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CONTENTS

Editorial Committee i
Content ii

Development and Performance Evaluation of a Baobab (Adansonia digitata L.) Seed Decorticator
Ola, F. A.; Ibrahim, S. O.; Sanusi, B. A.; Saleh, A. & Akande, F. B. 1 - 11

Processing Parameter Influence on the Mechanical Properties of Cast 7xxx Zinc-Modified Aluminium-Magnesium Alloy
Sekunowo, O. I.; Bolasodun, B. O. & Okpara, J. 12 - 19

Effect of Kaolin-based Zeolite and Cement on Physical Properties of Compacted Laterite Soil
James, O.; Sadiku, S.; Amadi, A. A. & Kovo, A. 20 - 28

Resource Assessment and Feasibility Study of River Oshin, Oro, Nigeria for Hydrokinetic Power Potential
Fagbenro, Oluwakemi Kehinde & Okewale, Oluwambo E. 29 - 37

Modelling of Groundwater Recharge of Otukpo Using Modified Soil Moisture Balance Methodology
Adesiji, A. R.; Adaudu, I. I.; Musa, J. J.; Gbadebo, A, O.; Asogwa, E. O. & Mangey, J. A. 38 - 46

Smart Bus Route Monitoring System for Federal University of Technology, Minna, Niger State
David, M.; Zubair, S.; Adejo, A. O.; Hamza, F.; Mamud, M. O. and Ebune E. 47 - 56

Evaluation of Groundwater Vulnerability to Pollution using Drastic-Based Fuzzy Logic System's Strategy for Selected Sites in Bwari Area Council, Federal Capital Territory, Nigeria
Otache, M. Y.; Adeoye, P. A.; Kuti, I. A. & Shaibu, R. 57 - 69

Review on Hierarchical Zeolite Beta from Kaolin: Synthesis Methods and Applications
Safiyanu, R. S.; Babashehu, A. S.; Afolabi, E. A.; Kovo, A. S. & Abdulkareem, A. S. 70 - 81

Paleoclimatic Reconstruction of Middle to Late Miocene Strata Evidenced from Palynological Study of Ida-4 Well, Eastern Niger Delta, Nigeria
Chukwuma-Orji, J. N. 82 - 93

Air Quality Sampling and Dispersion Model around a Power Generating Plant
Fagbenro, Oluwakemi Kehinde & Adediji, Victor Adebowale 94 - 106

Review on Hierarchical Zeolite Beta from Kaolin: Synthesis Methods and Applications

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Abstract

In order to overcome mass, diffusional transfer limitations and molecular accessibility in microporous zeolites, several researches have been carried out towards the synthesis of hierarchical Zeolite Beta catalysts comprising of micro/meso/macropores structures mainly using chemical reagent which are mostly hard to get and at times expensive . This review is focused on seeing the extent of research that have being done on the synthesis of hierarchical zeolite Beta from kaolin. Different synthetic methods and strategies of making Zeolite Beta as it relate to using readily available sources such as kaolin was discoursed and the catalytic application in various applications was highlighted .

Keywords: Zeolites, Beta, Hierarchical, Synthesis, Kaolin, Applications

Introduction

Zeolites are microporous, crystalline aluminosilicate minerals composed of 3-dimensional framework of silica (SiO_4) and alumina (AlO_4) tetrahydrally linked together by shared of oxygen atoms. The framework is an open structure where cations could locate within the materials pores. These cations neutralize the negative charge on the lattice of the framework. This movement of the cations gives the zeolite its unique ion-exchange and catalytic properties (Xu *et al.,* 2007). Although many zeolites exist in natural forms, most of the currently used zeolites are synthesized commercially or in autoclaves in the laboratory (Rissheng *et al.,* 2019). Zeolites are one of the most important groups of materials with wide range of applications in ion exchange, gas adsorption and catalysis (Li and Yu, 2014).

They are about 250 distinct framework structure of zeolites identified by the International Zeolite Association, but only 13 types have been used in commercial catalysis (Fernandez *et al.,* 2020), of these 13, only 5 (FERRIERITE, MORDENITE, ZSM-5 (five), FAUJASITE, and BETA) are produced in commercial quantity for catalytic application (Vogt *et al.,* 2015).

As one of the 5 most predominantly used zeolite materials, zeolite beta was first discovered in the laboratory by Mobil Research and Development in 1967. It possesses large micropores (0.55 x 0.55 nm and 0.76 x 0.64 nm) with 3-dimensionally 12-membered ring channels (Fernandez *et al.,* 2020), with high thermal and hydrothermal stability, high SiO_2 / Al_2O_3 ratio and outstanding catalytic properties (Shen *et al.,* 2008).

Zeolite beta has the following advantages:

- Due to its high Si/Al ratio, zeolite beta is hydrophobic and thermally stable at high temperatures, this property makes it useful in separation and catalytic applications such as vacuum gas oil hydrocracking and glucose alkylation (Du *et al.,* 2002),
- It is also applicable in hydrodewaxing and pour point lowering of petroleum (Tamer, 2006),
- Zeolite beta also possesses high acid strength (Bronsted and Lewis acids).

Even though, zeolite beta exhibit high performance superiority in diverse acid-catalyzed reactions, its practical application is greatly hindered by its high cost (Shen *et al.,* 2008,) and limited by mass transfer

diffusion when used as a microporous material (Yue *et al.,* 2016).

Therefore, much effort has been made by researchers to reduce its production cost (Xie *et al.,* 2008; Majano *et al.,* 2009; Lie *et al.,* 2010; Duan *et al.,* 2011) either by decreasing or eliminating the use of organic template which is expensive and also causes environmental pollution when the templates are removed from the zeolites by calcination and washing (Kamimura *et al.,* 2010a, 2010b) or substituting the synthetic organic chemical sources of silicon and aluminium with inexpensive, naturally occurring sources of silica and alumina such as Kaolinite, Rectorite and Diatomite (Duan *et al.,* 2011; Kovo, 2012; Yue *et al.,* 2016,). The use of these low-cost natural sources of aluminosilicate minerals with abundant reserves worldwide have been investigated by different researchers such as Caballero *et al.* (2007); Shen *et al.* (2008); Li *et al.* (2010); Holmes *et al.* (2011); Li *et al.* (2012); Ding *et al.* (2013); Liu *et al.* (2014); Yue *et al.* (2015); Yue *et al.* (2016); and Yue *et al.* (2019).

In addition to the high cost of zeolite synthesis, the diffusion limitation imposed by the sole presence of microporous channel system in zeolite is another challenge hindering the catalytic performance of zeolite beta (Tian *et al.,* 2016). To overcome this challenge, significant effort has been made by many researchers towards fabrication of hierarchical zeolite. Junliang *et al.* (2016), successfully synthesize hierarchical zeolite beta via the steam-assisted technique. Also, Yue *et al.* (2019), were able to successfully develop a green route to synthesized hierarchical zeolite beta from kaolin without the use of any organic template.

Hierarchical zeolite beta with bimodal pore systems integrating both microporous and macro/mesoporous structure have been employed to overcome the challenges faced by microporous zeolites (Yue *et al.,* 2014). H-Beta zeolites possesses enhanced intracrystalline diffusion rate of bulkier molecules, better catalytic performance and longer lifespan.

Kaolinite materials are abundant worldwide and have a Si/Al ratio (SiO_2 = 46.54 %; Al_2O_3 = 39.50 %; and H_2O = 13.96 %). Kaolin is a white colored solid with a brown-colored surface (Hartati *et al.,* 2020). The structure of kaolin is similar to that of zeolites, as such, kaolin has proven to be a good precursor in the synthesis of different kinds of zeolites. Kaolin have [$Al_2Si_2O_5(OH)_4$] chemical composition and can be converted to zeolites by hydrothermal action (Holmes *et al.,* 2011). This can be achieved by the thermal treatment of kaolin to obtain a more reactive phase metakaolin (Kovo *et al.,* 2009) and hydrothermal reaction of the metakaolin with an aqueous alkali medium to form the zeolite structure (Kovo, 2012). Kaolin consists of octahedral alumina sheets and tetrahedral silica sheets stacked alternately (Hartati *et al.*, 2020). Kaolin usually contains other minerals such as quartz, sulphur, micas, iron and titanium oxides. Therefore, the need to purify the kaolin before it can be used in synthesis. In 2015, Ayele *et al.,* synthesized zeolite A from kaolin via purification to remove quartz and mica impurities. Kaolin is extensively use as a raw material in the production of ceramics, paper coating, paper filling, rubber filler, plastic filler and cracking of catalyst or cement (Murray and Kogel, 2005).

Methods of Synthesizing Zeolites

Different synthetic methods such as solvothermal, hydrothermal, ionothermal, alkali fusion, alkali hydrothermal, alkali leaching, sol-gel, microwave and ultrasound energy methods have been employed from the literature to synthesize different types of zeolites (khaleque *et al.,* 2020). Among all the above methods, hydrothermal techniques is considered as the primary and simplest route to synthesized zeolite from kaolin and other aluminosilicate materials

(Cundy and Cox, 2005) via the following procedure:

1. Mixing of a reactant containing a silica and alumina source in an alkali medium (cation source),
2. Heating the reactant mixture at high temperature usually (> 100 ºC) in a sealed autoclave at autogenous pressure,
3. Increasing to synthesis parameters (temperature and time), the reactant mixture still remain amorphous,
4. Crystalline zeolite can then be detected after the above induction period,
5. The zeolite crystals can then be recovered by filtration, washing and drying (Hartati *et al.,* 2020)

The hydrothermal method is the only method that is capable of producing high-silica zeolites such as ZSM-5, Zeolite Beta and silicalites (Zhang *et al.,* 2017).

In 2016, Yue *et al.* synthesized pure-phase zeolite beta from natural aluminosilicate minerals (rectorite and diatomite) without quartz impurity. The synthesized zeolite beta with more brønsted acid sites exhibits excellent catalytic performance in the esterification of acetic acid with ethanol. The conversion of acetic acid and the selectivity to ethyl acetate was found to significantly increase by ca. 10% and ca. 7% respectively over the synthesized zeolite than over the reference.

Methods of Synthesizing Zeolite from Kaolin

Kaolin is transformed to zeolite by alkali fusion, direct transformation and metakaolinization.

2.1.1 Direct transformation of kaolin to zeolite:

Due to the unreactive nature of kaolin, only few successful researches have been published, on this challenging method. In 2008, Shen *et al.,* were able to synthesized zeolite beta using this method via hydrothermal process at 150 ºC 4 h by adding silicon in the crystallization reactions of kaolin with sodium hydroxide solution without calcination.

The role of Na_2O/SiO_2, SiO_2/Al_2O_3 and the ratio (amount) of TEAOH to SiO_2 are the most important parameters used to determine the formation of zeolite beta (Hartati *et al.,* 2020)

Other zeolites such as ZSM-5 (Hartati *et al.,* 2020), zeolite A, Sodalite and Cancrinite (Rios *et al.,* 2009) were also synthesized through the conventional hydrothermal method (Hartati *et al.,* 2020).

Transformation of kaolin to zeolites through metakaolinization:

Hydrothermal synthesis is the only method that can produce high silica zeolites such as Beta, ZSM-5, FER, and MFI etc. In this method, the kaolin is usually transformed into a more reactive phase (metakaolin) by calcining at a temperature of about 600 ºC. The heating process (dehydroxylation) removes water molecules from the kaolin to produce an amorphous aluminosilicate material (metakaolin) (Ilic *et al.,* 2010).

The silica/Alumina ratio will then be determined by adding a silica source or removal of alumina (dealumination). Zeolization is then carried out using hydrothermal process (Kovo and Holmes, 2010).

Fig. 1 illustrates general steps used during hydrothermal synthesis of converting kaolin to zeolite.

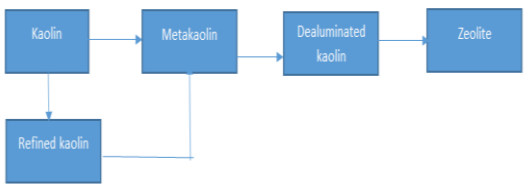

Fig 1.0 General steps for hydrothermal synthesis of kaolin to zeolite

Transformation of kaolin to zeolites by alkaline fusion:

This process is carried out by activating the kaolin with dry NaOH in a Teflon-coated porcelain crucible at about 600 ºC for 1 h. The mixture is then crushed and moisturized to the desired composition prior to the hydrothermal process. This is a bottom-up method. Only zeolite A (Ayele *et al.,* 2015 and Rios *et al.,* 2009), ZSM-5 (Hartati *et al.,* 2020), zeolite Y (Doyle *et al.,* 2016) and zeolite NaX (Chen and Lu, 2017) have been successfully developed using this method.

Table 1: Application of Kaolin in Synthesis of Beta zeolite and Hierarchical Zeolite Beta

S/N		Sources	Synthesis Method	Synthesis Parameters	Applications
1.	Xue *et al.*, 2019	Kaolin was used as alumina source Colloidal silica Zeolite Beta seed	Hydrothermal treatment Template-free synthesis	Crystallization Temp = 140 °C at 18 h. Calination Temp of 520 °C at 4 h.	Used in Esterification of acetic acid with benzyl alcohol
2.	Barakov *et al.*, 2019	Beta zeolite gel	Hydrothermal treatment	Crystallization Temp of 140 °C for 1-9 days $H_2O/Si = 2.5$-14.	Used in the reaction of bulky alcohols with 3,4-dihydro-2-pyran
3.	Tian *et al.*, 2016	Conventional Beta zeolite	Dealumination process	Calcined at 550 °C for 5 h. Urea Soln (5-20 wt %) At 80 °C for 1-8 h.	Applied in Nopol Synthesis
4.	Duan *et al.*, 2011	Kaolin used as the unique source of silica and alumina	In-situ hydrothermal crystallization method	SiO_2/Al_2O_3 = (~100) Crystallization temp of 170 °C for 30 h. Calination temp at 550 °C for 6 h.	FCC diesel hydrosulphurization
5.	Chandrasekar and Pramada 2004	Kaolin clay	Hydrothermal treatment	Calcination temp of 900 °C for 1 h	Used as a precursor for ceramics
6.	Wang *et al.*, 2007	Commercial Kaolin	Hydrothermal treatment	Calcined at 830 °C for 3 h	Catalyst for Naphta Aromatization

Synthesis of Hierarchical Zeolites

According to various literatures, hierarchical zeolites can be synthesized via two major techniques namely;

(1) Top-down and
(2) Bottom-up methods.

Top-Down Methods:

This method normally requires the post synthetic treatment of already commercial zeolite to create hierarchy or mesopores in the zeolite crystals. This is achieved by either etching way a part of the zeolite or recrystallization of the zeolite. These methods are usually considered to be destructive (Kerstens *et al.,* 2020). Here we have 3 major techniques according to previous literature. They are;

Dealumination: This is the oldest method used to introduce mesopores in a zeolite structure. It has been in use since mid-1960. It is used to remove Al from the framework of the zeolite, this alters the acidity, the Si/Al ratio and also increases the mesoporosity. Dealumination can be performed by; (a) steam, (b) acid, (c) heat treatment.

(a) Steam Treatment: These are generally performed at temperature higher than 500 ºC in water vapor atmosphere causing Al-O-Si bonds to break and cavity to be formed. The released Al will remain on the zeolite surface and in the pores as extra-framework Al (EFAl), while the less stable Si will move to the Al depleted regions to create a Si rich domain. The major drawback of this method is that it leads to wider pore size of the formed mesopores, causes low crystallinity and lack of connectivity of the formed framework of the zeolite to the surface.

(b) Acid Treatment: A mild acid treatment or acid wash is done to remove the debris and open the previously formed mesopores. Severe acid treatment are used to hydrolyze Si-O-Al bonds by extracting the Al from the framework, thereby increasing the Si/Al ratio and allowing the formation of mesopores without further need of an acid wash. The performance of the acid treatment depends on the type of zeolite, acid used and the pH of the acid solution (Zhang, 2018).

Zhao *et al.,* (2018) discussed the dealumination of Al-rich zeolite beta in a HNO_3 solution. The concentration of HNO_3 was varied between 4% and 15% and the dealumination temperature varied between 50 ºC and 100 ºC. Acid wash was carried

out using HCl to remove deposited extra framework alumina. The results shows that hierarchical zeolite beta with Si/Al ratio of 22 was an excellent catalyst in the conversion of 2,5-dimethlyfuran (2,5-DMF) to p-xylene, yielding 97 % p-xylene at 99 % DMF conversion.

Kowalska-kus *et al.* (2020) used citric acid followed by NaOH solution to obtain hierarchical beta zeolite with superior catalytic performance. It was used in ketalization of glycerol with acetone to obtain solketal with a conversion of 90 % and selectivity of 98 %.

Suarez *et al.* (2019) used HF/NH_4F as dealumination agent. The crystallinity was observed to be higher than 80 % as long as the HF concentration was lower than 0.5 M. the treatment was performed at temperature lower than 40 ^oC and 30 minutes. Low materials yields between 30 % and 60 % was observed. The HF/NH_4F treatment resulted in a higher Bronsted/Lewis acid sites ratio, which proved to cause a lower activity in the isomerization/disproportion reaction of m-xylene.

Li *et al.* (2017) performed dealumination and realumination using organic acids such as oxalic acid, di-malic acid and di-tartaric acid. Tartaric acid was found to have the highest realumination, hierarchical beta formed using malic acid exhibited the best performance in the esterification of acetic acid with sec-butyl alcohol.

Desilication: This is the removal of Si from the zeolite framework using an alkaline solution (diluted NaOH) which in turn aids the formation of mesopores. The morphology of the zeolites and the framework of Al play an important impact on this process (Verboekend and Perez-remirez, 2011; Moller and Bein, 2013; Chal *et al.,* 2011). Al is also considered to be a pore-directing agent during this process. The Al leached during the process are deposited as debris on the surface of the zeolites, thus blocking the micropores of the zeolite (Groen *et al.,* 2008). This Al debris can be removed by washing with mild acid to open the micropores again.

Leng *et al.* (2016), a beta zeolite was first desilicated in 0.2 M NaOH then refluxed in 12 M HNO_3 solution followed by an acid wash in 0.2 M HNO_3, then incorporating Ti into the framework. The hierarchical Ti-beta zeolites prepared by acid wash after desilication showed enhanced activity compared to hierarchical Ti-beta that was formed by direct dealumination or desilication.

During desilication, interconnected mesopores are easily formed while the zeolite largely retains its microporosity.

Sometimes SDA (TEAOH) salts are used during desilication in combination with a base as a pore-directing agent. This protects the zeolite during desilication by preventing the attack of the OH^- ions at the zeolite (Zhang *et al.,* 2016).

Dissolution / Recrystallization: This method involves two major steps;

i. A part of the zeolite is dissolved using an alkaline solution or structure depolymerization with glycerol. NaOH is commonly used as the alkaline agent in the presence of an organic template.

ii. The dissolved zeolite is recrystallized by reassembling the dissolved and dispersed species into a mesoporous phase. This recrystallization takes place during a hydrothermal treatment in the presence of a surfactant.

Zhang *et al.* (2018), synthesized hierarchical zeolites using different concentration of NaOH (0.2 M to 0.3 M). Catalytic tests in the conversion of benezyl alcohol with mesitylene showed that 0.2 M concentration was the optimal. This concentration was able preserve sufficient acidity and crystallinity during the

synthesis. The NaOH creates mesopores by extracting Si from the zeolite framework.

Cho *et al.* (2019), performed a final recrystallization step on a post synthesis of Sn/Beta in the presence of NH_4F and TEABr. The fluoride ions induced partial dissolution of silanol defects to form a 3D-ordered mesoporous imprinted catalyst and a nanocrystalline Sn/Beta catalyst. The two catalyst shows enhanced hydrophobic and mass transfer rate in the reaction involving bulky molecules such as lactose.

Bottom-Up Methods:

This method involves the creation of hierarchical system during the synthesis of zeolites. Thus, these methods are not considered to be destructive. Here mesopores are created during the synthesis of zeolites by the addition of a mesoporogen or template. This is referred to as mesoporogen method. This employed the use of either a hard or soft template (Zhang and Fernandez, 2019).

Mesoporogen-free (template-free) synthesis methods have also been developed. Hierarchical zeolites are synthesized using this method by seed assistance, steam assistance or kinetic regulation (Risheng *et al.,* 2019).

Soft-Template Method: Here an SDA and a mesoporogen is added during zeolite synthesis. The template is responsible for the formation of the micropores while the mesoporogen is responsible for the formation of the mesopores. Mesoporogens like surfactants, polymers or organosilanes are considered as soft templates (Kersten *et al.,* 2020).

Zheng *et al.* (2019), performed a one-step hydrothermal method. Here a cationic quateranary ammonium surfactant was able to interact with anionic aluminosilicate species to induce the formation of hallow beta zeolites. This followed a surface-to-core crystallization process. This process creates a larger inner cavity and a hierarchical structure which facilitates access to the acid sites.

Hallow directing agents are usually cost-effective and recyclable. Hallow zeolite beta have been tested in the alkylation of benzene and benzyl alcohol with isobutylene (Zhao *et al.,* 2019) and mesitylene respectively.

Wang *et al.* in 2018 employed analogous method to synthesized hierarchical beta support with another type of mesoporogen. This was categorized under “Gemini type” bifunctional multi quaternary ammonium surfactants. Although these templates are complicated, but they proved to be effective in the synthesis of combined micro/mesoporous zeolites.

Hard Templates Methods: Hard templates are solid materials with rigid structures. Examples; carbon materials, polymers and biological materials. These materials enable the control of the mesopores size. They can be easily removed after synthesis by calcination. They require high temperatures. This risks the loss of the product. Hierarchical zeolites synthesized using this method are often hydrothermally and mechanically less stable and the interconnectivity of the formed mesopores is relatively low due to the hydrophobic nature of the of these templates, their application is limited.

Soltani and Darian (2019) employed hydrothermal methods to synthesized H-BEA zeolites with three different templates (grahene oxide, carbon nanotubes and carbon Nanofibers) with additional SDA (TEAOH). It was observed that graphene oxide proved to be more effective as hard template in terms of final mesoporosity (0.61 to 0.19 $cm^3\ g^{-1}$) and pore size when compared to the template-free synthesized beta. This in turns increase the catalyst lifespan and catalytic performance on MTO reactions.

Yue *et al.* (2019), also uses white carbon black as hard template and PDADMAC as soft-template. This method produced nanomesoporous beta molecular sieves with large specific surface area, appropriate surface acidity and high chemical and thermal stability.

Template-Free Synthesis Method: As the name implies, this method does not require the use of any template/mesoporogen. This is a less expensive and green method because it does not release harmful gaseous chemicals into the environment.

In 2018, Zhao *et al.* successfully crystallized high Si-hierarchical beta zeolite by kinetic regulation of the crystallization process. It was seen that low water condition facilitated the nucleation and crystal growth and also ensured that the fusion of individual nanocrystal inside the particle is restrained. The developed catalyst was tested in the MTP reaction in which a longer catalyst lifespan and slower coking rate was noticed. This consequently improved the utilization of the interior acid sites and enhanced molecular diffusion.

Yue *et al.* (2019) employed seed assistance techniques to develop a green route and synthesized hierarchical zeolite beta from aluminosilicate materials (kaolin). The zeolite Beta seeds enhances the nucleation process of the BEA zeolite and the optimum crystallization conditions were found to be about 10% seed content, 1/30 Al_2O_3 / SiO_2 ratio, 0.3 Na_2O / SiO_2 ratio, 16.5 H_2O / SiO_2, and crystallization temperature of 140 ^oC for 18 h. The resultant zeolite Beta possesses great catalytic performance in the esterification reaction of benzyl alcohol with about 89.0 % conversion and 37.4 % yield of acetic acid.

Nanozeolites Assembly: This can be produced by using both top-down and bottom-up approaches.

Huang *et al.* (2017) hydrothermally formed hierarchical zeolite beta composed of uniform nanocrystals with high pore volume (0.67 cm^3 g^{-1}) and high external surface area (349 m^2 g^{-1}). Therefore, a layered silicate precursor (H-kanemite) was used as a silica source, which exhibits a huge number of silanols that easily dissoluted in alkaline media. Consequently, silica fragments were formed that were subsequently reassembled with Al species to construct the framework of nanosized beta crystals. Further assembly of these nanocrystals was assisted by TEAOH as SDA and eventually formed self-sustaining macrosized zeolitic aggregates with intracrystal microporosity, but also extremely high mesopores volumes and external surface areas.

Chaida-Chenni *et al.* (2018) used acidification of the beta seeds solution, without the use of an organic template. This method provided the best structured beta nanoparticles.

Conclusion

This review highlights some of the unique properties of kaolin clay which makes it a good precursor natural silica and alumina to synthesize zeolite Beta and hierarchical beta zeolite with high surface area, good acidity, and high silica to alumina ratio and improve catalytic performance in various acid catalyzed reactions. Different synthetic methods such as demetalization (dealumination and desilication), template and template free synthesis have been successfully used to synthesize hierarchical zeolite beta. Also template free synthesis method has also been proven to be a green and benign route in synthesizing hierarchical beta zeolites.

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