hydroxide as aluminum source, and sodium meta-silicate solution (from Hopkin and Williams Ltd., 8 wt.% Na₂O, 27 wt.% SiO₂ and 0.006 wt.% Impurities) as the source of silica, deionized water (supplied by Chemical Engineering Department Federal University of Technology Minna), zeolite Y and ZSM-5 as seeds (supplied by Zeolyst International, with 80 SiO₂/Al₂O₃, and 0.05 wt.% Na₂O).

Zeolite Y/ZSM-5 composite zeolite was synthesis in a Teflon-lined autoclave under static hydrothermal conditions by a two-step procedure. The first step was the preparation of micro-porous precursor gel (zeolite Y) using the batch molecular formula;



The seeding gel for the micro-porous precursor was developed by adding 1.2693g of zeolite Y to 3gH₂O at room temperature and stirred for two hours until a homogenous solution was formed. The feed stock gel (zeolite Y) was prepared by adding 1.2229g of NaOH to 9.0197g deionized water, the mixture was mixed thoroughly until homogenous, then 0.5016g aluminium oxide was added and mixed until all aluminium oxide was dissolved in the NaOH solution, lastly 6.9229g of Na₂SiO₃•9H₂O solution was slowly added under constant stirring for 2 hours at room temperature [4]. The seeding gel was added to resultant mixture, stirred thoroughly to give the micro-porous precursor gel which was aged in a plastic beaker for 2 days then transferred into a 50 ml Teflon-lined stainless steel autoclave and crystallized at 100°C for 7 hours in an oven [4]. After cooling at room temperature, the gel was obtained and used as the micro-porous precursor for the synthesis of Y/ZSM-5 composite.

The final step involved the synthesis of the composite Y/ZSM-5 molecular sieve having the batch molecular formula;



22.5427g sodium meta-silicate solution was added to 22ml deionized water and 0.4574g zeolite ZSM-5 (which served as seed for ZSM-5) was added to the resultant mixture, these was aged for 2 days at room temperature

and served as the structure directing agent for ZSM-5 in the composite with no additional organic template used, it also served as the source of extra silica for the composite, after aging it was introduced drop wise into the micro-porous precursor gel (zeolite Y) from step one and stirred thoroughly for 2 hour [4], the pH value of the solution was adjusted to a range of 11.0–11.5 by adding diluted aqueous H₂SO₄ in drops and stirred thoroughly. The resultant gel was transferred into a 50ml Teflon-line stainless steel autoclave and crystallized at 180°C for a period of 2 days [14]. The autoclave was removed from the oven and place in a stream of running cold water to quickly bring it temperature down to room temperature, after cooling the autoclave was opened, the solid product was recovered and washed on a filter paper with copious amount of distilled water and suction dried till all the water drains out, then dried over night at 100°C. The product gotten was weighed and designated as zeolite Y/ZSM-5 composite.

The synthesized zeolite Y/ZSM-5 composite sample was then characterized using X ray diffraction (XRD) to determine its structure, Fourier transform infrared (FTIR) technique to determine the functional groups, Scanning electron microscope (SEM) to determine its chemical composition and morphology, and Brunauer-Emmett-Teller (BET) to determine its surface area, pore size and architecture.

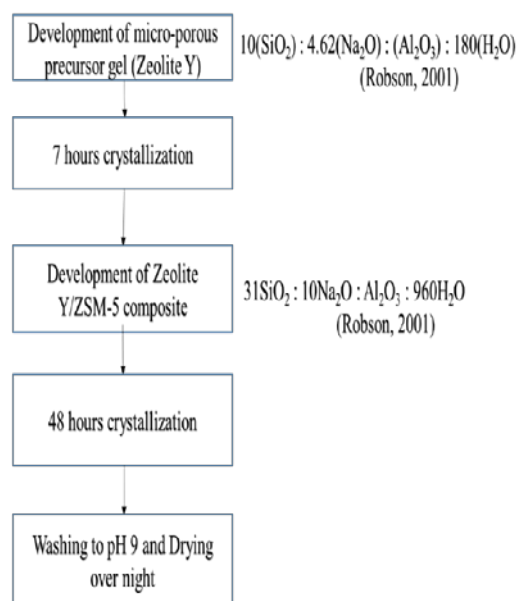


Figure 1. Illustration of the novel steps used

3. Results and Discussion

Powdered XRD was used to determine the sample crystallinity. Its Bragg's angle was scanned from 2 to 40°. XRD result obtained for the synthesized zeolite composite was used in calculating its percentage crystallinity [15] and a value of approximately 71% was obtained. These conclusively show the level of crystallization that took place as result of strong nucleation occasion by the presence of the seeds and subsequent crystal growth. The result gotten was similar to that gotten by Subotic [16]. The XRD pattern for the synthesized zeolite Y/ZSM-5 possessed both the characteristic peaks of standard zeolite

Y and that of zeolite ZSM-5, similar to that obtained by Tianbo [12]. The peaks for both Zeolite Y and ZSM-5 existed together, indicating that the two zeolite were fused together, the peak with the highest intensity was zeolite Y with a Bragg's angle of 12.17° , while that of ZSM-5 was obtained at 9.545° . These could be attributed to the fact that the nucleus of zeolite Y was synthesized first while ZSM-5 was an additive. The XRD pattern for commercial zeolite Y, ZSM-5 and synthesized zeolite Y/ZSM-5 composite are presented in Figure 2.

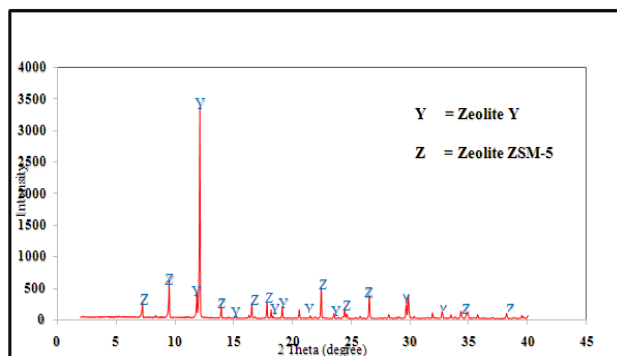


Figure 2. XRD pattern of the Synthesised Zeolite Y/ZSM-5 composite

The FTIR spectroscopy of the composite is shown in Figure 3. The result gotten tallied with that for standard zeolite material, where the most predominating band in zeolite occurs within the range 1250–950, 790-650, and 500-420 cm^{-1} [14], the most predominant band of the developed Y/ZSM-5 composite were observed at 1093.67, 693.33, and 482.22 cm^{-1} . Hence, the vibration band at 1093.67 represents asymmetrical stretching mode (OTO), 782.16 represents the symmetrical stretching mode (OTO), and 482.22 represents the T-O bending mode of TO4tetrahedra of the composite. The bands on 696.33 and 391.56 cm^{-1} were due to external linkage vibration and pore opening vibration respectively. The vibration band near 550 cm^{-1} has been assigned to the presence of five-membered ring structure, zeolite ZSM-5 in these case [17]. However these is absent in the result obtained, but Jensen pointed out that impure samples of Pentasil (ZSM-5) show an absorption band near 450 cm^{-1} in this case at 482.22 but does not show any at 550 cm^{-1} [17], these may be the reason for the absence of these band in the result obtained, since the product synthesized is not a single phase zeolite but a composite. The FTIR spectroscopy of the composite presents the vibrations band characteristics of zeolite ZSM-5 such as;

1. Asymmetrical stretch (external vibration) near 1225 cm^{-1} in these case 1424.48 cm^{-1}
2. Asymmetrical stretch (internal vibration) near 1093 cm^{-1} same as that gotten from the result at 1093.67 cm^{-1}
3. Symmetrical stretch (external vibration) near 790 cm^{-1} in the case 782.12 cm^{-1}
4. T-O bend at 450 cm^{-1} similar to that obtained at 482.22 cm^{-1} [17].

The FTIR spectroscopy also presents the vibrations band characteristics of zeolite Y such as 1108.14, 782.12 and 696.33 cm^{-1} indicating the vibration of tetrahedron similar to that gotten by Austin in his synthesis of zeolite Y [18].

Four hydroxyl group can be identified in the result obtained;

1. Vibration band at 3421.83 cm^{-1} normal polymeric OH stretch, these represent the hydrogen forms of fuajosite type zeolite (Y).
2. Vibration band at 3587.72 cm^{-1} represents OH group attached to Na^+ which compensates the negative charge of the framework.
3. Vibration band at 3741.06 cm^{-1} represents lattice termination silanol groups.
4. 3854.87 cm^{-1} OH bond, combination of stretching and bending.

Lewis acid site and Bronsted acid site are observed at band 1424.48 and 1654.98 cm^{-1} respectively, and their ratio (Lewis: Bronsted) was 0.287 which is low, but can be increased upon ion exchange to initiate the catalyst active site [19].

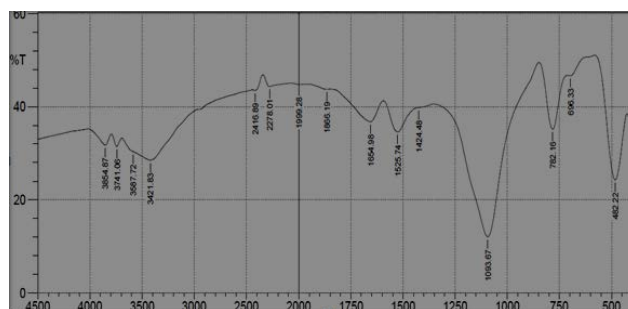


Figure 3. Morphology of zeolite Y/ZSM-5 composite

SEM was used to observe the morphology of the composite zeolite synthesized, its particle size as well as its silica to aluminum ratio. The result obtained showed the typical morphology of zeolite ZSM-5 which is an elongated hexagonal prismatic structure and that of zeolite Y which is octahedral, however these two structure appears to be fused together as seen in Figure 4. This is similar to that gotten by Hui [19]. These shows that the two zeolite were synthesized as a composite. The SEM result also showed that the composite zeolite synthesized has a sharp and clear crystallinity. The particle size of the synthesized zeolite from the SEM image was found to be 0.816 μm , while the silica to aluminum ratio was 42, these relatively high silica to aluminum ratio is due to the high silica requirement for the development of zeolite ZSM-5 these can however be further increased upon dealumination [14].

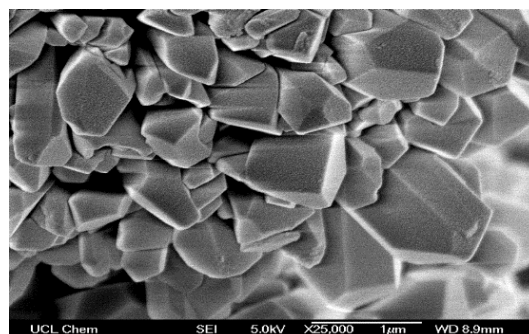


Figure 4. SEM image of the synthesised Zeolite Y/ZSM-5 composite

The synthesized zeolite Y/ZSM-5 composite exhibited a BET surface area 277.3 m^2/g this was same with the external surface area gotten using t-method, a micropore

volume of 0.089cc/g was determined using density Function Theory (DFT) method, while micropore half pore weight of 32.13Å was determine using Dubinin-Redushkevich (DR-plot) method and 0.1325µm pore radius was gotten using DFT method. The result gotten shows that the synthesized zeolite composite possess good surface area and pore volume necessary to make it an effective catalyst but these can be increased upon dealumination via ion exchange.

4. Conclusions

The result obtained from the synthesis and characterization of Zeolite Y/ZSM-5 composite via novel synthesis strategy showed that crystalline, micro-porous zeolite Y/ZSM-5 was successfully synthesized, since its morphology tallied with that for zeolite Y and ZSM-5. The characterization result for the composite showed that both zeolite Y and ZSM-5 were present in the composite. The synthesized composite possessed a DR pore diameter of 3.2×10^{-2} µm, Lewis to Bronsted acid site ratio of 0.287, particle size of 0.816 µm, Si/Al ratio of 42, pore volume of 0.089cc/g and BET surface area of 277.3 m²/g. Hence, the synthesized zeolite Y/ZSM-5 possesses good acid site, surface area, pore volume, particle size, high silica to alumina ratio and crystallinity.

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