Beyond traditional synthesis of zeolites: The impact of germanosilicate chemistry in the search for new materials

Ondřej Veselý [a], Russell E. Morris [b], Jiří Čejka [a],[*]

[a] Department of Physical and Macromolecular Chemistry & Charles University Center of Advanced Materials, Faculty of Science, Charles University, Hlavova 8, 12843, Prague, Czech Republic
[b] EaStChem School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, UK

A B S T R A C T

Zeolites are one of the key materials in the chemical industry with their applications ranging from water purification to gas separation or oil refining. In the recent years, the research of zeolites focuses more and more on specialised applications including fine chemical synthesis or separation of small organic compounds, which increase the demand for new types of zeolites with unique structural and chemical properties. Introduction of tailored organic structure-directing agents and especially the introduction of germanium stimulated the discovery of new zeolite frameworks and particularly led to a discovery of numerous new extra-large pore zeolites with attractive properties for selective catalysis. However, the germanosilicate chemistry also opened up an unparalleled opportunity for tailoring even more new zeolites and zeolite-derived materials by controlled post-synthetic transformation of the germanosilicates into layered zeolites or to new zeolite frameworks by solid-, liquid- or vapour-phase transformations such as the Assembly-Disassembly-Organisation-Reassembly process. The following research provided new strategies for preparation of porous materials with characteristics and properties tailored on-demand.

1. Introduction

Many chemical technologies ranging from large facilities for oil processing or small-scale processes for fine chemicals manufacturing employ zeolites as heterogeneous catalysts. Zeolites encompass a diverse group of crystalline microporous frameworks varying significantly in their structural features, pore sizes, pore connectivity but also their chemical composition or crystal morphology. Most widely used zeolites possess either small- (8-ring), medium- (10-ring) or large (12-ring) pores. However, numerous synthetic frameworks also contain pores wider than 12-rings, referred to as extra-large pore zeolites. Furthermore, individual zeolites vary in the connectivity of the channels, geometry of pore cavities as well as their elemental composition. These features directly influence their physical properties including the hydrothermal stability, surface area, pore accessibility or hydrophobicity and also their physico-chemical behaviours such as the ability to separate small compounds based on their size, shape and polarity, and their unparalleled shape-selective catalytic properties [1–3].

Large structural and compositional variability, emphasised by continuous discoveries of new distinct zeolite structures, prompted the research and application of zeolites to catalyse not only conversions of small simple compounds but also to focus on reactions of bulkier biological compounds using extra-large pore zeolites or even

enantioselective transformations in asymmetric catalytic processes using chiral zeolite frameworks (See Fig. 1 for examples) [4–9]. In addition, the transition from fossil fuel feedstocks towards renewables (such as biomass) poses new challenges [10]. Biomass-derived substrates tend to be more highly oxygenated than hydrocarbons, and this gives new challenges for optimising catalytic processes based on zeolites, including reactivity and stability issues especially in the presence of water, which is more common in bio-based systems [11,12]. Similarly, many bio-derived substrates may be more complex polymers, and so larger porosity (or more extensive hierarchical porosity) may be required. This means there remains a great incentive to develop new zeolites based on either a different chemistry or structural topology. Preparation of these highly specialised zeolites is still far from being a routine task and the synthesis protocols commonly rely on advanced synthetic methods.

This review intends to present an outline of the established as well as newer promising synthetic methods for preparation and targeted design of new zeolite structures. There will be a slight focus on using heteroatoms such as germanium to change both the toplogical and chemical properties of zeolites. In particular we will discuss how germanosilicates have enabled the synthesis of large pore zeolites and allowed novel transformation routes to new materials. However, zeolite synthesis is not just dependent on heteroatoms but is a complex interplay between

* Corresponding author.
  E-mail address: jiri.cejka@natur.cuni.cz (J. Čejka).

framework elements, synthesis conditions and the presence of structure-directing agents. We will also briefly discuss the latter in the context of zeolite synthesis.

2. Synthesis of new zeolites

Design of new zeolite structures commonly involves introduction of heteroelements into the framework, usage of elaborate organic structure directing agents (SDA) or uncommon synthesis conditions such as highly concentrated synthesis gels [6,7]. Although zeolites are most commonly described as silicates, numerous other tetrahedrally coordinated elements (B, Al, Ti, Fe, Zn, In, Ga, Ge, Zr, Sn …) can substitute the silicon in the framework positions [3,13–16]. The elements can not only significantly alter the chemical composition of the zeolite but even promote formation of new building units and thereby stabilise and favour formation of new structures [17–21].

Among the viable heteroelements, germanium holds a special position due to its ability to promote the formation of small 3- and 4-rings and double-4-rings (D4R) crucial in formation of zeolite structures with low framework density [6]. Avelino Corma was one of the pioneers in this area, developing the use of germanium substitution for the synthesis of large pore materials [22–25]. The larger size of the germanium atom compared to silicon provides an increased range of Ge-O-Ge bond angles (120–180°) compared to Si–O–Si (137–180°). As a result, the presence of germanium in the framework leads to relaxation of framework distortion and stabilises otherwise strained building units such as small four- or three-rings and D4R and D3R units. The small rings are particularly common in extra-large pore zeolites and structures with low framework density [8,18,26,27]. Fig. 2 illustrates a set of examples of zeolite structures containing the D4R units promoted by the germanium. Nevertheless, it needs to be stressed that exceptions to the rule also exist, such as the germanosilicate ITQ-69 which is free of D4R or D3R units despite crystallizing in presence of germanium [28].

The germanium possesses structure directing ability that stabilises small ring units, which would be less favourable or unstable in silicate form [17,20,30–32]. However, the presence of strained structural units also causes the regiospecificity in the distribution of the germanium throughout the framework. The germanosilicate ITQ-44 (**IRR**) acutely illustrates the inhomogeneous germanium distribution within its D3R and D4R units. Around 50% of the germanium resides in the highly strained D3R framework positions, 37% in the D4R positions and only 13% reside in the less strained framework sites. Ergo, while the germanium governs the formation of small ring units, the presence of such units governs the distribution of the framework germanium [33–37].

But germanium does not only have a structural effect: it also has a chemical one. The Ge–O bonds are also more susceptible to hydrolytic attack than the Si–O and so the introduction of germanium decreases the hydrothermal stability of the zeolite. Germanosilicates are particularly sensitive to water, which occasionally results in structure deterioration upon prolonged exposure to moisture [38–40]. The stability of a zeolite generally increases with decreasing germanium content; however, since the germanium provides the structural directing ability, its presence in the synthesis is often unavoidable and so there is a balance between stability of the final material and the need for Ge-induced structure direction. In addition, the phase selectivity of the synthesis also depends on the choice of the structure directing agent (SDA). Therefore, careful choice of suitable SDA may stabilise the zeolite and reduce the amount of germanium needed for a successful synthesis [41,42].

2.1. SDA design

One of the most significant breakthroughs in zeolite synthesis came with the introduction of organic structure directing agents (SDAs) which greatly accelerated and augmented the preparation and discovery of new zeolites [43,44]. The SDAs stabilise silica clathrate cages forming during the crystallisation and direct the growth towards a structure with specific cages or building units. The structural and chemical variety of organic SDAs exceeds that of the inorganic SDAs (e.g. alkali metal ions) considerably and provides more options for tuning the phase-selectivity and may facilitate formation zeolites with new compositions - most notably high-silica zeolites - under broader range of conditions, or preparation of entirely new and more complex zeolite structures [6,21, 45–47].

Proper choice of the SDA frequently decides the outcome of zeolite synthesis and its reliability. Though, disconcertingly, the nature of the structure-directing ability of SDAs is not understood in its entirety. On one hand, isolated examples of SDAs act as true templates, such as the triquaternary amine $C_{18}H_{36}N_3^+$ in synthesis of ZSM-18 (**MEI**) zeolite or $[Ni(en)_3]^{2+}$ in synthesis of CJ63 (**JST**) gallogermanate, both of which possesses the same symmetry as the respective SDA [8,27,46]. On the other hand, most SDAs show only loose relation to the respective zeolite structure and their structure-directing ability is not limited to just one zeolite. The stability of one zeolite structure over another depends on delicate interplay of weak interactions between the SDA and the framework during the crystallisation, which is further complicated by the high temperature (and thus SDA dynamics) under common zeolite synthesis conditions. As a result, one SDA can commonly stabilise multiple zeolite structures under varying synthesis conditions and conversely the same zeolite structure can form in the presence of several
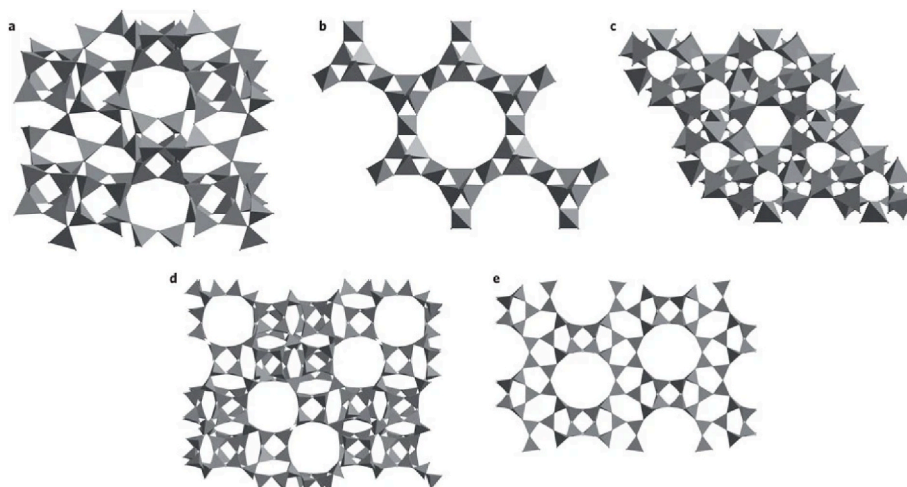

Fig. 1. Chiral and extra-large pore zeolites (a – **STW**; b – **OSO**; c – **CZP**; d – **-ITV, e – BEA** polymorph A) [4].
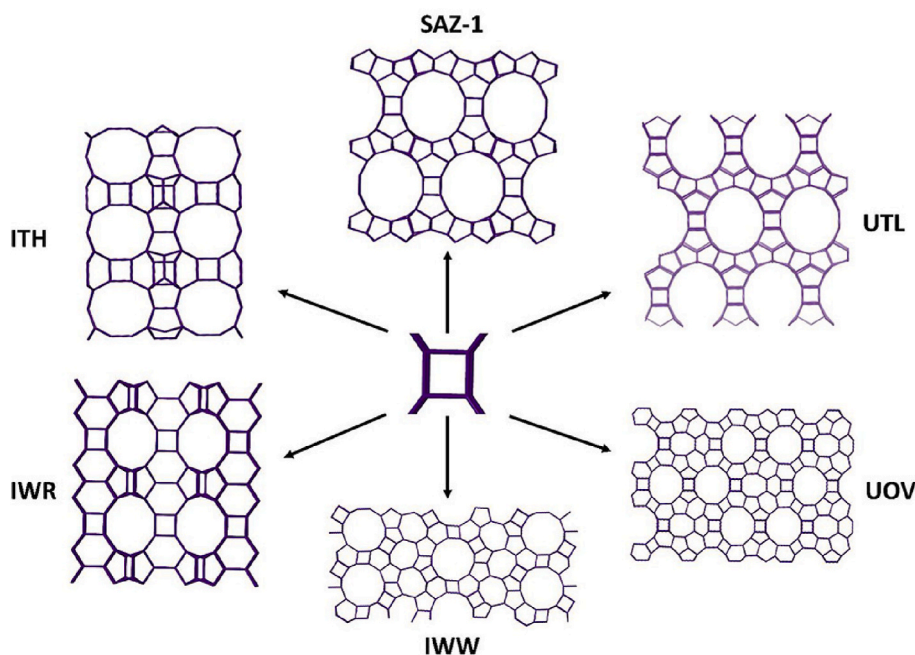
Fig. 2. Examples of germanosilicate zeolites containing the D4R units [29].

different SDA molecules. Therefore, it is commonly considered that the most important function of SDAs is to stabilise the zeolite by pore filling and charge balancing, rather than by true templating effects [46,48].

2.1.1. N-SDAs

The most common organic SDAs contain one or several quaternary nitrogen atoms substituted with alkyl groups or embedded into a cyclic molecule. The SDA molecules range from simple tetraalkylammonium cations to complex derivatives of imidazolium. The complexity and structure features of the SDA molecule including size and shape but also rigidity and charge density can considerably alter its properties [49,50]. Occasionally, replacement of one functional group switches the phase-selectivity towards an entirely different zeolite framework. For illustration, N-methyl-N′-ethylimidazolium favours the formation of the IM-16 (**UOS**) zeolite. However, substituting the ethyl group for more spatial butyl or p-methylbenzyl changes the phase selectivity towards IM-20 (**UWY**) and NUD-1 zeolites, respectively (Fig. 3) [51,52]. Similarly, zeolite SSZ-57 (***SFV***) crystalizes in a presence of N-butyl-N-cyclohexyl-pyrrolidinium. However, the same SDA with methyl or ethyl in place of the butyl group results in formation of ZSM-12 (**MTW**) instead [53].

Although the correlation between structures of the SDA and the zeolite formed is not entirely straightforward, more bulky compounds commonly favour formation of zeolites with large pores and cavities and lower framework density. Also, the phase-selectivity generally increases with rigidity of the SDA molecule and by balancing its C/N^+ ratio within 10–16 [47,49]. An example of this is the preparation of extra-large pore zeolites ITQ-44 (**IRR**) or IM-12 (**UTL**), which crystalize using bulky and rigid SDAs while more flexible SDA molecules, such as tetraethylammonium, produce zeolites **MTW**, ***BEA** or **BEC** [49,54,55].

Spatially rigid SDA molecules provide high phase selectivity, which is often a determining factor for preparation of zeolites with unique structural features or extra-large cavities. However, the tedious preparation of these SDAs limits their practical usage and thus they are often avoided in favour of assemblies of simpler and more accessible molecules. Smaller SDAs interacting by H-bonding or π-π interactions can assemble into dimers and cooperatively fill the cage of a zeolite in a similar manner as one large molecule, as illustrated by the synthesis of pure silica ITQ-29 (**LTA**) [56]. Analogous to small molecules, diquaternary ammonium SDAs containing rigid charged groups connected by flexible hydrocarbon chain can contort and fill the channels of varying zeolite structures. For instance, the hexamethonium SDA can produce
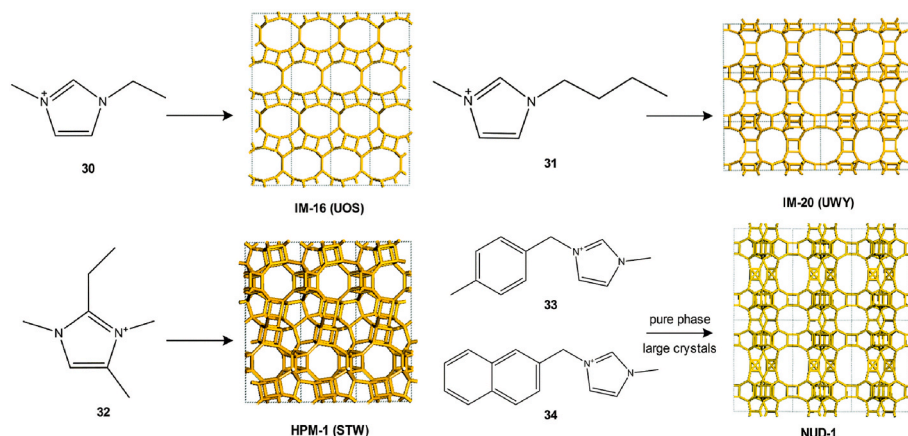

Fig. 3. Zeolites prepared using SDAs based on substituted imidazolium [46].

zeolites EU-1 (**EUO**), ZSM-48 (***MRE**) or ITQ-13 (**ITH**) [57,58]. The external conditions presumably prompt the SDA to adopt a specific conformation that determines its structural-directing ability. Furthermore, the hydrocarbon chain length also impacts the phase selectivity. For instance, the bis-(N-methylpyrrolidinium) connected with methylene chain favours formation of SSZ-74 (**–SVR**) zeolite when connected by a chain of six carbon atoms while IM-5 (**IMF**) and TNU-9 (**TUN**) zeolites for chain consisting of five and four carbons, respectively [46].

2.1.2. P-SDAs

Phosphorus-based SDAs (P-SDAs) including phosphonium, phosphazenes or aminophosphines provide an alternative to the nitrogen-based SDAs (N-SDAs). Although the use of P-SDAs is often avoided due to the concerns of their toxicity and availability, the P-SDAs possess several distinct advantages. First of all, the P-SDAs possess higher thermal stability and, unlike the N-SDAs, do not undergo Hoffmann degradation under high pH and temperature. Due to the enhanced thermal stability the P-SDAs can be used in synthesis requiring more severe conditions. Second, the P-SDAs can provide new types of phase-selectivity and stabilise zeolite structures uncommon for the N-SDAs [46]. The bis(trimethylphosphonium) illustrates this unique phase selectivity of P-SDAs in synthesis of ITQ-34 (**ITR**) where conventional bis-(trimethylammonium) SDA fails to produce any pure zeolite phase [59]. Other P-SDAs proved to be beneficial in synthesis of zeolites ITQ-26 (**IWS**), ITQ-27 (**IWV**), ITQ-34 (**ITR**) - polymorph B of the ITQ-13 (**ITH**), ITQ-40 (**-IRY**), ITQ-49 (**IRN**), or ITQ-52 (**IFW**) [59–64].

Additionally, P-SDAs also include phosphazene SDAs. The phosphazenes stand out for their easy construction, nearly unlimited structural variability and high basicity. The basicity enables them to produce hydroxide anions upon reaction with water [27,46]. Introduction of phosphazene SDAs most prominently enabled preparation of ITQ-47 with boggsite (**BOG**) structure, a natural aluminosilicate mineral which has proven to be exceptionally difficult to synthetize [65,66].

2.2. Highly concentrated gels

Crystallisation of zeolites commonly takes place in a basic to neutral aqueous solution containing dissolved SDA and sources of building elements such as various silicate, aluminate or germanate species [67]. However, high water content impedes the formation of some zeolites, especially germanosilicates, and then a synthesis from highly concentrated gels or solid phase is preferred. Synthesis conditions with low water content favour formation of zeolite structures with low framework density or structures prone to hydrolysis [68].

The synthesis under reduced water content includes crystallisation from highly concentrated gels, vapour-assisted crystallisation or dry gel conversion. Highly concentrated gel crystallisation uses a synthesis gel with H_2O/Si content bellow 10 [58,69]. The amount of water is commonly insufficient to dissolve the synthesis compounds and, hence, the synthesis gel is prepared from more dilute solutions and the excess water is subsequently evaporated to achieve the desired content before the crystallisation. However, in most aspects the synthesis procedure essentially resembles ordinary hydrothermal synthesis. On the other hand, vapour-assisted crystallisation and dry gel conversion differ significantly from the regular crystallisation, because the liquid water remains separated from the synthesis gel for the duration of the synthesis [69–72]. The synthesis of ZSM-5 (**MFI**) developed by Dong et al. proceeds from an amorphous synthesis gel and a mixture of water with ethylenediamine and trimethylamine located in separate compartments. The gel only comes in contact with the vapours during the synthesis. The water and amine vapours absorb into the gel and result in local dissolution of the oxide phase. The amines protonate upon contact with water, producing OH^- ions which mediate Si–O bond breaking and making and incite transformation of the amorphous gel into a crystalline ZSM-5 (**MFI**) zeolite. Additionally, newer studies also utilised similar synthetic methods to yield ***BEA**, **FAU** or **FER**, demonstrating the

variability of the method [69,73].

2.3. High-throughput synthesis

Zeolite synthesis gels are complex systems consisting of large number of compounds and the success of the synthesis further depends on numerous conditions such as temperature, pH, duration or even heating rate and agitation. Thereby discovery of new zeolites or optimising existing synthetic recipes requires extensive screening of synthetic conditions with large number of variables. Such experiments become physically inconceivable even for simple synthetic mixtures. However, thorough screening of synthetic procedures becomes manageable when combined with automation and large number of parallel small-volume reactors [74–76]. This high-throughput method takes advantage of automatic dispensing of individual reactants which facilitates and accelerates the preparation of the synthesis mixtures and may even enable higher precision in dosing of the synthetic compounds [77]. The synthesis proceeds in co-joined array of small-volume (e.g. 500 μl) autoclaves using only small volume of synthetic mixture for the experiment. The small volumes joined with automation of the dosing and characterisation enables simultaneous and efficient screening of dozens of synthetic parameters including concentrations of individual compounds or pH [75,78]. The high-throughput method, pioneered especially by the group of Avelino Corma, led to the discovery of several new zeolites, including extra-large pore ITQ-33 (**ITT**) with 18- and 10-ring channels [79] or ITQ-30 of the **MWW** family feasible within a wide range of Si/Al ratios (10–∞) [80].

The high-throughput experiments provide an extensive amount of data which can benefit from advanced computation analysis for evaluation. Most recently, the combination of high-throughput synthesis with machine learning appeared as a promising method of analysing the high-throughput synthesis data for determining the relations between synthetic conditions and the outcome [77,81,82]. The analysed data are most commonly presented as a series of phase diagrams and libraries of permutations of tested conditions. The trends and correlations observed from the data sets shed light on the fundamental relationships between the synthetic conditions and the outcome, pointing to the next target or predicting outcome of future experiments [83].

3. Transformations

3.1. Hydrothermal stability

Germanosilicate zeolites generally suffer from reduced hydrothermal stability compared to their purely siliceous analogues. The stability decreases due to the relatively labile character of the Ge–O bonds which are especially susceptible to hydrolysis by acidic solutions, liquid water or even air moisture [38,39,84,85]. Interaction with large amounts of water results in bond breaking and extraction of germanium. In zeolites with high framework content of germanium, the degermanation generally leads to structure deterioration and amorphization [39].

In contrast, zeolites with low germanium content retain their structure; nevertheless, the degermanation introduces defects into their structures impacting their textural properties and increasing hydrophilicity [40]. Increasing the stability of the low-germanium zeolites can be achieved by post-synthetic substitution of the germanium atoms with silicon. The silicon heals the defects formed by the degermanation and thus improves the hydrothermal stability of the zeolite framework [86,87].

High content of germanium makes the post-synthetic stabilisation of the framework more intricate. Zeolites with high germanium content often lose their structural integrity when treated with aqueous solutions due to leaching of significant number of framework germanium atoms. The degermanation thus proceeds too rapidly and extensively compared to the slow reinsertion of silicon species into the framework positions. Nevertheless, the substitution can successfully proceed on a zeolite

supported by SDA molecules in its pores (Fig. 4). The SDA molecules support the framework during the degermanation and provide increased stability and additional time for the silicon to heal the vacancies in the structure [88].

The structure can also be stabilised by other elements. For example, trivalent elements, such as aluminium can heal the vacancies and stabilise the zeolite in a similar way to silicon, but on top of that introduce catalytic activity in a form of Brønsted acidic sites. The method thus enables post synthetic functionalisation of the zeolites, which is especially noteworthy, since direct synthesis of aluminium-containing analogues of some germanosilicate zeolites has not been reported [87,89].

However, the degermanation also offers another unique opportunity. Due to the preferential location of the germanium in the D4R and D3R units, the germanium-rich domains can selectively hydrolyse and produce new materials. In zeolite structures such as IM-12 (**UTL**) or CIT-13 (***CTH**), the germanium-rich D4R units connect two-dimensional silica-rich layers into the three-dimensional framework. Hydrolysis of the germanium-rich D4R units effectively breaks the connections between the layers, resulting in a layered material (Fig. 5) [84,90].

3.2. ADOR transformation

Selective decomposition of germanosilicate UTL into a layered material opened up a new pathway to the development of ADOR (Assembly-Disassembly-Organisaion-Reassembly) transformation [91,92]. The ADOR transformation of the germanosilicate zeolites offers more direct and controllable alternative to the hydrothermal synthesis. The hydrothermal synthesis suffers from the lack of a clear and obvious relationship between the synthesis conditions and the resulting structure. On the other hand, the result of the ADOR is easily predictable due to transforming one zeolite structure into another by replacing certain structural units (e.g. D4Rs) [93,94].

The ADOR takes advantage of labile Ge–O bonds in zeolites such as **UTL** or ***CTH** to selectively hydrolyse the germanium rich D4R units and form layered precursors. The disconnected layers then participate as building blocks in the formation of new zeolite frameworks. Since the new frameworks consist of the same layers, only the interlayer connections and the respective layer positions determine the topology and porosity of the resulting materials. The interlayer connections directly affect the size of the micropores. The pore size decreases upon replacing the D4R units of the **UTL** by S4R units in IPC-2 (**OKO**) or oxygen linkages in IPC-4 (**PCR**) from 14-ring to 10-ring (see Fig. 7) [91,92]. The gradual and controlled decrease in pore size produces a family of isoreticular zeolites with identical layer structure and channel architecture but varying pore size. The isoreticular zeolites present a unique tool for studying relations between pore size and separation or catalytic properties with as few variables as possible [95–98]. On top of that, the ADOR process also enables altering the respective layer positions by introducing a mismatch between the layers. This structural mismatch
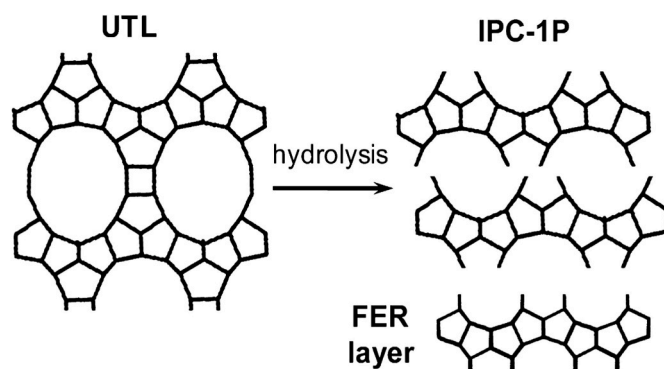

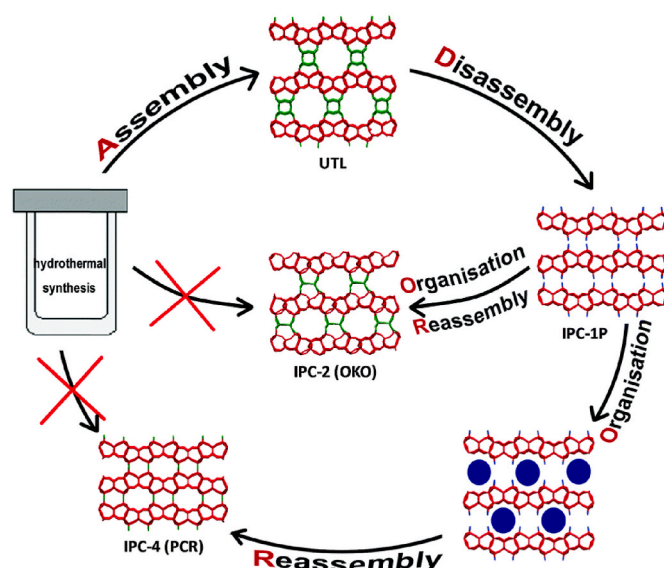**Fig. 5.** Transformation of **UTL** germanosilicate into a layered material IPC-1P [84].

Fig. 6. ADOR transformations of the **UTL** zeolite [92].

produces new high-energy structures, such as IPC-9 or IPC-10, which often do not obey the LID (local interatomic distances) criteria established for zeolites prepared by hydrothermal synthesis. The LID consist of several rules based on observations of existing zeolites which relate geometrical features of the framework (e.g. average T-T and T-O distances or T-O-T angles) and hydrothermal feasibility of the zeolite [99, 100]. However, zeolites such as IPC-9 and IPC-10 are considered "unfeasible" by the hydrothermal method. Moreover, they contain odd-ring pores (7-ring and 9-ring, respectively) with the potentially attractive
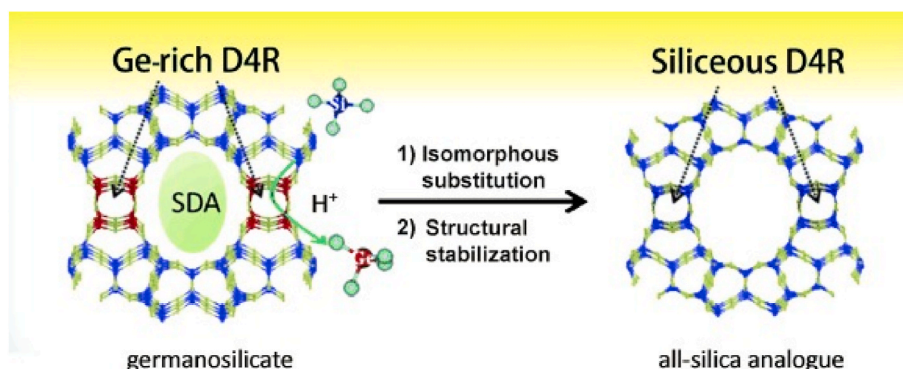

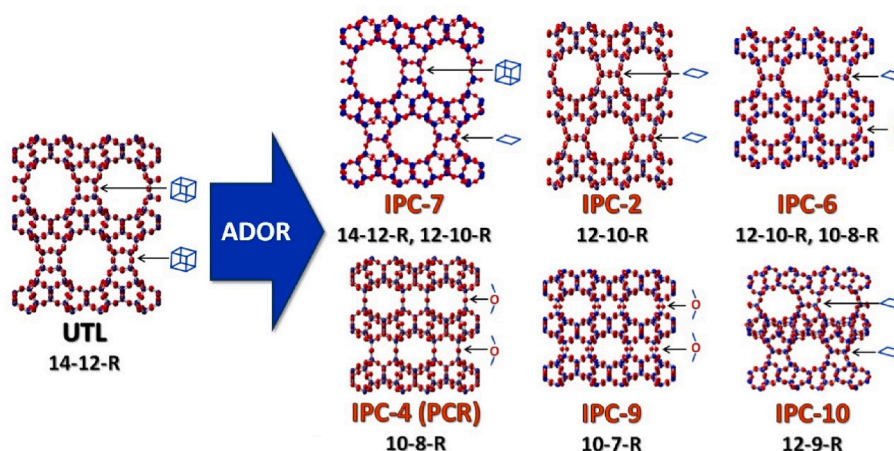**Fig. 4.** Stabilisation of Ge-rich **UTL** by isomorphous substitution with Si [88].

Fig. 7. UTL zeolite and the products of its ADOR transformations.

separation properties [101].

The ADOR process consists of four steps (Fig. 6):

1) Assembly

The first step of the ADOR process is the hydrothermal synthesis of the parent germanosilicate. The synthesis parameters determine two key properties of the parent material; the germanium content (Si/Ge molar ratio) and germanium distribution in the framework. The germanium promotes the formation of D4Rs and the Si/Ge ratio determines the amount of germanium within them. Lower Si/Ge results in higher number of germanium in the D4R positions which decreases the hydrothermal stability and facilitates the subsequent hydrolysis [90]. The stability also depends on the germanium distribution, namely its preference to occupy the D4R sites. The relative occupancy varies among individual framework types as well as the synthesis method. The germanosilicates synthesized under alkaline conditions generally contain majority of the germanium located in D4R sites. On the other hand, zeolites prepared in fluoride media show more even distribution of germanium throughout the framework [30].

2) Disassembly

Zeolites with high germanium content suffer from decreased stability against liquid water or even air moisture [39]. Small amounts of water (1 molecule per unit cell) can reversibly adsorb onto the zeolite without inducing any structural changes. However, higher water loadings (18 molecules per unit cell) enable thermodynamically highly favourable hydrolysis mechanisms and the water molecules react with the framework. The adsorbed water hydrolyses the labile Ge–O bonds, forming defects and extracting germanium [40].

The germanium preferentially occupies the D4R units that connect the silicon-rich layers in the framework [33,35]. Complete separation of the layers by hydrolysis occurs when the D4Rs contain at least four germanium atoms and no Si–O–Si linkages between the layers. The hydrolysis of the D4R units effectively removes the connections between the layers and the three-dimensional zeolite transforms into two-dimensional layered material. The layered materials contain characteristic silanol quadruplet defects left after the hydrolysis of the D4Rs. The unique arrangement and periodicity of the silanol quadruplets facilitate the subsequent condensation of the layered precursor to a new 3D-framework [92].

3) Organisation

Direct re-condensation of the as-hydrolysed layered precursor commonly produces a disordered material [84]. Formation of highly ordered zeolite requires enhancing the layer ordering prior to the condensation. Although the layers may self-organise spontaneously under favourable conditions, majority of the transformations involve assisted organisation through intercalation of sufficient organic agents [29,91,92,102,103]. The intercalation offers significantly higher control over the quality of the final material and enables further modification of its properties. Not only the ordering, but also the interlayer distance, pore size or relative layer spatial position depend on the choice of the intercalated agent. For example, intercalation of cationic surfactants neatly increases the interlayer distance and creates an expanded material with pore size exceeding that of common zeolites (up to 3,5 nm) [104]. Inversely, intercalation of small agents (e.g. choline) induces parallel shift in the respective layer position. The shifted layered precursor then produces zeolites with new interlayer connectivity and even uncommon structural features such as odd rings [101].

4) Reassembly

The re-condensation of the layered precursor into a three-dimensional zeolite differentiates the ADOR transformation from common hydrothermal synthesis. While the hydrothermal crystallisation is a reversible process, the 2D-3D condensation of the layered material is irreversible. Due to the irreversible nature of the last step, the ADOR transformation is able to produce high-energy configurations, structures which were previously described as unfeasible by hydrothermal synthesis. Furthermore, the irreversible condensation yielded unique structures such as odd-ring pore zeolites or interlayer expanded materials [99,105–107]. All hydrothermally synthesized zeolites obey the LID criteria. In contrast, the rules do not necessarily apply to zeolites prepared by the ADOR transformation, such as IPC-9 and IPC-10 [92, 101].

3.3. Liquid phase transformations

The ADOR transformation is most commonly carried out by immersing the parent germanosilicate in water or acidic solution to produce the layered precursor, subsequent intercalation of organics into the interlayer space to adjust the layer arrangement and finally, calcination. The outcome of the transformation depends on the concentration of the solution, temperature and acidity [108]. The rate of the hydrolysis depends on the amount of water in the system. High volumes of water boost the hydrolysis rate while low water content results in slower hydrolysis. Furthermore, the reaction rate increases with increasing temperature, resulting in faster hydrolysis [29,40,103].

The acidic environment promotes breaking and making of Si–O

bonds. Thus, highly acidic conditions facilitate leaching and re-insertion of Si (or other elements) from/into the framework and, consequently, in forming and healing defects and formation of new structural units; e.g. S4R [95]. The structure of the final zeolite also depends on the experimental conditions. Mildly acidic environment favours hydrolysis of the **UTL** to the layered IPC-1P material. The IPC-1P layers subsequently condensate into the IPC-4 (**PCR**) zeolite. On the other hand, moderately or highly acidic conditions promote the Si re-insertion, formation of S4R units and the IPC-2 (**OKO**) zeolite [91,92,95]. The preparation of the IPC-2 can also occur in two steps by intercalation of the layered IPC-1P with a source of Si and forming the S4R units by treatment with 1 M acid solution under raised temperature [108]. Lastly, the IPC-2 forms directly from the UTL upon hydrolysis in 12 M HCl through mechanism known as "inverse-sigma transformation". The inverse-sigma transformation proceeds through simultaneous cleaving of germanium from D4R units and their rearrangement to S4R [85].

3.4. Vapour phase transformations

The vapour-phase ADOR addresses numerous issues of the liquid-phase transformation which limit its application. The liquid-phase ADOR fails for "open framework" zeolites with low framework density, which typically degrade to amorphous phase or retain the original structure and only undergo degermanation [109,110]. On the contrary, the vapour-phase approach mitigates the downsides of working in large volume of liquid water by disassembling the zeolite by contact with acidic vapours. The disassembly takes place in a vessel with two compartments, separated by a porous membrane. First compartment contains the source of the vapours, such as solution of hydrochloric acid or pure ammonium chloride (Fig. 8). The second compartment contains the germanosilicate zeolite. Upon heating, the acidic vapours pass through the porous membrane to the second compartment and diffuse into the sample. Upon contact with the vapours the hydrolysis of the Ge–O bonds proceeds rapidly. The leached germanium forms volatile germanium chloride, which easily diffuses out of the zeolite. On the other hand, the migration of Si is hindered, preventing the healing and restoration of parent structure. Ergo, the absence of the liquid water not only provides more sensitive conditions for transforming labile zeolites but also affects the Si migration and reinsertion, resulting in formation of new zeolites [110].

The Si migration and re-insertion most notably impacts the outcome of the transformation of ITQ-22 (**IWW**) zeolite. The **IWW** contains interconnected system of 8-, 10- and 12-ring pores. The high pore connectivity facilitates the Si migration during the ADOR transformation. In the liquid phase, the fast Si migration promotes rapid healing of the defects from the disassembly. As a result, the liquid-phase ADOR of **IWW** commonly causes degermanation but results in a preservation of the **IWW** zeolite structure [109]. On the other hand, the vapour-phase setup restricts the Si migration and reinsertion during the ADOR. The vapour-phase ADOR thus enables transformation of the **IWW** and to IPC-18 with 8-, 8- and 12-ring pores and S4R connections in between the layers [110].

3.5. High pressure & mechanochemical transformations

Aside from the chemically mediated transformations, the literature describes several examples of germanosilicate transformations induced by high pressure. Applying high pressures on most germanosilicate zeolites commonly results in structural deterioration and amorphization. Nevertheless, notable structures, such as ITQ-29, can undergo controlled structural transformation. The silicate ITQ-29 possesses the **LTA** structure consisting of *sod* cages connected through *d4r* units. Under high pressure half of the *d4r* units converts to *sti* units accompanied by transformation of the *lta* cages to *ify*. The structural transformations manifest as 3D-3D conversion of the ITQ-29 (**LTA**) to ITQ-50 (**IFY**). The transformation is reversible up to moderate pressures around 1.2 GPa
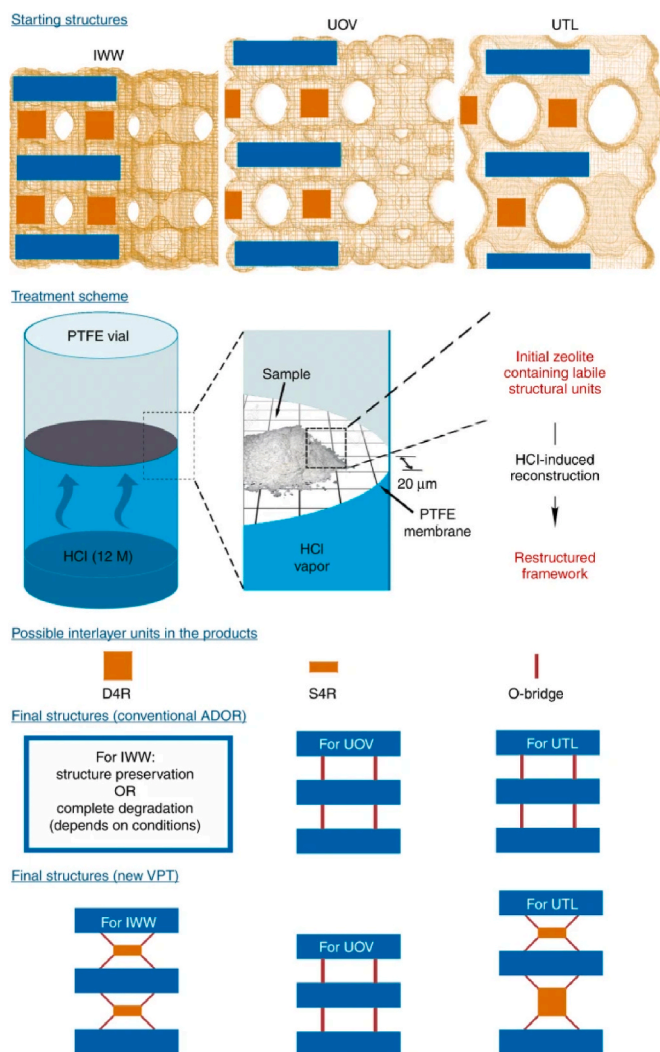

Fig. 8. Vapour-phase ADOR transformation of **IWW**, **UOV** and **UTL** germanosilicates [110].

and the ITQ-50 reverts back to ITQ-29 once the pressure decreases. However, higher pressures over 3.2 GPa cause irreversible changes and the zeolite retains the IFY structure even after the pressure is released [111].

Pressure-induced transformations also occur among the layered zeolite precursors. The layered IPC-1P obtained by hydrolysis of zeolite **UTL** undergoes condensation to IPC-2 (**OKO**) under 1 GPa and 200 °C. Contrary to the liquid-phase transformation of IPC-1P to IPC-2P, the high pressure 2D-3D transformation proceeds without a solvent and significantly reduces the experimental temperature from 550 °C to 200 °C. Interestingly, the high-pressure condensation of IPC-1P favours the formation of less dense IPC-2 (**OKO**) over the denser IPC-4 (**PCR**). The seemingly contra-intuitive behaviour originates from underlying reactions that accompany the 2D-3D transformation. The silanol groups on the IPC-1P condense to form the interlayer connections releasing water into the zeolite channels in the process. The formation of IPC-2 with micropores filled with water molecules thus becomes more favourable than IPC-4, because the total volume of the system containing both the released water and the zeolite is lower for IPC-2 [112].

3.6. Characterisation of ADOR products and mechanistic studies

The complex nature of the ADOR process means that characterising the intermediates, final products and the overall mechanism can be a

challenge. The essential 3D to 2D to 3D nature of overall transformation [113] means that there is great scope to lose and then regain crystalline order during the process itself. This means that both long range and short range characterisation techniques play a vital part.

As the initial parent and final daughter products are usually relatively crystalline, X-ray diffraction (XRD) is an obvious technique to use. However, during the process itself the long-range order (e.g., the register between layers in IPC-1P) is partially, but not completely, lost and XRD, while still useful in measuring, for example interlayer distances (Fig. 9) [29], does not give as much information as for highly crystalline solids. Since the extended layers from the parent material remain intact throughout the process the phase purity of the zeolite (usually measured using X-ray diffraction) is not usually a problem. However, the mechanism means that there is the possibility of significant disorder in the interlayer space and, as is common with the stacking/reconnection of any layered material there is the possibility of introducing stacking faults. The extent of disorder and faulting varies between materials, with some solids (such as the so-called unfeasible zeolites) being heavily faulted while others are well ordered and show few faults. Transmission electron microscopy, combined with XRD is often the best way to characterise these materials.

Other techniques, such as X-ray pair distribution function (PDF) analysis [114], positron annihilation spectroscopy [115] and computation [94] provide complementary and extremely useful information.

NMR spectroscopy is ideal for studying local structure, disorder and chemical reactivity in the solid state because of its sensitivity to the atomic-scale environment (without the need for any long-range order) [116]. This is particularly so for microporous materials where it provides information on both the framework and on any guest molecules incorporated in the pores or attached to metal centres [117]. Conventionally, rapid magic-angle spinning (MAS) is used to remove the anisotropic broadening found in NMR spectra of solids, but for nuclei with spin quantum number $I > 1/2$ (such as ^{17}O and ^{27}Al), more complex experiments (e.g. MQMAS and STMAS), are required to remove the quadrupolar broadening and resolve distinct species.

NMR spectroscopy has been particularly useful at following the nature of the silicon species in the process and by following how the oxygen species changes, especially on hydrolysis [118]. Techniques that probe local structural changes *in situ* during the process are particularly valuable for determining the overall mechanism. NMR [103] and PDF [119,120] analysis have both been vital tools in understanding the process.

4. Summary and perspectives

The development of germanosilicate chemistry on zeolite science has had two major impacts. First, the larger size of the germanium atom compared to silicon has led to the stabilisation of smaller multiple rings (D3R and D4R), which in turn has opened up new avenues in the preparation of large pore zeolites of 14-rings and above. The correlation between small rings in the frameworks and large pores is well known, and the work developed by Corma and others has opened up several new avenues in this area. Perhaps the most surprising result of all is the tendency of germanium to substitute for silicon in a regiospecific manner. It is unusual in zeolites to have quite such strong regiospecific substutions – and indeed a major synthetic challenge is to control where dopant atoms (especially aluminium) are located as it is these dopants that often control the reactivity of the materials. Understanding how the regiospecificity of germanium substitution works could well help our overall understanding of the process in all zeolitic solids.

The downside of germanium substitution in zeolite science is its susceptibility to hydrolysis. This makes the use of germanosilicates as active materials more difficult under many conditions. However, even this seeming disadvantage can be turned into an advantage as is shown by the various transformation routes including the ADOR process and related methods. This controlled disassembly/reassembly method is a
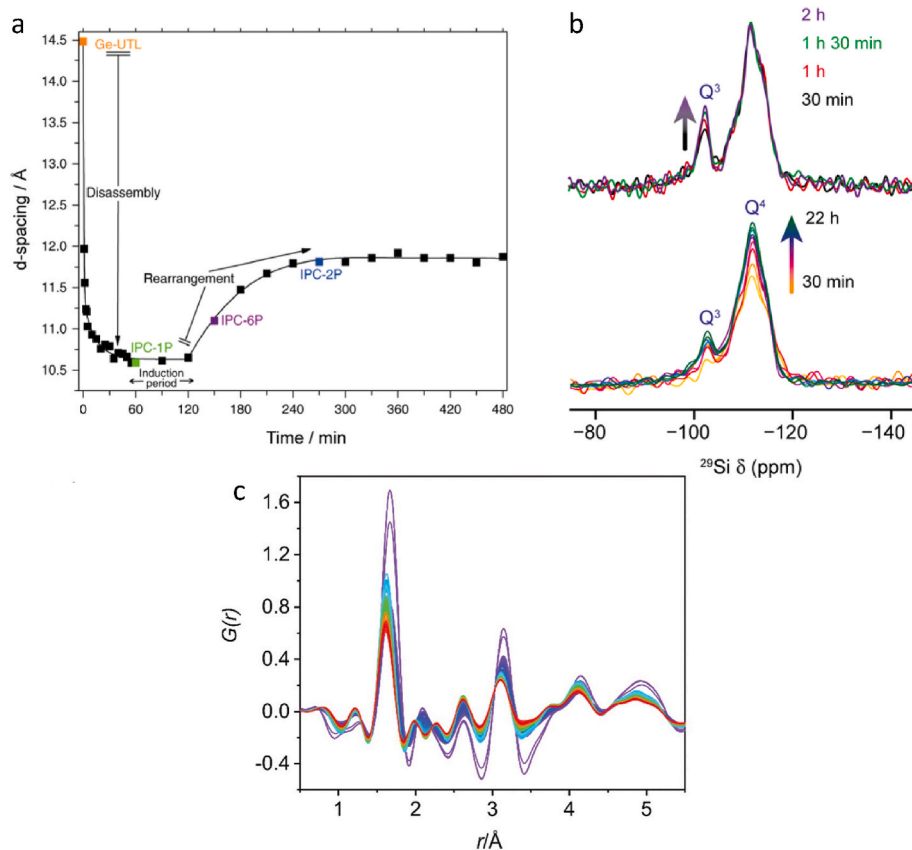
Fig. 9. Advanced characterisation of the ADOR process. (a) shows the variation of the d_{200} spacing (measured by XRD) as the process is ongoing. (b) shows *in situ* ^{29}Si MAS NMR studies of the process showing how the nature of silicon species in the materials change and (c) shows *in situ* X-ray PDF data, illustrating how interatomic distances change during the hydrolysis. Further details can be found in Refs. [29,118,119]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

fundamentally different synthetic procedure from traditional hydrothermal synthesis, relying as it does not on a crystallisation process but on condensation of large-scale intermediates. The primary importance of this is that mateirals that could be regarded as difficult to prepare (or unfeasible synthetic targets) using hydrothermal/solvothermal methods may indeed now become viable materials.

So what of the future of germanosilicate materials. Clearly there is a great deal of research still required to understand the impact of Ge (and indeed other substituting elements) on zeolite synthesis in general. The effects of different amounts of Ge in the synthesis on the structure and morphology of the resultant materials are only beginning to be understood. This is common with much zeolite synthesis mechanism studies. Improved *in situ* or *operando* characterisation techniques will surely play a part in developing our understanding of these processes. But there is also still a part to play in developing the breadth of feasible synthetic targets – we have certainly not exhausted the potential for the preparation of new topologies using either germanium in traditional hydrothermal synthesis or in the transformation syntheses like the ADOR process. There is much still to be done with exploring the interplay of designer SDAs with heteroatoms such as Ge and the scope for new material discovery is still a strong driver for future research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] J. Čejka, A. Corma, S. Zones, Zeolites and Catalysis, Wiley, 2010.

[2] R. Xu, W. Pang, J. Yu, Q. Huo, J. Chen, Introduction, in: R. Xu, W. Pang, J. Yu, Q. Huo, J. Chen (Eds.), Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure, Wiley, 2007, pp. 1–18.

[3] A. Corma, State of the art and future challenges of zeolites as catalysts, J. Catal. 216 (2003) 298–312.

[4] R.E. Morris, X. Bu, Induction of chiral porous solids containing only achiral building blocks, Nat. Chem. 2 (2010) 353–361.

[5] S.I. Zones, Translating new materials discoveries in zeolite research to commercial manufacture, Microporous Mesoporous Mater. 144 (2011) 1–8.

[6] J. Jiang, J. Yu, A. Corma, Extra-large-pore zeolites: bridging the gap between micro and mesoporous structures, Angew. Chem. Int. Ed. 49 (2010) 3120–3145.

[7] J. Yu, R. Xu, Rational approaches toward the design and synthesis of zeolitic inorganic open-framework materials, Acc. Chem. Res. 43 (2010) 1195–1204.

[8] Y. Han, Y. Li, J. Yu, R. Xu, A gallogermanate zeolite constructed exclusively by three-ring building units, Angew. Chem. Int. Ed. 50 (2011) 3003–3005.

[9] R. de la Serna, D. Nieto, D. Sainz, B. Bernardo-Maestro, Á. Mayoral, C. Márquez-Álvarez, J. Pérez-Pariente, L. Gómez-Hortigüela, GTM-3, an extra-large pore enantioselective chiral zeolitic catalyst, J. Am. Chem. Soc. 144 (2022) 8249–8256.

[10] D. Kubička, O. Kikhtyanin, Opportunities for zeolites in biomass upgrading—lessons from the refining and petrochemical industry, Catal. Today 243 (2015) 10–22.

[11] T. Ennaert, J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, D. Verboekend, B.F. Sels, Potential and challenges of zeolite chemistry in the catalytic conversion of biomass, Chem. Soc. Rev. 45 (2016) 584–611.

[12] P.A. Jacobs, M. Dusselier, B.F. Sels, Will zeolite-based catalysis be as relevant in future biorefineries as in crude oil refineries? Angew. Chem. Int. Ed. 53 (2014) 8621–8626.

[13] H. Xu, P. Wu, New progress in zeolite synthesis and catalysis, Natl. Sci. Rev. 9 (2022).

[14] M. Shamzhy, M. Opanasenko, P. Concepción, A. Martínez, New trends in tailoring active sites in zeolite-based catalysts, Chem. Soc. Rev. 48 (2019) 1095–1149.

[15] L. Gómez-Hortigüela, J. Pérez-Pariente, Synthesis and properties of zeolite materials guided by periodic considerations, in: D.M.P. Mingos (Ed.), The Periodic Table II: Catalytic, Materials, Biological and Medical Applications, Springer International Publishing, Cham, 2019, pp. 53–88.

[16] J. Čejka, A. Vondrová, B. Wichterlová, G. Vorbeck, R. Fricke, The effect of Al, Fe and in substitution in the MFI silicate structure on the aromatic hydrocarbon transformation: Si-OH-M site strength, Zeolites 14 (1994) 147–153.

[17] B.B. Schaack, W. Schrader, F. Schüth, How are heteroelements (Ga and Ge) incorporated in silicate oligomers? Chem. Eur J. 15 (2009) 5920–5925.

[18] J. Yu, Synthesis of zeolites, in: J. Čejka, H. van Bekkum, A. Corma, F. Schüth (Eds.), Studies in Surface Science and Catalysis, Elsevier, 2007, pp. 39–103.

[19] C.J. Heard, L. Grajciar, F. Uhlík, M. Shamzhy, M. Opanasenko, J. Čejka, P. Nachtigall, Zeolite (In)Stability under aqueous or steaming conditions, Adv. Mater. 32 (2020), 2003264.

[20] A. Corma, M.T. Navarro, F. Rey, J. Rius, S. Valencia, Pure polymorph C of zeolite beta synthesized by using framework isomorphous substitution as a structure-directing mechanism, Angew Chem. Int. Ed. Engl. 40 (2001) 2277–2280.

[21] R.F. Lobo, S.I. Zones, M.E. Davis, Structure-direction in zeolite synthesis, J. Inclusion Phenom. Mol. Recognit. Chem. 21 (1995) 47–78.

[22] R. Bai, Q. Sun, N. Wang, Y. Zou, G. Guo, S. Iborra, A. Corma, J. Yu, Simple quaternary ammonium cations-templated syntheses of extra-large pore germanosilicate zeolites, Chem. Mater. 28 (2016) 6455–6458.

[23] E. Kapaca, J. Jiang, J. Cho, J.L. Jordá, M.J. Díaz-Cabañas, X. Zou, A. Corma, T. Willhammar, Synthesis and structure of a 22 × 12 × 12 extra-large pore zeolite ITQ-56 determined by 3D electron diffraction, J. Am. Chem. Soc. 143 (2021) 8713–8719.

[24] Y. Yun, M. Hernández, W. Wan, X. Zou, J.L. Jordá, A. Cantín, F. Rey, A. Corma, The first zeolite with a tri-directional extra-large 14-ring pore system derived using a phosphonium-based organic molecule, Chem. Commun. 51 (2015) 7602–7605.

[25] J. Jiang, Y. Xu, P. Cheng, Q. Sun, J. Yu, A. Corma, R. Xu, Investigation of extra-large pore zeolite synthesis by a high-throughput approach, Chem. Mater. 23 (2011) 4709–4715.

[26] Y. Li, J. Yu, New stories of zeolite structures: their descriptions, determinations, predictions, and evaluations, Chem. Rev. 114 (2014) 7268–7316.

[27] Z. Wang, J. Yu, R. Xu, Needs and trends in rational synthesis of zeolitic materials, Chem. Soc. Rev. 41 (2012) 1729–1741.

[28] A. Sala, E. Pérez-Botella, J.L. Jordá, A. Cantín, F. Rey, S. Valencia, ITQ-69: a germanium-containing zeolite and its synthesis, structure determination, and adsorption properties, Angew. Chem. Int. Ed. 60 (2021) 11745–11750.

[29] S.E. Henkelis, M. Mazur, C.M. Rice, P.S. Wheatley, S.E. Ashbrook, R.E. Morris, Kinetics and mechanism of the hydrolysis and rearrangement processes within the assembly–disassembly–organization–reassembly synthesis of zeolites, J. Am. Chem. Soc. 141 (2019) 4453–4459.

[30] J.H. Kang, D. Xie, S.I. Zones, M.E. Davis, Fluoride-free synthesis of germanosilicate CIT-13 and its inverse sigma transformation to form CIT-14, Chem. Mater. 32 (2020) 2014–2024.

[31] M. Opanasenko, M. Shamzhy, Y. Wang, W. Yan, P. Nachtigall, J. Čejka, Synthesis and post-synthesis transformation of germanosilicate zeolites, Angew. Chem. Int. Ed. 59 (2020) 19380–19389.

[32] P. Kamakoti, T.A. Barckholtz, Role of germanium in the Formation of double four rings in zeolites, J. Phys. Chem. C 111 (2007) 3575–3583.

[33] S.O. Odoh, M.W. Deem, L. Gagliardi, Preferential location of germanium in the UTL and IPC-2a zeolites, J. Phys. Chem. C 118 (2014) 26939–26946.

[34] J.A. Vidal-Moya, T. Blasco, F. Rey, A. Corma, M. Puche, Distribution of fluorine and germanium in a new zeolite structure ITQ-13 studied by F-19 nuclear magnetic resonance, Chem. Mater. 15 (2003) 3961–3963.

[35] G. Sastre, A. Pulido, A. Corma, An attempt to predict and rationalize relative stabilities and preferential germanium location in Si/Ge zeolites, Microporous Mesoporous Mater. 82 (2005) 159–163.

[36] N. Kasian, A. Tuel, E. Verheyen, C.E.A. Kirschhock, F. Taulelle, J.A. Martens, NMR evidence for specific germanium siting in IM-12 zeolite, Chem. Mater. 26 (2014) 5556–5565.

[37] J.X. Jiang, J.L. Jorda, M.J. Diaz-Cabanas, J.H. Yu, A. Corma, The synthesis of an extra-large-pore zeolite with double three-ring building units and a low framework density, Angew. Chem., Int. Ed. 49 (2010) 4986–4988.

[38] L.A. Villaescusa, M.A. Camblor, Framework reduction of GeO2 zeolites during calcination, Chem. Mater. 28 (2016) 7544–7550.

[39] J.H. Kang, D. Xie, S.I. Zones, M.E. Davis, Transformation of extra-large pore germanosilicate CIT-13 molecular sieve into extra-large pore CIT-5 molecular sieve, Chem. Mater. 31 (2019) 9777–9787.

[40] M. Jin, O. Veselý, C.J. Heard, M. Kubů, P. Nachtigall, J. Čejka, L. Grajciar, The role of water loading and germanium content in germanosilicate hydrolysis, J. Phys. Chem. C 125 (2021) 23744–23757.

[41] P. Caullet, J.-L. Paillaud, A. Simon-Masseron, M. Soulard, J. Patarin, The fluoride route: a strategy to crystalline porous materials, Compt. Rendus Chem. 8 (2005) 245–266.

[42] J.L. Jorda, A. Cantin, A. Corma, M.J. Diaz-Cabanas, S. Leiva, M. Moliner, F. Rey, M.J. Sabater, S. Valencia, Structural Study of Pure Silica and Gecontaining Zeolite ITQ-24, Zeitschrift Fur Kristallographie, 2007, pp. 393–398.

[43] R.M. Barrer, P.J. Denny, 201. Hydrothermal chemistry of the silicates. Part IX. Nitrogenous aluminosilicates, J. Chem. Soc. (1961) 971–982.

[44] B.M. Lok, T.R. Cannan, C.A. Messina, The role of organic molecules in molecular sieve synthesis, Zeolites 3 (1983) 282–291.

[45] M. Moliner, F. Rey, A. Corma, Towards the rational design of efficient organic structure-directing agents for zeolite synthesis, Angew. Chem., Int. Ed. 52 (2013) 13880–13889.

[46] J. Li, A. Corma, J. Yu, Synthesis of new zeolite structures, Chem. Soc. Rev. 44 (2015) 7112–7127.

[47] Y. Kubota, M.M. Helmkamp, S.I. Zones, M.E. Davis, Properties of organic cations that lead to the structure-direction of high-silica molecular sieves, Microporous Mater. 6 (1996) 213–229.

[48] M.B. Park, S.J. Cho, S.B. Hong, Synthesis of aluminosilicate and gallosilicate zeolites via a charge density mismatch approach and their characterization, J. Am. Chem. Soc. 133 (2011) 1917–1934.

[49] O.V. Shvets, N. Kasian, A. Zukal, J. Pinkas, J. Čejka, The role of template structure and synergism between inorganic and organic structure directing agents in the synthesis of UTL zeolite, Chem. Mater. 22 (2010) 3482–3495.

[50] A. Jackowski, S.I. Zones, S.-J. Hwang, A.W. Burton, Diquaternary ammonium compounds in zeolite synthesis: cyclic and polycyclic N-heterocycles connected by methylene chains, J. Am. Chem. Soc. 131 (2009) 1092–1100.

[51] Y. Lorgouilloux, M. Dodin, J.-L. Paillaud, P. Caullet, L. Michelin, L. Josien, O. Ersen, N. Bats, IM-16, A new microporous germanosilicate with a novel framework topology containing d4r and mtw composite building units, J. Solid State Chem. 182 (2009) 622–629.

[52] M. Dodin, J.-L. Paillaud, Y. Lorgouilloux, P. Caullet, E. Elkaïm, N. Bats, A zeolitic material with a three-dimensional pore system formed by straight 12- and 10-ring channels synthesized with an imidazolium derivative as structure-directing agent, J. Am. Chem. Soc. 132 (2010) 10221–10223.

[53] C. Baerlocher, T. Weber, L.B. McCusker, L. Palatinus, S.I. Zones, Unraveling the perplexing structure of the zeolite SSZ-57, Science 333 (2011) 1134–1137.

[54] J. Sun, C. Bonneau, Á. Cantín, A. Corma, M.J. Díaz-Cabañas, M. Moliner, D. Zhang, M. Li, X. Zou, The ITQ-37 mesoporous chiral zeolite, Nature 458 (2009) 1154–1157.

[55] J. Jiang, J.L. Jorda, M.J. Diaz-Cabanas, J. Yu, A. Corma, The synthesis of an extra-large-pore zeolite with double three-ring building units and a low framework density, Angew. Chem. Int. Ed. 49 (2010) 4986–4988.

[56] A. Corma, F. Rey, J. Rius, M.J. Sabater, S. Valencia, Supramolecular self-assembled molecules as organic directing agent for synthesis of zeolites, Nature 431 (2004) 287–290.

[57] Q. Xu, Y. Gong, W. Xu, J. Xu, F. Deng, T. Dou, Synthesis of high-silica EU-1 zeolite in the presence of hexamethonium ions: a seeded approach for inhibiting ZSM-48, J. Colloid Interface Sci. 358 (2011) 252–260.

[58] X. Liu, U. Ravon, A. Tuel, Synthesis of all-silica zeolites from highly concentrated gels containing hexamethonium cations, Microporous Mesoporous Mater. 156 (2012) 257–261.

[59] A. Corma, M.J. Diaz-Cabanas, J.L. Jorda, F. Rey, G. Sastre, K.G. Strohmaier, A zeolitic structure (ITQ-34) with connected 9- and 10-ring channels obtained with phosphonium cations as structure directing agents, J. Am. Chem. Soc. 130 (2008) 16482–16483.

[60] D.L. Dorset, K.G. Strohmaier, C.E. Kliewer, A. Corma, M.J. Diaz-Cabanas, F. Rey, C.J. Gilmore, Crystal structure of ITQ-26, a 3D framework with extra-large pores, Chem. Mater. 20 (2008) 5325–5331.

[61] D.L. Dorset, G.J. Kennedy, K.G. Strohmaier, M.J. Diaz-Cabañas, F. Rey, A. Corma, P-derived organic cations as structure-directing agents: synthesis of a high-silica zeolite (ITQ-27) with a two-dimensional 12-ring channel system, J. Am. Chem. Soc. 128 (2006) 8862–8867.

[62] A. Corma, M.J. Díaz-Cabañas, J. Jiang, M. Afeworki, D.L. Dorset, S.L. Soled, K. G. Strohmaier, Extra-large pore zeolite (ITQ-40) with the lowest framework density containing double four- and double three-rings, Proc. Natl. Acad. Sci. USA 107 (2010) 13997–14002.

[63] M. Hernández-Rodríguez, J.L. Jordá, F. Rey, A. Corma, Synthesis and structure determination of a new microporous zeolite with large cavities connected by small pores, J. Am. Chem. Soc. 134 (2012) 13232–13235.

[64] R. Simancas, J.L. Jordá, F. Rey, A. Corma, A. Cantín, I. Peral, C. Popescu, A new microporous zeolitic silicoborate (ITQ-52) with interconnected small and medium pores, J. Am. Chem. Soc. 136 (2014) 3342–3345.

[65] R. Simancas, D. Dari, N. Velamazán, M.T. Navarro, A. Cantín, J.L. Jordá, G. Sastre, A. Corma, F. Rey, Modular organic structure-directing agents for the synthesis of zeolites, Science 330 (2010) 1219–1222.

[66] Q. Huang, N. Chen, L. Liu, K.S. Arias, S. Iborra, X. Yi, C. Ma, W. Liang, A. Zheng, C. Zhang, J. Hu, Z. Cai, Y. Liu, J. Jiang, A. Corma, Direct synthesis of the organic and Ge free Al containing BOG zeolite (ITQ-47) and its application for transformation of biomass derived molecules, Chem. Sci. 11 (2020) 12103–12108.

[67] C.S. Cundy, P.A. Cox, The hydrothermal synthesis of zeolites: precursors, intermediates and reaction mechanism, Microporous Mesoporous Mater. 82 (2005) 1–78.

[68] J. Grand, H. Awala, S. Mintova, Mechanism of zeolites crystal growth: new findings and open questions, CrystEngComm 18 (2016) 650–664.

[69] M.-H. Kim, H.-X. Li, M.E. Davis, Synthesis of zeolites by water—organic vapor-phase transport, Microporous Mater. 1 (1993) 191–200.

[70] M. Matsukata, M. Ogura, T. Osaki, P.R. Hari Prasad Rao, M. Nomura, E. Kikuchi, Conversion of dry gel to microporous crystals in gas phase, Top. Catal. 9 (1999) 77–92.

[71] M. Matsukata, N. Nishiyama, K. Ueyama, Synthesis of zeolites under vapor atmosphere: effect of synthetic conditions on zeolite structure, Microporous Mater. 1 (1993) 219–222.

[72] J. Weitkamp, M. Hunger, Preparation of zeolites via the dry-gel synthesis method, in: A. Gamba, C. Colella, S. Coluccia (Eds.), Studies in Surface Science and Catalysis, Elsevier, 2005, pp. 1–12.

[73] W. Xu, J. Dong, J. Li, J. Li, F. Wu, A novel method for the preparation of zeolite ZSM-5, J. Chem. Soc., Chem. Commun. (1990) 755–756.

[74] I.G. Clayson, D. Hewitt, M. Hutereau, T. Pope, B. Slater, High throughput methods in the synthesis, characterization, and optimization of porous materials, Adv. Mater. 32 (2020), 2002780.

[75] T.P. Caremans, C.E.A. Kirschhock, P. Verlooy, J.S. Paul, P.A. Jacobs, J.A. Martens, Prototype high-throughput system for hydrothermal synthesis and X-ray diffraction of microporous and mesoporous materials, Microporous Mesoporous Mater. 90 (2006) 62–68.

[76] J.M. Newsam, T. Bein, J. Klein, W.F. Maier, W. Stichert, High throughput experimentation for the synthesis of new crystalline microporous solids, Microporous Mesoporous Mater. 48 (2001) 355–365.

[77] M. Moliner, J.M. Serra, A. Corma, E. Argente, S. Valero, V. Botti, Application of artificial neural networks to high-throughput synthesis of zeolites, Microporous Mesoporous Mater. 78 (2005) 73–81.

[78] P.M. Forster, N. Stock, A.K. Cheetham, A high-throughput investigation of the role of pH, temperature, concentration, and time on the synthesis of hybrid inorganic–organic materials, Angew. Chem. Int. Ed. 44 (2005) 7608–7611.

[79] A. Corma, M.J. Diaz-Cabanas, J. Luis Jorda, C. Martinez, M. Moliner, High-throughput synthesis and catalytic properties of a molecular sieve with 18-and 10-member rings, Nature 443 (2006) 842–845.

[80] A. Corma, M.J. Díaz-Cabañas, M. Moliner, C. Martinez, Discovery of a new catalytically active and selective zeolite (ITQ-30) by high-throughput synthesis techniques, in: R. Xu, Z. Gao, J. Chen, W. Yan (Eds.), Studies in Surface Science and Catalysis, Elsevier, 2007, pp. 322–329.

[81] M. Moliner, Y. Román-Leshkov, A. Corma, Machine learning applied to zeolite synthesis: the missing link for realizing high-throughput discovery, Acc. Chem. Res. 52 (2019) 2971–2980.

[82] D. Schwalbe-Koda, S. Kwon, C. Paris, E. Bello-Jurado, Z. Jensen, E. Olivetti, T. Willhammar, A. Corma, Y. Román-Leshkov, M. Moliner, R. Gómez-Bombarelli, A priori control of zeolite phase competition and intergrowth with high-throughput simulations, Science 374 (2021) 308–315.

[83] A. Cantín, A. Corma, M.J. Diaz-Cabanas, J.L. Jordá, M. Moliner, Rational design and HT techniques allow the synthesis of new IWR zeolite polymorphs, J. Am. Chem. Soc. 128 (2006) 4216–4217.

[84] W.J. Roth, O.V. Shvets, M. Shamzhy, P. Chlubna, M. Kubu, P. Nachtigall, J. Čejka, Postsynthesis transformation of three-dimensional framework into a lamellar zeolite with modifiable architecture, J. Am. Chem. Soc. 133 (2011) 6130–6133.

[85] E. Verheyen, L. Joos, K. Van Havenbergh, E. Breynaert, N. Kasian, E. Gobechiya, K. Houthoofd, C. Martineau, M. Hinterstein, F. Taulelle, V. Van Speybroeck, M. Waroquier, S. Bals, G. Van Tendeloo, C.E.A. Kirschhock, J.A. Martens, Design of zeolite by inverse sigma transformation, Nat. Mater. 11 (2012) 1059–1064.

[86] L. Burel, N. Kasian, A. Tuel, Quasi all-silica zeolite obtained by isomorphous degermanation of an as-made germanium-containing precursor, Angew. Chem. Int. Ed. 53 (2014) 1360–1363.

[87] M.V. Shamzhy, P. Eliašová, D. Vitvarová, M.V. Opanasenko, D.S. Firth, R. E. Morris, Post-synthesis stabilization of germanosilicate zeolites ITH, IWW, and UTL by substitution of Ge for Al, Chem. Eur J. 22 (2016) 17377–17386.

[88] H. Xu, J.-g. Jiang, B. Yang, L. Zhang, M. He, P. Wu, Post-synthesis treatment gives highly stable siliceous zeolites through the isomorphous substitution of silicon for germanium in germanosilicates, Angew. Chem. Int. Ed. 53 (2014) 1355–1359.

[89] M. Mazur, V. Kasneryk, J. Přech, F. Brivio, C. Ochoa-Hernández, A. Mayoral, M. Kubů, J. Čejka, Zeolite framework functionalisation by tuneable incorporation of various metals into the IPC-2 zeolite, Inorg. Chem. Front. 5 (2018) 2746–2755.

[90] D.S. Firth, S.A. Morris, P.S. Wheatley, S.E. Russell, A.M.Z. Slawin, D.M. Dawson, A. Mayoral, M. Opanasenko, M. Položij, J. Čejka, P. Nachtigall, R.E. Morris, Assembly–disassembly–organization–reassembly synthesis of zeolites based on cfi-type layers, Chem. Mater. 29 (2017) 5605–5611.

[91] W.J. Roth, P. Nachtigall, R.E. Morris, P.S. Wheatley, V.R. Seymour, S. E. Ashbrook, P. Chlubna, L. Grajciar, M. Polozij, A. Zukal, O. Shvets, J. Čejka, A family of zeolites with controlled pore size prepared using a top-down method, Nat. Chem. 5 (2013) 628–633.

[92] P. Eliášová, M. Opanasenko, P.S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W.J. Roth, R.E. Morris, J. Čejka, The ADOR mechanism for the synthesis of new zeolites, Chem. Soc. Rev. 44 (2015) 7177–7206.

[93] M. Trachta, P. Nachtigall, O. Bludský, The ADOR synthesis of new zeolites: in silico investigation, Catal. Today (2014) 1007–1041, https://doi.org/10.1016/j. cattod.

[94] M. Trachta, O. Bludský, J. Čejka, R.E. Morris, P. Nachtigall, From double-four-ring germanosilicates to new zeolites: in silico investigation, ChemPhysChem 15 (2014) 2972–2976.

[95] P.S. Wheatley, P. Chlubná-Eliášová, H. Greer, W. Zhou, V.R. Seymour, D. M. Dawson, S.E. Ashbrook, A.B. Pinar, L.B. McCusker, M. Opanasenko, J. Čejka, R.E. Morris, Zeolites with continuously tuneable porosity, Angew. Chem. 126 (2014) 13426–13430.

[96] N. Žilková, P. Eliášová, S. Al-Khattaf, R.E. Morris, M. Mazur, J. Čejka, The effect of UTL layer connectivity in isoreticular zeolites on the catalytic performance in toluene alkylation, Catal. Today 277 (2016) 55–60.

[97] N. Remperová, J. Přech, M. Kubů, K. Gołąbek, J.F. Miñambres, M.-F. Hsieh, A. Turrina, M. Mazur, Gas-phase isomerisation of m-xylene on isoreticular zeolites with tuneable porosity, Catal. Today 390–391 (2022) 78–91.

[98] Y. Zhou, S.A. Kadam, M. Shamzhy, J. Čejka, M. Opanasenko, Isoreticular UTL-derived zeolites as model materials for probing pore size–activity relationship, ACS Catal. 9 (2019) 5136–5146.

[99] X. Li, M.W. Deem, Why zeolites have so few seven-membered rings, J. Phys. Chem. C 118 (2014) 15835–15839.

[100] Y. Li, J.H. Yu, R.R. Xu, Criteria for zeolite frameworks realizable for target synthesis, Angew. Chem., Int. Ed. 52 (2013) 1673–1677.

[101] M. Mazur, P.S. Wheatley, M. Navarro, W.J. Roth, M. Položij, A. Mayoral, P. Eliášová, P. Nachtigall, J. Čejka, R.E. Morris, Synthesis of 'unfeasible' zeolites, Nat. Chem. 8 (2016) 58–62.

[102] M. Mazur, P. Chlubná-Eliášová, W.J. Roth, J. Čejka, Intercalation chemistry of layered zeolite precursor IPC-1P, Catal. Today 227 (2014) 37–44.

[103] S.A. Morris, G.P.M. Bignami, Y. Tian, M. Navarro, D.S. Firth, J. Čejka, P. S. Wheatley, D.M. Dawson, W.A. Slawinski, D.S. Wragg, R.E. Morris, S. E. Ashbrook, In situ solid-state NMR and XRD studies of the ADOR process and the unusual structure of zeolite IPC-6, Nat. Chem. 9 (2017) 1012–1018.

[104] M. Shamzhy, M. Mazur, M. Opanasenko, W.J. Roth, J. Cejka, Swelling and pillaring of the layered precursor IPC-1P: tiny details determine everything, Dalton Trans. 43 (2014) 10548–10557.

[105] Z. Zhao, W. Zhang, P. Ren, X. Han, U. Müller, B. Yilmaz, M. Feyen, H. Gies, F.-S. Xiao, D. De Vos, T. Tatsumi, X. Bao, Insights into the topotactic conversion process from layered silicate RUB-36 to FER-type zeolite by layer reassembly, Chem. Mater. 25 (2013) 840–847.

[106] F.-S. Xiao, B. Xie, H. Zhang, L. Wang, X. Meng, W. Zhang, X. Bao, B. Yilmaz, U. Müller, H. Gies, H. Imai, T. Tatsumi, D. De Vos, Interlayer-expanded microporous titanosilicate catalysts with functionalized hydroxyl groups, ChemCatChem 3 (2011) 1442–1446.

[107] S. Inagaki, H. Imai, S. Tsujiuchi, H. Yakushiji, T. Yokoi, T. Tatsumi, Enhancement of catalytic properties of interlayer-expanded zeolite Al-MWW via the control of interlayer silylation conditions, Microporous Mesoporous Mater. 142 (2011) 354–362.

[108] M. Mazur, M. Kubů, P.S. Wheatley, P. Eliášová, Germanosilicate UTL and its rich chemistry of solid-state transformations towards IPC-2 (OKO) zeolite, Catal. Today 243 (2015) 23–31.

[109] P. Chlubná-Eliášová, Y. Tian, A.B. Pinar, M. Kubů, J. Čejka, R.E. Morris, The assembly-disassembly-organization-reassembly mechanism for 3D-2D-3D transformation of germanosilicate IWW zeolite, Angew. Chem. Int. Ed. 53 (2014) 7048–7052.

[110] V. Kasneryk, M. Shamzhy, J. Zhou, Q. Yue, M. Mazur, A. Mayoral, Z. Luo, R. E. Morris, J. Čejka, M. Opanasenko, Vapour-phase-transport rearrangement technique for the synthesis of new zeolites, Nat. Commun. 10 (2019) 5129.

[111] J.L. Jordá, F. Rey, G. Sastre, S. Valencia, M. Palomino, A. Corma, A. Segura, D. Errandonea, R. Lacomba, F.J. Manjón, Ó. Gomis, A.K. Kleppe, A.P. Jephcoat, M. Amboage, J.A. Rodríguez-Velamazán, Synthesis of a novel zeolite through a pressure-induced reconstructive phase transition process, Angew. Chem. Int. Ed. 52 (2013) 10458–10462.

[112] M. Mazur, Angel M. Arévalo-López, P.S. Wheatley, G.P.M. Bignami, S. E. Ashbrook, Á. Morales-García, P. Nachtigall, J.P. Attfield, J. Čejka, R.E. Morris, Pressure-induced chemistry for the 2D to 3D transformation of zeolites, J. Mater. Chem. 6 (2018) 5255–5259.

[113] P. Chlubna, W.J. Roth, H.F. Greer, W.Z. Zhou, O. Shvets, A. Zukal, J. Čejka, R. E. Morris, 3D to 2D routes to ultrathin and expanded zeolitic materials, Chem. Mater. 25 (2013) 542–547.

[114] S.A. Morris, P.S. Wheatley, M. Položij, P. Nachtigall, P. Eliášová, J. Čejka, T. C. Lucas, J.A. Hriljac, A.B. Pinar, R.E. Morris, Combined PDF and Rietveld studies of ADORable zeolites and the disordered intermediate IPC-1P, Dalton Trans. 45 (2016) 14124–14130.

[115] J. Jagiello, M. Sterling, P. Eliášová, M. Opanasenko, A. Zukal, R.E. Morris, M. Navaro, A. Mayoral, P. Crivelli, R. Warringham, S. Mitchell, J. Pérez-Ramírez, J. Čejka, Structural analysis of IPC zeolites and related materials using positron annihilation spectroscopy and high-resolution argon adsorption, Phys. Chem. Chem. Phys. 18 (2016) 15269–15277.

[116] B. Reif, S.E. Ashbrook, L. Emsley, M. Hong, Solid-state NMR spectroscopy, Nat. Rev. Method. Primers. 1 (2021) 2.

[117] S.E. Ashbrook, Z.H. Davis, R.E. Morris, C.M. Rice, 17O NMR spectroscopy of crystalline microporous materials, Chem. Sci. 12 (2021) 5016–5036.

[118] G.P.M. Bignami, D.M. Dawson, V.R. Seymour, P.S. Wheatley, R.E. Morris, S. E. Ashbrook, Synthesis, isotopic enrichment, and solid-state NMR characterization of zeolites derived from the assembly, disassembly, organization, reassembly process, J. Am. Chem. Soc. 139 (2017) 5140–5148.

[119] S.E. Henkelis, S.A. Morris, M. Mazur, P.S. Wheatley, L.N. McHugh, R.E. Morris, Monitoring the assembly–disassembly–organisation–reassembly process of germanosilicate UTL through in situ pair distribution function analysis, J. Mater. Chem. 6 (2018) 17011–17018.

[120] S.E. Russell, S.E. Henkelis, S.M. Vornholt, D.N. Rainer, K.W. Chapman, R. E. Morris, In situ flow pair distribution function analysis to probe the assembly–disassembly–organisation–reassembly (ADOR) mechanism of zeolite IPC-2 synthesis, Mater. Adv. 2 (2021) 7949–7955.