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Hierarchical Assembly of Zeolites: A Present Scenario

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Abstract

The never-ending demands of various industries for improvised and more efficient zeolites have led to an enormous amount of research in the development of hierarchical zeolites. By the introduction of a hierarchy of pore sizes into the zeolitic structures, the accessibility to the interior catalytic surface has been enhanced many times leading to improved catalytic activity. The secondary pores consist of meso- and macropores which serves as an additional space for active surface and for functionalization of the surface. The most attractive feature of hierarchical zeolite is their ability for catalysing reactions involving bulky molecules without being concerned about frequent regeneration and replacement of catalysts. A wide variety of novel strategies have been developed for synthesis of hierarchical zeolites. In this review, the different synthetic methods have been categorized as destructive and constructive methods. Destructive method comprises of demetallation and irradiation, whereas the constructive method comprises of dual templating techniques, zeolitization of materials, nano particle assembly, template assisted synthesis and zeolite seeds. This review also sheds light over the large variety of industrial applications of hierarchical zeolites.

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1. Introduction

Zeolites are three-dimensional, microporous, crystalline aluminosilicates. Swedish mineralogist Axel Fredrik Cronsted in 1765 discovered the mineral stilbite and described them as "boiling stones" therefore, the word zeolite originates from the Greek words zeo (to boil) and lithos (stone) *i.e.* a special kind of rock which traps water inside it. The zeolite framework consists of ordered networks of SiO_4^{4-} and AlO_4^{5-} tetrahedra that are interconnected by covalent bonding through oxygen bridges.[1] The presence of Al in the silicon oxide framework as the heteroatom makes the zeolite framework negatively charged, which requires one cation charge compensator per one Al atom. Usually, the cation can be alkali metal cation and they are easily exchangeable to other cations. In particular, when it is substituted with H^+, it can behave as strong Bronsted acid that can also be converted to Lewis acid sites through dehydroxylation.

Another distinguishing property is the pore size, which can vary from a few Angstroms to hundreds of nanometers. The International Union of Pure and Applied Chemistry (IUPAC) classifies the pores into three categories (1) microporous, with pores less than 2 nm in size; (2) mesoporous, with pores from 2 to 50 nm; and (3) macro porous, with pores between 50 and 1000 nm based on the different mechanisms occurring in these pores during N_2 isothermal adsorption studies.[2-7] The most common commercial zeolite, types A and X, have precisely defined ultra-micro pore size, which is 0.3, 0.4 and 0.5 nm for KA, NaA and CaA types respectively. The pore opening of the sodium form of zeolite X is approximately 0.8 nm.

The code for different zeolites is generally assigned from the name of the zeolite, for e.g., MFI stands for "Mobil 5", while FAU is an abbreviation of the name of the mineral faujasite. Depending on the framework composition, zeolites with a similar structure type can have different names. The MFI-type family includes an all-silica (Silicalite-1), an Al-containing (ZSM-5), and a Ti-containing (TS-1) member.[8]

Zeolites owes its high shape selectivity and high specific surface area to its well-defined pore systems and flexible chemical compositions. They are highly stable under harsh conditions, such as high temperatures, extreme pH condition and high pressure. These properties make zeolites indispensable materials for catalytic and separation processes. Despite their numerous advantages, zeolites also display diffusion limitations for branched molecules and transport of reagents with size similar to the size of the micropores is difficult. The delayed transport of reagents facilitates transformation of these molecules into undesired by-products, which clogs the micropores, which, consequently, leads to

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deactivation of the catalyst and lowering of turn over number and turn over frequency of the catalyst. As a whole, only the external surface of zeolite takes part in catalytic reaction while the interior remains catalytically unutilized. Therefore, a large amount of work has been done in the synthesis of zeolites with hierarchical porous structure since the last decade.

2. Hierarchical Zeolites

The present-day catalyst used in the refineries and chemical industry is fundamentally a zeolite, but it no longer sticks on to the old definition of zeolites, as zeolites have been modified a lot and is no more confined to be only microporous aluminosilicate. The term "hierarchical zeolites" refers to zeolites featuring at least one additional level of porosity besides the intrinsic micro pore system which is a characteristic of zeolites.

A whole lot of effort has been taken by the scientific community to overcome the diffusion limitations. Different synthesis methods have been preferred and adopted for hierarchical zeolite synthesis. To rationalize the efficiency of these hierarchical zeolites for a variety of applications, fine characterization methods are required. The decisive parameters are their pore size distribution, pore connectivity, morphology, and external surface chemistry. X-ray diffraction (XRD) is first used to probe the different crystalline phases and domain sizes coexisting in each sample. Electron microscopy at different scales (scanning and transmission microscopies) is also used to determine the morphology of the different porosity domains. N_2 adsorption provides a consolidated multiscale pore size distribution of each sample. The XRD patterns are termed as a fingerprint to confirm the zeolite structure. The line widths observed in the wide angle XRD powder patterns broaden as the crystal size decreases in nanocrystalline zeolites according to Scherrer equation.[9] The Scherrer formula depends on crystalline domain size and width of the peak at half of its height. Transmission Electron Microscopy (TEM) data gives a measure of the particle size and a detailed morphological analysis to visualize the whole matrix. Slight variations can be spotted while comparing the particle size calculated from TEM and average crystallite size calculated from XRD. XRD analysis using Scherrer (for spherical particles), produces only an average of crystalline size and will always have an experimental error from the Scherrer fitting. Therefore, the size measured from TEM analysis is considered to be more reliable than the XRD analysis.[10]

Various methods for pore size characterization and their application range are tabulated and published by IUPAC. The adsorption isotherms can be classified as a combination of type I (in the low-pressure range) and type IV (in the intermediate and high-pressure range). Type I is characteristic of micro porous materials with significant adsorption in the micropores at low relative pressures, while type IV is characteristic of mesoporous materials where capillary condensation occurs at higher relative pressures. The identification of a type IV adsorption isotherm for the different hierarchical zeolites is supported by the presence of capillary hysteresis loops. The N_2 adsorption isotherms of hierarchical zeolites are representative of materials with both micro pores and mesopores.[11,12] The porosity varies differently with strategies adopted for synthesis. In summary, few of the synthesis methods produce hierarchical zeolites with non-uniform porosity. Whereas quite a few methods brought forth higher controllability of the secondary porosity.[13]

The huge demand of hierarchical zeolites in various industries has led to tailoring of different synthesis techniques according to the need. There are many different techniques and they are broadly classified as destructive strategy and constructive strategy. A brief outline of the different strategies and the different methods used in each strategy is represented schematically in Fig. 1. The different destructive strategies adopted are also schematically represented in Fig. 1.

3. Synthesis strategies - destructive methods

The destructive methods used in the synthesis of hierarchical zeolites is by desilication, dealumination and by irradiation techniques. It is a sought of top-down method where leaching or boring of mesopores are done by destructing the already synthesized microporous zeolites. The different destructive techniques are schematically represented as Fig. 2.

3.1. Desilication

Desilication is a well-known post synthesis treatment and it is one of the simplest routes to hierarchical zeolites.[14-23] Desilication is done under alkaline conditions and the usual procedure is treating with sodium hydroxide (NaOH). The optimal value of the concentration of NaOH was found to be 0.2M and the optimal time for the treatment was found to be 120 secs.[14-16] Higher concentrations of NaOH was found to weaken the crystalline structure of the zeolite. In some of the works, after the desilication process ion exchanging with ammonium nitrate solution was done to get back the protonic form of the hierarchical zeolite.[16] The acidic nature of the zeolites was studied both with Ammonia- Temperature Programmed Desorption (NH_3-TPD) profile and Pyridine Fourier Transform Infrared Spectroscopy (FTIR). NH_3-TPD profile gives the total acidity *i.e.*, Bronsted and Lewis acid sites and the Pyridine FTIR distinguishes between the Bronsted and Lewis acid sites. Desilication provides more controllable mesoporosity and preserves the Bronsted acidity.[15,16] The TEM image of the resulting zeolite discloses the crystallite *i.e.*, the structural damage which indicates the removal of Si from the framework due to the desilication gives the evidence for the generation of mesoporosity in the zeolite after the treatment of alkali.

The amount of aluminium in the structure plays a crucial role in the leaching of framework Si and the related development of mesoporosity has been investigated. In the work done by J. C. Groen *et al*.[17], a broad range of Si/Al ratios were subjected to the alkaline treatment. Aluminium in

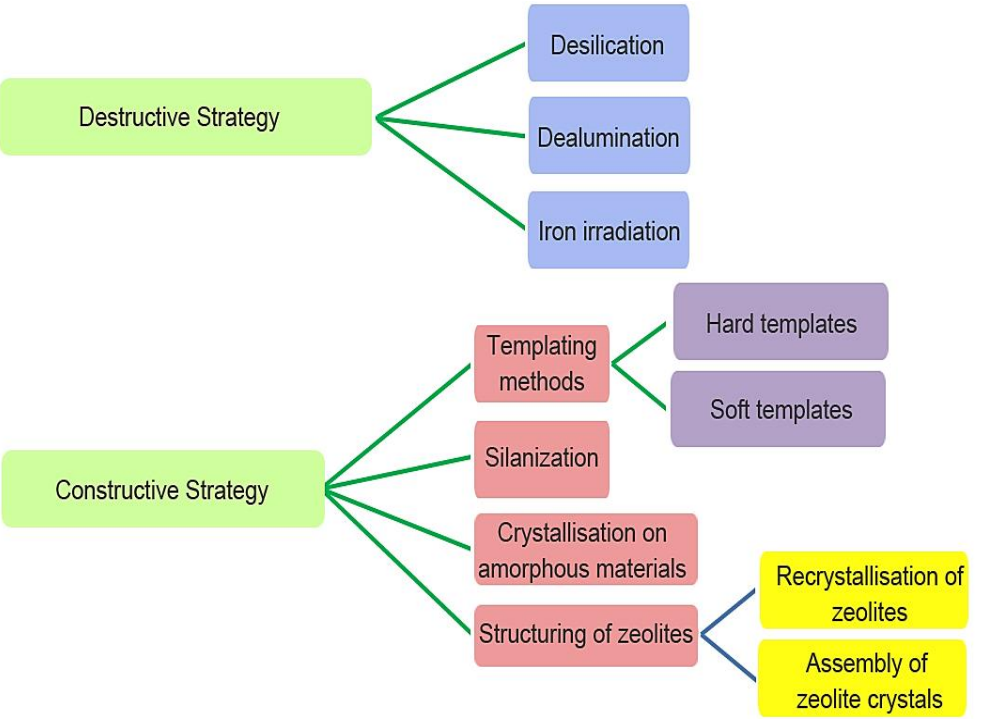

Fig. 1 Different methods for the synthesis of hierarchical zeolites.

framework positions directs the preferential extraction of framework Si upon alkaline treatment of MFI zeolites, leading to controlled mesopore formation. That is zeolites with higher Si/Al ratios, uncontrolled extraction of Si occurs, leading to large pores. While in low Si/Al ratio, hydrolysis of the Si- O - Al bond in the presence of OH^- is hindered compared with cleavage of the Si- O- Si bond in the absence of adjacent aluminium and most of the silicon atoms are stabilized by

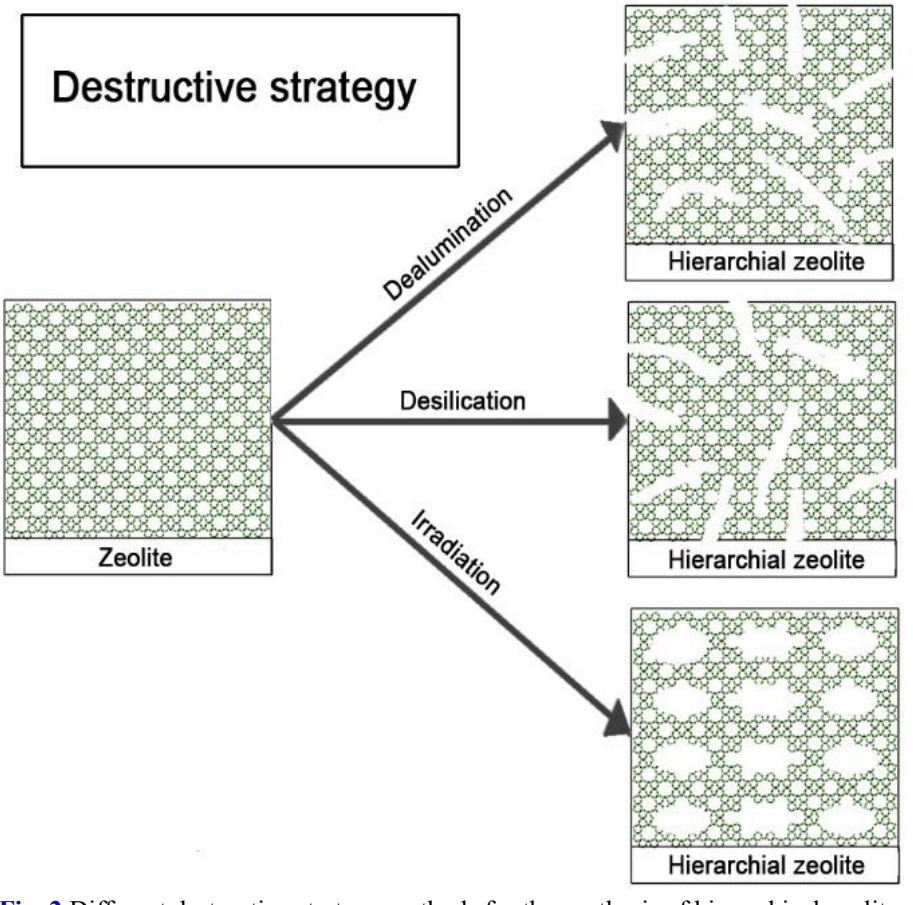

Fig. 2 Different destructive strategy methods for the synthesis of hierarchical zeolites.

AlO_4^- tetrahedra. This leads to restricted Si extraction and minor mesoporosity development. An intermediate framework Al content leads to well-controlled mesopores.

A novel desilication modification involving NaOH leaching in the presence of quaternary ammonium cations has been developed to tune the hierarchy factor in zeolites which enhance the mesopore surface area without severe penalization of the micropore volume.[18] The organic cations such as tetra propyl ammonium (TPA^+) or tetra butyl ammonium (TBA^+) acts as a pore-growth moderator in the crystal by OH^--assisted silicon extraction.[19,20] NaOH causes destruction of framework, So another method involves the use ammonia solution instead of NaOH solution.[21] Zeolite treated with ammonia contained mostly mesopores and significantly smaller contribution of micro pores and may constitute an inexpensive route.

Zhang *et al*. conducted a comparative study of the different desilication processes, such as direct alkali, and alkali with TPA cations and reaction with ammonium fluoride (NH_4F) solution.[22] In the presence of TPA^+, XRD results demonstrate excellent preservation of the structure integrity with high characteristic peak intensities. On the other hand, fluorinated sample experienced severe structural amorphization after treating in NaOH with significant peak broadening and intensity decline. The fluorination-desilication procedure was proposed as a facile approach towards the formation of hierarchical structures for high Al MFI-type zeolites. The formed Al-F complexation during the fluorination step facilitates the hydrolysis of the F-bearing tetrahedral Al species and the subsequent mesopore generation in the alkaline medium by an initial hydrolysis to Al hydroxy fluoride complexes. For the non-fluorinated high Al MFI zeolites, the fast saturation of Al hydroxides on the outer surfaces of zeolites terminates the mesoporosity development.

3.2 Dealumination

Dealuminated zeolite plays a major role in the refining industry, being one of the principal components of fluid catalytic cracking (FCC) and hydrocracking catalysts. Dealumination is one of the means to obtain hierarchical pore structure in zeolite by removing aluminium from zeolite structure by steaming and subsequent use of acid leaching.[24-26] Steaming is done at very high-temperatures (>500 °C) in a water vapour atmosphere which thereby extracts aluminium leading to vacancies in the zeolitic structure.[27-29] It results in a subsequent migration of silicon to those vacancies. The aluminium extracted from the framework is removed by a mild acid treatment. The aluminium extraction and the migration of silicon lead to an increase in the Si/Al ratio and the formation of mesopores.

Sasaki *et al.* also used TEM equipped with a high sensitivity slow scan CCD (SSC) camera to observe microstructure of zeolite Y.[30] From the TEM images of mesopores, the diameter of mesopores is estimated to be approximately 15–20 nm. The distribution of mesopores in a dealuminated hierarchical zeolite is random. This fact was proven by Feng *et al*.[31]

An investigation of the dealumination process was also done in presence of silicon source in the form of silicon tetrachloride.[32] Ammonium Fluorosilicate[33] (AFS) or ammonium hexafluorosilicate[34] (AHFS). Results show that although AFS treatments result in substantial pore enlargement. In general, the AHFS method is a selective one for preparing dealuminated zeolites with a high proportion of strong acid sites at relatively low dealumination degrees while the $SiCl_4$ method also results in a high proportion of strong acid sites, at relatively higher dealumination degrees.

3.3 Irradiation

Valtchev *et al*. employed an irradiation method with high energy heavy ^{238}U ion beam to form secondary porous structure in ZSM-5 crystals,[35] which were further subjected to attack with diluted HF solution and subsequently, washed with water. ZSM-5 crystals were prepared in fluoride media. Then subjected to ^{238}U irradiation under vacuum. Latent tracks are induced in most insulators where the linear energy transfer (LET) is above a threshold value. The ion and energy were chosen to ensure irradiation of a sufficient amount of matter with a large LET. Preparation of macropores in zeolite crystals includes two stages such as exposing zeolite crystals to a flow of swift heavy ions for inducing latent tracks and etching the latent tracks to create meso- or macropores. TEM observations also revealed that the pore diameter (50 nm) was constant along the crystal length as shown in the Fig. 3. In the present case, the formation of defect zones prior to chemical treatment makes possible the uniform extraction of framework cations. Interestingly, neither the microporosity nor the X-ray crystallinity of the ZSM-5 zeolite was impinged by the irradiation method. Consequently, comparing with other procedures, this method offers the remarkable advantage of creating a parallel distribution of meso/macropores.

4. Synthesis strategies - Constructive methods

Constructive methods involved in the synthesis of hierarchical zeolites is some of the most fascinating methods where the scientists have adopted different ideas to bring in different levels of porosity using microscopic techniques involving templates to create secondary porous structure.

4.1 Templating

The term templating is defined as the use of meso- or macroporogen to direct the formation of the additional porosity required, during the crystallization of zeolites in the presence of hard or soft templates. That is by using mixtures of micro- and mesopore-directing templates with aluminosilicate precursors. So, the term templating literally means dual templating.

Soft templating

Soft templating introduces either inter or intracrystalline

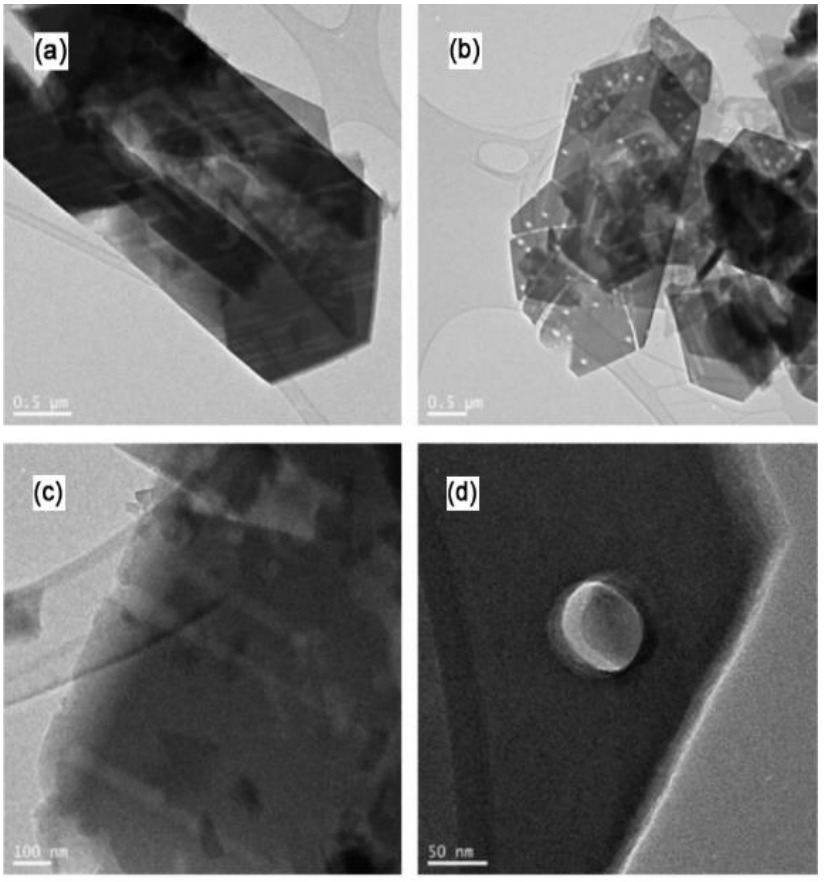

Fig. 3 TEM micrographs of ZSM-5 crystals with ordered systems of macropores (a and b) obtained by 238U irradiation followed by diluted HF acid etching. Side (c) and top (d) views of the macropores in ZSM-5 crystals showing that the pore diameter is around 50 nm. Reproduced with the permission from [35], Copyright 2011 American Chemical Society.

action of surfactant molecules, amphiphilic surfactants, cationic polymers, biopolymers, ionic liquids, organosilanes *etc*. Some of the well-known templates are surfactants such as: Cetyl Trimethyl Ammonium Bromide (CTAB) or Cetyl Trimethyl Ammonium Chloride (CTACl), whose molecules tend to form micelles in aqueous solutions. These micelles act as templates for the formation of mesostructures. Once the surfactant is removed by calcination or extraction, the space so released corresponds to the uniform mesopores found in these solids. Introduction of mesopores by soft templating method is schematically represented in the Fig. 4. Based on this background, many authors realized this soon by introducing mesoporosity in zeolites by means of treatment with surfactants according to the procedure known as dual templating.[36] This process prevents dissolution of crystals by providing interaction between the surfactant and zeolite and enables achieving almost total reorganization of the zeolite network around surfactant micelles.

TPA^+ is one of the most commonly used template for the synthesis of hierarchical zeolites.[37] The zeolite precursor solution along with the microporous structure directing agent (SDA) is stirred with TPA^+ cations. The mechanism proposed by authors for the formation of mesoporous aggregates is that, the negatively charged surface of zeolite crystal at reaction pH can interact with the excess TPA^+ cations present in the synthesis mixture. TPA^+ cations can electrostatically bind to the surface of the particles and participate in formation of mesopores between the nanocrystals provided the latter have a sufficiently small and uniform size. In the case of bigger ZSM-5 crystals, the effect of the TPA^+ cations layer around the particles does not lead to formation of mesopores because large crystals of irregular shape will stack and form macropores within the crystal aggregates. The smallest crystals were synthesized at a relatively low temperature of 140 °C and short hydrothermal treatment times with very good yields.

Synthesis strategy using these cationic surfactants via soft templating route resulted in some growth in the nanostructure. Park *et al*. investigated the structure directing ability of multi-quaternary ammonium surfactants with various structures for the generation of MFI zeolite nanosheets.[38]

The surfactants prepared by joining quaternary ammonium groups in series to an alkyl tail as in $C_{22}H_{45}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)]_{n-1}–C_6H_{13}$, where n was varied from 1 to 4. The spacers between ammonium groups were varied with $–C_3H_6–$, $–C_6H_{12}–$, and $–C_8H_{16}–$. The investigation of the role of spacer in MFI layers are done using $–C_6H_{12}–$and $–C_8H_{16}–$ using computer simulations. The multi-ammonium head acts as a zeolite SDA while the surfactant tails intermolecularly self-assemble into the lamellar-type

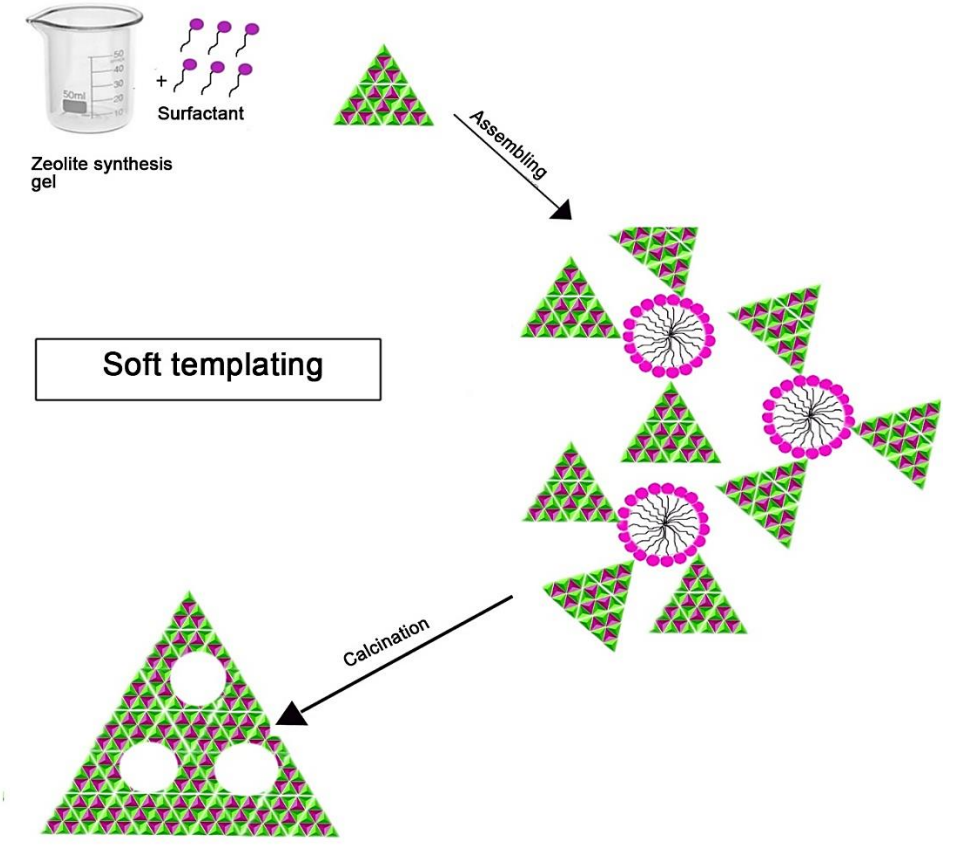

Fig. 4 Schematic representation of the soft templating technique using surfactants.

mesostructure because of the hydrophobic interaction. The thickness of the nanosheets progressively increased according to the number of ammonium groups which is evident from the SEM images given as Fig. 5. If SDA was $C_{22-6}N_2$, the small-angle diffraction pattern showed two Bragg diffractions at 2θ = 1.35° (d = 6.5 nm) and 4.05° (d = 2.2 nm). From this result, it was concluded that the $C_{22-6}N_2$ surfactant generated a multi lamellar structure composed of extremely thin MFI. When $C_{22-8}N_2$ was used as the SDA, the wide-angle XRD pattern was very similar to the result from $C_{22-6}N_2$. However, the small-angle peaks disappeared in its XRD. This indicate that the zeolite from $C_{22-8}N_2$ was an irregular assembly of nanosheets (unilamellar zeolite).[38]

The zeolite beta with a macropore-mesopore-micropore hierarchy was synthesized using quarternary ammonium surfactants by Cho *et al*.[39] Here six surfactants were synthesized. Four of them were double-tailed with -$C_{22}H_{45}$ or -$C_{16}H_{33}$ alkyl chains, and the others were single-tailed with -$C_{22}H_{45}$ alkyl chain. Silica sources such as diatomaceous earth and TEOS, was transformed into a crystalline zeolite via pseudomorphic transformation without migration into the solution phase. This leads to incorporate the macroporosity. High-resolution SEM images of as-synthesized solid precipitates collected from the synthesis mixture at various hydrothermal synthesis times using the C_{22}-N_8-C_{22} surfactant. Fig. 6. shows the change of external morphology during the crystallization of diatomaceous earth into zeolite β. XRD was recorded from 0 hour to 7 days. At the early stage of synthesis, XRD peaks were that of diatomaceous material and after 36 hours the peaks were completely of that of beta nanosponge.[39]

As per the Scherrer equation, XRD peaks of nanocrystalline materials exhibited broad peaks. The irregular arrangement of these nanoparticles leads to intercrystalline mesopores. For BEA, MTW and MRE zeolite framework, two typical diffraction peaks are observed in wide angle XRD at about 2θ=8° and 22.5°. Some of the peaks disappear and get merged because of the hydrophobic alkyl tails, which affect the formation of the framework structure.[40]

1, 4-diazabicyclo [2.2.2] octane (DABCO) is one of the other commonly used template.[41] DABCO has also been used as mesogenic template to prepare ZSM-5 zeolites with nanosheet morphology (10 nm crystal thickness) hydrothermally.[42] The surfactant is composed of a long alkyl chain (C_{18}). The mesopores are formed between the nearest-neighbouring nanosheets, therefore a larger pore diameter is observed for the ZSM-5 templated by larger SDA with longer nanosheet architecture. XRD patterns have similar structure for almost all zeolitic structures, but there were remarkable differences depending on the SDA used. The broad XRD patterns reveal that the particle sizes of these materials are smaller than those of other zeolite materials. Among the zeolite materials obtained by this synthesis procedure, a few

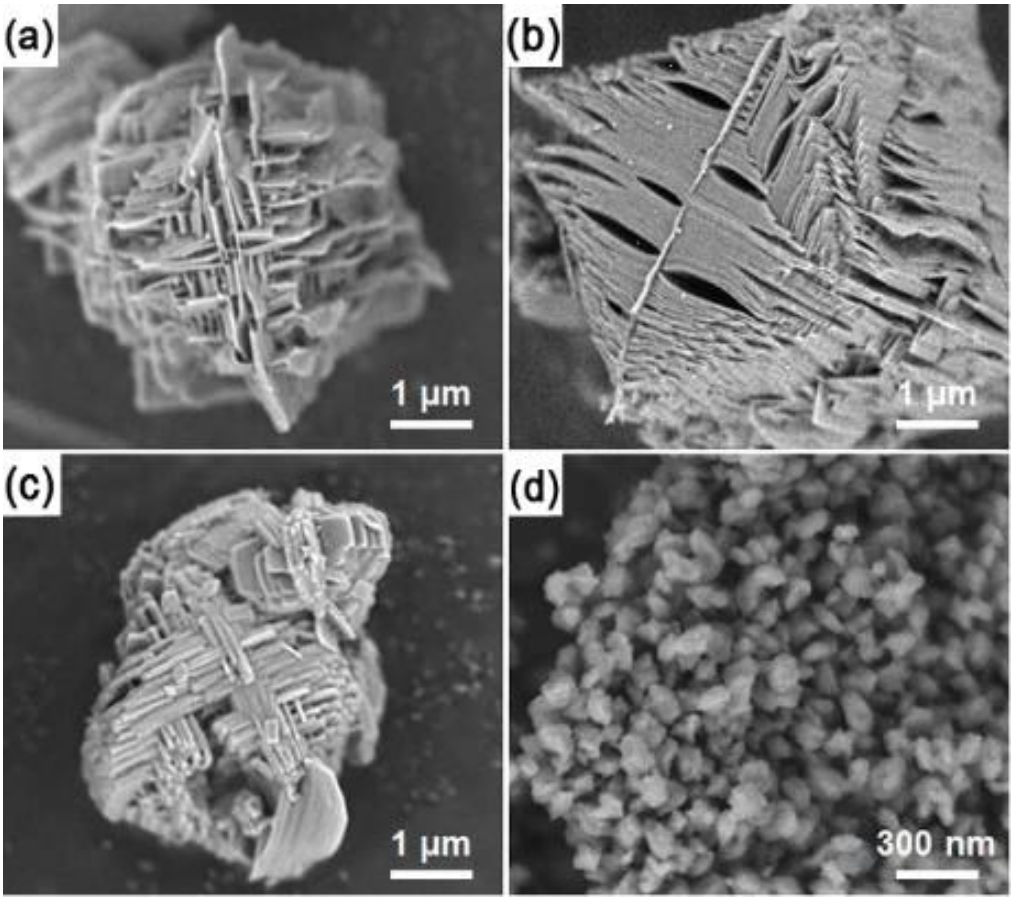

Fig. 5 High-resolution SEM images of as-synthesized products, which were obtained with (A) $C_{12-6}N_2Br_2$, (B) $C_{10-6}N_2Br_2$, (C) $C_{8-6}N_2Br_2$, and (D) $C_{6-6}N_2Br_2$ diquarternary ammoniums. Reproduced with the permission with permission from [38], Copyright 2011 American Chemical Society.

of them exhibited small-angle diffraction patterns, thus confirming the highly ordered crystalline nanoporous structure. Whereas, other zeolite materials obtained using this synthesis gel composition did not show well-resolved small-angle diffraction peaks, which confirms that they are disordered crystalline material.[42] TEM analysis confirms that zeolite growth has taken place in one direction and these unidirectionally grown zeolite nanosheets self-assembled to provide an interpenetrating nanoarchitecture.

Hierarchical ZSM-5 was synthesized by Zhu *et al.* in presence of CTAB.[43] To the precursor solution at room temperature, CTAB was added with ethanol. The zeolite precursor is mainly composed of silicate oligomers and nanoparticles of low polymerization degree, the self-assembly of TPA^+ around these low polymerized species can be destructed by strong interactions between the highly hydrophilic species and the hydrophilic ends of the CTAB molecules. This is a result of the competition between self-assembly (between the mesoporogens and the oligomers and/or nanoparticles) and crystallization of these species under the direction of the microporogens.

L. Jin introduced a new method to synthesize hierarchical ZSM-5 through the self-assembly of zeolite seeds by the assistance of CTAB without organic co-solvent or additive.[44] The multistep synthesis procedure avoids the competition between the dual templates. Here zeolite precursor solutions with seed are treated with CTAB and NaOH, resultant gels subjected to crystallization. The addition of NaOH not only increases the pH of zeolite precursor solution but also supplies some alkali metal ions Na^+ which are favourable to zeolite crystallization. Cationic surfactant CTAB can interact with these negative charged zeolite seeds through the ionic interactions. Its long chain alkyl group with a hydrophobic nature and bulky molecular size could not only prevent the zeolite-seed nanoparticles from integrating and growing into larger crystals or single crystal, but also serve as spacers to assemble the zeolite seeds into secondary zeolitic crystals, which contain a large quantity of uniform intercrystal mesopores. CTAB assisted hierarchical zeolite synthesis was modified with metal incorporation by keeping in mind an increase in Lewis acid sites.[45]

A whole lot of work has been done for modifying the alkyl tail of surfactants which plays a very vital role in the porous structure of the hierarchical zeolite generated.[46]

The ammonium group directly bonded to the C_{22}-alkyl tail looks like a turning point joining other ammonium groups to promote the zeolite structure-directing function. Here, the role of the $C_{22}-6N_n$ surfactant is two-fold. The multi-ammonium head acts as a zeolite SDA while the surfactant tails intermolecularly self-assemble into the lamellar-type

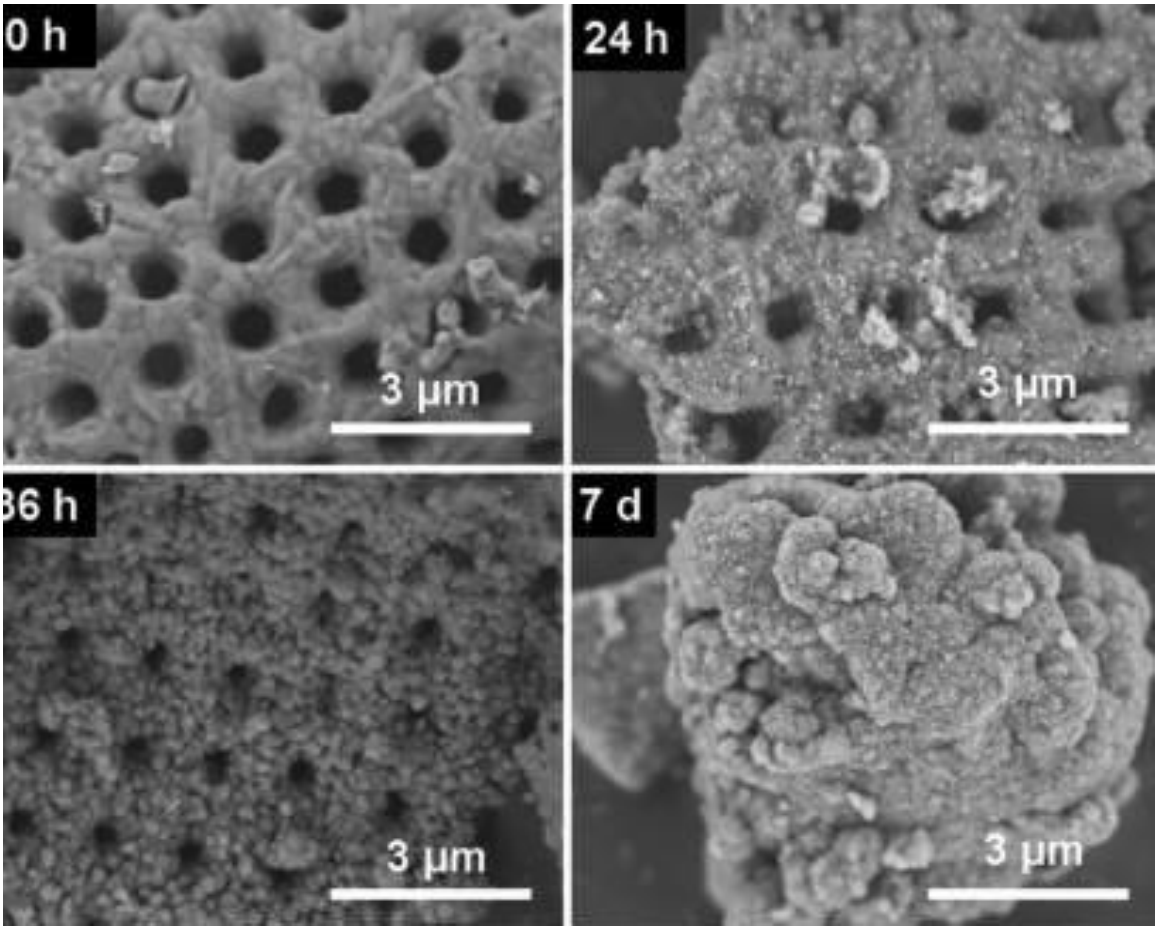

Fig. 6 High-resolution SEM images of as-synthesized solid precipitates collected from the synthesis mixture at various hydrothermal synthesis times using the C_{22}-N_8-C_{22} surfactant. The four upper images show the change of external morphology during the crystallization of diatomaceous earth into zeolite β by varying the crystallisation time. Reproduced with the permission from [39], 2012 American Chemical Society.

mesostructure because of the hydrophobic interaction. The thickness of the nanosheets progressively increased according to the number of ammonium groups.

Even though lots of work is being done in the area of hierarchical zeolite very few of them end up to be very economical thereby getting adopted by the industry.[47,48] A mesostructured Y zeolite was prepared by a CTAB templated process at the commercial scale and tested in a refinery. The ultra-stabilized mesostructured Y was milled and mixed with water, rare earth salts (to further stabilize the zeolite), kaolin (as a filler), and aluminium chlorohydrol (as a binder) and spray-dried into FCC catalyst microspheres. After proper calcination to set the binder, the final catalyst exhibits 250 m^2 g^{-1} zeolite surface area (ZSA), contributed by the micropores of the mesostructured zeolite Y, and 100 m^2 g^{-1} matrix surface area (MSA), contributed by the mesopores of the mesostructured zeolite Y.

Biopolymers have also contributed as soft templates in the synthesis of hierarchical zeolites. Briao *et al.* aimed to improve the structural properties and dye adsorption potential of ZSM–5 zeolite, through the use of chitin (low cost and available natural polymer) as template agent in the synthesis route.[49]

Cationic polymer

Another successful method under soft templating, for the synthesis of hierarchical zeolites is the use of a mixture of small organic ammonium salts which serve as a structure-generating agent of the zeolite and a mesoscopic cationic polymer. Polydiallyldimethylammonium chloride (PDADMAC) is one of the most commonly used cationic polymers. The cationic polymers could effectively interact with negatively charged inorganic silica species in alkaline media, resulting in the hierarchical mesoporosity. The molecular weight of the cationic polymer lies in the range 1 x 10^5 –1 x 10^6, and its size is estimated at 5–40 nm.[50]

Wang *et al.* synthesized hierarchical mesoporous beta(beta-H) and ZSM-5 zeolites by using cationic polymers of PDADMAC and dimethyldiallyl ammonium chloride acrylamide copolymer (PDDAM) respectively.[51] The two polymers can be easily dissolved in water and their decomposition temperatures are both higher than 200 °C, *i.e.* above the synthesis temperature. These features indicate that the cationic polymers can disperse in the synthesis solution and their structures are stable during the synthesis of zeolites. Barrett–Joyner–Halenda (BJH) pore size distribution study on beta zeolites and ZSM-5 confirms that the mesopore volumes

of Beta-H and ZSM-5 samples increased with added polymer. The larger amount of polymer added resulted in the larger porosity during the crystallization process. These results indicate the mesoporosity in Beta-H and ZSM-5 samples can be adjusted by adding different amounts of cationic polymers. The micropore volumes of ZSM-5 samples decreased with added amount of polymer, which are less than that of conventional ZSM-5. This indicates that the increased amounts of polymers affected the crystallization of ZSM-5 zeolite more. Authors reported that the high density of the positive charge on the polymer chains could be favourable for their interactions with the negatively-charged aluminosilicate. PDADMAC was also used in combination with other silica sources like CAB-O-SIL EH-5 and mesoporous silica Si514 for the synthesis of hierarchical beta zeolite.[52-54]

Ionic liquids

Ionic liquids (ILs) have been attracting considerable attention in recent times due to their unique properties, such as lack of measurable vapor pressure, non-flammability, catalytic activity and recyclability. Kore *et al*. synthesized dicationic ionic liquids (DCIL) for synthesizing hierarchical beta zeolite.[55] Cyclic and acyclic DCILs were prepared using commercially available piperidne, 4,4'-trimethylenebis(1-methylpiperidine) or imidazole as starting materials. Aluminium sulphate and sodium silicate mixed with as synthesized DCIL. The gel composition is subjected to crystallization. The presence of two ammonium groups in the same molecule could be most important for the generation of mesoporosity. XRD analysis of the product obtained using DCIL, shows that a pre-organized zeolite-like assembly was formed during gelation. This process reduced the nucleation time and the crystal growth took place rapidly to form hierarchical zeolite Beta. DCILs are able to generate a large number of zeolite seeds when compared with their mono ammonium analogues TEA^+.

Other soft templates

Xing *et al*. synthesized ZSM-5 by steam assisted conversion (SAC) approach with kaolin clay and hexadecyltrimethoxysilane (HTS).[56] A proper amount of templating agents Tetra Propyl Ammonium Hydroxide (TPAOH) and the mesoporogen (HTS), was added to ethanol under stirring at room temperature, followed by the addition of Tetra ethyl orthosilicate (TEOS), NaOH and deionized water. The gel obtained was mixed with kaolin into the solution. Then subjected to SAC. Authors calculated indexed hierarchy factor (IHF) to evaluate the mesoporosity development and found that IHF value for kaolin added ZSM-5 is high compared to conventional one.

Hard templating

Synthesis of hierarchical zeolites can be done using hard templates. Among hard templates are those containing carbon, aerogels, mesoporous silicates *etc*.

Carbonaceous templates

Different types of carbon, such as carbon black, three-dimensional ordered mesoporous (3Dom) carbon, carbon pearls *etc*. have been used as meso/macroporogen. SAC was employed for the synthesis of hierachical zeolites using carbonaceous templates.[57-62] Using SAC method, a dense precursor gel containing silicon, aluminium, the microtemplate and the carbonaceous template yielded a hierarchical zeolite material without using a mesoporogen. During the steam assisted treatment, water is vaporized and the SDA is contained in solid gel. The SAC of the highly concentrated precursor resulted in abundant nucleation and formation of nanocrystals. The additional steam treatment condenses the nanoparticles, thereby retaining the mesopores. This confined crystal growth on the ordered carbon provides uniformly shaped zeolite with ordered mesoporosity. TEM and SEM of the isolated crystalline domains reveal a networked structure composed of about 20 nm primary particles. This size is confirmed with the crystal size estimated from Scherrer analysis of the XRD data. Carbon Black Pearls also can be impregnated by incipient wetness method using a clear solution of TPAOH, NaOH, sodium aluminate, water, and ethanol.[63] Different types of carbon particles were also used to prepare hierarchical zeolites, such as carbon black with average particle diameter 18 nm and carbon black with average particle diameter 12 nm.[64] The use of different carbon sources enables different physical properties. The comparison of adsorption characteristics of thus synthesized samples showed that samples prepared from 18 nm carbon black provides a zeolite with higher porosity. Works with different concentration of carbon black was also used for the synthesis of mesoporous zeolite.[65] A schematic representation of the use of carbon as hard template is shown as Fig. 7.

The mesoporous zeolite materials like MFI, MEL and BEA, as well mesoporous zeotype materials like AFI and CHA are synthesized by including the direct introduction of carbon into reaction mixtures with 40 weight percentage of HF.[66] The behaviour of the fluoride ion is very similar to that of the hydroxide ion as a mineralizing agent and a complexing ion and it will also contribute to the formation of the molecular sieve structures. Dissimilar to the hydroxide mineralizer, the use of fluoride ions does not produce molecular sieve products even with gel pH below 5. In the crystallization of molecular sieve phases, fluoride ions act as agents solubilizing the framework-forming elements silicon and aluminium, slow down nucleation and growth rates, resulting in larger, more defect-free crystals.

Jacobsen *et al*. defined the confined space synthesis as preparation inside the pores. Many works report the crystallization of zeolites within the mesopore system of the inert carbon black material.[67-69] Carbon black was impregnated using incipient wetness impregnation method into the precursor solution and finally autoclaved.

Chen *et al*. synthesized various zeolites, including BEA, LTA, FAU, and LTL, with 3Dom –imprinted (3Dom-i)

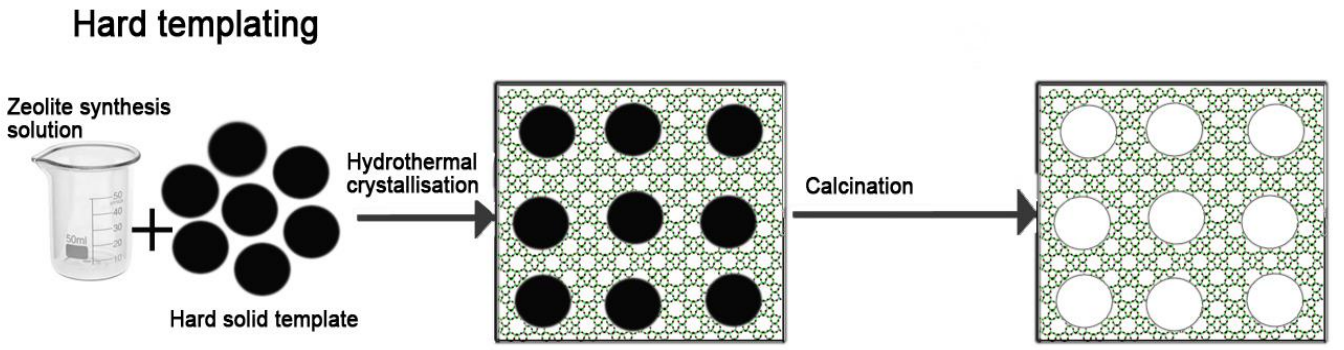

Fig. 7 A schematic representation of the use of carbon black as hard template leading to mesoporosity.

structure by conventional hydrothermal procedure rather than SAC.[70] They pointed out that the SAC often requires preparation of dense gels which cannot penetrate 3DOm carbon. Therefore, this synthesis had been done repeatedly by immersing carbon in the reaction mixture. BJH pore size analysis confirms the presence of marked mesoporosity in the 3DOm-i zeolites. Textural analysis reveals that the micropore volume of 3DOm-i zeolites are similar to that of conventional zeolites, indicating that the micropore structure of 3DOm-i zeolite is retained during the confined growth. TEM images of 3DOm-i zeolite crystals 3DOm-i zeolite crystals. TEM images of 3DOm-i LTA, FAU, BEA, and LTL grown within a 40 nm 3DOm carbon template is shown as Fig. 8.

Liu *et al.* also synthesized pillared MWW, pillared MFI, and 3DOm-i MFI.[71] The mesopore sizes of pillared MWW, pillared MFI, and 3DOm-i MFI, calculated from the BJH

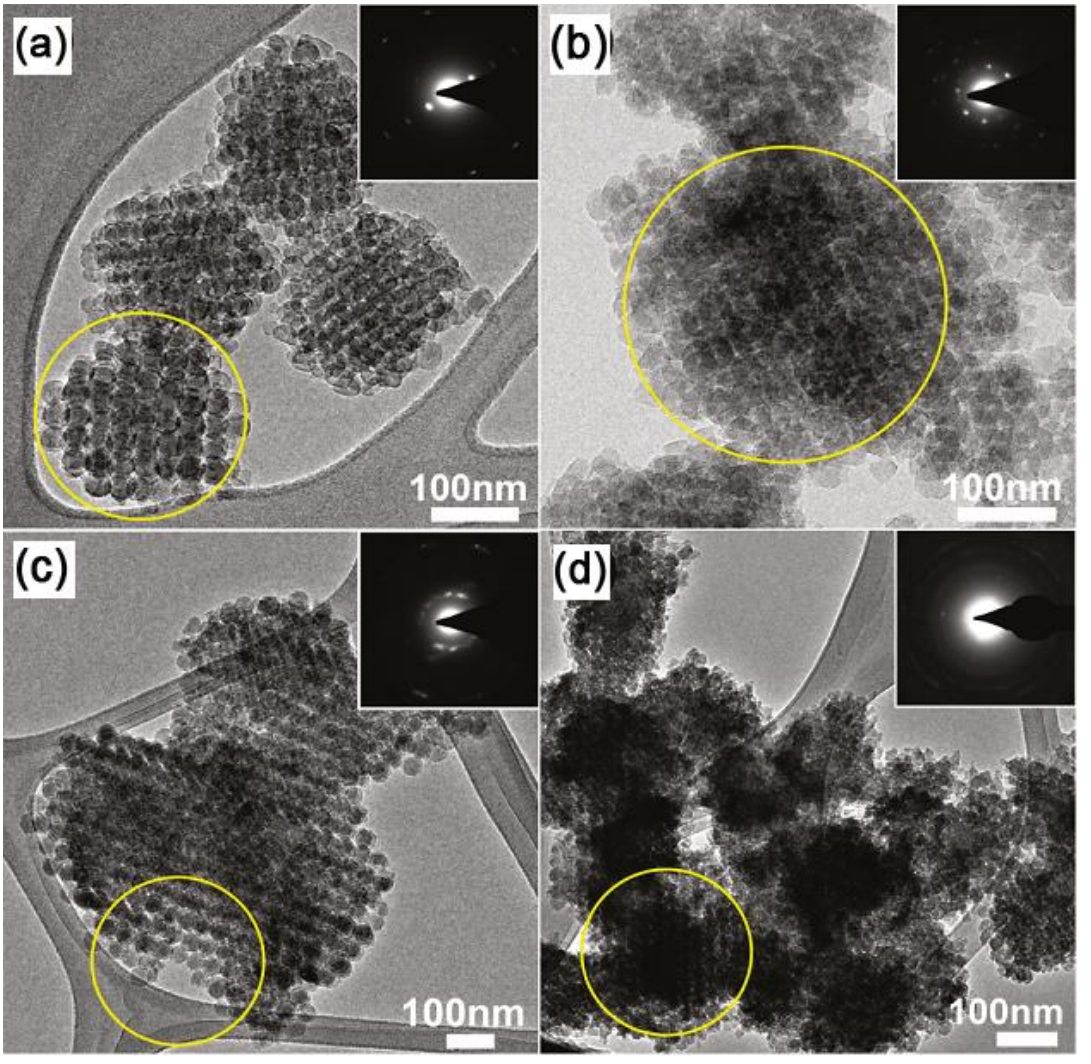

Fig. 8 3DOm-i zeolite crystals. TEM images of 3DOm-i LTA (a), FAU (b), BEA (c), and LTL (d) grown within a 40 nm 3DOm carbon template. Insets: electron diffraction patterns from the circled areas in the corresponding TEM images. Reproduced with the permission from [70], Copyright 2011 American Chemical Society.

model are 1.8 nm, 2.5 nm, and 6.0 nm respectively. The work claimed that the structure of 3DOm-i MFI, consists of spherical elements forming an opaline structure, in which each element is connected with the 12 other adjacent elements. The mesoporous space created between the ordered spherical elements in 3DOm-i MFI is highly connected and communicates with the micropores present in each spherical element.

Polymeric templates

Polymers act as excellent templates for the synthesis of hierarchical zeolites and resorcinol formaldehyde (RF) gel is one of the important mesoporous aerogels. RF gels were derived from the sol-gel polymerization of resorcinol and formaldehyde with a slight amount of sodium carbonate as a basic catalyst. Zeolite Y was prepared using RF solution.[72,73] The resultant carbon aerogel was then obtained in the form of vitreous black monoliths. This aerogel is transferred into cell containing zeolite precursor solution for carrying hydrothermal synthesis. The average crystallite size of meso-NaY is calculated to be 80 nm using the Scherrer equation. After characterizing with field emission scanning electron microscope (FESEM) authors reported that the mesopore structure of meso - NaY copies the frame structure of the carbon aerogel template. The meso-NaY has the FAU framework with relatively uniform mesoporous channels and the additional mesopore volume is as high as 1.37 cm^3g^{-1} with intrinsic mesoporosity.

Tao *et al.* did a comparative study on the pore structures of mesoporous ZSM-5 prepared from carbon aerogel (CA) and that prepared by RF gel.[74] The mesopore volumes of mesoporous ZSM-5 from RF templating are smaller than those from CA templating. The mesopore sizes and volumes of the mesoporous zeolites are closely related to the frame structures of the templates. RF has relatively smaller pore-wall volumes and then that of CA aerogels.

Multi walled carbon nano tubes (MWCNT) are also used for the synthesis of mesoporous zeolite.[75] Authors reported the synthesis of mesoporous zeolite silicalite -1 crystals on MWCNT. Nucleation of the zeolite takes place exclusively between the carbon nanotubes. The diameter of the carbon nano tubes varies closely around 12 nm with walls consisting of 6-8 graphene layers. The individual zeolite crystals have partly encapsulated the MWCNT material during growth. The use of MWCNTs acts as templates offering a high degree of control over the diameters and spatial arrangement of mesopores in solid materials.

Carbohydrate has been used as template for setting mesoporosity.[76] Sucrose dissolved in water and impregnated with silica is added into clear solution containing sodium aluminate and SDA. The method applies in situ generation of the carbon template from sucrose impregnated onto silica gel, and therefore the resulting material is readily available at low cost. Hg intrusion experiments shows that the mesopores are actually accessible and distributed over the interior volume of the zeolite crystals.

Katsuki *et al.* reported the implementation of rice husk for synthesizing ZSM-5 crystal.[77] Here rice husk was carbonized. The silica in the carbonized rice husk serves as a SiO_2 source for synthesizing zeolite crystals. The synthesis was carried out by microwave hydrothermal reaction. By the introduction of microwaves, the dissolution of silica from the carbonized rice husk was enhanced and the formation kinetics of ZSM-5 zeolite crystals increased by 3–4 times. In addition, Microwave hydrothermal reaction yielded small particles of 0.3–5 micrometer. Furthermore, smaller sized ZSM-5 zeolite crystals were promoted by rapid dissolution of silica with microwaves leading to supersaturation. The ZSM-5 zeolite/porous carbon composite were composed of microporous and mesoporous structures. The pore volumes of mesopores and micropores were 0.29 and 0.19 cc/g, respectively.

Wood has been utilized as macro template-support for the synthesis of silicalite-1.[78] A comparative study of the different calcinations method *i.e.* in presence of air and N_2 – air atmosphere has been done. Mesopore volumes are found to be 0.044 and 0.047 cm^3/g, respectively for the samples calcined in N_2+air and air. Hollow self-supported zeolite piece after calcination under the N_2+air atmosphere provides enough mechanical strength to the zeolitic body for handling and characterization. On the contrary, after calcination with air the zeolitic structure was destroyed and converted into powder and leads to breakage of the zeolitic structure because of hindering of combustion gases flow through micropores.

M. Fujiwara *et al.* brought forth another exciting method for the synthesis using polymeric templates. The silica-Alumina epoxy resin composite are readily prepared. Hydrothermal treatment of these composite materials with TPAOH crystallized the amorphous silica– alumina part to the MFI zeolite crystalline phase and induced the phase separation of epoxy-resin domain from the zeolite phase, generating both zeolite microporosity and mesoporosity in the solid catalyst after calcination.[79] Caramel,[80] Polystyrene,[81-83] natural rubber latex,[84] and starch gel[85] are the other polymeric templates used in the synthesis of hierarchical zeolites. Starch gel acts as a good template for the synthesis of mesoporous zeolite. SEM images of a calcined macroporous silicalite monolith prepared from a starch-silicalite gel template is shown in Fig. 9.

Other Solid templates

Zhu et al. described a new method by using cheap and easily available nanosized calcium carbonate ($CaCO_3$) hard template to synthesize silicalite-1 with intracrystal pores.[86] The homogeneous mixture containing nanosized $CaCO_3$, TPAOH, water and NaOH is subjected to hydrothermal crystallization. The composite was acid-treated to dissolve the nanosized $CaCO_3$, which released the secondary pores within the crystal. SEM analysis shows that average crystal size of silicalite-1 is in the range of 400–800 nm. Some mesopores and macropores

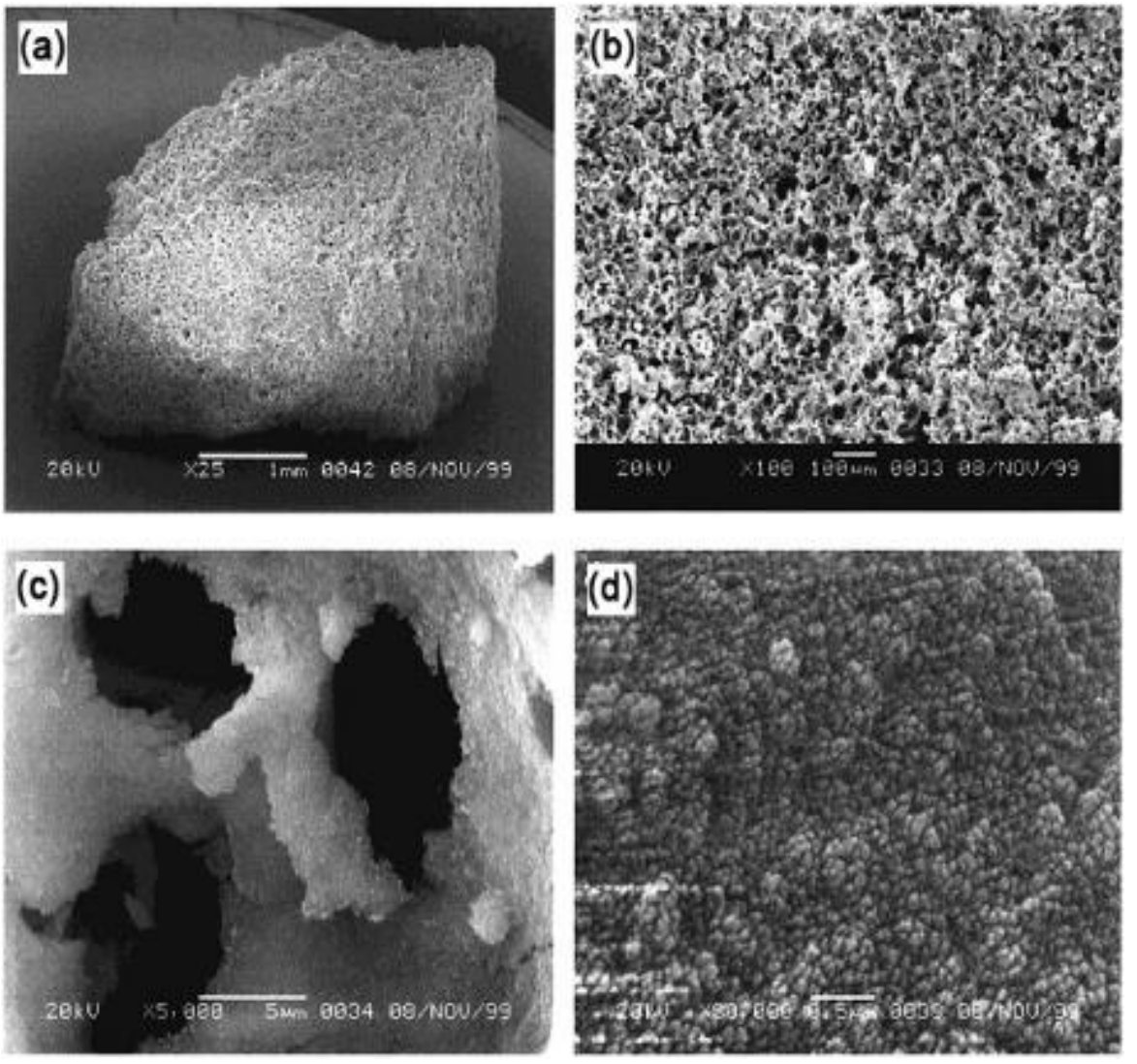

Fig. 9 SEM images of a calcined macroporous silicalite monolith prepared from a starch-silicalite gel template (a) Low-magnification image showing a fragment of the intact monolith (scale bar) 1 mm). (b-d) Higher-magnification images of a showing (b) macroporous texture (scale bar) 100 micrometer), (c) individual macropores (scale bar) 5 micrometer), and (d) mesoporous wall structure of aggregated silicalite nanoparticles (scale bar) 0.5 micrometer). Reproduced with the permission, from [85], 2002 American Chemical Society.

caused by the acid dissolution of $CaCO_3$ that are opening at the external surface of the silicalite-1 can be directly observed in the high-magnification SEM image of the is given as Fig. 10. The explanation given by the authors for the use of this template was that the highly active hydroxyl groups on the hydrophilic $CaCO_3$ can give rise to strong interaction between SiO_2 and $CaCO_3$ leading to the nanosized $CaCO_3$ dispersed in the silica gel which gets encapsulated into the crystal during the crystallization process.

Valtchev *et al*. showed that environmentally benign, inexpensive and renewable fresh silica-containing plant equisetum arvense transformed into zeolite beta with hierarchical porosity.[87] Leaves and stems are subjected to hydrothermal treatment with a zeolite Beta precursor solution. The zeolite readily crystallized in the vegetal tissues with the zeolite nucleation being induced by the highly reactive biomorphic silica deposited at the epidermal surface of the plant. The mesopore volumes, of the samples prepared at 100 and 150 °C have mesopore volumes 0.68 and 0.06 $cm^3\ g^{-1}$, respectively. Therefore, authors confirmed that, the synthesis conditions can also be employed to control the secondary porosity of the material.

Monolithic zeolites

A wide spread use of polyurethane foam (PUF) scaffolds in the synthesis of hierarchical zeolites have been experienced.[88,89] Li *et al.* synthesized ZSM-5 with unique macro-macro-meso-micropore.[90] SAC followed by removal of the PUF scaffold and TPAOH template led to tetra modal porosity. The first modes of macroporosity (33 micrometer) are formed after the removal of the PUF scaffolds. The second set of macro pores (0.2-1.7 micrometer) originate from the aggregation of ZSM-5 nanocrystals inside the macro pores of the PUF scaffolds. The third level of porosity from the

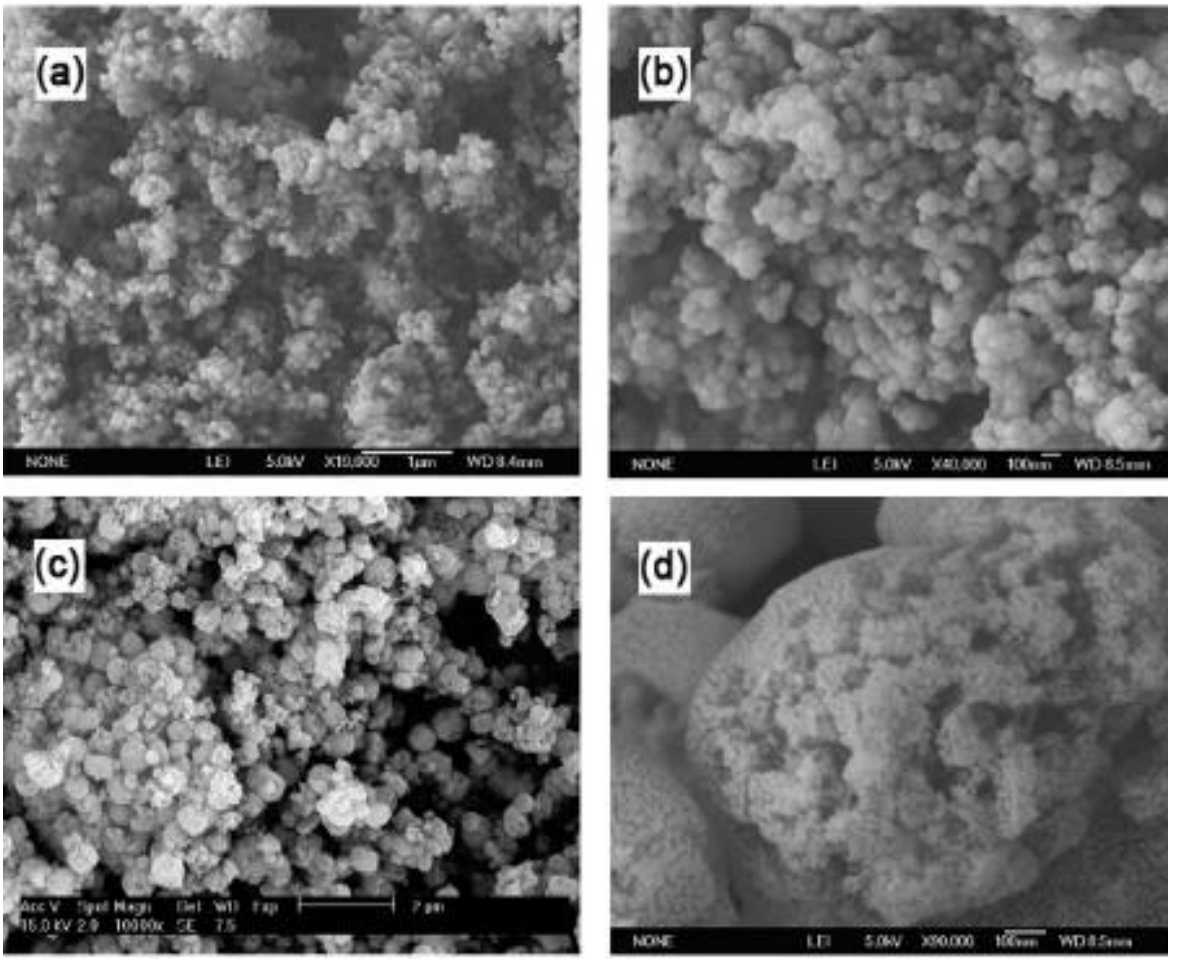

Fig. 10 Low- and high-magnification SEM image of nanosized $CaCO_3$(a and b). Low- and high-magnification SEM image of silicalite-1 with intracrystal pores(c and d). Reproduced with the permission from [86], 2008 American Chemical Society.

intracrystalline mesopores in each ZSM-5 crystal, along with the fourth intrinsic microporosity of zeolites.

Different types of monoliths are also used as templates for hierarchical zeolites.[91] Li *et al*. impregnated carbon aerogel to zeolite precursor solution.[92] Then subjected it to high temperature argon atmosphere. The obtained composite was then impregnated with silicalite-1 precursor solution again, followed by hydrothermal treatment. Second impregnation step with zeolite solution leads to mechanically stable and highly loaded silicalite -1. Authors gave an explanation for the route adopted by them that is the stress caused by the growth of zeolite crystals in the confined space of the carbon aerogel frame work may lead to a cracking of the carbon aerogel monolith.

The monolith silicalite exhibit high mechanical stability and hierarchical porosity with micropores within zeolite particles. Mesopores are formed by the packing of nanoparticles and a macropore system on the monolith level**.** TEM images of silicalite-1 obtained through the single step templating process show that less well-defined particles with not as distinctive morphologies are formed, which have sizes similar to the ones obtained through two-step templating. TEM images of silicalite -1 after double impregnation consists of well-defined, cube shaped crystals with sizes of 30-40 nm.

4.2 Silanization

Silanization is a bottom-up synthesis technique for hierarchical zeolites. Serrona *et al*. described this synthesis technique in four steps *i.e.*, Firstly, the precrystallization step, where the precursor gel containing protozeolitic MFI nanounits (seeds) is formed from clear solutions. Secondly, the Seed silanization agents (SSA) is added to the synthesis medium which reacts with the surface hydroxyls, being anchored onto the zeolite seeds (silanization step). Next is the crystallization of the funcionalized units and finally calcination. Serrona *et al*. have done a detailed study of all the four steps inorder to optimize the method and to end up with the most efficient hierarchical zeolites.

Serrona *et al*.[93] found that hydrothermal crystallization of the organo functionalized seeds leads to materials with macroscopic crystalline features and hierarchical porosity, because the presence of the silylating agent hinders the aggregation and densification of the nanounits. The materials prepared from silylated seeds exhibit significantly higher N_2 adsorption compared to the samples obtained omitting the silanization treatment. This enhanced adsorption is because of the presence of mesopores between the nanocrystals).

Serrano *et al*.[94] studied the influence of SSA in the porosity of hierarchical ZSM-5. Isobutyl triethoxysilane

(IBTES), octadecyltrimethoxysilane (ODTMS), 3-aminopropyltriethoxysilane (APTES), and phenyl amino propyl tri ethoxy silane (PHAPTES) are used as SSA. The strong hydrophilic nature and low incorporation degree of ODTMS leads to low silanization among the above four SSAs. Therefore, ODTMS is partially ineffective. When APTES and IBTES were used as silanization agents, ZSM-5 samples with larger surface areas were attained. Both samples are formed from 200–400 nm aggregates of smaller ZSM-5 units (10–20 nm). The most remarkable results were attained with PHAPTES which caused the highest increase of the surface area and the generation of a secondary porosity on the border between the micro- and mesopore ranges.

Serrano *et al*. confirms the importance of the precrystallization step to promote the formation of protozeolitic seeds before the addition of the silanization agent phenyl amino propyl trimethoxy silane (PHAPTMS).[95] In the absence of a precrystallization treatment, the silanization agent is mixed directly with the silica and aluminium sources each of which is collectively hydrolyzed and mutually co-condensed. Co-condensation reactions lead to the formation of organofunctionalized alumina silica oligomers that have nucleated. Solid state 1D & 2D Nuclear magnetic resonance (NMR) established that four coordinated Al atoms incorporated into the framework, TPA^+ cations located in the nanopores and PHAPTMS located on internal surface. The morphologies of the ZSM-5 products prepared from silanized seeds are significantly different. They consist of relatively large 300-nm sponge-like aggregates of much smaller nanoparticles. This relatively large size of the aggregates is a positive fact as it favours the recovery of the synthesis product by centrifugation, which otherwise would be very difficult if the nanocrystals were completely isolated.

Serrona *et al*.[96] introduced a novel method where the SSA is introduced into protozeolitic units with alcohol. The presence of alcohols increases the incorporation degree of the silanization agent due to the reduction of the gel viscosity caused by the alcohols, which favours the interaction and grafting of the organosilane with the protozeolitic nanounits, the alkoxylation reactions also occur by anchoring of the alcohols on the external surface of the protozeolitic units.

Hierarchical zeolite prepared by grafting PHAPTMS perturbs the aggregative growth.[97] The hybrid zeolite mesoporous materials formed by the addition of CTAB into the zeolite precursor gel led to the assembly of protozeolitic units around surfactant. The ammonia TPD test revealed that the hierarchical zeolite possesses weaker acidity since the acid strength of sites located on the mesopore external surface is lower than the acid site inside the micro pores. But the FTIR pyridine desorption show that hybrid zeolitic material exhibit high amount of Lewis acid sites. TEM images shows that hierarchical zeolite consist of aggregates, with a size in the range 400–600 nm. In the border of the aggregates, nanounits with sizes as small as 5 nm is observed.

A detailed study of the influence of the calcinations treatment on the catalytic properties of hierarchical ZSM-5 was done by Serrona *et al*.[98] Two different calcination methods were applied to hierarchical ZSM-5 samples in order to remove the organics contained in the as-synthesized materials. In the first one the materials were calcined under an air atmosphere. In the second calcination treatment, the as-synthesized materials were subjected first to a nitrogen atmosphere followed by calcination step under air. By studying the influence of these two methods, it was found that the concentration of Bronsted acid sites decreases by half for one-step air calcination, only a quarter when using a two-step nitrogen/air calcination, showing that the aluminium present in hierarchical ZSM-5 is very sensitive to the calcination conditions as it may undergo framework extraction and dehydroxylation phenomena. Therefore, ZSM-5 (N_2/air) sample exhibits a slightly higher anisole conversion than hierarchical zeolite treated under air atmosphere.

Carrero *et al*. synthesized ZSM-5 and Beta hierarchical zeolites from organo functionalized seeds for transesterification of Nannochloropsisgaditana.[99] Oleaginous microalgae are potential sources for biodiesel production as they accumulate high levels of lipids, The lipid extraction from Nannochloropsisgaditana was studied using three procedures (sonication, microwaves and magnetic stirring under reflux) with different extraction solvents. The highest lipid recovery was done using a magnetic stirring under reflux. Since this method causes a cell disruption stronger than sonication and microwaves. Wang *et al*. introduced a novel approach for making hierarchical zeolite by using silane functionalized polymer for intra crystal mesopores.[100] Silylated polymer formed from the reaction of (3-glycidoxypropyl) trimethoxysilane and polyethylenimine inserted into silica alumina reaction mixture by using SiO_3 units. Authors revealed that upon nucleation, polymer becomes phase separated and forms intracrystal polymer network, that covalently links with framework and its removal upon calcination results in uniform mesopores.

Solvent evaporation route to produce hierarchical MFI has been developed by Zhu *et al*.[101] Here Hexa decyl Trimethoxy Silane (HTS) is stirred with TEOS, and aluminium tritertbutoxide (ATTB) in ethanolic medium. After adding TPAOH it was subjected to evaporation resulting in a sol. As the ethanol evaporates, the whole mixture becomes more concentrated, accompanying a self-assembly and condensation process of the moieties, and eventually a dry gel. Transparent gel obtained was subjected to moisture assisted hydrothermal crystallization. SEM micrographs of ZSM-5-HTS after combustion removal of the organic SDA s is given as Fig. 11. Mesoporous Faujasite-type zeolite X with a low Si/Al molar ratio of 1.0–1.5 synthesized using the organosilane template 3-(trimethoxysilyl) propyl hexadecyl dimethyl ammonium chloride (TPHAC).[102,103] This pore system is constructed of zeolitic nanosheets in a house-of-cards-like assembly with wide macroporous interstices between the nanosheet stacks. Within each nanosheet there are

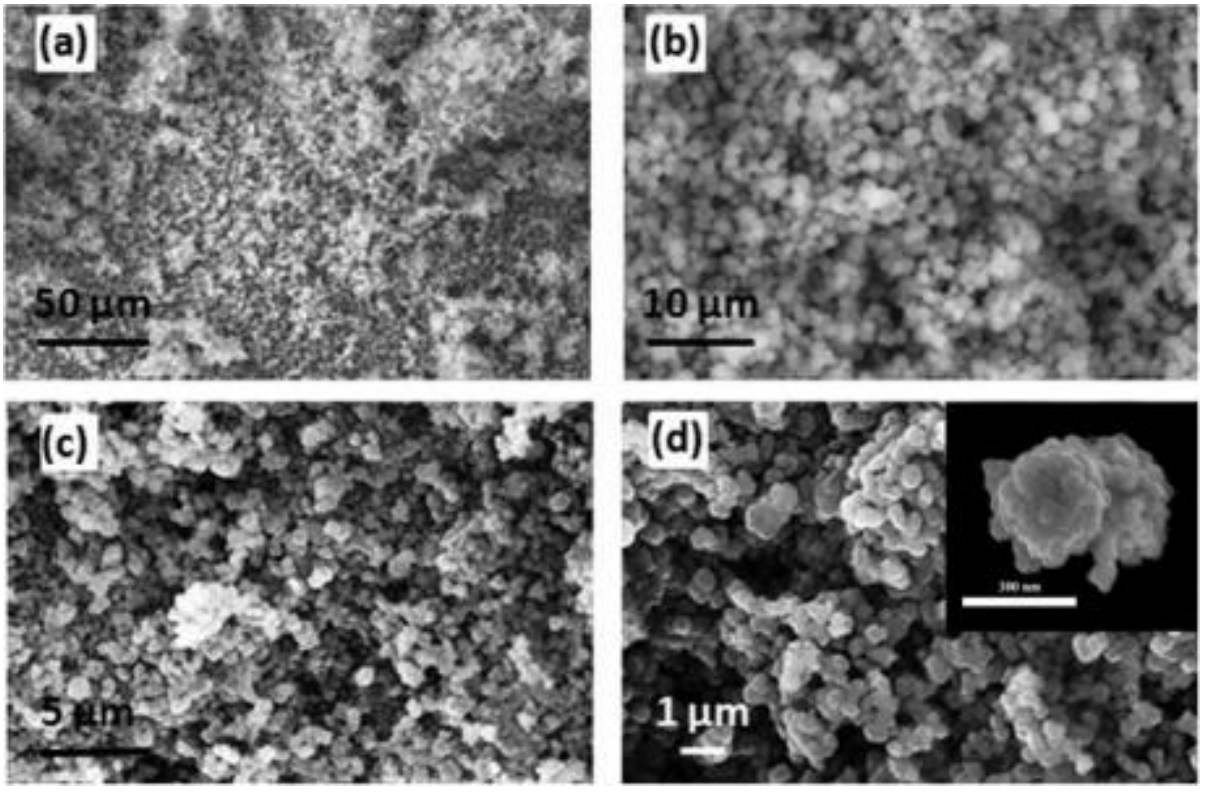

Fig. 11 SEM micrographs of ZSM-5-HTS after combustion removal of the organic structure directing agents, at low (a, b) and high (c, d) magnifications. Inset in Figure 11 d clearly shows one single secondary particle aggregate with primary nanozeolites. Reproduced with the permission from [101], 2011 American Chemical Society.

intracrystalline mesopores with diameters of around 7 nm from which the zeolitic micropores (0.74 nm wide pore openings) can be accessed. This hierarchical pore arrangement connects the zeolitic micropores through the mesopores and macroporous channels with the outside medium. The accessibility of the micropores and the zeolite surface from and to the outside has been greatly improved.

CTAB and 3-(trimethoxysilyl) propyl octadecyl dimethyl ammonium chloride) TPOAC[104] are the well-known surfactants which act as mesoporogen. Ahmadpour and Taghizadeh[105] studied effect of CTAB and TPOAC in different amounts of single and mixture of two mesoporogen templates. The hydrolysable methoxysilyl ($(CH_3O)_3Si$) group in the amphiphilic organosilane surfactant could strongly interact with the growing zeolite crystals through the covalent linkages with the soluble aluminosilicate species in the crystal-growth gel to avoid phase separation. The particle size of the sample prepared with the CTAB is greater than that of the sample prepared with TPOAC. By using mixed mesoporogens, the particle size was close to the sample prepared by only TPOAC. The long alkyl tails of the TPOAC surfactant with a hydrophobic nature linked on the surface of nanocrystals provide a capping effect, thus preventing the further crystal growth of the nanocrystals, the samples contain a large quantity of intercrystal pores in addition to regular intracrystal micropores. 1-methyl-3-[3′-(trimethoxysilyl) propyl] imidazolium chloride directed hierarchical zeolite Y was synthesized by Fu *et al*. using a novel ultrasonic/microwave synergistic synthesis (UMSS).[106] The results clearly demonstrated that the UMSS is a promising strategy to achieve zeolite Y with improved crystallinity, large surface area, bulky mesopore volume, well-dispersed morphology, small zeolite nanoparticle and reduced synthesis time.

Alkyl triethoxysilane (ATES) mediated MFI synthesis was reported by Srivastava *et al*.[107] Three different ATES with hydrolysable alkyl groups were used in the study. The alkyl groups are propyl, methyl or octyl. Authors studied the influence of hydrophobicity of ATES by varying the alkyl chain length in ATES used in the synthesis. The samples prepared with octyltriethoxysilane (OcTES), had the size of the crystal decreased, but no morphological changes were observed. The surface area of the obtained samples follows the order MFI-PrTES> MFI-MeTES>MFI-OcTES. This clearly indicates that moderate length alkyl-chain-containing organosilanes have a strong interaction with the growing crystals and, hence, effectively modulate the zeolite crystallization to form high surface area nanosized zeolite nanocrystals. The long-alkylchain hydrophobic ATES (OcTES) was found to be less effective, as it may be segregated from the aluminosilicate domain and unable to modulate the crystallization process by participating in crystal growth.

4.3 Zeolitization

Hierarchical zeolites are synthesized through the crystallization of mesoporous materials in the presence of

micro directing templates without using a second porogen.[108-112] Zeolitiation affords mesopores through controlled intergrowth of nanosized crystallites into an open network.[109] Use of highly concentrated precursor gels and SAC increase the nucleation rate that yields completely crystalline and highly porous materials at different scales. The mesoporosity is caused by the assembly of extremely small and uniformly sized crystalline particles whose growth is arrested by the dense packing in the gel. During steam conversion these nanoparticles condense into a porous network characterized by very high surface areas. A relatively larger amount of water must exist under reaction conditions.[110] This induces a more open gel structure, allowing for greater mobility with respect to rearrangement in the gel and/or nutrient transport.

4.4 Structuring of zeolites

Recrystallization of zeolite

Recrystallization process is a partly destructive and partly constructive strategy as firstly, the microporous zeolite is desilicated and then it is treated with a surfactant and reassembled and finally calcined to get mesoporous zeolite.[113,114] Desilication is done using NaOH[113-117] followed by addition of a surfactant which is commonly CTAB.[115,116] Addition of CTAB reassembles the zeolitic structure leading to mesopores. The pores formed are not uniform in nature. Pore formation in the zeolite with a diameter corresponding to the micelle diameter is explained by the stabilization of the micelle inside the pores during leaching of the zeolite phase. There is slight decrease in the amount and strength of acid site with respect to parent due to partial destruction of silicon and aluminium atoms. Recrystallization in mild condition leads to improved catalytic performance.[117] Recrystallization technique is schematically represented in the Fig. 12.

A comparative study between TPABr and CTABr was done by Verboekend *et al*.[118] Silicalite-1 and USY zeolites were subjected to treatment with additives, such as TPABr or CTABr added to the alkaline filtrate. The presence of TPA^+ and/or soluble aluminum hydroxide ions $[Al(OH)_4^-]$ in the Si-containing alkaline filtrate does not yield any solid product. On the contrary when CTA^+ is present during the treatment, ordered mesoporous materials (OMMs) are formed. Accordingly, zeolites desilicated in the presence of TPA^+ and/or $Al(OH)_4^-$ transform into highly crystalline hierarchical porous zeolites, while those alkaline-treated in the presence of CTA^+ are transformed into less crystalline zeolite/OMM composites. When micelle forming surfactant is used it forms

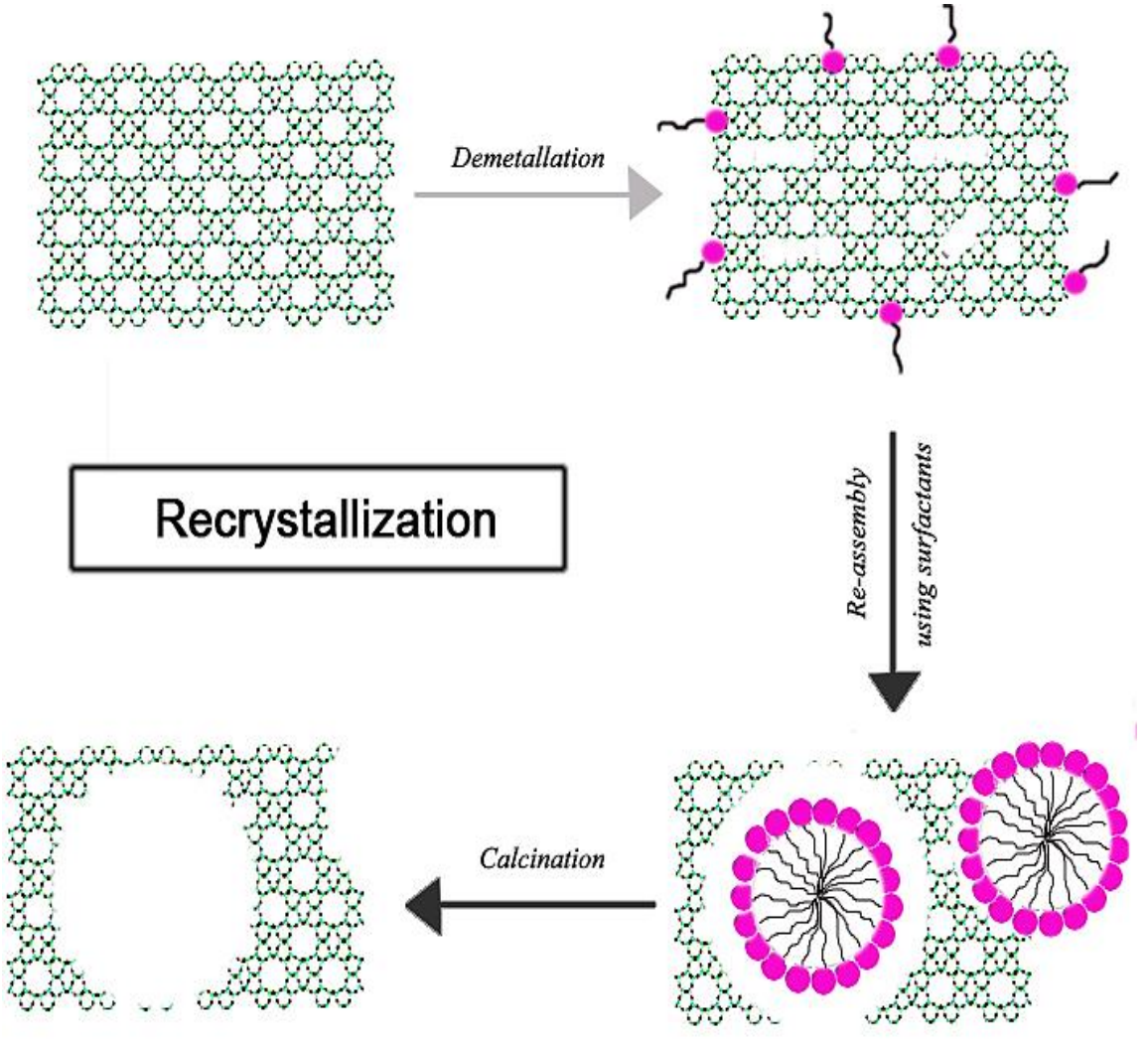

Fig. 12 Schematic representation of the recrystallization technique.

ordered mesoporous materials with intra crystalline mesopores.

Assembly of zeolites

Different techniques have been formulated in order to synthesize hierarchical zeolites in the form of nanoslab, grids, thin films, extrudates, granules *etc*. Hierarchical zeolite powders in protonic form was structured into mechanically stable granules by pan granulation with high-purity attapulgite or into extrudates by extrusion with kaolin by Gueudre *et al*.[119] The resulting complex shows trimodal network of micro-, meso-, and macropores. The introduction of mesopores, leads to a 6 times improved effective diffusivity in hierarchical with respect to conventional zeolite powders.

Martens *et al*. found that crystallization of silicalite from clear solution passes through different steps including nanoslabs and tablets.[120] The aggregation steps starting from the precursor were identified using different techniques such as cryo–TEM, Small angle X-ray scattering (SAXS), Atomic force microscopy (AFM), dynamic light scattering (DLS), diffuse reflectance IR, and Si NMR spectroscopy. The first type of material, denoted as zeogrid was obtained by reorganization of the correlated regions by addition of CTAB. The nanoslabs are stacked in concentric layers, intercalated by surfactant molecules. In the second type of hierarchical structure, denoted as zeotile nanoslabs are linked through their corners, edges or faces following patterns imposed by interaction with surfactant. A high meso structural order is typical for these assemblies.

Another method of assembling zeolites is the layer-by-layer deposition. TPA- silicalite-1 nanoparticle assembled into core-shell structures by layer-by layer deposition.[121] Multi-layered shells of silicalite-1 constructed on the latex beads by alternating the deposition of silicalite with a polycationic layer of PDADMAC. Zeolite membranes were prepared from silicalite colloidal nanocrystal suspension dispersed on mica substrates.[122] The microwave treatment imparts mesoporosity. Hydrogen bonds are formed between nanoparticles during self-assembly process. Calcination leads to self-standing zeolite membranes, with enhanced mechanical strength.

Pulsed current processing (PCP) is used to produce hierarchical monoliths from silicalite and ZSM-5.[123] Zeolite powders loaded in cylindrical graphite dies and treated in vacuum with a uniaxial pressure using a pulsed current processing apparatus. PCP or, as it is commonly called, spark plasma sintering, enables rapid thermal processing of zeolite powder assemblies with heating and cooling rates at 100 °C/minute or more, which results in the formation of strong powder bodies without any addition of secondary binders. The mercury intrusion data shows that PCP-treated silicalite -1 monoliths possess macropores with a size of around 3 μm and the ZSM-5 monoliths display a macroscopic pore size around 200-700 nm, and an additional mesoporosity with a pore size around 5-20 nm.

Efforts have been taken by Carr *et al.* to synthesize hierarchically ordered thin films. They used a silicalite precursor with a Pluronic P123 (Poly (ethylene glycol)-block-poly(propyleneglycol)-block-poly (ethylene glycol) surfactant template at low temperature for the synthesis of a micro-/mesoporous MFI/SBA-15 material.[124] Ordered thin films can be synthesized by employing low temperatures.

MCM- 36 was synthesized from MCM-22 by swelling and pillaring.[125] MCM-22 mixed with swelling precursor solution, which is made by adding TPAOH and CTAB. Then the material is added to TEOS. After that, the product was recovered by vacuum filtration, The dried powder was further hydrolyzed with an aqueous NaOH solution. The hydrolyzed product was obtained by centrifugation and dried overnight and finally, the recovered product is calcined in N_2 atmosphere followed by air atmosphere. In addition, through the swelling and pillaring process, the enclosed pore structures of 12-membered ring supercages and parts of 10-membered rings were opened. These orderly exposed structures allowed for controlling and desirably decreasing the residence time during which the encapsulated intermediates stayed inside the intralayer pores. The amount of carbon deposition was also found to decrease.

Chaikittisilp reported an alternative approach for the construction of hierarchically organized, honeycomb-like MFI zeolites(silicalite-1) by sequential intergrowth using dimers of the TPA cation, $(C_3H_7)_3N^+$- $(CH_2)nN^+(C_3H_7)_3$.[126]

Bai *et al*. synthesized ZSM-5 particle with scroll-like morphology and hierarchical pores (macropores, mesopores and micropores) in the presence of n-hexyltrimethy lammonium bromide (HTAB) and TPAOH.[127] Here zeolite particles were assembled by layer by layer wrapping of nanosheets.

Wang *et al*. applied a layer-by-layer zeolite assembly technique for the fabrication of zeolites such as silicalite-1, TS-1, ZSM-5 and beta zeolite with hierarchical pores using structured diatoms as templates.[128] Diatoms were positively charged by depositing a layer of cationic poly diallyl dimethyl ammonium chloride (PDDA). Then, the nanozeolite and PDDA were alternately deposited on the positively charged diatom substrates to form homogeneous nanozeolite/PDDA multilayers. Electrostatic attraction between the charged nanozeolite and oppositely charged polyelectrolyte is the effective driving force for the self-assembly of zeolite.

Liu *et al*. synthesized hierarchical macro-meso-micro porous ZSM-5 zeolite fibres via coaxial electrospinning.[129] Electrospinning was done by coaxial nozzle that create core-shell or hollow fibers in one-step. A suspension of ZSM-5 nanocrystals in polyvinylpyrrolidon (pvp)/ethanol solution worked as outer fluid and paraffin oil served as inner fluid for electospinning.

Assemblages were also synthesised using nanoclusters. The preformed zeolite Y nanoclusters is added to CTAB and assembled with kaolin in presence of NaOH.[130] XRD & SEM analysis confirms the absence of bulky microporous zeolite

phase in the composite. Microporous structure exists in mesoporous phase. The unique pore structure facilitates the mass transfer. Ammonia TPD analysis on Mesoporous zeolite Y/ Kaolin (MY/Kaolin) shows that lower percentage of strong acid sites which leads to lower catalytic activity for acid catalysed reaction. IR spectroscopy of adsorbed pyridine also confirms that there are less Bronsted acid sites and Lewis acid sites in the composite than parent Y.

Zheng *et al*. synthesized a series of zeolite composite by employing beta and Y zeolite as the nutrient for the other phase of zeolite growth.[131] BFZ (a composite zeolite prepared using beta zeolite as the core and Y zeolite as the shell) prepared by adding the pre-synthesized zeolite beta into mixture of sodium aluminate and seeds of Y zeolite, the solution was then stirred and subjected to hydrothermal treatment. BFZ-s (a composite zeolite prepared with zeolite-embedded aluminosilicate extrudates as the nutrients for Y zeolite growth) prepared by adding beta zeolite powder into mixture of aluminosilicate and zeolite Y seeds. It is then kneaded and extruded into cylindrically shaped extrudates with a diameter of 2.0 mm. After drying, beta extrudate Y zeolite seeds and NaOH were added to water and put in a stainless-steel autoclave for hydrothermal synthesis of BFZ-s.

5. Incorporation of metals in hierarchical zeolites

Incorporation of metal ions on hierarchical zeolites has received much attention during the last few decades due to their unique catalytic property in many industrially relevant reactions. Besides, hierarchical zeolites are facilitating diffusion of molecules into catalytic sites, the presence of mesopores increases the external surface of the zeolites considerably, which has a direct impact on the encapsulation of metal nanoparticle. Basically, metal ions are encapsulated by different strategies such as post-synthetic encapsulation strategy and in situ confinement strategy.[132] Here are some of the important works and their corresponding applications. Gold nanoparticles have also been impregnated in silicalite-1 mesoporous crystals by reduction. Au nanoparticles encapsulated silicalite-1 is very active in the gas phase oxidation of ethanol. Pt dispersed hierarchical ZSM-5 is very effective in suppression of the formation of ethyl benzene during the hydrogenation of ethylene to ethane. Moreover, Pt supported zeolites also acts as a good catalyst for hydrogenation of naphthalene in the presence of H_2S or dibenzothiophene. Titanium-containing silicalite-1 with gold particles shows its activity in mild oxidation, epoxidation and hydroxylation reactions in the presence of H_2O_2. Moreover, Cobalt oxide embedded ZSM-5 is very effective for Fischer–Tropsch.[133]

Synthesis of hierarchical self-assembled mesoporous zeolite structures were done by isomorphic substitution of Si with Mn and Al. It is shown that Mn-containing mesoporous zeolites are capable to form disulfide bonds with thiols in the presence of air. These hierarchical zeolitic materials have enhanced surface area, good pore-wall stability and possess reactive Mn^{4+} sites bringing forth a new era for the synthesis of value-added disulfides.[134] Hierarchical mesoporous iron encapsulated ZSM-5 is also found to possess maximum porosity and optimum metal content. It is found that the resulting szeolites are active and selective for the hydroxylation of benzene to phenol with nitrous oxide and oxidation of cyclohexene.[135,136] The ultrafine particles of various metal oxides (CeO_2, TiO_2, and $MnOx$) are encapsulated in zeolites. The method was extended to encapsulate noble metals (Au and Pt) in zeolites through their strong metal-support interactions with the metal oxides without the need of using any organic stabilizing ligands. If the metal clusters are incorporated by ion exchange method, it usually is in micro porous cavities as metal complex precursors or as solvated metal ions. Whereas, if the metal clusters are encapsulated by incipient wetness impregnation method, mesopores of these hierarchical zeolites can accommodate metal oxide particles. This work helped to pave an effective route to the encapsulation of noble metals in zeolite by making use of strong metal-support interactions without the need of any organic ligand to capture metal species. The catalyst exhibits benevolent catalytic activity and high selectivity for hydrogenation.[137] Metal nanoparticle is also encapsulated on Hierarchical zeolites through base-assisted chemo selective interaction between the silicon species on zeolite surface and metal salts. Flower-like nickel silicate precursor is prepared and coated on the polycrystalline particles of zeolite via base-assisted chemo selective interaction with corresponding metal source. The Nickel encapsulated ZSM-5 exhibits excellent catalytic activity and stability in the hydrodeoxygenation of stearic acid.[138] One-pot hydrothermal system using the metal stabilization by interacting with ethylene diamine tetra acetic acid (EDTA) as a ligand precursor is one of the most interesting techniques. This ultra-small metal nanoparticles on acid zeolite surfaces are advantageous for the mild 4-propylphenol hydrodeoxygenation as a model reaction for bio-oil upgradation application with a very high catalytic performance.[139] Cu^{2+} exchanged hierarchical ZSM-5 synthesized by the ion-exchange process enrouting$NaBH_4$ as a reducing agent. This catalyst exhibits superior activity for the synthesis of indolizine, chalcone and 1,2,3-triazole derivatives.[41] Furthermore, Bifunctional Cu/H-ZSM-5 zeolite with hierarchical porosity is effective for hydrocarbon abatement under cold-start conditions.[16] Hierarchical zeolites of faujasite (FAU) (zeolite Y) and BEA containing tin and Ruthenium oxide was synthesized and used in catalytic isomerization of dihydroxyacetone (DHA) to lactic acid and alkyl lactates.[45,140] In another work, the encapsulation of Zr^{4+}, increased the acid sites, as a result, increased catalytic activity of the zeolites was observed in the production of the unsymmetrical ether from anisaldehyde and 2-butanol.[141]

6. Stability and Application of Hierarchical Zeolites

Hierarchical Zeolites have considerable strength, flexibility

Table 1. Hierarchical zeolites in different types of catalytic reactions.

Type of hierarchical zeolite	Application	Metal modification	Route to hierarchical zeolite	Ref
BEA	Acetalization of glycerol with formaldehyde		Desilication	[15]
ZSM-5	Hydrocarbon abatement	Copper	Desilication	[16]
zeolite H-Y	Hydrocracking of n-hexadecane or squalane		Desilication	[145]
ZSM-5	Oxidation of cyclohexene	Iron oxide	Desilication	[146] [136]
ZSM-5	Pyrolysis of Biomass		Desilication	[147]
ZSM-5	Methylation of toluene to *p*-xylene, MTH reaction and isomerization of *p*-xylene		Desilication	[20]
ZSM-5	Biomass catalytic pyrolysis of oak		Desilication	[148]
Zeolite-Y	Isomerisation of α – pinene transformation to camphene and limonene.		Desilication	[21]
ZSM-5	Acylation (acylation of indole and benzoylation of resorcinol),		Surfactant as template	[42]
ZSM-5	Esterification (hexanoic acid with benzyl alcohol),		Surfactant as template	[42]
ZSM-5	Condensation (synthesis of vitamin E by the reaction of isophytol and 2,3,6-trimethylhydroquinone), and reactions.		Surfactant as template	[42]
ZSM-5	Hydroamination (aniline with methyl acrylate)		Surfactant as template	[42]
FAU or BEA	Isomerization of dihydroxyacetone (DHA) to alkyl lactates and lactic acid	Tin	Surfactant as template	[40]
ZSM-5	Methylation of 2-Methyl Naphthalene with methanol to 2, 6 DiMethylNaphthalene(2, 6-DMN)		Surfactant as template	[45]
BEA	Anisaldehyde and 2-butanol to 4-methoxybenzyl sec-butyl ether	Zirconium	Surfactant as template	[141]
ZSM-5	Removal of crystal violet		Chitin as template	[49]
ZSM-5	Alkylation of phenol with cyclohexene		Cationic polymer as template	[53]
Beta zeolites	Alkylation of benzene with isopropanol		Cationic polymer as template	[54]
Beta zeolites	Acylation of ferrocene with acetic anhydride		Dicationic ionic liquids	[55]
Beta zeolites	Transesterification of soyabean oil with methanol.		Dicationic ionic liquids	[56]
ZSM-5	Gas products of methanol aromatization		Kaolin clay modified	[56]
Pillared MWW, pillared MFI	Conversion of Propane and Isobutane.		Assembly	[71]

Continued

3DOm-i MFI zeolites	Conversion of Propane and Isobutane.		Hard template (3Dom carbon)	[71]
ZSM-5	Dealkylation of ethylbenzene		Carbon template	[59]
HZSM-11	Isomerization and cracking of n-hexadecane and		Hard templating (Carbon)	[64]
TS-2	Epoxidation of oct-1-ene and styrene.		Hard templating (Carbon)	[64]
ZSM-12	Cracking of tridecane and 1,3-dimethylcyclohexane.		Carbon black	[58]
Clinoptilolite	Removal of ionic contaminants from waste streams		Carbon from date stone	[149]
Fe-containing ZSM-5	Catalytic wet peroxide oxidation of lignin	Iron	Polystyrene beads	[83]
Fe-containing ZSM-5	Catalytic wet peroxide oxidation of EDTA	Iron	Polystyrene beads	[83]
ZSM-5	Alkylation of phenol to 2, 4-di-tert-butyl phenol selectivity		Polystyrene Sphere	[82]
ZSM-5 nanozeolite	Alkylation of phenol to 2, 4-di-tert-butyl phenol selectivity		Natural rubber latex	[84]
Hierarchical ZSM-5	Conversion of methanol to light olefins		Polyurethane foam	[88]
ZSM-5 monolith	Esterification between benzyl alcohol and hexanoic acid		Sponge	[91]
Monolith silicalite-1	Beckman rearrangement of cyclohexanone oxime to caprolactam		Organic aerogel	[92]
Self-supporting ZSM-5 monolith	Removal of trichloroethylene (TCE)		Polyurethane foam	[89]
Hierarchical ZSM-5 and hybrid zeolitic/ordered mesoporous materials	1,2-epoxyoctane isomerisation to octaldehyde (IV) and monounsaturated alcohols (V and VI)		Silanization	[89]
Hierarchical ZSM-5 and hybrid zeolitic/ordered mesoporous materials	Anisole acylation to para-methoxyacetophenone,		Silanization	[97]
Mesoporous ZSM-5	Gas-oil cracking		Silanization	[150]
ZSM-5-HTS	The acetone conversion to isobutene		Silanization	[101]
Meso[Fe]ZSM-5	Hydroxylation of benzene to phenol on the mesoporous ZSM-5		Silanization	[104]
ZSM-5	Jasminaldehyde (α-*n*-amylcinnamaldehyde) synthesis reaction.		Silanization	[103]

Continued

Mesoporous ZSM-5	Synthesis of vesidryl (2, 4, 4-trimethoxychalcone).	Silanization	[103]
Microporous HZSM-5	Conversion of triisopropylbenzene (TIPB) to isopropylbenzene and m-diisopropylbenzene	Zeolitization	[110]
MCM-41	Alkylation of naphthalene with cyclohexene	Recrystallization	[115]
Hierarchical ZSM-5	Self-condensation of cyclohexanone and methanol to chalcones	Assembly	[127]
Hierarchical ZSM-5	Cracking of isobutene	Assembly	[129]
Composite zeolite prepared by using beta zeolite as the core and Y zeolite as the shell	Cracking of isopropyl benzene and Dehydration of methanol to diethyl ether (DME)	Assembly	[131]

and excellent stability. The synthesis method plays an important role in determining the stability. The top-down method renders high stability whereas the bottom-up method renders the hierarchical zeolites with lower stability.[13] Hierarchical zeolites exhibits great activity and stability while catalyzing organic reactions. The presence of mesopores or macropores improves the catalytic stability by reducing the diffusion path length. Enhanced external surface increases the ability to overcome deactivation, moreover, it helps to avoid frequent regeneration.[142,143] The hierarchically structured monolith shows additional mechanical stability as well.

The mass transport limitations of purely micro porous zeolites make it ineffective and uneconomical in catalytic reactions. The low diffusivity of the reactants towards the active sites located in the micropores limits its role in industrial catalysis. The additional pores in the hierarchical zeolites improves the transport of larger substrates. Easier accessibility to acid sites is possible by the presence of multimodal pores. The monolithic zeolite are crystalline and attribute a hierarchically porous structure contain micro-, meso-, and macropores. The presence of meso and macropores facilitated the diffusion of reactants to the micropores and also reduced the extent of pressure drop associated with the use of conventional powder and pellet catalysts.

It is found that the industrially important reactions like alkylation and acylation over hierarchical zeolites leads to higher activity and lower deactivation of catalyst. Shorter diffusion path length, intracrystalline mesoporosity, uniform intercrystal mesopores and large external surface area of the hierarchical zeolites make them unavoidable in industrial catalysis at the present time in contrast with past. Ramirez demonstrated the large-scale preparation of hierarchical zeolites for the implementation of it into the industry rather than laboratory.[144] By the presence of intracrystal mesopores, there is a fourfold increase in the ethyl benzene selectivity over the pilot sample in the alkylation of benzene with ethylene. Since this monocyclic aromatic hydrocarbon is important in the petrochemical industry as an intermediate in the production of styrene.

Cracking reaction is one of the most efficiently done reactions by the use of hierarchical zeolites. The general finding is that hierarchical zeolites are comparable in activity to conventional zeolites for the cracking of small substrates. However, the mesopores lead to a great activity increase due to the enhanced accessible surface area for larger substrates. The combination of a good accessibility and strong Lewis acidity in hierarchical zeolite strongly improves their catalytic properties compared with conventional zeolites. Cracking reactions of large molecules which experiences diffusion and/or steric limitations in conventional zeolites is an excellent example of the advantage of hierarchical zeolites. Also, hierarchical zeolites have found application as catalysts for condensation reactions. This represent application of hierarchical zeolites in reactions that are conventionally away from the capacity of purely microporous zeolites due to the large molecular size of the reactants or products compared to the dimensions of the zeolite channels.

The slow diffusion of reactants and products through conventional zeolites led to the production of undesired oligomers and aromatics in the methanol conversion reaction leading to the deactivation of catalyst by blocking of carbon residue on the active site and channels. Propylene and light aromatics are commercially important by their applications in petrochemical industry and selectivity of it is difficult using microporous zeolites. The fast diffusion, multi modal porosity

and long catalytic life time of the hierarchical zeolites makes it a promising catalyst in methanol conversion reaction.

The presence of meso - macroporosity and highest external surface area of hierarchical zeolites allowed to increase adsorption capacity to very high values. Therefore, these hierarchical zeolites find applications in decontamination through adsorption and encapsulation of hazardous chemicals, ions and gaseous products from environment. The Table 1 represents the examples of hierarchical zeolites in different types catalytic reactions.

7. Summary and future perspectives

The idea of introducing hierarchical pores into otherwise microporous zeolites was a breakthrough in industrial catalysis. The chief advantages of these hierarchical zeolites over conventional microporous zeolites are their specific external surface area, which improve the reaction rate for diffusion limited reactions and transport properties with higher selectivity. The most interesting part is that, hierarchical zeolites exhibit slower deactivation kinetics or longer catalyst life time. This review gives a overview on the synthesis of hierarchical zeolites and its applications, It also describes how the newly added porosity is related to synthesis conditions and its effect on the heterogeneous catalysis.

The synthesis of hierarchical zeolites mainly categorized into two, they are destructive approach (through structure fracturing) such as dealumination, desilication and ion irradiation and constructive methods (structure fabrication) including Templating, silanization, structuring, and zeolitization. Each synthesis method has its own advantages which are to be selected based on the structural and functional requirement of desired applications. Different types of porosity such as, micro-meso, micro-macro, micro- meso-macro and micro-meso-macro- macroporous zeolites are obtained based on the synthesis procedures.

The constructive method or bottom-up method involves the use of carbon black, non carbon, polymers, silylated surfactant, amorphous materials, cationic polymers *etc*. for effective interaction with aluminosilicate species. Templating method is highly efficient and there are so many works reported using hard and soft templates. Hard Templating method involves the consumption of either porous or nonporous solid material during the zeolite synthesis to serve as a meso- or macroporogen for the formation of the additional porosity. However, the hard templating strategy is often limited by multistep procedures, relatively high costs and health hazards related to some of the hard templates used. Some of these limitations can be improved by using biological templates. Whereas the inter and intracrystal mesoporosity is obtained by using soft template approach.

Hierarchical zeolites can be used in numerous catalytic reactions such as alkylation, acylation, condensation and conversion of methanol. The application of hierarchical zeolites allows to reduce the diffusion limits in material pores, improve the heat and mass transfer properties, lower the pressure drops in reactors and facilitates regeneration of the catalyst.

The pace with which advancements are taking place in the field of hierarchical zeolites is immense. In the very near future, we can expect the use of hierarchical zeolites for a wider range of applications. The nanostructures of zeolites with hetero porosity would find great potentials in heterogeneous catalysis, adsorption, separation process and development of functionalized zeolitic materials. Moreover, the synthesis strategy applied to the synthesis of monoliths could be applicable for preparing advanced types of technically-relevant and mechanically stable hierarchical zeolites.

The near future would be witnessing the synthesis and use of smart and tunable hierarchical porous catalysts, which can tune the size of pores according to the needs of the reaction. These hierarchical catalysts with tunable porosity would surely possess very high turnover number and turn over frequency with literally no need for regeneration. These characteristics of catalyst would enable the scientists to use costly and efficient metals that top the Tafel's plot. These hierarchical zeolites would be way better than the conventional zeolites or mesoporous materials. It surely would be a promising catalyst in large scale production of chemicals.

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Not applicable.

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