Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design

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The introduction of synthetic zeolites has led to a paradigm shift in catalysis, separations, and adsorption processes, due to their unique properties such as crystallinity, high-surface area, acidity, ion-exchange capacity, and shape-selective character. However, the sole presence of micropores in these materials often imposes intracrystalline diffusion limitations, rendering low utilisation of the zeolite active volume in catalysed reactions. This *critical review* examines recent advances in the rapidly evolving area of zeolites with improved accessibility and molecular transport. Strategies to enhance catalyst effectiveness essentially comprise the synthesis of zeolites with wide pores and/or with short diffusion length. Available approaches are reviewed according to the principle, versatility, effectiveness, and degree of reality for practical implementation, establishing a firm link between the properties of the resulting materials and the catalytic function. We particularly dwell on the exciting field of hierarchical zeolites, which couple in a single material the catalytic power of micropores and the facilitated access and improved transport consequence of a complementary mesopore network. The carbon templating and desilication routes as examples of bottom-up and top-down methods, respectively, are reviewed in more detail to illustrate the benefits of hierarchical zeolites. Despite encircling the zeolite field, this review stimulates intuition into the design of related porous solids (116 references).

1. Evolution of porous materials: from disorder to hierarchy

1.1 Bright and dark sides of zeolites

Porous solids contribute to the welfare of society, mediating a multitude of applications in industry, environmental protection, and medicine, as well as in emerging areas such as nanotechnology, photonics, microelectronics, and bioengineering. The art, science, and engineering of making porous materials generally cover understanding and controlling the size, shape, and connectivity of the voids and channels built into solid frameworks, generally of inorganic nature. Over the last decade,

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we have witnessed great progress in the ability to fabricate new porous materials with defined structural, compositional, interfacial, and morphological properties.[1–6] This has created an impressive materials supermarket awaiting novel or improved applications.

Traditional porous solids used as catalysts, catalyst supports, and adsorbents, *e.g.* alumina, silica, and activated carbon, are mostly disordered in the sense of having random pore distributions covering indiscriminately the micro (<2 nm), meso (2–50 nm), and even macro (>50 nm) size ranges. The prime objective was, and in many cases still is, the attainment of several hundreds of square meters area per gram of solid without predefined pore geometry characteristics. The introduction of the first synthetic zeolites in the 1950s and the discovery of high-silica zeolites in the 1970s brought about a paradigm shift in the field of porous materials. Zeolites are a unique class of crystalline aluminosilicates with very high surface areas, being a consequence of ordered micropores of molecular dimensions (typically 0.25–1 nm) that enable shape-selective catalytic transformations. Fig. 1(a) illustrates a typical isotherm of the MFI-type ZSM-5 zeolite, containing a multi-dimensional network of micropores of 0.56 nm (Fig. 1(b)). Fundamental and practical interest of zeolites is largely a direct consequence of the fact that their bulk properties can be manipulated through variations in the atomic structure. Today, more than 170 different zeolite structures have been reported,[7] enabling the practice of *pore engineering* and offering seemingly endless possibilities to tailor these materials for chemical reactions.

However, zeolites and in general materials with active sites confined in micropores, are often victims of their own success, as the sole presence of micropores can impose severe mass-transfer constraints on the rate of catalysed reactions.[8–16] Diffusion, the main mechanism of mass transfer in micro- and mesoporous materials, is of crucial importance for their application in separation and catalysis, since the molecular mobility ultimately determines the rate of the overall processes.[8] Like the impeded human transit in crowded department stores and the dilatory traffic during rush hour in any metropolis, the intracrystalline motion of molecules in zeolite pores is intrinsically slow. The transport of a molecule in a pore of closely similar size is hindered, being further aggravated by the fact that reactants and products have different agendas: reactants enter while products abandon the pore system. Diffusion limitations due to restricted access and slow transport to/from the active site provoke low catalyst utilisation. This represents a major drawback in most industrial reactions catalysed by zeolites, *e.g.* cracking, oxidation, (hydro)isomerisation, alkylation, and esterification, as they do not operate at their full potential. In particular applications, *e.g.* the well-known methylation of toluene by methanol over H-ZSM-5, operation under strongly diffusion limited conditions is beneficial in order to enhance the fraction of *p*-xylene in the isomer distribution.[9,10] To this end, large zeolite crystals, *i.e.* long diffusion path lengths, and low acidity at the external surface are preferred. Bringing the accessibility problem to the extreme, the size exclusion principle of "to fit or not to fit" disables processing molecules larger than the pore entrance. According to industrial directives in terms of sharp conversions and intensified processes, future developments in zeolite catalysis should focus on more efficient catalyst utilisation for targeted reactions.

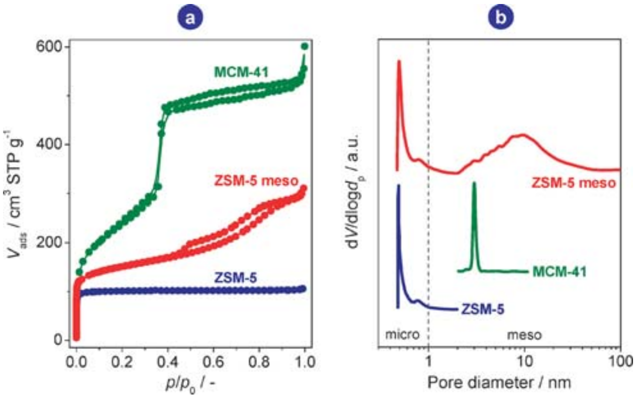
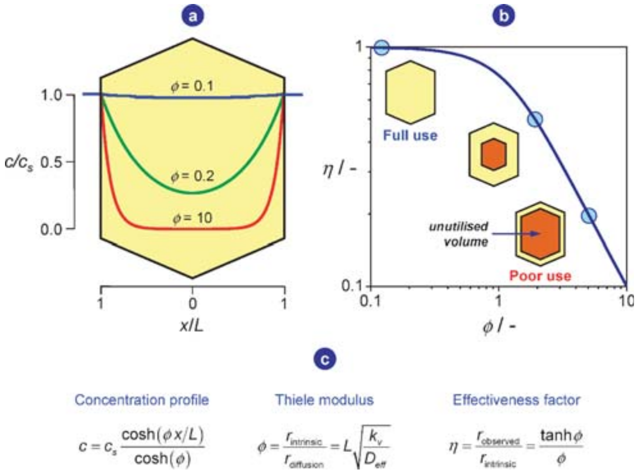


Fig. 1 Nitrogen isotherms at 77 K (a) and BJH pore size distributions (b) of characteristic porous solids. Purely microporous zeolites (*e.g.* ZSM-5) show N_2 uptake at low relative pressure followed by a plateau, the result of uniform micropores of 0.56 nm and the absence of larger pores. Ordered mesoporous materials (*e.g.* MCM-41) present N_2 uptake at intermediate relative pressure due to the presence of uniform mesopores of 3 nm, *ca.* 5 times larger than in typical zeolites. The isotherm of mesoporous ZSM-5, obtained by modification of the parent zeolite by desilication (details in text), shows N_2 uptake in various regions of the isotherm. The resulting material contains both micropores (0.56 nm) and mesopores (10 nm). The occurrence of a bimodal (or multimodal) pore distribution illustrates in broad terms what a hierarchical porous solid refers to.

1.2 Strategies to increase catalyst effectiveness

In reaction engineering, the degree of catalyst utilisation is classically described by the effectiveness factor (Fig. 2). Full utilisation of the catalyst particle ($\eta \rightarrow 1$) represents a situation where the observed reaction rate equals the intrinsic reaction rate due to operation in the chemical regime, *i.e.* free of any diffusion constraints. In terms of intraparticle transport, this is attained at low values of the Thiele modulus ($\phi \rightarrow 0$). Contrarily, $\phi = 10$ renders $\eta = 0.1$, meaning that only 10% of the catalyst volume is effectively used in the reaction. Transport limitations negatively impact not only on activity, but occasionally also on selectivity and stability (lifetime), *i.e.* the three distinctive features of any catalyst. Since the intrinsic rate coefficient k_v is fixed for a given reaction and zeolite, keeping the Thiele modulus small implies the practise of two basic strategies: shortening the diffusion length L and/or enhancing the effective diffusivity D_{eff} in the zeolite pores. In the latter line of thinking, ordered mesoporous materials (OMMs) with regular pores in the typical range of 2–15 nm have intensively been developed since the 1990s.[11–15] MCM-41 is prototypical in this category, displaying one-dimensional ordered arrays of non-intersecting hexagonal channels with controlled size in the range of 2–10 nm (Fig. 1). The diffusion regime in mesopore catalysts is typically bulk or Knudsen diffusion and this leads to diffusivities several orders of magnitude higher than in micropores, which often display an activated (configurational) diffusion mechanism. However,



$$c = c_s \frac{\cosh(\phi x/L)}{\cosh(\phi)} \qquad \phi = \frac{r_{\mathrm{intrinsic}}}{r_{\mathrm{diffusion}}} = L\sqrt{\frac{k_v}{D_{\mathrm{eff}}}} \qquad \eta = \frac{r_{\mathrm{observed}}}{r_{\mathrm{intrinsic}}} = \frac{\tanh\phi}{\phi}$$

Fig. 2 Concentration profiles across a zeolite crystal (slab geometry) at different values of the Thiele modulus, ϕ (a). The reactant concentration across a zeolite crystal is extinguished ($c/c_s = 0$) near the surface at $\phi = 10$, while being practically uniform and very similar to the surface concentration ($c/c_s = 1$) at $\phi = 0.1$. The dependence of the effectiveness factor on the Thiele modulus is shown in (b). Low Thiele moduli lead to full catalyst utilisation ($\phi \to 0$, $\eta \to 1$) while high Thiele moduli render a poorly utilised catalyst ($\phi \to \infty$, $\eta \to 1/\phi$). Relevant equations to construct the graphs (a) and (b) are given in (c). They were derived assuming steady-state diffusion and reaction, slab model, first-order irreversible reaction, and isothermal conditions. Baur and Krishna[116] addressed the applicability of classical definitions of Thiele modulus and effectiveness factor for zeolites.

the *a priori* very optimistic hopes for moving the zeolite catalysis to the meso-scale by using OMMs have so far not crystallised in industrial applications due to the limited success in mimicking the unique functionalities of zeolites. Consequently, research has primarily aimed at effective chemical modification of the amorphous walls in OMMs by *e.g.* grafting[16] or crystallisation[17,18] to generate active sites equivalent to those in zeolites.

From this key learning, the scientific community started to look for alternative strategies leading to improved accessibility of the active sites confined in zeolites, which are elaborated in the next section. Two fundamentally different approaches can be adopted: (1) increasing the width of the micropores or (2) shortening the micropore diffusion path length. For several decades, researchers have pursued the preparation of *new* "large-cavity" and "wide-pore" zeolites (up to 1.25 nm), containing rings of 12 or more T-atoms. Most of these low-framework density structures, among many others VPI-5,[19] UTD-1,[20] and ECR-34,[21] suffer from similar problems as OMMs, *i.e.* low thermal stability, low acidity, and unidirectional pore systems. Recently, wide-pore zeolites with multidirectional channels have indeed been obtained, *e.g.* ITQ-15,[22] ITQ-21,[23] and ITQ-33,[24] further realising the "promise of emptiness".[25]

For a given zeolite framework, the basic strategy to change the diffusion path length is altering crystal size and morphology using particular crystallisation conditions. Aiming at shorter diffusion path lengths in micropores of *existing* zeolites, "hierarchical" systems have been developed and have attracted rapidly growing attention. Broadly speaking, materials with structural hierarchy exhibit structure on more than one length scale.[26] Hierarchical porous materials integrate multiple levels of porosity. In zeolites, this can be attained by decreasing the crystal size or by introducing an additional (meso)pore system within an individual zeolite crystal. Importantly, for a material to be denoted hierarchical, it is required that each level of porosity has a distinct function; the functionality is the differentiating feature with respect to a disordered porous material. The topics of wide-pore and hierarchical zeolites have been presented in various reviews, mini-reviews, and perspectives covering particular synthetic approaches.[11,17,18,25,27–31] However, there exists an urgent need to quantitatively compare the various methods for their preparation, and not least to describe in detail the properties of the materials as well as to establish a firm link to catalysis. We set ourselves this task in this review, pinpointing which methods are most useful for different types of studies and applications. Although focus is on the zeolite field, we attempted to synthesise concepts that are generally applicable for the design of other types of porous materials.

1.3 Hierarchical systems

Generally speaking, hierarchical porous solids can be characterised by the number of porosity levels in the material and their individual geometry. As exemplified by the mesoporous ZSM-5 in Fig. 1, the prime aim of hierarchical zeolites is coupling in a single material the catalytic features of micropores and the improved access and transport consequence of additional pores of larger size. However, the connectivity between the various levels of pores is vital to maximise the benefits of hierarchy in catalysed reactions. Interconnected hierarchy refers to the network of voids generated in the intercrystalline space by fragmentation of the microporous crystal (Fig. 3(a)) into nanocrystals (Fig. 3(b)). Intraconnected hierarchy makes reference to the occurrence of mesopores in the microporous crystal (Fig. 3(c) and (d)). The schematic representations in Fig. 3(b)–(d) shorten the length of the micropores in a similar way with respect to Fig. 3(a) as the result of smaller crystals or intracrystalline voids. Besides, the three configurations could result in qualitatively similar N_2 isotherms and pore size distributions as that of mesoporous ZSM-5 in Fig. 1. A shorter diffusion length is necessary to increase the catalyst effectiveness, but it is not a sufficient condition. For example, the system in Fig. 3(d), which could well represent a hollow zeolite crystal, is transport-wise ineffective. This is due to the fact that the mesovoids are entrapped in the microporous matrix and thus only accessible *via* the micropores. Oppositely, the mesopores in Fig. 3(c) are directly accessible from the outer surface of the zeolite crystal, similarly to the intercrystalline space in nanocrystals (Fig. 3(b)). In the latter two cases, the condition that mesopores enhance the molecular transport to/from the active sites in the micropores has been satisfied. Thus, introducing mesopores in zeolites could be ineffective for application if not properly located in the crystal. Consequently, engineering hierarchical materials in general, and zeolites in particular, requires a careful design aiming not only at extensively generating large pores, but principally at locating them in

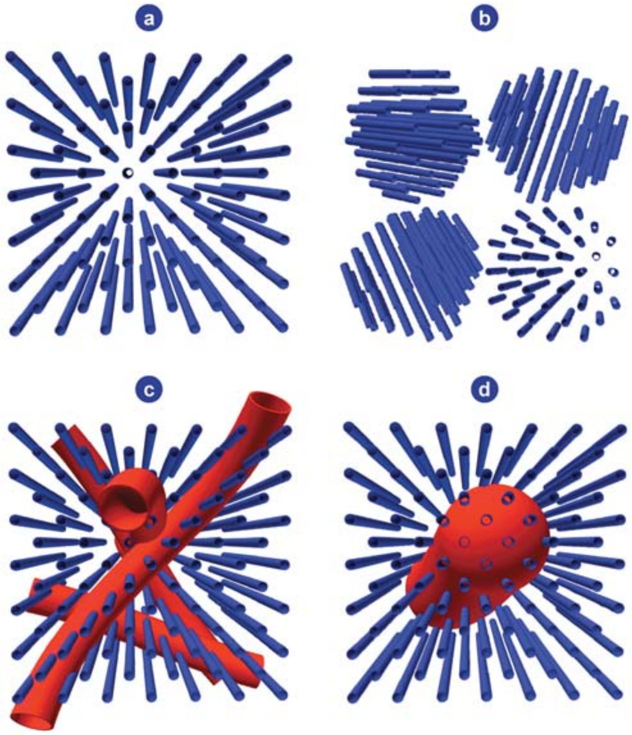


Fig. 3 Different degrees and types of hierarchy can be defined in porous materials. A purely microporous zeolite is considered as a non-hierarchical system according to the single dimension of the pores represented simplistically by the ordered blue sticks (a). The fragmentation of the zeolite into small nanocrystals engenders a network of mesopores constituting the intercrystalline space, leading to an interconnected hierarchical system (b). The term interconnected makes reference to the fact that the micropores in two crystals are bridged by interparticle voids. Intraconnected hierarchical systems are shown in (c) and (d). In these schemes, micropores are crossed by larger pores that are introduced within the zeolite crystal. Two extreme cases can be devised in this category: accessible mesopores that can be entered from the external surface of the zeolite crystals (c) and non-accessible mesovoids that are occluded in the microporous matrix (d). The systems (b), (c) and (d) could lead to similar N_2 isotherms and pore size distributions, resembling that of the mesoporous ZSM-5 in Fig. 1. However, the type and specific location of the mesoporosity largely determine whether the hierarchical system is a more efficient catalyst than the non-hierarchical (purely microporous) one.

harmony with the micropores. This is captured well by the quote by the French architect Robert Le Ricolais, which can be adapted to the topic of this review as "the art of making hierarchical materials is where to put the pore".

2. Zeolites with improved utilisation: materials and methods

As illustrated in Fig. 4, four different types of zeolite-based materials exist that offer improved accessibility to the catalytically active sites located in the microporous crystal:

1. *Wide-pore zeolites*, having substantially wider micropores than regular zeolite structures.

2. *Nanosized zeolites* having only intercrystalline pores or voids.

3. *Zeolite composites* featuring zeolite crystals supported on a material that is typically mesoporous or macroporous. In this case, the support material provides the pores required for improving mass transport to and from the zeolite crystals.

4. *Mesoporous zeolite crystals*, which exhibit intracrystalline mesopores. The introduction of mesopores into zeolite crystals can be conceived in two conceptually different ways. The mesopores are either introduced into the zeolite crystals directly during the crystallisation of the zeolite or they are introduced by a post-synthetic treatment step.

The materials in Fig. 4 can be categorised into two different groups according to the nature of their porosity. Thus, wide-pore zeolites are characterised by having a *unimodal* pore system, whereas nanosized zeolites, zeolite composites, and mesoporous zeolites are characterised by featuring *hierarchical* pore systems, since they combine the intracrystalline micropores having well-defined pore sizes and geometries determined by the crystal structure with larger pores that can be either intercrystalline (Fig. 3(b)) or intracrystalline (Fig. 3(c) and (d)).

Several synthesis strategies have been pursued to produce zeolite materials with improved accessibility. Most of the synthesis methods known today make use of templates in order to control the generation of mesopores. However, it is also possible to induce mesoporosity in zeolite materials without any template. Templating methods can be classified according to the nature of the interface between the zeolite crystal and the mesopore exactly when the mesopore starts to form.[28] In this categorisation, three classes of templating methodologies can be discerned: *solid templating*, *supramolecular templating*, and *indirect templating*. In solid and supramolecular templating, the zeolite crystal is in intimate contact with either a solid material or a supramolecular assembly of organised surfactant molecules that are subsequently removed to engender mesopores. Recently, the terms endo-templating and exo-templating have also been proposed to distinguish between these two approaches for introducing mesopores in materials.[32] In indirect templating, a preformed templated mesoporous material is either (partially) transformed into a mesoporous zeolite material or applied as a supporting material for controlled deposition of zeolite crystals. Both cases result in a composite material comprising zeolite crystals embedded in or deposited onto a mesoporous material. The non-templating methods fall under two general headings: *controlled crystallisation* and *demetallation*, and they entail either controlling the crystallisation conditions so that predominantly nanosized zeolite crystals are formed, or the preferential extraction of at least one of the constituent metallic elements of the zeolite framework, respectively.

2.1 Templating methods

Supramolecular and solid templates have been applied to control mesopore formation during zeolite crystallisation. Although a variety of solids have been used, it appears that the most general and versatile approach is to employ different types of porous carbons.[33–43] Carbon templating methods can be tuned to yield either nanosized zeolite crystals[34] or mesoporous zeolite crystals[35] and they will be dealt with in

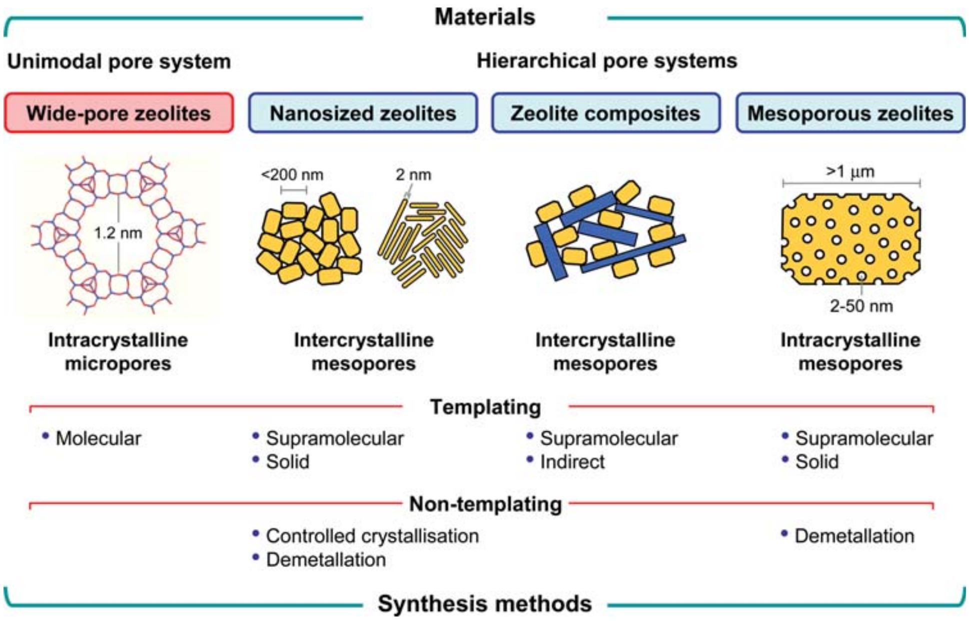


Fig. 4 Categorisation of zeolite materials with enhanced improved transport characteristics. Wide-pore zeolites increase the catalyst effectiveness by attaining higher intracrystalline diffusivity (D_{eff}), while the hierarchical pore systems reduce the characteristic diffusion length (L). Both approaches reduce the Thiele modulus defined in Fig. 2. The synthetic strategies leading to these architectures follow templating or non-templating routes, as detailed in the text.

detail in section 3.1. Other solid templates include resins,[44] organic aerogels,[45,46] and polymers,[47,48] biological templates such as bacteria,[49] plants,[50,51] and starch,[52] as well as purely inorganic compounds such as $Mg(OH)_2$[53] and $CaCO_3$.[53,54]

The supramolecular templating method involves the use of surfactant molecules to actively direct the synthesis of large micropores or mesopores. If we first consider the attempts to increase the pore size of the zeolite micropores, the only viable preparative strategy has proved to be the design of new molecular templates that lead to crystallisation of zeolite or zeotype framework structures with larger pore openings than those previously known. Over the last years, there have been numerous successful examples of wide-pore zeolites discovered with this approach,[20,22–24,55] and it has become possible to significantly accelerate this discovery process by applying high-throughput synthesis techniques.[24] However, it also appears clear that this approach has some severe limitations, since there are relatively few wide-pore zeolites. It is almost exclusively a trial-and-error approach and the operational window concerning chemical composition is relatively narrow.[25] As a consequence, parallel synthesis methodologies are of vital importance and there are still no real possibilities for predicting *e.g.*, the acidity or the hydrothermal stability of the resulting zeolites. Thus, even when a new wide-pore zeolite is obtained, there is no way of knowing in advance whether it will prove useful in a given catalytic application before testing it explicitly. Therefore, it is difficult to directly link the zeolite discovery work with ongoing catalyst development efforts. Besides, routes to large-cavity and wide-pore zeolites are "exotic" in the sense of the required incorporation of germanium and the presence of fluoride in the synthesis composition. In addition, the cost of the structure-directing agent is usually very high compared to more standard zeolites.

Besides zeolites featuring wide micropores, supramolecular approaches can be used to synthesise hierarchical zeolites. They can be classified as either primary or secondary methods, depending on whether the surfactant assists in the assembly of purely molecular species (primary) or partly crystalline species (secondary). There are two distinct approaches to primary supramolecular templating. One is when zeolite crystallisation takes place on the external surface of a surfactant assembly, another is when it takes place inside. There are not many successful examples of the first approach. In fact, the only general route is to apply tuneable organosilanes such as $[(CH_3O)SiC_3H_6N(CH_3)_2C_nH_{2n+1}]Cl$ as both a silica source and supramolecular template.[56,57] By varying the alkyl chain length, it is possible to obtain mesoporous materials with controlled mesopore diameters, up to 20 nm. The other primary supramolecular templating approach is to prepare microemulsions, or reverse micelles, and then apply the confined space within these nanodroplets as a means for controlling the sizes of the zeolite crystals during synthesis.[58,59]

On the other hand, there are three types of secondary supramolecular templating methods that are based on assembly of partly crystalline species. One is the application of surfactants to mediate the assembly of so-called zeolite embryos or seeds into mesoporous structures. Several types of composite materials have been prepared in this way. A class of materials commonly referred to as MSU[60,61] and MAS/MTS[15,62,63] have received attention in recent years partly owing to the fact that they are highly stable in steam at temperatures up to 1073 K. MSU materials have been assembled from zeolite embryos of several different structure types. Another type of secondary supramolecular templating is coating zeolite crystals with a thin layer of mesoporous material by aid of surfactants. Using this procedure, FAU coated with a 5–20 nm layer of MCM-41 structured materials have been produced, and this material exhibited higher conversion than ultra-stable Y in vacuum gas oil cracking of heavy molecules.[62] However, these materials have been shown to be less active and selective towards liquid gasoline products compared to similar mesoporous materials prepared by assembly of zeolite seeds in palm oil cracking using MCM-41/beta composites.[63] The third secondary supramolecular templating method is to apply surfactants to swell and exfoliate layered zeolite precursors into so-called delaminated zeolites. The delamination procedure results in layered zeolite structures, which typically exhibit improved accessibility of the active sites due to their nanosheet-like morphology. These materials, *e.g.* ITQ-2[64] (delaminated MCM-22(P)), ITQ-6[65] (delaminated PREFER), and ITQ-18[66] (delaminated NU-6(2)) typically possess very large external surface areas (600–800 m^2 g^{-1}). Unfortunately, the versatility of this approach is restricted to the few available zeolite precursors with layered structure.

In the indirect templating method, the hierarchical zeolite material is produced in the absence of a distinct mesopore or macropore template but instead from a partial transformation of an ordered zeolite precursor material or by controlled deposition of zeolite crystals onto a mesoporous supporting material.[17,18,28] In either case, the overall morphology of the mesoporous zeolite composite is more or less maintained during the zeolite crystallisation or deposition step. Thus, in this method the templating is indirect, and it can in fact be considered a borderline case between templating and non-templating methods. Typically, the indirect templating method gives composite materials consisting of supported nanosized zeolite crystals. Most reports on indirect templating are concerned with the partial (or secondary) crystallisation of mesoporous materials into zeolite structures.[67–70] Using this methodology, highly mesoporous and relatively stable zeolite materials have been prepared, particularly when thick-walled SBA-15 have been used as the starting material.[67,68] However, also crystallisation of zeolite seeds adsorbed on mesoporous materials such as SBA-15[69] and mesostructured cellular foams,[70] as well as zeolitisation of diatomaceous earth[71,72] are examples of indirect templating. Recently, the partial transformation of a disordered amorphous aluminosilicate into ZSM-5 zeolite/mesophase composite in the presence of TPAOH has been reported as a simple route to synthesise hierarchical systems *via* solid-phase crystallisation.[73]

2.2 Non-templating methods

The last two synthesis methods listed in Fig. 4, *i.e.* demetallation and controlled crystallisation, are non-templating methods. In the demetallation method, one constituent is preferentially extracted from a preformed zeolite material to form mesoporous zeolite crystals. The traditional method for introducing intracrystalline pores in zeolites is by dealumination, which involves preferential extraction of framework aluminium by steaming or acid leaching treatment.[30,31] Steam treatment is the presently used method in industry to induce mesoporosity in zeolites. A more powerful strategy is the selective removal of framework silicon,[74] which will be dealt with in detail in the following section. Recently, partial leaching of titanium and silicon in ETS-10, a titanosilicate material, by treatment in H_2O_2 under microwave irradiation, resulted in intracrystalline mesoporosity and improved catalytic performance in the Beckmann rearrangement of cyclohexanone oxime.[75]

In the controlled crystallisation method,[76,77] the crystallisation conditions are regulated to favour nucleation over crystal growth. In many ways, this is a very desirable way to improve the accessibility of the active sites in zeolite catalysts since it does not require discovery of an entirely new structure type but 'merely' the development of a modified synthesis procedure that favours nucleation over growth for the desired zeolite material. Thus, when it becomes clear that a particular zeolite shows promise in a given catalytic application, it is relatively straightforward to target modified synthesis methods that lead to decreased zeolite crystal sizes. This can be achieved by adding growth inhibitors, by increasing the supersaturation, or by quenched crystallisation. Despite the fact that considerable success has been achieved throughout the last decades in the synthesis of nanosized zeolite crystals,[76,77] unfortunately no generic approach to achieve nanosized crystals of the many available zeolite structures is known.[28] Accordingly, this approach typically also involves massive screening of zeolite synthesis schemes, similar to the approach to obtain large-cavity and wide-pore zeolites. Application of nanocrystals engenders issues related to separation in order to avoid contamination of the final product.[76] In addition, nanocrystals typically possess a relatively low internal surface area due to the decrease in microporosity with decreasing crystal size.[77]

3. Bottom-up *vs.* top-down approaches

In this section, hierarchical zeolites obtained by two particular routes, *i.e.* carbon templating and desilication are elaborated as selected examples of bottom-up and top-down synthetic approaches, respectively. Both routes are contrasted in terms of versatility, effectiveness in porosity generation, diffusion, and catalysis, and last but not least scalability. In fact, both methodologies are amenable to practical implementation.

3.1 Carbon templating

Originally, the carbon-templating approach was conceived in an attempt to develop a general method for synthesizing nanosized zeolite crystals with controlled size distributions.[34] The simple, underlying idea is that crystallisation of a zeolite inside the pores of an inert matrix would prevent the zeolite crystals from growing any larger than the size of the pores in the matrix material. Thus, the zeolite was synthesised in such a way that the entire synthesis gel was loaded exclusively into the pores of the matrix before the crystallisation was initiated. This proved to be a viable approach to give high-quality, nanosized zeolite crystals with MFI and BEA structures and with crystal size distributions controlled largely by the pore size distribution of the chosen matrix. By use of carbon, it was possible to recover the pure zeolite by simply combusting the auxiliary template.[78] This methodology was coined "confined space synthesis" to emphasise that the growth of the zeolite crystals occurred inside the pores of carbon. Clearly, the nanosized zeolite crystals obtained by this method feature the intracrystalline micropores characteristic of ordinary zeolites plus an additional mesopore system resulting from the packing of the small zeolite crystals, *i.e.* intercrystalline pores or voids (Fig. 3(b)). However, attempts to further develop this methodology showed serendipitously that a completely different class of materials could be obtained by essentially applying the same approach. In fact, by only changing the crystallisation conditions slightly, it proved possible for zeolite crystals not only to nucleate inside the carbon matrix but also to continue their growth through the surrounding carbon pore system in such a way that the zeolite crystals encapsulate part of the carbon matrix. Thus, the zeolite crystals essentially become replicas of the carbon pore systems in which they are grown, and when the carbon matrix is removed by combustion relatively large zeolite crystals featuring an intracrystalline mesopore system result (Fig. 5(a)).

Zeolite materials produced by carbon templating are called mesoporous zeolite crystals. The materials are highly defected structures (see the scanning electron micrograph in Fig. 5(b)) that can have intracrystalline mesopore volumes exceeding 1 cm^3 g^{-1}. High-resolution transmission electron microscopy (TEM) coupled with selected area electron diffraction (SAED)[35,79] (Fig. 5(c)) proved that they can still be considered single crystals. Thus, it is noteworthy that the introduction of a zeolite gel into a porous carbon can lead to two fundamentally different types of materials. Whether the use of carbon as a template results in the formation of nanosized zeolite crystals or in mesoporous zeolite single crystals depends solely on the rate of nucleation relative to the rate of zeolite growth, and this must be determined experimentally for any given zeolite recipe. For the mesoporous zeolite single crystals, the pore size of the intracrystalline mesopores directly reflect the size, shape, and connectivity of the carbon particles in the matrix, and accordingly it is appropriate to classify the carbon as a template. This was clearly demonstrated by using carbon templates with different sizes and different morphologies.[80] In particular, it was shown that by using carbon nanotubes, it was possible to obtain zeolite crystals with mesopore systems that exactly replicated the structure of the original carbon nanotube template.[81] By use of stereo-TEM[80] and TEM tomography,[82] the mesopore system of the treated zeolites can be mapped in great detail. The mesopores extend throughout the entire zeolite crystal and thereby provide improved access to the zeolite micropores. Fig. 5(d) shows the nitrogen isotherm and pore size distribution plot (inset) of mesoporous silicalite-1 prepared by carbon templating, whose morphology is presented in Fig. 5(b). The pore size distribution shows that the additional porosity induced by carbon-templating is typically in the mesopore range. The increased mesoporosity is also evident from comparative diffusion experiments conducted with mesoporous and conventional zeolites.[83] This is depicted in Fig. 5(e), which shows that desorption of isobutane proceeds significantly faster out of mesoporous ZSM-5 than it does out of conventional ZSM-5. Naturally, the increased rate of diffusion observed for mesoporous zeolite crystals also has implications on their performance as catalysts. Thus, mesoporous zeolite crystals are typically more active as catalysts than conventional crystals, as exemplified in Fig. 5(f) for the vapour-phase benzene alkylation with ethylene to ethylbenzene.[84] Due to the alleviated diffusion limitation, the apparent activation energy of the mesoporous zeolite (slope of the Arrhenius plot) was higher than that of the purely microporous zeolite (77 *vs.* 59 kJ mol^{-1}). What is perhaps less obvious is why these catalysts, and hierarchical zeolites in general, also offer a higher selectivity to the monoalkylated

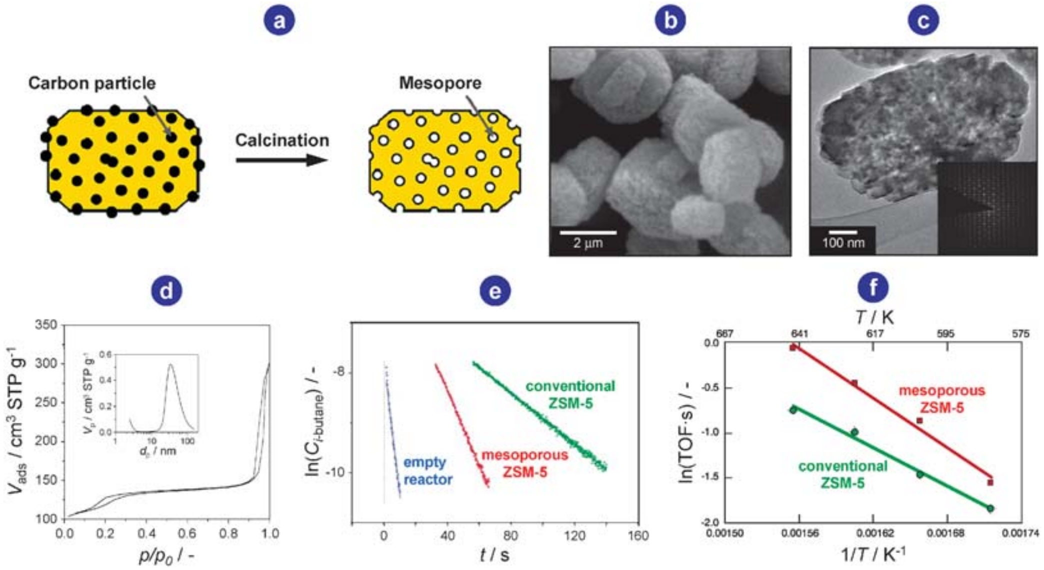


Fig. 5 Schematic illustration of zeolite crystallisation in the presence of an auxiliary carbon template resulting in hierarchical microporous–mesoporous zeolite crystals (a). Representative SEM (b) and TEM (c) images of the templated zeolites, including the electron diffraction pattern. The zeolite prepared by carbon templating evidences extensive mesoporosity as revealed by N_2 adsorption, with pores centered at 40 nm (d). The elution of isobutane (e) and the turnover frequency in the vapour-phase benzene alkylation (f) over the hierarchical zeolite (mesoporous ZSM-5) is largely improved compared to the microporous counterpart (conventional ZSM-5).

benzene in comparison with the purely microporous analogues. This can be explained by the shortened diffusion path length that decreases the average residence time of reacted molecules in the micropores. This suppresses successive alkylation steps of the desired ethylbenzene to polyalkylbenzenes.

Today, a wide range of zeolite structure types (MFI,[32] MEL,[85] BEA,[86] MTW,[87] CHA,[88] AFI[88]) has become available in the form of mesoporous single crystals, and it appears that other structures should be available analogously. Thus, the carbon-templating approach seems to be a versatile method for introducing mesopores into zeolites and it also provides some opportunities for tailoring the pore system to the desired application by choosing suitable carbon templates. Importantly, the method is applicable to all zeolites irrespective of their chemical composition, and therefore also to zeotype materials that do not necessarily contain silicon or aluminium. Furthermore, carbon-templating allows independent control of the mesoporosity and the acidity.

Industrial use of the method might be hampered by the fact that the suitable carbon templates (in terms of morphology, porosity, and purity) can be quite expensive, and because efficient introduction of the zeolite gel into the carbon can require more elaborate synthesis steps. Recently these hurdles were alleviated to some extent by the so-called *in situ* carbon templating method, in which the carbon template is generated by decomposing a carbohydrate, *e.g.* sugar, inside the pores of the silica source used for the zeolite crystallisation.[89] Compared to the original carbon-templating method, this approach provides less control of the pore size and geometry but instead it allows careful tailoring of the mesopore volume since this can be controlled simply by adjusting the amount of carbohydrate decomposed inside the silica. In any case, the removal of the template by combustion is a critical step to obtain high quality mesoporous zeolites. This aspect requires careful consideration, particularly in large-scale production.

3.2 Desilication

Despite numerous works available on (partial) dissolution of silicon from amorphous or even crystalline silica entities, the potential of this post-synthesis method for controlled porosity development has been unrecognised for a long time. In the early 1990s, Dessau *et al.*[90] reported an anisotropic and excessive dissolution of ZSM-5 crystals upon treatment in hot alkaline Na_2CO_3 solution, which has been speculatively attributed to the presence of an aluminium gradient in the zeolite crystals. In 1997, a distinctive role of aluminium on the kinetics of silicon dissolution upon treatment of silicalite-1 and ZSM-5 in concentrated NaOH solutions was identified by Čižmek *et al.*[91] The presence of aluminium in the zeolite framework dramatically slowed down the dissolution kinetics. In these works, however, no attention was paid to the structural, morphological, and textural changes of the treated materials. The first paper highlighting the presence of mesopores in ZSM-5 zeolites by framework silicon extraction in alkaline medium appeared in the year 2000 by the Matsukata group.[92] Although the newly obtained mesoporosity was initially attributed to intercrystalline pores by dissolution of crystal boundaries, subsequent systematic studies by Groen *et al.*[93,94] over ZSM-5 confirmed that controlled desilication mainly induces intracrystalline mesoporosity whereas preserving most of the original microporosity. A combinatorial-type program was conducted to elucidate the role of both treatment variables such as time, temperature, and stirring speed and material related parameters like framework Si/Al ratio, crystal size, and different framework types.[95,96] These studies pointed towards a key role of framework aluminium that highly determines the alkaline treatment's chance of success (Fig. 6). The alkaline-assisted hydrolysis of the Si–O–Si bonds from the zeolite framework can be directed towards mesoporosity development when operating in an appropriate window of Si/Al ratios. Aluminium in framework positions suppresses the extraction of neighbouring silicon species. Besides aluminium, also other trivalent cations such as iron have proven to be as effective as aluminium in directing the silicon extraction towards mesoporosity development.[97] This knowledge has been used to fabricate hollow zeolite crystals upon desilication of Al-zoned ZSM-5 crystals, though the resulting system is a hierarchical system with occluded extra porosity (Fig. 7(a)).[98] Due to the presence of entrapped mesoporosity, hollow crystals are not optimal architectures to improve the catalytic activity of zeolites in diffusion-limited reactions, despite the shorter diffusion lengths by dissolution of the crystals' interior. Accordingly, the removal of framework species should desirably generate accessible mesopores from the external surface, such as those in Fig. 3(c). A uniform incorporation of accessible mesoporosity in the microporous matrix has been achieved by desilication of ZSM-5 with an isotropic distribution of aluminium in the crystal and analogous extraction of silicon (Fig. 7(b)).[99] The so-obtained materials present an accessible hierarchically architectured micro- and mesoporous system. An important feature of the alkaline-treated mesoporous zeolites is the preservation of the intrinsic Brønsted acidity of the zeolite framework, which is in contrast to zeolites modified by the traditional dealumination post-treatment (Fig. 7(c)). Besides, the mesoporosity achieved upon the latter treatment is frequently occluded in the microporous matrix[100,101] and thus less effective as compared to the hierarchical system in the uniformly desilicated zeolite crystals.[99] The presence of extra-framework aluminium species, *e.g.* obtained by a dealumination post-treatment, inhibits the extraction of framework silicon during alkaline treatment of ZSM-5. Accordingly, an independent tailoring of porous and acidic properties can only be successfully achieved by a successive combination of treatments in which the desilication treatment is performed first followed by dealumination.[102]

Successful extrapolation of the alkaline treatment to MOR[103] and MTW[104] topologies have confirmed the crucial role of framework aluminium and the generality of the desilication approach. For these zeolite types, similar ranges of framework Si/Al ratios were a prerequisite for achieving controlled mesoporosity development coupled to preserved acidity. However, operating in the optimal Si/Al ratio window of 25–50 is not the only intrinsic condition for treatment's success. Additionally, a high stability of framework aluminium is crucial to exert its pore-directing role. This has

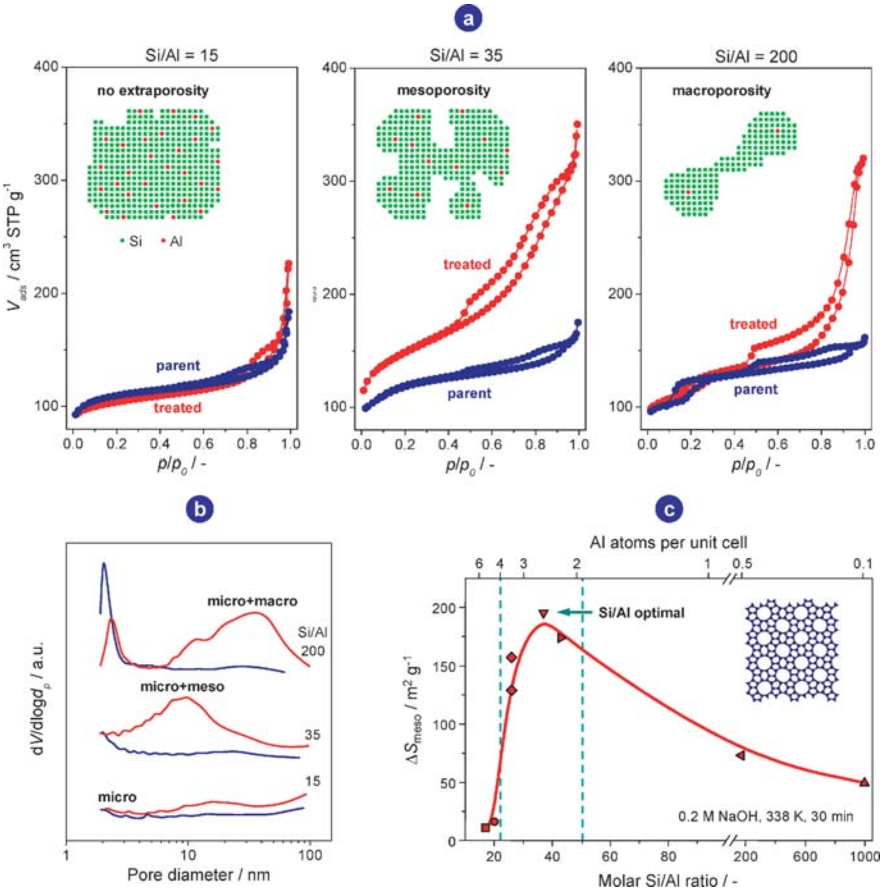


Fig. 6 The nitrogen isotherms of parent and alkaline-treated ZSM-5 zeolites of different starting Si/Al ratios (a) show the impact of the alkali treatment on the porous properties of the resulting materials. At low Si/Al ratios, a minor change in porosity has been concluded whereas at higher Si/Al a remarkably increased uptake is achieved in the treated samples, indicative of enhanced porosity. The insets in (a) represent a simplified schematic representation of the influence of the Si/Al ratio on the porosity development. The BJH pore size distribution (b) obtained from the adsorption branch of the N_2 isotherms in (a) quantitatively describes the porosity development in the ZSM-5 zeolites. A negligible extraporosity generation in the zeolites of low Si/Al ratio is obtained, which thus remain a purely microporous system, a combined micro- and mesoporous architecture in the case of intermediate Si/Al ratios, and combined micro- and macroporosity in the high-silica ZSM-5 zeolites. The different extent of extraporosity development in the ZSM-5 zeolites by varying the Si/Al ratio impacts on the newly developed mesopore surface area (c). At low and high Si/Al ratios, the minor extraporosity and macroporosity, respectively, moderately increase the mesopore surface area. At Si/Al ratios in the range of 20–50, controlled desilication leads to an impressive increase in mesopore surface area up to 200 m^2 g^{-1}, which effectively contributes to the more efficient utilisation of the hierarchical porous architecture. In this optimal range of Si/Al ratios, the original micropore volume is decreased by only 25% maximally with a preserved micropore size.

been supported by systematic investigations of the alkaline treatment over beta zeolite crystals synthesised in fluoride-medium. The relatively low stability of aluminium in the four-membered rings of the BEA framework turned out to be incapable of directing the mesoporosity development coupled to a preservation of the Brønsted acidity.[105] Consequently, the characteristics of the starting zeolite in terms of amount (Si/Al ratio), nature (framework or extra-framework), and distribution of metal species in the crystal volume are important aspects to tailor mesoporous zeolites by desilication.

The newly introduced mesoporosity achieved by selective silicon removal leads to a greatly improved physical transport in the zeolite crystals as was revealed by transient uptake experiments of neopentane in ZSM-5 crystals[99] (Fig. 7(d)) and diffusion studies of *n*-heptane, 1,3-dimethylcyclohexane, *n*-undecane in mesoporous ZSM-12,[104] and diffusion and adsorption studies of cumene in mesopore structured ZSM-5.[106] Up to three orders of magnitude enhanced rates of diffusion were concluded in the hierarchical systems as compared to their purely microporous precursors due to improved accessibility and a distinct shortening of the micropores. Catalytic testing of various mesoporous zeolites has proven the effectiveness of the desilication approach. A 20 times higher activity of alkaline-treated ZSM-5 has been concluded by Choi *et al.*[107] in the liquid-phase degradation of HDPE. Zhao *et al.*[106] reported doubled conversion in cumene cracking over desilicated ZSM-5 compared to the parent zeolite. A recent *in situ* microspectroscopic study on the oligomerisation of styrene derivatives revealed a greatly enhanced accessibility of the micropores in the hierarchical ZSM-5 zeolites obtained by desilication (Fig. 7(e)).[108] Application of mordenite[103] and ZSM-5[105] in the liquid-phase benzene alkylation evidenced a higher activity and selectivity

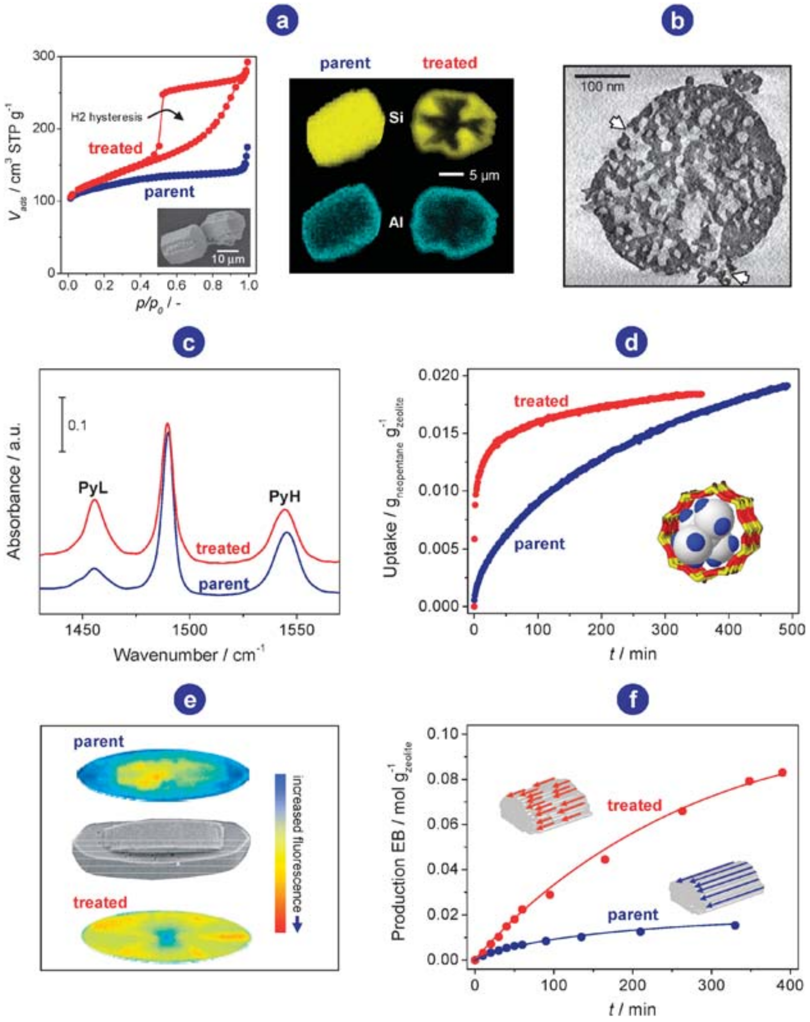


Fig. 7 SEM-EDX micrographs of large, in TPAOH-synthesised, ZSM-5 crystals evidence an anisotropic aluminium profile across the crystal volume, which shows an up to 30 times higher concentration of aluminium in the outer rim as compared to the interior of the crystals. Desilication of such zeolite crystals induces encapsulated porosity as shown by the IUPAC H2-type hysteresis loop of the N_2 adsorption isotherm (a). This observation emphasises the crucial role of the distribution of framework aluminium on the porosity development upon silicon extraction and points to the importance of the quality of the parent material. A 3-D TEM virtual cross section proves that desilication of ZSM-5 with a uniform incorporation of aluminium in the zeolite framework homogeneously generates extensive intracrystalline mesoporosity (b); arrows indicate access points to the mesopores from the external surface. Pyridine adsorption on the parent and desilicated ZSM-5 zeolites confirms preservation of the original Brønsted acidity (PyH) and generation of new Lewis acid sites (PyL) (c). The latter is the result of realumination of the zeolite framework during the alkaline treatment. Transient uptake experiments of neopentane at 393 K conclude a 2–3 orders of magnitude enhanced rate of diffusion in the desilicated hierarchical ZSM-5 crystals compared to the purely microporous parent crystals (d). *In situ* confocal fluorescence spectroscopy measured during oligomerisation of 4-methoxystyrene at 373 K reveals a more uniform yellow coloration in large-crystal mesoporous ZSM-5 zeolites due to the improved diffusion and accessibility of the treated zeolite crystals as compared to the microporous counterparts (e). Liquid-phase benzene alkylation with ethylene over mordenite greatly benefits from the introduced mesoporosity upon desilication, from 5 m^2 g^{-1} in the parent zeolite to 100 m^2 g^{-1} in the treated zeolite (f). An up to six times higher productivity of ethylbenzene coupled to minimised deactivation by coke is obtained in the mesoporous mordenite due the effectively shortened diffusion path length that greatly relieves the single file diffusion penalty in the one-dimensional zeolite structure.

to ethylbenzene of the mesoporous zeolites (Fig. 7(f)). Song *et al.*[109] reported a higher stability of desilicated ZSM-5 in butane aromatisation. The benefits of alkaline treatment on the activity, selectivity, and stability of ZSM-5 in the conversion of methanol to gasoline[110] and methanol to propylene[111] have also been demonstrated. The interplay between enhanced mass transport due the shorter diffusion path length and the preserved acidity has proven to be essential in achieving the greatly improved performance over these mesoporous zeolite crystals. In addition, an enhanced ion-exchange capability by the higher aluminium concentration in desilicated zeolites with ameliorated access to the ion-exchange sites[112] or alteration of the active sites by the desilication treatment[113] results in more effective (redox) catalysts. The highly chemically controlled nature of the desilication treatment in alkaline medium makes scaling up rather straightforward and thus amenable to practical implementation. A first scaling up from the milligram to the kilogram scale has successfully been realised by means of a

6-liter stirred tank reactor with an increased solid–liquid ratio with no deterioration of the properties of the resulting materials.[96]

As noted above, desilication mostly creates intracrystalline porosity in channel-type zeolites such as ZSM-5, ZSM-12, mordenite, and beta. Recently, it has shown that silicon leaching can be also used to fabricate octadecasil nanocrystals (10–25 nm) with a high degree of intercrystalline porosity (*ca.* 200 $m^2 g^{-1}$) and a preserved structure.[114] Clathrasils, *i.e.* zeolite-related materials consisting of window-connected cages, are impenetrable to typical sorbate molecules such as N_2 or reactants such as hydrocarbons, and hence have no prospective for catalytic applications. The zero-dimensional character of these materials conditions the alkaline to operate in a different manner, as the cages cannot be accessed. Therefore, instead of attaining perforated crystals as in channel-type zeolites, clathrasil crystals are fragmented and peeled by the base, resulting in nanosized crystals. This widens the scope of these compounds, opening room for application as catalysts and/or catalyst supports.

4. Conclusions and outlook

During the last decade, hierarchical zeolites have emerged as an important class of materials in zeolite science and technology, and they attract continuously increasing interest. The optimal design of hierarchical zeolites requires the generation of multiple levels of porosity being appropriately connected in order to maximise the benefits of hierarchy in catalysed reactions. Ultimately, the art of making hierarchical materials is where to put the pore. Today, several different types of hierarchically organised zeolitic materials are available and a multitude of preparative methods have been developed to target the synthesis of specific materials. It has been shown conclusively, and in accordance with expectations, that in these materials, the micropores are indeed much more accessible due to significantly improved mass transport in the hierarchical zeolites compared with conventional zeolites featuring only micropores. The improved catalytic performance of hierarchical porous zeolite structures has been automatically attributed to enhanced transport, most of the times without direct evidence of the diffusion characteristics. Consequently, the diffusion studies should increasingly accompany papers dealing with the synthesis and catalytic application of hierarchical zeolites.

So far, the improved accessibility has been the main motivation for developing this class of materials. Herein, we tried to categorise these materials and the methods for their synthesis, and to highlight examples in which superior catalytic performance of the hierarchical zeolites appears to be directly related to the improved mass transport. To illustrate state-of-the-art achievements in the field, we have presented prominent examples of the various approaches available to prepare hierarchical zeolites. It should be clear that each method has its advantages and disadvantages, and more importantly, that there is ample room for extending and improving all the currently known methods. In fact, it appears likely that entirely new methods will emerge and contribute to the existing options for designing hierarchical zeolites. Besides zeolite composites, substantial efforts have been devoted to the development of the carbon-templating method and the desilication method. For the latter two methods, quantitative studies related to the improved diffusion, detailed characterisation studies, and also several examples of improved catalytic performance have been reported. Therefore, we have focused on these methods to in-depth illustrate the opportunities with hierarchical zeolite materials and to clearly establish the link between materials design and catalytic performance. However, with the different materials available and the various preparative methods ready to hand, it is interesting to discuss which materials and which of the currently known methods are indeed the most promising, going beyond laboratory scale toward implementation. This is clearly a most difficult question, and the answer appears to depend on many factors in a quite complicated way. If we, for simplicity, limit our discussion to pure zeolite materials, it appears that there are no obvious advantages of any particular type of zeolite material, *i.e.* nanosized zeolite crystals and hierarchical zeolite crystals are expected to have quite similar properties thereby showing analogous catalytic performance. However, there could easily be some more subtle differences *e.g.* in the thermal and hydrothermal stability of the different materials or in the handling of the materials, but such studies have not yet crystallised. Thus, in selecting one particular method for synthesizing hierarchical zeolites, the most important thing is to consider the objective of the study. If it is imperative to achieve very accurate control over the pore size distribution *e.g.*, to tailor systems for fundamental studies, clearly the supramolecular templating methods appear most promising, and in particular the method by the group of Ryoo seems to allow the most precise control of the pore system.[27,56] A most recent work by the same group claims distinctive catalytic activity of the mesopores in hierarchical MFI zeolites,[115] implying a dual functionality of the mesoporosity in hierarchical systems as transport facilitator and active catalyst. This opens wide avenues for dedicated transformations of larger molecules. Still, a point of concern is the fact that the supramolecular templating methods are in general economically prohibitive for the vast majority of possible industrial applications of these hierarchical zeolites. In this case, desilication and *in situ* carbon templating methods appear much more viable. If the desilication method can be made to work with the desired zeolite structure and the relevant Si/Al ratio, this would be the obvious choice due to its simplicity, scalability, and low cost. In desilication, the flexibility to tailor the mesoporosity is so far basically limited to the Si/Al ratio, temperature, and time. Accordingly, research efforts should be directed toward increasing the tuning capabilities of the desilication treatment and to widen the applicability of this treatment to other frameworks. In other cases, the carbon-templating route would be the preferred alternative, since this method is versatile and allows more control over the pore size distribution though not nearly to the same degree as that reported with the supramolecular templating methods. Mei *et al.*[111] have for the first time compared in the same study mesoporous ZSM-5 obtained by templating with starch and by desilication for the methanol-to-propylene reaction. The template route led to enhanced mesoporosity in the zeolite crystals compared with alkaline treatment. However the mesopores in the former sample were mainly located inside the zeolite body and played a limited role in the diffusion of gas molecules. In contrast, the open mesopores in the desilicated zeolite catalyst enhanced the diffusion of the primary olefin products (propylene and butylene), and inhibited undesirable secondary reactions. As a result, the propylene-to-ethylene ratio and propylene selectivity were most effectively enhanced in the alkaline-treated catalyst. Clearly, there can be many other factors to consider than those presented here. Moreover, it is anticipated that improved insight into the capabilities of the different synthetic methods will appear during the coming years and this can obviously refine these considerations. Accordingly, it is concluded that the field of hierarchical zeolites will continue to attract increasing attention during the years to come. These new efforts will lead to a substantial improvement in our understanding of zeolite catalysis and possibly also to significant technological developments through the implementation of hierarchical zeolites in industrial processes.

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