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Zeolite Synthesis in Hydrated Silicate Ionic Liquids

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Hydrated alkali silicate ionic liquids (HSIL) were prepared by hydrolysis of tetraethoxysilane (TEOS) in alkali hydroxide-water mixtures, inducing coacervation and phase separation. The resulting optically clear, homogenous silicate ionic liquid offers exceptional potential for monitoring zeolite crystallisation. This enhanced synthesis route provides access to analysis of speciation, mechanistic details of zeolite formation, and brings organic-template-free zeolite synthesis by design within reach.

1 Introduction

Over the past half century the industrial interest in zeolite materials for application in catalysis¹, molecular separation purification², and detergents³ has stimulated intensive investigation of zeolite synthesis. Despite of this intense research, some basic scientific questions persist⁴ and zeolite formation remains a source for some of the most resistant conundrums in crystallisation science: How come so many hypothetical networks can be predicted while so few frameworks are actually obtained?^{5, 6} Why are so few data available about zeolite solubility?⁷ Why does crystallisation of natural zeolite topologies from homogeneous liquids fail in the laboratory?⁸ As these questions remain, despite of the dozens of zeolite frameworks successfully obtained through what is known as the hydrothermal gel method, a paradigm shift is essential to unravel zeolite formation on molecular scale. In this paper we propose zeolite synthesis from homogeneous hydrated silicate ionic liquids.

Hydrolysis of TEOS in aqueous hydroxide solution can induce coacervation, resulting in the separation of a dense liquid silicate phase and a water-ethanol phase. The dense phase is a hydrated silicate ionic liquid (HSIL); i.e. the number of water molecules in this phase does not exceed the coordination number of the alkaline cation (4-8).⁹ Doping such HSILs with traces of aluminate, followed by controlled heating, yields a number of homo-ionic zeolites with natural zeolite topologies. The outcome of these syntheses depends on choice of the alkaline cations, the Si/OH ratio, the H₂O/MOH ratio and temperature. It was observed presence of aluminate is essential to obtain zeolite phases and commonly the yield of the product approaches 100% yield in aluminium. In contrast with the hydrothermal gel method, the optically transparent HSILs offer the exceptional potential for monitoring zeolite crystallisation with unprecedented accuracy.

Inspired by natural zeolite formation, the pioneers of zeolite synthesis departed from purely inorganic systems. Breck and Flanigen for example thoroughly studied zeolite crystallisation in the Na₂O-SiO₂-Al₂O₃-H₂O phase diagram.¹⁰ Crystallisation

of these traditional mixtures, readily forming complex gels and strongly depending on structure directing effects of inorganic cations, has generated most of the industrially exploited framework types of the synthetic zeolite collection.⁶⁻⁹ These syntheses typically yield zeolites with high cation exchange capacity that are of practical importance in many fields, and particularly in pollution abatement, CO₂ sequestration, and catalysis for renewables.¹¹

The introduction of organic structure directing agents (SDAs) allowed to synthesize high silica zeolites¹² and led to the discovery of a score of new framework types. Despite of their success, these templates are costly, often involve complicated synthesis, and in most cases cannot be recovered after zeolite formation but need to be sacrificed in calcination. Similar to traditional inorganic zeolite synthesis mixtures, most of these compositions still form complex gels that impair complete characterization of zeolite precursors and study of the mechanism of zeolite formation.

Some compositions however yielded clear liquid ('sol'-type) precursors, thereby allowing improved characterization of the precursor with NMR, mass spectrometry and photon scattering techniques such as SAXS and DLS.¹³ This has been demonstrated for the synthesis of silicalite-1 from TEOS-tetrapropylammonium precursors that historically were called 'clear solutions',¹⁴ but actually are clear sols containing 1-2 nm objects, i.e., assembly of silicate oligomers and templates, and wherein the zeolite formation is initiated. Owing to the clear appearance of these suspensions a combination of different characterization techniques led to considerable insight into the formation process.^{14, 15} Today such knowledge is still absent for purely inorganic syntheses where the commonly encountered gel phase prevents thorough characterization. In few cases, colloidal suspensions ('sol') consisting of gel particles with uniform and very small size are generated by mixing aluminium and silicon sources.^{16, 17} Ng *et al.* for example devised a Na-based organic template free synthesis of Na-EMT, a zeolite synthesis originally involving the use of 18-crown-6 ether template.^{17, 18} This achievement is in full accordance with the predicted phase diagram.¹⁹ However, also in these cases NMR characterization suffers from line broadening as crystallisation occurs within the particles. To allow full exploitation of high resolution NMR for mechanistic studies on template free, alkaline zeolite synthesis, clear precursor solutions are essential.

This manuscript presents the concept of homogeneous liquids of simple preparation, being room temperature hydrated molten silicate salts, which readily crystallise into zeolites. While other clear zeolite precursors using Na or K have been reported earlier, creation of such mixtures required heating and/or the introduction of other elements (anions).²⁰ The current method is based on hydrated alkali silicate ionic liquids (HSILs) which significantly differs from ionothermal syntheses,²¹⁻²⁴ the ionic liquid anions being the silicates themselves. The inorganic ionic liquids are essentially solvent free, exclusively containing water molecules locked into the primary hydration shell of cations and oligomeric silicate units.

2. Experimental details

Mixing TEOS (Acros Organics, 98%):KOH (AnalaR Normapur, 86%):H₂O (MilliQ) with ratio 1:1:20 or Al(^tOPr)₃ (Acros Organics, 98%):KOH:H₂O with ratio 0.1:1:3, under vigorous stirring, initially yields a homogeneous emulsion. Upon complete hydrolysis these alkoxide emulsions spontaneously undergo phase

separation into two liquid systems.

Gravimetry revealed the composition of the lower, dense silicate phase as SiO₂:KOH:H₂O in a 1:1:6 molar ratio, while the upper phase was identified as pure ethanol-water mixture resulting from TEOS hydrolysis. The composition of both phases was analysed with ¹H, ²⁹Si, and ³⁹K NMR. After removal of the upper, ethanol-water phase, the SiO₂/H₂O/KOH ratio of the silicate phase can be adjusted by addition of KOH-H₂O mixture, while keeping a clear ionic liquid.

Table 1: Chemical composition leading to de-mixing into two clear solutions.

TEOS	Molar composition		Outcome
	KOH	H ₂ O	
0.25	1	20	solution, clear single phase
0.50	1	20	
0.75	1	20	coacervation, 2 clear liquids
1.00	1	20	
1.25	1	20	
1.50	1	10	coacervation, gel + liquid

By dissolution of Al(OH)₃ in KOH-H₂O mixture or by exploiting the phase separation in the Al(ⁱOPr)₃:KOH:H₂O system, addition of small volumes of aluminate homogeneous liquid with final composition 0.1:1:2.85 allowed introduction of up to 5% of T-atoms as Al without provoking gel formation. The resulting homogeneous liquids can be used to crystallise zeolites as demonstrated by formation of MER zeolite, obtained by autoclaving such a precursor with composition: 0.5 SiO₂: 1 KOH: 8 H₂O: 0.013 Al₂O₃ in a temperature range from 60 to 170 °C.

The HSIL precursors were investigated by DLS on a ALV/CGS-3 instrument (ALV, Langen, Germany). 60 s measurements were performed at scattering angles from 30 to 150 and a wavelength of 632.8 nm. SAXS was measured at room temperature on a SAXSess MC² instrument (Anton Paar) with line-collimated CuK_α radiation.

SEM images of the zeolite products were made on a Nova NanoSEM 450.

XRD patterns were recorded on a STOE STADI MP diffractometer with focusing Ge(111) monochromator (CuK_{α1} radiation) in Debye-Scherrer geometry with a linear position sensitive detector (PSD) (6 2^θ window) with a step width of 0.5 degree and internal PSD resolution 0.01 degree.

3. Results and Discussion

TEOS hydrolysis is considered a reproducible route to molecular, monomeric silicic acid and is therefore preferred for mechanistic studies of zeolite formation. Despite this advantage, ethanol released during hydrolysis tends to decrease the dielectric constant of the liquid, favouring sol formation and precipitation.²⁵ In zeolite synthesis mixtures, the essential introduction of aluminate amplifies this effect by its strong tendency towards flocculation and gelation.

Zeolites from ionic liquid precursors

In this study TEOS based silicate systems with composition SiO₂:KOH:H₂O:EtOH in *n*:1:20:4*n* ratio were observed to spontaneously de-mix upon full TEOS hydrolysis for some values of *n*.⁹ This phase separation into two clear liquids

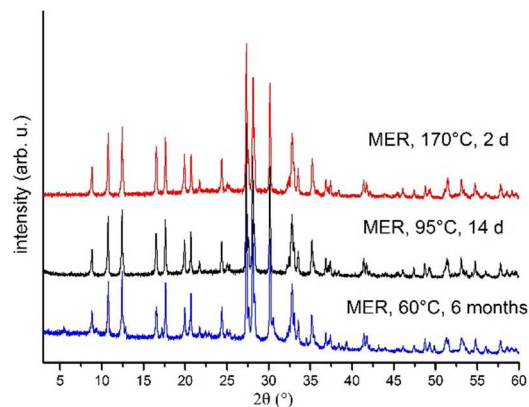


Figure 1: XRD patterns of MER type zeolite recovered after hydrothermal treatment of potassium aluminosilicate ionic liquid in the system 0.5 SiO₂: 1 KOH: 8 H₂O: 0.013 Al₂O₃ at 170°C (2 d), 95 °C (14 d), and 60 °C (6 m). Small reflections belonging to CHA (e.g. at 12.85, 17.20 and 30.55° 2θ) were present in the 60°C sample.

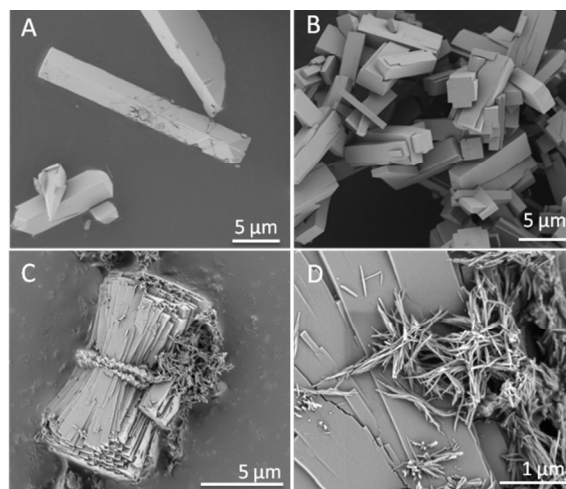


Figure 2: SEM images of the products crystallised at 170°C for 16 h (A), at 90°C for 30 days (B) and at 60°C for 6 months (C and D) from the precursor with composition 0.5 SiO₂: 1 KOH: 8 H₂O: 0.013 Al₂O₃.

exclusively occurs in the range from ca. 0.75:1:20:3 to 1.25:1:20:5 and strictly depends on the amount of water per Si. Upon dilution of the system with water, the phase separation disappears, returning the system to a transparent homogeneous solution. TEOS concentrations outside the indicated range result in formation of gels or apparently single-phase liquids (Table 1). In contrast to the true ionic liquids obtained after successful coacervation, the apparent single-phase systems with ethanol contain nano-aggregates and are better described as colloidal suspensions or ‘sols’.²⁶ Similar coacervation phenomena have been described for aqueous solutions combining sodium silicate and salts of small tetra-alkylammonium ions, or ethanol.^{27, 28}

To demonstrate effective zeolite crystallisation from the HSILs, precursors with different water and aluminium content were prepared by addition of KOH-H₂O

mixture and/or an aluminate mixture of composition 0.1Al:1 KOH:2.85 H₂O. In the evaluated systems, the SiO₂/KOH ratio was fixed at 0.5. This resulted in the crystallisation of phase pure zeolites even for very low H₂O:KOH ratio (≥ 4), much below a fully hydrated K ion, with a typical coordination number of 8.

Phase pure **MER** type zeolite was obtained from an HSIL precursor with composition 0.5 SiO₂: 1 KOH: 8 H₂O: 0.013 Al₂O₃ (Figure 1). The HSIL precursor was clear to the eye and according to DLS and SAXS did not contain any object larger than 1 nm radius. The absence of peak broadening in ²⁹Si NMR spectra further confirmed the absence nano-aggregates, or nanoparticles in the precursor liquid at room temperature, while detailed spectral analysis revealed these precursors exclusively contained small oligomers.²⁹

In contrast with the low content of aluminium in the above precursor, **MER** type zeolites are typically obtained from gels with the Si/Al ratio 2.5,³⁰ resulting in a ratio around 1.8 in the final framework. In this work, **MER** with a typical Si/Al ratio around 2, was formed from precursors with Si/Al ratios as high as 36. As no congruent liquid to crystal conditions are used the yield must be calculated on the element of lowest concentration. It reaches 100% related to aluminium content. **MER** crystal morphology was observed to be dependent on the Al content of the precursor liquid and on the crystallisation temperature. While low aluminium (and water) content precursor compositions yield very large (up to 150 μ m) isolated single crystals of high quality, other conditions resulted in lath shaped crystals and bundles of these.⁴³

MER zeolite formed at temperatures from 60°C to 170°C (Figure 2). At 60°C, traces of **CHA** were detected by XRD and SEM. In more diluted conditions, (0.8 SiO₂: 1 KOH: 92 H₂O: 0.013 Al₂O₃) combined with higher Si/OH ratio, **LTL** formed at 85°C, consistent with synthesis conditions reported for classical gel systems.³¹⁻³³ In accordance with the phase diagram established by Lillerud et al.,³³ phase pure **CHA** could not yet be obtained because the maximum Si/KOH ratio for a clear precursor is not high enough.

The principle of preparing HSILs in the TEOS-KOH-H₂O system can also be exploited with other alkali cations, such as Na. Also in this case, a coacervation process takes place, but Na was observed to have stronger affinity for gel formation at lower Si/OH ratio. Here again, two separate phases were obtained at 0.75 SiO₂: 1 NaOH: 20 H₂O. Instead of dissolving as in the KOH system, Al(iOPr)₃ precipitated as Al(OH)₃ in the NaOH-H₂O mixture. Therefore a mixture with adjusted composition of 0.1 Al(OH)₃: 1.3 NaOH: 6 H₂O was chosen as Al source. A Na based precursor with final composition 0.5 SiO₂: 1 NaOH: 8 H₂O: 0.013 Al₂O₃ yielded phase pure **GIS** at 90°C after 3 days. Combination of Na and K based HSILs yielded pure **GIS** for $x = \text{Na}/(\text{Na}+\text{K}) = 1$, pure **PHI** for $x = 0.75$ to 0.50, and pure **MER** for $x = 0.25$ to 0.00. The same zeolite types were encountered by Donahoe et al. in the Na₂O: K₂O: Al₂O₃: SiO₂ gel systems.²⁰

Mechanism of formation of zeolites

A recent review by Cundy et Cox³⁴ lists an impressive number of contributions proposing mechanisms of formation of zeolites. Despite of the wealth of literature on this topic a comprehensive description can yet not be reached due to a lack of information about the molecular steps of the lattice construction. With the advent of HSILs, alternative routes to elucidate those elementary steps are within reach. In the next paragraphs, the steps of zeolite formation derived from previous contributions

and from these novel silicate ionic liquid precursors will be enumerated in relation to the reaction types indicated in Table 2.

Table 2: Reactions for the different stages of TEOS hydrolysis into silicic acid, its deprotonation,, successive condensation and dehydration stages. The H₂O subscript indicates solvated species.

	Reactions	Main characteristic	Parameter observable
1	$\text{Si(OEt)}_4 \text{ pure} + 4 \text{ H}_2\text{O} = \text{Si(OH)}_4 + 4 \text{ EtOH}$	hydrolysis	solubility
2	$\text{Si(OH)}_4 + \text{MOH}_{\text{H}_2\text{O}} = \text{Si(OH)}_3\text{O}^-\text{M}^+ + \text{H}_2\text{O}$	deprotonation, acidity	titration
3	$\begin{aligned} &(\text{OH})_3\text{Si(OH)}_{\text{H}_2\text{O}} + \text{H}_2\text{O}(\text{OH})\text{Si(OH)}_2\text{O}^- \\ &= \\ &(\text{OH})_3\text{Si-O-Si(OH)}_2\text{O}^- + \text{H}_2\text{O} \end{aligned}$	dimerization condensation	oligomers formation, increase of <n>
4	$n \text{ Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}} = \text{Si}_n\text{O}_p(\text{OH})_{3n-2p}\text{O}^{n-p}(\text{M}^+)_n + p \text{ H}_2\text{O}$	oligomerization condensation	increase of <n> Si/OH < 1
5	$\begin{aligned} &\text{Si}_n\text{O}_p(\text{OH})_{3n-2p}\text{O}^{n-p} + \text{Si}_q\text{O}_r(\text{OH})_{3q-2r}\text{O}^{q-r} \\ &= \\ &\text{Si}_j\text{O}_k(\text{OH})_{3j-2k}\text{O}^{j-k} + \text{Si}_i\text{O}_m(\text{OH})_{3i-2m}\text{O}^{i-m} \end{aligned}$	exchange	Interconversion <n> invariant
6	$\begin{aligned} &n[\text{Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}}] \\ &= \\ &[\text{Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}}]_n + n(x-p) \text{ H}_2\text{O} \end{aligned}$	aggregation, dehydration coacervation or demixing	<n> invariant after Si/MOH=1 or 0.5
7	$n \text{ Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}} = \text{Si}_n\text{O}_p(\text{OH})_{3n-2p}\text{O}^{n-p}(\text{M}^+)_n + p \text{ H}_2\text{O}$	oligomerization condensation within nanoaggregates, and water exclusion/dehydration	<n> increases Si/OH > 1
8	$\begin{aligned} &\text{Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}} + \text{HOSi(OH)}_3 \\ &= \\ &\text{Si}_2\text{O(OH)}_5\text{O}^- + \text{OH}^-\text{M}^+_{\text{H}_2\text{O}} \end{aligned}$	condensation, MOH release	<n> invariant by dismutation with T if <n> > 3.0
9	$\begin{aligned} &\text{Si(OH)}_3\text{O}^-\text{M}^+_{\text{H}_2\text{O}} + \text{M}^+\text{OSi(OH)}_3 + \text{H}_2\text{O} \\ &= \\ &\text{Si}_2\text{O(OH)}_5\text{O}^- + 2 \text{ OH}^-\text{M}^+_{\text{H}_2\text{O}} \end{aligned}$	condensation, M ₂ O release O ²⁻ M ⁺ ₂ and reaction with H ₂ O	<n> > 3

Silicic acid formation and deprotonation

The monomeric silicon source TEOS slowly hydrolyses into silicic acid in a water-alkali hydroxide mixture. TEOS does not mix with the water phase spontaneously, so energetic stirring is indicated (reaction 1 of Table 2). In the highly alkaline solution (about pH 13), silicic acid readily deprotonates (reaction 2 of Table 2). This deprotonation is approximately limited to one proton per Si(OH)₄ producing a silicate anion ion-paired to an alkaline cation, Si(OH)₃O⁻ ...M⁺. When prepared with 20 water molecules per MOH, and 0.5 to 1.2 TEOS, this liquid mixture separates into a water-ethanol upper phase and a denser hyposolvated alkali-silicate phase. The dense phase is an ionic liquid with a number of water molecules not exceeding the coordination number of the alkaline cation (4-8).⁴

Limited Condensation by oxolation

With a progressively increasing Si/OH ratio due to hydrolysis, small oligomers develop. The main reaction involved is Si-O-Si formation by an oxolation reaction, (reaction 3 and 4 of Table 2). The average connectivity, the number of bridging O, varies progressively from 0 in the monomer to about 3.0 for a Si/OH ratio of 3. Those oligomers interconvert slowly, which can be detected by 2D EXSY NMR experiments (reaction 5 of Table 2).³⁵ The oligomers formed have a progressively increasing nuclearity, i.e., an increasing number of silicon atoms per oligomer. At the maximum oligomer connectivity of ca. 3.0 most species are still below a nuclearity of about twelve. A small fraction of the population however exhibits nuclearity as high as 31 as detected by mass spectrometry.³⁶ This condensation stage has already been identified as early as the beginning of zeolite syntheses studies by Barrer.^{37, 38}

Si/OH ratio, the titration of OH by Si(OH)₄

Titration of hydroxides by silicic acid can be observed by the pH decrease with corresponding increase of the Si/OH ratio. In non-separated hydro-alcoholic systems nano-aggregation occurs when reaching a Si/OH ratio of one, as detected by DLS and SAXS. In hyposolvated mixtures (with H₂O/MOH ≤ 20) de-mixing occurs, resulting in a dense silicate ionic liquid with composition $x \text{ Si(OH)}_4 : 1 \text{ MOH} : y \text{ H}_2\text{O}$ and a y value of about 6 for potassium. This silicate ionic liquid producing phase separation occurs for x values between 0.5 and 1. The resulting ionic liquids exhibit "dressed" cations, coordinated by water molecules and/or silicate species, thereby representing ion pairs of silicate anions with fully or partially hydrated cations. The free energy of formation arises from the Coulombic energy between ions, with an additional stabilization by coordinative hydration of the cation. Additional water would progressively lead to aqueous solutions, where the lattice energy would be dominated by solvation of both ions, rather than by Coulombic interaction as the ions are progressively separated by dilution. The latter case is conventionally described by the Debye-Hückel solvent model. The former case resembling a molten alkali-silicate hydrate has been coined as hydrated or solvated ionic liquids by C. A. Angell since 1965.³⁹

Nano-aggregation, or coacervation, or de-mixing. Ionic liquid formation.

Increasing concentrations of silicate salts go hand in hand with an increasing degree of silicate oligomerization, corresponding to H₂O release (reaction 3 of Table 2, oxolation), MOH release (reaction 8 of Table 2), or M₂O/2MOH release (reaction 9 of Table 2). With increasing oligomerisation, the dielectric constant of the medium changes, initially fairly gradual, but at Si/OH ≅ 1.0 for ethanol containing mixtures or at Si/OH ≅ 0.5 in spontaneously de-mixing systems, quite abruptly. The macroscopic effect of the resulting coacervation phenomenon depends on the solubility of the hydroxide cation M⁺ in ionic liquid compared to the ethanol-water phase of the source solution. Depending on this solubility it leads to formation of suspended nanoaggregates²⁶ (high solubility) or to separation into a dense liquid silicate and a water-ethanol phase (low solubility).⁴³ This results in the formation of nano-aggregates in the former case and in complete phase separation in the latter. Both processes are related, and have been designated with a variety of names such as coacervation, liquid-liquid de-mixing and even ion-pairing, with or without a potential spinodal decomposition when slow conformation rearrangements of

complex organic cations occur. Though a general theory describing these liquid-liquid de-mixing processes is lacking, their main characteristic is that the inorganic phases de-mix on macroscopic or nanoscale, consequently leading to phase separation or the formation of nano-aggregates. In both cases, the denser phase contains the inorganic species in significantly hyposolvated state compared to the initial mixture.

This dehydration step is analogous to a salting out process, or more adequately described, an ethanol "washing out" process.⁴⁴ Most noteworthy, this process does not directly affect the connectivity of the oligomer distribution, thereby indicating that the dominant aspect of this stage is a free energy discontinuity resulting from dehydration and Coulombic lattice energy development (reaction 7 of Table 2).

Condensation by hydroxide release, pores formation

Provision of additional energy to the nano-aggregate precursors by heating liquid precursors with a Si/OH ratio of 3.0 corresponding an average connectivity $\langle n \rangle$ of 3, initiates a second stage of aggregation with particles increasing in size from nano-aggregates about 2-3 nm, to 6 to 100 nm, before crystallisation. This period of induction, lasting about 24 h at 95°C for a clear silicalite precursor sol, exhibits no change in $\langle n \rangle$ though the size of particles grows considerably. At this stage no Bragg crystallinity is detected by in-situ X-ray diffraction.

Until a Si/OH ratio of 1.0, silicic acid is deprotonated only once, which allows to reach an average connectivity $\langle n \rangle$ of 3 by oxolation only. At increasing Si/OH ratios this situation changes. For example at Si/OH = 3.0, and when $\langle n \rangle$ has already reached 3 by further addition of silicic acid, so that each silicon in average is connected to 3 neighbours, 1/3 of the silicon atoms are deprotonated, presenting one SiO⁻ group while 2/3 still exhibit a SiOH function. These are the groups left available for further condensation, as described by reaction 8 of Table 2. Since this reaction forms a Si-O-Si bond by releasing an OH⁻ group, the latter can attack a Si-O-Si bond and open it. Consequently $\langle n \rangle$ does not vary globally during this stage. Instead, two phenomena take place: super-aggregation of higher connectivity silicon atoms in a network and release of lesser connectivity silicon inside nano-aggregates. During this induction period, Si-O-Si bond breaking and bond formation allow for the initiation of network formation. The network connects but does not yet reach the periodic organization of the crystal. It is formally analogous to the correction scheme of supramolecular crystal formation. The dominant process is driven by the free energy evolution of the lattice by the pore formation enclosing hydrated cations or template molecules, which is essentially an entropic contribution.

Heating a HSIL, at a Si/OH ratio of 0.5 leads to a similar situation. Heating decreases the dielectric constant of the medium, and density fluctuations take place. The process might be faster as compared to the nano-aggregate condensation-super aggregation of sols. The presence of OH⁻ groups, with a $\langle n \rangle$ of c.a. 1.5 allows to overlap oxolation and MOH release condensations, which are therefore no longer fully separated reaction steps. The limited number of water molecules favours formation of clathrate types or clusters around the cations. Si-O-Si bonds formation at this stage requires heat, due to a higher activation energy of the water/OH assisted bond breaking and bond reformation, in which the water clusters around cations have to contribute their coordination water.

Crystallisation, condensation by hydroxide/oxide release

Finally at crystallisation a dramatic change occurs, hallmarked by an entropy driven free energy evolution. Organisation of the almost connected network fragments into a periodically ordered crystal represents a first order phase transition. At this stage reactions 8 and 9 of Table 2 take place, two reactions generating massive release of OH⁻ and an increase of pH, which almost returns to its initial value of the MOH water mixture before introduction of TEOS. The phase obtained at this stage is a dense phase with pores filled by water or cation-cluster clathrate-like structures.

Though this mechanism of formation has only been established on few studies of the formation of MFI, BEA, MER, CHA, LTL, GIS, or PHI, it overlaps consistently with most of the observations or assumptions described in Table 1 of Cundy and Cox (2005).³⁴ The nature of chemical origin of activation energy for Si-O-Si bond breaking and reformation is related to the different water assisted mechanisms of condensation controlling its formation at each stage. They depend on the cation type, the water clathrate structure, the composition of the ionic liquid, and the concerted reaction involving the reagents with Si-O-Si.

The limitation of zeolites to a severely restricted number of real topologies compared to the innumerable list of hypothetical ones can also be explained by the small number of units, cages and rings, exhibiting enough stability to be found within zeolite networks, thereby leading to a limited set of crystals formed with minimal lattice energy.⁵

The templating effect of organic as well as alkaline cations of zeolites can be revisited using this new paradigm. As Barrer indicated,⁴¹ the chemical potential of the hydrated, clathrate-like structure of cations has to be taken into account for calculating the chemical potential of the crystal. Since zeolites form as dense crystals with hydrated cations or organic templates filling the cavity system, their nanoporous character appears only at the post-crystallisation stage when pores are emptied. It will be essential to re-determine the crystal structures of zeolites filled with cations⁴¹ and water to derive rules of stabilization of the large cages as suggested by the work of Blatov and Proserpio.⁴²

The global scheme depicting the description of the zeolite formation discussed above is provided in Figure 3.

Data still missing

This paper demonstrates a new practical route for synthesis of natural zeolites from silicate ionic liquids. In contrast with traditional zeolite synthesis, zeolites can now be crystallised from a hydrated silicate ionic liquid. In case of excess aluminium, gels phases are obtained which coexist with HSIL. The excess aluminium used in gel syntheses, serves several purposes: as aluminium source, as nucleation surface for heterogeneous nucleation and as diffusion slowing agent.

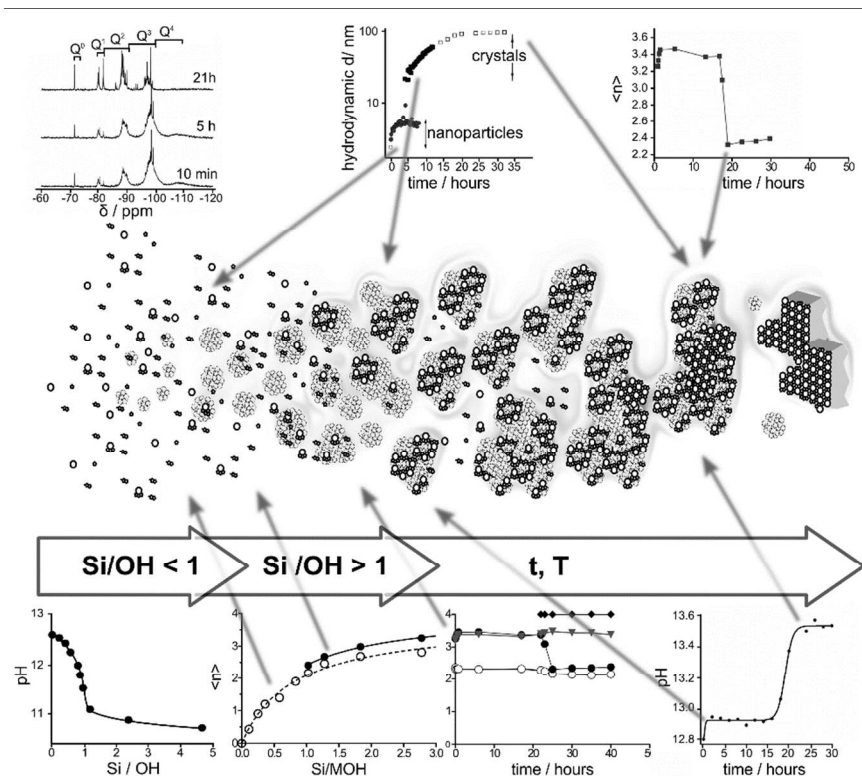


Figure 3: Mechanism of homogeneous liquid with nanoaggregation or ionic liquid formation from room temperature precursor formation to hydrothermal heating of precursor into zeolite crystal. Precursor state varies with Si/OH . Before $Si/OH = 1$, neither aggregation nor de-mixing occurs. For $Si/OH > 1.0$ nano-aggregation occurs for ethanol containing sols. De-mixing with ethanol exclusion and hypohydrated ionic liquid starts at Si/OH of 0.5. When heating an induction phase starts, and ends at crystallisation. NMR, pH, Dynamic Light Scattering and $\langle n \rangle$ determined from NMR are plotted in insets.

Silicate ionic liquid synthesis of zeolites will enable to study all molecular aspects of the syntheses, in conditions very comparable to gel phases, with very low water content. This is a requirement to assign activation energy and free energy of each stage of the synthesis to a definite molecular process. There are however missing data still to be acquired. Among them, one can cite the densities of the HSIL, their viscosities and conductivities. Solubility measurements in HSIL would be directly accessible, even in non congruent crystallisation conditions by using the analytical power of in-situ NMR for all nuclei. Solubility of direct or retrograde character will therefore be accessible and formulated unambiguously. This represents an essential step to allow formalising the crystallisation of zeolites. In addition to direct solubility measurements, also interconversion of zeolites could lead to critical assessment of the proper understanding of zeolite formation. Indeed, the interconversion also is determined by crystallisation kinetics and thermodynamics which depend on the activation energy of the slowest crystallisation step and the solubility of the zeolites involved.

4. Conclusions

In this contribution a new formalism to zeolite formation has been proposed. It was

necessary to identify that the phase from which zeolites nucleate, and at a later stage crystallise, is in a state of low hydration, a hydrated silicate ionic liquid (HSIL). The latter cannot be confused with standard water solutions, as the amount of water does not exceed the water molecules in the coordination sphere of the silicate salt cation. Their study will lead to understanding of any type of zeolite precursors, clear solutions, sols or gels. Additionally, depending on the presence of an excess of solid reagent like the aluminium source, heterogeneous nucleation can take over. This will allow also to evaluate the change of homogeneous to heterogeneous nucleation. The reacting medium from which zeolites form in a traditional gel synthesis is probably an interstitial ionic liquid formed by salting out the excess water. The HSIL route will allow application of most methods of molecular-level characterisation. This can lead to unification of the different zeolite synthesis routes.

With the actual results presented in this study, it seems that zeolite crystallisation from hydrated alkaline silicate ionic liquids does not represent any exception from classical crystallisation mechanisms. In contradiction to common claims in literature depicting zeolite formation as special case, zeolite crystallisation, like classical crystallisation, is governed by well-defined physico-chemical rules. This is where the paradigm shift lies. However, compared to classical crystallisations zeolite crystallisation proceeds in slow motion. By studying the HSIL precursors, one can establish and quantify a wealth of parameters for molecular processes related to nucleation and growth that are relevant not only for zeolites, but also can shed light on crystallisation phenomena in general. With the identification of the complexity of all stages of zeolite formation, the proposal of a grand scheme for crystallisation is within reach, covering different interconnected models of different grain sizes from coarse to fine. This is yet to come.

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