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Lu, P.; Villaescusa Alonso, LA.; Cambor, MA. (2018). Driving the Crystallization of Zeolites. *The Chemical Record*. 18(7-8):713-723. <https://doi.org/10.1002/tcr.201700092>



The final publication is available at

<https://doi.org/10.1002/tcr.201700092>

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Additional Information

Driving the Crystallization of Zeolites

Peng Lu,^[a] Luis A. Villaescusa^[b] and M.A. Cambor*^[a]

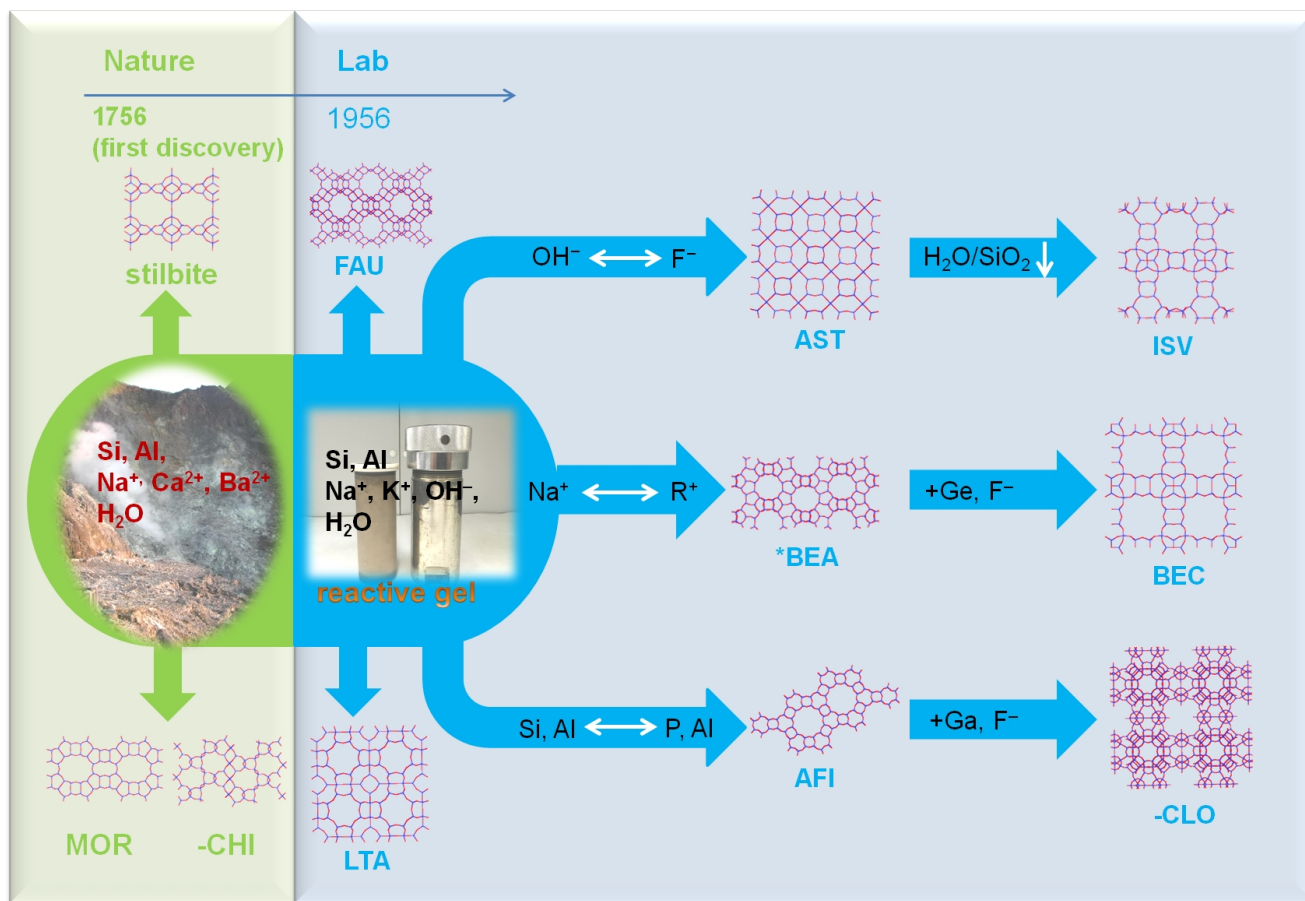
Dedicated with our warm regards to Professor Eduardo Ruiz-Hitzky

Abstract:

The synthesis of zeolites with new structures and/or improved properties heavily relies on trial and error efforts that are not entirely blind, as the large empirical background accumulated for the last 7 decades can be, to some extent, rationalized and purposefully used to make new materials. The so-called structure-directing factors may be combined to promote (or frustrate) the crystallization of a particular structure. This personal account opens with the concept of geoinspiration, as suggested by Prof. Ruiz-Hitzky, and its application to zeolite synthesis. We then provide a concise overview of structure-direction in the synthesis of zeolites and detail examples, both new and from the literature, on how they can be combined to drive the crystallization towards (or away from) structures displaying particular features.

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Peng ‘Jacky’ Lu was born in Shandong, China. He received his Master’s degree in chemical engineering from Qingdao University of Science and Technology from 2009-2012. He is currently a Ph.D. student in Dalian Institute of Chemical Physics, Chinese Academy of Sciences under supervision of Prof. Lei Xu and also a joint Ph.D. student, sponsored by Chinese Scholarship Council (CSC), in the Institute of Materials Chemistry of Madrid (ICMM-CSIC) under supervision of Prof. Miguel A. Cambor. His research includes synthesis of pure silica and germanosilicate zeolites using imidazolium-derivatives as structure-directing agents in fluoride medium and the corresponding structure characterization and catalytic evaluation. He is a keen singer.

Luis A. Villaescusa started his route to zeolites by tossing a coin whose result eventually lead him contact Instituto de Tecnología Química (ITQ) in Valencia. There, he obtained his PhD under the supervision of M.A. Cambor, the peculiar guy here below, in 1999. After a two year postdoctoral stay in the School of Chemistry in St. Andrews (Scotland), he got a “Ramón y Cajal” fellowship to work in the Department of Chemistry of the Universitat Politècnica de València (UPV). There, he became associate professor in 2004 and tenured professor in 2011. His main interests are around synthesis and applications of porous materials and, lately, he has started to learn music and to play trumpet.

Miguel A. Cambor (*aka* MSax) was born in Avilés (Asturias) and received his Ph.D. in Chemistry from the Universidad Autónoma de Madrid in 1991 for work developed under the supervision of Prof. J. Pérez-Pariente. He has been a postdoctoral Fulbright Fellow at Caltech (1992-1994), a Tenured Scientist at the Spanish National Research Council (CSIC, 1993-2000), the Director of the R+D department of IQE, S.A. (Zaragoza, Spain 2000-2002) and a Senior Scientist (2002-2009) and then a Research Professor (since 2009) at the Institute of Materials Science of Madrid (ICMM-CSIC). His main research interests are structure-direction and the structural and physicochemical characterization of zeolites. He also plays tenor sax in a number of bands.

1. Introduction

Zeolites constitute a technologically and scientifically important class of materials due to their large diversity, interesting properties, applicability in a wide range of processes and capability for fine tuning their attributes. This diversity is due to the wide compositional and structural variability that this type of microporous solids can display. Zeolites may be defined as crystalline materials possessing a non-dense three-dimensional fully connected (4;2) network, meaning that they are built by atoms acting as four coordinated nodes connected through two coordinated bridges. There are currently 216 such networks recognized by the International Zeolite Association as having been realized, plus 12 interrupted frameworks (i.e., with not fully connected networks) and 7 partially disordered materials (i.e. composed of intergrowths of different polymorphs, at least one of them having not been realized as an ordered material). This recognized Zeolite Framework Types (ZFT) are assigned a code of three letters (like, for instance, MFI for the technologically important ZSM-5).^[1] For the last 10 years the number of recognized ZFT networks has kept growing at about half a dozen new structure types per year. Most of these newly discovered zeolites are synthetic.

In our view, the goal of zeolite synthesis is to master the crystallization of zeolites so as to be able to:

- 1) design/predict the crystallization of structures with particular features aimed to targeted applications
- 2) produce zeolites with a different composition and properties, such as a new type of catalytic site, an improved thermal stability or an increased hydrophobicity.
- 3) modify textural properties (crystal size, hierarchical arrangement of pores) that may imply a different performance in a given application

The four-coordinated nodes and two-coordinated bridges of the framework may vary widely, giving an impressive compositional variability of zeolites. Nodes may comprise Si, Al, P, Ge, Ti, V, As, Ga, B, Zn, Be, Li, Sb, Sn, Ni, Fe, Co... although not all possible combinations of those have been realized. On the other hand, oxygen is by far the most frequent bridge, although examples exist in which S, Se and even N act as bridges. However, the compositional variability appears to depend on the zeolite structure type. In this personal account we will deal only with oxide phases, mainly silica-based zeolites.

2. Geoinspired synthesis

Professor Ruiz-Hitzky suggested the concept of geoinspiration to one of the authors (MAC) around 2005. Geoinspiration could be defined as the wealth of motivation that materials scientists may borrow from the mineral world, both in terms of ‘design’ of useful materials and of feasible chemical pathways to prepare them. The referred author realized that the concept could be applied in retrospect to the synthetic zeolites and their evolution.^[2,3] Consequently, as well, it could be applied to a good portion of

his own scientific career, the last fifteen years of which has been happily developed at the Nanostructured **H**ybrid, **B**iohybrid and **P**orous **M**aterials Group that Ruiz-Hitzky successfully lead for several decades. The zeolites materials we discovered in this group are denoted upon the name of the group as **HPM-n**, where n is a sequence number (up to 9, so far).

There have been many reviews on the synthesis of zeolites and its historical evolution.^[3,4] Very briefly, the field started with the works by Barrer,^[5] the “founding father of zeolite chemistry”,^[6] on one hand, and Milton in the other,^[7] and their respective coworkers. While, initially, Barrer tried to directly emulate the expected natural crystallization of zeolites from volcanic glasses and saline water at relatively high temperature, Milton started with more reactive ingredients, looking for lower crystallization temperatures that could result in more hydrated and less dense materials.^[8] From the point of view of discovering new zeolites, Milton’s approach was extremely successful since it rapidly yielded several new zeolites, two of which met an immediate, enormous and still lasting commercial success (zeolites X and A). The substitution of the natural reactants by more reactive ones exemplifies well the geoinspiration concept, in which modifying the ‘geological’ route affords new materials with a similarly ‘good design’. Here, we are borrowing terms from a definition of biomimetics by Vincent who, incidentally, considered zeolites as nonbiological functional mimics of enzymes.^[9] Also incidentally, and far more surprisingly, natural zeolites have been considered to mimic in properties their synthetic counterparts.^[10]

Milton’s success relies on metastability: zeolites are in principle less stable than their denser counterparts (quartz in the case of pure silica compositions),^[11] and using more reactive reagents at a lower temperature increases the chances to stay away of the thermodynamic phase. When looking for new phases, especially zeolites with high porosity, kinetic control appears to be mandatory in order to stay away from the thermodynamically more stable phase.

3. Structure-Direction

The geoinspired strategy to discover new zeolite structures relies on the substitution of elements of the crystallization pool by others that may individually or collectively result in a different crystalline product under soft conditions, thus allowing kinetic control.^[3] The factors that govern the crystallization and drive it towards a given zeolite instead of any other zeolite or dense phase are generally called ‘structure-directing effects’. There have been many reviews on these topics, so we will just very briefly summarize these effects.

3.1 Organic cations

In natural zeolites, alkaline and alkaline-earth cations occluded in the framework voids provide the necessary counterbalance of the negative charge introduced in the framework by aluminum. They are typically hydrated and may of course display some structure-direction of their own. Since the pioneering work by Barrer and Denny,^[12] on one hand, and Kerr and coworkers on the other,^[13] organic cations have substituted, totally or in part, for inorganic cations in the crystallization of zeolites. There are two important effects to note: a) organic cations have typically a much lower charge-to-size ratio so they promote the formation of zeolites with a lower charge density, increasing in this way the zeolite stability; b) they may show a tendency to promote a particular zeolite structure. This effect may be more or less strong and specific and, hence, it may rank from a loose “pore filling effect” with a weak stabilization to a “template effect” with a strong stabilization and specificity and a strong geometrical correspondence between the organic cation and the void space it occupies.^[14] Neutral amines may also serve as structure-directing agents in the synthesis of pure or high silica materials.^[15] Phases intrinsically stable that crystallize in the absence of a strong directing agent and only need a mere pore filling are usually called “default structures”.^[16] The reader may find recent reviews on organic structure-directing agents in the literature.^[17]

Additionally, in certain instances, it is a subtle interplay between organic and inorganic cations and aluminium content what directs the crystallization towards a specific zeolite. This has been shown by Prof. S. B. Hong’s group, which provided several examples in which a given flexible organic cation

plus an inorganic cation that varies in nature or relative amount produced different zeolites. For instance, the flexible hexamethylpentanediammonium cation can produce up to four different zeolites (EUO, MRE, MTW or MWW) depending on the amount of Al and type and concentration of the inorganic cation used.^[18] A similar behaviour was observed for 1,4-bis(N-methylpyrrolidinium)butane, which was able to produce several zeolites, including the new zeolite TNU-9 only in a narrow range of Al and NaOH contents. These effects have been ascribed to the flexibility of the organic cation allowing different conformations depending on the nature and extent of organic-inorganic interactions.^[19]

3.2 The Fluoride Route and the *Zicovich-Wilson Effect*

In nature the crystallization of zeolites occurs in aqueous environments, normally in the presence of hydroxide as a mineralizer that increases the solubility of the reactants and catalyzes the breaking and formation of T-O bonds (T=Si, Al).^[20] The synthesis of zeolites started by emulating their natural crystallization in alkaline conditions. Later on, however, Flanigen and Patton made a major departure from conventional zeolite synthesis by substituting OH⁻ by F⁻.^[21] This afforded the crystallization at nearly neutral pH. The fluoride route proved very well suited for pure silica or very high silica materials,^[22] although it may be applied to other compositions,^[23] and yielded zeolites that, contrarily to high silica zeolites prepared in alkaline conditions,^[24] are essentially free of ‘connectivity defects’ (i.e., dangling Si-O bonds).^[25] We proved by water adsorption experiments that the calcined pure SiO₂ zeolites are strictly hydrophobic.^[26]

In addition, fluoride was proposed to exert some structure-direction of its own towards structures with small cages, particularly, structures with double four-ring cages (D4R).^[27] In a long and extremely fruitful collaboration with the late Prof. Claudio M. Zicovich-Wilson, a brilliant quantum chemist and our very close friend, he found out the reasons for this effect: the electronic interaction of fluoride and the organic cations with the silica framework induces a polarization of the Si-O bond, reducing the spatially oriented covalent character and, thus, making the SiO₂ framework more flexible in the as-made zeolite (Figure XX).^[28] We think this interpretation of structure-direction by fluoride should be termed the “Zicovich-Wilson effect” to honor his main contributor. We also call it ‘the Clau Effect’, because Clau was our friend’s nickname and also because ‘clau’ means ‘key’ in Valencian and we think this is truly a key effect to understand this system. Thus, D4R structures, that for silica compositions are significantly strained, are relaxed in the as-made state. Rather than specifically directing towards any given structure, we can consider that fluoride makes D4R-containing structures reachable for crystallization by enhancing their ionicity and flexibility. The effect was strong enough as to revert the order of stability of zeolite phases, allowing the in situ transformation of a dense and stable phase (TON) into a zeolite with a more open and, in the absence of guests, more strained structure (ITW).^[29] Subsequently, this kind of transformation was observed also for other phases.^[30,31] These observations constitute examples in which, out of several materials that actually crystallize, the final zeolite is selected by a thermodynamic rather than kinetic control.

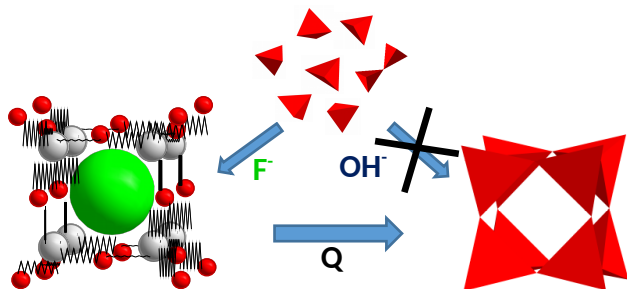


Figure 1. An illustration of the *Zicovich-Wilson (or Clau) effect*. Structures containing D4R units (right) are strained for pure silica zeolites because of the covalent character of the Si-O bond and the

rigid nature of the $[\text{SiO}_{4/2}]$ tetrahedra (red). Hence they cannot be directly synthesized by the hydroxide route. However, host-guest interactions in materials containing fluoride occluded in that cavity (left) make the bond more ionic and the structure more flexible and relaxed, rendered here as spring bonded atoms.^[28,29,30] The crystallization of those materials is thus possible by the fluoride route. Calcination at high enough temperatures removes the fluoride anion.^[32]

Table 1. Zeolites that could be synthesized for the first time as pure silica polymorphs by the fluoride route in highly concentrated conditions.

Zeolite	ZTF Code	known? ^[a]	Channels	Ref. ^[b]
Beta	-BEA	Yes ^[33]	3D-12MR	[34]
ITQ-3	ITE	No	2D-8MR	[35]
ITQ-4	IFR	No	1D-12MR	[36]
CHA	CHA	Yes ^[37]	3D-8MR	[38]
ITQ-9	STF	No	1D-10MR	[39]
ITQ-7	ISV	No	3D-12MR	[40]
ITQ-12	ITW	No	2D-8MR	[41]
ZSM-35	MTF	Yes ^[42]	1D-8MR	[43]
ITQ-14 ^[c]	BEC	Yes ^[44]	3D-12MR	[45]
ITQ-13	ITH	No	3D-10,10,9MR	[46]
HPM-1	STW	Yes ^[47]	3D-10,8,8MR	[48]
SSZ-55	ATS	Yes ^[49]	1D-12MR	[50]
ITQ-39	-ITN	No	3D-12,12,10MR	[51]
ITQ-29	LTA	Yes ^[7]	3D-8MR	[52]
SSZ-50	RTH	Yes ^[53]	2D-8MR	[54]
SSZ-37	NES	Yes ^[55]	2D-10MR	[56]
Eu-1	EUO	Yes ^[57]	1D-10MR+pockets	[58,59]
SSZ-33	CON	Yes ^[60]	3D-12,12,10MR	[56]
SSZ-73	SAS	Yes ^[61]	1D-8MR	[62]
ITQ-27	IWV	No	2D-12MR	[63]
SSZ-74	-SVR	No	3D-10MR	[64]
ITQ-24	IWR	Yes ^[65]	3D-12,10,10	[66]

[a] Whether or not the structure was previously realized with a different composition. [b] First report of the pure SiO₂ material by the fluoride route. [c] Pure silica BEC overgrown on pure silica *BEA.

3.3 Concentration and the *Villaescusa's Rule*

The use of fluoride in zeolite syntheses allowed to prepare defect-free pure silica zeolites, but it didn't produce at first many new structures. The most relevant was pure silica octadecasil (AST) because it was the first example of a pure silica zeolite containing D4R units.^[67] However, when we systematically studied the fluoride synthesis in highly concentrated conditions, a number of new zeolite structures as well as a number of new silica phases with already known topologies were obtained (see Table 1).^[22] From these studies a useful empirical rule, known as the Villaescusa's rule (named after one of the authors, LAV, *the man with a rule*),^[3] emerged: in the synthesis of pure silica zeolites by the fluoride route, the less dense phases are favored at the most concentrated conditions.^[22]

The Villaescusa's rule has been confirmed by many subsequent studies but still lacks a good explanation.^[60,68] It seems to hold not only for pure silica compositions but also for Germanate zeolites and aluminophosphate phases prepared by the fluoride route, as illustrated in Figure 2: the depicted dimethylbicyclooctane cation had been successfully used to crystallize several silicate zeolites, and shows the only exception to the rule that we are aware of so far (see the caption to the figure). Due to the Villaescusa's rule, the variation of the water content has become a must in the screening of synthesis conditions when searching for new zeolite structures by the fluoride route. When the synthesis was extended to germanate and aluminophosphate compositions, the less dense materials are still favored when decreasing the H₂O/TO₂ ratio (where T means in this case Si, Ge or Al and P). On the contrary, the applicability of the rule to the hydroxide route could be possibly severely hampered by the high pH causing a low stability of the organic cation as well as a largely increased solubility of silica.

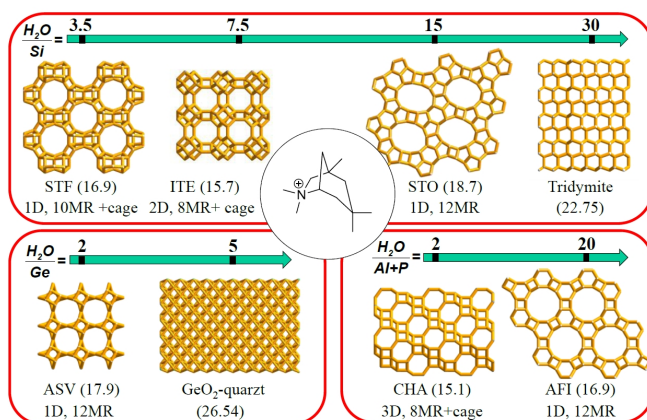


Figure 2. The general prevalence of the Villaescusa's rule in different systems is exemplified here by the fluoride mediated crystallization of three different kinds of framework compositions using 1,3,3,6,6-pentamethyl-6-azoniabicyclo[3.2.1]octane (DMABO⁺). For each one of the SiO₂, GeO₂ and AlPO₄ systems, the phase selected depends on the water/TO₂ ratio, with the less dense phases generally appearing as the concentration increases. The crystallization of STF (FD=16.9) at lower water/silica ratios than ITE (FD=15.7) may constitute the sole exception to the Villaescusa's rule that we are aware of. We note, nevertheless, that both zeolites occlude the same concentration of guests (2 SDA/32Si) and have the same micropore volume in their calcined state (0.21cm³/g).

3.4 Heteroatom substitution

The Si-O-T is generally considered to have a broad range of possible values, specially for T=Si and also Al, with not a large preference for a very specific value (i.e., the angular potential curve appears a

rather flat-bottomed well).^[69] In fact, zeolites are considered to possess a “floppy/stiff duality”, meaning that forces internal to the tetrahedra are stronger than those between tetrahedra.^[70] Thus, very frequently, zeolites can be taken as rigid tetrahedra joined through flexible hinges (see below). This may be in part responsible for the large compositional variability of zeolites as it is frequently possible to change a T atom by another without introducing much stress to the framework.

However, for some tetrahedral atoms this is clearly not the case. For instance, Be and Zn tend to prefer more acute Si-O-T angles, and have been shown to promote structures with 3MR. This was first observed in the natural berillosilicate zeolite Lovdarite,^[71] for which a synthetic analogue also exists,^[72] and because of a proposed relationship between maximum porosity and size of the smallest ring in the structure,^[73] this prompted a genuinely geoinspired approach to synthesize 3MR zeolites. This was initially undertaken by using Zn instead of Be, because Zn is safer (Be reactants are frequently toxic) and Zn silicates show certain similarities with Be silicates. The approach led to the synthesis of the zincosilicates VPI-7 (VSV),^[74] VPI-9 (VNI)^[75] and RUB-17 (RSN),^[76] all of which are porous zincosilicates with 3MR.

In these materials, Be or Zn belong to a 3MR and a high degree of order in the distribution of Si and Be or Zn over the available tetrahedral sites was observed.^[71,75,76,77,78] 3MR have been found in materials with similar or more exotic compositions: in natural berillosilicates *roggianite* (-RON),^[79] and *nabesite* (NAB),^[80] synthetic berillosilicate OBS-2 (OBW),^[81] natural berillophosphate *weinebenite* (WEI),^[82] natural zincosilicate *gaultite* (isomorphous to VPI-7, VSV),^[83] the synthetic beriloarsenate BOZ,^[84] and oxonitridophosphate-2 (NPT).^[85] And at least one lithium silicate with a true 4,2-3D zeolitic nature and containing 3MR, RUB-23, was also synthesized.^[86]

Germanium is also proposed to exert a certain structure-directing effect towards structures containing D4R units. To the best of our knowledge, this was first proposed in a PhD thesis supervised by one of the authors (MAC).^[45] That work led to a patent on a family of zeolites named as ITQ-5, synthesized with tetraethylammonium, fluoride and increasing Ge contents and showing a smooth transition from Beta to BEC (the then hypothetical polymorph C of zeolite Beta, containing a high density of D4R).^[87] Although at the time of the PhD defense (1997) the BEC end member was unpurified with some unknown phase, few months later it was prepared very pure for a Ge/(Ge+Si) molar fraction of 2/3, as seen in Figure 14 of ref. [88]. Later on, FOS-5, a pure germanate was reported,^[89] which is currently the “type material” for the BEC framework type.^[1]

Many germanates or germanosilicates with D4R and even a couple with D3R (double 3-membered ring) have been reported after that, and Ge shows a strong tendency to occupy positions in these units.^[90] It has been argued that Ge favors units with small Ge-O-T angles, because of its relatively long Ge-O bond distance and consequently acute Ge-O-T angles.^[91]

It is interesting to note that no natural zeolite of any composition exists that contain D4R units. D4R zeolites are genuine representatives of the geoinspired route to zeolites, as shown in Figure 3. The evolution of the discovery of D4R zeolites is marked by three major geoinspired events: the synthesis of LTA from reactive gels, the first fluoride containing pure silica D4R zeolite (AST) and the substitution of Si by Ge leading to D4R zeolites.

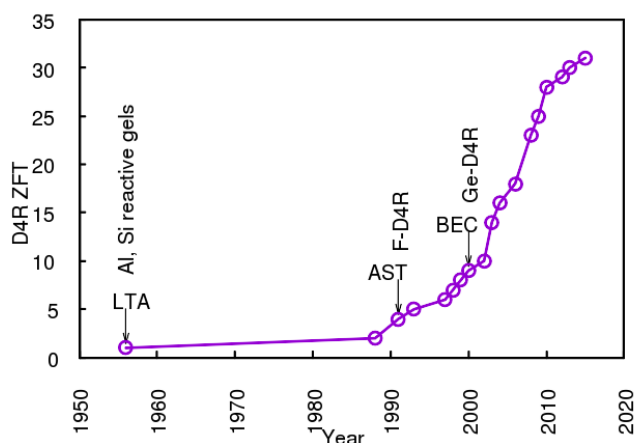


Figure 3. The evolution of the discovery of D4R containing zeolites. The year refers to the publication of the structure of the type material according to the Database of Zeolite Structures,^[1] and is not necessarily the year of the synthesis report.

3.5 The importance of being flexible

The large structure variability of zeolites is made possible by the flexibility of tetrahedral $(\text{Si,T})\text{O}_{4/2}$ frameworks. Such flexibility, understood as the capability to deform easily, largely depends on the topology and composition and may also depend on host-guest interactions, as commented above in relation to the Zicovich-Wilson effect. Recently, Sartbaeva et al. introduced the concept of “*flexibility window*” and emphasized the importance of flexibility in relation to the feasibility of particular zeolite topologies.^[92] There, the flexibility window was defined as the range of densities that a structure can withstand without losing the ideal shape of its constituent units, such as tetrahedra in the case of zeolites. Sartbaeva and coworkers conjecture that “realizable zeolites” need to have a wide flexibility window and they found, quite surprisingly, that actual zeolites tend to adopt a configuration close to the lowest density end within that window. This was explained as the result of a “Coulomb inflation”.

We have argued that the existence of a flexibility window may enhance the chance of achieving an optimal host-guest fit and, hence, of providing enough stabilization to make the material reachable for crystallization.^[93] And we have also argued that the flexibility that matters is that of the material that actually crystallizes (the as-made material, rather than the calcined one), so that host-guest interactions, including the Zicovich-Wilson effect, may provide additional flexibility to otherwise too rigid frameworks. This explains our synthesis of the chiral pure silica zeolite STW,^[48] despite predictions on the contrary that were based either on computational analysis relying on rigid tetrahedra interconnected through flexible joints,^[94] or on energetic calculations of guest-free phases.^[95]

4. Enhancing or frustrating structure-direction

Frequently, it is possible to shift structure-direction towards or away from a given zeolite structure either by combining several of the factors summarized above or by profiting from certain chemical and topological issues that we shall discuss below. This is particularly interesting when a set of crystallization conditions is unable to yield anything else than a “default structure”, i.e. a stable structure not very demanding of specific structure-direction (and, almost by definition, a probably known phase).^[16]

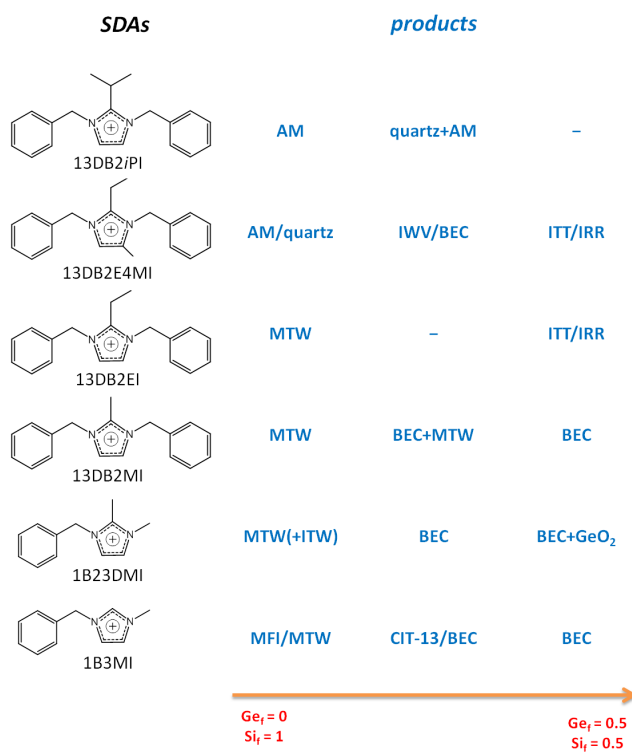


Figure 4. Summary of our most recent synthesis results using organic cations containing both imidazolium and benzyl moieties. AM stands for “amorphous phase”. The ITW appearing with 1B23DMI is the result of degradation of the cation to yield 1,2,3-trimethylimidazolium.^[96]

For instance, Figure 4 summarizes our study of structure direction by a number of organic cations containing both imidazolium and benzyl moieties. This set of cations do not appear to be able to provide a specific structure-direction in pure silica conditions, since almost all of them tend to yield only MTW, which we consider a default structure in pure silica conditions by the fluoride route. Only for the smallest cation, 1M3BI, under conditions of high concentration, MFI can be crystallized instead,^[96] while the two largest cations are unable to promote the crystallization of any phase.

The ITW impurities appearing with 1B23DMI are due to degradation and rearrangement of this cation to yield the much smaller 1,2,3-trimethylimidazolium (123TMI).^[96] When a fraction of Si is substituted by Ge, the tendency of Ge to promote D4R structures significantly changes the crystallization landscape: now, most syntheses produce BEC, which may be considered to be a default structure in fluoride mediated syntheses with Si and Ge under concentrated conditions. But, interestingly, four very recently discovered new phases also appeared: CIT-13, with the smallest cation and ITT, IRR and IWV with two of the largest cations (Figure 5). CIT-13 is a new extra large pore germanosilicate zeolite very recently reported, and it was synthesized with imidazolium cations having also benzyl moieties but containing additional methyl substituent in the benzene ring.^[97] The structure of CIT-13 contains D4R units, in addition to a bidimensional system of channels of 14 and 10 MR pores, respectively.^[98] With regard to IRR and ITT, here they appear as disordered intergrowths (Figure 5) when using two closely similar cations containing two benzyl moieties, 13DB2EI and 13DB2E4MI at high degree of Si substitution ($Ge_f=0.5$). The synthesis and structure of ITT and IRR were very recently reported.^[99] Both contain extra-large pores (18MR), as well as D4R and 3R units (D3R in the case of IRR) and were synthesized by the fluoride route in very highly concentrated conditions using Ge and organic SDAs without imidazolium moieties. The existence of disordered ITT/IRR materials is not surprising, since they both can be built from the same layers either by sharing the 3MR (ITT) or by linking the 3R to produce D3R (IRR).

In our experiments (Figure 4) we also obtained zeolite IWV but only with 13DB2E4MI at small degrees of Si/Ge substitutions. This large pore material was originally synthesized without Ge using a non-imidazolium SDA that also contains two benzene rings (dimethyldiphenylphosphonium).^[100] However, both SDA are radically different in size and nature. Finally, the cation with two benzyl moieties but with an isopropyl substituent at C(2) of the imidazole ring, 13DB2iPI, proved inactive as an SDA either in the presence or absence of Ge. The crystallization of dense TO2 phases (quartz and argutite) may suggest this cation is not able to interact strongly enough with the inorganic components of the synthesis mixture.

It is also possible to frustrate structure direction, i.e., to conduct the crystallization away from the expected structure, rather than towards any particular one. We have done this by at least two different routes, one based on topological considerations, the other on destabilizing the D4R units. To illustrate this, let's take the case of 123TMI, which is without any doubt the best SDA for the synthesis of ITW, a small pore zeolite that we have so far prepared with five different imidazolium cations via the fluoride route.^[17,29,30] ITW contains both D4R units (which for pure silica materials need to be synthesized with occluded fluoride) and 5MR. We could get rid of ITW by:

- shifting the composition to AlPO_4 , which cannot display topologies with odd number of rings (like the 5MR in ITW) because Al and P strictly alternate in AlPO_4 frameworks.^[101]

- avoiding the use of fluoride and working instead in aluminosilicate composition, so that D4R would be destabilized.

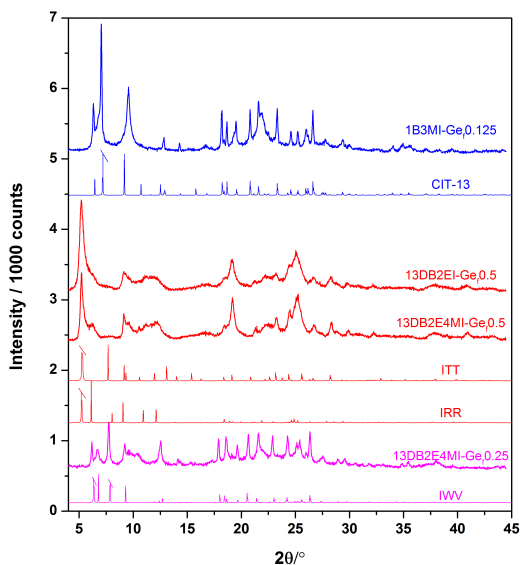


Figure 5. XRD patterns of new zeolites obtained according to Figure 4, with the simulated patterns included for comparison.

Of course, both strategies actually departed from ITW. The first strategy produced three AlPO_4 phases depending on concentration: a triclinic form of AlPO_4 -34 (CHA), a monoclinic form of AlPO_4 -5 (AFI) and the new HPM-3 material, with still an unknown structure.^[102] The second strategy allowed the synthesis of the aluminosilicate zeolite RTH.^[103]

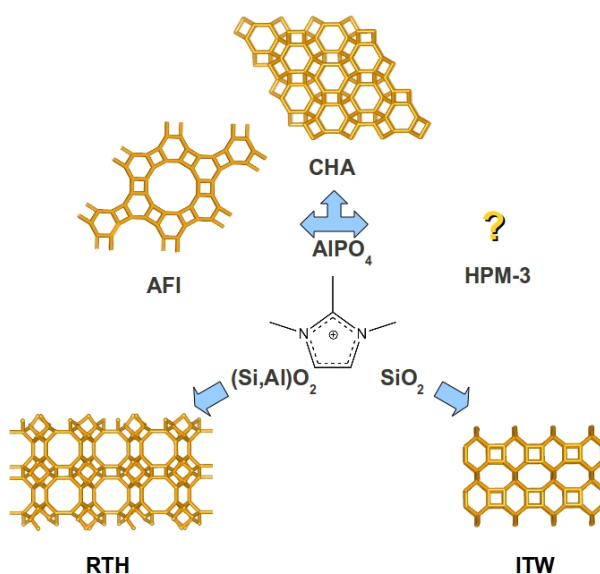


Figure 6. 1,2,3-dimethylimidazolium is the most specific SDA for the synthesis of pure silica ITW (bottom right). However, this structure-direction is frustrated, and other materials crystallizes instead, when Al replaces F for charge balance, and when an structure with only even rings (AlPO_4) is targeted.

5. Homochiral zeolites

As a final example showing how it is possible to drive zeolite crystallization towards new materials with improved properties, we shall mention the recent production of scalemic conglomerates of zeolite STW by Davis's group.^[104] After discovering that a particular imidazolium-based dication would yield STW with both imidazolium moieties in adjacent cages, a modified chiral dication in homochiral form was used to produce enantiomerically enriched zeolites. In short, by enhancing the probability that the next cage is tilted by some 60° in one, rather than the other, direction, the crystallization was preferentially driven to one enantiomer over the other. The crystallized (alumino)germanosilicates were shown to enantioselectively adsorb a chiral adsorbate (2-butanol) and to catalyze the ring opening of epoxides with moderate but significant enantiomeric excess. Given that germanosilicates show moderate thermal and hydrothermal stability and that the improved flexibility imparted by Ge may play in detriment of the necessary close fit warranting enantiomeric discrimination, we believe an enhanced enantiomeric selectivity in adsorption and catalysis could be achieved with pure silica STW, and we have made some advances in this respect that will be reported in due time.^[31]

Acknowledgements

Financial support by the Spanish Ministry of Economy and Competitiveness (MAT2015-71117-R and AGL2015-70235-C2-R) is acknowledged. P. L. is grateful to the China Scholarship Council (CSC) for a fellowship and to the Dalian Institute of Chemical Physics for permission to leave. Thanks are also due to Wikimedia Commons and Mr. A. T. Chang for the picture of the hot springs included in the frontispiece.

Keywords: Zeolites • Synthesis • Structure-direction • Geoinspiration

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