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Zeolite Synthesis

Towards the Rational Design of Efficient Organic Structure-Directing Agents for Zeolite Synthesis

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Zeolites are crystalline microporous materials with application in diverse fields, especially in catalysis. The ability to prepare zeolites with targeted physicochemical properties for a specific catalytic application is a matter of great interest, because it allows the efficiency of the entire chemical process to be increased (higher product yields, lower undesired by-products, less energy consumption, and cost savings, etc). Nevertheless, directing the zeolite crystallization towards the material with the desired framework topology, crystal size, or chemical composition is not an easy task, since several variables influence the nucleation and crystallization processes. The combination of accumulated knowledge, rationalization, and innovation has allowed the synthesis of unique zeolitic structures in the last few years. This is especially true in terms of the design of organic and inorganic structure-directing agents (SDAs). In this Minireview we will present the rationale we have followed in our studies to synthesize new zeolite structures, while putting this in perspective with the advances made by other researchers of the zeolite community.

1. Introduction

Zeolites and related zeotypes are crystalline microporous materials with well-defined pores and cavities of molecular dimensions. Their frameworks are composed of TO_4 tetrahedra (with T = Si, Al, P, Ti, Sn) connected by oxygen atoms.[1] The ability to synthesize zeolites with different porous architectures and chemical compositions has allowed an important number of applications in relevant fields, such as catalysis, gas adsorption, gas separation, ion exchange, electronics, and biomedicine.[2]

Despite the fact that there are more than 200 different zeolites accepted by the International Zeolite Association (IZA),[3] the mechanisms involving the nucleation and crystallization of zeolites still remains unclear.[4] Significant studies have been performed to provide fundamental physicochemical knowledge on the initial stages of zeolite growth, but most of them have been applied to very simple systems, and consequently, the conclusions obtained cannot be fully extended to typical complex systems.[5] However, the insight achieved since the early systematic synthesis studies by Barrer and Breck[6] has allowed some understanding of the influence of the many variables involved in the synthesis of zeolites.

Zeolites are generally synthesized under hydrothermal conditions at temperatures ranging between 100 and 200 °C from mixtures of the required sources of framework atoms (Si, Al, Ti, Sn, Ge, etc), mineralizing agents (such as hydroxy or fluoride anions), and inorganic and/or organic cations that act as structure-directing agents (SDAs).[2a,4]

It must be pointed out that by properly selecting the inorganic framework cations one may direct the formation of specific secondary building units (SBUs) that direct the crystallization of, otherwise, less stable zeolitic structures.[2a] The presence of those specific secondary building units clearly determines the framework and pore topology. In 1989, Brunner and Meier predicted from theoretical studies on pure silica zeolites a relationship between zeolites with low framework densities (FD, number of tetrahedral atoms per 1000 $Å^3$) and the presence of 3- and 4-rings in their structures.[7] They concluded that it should be possible to obtain zeolites with low FD and, consequently, with large micropore volumes provided that the framework was built

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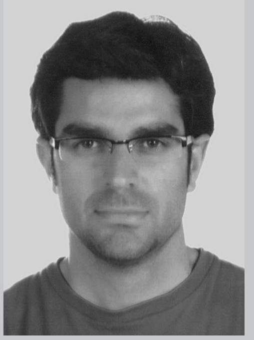
with a large number of 3- and 4-rings. However, 3- and 4-silica rings in zeolites are less stable than 5- or 6-rings and, therefore, the possibility of producing zeolites with very low FD and high pore volume, namely three-dimensional zeolites with extra-large pores, should be low when working with pure silica or even silicoaluminate polymorphs. Based on that theoretical work and the fact that many pure germanates contain double 4-ring (D4R) cages, we hypothesized that the introduction of Ge could facilitate the formation of D4R cages. Indeed, Ge-O-Ge or Si-O-Ge bond angles would be better than Si-O-Si for stabilizing those D4R units, and even D3R units. Indeed, by theoretical calculations we observed that the introduction of up to three Ge atoms in the D4R cages clearly stabilizes the formation of those units, something that was also shown experimentally.[8] Since then, we have been able to synthesize numerous silicogermanates with low framework densities that show diverse and fascinating framework architectures (Figure 1),[9] all of them containing small D4R cages, and more recently D3R, in their structures.[10] Interestingly, zeolites combining the lowest framework densities reported for zeolitic materials and the largest pore diameters (reaching even mesopores) have been achieved thanks to the introduction of germanium in the synthesis media.[9b,c,e,11] Zn and Be are other examples of heteroatoms that direct the formation of specific small rings, both favoring the crystallization of zeolites with 3-rings.[12] In this way, it has been possible to synthesize one extra-large-pore zeolite with a 14-ring aperture by using Be.[12b] However, Zn, while directing the synthesis to the formation of 3-rings, has not resulted in the generation, so far, of any zeolite with extra-large pores.

The mineralizing agent is the chemical species that controls the solubility and mobility of the framework atom sources in the synthesis gel by dissolution and precipitation processes.[13] The most widely used mineralizing agent is the hydroxy anion, which allows the zeolite crystallization to be performed in alkaline media ($pH > 10$). However, there are cases where it would be convenient to perform the zeolite synthesis at a neutral pH value. This is particularly the case when the organic SDA is not stable at a high pH value at the temperature required for the synthesis. In those cases, fluoride anions can be used as mineralizing agents. Nevertheless, the role of F^- ions during zeolite synthesis can go beyond the silica mineralizing effect, since F^- ions can be included in small cage units, thereby increasing their stability.[14]

Researchers at the Instituto de Tecnología Química (ITQ) reported that it was possible to synthesize open hydrophobic high-silica zeolites, such as Beta,[15] ITQ-4,[16] ITQ-7,[17] ITQ-17,[18] or ITQ-24, by working with F^- ions and concentrated gels.[19] In particular, the synthesis of hydrophobic pure silica Beta zeolite in fluoride media was an important achievement since it then allowed the isomorphic substitution of different isolated metals, such as titanium,[20] tin,[21] tantalum, or niobium,[22] in its structure by direct methods. Those metal-containing Beta zeolites have been used as water-resistant environmentally friendly solid acid catalysts in fine chemistry and biomass processes.[23]

Avelino Corma was born in Moncófar, Spain, in 1951. He studied Chemistry at the Universidad de Valencia (1967–1973), and received his PhD at the Universidad Complutense de Madrid in 1976. He carried out postdoctoral research in the Department of chemical engineering at Queen's University (Canada, 1977–1979), and since 1990 has been research professor at the Instituto de Tecnología Química (UPV-CSIC) at the Universidad Politécnica de Valencia. His research focuses on acid-base and redox catalysis, and he is co-author of more than 900 publications and 100 patents.



Manuel Moliner was born in Valencia in 1979. He obtained his BS in Chemical Engineering at the University of Valencia in 2003 and completed his PhD in Chemistry at the Polytechnic University of Valencia (UPV) under the guidance of Prof. Avelino Corma and Dr. Maria J. Díaz. After two years postdoctoral research at Caltech with Prof. Mark Davis, he joined the "Instituto de Tecnología Química" (ITQ) as "Ramón y Cajal Researcher". His research lies at the interface of materials design and heterogeneous catalysis.

Fernando Rey (1963) received the PhD in 1992 under the supervision of Prof. Vicente Fornés. He then joined Prof. John M. Thomas as a Postdoctoral Researcher at the Royal Institution working on the development of synchrotron characterization methods for understanding micro- and mesoporous catalysts. He returned to the ITQ in 1995, and was promoted to Research Professor of the CSIC in 2007. His research focuses on the synthesis and characterization of zeolites with application in catalysis and adsorption. He is co-author of more than 120 papers and more than 40 patents.

Besides framework cations, other inorganic cations, such as alkali or alkaline-earth cations, were used as structure-directing agents (SDAs) in zeolite synthesis. These enabled the formation of the first synthetic silicoaluminates with very low Si/Al ratios.[6] In addition to the inorganic directing effect, the presence of alkali or alkaline-earth cations in the gel increases the nucleation rate, thereby considerably reducing the crystallization time.[24] Whereas only low Si/Al zeolites were previously obtained with alkali or alkaline-earth cations, today it is possible to crystallize a number of high-silica zeolites in the presence only of inorganic cations. In those cases, the presence of relatively large amounts of seeds has been mandatory for growing higher silica zeolites.[25]

Finally, the introduction of organic molecules, such as quaternary ammonium cations or amines, as pioneered by Barrer et al.[26] and Kerr,[27] has permitted the preparation of a large number of new zeolitic structures with unique frameworks and chemical compositions that have been applied as exceptional industrial acid catalysts.[28]

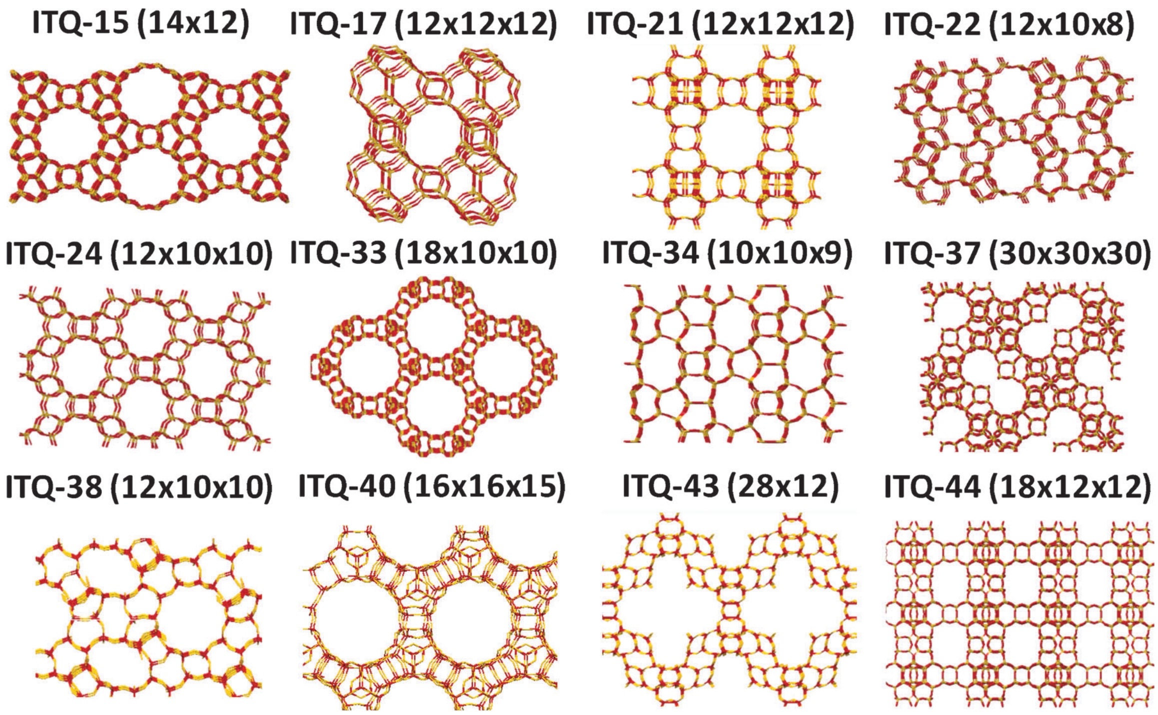


Figure 1. New germanosilicates (synthesized at ITQ).

In this Minireview we will concentrate on the organic structure-directing agents (OSDAs), and we will show how it has been possible to develop different families of OSDAs, each one of them with specific characteristics that influence the synthesis of a large number of zeolites. However, we want to emphasize again the interdependence of the synthesis variables, as it has been critically reviewed in the literature.[4,29]

2. Directing Role of Different OSDAs

2.1. First Ammonium OSDAs and Systematic Studies of Zeolite Synthesis

As stated above, the first described synthesis of zeolites through the use of organic molecules, such as tetraalkylammonium cations, was reported in 1961 by Barrer and Denny.[26a] They described the preparation of different methylammonium aluminosilicates analogous to their alkali metal aluminosilicates counterparts, such as sodalites, faujasites, and Linde molecular sieve A. The authors hypothesized that those zeolites containing organic moieties must be silica-rich relative to their analogues containing only inorganic cations. This could be easily explained on the basis that the relatively large organic molecules introduce a lower number of positive charges than small inorganic cations (i.e. Na^+ or K^+) within the zeolite cages, thus requiring a lower number of balancing negative charges in the framework and, consequently, a lower number of T^{III} elements. In other words, the size of the quaternary organic ammonium OSDA could determine the concentration of trivalent elements in the zeolite framework, that is, the number of aluminum atoms. This was a very significant discovery, since the synthesis of high-silica zeolites, with Si/Al ratios higher than 10:1, provides high hydrothermally stable materials with strong Brönsted acidities (protons are placed close to aluminum atoms after removing the organic moieties by calcination). In fact, two of the most successful acid zeolites used today in industry, ZSM-5 and Beta, were synthesized in the 1960s by Mobil researchers by using tetrapropylammonium and tetraethylammonium cations, respectively, as OSDAs.[30]

Many studies were subsequently devoted to vary the shape, size, hydrophobicity, and number of charges of the OSDAs, with the aim of controlling the pore dimensions and cavities of the synthesized zeolites. In this sense, Gies and Marler, and Nakagawa and Zones performed systematic studies by changing the nature of the OSDAs. Gies and Marler studied intensively the synthesis of clathrasils (zeolites with apertures lower than 8-rings) by using OSDAs with different size. They were able to correlate the size of the clathrasil cavity with the size of the OSDA used.[31]

Nakagawa and Zones showed that it was possible to obtain more open structures by increasing the size of the OSDA.[32] The same research group also studied the possible "templating" effect of the OSDAs, and they found that the specificity of the OSDAs increases when going from small and flexible to large and rigid organic moieties.[28] A number of different families of organic molecules have been systematically studied in the literature. Of these, polycyclic molecules synthesized by Diels–Alder reactions[33] have resulted in rigid OSDAs that allow the synthesis of zeolites with large pores or cavities in their framework.[19,34] As shown in Figure 2 A, we have synthesized new zeolitic structures by varying the size

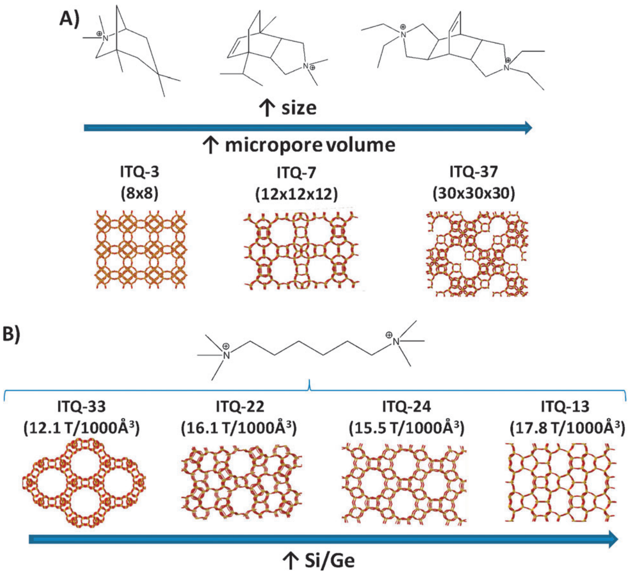


Figure 2. New zeolites prepared by systematic studies using A) Diels–Alder OSDAs, and B) flexible linear diquaternary ammonium cations (diquats).

and shape of the polycyclic OSDAs and, in general, larger pores and cavities are obtained when the size of the OSDA is increased.

The effect of the methylene chain length of flexible linear diquaternary ammonium cations (diquats) has also been intensively studied.[35] The high flexibility offered by these linear diquats has allowed the synthesis of a large number of zeolites with different topologies, ranging from zeolites with small to extra-large pores. The advantage of using those flexible molecules is a higher probability of crystallizing zeolites under more or less conventional synthesis conditions. However, this virtue can turn into a limitation because of the low specificity for directing into a particular structure, thus resulting in a mixture of different structures in many cases. This was the driving force for our use of high-throughput (HT) synthesis techniques in combination with statistical experimental designs and powerful data-mining techniques.[36] This approach allowed us to find the synthesis space to obtain a particular zeolite from a mixture of several structures in a short period of time.

In this way, and by using the flexible hexamethonium cation as the OSDA, we have synthesized a large number of new microporous materials, that is, ITQ-13, ITQ-22, ITQ-24, and ITQ-33, zeolites which range from small to extra-large (18-ring) pores (Figure 2B).[9b,19,35d] ITQ-33 is a particularly interesting structure that combines 18- and 10-ring pores, and shows a unique catalytic behavior for cracking vacuum gasoil, since it allows maximization of the yields of diesel and propylene at the same time.[9b]

The use of other organic molecules as OSDAs, such as azoniaspiro alkanes, crown ethers, fluoroamines, have been described and systematically studied in the literature. We refer the reader to an excellent review by Burton and Zones which lists preparation protocols of OSDA families and their role in zeolite synthesis.[37]

The systematic study of OSDA families has allowed the discovery of new attractive zeolites and it seems clear today that the size and shape of the organic additive plays a fundamental role in determining the framework topology. However, actual predictions of suitable templates for a given framework were rarely described, despite the efforts made by using computer modeling.[38] For example, Lewis et al. developed a de novo design for predicting potential organic molecules able to direct known or hypothetical zeolites,[39] but this method still has room for improvement.

Despite the complexity in predicting the exact interaction between OSDAs and zeolites, it would be interesting to go beyond the generation of OSDAs by systematic modification of well-known organic molecules, and direct the efforts to the "ab initio" design of the organic moiety to prepare a desired structure from the thousands predicted as being possible by molecular modeling studies.[40] In this regard, different research groups, and particularly our group at ITQ, have been making efforts in the last few years to prepare specific and novel OSDAs for challenging zeolite synthesis.

Indeed, some organic molecules with a priori rationalized shape and chemical functionalities have allowed: the recovery and reuse of the OSDA molecule without calcination;[41] new non-ammonium cations that can be used under synthesis conditions where other OSDAs are degraded;[42] the synthesis of zeolites under atmospheric pressure;[43] the supramolecular self-assembly of OSDAs for templating cage-based zeolites;[44] the application of modular organic molecules with high basicity for the synthesis of multipore zeolites;[45] the synthesis of extra-large-pore zeolites by using bulky proton sponges;[46] and the application of multifunctional OSDAs for the preparation of multipore zeolites[47] and zeolitic nanosheets.[48]

Those are, in our opinion, some of the most relevant recent achievements related to the guided design of organic molecules for their application in zeolite synthesis. All those rationalized organic molecules are novel ammonium cations, proton sponges, phosphonium cations, and phosphazenes.

2.2. Novel Quaternary Ammonium Cations

Davis and co-workers[41] and Morris and co-workers[43] have rationalized the design and use of new ammonium cations as OSDAs, thereby allowing the improvement of the procedures for zeolite synthesis. Davis and co-workers described a family of organic molecules that can be easily formed by reacting two components and forming covalent bonds, as is the case in the synthesis of acetals for use as stable OSDAs under zeolite synthesis conditions.[41] Once the zeolite is crystallized, the OSDA acetal can be hydrolyzed in acid media, thus extracting the initial small organic fragments from the inorganic framework and, recombining them for reuse. This method avoids the calcination of the occluded OSDA molecules, which are usually the most expensive components in zeolite synthesis. This concept has been shown for the synthesis of one of the most industrially relevant zeolites, ZSM-5, by using a cyclic ketal molecule, which is easily assembled/dissembled depending on the pH value

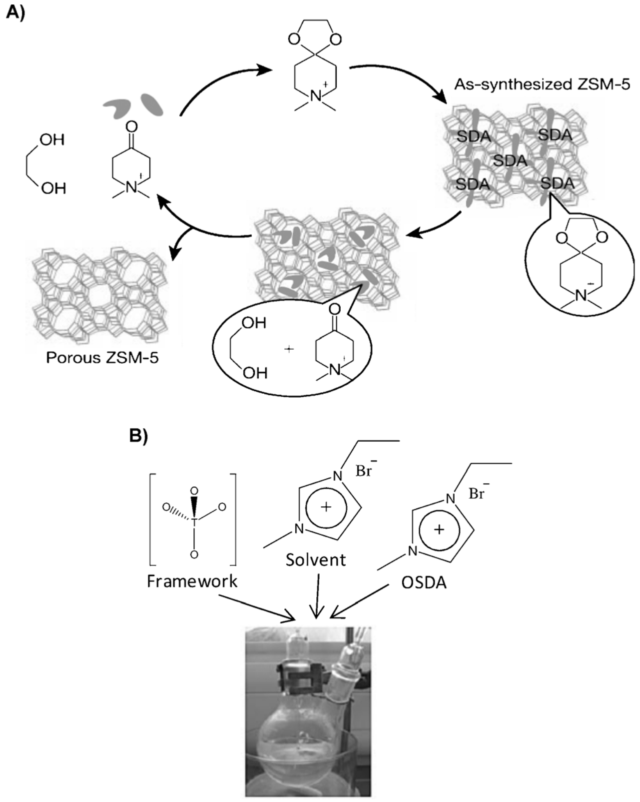


Figure 3. A) Cyclic ketals for the combustion-free method developed by Davis et al. Reproduced from Ref. [41]. B) Ionothermal zeolite synthesis at ambient pressure. Reproduced from Ref. [50].

(Figure 3 A). Morris and co-workers reported the synthesis of molecular sieves under atmospheric pressure by using ionic liquids as OSDAs.[43] This is a significant advancement, since the conventional synthesis of zeolites is performed in sealed autoclaves under elevated pressures,[49] and thus the preparation of zeolitic materials under atmospheric pressures is a matter of much interest for safety reasons (Figure 3 B). Morris and co-workers rationalized the use of imidazolium salts (which are the most common ionic liquids) as OSDAs, since those molecules have low vapor pressure and the required properties to act simultaneously as both the OSDA and solvent.[50] New zeotype structures with different pore architectures have been described by following this ionothermal method.[43,51] Some water has to be present in the synthesis media to produce aluminosilicates.

A new concept has been introduced recently to prepare a priori designed OSDAs. This approach is based on the supramolecular self-assembly of two aromatic anilinium-derived molecules through π-π interactions (Figure 4).[44] Since the π-π distances are much larger than C−C bonds, this results in a bulky self-assembled organic moiety that has the proper C/N ratio for templating zeolites. Following this strategy, the size to charge ratio of the OSDA can be maximized, which is highly desirable to synthesize hydrophobic high-silica zeolites in general, and for high-silica zeolites with large cavities in particular.[28] Indeed, high-silica zeolites with large cavities and small pore openings are of interest for reactions such as the methanol to olefin reaction (MTO),[52] the selective catalytic reduction (SCR) of nitrogen oxides (NO_x),[53] or the separation of hydrocarbons.[54] Of all the described small-pore zeolites, LTA is probably one of the most interesting molecular sieves with very high void volumes. Unfortunately, the applicability of this molecular sieve as a catalyst and adsorbent was limited because of its low Si/Al ratio (<3:1), which results in low hydrothermal stability, low acidity, and high hydrophilicity. To increase the Si/Al ratio in LTA a bulky OSDA must be designed that fits the very large cavity of LTA. Interestingly, the supramolecular OSDA fits perfectly in the spherical cavities of LTA (Figure 5), thereby providing unique directing effects towards LTA cavities. High-silica LTA samples and, even the pure silica polymorph (ITQ-29), were synthesized for the first time by using this supramolecular approach.[44] This material showed an excellent capability to separate hydrocarbons such as C_3 and C_4 olefins and paraffins without undesired oligomerization reactions.[44]

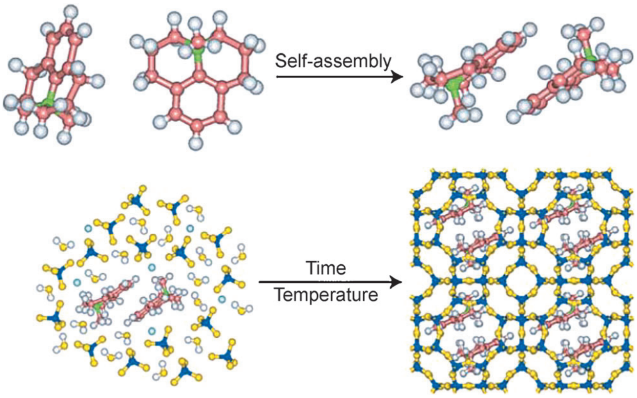


Figure 4. Supramolecular self-assembling OSDA method for zeolite synthesis. Reproduced from Ref. [44].

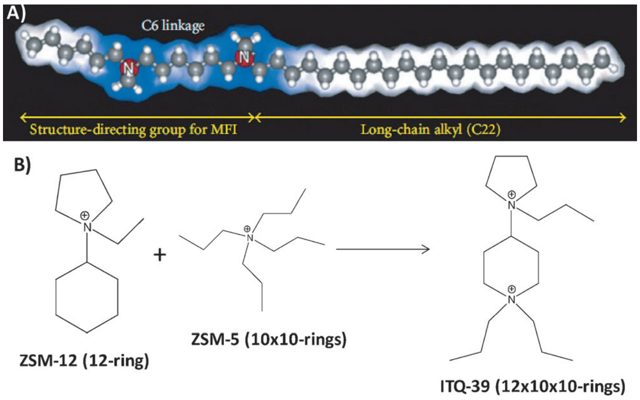


Figure 5. A) Multifunctional OSDA designed by Ryoo et al. for the direct synthesis of zeolitic nanosheets. Reproduced from Ref. [48]. B) Multifunctional OSDA designed by Corma et al. for the synthesis of multipore zeolites.

Two important synthesis methods involving multifunctional quaternary ammonium cations have been reported by Ryoo and co-workers[48] and our research group[47] to guide the preparation of ultrathin and multipore zeolites, respectively. On the one hand, it is known that serious diffusion problems can occur through the zeolite crystals when bulky reactants or products are involved in a chemical process. To improve the accessibility of bulky molecules to the active sites we described for the first time the preparation of ultrathin zeolites, such as ITQ-2 and ITQ-6, by delamination of layered zeolite precursors several years ago.[55] Our method, based on a two-step procedure, permits the synthesis of ultrathin zeolites with thicknesses below 3 nm and very high external surface areas, thus favoring access of the reactants to the active sites. Ryoo and co-workers used specific multifunctional OSDAs for the direct synthesis of ultrathin zeolites, called nanosheets.[48] These OSDAs possess a long-chain alkyl group and also two quaternary ammonium groups spaced by a short alkyl chain, typically C_6 (Figure 5 a). The diammonium group allows the formation of crystalline zeolite layers, while the long hydrophobic chain prevents zeolite growth in the normal direction of the sheet by the formation of a micellar structure. This method has allowed the synthesis of 2 nm thick MFI nanosheets with different Si/Al ratios and large external surface areas ($>700\,m^2g^{-1}$).[48] The same authors have also demonstrated that the number of layers in the nanosheets can be tuned by modifying the number of quaternary ammonium groups in the multifunctional OSDA.[56] Very recently, Ryoo and co-workers have extended their method based on multifunctional OSDAs to other zeolite-related nanosheets, both aluminosilicates (Beta, MTW, and MRE structures),[57] and aluminophosphates (AEL, AEI, and ATO structures).[58]

On the other hand, one must take advantage of the porous systems of the zeolites when shape selectivity is desired. In this sense, the synthesis of zeolites containing interconnected discrete pores with different ring sizes is highly desired in catalysis because they can offer unique diffusion pathways to reactants and products. For example, molecular sieves with interconnected large and medium pores could be of interest for industrially relevant processes, since they can combine the catalytic behavior of two of the most successful industrial zeolites, Beta and ZSM-5. The design of a new dicationic piperidine-derived molecule containing the adequate potential functionalities for directing the crystallization of molecular sieves with interconnected large and medium pores was rationalized.[59] As shown in Figure 5 B, this OSDA combines the rigidity to direct the formation of large-pore zeolites, as previously reported for the synthesis of large pore ZSM-12,[60] and the flexibility to direct the formation of medium-pore zeolites, as reported extensively for the medium pore ZSM-5.[61] The use of this dicationic molecule in zeolite synthesis has allowed the preparation of a new zeolite (ITQ-39, Figure 6) under a broad range of synthesis conditions.[47,59,62] Thanks to its unique pore topology with large and medium pores, the multipore ITQ-39 zeolite shows an exceptional catalytic behavior for the alkylation of aromatic naphtha to produce diesel.[47] A similar dicationic OSDA has allowed the synthesis of ITQ-38, a new zeolite also with large and medium pores in its structure.[63]

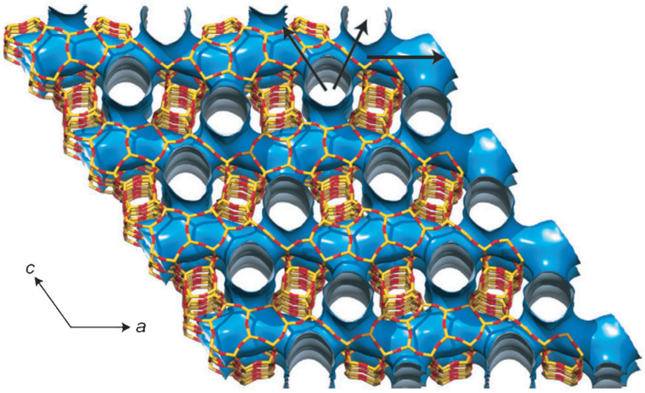


Figure 6. Structure of ITQ-39 zeolite with different pores. Reproduced from Ref. [47].

2.3. Proton Sponges

One of the main goals in zeolite synthesis is the preparation of stable extra-large-pore zeolites for application in the petrochemical and chemical industries. For example, extra-large-pore zeolites can have a positive impact in catalytic cracking and hydrocracking processes by increasing the catalytic activity and selectivity to distillates. In this sense, some extra-large-pore zeolites with 14-ring openings (UTD-1, CIT-5, SSZ-53, SSZ-59) were prepared by using relative large and rigid OSDAs.[64] However, zeolites with the largest openings have been achieved in the last few years by introducing germanium in the zeolite synthesis.[2a] The efficient inorganic directing effect of Ge towards small rings and cages formed primarily by 3- and 4-rings[8,9b,10] allowed the synthesis of very open silicogermanates (Figure 1). Nevertheless, silicogermanates show low hydrothermal stabilities, and their potential industrial application is prevented by this low hydrothermal stability as well as economic reasons.[65] In the last few years, some attractive improvements have been reported that increase the stability of those materials through post-synthetic procedures, either by replacing germanium by other heteroatoms in the zeolite framework[65] or by transforming the as-prepared silicogermanate into zeolitic high-silica sheets[66] and other related zeolites.[67] These procedures may open new possibilities for a large number of silicogermanates and silicoaluminogermanates.

We have also explored the use of “proton sponges” as suitable bulky OSDAs for the synthesis of extra-large-pore zeolites.[46] Indeed, “proton sponges” are bulky aromatic diamines in which the amine groups are in proximity (Figure 7). As a consequence, these materials have a high unusual basicity because of repulsion of the close lone pairs of electrons ($pK_a > 12.1$).[68] Their high basicity would allow their protonation in the synthesis media, thereby favoring organic–inorganic interactions during nucleation. Their large size and rigidity may confer “proton sponges” with adequate molecular structure for templating extra-large pores.

The potential of “proton sponges” as OSDAs to synthesize extra-large-pore zeolites has been proved by using the commercially available 1,8-bis(dimethylamino)naphthalene

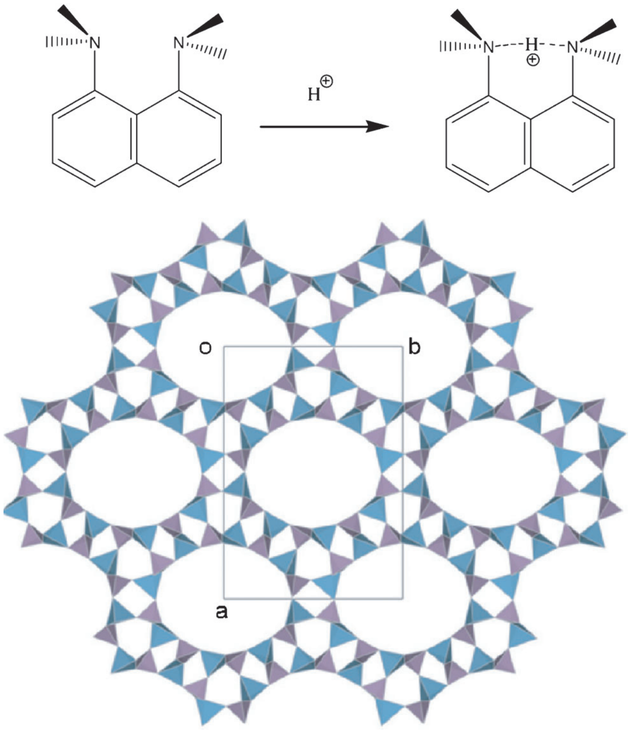


Figure 7. Bulky proton sponges as OSDAs for synthesizing stable extra-large zeotypes. Reproduced from Ref. [46].

for the preparation of the ITQ-51 zeotype (Figure 7).[46] This is the first reported stable molecular sieve with 16-ring pores.

2.4. Phosphonium Cations

The most frequently used OSDAs are alkylammonium cations. However, they can undergo Hoffman degradation reactions in aqueous media at high pH values and high temperatures to give an amine degradation product and an alkene or alcohol.[37] In the last few years we have rationalized the use of tetraalkylphosphonium cations as organic structure-directing agents for zeolite synthesis, since these organic molecules do not undergo the Hoffman degradation reaction and they could, in principle, allow the syntheses to be carried out under more severe conditions.[42]

We have demonstrated the validity of using phosphonium cations as templates with the synthesis of ITQ-27, a new two-dimensional large-pore high-silica zeolite. In this case, diphenyldimethylphosphonium was selected as the OSDA (Figure 8).[42] The synthesis of the first three-dimensional zeolite with intersecting extra-large channels of 16 × 16 × 15-ring pores was also achieved by using diphenyldiethylphosphonium in combination with germanium atoms.[10] Moreover, molecular modeling studies have guided the synthesis of the new ITQ-34 zeolite, which consists of structure-connecting 9- and 10-ring pores, by using propane-1,3-bis(trimethylphosphonium) cation as OSDA.[69]

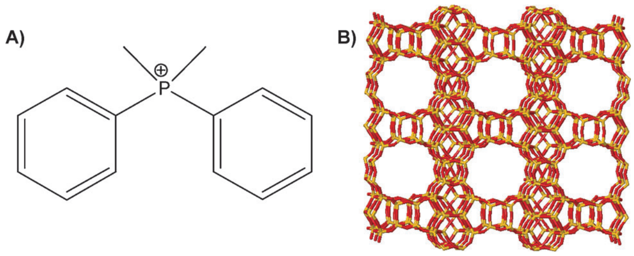


Figure 8. A) Phosphoinium cations as the OSDA for the synthesis of ITQ-27. B) Structure of the ITQ-27 zeolite.

Recently, Tsapatsis and co-workers have been able to synthesize a hierarchical self-pillared MFI zeolite composed of single unit cell lamellae (2 nm thick) by a one-step synthesis by using tetrabutylphosphonium as the single OSDA.[70] These nanosheets form a "house-of-cards" arrangement with 2- to 7 nm mesopores, which results in a lower diffusion limitation to bulky organic molecules compared to conventional zeolites. The authors report that self-pillared MFI nanosheets perform better than conventional crystalline zeolites for the synthesis of the desirable bio-based intermediate 5,5′-oxy(bismethylene)-2-furaldehyde (OBMF) through the etherification of 5-hydroxymethyl-2-furaldehyde (HMF).[70,71]

2.5. Superbasic Phosphazenes

We have introduced superbasic phosphazenes as a new type of OSDAs for zeolite synthesis.[45] These molecules can mobilize silica and other heteroatoms in the preparative gels through their high basicities. Moreover, this family of organic molecules can be easily prepared with very different shapes and volumes by constructing them from different organic blocks, in a similar way to "Lego chemistry" (Figure 9 A). It is feasible to create phosphazenes with a large variety of substituents, thereby creating nearly unlimited flexibility in terms of synthesis (Figure 9 B). Interestingly, the potential of phosphazene structures with adequate directing effects towards the synthesis of zeolites with interconnected large and medium pores can be rationalized by "ab initio" molecular modeling studies. As described above, these zeolitic structures are highly desired in catalysis because they allow the unique diffusion of reactants and products of different molecular dimensions through their different-sized channels and, consequently, can provide unique catalytic properties. *tert*-Butyliminotris(dimethylamino)phosphorane was a potential OSDA for the synthesis of the boggsite zeolite. This molecular sieve, which has interconnected large and medium pores in its structure, had not been synthesized in the laboratory, and therefore, its application as a catalyst was not possible. Boggsite was synthesized experimentally by introducing *tert*-butyliminotris(dimethylamino)phosphorane in the synthesis media.[45] This material shows an exceptional catalytic behavior in the preparation of the industrially relevant cumene through the alkylation of benzene with propylene.[45]

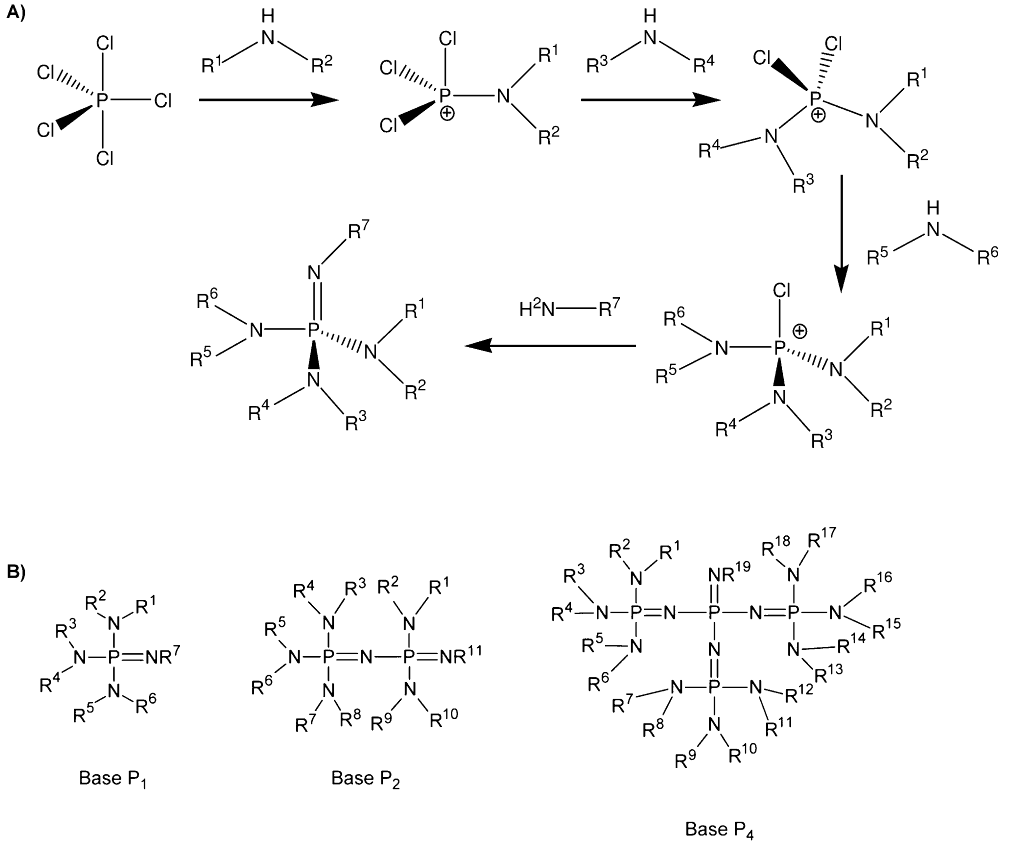


Figure 9. A) Schematic representation of the potential of "Lego chemistry" for the preparation of phosphazenes. B) Some examples of modular OSDAs based on superbasic phosphazenes. Reproduced from Ref. [45].

3. Future Perspectives

In this Minireview we have shown the recent advances achieved in zeolite synthesis by applying different and novel OSDAs. It is clear that guided OSDAs allow the preparation of targeted zeolites with specific physicochemical properties, and by following similar principles, novel or improved zeolitic frameworks will be synthesized in the very near future.

For example, the preparation of new stable large-pore zeolites with large cavities would be very attractive for application as catalysts, and the use of supramolecular OSDAs through self-assembly could be helpful for this objective. A challenging and relevant objective would be the synthesis of zeolites with large pores and cavities with high Si/Al ratios.

The use of a single enantiomer of a chiral zeolite would also be a scientific challenge that may result in materials with interest for use in separation, catalysis, and photocatalysis processes.[72] Up to now, several chiral zeotypes have been described in the literature, such as zinc phosphate CZP,[73] berosilicate OSB-1,[12b] germanosilicate SU-32a,[74] the mesoporous zeolite ITQ-37,[9c] and HPM-1 silicate.[75] However, a single enantiomer has not been presented. It is worth mentioning that in most of those cases the OSDAs used in their preparation were achiral templates, thus making it difficult to understand the real role of these achiral OSDAs in templating chiral structures. In those cases, the chiral frameworks probably occur by the chiral organization of achiral structure units through noncovalent host–guest interactions, such as hydrogen bonds.[76] On the other hand, chiral organic templates have been employed in the synthesis of high-silica zeolites, but only achiral frameworks have been achieved.[77] Davis has proposed that the high mobility of the OSDA under reaction conditions could limit the noncovalent interactions to fix the chiral organic template in three-dimensional space, thus preventing chirality transfer from the OSDA to the inorganic framework.[77] The increase in the noncovalent interactions in the nucleation process, such as for example by introducing fluoride anions, could assist the arrangement and fixation of the organic moiety in the porous matrix. Consequently, this fixed fluoride–organic complex can provide an opportunity to create chiral molecular sieves if the organic molecule is also chiral.[77] Other possible alternatives could be the attachment of the chiral organic molecule during the nucleation process through covalent bonds to the inorganic matrix, for example by using chiral organosilane molecules as OSDAs.[78] This would avoid the "free rotation" of chiral organic molecules. Thus, the synthesis of stable chiral inorganic molecular sieves for their application in asymmetric catalysis and separations offers opportunities in biochemistry and pharmacy.

As a general remark, we can assert that original and innovative future advances in the rational design of OSDAs will allow novel or improved zeolites to be engineered with unique frameworks and chemical compositions, which may have significant implications in relevant chemical processes.

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