HIERARCHICAL ZEOLITES AS A NEW FRONTIER IN FCC CATALYSIS: A SHORT REVIEW

Nakakana, S.[1], Atta, A. Y.[1], *El-Yakubu, B. J.[1], Ahmed, A.S.[1] and Adefila, S. S.[2]

[1]Department of Chemical Engineering, Ahmadu Bello University Zaria, Nigeria

Engineering and Environmental Management Services Limited, Abuja, Nigeria

*Email address of the corresponding author: byjibril@gmail.com

ABSTRACT

Zeolites Y and ZSM-5 has been used extensively as part of Fluid Catalytic Cracking (FCC) catalyst blend. Owing to the dwindling global light oil reserves and large volume of heavy feedstock, it is important to optimize such catalysts and design new ones. One approach for improving the performances of zeolite catalyst is to develop its hierarchical structure. In the present review, various strategies employed for developing hierarchical structures are considered, with emphasis on the Top-Down and Bottom-Up approaches. These involved operations such as Dealumination, Desilication, Irridation, Mixed approach, Soft templating, Zeolitization and Hard templating strategies. Hierarchical ZSM-5 has currently being used along with USY in Vacuum Gas Oil (VGO) and Heavy Gas Oil (HGO) processing for possible use in the FCC. While top-down approaches (Dealumination, Desilication, Irradiation, Mixed approach), with specific emphasis on demetallation, are currently being employed on an industrial scale due to their facile nature, more specialized methods i.e. the bottom-up methods are currently being harnessed to become facile, and are generally more efficient in producing ordered hierarchical structures, with hard templating using carbonaceous materials showing the most promise, and therefore given particular attention. Our current approach on hierarchical zeolite Y for FCC catalysis is going to be emphasized.

Keywords: ZSM-5, Hierarchical, FCC, Top-down, Bottom-up, Carbonaceous

1.0 INTRODUCTION

Zeolites are a family of aluminosilicate crystalline mineral, which are also synthesized, whose intrinsic structure, composing of a regular array of uniform micropores, framework stability and acidity make it a prime candidate of choice in a vast array of applications including as molecular sieves for adsorption, separation and catalysis. Zeolites enjoy wide use as solid catalysts in oil refining, petrochemical processing and organic synthesis (Zeolites occupy more than 40% of the entire solid catalysts in the current chemical industry (Na *et al*, 2013). New applications are under research and consideration in drug delivery, sensing and opto-electronics (Na *et al*, 2013). Among the different properties of zeolites, the shape, size and interconnectivity of its pores have a dominant impact on their functionality across all applications, by imparting the zeolites with unique and important capabilities such as shape and size selectivity, but also preventing the diffusion or movement of large molecules of feed into them: that is, the pore size distribution is in the micropore range (<2nm). This restriction of fluid movement into and out of its pores limits the application

of the zeolites when bulky molecules are to be processed, via imposing severe mass transfer constraints, resulting in poor catalytic performance. This diffusion limitation also results in coking which deactivates the catalysts, thereby shortening the catalyst's life (Zhang and Ostraat, 2016). This diffusion conundrum has been the subject of intensive research since the early days of utilizing zeolites in catalytic processes.

Increasing the pores of the zeolites has been considered as a solution to this problem. But, with time, it was discovered that this also comes along with its own problems such as reducing the framework stability and acidity/activity of zeolites. This led to the understanding that a scheme had to be developed which, while increasing the accessibility of the active sites of the zeolites, hence its diffusion characteristics, would also maintain the framework stability and acidity/activity of the zeolites (Zhu *et al*, 2013). This culminated in the production of modern hierarchical zeolites. Different methods/approaches have been outlined in attempting to install the property of hierarchy within zeolites (Na and

Somorjai, 2015). There are generally two broad schemes by which it was sought viz.: top down and bottom up approaches. Hierarchical zeolites have been used in a wide variety of applications, most prominent of which is in oil refining (Zhu *et al*, 2013). They have been found to improve yield of more desired fractions obtained during Fluid Catalytic Cracking (FCC), Alkylation, Isomerization, Hydrogenation and Hydrodesulphurization (Zhu *et al*, 2013).

The earliest attempts at hierarchicalizing zeolites for FCC use were approached by steam treatment (Pavol, 2011) leading to the production of USY. This was later followed by chemical treatment, hard templating and soft templating. In the continuing search for better conversion of FCC feed stock (VGO), with an ever-increasing demand of gasoline and other light end fractions worldwide, the need for improved yield from the FCC unit, which gives the gasoline its required octane number, cannot be over emphasized. Thus, from ultra-stable zeolite Y to the experimental ITQ-39, the various frameworks and combinations of hierarchical zeolites produced by various routes for this use, have been tested (Vogt and Weckhuysen, 2015). Of important note is hierarchical ZSM-5 which has developed much interest due to its worldwide application in catalytic cracking (Ishihara *et al*, 2012). This work is designed to propound or attenuate the viability of hierarchical ZSM-5 use as FCC catalyst.

2.0 HIERARCHICAL ZEOLITES

For a material to be termed hierarchical, it must fulfil two basic criteria:

(i).   It's structural elements have to be characterized by more than one length scale.

(ii).   Each of these structural elements must have a very distinct, but complementary function (Schweiger *et al*, 2015).

Hierarchical materials have been known to outperform their individual entities by far e.g. the exceptional physical properties of natural materials (i.e. bones, wood) are typically ensured by a hierarchical arrangement of entities of either the same material having different dimensions, or of entities of different materials (Schweiger *et al*, 2015).

Leading from the above explanation, hierarchical zeolites are usually used in reference to zeolites materials having bi, tri or tetra modal (or more) porosities (Serrano *et al*, 2013). Typically, a hierarchical zeolite would have a minimum of one secondary porosity, in addition to it's primary porosity (micro porosity). More frequently than not, the secondary

porosity would be in the mesopore range; the pore size depending on the synthesis strategy used in its processing (Serrano *et al*, 2013).

In comparison with conventional zeolite catalysts, hierarchical zeolites have shown a remarkable increase in performance in most cases. This is ever so prominent when dealing with bulky substrates feed. This is premised on the following advantages noticed during their use:

i.   (Reduction of steric limitations in converting bulky substrates: The active sites located on the secondary pore surface of the hierarchical zeolite are not sterically hindered, i.e. not restricted due to their position and thus may catalyse reactions involving bulky substrates, making it possible to see the use of these zeolites in other fields e.g. fine chemicals synthesis

ii.   .Increase in the rate of intracrystalline diffusion: Due to slow diffusion characteristics when molecular size of diffusion species approaches the dimensions of zeolite channels, intracrystalline transports determine the rate of many adsorption and catalytic processes when using them. Hierarchical zeolites attenuate this problem by decreasing the diffusion pathway followed by the substrates, leading to an increase in diffusional rate and thus the rate of the processes under consideration.

iii.   Variation of selectivity toward the target products: Although some processes like xylene isomerization are affected negatively in terms of selectivity due to the presence of mesopores in the hierarchical zeolites, in other processes like toluene disproportionation, the shorter residence time within the zeolite micropores led to a reduction in conversion of the primary products (xylene) through non-desired secondary reactions.

iv.   Decrease in coke enhanced deactivation: Generally, a higher amount of coke is usually formed over hierarchical zeolites but it has a lower deactivating effect when compared with conventional zeolites. Deactivation occurs by site coverage, micropore blockage and deposition over zeolite crystals external surface. This is very prominent in zeolites with large crystal sizes, but reduced in nanocrystalline zeolites and by extension hierarchical zeolites (Zhu *et al*, 2013).

These factors all contribute to the overall effectiveness of hierarchical zeolites use over conventional zeolites provided that the substrates lead to steric or diffusion problems and the coking enhanced deactivation is significant.

3.0 HIERARCHICAL ZEOLITE SYNTHESIS

Over the last decade, a lot of research work has gone into the development of hierarchical zeolites. As has been stated earlier in introduction, there are two major sub divisions of the methods i.e. top down and bottom up. These two can be further reclassified into seven (7) different strategies viz. (Serrano *et al*, 2013):

Top Down: (a) Dealumination (b) Desilication (c) Irradiation (d) Mixed Approach.

Bottom Up:

(e) Soft Templating,

    (i)   Dual templating with surfactants

    (ii)   Silanization based methods:

        Crystallization of silanized protozeolitic nanounits

        Crystallization using sylilated polymers

        Crystallization using amphiphilic organosilanes

(f) Zeolitization of preformed solids:

    (i)   Nanozeolitic assemblies by cyclic or linear diamino or diamine structure directing agents

    (ii)   Nanozeolite assemblies by multistep pretreatment procedures

    (iii)   Nanozeolite assembles from concentrated gels

(g) Hard templating methods:

    (i)   Carbonaceous templates

    (ii)   Polymeric templates

    (iii)   Other solid templates

3.1 Top Down approaches:

Being the earliest of all processes used in developing hierarchical zeolites, top down approaches have been widely researched upon and the zeolites thus produced have been put to industrial use (Pavol, 2011). They are thus far accepted as the cheapest and simplest route to achieving hierarchy in zeolites. They basically involve demetallation, that is, removal of frame work atoms from the zeolite crystals through acid or alkali treatment, radiation, steaming or a combination of some of the methods.

3.2 Dealumination:

This is a well-known process employed to produce zeolites with high Si/Al ratios and enhanced diffusion characteristics from high alumina zeolites. It is formed by hydrothermal treatment or chemical treatment of which high temperature steaming and acid leaching are the commonest procedures. The primary reason for dealumination was to control the concentration strength of the acid sites by increasing the Si/Al ratio of high alumina zeolites, often with the secondary porosity as a pleasant surprising consequence. As stated earlier, dealumination is used, sometimes by combination of the two procedures, to produce ultra-stable zeolite Y (USY) which is currently used as FCC catalyst. Drawbacks of this process include a partial collapse of the crystal framework and irregularity of the mesopores formed i.e. low inter-connectivity and wide size distribution (Serrano *et al*, 2013). These have led to a gradual decline in proponents for this method, although it has been suggested that this process could be used in conjunction with desilication to produce novel zeolites (Yuan *et al*, 2014).

3.3 Desilication:

Arguably the most researched upon method, desilication involves the controlled dislodgement of silica from the zeolite crystals causing a decrease in the Si/Al ratio of the crystals. The first reported case of desilication was in 2000 (Serrano *et al*, 2013). Since then, a lot of interest has been developed in this field. An optimum Si/Al ratio is required in the zeolite to be desilicated in order to prevent over leaching or little-to-no leaching and to generate enhanced mesoporosity. Leaching is usually in the presence of a base. The crystalline morphology of the zeolite used affects desilication, and hence concentration of base used as leaching agent (Moller and Bein, 2013).

The drawbacks of this method include amorphization with extreme dissolution and micropore volume loss, accompanied by a loss in crystallinity. Sometimes, in order to mitigate excess leaching, a surfactant or alternative reagents are added to the leaching base or a partial removal of the template is followed by the leaching base (Moller and Bein, 2013).

3.4 Irradiation:

This method employs the use of radiation ([238]U) in order to create latent tracks inside the crystalline zeolite. Sequentially the irradiated zeolite is leached with diluted HF acid and washed with water. This leads to the formation of uniform meso/macropores in parallel orientation within the zeolite crystal. Notedly, neither the crystallinity or micropore volume are impinged upon by the irradiation process. Drawback of this process is the use of uranium with its attendant complexity.

3.5 Mixed approach:

This method is similar to the one reported in desilication using surfactant but it comes with a twist. It was found that, using a particular surfactant, Cetyl trimethylammonium bromide (CTAB), and NaOH as the leaching base, a rearrangement of the zeolite framework occurred (Li *et al*, 2015a). This could be tuned in such a way that you can have a completely different material, having either a bimodal micropore/mesopore structure, or a completely mesoporous material, by adjusting NaOH concentration. Another variation to conventional dealumination and desilication involves using both simultaneously (Yuan *et al*, 2014). Drawbacks of this include the toxicity of the template used and its relatively high cost.

3.6 Bottom Up approaches:

These refer to generally all hierarchical zeolite synthesis methods that utilize zeolite precursors in producing multi-modal pores in the zeolite structure. They may be grouped as hard templating, soft templating and non-templating synthesis procedures. These templating methods employ conventional hydrothermal synthesis processes for the production of the hierarchical zeolites. But, instead of using only one Structure Directing Agent (SDA), a second, larger template is also used to impart hierarchical pores on the zeolite. However, there are reports indicating the use of a single template (soft) in determining both bi-modal pores (Liu *et al*, 2014a). Non-templating synthesis procedures include the zeolitization of preformed solids.

3.7 Soft templating:

(i)   Dual templating: this strategy combines both the use of SDA to build the conventional zeolite framework and subsequent addition of surfactant leading directly to the formation of micelles which serves as a template for the meso-structure. The process involves the formation of protozeolitic units, to be subsequently templated by the surfactant. This sequence was informed as a succour to the phase separations experienced when both templates were utilized simultaneously (Jin *et al*, 2014). Drawbacks of this method are the relatively high cost of templates and environmental concerns regarding its toxicity.

(ii)   Silianization based methods: Organosilanes have found extensive use in research as soft templates (mesoporogens) for hierarchical zeolite synthesis. This is due to their tunability i.e. ability to transform them by addition of functional groups to enhance their zeolitization utility. Three silanization based methods

have been distinguished, in accordance with the type of silanization agent used and the role it plays in zeolite crystal formation, viz.:

Crystallization of silanized protozeolitic nanounits: This method follows these synthesis steps accordingly: pre-crystallization of the zeolite synthesis gel to form protozeolitic nanounits (zeolitic seeds); functionalization of protozeolitic nanounits on their external surface from the reaction with the organosilane, forming a protective layer; crystallization to complete zeolitization of the functionalized protozeolitic units; calcination in air to remove SDA and mesoporogen leaving uniform interconnected mesopores behind (pore size typically ~2-5nm).

Crystallization using sylilated polymers: A typical synthesis procedure includes the addition of a sylilated polymer to a zeolite seed gel. This leads to the aggregation of protozeolitic units forming large crystals. Mesopores are formed due to phase segregation of the space occupied by the sylilated polymer from the zeolite (pore size range ~2-5nm).

Crystallization of amphiphilic organosilanes: Amphiphilic organosilanes were developed in response to the phase segregation witnessed when simultaneously adding both templates (micro/mesoporous) into the reaction mix. They are usually utilized following conventional synthesis procedures (pores size range ~2-20nm).

3.8 Zeolitization of preformed solids:

A lot of attention has been given to this method due to the synthesis of nanocrystalline zeolite phases in hierarchical porous materials having 2D and 3D microporous stability, large surface area, strong acidity and high absorption capacity (Yang *et al*, 2017). There are two general synthesis procedures: Vapour Phase Transport (VPT), where a mixture of water and SDA is vaporized and contacted with the dry gel; steam assisted conversion (SAC), where only water is vaporized, the SDA (non-volatile compounds) having being already included in the solid gel. This method presents a number of advantages including faster crystallization, minimal SDA use and stable SiO/M_xO_y ratio in seed and crystal. A few schemes have been identified for the synthesis of the nanozeolites, listed as follows:

(i)   Nanozeolites assemblies by cyclic or linear diamino or diamine SDAs: These SDAs cause a pseudomorphic crystallization of zeolite precursor gels

into zeolite nanocrystal assemblies, maintaining the gel structural features.

(ii) Nanozeolite assembles by multiple step pretreatment procedures: In this process, pre-prepared zeolite seeds are added in small quantities to the reaction gels, thereby promoting nucleation of the desired phase. This suppresses any side products and usually significantly reduces the reaction time.

(iii) Nanozeolite assembles from concentrated gels: SAC assists in the synthesis of nanocrystals from dry synthesis gel. The drying of the precursor gel further implies a localized concentration of the constituents in the synthesis mix, an ideal condition for controlled massive nucleation.

3.9 Hard templating:

Hard templating involves the use of porous solids as matrices within which zeolitization of zeolite seeds proceeds. The process consists of 3 basic steps: impregnation of pores of the hard template with the zeolite precursor; crystallization of zeolite within the pores of the template by heat treatment; removal of template by calcination (organic templates) or dissolution (inorganic templates). Nano crystalline materials have been reportedly formed using this method (Na et al, 2013). The zeolite crystal size is determined by the pore size distribution of the template. Drawbacks are the relative cost of template, environmental hazards involved with template pyrolysis, and inhomogenous mix of zeolite seeds and template leading to irregular pore size distribution.

(i) Carbonaceous templates: These include carbon black, carbon nanotubes or nanofibres, ordered mesoporous carbons, carbon aerogels and mesoporous carbons, pyrolysed wood, carbonized rice husk, carbonized sugarcane bagasse, among others. The concentration and volume of the zeolite seed gel, along with the porous properties of the carbon template are very important variables in determining the final characteristics of the hierarchical zeolites formed. The use of specialized carbonated material e.g. CMK leads to narrow pore size ranged, ordered nanoporous zeolites (Fang and Hu, 2006). For carbon nanotubes and nanofibres, the procedures for incorporating the synthesis gel into the template matrix is crucial for obtaining single crystals with intraparticle mesoporosity (Serrano et al, 2013). Colloidal silica has also been used in producing mesoporous carbons, which are

subsequently employed as templates for hierarchical zeolites (Serrano et al, 2013). Finally, the effect of the nature of carbon pores templates used on zeolite crystal growth was demonstrated using graphene and graphene oxide. Hydrophilic graphene oxide sheets promote zeolite crystallization, with the formation of large crystals as opposed to hydrophobic graphene sheets which act as barriers to confine zeolite crystal growth and result in smaller crystals (Zhang and Ostraat, 2016).

(ii) Polymeric templates: Polymers have also seen wide application as templates, usually as scaffolds, for hierarchical zeolite synthesis. Some materials used are polystyrene, polyurethane foams and polymeric aerogels. Natural polymeric materials (e.g. starch derived templates) have been explored for use as templates as they have the advantages of being relatively cheap and non-toxic, with good hydrophilicity. The zeolites may be synthesized by addition of starch to zeolite synthesis gel, then proceeding with conventional zeolite synthesis, followed by calcination to remove the template and hence impart mesoporosity on the zeolite formed.

(iii) Other solids as templates: other materials that have been explored for possible use as hard templates in hierarchical zeolites synthesis include $CaCO_3$, bacterial threads, natural sponges (luffa sponge) and leaves of plants. Little research work has been done in this realm, thereby leading to a paucity of data regarding critical zeolitic parameters like mechanical stability and catalytic features.

Reflectingly, it must be said that qualitatively different mesoporosity in hierarchical zeolites is created by the varying processing techniques. Tiny variations in synthesis conditions (rotating or static) can lead to vast differences in material properties (Liu et al, 2014b). This may be manifested in pore volume or surface area, intra or inter crystalline, inter connecting of secondary pores, or size distribution. The different methods may also indicate differences in microporosity, acidity, hydrothermal stability and crystallinity. Efforts have been made to have generalized correlations for comparing the hierarchical zeolites prepared by varying techniques.

One of these is the hierarchical factor (HF) defined as the product of S_{meso}/S_{total} and V_{micro}/V_{total} (Li et al, 2014a). Care has to be taken when comparing the HF obtained using different gas-adsorption determination equipment. Although this HF appears viable, its

reliability has not been confirmed, since the relationship between HF and catalytic performance is hitherto unestablished.

4.0 HIERARCHICAL ZEOLITES IN OIL REFINING

Zeolites have been regarded as one of the catalysts in high demand in the petrochemical industry owing to their excellent catalytic performance. Hierarchical zeolites were first introduced in oil refining as ultra-stable zeolite Y (USY), an accidental benefit attained as a consequence of an attempt to reduce the activity of Zeolite Y (Pavol, 2011). The perks gained include diffusion of greater molecules to strong acid centers within the zeolite crystal structure, leading to an increase in overall conversion of substrate into gasoline, in comparison with conventional zeolite Y. Over the years, there has been an intense interest in the usage of hierarchical zeolites as catalysts or catalyst supports (Li *et al*, 2013). This interest has been driven by the demand to add value to an increasing volume of less valuable substrates. In oil refining, this has become more evident as new oil sources are being discovered (Vogt and Weckhuysen, 2015). The FCC unit being at the heart of the oil refinery operations, and accounting for a great tonnage of catalyst use in the oil refining industry, has taken a central stage in the use as proposed of new hierarchical zeolites, in order to enhance gasoline and diesel yield.

Zeolite Y in its various forms has been the main component of FCC catalysts since 1964 (Vogt and Weckhuysen, 2015). ZSM-5 has also found large scale usage in FCC. It has been found to improve the yield of propylene, an important precursor of plastics. As conventional FCC feedstocks get heavier, the need to tweak the system for better functionality to enable them handle these substances is required. This may be seen as engendering increased metal tolerance, flue gas emissions control, petrochemical feedstock maximization (e.g. propylene), light cycle oil (LCO) maximization (e.g. diesel flexibility) and lowering coke yield. Some strategies employed in furthering these include using composite zeolite Y / ZSM-5 zeolites (Pavol, 2011), and having over 65% of tonnage of FCC catalysts sold in the USA containing ultra-stable zeolite Y (USY) (Li *et al*, 2013).

In a number of research applications, hierarchically porous zeolites have been found to outperform their conventional counterparts with the increase in diffusion rates of reactants and higher conversion of bulky materials deemed the reasons for this outcome. Catalyst deactivation due to coke deposition on the catalyst would hence been minimized. As an example, mesostructured zeolite Y, with ordered mesoporosity and high hydrothermal stability, prepared by a surfactant method was used as an FCC catalyst (Zhu *et al*, 2013). The mesostructured zeolite Y produced more gasoline and LCO as well as less bottoms and coke than conventional zeolite Y because the presence of mesopores allows larger molecules in the vacuum gas oil (VGO) access to active sites within the zeolite crystal.

In another instance, bimodal Zeolite Y nanoclusters were synthesized using a triblock polymer as a template (Zhu *et al*, 2013). This zeolite produced a higher yield of light fractions (53%) than conventional zeolite Y (40%) in FCC, with heavy oil as feed.

In April 2013, Rive Technology began the ongoing supply of a commercial FCC catalyst, with mesoporous Zeolite Y made by a surfactant template post-synthetic modification, heralding a new age in the commercial application of hierarchical zeolites (Li *et al*, 2014a).

Hierarchical ZSM-5 has also been used for catalytic cracking. They can be used as additives to USY in FCC for improving catalytic activity and selectivity towards light olefins without affecting the gas oil yield (Zhu *et al*, 2013). Mesopores were understood to be the key determinant to enhancing the preferential production of propylene, suppressing secondary and hydrogen transfer reactions and offering easier access to its active sites.

Similarly, two ZSM 5 mesoporous catalysts (~2.2 and 5.2nm) with intracrystal mesopores formed using organosilane polymer templates were used in cracking VGO (Zhu *et al*, 2013). They both displayed higher reactivity and selectivity towards light olefins, with gasoline yield increasing from 12% to 19% as compared to conventional ZSM %, and overall VGO conversions from 33% to 48% which was attributed to the formation of olefin precursor in small intracrystal mesopores and subsequent formation of olefins in the micropores. Finally, slurry phase catalytic cracking of n-hexadecane showed pronounced increase in activity using mesoporous ZSM 5 as catalyst than conventional ZSM 5 (Perez Page *et al*, 2016).

Reflectingly, juxtaposing the interest and research on use of hierarchical zeolites as FCC catalyst, and the fact

that most of these remain in academia, is a paradox. But with recent commercialization of hierarchically mesoporous zeolite Y by Rive Technology in the USA, and with the discovery of facile and cheaper routes for hierarchy in zeolites, it is not out of place that there remains great interest in their use.

5.0 ADVANCES IN SYNTHESIS METHODS

Due to the level of interest in hierarchical zeolites, research is abundant on synthesis methods for all the various strategies, engineering a progressive advancement reflected in the quality of synthesis product thus obtained. Carbonaceous templates so far appear the most promising of the lot, giving a viable product when all the process parameters are considered, of which cost and toxicity are included among others. Here we present a few of the more prominent strategies, and research progress made so far:

Dealumination:

Due to recent advances in hierarchical zeolite synthesis, this primary process is gradually losing its panache and importance. Most research work involving dealumination usually considers it in association with another supporting process (eg, desilication). Nevertheless, some research in recent past concerning simulations on dealumination of mordernite was conducted (Ban *et al*, 2010). It was a successful effort as the simulation results were in good agreement with experimental results from Si NMR, XRD and N_2 and Ar desorption. The effort also successfully demonstrated the enlargement of micropores and creation of mesopores in the zeolite.

Desilication:

Desilication is one of the more popular strategies, and occurs in the presence of a base. Groen *et al* (2004) tried to optimize the desilication process, by studying the influence of Si/Al on the process. It was observed that a Si/Al range of 25-50 appeared to be optimal for mesopore formation. The tetrahedrally coordinated aluminum controlled the mechanism of mesopore formation.

More recently, desilication takes place in the presence of template (e.g. surfactant). In view of this, Wang *et al* (2015) produced mesoporous ZSM-5 zeolites using NaOH and a small molecular organic amine (piperidine). The piperidine added successfully prevented the excessive leaching of the zeolite by the base. From N_2 adsorption measurements, noticed was a significant change in micropore volume (from 0.16 to 0.11cm^3g^{-1}) in the NaOH treated ZSM-5 without piperidine (PI) as compared to minimal change in that obtained with various molar volumes of piperidine at the same NaOH concentration, while still having a greater mesopore volume at low PI loading. Catalytic cracking of n-hexane over conventional ZSM-5, NaOH treated ZSM-5 and piperidine+NaOH treated ZSM-5 was investigated, with the PI treated showing a better overall performance over the others in this order: PI+NaOH ZSM-5> ZSM-5> NaOH ZSM-5.

Tarach *et al* (2016) preferred tetrabutylammonium hydroxide (TBAOH) as low-leaching template i.e. mixing it with NaOH. The TBAOH + NaOH treated ZSM-5 zeolites were less leached than those treated with NaOH alone, showing the protection offered by the template. The mesopore size distribution was also narrower than TBAOH+NaOH treated ZSM-5 as opposed to NaOH treated, which had a longer range. Cracking of n-decane, TIPB and VGO was investigated on the 3 catalysts. Parent ZSM-5 showed the best n-decane values, followed by TBAOH + NaOH ZSM-5. This was attributed to the greater activity of the parent ZSM-5, decreasing in that order. In TIPB, greater accessibility to the acid sites lead to a better conversion for the treated zeolites than parent ZSM-5, with TBAOH + NaOH ZSM-5 giving the highest values. VGO cracking produced inconclusive results, with the major standout point being the preference of olefinic components observed for the treated zeolites.

Finally, in congruence with the work by Tarach *et al* (2016), Wan *et al* (2006) found a significant difference in the degree of leaching when using tetrapropylammonium hydroxide (TPAOH) with NaOH, as opposed to only NaOH. This was attributed to size distribution of mesopores formed in both cases, with TPAOH + NaOH ZSM-5 having a shorter range of size and smaller mesopores. The catalysts performance was then studied with cracking of methanol. Even though their conversion was comparable, the TPAOH+ NaOH ZSM-5 had greater catalytic longevity than parent ZSM-5 and NaOH ZSM-5. This was attributed to the mesopores which prevented retention of coke precursors within its pores by shortening diffusion pathways. The increased external surface area in TPAOH + NaOH ZSM-5 was indicated as being responsible for its better longevity as compared with NaOH ZSM-5, though also mesoporous.

Mixed Approach:

Mixed methods were developed in order to mitigate the problems associated with desilication and dealumination. Yuan *et al* (2014) produced hierarchical ZSM5 by acid leaching of parent ZSM-5 mixed with sodium aluminate (NaAlO$_2$), varying a number of process conditions (e.g. treatment time, temperature). The doubly treated ZSM-5 showed greater mesopore volume than parent ZSM-5, and greater crystallinity when compared with a NaOH treated ZSM-5, under similar conditions. This indicates that even though mesopores are formed in the doubly treated ZSM-5, their formation is controlled so as to largely maintain its crystal structure. From micro reaction activity tests, doubly treated ZSM-5 showed greater catalytic activity than the parent ZSM-5 accounted for by the reduction in diffusion restrictions.

Li *et al* (2015a), instead of using PI as in Wang *et al* (2015), replaced PI with an ammonium surfactant (cetyltrimethylammonium bromide (CTAB)), but as a recrystallization template. N$_2$ adsorption measurements showed an increase in specific surface area, as compared with the parent ZSM-5, an indication of the formation of mesopores. The zeolites were transformed into a ZSM-5/MCM-41 composite due to partial recrystallization of the zeolites enhanced by the surfactant. The composite zeolites thus formed exhibited superior performance in the catalytic cracking of n-dodecane, when compared with untreated zeolites.

Sun *et al* (2017) went a step further, in trying to propose a scheme by which mesoporous zeolites produced by mixed approach (sequential desilication and dealumination) can be put into commercial use. They used NaOH instead of NaAlO$_2$ as the leaching base, retaining HCl as the leaching acid. The scaled up process (50L) was found to show the formation of mesopores leading to a corresponding rise in specific surface area. In cracking VGO, a remarkable rise in preferred products (gasoline, propylene) is noticed when compared with parent ZSM-5, an increase in coke yield not affecting the overall conversion.

Zeolitization:

Efforts are underway for meso-template-free synthesis of zeolites. These have been hailed for their 'green' outlook, since they don't involve the use of mostly toxic templates. Ding *et al* (2013) synthesized hierarchical ZSM-5 zeolite from rectorite without the use of template. Undissolved rectorite debris acted as seed crystals and played a structure directing role, effectively substituting templates. N$_2$ adsorption measurements showed an increase in mesopore volume, along with attendant increase in specific surface area, which is attributed to the aggregation of nanorods that make large spherical ZSM-5 particles, and consequent intercrystal mesopores. Hierachical ZSM-5 (Hc ZSM-5) showed greater hydrothermal stability when juxtaposed with conventional ZSM5 (R ZSM-5), as buttressed by its higher crystallinity after steam treatment. To test the catalytic performance of the zeolites, 1,3,5-tri-isopropylbenzene (TIPB) was cracked over both Hc ZSM5, R ZSM-5, and desilicated ZSM-5, with Hc ZSM-5 coming out tops in conversion. Heavy gas oil was then cracked over the three candidate catalysts above, with Hc ZSM-5 being better than the rest, with a reduction in coke and dry gas yield. Wang *et al* (2014a) synthesized Hc ZSM-5 by a CO$_2$-in-water microemulsion method. The Hc ZSM-5 formed had a wide mesopore range (10-40nm) with a greater pore volume than R ZSM-5. It also took much less time to crystallize than R ZSM-5 with similar crystallinity.

Yuan *et al* (2014) synthesized Hc ZSM-5 by depolymerization and subsequent rearrangement of the synthesis mix containing one aluminium-rich (diatomite) and silicon-rich (rectorite) aluminosilicate mineral. It had a greater hierarchical factor (HF) than R ZSM-5. The crystallization follows a similar scheme as Wang *et al* (2014a), producing primary nanocrystals, and then nanosheets after aggregation. Cracking of TIPB and Heavy gas oil (HGO) were all more favorable on the Hc ZSM-5 when compared with commercial ZSM-5, with a boost in gasoline/diesel and propylene yield, and reduction in coke formation.

Zheng *et al* (2016) also produced nanocrystalline mesoporous zeolite following a traditional hydrothermal route, while adjusting parameters resulting in higher degree of supersaturation and nucleation to growth rates. As expected, the total pore volume and specific surface area (SSA) of the Hc ZSM-5 surpassed that of R ZSM-5. Cracking of TIPB over both catalysts was undertaken, with Hc ZSM-5 showing better conversion. Though the acid sites in R ZSM-5 are stronger than those in Hc ZSM-5, increased access to the interior of the Hc ZSM-5 catalyst led to a better conversion. This work is similar to that by Li *et al* (2015b), the main difference being the use of different silica types as precursors.

Finally, kinetic regulation was propounded by Ding *et al* (2015), implying the possible regulation of nucleation kinetics to form nanocrystalline MFI zeolites. The main

idea was to avoid Ostwald ripening at lower temperatures, allowing the retention of defects generated in the oriented attachment process. When tested for cracking as a composite with USY zeolite in the FCC unit, a higher gas oil conversion, and less coke formation was observed, with increased olefin selectivity, as compared with R ZSM-5.

Surfactants:

Surfactants are a group of complex compounds that have gotten wide use in synthesis of zeolites. There have been reports of surfactants being used in controlled desilication, and commercial quantities of the zeolites have been produced (Li *et al*, 2014a).

In 2011, Na *et al* synthesized C_{n-6-6} Br_2 (n=12, 16 or 22) surfactants for use as SDA for the synthesis of Hc MFI zeolites to from unilamellar, and after aging under specific conditions, multilamellar crystals sequentially. The unilamellar crystals showed great mechanical stability under pressure, giving promise for possible use in high pressure environment (FCC). C_{22-6-6} was found to have the largest pore volume, showing a large mesopore volume and hence, better prospects for use. Liu *et al* (2014b) studied the effect of synthesis conditions (rotation or static) on the nature of Hc ZSM-5 produced using a dual porogenic surfactant (C_{22}-N_4-C_{22}). The Hc ZSM-5 produced with rotation during synthesis produced the most mesopores when compared with Hc ZSM-5 Static and R ZSM-5. Thus, Hc ZSM-5 rotation was adjudged to have the best diffusion characteristics.

A gemini surfactant ($C_{18-3-18}$) was synthesized by Wang *et al* (2014b) for use as SDA to produce Hc ZSM-5. Hc ZSM-5 crystals formed had a small range of pore size distribution, as is common with surfactant SDAs. A relatively low crystalline temperature was required for the crystallization process. Liu *et al* (2014a) used bolaform quarternary ammonium surfactants ($C_{6-6-diphe}$) as SDAs. They work in such a way that allows crystal growth only along certain planes, due to the nature of functional groups that make them up. The Hc ZSM-5 crystals produced were arranged in a multilamellar form. Jin *et al* (2014) used cetyl trimethylammonium bromide (CTAB) as the only SDA in synthesis of Hc ZSM-5. This was achieved through the self-assembly of zeolites seeds with the help of CTAB. The crystals produced were in nanoscale (10nm). The CTAB prevents aggregation of the nanoparticles into larger crystals. Finally, Keoh *et al* (2016) used simple diquarternary ammonium SDA (Prediquat-5) to synthesize

hierarchically and sequentially intergrown ZSM-5, giving thin crystalline plates.

Silanization:

Organosilanes are a group of recently developed templates used as SDAs in hierarchical zeolite synthesis. They are characterized as having the silane group. Being surfactants, their functionality is similar to those of that group. Guo *et al* (2011) synthesized Hc ZSM-5 using organosilanes by two methods: A sequential addition of template to the zeolite seeds before crystallization; and making the template part of the reaction solution. The Hc ZSM-5 thus produced indicated the presence of mesopores of 2.8nm size and supermicropores of 1.4nm size. This process, like surfactant use, leads to the formation of nanocrystals, with their attendant benefits. The two synthesis schemes employed didn't exhibit any deviation in the functionality of Hc ZSM-5 synthesized by their routes. 3-Aminopropyltrimethoxysilane (APTMS) was found to give the best crystallinity, indicating the formation of excellent nanosized crystals.

Zhu *et al* (2011) produced some Hc ZSM-5 nanocrystals (12nm) using another silane (hexadecyltrimethoxysilane) dissolved in ethanol solution containing zeolite precursors. The Hc ZSM-5 produced had trimodal pores, increasing its SSA and pore volume, as compared with R ZSM-5. Uniquely, the nanozeolites formed shared the same crystalline orientation. Hc ZSM-5 microspheres were synthesized by Xiao *et al* (2013), leaving the nanocrystalline trend for surfactants. The silane used, 3-aminopropyltriethoxysilane (APTES), plays a retarding role in the development of crystallinity of Hc ZSM-5, leading to the formation of microspheres.

He and Liu (2014) synthesized Hc ZSM-5 with chain-like morphology with the help of a carbamate linked organosilane. TEM images and N_2 adsorption measurements were used to confirm the formation of mesopores in the Hc ZSM-5 crystals, with SSA of $378m^2/g$ and mesopore volume of $0.3cm^3/g$ respectively.

Zhu *et al* (2016) followed up their 2011 work with the use of a mesoporogen, an organosilane, with a gemini type structure to synthesize Hc ZSM-5. The mesopores formed are quite irregular, but can be tuned by changing organosilane/silica ratio, showing organosilane flexibility. The mesopore volume increased with increased SDA/silica ratio. Mesopore size distribution is 10-30nm. Wang and Liu (2016) used an organosilane (TABDPI) with double oxycarbonyl carbon chains in the

synthesis of Hc ZSM-5. N_2 adsorption measurements discovered a mesopore size distribution at about 4nm. Porous volume was $0.2cm^3/g$. Well organized crystals were formed, leading to the formation of mesopores.

Finally, nanocrystalline aggregates were produced from the hydrothermal synthesis from zeolite precursors (mesoporous silica) in the presence of an organosilane phenylaminopropylmethoxysilane (PHAPTMS) following a conventional synthesis method (Wang *et al*, 2017). Tunability of mesopore volume was also found to be viable by this process. Pore size distribution was found to be 2-10nm, with a concentration around 2.5nm and 5.5nm.

Polymers:
Polymers have extensive use as templates in Hc ZSM-5 synthesis. Natural polymers (Luffa sponge) have long been touted as 'green' templates for use. One such attempt at synthesis of Hc ZSM-5 with the use of polymers as templates involved block co polymers (Zhou *et al*, 2011). The co polymers act as a scaffold, supporting the synthesized zeolite, and imparting mesoporosity on the ZSM-5 crystals after removal by calcination. Steam treatment was used in the synthesis of the dried ZSM-5-in-co polymer matrix gel, dried so as to prevent phase separation between the silicon phase and template. Total pore volume of Hc ZSM-5 was far greater than that for R ZSM-5, having an average pore size of 9.8nm. The micropore volume for R ZSM-5 only slightly changed ($.02cm^3/g$) as compared with the Hc ZSM-5. The mesopore volume and average diameter can be tuned, as is same for most hard templates, by changing the mass of template used. TIPB was cracked over both Hc ZSM-5 and R ZSM-5, with Hc ZSM-5 showing better ratings with regards to conversion, and coke induced deactivation, accounted for by improved diffusion characteristics (nearly 100 times diffusion length reduction).

Subsequently, efforts were made to produce ordered mesostructure in Hc ZSM-5 using polymers, expecting an improvement in overall catalytic performance due to organized linkage of pores. Thus, a cationic amphiphilic copolymer was used in one such attempt (Liu *et al*, 2012), with b-aligned mesopores formed by this process. N_2 adsorption measurements gave a mesopore size distribution of 6-60nm. The Hc ZSM-5 showed great hydrothermal stability under steam treatment. From the catalytic conversion of benzaldehyde, the copolymer synthesized ZSM-5 outperformed disordered hierarchical ZSM-5 and multilamellar and unilamellar nanosheets, prompting a positive outlook with regards its use in the FCC unit.

From the success achieved with ordered mesoporous Hc ZSM-5 templated by polymers, ways by which to increase the total pore volume as a way forward were proposed. In this vein, Tao *et al* (2013) and Li *et al* (2014b) both produced Hc ZSM-5 with intracrystalline and intercrystalline mesopores using polyethylene glycol (PEG) and polyurethane (PUF) as scaffolding templates respectively. Tao *et al* (2013) successfully generated irregular intracrystalline mesopores (2-10nm) after removal of template, while intercrystalline mesopores were formed due to the aggregation of well crystallized ZSM-5 nanocrystals (50-200nm). A trimodal porosity distribution was obtained. Activity of the Hc ZSM-5 synthesized was compared with nano ZSM-5 and R ZSM-5 by the conversion of benzenaldehyde. Hc ZSM-5 (56.5%) compared favourably with nano ZSM-5 (56.7%), and outperformed R ZSM-5 (18.3%) by more than three fold.

Considering the challenges associated with separating nano ZSM-5 from product, Hc ZSM-5 appears the standalone victor in this quest. For PUF templated Hc ZSM-5, a monolithic solid crystalline structure of ZSM-5 was obtained with tetramodal porosity. Pore volume was found to be $0.21cm^3/g$. Intracrystalline mesopores were created by voids formed by the initial dry precursors, which transformed and were preserved in the Hc ZSM-5 crystal.

Finally, due to problems associated with the use of binders in catalyst formulation for industrial applications, Hu *et al* (2017) set out to synthesize standalone zeolites capable of direct industrial application. Their approach involved the use of a sponge as polymeric template. The Hc ZSM-5 produced had a considerably large pore volume ($0.62cm^3/g$) as opposed to R ZSM-5 ($0.22cm^3/g$).

Carbonaceous Material:
This class of materials gives one of the classic attempts at hierarchicalization of zeolites. From carbon black to CMK, they have been widely researched on with new solutions generated by the day. One of the earliest attempts at hierarchicalization using carbonaceous materials in recent times involved the use of carbon aerogels (resorcinol-formaldehyde (RF)) (Tao *et al*, 2002). Hc ZSM-5 Synthesis followed the conventional route, with the aerogel incorporated into the process. N_2 adsorption isotherms gave an SSA of $1330m^2/g$, and

mesopore volume as $0.2cm^3/g$ with pore size distribution of 9-13nm. Micropore volume difference between Hc ZSM-5 and R ZSM-5 is $0.03cm^3/g$.

Subsequently, an attempt at making ordered Hc ZSM-5 was made using CMK, known for its monolithic ordered structure. (Fang and Hu, 2006). Al/SBA-15 (mesoporous silica) was used as zeolite precursor. N_2 adsorption measurements confirmed the creation of mesopores (5nm) in the ZSM-5 crystal. The mesopore volume was found to be $0.5cm^3/g$, indicating complete crystallization of Al/SBA-15. This was supported by FTIR spectra. Hydrothermal stability of Hc ZSM-5 was determined by steam treatment, after which it remained stable, as confirmed by XRD and TEM Imagery. Finally, metal assisted Hc ZSM-5 gave better results as compared with metal assisted R ZSM-5 in the methylation of 2-methylnaphtalene with methanol.

In the pursuit of perfection, a new scheme was proposed in which the use of a specialty carbonaceous template (3DOM carbon) was used in so called 'confined' synthesis (Yoo *et al*, 2009). This involves impregnating the pores of the 3DOM carbon pieces with zeolite precursor mix and subsequent low temperature crystallization followed by calcination to remove the template. This led to formation of MFI (silicalite) nanocrystals, a rare occurrence when using carbonaceous templating methods. High precursor concentrations (nucleation dominant conditions) led to polycrystalline zeolite particles, whereas growth dominant conditions led to large single crystals.

Going further, problems associated with cost and environmental hazards associated with choice of carbonaceous template led to the search for more eco-friendly cost effective solutions. Nandan *et al* (2014) presented one such example, using glucose as a template. Hc ZSM-5 was synthesized by conventional methods. Mesopore/macropore volume was considerably higher ($0.22cm^3/g$) when compared with R ZSM-5 ($0.10cm^3/g$), although there was a significant change in micropore volume ($0.07cm^3/g$). It was also noticed that activity decreased with increase in glucose concentration. Catalytic conversion of phenol was found to be greatly enhanced in the Hc ZSM-5 (46.6%) as compared with R ZSM-5 (13.7%). This may be attributed to the ease of diffusion in the Hc ZSM-5, as R ZSM-5 has been proven to have more activity.

Due to irregularities in pore formation associated with the glucose templated Hc ZSM-5, more research

unearthed a new template synthesized from biological material (biomass) for Hc ZSM-5 synthesis (White *et al*, 2014). This template, NDC (Nitrogen doped Carbonaceous) monolith was found to have a desirable mesopore generating length scale (12-16nm) and was successfully employed in the synthesis of Hc ZSM-5 via conventional zeolite synthesis procedure. Interestingly, N_2 adsorption measurements showed that micropore volume was not significantly altered by the presence of NDC monolith in the synthesis, as compared with R ZSM5($\sim0.13cm^3/g$). Pore size distribution of Hc ZSM-5 had a maxima around 10-20nm considerably repeating the structure of NDC monolith in the ZSM-5 crystal to create mesopores. Volume of mesopores was found to be $0.13cm^3/g$, giving a 50:50 ratio between micopores and mesopores. High crystallinity was noticed when using high resolution TEM imagery. Mesoporosity was also tunable, by varying precursor concentration, solvent volume etc. Given the 3D nature of the NDC monolith, intracrystallinity in the zeolite can be engineered by impregnation as was done with 3DOM carbon, producing nanocrystals. These NDC monoliths have prospective comparability in performance to the more acclaimed 3DOM Carbon, and are without their cost and environmental malaise.

Finally, a modification of a template that can be wittingly referred to as the old lady in hierarchicalization of zeolites using carbonaceous templates was considered, being that it was one of the more facile routes, and considering it's known environmental dynamics(Han *et al*, 2016). Carbon black was used in the synthesis of mesoporous ZSM-5 zeolites as carbonaceous template. The hydrophobic carbon black was first oxidized to gain hydrophilicity via the action of sodium hypochlorite solution. This induced the uniformity of mesopore distribution within the synthesized Hc ZSM-5. Conventional zeolite synthesis method was then followed. A narrow mesopore range (5-18nm) was identified using N_2 adsorption measurements. It was also found that changing the carbon black content regulated both the textural properties and acidity of the Hc ZSM-5, as determined by BET/SEM/TEM and NH_3 TPD measurements respectively. When used for toluene disproportionation, Hc ZSM-5 was comparable to commercial ZSM-5, having a better conversion and xylene selectivity, and almost identical p-xylene selectivity.

5.0   CONCLUSION
Considering all that has been discussed, it has been seen that all the various strategies by which hierarchical

zeolites are produced have been elaborated upon. Their application has also been reviewed when it comes to FCC operation. Finally, previous works related to hierarchicalization of zeolites, and its respective application in FCC and allied operations, with special emphasis on Hc ZSM5, have been considered. It is hoped that armed with this information, a better picture About the scope and extent of research regarding hierarchical ZSM-5 use in oil refining and FCC has been visualized. Going forward, as more research is conducted in this field, it can be appropriately deduced as adduced from the prevailing literature that an optimal strategy for Hc ZSM-5 catalyst synthesis for the process should fulfill the following: induce hydrothermal stability with excellent mechanical strength; be economically suitable; environmentally friendly; have a facile process of application; optimize catalytic activity; ingrain order in the catalyst; and enable tuning of catalyst parameters to suit prevailing conditions of service and extend its functionality. Accordingly, the biomass engineered template (NDC) shows great prospects for the future, although there remains a considerable gulf in quality between the optimum product and its present condition.

ACKNOWLEDGEMENT

ABBREVIATIONS

Hc – Hierarchical
SDA- Structure Directing Agent
VPT- Vapour Phase Transport
SAC- Steam Assisted Conversion
TIPB- (1,3,5 tri-isopropylbenzene)
CTAB- cetyltrimethylammonium bromide
PI- Piperidine
R- Conventional
HF- Hierarchical Factor
APTMS- 3-Aminopropyltrimethoxysilane
APTES- 3-Aminopropyltriethoxysilane
PHAPTMS- Phenylaminopropylmethoxysilane
RF- Resorcinol-Formaldehyde
SSA- Specific Surface Area
NDC- Nitrogen Doped Carbonaceous

REFERENCES

Ban, S., Van laak, A.N.C., Landers, J., Neimark, A.V., Jongh, P.E, and Vlugt, T.G.H. (2010) Insight into the Effect of Dealumination on Mordenite Using Experimentally Validated Simulations, *Journal of Physical Chemistry C*, 114, pp. 2056 – 2065.

Ding, J., Liu, H., Yuan, P., Shi, G., and Bao, X. (2013) Catalytic Properties of a hierarchical Zeolite Synthesized from a Natural Aluminosilicate Mineral without the use of a Secondary Mesoscale Template, *ChemCatChem*, 5, pp. 2258 – 2269.

Ding, K., Corma, A., Macia-Agullo, J.A., Hu, J.G., Kramer, S., Stair, P.C., and Stucky, G.D. (2015) Constructing Hierarchical Porous Zeolites via Kinetic Regulation, *Journal of American Chemical Society*, 137, pp. 11238 – 11241.

Fang, Y., and Hu, H. (2006) An Ordered Mesoporous Aluminosilicate with Completely Crystalline Zeolite Wall Structure, *Journal of American Chemical Society*, 128, pp. 10636- 10637.

Groen, J.C., Jansen, J.C., Moulijn, J.A., and Perez-Ramirez, J. (2004) Optimal Aluminum-Assisted Mesoporosity Development in MFI Zeolites by Desilication, *Journal of Physical. Chemistry B*, 108, pp. 13062 – 13065.

Guo, Y.P., Wang, H., Guo, Y.J., Guo, L., Chu, L., and Guo, C. (2011) Fabrication and Characterization of Hierarchical ZSM-5 Zeolites by Using Organosilanes as Additives, *Chemical Engineering Journal, Elsevier*, 166, pp. 391 – 400.

Han, S., Wang, Z., Meng, L., and Jiang, N. (2016) Synthesis of Mesoporous ZSM 5 usingHydrophilic Carbon as Hard Template, *Materials Chemistry and Physics, Elsevier*, 177, pp. 112-117.

He, D., and Liu, D. (2014) Amphiphilic Organosilane-Directed Synthesis of Mesoporous ZSM-5 Zeolite Crystals with a Chainlike Morphology, *Chemistry Letters*, 43, pp. 1616 – 1618.

Hu, T., Liu, J., Cao, C., and Song, W. (2017) Synthesis of ZSM-5 Monolith with HierarchicalPorosity through a Steam-Assisted Crystallization Method Using Sponges as Scaffolds *Chinese Journal of Catalysis*, 38, pp. 872 – 878.

Ishihara, A., Kimura, K., Onaki, A., Inui, K., Hashimoto, T., and Nasu, H. (2012) Catalytic Cracking of VGO by Hierarchical ZSM 5 Zeolite Containing Mesoporous Silica Aluminas using Curie Point

Pyrolyser, *Catalysis Communications, Elsevier*, 28, pp. 163.

Jin, L., Liu, S., Xie, T., Wang, Y., Guo, X., and Hu, H. (2014) Synthesis of Hierarchical ZSM-5 by Cetyltrimethylammonium Bromide Assisted Self-Assembly of Zeolite Seeds and its Catalytic Performances, *Reaction Kinetics Mechanisms and Catalysis, Springer*, 113, pp.575 – 584.

Keoh, S.H., Chaikittisilp, W., Muraoka, K., Mukti, R.R., Shimojima, A., Kumar, P., Tsapatsis,M., and Okubo, T. (2016) Factors Governing the Formation of Hierarchically and Sequentially Intergrown MFI Zeolites by Using Simple Diquaternary Ammonium Structure-Directing Agents, *Chemistry of Materials*, 28, pp. 8997 – 9007.

Li, B., Hu, Z., Kong, B., Wang, J., Li, W., Sun, Z., … Zhao, D. (2014b) Hierarchically Tetramodal-Porous Zeolite ZSM-5 Monoliths with Template-Free-Delivered Intracrystalline Mesopores, *Chemical Science*, 5, pp. 1565 – 1573.

Li, G., Diao, Z., Na, J., and Wang, L. (2015a) Exploring Suitable ZSM-5/MCM-41 Zeolites for Catalytic Cracking of n-dodecane: Effect of Initial Particle Size and Si/Al Ratio, *Chinese Journal of Chemical Engineering*, 23, pp. 1655 – 1661.

Li, K, Valla, J., and Martinez, J.G. (2014a) Realizing the Commercial Potential of Hierachical Zeolites: New Opportunities in Catalytic Cracking, *ChemCatChem Reviews*, 6, pp. 51, 52, 57.

Li, W., Ma, T., Zhang, Y., Gong, Y., Wu, Z., and Dou, T. (2015b) Facile Control on Inter-Crystalline Porosity in the Synthesis of Size-Controlled Mesoporous MFI Zeolites Via In Situ Conversion on Silica Gel into Zeolite Nanocrystals for Catalytic Cracking, *CrystEngComm*, 17, pp. 5680 – 5689.

Li, X., Sun, M., Rooke, J.C., Chen, L., and Su, B. (2013) Synthesis and Applications of Hierarchically Porous Catalysts, *Chinese Journal of Catalysis*, 34, pp. 22, 23.

Liu, B., Duan, Q., Li, C., Zhu, Z., Xi, H., and Qian, Y. (2014a) Template Synthesis of the Hierachical Structured MFI Zeolite with Nanosheet Frameworks and Tailored Structure, *New Journal of Chemistry*, 38, pp. 4380-4388.

Liu, B., Zheng, L., Zhu, Z., Zhang, K., Xi, H., Qian, Y. (2014b) Effect of Synthesis Conditions on the Structural and Catalytic Properties of Hierarchically Structured ZSM-5 Zeolites, *Royal Society of Chemistry Advances*, 4, pp. 13831 – 13838.

Liu, F., Willhammar, T., Wang, L., Zhu, L., Sun, Q., Meng, X., … Xiao, F. (2012) ZSM-5Zeolite Single Crystals with B-Axis Aligned Mesoporous Channels as an Efficient Catalyst for Conversion of Bulky Organic Molecules, *Journal of American Chemical Society*, 134, pp. 604 – 610.

Moller, K., and Bein, T. (2013) Mesoporosity: A New Dimension for Zeolites, *Chemical Society Reviews*, 44, pp. 3703, 3694.

Na, K, and Somorjai, G.A. (2015) Hierarchically Nanoporous Zeolites and Their HeterogeneousCatalysis: Current Status and Future Perspectives, *Catalysis Letters, Springer*, 145, pp. 193 – 213.

Na, K., Choi, M., and Ryoo, R. (2013) Recent Advances in the Synthesis of Hierarchical Nanoporous Zeolites, *Microporous and Mesoporous Materials, Elsevier*, 166, pp. 4-6.

Na, K., Park, W., Seo, Y., and Ryoo, R. (2011) Disordered Assembly of MFI Zeolite Nanosheets with a Large Volume of Intersheet Mesopores, *Chemistry of Materials*, 2, pp. 1273 – 1279.

Nandan, D., Saxena, S.K., and Viswanadham, N. (2014) Synthesis of Hierachical ZSM 5 using Glucose as a Templating Precursor, *Journal of Materials Chemistry A*, 2, pp. 1054-1059.

Pavol, H. (2011, June) *FCC Catalyst - Key Element in Refinery Technology*, Paper Prensented at the 45th International Petroleum Conference, Bratislava, Slovak Republic, pp. 9, 11.

Perez-Page, M., Yu, E., Li, J., Rahman, M., Dryden, D.M., Vidu, R., and Stroeve, P. (2016) Template-Based Synthesis for Shape Controlled Nanostructures, *Advances in Colloid and Interface Science, Elsevier*, w234, pp. 69.

Schwieger, W., Machoke, A.G., Weissenberger, T., Inayat, A., Selvam, T., Klump, M., and Inayat, A. (2016) Hierachy Concepts: Classification and Preparation Strategies for Zeolite Containing Materials

with Hierachical Porosity, *Chemical Society Reviews*, 45, pp. 3353.

Serrano, D.P., Escola, J.M., and Pizarro, P. (2013) Synthesis Strategies in Search of Hierachical Zeolites, *Chemical Society Reviews*, 42, pp. 4004, 4009.

Tao, H., Yang, H., Liu, X., Ren, J., Wang, Y., and Lu, G. (2013) Highly Stable Hierarchical ZSM-5 Zeolite with Intra- and Inter-Crystalline Porous Structures, *Chemical Engineering Journal, Elsevier*, 225, pp. 686 – 694.

Tao, Y., Kanoh, H., and Kaneko, K. (2002) ZSM-5 Monolith of Uniform Mesoporous Channels, *Journal of American Chemical Society*, 125, pp. 6044 – 6045.

Tarach, K.A., Martinez-Triguero, J., Rey, F., and Gora-Marek, K. (2016) Hydrothermal Stability and Catalytic Performance of Desilicated Highly Siliceous Zeolites ZSM-5, *Journal of Catalysis, Elsevier*, 339, pp. 256 – 269.

Vogt, E.T.C., and Weckhuysen, B.M. (2015) FCC: Recent Development on the Grand Old Lady of Zeolite Catalysis, *Chemical Society Reviews*, 44, pp. 7342 – 7370.

Wan, W., Fu, T., Qi, R., Shao, J., and Li, Z. (2016) Coeffect of Na+ and Tetrapropylammonium (TPA+) in Alkali Treatment on the Fabrication of Mesoporous ZSM-5 Catalyst for Methanol-to-Hydrocarbons Reactions*, Industrial and Engineering Chemistry Research*, 55, pp. 13040 – 13049.

Wang, C., Li, J., Yan, J., and Sun, J. (2014a) Investigation on the Morphology of Hierarchical Mesoporous ZSM-5 Zeolite Prepared by the CO2-in-Water Microemulsion Method, *Korean Journal of Chemical Engineering*, 31, pp. 1547 – 1552.

Wang, D., Zhang, L., Chen, L., Wu, H., and Wu, P. (2015) Post-synthesis of Mesoporous ZSM-5 Zeolite by Piperidine Assisted Desilication and its Superior Catalytic Properties in Hydrocracking, *Journal of Materials Chemistry A.*, 3, pp. 3511-3521.

Wang, Q., Wei, Y., Xu, S., Zhang, M., Meng, S., Fan, D., … Liu, Z. (2014b) Synthesis of Mesoporous ZSM-5 Using a New Gemini Surfactant as a Mesoporous Directing Agent: A Crystallization Transformation Process, *Chinese Journal of Catalysis*, 35, pp. 1727 – 1739.

Wang, Y., and Liu, D. (2016) Synthesis of Mesoporous ZSM-5 Zeolite Crystals by a NewOrganosilane Template with Double-Oxycarbonyl Carbon Chains, *Chemistry Letters*, 45, pp. 1012 – 1014.

Wang, Y., Ma, J., Ren, F., Du, J., and Li, R. (2017) Hierarchical Architectures of ZSM-5Nanocrystalline Aggregates with Particular Catalysis for Larger Molecule Reaction, *Microporous and Mesoporous Materials, Elsevier*, 240, pp. 22 – 30.

Wei, Y., Parmentier, J.E., de Jong, K.P., and Zecevic, J. (2015) Tailoring and Visualizing the Pore Architecture of Hierachical Zeolites, *Chemical Society Reviews*, 44, pp. 7234-7261.

White, R.J., Fischer, A., Goebel, C., and Thomas, A. (2014) A Sustainable Template for Mesoporous Zeolite Synthesis, *Journal of American Chemical Society*, 136, pp. 2715-2718.

Xiao, Q., Yao, Q., Zhuang, J., Liu, G., Zhong, Y., and Zhu, W. (2013) A Localized Crystallization to Hierarchical ZSM-5 Microspheres Aided by Silane Coupling Agent, *Journal Colloid and Interface Science, Elsevier*, 394, pp. 604 – 610.

Yang, X.Y., Chen, L.H., Li, Y., Rooke, J.C., Sanchez, C., and Su, B.L. (2017) Hierachically Porous Materials: Synthesis Strategies and Structure Design, *Chemical Society Reviews*, 46, 481, pp. 493.

Yoo, W.C., Kumar, S., Penn, R.L., Tsapatsis, M., and Stein, A. (2009) Growth Patterns and Shape Development of Zeolite Nanocrystals in Confined Syntheses, *Journal of American Chemical. Society*, 131, pp. 12377 – 12383.

Yuan, E., Tang, Z., and Mo, Z. (2014) A New Method to Construct Hierarchical ZSM-5 Zeolites with Excellent Catalytic Activity, *Journal of Porous Materials, Springer*, 21, pp. 957 – 965.

Yue, Y., Liu, H., Yuan, P., Li, T., Yu, C., Bi, H., and Bao, X. (2014) From Natural Aluminosilicate Minerals to Hierarchical ZSM-5 Zeolites: A Nanoscale Depolymerization-Reorganisation Approach, *Journal of Catalysis, Elsevier*, 319, pp. 200-210.

Zhang, K., and Ostraat, M.L. (2016) Innovations in hierarchical Zeolite Synthesis, *Catalysis Today, Elsevier*, 264, pp. 3, 6.

Zheng, J., Zhang, H., Liu, Y., Wang, G., Kong, Q., Pan, M., Tian, H., Li, R. (2016) Synthesis of Wool-Ball-Like ZSM-5 with Enlarged External Surfaces and Improved Diffusion: A Potential Highly-Efficient FCC Catalyst Component for Elevating Pre-Cracking of Large Molecules and Catalytic Longevity, *Catalysis Letters, Springer*, 146, pp. 1457 – 1469.

Zhou, J., Hua, Z., Lin, Z., Wu, W., Zhu, Y., and Shi, J. (2011) Direct Synthetic Strategy of Mesoporous ZSM-5 Zeolites by Using Conventional Block Copolymer Templates and the Improved Catalytic Properties, *ACS Catalysis*, 1, pp. 287 – 291.

Zhu, H., Abou-Hamaad, E., Chen, Y., Saih, Y., Liu, W., Samal, A.K., and Basset, J. (2016)Organosilane with Gemini-Type Structure as the Mesoporogen for the Synthesis of the Hierarchical Porous ZSM-5 Zeolite, *Langmuir*, 32, pp. 2085 – 2092.

Zhu, J., Meng, X., and Xiao, F., (2013) Mesoporous Zeolites as Efficient Catalyst for Oil Refining and Natural Gas Conversion, *Frontiers of Chemical Science and Engineering*, 7(2), pp. 233 – 248.

Zhu, K., Sun, J., Liu, J., Wang, L., Wan, H., Hu, J., … Nie, Z. (2011) Solvent Evaporation Assisted Preparation of Oriented Nanocrystalline Mesoporous MFI Zeolites, *ACS Catalysis*, 1, pp. 682 – 690.