A facile approach towards Hierarchical Zeolite Y Synthesis from Inexpensive Precursor

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Research Article

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Abstract

Microporous zeolite is one of the most utilized heterogeneous catalyst in many chemical reactions in process industries. It has a unique selectivity property, stability in high thermal reaction and porosity to enhance chemical reaction. The micropore associated with the conventional zeolites poses some constrains in reaction involving bulky reactant thereby causing deactivation of zeolite catalyst. Therefore, to overcome this constrain, a hierarchical structured zeolite catalytic material was proposed as it is known to have pores of difference dimensions which can overcome inaccessibility experienced in the smaller pore zeolites. In this work, a hierarchical zeolite Y catalyst was synthesized using a poorly crystalline inexpensive Aloji Kaolin from Nigeria as an aluminosilicate material through a facile modified Top down approach in which the zeolite Y was initially prepared from the kaolin via hydrothermal method and then followed by desilication using mild solution of sodium hydroxide. The synthesized hierarchical zeolite Y was characterized with the aid of powder X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), Brunauer-Emmett-Teller (BET) analysis. The synthesized hierarchical Y has crystallite size of 35.67nm, surface area of 18.1114m^2/g, pore size 50.676Å, and pore volume 0. 23178cm^3/g.

1. Introduction

Zeolite catalyst possesses unique structural pattern of regular arrays of pores, cages, channels and cavities of molecular dimensional orders. Zeolites Y are mainly used as catalyst due to their acidity, special pore structures, high thermal and hydrothermal stability [1]. The application of zeolite catalyst depends largely on their micropores which possess some constrain to bulky reactant and product. However, the small pore sizes impose restriction on molecular diffusion and mass transport within zeolite crystals and prohibit large molecules from accessing the intra-crystalline active sites [2]. Consequently, adsorption processes and catalytic reactions based on zeolites are often limited by slow diffusion, and zeolites are incapable of catalyzing reactions involving large molecules [3]

The development of hierarchical zeolite with qualities such as longer lifetime, high catalytic performance, postponed coking and deactivation will reduce the constrain observed in the conventional zeolite catalyst. Hierarchically structured zeolites combine the qualities of microporous zeolites and mesoporous materials to offer enhanced molecular diffusion and mass transfer without compromising the inherent catalytic activities and selectivity of zeolites. They are defined by the difference in their physical properties mainly pore size distribution. It contains more types of pores of difference sizes (micropores, mesopores and macro-pores) which can overcome transport limitation of the smaller pore' zeolites. It encompasses zeolite with at least a secondary pore – structure system [4]. Three are two methods of creating interconnectivity of mesoporous and microporous pore systems in zeolites [2]. There are two main approaches in hierarchical zeolite production, top-down and bottom-up. Top-down methods are used when available, or commercial zeolites are treated to create additional pores by etching part of it. The bottom-up approach is the creation of an additional pore in the zeolites during the synthesis of the zeolites by incorporating a pore directing substances (Mesoporogen) in the precursor gel. Hierarchical zeolites are mostly synthesized by either desilication or recrystallization of commercial zeolites [5–6]. Development of hierarchical zeolite is therefore, aimed at obtaining a catalyst with improved properties over that of the conventional microporous counterpart to enhanced their performance [7]. The hierarchical type zeolite is essentially more active and perform better in diffusion constrained reactions, such as those involving the transformation of larger substrate or those undertaken in the liquid phase. They have the essential attributes of activity, stability, selectivity, regenerability, longer lifetime, postponed coking and deactivation. The post-treatment of microporous zeolites enhances the catalytic performance and catalytic lifetime [8] [9][10]. There are many approaches to introducing mesopores into zeolites in the post treatment of parent zeolites. They are called top down method that includes dealumination [11] steam treatment [12], Dissolution-Recrystallization [13] and desilication. The zeolites have minor deactivation rate due to the high external surface area, mesopore volume, and pore mouth. The introduction of mesopores in a zeolite through desilication was performed with NaOH[14–19] and the alkaline treatment of zeolites Y mostly at 1–2 wt% NaOH at room temperature has revealed incredible mesopores formation as detected in the modification that led to Si-O-(OH)-Al bond[20].The silica extraction formed a framework structure creating tetrahedral extra framework lewis acidic aluminium [21]. There are other reagents that has been used to introduce mesopores in zeolites synthesis: Cetylmethlylammonium bromide (CTAB) (Tewodros *et al.*, 2021), Oxalic acid [22] NaHCO[23]. These reactions mostly occur in the presence of surfactants and involves high synthetic costs. Desilication processes as a means of introducing mesopores has mostly been conducted using commercial zeolites [24–29]. Hierarchical zeolite Y in this work was synthesized by post treatment of a conventional synthesized zeolites Y from Aloji Nigeria kaolin (ANK) by mild solution of sodium hydroxide, and protonating with ammonium sulphate. Researchers in the past two or three decades have investigated the suitability of kaolinite minerals for zeolite catalyst synthesis [29]. The synthesis of hierarchical mesoporous zeolites from kaolin is yet an unexplored area. The use of kaolin for the production of hierarchical zeolites catalyst is a research area that is just evolving and, in this work, ANK will be investigated as a potential source of silica and alumina for development of hierarchical zeolites Y.

2. Experimental Section

2.1 Kaolin Beneficiation and Dehydroxylation.

Raw ANK was mildly crushed to powder with mortar and pestle. 60g of raw kaolin was measured into a 250ml measuring cylinder containing 180ml of deionized water [30]. These was agitated to form slurry and allowed to free settle for 20 minutes. At the end of the settling time, the heavier (coarse) component settled and the kaolin sample (lighter fraction) remains as supernatant. The supernatant was decanted into different measuring cylinder and was allowed to settle for 24h. The settled clay sample, (the fine fraction, < 2 μm) was obtained after decanting the suspended deionized water. The clay sample was dried in an oven at 90 ^{0}C for 24h. and a refined ANK was obtained. Metakaolinization of ANK was achieved at temperature of 650^{o}C for 3 hours. The raw and calcined ANK was crushed and kept in a sealed container for XRD, SEM, TEM and BET analysis.

2.2 Synthesis of Hierarchical Zeolite Y by Modified Top Down Approach (Desilication).

These procedures are modification of the work of Van Aelst, *et al* [31] using a locally sourced, poorly crystalline kaolin Aloji kaolin as a source of aluminosilicate material and desilicating with a mild solution of NaOH. Sodium hydroxide pellets of mass 1.3 grammes was dissolved in 2 grammes of distilled water. The above solution was divided into two equal halves. 2.46 grammes of sodium meta silicate was added to one and 1.0 gramme of metakaolin to the other solution. The two mixtures were rigorously stirred for complete dissolution. The combined aluminosilicate gel was aged at 10 hours and crystalline in a Teflon-line stainless steel autoclave at 80^{o}C crystallization temperatures for 9 hours. The crystallized zeolite was washed with deionized water to a pH of 9 and dried at 110^{0} C for 8h. The as synthesized zeolite was denoted by YT5n.

The desilication of YT5n to hierarchical zeolite was conducted as follows.

A gram of synthesized conventional zeolite from ANK was treated with a mild solution of 0.2M Sodium hydroxide at 65 ^{o}C for 30 minutes. This zeolite was washed with deionized water to a pH of 9 and dried again at 110 ^{o}C for 8h. This mesoporous zeolite Y was protonated by ion exchange with 10ml 1.0 M NH_2SO_4 solution per gram of synthesized zeolite by soaking in the above solution for 24 h. The sample was filtered, dried in the oven at 100 ^{o}C for 3h and calcined at 550 ^{o}C for 3h. This hierarchical zeolite catalyst was denoted YT5.

3. Characterization

The synthesized zeolite was investigated for its crystallinity, morphology, textural structures and porosity by XRD, SEM, TEM and BET analysis. The X-ray diffraction pattern of as-synthesized hierarchical zeolite (YT5) was recorded on Bruker AXSD8 using nickel filtered CuKα X-ray radiation at 40kV and 30mA. The two-theta degree range was scanned from 5^{o} to 90^{o} with a scanning rate of 20^{o}/min. The morphology of YT5 was examined using a Hitachi SU-8010 scanning electron microscope. The composition of YT5 zeolite particles was analyzed with the energy-dispersion X-ray spectrometer (EDS) attached to the SEM. Transmission electron microscopy (TEM) was recorded by JEOL.JEM-2100 electron microscope operating at 200kV and the isotherms of nitrogen were measured at nitrogen gas temperature of 77K as adsorbate employed to obtain the Brunauaer-Emmett-Teller (BET) surface area adsorption, average pore size and pore volume of the hierarchical zeolites Y (YT5).

4. Results And Discussion

4.1 Refining and Dehydroxylation of Kaolin

The SEM images shows the kaolinite and a considerable high amount of quartz. The angular orientation of SEM of raw ANK denotes the high occurrences of quartz within the clay. Quartz is an insoluble mineral that exist within the kaolinite mineral. The SEM image of the refined ANK shows a platy morphology and hexagonal outline and are loosely packed which are attributes of kaolinite clay. The elemental composition of ANK has its Si/Al ratio approximately I.12.as indicated by the EDX Spectrum. The ANK has been adjourned to be a poorly crystalline kaolinite mineral with appreciable quartz content when compared with kaolin sourced from. Chokocho, Kankara, Egypt, Iraq and England with Si/Al ratio of 2.0, 1.23, 1.66, 1.53 and 1.17 respectively [32–33].

HRTEM analysis of the refined ANK shows a platy morphology and a hexagonal shape confirming the results of the SEM image of same kaolin in Fig. 2. The results of HRTEM image 2(a) shows that quartz is also agglomerated within the clay. The lattice plain is seen in the same direction typical of mono or single crystalline and single grain material in 2(b). The Selected Area Electron Diffraction (SAED) (c) has many isolated spots single crystalline scattered without distinct ring denoting single crystalline material [34].

The adsorption isotherm is a type IV and hysteresis of H4 according to IUPAC classification for a porous material. The hysteresis H4 is associated with narrow pores and internal voids of irregular shape that are connected [35]. The partial appearance of hysteresis loop signifies the inadequate pore in the kaolin. ANK has BET Surface Area of 14.1544 m^2/g, pore volume 0.071077 cm^3/g and pore size 18.3149nm.

4.2 Metakaolinization

The peaks of kaolin mineral are identified by comparing the compositional component of peaks diffraction intensity (Two Theta Degree) with the standard, the Joint Committee for Powder Diffraction Standard {JCPDS}. The peaks intensity of kaolin is the absorption peak at 2θ degree of 12.22^o. 24.81^o, quartz at 21.22^o, 26.27^o, cristobalite was 22.96^o and halloysite mineral at 11.68^o.

The use of kaolin as a source of aluminosilicate for synthesis of zeolite requires an improvement either by chemical method or by thermal treatment. The chemical treatment of kaolin is very difficult due to its low reactivity. The most effective way of improving kaolin is by thermal treatment (calcination) to obtain more reactive phase with loss of structural water and structural reorganization. The conditions of the kaolin calcination strongly influence the reactivity of the obtained solids. Kaolin dehydroxylates between 530 ^oC and 630 ^oC. The process is endothermic due to higher amount of energy required for the removal of the chemical bond of hydroxyl ions. The best conditions for obtaining a very reactive metakaolin have been discussed by several authors who reported values between 600–850°C [36–38]. The calcinations of Aloji kaolin was done at 650^0C for 3hours.The SEM and XRD results of the refined kaolin shows that the kaolin has a lot of impurities even after the refinement and for a reactive metakaolin to be achieved from such a low-grade kaolin. The XRD pattern of metakaolin exhibit some changes compared to that of kaolin. The disappearance of the diffraction peaks of kaolin, appearance of amorphous aluminosilicate as a result of thermal treatment of the raw Aloji kaolin. Metakaolin is an amorphous material. The highest diffraction peaks correspond to the presence of some crystalline phases of quartz at two theta value of

26.65^0[36]. It is due to the thermal stability of quartz which is an impurity in some synthesized zeolite from kaolinite. The SEM image of metakaolin is showing the amorphous phases and has no platy morphology and the characteristic crystallinity of kaolin has disappeared due to the thermal treatment [37].

4.3 Synthesis of Hierarchical Zeolite Y by modified Top Down Approach.

The results obtained from the characterization of as-synthesized zeolites Y (YT5) were as follow.

The XRD plots of as synthesized Hierarchical zeolites Y obtained by Bottom-Up approaches with YT5 synthesized using NaOH of 1.3 grammes, crystallized at 110 ^oC for 9 hours after aging for 10 hours. The peaks at 2 theta values of $6,13^o$, 10.34^o, 12.14^o, 14.65^o and 15.97^0. and more denotes zeolites Y. However, the peaks of 26.65^0 and 36.55^0 denotes the presence of quartz which is an impurity in synthesis of zeolites from kaolin. The crystallite size of 35.77nm was calculated from the XRD Pattern of YT5 zeolite with percentage crystallinity of 85.12%.

The SEM image of YT5 zeolites showing a spherical shape of hierarchical zeolites Y. These figures agree with the work of Bellaabed *et al.*, [39] who obtain a spherical shaped NaY. The EDX spectra revealed the elemental composition of YT5 zeolite showing the presence of Fe, Ti, S and Na. These elements are the impurities in the kaolin which depend largely on the source of the kaolin. However, the high percentage of Si in YT5 zeolite is expected of a faujasite zeolites framework [2]. They observed that the framework composition (Si/Al ratio) of zeolite catalyst can be tuned from 1 to infinite by altering the hydrothermal synthesis or post-synthetic modifications. Using Image J software, the diameter distribution was obtained, the higher distribution between 50 to 470nm give an average crystallite diameter of 225.19nm.

HRTEM analysis has been utilized as reputable method of characterization of textural material that afford a lot of proof of mesoporosity in hierarchical zeolites. It explains the internal structures of a hierarchical zeolites. It also provides better imaging resolution and perception into the interior structure of material. In view of the statement above, HRTEM analysis of YT5 zeolites was done and the images of Figs. 8 was obtained. At a magnification of 200nm, a Spherical shaped YT5 Zeolites was observed confirming the SEM image [39]. The results of HRTEM images (a) shows a spherical shape with flakes and white patches within the shape showing a porous YT5 zeolites. Quartz is also agglomerated within the crystal as an impurity in the synthesized YT5 zeolite. Grains formation is depicted by the lattice of different orientation in (b) and fringes measured using image j software to be 0.269nm. The higher magnification of the HRTEM images of as synthesized has notable numbers of grains in (b) typical of polycrystalline or nanomaterial [40]. The white patches in the images denote a porous material. The smaller grains and many pores in the magnified image of HRTEM will be responsible for large surface area.

The Selected Area Electron Diffraction (SAED) (c) has many small spots forming a diffusing ring, these crystallites give the spots arising from Bragg reflections giving rise to numerous spots forming diffused rings. The diffusing ring is due to the amorphization of the parent zeolite during mild alkaline treatment of YT5n to form hierarchical zeolites [41]. This phenomenon rings are that of polycrystalline or hierarchical material [34].

Nitrogen adsorption has been used to analyses the surface area and pore size distribution of porous materials. The pore size distribution, surface area and pore volume are the core characteristics of catalyst that determines the selectivity and accessibility of a probing molecules during a catalyzed reaction. The thermodynamic and transport of molecules in and out of the catalyst are determine by the porosity of the catalyst. The BET analysis of YT5 and YT5n was conducted and the following results were obtained. The gas adsorption desorption isotherm graph was plotted and shown in Fig. 9

The adsorption isotherm is a type IV and hysteresis of H4 according to IUPAC classification for a porous material. The hysteresis H4 is associated with narrow pores and internal voids of irregular shape that are connected. The narrow hysteresis loop observed at low pressure region of p/p^o of less than 0.2, is an evidence of presence of mesopores [35]. The presence of hysteresis loop at high pressure region of p/p^o greater than 0.2 is an indication of mesopores and macropores in the as synthesized zeolite YT5. This is an indication of silicon extraction by the mild alkaline treatment of the synthesized hierarchical zeolite. However, the adsorption capacity of YT5 is moderate due to the presence of quartz in the as-synthesized zeolites. The adsorption- desorption isotherm loop indicates a monolayer and multilayer adsorption in both the YT5n and YT5. The as-synthesized zeolite YT5 has BET surface area of $18.1114 m^2/g$, pore volume of $0.023178 cm^3/g$ and pore size of 50.676Å or 5.0676nm while YT5n has BET surface area of $11.0112 m^2/g$, pore volume of $0.040299 cm^3/g$ and pore size of 132.364Å or 13.236nm. The increase in the mesopores surface area of YT5 after desilication steps of YT5n proves that, there was a high dispersion of pores size in YT5 [28]. However, the different in pore size and pore volume observed in the YT5n and YT5 zeolites are due to dissolution and partial amorphization of YT5n during mild alkaline treatment. The etching of YT5n to the partial amorphization of the framework leads to blocking of pores with debris and silicon scraps etched from the framework [41].

The Barret- Jovner-Halenda (BJH) pore size distribution derived from the desorption branch of the isotherm revealed the presence of multi modal and hierarchical porosity. The sample YT5n has the highest peak at > 20Å and pore size ranging from 2nm to 65nm while the YT5 has its highest peaks at < 50Å and pore size ranging from 5nm to 90nm. The presence of large amount of micropores is expected in samples YT5n. However, the micropore has a remarkable reduction in YT5 owning to the desilication treatment with mild solution of NaOH which resulted in generation of larger pores of about 900Å. Aloji Nigeria kaolin has been utilized to developed a hierarchically structured zeolites Y.

Conclusions

Hierarchical zeolite Y was successively synthesized for the first time from poorly crystalline Aloji kaolin by modified desilication of parent zeolite synthesized from Aloji kaolin using 0.2M of sodium Hydroxide solution at 65^oC for 30 minutes. The Structure and the morphology of the synthesized zeolite was characterized with BET, XRD, FESEM and HRTEM. The results suggested that the modified top-down method was able to create a pore ranging from 2 nm to 90 nm as observed in the BJH plot for pore size distribution. A hierarchical zeolite Y with micro-mesopore was synthesized with spherical shape, polycrystalline structure and numerous grains. The mesopores zeolites Y has a crystallite size of 35.67nm, average crystallite diameter of 225nm, surface area of 18.1114m^2/g, pore size 50.676Å, and pore volume 0. 23178cm^3/g.

Declarations

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Conflict of interest

This research is solely the work of the authors and hereby declare no conflicts of interest.

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Figures

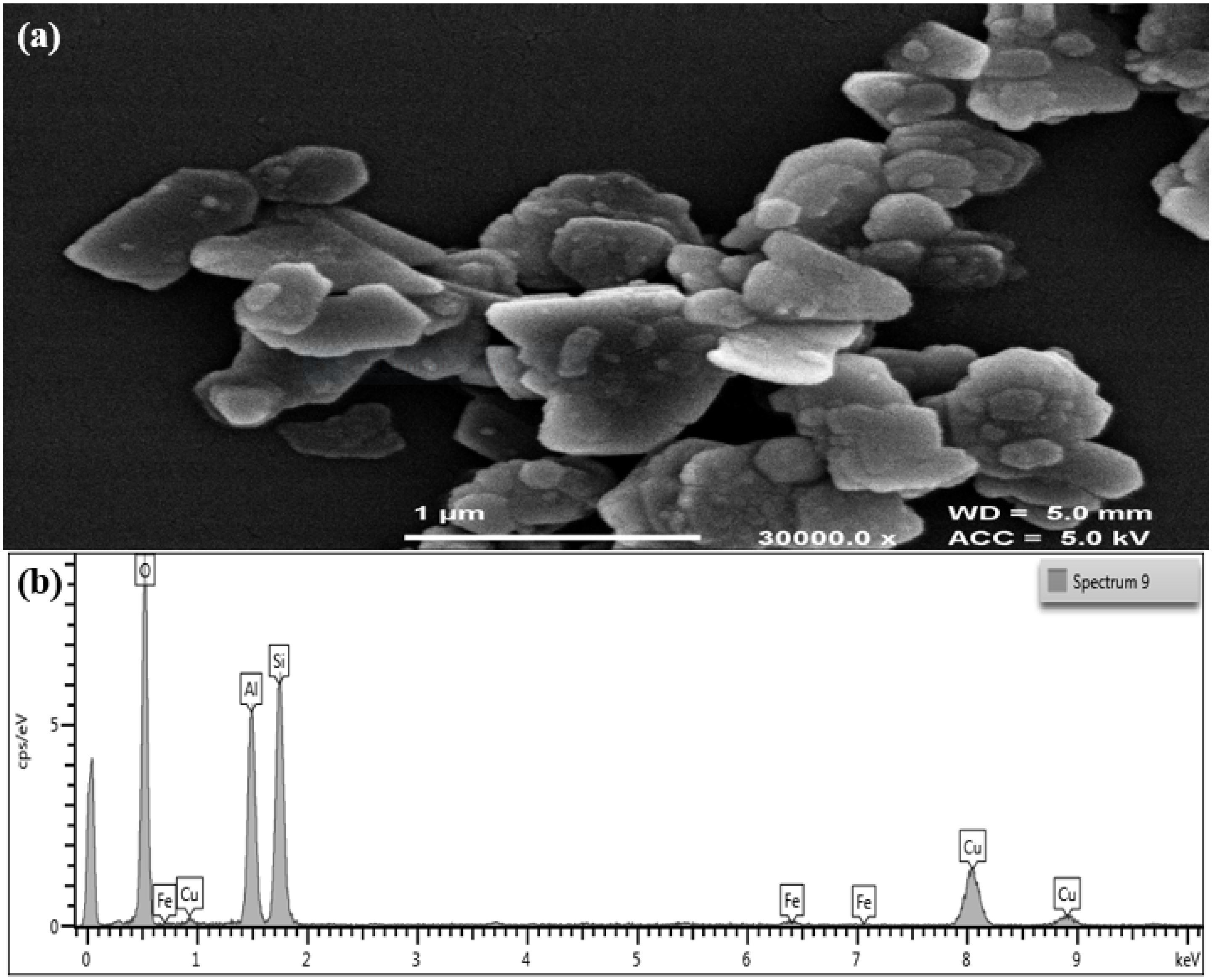

Figure 1

SEM image and EDX spectra of Refined Aloji kaolin

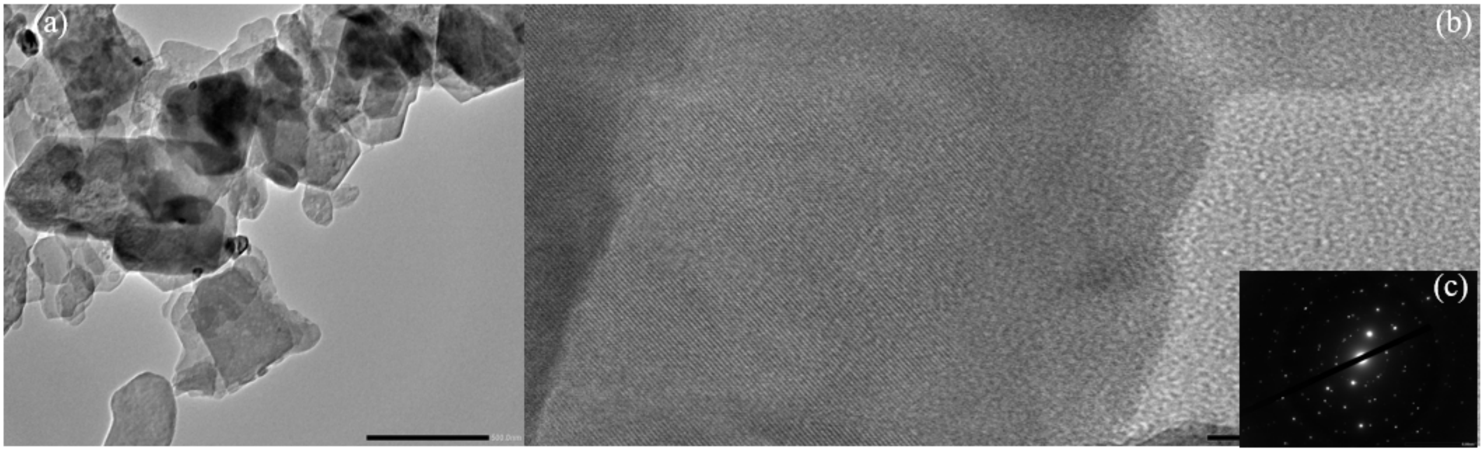

Figure 2

TEM images of Refined Aloji kaolin

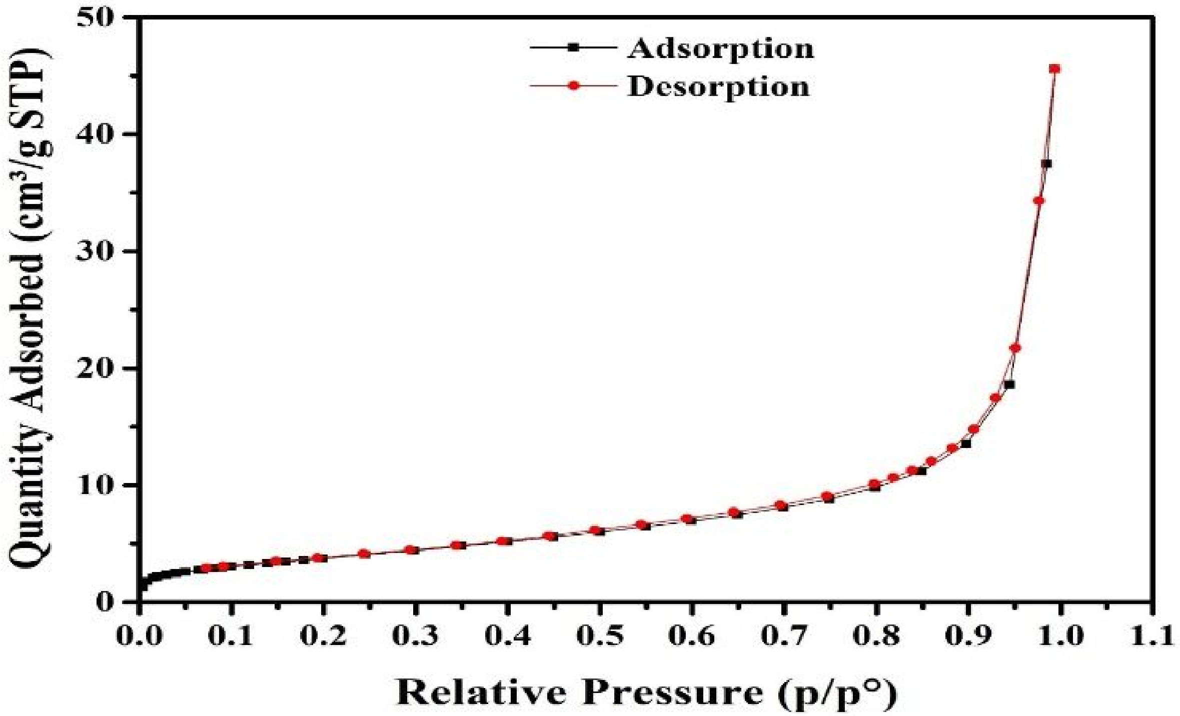

Figure 3

Nitrogen adsorption – desorption isotherm loops of ANK

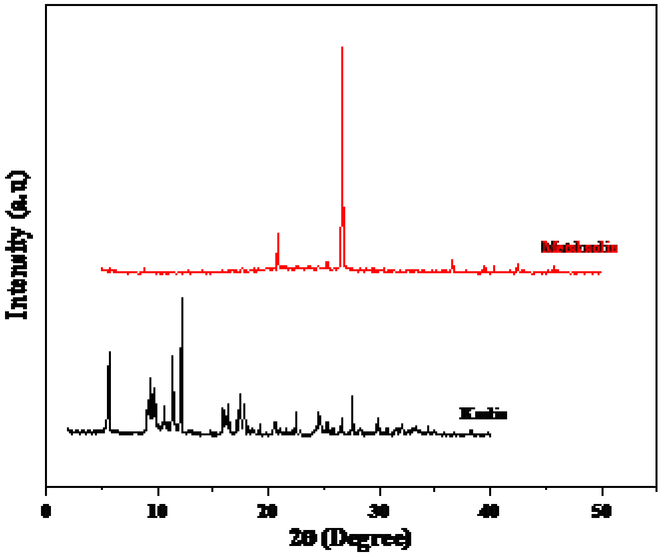

Figure 4

XRD Pattern of Refined ANK and Metakaolin calcined at 650^{O}C for 3h.

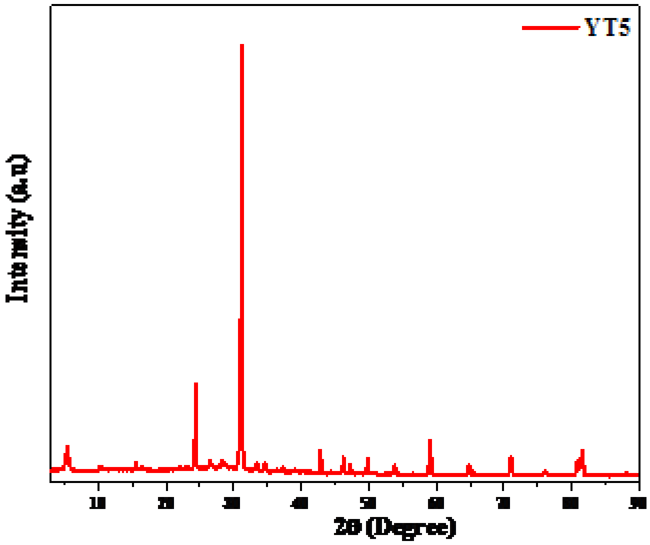

Figure 5

The XRD Pattern of Hierarchical zeolites Y (YT5).

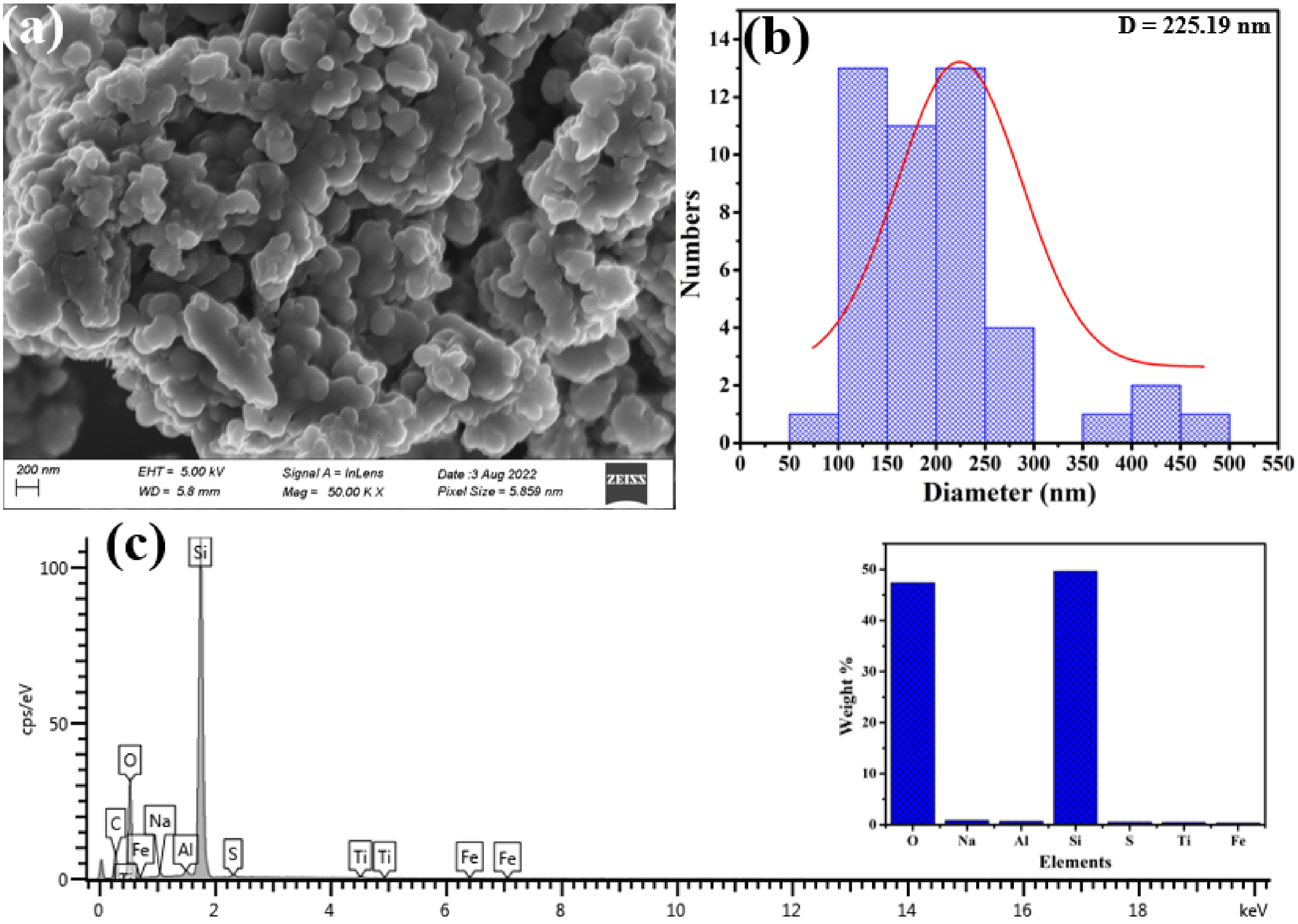

Figure 6

SEM images (a), crystallite diameter distribution (b) EDX spectra and Elemental percentage weight of YT5 zeolite

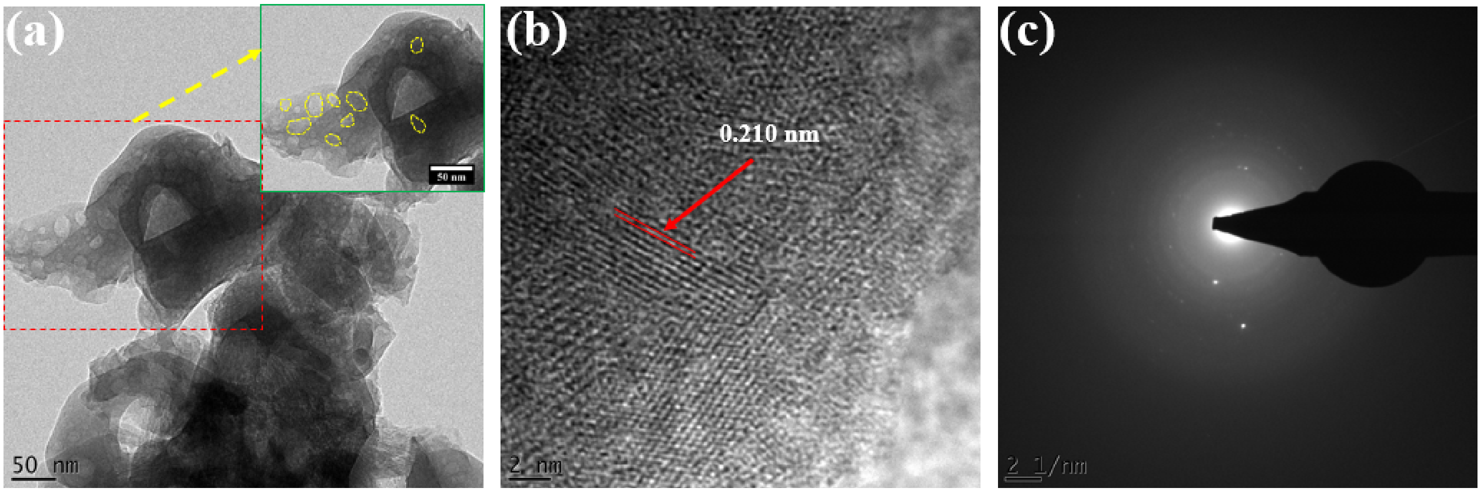

Figure 7

TEM image of YT5 Zeolite

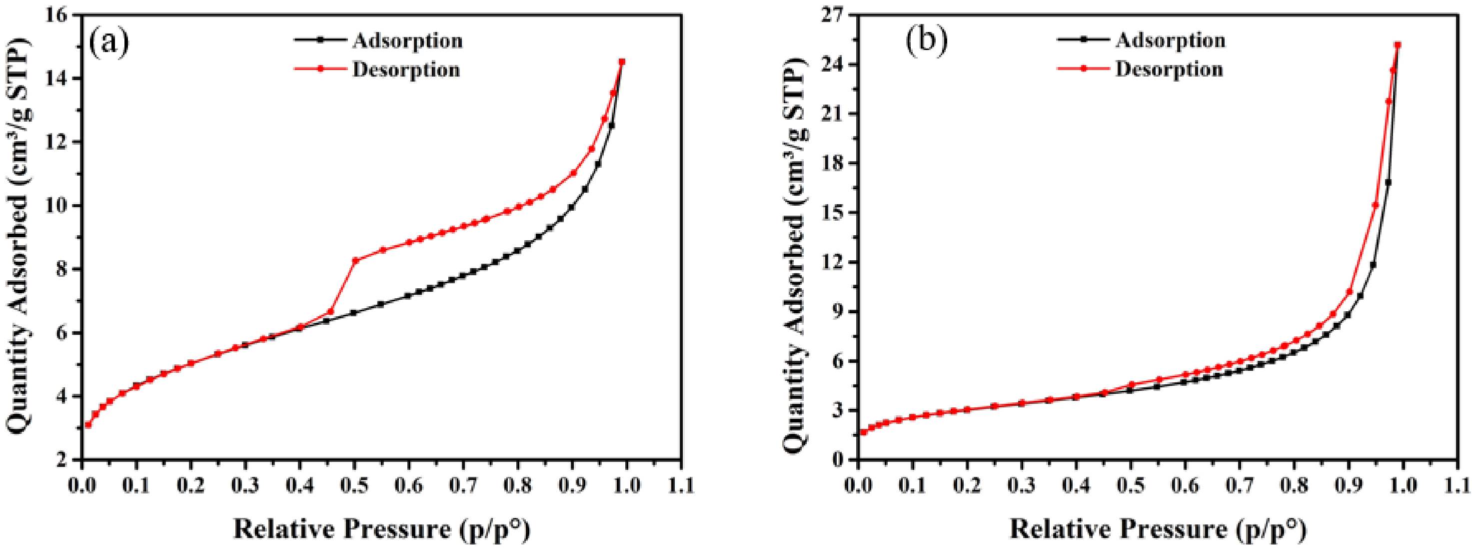

Figure 8

Nitrogen adsorption – desorption isotherm loops of (a) YT5 and (b)YT5n.

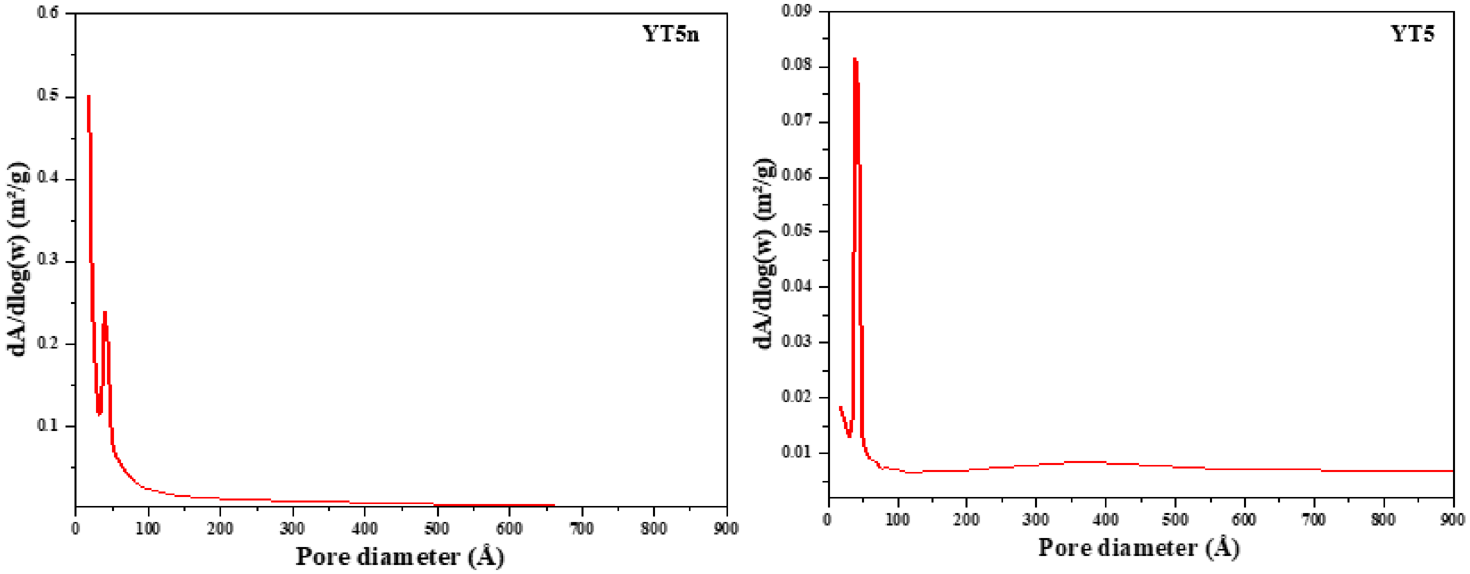

Figure 9

Surface area distribution of YT5n and YT5

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- floatimage1.png