Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity

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‘Hierarchy’ is a property which can be attributed to a manifold of different immaterial systems, such as ideas, items and organisations or material ones like biological systems within living organisms or artificial, man-made constructions. The property ‘hierarchy’ is mainly characterised by a certain ordering of individual elements relative to each other, often in combination with a certain degree of branching. Especially mass-flow related systems in the natural environment feature special hierarchically branched patterns. This review is a survey into the world of hierarchical systems with special focus on hierarchically porous zeolite materials. A classification of hierarchical porosity is proposed based on the flow distribution pattern within the respective pore systems. In addition, this review might serve as a toolbox providing several synthetic and post-synthetic strategies to prepare zeolitic or zeolite containing material with tailored hierarchical porosity. Very often, such strategies with their underlying principles were developed for improving the performance of the final materials in different technical applications like adsorptive or catalytic processes. In the present review, besides on the hierarchically porous all-zeolite material, special focus is laid on the preparation of zeolitic composite materials with hierarchical porosity capable to face the demands of industrial application.

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1 Hierarchical aspects in materials: classification and definition

The expression ‘Hierarchy’ goes back to the Greek word ‘ἱεραρχία’ (hierarchia): "rule of a high priest" and it describes in general a ranking of something like, e.g., items, ideas, values, concepts and organisations. From the viewpoint of natural scientists hierarchical systems are mostly connected with a function, e.g. stability, strength and flexibility of a material.

Materials which are organised hierarchically by the combination of entities, compositions and/or geometrical structures form compartments or paths of matter with different properties (e.g. densities and viscosities) in one single system. In addition, hierarchical systems can be organised in a continuous or discontinuous and/or in a homogeneous or heterogeneous way and are very often composed of elements of very different sizes bridging several orders of magnitude. Therefore, to be termed ‘hierarchical’, a material has to fulfil two basic criteria: Firstly, its structural elements (compartments) have to be characterised by more than one length scale, and secondly each of these structural elements has to have a very distinct but complementary function.1,2 As a result, just by organizing individual entities/structures in a hierarchical manner, a specific property of the resulting hierarchical material can outperform the very individual entities/structure by far. For instance, the exceptional physical properties of natural materials (e.g. physical strength of wood and bones) is typically be ensured by a hierarchical arrangement of entities either of the same material having different dimensions or of entities of different materials.3

For chemical engineers, the aim to design and optimise a certain property (or function) of a material is always a central aspect of their work pattern. Thus, from the viewpoint of designing such a property or function, three different forms of hierarchy can be distinguished:

Structural hierarchy: enables very stable construction by a tactical repetitive combination of structural elements (e.g. wood, ceramics and bones)

Transport hierarchy – hierarchy in fluid systems: enables fast transport and/or high degree of distribution of a flow (e.g. lung, river delta and information system).

Compositional hierarchy: arranging the parts of a material (e.g. atoms, molecules and larger entities) enables the formation of a system with locally and systematically variable composition by rearrangement/self-organisation mechanism induced by small forces (e.g. human body, ordered alloys and biomolecules).

Structural hierarchy often describes a very specific arrangement of material entities with functional subunits.4 There, structural elements, which themselves contain a certain individual structure, are organised over different length scales and all together form the macroscopic “super-element”, like the arrangement of the cellular structure in a bone. Compared to materials with only one homogeneous bulk structure, hierarchical structures can exhibit unusual properties, such as a higher compressive strength, extreme behaviour concerning thermal expansion or an oriented piezoelectricity.4 In contrast to the structural hierarchy, transport based hierarchical systems are related to well-organised open (transport) pathways like in an efficient interconnected pore system.

In this respect, the different forms of hierarchy seem to be implemented in the multiple scale constitutions, which we face in technical catalytic processes, e.g. catalytically active site → pore geometry → catalyst particle (crystal) → shaped catalyst body → packing of the catalyst → the reactor itself, thus bridging such entities with different chemical properties (e.g. composition of the catalytically active sites) and functions (e.g. strength of the packing: pellet or monolith) over more than 10 orders of magnitude (Fig. 1). Besides these chemical and structural aspects, the fluid phases (reactants and products) have to find their flow and diffusion path throughout the whole complex system, which is illustrated in Fig. 1. In the following sections we will only focus on different aspects of the transport-related form of hierarchy, i.e. hierarchical porosity.
1.1 Hierarchy from different points of view

There are various types of hierarchical systems – often also called networks – in the world, reaching from social and technical to biological systems, like the organisations in human society, the data distribution in informatics (illustrated schematically in Fig. 2) and the well-known transport systems in the human body.

Concerning the structure of such hierarchical systems, Clauset et al.4 wrote: “Recent studies suggest that networks often exhibit hierarchical organisation, in which vertices divide into groups that further subdivide into groups of groups, and so forth over multiple scales. In many cases, the groups are found to correspond to known functional units, such as ecological niches in food webs, modules in biochemical networks (protein interaction networks, metabolic networks or genetic regulatory networks) or communities in social networks”. Accordingly, the levels of the entities in hierarchical systems have to be interconnected forming a branched or a flat hierarchical arrangement.

Also technical systems like the electricity networks and the water and gas supply systems in every city are hierarchical, representing branched systems. Even a consumer product like diapers with their very fast soaking and effective long lasting storage ability for liquid in their pore system are hierarchical. They are designed in such a way that they contain a main flow pathway for the fast transport of fluid phase which diverges directly into small storage compartments, representing an example for a flat hierarchy.

Especially, many flow systems in nature show hierarchical patterns sometimes with different but very specific structures. Some typical examples are summarised in Fig. 3 to illustrate the diversity of the occurrence of the hierarchical property.

Hierarchical patterns can also be observed in ecological systems like river deltas, in which the horizontal distribution of the water is increased, which leads to lower flow velocity and thus decreased soil discharge into the ocean as compared to a straight river (Fig. 3a). Even lightning and nerves exhibit hierarchical shape for fast transport and efficient distribution of the energy and information, respectively (Fig. 3b and g). In Fig. 3c and d parts of a tree, i.e. the roots and a fraction of a leaf are shown. The pictures indicate the occurrence of two different hierarchical directions: the system of the roots collects the mineral containing water using widely distributed tiny flow paths at the beginning, passes the collected water and nutrients onto a higher level of the hierarchical system, which is here realised by the wider transportation channels in the stem of the tree. Finally, the water is released via the leaves in which the distribution of the flow is mainly realised by a two-level hierarchy consisting of the ‘main pathways’ – here the veins of the leaf – which distribute the flow into a large network of smaller capillaries.

Very prominent hierarchy examples are our lung and the blood circuit (Fig. 3e and f). The combination of the broad single channel trachea between nose and lung and the large amount of pulmonary alveoli, which cause a huge increase of the surface area of the lung, is a very efficient natural construction enabling both, fast transport with a minimum of resistance (pressure drop of less than 1 bar!) and fast and effective oxygen and CO₂ exchange between air and blood. Also, the blood circuit is a closed system, thus it exhibits similar flow at the beginning and at the end of each split-up region (→ hierarchical distribution and hierarchical re-collection). The cardiovascular system splits up and fuses depending on the need for fast blood transport through the body or efficient exchange with the tissue.

Town maps can be used to illustrate very descriptively the structural aspects and their advantage in respect to an effective transport (in this case the traffic flow) in differently organised systems: non ordered arrangements of streets in an old downtown area versus the well-organised (hierarchical) street systems of the so-called ‘planned cities’ where main streets are reaching even the centre of the town or certain residential areas directly.9
2 Hierarchically porous zeolite systems

Preparation of porous materials in general

Porosity in general results from the combination of arrangements of elements in the form of complexes, subunits, building blocks, crystals or particles themselves. Nowadays, a huge variety of different strategies exists in which nearly every chemical element can contribute to the construction of a porous system. These strategies are not limited to bottom-up methods but can also involve top-down methods or a combination thereof.

Comprehensive reviews on the preparation principles and synthetic strategies of porous materials with pore sizes in the micro- (<2 nm), meso- (2-50 nm) or macropore (>50 nm) regime are given in the open literature. The most important preparation methods are: (i) hydro- (or solvothermal) synthesis like in the synthesis of zeolites, AlPOs or MOFs, (ii) sol-gel processing and (iii) precipitation methods like in the preparation of silica gels and precipitated silicas, respectively, (iv) templating with supramolecular arrays like LIGA technique, (v) (nano)casting methods, (vi) phase separation (e.g. porous glass), (vii) structuring methods like the LIGA technique, (viii) physically and/or chemically induced foaming leading to polymeric, ceramic and metallic foams, and (ix) methods belonging to additive manufacturing (e.g. selective electron beam melting SEBM).

In general, all these methods usually yield materials with a non-hierarchical pore system. To create hierarchically porous materials, the above mentioned preparation methods have to be either adapted or combined, post-synthetic preparation...
steps have to be applied or pre-manufactured materials with different pore systems have to be combined in a suitable manner.

For zeolite-based materials, these different preparation routes towards hierarchically porous materials usually yield in materials with short diffusion path lengths. Compared to common microporous systems, the shortening of the diffusion path length results in improved mass transfer properties. This improvement enables higher activities and/or improved kinetics of catalytic and sorptive processes which is kind of the “driving force” for the growing interest in hierarchically porous materials in general.34–37

In the following, zeolite-based hierarchical materials shall be discussed according to their compositional, textural and structural properties as well as according to the underlying preparation principles.

Different hierarchically porous zeolitic materials

Inherently, crystalline zeolitic materials exhibit a well-defined pore system with pore sizes in the micropore regime and, thus, do not feature hierarchical porosity. To introduce an additional pore system into zeolitic materials which is integrated in a hierarchical manner (as illustrated in Fig. 5) and thereby creating hierarchical porosity, several preparation strategies are described in the literature. Interestingly, all these strategies are based on just a few general preparation principles, namely crystallisation, aggregation and extraction (or combinations thereof) with their underlying different physical and chemical laws. In a very general way, one can distinguish between attempts to:

- combine the microporous nature of the zeolitic material with the porosity characteristics of (at least) one second material, thus, resulting in (i) hierarchical zeolite composite materials or (ii) hierarchical all-zeolite materials after complete crystallisation/ transformation.

In the following paragraphs, these two attempts shall be discussed in detail.

Fig. 6 gives an overview over hierarchical zeolites according to their constitution, i.e. it subdivides hierarchical zeolites into all-zeolite materials and composite materials. However, it should be underlined, that even though the compilation in Fig. 6 might cover today’s most established examples, all the preparation routes and materials could theoretically be combined, yielding a large number of different (new) hierarchical zeolitic materials.

Hierarchical all-zeolite materials are characterised by the inherent microporosity dictated by the crystalline structure of the zeolite and an additional hierarchically connected pore system which might be either inter- or intracrystalline or even a combination thereof. The preparation of such all-zeolite materials is mostly performed using bottom-up principles, where the additional porosity is either generated during the course of the crystallisation of the zeolite crystals or by a purposeful aggregation of individual zeolite crystals. On the other hand, some preparation routes follow top-down approaches, such as selective extraction of specific framework constituents of the already synthesised microporous zeolite (e.g. via desilication). These top-down approaches always include a post synthesist step such as leaching with alkaline media. Obviously, such a post-synthetic method is not limited to pristine zeolite systems to form hierarchical zeolite materials.
crystals, but might also be applied to create an additional level of porosity in already hierarchical zeolitic systems. Depending on the configuration of the resulting hierarchical all-zeolite material one can further distinguish (i) hierarchical zeolite single crystals, (ii) hierarchical monolithic zeolite materials, (iii) hierarchical intergrown zeolite sheets and (iv) hierarchical porous aggregates of e.g. zeolite nanocrystals.

The group of hierarchical zeolite composite materials contains per definition at least one pre-fabricated material acting as a composite partner for the zeolite and providing or building the additional porosity needed for the creation of a hierarchical pore system within the final composite material. According to the right hand side of Fig. 6, the composite partner might either (i) serve as a constructive binder (not necessarily porous) enabling the durable aggregation of the zeolite crystals in the form of zeolite shapes with intercrystalline porosity resulting from the aggregation during the compaction/shaping process or (ii) exhibit an intrinsic porosity and act as a support for the zeolite, which leads to a zeolite-coated support. The additional porosity in the former case is highly dependent on the binder material, zeolite crystal size and the processing technique, while in the latter case the additional porosity is dictated by the porosity of the support material. A review about a wide range of shaping techniques for porous powders has been published recently.38

While both aforementioned methods (shaping and coating) can be assigned to the ‘bottom-up’ approaches, the (iii) partial transformation (also referred to as ‘reactive coating’) of a reactive preform rather belongs to the ‘top-down’ approaches. Here a porous pre-shaped material (usually meso- or macroporous) containing at least one ingredient (mostly SiO₂) for zeolite crystallisation is set into conditions enabling zeolite synthesis and thereby delivering the required nutrient(s) for a partial (re)crystallisation. As a result, the parent material is (partially) transformed into zeolite resulting in a composite material which is characterised by a very strong intergrowth between the zeolite coating and the remaining support. It is worth mentioning that in principle, for some materials, the transformation into zeolite can be performed to 100% – in that case, however, the resulting material is rather to be assigned to ‘all-zeolite materials’ than to ‘composite materials’. With the prerequisite of the binder being transformable, the aforementioned transformation principle can also be applied to ‘shaped zeolite composites’ resulting in an ‘all-zeolite system’.

### 3 Preparation routes to hierarchically porous all-zeolite materials

In order to form hierarchical all-zeolite materials, an additional pore system needs to be introduced with an hierarchical interconnectivity with the inherent micropore system dictated by the zeolitic framework structure. Such an additional pore system can be introduced.
• directly during the crystallisation of zeolites in the presence or absence of hard or soft templates (bottom-up approaches) as summarised in Table 1. Here, the term templating refers to the use of meso- or macroporogen to direct the formation of the additional porosity.
• by post-synthetic methods like metal extraction (top-down approach), aggregation of already existing zeolite particles (bottom-up approach) or (re)arrangement, e.g. delamination/ reassembly of layered zeolites.

3.1 Hard/solid templating methods

This method involves the utilisation of either porous or nonporous solid material during the zeolite synthesis to serve as a meso- or macroporogen for the formation of the additional porosity.66 The actual procedure includes the preparation of the zeolite synthesis mixture, addition of the solid template, crystallisation of the zeolite precursors in the presence of the solid template and the post-synthetic removal of this solid template via calcination or dissolution in acids. Carbonaceous materials, biological materials, polymers as well as inorganic solid materials have been applied as hard templates to prepare hierarchically porous materials.67 Among these, especially the carbonaceous materials of different shapes, sizes and porosities belong to the widely used hard templates as summarised in Table 1. Furthermore, organic aerogels (resorcinol-formaldehyde-based) with uniform mesopores have also been used as templates for the synthesis of hierarchically porous ZSM-5 and silicalite-168 monoliths under conventional hydrothermal synthesis conditions. Very recently, the synthesis of ZSM-5 monoliths with hierarchical tetramodal porosity has been realised using a polyurethane foam as a rigid scaffold via steam-assisted crystallisation.

The use of hard templates allows the control of properties like the meso- and/or macropore size and the pore size distribution of the resulting zeolitic materials. As the solid template is usually chemically inert during zeolite synthesis, the hard templating method can be applied for a wide range of zeolite structures, such as MFI,69 FAU49 and BEA.70

Furthermore, the hard templating method is also used to prepare monolithic three-dimensionally ordered meso-/macroporous (3DOM) zeolites with intercrystalline meso- or macroporosity. Such 3DOM zeolites are characterised by an ordered arrangement of the additional pores within the resulting polycrystalline monolith, which stems from an ordered arrangement of the usually spherical meso- or macroporogens. Mostly, 3DOM carbons have been used as macroporogens for 3DOM zeolite materials, which required a post-synthetic removal of the template by calcination.71

However, the removal of the hard template has been reported to damage the final zeolite structure.72 Alternatively, mesoporous silica particles can be applied as hard templates to overcome the critical hard template removal step, because they act as both a mesoporogen or macroporogen and as a silica source, which leads to their consumption during zeolite crystallisation.73 3DOM zeolite structures have been successfully prepared by using sacrificial silica templates. Very recently, this method was even adopted for the preparation of zeolitic single crystals with intracrystalline macroporosity as schematically depicted in Fig. 7. This approach utilises the steam-assisted crystallisation of mesoporous silica particles (MSPs) after their impregnation

<table>
<thead>
<tr>
<th>Route</th>
<th>Type of meso- or macroporogen</th>
<th>Additional pore type</th>
<th>Framework type and reference</th>
</tr>
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<tbody>
<tr>
<td>Hard templating</td>
<td>Carbonaceous templates</td>
<td></td>
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<tr>
<td></td>
<td>• Carbon particles</td>
<td>Mesopores</td>
<td>MTW, MFI and MEL, BEA, CHA and MWW</td>
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<td></td>
<td>• Carbon fibers</td>
<td>Mesopores</td>
<td>MFI</td>
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<td></td>
<td>• Carbon nanotubes</td>
<td>Meso- or macropores</td>
<td>MFI</td>
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<td></td>
<td>• Colloidal imprinted carbon</td>
<td>Meso- or macropores</td>
<td>MFI</td>
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<tr>
<td></td>
<td>Aerogel/polymer/resin</td>
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<td></td>
<td>• Polystyrene, polyurethane</td>
<td>Meso- or macropores</td>
<td>MFI</td>
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<td></td>
<td>• Carbon aerogel</td>
<td>Mesopores</td>
<td>FAU, MFI</td>
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<td></td>
<td>• Resorcinol-formaldehyde aerogel</td>
<td>Mesopores</td>
<td>LTA, MFI</td>
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<td>Biological</td>
<td>• Starch, bacteria, wood, luffa cylindrical</td>
<td>Meso/macro</td>
<td>MFI</td>
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<td>Inorganic</td>
<td>• Silica</td>
<td>Meso- or macropores</td>
<td>MFI</td>
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<td></td>
<td>• CaCO₃</td>
<td>Macropores</td>
<td>MFI</td>
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<tr>
<td>Soft templating</td>
<td>Dual templating</td>
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<td></td>
<td>• [Amphiphilic] surfactants</td>
<td>Mesopores</td>
<td>MFI, FAU</td>
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<td></td>
<td>• Organosilanes</td>
<td>Mesopores</td>
<td>FAU, MFI</td>
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<tr>
<td>Microemulsion, reverse micelles</td>
<td>Emulsion agents</td>
<td>Macropores</td>
<td>MFI</td>
</tr>
<tr>
<td>Surfactant mediated assembly of seeds</td>
<td>Mesopores</td>
<td>MFI</td>
<td></td>
</tr>
<tr>
<td>Non-templating</td>
<td>None</td>
<td>Meso- or macropores</td>
<td>MFI</td>
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</table>

Table 1 Overview of the different bottom-up routes used to prepare hierarchical all-zeolite materials during synthesis
with tetrapropylammonium hydroxide (TPAOH) acting as the zeolite structure directing agent and source of alkalinity. Nevertheless, the hard templating strategy is often limited by multistep procedures, relatively high costs and health hazards related to some of the hard templates used. Some of these limitations can be alleviated by using biological templates like starch and bacteria. Such biological materials are abundant, mostly less toxic and can be available at a more reasonable price.

3.2 Soft templating methods

In this strategy, either inter- or intracrystalline mesopores can be introduced in different zeolitic materials by the templating action of (i) specially designed surfactant molecules, (ii) surfactant arrays to induce the assembly of subnano pre-crystalline zeolite species or (iii) emulsion forming agents. As also shown in Fig. 8, these strategies can be further subdivided into primary methods, in which all components (including the surfactant) are added at the beginning of a one-step synthesis procedure and secondary methods, which are characterised by a two-steps procedure, where all components except the surfactant are added in the first step, while the surfactant is added in the last step prior to the hydrothermal synthesis.

In primary methods, surfactants assist the assembly of purely molecular species (framework building units) to form zeolite crystals with additional intra- or intercrystalline porosity. Mostly, the surfactant fulfils two functions. The first function, related to the hydrophilic part of the surfactant, is to direct the zeolite structure formation, and/or to ‘anchor’ the surfactant into the zeolite framework, e.g. in the case of organosilane surfactants. The second function, related to the hydrophobic part of the surfactant molecules, is to initiate the formation of organic domains between the inorganic fractions and thus, the surfactant can act as a mesoporogenic or spacer phase during crystallisation. This finally leads either to mesoporous zeolite crystals or a layered assembly of zeolitic nanosheets.

For example, depending on the choice of the surfactant and targeted zeolite framework type, very thin zeolitic MFI-type nanosheets with intracrystalline mesopores were obtained in the presence of a specially designed diquarternary ammonium-type surfactant. In this approach (during the synthesis), the hydrophilic ammonium groups directed the formation of the microporous zeolite structure, whereas the hydrophobic surfactant chains were used to limit the further growth of the zeolite network along the b-direction. Thus, very thin zeolite layers were obtained. By either changing the synthesis conditions or modifying the template, it is possible to prepare these thin zeolite layers as single randomly oriented nanosheets (unilamellar) or as a lamellar stacking of several nanosheets (multilamellar). Another example of primary methods is the use of organosilane surfactants to form zeolitic nanosheet assemblies with intracrystalline mesopores in the case of FAU-type zeolite and mesoporous sponge-like crystals in the case of MFI-type zeolite as summarised in Fig. 9 (right), respectively.

Although the use of these surfactants results in hierarchical zeolites with high degree of interconnected mesopores, most of these surfactants are not commercially available and must be prepared prior to zeolite synthesis. This makes the primary methods very laborious and very expensive. To overcome these limitations, conventional surfactants, like cetyltrimethylammonium bromide (CTAB) can be utilised. However, many attempts to prepare hierarchical zeolites by using CTAB yielded composite materials due to phase separation (physical mixture of amorphous mesoporous silica and crystalline zeolitic phase) during the hydrothermal synthesis.
Alternatively, secondary methods have been developed, which in contrast to the primary methods utilise conventional surfactants like CTAB to assist the assembly of subnano pre-crystalline zeolite species induced by surfactant arrays into zeolitic assemblies exhibiting intercrystalline or intracrystalline mesoporosity. This has been realised via a two-step synthesis procedure. In the first step, zeolite synthesis gel was allowed to age in the absence of the surfactant at 100 °C for different periods of time to form seeds (subnanocrystals) with different degree of polymerisation. In the subsequent step, the surfactant (in this case CTAB) dissolved in ethanol solution was added to direct the self-assembly of these subnano pre-crystalline zeolite species via hydrothermal synthesis.

As also shown in Fig. 10, depending on the aging time ($t_{age}$) of the initial gel, either a mixture of zeolite and mesoporous silica (when the aging time was too short) or cubic shaped crystals of MFI-type zeolites perforated with mesopores (after 2–3 days of aging time) or just aggregates of nanocrystals with intercrystalline mesopores (when the aging time was too long) were obtained.

In addition to the soft templating role, surfactants have also been used to introduce additional porosity in zeolites via the generation of a biphasic emulsion. The main principle behind the emulsion approaches is a phase-separation process during the zeolite formation: A mixture consisting of an organic and an aqueous phase undergoes a phase-separation under the applied synthesis conditions in such a way that the zeolite mixture (aqueous phase) and the organic fraction (future pore/void) form a stable, biphasic (and potentially bicontinuous) emulsion. To achieve this objective, in most cases surfactants and co-surfactants are necessary to prevent the micro- or mini-emulsion from complete phase-separation. Lee and Shantz used polyoxyethylenenonylphenyl ether as surfactant and butanol as co-surfactant to emulsify the aqueous droplets of a silicalite-1 synthesis mixture (tetrathoxysilane (TEOS)/TPAOH/water) in heptane serving as the organic phase. During the hydrothermal synthesis, the aqueous droplets act as ‘nano-reactors’ (‘synthesis in confined space’) wherein the zeolite can crystallise isolated from neighbouring droplets. According to the authors, once the particle within each droplet reached a certain size (approx. 100 nm) the effect of surfactant adsorption became more pronounced leading to an aggregation of those nanometersized particles. This eventually resulted in spherical, micrometersized particles each composed of zeolite nanocrystals. Thus, next to the inherent zeolitic microporosity, the material obtained exhibits intercrystalline meso-/macropores within each particle as well as macropores between the individual particles. Both, crystallinity and size of the resulting aggregates can be tailored by adapting the share of the aqueous phase and the concentration of water therein.

Li et al. also made use of the formation of an emulsion composed of a zeolite synthesis mixture and an organic phase. In contrast to the ‘synthesis in confined spaces’ described above, the authors used a two-step approach. Firstly, organic micelles (CTAB surfactant in ethanol) were emulsified within the aqueous silicalite-1 synthesis mixture (TEOS/tetrabutylammonium...
bromide (TBABr)/water. After aging for 24 hours, the emulsion was dried at 60 °C resulting in an amorphous dry gel composed of all the constituents for the zeolite synthesis (framework atoms silicon and oxygen, structure directing agent TPABr) plus inclusion of CTAB micelles (mesoporogen) plus inclusion of former ethanol/CTAB droplets serving as a soft template for the generation of the macropores within the final product. The actual crystallisation was performed following the ‘steam-assisted conversion’ method: The dry gel was put in a small PTFE container which was placed in an autoclave containing a small amount of water at the very bottom. After 36 hours at 150 °C, crystalline silicalite-1 was obtained showing a trimodal pore size distribution (shown by nitrogen sorption and mercury intrusion). According to the authors, the pores are interconnected and therefore this material can be assigned to the materials with type-II hierarchical porosity (according to the classification in Fig. 5). It is worth mentioning, that the method of Li et al. can also be understood as a two-step process within which the generation of the pores is separated from the actual crystallisation of the zeolite. In other words, here, the hierarchical character of the resulting porosity is generated by the crystallisation of a porous (still amorphous) preform, and thus, this approach can be assigned to the transformation methods (which will be discussed in detail in Section 5.1) as well as to the soft templating methods.

### 3.3 Non-templating methods

These methods enable the creation of additional porosity in all-zeolite materials without any templating action of meso- or macropore templates (in the absence of meso- or macroporogens). Non-templating methods are either based on the aggregation of nanocrystals to form intercrystalline mesopores or on the controlled crystallisation of amorphous gels into zeolite crystals with intracrystalline mesopores or on the selective modification of the zeolitic crystal growth direction (winning).

The aggregation or self-assembly of nanocrystals is the widespread method to create additional porosity without utilising any mesoporogen. Although promising, the self-assembly of nanocrystals results in unstable intercrystalline mesopores or macropores, which can be easily lost due to the (sometimes) very tight agglomeration of the nanocrystals, especially due to treatment stresses during catalytic applications. Alternatively, the non-templating approach has been utilised to form zeolite crystals with intracrystalline mesopores by preserving the mesopores/voids of a dry synthesis gel which was crystallised in water vapor atmosphere. Another impressive example for the non-templating approach is the preparation of self-pillared MFI-type zeolitic nanosheets. Their hierarchical porosity consists of the zeolitic micropores and additional intercrystalline porosity created by the three-dimensional nanosheet assembly. The repetitive branching of the MFI-type zeolite nanosheets was found to be based on a twinning mechanism due to the formation of MEL-type zeolite domains within the MFI structure. MEL and MFI are isomorphous (structural twins), The MEL formation was induced by the presence of certain organic structure directing agents (micropore templates), e.g. tetrabutylphosphonium ions, during the zeolite crystallisation (Fig. 11). A similar effect was observed for FAU crystallisation in the presence of organosilane molecules (e.g. 3-(trimethoxysilyl)propyl hexadecyl-dimethylammonium chloride (TPHAC)), which can act not only as soft templates for mesopores (as shown in Fig. 9), but also as ‘morphology modifiers’ by inducing twin formation.

However, such organic molecules are often difficult to prepare and require a post-synthetic treatment for their removal.

Recently, an alternative approach for the induction of structural twin formation was reported for FAU-type zeolite. Here, simple inorganic salts like zinc nitrate and lithium carbonate instead of organic molecules have been used as ‘morphology modifiers’ to form EMT (structural twin of FAU) domains within the FAU structure. A schematic drawing of the twinning principle as well as SEM pictures of the resulting self-pillared aggregates are illustrated in Fig. 11.

Furthermore, it is also possible to apply growth modifying agents for the formation of layered zeolite crystals. Growth modifying agents are molecules, which selectively adsorb on certain crystal faces and change their growth rate. The zeolite materials obtained in this way might exhibit intercrystalline mesoporosity, if the layered crystals are assembled in the form of aggregates to – as a result of this aggregation process – span meso- and/or macropores between the layers.

### 3.4 Demetalation

Demetalation belongs to the widely used and most researched method to introduce mesopores or macropores into an already existing zeolite crystal. The principle behind this method is
based on the selective removal or extraction of framework atoms \([\text{Al, Si, B or Ti}]\) from crystalline zeolitic materials through acid or alkali treatment, steaming, radiation or a combination of them.\(^7\)

Acid treatment at temperatures between 50 and 100 °C results in dealumination.\(^67\) This treatment creates voids, which consequently serve as intracrystalline meso- or macropores. Alternatively, framework aluminium atoms can also be removed by steaming the zeolite at temperatures between 300 and 600 °C. The removal of framework aluminium does not only create additional intracrystalline porosity, but also alters the Si/Al ratio and hence the acidic properties of a given zeolite. This feature has been utilised to tune (reduce) the catalytic activity of different zeolitic materials, the most prominent being zeolite Y.\(^88\)

Dealumination by steaming may also result in extra-framework aluminium. These extra-framework species potentially form Lewis acid sites, which can be advantageous in some catalytic reactions. However, in other catalytic reactions, Lewis acid sites may promote coke formation and thus speed-up the catalyst deactivation.\(^89\) In addition, the dealumination process is limited to aluminium-rich zeolites, forms mesopores in a random manner and is very difficult to control. Furthermore, the mesopores created by dealumination are poorly interconnected. Besides, this method may result in a partial blockage of both meso- and micropores due to the deposition of amorphous material in these pores.

Apart from dealumination, desilication is another prominent and efficient post-synthetic demetallation approach for creating hierarchy in zeolite crystals. It involves the selective extraction of silicon from the zeolite framework via treatment with diluted alkaline solutions at temperatures between 50 and 80 °C.\(^90,91\) This method can be used to introduce intracrystalline mesopores with high degree of interconnectivity in zeolite crystals of different framework types.\(^36,92–96\) In contrast to dealumination, desilication does not significantly affect the acidity and the crystalline structure of zeolites.\(^97\) As also depicted schematically in Fig. 12, the desilication treatment is most effective for zeolites with Si/Al molar ratios between approx. 20 and 50.\(^35,98,99\) However, it has recently been shown that the partial coverage of the outer crystal surface with organic molecules allows the controlled desilication even of aluminium-free zeolites,\(^98\) while a combined acid-base treatment allows the desilication even of Al-rich zeolites.\(^100,101\)

### 3.5 Delamination and assembly

The search for zeolitic materials with better catalytic and adsorptive properties has led to the development of 2D zeolites or layered zeolites (MCM-22(P), PreFER, MCM-56, RUB-15, PreAFO, MFI, etc.).\(^102,103\) These materials combine the classical properties of microporous zeolites with the typical structure related, geometrical anisotropic properties of 2D materials, as it is known from clays or clay-like (or more general: layered) materials. Thus, it is possible to develop novel catalysts and adsorbents with very open structures and high external surface areas, which may allow many processes to proceed directly on the surface of the zeolite and not deep within the 3D crystals. However, many precursors of the existing layered zeolites condense upon the removal of the organic template and thus form 3D zeolite frameworks.\(^77\) This limitation can be easily overcome by post-modifying the structure or composition of the 2D zeolite precursor. These post-modifications have been achieved by utilizing the well-known post-synthetic procedures available to modify layered silicate materials, like swelling, intercalation, delamination and pillaring as illustrated in Fig. 13.

During delamination, the layered zeolite precursor is treated in alkaline solutions to expand the interlayer distance by using surfactants. The expanded layers are then completely separated by sonication to form a collection of poorly ordered zeolite layers, which are not connected with each other. Finally, the delaminated material is calcined to remove the surfactants. The material obtained in this way is usually characterised by a high degree of intercrystalline (interlamellar) mesoporosity.\(^104\) Different hierarchical zeolites like ITQ-2,\(^105\) ITQ-6,\(^106\) and NSI-ITQ-18\(^107\) have been successfully delaminated from their precursors, MCM-22(P) or MCM-56, FER, NSI, respectively. Out of these, the delamination of MCM-22(P) belongs to the most widely studied system and the improved catalytic performance of its delaminated 2D zeolite (ITQ-2) has been successfully demonstrated in different reactions.\(^104,105\) One of the biggest challenges of delamination is the high surfactant content and alkalinity used during swelling as such alkaline conditions can result in partial dissolution of the zeolite framework.

Alternatively, a pillaring step can be used to create or to preserve an organically pre-set porosity in layered zeolitic materials. Classically, pillaring is achieved by intercalating surfactant molecules in the interlamellar space to expand the interlamellar distance.\(^102\) When the interlamellar space of a layered precursor is large enough, this step is not necessary.\(^108\) The actual pillaring step starts by impregnating the surfactant chains in the interlamellar space with a soluble material (e.g. TEOS).
Finally, the impregnated material is hydrolysed in an aqueous environment and after subsequent calcination, stable pillars are obtained. Thus, a layered material is obtained with permanently expanded interlayer space serving as intercrystalline (interlamellar) mesopores.102,108 Pillaring has been successfully applied to prepare hierarchical MCM-36 from a purely microporous MCM-22(P).104 Recently, layered MFI precursor (multilamellar MFI) has been successfully pillared without any swelling step to form a well-ordered hierarchically porous MFI-type zeolite and thereby minimising the collapse of multilamellar stacking.108

Although delamination and pillaring have proven to be useful tools to prepare hierarchically porous zeolites, their industrial exploitation is still challenging due to the high costs of the surfactants needed to expand the interlayer space.

3.6 Comparison of the different strategies

From the discussion of the different routes to prepare zeolites with hierarchical porosity, it is evident that one needs to consider the advantages and disadvantages of each route with respect to the final material properties as well as preparative challenges before selecting a certain strategy to prepare hierarchically porous zeolites. Different aspects of the most important routes to achieve this objective are compared in Table 2.

4 Preparation routes to hierarchically porous zeolite containing composites

In contrast to all-zeolite materials, zeolitic composite materials contain at least one additional material next to the zeolite. In order to build a hierarchical pore system within the zeolite containing composite material, the composite partner has to be either porous itself (e.g. open-cell foams, periodic open cellular structures (POCS)) or needs to help the generation of intercrystalline porosity between the zeolite crystals (e.g. a binder material), as it was already defined in Section 2. In addition, the

Table 2 Strengths and limitations of different preparative routes towards hierarchically all-zeolite materials

<table>
<thead>
<tr>
<th>Approach</th>
<th>Route</th>
<th>Advantages</th>
<th>Limitations</th>
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</thead>
<tbody>
<tr>
<td>Bottom-up</td>
<td>Hard templating</td>
<td>• High zeolitic character</td>
<td>• Pore connectivity can be challenging</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Variation of Si/Al possible</td>
<td>• High production costs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Applicable to different zeolites</td>
<td>• Tuning of the additional porosity is still a challenge</td>
</tr>
<tr>
<td></td>
<td>Soft templating</td>
<td>• Tunable mesoporosity</td>
<td>• High production costs</td>
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<tr>
<td></td>
<td></td>
<td>• Variation of Si/Al possible</td>
<td>• Low to medium zeolitic character</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Applicable to different zeolites</td>
<td>• Most templates are not available commercially</td>
</tr>
<tr>
<td></td>
<td>Non templating</td>
<td>• Eco-friendly</td>
<td>• Tuning of the additional porosity is still a challenge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Cost-effective</td>
<td>• Applicable to few zeolites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Medium zeolitic character</td>
<td></td>
</tr>
<tr>
<td>Top-down</td>
<td>Demetalation</td>
<td>• High zeolitic character</td>
<td>• Low pore interconnectivity (dealumination)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Applicable to different zeolites</td>
<td>• Dealumination is applicable to Al-rich zeolites only</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Applicable to wide Si/Al ratios</td>
<td>• Expensive when organic templates/ acids are involved</td>
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<tr>
<td></td>
<td></td>
<td>• Cost-effective</td>
<td>• May alter the Si/Al ratio of the parent zeolite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High pore connectivity possible with desilication</td>
<td>• Tuning of the additional porosity is still a challenge</td>
</tr>
<tr>
<td></td>
<td>Delamination and</td>
<td>• High degree of additional porosity</td>
<td>• High production costs</td>
</tr>
<tr>
<td></td>
<td>assembly</td>
<td>• Applicable to many layered zeolites</td>
<td>• Low zeolitic character</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Partial dissolution of silica is possible</td>
</tr>
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<td></td>
<td></td>
<td>• Scale-up is still challenging</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Delamination is easily applicable to certain Si/Al ratio</td>
</tr>
</tbody>
</table>
preparation of zeolitic composite materials can lead to geometrically well-defined shapes, which has various application-oriented advantages as will be discussed in the following sections.

Shaped zeolitic bodies are the traditional type of zeolitic composite materials, which on the one hand contain a hierarchical pore system due to the interconnected intercrystalline porosity within each shaped particle/body and on the other hand allow the generation of interparticle macropores on the packed bed level, e.g. when they are used as reactor fillings. Such zeolitic composite bodies are usually prepared by aggregating a pasty mixture of a desired zeolite (mostly in the powder form) and a binder material using compacting and shaping techniques to obtain pellets, beads, cylinders etc. as depicted in Fig. 14 (left). The resulting zeolitic shaped particles can be considered as granular systems and are widely used as unconsolidated packings in reactors/columns for different industrial applications. Unconsolidated packings are usually characterised by an irregular arrangement of individual particles (i.e. not interconnected), see also Fig. 15.

In contrast to the (from the reactor-filling point of view) unconsolidated packing of granular zeolitic composites, consolidated zeolite composites consist of a solid macroporous support (e.g. honeycomb or solid open-cell foam, mostly referred to as structured monolith) with a functional surface in the form of a zeolitic coating (Fig. 14, right). Thus, such consolidated zeolite containing systems (also referred to as monolithic zeolite composites) combine the different porosity levels (macro–micro or even macro–meso–micro) of the composite partners on a large length-scale.

When discussing such zeolite composite systems in the context of chemical reaction engineering (e.g. for the usage as reactor internals), the advantages of consolidated zeolite composites in comparison to their unconsolidated counterpart (packing of zeolite shapes) are manifold. Just to name a few, the consolidated composites allow tailoring the size and shape of the macropore system independently from the zeolite material already during the preparation of the consolidated support material. Furthermore, consolidated support materials are characterised by a better heat transfer performance due to the continuous solid phase when used as a single reactor packing combined with improved mass transfer characteristics (decrease in pressure drop) as well as higher mechanical stability. For these reasons, in Section 4.2 special focus shall be paid on the macroporous consolidated support materials themselves as well as on the methods for their functionalisation (“zeolitisation”) which lead to hierarchical porosity for a fast transport to and from the reactive/adsorptive sites in the zeolitic micropores.

4.1 Granular zeolite composites via compaction

Binder containing granular zeolitic composites. Starting from a pasty mixture of pre-synthesised zeolites and usually a binder fraction, zeolite containing shaped bodies can be

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Fig. 14 Schematic comparison of compaction and coating approaches: preparation routes for hierarchical zeolitic composites either based on zeolite shaping methods (left) or on ex situ and in situ zeolite coating on consolidated supports (right, exemplarily shown for open-cell solid foam supports). The characteristics of the resulting products are shown schematically (middle, black: binder, grey: support, zeolite: white) and by photographs and SEM images (bottom).
prepared by aggregation via compacting routes. These routes consist at least of a shaping step and a subsequent thermal treatment, which induces the solidification of the shaped composite material, thus enhancing the mechanical strength of the resulting shaped bodies.

Consequently, shaped zeolite containing composite bodies are obtained which contain a fixed additional porosity between the individual zeolite crystals throughout the shaped body. Depending on the compaction method applied, it is possible to produce the granular zeolitic composites in a huge variety of different shapes and dimensions, as it was reviewed recently by Akthar et al. 38

Inorganic (silica, alumina, silica–alumina mixtures and clays) as well as organic (cellulose) binders are commonly used to shape such zeolite powders in the form of beads, pellets or extrudates via spray drying, granulation, tableting or extrusion. 38,109,110 In general, both organic and inorganic binders themselves or also in combination have proven to be effective for improving the mechanical strength, chemical and attrition resistances of the shaped material and for an efficient handling in industrial adsorption, separation and catalytic processes.

To increase and tailor the porosity within the shaped bodies, hard templates can also be used during the shaping process: Akthar et al. 110 prepared zeolite 13X and silicalite-1 shapes (cylindrical monoliths with 10 mm diameter and 6–8 mm height) with large macro channels and high tensile strengths (up to 1 MPa) from a mixture of zeolite powders with glassy carbon spheres and fibres acting as hard templates. Here, kaolin was used as a binder.

Binder-free granular zeolite shapes by binder exclusion or removal. In general, binders reduce the specific efficiency of the zeolitic system indirectly by diluting the active zeolite phase (reduced density of active sites) and/or directly by blocking the pores and/or by hindering the access to the active sites and by limiting heat and mass transfer. However, the mechanical stability of the final zeolitic shaped body is based on the presence of the binder material 38 and, thus, its utilisation is in most cases inevitable.

Nevertheless, attempts have been made to avoid a binder in the final zeolite shape and still to guarantee a sufficient mechanical stability by sintering the zeolite crystals. Here, special attention has to be paid on the maximum temperature and duration of the sintering process in order to reduce amorphisation and thereby maintaining the zeolitic (micro-porous) character of the material. In doing so, binder-free zeolite shapes have been prepared by slip casting of an alkaline suspension of zeolite 13X and polyethylene glycol (as an organic intermediate binder) followed by thermal treatment to remove the organic binder and to actually consolidate (via sintering) the shaped bodies. 111 It was shown, that the optimum stability and crystallinity can be achieved for a consolidation temperature of 800 °C without any isothermal holding time. Besides the two step process of shaping (with intermediate binder) plus thermal treatment, recently, the so-called ‘spark-plasma sintering’ (also referred to as ‘pulsed current processing’, PCP) was used for the preparation of binder-free zeolitic compacts. Here, the pressing and the consolidation via sintering is performed in one single step with the sintering temperature being generated by pulsed current through the zeolite shape. This allows for extremely high heating and cooling rates (several 100 K min⁻¹) and, thus, shorter period of high temperature and consequently less severe damages of the crystalline structure. In addition, because of the shaping and consolidation process are performed in parallel, no (intermediate) binder is needed. Bergström and co-workers used this technique to prepare MFI-type zeolite (silicalite-1 and ZSM-5) cylinders with a diameter of 12 mm and reasonable tensile strength (up to 2.4 MPa) 112 as well as silicalite-1 discs with 2.5 cm in diameter. 113

Binder-free granular zeolite shapes via binder transformation. To overcome the disadvantages accompanied with inert binder materials as well as weak mechanical strength in the absence of binder, the concept of binder transformation...
has been developed. This concept aims at the preparation of binder-free zeolite shapes which eventually still retain the mechanical strength primarily assured by the presence of the binder. In particular, Schumann et al.\textsuperscript{114-116} have recently reported the preparation of mechanically stable binder-free shaped zeolites (13X and LTA) by additional hydrothermal treatment of binder-containing zeolite beads under alkaline conditions, thereby transforming the binder components into zeolite material. Such hierarchical binder-free zeolite 13X beads exhibited higher adsorption capacities than the conventional binder-containing shaped zeolite 13X, as it was shown for CO\textsubscript{2} and H\textsubscript{2}O adsorption. In addition, pulsed field gradient (PFG) NMR diffusometry measurements revealed that binder-free shaped zeolites (13X and LTA) showed improved mass transfer for H\textsubscript{2}O molecules due to their hierarchical nature compared to conventional solely microporous adsorbents.\textsuperscript{117} Such binder-free zeolite beads are already commercially available, e.g. from the German company Chemiwerk Bad Köstritz (CWK).

Another transformation approach aiming at the preparation of all-zeolite shapes started from extrudates, which were prepared from a mixture of zeolite beta (BEA), sodium aluminate, fumed silica and silica sol.\textsuperscript{118} Sodium aluminate, fumed silica and silica sol acted as both, temporary binder and source of zeolite framework constituents. After extrusion, solidification was performed by a subsequent thermal treatment. For the hydrothermal transformation of the binder fraction as well as for the recrystallisation of the zeolite beta within the shaped bodies, tetrapropylammonium bromide (TPABr) and sodium hydroxide were used as the template and source of alkalinity, respectively. As a result, pure ZSM-5 shaped bodies with intercrystalline porosity were obtained. This journal is © The Royal Society of Chemistry 2016

\section{Zeolites on consolidated (structured) supports via coating}

Consolidated supports are monolithic materials that can be used as single reactor internals. They exhibit a continuous solid phase throughout the entire cross section of the reactor (only the coupling to the reactor wall might induce a discontinuity\textsuperscript{120}) as well as throughout the entire length of the monolithic material, which distinguishes them from conventional unconsolidated reactor fillings like fixed beds of granular zeolitic shapes (Fig. 15).

Supporting zeolites on consolidated supports introduces a number of beneficial properties to the resulting composite material, such as improved (and tailored) heat- and mass transfer characteristics. Nowadays, such consolidated composite systems are of huge interest and shall therefore be discussed in terms of their support characteristics in general and concerning the different coating routes (here: “surface zeolitisation”).

**Consolidated support systems.** As mentioned above, the preparation of consolidated zeolite composites needs a solid macroporous support (composite partner for the zeolite) which can be a honeycomb monolith, a solid open-cell foam monolith or even a periodic open cellular structure (POCS). In contrast to (from the reactor-filling point of view) unconsolidated packings of hierarchical zeolitic composite materials, such as granular zeolites bodies, the consolidated (or ‘structured’) supports feature remarkable and also tailorable characteristics which they also bring into the final composite material. These characteristics include geometry related (e.g. high surface area, high porosity and low resulting pressure drop) but also material related (e.g. high thermal conductivity) properties. Hence, in consolidated systems, the aforementioned properties can be tuned independently by choosing an appropriate geometry and material for the structured support, respectively. Consequently, this can provide a thorough reaction-engineering control on the characteristics of the composite systems used as consolidated reactor internals.\textsuperscript{121-123}

Fig. 15c-e schematically shows different consolidated supports (Fig. 15) in comparison to a conventional randomly (irregularly) packed bed of shaped bodies (Fig. 15a), a regularly packed bed of shaped bodies (theoretical, e.g. face-centered cubic FCC; Fig. 15b) and two planar reactor concepts for zeolitic catalysts (Fig. 15f-g).

In Table 3, some important properties of the two most prominent examples of reactor fillings for catalytic systems, namely the packed bed of shaped bodies as well as the honeycomb support, are compared with solid open-cell foam as one representative of highly porous consolidated catalyst support materials. Monolithic honeycombs offer clear advantages over packed bed systems in terms of pressure drop, which is an important parameter for reactor design as it plays a vital economic role in the applications that involve high space velocities.

Honeycombs were developed and introduced in the 70s and today they have become standard catalyst supports in most environmental catalytic applications e.g., in the treatment of exhaust gas from both stationary and mobile sources.\textsuperscript{125,126} Though honeycombs have much lower pressure drop as compared to packed bed systems, they lack other important features, e.g. radial mass flow, radial heat exchange and tortuosity, which are present in packed bed configurations to a fair extent.\textsuperscript{124} Solid open-cell foams (also referred to as ‘sponges’) on the other hand tend to combine the advantages of packed beds and honeycombs, as they offer low pressure drop combined with radial heat and mass transfer. Therefore, among different consolidated catalyst supports, solid open-cell foams are gaining more and more importance.\textsuperscript{122,124}

While replication techniques lead to consolidated monolithic structures (foams) with rather irregular pore geometry and broad distribution of pore size and solid material, additive manufacturing techniques nowadays offer the possibility to tailor the 3D structure of such monoliths. In this way, highly
periodic open-cellular structures (POCS) can be precisely designed to the requirements of the target application.\textsuperscript{13,127}

The past decade has witnessed various strategies for the coating of such consolidated support systems to form a zeolitic composite material with high transport porosity.\textsuperscript{128,129} As already mentioned, the support material itself carries important physical properties which should preferably be retained in the final composite material. For this reason, the zeolite crystals are usually just anchored on the surface of the support material without destroying its consolidated nature. Therefore, the preparation of such composite materials can be termed “surface zeolitisation”. The common surface zeolitisation strategies will be reviewed in the following section.

Coating of consolidated supports. The functionalisation of the consolidated support surface with zeolitic material, i.e. ‘surface zeolitisation’, allows the development of hierarchically organised materials with two (micro–macro) or three (micro–meso–macro) levels of porosity. These hierarchically porous zeolitic composites can be prepared either by direct hydrothermal synthesis (so-called ‘in situ coating’) of zeolite on the support surface or by depositing a layer of pre-synthesised zeolite crystals (‘ex situ coating’) with the help of a binder material, e.g. by dip-coating) on the support (Fig. 16, left).\textsuperscript{67,122,130} Some examples of consolidated zeolitic composites from the open literature, prepared by ex situ coating techniques are summarised in Table 4.

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The in situ coating technique can be further subdivided into in situ coating on inert supports and in situ coating on reactive supports. in situ coating on inert supports relies on the crystallisation of zeolite right on the outer surface of the support without changing the support itself. In contrast, in situ coating on reactive supports consumes a part of the support material (usually a part of the SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3} components, see also Section 5.1) and incorporates it into the zeolite framework, which leads to a strong intergrowth between the zeolite layer and the remaining support material (see Fig. 14, right and Fig. 16, right). Some examples of zeolitic composites from the open literature, prepared by in situ coating techniques on both, reactive and inert supports are summarised in Table 5.

5 Special systems and methods

5.1 Transformation of silicious materials

The (partial) transformation of mesoporous preforms such as ordered mesoporous silica (OMS) materials and porous glass shapes (spheres, plates, etc.) is another way to prepare a zeolitic material with hierarchical porosity. As a prerequisite, the preform must consist of at least one component which might be able to form building blocks for the zeolite formation (e.g. SiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}). If the starting material is only partially transformed into zeolite, a zeolite-containing composite material is obtained, whereas a complete transformation yields an all-zeolite material. The transformation products exhibit a hierarchical pore system if the transformation is either pseudomorphic (i.e. the pore walls of the starting material are transformed into zeolite while retaining the initial pore system of the starting material) or if at least intercrystalline porosity exists within the transformed material, which has to be still directly accessible from the outside medium (compare Fig. 5, type II hierarchy).

Transformation of (meso)porous silica. Seed-assisted hydrothermal transformation of mesoporous silica spheres has been successfully applied to prepare hierarchical MFI-type zeolite material (silicalite-1) using TPAOH as the structure directing agent.\textsuperscript{147} Similarly, Lei et al.\textsuperscript{148} have transformed bimodal porous silica monoliths into hierarchical zeolite beta monoliths with the help of deposited zeolite seeds, but the transformation was conducted in a vapour atmosphere and not in solution. In addition, Tong et al. reported a ‘pore-protected’ synthesis of monolithic zeolite beta with interconnected hierarchical porosity via the hydrothermal transformation of a composite (carbon/silica) monolith.\textsuperscript{149} In such case, the carbon acts as a solid template which preserves the pore channels of the silica monolith and protects the monolith as a whole from collapsing during the conversion of the amorphous walls of the silica monolith into zeolite beta under hydrothermal conditions.

Transformation of porous glass. A very promising method for the manufacturing of hierarchical zeolitic material with a
very high degree of freedom concerning the geometry and shape of the granules, plates or larger monoliths as well as the type of the zeolite material is the (partial) transformation of porous glass. Compared to shaped zeolitic bodies prepared by a compacting approach, porous glass is a very dense and stable amorphous material which can be produced in nearly every geometric form using standard glass-shaping techniques. Thus, porous glasses have been widely used as substrate for the fabrication of numerous hierarchical porous glass/zeolite composites, e.g. in the form of membranes obtained by hydrothermal,150–154 and vapour-phase transport 155–158 methods. In previous contributions, we have shown the preparation of ZSM-5 granules (Fig. 17) with hierarchical porosity by hydrothermal transformation of porous glass granules using propylamine as the template.159–161 This approach has the advantages of combining the fabrication of the hierarchical system with a high loading of zeolite (84%) and a reasonable mechanical strength (10 N mm$^{-2}$). Apart from porous glass granules, macroporous glass beads have been transformed into zeolite ZSM-5 and zeolite beta beads under hydrothermal conditions using dipropylamine and tetraethylammonium hydroxide (TEAOH), respectively. Furthermore, the transformation of the top layer of porous glass discs into zeolites yields glass-supported zeolitic membranes,158,165 which exhibit a type I hierarchy according to the hierarchy classification given in Fig. 5.

5.2 Zeolitic monoliths via freeze casting

Consolidated (‘monolithic’), multimodal porous systems with hierarchical porosity can be obtained from a large variety of processes as discussed above and especially from combinations

Table 4  Zeolite coating on consolidated supports by ex situ coating (adapted from ref. 67, Copyright 2011, Wiley-VCH Verlag GmbH Co. KGaA)

<table>
<thead>
<tr>
<th>Coating technique</th>
<th>Zeolite type</th>
<th>Support material</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash coating</td>
<td>MFI</td>
<td>Alumina-mullite foam</td>
<td>Patcas$^{131}$</td>
</tr>
<tr>
<td></td>
<td>MFI</td>
<td>Alumina-mullite foam</td>
<td>Buciuman and Kraushaar-Czarnetzki$^{132}$</td>
</tr>
<tr>
<td></td>
<td>MOR, MFI, BEA, FAU</td>
<td>Cordierite monolith</td>
<td>Mitra et al.$^{133}$</td>
</tr>
<tr>
<td></td>
<td>Cu-MFI</td>
<td>Cordierite monolith</td>
<td>Lisi et al.$^{134}$</td>
</tr>
<tr>
<td>Dip coating</td>
<td>BEA</td>
<td>Silica and cordierite monoliths</td>
<td>Beers et al.$^{135}$</td>
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<tr>
<td></td>
<td>MFI</td>
<td>SSiC foam</td>
<td>Inayat$^{122}$</td>
</tr>
<tr>
<td>Slurry coating</td>
<td>Fe-MFI</td>
<td>Stainless-steel plate</td>
<td>Hiemer et al.$^{136}$</td>
</tr>
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</table>

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<table>
<thead>
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<th>Support type</th>
<th>Zeolite type</th>
<th>Support material</th>
<th>Ref.</th>
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<td>Reactive support</td>
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<td>CHA/AEI/AFI</td>
<td>Al foil</td>
<td>Bauer et al.$^{137}$</td>
</tr>
<tr>
<td></td>
<td>MFI</td>
<td>SiSiC ceramic</td>
<td>Zampieri$^{139}$</td>
</tr>
<tr>
<td></td>
<td>FAU</td>
<td>Al/ceramic foam</td>
<td>Barg et al.$^{140}$</td>
</tr>
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<td></td>
<td>BEA</td>
<td>Mesoporous TUD-1</td>
<td>Waller et al.$^{141}$</td>
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<td></td>
<td>MFI (ZSM-5)</td>
<td>Silica</td>
<td>Landau$^{142}$</td>
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<td></td>
<td>MFI (ZSM-5)</td>
<td>Porous glass monolith</td>
<td>Louis et al.$^{143}$</td>
</tr>
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<td>Inert support</td>
<td>MFI</td>
<td>SiC/Si–O–C foam</td>
<td>Zampieri et al.$^{144}$</td>
</tr>
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<td></td>
<td>MFI/BEA</td>
<td>g-Al$_2$O$_3$</td>
<td>Puil et al.$^{145}$</td>
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<td></td>
<td>MFI</td>
<td>SiC foam</td>
<td>Ivanova et al.$^{146}$</td>
</tr>
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Fig. 17  Transformation of porous glass granules to ZSM-5 granules: SEM images of (a) starting material and (b) final ZSM-5 granules after 72 h of crystallisation time (left: overview, scale-bar 300 µm. Right: surface, scale-bar: 2 µm). (c) Time-dependency of the transformation process shown by X-ray powder diffraction patterns taken after different crystallisation times (0 h, 24 h, 36 h, 49 h 55 h, 61 h, 72 h). Adapted from ref. 161, Copyright 2004, with permission from Elsevier.
The freeze casting technique is a versatile route to create consolidated (monolithic) porous materials by the controlled freezing of the dispersant of a suspension (slurry) which contains the accordant constituent(s) for the targeted porous material. During cooling, the dispersant freezes and thus segregates from the particle-rich domains and acts as a macroporogen, which is finally removed by sublimation. Next to aqueous suspensions, freeze casting based on organic dispersants, such as tert-butyl-alcohol, or 1,4-dioxane has been reported in the literature. The pores generated by the freeze casting technique are usually in the range of 1 μm up to several hundreds of micrometres. In general, all systems have in common, that the freezing mechanism starts at the very interface between the suspension and the cooling plate and spreads unidirectional along the temperature profile imposed by the external cooling (see also Fig. 18a). The pore morphology strongly depends upon the dispersant and its crystallisation behaviour during freezing at the given temperature. Exemplarily, for water as initial dispersant, lamellar pores have been found, while for camphene reported channels of rather hexagonal cross sectional area.

Technically, the freezing of the suspension is performed in a mould of at least one metallic, externally cooled part. The cooling is realised by e.g. liquid nitrogen or an appropriate coolant set to a temperature suitable for the dispersant used (e.g. ethanol at −100 °C for freezing of tert-butyl alcohol (TBA) or +20 °C water bath for the freezing of camphene). It is worth mentioning, that during freezing, the velocity of the freezing front decreases with increasing distance to the cooling part for the reason of which, some pore characteristics (e.g. interconnectivity and size) in the final material depend on its initial position within the mould. Though, the freedom of design is to some extent limited by the necessity of using a mould (to carry the liquid) with the accompanying requirement of removing the mould after freezing. In addition, for a controlled freezing, the mould – and in particular the cooling part of it – has to be designed in accordance with the desired temperature profile. Therefore, such monolithic materials mostly are freeze casted in the shape of cylinders and tubes. Once frozen, the ice-template has to be removed by sublimation which usually is performed via freeze drying in vacuum. Subsequently, the obtained ‘green body’ has to be consolidated via a final solidification step (e.g. via sintering). For materials which are not able to solidify themselves, binders are usually added to the initial suspension, which are then responsible for the durable solidification (see also Section 4.1).

Due to the basic underlying principles, the freeze casting technique can also be assigned to the hard templating approach. In contrast to hard templating methods discussed in Section 3.1, here, the hard template (frozen dispersant) is formed in situ via a temperature induced phase separation, which is the same underlying preparation principle as in the case of porous glass. Nevertheless, compared to the other hard templating methods, the freeze casting technique offers not only the possibility to tailor the direction of the pores, the pore size distribution and its gradient along the freezing direction, but also e.g. the porosity of the resulting solid by adjusting the process parameters such as temporal and spatial temperature profile and the solid concentration.

The applicability of this method was shown for the production of porous monoliths of a large variety of inorganic material such as alumina, silica gel, mullite, YSZ and SiN.
as well as of organic materials, such as poly(ε-lactic acid)\textsuperscript{171} and PEG-methacrylate-based polymers.\textsuperscript{178}

When freeze casting a suspension of a microporous material such as zeolites (usually together with a binder material), the resulting consolidated material comprises the inherent microporosity of the zeolite material next to the intercrystalline porosity within the consolidated solid and the macroporosity originating from the templating effect of the frozen dispersant. Thus, a zeolite material prepared by freeze casting, intrinsically exhibits a type II hierarchical porosity (see Fig. 5) while closed cavities are unlikely to be present.

For the preparation of cylindrical zeolite A (LTA)\textsuperscript{175} and zeolite 13X (FAU) monoliths,\textsuperscript{166} Ojuva \textit{et al.} used bentonite and polyethylene glycol (PEG) as inorganic binder and intermittent binder, respectively (see also Fig. 18b). In order to deagglomerate the zeolite crystals, an aqueous slurry containing the binders and the powdery zeolite was ball-milled for several hours, degassed and freeze casted using liquid nitrogen as coolant. The removal of the ‘template’ ice via sublimation was performed in a vacuum freeze dryer for two days before the final thermal treatment provoked both, removal of the intermittent binder as well as the actual consolidation by the help of the inorganic binder bentonite. This led to zeolitic monoliths with reasonable mechanical strength and excellent mass-transfer characteristics, which was shown for the 13X monolith by an increase in CO\textsubscript{2} adsorption rate as compared to the conventional packed bed adsorber configuration (pellets of the same composition).

As already mentioned in Section 4.1, the use of a binder material for the consolidation of a zeolitic material is always accompanied by a decrease in activity due to the dilution effect and potential blockage of pores and active sites of the zeolite. These circumstances motivated Mori and co-workers to develop a preparation route for all-zeolite monoliths. In their contribution,\textsuperscript{177} the authors showed the preparation of silicalite-1 all-zeolite monoliths via a combination of the freeze casting technique and a transformation method (see Section 5.1). Here, first an amorphous silica gel monolith was prepared by freeze casting which then served as a substrate for the transformation process. The transformation was conducted under water vapour atmosphere (so-called steam-assisted crystallisation) using TPAOH as a structure-directing agent. Eventually, a purely crystalline all-zeolite (MFI-type) monolith was obtained with type-I hierarchical porosity.

### 5.3 Core–shell composites

In recent years, zeolite-based core–shell systems have gained enormous attention. This is due to the fact, that the controlled combination of a microporous zeolite material and a mesoporous material in a core–shell like manner gives rise to outstanding catalytic and sorption properties in comparison to the pristine core and shell materials or a physical mixture thereof. In particular, by enwrapping the actual zeolite material in a mesoporous shell, the catalyst performance in terms of \textit{e.g.} lifetime,\textsuperscript{179} activity\textsuperscript{180} and selectivity\textsuperscript{181} was shown to be higher in comparison to the reference material due to the beneficial interplay of the properties of core and shell material in terms of catalytic activity (\textit{e.g.} pre-cracking of bulky molecules by the active sites in the mesoporous shell),\textsuperscript{180} surface acidity and sorption behaviour.\textsuperscript{191} Zeolites, such as MFI (ZSM-5\textsuperscript{181,182} and silicalite-1\textsuperscript{183}), LTA\textsuperscript{183} TS-1,\textsuperscript{184} Ti-MWW\textsuperscript{179} and FAU (zeolite Y)\textsuperscript{185,186} have been successfully encapsulated in mesoporous silica shells (\textit{e.g.} MCM-41, MCM-48 and SBA-15) yielding core–shell catalysts with hierarchical porosity.

Moreover, the mesoporous silica shell can also act as a support for an additional catalytically active component. For example, a mesoporous silica shell enwrapping MFI-type zeolite TS-1 was used as a support for Au nanoparticles. This bifunctional catalyst showed higher propylene oxide selectivity and longer lifetime in the selective epoxidation of propylene as compared to Au supported by pristine TS-1 zeolite which was attributed to the confining effect of the mesopores preventing the gold nanoparticles from aggregating.\textsuperscript{187}

According to the definition in Fig. 5, such systems containing a mesoporous shell enwrapping a microporous core, together with their ‘planar counterparts’ namely porous membranes, are typical examples for type I hierarchical porosity. The respective arrangement of the two porous composite partners is schematically illustrated in Fig. 19. In addition to the micro-/mesoporous core–shell materials mentioned above, all-zeolite core–shell systems have also been reported, where usually a single-crystal zeolite core is encapsulated by a polycrystalline shell. In such systems, the ‘core’ is the actual active material carrying the catalytic activity or gas sorption capacity, while the ‘shell’ provides an additional function. Thus, the all-zeolite core–shell arrangement likewise increases the performance of the composite system as compared to the bare core zeolite material in gas separation (\textit{e.g.} separation of hexane isomers by beta/ silicalite-1\textsuperscript{188}) and especially in catalysis: the zeolite shell can be used to fine-tune the catalytic activity of the composite core–shell material, \textit{e.g.} by covering and, thus, passivating the active sites of the bare core-zeolites’ outer surface. This passivation increases the share of active sites within the micropores and therefore increases the selectivity of a certain shape-selective reaction product.\textsuperscript{189} Such an effect for instance was found for a silicalite-1/ZSM-5 core–shell material catalysing the selective synthesis of \textit{p}-xylene from toluene.\textsuperscript{190,191} Various combinations of zeolite structures were reported to form such zeolite-core/ zeolite-shell materials, such as beta/ZSM-5,\textsuperscript{192,193} beta/Y,\textsuperscript{194} ZSM-5/silicalite-1,\textsuperscript{191,193} X/LTA,\textsuperscript{195} SOD/LTA,\textsuperscript{193} beta/LTA\textsuperscript{193}

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Fig. 19 Schematic illustrations of two examples for zeolite containing composite materials with a hierarchical porosity with a layered like arrangement (porosity type I according to Fig. 5).
6 Summary and conclusions

Zeolites are industrially important materials in various adsorption, separation and catalytic processes. However, conventional zeolite materials face some limitations, e.g. reduced accessibility of the active sites and diffusion restriction due to the long microporous pathways often resulting in a fast deactivation of zeolite containing catalysts. Thus, hierarchically porous zeolites offer an effective solution to the mass transfer problem associated with conventional zeolites, because they couple, in a single system, the catalytic features of micropores and the improved access and transport properties of the additional porosity (meso- or macropores).

‘Hierarchy’ in general is a property of a large variety of social, technical and in particular of natural systems. Especially transport related hierarchical systems are widely found in the human body and in our natural environment like the hierarchical pattern of our lung and of our blood circuit, the branching of the trees’ roots and their branches or the structure of river deltas.

After a general definition and classification of hierarchical systems, we have summarised herein the recent developments in the field of hierarchically porous zeolites, including various preparation strategies which result in a large number of hierarchically porous all-zeolite materials as well as zeolitic composites.

The preparation strategies for hierarchically porous all-zeolite materials involve different approaches, such as hard and soft templating, non-templating, demetalation and delamination-reassembly. Each synthetic method has its own advantages and disadvantages and has to be selected based on the structural, textural and functional requirements of the different and desired applications. Interestingly, almost always at least two different principles have to be combined in order to prepare an all-zeolite material with at least two different pore systems interconnected in a hierarchical manner. An exception represents – from our viewpoint – the formation of intergrown zeolite sheets where just one single crystallisation process is needed to create an all-zeolite material with at least two hierarchically organised pore systems.

Besides the particulate (or granular) systems, structured zeolitic composites are also considered as hierarchically porous materials with two (micro–macro) or three (micro–meso–macro) levels of porosity. They are generally prepared by surface functionalisation or modification of a pre-prepared structured supports (e.g. monolithic honeycombs and solid open-cellular foams) with zeolitic materials by different ex situ coating methods or by direct in situ hydrothermal synthesis. In the literature, various reactive or inert materials have been used as supports for the in situ preparation of structured zeolite composites. Among the reactive supports, porous glasses are very useful for the preparation of monolithic zeolite composites having hierarchical porosity. Zeolite-based hierarchical core–shell catalysts are another class of hierarchical materials, which contain zeolites as core wrapped by mesoporous materials or zeolites as shell. In recent years, these zeolitic core–shell materials have gained increasing attention due to their dual functions in catalysis (i.e. shell for separation and core with catalytic function).

In general, according to the proposed classification of ‘hierarchical porosity’ given in Fig. 5, all the discussed materials typically exhibit a type II hierarchical pore system, i.e. large pores acting as ‘main roads’ from which the flow can detour into the small channels of the microporous zeolite structure. In contrast, examples for zeolitic materials exhibiting a type I hierarchical porosity are very rare and are mainly limited to membranes (planar system) and core shell materials with zeolitic core, which can be regarded as the round counterpart to zeolitic membranes. Very often it is still difficult to characterise the interconnectivity of the existing – at least two different – pore systems with the different length scales precisely. Few recent papers have shown the progress in this respect in specified methods such as 3D reconstruction from data by STEM-tomography or by face-scanning techniques. spectroscopic techniques such as positron annihilation lifetime spectroscopy or continuously improved conventional methods like physical sorption.

Alternatively, molecular uptake and release studies have been performed to demonstrate the role of pore interconnectivity and the enhancement of mass transport properties of zeolites with hierarchical porosity. Since these methods require a very specific methodology and often costly technical setups, a variety of catalytic reactions are commonly used to study the positive effect of the hierarchical porosity in zeolite systems on their catalytic performance, i.e. increase in conversion and/or selectivity as well as better resistance to coke formation. Based on the very promising results, attempts to commercialise hierarchically porous zeolites have been initiated and are still in progress. Although the results of such catalytic studies indicate the potential for technical applications for hierarchically porous systems, from the scientific point of view their interpretation in terms of mass transport/reaction relationships is still a challenging task and matter of debate.

In spite of the limitation in the field of the characterisation of such materials, this review might have shown that a huge toolbox of synthetic methods as well as shaping techniques is nowadays available which would enable the preparation of hierarchical pore systems on the structured reactors length scale, e.g. optimised via additive manufacturing like 3D printing, as well as on the nanoscale, e.g. via partial incorporation of a continuous zeolite phase into the meso- or macropores of a host material. Comparative studies on the performance of type I and II hierarchical materials in various catalytic as well as other transport-related applications would surely be among the most interesting areas of future research in the field of hierarchically porous materials.

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References
