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Review

Present and future synthesis challenges for zeolites

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ABSTRACT

This work seeks to establish possible synthesis challenges in the zeolitic material field over the coming years. The choice may be subjective but it is worth reflecting on such an important question. The most pressing synthesis challenges in the opinion of the authors described in the following pages are: (1) elucidation of the nucleation and growth mechanism of zeolites; (2) controlling zeolite crystal size and growth habit; (3) preparation of extra-large pore zeolites; (4) synthesis of zeolitized mesoporous materials; (5) synthesis of chiral zeolites; (6) preparation and modification of layered zeolites; (7) and preparation of true molecular sieve membranes.

1. Introduction

Zeolites are crystalline, hydrated aluminosilicates having microporous, regular structures. The zeolite micropores are of molecular size which give them adsorption, catalytic and ion exchange properties of paramount importance in both the chemical industrial field and the study of new applications related to process intensification [1], green chemistry [2], hybrid materials [3], medicine [4], animal food uses [5], optical and electrical based applications [6], reaction [7] and sensing [8] microsystems, and nanotechnology [9]. Furthermore, the concept of zeolite can be extended to the so-called porous-tailored materials. This would include: oxide molecular sieves, porous coordination solids {such as metal organic frameworks (MOFs), or more specifically isoreticular MOFs (IRMORs), MMOFs (microporous MOFs) or porous coordination polymers (PCP) [10,11]}, porous carbons, sol–gel-derived oxides, and porous heteropolyanion salts [12]. In consequence, the term zeolitic materials is frequently used in a very broad sense. This is the reason why even though this perspective is focused mainly on zeolites, mention to zeotypes and ordered mesoporous sieves will be done alone the paper.

Fig. 1 illustrates another point of view for the approach from porous materials to zeolites: starting from porous materials, passing though nanostructured solids (this would include materials such as MCM-41 and MCM-48) [13] and crystalline porous solids such as octahedral–pentahedral–tetrahedal framework silicates (ETS-4, ETS-10, etc.) [14], this classification would converge to the classical zeolites after zeotypes, i.e. SAPOs and AlPOs having zeolite type structures but incorporating other different metals from Si and Al in their composition [15]. Ultimately, the four main characteristics of zeolites are their tetrahedral framework, their cavity system, and the presence of water and charge compensating cations in well defined crystallographical positions. The last two would not be strictly applicable in all cases but depend on the chemical composition (Si/Al ratio) of the zeolite. Besides, from a practical point of view, zeolites are environmental-friendly in technological processes [16].

2. Elucidation of nucleation and growth mechanism of zeolites

Although it is true that zeolites can be prepared by the so-called dry gel method [17], more common is the crystallization of zeolites from solution. The goal can be the synthesis of either nanocrystals or large single crystals. Both situations would require the control of the nucleation [18,19] and growth [20] processes related to the synthesis of a certain zeolitic material. Zeolites together with proteins are two systems crystallizing from solution, the formation mechanism of which has been studied in depth [21]; however, despite the many experimental studies that have been carried out on the synthesis of different zeolites (but most frequently on silicalite-1), understanding is still far from total [22–24].

As Fig. 2 shows, starting from nutrients, hydrolysis, silica oligomerization and condensation reactions catalyzed by hydroxyls lead to entities of different size (and hence stability) and order. Depending on the synthesis conditions (pH, temperature, and presence of structure-directing agents) an amorphous phase can be obtained as either intermediate phase (which would either

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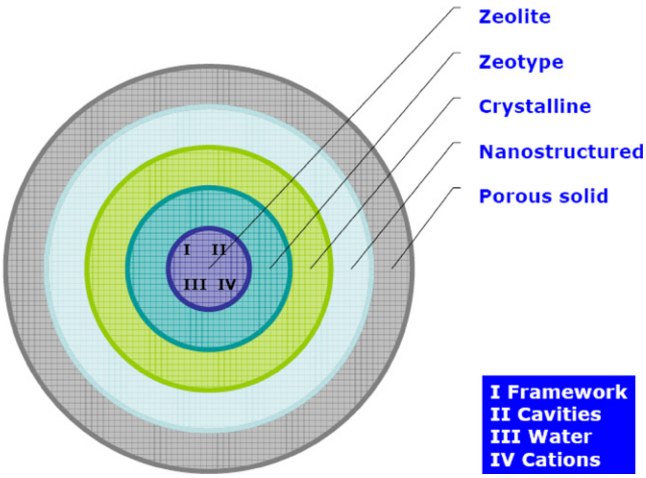

Fig. 1. Porous solids and zeolites.

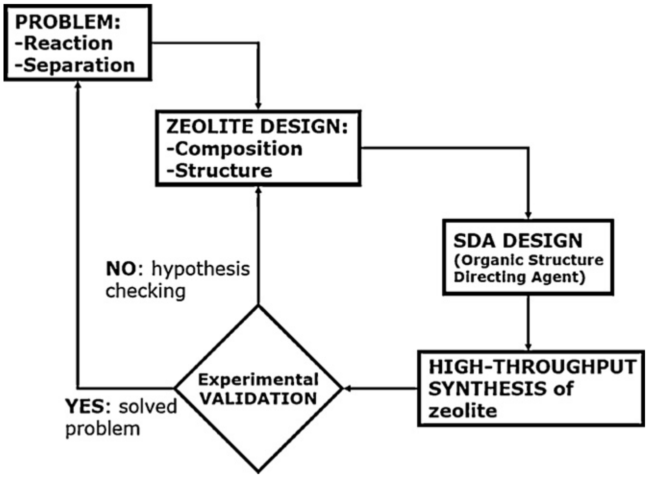

Fig. 3. Optimization of zeolite synthesis and application.

transform into a crystalline phase or dissolve to be incorporated into a more stable product) or final product. In this scheme, the role of hydroxyl ions has been well described in breaking and remaking Si,Al–Si,Al bonds in the corresponding condensation and rearranging reactions leading to pre-nuclei and then to nuclei particles [23]; the concept of hydrophobic hydration has been introduced [25] to explain how some organic molecules can organize silica and how others cannot [26]; and finally subcolloidal or precursor nanoparticles which could be the previously mentioned pre-nuclei have been identified by means of NMR, TEM, DLS and SAXS techniques [27,28]. In fact, some of these particles, called nanoslabs (slab shaped particles), have been claimed to be of defined sizes of 1.3 nm × 4 nm × 4 nm, each one containing a TPA$^+$ cation [27], even if this finding has been the subject of serious controversy [29,30]. Another aspect recently introduced is the concept of molecular recognition to describe the early interaction between silica complexes and template molecules to form clusters from which ordered structures may grow [31].

Returning to Fig. 2, to increase the understanding about how zeolites nucleate and crystallize, since direct evidence for crystal layer growth has been established through, for instance, atomic force microscopy for several zeolites [20,32,33], a challenge would be the identification and monitoring of pre-nuclei species, established around a single template molecule or a simple supramolecular entity, as they progress towards ordered structures, either in solution or in possible intermediate amorphous species.

A complementary approach to the previous discussion may arise from parallel or high-throughput synthesis, a concept that was introduced in inorganic chemistry and materials science in 1995 [34]. As regards zeolites, this technique was applied for the first time in 1998 [35] and then diversified to the preparation of zeolite films [36], coatings [37] and exchanged zeolites [38], and to the identification of the synthesis conditions leading to new zeolites [39]. High-throughput experimentation involving catalyst synthesis (Ti-MCM-41 and Ti-MCM-48) postsynthesis treatments and reaction testing, and combined with genetic algorithms assisted by artificial neural networks, were used to optimize several olefin (cyclohexene, 1-hexene, 1-decene and 1-dodecene) epoxidation processes [40]. This example suggests (see Fig. 3) that in the future both reaction yield or separation selectivity and catalyst or adsorbent design, perhaps based on hypothetical structures enumerated using combinatorial tiling theory [41], and preparation (i.e. zeolite nucleation and growth) could be parameters of the same optimization problem, even though a new and specific organic structure-directing agent might be found through a parallel scheme.

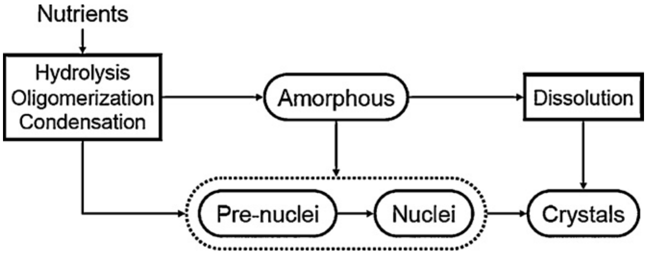

Fig. 2. Progress from nutrients to zeolite crystals.

3. Controlling zeolite crystal size and growth habit

The control of the size and growth habit when synthesizing a zeolite is critical whether the goal is either a catalytic process [42] or an adsorption application [43], but also when the target is the use of zeolites as fillers for mixed matrix membranes [44] or when crystallizing a continuous layer of zeolite [3]. The range of useful particle sizes is wide, from colloidal zeolites, a few tens of nm in size, to large crystals in the mm range. Colloidal zeolites can be used as seeds for secondary seeded growth and growing larger crystals or membranes, and are also interesting for catalytic and adsorptive applications in view of their high external specific surface areas and reduced diffusion path lengths. Nanozeolites may present inherent problems of pressure drop and safe management due to the possibility of forming respirable aerosols, among others, which have been overcome through the formation of hierarchical pore system materials [45,46]. Recently, techniques for the growth of large single crystals of various zeolites have been established [47,48]. Large zeolitic crystals can be of interest for structure refining [49], characterization [50], catalytic [48], electronic [51] and sensing [48] applications, *in situ* reaction studies [52,53], and for the study of chemical and physical processes difficult to observe on nanometric or micrometric particles [52,54,55].

The growth habits of zeolites can be modified through templating using alkylammonium polycations. As has been demonstrated for silicalite-1 [56,57], this is of particular interest when preferential orientation of zeolite channels with respect to crystal shape and dimensions is a key issue, as in the case of silicalite-1 membranes [58]. An alternative for crystal growth (habit and size) control would use the same specific template while buffering the synthesis medium with a different organic compound, as in the case of the growth of dodecasil 3C in presence of amino acid histidine [59].

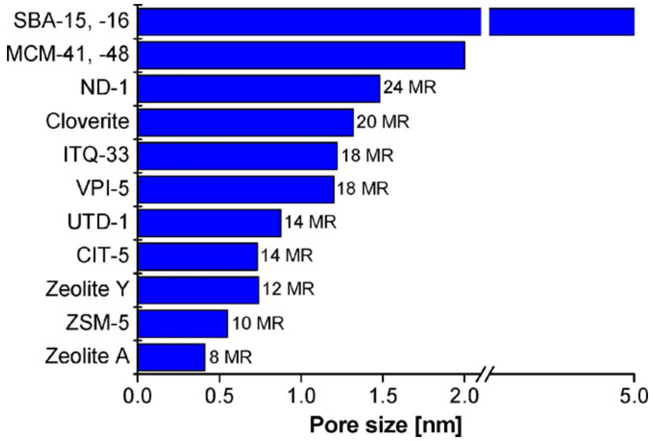

Fig. 4. Pore size of different porous-tailored materials. MCM-41 and MCM-48, and SBA-15 and SBA-16 can be prepared with pore sizes up to 10 and 30 nm, respectively.

In any event, the strategies developed for silicalite-1 in terms of growth habit control are far from be extended to other zeolite phases, while only a few zeolites (for instance silicalite-1 [60], zeolite A [19], zeolite Y [61], sodalite [62], gismondine [63]) have been prepared until now as discrete colloidal zeolites. Recent approaches to the synthesis of colloidal zeolites have been focussing on obtaining monomodal distributions in the 10–40 nm range [64–66].

Concerning the synthesis of giant crystals, template removal remains a challenge to be overcome, even though new template removal strategies have been reported for zeolitic materials [67–69]. Furthermore, template removal at high temperature is a good way of producing aggregation, structural defects, undesired phase and composition changes, loss of crystallinity and cracks in large crystals or in polycrystalline structures, among other possible effects, so that low temperature template degradation [67,68] and ion exchange removal [69,70] are possible routes for activation of zeolite microporosity. Alternatively, many microporous materials are synthesized without the use of organic templates in very limited conditions, and if these are not respected impurities are obtained. Again, and this would be a utopian challenge, high-throughput approaches, perhaps combined with seeding in certain situations, could be useful for investigating the precise conditions leading to the obtaining of already known pure zeolites of the desired size without the use of organic structure-directing agents.

4. Preparation of extra-large pore zeolites

One limitation on the use of zeolites may arise from their pore size being able to process relatively small molecules. For instance, ITQ-33, a zeolite with 18-member rings, is able to produce more diesel and less gasoline during the catalytic cracking of vacuum gasoil than USY (ultra stable zeolite Y) with 12-member rings [39], while other zeolitic materials with 14- [71–73], 18- [74], 20- [75] and 24-member [76] rings have also been synthesized showing differential catalysis and adsorption behaviour versus large molecules. On the other hand, MTS (mesoporous templated silicates) materials cover the 1.5–30 nm range of pore size [77], although they lack the chemical and hydrothermal stability of zeolites, as will be discussed in the next section. For instance, it has been reported that ECR-34 (18-member rings) [74] and ITQ-15 (14-member rings) [73] are stable to 800 and 1000 °C, respectively. Fig. 4 shows an overview of some selected extra-large pore zeolitic materials.

Zwijnenburg et al. [78] related topology and energetic considerations of large pore/channel zeolites, finding that the presence of sufficient small rings was critical for their stabilities, in particular of 3- and 4-member rings, as had been previously suggested by Brunner and Meier [79]. Otherwise the more energetically stable polyhedra would result in clathrasils rather than extra-large-pore zeolites. Methods to stabilize these rings consist in carrying out the synthesis in fluoride media and in the introduction of Ge [26] to produce silicogermanates [39] and gallogermanates [80].

As can be seen in Fig. 4, there is some continuous progression in terms of pore size from zeolite A (0.41 nm) to zinc phosphate ND-1 (1.48 nm) [76] but, forgetting stability (phosphate-based materials might have limited stability [15]) and other functional considerations (such as limitations due to pore blocking [81]), there is an important gap up to 2–3 nm to fill for crystalline porous-tailored materials. By filling this gap, crystalline porous materials could be used to perform processes usually carried out by less stable mesoporous materials (e.g. treatment of large reactant molecules, especially in liquid phase [82]). Another challenge would be the synthesis itself of all these useful materials with the classical chemical composition of silicoaluminates, what would help control adsorption and acid catalysis properties.

5. Synthesis of zeolitized mesoporous materials

It has been recognized that the thermal, hydrothermal and mechanical stability of as-synthesized mesoporous templated silicates is limited [77]. A perfectly zeolitized material, e.g. M41S (MCM-41, -48, -50) having walls of ZSM-5 or zeolite beta, would continue the increasing pore size trend established in Fig. 4. One may imagine such a zeolitized material as an extra-large pore zeolite with walls made of pentasil rings (in the case of stabilizing using the MFI-type zeolite). For this purpose, typical zeolite organic structure-directing agents can be added to the corresponding synthesis solution, and as a result nanoparticles of zeolite are found imbedded in the amorphous wall of the mesoporous material [83]. This gives rise to micro/mesoporous composites combining microporosity of zeolite units with mesoporous of amorphous phases, and to synergies in terms of properties and potential application of the new types of hierarchic materials obtained [84]. This situation, even if not perfect, usually leads to an improvement of the hydrothermal stability and catalytic performance of the modified mesoporous material [85,86], even in the cracking of bulky reactants such as high-density polyethylene [87]. However, other stabilization strategies such as silylation [88], the addition of different inorganic and organic salts during the synthesis process [89] or the post-synthetic hydrothermal treatment or recrystallization [90] have also been shown to be effective. Two complementary strategies to produce micro/mesoporous systems involve [16]: (i) the embedding of carbon precursors of narrow particle size distribution in zeolite crystals and their removal by calcination, and (ii) the controlled desilication of zeolites in alkaline medium.

Since thermal stability has in part been found to be linked to the thickness of the pore walls [77], another possibility consists of obtaining silica mesostructures with thicker framework walls than those of M41S (1.0–1.5 nm for MCM-41): for example, those related to HMS- (1.7–3.0 nm) [91] and SBA-type (3.1–6.4 nm) [92] mesoporous materials. These bulkier materials would also be better disposed towards the conversion of their walls into zeolite. In any event, the solution of the problem posed here needs of a better understanding of sol–gel chemistry and quasi-crystalline solids [93], although some approach from the extra-large pore zeolites could solve in part it.

6. Synthesis of chiral zeolites

Chiral porous materials could be of application in enantioselective adsorption and catalysis processes [94], and it seems logical to think that in the near future chiral zeolites, or in a wide sense chiral ordered porous materials, will make a decisive contribution to obtaining enantiopure compounds. It has also been recognized the challenge of obtaining an enantiopure porous tetrahedral framework and, in principle, a chiral organic structure-directing agent would be needed for synthesizing a chiral porous solid [95]. In this context, a large fraction of chiral polymorph A (>92%, the rest being polymorph B) of zeolite beta has been crystallized in the presence of chiral amine or rhodium complex acting as templates in conditions of thermal and racemization stability [96]. Other more successful (at least in terms of product purity) examples are several zeolite-like materials (zinc and beryllium arsenates and a gallogermanate) called UCSB-7 with three-dimensional helical pores [97] and a zeolite-like galloborate having 11-member ring channels and solvothermally prepared [98]. It is worth mentioning that in these two instances no chiral template was employed, and the same was true in the case of a porous gallophosphate templated by achiral triamine [99]. Recently, it has been discovered zeolite ITQ-37, which is the first chiral zeolite with a single giroid channel and with pore size dimension (4.3 Å × 19.3 Å asymmetric openings) approaching the mesoporous range [100]. This zeolite was obtained by means of a structure-directing agent containing four chiral centres, which make the overall molecule achiral. On the other hand, an anionic surfactant based on the amino acid alanine (N-myristoy-L-alanine sodium salt) templated the synthesis of chiral ordered mesoporous silica [101,102].

In any event, even if there exist about 20 chiral silicate zeolites, only very recently it has been reported enantioselective recognition of enantiomers by some natural zeolites (goosecreekite and nabesite) [103]. The hypothetical advantage of having zeolites able of enantioselective performance would mainly be related to their stability. Several chiral non-ordered silicas have been obtained combining sol–gel chemistry and molecular imprint but they loose enantioselectivity upon calcination [104].

As in other challenging situations, computational methods have been used to predict feasible chiral zeolite frameworks with desired channel geometries, which could be an aid for systematic research [105].

7. Preparation and modification of layered zeolites

Layered precursors have been found during the crystallization of several zeolites [106,107], while MCM22-P [108] together with PREFER [109] and Nu(6)-1 [110] are examples of layered zeolites invoked many times as feasible options for treating large molecules upon pillaring and delamination or exfoliation to increase accessibility while preserving thermal stability, homogeneous distribution of pores and silanol groups, and acidic character. Corma et al. have shown how it is possible to prepare delaminated zeolites such as ITQ-2 [111] from MCM-22P, ITQ-6 [112] from PREFER, and ITQ-18 [113] from Nu-6(1). Delaminated zeolites have been used for catalysis [111,114], adsorption after be functionalized with amines [115], and enzyme immobilization [116] showing in these cases advantages over, for instance, conventional zeolites or ordered mesoporous materials.

To identify targets in this section, it is worth describing how delamination proceeds. This consists of a first step of swelling of the solids by intercalation of surfactant cations in the presence of TPAOH molecules. Due to the size of the surfactant cations, the intercalation produces an increase in the layer spacing that can be monitored by X-ray diffraction. The high pH induced by the TPAOH molecules favours layer separation (negatively charged) and the attraction of surfactant cations, while the corresponding countercation (TPA^+) cannot interfere because of its relatively large size [117]. This is not only because of its large size for occupying exchange positions, but also because the smaller size of, for instance, Na^+ would better stabilize the silicate species fruit of an eventual dissolution process [118]. After the swelling, the material can be delaminated by means of sonication. As a result, in such materials the external surface area is around 10 times higher than that of the parent zeolite [111].

The swelling and exfoliation processes are normally carried out in excess of surfactant cation and reaction time and at relatively high temperatures and pH, which is not only responsible for the irreversibility of the swelling [119] but may also produce the dissolution of a significant amount of the treated zeolite and the by-product/contaminant MCM-41 [120]. The consequence is a low yield of the whole delamination process in terms of solid collected and perhaps also specific surface area achieved. In conclusion, a rationalization of these processes should lead to both a better understanding of the changes experienced by the zeolite and a higher quality of the delaminated product obtained. Furthermore, similarly to the synthesis of colloidal zeolites [121], it would be challenging to obtain the delaminated zeolites (i.e. particles having the desired topology but with a tremendous aspect ratio) as the fruit of a single hydrothermal crystallization stage, i.e. avoiding the synthesis of the lamellar precursor and then the subsequent, sometimes uncertain, delamination process. For instance, starting from the same lamellar zeolite Nu(6)-1, the delamination yield can be found in terms of BET specific surface area in the 150–600 m^2/g range [113,122,123].

8. Preparation of true molecular sieve membranes

Zeolites are potentially very useful and versatile materials for the preparation of selective membranes for molecular separations and for integrating reaction and separation in a solo device [124–129]. These are always supported membranes on mainly stainless steel or alumina porous supports, and a peculiarity they have is their lack of reproducibility [130], at least when the behaviour of membranes of the same zeolitic phase but prepared in different laboratories are compared. This means that one can find, for instance, MFI-type zeolite membranes (silicalite-1 and ZSM-5, the zeolites most synthesized as membranes) presenting not only different values of permeance and selectivity (related to the thickness of the membrane and the presence of a different number of intercrystalline defects) but also different qualitative behaviours. There are MFI-type membranes that separate the n/i-butane mixture (usually used to test the quality of these membranes) at high temperature [131], others only at low temperature [132] and others that cannot do this at all [133]. A few (very high quality) membranes can separate xylene isomer mixtures [134–136]; some silicalite-1 membranes show activation with temperature for single H_2 permeance [133], while others do not [137]; etc. The reasons for all these discrepancies are related not only to the different quality and crystallographical orientation of the membrane [58,138], but also to the influence of the porosity and chemical composition of the support [132,139]. Quite often the zeolite is synthesized inside the support pores (thus it is not possible to know the thickness of the membrane and the contribution to the transport of zeolitic material inside the pores even though this is not as a continuous composite layer) [140], while frequently the support is attacked by the precursor gel of the zeolite and the result is the incorporation of reactants to the zeolitic phase changing its chemical composition [141] and in consequence its transport properties.

The secondary (seeded) growth method implemented for silicalite-1 membranes [58,138], among other advantages, reduces the influence of the support in the permeation properties of the resulting zeolite membrane. The seeding with nanometric silicalite-1 crystals can be made to orient one of the crystallographic directions of these crystals perpendicular to the support

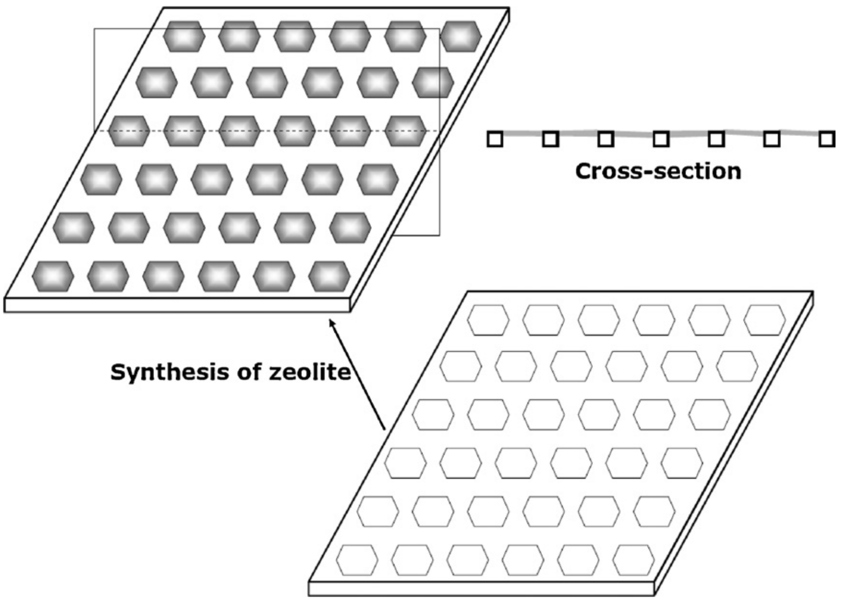

Fig. 5. Proposal of zeolite membrane from a support having holes of the morphology and size of the expected crystals.

[142]. Given the anisotropic pore system of the MFI-type zeolite, this method allows the control of an important factor concerning the transport properties of silicalite-1 membranes when compared to those of randomly oriented membranes, as demonstrated by Tsapatsis and coworkers who established that the performance of silicalite-1 membranes depended strongly on their microstructure [135], as expected but frequently unobserved because of the membrane meso and/or macrostructure.

Here the challenges are several. First, to produce reproducible, defect-free oriented (when the zeolite has an anisotropic structure) membranes of other zeolites different from the MFI-type. Second, and from another point of view, to implement for their preparation successful sol–gel based techniques (e.g. those used to produce commercial asymmetric mesoporous γ-Al_2O_3, TiO_2 membranes). Sols of zeolitic nanoparticles (such as zeolite nanoslabs [27] and protozeolites [143]) could be used to coat supports with thin layers of precursors to be then stabilized in some way. A process like this would be probably more reproducible, avoiding the inherent risks related to the heterogeneous crystallization of a zeolitic phase on a given support, and closer to an industrial strategy. Nishiyama et al. claimed the preparation of a H_2-selective membrane from zeolite A nano-blocks obtained from the dissolution in HCl of commercial zeolite NaA crystals [144]. A third challenge may arise from the preparation of self-supported membranes from, for instance, geometrically homogeneous porous supports (Fig. 5). These supports could be of Si or stainless steel, created *ad hoc* by a laser [145,146] or using microelectronic techniques [147] and having hole geometry in concordance with crystal growth habit. Finally, both membrane preparation through alternative procedures (e.g. using continuous systems [148,149], microwave heating [150,151], or ionic liquids [152] so that solvothermal synthesis at atmospheric pressure would be possible) and membrane activation to produce defect-free membranes [153–155] are research topics to be developed to approach practical specifications.

9. Conclusions

There is no doubt of the great importance of zeolites in the general subject of materials science. Zeolites, and in a broader sense zeolitic materials, are today studied and applied in many different ways and fields, even though some of their essential features are not wholly understood, and many challenges remain for the future.

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