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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.¹

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^{2,3} or even framework elements from their structure.⁴ 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.

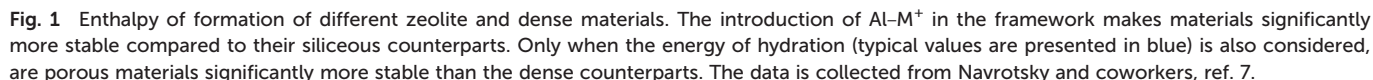
Siliceous zeolites

From a thermodynamic perspective, the enthalpy of formation for purely siliceous (empty) zeolites falls within a narrow range, metastable compared to α -quartz by 7 to about 15 kJ mol⁻¹ (Fig. 1(a), "Silica Polymorphs"). Interestingly, also amorphous silica fits into this window (Fig. 1(b)).^{5,6} The calorimetric data thus suggests that transforming silica into a zeolite framework is not energetically hindered under standard synthesis conditions.^{5,7} 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.⁸ 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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Since the energetic aspects of templating by organic molecules have already been discussed extensively in literature, in particular by the group of Navrotsky,^{5-8,15-17} 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^{4,18} will not be discussed.

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

The inclusion of more cations in a given framework results in a more densely packed pore space and thus more stable structures.²⁸ 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.²⁴ 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,²⁶ these

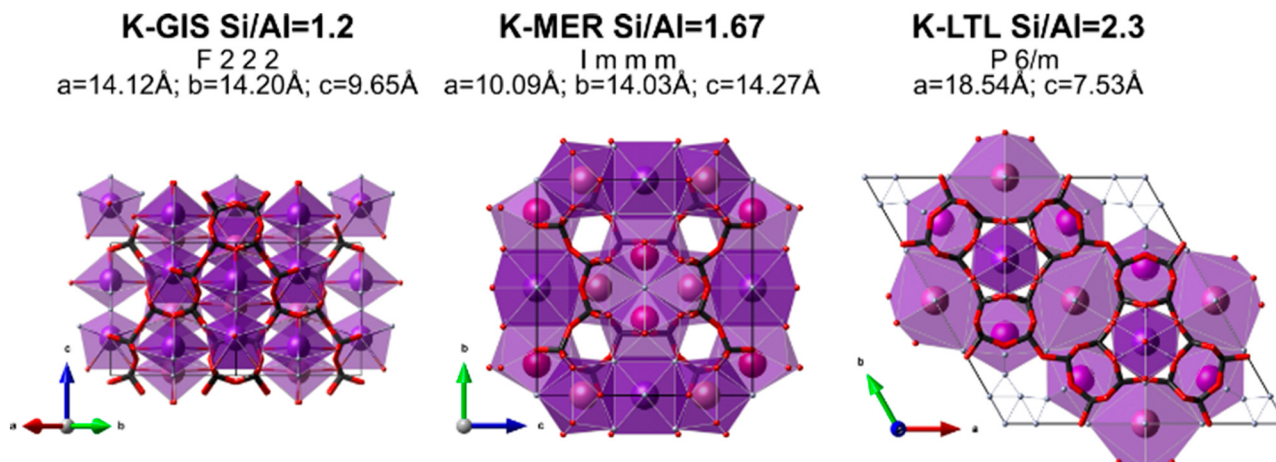


Fig. 2 At the lowest possible Si/Al ratio of a given framework, all framework oxygens are in contact with at least one cation, so the whole framework is fully encased by charge compensating cations. Coordination spheres of cations are complemented by water molecules and larger volumes (e.g. the 12-r 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.

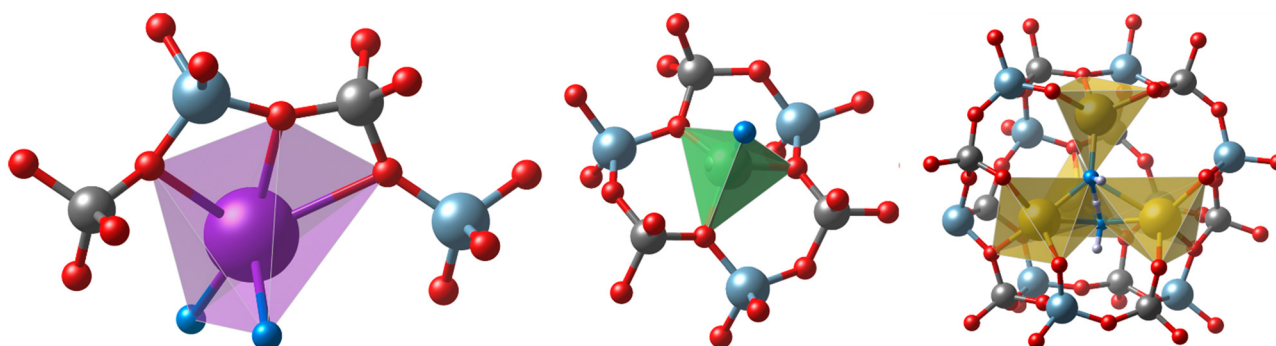


Fig. 3 The coordination environment of cations and water in the zeolite framework. JBW (left) features chains of alternating K ions and water molecules.²¹ ABW (middle) is templated rather by $\text{Li}(\text{H}_2\text{O})^+$ than anhydrous Li.²⁰ Hydroxy-sodalite (right) features Zundel-like ions $[\text{Na}_4\text{H}_3\text{O}_2]^{3+}$, motives that can be found in the synthesis medium as well.²⁶ 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.^{26,29–33}

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.^{34,35} 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 Na^+ in the ANA topology than 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 2.²⁴

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.^{24,34} 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.²⁴ 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



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In a given system, the degree of ion association is dependent on the cation type, the system temperature and the chemical composition.⁴⁹ Using hydrated silicate ionic liquids (HSILs), Asselman and coworkers investigated phase selection in water-deprived systems.^{34,59} In the most extreme case, the nominal cation hydration ($\text{H}_2\text{O}/\text{KOH}$) was as low as 4, below the inner coordination number of alkali cations in hydrated solutions, which is 4–8.⁶⁰ 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.^{34,59} 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.⁶¹ The progression is indeed accompanied by an increasing density. Further support for this argument is also given by Chawla for potassium systems.⁶² 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.⁶³

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.^{24,34} 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.⁵⁹ 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.^{34,59} 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 aluminosilicate 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.^{20,57} In a few individual cases was it 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.²⁶ 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 aluminosilicate species rather than isolated alkali metals (Fig. 3; right). Also halite sodalites are known to form super-ions that template the final structure.²⁰ Another example is presented by Li-ABW, where the hydration enthalpy of Li and the water positions in the cage indicate that $\text{Li}(\text{H}_2\text{O})^+$ is more likely to be the structuring agent, rather than anhydrous Li (Fig. 3; middle).²⁰

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.^{34,45,64} Water impacts this process by competing with aluminosilicate species to coordinate with cations. This phenomenon can be monitored using (*in situ*) differential impedance spectroscopy (DIS),^{65–67} 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.^{68,69} 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.^{24,34,49,64} 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-reprecipitation 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).^{4,34,48} 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,⁷⁰ into a thermodynamically preferred phase with exactly the same chemical composition as the kinetically preferred phase, the kinetic influence on the formation of

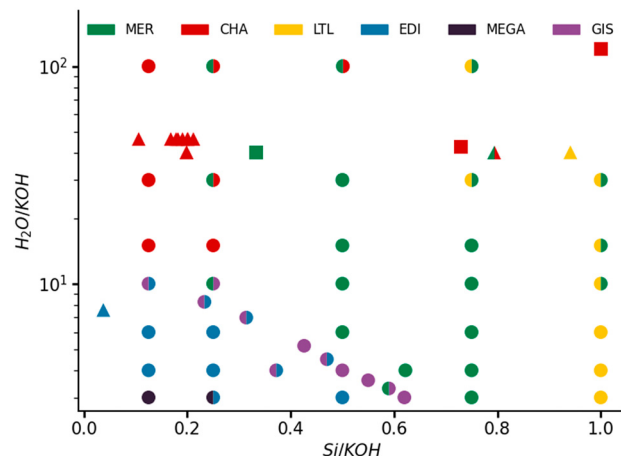


Fig. 5 The HSIL-based phase selection (ref. 34, circles) is compared against interzeolite conversions published by Van Tendeloo in 2013 (ref. 48, squares) and 2017 (ref. 4, triangles). The good match is an additional argument for a thermodynamic treatment of phase selection.

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.⁴

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.^{71–73} Ren and coworkers showed that the use of sodium metasilicate, containing 1–4.5 water per Na⁺, are excellent silicon sources for at least 6 different zeolites (MFI, SOD, MTN, MOR, BEA, FAU) under solvent-free conditions.⁷¹ 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.^{49,74}

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

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solvent-free synthesis from fully anhydrous silicate sources—is not possible without the introduction of fluoride.⁷³ 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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Notes and references

- W. Vermeiren and J.-P. Gilson, Impact of Zeolites on the Petroleum and Petrochemical Industry, *Top. Catal.*, 2009, **52**(9), 1131–1161, DOI: [10.1007/s11244-009-9271-8](#).
- J. Devos, V. L. Sushkevich, I. Khalil, S. Robijns, R. de Oliveira-Silva, D. Sakellariou, J. van Bokhoven and M. Dusselier, Enhancing the Acidity Window of Zeolites by Low-Temperature Template Oxidation with Ozone, *J. Am. Chem. Soc.*, 2024, **146**(39), 27047–27059, DOI: [10.1021/jacs.4c08123](#).
- H. Lee, S. I. Zones and M. E. Davis, A Combustion-Free Methodology for Synthesizing Zeolites and Zeolite-like Materials, *Nature*, 2003, **425**(6956), 385–388, DOI: [10.1038/nature01980](#).
- L. Van Tendeloo, W. Wangermez, A. Vandekerckhove, T. Willhammar, S. Bals, A. Maes, J. A. Martens, C. E. A. Kirschhock and E. Breynaert, Postsynthetic High-Alumina Zeolite Crystal Engineering in Organic-Free Hyper-Alkaline Media, *Chem. Mater.*, 2017, **29**(2), 629–638, DOI: [10.1021/acs.chemmater.6b04052](#).
- P. M. Piccione, C. Laberty, S. Yang, M. A. Cambor, A. Navrotsky and M. E. Davis, Thermochemistry of Pure-Silica Zeolites, *J. Phys. Chem. B*, 2000, **104**(43), 10001–10011, DOI: [10.1021/jp002148a](#).
- I. Petrovic, A. Navrotsky, M. E. Davis and S. I. Zones, Thermochemical Study of the Stability of Frameworks in High Silica Zeolites, *Chem. Mater.*, 1993, **5**(12), 1805–1813, DOI: [10.1021/cm00036a019](#).
- A. Navrotsky, O. Trofymuk and A. A. Levchenko, Thermochemistry of Microporous and Mesoporous Materials, *Chem. Rev.*, 2009, **109**(9), 3885–3902, DOI: [10.1021/cr800495t](#).
- J. Boerio-Goates, R. Stevens, B. K. Hom, B. F. Woodfield, P. M. Piccione, M. E. Davis and A. Navrotsky, Heat Capacities, Third-Law Entropies and Thermodynamic Functions of SiO₂molecular Sieves from T = 0 K to 400 K, *J. Chem. Thermodyn.*, 2002, **34**(2), 205–227, DOI: [10.1006/jcht.2001.0900](#).
- C. S. Cundy and P. A. Cox, The Hydrothermal Synthesis of Zeolites: Precursors, Intermediates and Reaction



- Mechanism, *Microporous Mesoporous Mater.*, 2005, **82**(1), 1–78, DOI: [10.1016/j.micromeso.2005.02.016](https://doi.org/10.1016/j.micromeso.2005.02.016).
- 10 L. Gómez-Hortigüela and M. Á. Camblor, Introduction to the Zeolite Structure-Directing Phenomenon by Organic Species: General Aspects. in *Insights into the Chemistry of Organic Structure-Directing Agents in the Synthesis of Zeolitic Materials*, ed. L. Gómez-Hortigüela, Springer International Publishing, Cham, 2018, pp. 1–41, DOI: [10.1007/430_2017_8](https://doi.org/10.1007/430_2017_8).
 - 11 M. Moliner, F. Rey and A. Corma, Towards the Rational Design of Efficient Organic Structure-Directing Agents for Zeolite Synthesis, *Angew. Chem., Int. Ed.*, 2013, **52**(52), 13880–13889, DOI: [10.1002/anie.201304713](https://doi.org/10.1002/anie.201304713).
 - 12 H. Gies and B. Marler, The structure-controlling role of organic templates for the synthesis of porosils in the system SiO₂/template/H₂O, *Zeolites*, 1992, **12**, 42–49.
 - 13 J. E. Schmidt, D. Fu, M. W. Deem and B. M. Weckhuysen, Template–Framework Interactions in Tetraethylammonium-Directed Zeolite Synthesis, *Angew. Chem., Int. Ed.*, 2016, **55**(52), 16044–16048, DOI: [10.1002/anie.201609053](https://doi.org/10.1002/anie.201609053).
 - 14 M. B. Park, D. Jo, H. C. Jeon, C. P. Nicholas, G. J. Lewis and S. B. Hong, Zeolite Synthesis from a Charge Density Perspective: The Charge Density Mismatch Synthesis of UZM-5 and UZM-9, *Chem. Mater.*, 2014, **26**(23), 6684–6694, DOI: [10.1021/cm501919d](https://doi.org/10.1021/cm501919d).
 - 15 S. I. Zones, K. Jayanthi, J. Pascual, D. Xie and A. Navrotsky, Energetics of the Local Environment of Structure-Directing Agents Influence Zeolite Synthesis, *Chem. Mater.*, 2021, **33**(6), 2126–2138, DOI: [10.1021/acs.chemmater.0c04796](https://doi.org/10.1021/acs.chemmater.0c04796).
 - 16 K. Jayanthi, S. I. Zones, I. Stacey and A. Navrotsky, Energetic Insights into the Role of Quaternary Ammonium Cations in Zeolite Synthesis, *Cryst. Growth Des.*, 2023, **23**(8), 5583–5588, DOI: [10.1021/acs.cgd.3c00238](https://doi.org/10.1021/acs.cgd.3c00238).
 - 17 A. Navrotsky, Calorimetric Insights into the Synthesis of Templated Materials, *Curr. Opin. Colloid Interface Sci.*, 2005, **10**(5), 195–202, DOI: [10.1016/j.cocis.2005.08.001](https://doi.org/10.1016/j.cocis.2005.08.001).
 - 18 W. Schwieger, A. Gonche Machoke, T. Weissenberger, A. Inayat, T. Selvam, M. Klumpp and A. Inayat, Hierarchy Concepts: Classification and Preparation Strategies for Zeolite Containing Materials with Hierarchical Porosity, *Chem. Soc. Rev.*, 2016, **45**(12), 3353–3376, DOI: [10.1039/C5CS00599J](https://doi.org/10.1039/C5CS00599J).
 - 19 IZA Database. Zeolite framework types. https://europe.iza-structure.org/IZA-SC/ftc_table.php (accessed 2024-05-14).
 - 20 M. A. Zwijnenburg and S. T. Bromley, Zeolite Synthesis: An Energetic Perspective, *Phys. Chem. Chem. Phys.*, 2010, **12**(43), 14579, DOI: [10.1039/c0cp01045f](https://doi.org/10.1039/c0cp01045f).
 - 21 K. Asselman, S. Radhakrishnan, N. Pellens, C. V. Chandran, M. Houlléberghs, Y. Xu, J. A. Martens, S. P. Sree, C. E. A. Kirschhock and E. Breynaert, HSIL-Based Synthesis of Ultracrystalline K₂Na₂JBW, a Zeolite Exhibiting Exceptional Framework Ordering and Flexibility, *Chem. Mater.*, 2022, **34**(16), 7159–7166, DOI: [10.1021/acs.chemmater.2c01059](https://doi.org/10.1021/acs.chemmater.2c01059).
 - 22 H. Geerts-Claes, G. Vanbutsele, S. Pulinthanathu Sree, S. Radhakrishnan, C. V. Chandran, E. Breynaert, J. A. Martens and S. Smet, RHO Zeolites with High Hydrothermal Stability, *Cryst. Growth Des.*, 2023, **23**(11), 7829–7840, DOI: [10.1021/acs.cgd.3c00643](https://doi.org/10.1021/acs.cgd.3c00643).
 - 23 *Molecular Sieves—II*, ed. J. R. Katzer, ACS Symposium Series, American Chemical Society, Washington, D. C., 1977, vol. 40, DOI: [10.1021/bk-1977-0040](https://doi.org/10.1021/bk-1977-0040).
 - 24 K. Asselman, D. Vandenabeele, N. Pellens, N. Doppelhammer, C. E. A. Kirschhock and E. Breynaert, Structural Aspects Affecting Phase Selection in Inorganic Zeolite Synthesis, *Chem. Mater.*, 2022, **34**(24), 11081–11092, DOI: [10.1021/acs.chemmater.2c03204](https://doi.org/10.1021/acs.chemmater.2c03204).
 - 25 M. M. Lozinska, E. L. Bruce, J. Mattock, R. G. Chitac, P. A. Cox, A. Turrina and P. A. Wright, Understanding the Anion-Templated, OSDA-Free, Interzeolite Conversion Synthesis of High Silica Zeolite ZK-5**, *Chem. - Eur. J.*, 2022, **28**(56), e202201689, DOI: [10.1002/chem.202201689](https://doi.org/10.1002/chem.202201689).
 - 26 K. Asselman, N. Pellens, S. Radhakrishnan, C. V. Chandran, J. A. Martens, F. Taulelle, T. Verstraelen, M. Hellström, E. Breynaert and C. E. A. Kirschhock, Super-Ions of Sodium Cations with Hydrated Hydroxide Anions: Inorganic Structure-Directing Agents in Zeolite Synthesis, *Mater. Horiz.*, 2021, **8**(9), 2576–2583, DOI: [10.1039/D1MH00733E](https://doi.org/10.1039/D1MH00733E).
 - 27 H. J. Choi, J. G. Min, S. H. Ahn, J. Shin, S. B. Hong, S. Radhakrishnan, C. V. Chandran, R. G. Bell, E. Breynaert and C. E. A. Kirschhock, Framework Flexibility-Driven CO₂ Adsorption on a Zeolite, *Mater. Horiz.*, 2020, **7**(6), 1528–1532, DOI: [10.1039/D0MH00307G](https://doi.org/10.1039/D0MH00307G).
 - 28 A. Navrotsky and Z.-R. Tian, Systematics in the Enthalpies of Formation of Anhydrous Aluminosilicate Zeolites, Glasses, and Dense Phases, *Chem. - Eur. J.*, 2001, **7**(4), 769–774, DOI: [10.1002/1521-3765\(20010216\)7:4<769::AID-CHEM769>3.0.CO;2-J](https://doi.org/10.1002/1521-3765(20010216)7:4<769::AID-CHEM769>3.0.CO;2-J).
 - 29 W. Loewenstein, The Distribution of Aluminum in the Tetrahedra of Silicates and Aluminates, *Am. Mineral.*, 1954, **39**(1–2), 92–96.
 - 30 P. J. Mead and M. Weller, Synthesis, Structure, and Characterization of Halate Sodalites: Me[AlSiO₄]₂[e(XO₃)₂]_x(OH)_z; M = Na, Li, or K; X = Cl, Br, or I, *Zeolites*, 1995, **15**, 561–568.
 - 31 E. Tambuyzer and H. J. Bosmans, The Crystal Structure of Synthetic Zeolite K–F, *Acta Crystallogr., Sect. B*, 1976, **32**(6), 1714–1719, DOI: [10.1107/S0567740876006286](https://doi.org/10.1107/S0567740876006286).
 - 32 S. Ghose, Y. Hexiong and J. Weidner, Crystal Growth and Structure of KrAlrSi₃O₈.KCl A New Anhydrous Zeolite-Type phase with the Edingtonite framework, *Am. Mineral.*, 1990, **75**, 947–950.
 - 33 K. Hackbarth, T. M. Gesing, M. Fechtelkord, F. Stief and J.-C. Buhl, Synthesis and Crystal Structure of Carbonate Cancrinite Na₈[AlSiO₄]₆CO₃(H₂O)_{3.4}, Grown under Low-Temperature Hydrothermal Conditions, *Microporous Mesoporous Mater.*, 1999, **30**(2), 347–358, DOI: [10.1016/S1387-1811\(99\)00046-3](https://doi.org/10.1016/S1387-1811(99)00046-3).
 - 34 K. Asselman, N. Pellens, B. Thijs, N. Doppelhammer, M. Haouas, F. Taulelle, J. A. Martens, E. Breynaert and C. E. A. Kirschhock, Ion-Pairs in Aluminosilicate-Alkali Synthesis Liquids Determine the Aluminum Content and Topology of



- Crystallizing Zeolites, *Chem. Mater.*, 2022, **34**(16), 7150–7158, DOI: [10.1021/acs.chemmater.2c00773](https://doi.org/10.1021/acs.chemmater.2c00773).
- 35 V. V. Bakakin, Quasipollucites and Their Mixed Frameworks, Block Isomorphism, and Superstructures, *Crystallogr. Rep.*, 2009, **54**(5), 763–769, DOI: [10.1134/S1063774509050083](https://doi.org/10.1134/S1063774509050083).
- 36 V. Pashkova, S. Sklenak, P. Klein, M. Urbanova and J. Dědeček, Location of Framework Al Atoms in the Channels of ZSM-5: Effect of the (Hydrothermal) Synthesis, *Chem. - Eur. J.*, 2016, **22**(12), 3937–3941, DOI: [10.1002/chem.201503758](https://doi.org/10.1002/chem.201503758).
- 37 S. Radhakrishnan, C. Lejaegere, K. Duerinckx, W.-S. Lo, A. F. Morais, D. Dom, C. V. Chandran, I. Hermans, J. A. Martens and E. Breynaert, Hydrogen Bonding to Oxygen in Siloxane Bonds Drives Liquid Phase Adsorption of Primary Alcohols in High-Silica Zeolites, *Mater. Horiz.*, 2023, **10**(9), 3702–3711, DOI: [10.1039/D3MH00888F](https://doi.org/10.1039/D3MH00888F).
- 38 A. F. Morais, *et al.*, Noncontact In Situ Multidiagnostic NMR/Dielectric Spectroscopy, *Anal. Chem.*, 2024, **96**(13), 5071–5077.
- 39 I. Kiseleva, A. Navrotsky, I. A. Belitsky and B. A. Fursenko, Thermochemistry and Phase Equilibria in Calcium Zeolites, *Am. Mineral.*, 1996, **81**(5–6), 658–667, DOI: [10.2138/am-1996-5-613](https://doi.org/10.2138/am-1996-5-613).
- 40 A. Alberti, G. Vezzalini, S. Quartieri, G. Cruciani and S. Bordiga, Rehydration Mechanisms in Zeolites: Reversibility of T–O–T Breaking and of Tetrahedral Cation Migration in Brewsterite, *Microporous Mesoporous Mater.*, 2001, **42**(2), 277–287, DOI: [10.1016/S1387-1811\(00\)00330-9](https://doi.org/10.1016/S1387-1811(00)00330-9).
- 41 M. Zema, S. C. Tarantino and G. Montagna, Hydration/Dehydration and Cation Migration Processes at High Temperature in Zeolite Chabazite, *Chem. Mater.*, 2008, **20**(18), 5876–5887, DOI: [10.1021/cm800781t](https://doi.org/10.1021/cm800781t).
- 42 G. Cruciani, Zeolites upon Heating: Factors Governing Their Thermal Stability and Structural Changes, *J. Phys. Chem. Solids*, 2006, **67**(9), 1973–1994, DOI: [10.1016/j.jpcs.2006.05.057](https://doi.org/10.1016/j.jpcs.2006.05.057).
- 43 V. M. Georgieva, E. L. Bruce, M. C. Verbraeken, A. R. Scott, W. J. Casteel Jr., S. Brandani and P. A. Wright, Triggered Gate Opening and Breathing Effects during Selective CO₂ Adsorption by Merlinoite Zeolite, *J. Am. Chem. Soc.*, 2019, **141**(32), 12744–12759, DOI: [10.1021/jacs.9b05539](https://doi.org/10.1021/jacs.9b05539).
- 44 M. M. Lozinska, E. Mangano, J. P. S. Mowat, A. M. Shepherd, R. F. Howe, S. P. Thompson, J. E. Parker, S. Brandani and P. A. Wright, Understanding Carbon Dioxide Adsorption on Univalent Cation Forms of the Flexible Zeolite Rho at Conditions Relevant to Carbon Capture from Flue Gases, *J. Am. Chem. Soc.*, 2012, **134**(42), 17628–17642, DOI: [10.1021/ja3070864](https://doi.org/10.1021/ja3070864).
- 45 J. Šefčík and A. V. McCormick, Prediction of Crystallization Diagrams for Synthesis of Zeolites, *Chem. Eng. Sci.*, 1999, **54**(15–16), 3513–3519, DOI: [10.1016/S0009-2509\(98\)00522-3](https://doi.org/10.1016/S0009-2509(98)00522-3).
- 46 N. Jakupec, K. J. Ardila-Fierro, V. Martinez, I. Halasz, J. Volavšek, G. Algara-Siller, M. Etter, V. Valtchev, K. Užarević and A. Palčić, Mechanochemically Induced OSDA-Free Interzeolite Conversion, *ACS Sustainable Chem. Eng.*, 2024, **12**(13), 5220–5228, DOI: [10.1021/acssuschemeng.3c08477](https://doi.org/10.1021/acssuschemeng.3c08477).
- 47 S. Robijns, J. Devos, B. Baeckelmans, T. De Frene, M. Torka Beydokhti, R. de Oliveira-Silva, N. De Witte, D. Sakellariou, T. R. C. Van Assche and M. Dusselier, Split Syntheses: Introducing Bottom-Up Control over Aluminum in SSZ-13 and ZSM-5 Zeolites, *JACS Au*, 2025, **5**(2), 593–605, DOI: [10.1021/jacsau.4c00551](https://doi.org/10.1021/jacsau.4c00551).
- 48 L. V. Tendeloo, E. Gobechiya, E. Breynaert, J. A. Martens and C. E. A. Kirschhock, Alkaline Cations Directing the Transformation of FAU Zeolites into Five Different Framework Types, *Chem. Commun.*, 2013, **49**(100), 11737–11739, DOI: [10.1039/C3CC47292B](https://doi.org/10.1039/C3CC47292B).
- 49 D. Vandenabeele, N. Doppelhammer, S. Radhakrishnan, C. V. Chandran, W. Wangermez, A. Rais, E. Vandeurzen, B. Jakoby, C. Kirschhock and E. Breynaert, Hydrated Silicate Ionic Liquids: Ionic Liquids for Silicate Material Synthesis, *J. Mol. Liq.*, 2024, 126603, DOI: [10.1016/j.molliq.2024.126603](https://doi.org/10.1016/j.molliq.2024.126603).
- 50 J. Šefčík and A. V. McCormick, What Is the Solubility of Zeolite A?, *Microporous Mater.*, 1997, **10**, 173–179.
- 51 J. Šefčík and A. V. McCormick, Thermochemistry of Aqueous Silicate Solution Precursors to Ceramics, *AIChE J.*, 1997, **43**(S11), 2773–2784, DOI: [10.1002/aic.690431324](https://doi.org/10.1002/aic.690431324).
- 52 J. J. De Yoreo, P. U. P. A. Gilbert, N. A. J. M. Sommerdijk, R. L. Penn, S. Whitelam, D. Joester, H. Zhang, J. D. Rimer, A. Navrotsky, J. F. Banfield, A. F. Wallace, F. M. Michel, F. C. Meldrum, H. Cölfen and P. M. Dove, Crystallization by Particle Attachment in Synthetic, Biogenic, and Geologic Environments, *Science*, 2015, **349**(6247), aaa6760, DOI: [10.1126/science.aaa6760](https://doi.org/10.1126/science.aaa6760).
- 53 D. Vandenabeele, N. Doppelhammer, S. Radhakrishnan, C. V. Chandran, W. Wangermez, A. Rais, E. Vandeurzen, B. Jakoby, C. Kirschhock and E. Breynaert, Hydrated silicate ionic liquids: Ionic liquids for silicate material synthesis, *J. Mol. Liq.*, 2025, **417**, 126603.
- 54 A. V. McCormick, A. T. Bell and C. J. Radke, Multinuclear NMR Investigation of the Formation of Aluminosilicate Anions, *J. Phys. Chem.*, 1989, **93**(5), 1741–1744, DOI: [10.1021/j100342a015](https://doi.org/10.1021/j100342a015).
- 55 A. V. McCormick, A. T. Bell and C. J. Radke, The Influence of Alkali Metal Hydroxides on Silica Condensation Rates: The Role of Ion Pairing, *MRS Online Proc. Libr.*, 1988, **121**, 67, DOI: [10.1557/PROC-121-67](https://doi.org/10.1557/PROC-121-67).
- 56 A. V. McCormick, A. T. Bell and C. J. Radke, Evidence from Alkali-Metal NMR Spectroscopy for Ion Pairing in Alkaline Silicate Solutions, *J. Phys. Chem.*, 1989, **93**(5), 1733–1737, DOI: [10.1021/j100342a013](https://doi.org/10.1021/j100342a013).
- 57 N. Pellens, N. Doppelhammer, S. Radhakrishnan, K. Asselman, C. V. Chandran, D. Vandenabeele, B. Jakoby, J. A. Martens, F. Taulelle, E. K. Reichel, E. Breynaert and C. E. A. Kirschhock, Nucleation of Porous Crystals from Ion-Paired Prenucleation Clusters, *Chem. Mater.*, 2022, **34**(16), 7139–7149, DOI: [10.1021/acs.chemmater.2c00418](https://doi.org/10.1021/acs.chemmater.2c00418).
- 58 J. Vekeman, D. Vandenabeele, N. Doppelhammer, E. Vandeurzen, E. Breynaert, C. E. A. Kirschhock and T. Verstraelen, Simple Molecular Model for Hydrated Silicate Ionic Liquids, a Realistic Zeolite Precursor, *Chem. Mater.*,



- 2024, **36**(8), 3886–3897, DOI: [10.1021/acs.chemmater.4c00285](https://doi.org/10.1021/acs.chemmater.4c00285).
- 59 K. Asselman, M. Haouas, M. Houleberghs, S. Radhakrishnan, W. Wangermez, C. E. A. Kirschhock and E. Breynaert, Does Water Enable Porosity in Aluminosilicate Zeolites? Porous Frameworks versus Dense Minerals, *Cryst. Growth Des.*, 2023, **23**(5), 3338–3348, DOI: [10.1021/acs.cgd.2c01476](https://doi.org/10.1021/acs.cgd.2c01476).
- 60 H. Ohtaki and T. Radnai, Structure and Dynamics of Hydrated Ions, *Chem. Rev.*, 1993, **93**(3), 1157–1204, DOI: [10.1021/cr00019a014](https://doi.org/10.1021/cr00019a014).
- 61 M. Maldonado, M. D. Oleksiak, S. Chinta and J. D. Rimer, Controlling Crystal Polymorphism in Organic-Free Synthesis of Na-Zeolites, *J. Am. Chem. Soc.*, 2013, **135**(7), 2641–2652, DOI: [10.1021/ja3105939](https://doi.org/10.1021/ja3105939).
- 62 A. Chawla, A. J. Mallette, R. Jain, N. Le, F. C. Robles Hernández and J. D. Rimer, Crystallization of Potassium-Zeolites in Organic-Free Media, *Microporous Mesoporous Mater.*, 2022, **341**, 112026, DOI: [10.1016/j.micromeso.2022.112026](https://doi.org/10.1016/j.micromeso.2022.112026).
- 63 M. Houleberghs, E. Breynaert, K. Asselman, E. Vaneeckhaute, S. Radhakrishnan, M. W. Anderson, F. Taulelle, M. Haouas, J. A. Martens and C. E. A. Kirschhock, Evolution of the Crystal Growth Mechanism of Zeolite W (MER) with Temperature, *Microporous Mesoporous Mater.*, 2019, **274**, 379–384, DOI: [10.1016/j.micromeso.2018.09.012](https://doi.org/10.1016/j.micromeso.2018.09.012).
- 64 H. Lechert, P. Staelin and C. Kuntz, Quantitative Relations of the Batch Composition and the Si/Al Ratio in the Product of Zeolites, *Zeolites*, 1996, **16**, 149–156.
- 65 N. Doppelhammer, D. Vandenabeele, K. Asselman, E. Breynaert, B. Jakoby and C. E. A. Kirschhock, In-Situ Polymerization Measurement During Zeolite Formation Employing a Differential Impedance Approach, In *2023 International Workshop on Impedance Spectroscopy (IWIS)*, IEEE, Chemnitz, Germany, 2023, pp. 51–55, DOI: [10.1109/IWIS61214.2023.10302782](https://doi.org/10.1109/IWIS61214.2023.10302782).
- 66 N. Doppelhammer, N. Pellens, B. Jakoby, C. E. A. Kirschhock and E. K. Reichel, Monitoring Zeolite Formation with Moving Electrode Conductometry. In *2021 IEEE Sensors*, IEEE, Sydney, Australia, 2021, pp. 1–4, DOI: [10.1109/SENSOR47087.2021.9639654](https://doi.org/10.1109/SENSOR47087.2021.9639654).
- 67 D. Vandenabeele, N. Doppelhammer, S. Radhakrishnan, C. Chandran, B. Jakoby, C. Kirschhock and E. Breynaert, Can the Combination of in Situ Differential Impedance Spectroscopy and ²⁷Al NMR Detect Incongruent Zeolite Crystallization?, *Microporous Mesoporous Mater.*, 2024, **374**, 113141, DOI: [10.1016/j.micromeso.2024.113141](https://doi.org/10.1016/j.micromeso.2024.113141).
- 68 L. Van Tendeloo, M. Haouas, J. A. Martens, C. E. A. Kirschhock, E. Breynaert and F. Taulelle, Zeolite Synthesis in Hydrated Silicate Ionic Liquids, *Faraday Discuss.*, 2015, **179**, 437–449, DOI: [10.1039/C4FD00234B](https://doi.org/10.1039/C4FD00234B).
- 69 M. Haouas, L. Lakiss, C. Martineau, J. El Fallah, V. Valtchev and F. Taulelle, Silicate Ionic Liquid Synthesis of Zeolite Merlinoite: Crystal Size Control from Crystalline Nanoaggregates to Micron-Sized Single-Crystals, *Microporous Mesoporous Mater.*, 2014, **198**, 35–44, DOI: [10.1016/j.micromeso.2014.07.011](https://doi.org/10.1016/j.micromeso.2014.07.011).
- 70 A. Putnis and C. V. Putnis, The Mechanism of Re-equilibration of Solids in the Presence of a Fluid Phase, *J. Solid State Chem.*, 2007, **180**(5), 1783–1786, DOI: [10.1016/j.jssc.2007.03.023](https://doi.org/10.1016/j.jssc.2007.03.023).
- 71 L. Ren, Q. Wu, C. Yang, L. Zhu, C. Li, P. Zhang, H. Zhang, X. Meng and F.-S. Xiao, Solvent-Free Synthesis of Zeolites from Solid Raw Materials, *J. Am. Chem. Soc.*, 2012, **134**(37), 15173–15176, DOI: [10.1021/ja3044954](https://doi.org/10.1021/ja3044954).
- 72 Q. Wu, X. Meng, X. Gao and F.-S. Xiao, Solvent-Free Synthesis of Zeolites: Mechanism and Utility, *Acc. Chem. Res.*, 2018, **51**(6), 1396–1403, DOI: [10.1021/acs.accounts.8b00057](https://doi.org/10.1021/acs.accounts.8b00057).
- 73 Q. Wu, X. Liu, L. Zhu, L. Ding, P. Gao, X. Wang, S. Pan, C. Bian, X. Meng, J. Xu, F. Deng, S. Maurer, U. Müller and F.-S. Xiao, Solvent-Free Synthesis of Zeolites from Anhydrous Starting Raw Solids, *J. Am. Chem. Soc.*, 2015, **137**(3), 1052–1055, DOI: [10.1021/ja5124013](https://doi.org/10.1021/ja5124013).
- 74 N. A. MacGillp, An Investigation of Some Properties of Sodium Silicates and Their Use in Zeolite Synthesis, *Doctoral dissertation*, University of Edinburgh, 1976.

