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## What drives porosity in aluminosilicate zeolites?

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Discovery of their commercial potential gave rise to a massive implementation of zeolites in industrial (petro-)chemical processes. Their robustness and molecular scale porosity in combination with acidic and/or ion exchange properties makes zeolites nearly indispensable for most of these applications. This highlight explores the origins of zeolite porosity. As microporosity is an inherent feature of the formed topology, we emphasize the link with phase selection. For zeolites, phase selection is driven by competition between water and framework elements to coordinate with extra-framework species. This competition is important in the final product, where such coordinations provide thermodynamic stability, as well as in the crystallization medium where supermolecular structures can play a templating role. Synthesis experiments using hydrated silicate ionic liquids show that limited water availability prompts the formation of less porous (or even dense) phases, while moderate hydration supports the development of more open frameworks. Understanding these interactions is key to deepening the insight into zeolite genesis and can guide strategies for tailoring material properties for industrial applications.

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## Introduction

Zeolites are naturally occurring crystalline aluminosilicates with unique frameworks of interconnected pores and channels. Since the start of their commercial production in the 1950's, they have evolved into critical players in industrial processes involving catalysis, adsorption and/or ion exchange, owing to their vast surface area, immense pore volume and chemical properties.<sup>1</sup>

Zeolites are known for their extremely high porosity. Yet it is intrinsically impossible to crystallize empty space. So where does the porosity of zeolites originate? A superficial answer can be given easily: zeolites inevitably crystallize as dense phases, their pores filled with water and other pore-filling agents. Porosity is only generated following their initial crystallization, by removal of non-framework species<sup>2,3</sup> or even framework elements from their structure.<sup>4</sup> Why zeolite frameworks incorporate extra-framework species during crystallization, encapsulating them in pore, channel and cage-like framework structures is the topic of this highlight. Starting with a brief discussion about high-silica materials, the manuscript outlines how the interplay of enthalpy and entropy impacts the formation of high-alumina zeolites. Structural insights into this subject were compiled from recent work on zeolite formation in hydrated silicate ionic

liquids (HSILs), which provide a convenient avenue to investigate such relations. Emphasis is placed on the templating effect of water and cations, as well as on the temperature-dependent modulation of these effects by water. In addition to modulating phase selection and Si/Al ratio, water also acts as a catalyst for the formation of (alumino-)silicate bonds. This aspect is specifically addressed in the final section of this highlight.

## Siliceous zeolites

From a thermodynamic perspective, the enthalpy of formation for purely siliceous (empty) zeolites falls within a narrow range, metastable compared to  $\alpha$ -quartz by 7 to about 15 kJ mol<sup>-1</sup> (Fig. 1(a), "Silica Polymorphs"). Interestingly, also amorphous silica fits into this window (Fig. 1(b)).<sup>5,6</sup> The calorimetric data thus suggests that transforming silica into a zeolite framework is not energetically hindered under standard synthesis conditions.<sup>5,7</sup> Also entropic factors, which can be estimated *via* adiabatic calorimetry, are not dominating zeolite stability. Boerio-Goates and coworkers showed that the entropy-term is identical for at least 4 different topologies (BEA, MFI, MTT and FAU) at relevant temperatures (298 K), owing to the similarity of the strong tetrahedral silicon framework.<sup>8</sup> The organic structure-directing agents (OSDA's) required to form high- and all-silica materials are therefore templating structures with intrinsic stability. Rather than enabling structures that otherwise would be very unstable, they provide favourable pathways by stabilizing specific framework motives (pores,

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Fig. 1 Enthalpy of formation of different zeolite and dense materials. The introduction of Al-M<sup>+</sup> in the framework makes materials significantly more stable compared to their siliceous counterparts. Only when the energy of hydration (typical values are presented in blue) is also considered, are porous materials significantly more stable than the dense counterparts. The data is collected from Navrotsky and coworkers, ref. 7.

channels, cages) through a combination of coulombic and dispersion interactions.<sup>5</sup> Looking at the stability of the zeolite inside the synthesis environment, also considering the liquid silicate speciation, should therefore provide a better insight into the phase selection of siliceous zeolites.<sup>7</sup>

OSDA's are typically organic quaternary ammonium cations that remain encapsulated after synthesis and thus require thermal or chemical decomposition to open the pores.<sup>2,3,9</sup> Although clear trends between the structure of these molecules and the final topology of a zeolite material have been observed in some cases,<sup>10–12</sup> a complete rationalization remains challenging. Synthesis-related factors such as concentration, charge density and template flexibility play vital roles,<sup>10,11,13,14</sup> again stressing the need to consider the synthesis medium.

Since the energetic aspects of templating by organic molecules have already been discussed extensively in literature, in particular by the group of Navrotsky,<sup>5–8,15–17</sup> this highlight will further focus on the case of aluminosilicate zeolites with a low Si/Al ratio, which crystallize in the absence of organic species. Also generation of randomly distributed mesopores by post-synthetic modification<sup>4,18</sup> will not be discussed.

## Stability of aluminosilicate zeolites: cations and aluminium

The topological description of zeolites is based on the concept of 4-coordinated nets, consisting of corner-sharing tetrahedra, with typical framework densities ranging between 12 and 21 tetrahedra per 1000 Å<sup>3</sup>. This implies that many different topologies with different pore volumes exist, as evident from the zeolite database of the International Zeolite Association (IZA).<sup>19</sup> Understanding the origins of varying porosity in zeolites in general, and high alumina zeolites specifically, therefore comes down to a discussion on phase selection.

The incorporation of heteroatoms such as aluminium, having a different valence than silicon, induces a permanent

charge in the silicate network which has to be compensated by extra-framework cations. Residing in the zeolite structure, the cations coordinate to oxygen atoms present in the framework and/or hydrating water molecules in the pore space. As cations vary in ionic potential (charge/size), softness and hydration energies, they prefer different coordination environments.<sup>7,20</sup> It is therefore not surprising that some zeolites are only forming with specific cations (or combinations of cations),<sup>21–23</sup> stabilizing specific framework motifs. Na<sup>+</sup> for example typically resides in 6-rings, often also including water as complementing coordination partner, whereas K<sup>+</sup> has a stronger preference for 8-rings, with lower tendency for water coordination. Cs<sup>+</sup>, being even larger and more polarizable, usually resides in cages where it can coordinate to 8 or more framework oxygens, having no or very few water molecules in the first coordination sphere.<sup>24</sup> Besides hydration water and framework oxygens, cations can also partly fulfil their coordination requirements with other molecules, e.g. anions or gasses.<sup>25–27</sup>

The inclusion of more cations in a given framework results in a more densely packed pore space and thus more stable structures.<sup>28</sup> In other words, it is enthalpically favourable to introduce more aluminium in a given framework so that more cations can be introduced. Of course, this is limited to a Si/Al ratio of unity, as dictated by the Löwenstein rule, which prohibits the formation of Al–O–Al bonds. Yet, more often than not, it is challenging or even impossible to synthesize frameworks with such a high aluminium content. Each topology only offers a limited number of viable cation positions, resulting in a maximal Al-content which can be charge-balanced. For example, the unit cell of K-MER, presented in the highest topological symmetry, has 12 positions for K and 32 for framework elements. A full cation occupancy would require 12 Al-atoms in the framework, resulting in a Si/Al ratio of 1.7, a commonly observed value for K-MER.<sup>24</sup> Some topologies such as EDI, CAN or SOD, do have more cation positions than can be compensated for by the framework. By incorporating superions consisting of cations, anions and water,<sup>26</sup> these





**Fig. 2** At the lowest possible Si/Al ratio of a given framework, all framework oxygens are in contact with at least one cation, so the whole framework is fully encased by charge compensating cations. Coordination spheres of cations are complemented by water molecules and larger volumes (e.g. the 12-r channel of LTL contain a hydrogen bonded network of water molecules). The T sites are given in black, the framework oxygens in red, the coordination polyhedral in violet and hydration water in grey, also showing mutual H-bonding distances.



**Fig. 3** The coordination environment of cations and water in the zeolite framework. JBW (left) features chains of alternating K ions and water molecules.<sup>21</sup> ABW (middle) is templated rather by  $\text{Li}(\text{H}_2\text{O})^+$  than anhydrous  $\text{Li}$ .<sup>20</sup> Hydroxy-sodalite (right) features Zundel-like ions  $[\text{Na}_4\text{H}_3\text{O}_2]^{3+}$ , motives that can be found in the synthesis medium as well.<sup>26</sup> The water oxygens are indicated in blue, K, Li and Na ions in purple, green and yellow. Framework oxygens are presented in red for clarity. Si and Al are shown in steel blue and grey.

topologies can still fully occupy all cation positions without violating the Löwenstein rule.<sup>26,29–33</sup>

As stated earlier, cations prefer different coordination environments. The number of cation positions in a given topology is therefore also dependent on the cation type. ANA forms a prime example to illustrate this effect. It forms with at least 6 different cations and exhibits a very large compositional window.<sup>34,35</sup> Comparing pollucite (Cs-ANA) with analcime (Na-ANA) for instance, the cations have distinctly different preferred cation positions so that it is possible to include twice as many  $\text{Na}^+$  in the ANA topology than  $\text{Cs}^+$ . The resulting minimal Si/Al ratio is therefore 1 for analcime and 2 for pollucite. In leucite (K-ANA) the cations occupy the same positions as those found in pollucite. The minimal Si/Al ratio is therefore also 2.<sup>24</sup>

While the lower bounds are determined by the topology, it is theoretically possible for any framework to be fully siliceous by virtually substituting the framework Al and their charge-compensating cation for Si and water. However, this leads to framework oxygen atoms not interacting with a

cation close by, and a less efficient pore filling. Indeed, experimentally, we find that the upper compositional limit is determined by the lower limit of another topology.<sup>24,34</sup> Revisiting MER, literature describes a Si/Al ratio window of 1.7–2.3, the upper limit determined by the lower limit of LTL. At a framework composition of 2.3, LTL exhibits full cation occupancy, whereas MER would only have about 80% of its cation positions occupied.<sup>24</sup> Consequently, at this composition, the LTL topology is more densely packed and thus becomes more stable than MER. These observations exemplify the dominant impact of the Coulombic component of the crystal energy on the enthalpy of formation, suggesting that for a given Si/Al ratio zeolite-forming systems minimize the occurrence of unoccupied cation positions to maximize Coulombic energy, while obtaining a homogeneous charge distribution.

As a rule of thumb, for a given Si/Al ratio and cation, the topology with the densest packing will form. Additionally, an alkali-zeolite with a Si/Al ratio allowing full occupation of all viable cation sites, all framework oxygen atoms are in



interaction distance to at least one cation. The coordination of cations is completed by water molecules if pores space is not adequately filled (Fig. 2).

Finally, it is also worth mentioning that the cation's coordination environment co-determines the preferred aluminium positions in the framework.<sup>36</sup>

## Stability of aluminosilicate zeolites: water

Fig. 1 demonstrates that the introduction of aluminum, accompanied by cations, is often sufficient to make the formation of aluminosilicates more favourable than that of quartz. The figure does not discriminate between frameworks and counterions to highlight the general trends, only a FAU-series with different cations, yet the same Si/Al ratio, is highlighted to demonstrate that also the cation-type co-determines stability. While topologies can differ significantly in stability for a given framework composition, the anhydrous porous frameworks still have a comparable formation enthalpy as the respective dense phases (Fig. 1). The difference is overcome by the favourable hydration enthalpy by water (20–40 kJ mol<sup>-1</sup> near room temperature).<sup>7</sup> For example, in absence of water Li-[AlSiO<sub>4</sub>] mixtures crystallizes as doped quartz, yet the same mixture forms Li-ABW when water is available.<sup>20</sup> Zeolites generate an environment where individual water molecules can coordinate with cations and hydrogen bond to siloxane bridges. Such configurations efficiently fill the pore space and assist in screening of the positive charge of adjacent cations.<sup>7,21</sup> It is thus not only direct ionic framework-cation coordination, but also hydrogen bonding interactions that stabilize the structure.<sup>20,28,37</sup> If no water is available to shield the cations, they require to be encapsulated entirely by framework elements, resulting in the formation of anhydrous, dense topologies.<sup>24</sup> In zeolites with a large diameter pores, *e.g.* LTL (Fig. 2), already at relatively low concentrations, water almost behaves as bulk rather cation hydration or confined water.<sup>7</sup> Such phenomena could be evaluated by probing the dielectric properties of the enclosed water using combined NMR/impedance spectroscopy.<sup>38</sup> Several zeolites have both kinds of water sites, so that water incorporation into a dehydrated zeolite framework does not follow a single mechanism. When it is distributed in specific positions, hydration shows distinct phases with a stoichiometric water content, as is the case for instance for Leonhardtite.<sup>39</sup> In other cases, hydration appears to be a continuous process as is observed for clinoptilolite.<sup>7</sup> Independent on the coordination environment, the hydration is more exothermic at low water contents and becomes increasingly less favourable when the amount of incorporated water increases. Even though the enthalpy of hydration is negative for all cations, reducing the freedom of water is costly in terms of entropy. While this is a relatively small component at low temperatures, it starts to dominate around

500 K, so that the Gibbs free energy becomes positive, favouring formation of more dense aluminosilicates.<sup>7</sup>

Entropic considerations also explain why dehydration of a zeolite outside of the synthesis medium often leads to structural changes. While these can be fully reversible,<sup>27,40,41</sup> in other cases they corrupt the structural integrity of the framework, causing collapse.<sup>42</sup> JBW, composed of distinct 6- and 8-ring channels, forms an interesting case. Its 6-ring channels are occupied by Na<sup>+</sup>, while the 8-ring channels are occupied by alternating water and K ions (Fig. 3; left). The isolated water molecules are well positioned to hydrogen bond to the zeolite framework and are in interaction distance to K-ions, effectively stabilizing the structure. Upon dehydrating the framework at 473 K under vacuum, the zigzag chains separating the 8R channels rotate, resulting in a diagonal contraction of the channel. Interestingly, these structural changes are irreversible (Fig. 4). Even though, upon rehydration, the framework does return to its original chemical composition, the combination of XRD and <sup>1</sup>H-NMR analysis revealed a changed framework structure and pore-water ordering.<sup>21</sup> Note that the structural strain invoked by dehydration offers opportunities for adsorption of gas molecules which can be beneficial for carbon-capture applications.<sup>27,43,44</sup>

## Stability relative to the liquid

In the final step, the thermodynamics of zeolite genesis should be considered in relation to the crystallizing medium. This approach suggests that a framework that does not naturally form in a given liquid will dissolve in that liquid.<sup>45</sup> This led to the development of 'interzeolite conversion', a well-established synthesis route with various experimental variations, in which one or more zeolites serve as precursors for the formation of a new framework.<sup>4,25,46–48</sup>

Secondly, this also implies that the liquid features responsible for structuring the zeolite, should be present in the liquid already. Unfortunately, silicate speciation is notoriously complex to monitor, except for a few highly alkaline cases where the silicates are restricted to small oligomers.<sup>45,49–51</sup> Therefore, it is also challenging to assess the growth units and thus the crystallization mechanism.



Fig. 4 Removal of the hydration water in JBW leads to irreversible structural changes.



## Highlight

Even though there is experimental support for multiple crystallization pathways,<sup>52,53</sup> it is generally accepted that zeolites formation is critically affected by ion association of (alumino-)silicate species and cations.<sup>54–58</sup> In other words, insight into this phenomenon can help to bridge the liquid and the solid structure.

In a given system, the degree of ion association is dependent on the cation type, the system temperature and the chemical composition.<sup>49</sup> Using hydrated silicate ionic liquids (HSILs), Asselman and coworkers investigated phase selection in water-deprived systems.<sup>34,59</sup> In the most extreme case, the nominal cation hydration ( $H_2O/KOH$ ) was as low as 4, below the inner coordination number of alkali cations in hydrated solutions, which is 4–8.<sup>60</sup> Considering that also alumino-silicate oligomers are hydrated, we can safely assume that the amount of water in the system is insufficient to fully hydrate the ions. Hydrothermal treatment of a K-containing system at high temperatures (170 °C in this study) results in the formation of Megakalsilite (MEGA). MEGA is an anhydrous potassium feldspar, characterized by a Si/Al ratio of 1. A more moderate thermal treatment (90 °C) yields a hydrated K-GIS phase with a Si/Al ratio of 1.4.<sup>34,59</sup> Similar to the assessment made for zeolite materials removed from their synthesis medium, framework hydration is thus also during synthesis governed by a balance between hydration enthalpy and increasing entropy associated to free water. At synthesis temperatures as high as 170 °C, the entropic penalty of hydration is clearly too large, resulting in denser frameworks with low water content or anhydrous nature. At lower temperatures hydration enthalpy outweighs entropy, so that hydration remains favourable, yielding more porous, hydrated zeolites. The same effect is even visible between different zeolite materials. Zeolites synthesized at higher synthesis temperatures generally feature lower water contents in the as synthesised zeolites, consequently resulting in denser frameworks. Maldonado and coworkers for example describe how an identical synthesis mixture employing Na as charge-balancing ion crystallizes FAU at 65 °C, GIS at 100 °C and ANA at 180 °C.<sup>61</sup> The progression is indeed accompanied by an increasing density. Further support for this argument is also given by Chawla for potassium systems.<sup>62</sup> This study finds zeolites with a higher porosity such as BPH at lower temperatures (<85 °C), while similar systems at higher temperatures form topologies with a higher cation-framework coordination number such as EDI. We can therefore deduce that also here the high temperature favours cation-silicate interactions over cation hydration. Note that the synthesis temperature not only impacts Si/Al ratio and porosity, it has been reported to also influence the supersaturation and thereby the growth mechanism of MER, shifting from “birth-and-spread” to spiral growth when increasing the temperature from 90 °C to 175 °C.<sup>63</sup>

Also the composition of the synthesis medium is a critical factor influencing ion association. While hard cations, such as Na, have a strong affinity for water, in the framework as well as in the synthesis medium, softer cations, such as Cs,

prefer interactions with silicates, often resulting in anhydrous, dense frameworks like pollucite.<sup>24,34</sup> Water also plays an important role determining the framework composition and thus porosity. The previously mentioned study reported by Asselman also investigates the effect of (moderate) dilution on the synthesis product.<sup>59</sup> For nominal cation hydration ratios of 8 and 12 in the synthesis medium, the resulting zeolite topology is MER, independent of the synthesis temperature. At 170 °C, the Si/Al ratio of the products was determined as 1.9 and 2.4, respectively. At 90 °C, the Si/Al range obtained for similar synthesis mixtures spans 1.6 to 2.<sup>34,59</sup> With a higher water content in the synthesis medium, the entropic penalty of cation hydration clearly is less severe so that the product is a porous structure.

The effects of temperature and composition indeed show a significant role for hydration and ion association in the synthesis liquid. The competition between alumino-silicate oligomers and water to interact with cations affects locally and temporally stable structures, which already exhibit configurations related to framework elements. Such configurations can be brought into context with the concept of pre-nucleation clusters as described for the formation of gismondine from Na-HSIL. When considering the structure directing role of (inorganic) cations, these cannot be considered as isolated entities.<sup>20,57</sup> In a few individual cases it was possible to identify the units responsible for structuring the zeolite framework. One of these cases is hydroxy-sodalite, which only forms in presence of an abundance of NaOH (molar concentrations up to 22 M) where super-ionic configurations are prevalent.<sup>26</sup> These configurations are composed of four sodium ions, centred around a Zundel- or extended Zundel-ion ( $H_3O_2^-$  or  $H_5O_3^-$ ). The structural resemblance of solution species and pore-filling agents strongly indicates the option of a structuring role of super-ions associated to alumino-silicate species rather than isolated alkali metals (Fig. 3; right). Also halite sodalites are known to form super-ions that template the final structure.<sup>20</sup> Another example is presented by Li-ABW, where the hydration enthalpy of Li and the water positions in the cage indicate that  $Li(H_2O)^+$  is more likely to be the structuring agent, rather than anhydrous Li (Fig. 3; middle).<sup>20</sup>

While a full molecular understanding of the structure directing role of the cations remains obsolete, the direct link between the composition of the synthesis liquids and the composition and porosity of the final zeolite products is clear.<sup>34,45,64</sup> Water impacts this process by competing with alumino-silicate species to coordinate with cations. This phenomenon can be monitored using (*in situ*) differential impedance spectroscopy (DIS),<sup>65–67</sup> provided that the data is not obscured by other charge-modulating processes. Hydrated silicate ionic liquids provide a homogeneous synthesis medium, allowing individual parameters to be studied in a straightforward way.<sup>68,69</sup> Even though this report mainly highlights the role of water, also the alkalinity of the crystallization liquid is known to crucially affect the



speciation of the aluminosilicates (connectivity and ionization) and the final framework composition.<sup>24,34,49,64</sup> The combination of such a controllable synthesis platform and dedicated measurement equipment provides a promising avenue to deepen our understanding of the formation of porous silicates.

## Thermodynamics vs. the Ostwald rule of stages

It is often suggested that also kinetic factors influence phase selection, for instance to explain the occurrence of mixtures of different phase. The so-called Ostwald rule of stages, assumes that more stable phases are kinetically hindered, allowing less stable structures to form first. Higher temperatures or longer crystallization times would therefore inevitably lead to the formation of the most stable structure. If one assumes the increased temperature does not influence the state of the liquid and only provides additional energy to overcome kinetic barriers, this would lead to structures with the lowest molar volume.

Even though in a limited number of cases, kinetics could indeed influence the evolution of a crystallization system, its impact is almost always translated into a thermodynamic effect. If a certain dense or porous, crystalline or amorphous solid phase forms kinetically, before formation of the thermodynamically stable phase(s), phase separation of such kinetic phase always affects the composition of the relevant supernatant. The next phase that forms, naturally exhibits a lower solubility, turning the initial effect into a thermodynamic effect, often leading to the re-dissolution of the initially formed phase in favor of the thermodynamically more stable phase.

Gel-based syntheses are inherently non-equilibrium systems, featuring large compositional changes during the crystallization. In such systems, such dissolution-precipitation sequences are therefore more likely to occur. Such a process more resembles interzeolite conversion than Ostwald's rule of stages. This is highlighted by the fact that products of (partial) interzeolite conversion syntheses correspond very well to HSIL-based syntheses with comparable compositions (Fig. 5).<sup>4,34,48</sup> As one can safely assume kinetic barriers to be totally different for two completely different crystallization routes this observation presents another argument in favor of the primarily thermodynamic nature of phase selection.

The elegance of the HSIL-based zeolite crystallization systems is their homogeneous nature, which easily allows to determine when systems reach equilibrium. It provides options to easily detect the the impact of any kinetic effects. Despite the general validity of the previous statement, there is however one potential exception. If a kinetically preferred phase would transform, by ultra-fast dissolution-precipitation,<sup>70</sup> into a thermodynamically preferred phase with exactly the same chemical composition as the kinetically preferred phase, the kinetic influence on the formation of



Fig. 5 The HSIL-based phase selection (ref. 34, circles) is compared against interzeolite conversions published by Van Tendeloo in 2013 (ref. 48, squares) and 2017 (ref. 4, triangles). The good match is an additional argument for a thermodynamic treatment of phase selection.

the initial phase could be missed. Hitherto, there are however no indications for the occurrence of such behavior, not in HSIL-systems, nor in inter-zeolite conversion systems. Changes were always observed in the chemical composition of the supernatant liquid, both during initial dissolution of the starting zeolite, as well as during the crystallization of the new phase.<sup>4</sup>

This means that the occurrence of progressively denser phases with increasing temperature or crystallization time is most likely a thermodynamic, rather than a kinetic (Ostwald) effect. Temperature-induced changes can be readily explained by the balance between enthalpic gain and the entropic penalty of hydration, as elaborated above. Phase progression during prolonged crystallization should, if observed, be considered in relation to changes in the crystallization liquid, which can induce recrystallization.

## Water as oxolation catalyst

Reducing the water content beyond the HSIL domain reveals a second function of water: its role as catalyst for the formation of Si–O–T bonds (T = Al or Si). These syntheses, often referred to as ‘solvent-free’ or ‘solid-state’ synthesis, minimize aqueous waste and reduce the pressures typically generated during traditional hydrothermal conversion, making them attractive for industrial applications.<sup>71–73</sup> Ren and coworkers showed that the use of sodium metasilicate, containing 1–4.5 water per Na<sup>+</sup>, are excellent silicon sources for at least 6 different zeolites (MFI, SOD, MTN, MOR, BEA, FAU) under solvent-free conditions.<sup>71</sup> Note that the hydrated metasilicates typically used in these solid-state syntheses are essentially crystallized hydrated alkali silicates with melting points in the range of synthesis conditions and compositions extremely close to the most concentrated HSILs.<sup>49,74</sup>

Although this route can effectively produce zeolite materials, completely eliminating water—*i.e.*, achieving



## Highlight

solvent-free synthesis from fully anhydrous silicate sources—is not possible without the introduction of fluoride.<sup>7,3</sup> Water is namely indispensable as a catalyst for oxolation reactions enabling formation of siloxane bridges from deprotonated silanol groups. In presence of fluoride, silicate condensation can occur *via* a completely different mechanism than in presence of water, involving penta- and hexa-coordinated silicate cations. This enables zeolite formation from fully anhydrous silicate sources as long as organic SDAs are available to fill the pore space.

## Conclusions

Water plays a vital role in the creation of porous aluminosilicates. Their interaction energy benefits the thermodynamic stability *via* a structuring role in tandem with the cations. Water can coordinate with the framework and shields the charges of neighbouring cations. At high temperatures, the entropic penalty related to constrained water in a zeolite material exceeds the enthalpic gains, often resulting in deformed or even collapsed structures.

The structure forming role of water already manifests in the synthesis liquid. Although the link between the solid and liquid phases has been established for certain cases, such as hydroxy-sodalite and Na-GIS, the formation of most high-alumina zeolites can currently only be explained using empirical rules. Lower temperatures, higher water content, as well as hard cations promote hydrated cation-framework assemblies, resulting in more porous materials, while denser frameworks are typically observed at high temperatures, low water availability and softer cations in the medium. Such observations are commonly misinterpreted as kinetics, using the Ostwald rule of stages.

Finally, water availability is a crucial factor in fluoride-free zeolite formation. Full anhydrous conversions are not yet reported as the water is required for its catalytic role.

## Data availability

The data supporting the findings of this study are available in the referenced original published materials. As no new data were generated or analyzed in this study, data sharing does not apply.

## Author contributions

D. V. and E. B.: conceptualization; D. V., A. R and E. B.: writing – original draft preparation; C. K. and E. B.: writing – review and editing, supervision and funding Acquisition.

## Conflicts of interest

“There are no conflicts to declare”.

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