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CHAPTER 2

Modern Synthesis Routes to Hierarchically-Structured Porous Materials

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2.1. Introduction

Many processes of societal and industrial importance, with heterogeneous catalysis and separation technologies being prominent examples (see Vol. 2, Chaps. 1 and 2; and Vol. 3, Chap. 1), involve the adsorption of molecules (or ionic compounds) on the surface of a material. Since adsorption is a surface-related phenomenon, these processes benefit from the use of materials with high, accessible surface area. The magnitude and the accessibility of the surface area are both crucial for achieving high performance and many research efforts have been devoted to the development of materials that combine these two features together with the specific properties for the desired application (as for example the active sites of a catalytic material). The two main strategies for maximising the specific surface area of a functional material consist in designing highly porous materials, and/or to prepare nanomaterials (e.g. nanoparticles, nanorods, nanotubes), which are characterised by a large surface-to-volume ratio. In the case of porous materials, the size of the pores and their connectivity should be carefully controlled in order to achieve the desired high surface area while granting its accessibility to the target molecules. For practical applications,

these features should be combined to high chemical and thermal stability of the material. Considering that the kinetic diameter of the majority of molecules produced by the chemical industry (e.g. the main bulk chemicals and several fine chemicals) is below 1 nm, developing materials with a highly porous structure and with uniform pore size in the nanometre range would allow achieving the desired high, accessible surface area.

Micropores 0.3 to 2 nm.
Mesopores 2 to 50 nm
Macropores > 50 nm

According to IUPAC, the pores in such materials are categorised in three groups: micropores ($d < 2$ nm), mesopores ($2 \text{ nm} \leq d \leq 50$ nm) and macropores ($d > 50$ nm). Theoretically, smaller pores would lead to higher specific surface area (m^2/g), though this quantity also depends on the thickness of the pores walls and on the atomic mass of the elements constituting the material. However, if the pore size is only slightly larger than the size of the molecules that have to diffuse through it, mass transport limitations will occur. In this context, three types of diffusion in (ideal) cylindrical pores can be distinguished (Figs. 2.1(A–C)):

- Molecular diffusion, which occurs when the collision with another molecule is more likely than the collision with the pore walls. Under such condition, the diffusivity is similar to that in a non-confined space and is proportional to the mean free path (i.e. the average distance that a molecule travels between successive collisions, at a certain temperature and pressure).
- Knudsen diffusion, which occurs when the pore diameter is comparable to or smaller than the mean free path of the molecule diffusing through the pore. Under this condition, the collision with the pore walls becomes gradually more likely and the diffusivity is lower compared to regular diffusion.
- Configurational diffusion, which happens if the molecules have comparable size to that of the pore. Under this condition, the diffusivity is orders of magnitude lower compared to molecular

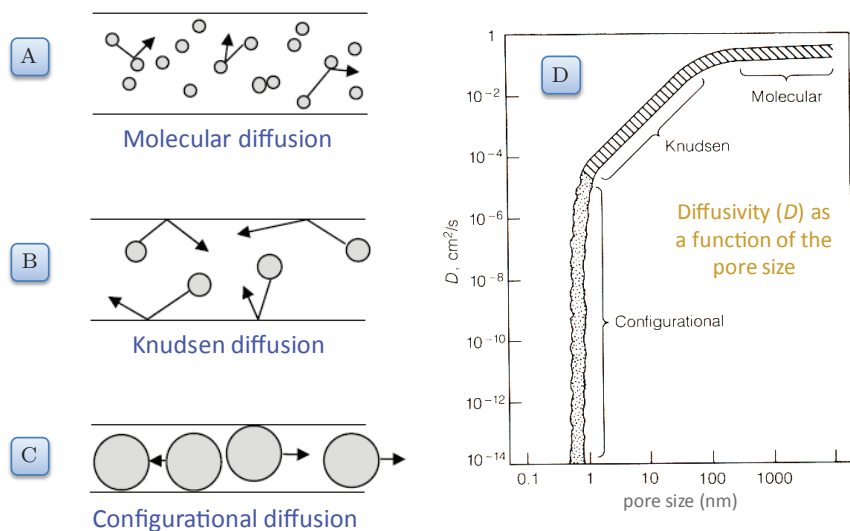


Fig. 2.1. Types of diffusion in porous materials (A–C) and dependence of diffusivity on pore size (D).

diffusion and small differences in structure and, thus, in kinetic diameter of the molecule cause large differences in diffusivity (Fig. 2.1(D)).

Depending on the specific size of the pore and of the molecules, diffusion in microporous materials is either in the configurational or Knudsen regime, whereas diffusion in mesoporous materials is typically of Knudsen or molecular type.

In general, configurational diffusion is a shortcoming, as it causes mass transport limitations that decrease the effectiveness of a functional material (e.g. a catalyst). However, in specific cases it can also represent an asset. This is exemplified by **zeolites**, which are a very important class of microporous materials finding large-scale applications as heterogeneous catalysts, adsorbents and ion-exchangers.¹ Zeolites belong to the silicates class and are thus characterised by tetrahedral SiO_4^{4-} units connected to each other through O-bridges, generating a three-dimensional crystalline microporous structure (with micropores typically in the range 0.3 – 1 nm). Most zeolites contain other elements that partially substitute Si in the tetrahedral positions in the framework, with Al being the

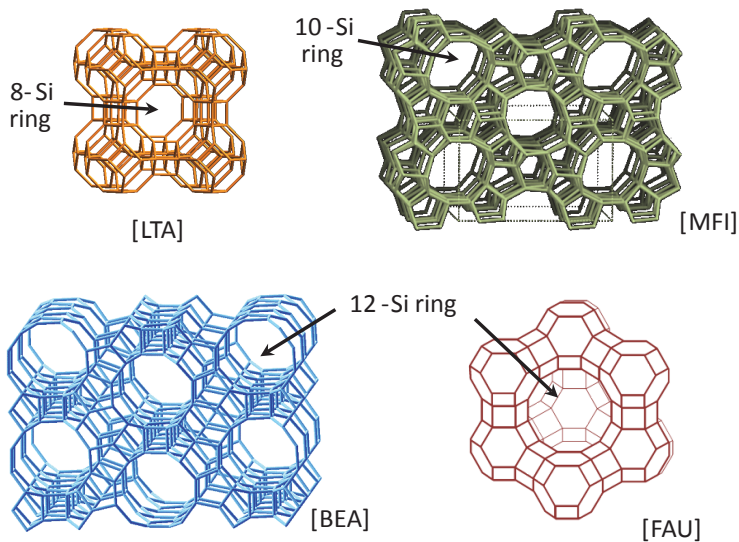


Fig. 2.2. Selected types of zeolite frameworks.

most common substituent. Therefore, zeolites are often referred to as aluminosilicates, although several zeolitic structures containing metal atoms (e.g. Ti or Sn) partially replacing Si in the crystalline framework have also been reported. A large number of natural and synthetic zeolite structures exist, with different types and sizes of channels and cages (Fig. 2.2). The interested reader can find an updated database of zeolite structures in the online database of the International Zeolite Association (IZA).² As a consequence of their microporous structure, virtually all atoms of zeolites are located at the surface. This imparts a very high specific surface area to zeolites (typically in the range 400 to 700 m²/g), with most of this surface area originating from the internal surface (i.e. from the porous structure). The large surface area is highly attractive for the adsorption of molecules and, when combined with the sites generated by isomorphous substitution of part of the Si atoms with other elements, for applications in heterogeneous catalysis and ion-exchange. In aluminosilicate zeolites, the presence of each Al (oxidation state +3) instead of Si (+4) requires an additional positive charge to balance the framework: these counterions can be

monovalent (e.g. H^+ , Na^+) or polyvalent cations (e.g. Ca^{2+} , Mg^{2+} , La^{3+}). The ability of these zeolites to exchange their counterions when in contact with a solution of another cation is the basis for their application as ion-exchanging materials (e.g. in detergents, where they are used to decrease the hardness of water by exchanging Ca^{2+} with Na^+). If the counterion is a proton (H^+), the zeolite displays strong Brønsted acidity, with the number and strength of the acid sites being determined by the Si/Al ratio.³ Zeolites in their H-form find broad application as solid acid catalysts in important reactions such as isomerisations, alkylations and cracking, particularly in the petrochemical industry. Zeolites owe their applicability not only to the combination of large specific surface area and functional sites, but also to their high chemical and thermal stability. In the catalytic application of zeolites, the occurrence of configurational diffusion has been exploited to achieve an increased selectivity in the formation of a desired product compared to what would be expected based on thermodynamics. This shape selectivity is based on the difference in diffusivity of molecules with different size and can involve:

- (i) the reactants, in which case a reactant is so large that it diffuses very slowly or does not to diffuse at all through the pores (for this feature zeolites are often referred to as ‘molecular sieves’);
- (ii) the products, in which case a specific product is smaller than the others and thus diffuses more rapidly through the pores of the zeolite;
- (iii) a transition state requiring an arrangement of the molecules that does not fit in the pores, thus preventing that specific reaction path from being followed.

A well-known example of product shape selectivity is the industrially relevant reaction of toluene with methanol to produce *para*-xylene (which in turn can be oxidised to terephthalic acid, which is then reacted with ethylene glycol to produce polyethylene terephthalate, better known with its acronym, PET). The synthesis of *para*-xylene is catalysed by zeolite H-ZSM-5 [MFI], which is characterised by interconnected channels with uniform pore size defined by 10 Si-atoms rings (0.53–0.56 nm aperture, Fig. 2.2). The

three isomers of xylene tend to form in the cages defined by the intersection of the channels of ZSM-5. The pore diameter of ZSM-5 allows the diffusion of the linear *para*-xylene, whereas the *ortho*- and *meta*-isomers are bulkier and, therefore, their diffusivity through the zeolitic pores is much lower. As a consequence, *para*-xylene molecules diffuse out of the zeolite once they form, while the *ortho*- and *meta*-isomers tend to remain in the cage where they isomerise, thus re-establishing the local equilibrium with *para*-xylene. Eventually, this leads to the desired higher selectivity towards the *para*-xylene product.

Apart from the advantages related to shape selectivity, configurational diffusion in zeolites is generally a drawback as mass transport limitations negatively affect the catalytic activity as a consequence of an incomplete utilisation of the active sites, with the sites requiring a longer path to be reached being the least accessed. Additionally, diffusion limitations can also have a negative impact on the catalyst selectivity and on its lifetime (by promoting deposition of reaction intermediates and products, with consequent coking).

Different strategies have been developed in order to overcome the mass transport limitations in zeolites:

- One approach consists in developing porous silicate materials that display a larger pore size compared to zeolites. Since the 1990s, several ordered mesoporous silicate materials with pores of uniform size in the range 2–15 nm have been developed. Two widely studied and applied materials in this class are MCM-41 and SBA-15 silicates. Both these materials are characterised by a hexagonal array of parallel mesopores, which are generated by synthesising the materials in the presence of surfactants that organise themselves in micelles,^a and thus act as structure-directing agent around which the ordered mesoporous silicates form. In MCM-41, the mesopores (typically between 2 and 3 nm)

^aIn polar solvents, surfactants organise themselves to have the lowest energy in the solution by assembling into micelles with their hydrophilic heads pointing towards the polar solution and the hydrophobic tails forming the interior structure of the micelle.

are isolated from each other, whereas the channels in SBA-15, besides being larger (generally 4–10 nm), are often interconnected through micropores. Although their structure is ordered, the walls around the channels of these mesoporous materials are amorphous. Similarly to zeolites, these ordered mesoporous materials can be prepared with metal atoms (e.g. Al, Ga, Ti, Zr, Sn) partially replacing Si atoms in the silicate framework, thus generating catalytic active sites (i.e. Brønsted acid sites with the metals with oxidation state +3 and Lewis acid sites with the metals with oxidation state +4). Owing to their highly porous structure, MCM-41 and SBA-15 materials can reach very high surface area (e.g. around 1000 m²/g). This feature, combined with the presence of active sites and the diffusion in the Knudsen and molecular regime that characterises mesoporous materials seemed very promising for catalytic applications. Indeed, metal-substituted MCM-41 and SBA-15 have found several applications as heterogeneous catalysts, displaying significantly higher activity than zeolites with substrates that are sterically too bulky for diffusing efficiently through the zeolitic micropores. However, the amorphous nature of these materials implies a lower thermal and chemical stability compared with the crystalline zeolites, and the metal sites are generally less active and more prone to leaching compared to their counterparts in zeolites. These drawbacks prevented the widespread industrial application of these ordered mesoporous silicates and stimulated research towards alternative approaches.^{4–7}

- With the aim of maintaining the specific assets of zeolites while increasing the accessibility of the active sites, research efforts were devoted to the synthesis of zeolites with wider micropores (i.e. >1 nm). Remarkable advances were achieved in this field of research in recent years and zeolites with pores with more than 12 Si atoms and large cavities were prepared. The presence of Ge in the framework and the tailored design of organic templates were key factors for the development of many of these large-pore zeolites.^{6a} Although many of these materials did prove to be advantageous compared to conventional zeolites with narrower micropores in terms of catalytic conversion of bulky substrates,

their lower thermal stability and the high cost of the needed organic templates are still hampering their widespread application.

- Another strategy that aims at preserving the crystalline microporous framework and active sites of zeolites while improving their accessibility focuses on decreasing the diffusion path length within the micropores by preparing zeolites in the form of nanosized crystals. This inherently decreases the mass transport limitations experienced by reactants and products within the micropores and increases the fraction of the material that can effectively act as a catalyst. As a consequence of their decreased particle size, zeolite nanocrystals present a larger surface-to-volume ratio and thus a much higher external surface area (in m^2/g) compared to conventional zeolite crystals. Several approaches have been developed to prepare zeolite nanocrystals.⁵ One approach consists in tuning conventional hydrothermal synthesis methods to promote nucleation over growth, thus generating many small crystals rather than few with larger size. This can be achieved by performing the synthesis in diluted systems and at relatively low temperature (clear suspension method), although this approach typically gives low yields of zeolite product. An alternative approach is the confined-space synthesis, in which the zeolite crystals are grown within the voids of a hard template (e.g. porous carbon), which is then removed by combustion. Other methods based on the restriction of the zeolite growth involve the use of multivalent surfactants or of water-in-oil microemulsions. Yet another method consists in limiting the growth of the zeolite crystals by functionalisation of their surface with silanes containing amino, thiol or allyl groups.

A major limitation to the practical application of nanosized zeolites as heterogeneous catalysts in liquid-phase reactions in batch reactors is their cumbersome separation from the reaction mixture, which normally requires high-speed centrifugation or special filtration and typically leads to incomplete recovery of the zeolite catalyst. Also for gas-phase catalytic reactions, the use of zeolite nanocrystals is not ideal as these would need to be shaped into pellets with the help of binders to avoid severe pressure drops across the catalyst bed in the continuous flow reactors, and this

would cause a significant loss of the advantages related to the large external surface area.

- Another approach to increase the accessibility to the active sites by decreasing the diffusion path within the micropores is the delamination^b of zeolites to produce layered structures consisting of zeolite nanosheets (i.e. extensive crystals in two dimensions, but with thickness at the nanoscale).^{6,7} The delamination is typically achieved by sonication in the presence of a surfactant (e.g. cetyltrimethylammonium bromide), which causes swelling and exfoliation of the layered zeolite precursor. The obtained zeolite nanosheets are not connected with each other and typically possess extremely large external surface area (600–800 m²/g). A clear limitation of this approach is that it is restricted to the few zeolite framework types that are characterised by a layered structure. Another issue in this method is that the alkaline conditions typically employed in the swelling step can result in partial dissolution of the zeolite framework.
- A final strategy, and the one that will be discussed more in detail within this chapter, attempts to combine the benefits of the shorter diffusion path length characteristic of zeolite nanocrystals with the efficient diffusion through mesoporous and macroporous materials. The target is to generate a material with **hierarchical porosity**, in which the microporous zeolitic domains are accessed through larger pores in the meso- or macropore range. If the design of the material is correctly realised, it should enable to combine the assets of all the above strategies while limiting their shortcomings.

2.2. Hierarchical Porous Materials

Before discussing the types of hierarchically-structured porous materials and the methods that can be employed to synthesise them, it is important to provide a clear definition of what is intended with hierarchy when referring to the structure of a porous material. In a general definition derived by those provided by the Oxford dictionary,

^bNot to be confused with the dealumination described in Section 2.2.1.3.1.

a hierarchy is a system in which people or things are ranked with respect to each other according to their relative importance in exerting a specific function. Circumscribing the definition to the context of porous materials, a hierarchical porosity should refer to the presence of pore systems with different magnitudes, which are interconnected in such a way that the smaller pores are accessed through larger ones. However, the reader should be aware that in the scientific literature the term hierarchical porosity is often used in a broader and not always appropriate way to refer to systems containing pores of different sizes, independently of whether or how these pore systems are interconnected.⁸

In the following sections, the main strategies that have been developed to prepare hierarchically-structured porous materials will be presented for the specific case of zeolites (Section 2.2.1), followed by a brief overview of other materials with hierarchical porosity and of the synthesis routes used to prepare them (Section 2.2.2).

2.2.1. *Strategies for preparing zeolites with hierarchical porosity*

The development of zeolites with hierarchical porosity has been a lively field of research in recent years.^{7,9–12} This was triggered by the broad scope of catalytic applications of zeolites and by the growing interest in the upgrade of bio-based feedstock, which includes bulky compounds. In order to enhance the diffusion of bulky molecules, it is crucial that the larger pores providing access to the micropores are connected to the surface of the crystals or are connected to the outside through other meso- or macropores (Fig. 2.3(A)). On the other hand, a structure that contains large pores that are accessible only through micropores (Fig. 2.3(B)) should not be considered to display hierarchical porosity according to the definition provided above and, more importantly, would not be advantageous in terms of diffusivity.⁷ Therefore, only a truly hierarchical structure would be beneficial for enhancing the mass transport of (bulky) reactants and/or products and thus the catalytic performance of the zeolitic material. Indeed, hierarchical zeolites typically display superior catalytic activity compared to their counterparts devoid

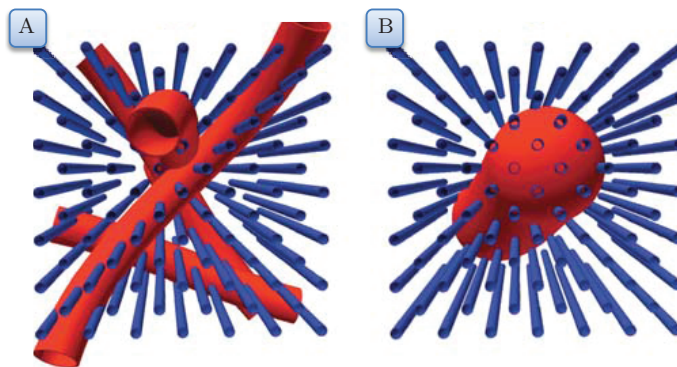


Fig. 2.3. Schematic representation of: (A) a truly hierarchical porous structure and (B) a structure in which the larger pores are trapped by smaller ones [adapted from Ref. 7].

of meso- or macroporosity in a wide variety of reactions including alkylations, isomerisations and (hydro)cracking.^{13–16} Additionally, the shorter diffusion path length that characterises hierarchical zeolites compared with their purely microporous analogues implies shorter average residence time of molecules in the micropores. This can limit deactivation by coking and can lead to enhanced product selectivity by suppressing further reaction of the formed molecules (e.g. higher selectivity towards the monoalkylated product in the alkylation of benzene).^{7,13}

Several approaches have been developed to create mesoporosity (and, less frequently and less preferably, macroporosity) in zeolite structures. These approaches are labelled as *hard templating*, *soft templating*, and *post-synthetic treatments*.

2.2.1.1. *Hard templating methods*

A template is a compound around which, or in the pores of which, a material can grow. Removal of the template at the end of the crystallisation of the zeolite leaves void spaces behind, which generate the desired hierarchical porosity in the final zeolitic material. When the template is a solid material it is referred to as a hard template. Different types of carbon-based nanomaterials have been successfully employed as hard templates, including carbon nanoparticles and

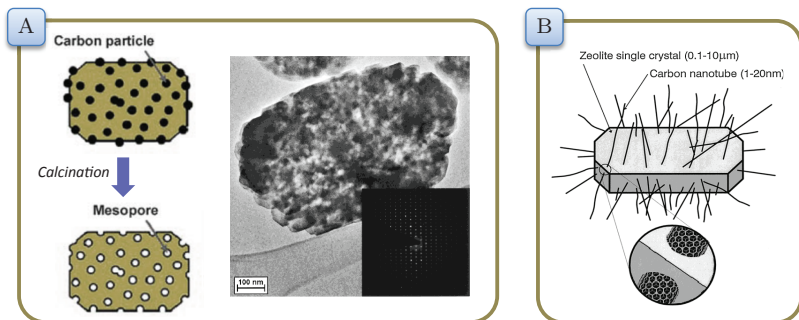


Fig. 2.4. Schematic representation of carbon-based hard templating for the synthesis of mesopore-containing zeolites: (A) with carbon nanoparticles with average size of 12 nm, including a TEM image of the obtained material; (B) with carbon nanotubes [adapted from Refs. 17 and 18].

nanotubes (Fig. 2.4).^{17,18} By carefully tuning the ratio between zeolite precursors and carbon template, as well as the remaining synthesis conditions, it is possible to let zeolite crystals grow around the carbon nanomaterials. The encapsulated carbon species can be removed by calcination, leaving behind a mesoporous structure. A mesoporous ZSM-5 zeolite prepared with this approach and using carbon nanoparticles with an average size of 12 nm as hard template (Fig. 2.4(A)), led to higher rates of diffusion and improved catalytic activity compared to the corresponding conventional zeolite.¹⁹ However, it should be noted that part of the formed mesopores in this type of materials are likely to be trapped by micropores (Fig. 2.3(B)) and thus will not improve the mass transport.

When using carbon nanotubes as hard templates (Fig. 2.4(B)), it was possible to obtain zeolites with mesopores having size and geometry that corresponded well with those of the nanotubes. Such mesopores extended throughout the whole zeolite and thus provided enhanced accessibility to the micropores.

Hard template methods based on carbon nanosized materials are versatile and currently allow the synthesis of a variety of mesopore-containing zeolite frameworks (e.g. CHA, MFI, BEA).

A related yet different approach in hard templating employs porous carbon materials to provide a confined environment within

which zeolite crystals can grow.^{9,11} This confined-space synthesis promotes the formation of zeolite nanocrystals (see also Section 2.1). Tuning the synthesis conditions can lead to intergrowth between the zeolite particles, and in such case the voids between the nanocrystals can be considered structural. The utilisation of three-dimensionally ordered mesoporous carbon templates with narrow pore size distribution enabled the synthesis of materials consisting of an ordered arrangement of zeolite nanocrystals with uniform size (Fig. 2.5).²⁰ However, it is generally difficult to establish the degree of intergrowth between the primary zeolite particles in these materials. As a consequence, the mechanical and thermal stability should be assessed to establish whether the hierarchical porosity of these materials would be preserved under operating conditions in catalytic or adsorption applications.

Organic polymers that are insoluble in the synthesis mixture have been extensively studied as another class of hard templates for the synthesis of zeolites with hierarchical porosity.⁹ Once the zeolite has formed, the polymeric template can be readily removed by calcination. A limitation when using polymers as templates is that the temperature of the hydrothermal synthesis of the zeolite (which generally ranges between 100 and 240°C) should be kept below the glass transition temperature (T_g) of the polymer, to prevent softening that would change its templating behaviour. Many polymers are commercially available in the form of macroscopic solid beads, with

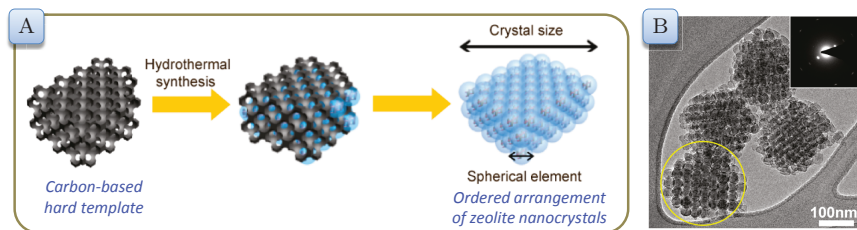


Fig. 2.5. Schematic representation of the formation of three-dimensionally ordered zeolite nanocrystals templated by three-dimensionally ordered mesoporous carbon (A). TEM image of an LTA zeolite prepared with this approach (B); the inset shows the electron diffraction pattern of the circled area [adapted from Ref. 20].

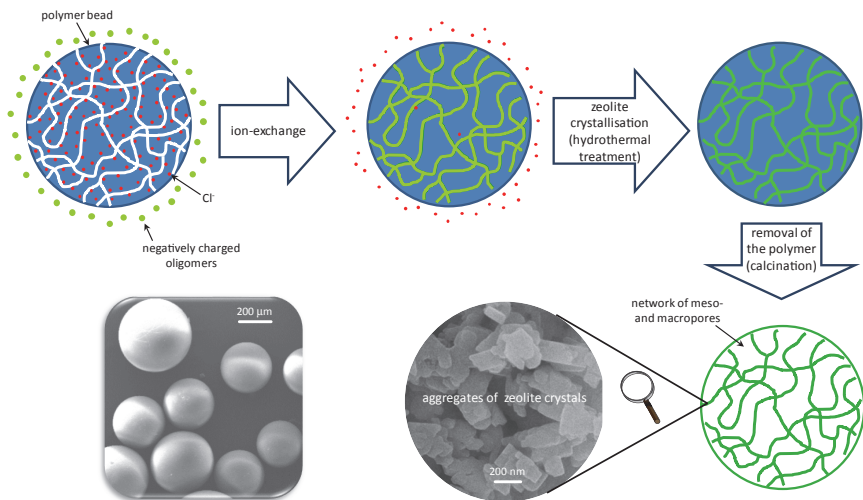


Fig. 2.6. Proposed steps leading to the formation of zeolite beads with hierarchical porosity, via hard templating with anion-exchange polymer beads [adapted from Ref. 23].

a typical diameter between 0.3 and 1 mm (i.e. similar to the size of the metal sphere at the tip of a ball pen). By employing polymer beads with ion-exchange properties as hard templates combined to careful tuning of the conditions of the hydrothermal synthesis, it is possible to prepare zeolites in the form of hierarchically porous beads (Fig. 2.6).^{21–23} Typically, the obtained materials consist of zeolite nanocrystals forming a network of connected large meso/macropores and organised in a macroscopic bead shape, with a slightly smaller diameter (0.2–0.8 mm) compared to that of the polymer template. Therefore, the polymer beads act as shape- and structure-directing agent in the synthesis of these materials. The notable feature of these materials is that they combine macroscopic shaping into a bead format with hierarchical porosity within the material, with meso- and macropores providing the access to the microporous zeolitic domains. The bead format is advantageous for catalytic applications in batch reactors, as it allows recovering the catalyst without centrifugation or filtration. It is also attractive for application in continuous flow reactors, as it provides binder-free shaping of the

zeolite. The challenge in the synthesis of these materials is to generate zeolite beads with good mechanical stability and with high degree of crystallinity.

Hard templating strategies are versatile but typically still suffer from a number of downsides.^{7,9} The synthesis procedures can be complex and require multiple steps. The species used as hard templates are often expensive (e.g. carbon nanotubes) and are destroyed by calcination at the end of the synthesis. Additionally, this thermal treatment can be detrimental for the zeolite structure. All these drawbacks pose important challenges, and may hinder the large-scale application of hard templating.

2.2.1.2. *Soft templating methods*

The role of the template is to direct the growth of the material towards a desired structure. In the synthesis of many conventional zeolites, organic templates are used to promote the formation of a specific microporous framework (e.g. tetrapropylammonium cations, TPA⁺, for the synthesis of MFI zeolites). In the synthesis of ordered mesoporous materials (e.g. MCM-41, SBA-14, see also Section 2.1) the tendency of specific surfactants to organise themselves in cylindrical micelles in a polar solvent is exploited to induce the formation of silicates with a hexagonal array of parallel mesopores. These structure-directing agents lack the rigidity of the hard templates discussed in Section 2.2.1.1 and are thus referred to as soft templates. At the end of the synthesis, these templates are typically removed by calcination, though other techniques (e.g. based on acid treatment) have been used for removing and, in some cases, recovering the compounds used as templates.^{24–27} Soft templating methods can be subdivided into two groups: primary methods, in which the template and all other components of the synthesis mixture are added together; and secondary methods, in which first all components except the template are mixed, followed by addition of the template in a second, separate step. The first attempts to apply soft templating to the synthesis of zeolites with hierarchical porosity were based on combining a structure-directing agent for the synthesis of the zeolite and a surfactant for generating mesoporosity. However, this

approach tends to lead to segregation and consequent formation of either the zeolite, the mesoporous silicate or a physical mixture of the two.⁹ Nevertheless, the hydrothermal synthesis of zeolites with hierarchical porosity at the mesoscale was eventually achieved by thorough tuning of the ammonium salt used as template for the zeolite structure and of the polymeric surfactant employed to induce mesoporosity, and by adding the surfactant 1 hour after having mixed all other components.²⁸ This method was demonstrated by preparing a zeolite Beta [BEA] with partially-connected mesopores in the 5–40 nm range, by using tetraethylammonium hydroxide (TEAOH) and polydiallyldimethylammonium chloride as dual templating system. An alternative, elegant strategy that was developed to prevent the risk of formation of separate microporous and mesoporous phases consists in designing templates that contain in a single compound both ammonium moieties that act as template for the micropores of the zeolite and long alkyl chains that promote the formation of the micelles that lead to the generation of the mesostructure.²⁹ An example of these multifunctional template compounds is $C_{18}H_{37}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_{18}H_{37}(Br^-)_3$ (Fig. 2.7), which allowed preparing a mesopore-containing MFI zeolite with a remarkably high specific surface area ($1190\text{ m}^2/\text{g}$). In general, the size of the mesopores in these materials could be tuned in the 4–21 nm range by changing the alkyl chain and by adding a swelling agent as 1,3,5-trimethylbenzene, whereas the thickness of the zeolitic pore walls could be controlled by increasing the number of ammonium units in the template from 3 (1.7 nm thickness) to 8 (5.1 nm). A related method employs a multifunctional template that, besides a quaternary ammonium moiety and a long hydrophobic chain, contains a trimethoxysilane end group $[(CH_3O)SiC_3H_6N(CH_3)_2C_{16}H_{33}]Cl$.³⁰ Under the hydrothermal conditions used, the methoxy groups of the silane hydrolysed and condensed together with tetraethylorthosilicate (TEOS) and sodium aluminate, leading to the formation of a mesoporous aluminosilicate zeolite with MFI framework type. The surface area of the material ($590\text{ m}^2/\text{g}$) was higher than that of the corresponding conventional zeolite. The mesopores had a relatively narrow size distribution

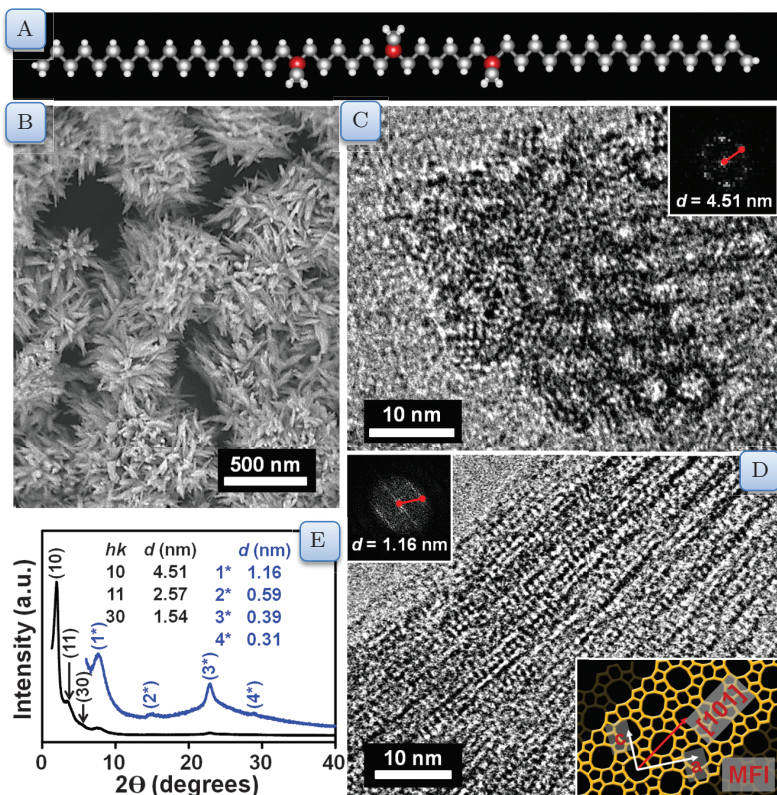


Fig. 2.7. Synthesis of a mesoporous aluminosilicate zeolite with MFI framework type. (A) The surfactant used in the synthesis (H: white spheres; C: grey spheres; N: red spheres). Characterisation of the material by SEM (B), TEM (C and D), Fourier diffractogram [insets of C and D], XRD (E). A model of the MFI framework is given in the bottom right inset of D [adapted from Ref. 29].

centred at 3 nm, which could be increased to 8 nm with longer synthesis times. Titration of the acid sites with a bulky probe that cannot access the micropores (2,6-di-tert-butylpyridine) allowed to estimate that around 25% of the acid sites of this hierarchical zeolite were accessible to bulky molecules, which is a much larger fraction compared to that in the corresponding conventional MFI zeolite (~6%).³¹ The method based on organosilane multifunctional soft templates proved versatile in the synthesis of a variety of other hierarchical zeolite structures (e.g. LTA, BEA, FAU).^{9,13}

A general limitation of soft templating techniques is that the employed surfactants typically require a complex, multi-step synthesis, making them expensive and thus hindering the upscaling to industrial production.

2.2.1.3. *Post-synthetic methods*

The controlled removal of a fraction of the Si or Al atoms from their tetrahedral sites in the framework of zeolites can lead to the formation of mesopores, ideally without significantly compromising the crystallinity of the material. For this purpose, the zeolites are prepared according to conventional methods and then subjected to a selected post-synthetic step that can involve treatment with an acid or a base, steaming, irradiation or a combination of them.⁹ The type of treatment to be employed and the features of the obtained material vary significantly depending on whether the method aims at extracting aluminium or silicon from the zeolite framework.

2.2.1.3.1. Dealumination

Post-synthetic treatments leading to the dealumination of zeolites have been widely employed to increase the Si/Al ratio of zeolites.⁹ The most known example thereof is the modification of zeolite Y [FAU] by steam and acid treatments, which allows tuning the Si/Al ratio of the material while largely retaining its crystallinity. The obtained zeolites are known as ultrastable Y (USY) as they display improved hydrothermal stability, and find large-scale industrial application as (hydro)cracking catalysts.¹³

The most common approach towards dealumination of zeolites involves steaming at high temperatures (600–800°C), typically followed by a mild acid leaching treatment, with either inorganic or organic acids. The steaming step causes the hydrolysis of a fraction of the Al-O-Si bonds with consequent extraction of Al atoms from the tetrahedral sites in the framework, which leads to the formation of extra-framework Al species (mostly with octahedral coordination). The acid leaching step removes these extra-framework species from the internal and external surface of the zeolite, thus preventing partial blockage of the pores.

Dealumination can also be achieved only through acid treatment at temperatures in the range 50–100°C.¹¹

The dealumination process can be accompanied by a rearrangement of the Si species leading to a stabilisation of the framework.¹³ Additionally, dealumination treatments generally lead to the creation of mesoporosity in the zeolite structure. However, these mesopores are not or scarcely interconnected to each other or to the external surface (as depicted in Fig. 2.3(B)) and thus do not lead to a clear enhancement of the diffusion properties.⁹

The extraction of aluminium atoms from tetrahedral framework sites also leads to a modification of the acid properties of the zeolite: the number of Brønsted acid sites stemming from tetrahedral Al sites decreases, whereas the formed extra framework aluminium species, if not removed, can behave as Lewis acid sites. As a consequence, the catalytic properties of dealuminated zeolites differ from those of their untreated counterparts. These changes can be beneficial or detrimental to the activity and selectivity of the catalyst, depending on the nature of the target reaction.¹¹

The poor interconnectivity of the mesopores and thus the limited advantages in mass transfer combined with the possible damages to the crystalline microporous framework under the severe treatment conditions, make dealumination less suitable than desilication (see below) as post-synthetic method to introduce hierarchical porosity in zeolites.

2.2.1.3.2. Desilication

Preparation of zeolites with hierarchical porosity by desilication has proven to be a versatile and efficient method that has the potential to be upscaled to industrial production.³² This post-synthetic method involves the partial removal of Si atoms from a chosen zeolite framework by means of a treatment in alkaline medium under relatively mild conditions (e.g. 0.2 M NaOH at temperature between 50 and 100°C). In such basic environment, the Si atoms are preferentially removed from the zeolite crystal, whereas the Al atoms are largely preserved, causing a decrease in the Si/Al ratio of the zeolite. The creation of mesopores by desilication was first reported for zeolite

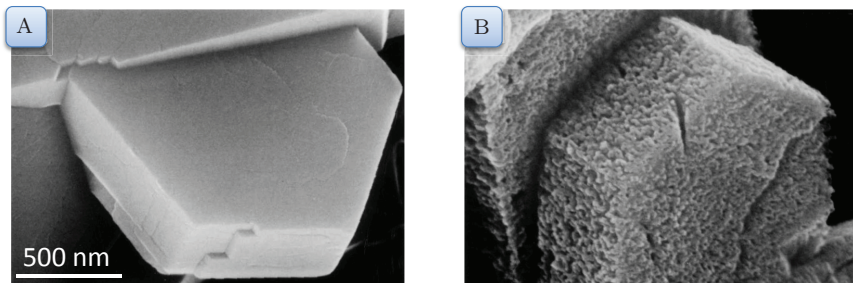


Fig. 2.8. Desilication of zeolite ZSM-5: (A) SEM images of the original ZSM-5 zeolite and (B) of the material obtained after alkaline treatment, in which the porosity generated by desilication is visible [adapted from Ref. 33].

ZSM-5 [MFI] (Fig. 2.8(A-B)).³³ These early studies evidenced that by tuning the NaOH concentration (0.2 M) and the treatment time, it was possible to increase the mesopore volume from $0.072 \text{ cm}^3/\text{g}$ of the parent zeolite to values $>0.150 \text{ cm}^3/\text{g}$ without negatively affecting the crystallinity of the material. Treatments with higher NaOH concentration (e.g. 1 M) caused a decrease in the crystallinity of the zeolite.

More recent work investigated systematically how the desilication process varies as a function of the Si/Al ratio of the parent ZSM-5 zeolite (Fig. 2.9).³⁴ In all cases, the treatment is highly selective towards the removal of Si atoms from the zeolite framework through hydrolysis of the Si-O-Si bonds, whereas the number and tetrahedral coordination of the Al sites in the framework is largely unaffected. For zeolites with Si/Al ratio in the 25–50 range, the desilication method is highly effective in creating mesopores with a diameter between 5 and 20 nm and high mesopore surface area up to $200 \text{ m}^2/\text{g}$. These mesopores are connected to the external surface and are therefore easily accessible, thus proving the truly hierarchical nature of the porous system (Fig. 2.9(B)). For zeolites with $\text{Si/Al} < 25$, the high aluminium content prevents the removal of the silicon atoms from the framework and, therefore, limits the formation of mesopores (Fig. 2.9(A)). On the other hand, zeolites with $\text{Si/Al} > 50$ tend to dissolve to an excessive extent, giving rise to macropores rather than mesopores (Fig. 2.9(C)).⁷

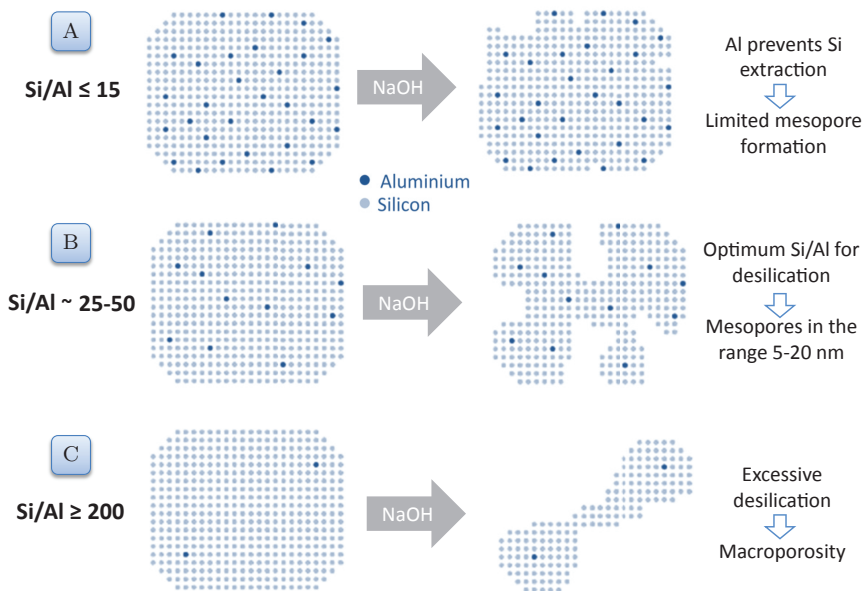


Fig. 2.9. Schematic representation of the desilication of zeolite ZSM-5 by alkaline treatment with NaOH, as a function of the Si/Al ratio in the parent zeolite framework [adapted from Ref. 34].

The beneficial effect of the creation of hierarchical porosity by desilication of zeolite ZSM-5 was demonstrated by monitoring by FTIR spectroscopy the adsorption of molecular probes of different size on the Brønsted acid sites of samples with different mesopore surface area.³⁵ On the basis of the ratio between the number of Brønsted acid sites probed by 2,6-lutidine (which is a relatively large organic base that is able to access only \sim 50% of the acid sites of the parent zeolite) and those probed by pyridine (which is a less sterically-hindered organic base that is conventionally used to estimate the number of acid sites of zeolites) it was possible to estimate to which extent the desilication improved the accessibility of the acid sites. It was found that the accessibility increased clearly for mesopore surface area $>200\text{ m}^2/\text{g}$, with an analogous number of acid sites being accessible to the two probes for the most severely desilicated ZSM-5 zeolite, which had a mesopore surface area of $277\text{ m}^2/\text{g}$. However, it should be noted that this

more extreme desilication was also accompanied by the undesired loss of approximately half of the original micropore volume, which indicates a deterioration of the crystalline framework. With the aim of minimising the loss of microporosity while maximising the mesoporosity, methods were developed in which a weaker base (e.g. TPAOH) was used as desilicating agent instead of NaOH.³⁶ This led to lower desilication rates, making the process more controllable and allowing to preserve better the microporosity. Additionally, this approach has the advantage of generating readily the H-form zeolite upon calcination, whereas an ion-exchange step is needed to remove the sodium cations if the desilication is carried out using NaOH. On the other hand, this method also has drawbacks as it does not allow reaching very high mesopore surface area (125–180 m²/g) and the slower extraction of Si from the framework leads to a higher extent of Al leaching compared to the treatment with NaOH. Further optimisation of this method was achieved by using mixtures of TPAOH and NaOH as desilicating agent. The total concentration of OH⁻ was kept constant at 0.2 M, whereas the effect of varying the ratio between TPAOH and NaOH was investigated.³⁷ This allowed controlling the average size of the mesopores in the range between 10 nm (no TPA⁺ present) to 4–5 nm (TPA⁺/Na⁺ ratio = 2/3). The use of TPAOH in combination with NaOH also allowed a better control of the desilication of zeolites with high Si/Al ratio.³⁸ Whereas with pure NaOH excessive dissolution of the material is observed (Fig. 2.9(C)), in the presence of TPAOH the desilication process is milder, leading to zeolites with high mesopore surface areas (>200 m²/g).

An alternative and elegant method to preserve the microporosity of the zeolite during the desilication process is based on the observation that zeolites that still contain the organic template used in their synthesis are nearly immune to Si extraction when treated with aqueous NaOH solutions.³⁹ This allowed developing a method in which the template was only partially removed by mild calcination (230 or 330°C), followed by desilication with generation of mesopores in the regions of the zeolite from which the template had been removed. A second calcination step at higher temperature (550°C) allowed removing the remaining organic template, thus

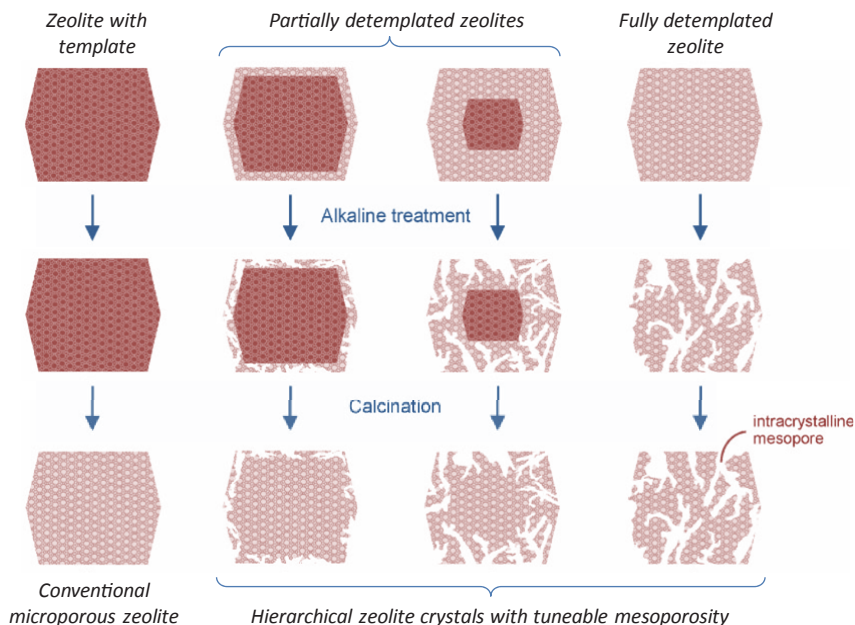


Fig. 2.10. Schematic depiction of effect of the amount of the template present in the zeolite framework on the degree of formation of mesopores by desilication upon alkaline treatment [adapted from Ref. 39].

freeing the preserved micropores. By tuning the temperature of the first calcination step it was possible to adjust the degree of mesopore formation in the zeolite ($20\text{--}230\text{ m}^2/\text{g}$) upon alkaline treatment (Fig. 2.10). This method is particularly interesting for zeolites as Beta, for which the desilication process is difficult to control due to the relatively lower stability of Al in this framework.

Most of the research on the utilisation of desilication to generate hierarchical porosity in zeolites has been performed on ZSM-5 frameworks with Si/Al ratio between 25 and 50. The low tendency of silicon atoms that neighbour aluminium atoms in framework positions to undergo extraction by alkaline treatment poses a challenge in the application of desilication approaches to zeolites with lower Si/Al ratio,⁷ of which zeolite Y is the most important example in terms of industrial applications. Several strategies have been devised to overcome this limitation.¹³ The most efficient approach combines

an initial acid treatment with an aqueous solution of H_4EDTA , followed by an alkaline treatment with $NaOH$.⁴⁰ The acid treatment causes the partial dealumination of the zeolite Y framework (see Section 2.2.1.3.1), leading to an increase of the Si/Al from 2.4 in the parent zeolite to $Si/Al > 4$. This feature makes the zeolite more prone to undergo desilication and thus to generate a hierarchical zeolite with large mesopore surface area (up to $\sim 200\text{ m}^2/\text{g}$). During the alkaline treatment, the aluminosilicate debris formed during the dealumination step provides Al species that are reinserted in the zeolite framework. Although these Al species are tetrahedrally coordinated, they do not behave as conventional framework sites and can be detrimental to the catalytic performance of the material.¹³ These Al species can be removed efficiently by means of a mild acid treatment with an aqueous solution of Na_2H_2EDTA .⁴⁰

It can be concluded that desilication is a versatile and efficient approach for generating zeolites with hierarchical porosity as it allows the creation of mesopores with high degree of interconnectivity in zeolites with different Si/Al ratios and with different framework types (e.g. CHA, MFI, BEA, FAU).^{9,11} An additional asset is that, differently from dealumination, the desilication process does not affect significantly the acid sites of zeolites. In the perspective of large-scale industrial application, it is also important to note that hierarchical zeolites prepared by desilication have been reported to display good mechanical stability under the conditions that would be employed for preparing pellets by compression.⁹

2.2.1.4. *Other methods for preparing of hierarchically porous zeolites*

Besides the main methods presented in Sections 2.2.1.3, a few other approaches have been designed with the purpose of preparing zeolites with hierarchical porosity.

Organosilanes ($RSiX_3$, where R is an organic group and X is either an alkoxide or a chloride) can be used to promote the formation of hierarchical structures by exploiting the tendency of these compounds to react with the silanol groups at the surface of silicates.^{41,42} The addition of organosilanes into the synthesis gel at

the initial stages of the crystallisation of zeolite ZSM-5 results in their anchoring on the external surface of the protozeolitic units present in the reaction mixture.⁴¹ The organic groups from the organosilanes hinder the growth of these protozeolitic units into a conventional large crystal, leading instead to the formation of a material that, after calcination to remove the organic moieties, consists of MFI nanocrystals (5–10 nm) with a high degree of intergrowth and organised in large aggregates (300–400 nm). The obtained material displayed higher specific surface area (670 m²/g vs. 435 m²/g) and external surface area (478 m²/g vs. 89 m²/g) compared to a conventional ZSM-5 zeolite, although this was at the expense of a drop in micropore surface area (192 m²/g vs. 346 m²/g). An additional drawback of this type of materials is the smaller number and lower strength of their acid sites compared to those in conventional ZSM-5 zeolite.⁹ This feature represents a serious limitation for potential catalytic applications.

Another approach that has been investigated for the creation of zeolites with hierarchical porosity is the steam-assisted conversion of amorphous silicates into zeolites. However, in most of the cases this method leads to only partial conversion of the amorphous parent material into a crystalline zeolite framework.⁹ A promising material prepared by steam-assisted conversion is a MFI-type zeolite with high crystallinity and with intracrystalline macropores with diameter between 250 and 500 nm, which was obtained by gradual dissolution and zeolitisation of mesoporous silica spheres with diameter of around 600 nm.⁴³

2.2.2. *Preparing other materials with hierarchical porosity*

Zeolites are probably the class of materials for which synthetic strategies to generate hierarchical porosity have been investigated more extensively. However, other classes of materials can also be prepared with a porous hierarchical structure.^{44–46} The methods employed for this purpose are typically related to those developed for preparing hierarchical zeolites and described in detail in Section 2.2.1, with hard and soft templating techniques being the most commonly

employed approaches. The type of materials that can be prepared with hierarchically-structured pores range from metal oxides^{44,45} to carbon-based materials.^{45,46}

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