

Formation of Zeolites Responsible for Waste Glass Rate Acceleration:

An Experimental and Computational
Study for Understanding
Thermodynamic and Kinetic Processes

April 2023

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U.S. DEPARTMENT
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Project Background

Before nuclear waste glasses can be disposed at geological disposal facilities, a performance assessment (PA) must be conducted to provide confidence to the regulators and public that the release rates of radioisotopes and hazardous materials into the environment are below the regulatory limits. Because the release rate of radionuclides is directly related to the dissolution rate of the radionuclide-containing glass, the corrosion behavior of the glass must be well understood for the disposal site lifetime. For simplicity, glass dissolution in static conditions has been categorized into three different stages, referred to as initial rate (Stage I), residual rate (Stage II) and, depending upon the secondary phases formed, a possible delayed resumption in the alteration rate (Stage III).¹ The last of these stages is the least understood and has the possibility to drive radionuclide release rates above regulatory thresholds.

At present, neither the glass composition nor experimental duration can be used to predict the occurrence of Stage III dissolution behavior. Currently available data on Stage III is generally limited to static dissolution tests at 90 °C or higher and relatively high glass-surface-to-solution-volume (S/V) ratios. There are several key points based on previous observations in literature: (1) not all glasses undergo Stage III behavior in the experimental time period, (2) the onset of Stage III behavior occurs at different time periods, and (3) the apparent Stage III dissolution rate changes with glass composition. However, there are some consistencies between glasses that demonstrate Stage III behavior, which is linked to the formation of a secondary phase(s).² Post-reaction analysis of solids often identifies these phases as zeolites.³⁻⁵

Geochemical modeling has been used to describe the onset of Stage III dissolution through reasoning that the formation of these secondary phases consumes silica from solution, which, through an affinity-based relationship, drives further glass dissolution. The models have been based on a combination of thermodynamic^{6,7} and kinetic⁸ considerations. Another mechanism responsible for Stage III dissolution is

that zeolites consume elements from the passivating alteration layer formed on the glass surface, which, in turn, reduces the passivating properties of the layer.⁹ Regardless of the mechanism responsible for its onset, a recent study has identified zeolite gismondine (GIS) framework topology, or zeolite P2, as the phase responsible for initiating Stage III behavior at 90 °C.⁹

Prior studies have identified methods to synthetically generate P2 relative to its polymorph P1 and related isostructures that crystallize under similar conditions.¹⁰ Experimental analyses reveal that P2 is thermally stable and largely inaccessible to sorbates owing to the presence of sodium ions. The latter are extra-framework cations that balance the negative charges of framework aluminum and serve as an inorganic structure-directing agent (SDA) for many zeolite framework types.¹¹ Density functional theory (DFT) calculations of P2 show that molecular adsorption, as well as thermal stability, is dependent upon the Si/Al ratio and selection of extra-framework cations.¹⁰ Notwithstanding prior studies of P2, many aspects pertaining to the kinetics and thermodynamics of its formation remain elusive.

Zeolite crystallization is dependent upon the use of inorganic and/or organic structure-directing agents, which help facilitate the formation of CBUs and pores.¹² The formation of zeolites in geological repositories relies solely on inorganic SDAs (e.g., alkali metals) to facilitate crystallization. Alkali metals can be highly selective in directing the formation of different crystal structures.^{13, 14} These extra-framework cations reside on oxygens adjacent to framework Al. The occlusion of inorganic SDAs in small pore zeolites, such as P2, occupy much of the available pore volume and can have a significant impact on the hydrothermal stability of the structure. For many zeolite framework types, the thermodynamics of aluminum inclusion and the impact of alkali metals on (alumino)silicate speciation are not well understood.

A common phenomenon in zeolite synthesis is intercrystalline transformations¹⁵ wherein a metastable structure initially forms and proceeds to transform into more thermodynamically stable (i.e., higher density) structures with increased time or higher temperature. This process seemingly abides by the Ostwald rule of stages¹⁶, which is a ubiquitous phenomenological process in many systems where kinetic factors dictate the initial formation of a metastable structure (often an amorphous precursor) that undergoes a series of transformations to more energetically favorable products. The factors governing the sequences of structures as well as the kinetics of their formation (and transformation) are largely unknown. Further understanding of these processes as a function of temperature and growth conditions (particularly pH and ionic strength) expected in a geological repository would greatly aid in the technical underpinning associated with the long-term storage of nuclear waste glasses. A more fundamental knowledge of zeolite formation, and their effect on Stage III glass dissolution, requires combined experimental and computational studies to elucidate both the thermodynamic and kinetic processes of zeolite crystallization.

Project Outcomes

The project resulted in 4 publications that resulted in the following insights:

Section 1: *We have identified accelerants and inhibitors of zeolite GIS formation.* These studies are a valuable and efficient tool in assessing the likelihood that zeolites will precipitate during glass corrosion experiments. Calcium was identified as an accelerant of zeolite GIS crystallization and both tin and lithium as inhibitors. This information can be used as a guide to design nuclear waste glass compositions that may be less susceptible to Stage III behavior.

Section 2: *We focus on the impact of Zn on the kinetics and identity of certain zeolites.* Multivalent metals have diverse effects on zeolite crystallization. We have used a combination of experimental and computational approaches to develop a deeper understanding of how heteroatoms can influence zeolite crystallization. We specifically addressed their impact on FAU-to-GIS IZT by assessing how the addition of various metals to synthesis media impact nucleation of both parent and daughter zeolites. In the absence

of zinc, we showed that the nucleation of GIS (daughter) is independent of the presence of FAU (parent). Introduction of zinc into the growth medium can have several effects based on its concentration. At high concentration, zinc suppresses zeolite nucleation and leads to an amorphous product. At low concentration, zinc inhibits the FAU-to-GIS IZT and also shifts the final GIS product from polymorph P2 to P1. At an intermediate concentration, zinc completely suppresses GIS nucleation leading to a stable FAU product. This information helps explain how glasses with higher Zn content might be shown to be more durable in Vapor Hydration Tests.

Section 3: *We investigate how the presence of Ca may lead to a higher likelihood of Stage III behavior.* We have investigated the thermodynamics of oligomerization reactions in zeolite growth for systems with varied compositions. Overall, the oligomerization of the silicate system was found to be slightly exothermic, whereas the aluminosilicate system was found to be significantly more exothermic, with the presence of aluminum increasing the exothermicity of oligomerization. The thermodynamics of silicate complexes growth were also evaluated in the presence of Na^+ and Ca^{2+} . Both cations increase the exothermicity of silicate oligomerization, with Ca^{2+} exhibiting the most exothermic path, which is particularly interesting as Ca^{2+} is often found in naturally occurring zeolites. Apart from the dimer species, cyclization was found to be favorable for all silicate and aluminosilicate complexes both in the presence and absence of cations.

Section 4: *In this work, we further the understanding of how zeolites form, a finding that provides defense in depth on the possibility of Stage III glass dissolution behavior.* In this work, we studied the formation thermodynamics of a wide range of zeolitic precursor species by applying density functional theory calculations. Findings reveal that the effects of cations on formation thermodynamics of cages depend highly on cation charge and size, cage size, and the presence of aluminum, which alters electrostatic interactions. Calculations support the experimental observations that alkali metal cations can direct growth of many aluminosilicate zeolites, whereas highly siliceous zeolites require the use of bulky organic cations or seed crystals.

Project Deliverables:

This collaborative project involving both experiments and computational research efforts resulted in four publications, which will be described in the following sections of this final report.

Section 1: The Effect of Metals on Zeolite Crystallization Kinetics with Relevance to Nuclear Waste Glass Corrosion

Mallette, A.J., Reiser, J.T., Mpourmpakis, G., Motkuri, R.K., Neeway, J.J., Rimer, J.D.: “npj Mater. Degrad. (2023) In Press

Section 2: Heteroatom Manipulation of Zeolite Crystallization: Stabilizing Zn-FAU against Interzeolite Transformation

Mallette, A.J., Hong, S., Freeman, E.E., Saslow, S.A., Mergelsberg, S., Motkuri, R.K., Neeway, J.J., Mpourmpakis, G., Rimer, J.D.: JACS Au 2 (2022) 2295-2306, DOI: 10.1021/jacsau.2c00325

Section 3: Understanding Initial Zeolite Oligomerization Steps with First Principles Calculations

Freeman, E.E., Neeway, J.J., Motkuri, R.K., Rimer, J.D., Mpourmpakis, G.: AIChE J. e17107 (2020) 1-11, DOI: 10.1002/aic.17107

Section 4: Understanding Formation Thermodynamics of Molecular Zeolitic Species with First Principles Calculations

Hong, S., Mallette, A.J., Neeway, J.J., Motkuri, R.K., Rimer, J.D., Mpourmpakis, G.: J. Chem. Soc., Dalton Trans. (2023) In Press

Section 1: The Effect of Metals on Zeolite Crystallization Kinetics with Relevance to Nuclear Waste Glass Corrosion

Vitrification and geologic disposal of radioactive material is planned in several countries, but there are remaining uncertainties related to the long-term stability of glass exposed to groundwater. Specifically, the crystallization of aluminosilicate zeolite minerals can accelerate the rate at which glass corrodes and radioactive material is released into the biosphere. In this study, we identify elemental species that may accelerate or suppress zeolite formation using a protocol to examine their effects on zeolite synthesis over a three-day duration. Our results are consistent with previous works demonstrating glass corrosion acceleration in the presence of calcium. Furthermore, we identify two elements – tin and lithium – as inhibitors of zeolite P2 (GIS type, or gismondine) nucleation and, thus, promising species for promoting the long-term durability of glass waste forms.

Introduction

Radionuclides from nuclear waste can be incorporated into borosilicate glass matrices via vitrification to limit their release into the environment after geological disposal. To date, a wide range of proposed or actual glass compositions have been developed, which corrode at various rates upon exposure to water. In general, glasses corrode rapidly at first (Stage I) before dissolution rates are reduced to a much slower and (nearly) constant level (Stage II)^{17, 18}. In some cases, however, as the duration of the experiment increases, zeolite crystals are formed, whereupon the rate of glass dissolution precipitously increases (Stage III)^{7, 19-22}. Several zeolites either have been identified once a glass demonstrates Stage III behavior or are known to induce Stage III behavior when added to the system, including framework types CHA, ANA, and GIS (the three-letter codes refer to crystal structures designated by the International Zeolite Association). The focus of this study is to understand which oxides in the glass affect (either enhance or inhibit) the formation of zeolitic phases that result in Stage III dissolution behavior.

A vast array of oxides is used in glass formulations, but deconvoluting which elements promote or suppress zeolite nucleation remains challenging. In zeolite synthesis research, various elements in growth mixtures are understood to have distinct and significant effects on crystallization which are briefly surveyed here to summarize reported effects of elements known to alter zeolite formation. Besides Si and Al, which comprise the basic building blocks of natural and most synthetic zeolites, alkali metals are common extra-framework elements in zeolites. Indeed, these ions are often required to achieve fully crystalline products for many framework types because they balance negatively-charged AlO_4^- framework sites^{15, 23-28}. Alkali cations also function as structure-directing agents (SDAs) to facilitate the formation of a particular structure²⁸. For instance, Kirschhock and coworkers¹⁴ demonstrated that the product of seeded zeolite syntheses can be controlled simply by exchanging alkali cations (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+). Previously, the composition space of zeolites that form in sodium¹⁵ and potassium¹⁹ media has been mapped. Compared to alkali metals, alkaline earth metals (Group II) are rarely used as SDAs in zeolite synthesis; however, these cations are often present in natural zeolites, suggesting their influential role in geologic zeolite formation^{29, 30}. For instance, calcium³¹, magnesium³² and strontium³³ have each been shown to increase zeolite crystallization rates. Compared to cations, anionic halides (Group VII) have a minimal effect on zeolite syntheses^{28, 34} with one exception: fluoride – which can replace hydroxide as a mineralizing agent (i.e., zeolite accelerant) that facilitates crystal formation with fewer defects³⁵⁻⁴¹. The motive for adding elements in the transition metal block and groups III-V to the growth mixture is generally to isomorphically substitute heteroatoms (e.g., Zn, Sn, and Ga) into the crystal structure to enhance catalytic activity. These elements can have diverse effects on zeolite crystallization, which tends to be highly sensitive to the presence of inorganic additives. For example, small amounts of tin (Si/Sn molar ratio = 100) and zinc (Si/Zn molar ratio = 50) can extend the time required to synthesize zeolites BEA⁴² and FAU²⁷, respectively, while germanium can accelerate the synthesis time for various framework types⁴³. Owing to the complexity of zeolite synthesis mixtures, the underlying mechanistic causes of these phenomena are typically challenging to deconvolute.

To elucidate the effects of certain elemental oxides on glass corrosion, Crum et al.⁴⁴ designed a matrix of 24 waste glasses called the enhanced low-activity waste (eLAW) matrix. In particular, the matrix was subjected to a series of tests where zeolite P2 (GIS type, or gismondine) seeds were added to the glass-water system at pre-determined durations to help understand the propensity for various glass compositions to exhibit induced Stage III behavior. The statistically-designed matrix was developed for compositions pertinent to the Hanford Waste Treatment and Immobilization Plant (WTP)⁴⁵. Seven major components (Al_2O_3 , B_2O_3 , CaO , Na_2O , SiO_2 , SnO_2 , and ZrO_2) were varied independently, while all remaining species were grouped into an eighth component (listed generically as “others”), which was also varied. The matrix was designed such that the individual effects of the seven major components and *others* could be isolated. In the study by Crum et al.⁴⁴, each of the 24 glasses was allowed to react with deionized water at 90°C in a stainless steel vessel for 28 days. Then, seeds of zeolite P2 (GIS type) were added to the system and the experiment continued at 90°C to observe whether or not the presence of the zeolite seeds affected the glass dissolution rate over the following twelve months. The addition of zeolite seeds has the potential to induce Stage III glass behavior on reasonable time scales²², and zeolite P2 is used because it is one of the most common zeolites known to induce Stage III glass behavior⁴⁶. Zeolite P2 is one of two common polymorphs possessing the GIS framework; the other is P1 (Fig. 1.1a), which is differentiated by a slight twist in the channel geometry that has been described in detail elsewhere^{27,47}. Crum et al.⁴⁴ distinguished 4 types of glass behaviors depending on their composition: (Type 1) no effect of the seed, (Type 2) an immediate increase in the glass dissolution rate until all of the glass dissolved, (Type 3) an immediate increase in the glass dissolution followed by an eventual slowing in the rate, and (Type 4) an increase in the glass dissolution rate that was offset with respect to the time that the seeds were added. Most significantly, glasses with low calcium content resisted Stage III behavior significantly better than those with relatively high calcium content.

Though previous observations have been helpful in identifying the glass compositions that may be susceptible to Stage III dissolution behavior, the role of zeolite crystallization kinetics is still unclear as the zeolite seeds were added to the system, thus bypassing nucleation. Herein, we attempt to isolate the role of crystallization kinetics by simulating the glass composition in solution (except for Na_2O , which was added in excess to attain a high solution pH) and identifying the resulting zeolite-containing product. This method allows us to bypass certain experimental constraints in the glass dissolution tests and isolate the role of select zeolite accelerants and suppressors. Herein, we investigate the consequences of various elements on zeolite crystallization kinetics in conventional synthesis mixtures. Selecting elements present in waste glass at higher compositions, we perform systematic studies using zeolite synthesis mixtures that more accurately replicate the glass composition. We show that modifications to zeolite growth mixtures by alkali metal substitution and/or alkaline earth metal addition can significantly alter crystallization rates. This approach aids the identification of certain glass compositions that may be susceptible to Stage III behavior in the environment and allow nuclear disposal facilities to potentially mitigate the effects of possible Stage III behavior due to zeolite crystallization.

Results and Discussion

The effects of many elements present in the eLAW glass compositional matrix were investigated by adding each to a conventional synthesis⁴⁷ of zeolite P2 (GIS), one of the most common frameworks observed as an accelerant of nuclear waste glass dissolution rates (Fig. 1.1a)⁴⁸. Synthesis mixtures have a molar composition of 9 SiO_2 :0.5 Al_2O_3 :5.5 Na_2O :0.2 M_xO_y :190 H_2O (where M = metal, x = number for M atoms, and y = number of O atoms) and were treated for 3 days at 100°C, which is sufficient for complete crystallization of GIS, by way of a FAU pathway, in a conventional zeolite synthesis (i.e., M = 0). The hydrothermal treatment temperature was selected to be consistent with well-characterized zeolite syntheses.^{15,47} Bulk crystallization assays where Na is combined with a range of different metals demonstrate that many higher valence elements (e.g., Cr, B, Zn, Sn, Fe) suppress GIS formation (Fig. 1.2,

blue). Most notably, tin and zinc completely inhibit GIS crystallization for longer than 28 days of heating. The presence of a small FAU impurity used to distinguish elements that do not appear to alter crystallization rates (Mg, Sr, Zr, and Mn, Fig. 1.2, yellow) from those that accelerate the formation of zeolite products (notably, Na, Li, and Ca; Fig. 1.2, red), in conventional growth media used to prepare GIS crystals⁴⁷.

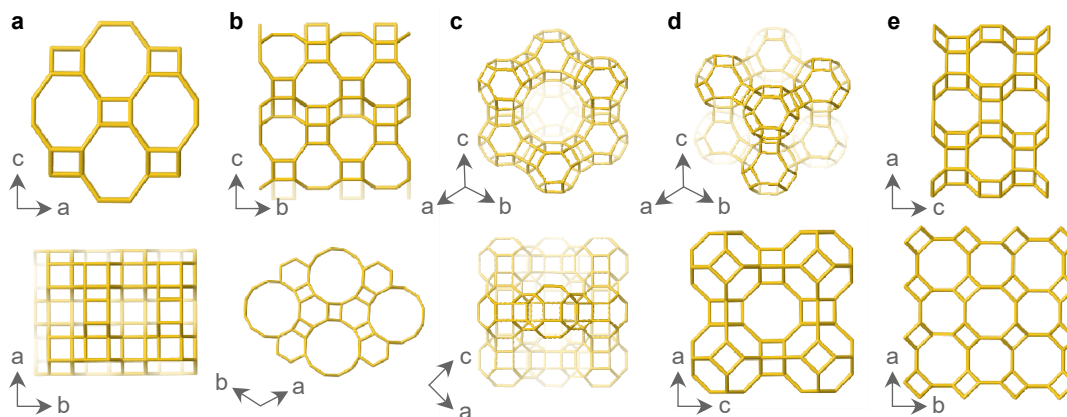


Fig. 1.1 Zeolite frameworks. Crystal structures of zeolite framework types synthesized in this study: (a) GIS, (P1 polymorph) (b) FAU, (c) LTA, (d) GME, and (e) MER.

I												VIII					
1 H Hydrogen 1.01												2 He Helium 4.00					
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 67.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.75	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.90	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.20	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)

Fig. 1.2 Periodic table. Effect of elemental species on zeolite GIS crystallization rates using conventional synthesis conditions. Each synthesis was carried out for 3 days at 100°C using a growth mixture with a molar composition of 9 SiO₂:0.5 Al₂O₃:5.5 Na₂O:0.2 M_xO_y:190 H₂O. Growth mixtures have a pH value of ~13. Reagent “M” corresponds to elements added, which is color-coded according to its effect on the crystallization rate: accelerant (red), suppressor (blue), or neutral (yellow).

Following the initial survey of elements under conditions that are typical of synthetic zeolites, we sought to explore the effect of different elements when synthesis mixtures more accurately reflect the complex environment of altered nuclear waste glass. Our assumption is that all glass components are released congruently from the glass into solution whereas it is well known that the release of species from the glass is incongruent in static dissolution tests. Additionally, the present set of experiments ignores the possible

effect that an altered glass substrate may play in zeolite nucleation kinetics. For a basis, we selected the seven major components (Al, B, Ca, Na, Si, Sn, and Zr) present in the eLAW series of 24 glasses assayed by Crum et al.⁴⁴ In the study carried out by Crum et al.⁴⁴, observations after seeding (Fig. 1.3a) could be described with four different behaviors types (and general compositional trends): (Type 1) no effect of the seed (low CaO), (Type 2) an immediate increase in the glass dissolution rate until all of the glass dissolved (high CaO, Al₂O₃, and ZrO₂), (Type 3) an immediate increase in the glass dissolution followed by an eventual slowing in the rate (high CaO, B₂O₃, low Al₂O₃), and (Type 4) an increase in the glass dissolution rate that was offset with respect to the time that the seeds were added (high CaO, Al₂O₃, low ZrO₂). These glass classification types were made based on the general composition properties of a group of glasses that behaved similarly in glass dissolution relationship. For instance, not every glass in the latter group (high CaO, Al₂O₃, low ZrO₂) necessarily has a high CaO content. For the zeolite syntheses, the appropriate molar ratios were calculated where several values (H₂O, OH, and Si based on previous studies^{15, 28}) were held constant to maintain consistency across synthesis mixtures. To assess the effects of changing molar ratios, we heated each of the 24 mixtures, labeled eLAW-*X* (*X* = 1 – 24), for 7 days at 100°C. In most cases, we observed a mixture of amorphous and crystalline (both zeolitic and non-zeolitic) phases in the products. Quantitative analysis of crystalline phase(s) was performed by refining powder X-ray diffraction (PXRD) patterns with the software Topas using MgO as an internal standard. In most cases, the dominant zeolite phase is GIS, but in select cases we observed crystals of metastable zeolite frameworks FAU (Fig. 1.1b) and LTA (Fig. 1.1c) that often form at similar synthesis conditions^{15, 49-53}. Among non-zeolitic phases, the most prominent is burtite, or calcium hexahydroxystannate (Ca[Sn(OH)₆]), which varies in weight fraction across the syntheses where it was detected. Other precipitated non-zeolitic phases include calcium hydroxide (Ca(OH)₂) and zirconium oxide (ZrO₂), but neither Ca nor Zr appeared to influence zeolite crystallization in these experiments since their composition in the growth mixture could not be correlated to the fraction of GIS product.

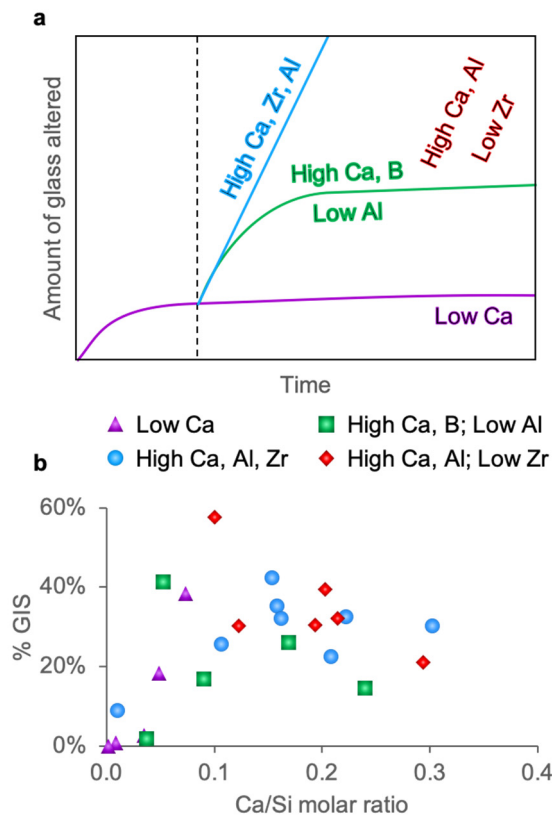


Fig. 1.3 Effect of Ca. (a) Qualitative response curves of eLAW glasses in dissolution studies performed in the presence of zeolite seeds, as reported by Crum et al.⁴⁴. Seed addition (dashed vertical line) allows for

glass responses to be assayed on a reasonable timeframe. Glasses are characterized and grouped according to their compositions: Type 1, low CaO (purple); Type 2, high Ca, Al, Zr (blue); Type 3, high Ca, B, and low Al (green); and Type 4, high Ca, Al, and low Zr (red). (b) Experimentally observed weight fraction of zeolite GIS phase in the product of bulk crystallization versus Ca/Si molar ratio in the initial synthesis mixtures designed to mimic eLAW glass conditions⁴⁴. Color coding of data points is based on the classification of each glass according to panel A, which corresponds to alteration responses for glasses with low CaO (purple triangles); high CaO, Al₂O₃, ZrO₂ (blue circles); high CaO, B₂O₃, and low Al₂O₃ (green squares); and high CaO, Al₂O₃, and low ZrO₂ (red diamonds).

The phase outcomes of 24 eLAW zeolite syntheses from this study produced several noteworthy correlations to the behaviors presented in Fig 1.3a. First, these findings revealed that short (<7 days) and facile experiments may be capable of quickly assessing the susceptibility of certain glass compositions to precipitate zeolites much more rapidly than glass dissolution tests, which are both time- and resource-intensive. Among the seven components investigated, we identified two (calcium and tin) that most significantly impact zeolite crystallization; the fraction of zeolite GIS is not directly correlated with any other element. These observations corroborate the results reported by Crum et al.⁴⁴ which suggest higher calcium content promotes zeolite formation and Stage III behavior (Fig. 1.3a). Indeed, a significant increase in the fraction of zeolite GIS product is apparent as the amount of calcium in the growth mixture increases (Fig. 1.3b). Synthesis mixtures with the lowest amount of calcium (Ca/Si < 0.1) led to largely amorphous products and/or metastable zeolite phases, which suggests that a longer time is required for GIS crystallization. Increasing the amount of calcium to intermediate levels (0.1 < Ca/Si < 0.2) led to a significant increase in the amount of zeolite GIS formed. High calcium content (i.e. Ca/Si > 0.2) may slightly decrease the relative amount of zeolite GIS, which may be related to the limited solubility of Ca²⁺ ions in alkaline solutions and the tendency to precipitate as Ca(OH)₂. This effect is particularly evident in the case of glasses with high Ca and Al content and low Zr content (Fig. 1.2a, red curve). Our findings that calcium promotes the nucleation of zeolite GIS aligns with computational investigations by Mpourmpakis and coworkers⁵⁴, who demonstrated that calcium cations substantively enhance the thermodynamic favorability of (alumino)silicate oligomerization.

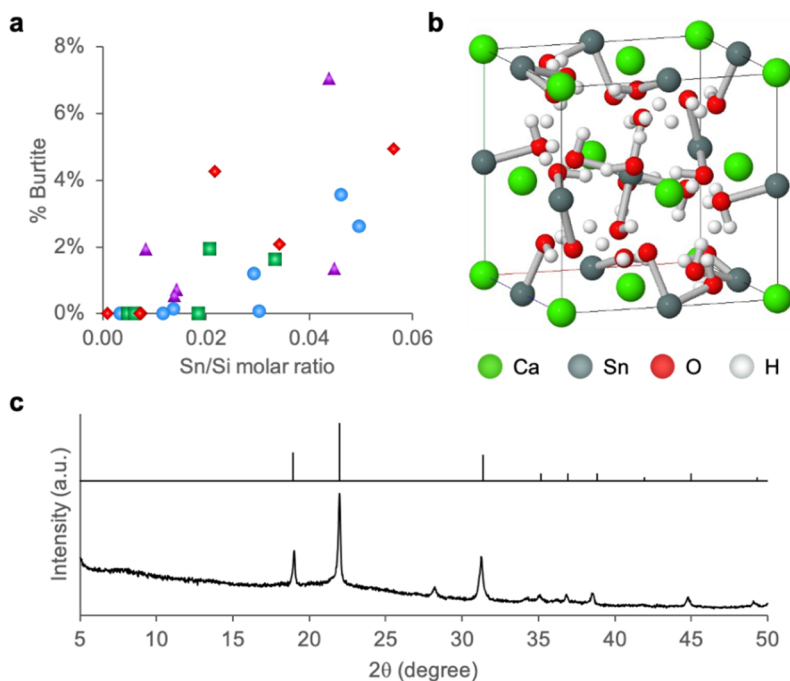


Fig. 1.4 Effect of Sn. (a) Graphical relationship illustrating the positive correlation between the weight fraction of burtite in products of eLAW zeolite synthesis series and the amount of tin in the growth mixture. Refer to the legend in Fig. 1.3b for symbol descriptions. (b) Burtite crystal structure, adapted with permission⁵⁵. (c) PXRD pattern of burtite (bottom) synthesized by aging zeolite growth mixture eLAW-24 which had the highest Sn molar ratio for 24 h at room temperature without hydrothermal treatment. Reference pattern for burtite (top) was obtained from the American Mineralogist Crystal Structure Database.

The precise effect of tin on these systems is more challenging to discern compared to calcium given that several experimental observations are in apparent contradiction. First, our findings reveal that there is no clear correlation between the initial tin composition and the fraction of zeolite GIS product. The quantity of tin is, however, correlated with the amount of burtite in the solid product (Fig. 1.4a), which is not observed for other elements. Burtite is a crystalline structure that contains calcium (Fig. 1.4b); therefore, we hypothesize that tin plays a minor role in the suppression of GIS by sequestering calcium in the form of a solid mineral where it cannot promote zeolite nucleation. To this end, we demonstrated that burtite crystallizes prior to zeolite phases (Fig. 1.4c), which agrees with previous findings⁵⁵ and supports our hypothesis that burtite formation reduces the amount of calcium available for promoting zeolite nucleation. In a standard static glass corrosion experiment, this phase may not be observed; however, tin may play a role in preventing the release of calcium into solution.

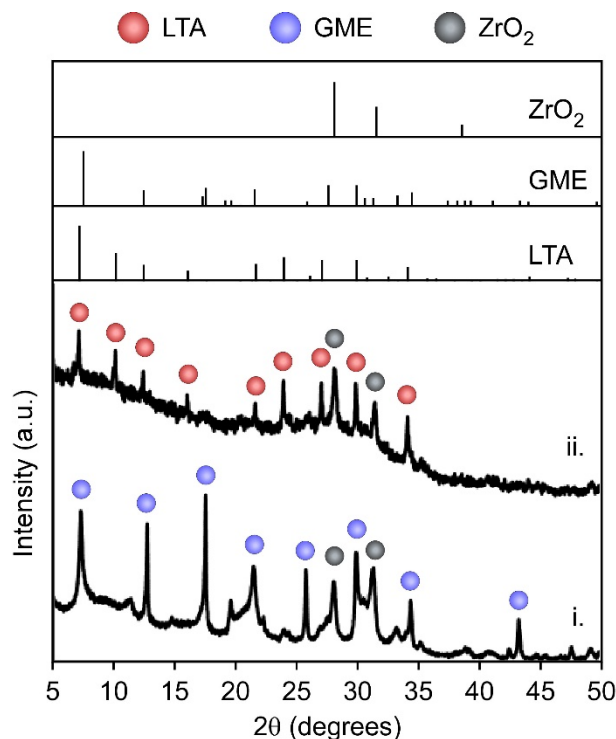


Fig. 1.5 Deconvoluting Sn and Ca. PXRD patterns illustrating the effect of tin on samples synthesized with a molar composition similar to that of eLAW-21. (i) eLAW-21 synthesis repeated in the absence of Ca and Sn. (ii) eLAW-21 synthesis repeated in the absence of Ca and in the presence of Sn. Solid products were extracted from syntheses after 7 days at 100°C. Reference patterns of ZrO₂, GME, and LTA are provided.

It is well-known that zeolite crystallization is commonly suppressed by the presence of tin^{42, 56-58} even in the absence of calcium, which we have confirmed using a conventional zeolite synthesis mixture (Fig. 1.2).

In this analysis, we aimed to deconvolute the effects of tin and calcium by removing the latter from the growth mixture and comparing the result to a case where both calcium and tin were absent. We selected eLAW-21 for this study because it led to a large amount of GIS product. For the control synthesis using tin- and calcium-free media, we observed the formation of a zeolite product predominantly comprised of GME (Fig. 1.5, pattern *i*), which has a structure (Fig. 1.1d) similar to that of GIS (Fig. 1.1a). When tin was added to the synthesis mixture, we observed a largely amorphous product (Fig. 1.5, pattern *ii*) with a minor zeolite LTA phase. Therefore, tin clearly suppresses zeolite crystallization in syntheses replicating glass compositions irrespective of calcium content. Notably, tin seemingly affects the propensity of zeolite nucleation to occur in glass solution systems wherein we posit two potential mechanisms for its mode of action: (i) tin sequesters calcium accelerants and/or (ii) stannosilicate oligomers scavenge silica to form species that are putatively less amenable to zeolite nucleation compared to aluminosilicates⁵⁸. The fraction of GIS product is more directly correlated with the concentration of calcium than that of tin (Fig. 1.3). This is partly attributed to the relatively high Ca/Si ratio in zeolite growth mixtures, but is more likely due to tin favoring burtite crystallization over that of GIS, as reflected in the changing product distribution as a function of Sn/Ca ratio (Fig. 1.6).

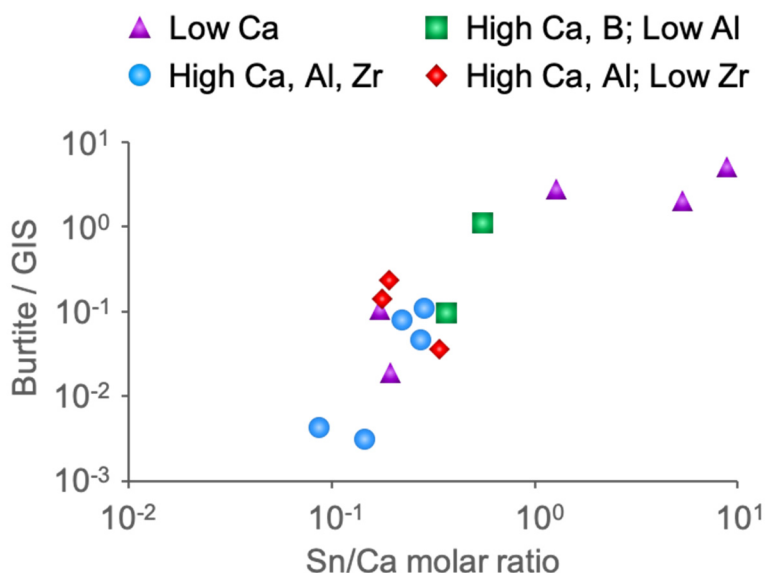


Fig. 1.6 Effect of Sn/Ca ratio. Logarithmic relationship between the relative amounts of burtite and GIS by weight in the final product (calculated from PXRD patterns using MgO as an internal standard) as a function of the initial Sn/Ca molar ratio of the growth mixture. Color coding of data points is based on the classification of each glass according to Fig. 1.3a, which corresponds to alteration responses for glasses with low CaO (purple triangles); high CaO, Al₂O₃, ZrO₂ (blue circles); high CaO, B₂O₃, and low Al₂O₃ (green squares); and high CaO, Al₂O₃, and low ZrO₂ (red diamonds). Some samples are not plotted which do not contain a quantifiable amount of burtite according to their PXRD pattern.

In these studies, the P1 polymorph of zeolite GIS was observed. The prevalence of zeolite P1 in the present study is suspected to be due to the limited quantity of available Si species as prior research⁴⁷ has established that zeolite P1 preferentially nucleates rather than zeolite P2 at low Si/OH ratios. Owing to the highly viscous synthesis mixture and diversity of sol-gel species, most of the Si species present may not be available for nucleation, lowering the effective Si/OH ratio. Since previous glass dissolution studies showed similar responses regardless of whether zeolites P1 or P2 seeds were added to the system^{46, 59}, the observed trends from this study would likely not substantively change if zeolite P2 were to nucleate rather than zeolite P1.

Sodium is the most common alkali metal used to promote zeolite synthesis, so its prevalence in many nuclear waste glass compositions suggests that the partial substitution of sodium with alternative alkali metals may enhance glass stability with respect to Stage III behavior. We used eLAW-21 as the basis for these syntheses since it leads to a product with a relatively high fraction of zeolite GIS. Increasing the sodium content in the growth mixture to 120% of its original value leads to minimal changes, as expected (Fig. 1.7, pattern *i*). When potassium is added to the synthesis mixture (Na/K = 5), a partial zeolite MER phase is observed in the product (Fig. 1.1e; and Fig. 1.7, pattern *ii*), which is consistent with conventional zeolite syntheses where K^+ directs MER formation under otherwise similar conditions as GIS. Given that Li^+ is known to promote zeolite ABW¹⁴, its addition was expected to lead to a dual mixture of GIS and ABW. Contrary to expectations, adding lithium to the synthesis mixture (Na/Li = 5) led to a largely amorphous product with a relatively small quantity of zeolite GIS product (Fig. 7, pattern *iii*), as indicated by the higher background intensity of the normalized pattern. This result is particularly surprising since the addition of lithium to a similar synthesis using conventional conditions (i.e., in the absence of the extra components used to mimic the glass composition) accelerates GIS crystallization. This suggests that lithium may be altering the physicochemical structure of amorphous precursors or the nature of calcium species in such a way that significantly inhibits zeolite nucleation. Collectively, this result illustrates the importance of using synthesis mixtures that isolate the impacts of individual elements better than the more complex environment surrounding nuclear waste glass. Furthermore, simple modifications to glass (or synthesis mixture) compositions can significantly reduce the likelihood of zeolite nucleation, with the potential to dramatically enhance the durability of waste glass.

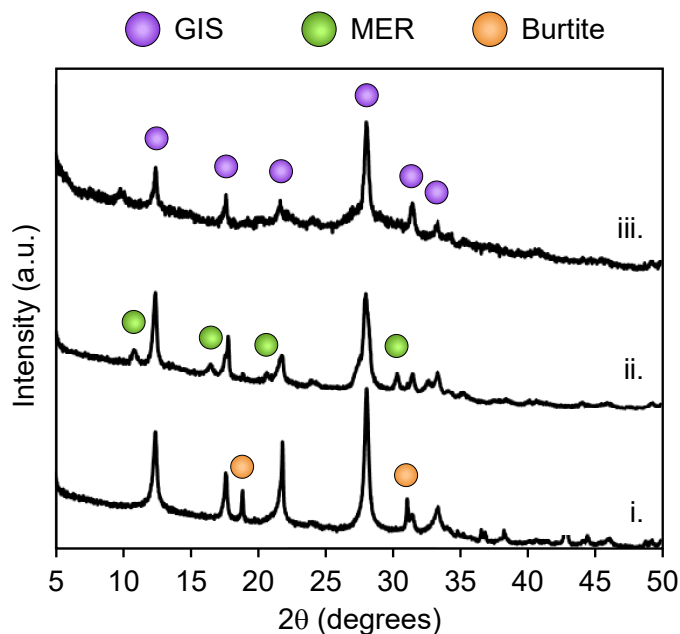


Fig. 1.7 Alkali metal substitution. Normalized PXRD patterns of products generated from a synthesis mixture designed to replicate the glass composition of eLAW-21 with variations in the alkali metal content. Growth mixtures were prepared with molar compositions of 60.5 SiO_2 :8.7 Al_2O_3 :29.8 Na_2O :6 M_2O :11.2 B_2O_3 :2.0 ZrO_2 :6.1 CaO : 2.1 SnO_2 :1270 H_2O where $M = Na$ (i), K (ii), and Li (iii). All syntheses were carried out for 7 days at 100°C. Synthesis (i) contains 120% the amount of sodium present in eLAW-21. PXRD patterns are normalized for clarity.

Conclusions

Zeolite synthesis studies where crystals nucleate from a mixture designed to replicate expected glass compositions are a valuable and efficient tool in assessing the likelihood that zeolites will precipitate during glass corrosion experiments. Results presented herein correlate well with expectations based on prior dissolution studies,⁴⁴ where glasses with low calcium content were the least likely to have increased dissolution rates when zeolite seeds were added, even if the synthesis mixtures having a higher pH (~13) than typical glass corrosion experiments (~pH 10). Although deconvoluting the effects of diverse species is challenging, chemical insights from this study can provide a basis for future work towards predicting nuclear waste glass stability in a disposal scenario. We identify calcium as an accelerant of zeolite GIS crystallization and both tin and lithium as inhibitors. Additional accelerants and inhibitors have also been identified in conventional zeolite synthesis mixtures, but the correlation between these syntheses and glass compositions is less clear, especially in light of the retention of certain species in the alteration layer during glass corrosion. This information can be used as a guide to design nuclear waste glass compositions that may be less susceptible to Stage III behavior.

Insights from this study also benefit the zeolite synthesis community. The systematic way this study was conducted provides a unique strategy for investigating the effects of diverse species on zeolite syntheses. Perhaps one of the more surprising aspects of these results is that some elements (i.e., Ca and Sn) have a dramatic effect on crystallization outcomes while others (i.e., Zr and B) do not appear to have a substantial effect. However, the findings for this system may not be generalizable to syntheses of other zeolite topologies. Future investigation will be necessary to broaden the scope of this research to develop a more holistic understanding of how heteroatoms and other additives alter crystallization mechanisms across the ever-expanding library of zeolite framework types.

Section 2: Heteroatom Manipulation of Zeolite Crystallization: Stabilizing Zn-FAU against Interzeolite Transformation

The preparation of metastable zeolites is often restricted to a limited range of synthesis conditions, which is exemplified in commercial syntheses lacking organics to stabilize the crystal structure. In the absence of an organic structure-directing agent, interzeolite transformation is a common phenomenon that leads to undesirable products or impurities. Many studies have investigated the substitution of Si and Al in zeolite frameworks with alternative elements (heteroatoms) as a means of tailoring the properties of zeolites; however, relatively few studies have systematically explored the impact of heteroatoms on interzeolite transformations and their concomitant effects on zeolite crystallization. In this study, we examine methods to prepare isostructures of faujasite (FAU), which is one of the most commercially relevant zeolites and also a thermodynamically meta-stable structure. A survey of multivalent elements revealed that zinc is capable of stabilizing FAU at high temperatures and inhibiting its frequent transformation to zeolite GIS. Using combined experimental and computational studies, we show that zinc alters the chemical nature of growth mixtures by sequestering silicates. Zinc heteroatoms incorporate in the FAU framework with a loading-dependent coordination. Our collective findings provide an improved understanding of driving forces for the FAU-to-GIS interzeolite transformation where we observe heteroatoms (e.g. zinc) can stabilize zeolite FAU over a broad range of synthesis conditions. Given the growing interest in heteroatom-substituted zeolites, this approach to preparing zinc-containing FAU may prove applicable to a broader range of zeolite structures.

Introduction

The versatility of zeolites as stable solid-acid catalysts has led to their widespread implementation across multiple industries. These nanoporous aluminosilicates can be synthesized with over 250 distinct framework topologies possessing diverse pore geometries, compositions, and crystal morphologies. Tetrahedrally coordinated aluminum sites are balanced by extra-framework cations, often hydrogen (i.e. Brønsted acid sites), where the concentration and siting⁶⁰ of Al atoms can strongly influence catalyst performance and stability^{61, 62}. Zeolites can also be synthesized with a wide range of framework composition, referred to as zeotypes (or zeolite isostructures) when tetrahedral sites (T-sites) are occupied by “heteroatoms”, which are elements other than Si and Al. Heteroatom substitution with diverse species has garnered significant interest in recent years⁶³ as a method to enhance zeolite properties – most notably the nature and strength of Brønsted and/or Lewis acid sites⁶⁴. For example, tin⁶⁵, hafnium⁶⁶, and zirconium⁶⁷ have been incorporated into the *BEA structure for applications in biomass conversion. Previous studies have also shown that heteroatoms, such as titanium⁶⁸, zinc⁶⁹, and gallium⁷⁰, can enhance the catalytic activity of MFI. Furthermore, incorporation of some elements (e.g. Fe⁷¹, Sn⁷², and Zn^{73, 74}) can lead to mesoporous structures by promoting defects. The ability to synthesize zeolites with isomorphically substituted heteroatoms is specific to both the element and framework of interest⁷⁵, where many combinations can only be synthesized after prohibitively long synthesis times⁶³. It has been suggested that the addition of heteroatom precursors to zeolite syntheses alters crystallization kinetics by modifying physicochemical properties of the growth mixture⁷⁶ or facilitating the formation of thermodynamically unstable crystal structures owing to heteroatom incorporation⁷⁷. Investigating these hypotheses, however, is nontrivial since complex synthesis media and nonclassical crystallization mechanisms obfuscate attempts to identify causal relationships between synthesis parameters and growth kinetics or properties of zeolites/zeotypes^{26, 78}.

Owing to the relatively high geologic abundance of zinc and its ability to coordinate to zeolites as framework sites or extra-framework species, zinc is commonly investigated for its potential to enhance zeolite properties. The nature of zinc in zeolite crystals can be difficult to establish since it can be present in many forms: zinc oxide⁷⁹ or zinc hydroxide⁸⁰ occlusion, framework sites^{80, 81}, or extra-framework cations

(Zn^{2+} , ZnOH^+ , or $[\text{Zn-O-Zn}]^{2+}$)⁸². Zinc incorporation in zeolites can alter Si/Al ratios⁷⁶, promote intergrowths (i.e., hierarchical architectures)⁷³, or introduce Lewis acidity^{69, 80}. Zinc can be incorporated top-down by either impregnation or ion exchange, or it can be introduced bottom-up by adding a precursor (e.g. $\text{Zn}(\text{NO}_3)_2$) to the synthesis mixture⁷⁶, which leads to better dispersion and stability⁷⁴. Understanding of the effects of zinc on crystallization pathways can lead to more effective strategies for preparing Zn-zeolites without deleterious effects.

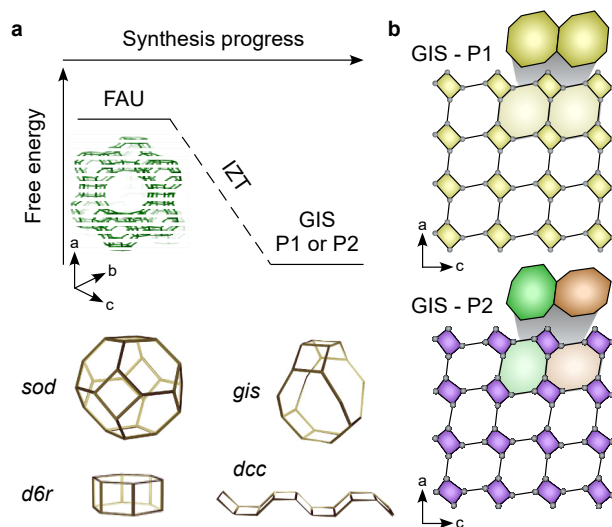


Fig. 2.1. (a) FAU-to-GIS interzeolite transformation (IZT) involves a reduction in free energy for two zeolites that do not share a common CBU. (b) Side-by-side comparison of P1 and P2 polymorphs of GIS. P1 exhibits identical pore mouths (yellow) whereas alternating four-membered rings in P2 lead to slight variations in pore mouth geometry (green and orange).

One topic that has received little attention is the impact of heteroatoms on zeolite growth mechanisms. This is particularly relevant for organic-free syntheses where polymorphism and interzeolite transformations (IZTs) are common phenomena^{15, 26, 63}. IZT is frequently encountered when using inorganic structure-directing agents (ISDAs), which are less selective for syntheses of pure framework types than their organic counterparts. Transformations purportedly abide by the Ostwald rule of stages where the sequence of events in the direction of increased thermodynamic stability^{15, 78} involve the initial formation of a metastable (parent) zeolite followed by the subsequent nucleation and growth of a second (daughter) phase with concomitant disappearance of the parent. The sequence of IZT stages can be difficult to predict. Numerous parent-daughter pairings involve zeolites with at least one shared composite building unit (CBU)²⁶, while other cases comprise zeolites with no apparent structural similarity¹⁵. One example of the latter is the transformation from faujasite (FAU) to gismondine (GIS) once synthesis temperature approaches 100°C (Fig. 2.1a). Both of these structures form naturally and are also industrially relevant⁸³. FAU is the most widely used fluidized catalytic cracking (FCC) catalyst⁸⁴. Syntheses of FAU often lead to impurity phases, such as GIS, which crystallizes as polymorphs P1 or P2 (Fig. 2.1b)¹⁴. Kinetics of FAU, GIS, and other zeolites in complex systems are also of interest in nuclear waste glass disposal as the acceleration or inhibition of growth of certain zeolites can impact the alteration behavior of a glass²⁰.

In zeolite syntheses the partitioning of solute between solid (amorphous precursor) and solution (supernatant) leads to changes in the growth environment over the course of zeolite crystallization. The impact of these changes on IZT events and the ability to manipulate these processes via the introduction of

heteroatoms is elusive. In this study, we report methods to prepare Zn-FAU in organic-free media and investigate the impact of zinc and other multivalent metals on the FAU-to-GIS transformation. Our findings reveal that zinc is an efficient inhibitor of IZT, which enables Zn-FAU to be prepared over a broad range of synthesis conditions.

Results and Discussion

We investigated the effects of diverse multivalent species, M, on the FAU-to-GIS IZT using synthesis gels with a molar composition ($9 \text{ SiO}_2:0.5 \text{ Al}_2\text{O}_3:z \text{ M}^{n+}:11 \text{ NaOH}:190 \text{ H}_2\text{O}$) that is typical for the preparation of GIS – P2⁸⁵. The nominal condition for synthesis ($z = 0$, control) was used to benchmark crystallization kinetics for comparison with growth mixtures containing multivalent additives. The FAU-to-GIS transformation is monitored quantitatively by powder X-ray diffraction (XRD) and qualitatively by electron microscopy owing to the distinct size and shape of FAU (Fig. 2.2a) and GIS (Fig. 2.2b) crystals. In the control synthesis, faujasite (FAU) forms within 4 h of hydrothermal treatment at 100°C. Within 24 h, we observe the emergence of Bragg peaks in powder XRD patterns that are indicative of GIS-type zeolite nucleation. Additional hydrothermal treatment results in the reduction of faujasite peaks in XRD patterns with a concomitant shift to pure GIS – P2 within 4 days. The same synthesis was repeated multiple times with the addition of various multivalent species to the synthesis gel ($z = 0.2$) using a fixed hydrothermal treatment of 4 days at 100°C to investigate which multivalent species alter crystallization time and/or polymorph selection. Multivalent species selected for this study included four divalent alkaline earth metals (Ca, Mg, Sr, Ba), a divalent transition metal (Zn), and four higher valence species (B, Ga, Ge, In) to assess a diverse range of chemical properties. As shown in Fig. 2.2c, screening multivalent additives revealed differences in the final product being faujasite (green shading), GIS – P2 (purple shading), or mixtures of both.

An interesting observation is the dichotomy between alkaline earth metals (Fig. 2.2c, left) and multivalent species with higher valence states (Fig. 2.2c, right). Group II elements do not suppress the FAU-to-GIS IZT, whereas other assayed elements either partially or completely suppress GIS – P2 formation. Among Group III (B, Ga, In) and fourth row (Zn, Ga, Ge) elements, IZT is generally suppressed with increasing atomic size of multivalent species. When Zn is used, transformation to GIS is suppressed for longer than 28 days, regardless of whether $\text{Zn}(\text{NO}_3)_2$ or ZnO is used as the zinc source. This is consistent with studies by Schwieger and coworkers⁷³ who showed that zinc stabilized FAU at a synthesis temperature of 75 °C, which is higher than many reported syntheses. Prior studies indicate that metallosilicate condensation varies depending on metal selection⁸⁶ wherein the angle and flexibility of Si-O-M bonds varies for distinct multivalent species. Indeed, some heteroatoms tend to condense silicates more readily than others^{86, 87}, which may be related to the ability of each species to suppress FAU-to-GIS IZT. We surmise these effects could be attributed to several factors: (i) different bond angles of metallosilicates relative to aluminosilicates may render the former less amenable to GIS nucleation and/or growth, potentially due to the fact that GIS is a denser structure; (ii) metallosilicate condensation may unfavorably alter the chemical potential of the growth solution; or (iii) heteroatoms may alter parent (FAU) properties such as crystal stability (*vide infra*).

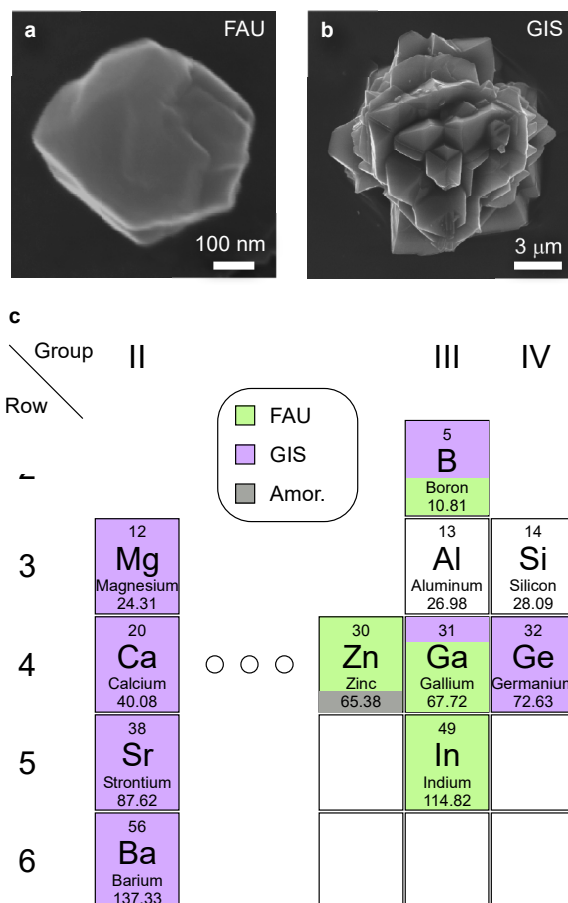


Fig. 2.2. (a and b) Representative scanning electron micrographs of zeolites (a) FAU and (b) GIS – P1. The morphology of GIS – P2 is nearly identical to the latter (see Fig. 2.8d). (c) Screening of Group II, III, and IV heteroatoms used in zeolite synthesis mixtures compared to Zn (the sole transition metal investigated in this study). The effects of various multivalent metals were assessed using a fixed molar composition of 9 SiO₂:0.5 Al₂O₃:0.2 M:11 NaOH:190 H₂O where *M* represents the highlighted multivalent species. Growth mixtures were hydrothermally treated at 100°C for 4 days. Color coding is purple (GIS) and green (FAU) with mixed colors indicating binary combinations (with shaded areas representing approximate percentages of each framework). The principal components of each zeolite (Si and Al) are shown for reference.

Trends in Fig. 2.2c can be rationalized by differences in the ionic structure these elements adopt in the highly alkaline solutions used in zeolite synthesis. Under these conditions, alkaline earth metals dissociate (either completely or partially) into their constituent ions. The latter can function as ISDAs in addition to sodium, which is present at a much higher concentration than the additives (i.e. molar ratio Na⁺/M²⁺ = 55). When the ratio of Na⁺/M²⁺ is small, alkaline earth metals can inhibit FAU crystallization by reducing the pH⁸⁸; however, in this study, the effect of sodium on zeolite crystallization seemingly far outweighs that of any alkaline earth metal. Conversely, higher valence species (hereafter referred to as “heteroatoms”) are not present as cations, but rather as anionic metal hydroxide complexes in high-pH media^{86, 87} akin to those formed by silicon (silicates) and aluminum (aluminates). We posit the primary role of these species is less that of an ISDA and more related to a pseudo sequestering agent based on their ability to promote metallo-(alumino)silicate oligomerization. Moreover, isomorphic substitution of metal heteroatoms in zeolite

frameworks can alter crystallization. Herein we analyze heteroatom impact on IZT and polymorphism, focusing on zinc as the sole multivalent additive.

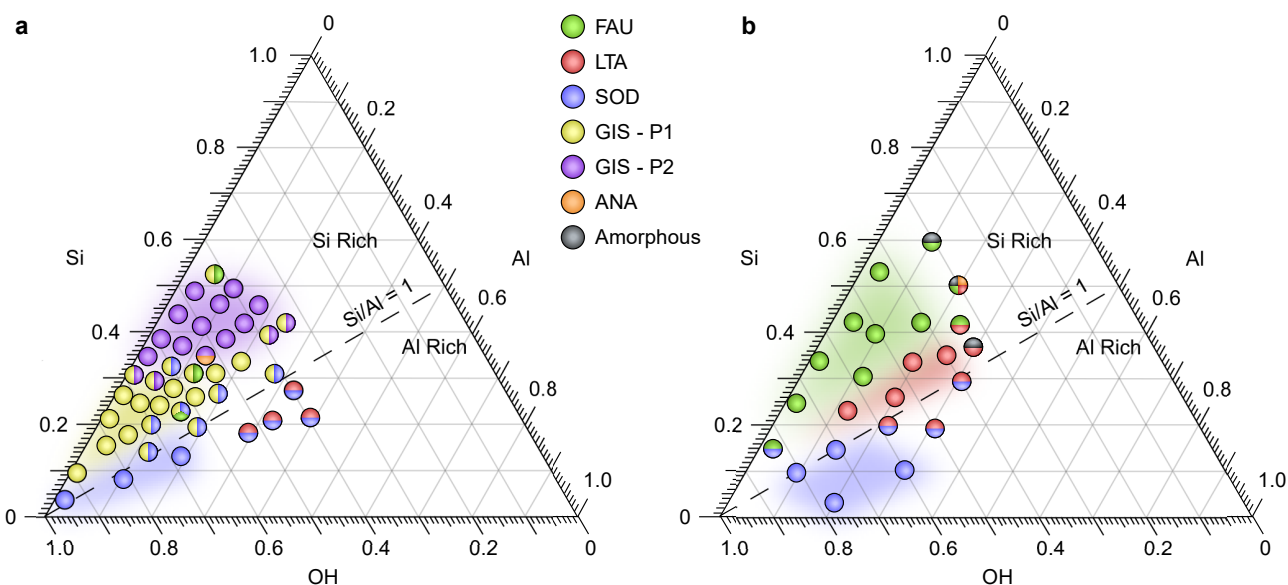


Fig. 2.3. Kinetic ternary phase diagrams with molar compositions x Si: y Al: z Zn:11 NaOH:190 H₂O comparing conditions with (a) no zinc ($z = 0$) and (b) a fixed zinc concentration ($z = 0.2$). Data in panel (a) were previously reported by Oleksiak et al.⁸⁵ and Maldonado et al.¹⁵ Symbols are color coded based on the final zeolite structure after 7 days of synthesis at 100°C. Symbols of a single color are pure zeolite phases whereas mixed symbols indicate binary or ternary mixtures based on analysis of powder XRD patterns.

We compiled kinetic phase diagrams of sodium-containing syntheses (7 days, 100°C) in the absence (Fig. 2.3a) and presence (Fig. 2.3b) of zinc. In a previous study⁸⁵, we showed that zeolite GIS is the dominant phase in Si-rich media with polymorphs P1 and P2 forming in more and less alkaline conditions, respectively. The addition of zinc at a constant concentration (molar ratio Zn/H₂O = 0.001) completely suppresses the GIS phase (Fig. 2.3b) and transforms the kinetic phase diagram into one resembling low-temperature (i.e. 65°C) Na-zeolite syntheses¹⁵ in the Si-rich region. The Al-rich region remains characteristic of 100°C Na-zeolite syntheses, irrespective of zinc addition, with sodalite (SOD) formed in more alkaline media. Interestingly, both FAU and LTA are metastable zeolites known for their rapid conversion to more stable (i.e., higher framework density) phases when the temperature is raised from 65°C to around 100°C; however, in the presence of zinc, both phases are stabilized and the LTA region shifts towards higher Si/Al ratios. Overall, these results reveal that zinc inhibits GIS formation regardless of synthesis gel compositions tested.

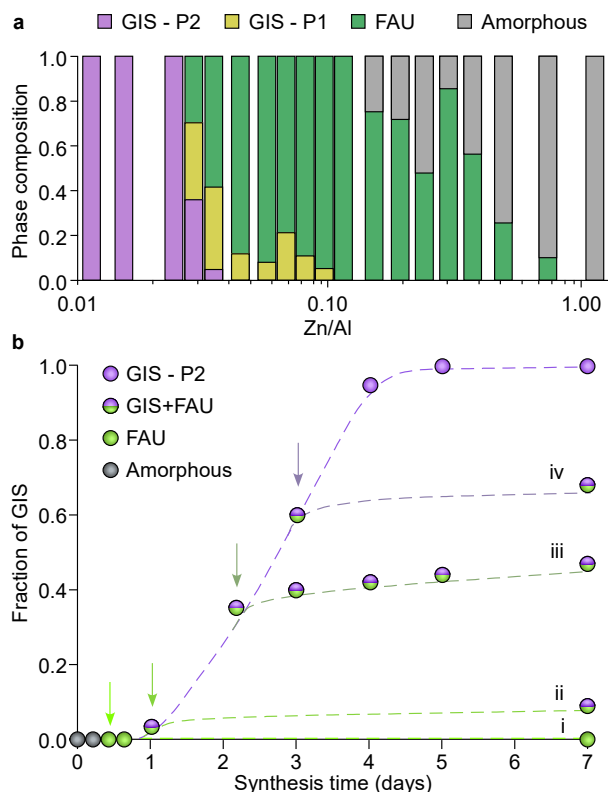


Fig. 2.4. (a) Phase purity of solids extracted from syntheses after 4 days at 100°C using a molar composition of 9 SiO₂:0.5 Al₂O₃:11 NaOH: *z* Zn:190 H₂O. The approximate percentage of each zeolite is based on relative peak area for each phase in powder XRD patterns. (b) Fraction of FAU converted to GIS during a synthesis at 100°C where Zn(NO₃)₂ is added to the gel (to yield a molar ratio of 0.2 Zn:190 H₂O) after 0.5 (i), 1 (ii), 2 (iii), and 3 (iv) days (indicated by arrows). Fractions of GIS are based on powder XRD analysis of extracted solids. Dashed lines are visual guides for the eye.

We investigated the impact of zinc concentration on the final zeolite product after hydrothermal treatment at 100°C for 4 days, which is the time required to achieve fully crystalline GIS in the absence of zinc. Comparison of powder XRD patterns at increasing Zn/Al molar ratio reveal a threshold zinc concentration (Zn/Al ~0.02) below which GIS – P2 formation is unhindered and above which we observe residual faujasite, consistent with our observation that zinc suppresses the FAU-to-GIS IZT. The first evidence of GIS inhibition shows that the presence of zinc also shifts the GIS polymorph to P1 (rather than the nominal P2). We posit that this effect is related to the ability of zinc to sequester silicates, thus leading to a growth mixture with a lower effective Si/Al ratio, which favors P1 (Fig. 2.3a)⁸⁵. Further increase in zinc concentration (Zn/Al ~0.1) results in pure faujasite, whereas higher zinc content stunts zeolite nucleation and leads to a purely amorphous product at Zn/Al > 1. This indicates there is an optimum amount of zinc to stabilize FAU, which depends on synthesis time and temperature. The full sequence of heteroatom effects on fractions of zeolite/amorphous products is highlighted in Fig. 2.4a.

We performed a series of experiments where zinc was introduced into the synthesis gel at periodic times of heating to assess whether its presence prior to FAU and/or GIS nucleation impacted the ability of zinc to suppress the FAU-to-GIS transformation. We selected synthesis times corresponding to complete FAU crystallization (prior to IZT) and periodic stages during GIS growth. In all cases, mid-synthesis addition of zinc (arrows in Fig. 2.4b) caused immediate cessation of GIS formation. This seems to indicate that the presence of zinc impacts the chemical potential of the synthesis medium. For instance, it would be expected that GIS being a more thermodynamically stable zeolite than FAU would continue to grow if the chemical potential of the medium remained favorable for interzeolite transformation; however, our findings reveal that zinc’s mode of action is independent of the properties of the growth mixture prior to its addition.

Here we explore whether the presence of zinc in solution or in the solid state (i.e. amorphous precursor or FAU parent crystals) has a more critical influence on the chemical evolution of the growth mixture. Inductively coupled

plasma-mass spectrometry (ICP-MS) was used to track the elemental composition of supernatant solutions extracted at periodic times during FAU synthesis. For these studies we used a lower synthesis temperature of 80°C to reduce the kinetics of zeolite crystallization, thereby enabling more samples to be collected as a function of reaction progress. Prior to heating, zinc and aluminum are present at similar concentrations in the supernatant. During the induction period, both of these elements are gradually incorporated into the solid phase prior to the onset of Bragg peaks detected in powder XRD patterns of extracted solids. This resulting decrease in supernatant Zn and Al concentrations reaches an apparent plateau around the time of nucleation (ca. 1.7 days). Beyond this time, we observe a stark difference in temporal variations of these two species in the supernatant with increasing time during FAU crystallization. Notably, zinc gradually relocates from solid to solution as aluminum incorporates into FAU crystals (i.e. the Zn/Al ratio of the supernatant increases with time).

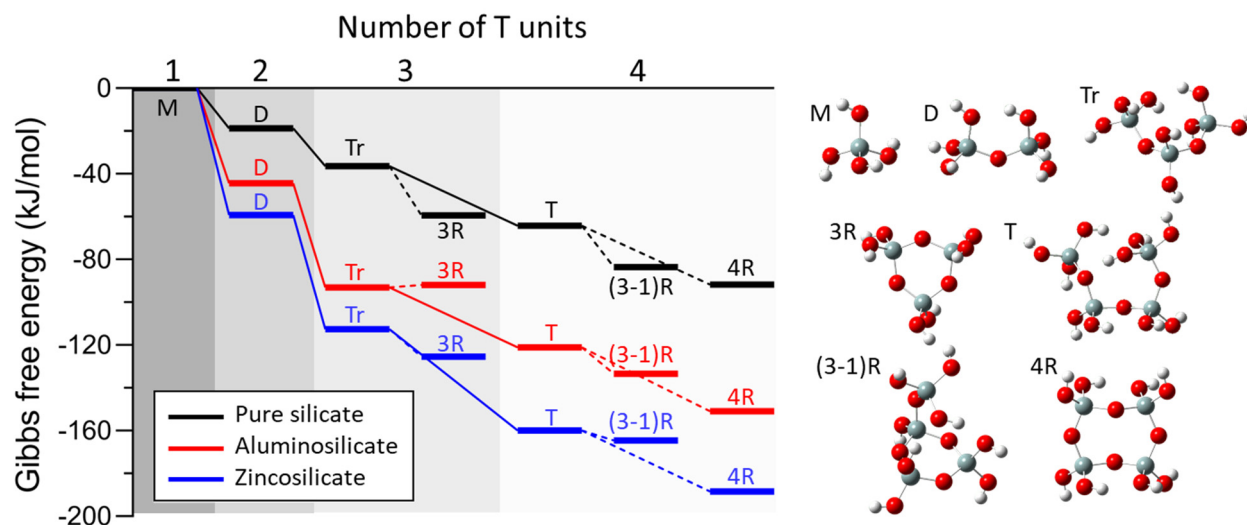


Fig. 2.5. Formation Gibbs free energies of oligomers (up to $n = 4$, where n is the number of tetrahedral species, i.e., Si, Al, or Zn) calculated using DFT (M = monomer, D = dimer, Tr = trimer, 3R = 3-membered ring, T = tetramer, (3-1)R = 3-membered ring with one acyclic silicon, and 4R = 4-membered ring). Oligomer growth via condensation is represented by solid lines and cyclization is represented by dotted lines. Aluminosilicate and zincosilicate isomers with the most exothermic formation energy values are reported. Optimized molecular structures of pure-silicate oligomers are provided with color-coded balls representing silicon (grey), oxygen (red), and hydrogen (white) atoms.

A prior study by Anseau and coworkers⁸⁷ revealed the importance of the Zn/Al molar ratio on oligomer speciation in highly alkaline solutions containing zinc, aluminum, and silicon at similar ratios as those used in our study. They found that although zinc and aluminum do not oligomerize with one another, they compete for available silicon to generate zincosilicate and aluminosilicate oligomers, respectively. This was demonstrated using ²⁹Si NMR spectroscopy to show that silicates have a slight preference to form oligomers with zinc. Previous research has shown that there are clear differences in the oligomerization behavior and crystallization of zincosilicates relative to aluminosilicates⁸⁷. For example, it has been demonstrated that zincosilicate zeotypes possess 3-membered rings (3R), which are not typically observed in aluminosilicate zeolites^{80, 81}. Furthermore, zinc-containing zeotypes typically require high synthesis temperatures, suggesting larger energetic barriers to nucleation compared to those for aluminosilicates. For the synthesis conditions used in this study, increased temperature (from 100 to 150°C) and replacement of aluminum with zinc results in the formation of VPI-7, which is a zincosilicate zeotype (VSV type)⁸¹.

We used density functional theory (DFT) calculations to compare the condensation and oligomerization energetics of silicate, zincosilicate, and aluminosilicate species. Formation energies of experimentally identified silicate oligomers^{89, 90} were calculated for $n = 1 - 4$ (Fig. 2.5) where n is the number of tetrahedral species (T = Si, Al, or Zn). Growth of linear complexes (monomer (M) → dimer (D) → trimer (Tr) → tetramer (T)) in the pure-silicate system shows a downhill energetic trend (exothermic). The formation of cyclic structures (3-membered ring (3R), 3-membered ring with one acyclic silicon ((3-1)R), and 4-membered ring (4R)) from their corresponding linear structures is also calculated and appears to be generally favorable (i.e., cyclic complexes are more stable than linear). Formation thermodynamics agree well with oligomerization energies reported by Mora-Fonz et al.⁹¹

assuming an alkaline condition (i.e., considering the presence of negatively charged species) with an implicit solvation model. The 4R silicate species is the most stable among cyclic structures investigated, which is consistent with observations of its dominant population in aqueous solutions⁸⁹ and in many zeolite frameworks.

The presence of Al or Zn significantly affects oligomerization thermodynamics. Overall, zincosilicate species (Fig. 2.5, blue) show more exothermic formation energy than corresponding aluminosilicates (Fig. 2.5, red), followed by the least exothermic silicate species (Fig. 2.5, black). Freeman et al.⁵⁴ reported a more exothermic formation of aluminosilicate oligomers relative to their pure silicate counterparts. Energetic differences in reaction pathways containing Al or Zn are primarily owing to the monomer addition step rather than condensation or cyclization. As expected from the thermodynamic calculations, kinetics of oligomerization is found to be fastest for zincosilicates, followed by that for aluminosilicates. The observed oligomerization thermodynamics are consistent with solution ²⁹Si NMR spectra reported by Anseau et al.⁸⁷ showing a higher percentage of silicate dimerization with zincate species than those of aluminate. While the presence of Al or Zn significantly affects the oligomerization thermodynamics, it does not alter the preference among different species; thus the energetic preferences of pure-silicate species (4R > (3-1)R > T > 3R > Tr > D > M) is true for all systems with one exception: the inversion between aluminosilicate Tr and 3R (although with a small energy difference). These findings indicate that aluminate and zincate species play an important role in pre-nucleation chemistry and oligomer composition, but less so for oligomer size and structure.

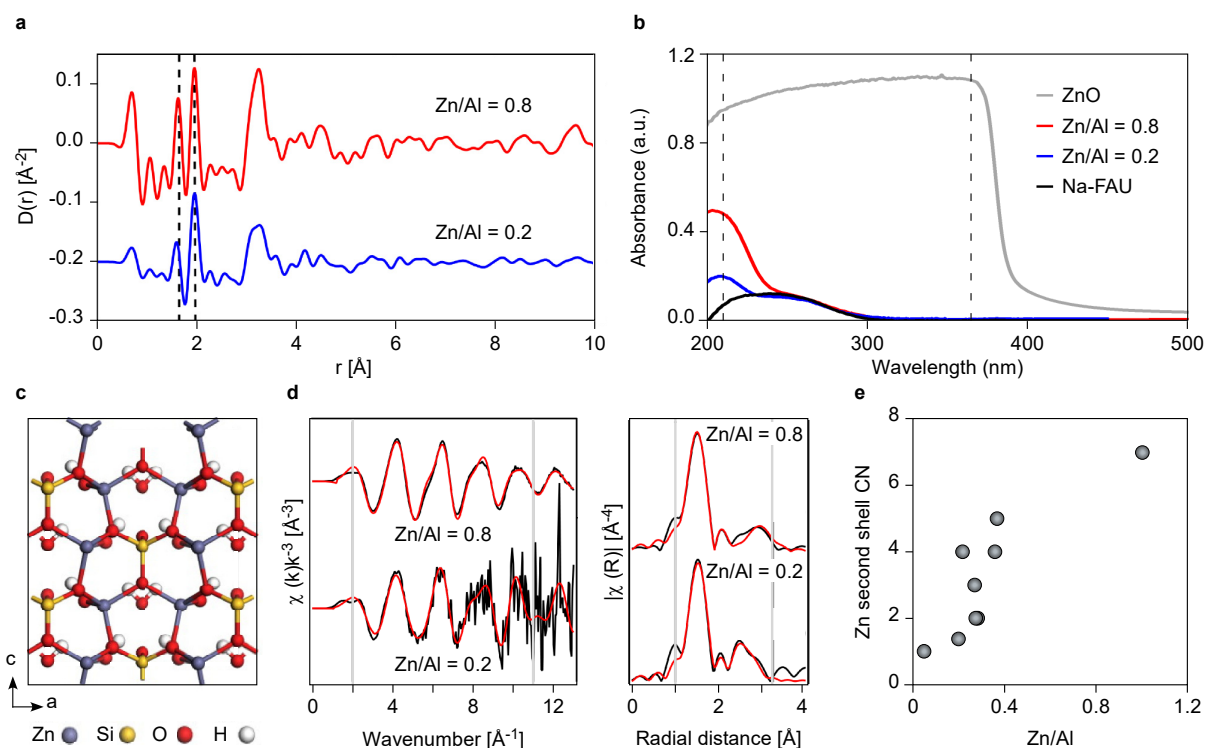


Fig. 2.6. (a) Differential X-ray PDF (dPDF) of Zn,Na-FAU samples. Dashed lines indicate the Al/Si – O distance in faujasite (1.64 Å) and the Zn – O distance in hemimorphite (1.96 Å). The loss of intensity beyond 4 Å indicates the Zn-associated disorder is primarily short- to medium-order in scale, extending to approximately 5 Å at low Zn and to approximately 10 Å at high Zn. (b) UV-Vis spectra of Na-FAU (black), Zn,Na-FAU synthesized with Zn/Al ratios of 0.8 (red) and 0.2 (blue), and commercial ZnO (gray) as a reference. Dashed lines indicate peaks at 210 and 365 nm. (c) Crystal structure of hemimorphite (nonporous zincosilicate). Reproduced with permission from ref.⁹². Copyright 2010 Elsevier. (d) EXAFS measurements of Zn,Na-FAU samples washed with deionized water prior to centrifugation. (Left) Zn K-edge EXAFS spectra (black) for Zn,Na-FAU samples. Shell-by-shell fits (red) were produced using FAU framework and hemimorphite reference structures for low and high Zn/Al samples, respectively. (Right) Fourier transforms of the Zn EXAFS data. Grey lines define the fit window of 2 – 11 Å⁻¹ (k space) and 1 – 3.25 Å (R space). (e) Dependence of zinc coordination number (CN) on the amount of zinc present in the Zn,Na-FAU synthesis mixture.

Here we use a combination of experimental and computational techniques to examine how Zn heteroatoms incorporate in zeolite crystals. Elemental analysis of Zn,Na-FAU crystals reveals a non-uniform distribution of Zn and Al atoms throughout the crystal. As shown in Table 2.1, two methods were used to evaluate the Si/Al and Si/Zn ratios. X-ray photoelectron spectroscopy (XPS) was used to extract the molar ratios at the outermost surface (i.e. depth of ca. 8 nm) whereas energy dispersive spectroscopy (EDS) was used to evaluate the overall composition (depth of ca. 1 μ m) of each sample. Comparison of EDS and XPS data for Na-FAU reveals a similar Si/Al ratio, indicating a homogeneous distribution of Al without evidence of either Al- or Si-zoning⁶². For Zn,Na-FAU we observe a higher Si/Al ratio from XPS relative to EDS, which indicates minor Si-zoning in the outer rim of these crystals. The loss of Al sites at the exterior surface is compensated by the increased occlusion of zinc, which is confirmed by the lower Si/Zn ratio from XPS measurements (Table 2.1). This anti-correlated relationship between zinc and aluminum was observed previously in Zn-FAU samples⁷⁶. Potential explanations for Zn-zoning in FAU and its putative role in suppressing GIS nucleation are provided in the following sections.

Table 2.1. Composition of FAU crystals.

Molar ratio	Method	Na-FAU*		Zn,Na-FAU (Zn/Al 0.2)	Zn,Na-FAU (Zn/Al 0.4)
Si/Al	EDS	2.2 $\pm$ 0.3		2.0 $\pm$ 0.1	2.4 $\pm$ 0.3
Si/Al	XPS	2.1 $\pm$ 0.2		3.5 $\pm$ 0.3	4.6 $\pm$ 0.3
Si/Zn	EDS	n.a.		40 $\pm$ 20	11 $\pm$ 3
Si/Zn	XPS	n.a.		4.3 $\pm$ 0.8	5.5 $\pm$ 0.6

*Solids were extracted from growth mixtures by decanting the supernatant solutions prior to washing with DI water

There are multiple possibilities for zinc coordination in zeolites. We performed tests to eliminate several options for zinc coordination in Zn,Na-FAU samples. X-ray pair distribution function (PDF) analysis was also performed on as-synthesized samples (Fig. 2.6a), revealing the absence of O–Zn²⁺ bonds, which are signatures of extra-framework Zn²⁺ ions associated with framework oxygen. We attempted to remove any potential extra-framework zinc complexes by ion exchange with monovalent (Na⁺ and K⁺) and divalent (Co²⁺) cations; however, these treatments had a minimal effect on Si/Zn ratios, indicating the absence of extra-framework zinc species. The potential incorporation of ZnO particles was also investigated by UV-Vis spectroscopy, which can detect relatively small amounts of metals⁹³.

Table 2.2. Shell-by-shell fits to Zn EXAFS spectra.

Sample	Neighbor	CN	R + ΔR (Å)	σ^2	p(F)	ΔE_0	R factor	Fit profile
Zn,N _a -FAU (Zn/Al = 0.2)	O	4*	1.945(6)	0.0029(4)	<0.001	4(1)	0.012	FAU
	Zn	1*	2.920(9)	0.003(1)	<0.001			
Zn,N _a -FAU (Zn/Al = 0.8)**	O	5.30*	1.947(5)	0.0060(4)	<0.001	5.6(7)	0.007	Hemimorphite ⁹⁴
	Zn	7(3)	3.32(1)	0.017(4)	<0.001			
Zn,N _a -FAU (Zn/Al = 0.8)**	O	5.30*	1.947(4)	0.0058(5)	<0.001	5.6(6)	0.004	Hemimorphite ⁹⁴
	Si	1.33*	3.14(3)	0.009(5)	0.176			
	Zn	7.70*	3.32(2)	0.021(3)	0.003			

$S_0^2 = 0.8$; coordination number (CN); k space fit window 2 – 11 Å⁻¹, Fourier transform fit window 1 – 3.25 Å; interatomic distance (R + ΔR); disorder parameter (σ^2); F-test [p(F)]; energy shift (ΔE_0); goodness of fit parameter (R factor). *Fixed Value. **Na,Zn-FAU (Zn/Al = 0.8) was fit using two methods where Si next-nearest neighbors were ignored (top) or included (bottom). FAU framework standard generated in VASP⁹⁵

Spectra were assessed for Zn,N_a-FAU samples prepared with two Zn/Al ratios (Fig. 2.6b). Low zinc content (Zn/Al = 0.2) results in only one peak at 210 nm, which is commonly associated with framework zinc, although this assignment is ambiguous^{80, 82}. For samples with high zinc content (Zn/Al = 0.8), we observed differences in spectra based on the washing protocol.

The nature of zinc incorporation in FAU samples was further assessed using extended X-ray absorption spectroscopy (EXAFS) in combination with PDF analysis. The Zn EXAFS spectra of Zn,N_a-FAU samples, similar to UV-Vis measurements, were dependent on zinc loading (Fig. 2.6d). For samples with Zn/Al < 0.2, the EXAFS data can be fit with the FAU structure; however, samples with Zn/Al > 0.2 are best fit with a hemimorphite-like structure. For all samples, hemimorphite is not evident in XRD patterns, consistent with PDF profiles indicating these species do not possess long-range order. Hemimorphite (Zn₄(Si₂O₇)(OH)₂·H₂O) is a naturally occurring zincosilicate crystal with a nonporous structure (Fig. 2.6c). The appropriateness of using hemimorphite to fit the EXAFS Zn spectra is due to the increased Zn–O–Zn bond length within the zeolite structure. As shown in Fig. 2.6e, the Zn coordination number increases with increasing zinc loading, consistent with the presence of a more ZnO-like phase, and the Zn–O–Zn bond length increases from 2.9 Å (FAU) to 3.3 Å (hemimorphite). However, the lack of shell-by-shell fit sensitivity (p(F) value >0.05) to the inclusion of Zn–O–Si bonds in the coordination environment of zinc supports that an ordered hemimorphite phase is not present and that this model fit structure is likely best at capturing the increase in the Zn–O–Zn bond length (Table 2.2).

Shell-by-shell fitting of EXAFS spectra to determine the precise Zn coordination environment was particularly challenging due to heterogeneous or disordered environments. The proposed increase in bond length of the 0.8 Zn/Al sample is corroborated using PDF, which shows that when zinc is present in low quantities, its effect on crystal order is limited to distances less than 10 Å. These short-range shifts in Si–O and Zn–O bond lengths are more prominent with higher Zn/Al ratios (Fig. 2.6a) and indicate the presence

of a hemimorphite-like structure with medium-range disorder. Collectively, EXAFS and PDF results suggest that a small quantity of zinc can be incorporated into the FAU crystal, but the zinc coordination environment changes as the Zn/Al molar ratio increases (Fig. 2.6e), approaching a partially disordered hemimorphite-like structure at the highest loadings tested. The apparent imprecision suggests that the zinc coordination is challenging to identify in these structures owing to non-homogeneous or disordered environments. Further evidence of this possibility involves the lack of shell-by-shell fit sensitivity to the inclusion of Zn–O–Si bonds in the coordination environment of zinc (Table 2.2). As zinc loading increases, the Zn coordination increases (Fig. 2.6e), consistent with the presence of a ZnO-like phase with a Zn–O–Zn bond of 3.3 Å (Table 2.2), in good agreement with hemimorphite.

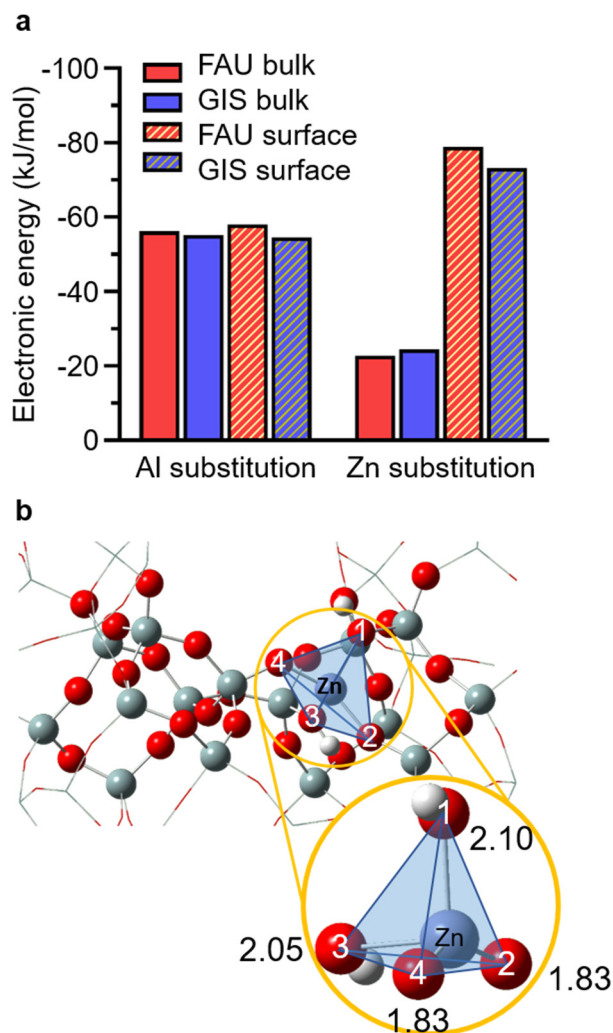


Fig. 2.7. (a) Calculated energies of Al- and Zn-substitution on FAU and GIS frameworks in bulk (solid bars) and surface (striped bars) locations. (b) Optimized local geometry around Zn in the bulk position of the FAU framework with Zn-O bond lengths labelled (in Å).

To investigate whether zinc incorporation is thermodynamically feasible in FAU and GIS, we calculated energetic changes of replacing a tetrahedral Si site by Al and Zn. Here, DFT calculations are combined with a semi-empirical method to compare Al and Zn substitution energies at different T-sites. Both frameworks were evaluated using two DFT regimes in the crystal: one at the surface and one in the bulk where all other atoms were included in the semi-empirical regime. As shown in Fig. 2.7a, regardless of framework type (FAU or GIS) and substitution location (surface or bulk), the substitution energy of aluminum is around -55 kJ/mol, which is consistent with experimental observations of homogeneously distributed Al in the absence of Zn (Table 2.1). On the other hand, Zn substitution energetics depend on the location of the T-site; in both frameworks, bulk T-sites do not strongly favor zinc incorporation, whereas the surface shows increased exothermicity. Hence, aluminum is preferred over zinc in the bulk, but zinc is preferentially located near the exterior surface (Fig. 2.7a), which is consistent with elemental analysis (Table 2.1) showing Zn,Na-FAU crystals with Zn-rich and Al-poor surfaces relative to their overall (or bulk) composition.

The strong preference of zinc to populate surface sites is attributed to changes in the local coordination environment. We observed increased bond lengths wherein oxygen atoms move further away from a T-site after substitution with Zn compared to Al. This bond elongation is greater for oxygens with the Brønsted acid. For example, an Al site has three Al-O bonds at around 1.72 Å and one Al-O(H) bond at 1.89 Å, which is consistent with values reported in literature⁹⁶. Conversely, Zn sites have two Zn-O bonds, which are around 1.83 Å and two Zn-O(H) bonds at 2.05 and 2.10 Å (Fig. 2.7b), the average of which (1.95 Å) corresponds well with results from EXAFS (Table 2.2). This configuration breaks the symmetry of the regular tetrahedron (SiO₄) and distorts the local geometry. The average distortion of the tetrahedral (TO₄) bond upon Al or Zn substitution is quantified based on the deviation of positions of oxygen atoms from the four vertices of a corresponding regular tetrahedron⁹⁷. The original site (SiO₄) is very close to a regular tetrahedron with a consistent Si-O length of 1.6 Å. Aluminum substitution results in a longer average T-O bond length with minimal angular distortion (< 5 %), which does not depend on location. On the other hand, zincate tetrahedra are substantially enlarged and distorted from the silicate tetrahedron, especially at T-sites on external surfaces. Indeed, a T-site located within the bulk is more constrained than a surface site since the former is embedded in the rigid crystalline structure, which promotes selective substitution of Zn on surface sites.

Considering the computational evidence regarding favorable zinc incorporation on zeolite surfaces, Zn-zoning is predicted, consistent with results in Table 2.1 showing a lower Si/Zn ratio at the exterior surface of FAU. The presence of framework zinc in FAU is not fully resolved; however, collective results from ONIOM calculations (DFT combined with a semi-empirical method) and EXAFS measurements suggest zinc can incorporate in the framework with a coordination less than that of aluminum. These sites introduce defects in the FAU crystal structure that may be responsible for changes in bulk crystal morphology. For instance, synthesis of FAU in the presence of zinc leads to apparent intergrowths.

ONIOM calculations revealing energetic equivalence of zinc incorporation in FAU and GIS supports the hypothesis that zinc in the solution phase is responsible for disrupting the FAU-to-GIS transformation. Here we tested this idea by deconvoluting the effects of zinc in the solid (FAU) and solution (supernatant) phases. We synthesized FAU crystals in the presence (Zn,Na-FAU) and absence (Na-FAU) of zinc and in each case isolated their respective supernatants. A series of four seeded growth experiments were performed where all combinations of FAU crystals and supernatant solutions were combined and heated for 3 days at 100°C to determine under which conditions we observed a FAU-to-GIS transformation. All combinations where zinc was present in the supernatant did not result in GIS formation. For the case where Zn,Na-FAU seeds were suspended in a zinc-free supernatant, we observed partial transformation of FAU to GIS, indicating zinc within the solid crystal was insufficient to suppress the onset of IZT; however, release of zinc from the FAU crystal into solution may be the reason for FAU-to-GIS IZT to cease within the timeframe of the

experiment. In another set of experiments, we heated only the supernatant solutions (without seed addition) and observed no crystals after 3 days for the zinc-containing solution; however, the supernatant without zinc resulted in direct GIS crystallization, thus corroborating previous suggestions that GIS does not nucleate epitaxially on FAU surfaces^{98, 99}.

In a recent Perspective article²⁶, we postulated that IZTs can be bypassed if the chemical potential $\Delta\mu$ of the synthesis medium could be altered in a way that favors nucleation of the more thermodynamically stable zeolite. Zeolite synthesis mixtures are heterogeneous with the majority of silica retained within undissolved sources; thus, the inaccessibility of silica at early stages of synthesis creates a pseudo environment in both solution and solid states that differs from the overall molar composition of the synthesis mixture¹⁰⁰. Although chemical potential is a nebulous parameter that is difficult to quantify, we proposed a general trend in $\Delta\mu$ as a function of synthesis progress (Fig. 2.8a) where the driving force leads to the initial metastable zeolite FAU but changes later in the synthesis to favor growth of GIS. We hypothesized that it could be possible to directly nucleate GIS if $\Delta\mu$ of the initial solution was altered. Here we show that the FAU supernatant solution is still sufficiently supersaturated to crystallize GIS. We prepared growth mixtures with identical concentrations as the supernatant solution after Na-FAU synthesis: growth mixture β (Fig. 2.8a) has a molar composition of 164 SiO₂:0.5 Al₂O₃:209 NaOH:5115 H₂O. Preparation and hydrothermal treatment of growth mixture β revealed direct GIS crystallization in less than 3 days (Fig. 2.8b) whereas the addition of a small amount of zinc (i.e. Zn/Al = 0.2) inhibited zeolite nucleation. Most notably, FAU intermediates are absent, unlike the nominal growth conditions in this study (growth mixture α , Fig. 2.8a and c). We also observe that growth mixtures α and β lead to crystals with subtly distinct morphological features (Fig. 2.8d and e, respectively).

Conditions in this study that lead to the direct formation of GIS are similar to the few studies in literature reporting the direct nucleation of GIS without first observing crystalline FAU as a metastable intermediate^{101, 102}. In such cases, the growth medium is dilute with low solute concentration^{98, 101, 103} and often has a high Si/Al ratio^{98, 104}. When we compare GIS nucleation during IZT to that in the extracted supernatant, the induction times are approximately identical. This indicates that FAU crystals do not appreciably accelerate GIS nucleation. During synthesis progress, FAU crystallization leads to substantive changes in the growth mixture composition and distribution of Si and Al species (i.e. the growth medium progressively becomes more Si-rich). As postulated in Fig. 2.8a, these changes alter the chemical potential in ways that favor GIS nucleation, and several experiments confirmed that increased Si availability promotes GIS crystallization. Interestingly, Okubo and coworkers¹⁰⁵ modeled Al incorporation in the GIS framework by molecular mechanics and reported it is most thermodynamically stable at Si/Al molar ratios ≥ 3 , compared to FAU that reaches its maximum stability at Si/Al < 3 ¹⁰⁶. This is consistent with findings in this study that Zn acts as an inhibitor of GIS crystallization. GIS nucleates in media with a higher Si/Al ratio and given that Zn is an efficient scavenger of silicates (i.e. reduces supernatant Si/Al ratio), this inhibits GIS crystallization.

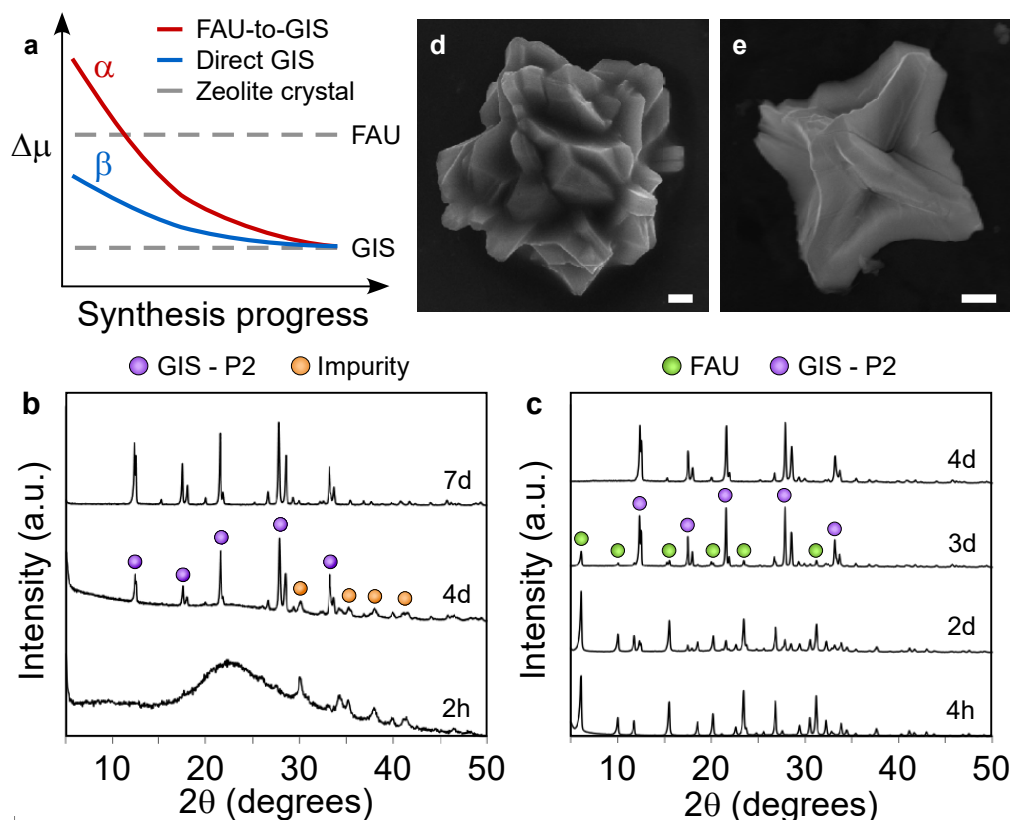


Fig. 2.8. (a) Hypothetical changes in chemical potential, $\Delta\mu$, with synthesis progress, adapted from the IZT concept proposed⁶⁷ for different growth solutions (α and β) and zeolite products (FAU and GIS). Growth mixture α refers to the nominal synthesis condition resulting in a FAU-to-GIS transformation. Growth mixture β is the supernatant of the previous mixture extracted at a time corresponding to full FAU crystallinity prior to the onset of GIS nucleation, where continued heating results in direct crystallization of GIS. (b and c) Time-resolved powder XRD patterns of solids extracted from growth mixtures β (b) and α (c). Select peaks of FAU, GIS – P2, and impurity phases are indicated by green, purple, and orange circles, respectively. (d and e) Scanning electron micrographs of GIS – P2 products obtained after 7 days of hydrothermal treatment of growth mixtures (d) α and (e) β . Scale bars represent 1 μm .

Conclusions

Multivalent metals have diverse effects on zeolite crystallization. In this study, we specifically addressed their impact on FAU-to-GIS IZT by assessing how the addition of various metals to synthesis media impact nucleation of both parent and daughter zeolites. Elements selected from Group III and IV as well as zinc (the sole transition metal selected for this study) can serve as heteroatoms in zeolite frameworks and have a more pronounced impact on crystallization pathways than Group II elements. Here we focused on zinc as an effective modifier of IZT pathways.

Working in the absence of zinc we showed that the nucleation of GIS (daughter) is independent of the presence of FAU (parent). The direct nucleation of GIS from the supernatant solution of a FAU synthesis tested the hypothesis that changes in the initial composition (or chemical potential) can alter the trajectory

of IZT. This also suggests that metastable FAU has a less active role in GIS nucleation, and likely serves only as a source of aluminosilicate solute to allow continued growth of GIS crystals. Introduction of zinc into the growth medium can have several effects based on its concentration. At high concentration, zinc suppresses zeolite nucleation and leads to an amorphous product. At low concentration, zinc inhibits the FAU-to-GIS IZT and also shifts the final GIS product from polymorph P2 to P1. At an intermediate concentration, zinc completely suppresses GIS nucleation leading to a stable FAU product. Surprisingly, zinc can stabilize FAU crystals at temperatures around 100°C, which is much higher than typical synthesis conditions for this metastable zeolite. The ability of zinc to suppress GIS nucleation is independent of when the heteroatom is added to the synthesis medium.

In the presence of zinc, we posit that aluminate and zincate species compete to condense alumino-/zincosilicate oligomers, where the extent of zincosilicate formation depends on the Zn/Al ratio. At intermediate zinc compositions ($0.1 < \text{Zn/Al} < 0.2$), zinc prevents the level of chemical evolution necessary for GIS nucleation by sequestering much of the remaining silicate species. This draws greater attention to the role of the solution phase where soluble zincosilicate species seemingly have a more pronounced effect on zeolite phase transition. This was confirmed by DFT calculations, which show that zincosilicate oligomerization is more favorable than that of (alumino)silicate species. Using EXAFS measurements, we showed that zinc heteroatoms are not fully coordinated when incorporated into the FAU framework. Our findings have not conclusively resolved the local structure of zinc species, but have revealed that framework zinc has a local coordination that more closely resembles a zincosilicate mineral, hemimorphite, and is preferentially located near the surface of zeolite crystals. The selective incorporation of Zn on the crystal surface is rationalized by ONIOM calculations, which showed that Zn substitution on the surface is promoted by the more flexible coordination environment on the surface relative to the bulk crystal.

In summary, we have used a combination of experimental and computational approaches to develop a deeper understanding of how heteroatoms can influence zeolite crystallization. There is increased interest in designing zeolites with a variety of heteroatoms as potential sites for catalytic reactions. Here, we focus on zinc and highlight the challenges of conclusively identifying heteroatom coordination in zeolites. One previously unrecognized benefit of heteroatoms in zeolite synthesis that we observe in this study is their ability to stabilize FAU over a broad temperature range, thus avoiding unwanted impurities and expanding the synthesis space of this commercially relevant zeolite. Two key observations in this study related to IZTs are that daughter nucleation does not necessarily occur on the surface of the parent crystal; and that the pathway of zeolite nucleation can be altered by changing the solution state, which is counter to many nonclassical pathways of zeolite crystallization that focus on the role of precursors (i.e. gel or solid state). Future studies of other heteroatoms and zeolite frameworks may prove how generally these observations apply to syntheses of other materials.

Section 3: Understanding Initial Zeolite Oligomerization Steps with First Principles Calculations

Zeolites are porous aluminosilicate materials that find various applications in the chemical industry in separations, catalysis, ion exchange, etc. However, despite their widespread use, the reaction mechanisms occurring during zeolite growth are still unclear. Herein, we use Density Functional Theory calculations to gain insights into the thermodynamics of oligomerization, which constitute the initial steps of zeolite growth. By taking into consideration solvent and temperature effects, our results demonstrate that the growth of aluminosilicate systems is significantly more exothermic than their pure silicate counterparts. Under pH neutral conditions, water prefers to dissociate on the early-growth-stage aluminosilicate complexes rather than desorb, thus generating potential Brønsted acid sites on the oligomers. Additionally, (alumino)silicate growth pathways are evaluated in the presence of Na^+ cation, as well as the Ca^{2+} cation for the pure silicate pathway. The presence of cations increases the exothermicity of growth, with Ca^{2+} exhibiting the most energetically favorable growth environment for the silicate systems. Importantly, we demonstrate through reaction extent analysis that the presence of cations modulates the speciation of the formed oligomers, with Na^+ favoring linear species in addition to the generally preferred cyclic ones. Overall, this work provides a fundamental understanding of the thermodynamics of complex reaction paths that occur during early stages of zeolite growth and suggests that the initial growth steps can have significant impact on the final zeolite structure.

Introduction

Zeolites are porous aluminosilicates that are both naturally occurring and synthetically produced. Zeolites can be synthesized with detailed control of their physiochemical properties which makes them excellent materials for applications in fields such as separations^{107, 108}, ion exchange¹⁰⁹, and catalysis^{110, 111}. The ability to control the structural and chemical functionalities of a given zeolite is extremely important for its end application. For example, ZSM-5 (MFI type) is one of the most commonly used industrial catalysts in the cracking of long hydrocarbon chains to produce light olefins due to its acidic properties and (hydro)thermal stability¹¹². Additionally, zeolite growth has an important role in nuclear waste glass performance at disposal facilities. The formation of zeolites has been shown to cause a delayed acceleration in the corrosion rate of certain glasses (Stage III); therefore, it is essential that zeolite growth be well understood in order to be applied in the field of waste glass corrosion^{9, 20-22, 113, 114}. Obtaining a detailed understanding of the mechanisms involved in early zeolite nucleation steps, and the effects of system composition on growth will enhance the ability to estimate nuclear waste glass dissolution rates in a long-term disposal facility.

Zeolite synthesis has significantly advanced over the years in terms of controlling their final structures; however, despite the progress that has been made in zeolite synthesis, the detailed mechanisms for zeolite crystallization are far from being determined due to the complexity of their growth media. The largest gap in understanding how zeolites grow remains in the initial oligomerization steps of pre-nucleation (alumino)silicate species (oligomers, clusters, particles). The impact of the first steps of nucleation on the final zeolite product is of great interest in the field of zeolite synthesis^{115, 116}. Therefore, gaining a deeper understanding of the mechanism(s) that drives these reactions is imperative to achieve better control during synthesis and eventually control the final zeolite structure. Such control would allow the development of novel zeolite structures, thus furthering the range of applications.

Many investigations, both experimental and computational, have attempted to clarify how initial oligomerization steps progress using several techniques such as nuclear magnetic resonance (NMR)¹¹⁷, Density Functional Theory (DFT) calculations^{91, 118-122}, and Monte Carlo simulations^{121, 123, 124}. Experimental studies have offered insights into the effects of reactant composition and synthesis environment on the species formed during nucleation, which has direct impact on zeolite size, topology,

and functionality¹²⁵. However, it is difficult to experimentally observe the exact species (and their concentrations) formed during nucleation due to the extreme synthesis conditions (e.g. high ionic strength, pH, temperature, etc.), as well as the rate at which these reactions occur¹²¹. On the other hand, deeper mechanistic understanding of early growth stages of materials can be achieved using DFT methods¹²⁶. Specifically for zeolitic (alumino)silicate systems, studies have focused on probing mechanisms of the early oligomerization reactions, with extensive work being done on the dimerization of silicates^{120, 127}; however, there is little consistency within these studies in terms of reactant species, simulated synthesis environment, solvation considerations, and reported energetics.

Several computational studies have probed the impact of pH on oligomerization in aluminosilicate systems, with most calculations being performed in the pH range of 8-11, where alkaline environments lend to the deprotonation of a given silanol group to facilitate further oligomerization^{118, 121}. This deprotonation step has resulted in a proposed anionic pathway of silicate oligomerization¹²⁷. Systems that are highly alkaline (e.g. pH=11) have been shown to give preference to cyclic structure formation over their linear counterparts¹²⁸. To better understand the role of solvent, the first oligomerization steps have been investigated using DFT calculations in various environments: the gas phase, implicitly solvated, explicitly solvated, and a combination of the latter two. White et al.¹²⁷ found that in order to obtain pK_a values that were consistent with experimental data, it was necessary to use a combination of an implicit solvation model and explicit water molecules interacting with the structure of interest. This agrees with Catlow and coworkers who also showed that energies obtained using an implicit solvation model along with explicit solvent molecules were found to best agree with experimental values¹²⁹.

While the contributions of pH and solvation on the nucleation steps of zeolite growth have been addressed computationally¹²¹, there remains a sizable gap in zeolite nucleation knowledge that has been untouched by computational studies. For instance, although zeolites are aluminosilicate materials, most of the computational studies focus only on oligomerization of pure silicate systems^{91, 118-124}. Additionally, cations present in the synthesis environment can assume various roles during growth. Cationic species can perform as inorganic structural-directing agents, which serve to direct growth towards a desired structural conformation and can determine structural characteristics in the final zeolite product¹³⁰. Cations are also found in zeolites as counterions which stabilize charges in the zeolite framework that result from incorporation of tetrahedral aluminum sites. Though the effects of counterions in zeolite growth have been investigated previously¹³¹⁻¹³³, most computational studies focus on monovalent cations and rarely include divalent alkaline earth metals which are commonly found in natural zeolites. Contributions of cations during growth as well as their spatial positioning in the final zeolite product remain unclear.

In this work, we seek to shed light into the early stages of zeolite growth. We apply DFT calculations to gain a detailed understanding of the energetic profiles in the initial oligomerization steps of zeolite growth up to the formation of a cyclic tetramer for silicate and aluminosilicate systems (with Si/Al ratios of 1 and 3). In order to uncover the role of cations during early-growth stages, we investigate the oligomerization steps in the presence of monovalent Na^+ and divalent Ca^{2+} cations (from NaOH and $Ca(OH)_2$ addition). Moreover, we address the effect of H_2O molecules produced during oligomerization (condensation) reactions on the formation of Brønsted acid sites found on aluminosilicate species. Finally, we reveal the detailed speciation of the formed complexes based on the thermodynamics of the oligomerization elementary steps. Overall, our work reveals not only the complexation thermodynamics of how zeolite precursor structures are formed prior to crystal growth, but also the role of cations and solvent on their structure and speciation.

Results and Discussion

In order to develop a detailed mechanistic understanding of how zeolites grow, we focus on the initial oligomerization steps in (alumino)silicate systems. We have investigated the free energy pathways of these

initial steps for both silicate and aluminosilicate systems, as shown in Fig. 3.1. The Gibbs free energy (not shown here) includes enthalpic and entropic contributions to the total electronic energy. For each system, we have investigated oligomerization from the monomer, $\text{Si}(\text{OH})_4$ and $\text{Al}(\text{OH})_3$, up to formation of the cyclic tetramer complex.

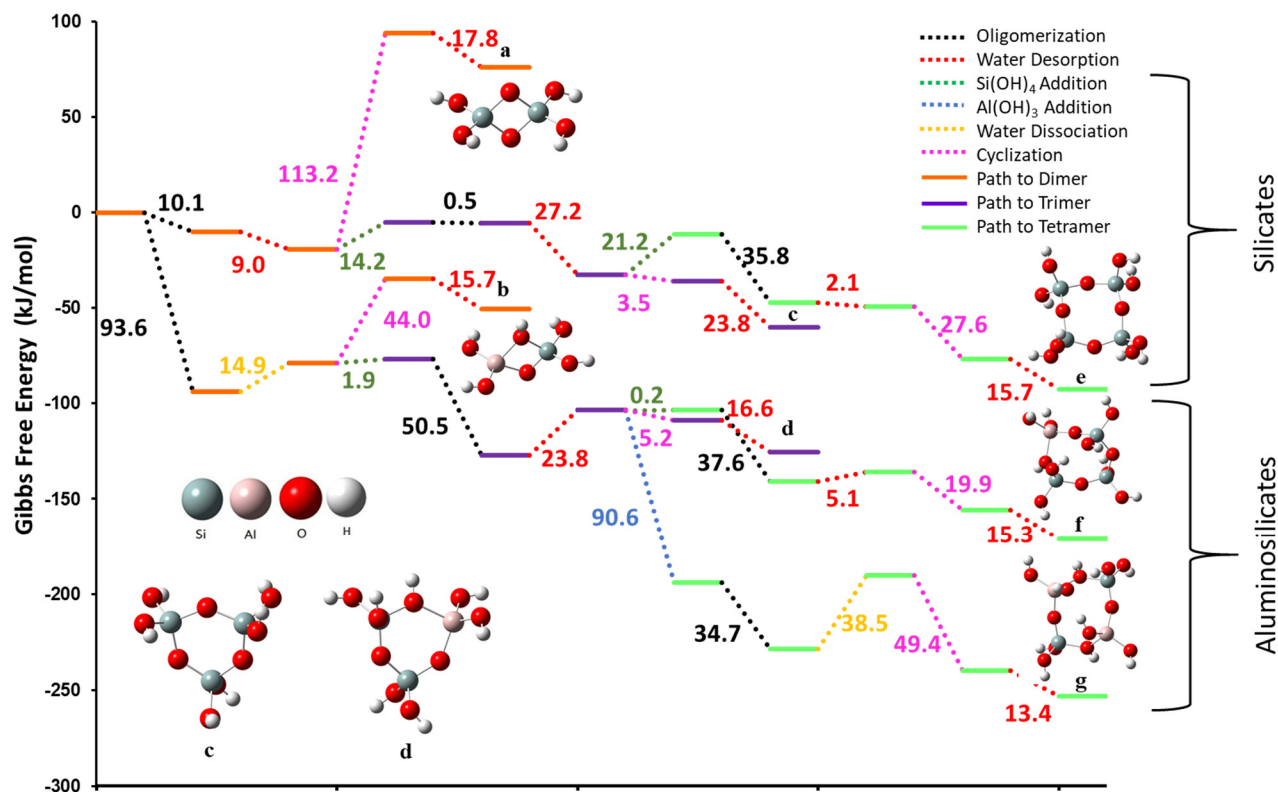


Fig. 3.1. Free energy reaction profile for oligomerization of silicate and aluminosilicate systems. The initial reactants for the silicate and aluminosilicate systems are $\text{Si}(\text{OH})_4 + \text{Si}(\text{OH})_4$ (top pathway) and $\text{Si}(\text{OH})_4 + \text{Al}(\text{OH})_3$ (bottom pathway), respectively. The number listed by each step represents the absolute value of the change in Gibbs free energy between the two corresponding states (kJ/mol). Each number is color-coded to indicate the specific reaction step and is consistent with the coloring of the dashed lines. Colors of dashed lines in the figure indicate the following steps: black - oligomerization; red - water desorption; green - $\text{Si}(\text{OH})_4$ addition; blue - $\text{Al}(\text{OH})_3$ addition; yellow - water dissociation; and pink - cyclization. The solid lines are color-coded to highlight the paths forming oligomers of different size: orange – dimer species; purple – trimer species; and green – tetramer species. The profile shows the energetics for the formation of both the linear and cyclic structures through the tetramer. Terminal structures (states a-g) are shown for each pathway.

Dimer Formation. The first oligomerization step is a condensation reaction between two monomers ($\text{Si}(\text{OH})_4 + \text{Si}(\text{OH})_4$, or $\text{Si}(\text{OH})_4 + \text{Al}(\text{OH})_3$) to form the dimers $\text{Si}_2\text{O}_7\text{H}_6(\text{H}_2\text{O})$ or $\text{SiAlO}_6\text{H}_6(\text{H}_2\text{O})$. Though the dimerization step in the silicate system is exothermic at -10.1 kJ/mol, the same step in the aluminosilicate system is significantly more exothermic at -93.6 kJ/mol. White et al.¹²⁷ reports the same trend when comparing silicate and aluminosilicate dimerization at pH 11, with a silicate dimerization free energy of -1.8 kJ/mol, while the dimerization of its aluminosilicate counterpart ($\text{Si}(\text{OH})_4 + \text{Al}(\text{OH})_4^- \cdot \text{Na}^+$ as initial reactants) under the same conditions having a free energy of -21.2 kJ/mol. Furthermore, the silicate dimerization reaction step was reported to have a Gibbs free energy of -14.2 kJ/mol (at pH 7) by White et al.¹²⁷ and 0 kJ/mol by Mora-Fonz et al.⁹¹, demonstrating that our numbers are within the reported range in

literature. The energetic differences can be attributed to temperature and solvation effects. White et al. models solvation effects using the conductor-like screening model (COSMO) and includes explicit water molecules at a temperature of 298 K, whereas Mora-Fonz et al. reports energetics at 450 K using COSMO without considering explicit water molecules. In this work we evaluate these reactions at 373K using an implicit solvation model (CPCM) and include single explicit water molecules upon their formation during condensation reactions (oligomerization steps).

Trimer Formation. The next oligomerization step following formation of the dimer is the trimerization reaction. Here, a silicic acid monomer ($\text{Si}(\text{OH})_4$) is added as reactant to with the linear dimer ($\text{Si}_2\text{O}_7\text{H}_6(\text{H}_2\text{O})$ or $\text{SiAlO}_6\text{H}_6(\text{H}_2\text{O})$) to produce a trimer product. Trimerization occurs after water desorption or water dissociation steps in the silicate and aluminosilicate systems, respectively. The trimer $\text{Al}_2\text{SiO}_9\text{H}_8(\text{H}_2\text{O})$ (with Si/Al ratio of 0.5) formed upon addition of aluminum hydroxide species ($\text{Al}(\text{OH})_3$) was not considered in order to maintain a Si/Al molar ratio of 1 or greater, which is an attribute of many zeolite topologies, and remains in accordance with Löwenstein's rule which suggests the formation of Al-O-Al bonds is unfavorable in these systems¹³⁴. The same trend found in the dimerization steps is also observed in the trimerization reactions. Trimerization of the aluminosilicate system was found to be more exothermic at -50.5 kJ/mol than its silicate counterpart at -0.5 kJ/mol. To our knowledge, there is little work reported in the literature on silicate trimerization^{118, 135}, none of which has been conducted at 373 K. Trimerization in the silicate system at 450 K is reported by Mora-Fonz et al.¹¹⁸ to be 6 kJ/mol (BLYP/DNP, COSMO), which again confirms our agreement with literature that silicate trimerization is relatively thermoneutral.

Tetramer Formation. The Si/Al molar ratios have been shown to have a direct impact on final zeolite structure and composition¹³⁶. Therefore, two different Si/Al ratios for the aluminosilicate system were evaluated to examine the impact of aluminum and silicon composition on the energetics of oligomerization. In the aluminosilicate system, the growth path splits upon reactant addition to the trimer $\text{Si}_2\text{AlO}_{10}\text{H}_9$. The tetramer can be formed by adding either an $\text{Si}(\text{OH})_4$, or an $\text{Al}(\text{OH})_3$ monomer to the trimer complex. The addition of $\text{Si}(\text{OH})_4$ produces a tetramer ($\text{Si}_3\text{AlO}_{13}\text{H}_{11}$) with an Si/Al ratio of 3, while the addition of $\text{Al}(\text{OH})_3$ produces a tetramer ($\text{Si}_2\text{Al}_2\text{O}_{13}\text{H}_{12}$) with an Si/Al ratio of 1.

Tetramerization steps for all systems display similar energetics, with Gibbs free energies between -34 and -38 kJ/mol. At first glance, this suggests that the energetics of tetramerization are not strongly affected by the composition of the system; however, upon evaluation of the electronic energies we observe that this is not the case. In the silicate and aluminosilicate systems with Si/Al=3, the electronic energies were found to be -53.5 and -54.3 kJ/mol, respectively, whereas the electronic energy of the Si/Al=1 aluminosilicate system was found to be -35.8 kJ/mol. This indicates that entropic effects are more pronounced in systems where $\text{Si}(\text{OH})_4$ is added to the trimer species (ΔS term is -0.041 kJ/mol-K for both pure silicate and Si/Al=3 tetramerization steps) rather than $\text{Al}(\text{OH})_3$ (ΔS is -0.003 kJ/mol K for Si/Al=1 tetramerization). This difference can be explained by the interaction between the water molecule produced during the formation of the aluminosilicate tetramer and the second aluminum atom. Upon formation of the linear tetramer in the Si/Al=1 aluminosilicate system, the aluminum atom strongly interacts with the oxygen atom of the water molecule, which would explain why the entropic effects in this system are much smaller than in its counterparts.

Cyclization. Cyclization of (alumino)silicate complexes is critical to zeolite growth as many of the produced ring species are recognized as composite building units of zeolite framework structures¹¹⁸. The cyclization step occurs via a condensation reaction between the two ends of a linear chain, which produces a cyclic conformation of the oligomer complex and a water molecule. For both silicate and aluminosilicate systems, cyclization reactions were found to be favorable for the trimer and tetramer species, which is consistent with literature¹¹⁸. For both the silicate and aluminosilicate systems, we have investigated a configuration of the dimer species analogous to a cyclic configuration, where the two tetrahedral metal atoms share two oxygen atoms (shown respectively as states *a* and *b* in Fig. 3.1, for silicate and aluminosilicate systems).

The condensation steps necessary to form these dimer configurations are highly endothermic (113.2 and 44.0 kJ/mol in silicate and aluminosilicate systems, respectively) which suggests that they are unlikely to occur. Cyclization steps following dimerization were found to be exothermic. Gibbs free energies of trimer cyclization for the silicate (Fig. 3.1, state *c*) and aluminosilicate (Fig. 3.1, state *d*) systems are -3.5 and -5.2 kJ/mol, respectively. Tetramer cyclization was found to be the most exothermic of the cyclization reactions for all oligomer systems studied, which agrees with the observation that cyclic tetramer structures are common in several zeolite topologies. Cyclic tetramer structures are shown in Fig. 3.1 as *e*, *f*, and *g* for the silicate, Si/Al=3 aluminosilicate, and Si/Al=1 aluminosilicate systems, respectively. The oligomerization paths explored in this work considers oligomerization to occur in linear structures. Cyclization of linear oligomer structures produces terminal states in the growth pathway, therefore growth occurring on cyclic complexes is not investigated in this work.

H₂O Desorption vs. H₂O Dissociation in Aluminosilicates. To further understand how pre-nucleation species assemble and grow, we now focus on the step subsequent to an oligomerization step. Each oligomerization reaction produces an H₂O molecule in addition to the (alumino)silicate complex. In order to maintain consistency in all calculations, the product H₂O molecule was either desorbed (to the liquid phase) or dissociated on the complex, as shown in Fig. 3.2. For the aluminosilicate system, we evaluated the energetics of the reaction path in the same step order (oligomerization step followed by H₂O desorption step) as its silicate-only counterpart. We found the energetics of water removal steps in the aluminosilicate system to be significantly more endothermic than those of the silicate system. The H₂O desorption step following the dimerization reaction in the aluminosilicate system (shown as step *a-b* in Fig. 3.2) has a Gibbs free energy of +69.7 kJ/mol. That same water removal step in the silicate system has a value of -9.0 kJ/mol. Silicates are known to be hydrophobic, which is captured by the exothermic water desorption step. However, in the aluminosilicate system we observe an endothermic H₂O desorption because upon H₂O formation during oligomerization, the H₂O molecule strongly associates with the aluminum atom on the aluminosilicate complex, which stabilizes the structure. This allows the aluminum atom to obtain its preferred tetrahedral coordination, which enhances the overall stability of the complex.

To further address this thermodynamically unfavorable step in aluminosilicate systems, we explored the dissociation of water as an alternative to water desorption. Upon dissociation of the H₂O molecule, a hydroxide group stays associated with the aluminum atom, while the remaining H⁺ is bound to the bridging oxygen of the Si-O-Al bond, resulting in the formation of a Brønsted acid site. Fig. 3.2 shows that the dissociation of H₂O is energetically more favorable than H₂O desorption for species where an H₂O molecule interacts with an aluminum atom (highlighted in Fig. 3.2 as red and yellow arrows, respectively). For the H₂O desorption step following dimerization where the Gibbs free energy was found to be +69.7 kJ/mol (step *a-b* in Fig. 3.2), the alternative option of dissociating the H₂O molecule (*a* to *c*) exhibits a free energy of +14.9 kJ/mol, which is significantly less endothermic than water desorption. The same trend is observed following the oligomerization step forming the Si/Al=1 tetramer, in which H₂O desorption (step *d* to *e*) has a free energy of +97.9 kJ/mol, and H₂O dissociation (step *d* to *f*) is at +38.5 kJ/mol. This energetic preference of H₂O dissociation over H₂O desorption in the aluminosilicate system occurs due to the aluminum atom's preference to be tetrahedrally coordinated. By dissociating the water molecule, the aluminum atom remains tetrahedrally coordinated unlike in H₂O desorption steps. Importantly, these observations indicate that Brønsted acid sites may be formed on intermediate species during these first steps of zeolite growth.

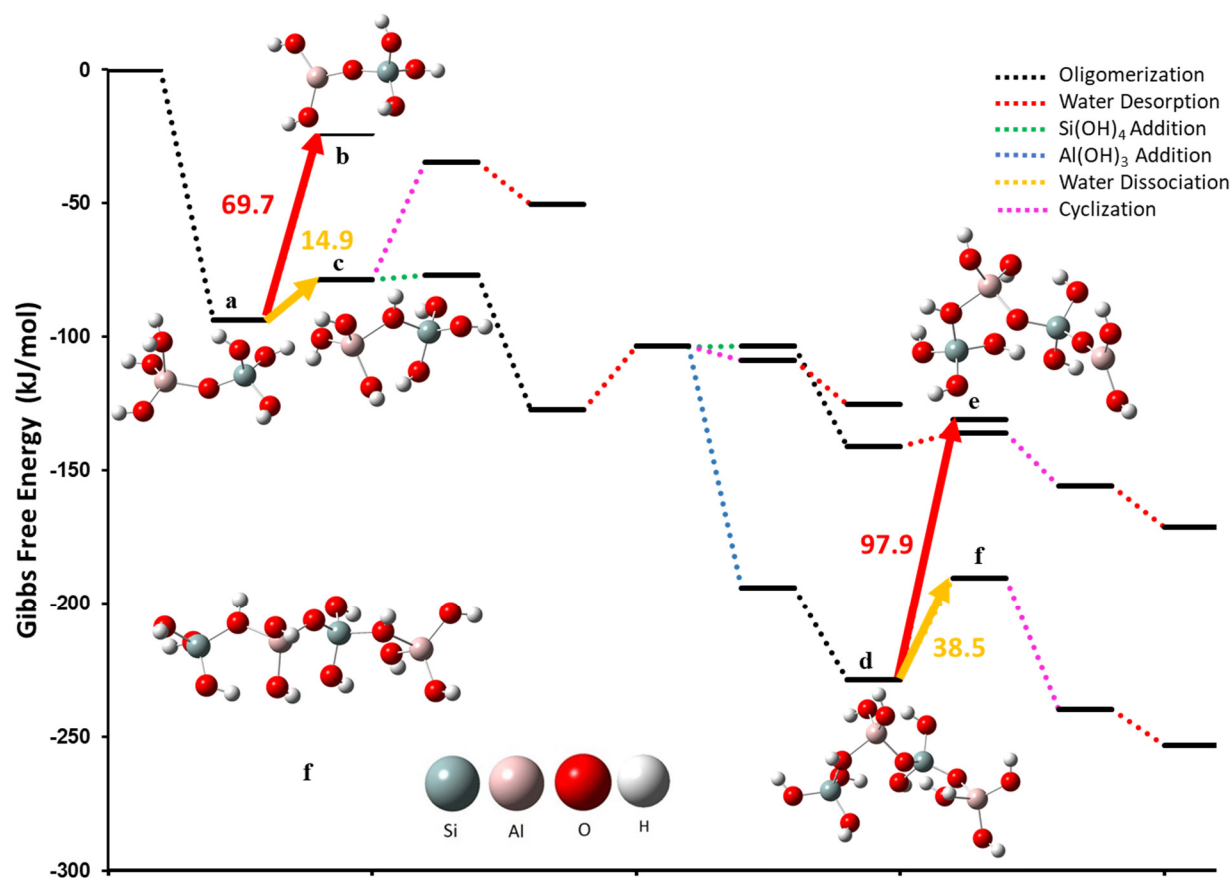


Fig. 3.2. Free energy reaction profile for oligomerization of the aluminosilicate system (note that this is a subset of information shown in Fig. 3.1), demonstrating the energetics for water dissociation and water desorption after each $\text{Al}(\text{OH})_3$ addition. The water dissociation and desorption steps have been highlighted in red and yellow arrows, respectively. The number listed by each step represents the absolute value of the change in Gibbs free energy between the two corresponding states. Each number is color-coded to indicate the process that is occurring in that specific step and is consistent with the coloring of the dashed lines, details of which are given in Fig. 3.1. Water prefers to dissociate on SiAlO_6H_5 and $\text{Si}_2\text{Al}_2\text{O}_{12}\text{H}_{10}$ rather than desorb, generating acidic hydrogens (Brønsted acid sites). Structures of states associated with water dissociation and desorption are shown as insets (states a-f).

Cation Effect on Energetics of Silicate Growth. As an effort to elucidate the role of cationic species in the initial steps of zeolite growth, we have investigated how the thermodynamics of growth change in the presence of Na^+ and Ca^{2+} . To this end, a proton on the $\text{Si}(\text{OH})_4$ molecule was substituted with either Na^+ or $\text{Ca}(\text{OH})^+$ (representing experimental NaOH and $\text{Ca}(\text{OH})_2$ addition, respectively) with the overall systems retaining their charge neutrality. We found that the presence of these cations (Na^+ and Ca^{2+}) shifts the reaction pathway to become more exothermic, as shown in Fig. 3.3. Overall, we observe that the Ca^{2+} oligomerization path is the most exothermic, followed in exothermicity by Na^+ and then by the pure silicate. This is an interesting observation; taking into consideration that naturally formed zeolites typically contain Ca^{2+} cations, here we demonstrate that the presence of Ca^{2+} cations thermodynamically facilitate oligomerization. The dimerization reaction for silicate oligomerization in the absence of cations has a free energy of -10.1 kJ/mol, whereas this reaction in the presence of Na^+ becomes more exothermic with a free energy of -36.9 kJ/mol. Although the overall reaction path is most exothermic in the presence of Ca^{2+} , the respective dimerization step (second oligomerization step in Ca^{2+} pathway) is less exothermic (compared

to Na^+ and pure silicate paths) with a free energy value of -0.6 kJ/mol. The reduced exothermicity of the dimerization reaction in the presence of Ca^{2+} can be explained by the calcium-oxygen interactions upon the addition of a $\text{Si}(\text{OH})_4$ molecule. The formation of the Si-O-Si bond during dimerization decreases the number of silicon-bonded oxygens that Ca^{2+} has available to interact with. The overall high exothermicity of the calcium-containing pathway can be partially explained by the exothermicity (-89.7 kJ/mol) of the substitution step, where $\text{Si}(\text{OH})_4$ and $\text{Ca}(\text{OH})_2$ react to form the Ca^{2+} substituted monomer $\text{Si}(\text{OH})_3\text{OCa}(\text{OH})$. Neither the addition of Na^+ or Ca^{2+} produced a significant change in the energetics of dimer cyclization (edge-sharing tetrahedra configurations), which is endothermic for all systems. The edge-sharing dimer species $\text{Si}_2\text{O}_6\text{H}_3\text{Na}(\text{H}_2\text{O})$ and $\text{Si}_2\text{O}_7\text{H}_4\text{Ca}(\text{H}_2\text{O})$ have formation Gibbs free energies of 124.4, and 171.6 kJ/mol, respectively.

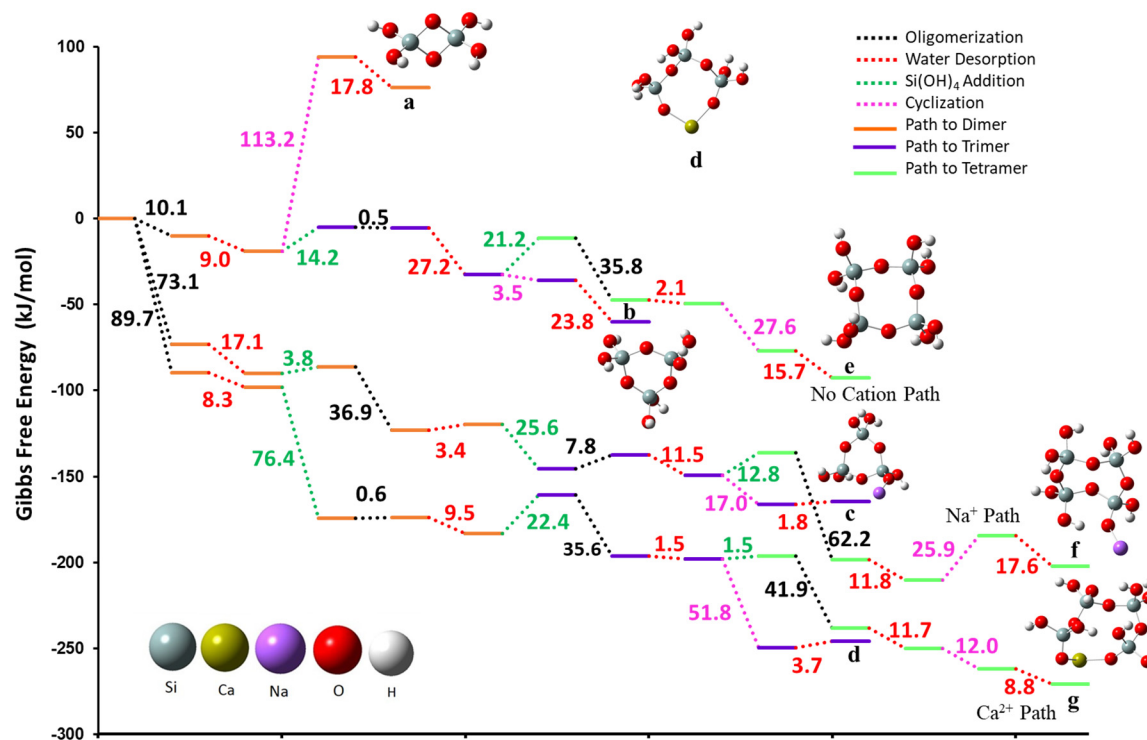


Fig. 3.3. Free energy reaction profiles for oligomerization of silicates in the absence and presence of Na^+ and Ca^{2+} cations (NaOH and $\text{Ca}(\text{OH})_2$ addition). The initial reactants for the systems are $\text{Si}(\text{OH})_4 + \text{Si}(\text{OH})_4$, $\text{Si}(\text{OH})_4 + \text{NaOH}$ and $\text{Si}(\text{OH})_4 + \text{Ca}(\text{OH})_2$, respectively. The number listed by each step represents the absolute value of the change in Gibbs free energy between the two corresponding states. Each number is color-coded to indicate the process that is occurring in that specific step and is consistent with the coloring of the dashed lines, details of which are given in Fig. 3.1. The solid lines are color-coded to highlight the paths forming oligomers of different size as in Fig. 3.1. The profile shows the energetics for the formation of both the linear and cyclic structures for each species through the tetramer. Terminal structures are shown for each pathway.

In addition to highly exothermic energetics, the introduction of Ca^{2+} into the silicate system was found to open an alternative oligomerization pathway. As a divalent atom, calcium can form two Ca-O bonds and incorporate itself into the zeolite primary units formed during these initial steps, which could result in integration into the zeolite framework. This produces the formation of an O-Ca-O bridge between two tetrahedral (Si, Al) atoms. Upon the addition of a second $\text{Si}(\text{OH})_4$ to the $\text{Ca}(\text{OH})$ substituted monomer ($\text{Si}(\text{OH})_3\text{OCaOH}$) the pathway splits to form either a Si-O-Si bond or an O-Ca-O bond. We investigated all

reaction steps in the silicate system containing Ca^{2+} (with the exception of the cyclic dimer) using structures that contain an O-Ca-O bond rather than structures that include an O-Ca-OH bond. It is also worth noting that in addition to zeolites, calcium silicates also play an important role in the composition of Portland cement, and thus have significant environmental impact¹³⁷. There has been much work done in the field of cement science that seeks to optimize cement composition, improve cement hydration rates, and in turn lower the carbon footprint of global cement use¹³⁸⁻¹⁴⁰.

Cation Effect on Energetics of Aluminosilicate Growth. Following the approach used to explore the effects of cations on the reaction pathway of silicate oligomerization, the impact of Na^+ was also investigated in the aluminosilicate systems (Fig. 3.4). Here we substitute the Na^+ cation onto the $\text{Al}(\text{OH})_3$ molecule rather than $\text{Si}(\text{OH})_4$, forming the $\text{Al}(\text{OH})_2\text{ONa}$ monomer. Though the substitution of Na^+ on $\text{Si}(\text{OH})_4$ is thermodynamically preferred (-73.1 kJ/mol, Fig. 3.3) over substitution on $\text{Al}(\text{OH})_3$ (-30.8 kJ/mol, Fig. 3.4), the aluminosilicate system containing sodium is evaluated starting from the substituted $\text{Al}(\text{OH})_3$ complex ($\text{Al}(\text{OH})_2\text{ONa}$). We chose to evaluate this pathway in order to understand the effects of aluminosilicate growth when Na^+ is substituted on $\text{Al}(\text{OH})_3$, which is compared with the respective growth energetics when Na^+ is substituted on $\text{Si}(\text{OH})_4$ groups (Fig. 3.3). Despite there being some differences in the energetics of the individual steps along the growth path, the overall thermodynamics converge upon formation of the dimer when in both systems we consider the Na^+ atom to be positioned on the bridging oxygen, which results in the same dimer product regardless of which tetrahedral atom (Si, Al) the Na^+ is first associated with. Consistent with what was observed in the silicate system, the growth pathways of the aluminosilicate system are found to become more exothermic in the presence of NaOH. We observe that Na^+ behaves as an aggregation center for the small aluminosilicates, which promotes the growth of larger oligomer complexes.

As discussed above, a condensation reaction involving $\text{Al}(\text{OH})_3$ is followed by a H_2O dissociation step, forming a Brønsted acid site on the bridging oxygen. In aluminosilicate systems containing Na^+ counterions, we consider the Na^+ atom to take the place of the H^+ on the acid site (similar to ion exchange). In this case, the $\text{Al}(\text{OH})_2\text{ONa}$ molecule reacts with a $\text{Si}(\text{OH})_4$ monomer, forming an Al-O-Si bond with Na^+ positioned on the bridging oxygen atom (similar to positions assumed by extra-framework cations in zeolites). In the same step a hydroxide group coordinates with the aluminum atom producing the dimer complex $\text{AlSiNaO}_7\text{H}_6$, where the aluminum atom is tetrahedrally coordinated and Na^+ is stabilized on a bridging oxygen of the dimer, resulting in a highly exothermic (-292.1 kJ/mol) oligomerization step. As we have only added one NaOH molecule to our system, the Na^+ atom is associated with the position that was the Brønsted acid site in the pure aluminosilicate system. In the case that we form the tetramer with a Si/Al ratio of 1 (i.e. presence of 2 Al atoms), the additional negative charge of the oligomer is counterbalanced by H^+ occupying the oxygen bridging the silicon and aluminum atoms. This produces an aluminosilicate tetramer that contains both a typical Brønsted acid site and a Na^+ cation that is associated with a bridging oxygen. Interestingly, we see that in this case the H_2O dissociation step becomes slightly exothermic (-12.4 kJ/mol), whereas H_2O dissociation steps in all other systems are endothermic. This could be due to enhanced interactions of the Na^+ cation with oxygens on the silicon atom involved in the new Si-O-Al bond being formed via tetramerization.

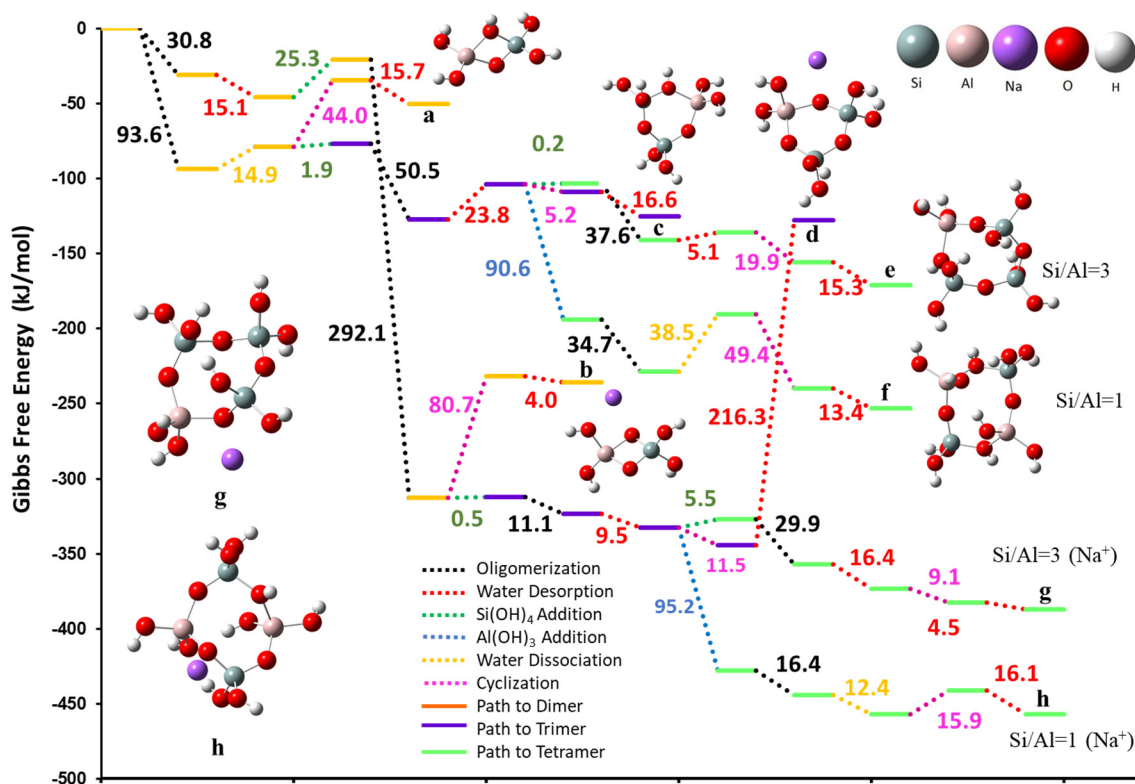


Fig. 3.4. Free energy reaction profile for oligomerization of aluminosilicate system in the absence and presence of NaOH. The initial reactants for the systems are Si(OH)₄ + Al(OH)₃ (-93.6 kJ/mol) and Al(OH)₃ + Na(OH) (30.8 kJ/mol), respectively. The number listed by each step represents the absolute value of the change in Gibbs free energy between the two corresponding states. Each number is color-coded to indicate the process that is occurring in that specific step and is consistent with the coloring of the dashed lines, details of which are given in Fig. 3.1. The solid lines are color-coded to highlight the paths forming oligomers of different size as in Fig. 3.1. The profile shows the energetics for the formation of both the linear and cyclic structures for each species through the tetramer. Terminal structures are shown for each pathway.

Reaction Extent Analysis

Quantification of species in solution has been a well-investigated topic in the materials growth field for many years. Many approaches, both experimental and computational, such as NMR^{141, 142}, Kinetic Monte Carlo¹⁴³, Mass Spectrometry^{144, 145}, etc. have been employed to quantify the species present in a growth environment. Pelster et. al. investigated the species present during synthesis of various pure-silicate zeolites using Mass Spectrometry¹⁴⁵. The most prevalent species found in the synthesis media was a 32-unit oligomer, however, they also detected the presence of smaller 6- and 8-unit species at lower concentrations. Kirschhock et. al. performed a study using NMR and infrared spectroscopy to identify the polycondensation products formed during growth of the MFI zeolite, where the most predominant species was a 33 Si atom complex¹⁴². Several smaller species were also observed at various times throughout the synthesis such as the three-ring, bicyclic pentamer, and double five-ring complexes (five-ring containing species are common in the MFI topology). Experimentally determining the species present at these very initial stages of growth remains challenging due to the small size of the pre-nucleation species, fast time-scales of nucleation, and complex growth environment. It is also worth noting that both aforementioned studies have different

synthesis conditions (temperature, time-scale, reactant materials, etc.), which can have significant impact on the species found during growth.

Here, in an effort to determine if early growth will be limited by the endothermic steps on the reaction pathways and find the relative concentrations of each species along the reaction pathway, a reaction extent analysis was performed. Each pathway was evaluated individually in order to determine which species were most prevalent for each system under thermodynamic equilibrium at 373K. For the three silicate systems shown in Fig. 3.5A, each calculation was performed with an initial Si concentration of 4 mol, and 1 mol for the cation reactant species, NaOH or $\text{Ca}(\text{OH})_2$. The four aluminosilicate pathways, displayed in Fig. 3.5B, had initial concentrations (Si:Al:Na) of 3:1:0, 2:2:0, 3:1:1, and 2:2:1 for aluminosilicate Si/Al=3, aluminosilicate Si/Al=1, aluminosilicate with Na^+ and Si/Al=3, and aluminosilicate with Na^+ and Si/Al=1, respectively. The percentages reported in Fig. 3.5 correspond to the Si-content converted to products with respect to the initial Si of the system.

The silicate system in the absence of cations (red pathway in Fig. 3.5A) was found to proceed until 97% of initial Si was converted to the cyclic tetramer complex (Fig. 3.5A, state c). Upon the addition of NaOH (purple pathway in Fig. 3.5A), 91% of initial Si was converted to the linear tetramer complex (Fig. 3.5A, state e), with only 1% of initial Si progressing to the cyclic tetramer (Fig. 3.5A, state f). This indicates that the endothermic tetramer cyclization step (25.9 kJ/mol) limits growth past the linear tetramer in the presence of NaOH. The silicate with $\text{Ca}(\text{OH})_2$ produced two complexes, 22% for the cyclic tetramer— H_2O (hydrated complex) and 78% of the cyclic (dehydrated) tetramer (hydrated and dehydrated states shown in Fig. 3.5A as states g and h, respectively).

As shown in Fig. 3.5B, the aluminosilicate system and aluminosilicate system with Na^+ , for pathways with Si/Al=3 (red and purple paths, respectively), the cyclic tetramer species (Fig. 3.5B, states b and g, respectively) were most prevalent with 98% total Si content in each case. For the Si/Al=1 pathway involving pure aluminosilicate, the cyclic tetramer (Fig. 3.5B, state e) and linear tetramer— H_2O (Fig. 3.5B, state c) complexes were found at concentrations of 42% Si and 57% Si, respectively. Similarly, the Si/Al=1 pathway for the aluminosilicate system with Na^+ is also split with the cyclic tetramer (Fig. 3.5B, state j) and linear tetramer (Fig. 3.5B, state i) complexes, with Si concentrations of 50% and 49%, respectively.

The key difference between the two Si/Al=1 pathways is that in the pure aluminosilicate system, the H_2O molecule produced during tetramerization is still associated with the linear tetramer, whereas in the system of aluminosilicate with Na^+ , the prevalent species is the linear tetramer with water dissociated. This can be attributed to the respective H_2O dissociation steps being exothermic (-12.4 kJ/mol) in the Na^+ containing system and endothermic (38.5 kJ/mol) in the pure aluminosilicate system. In the case of the Na^+ containing aluminosilicate system with Si/Al=1, the tetramer cyclization step is endothermic (15.9 kJ/mol), resulting in an almost even split between the linear and cyclic tetramer products as explained by the almost isoenergetic nature of these states (5B, states i and j).

Overall, the reaction extent analysis reveals that the growth pathways will progress to formation of the tetramer species. Interestingly, it suggests that the presence of Na^+ results in a higher percentage of total Si remaining in the linear tetramer configuration rather than forming the cyclic tetramer species, as in every other growth pathway. This is evidenced by the silicate system with Na^+ (purple path in Fig. 3.5A) and the aluminosilicate system with Na^+ and Si/Al=1.

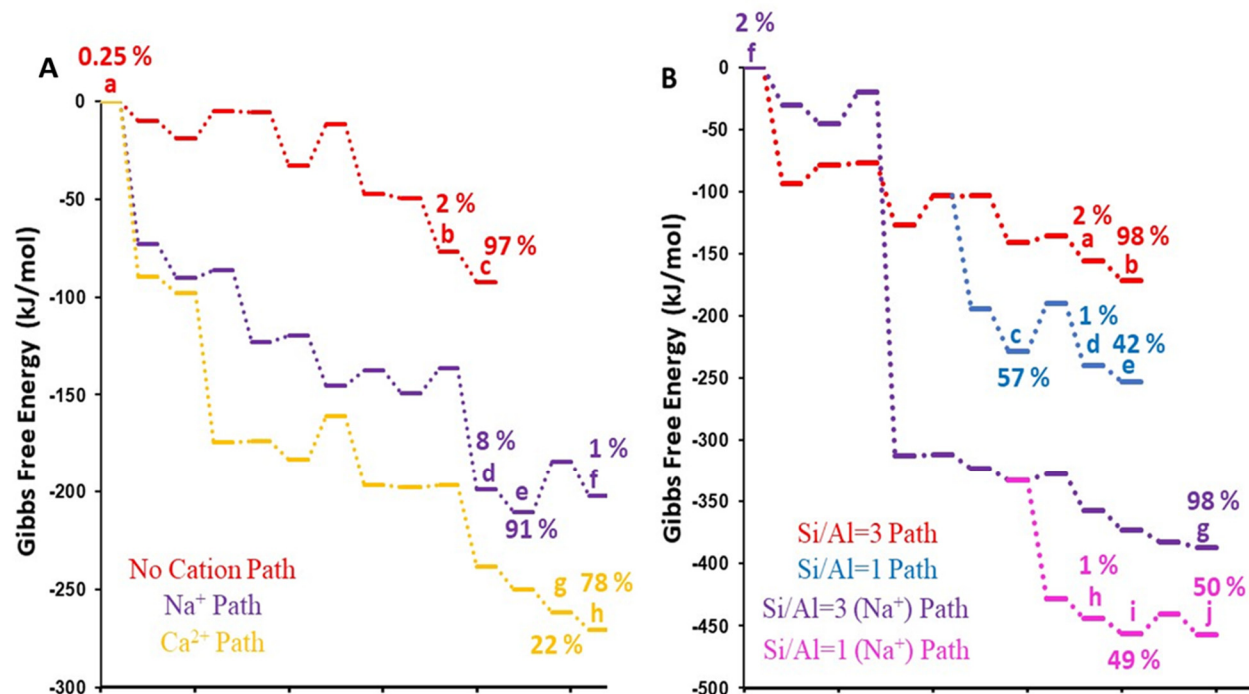


Fig. 3.5. Free energy reaction profiles for oligomerization of A) silicate system in the absence of cations (red) and in the presence of NaOH (purple) and Ca(OH)₂ (yellow), and of B) aluminosilicate system in the absence of cations with Si/Al=3 (red) and Si/Al=1 (blue) and in the presence of NaOH with Si/Al=3 (purple) and Si/Al=1 (pink). States labeled (a, b, etc.) along the pathways indicate the complexes that are found to be in highest concentration within each individual path based on reaction extent calculations. Percentages shown for each labeled state correspond to the mol % of Si in each respective complex and are color-coded to indicate the path to which they belong. The species in panel A are as follows: a - Si(OH)₄, b - cyclic tetramer + H₂O, c - cyclic tetramer, d - linear tetramer with Na⁺ + H₂O, e - linear tetramer with Na⁺, f - cyclic tetramer with Na⁺, g - cyclic tetramer with Ca²⁺ + H₂O, and h - cyclic tetramer with Ca²⁺. The species in panel B are as follows: a - cyclic tetramer (Si/Al=3) + H₂O, b - cyclic tetramer (Si/Al=3), c - linear tetramer (Si/Al=1) + H₂O, d - cyclic tetramer (Si/Al=1) + H₂O, e - cyclic tetramer (Si/Al=1), f - Si(OH)₄, g - cyclic tetramer with Na⁺ (Si/Al=3), h - linear tetramer with Na⁺ (Si/Al=1) + H₂O, i - linear tetramer with Na⁺ (Si/Al=1), and j - cyclic tetramer with Na⁺ (Si/Al=1). The growth pathways progress to convert most Si content to the tetramer species, either linear or cyclic, with the linear complexes often appearing in the media containing Na⁺.

Conclusions

In summary, we have investigated the thermodynamics of oligomerization reactions in zeolite growth for systems with varied compositions. Overall, the oligomerization of the silicate system was found to be slightly exothermic, whereas the aluminosilicate system was found to be significantly more exothermic, with the presence of aluminum increasing the exothermicity of oligomerization. We found that in aluminosilicate complexes, H₂O dissociation on the complex is energetically preferred over H₂O desorption, which may result in the formation of Brønsted acid sites on bridging oxygens (Si-O-Al). This suggests that Brønsted acid sites, responsible for zeolite acidity, may be first introduced during the early stages of growth as an intermediate species which then could participate in ion exchange (in the presence of cations). The thermodynamics of silicate complexes growth were also evaluated in the presence of Na⁺ and Ca²⁺. Both cations increase the exothermicity of silicate oligomerization, with Ca²⁺ exhibiting the most

exothermic path, which is particularly interesting as Ca^{2+} is often found in naturally occurring zeolites. Furthermore, introducing Ca^{2+} into the silicate system provided an alternative growth pathway due to the divalent nature of calcium, acting as a bridge between two Si atoms by the formation of OCaO bonds. Moreover, to elucidate the cation effect in aluminosilicate growth, we considered the presence of Na^+ , which increased the exothermicity of the reaction pathways similarly to case of silicates. Cyclic structure formation was evaluated for each (alumino)silicate complex (dimer, trimer, etc.). Apart from the dimer species, cyclization was found to be favorable for all silicate and aluminosilicate complexes both in the presence and absence of cations. Reaction extent analysis suggests that all growth pathways will progress to convert most Si introduced as a reactant to the tetramer species, either linear or cyclic, with the linear complexes appearing in the media containing Na^+ . Overall, our computational work reveals the oligomerization thermodynamics during early stages of zeolite growth and the impact of cations on altering the speciation of preferred complexes. This work unravels the complexity of reaction steps taking place during early nucleation stages of zeolite growth, which can further aid the control of materials synthesis. With the early stages of zeolite growth being practically infeasible to track with experiments, this computational work demonstrates the detailed thermodynamics of oligomerization and how speciation changes in the presence of cations. Looking ahead, computational efforts should focus on larger oligomers and their overall impact on zeolite structure. For instance, although at the conditions of interest we revealed a polymeric behavior of oligomerization, it is unclear if oligomers growth stops at larger complexes (of specific size) or continues this polymeric behavior. Oligomers stabilized at specific sizes can in turn act as building blocks in zeolite growth. Theory and experiments should be tightly coupled together to understand if highly stable oligomers formed at the early growth stages act as building units for zeolites or as spectator species.

Section 4: Understanding Formation Thermodynamics of Molecular Zeolitic Species with First Principles Calculations

The mechanisms of many zeolitic processes, including nucleation and interzeolite transformation are not fully understood owing to complex growth mixtures that obfuscate in situ monitoring of molecular events. In this work, we provide insights into zeolite chemistry by investigating the formation thermodynamics of small zeolitic species using first principles calculations. We systematically study how formation energies of pure-silicate and aluminosilicate species differ by structure type and size, temperature, and the presence of alkali or alkaline earth metal cations (Na^+ , K^+ , and Ca^{2+}). Highly condensed (cage-like) species are found to be strongly preferred to simple rings in the pure-silicate system, and this thermodynamic preference increases with temperature. Introducing aluminum leads to more favorable formation thermodynamics for all species. Moreover, with a low Si/Al ratio (≤ 2), a thermodynamic preference no longer exists among structure types and a pool of diverse aluminosilicate structures compete in formation. Metal cation effects strongly depend on the presence of aluminum, cage size, cation type, and location since each of these factors can alter electrostatic interactions between cation and zeolitic species. We reveal that confined metal cations may destabilize pure-silicate cages due to localized interactions; conversely, they stabilize aluminosilicates due to strong cation-framework attractions in sufficiently large cages. Importantly, this work rationalizes a series of experimental observations and can potentially guide efforts for controlling zeolite nucleation/crystallization processes.

Introduction

Elucidating mechanisms of nucleation and growth of zeolites, including interzeolite transformations, remain one of the most difficult challenges for controlling zeolite synthesis outcomes. An early concept introduced by Barrer and coworkers postulated that zeolite crystals could directly result from the sequential addition of prefabricated building units, which was based on the observation that the crystals are composed of small repeating units¹⁴⁶. Through technological advances in spectroscopy (Raman, Infrared, and NMR) over several decades, it became possible to identify silicate speciation in solution¹⁴⁷⁻¹⁵¹. Notably, some research groups observed strong structural similarities between the soluble species and final crystals, which directly supported the idea of the “assembly of precursors”¹⁵²⁻¹⁵⁶. However, both the mechanism and the supporting evidence have been disputed in literature^{116, 157-159}. For instance, Houssin et al.¹⁵⁶ proposed new molecular precursors (pentacyclic dodecamer) for MFI-type zeolites based on ^{29}Si NMR spectra, but Knight et al.¹¹⁶ pointed out that the peaks ascribed to such precursors arise from smaller soluble species, and therefore the existence of the precursors was not fully supported. In fact, none of the ~ 40 unique silicate structures that have been confirmed are composed of more than 9 silicon atoms, and no “molecular precursor” exists exclusively for a targeted topology^{116, 157, 159, 160}. This shows that there is no clear correlation between the soluble species and resulting zeolite crystals, which appears to contradict the assembly mechanism. Instead, potential alternative mechanisms for zeolite crystallization have been suggested including: (1) the release of small soluble species from an amorphous gel into the solution phase and their nucleation to grow crystals^{161, 162}, and (2) the reorganization of amorphous structures towards crystals via breakage and recombination of siloxane bonds under hydrothermal conditions¹⁶³⁻¹⁶⁵. The crystallization of zeolites involves kinetic processes that are highly affected by many factors (e.g., temperature, cation, elemental composition, and source selection for silicon and aluminum). Therefore, revealing zeolite formation mechanisms requires integrated observations and knowledge in a wide range of zeolitic structures in multiple phases, from aqueous oligomers to solid particles.

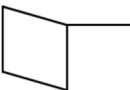
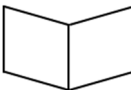
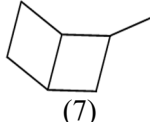
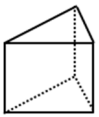
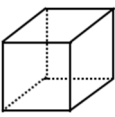
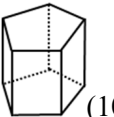
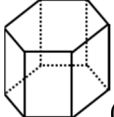
Examining amorphous/crystalline solid particles that appear during a crystallization process is no longer technically limited owing to the advances in microscopy and crystallography^{166, 167}. In contrast, small solution species are difficult to study experimentally. Although there have been extensive efforts to identify (alumino)silicate species in solution using spectroscopies^{148-151, 168-171}, our understanding of the molecular

events during zeolite nucleation processes is limited due to the hurdles of in situ monitoring. Thus, theoretical studies have been carried out using quantum mechanical methods^{54, 127, 172, 173} and kinetic simulations^{123, 174, 175}. Especially, the initial stage of nucleation, i.e., oligomerization of silicate monomers ($\text{Si}(\text{OH})_4$) and cyclization of linear oligomers, has been of particular interest. Most of the studies^{54, 123, 127, 173-175} have focused on the formation of up to tetrameric species (consisting of 4 tetrahedral (T) atoms), since they are abundant in solution and do not require high computational cost to simulate. However, mid-sized species (i.e., larger than 4 T-units but smaller than experimentally accessible solid particles) have not attracted much attention, albeit they are also essential for understanding zeolite chemistry. Therefore, theoretical investigation of species falling into the mesoscale range is necessary to fill the gap in our understanding of how zeolite precursors evolve.

Furthermore, the building units that appear in topologies but not in solution (many composite building units (CBUs) and secondary building units (SBUs); for example, double-6-membered ring (*d6r*) or hexagonal prism) contain information of a particular framework since its geometry and topology result from thermodynamics and kinetics of nucleation/growth processes. For instance, Blatov and coworkers proposed a packing model of zeolite building units, which explained why only a limited number of zeolites have been experimentally realized out of millions of hypothetical zeolites¹⁷⁶ and predicted the existence of zeolites that have not been synthesized yet¹⁷⁷. Moreover, zeolite building units are putatively of great importance in interzeolite transformation. There are many parent-daughter transformation pairs that share a CBU (e.g., *d6r* in LEV-to-CHA conversion¹⁷⁸ and *mor* for BEA-to-MFI¹⁷⁹). It was found that there is a remarkable similarity in graph representation of the parent and daughter crystals transformation pairs that do have a common CBU¹⁸⁰, which indicates that geometry may play a significant role in transformation processes.

Understanding the role of cations during zeolite crystallization and interzeolite transformation processes is also of high importance. Zeolites are always produced in the presence of cations, which can significantly affect crystallization chemistry¹⁸¹ and physicochemical properties of the products¹⁸². The roles of extra-framework cations include counterbalancing negative framework charges that result from the presence of trivalent atoms in tetrahedrally coordinated environments (e.g., Al^{3+} and Fe^{3+})¹⁶⁴, and directing the formation of target topologies¹⁸³. While alkali metal cations (Na^+ , K^+ , Cs^+ , etc.) are the most common in naturally occurring or synthetic zeolites, highly siliceous zeolite crystals ($\text{Si}/\text{Al} > 10$) typically require cationic organic structure-directing agents (OSDAs)¹⁸³⁻¹⁸⁶. Since siliceous zeolites have low framework charge and intrinsic hydrophobicity, bulky organic cations can direct these frameworks effectively by simultaneously filling pores and compensating for negative framework charges¹⁸⁷⁻¹⁹⁰. Despite their effectiveness, OSDAs suffer from high synthesis costs and significant pollution during their removal¹⁹¹, which has spurred extensive efforts towards OSDA-free synthesis, often by introducing seed crystals to direct desired products^{187, 190, 192-195}. Although the mechanism of the process has not been fully understood, it has been suggested that the transformation is mediated by zeolitic species in a solution phase. Kamimura and coworkers claimed that the dissolved fragments of zeolite beta (*BEA) seeds in alkaline solution induce zeolite MTW crystallization¹⁹⁵. Similarly, Zhang et al. showed small building units originating from zeolite CDO seed crystals enable OSDA-free synthesis of FER-type zeolites¹⁹², where the interactions between the fragments and alkali metal cations play a key role¹⁹⁶. Furthermore, Tendeloo et al. reported that FAU crystals could evolve to four different topologies (ABW, CHA, MER, and ANA) depending on which alkali species is present (Li^+ , K^+ , Rb^+ , and Cs^+ , respectively)¹⁴. These findings demonstrate that a better understanding of the interactions between zeolitic species and inorganic cations is crucial for effectively controlled zeolite syntheses.

Table 4.1. Names and graphics of the selected structures of three different families of zeolite subunits (monocycles, multicycles, and cages).

Monocycles	Name	3MR	4MR	5MR	6MR
	Structure	 (3)	 (4)	 (5)	 (6)
	Conventional name	cyclic trimer	cyclic tetramer	cyclic pentamer	cyclic hexamer
	SBU name	3	4	.	6
	CBU name	.	.	.	.
Multi-cycles	Name	Mono-ring	Branched mono-ring	Di-ring	Branched di-ring
	Structure	 (4)	 (5)	 (6)	 (7)
	Conventional name	cyclic tetramer	substituted cyclic tetramer	bicyclic hexamer	.
	SBU name	4	4-1	4-2	.
	CBU name	.	.	.	.
Cages	Name	Trigonal prism	Tetragonal prism	Pentagonal prism	Hexagonal prism
	Structure	 (6)	 (8)	 (10)	 (12)
	Conventional name	prismatic hexamer	cubic octamer	.	.
	SBU name	.	4-4	.	6-6
	CBU name	d3r	d4r	d5r	d6r

“MR” in monocycles stands for “membered ring”. In graphical representations, each vertex and edge represents a T (tetrahedral, Si or Al) atom and oxygen bridge, respectively, with terminal non-bridging oxygen (as hydroxyls or water) being omitted. Numbers in parenthesis alongside graphics stand for the number of T atoms in the structures. Conventional names of structures and SBU and CBU classifications¹⁹⁸ are given for reference (dots represent non-existing name convention).

Herein, we use first principles calculations to understand the formation thermodynamics of structurally diverse zeolitic oligomers that are relevant to a wide range of zeolite synthesis and transformation processes. First, we explore how the formation energy of zeolitic species depends on the structure type (from simple rings to cages), structure size, temperature, and the presence of framework aluminum. Next, we investigate the effects of select alkali and alkaline earth metal cations on the formation thermodynamics of cage structures. The formation energy profiles provided herein reveal a thermodynamic preference for growth of (alumino)silicates under hydrothermal conditions. Also, our calculations rationalize the wider window of experimentally accessible Al-rich zeolite crystals compared to that of highly siliceous crystals¹⁹⁷. Moreover, we unravel effects from inorganic cations in the formation thermodynamics of pure-silicate/aluminosilicate cages, shedding light on the roles and limitations of cations for directing target zeolite frameworks. Taken together, our results rationalize the presence of zeolitic species and frameworks under specific experimental conditions and compositions, which can guide experimental efforts to efficiently synthesize a wide range of zeolite crystals.

Zeolitic Systems. Among various subunits of zeolite structures (e.g., soluble units, SBUs, and CBUs), we selected three families of species to study: monocycles, multicycles, and cages. Table 4.1 shows the four smallest structures in each family with graphical representations and names. Monocycles are cyclic structures composed of 3 or more T atoms, investigated up to dodecamer (12 T units). Each structure is named n MR for convenience (n = number of T units, i.e., $x + y$ in equation 1, and MR stands for “membered ring”). Another type of structure is a multicycle, which is linked 4MR, resembling the most frequently found “chains” in zeolite topologies (dzc, dcc, or dsc)¹⁹⁸. Multicycles are named mono-ring, di-ring, etc., depending on the number of 4MR found in each structure. Note that the smallest multicycle, mono-ring, is identical to a 4MR species. The largest multicyclic structure (penta-ring) is composed of 12 T units. The *branched* multicyclic structures are also considered as intermediates connecting two complete multicycles. Finally, cages are prismatic structures, which are characterized by base size, i.e., trigonal prism, tetragonal prism, and so on. The largest cage investigated is an octagonal prism (16 T units).

Results and Discussion

Structure and temperature effects

Pure-silicate system. For pure-silicate species, we first study the dependence of formation energy on structure type and temperature in a cation-free environment. Fig. 4.1 shows the formation electronic energies and Gibbs free energies of three different types of structures up to the 12 T-unit size. In terms of electronic energy (Fig. 4.1(a)), monocycles compete with multicycles up to T=8 (i.e., 8MR and tri-ring) whereupon monocycles become more favorable, while cages of all sizes show far less negative formation energy. Also, size effects are significant in monocycles, i.e., they prefer to form larger rings, whereas all multicycles and cages larger than trigonal prism do not show a significant size dependence. Conversely, trends change drastically in the formation Gibbs free energies when one accounts for temperature and entropic effects. At 50 °C (Fig. 4.1(b)), cage formation becomes the most exergonic for all sizes except the smallest (trigonal prism), with progressively lower thermodynamic stability for multicycles and monocycles. In addition, multicycles show a clear size dependence favoring larger species, whereas the ΔG_f of monocycles does not have a strong dependence on size. Increasing system temperature (50 °C $\rightarrow$ 150 °C) amplifies these differences such that the ΔG_f of monocycles become size-independent, whereas the cage formation becomes increasingly exergonic at 150 °C. Hence, under typical zeolite synthesis (hydrothermal) conditions, silicate species prefer to exist in a more condensed form, which aligns well with experimental observations of a relatively high concentration of condensed silicates in solution^{157, 199}. It is worth noting that there is no thermodynamic driving force for silicate cages to grow larger than a tetragonal prism as seen by the nearly identical formation Gibbs free energies from tetragonal to hexagonal prisms. This may explain the abundance of tetragonal prisms in silicate solutions under some experimental setups^{169, 199} and final topologies¹⁹⁸.

The changes in trends between ΔE_f and ΔG_f are attributed to entropic contributions since more condensed structures release more water molecules upon their formation. According to eqn.1-4, at the same number of T units ($= x + y$), the coefficient associated with water is always larger in cages, followed by multicycles and monocycles. This results in significantly positive formation entropy for cages, which negatively contributes (i.e., more exergonic) to the ΔG_f . In contrast, the formation entropy is negative (i.e., endergonic contribution to ΔG_f) in monocycles (except 3MR and 4MR), and insignificant in multicycles. The temperature effects described here, which make the more condensed structures be thermodynamically favored, may explain why zeolite crystallization typically requires thermal treatment. We note that it was experimentally observed that the equilibrium among soluble silicate species shifts ~~is shifted~~ towards lower molecular weights at higher temperature^{151, 200}, which seems to contradict our findings. In fact, our results suggest that condensed species would be thermodynamically more stable than less condensed species at a higher temperature, regardless of how species populate in solution on observable time scales. In other words, polymerization kinetics, interactions between the species and structure-directing agents (SDAs), and pH effects should all be considered to explain experimental findings in aqueous silica solutions. This highlights the complexity of silicate solution chemistry, where formation thermodynamics may not dominate species growth and many factors contribute simultaneously. Nevertheless, our results clearly demonstrate that temperature significantly alters formation thermodynamics of zeolitic oligomers (due to entropic contributions), which in turn may lead to changes in precursor size, nucleation/growth rates, and reaction kinetics.

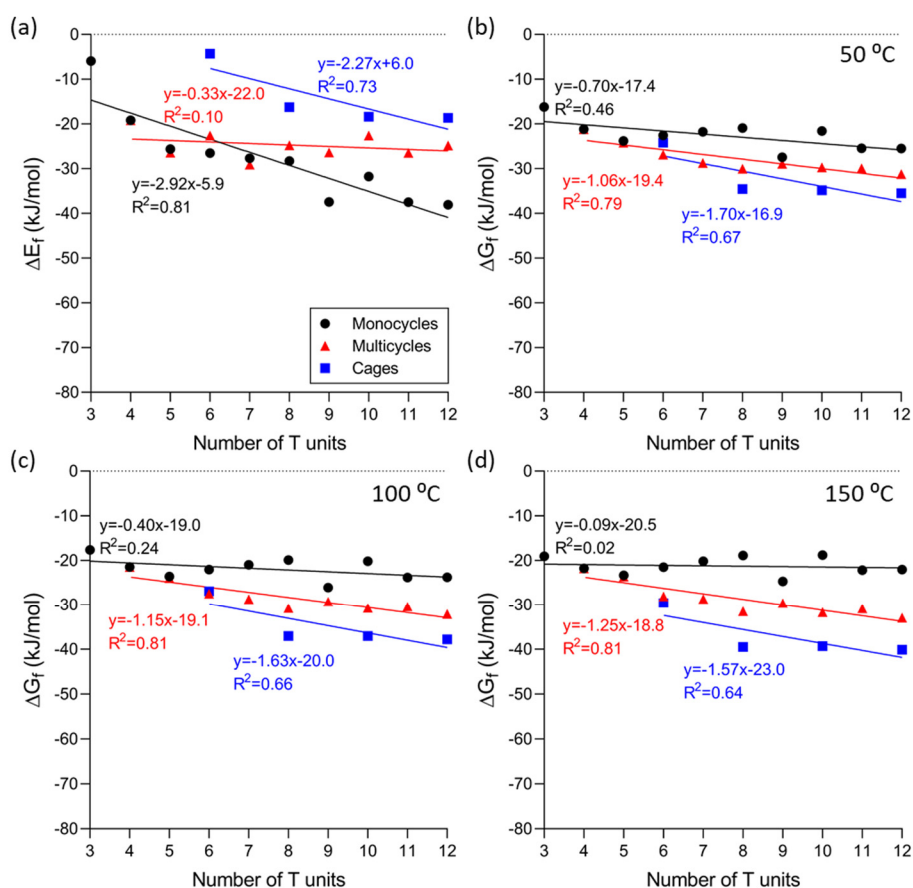


Fig. 4.1. (a) Normalized formation electronic energies (ΔE_f) of pure-silicate structures, and their normalized formation Gibbs free energies (ΔG_f) determined at (b) 50 °C, (c) 100 °C, and (d) 150 °C. Fitted lines (determined by least square regression) serve as a guide to the eye for formation energy trends as a function of the structure size.

Aluminosilicate system. Here, we repeat the same calculations as above (formation electronic/Gibbs free energies of 3 families of species) for aluminosilicate structures, where the maximum possible number of aluminum atoms are included in the framework ($\text{Si}/\text{Al} \approx 1$), obeying Löwenstein's rule²⁰¹ (i.e., there are no Al-O-Al bridges). Monocycles and multicycles composed of an even number of T units have a Si/Al ratio of unity, while the other mono/multicycles have $\text{Si}/\text{Al} > 1$. For instance, a 3MR species has two Si and one Al ($\text{Si}/\text{Al} = 2$), and a 5MR has 3 Si and 2 Al ($\text{Si}/\text{Al} = 1.5$). Likewise, cages with an even-numbered base (tetragonal, hexagonal, and octagonal prisms) have $\text{Si}/\text{Al} = 1$, while others have $\text{Si}/\text{Al} > 1$. Using the lowest possible Si/Al ratio facilitates the identification of aluminum effects across different types of structures. It should be noted that aluminosilicate multicycle and cage structures are not major species in solution. While Al-containing soluble species have been detected using NMR techniques, which include 3MR, 4MR, trigonal prism, and tetragonal prism, none of them contains more than two aluminum atoms^{170, 171, 202-205}. Furthermore, those species are not abundant nor active enough to significantly contribute to zeolite crystal formation; rather, unstable and reactive small species (2-4 T units) are likely to take part in zeolite growth^{170, 205}. Therefore, while the results shown below are not directly applicable to aluminosilicate solution chemistry, they are meaningful within the context of the thermodynamic stability of independent species and possibly crystals.

The inclusion of aluminum significantly alters formation energies compared to pure-silica structures, as shown in Fig. 4.2. Aluminum enhances formation thermodynamics regardless of structure type and size and increases the size-dependency (more negative slopes). The formation electronic energy exhibits a similar trend as for silicates (more negative in the order of monocycles > multicycles > cages), but the energy difference between different families becomes more significant in aluminosilicates. Hence, accounting for entropic contributions results in eliminating the thermodynamic preference among different structure types in terms of Gibbs free energy at 50 °C, instead of inverting the order as observed in pure silicates. The increase in temperature plays the same role as that observed in the pure-silicate system, i.e., monocycles and cages become less and more exergonic, respectively, with only minimal effects being observed in multicycles. However, the formation energy difference among the three families is minimal at any size, even at 150 °C. Therefore, the effects of aluminum on the formation energy of zeolitic species are two-fold: (1) enhancing exergonicity and size-dependency, and (2) eliminating dependence on the structure type.

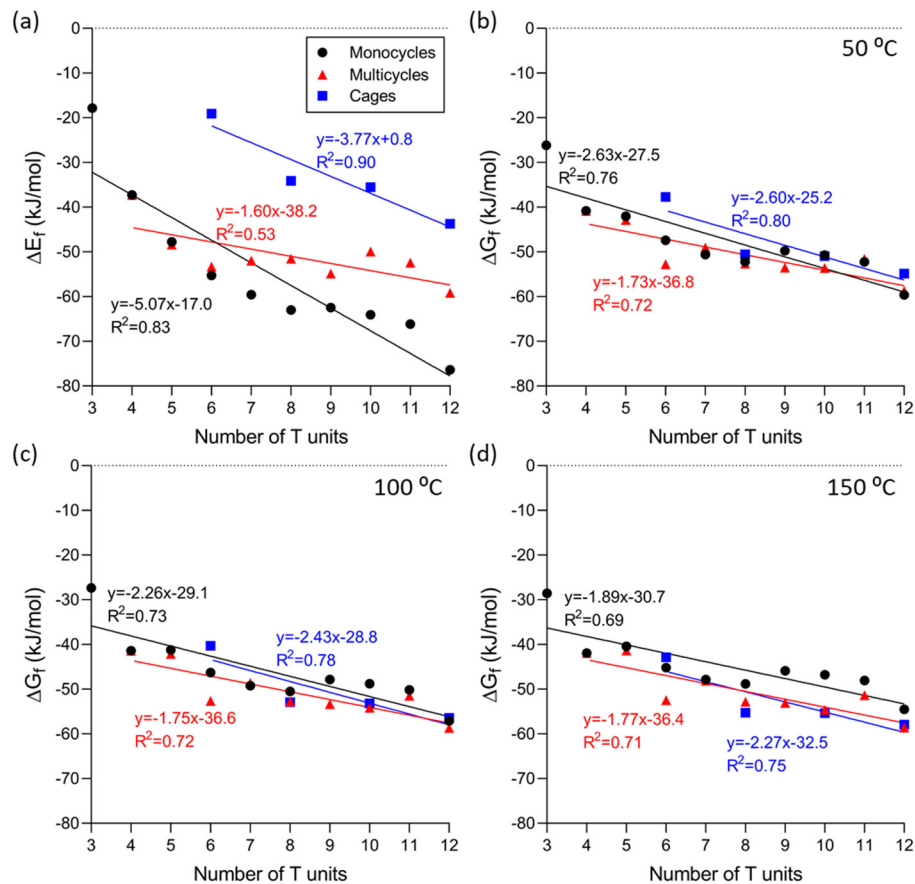


Fig. 4.2. (a) Normalized formation electronic formation energies (ΔE_f) of aluminosilicate structures (Si/Al $\approx$ 1), and their normalized formation Gibbs free energies (ΔG_f) determined at (b) 50 °C, (c) 100 °C, and (d) 150 °C.

The enhanced formation thermodynamics and size-dependence in the presence of aluminum may imply the thermodynamically favorable crystallization of aluminosilicates compared to the pure-silicates. Using DFT calculations, Freeman and coworkers⁵⁴ also reported the more favorable formation of aluminosilicate oligomers (number of T units $\leq$ 4) compared to silicates of the same size, where the most negative formation energy is achieved at the lowest possible Si/Al ratio ($=$ 1). Likewise, Muraoka et al. showed that higher aluminum content increases the thermodynamic stability of zeolite topologies that normally have a low Si/Al ratio¹⁰⁵. Herein, the effects of the Si/Al ratio are also demonstrated in the formation Gibbs free energies of the small aluminosilicate species. At all temperatures, the formation of 5MR (Si/Al = 1.5) is not favored over 4MR (Si/Al = 1) (Fig. 4.2), which is against the overall tendency that the larger species show more negative formation energies. Likewise, for multicycles, a branched mono-ring (Si/Al = 1.5) shows similar formation exergonicity with mono-ring (Si/Al = 1), and a branched di-ring (Si/Al = 1.33) is less exergonic than a di-ring (Si/Al = 1). Finally, a trigonal cage (Si/Al = 2) is less favorable than a di-ring (Si/Al = 1), which is against the other cages that showed similar ΔG_f with the multicycles of the same size. Although we have not systematically investigated the effect of Si/Al ratio on formation thermodynamics, the above examples reveal the general trend that lower Si/Al ratios allow for greater formation exergonicity. For species larger than those mentioned above, the effects of Si/Al ratio are not pronounced since it does not vary significantly. In fact, low-temperature (i.e., room temperature) crystallization has been successful only for low-silica zeolites, including zeolite A^{206, 207} (Si/Al = 1), zeolite X (Si/Al = 1.14-1.20)^{208, 209}, zeolite Y (Si/Al = 1.95-2.52)²¹⁰, and EMT zeolite (Si/Al = 1.14)²¹¹, whereas highly siliceous zeolites typically

require moderate to high temperature²¹²⁻²¹⁴. Therefore, we posit that aluminum has a crucial role in facilitating the crystallization of zeolites by introducing a thermodynamic driving force.

Table 4.2. Structural information of select highly siliceous zeolites.

Material (topology)	Si/Al ratio	Framework density* (T/1000 Å ³)
ZSM-5 (MFI)	$\geq 15^{215, 216}$	18.4
ZSM-11 (MEL)	$\geq 15^{214, 217}$	17.4
ZSM-12 (MTW)	$\geq 30^{218}$	18.2
ZSM-22 and Theta-1 (TON)	$\geq 25^{219, 220}$	18.1
ZSM-23 and SSZ-32 (MTT)	$\geq 20^{221, 222}$	18.2
ZSM-48 (*MRE)	$\geq 30^{223}$	19.7

*Data sourced from the International Zeolite Association¹⁹⁸.

The second effect (i.e., no strong preference towards condensed aluminosilicates) indicates that the presence of aluminum results in generating a diverse pool of thermodynamically stable aluminosilicate structures. Table 4.2 shows structure information of some highly siliceous zeolites that can be hydrothermally synthesized in an alkaline media³⁷ and do not contain heteroatomic framework elements (i.e., elements besides Si and Al). Their framework densities, listed in units of T/1000 Å³, are high (>17) relative to all reported zeolites (13-21)¹⁹⁷, whereas those of low-silica aluminosilicate zeolites have a wider range and can be as low as 13 (e.g., FAU and LTA). Our calculations combined with structural information presented in Table 4.2 collectively indicate that aluminum-based stabilization of a pool of different structures (besides cages) may enable the synthesis of more metastable and diverse topologies. Some frameworks contradict this argument; for instance, certain ITQ-family structures are purely siliceous zeolites with extra-large pores and relatively low framework density¹⁹⁸. However, experimental factors for their synthesis (HF media with bulky OSDAs^{224, 225} or pressure-induced phase transformations²²⁶) are far from conventional hydrothermal methods and not considered in our computation results. Overall, Fig. 4.2 reveals the general tendency that aluminosilicates allow for greater framework diversity because of the strong stabilization effects of aluminum on the formation of various types of species (i.e., monocycles, multicycles and cages). This is contrary to what is observed on the purely siliceous species, which show a strong thermodynamic preference towards highly condensed structures (i.e., cages) (Fig. 4.1).

Cages with alkali/alkaline earth metal cations

After we investigated the formation thermodynamics of pure-silicate and aluminosilicate cages, we systematically studied the effects of alkali and alkaline earth metal cations (i.e., Na⁺, K⁺, and Ca²⁺). These cations counterbalance the negatively charged cages, which emerge from either the highly alkaline synthesis environment or the presence of trivalent aluminum in tetrahedral framework positions. We focus on cages because they represent interactions between zeolite crystals and cations better than less condensed species (i.e., monocycles and multicycles). In addition, the formation of oligomers in the presence of cations has been investigated in detail with DFT calculations^{54, 127, 168}.

External cations. Since cages are 3-dimensional structures with internal volume, cations can be located either externally or internally. A cation can be placed in various external positions as depicted in Fig. 4.3. As mentioned in the Computational Details section, cations are introduced to the system assuming a dehydration reaction between a zeolitic cage and cation hydroxide, which results in a charge-neutral species. Essentially, alkali metal cations replace one proton on either hydroxyl (on Si in pure-silicates) or water (on Al in aluminosilicates) from different positions of the optimized cation-free cages. Likewise, two protons are removed to add a calcium cation. The vertex position represents that a cation is introduced taking the original position of the removed proton, resulting in a single terminal cation-oxygen pair. If a cation replaces a proton but interacts with another nearby terminal or framework oxygen simultaneously, the cation resides at an edge position. A surface position represents that a cation is not in the proximity of the terminal oxygen or hydroxyl (from which a proton is removed) but strongly interacts only with the framework oxygens.

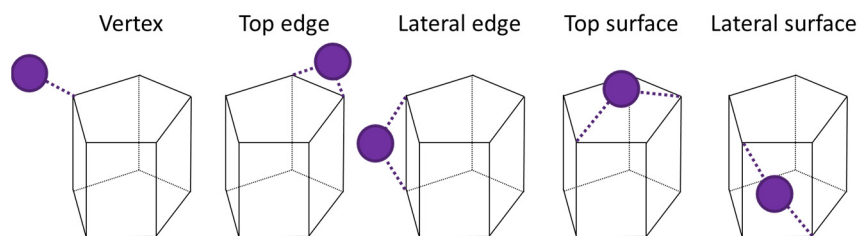


Fig. 4.3. Possible external positions of cation associated with (alumino)silicate cages. Each vertex and edge in black represent a T atom and oxygen bridge, respectively, with terminal non-bridging oxygen (as hydroxyls or water) omitted. The purple sphere indicates a single cation. Note that there is no distinction between the top and side edges nor between the top and side surfaces in the tetragonal prism.

Fig. 4.4 shows the relative Gibbs free energies of formation ($\Delta\Delta G_f$) of cages with an external cation, which are calculated by equation (1):

$$\Delta\Delta G_f = \Delta G_f - \Delta G_f^{\text{ref}} \quad (1)$$

where ΔG_f is the formation Gibbs free energy determined by equation (4) in the presence of cation ($i = 1$), and ΔG_f^{ref} is that of the corresponding cation-free structure ($i = 0$). Overall, external cations enhance exergonicity of cage formation regardless of cage size and cation type, which indicates that interactions between (alumino)silicate species and cations can facilitate zeolite formation. Thermodynamic stabilization by cations is the primary reason why zeolite nucleation/growth always occurs in the presence of cations¹⁶⁴. Also, it is consistently observed that cation effects are more significant in smaller cages. Considering that the calculated formation energies are normalized by the number of T units in cages, the decrease in exergonicity of $\Delta\Delta G_f$ with size indicates that cation effects *per T unit* decrease with size, rather than interactions between cation and cages diminish with cage size.

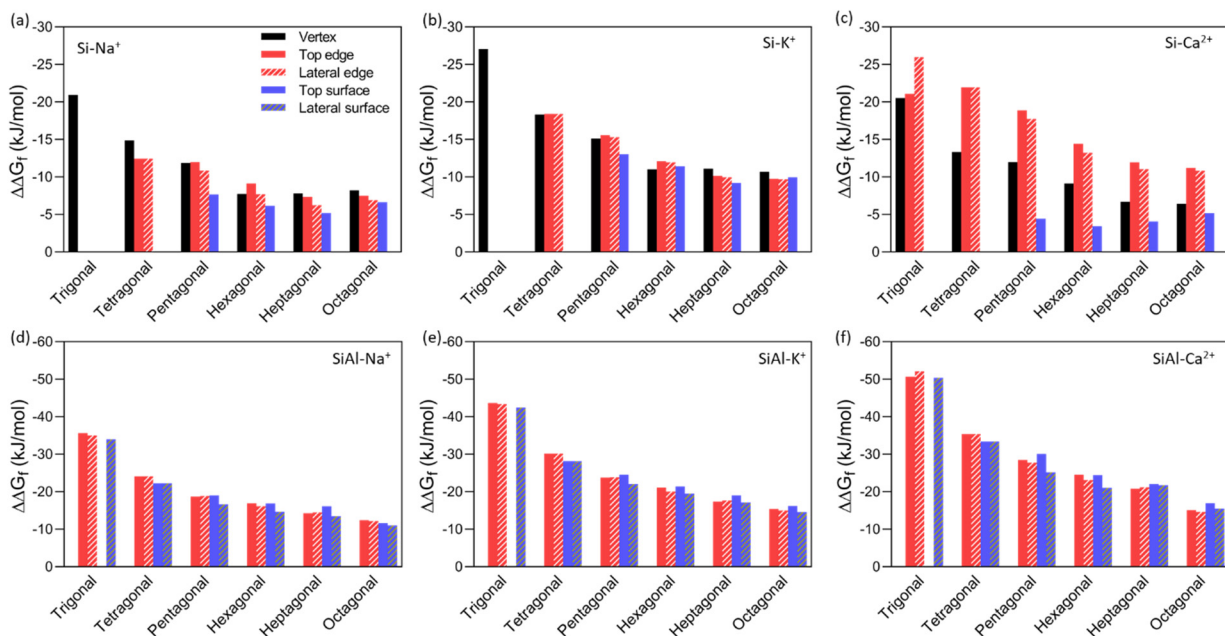


Fig4. 4. Relative formation Gibbs free energies ($\Delta\Delta G_f$) of silicate (a-c) and aluminosilicate ($\text{Si}/\text{Al} \approx 1$, d-f) cages with an alkali or alkaline metal cation (Na^+ , K^+ , or Ca^{2+}) located at an external position (vertex, top edge, lateral edge, top surface, or lateral surface). The Gibbs free energies are determined at 100 °C. Missing data points indicate that the cation at the corresponding position moves to another position during optimization.

For pure-silicate cages with alkali metal cations (Fig. 4.4(a) and (b)), the vertex position is equally or more favorable compared with top/lateral edge positions. On the other hand, the divalent cation (Ca^{2+}) has a strong thermodynamic preference for edge positions rather than vertex positions (Fig. 4.4(c)), which is attributed to the cation valence. The interactions between the monovalent cation and cage are maximized with the presence of one cation-oxygen pair, and additional interactions do not significantly contribute to formation thermodynamics. In contrast, calcium can strongly interact with two negatively charged terminal oxygen atoms simultaneously, i.e., edge positions. Compared to edge/vertex positions, cations located on the surface have less impact on the formation thermodynamics of pure-silicate cages. Surfaces that are smaller than 5MR (i.e., the top surface of the trigonal and tetragonal cages, and the lateral surfaces of cages of any size) are unable to hold a cation (the cation initially located at those locations moved to nearby vertex or edge during optimization). Furthermore, larger rings (top surfaces of pentagonal and larger cages) show less negative $\Delta\Delta G_f$ compared to vertex/edge positions. Fig. 4.5(a) shows the charge distribution on the surface of single negatively charged silicate tetragonal prisms calculated with Natural Bond Orbital (NBO) analysis²²⁷ as implemented in Gaussian 09, at the same level of theory (M062X/6-311g(d,p)). The terminal oxygen is the most negatively charged (-1.36) because of proton removal, which is therefore capable of strong interactions with a cation. Although framework oxygen atoms are also negatively charged (around -1.29), highly positive framework silicon atoms (≥ 2.39) prevent strong attraction between the cation and the cage body. As ring size increases, framework oxygen atoms become more accessible to cations, but surface positions consistently show the least negative $\Delta\Delta G_f$ (Fig. 4.4(a-c)), with only one exception at the largest ring with K^+ (top surface of the octagonal prism, Fig. 4.4(b)). The charge distribution calculated with the NBO method aligns well with reported values for the BEA zeolite structure²²⁸ determined by GGA-PBE exchange-correlation functional, coupled with the Iterative Hirshfeld or Density Derived Electrostatic and Chemical charge method: +2.55 to +2.62 for Si and -1.26 to -1.31 for O. Additionally, the authors identified the Extended Charge Equilibration semi-empirical method showing very good agreement with the DFT calculated charges: +2.53 for Si and -1.26 for O. In comparison, most molecular dynamics studies

have used atomic charges (Si: +1.6 to +2.1, Al: +1.2 to +1.8, and O: -0.8 to -1.2), which are smaller in magnitude than the values reported here to account for the framework-cation or framework-adsorbate Coulombic interactions²²⁹⁻²³². Hence, the atomic charge density determined at the high level of theory in this work may be used in future studies for more accurate description of electrostatic interactions.

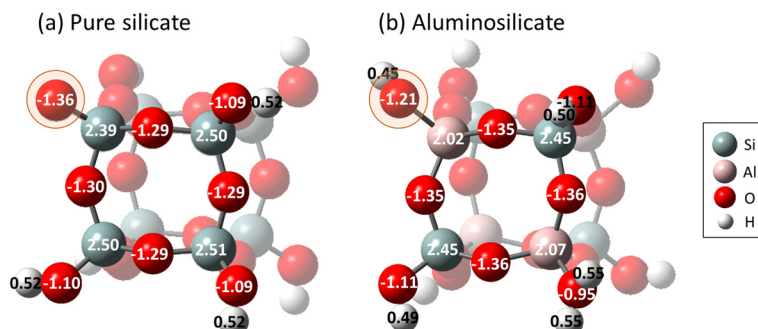


Fig. 4.5. Atomic charges on one plane of the cation-free pure-silicate (a) and aluminosilicate (b) tetragonal prisms, which possess a -1 overall charge by removing one terminal proton (left top, highlighted by orange circle) from the optimized neutral species. The atomic charge is calculated by Natural Bond Orbital analysis²²⁷.

As expected, Fig. 4.4(d-f) reveals that aluminosilicate cages interact with cations very differently compared to pure-silicates, which is attributed to the different charge distribution on the framework atoms (Fig. 4.5(b)). The negative charge of the terminal hydroxyl on aluminum (generated by removing one proton from terminal water; -1.21) is smaller in magnitude than that of the terminal oxygen of pure-silicates (-1.36), whereas framework oxygen atoms in aluminosilicates are more negatively charged (-1.35 or -1.36) than those in silicates (-1.29 or -1.30). At the same time, aluminum is less positively charged than silicon. These differences strongly favor cationic attraction on edge positions as they allow cations to interact with terminal and framework oxygen simultaneously. As a result, a cation located at a vertex position always moves to edge/surface positions during geometry optimization, as indicated by the missing data for the vertex position (Fig. 4.4 (d-f)). Moreover, the top surface positions of cages larger than tetragonal prisms ($\geq 5\text{MR}$) attract cations as strongly as edges because the cations can strongly interact with framework oxygens. In fact, framework oxygen atoms are more negatively charged than the oxygen of the terminal hydroxyl (-1.35 or -1.36 vs. -1.21, Fig. 4.5(b)). This indicates that cation – cage interactions are less localized in the aluminosilicate system compared to the pure-silicates. This phenomenon is putatively due to the presence of aluminum changing the charge distribution of multiple neighboring atoms, especially since the investigated systems possess high aluminum content (i.e., aluminum is spread throughout the cages).

The differences in the effects of cations are also worth noting. Essentially, monovalent cations (Na^+ and K^+) show similar trends of $\Delta\Delta G_f$ with cage size and cation position in each system (Fig. 4.4(a) and (b) for pure-silicates and Fig. 4.4(d) and (e) for aluminosilicates). However, the effects of potassium are consistently stronger (more negative $\Delta\Delta G_f$) than sodium. This does not necessarily indicate that potassium more effectively directs the same type of crystal structures as sodium. Instead, the different formation thermodynamics can significantly alter the crystallization kinetics and therefore final zeolite topologies. Indeed, it has been well demonstrated that different alkali metal cations can have various structure-directing effects. In the pioneering work of Barrer et al. in the 1950s^{233,234}, it was found that aluminosilicate gels with identical chemical compositions except for alkali metal cation selection ($M_2\text{O}-\text{Al}_2\text{O}_3-n\text{SiO}_2$, where $M = \text{Na}$ or K and $1 < n < 12$) can result in either the same or different types of zeolite/aluminosilicate minerals, depending on the hydrothermal synthesis conditions. Further, they revealed that the Na^+/K^+ ratio is a key factor to determine the product crystals when both cations are used together, which demonstrated that Na^+

and K^+ can play different structure-directing roles¹⁴⁶. Likewise, Iwama et al.²³⁵ showed that the controlled addition of potassium could change the selectivity of FAU-type zeolite over LTA by altering the aluminosilicate precursor assembly. Tendeloo et al.¹⁴ synthesized various zeolite crystals (ABW, CHA, MER, and ANA) via interzeolite transformation from zeolite Y using different alkali metals. Moreover, the distinct roles of alkali metal cations (Na^+ , K^+ , and Cs^+) during the synthesis of CHA nanocrystals were identified by Ghossein et al.²³⁶, where a mixture of the cations was used. Rimer et al. showed that the zeolite synthesis phase diagram constructed with K^+ is completely different from that with Na^+ , which demonstrates the significant effect of the cations in altering crystallization kinetics^{15, 237}.

The effects of calcium on the formation energy of (alumino)silicates are different from those of monovalent cations (Fig. 4.4(c) and (f) for pure-silicates and aluminosilicates, respectively). These effects can be attributed to a higher valence state (+2 rather than +1). In the aluminosilicate system, the trends of $\Delta\Delta G_f$ with the cage size and cation position are similar for all cations, but calcium consistently shows the most negative $\Delta\Delta G_f$ (Fig. 4.4(d-f)). This is because the higher-valent cation has stronger electrostatic interactions with terminal/framework oxygen atoms. Interestingly, in the pure-silicate system, we show that the dependence of $\Delta\Delta G_f$ on cation position is significantly different in calcium compared to the alkali metals, where the edge positions surpass the vertex in exergonicity. These observations indicate that the divalent cation can play a considerably different structure-directing role than those of monovalent cations. Compared with alkali metal cations, relatively little attention has been devoted to exploring the possibilities of altering crystallization pathways using divalent cations; however, divalent cations such as Ca^{2+} and Mg^{2+} are present in a number of naturally-forming zeolites (e.g., GIS²³⁸, CHA²³⁹, and FER²⁴⁰), and it has been shown that introducing divalent cations into zeolite growth mixture has a potential to alter zeolite crystallization pathways. For example, Liang et al. recently observed that introducing Sr^{2+} in K-CHA growth mixtures can lead to a dramatic reduction in CHA crystallization time³³. Similarly, it has been demonstrated that Mg^{2+} can promote zeolite *BEA²⁴¹. Collectively, previous studies have shown that the use of different cations can direct structure and/or accelerate zeolite kinetics, and our findings suggest that this may be attributed to electrostatic effects on the formation thermodynamics of small zeolitic species, which stem from the difference in cation size and charge. Although our study addresses formation thermodynamics of small zeolitic structures, it should be noted that changes in reaction free energies can affect kinetics of zeolite crystallization through the well-known Brønsted-Evans-Polanyi relationships²⁴², which have been shown to play a role in both nucleation and growth of nanoparticles²⁴³.

Internal cations. In addition to external positions, we investigated the thermodynamic effects of cations occupying the center of the cage. The formation Gibbs free energies of cages confining cations are shown in Fig. 4.6, along with those of cation-free cages and cages with the external cations at the most stable positions (shown in Fig. 4.4). Interestingly, the pure-silicate trigonal prism with an internal cation shows significantly endergonic formation energies (Fig. 4.6(a)). Additionally, the formation of pure-silicate tetragonal and pentagonal prisms (for all cations) and the hexagonal prism (for calcium) is less favored than the corresponding cation-free cages. In contrast, larger silicate cages (heptagonal prism with alkali metal cations and octagonal prism with all cations) show enhanced formation exergonicity relative to the cation-free cages (black), which indicates the cage size should be sufficiently large for an internal cation to provide thermodynamic stabilization. However, the effects of internal cations on aluminosilicate cages are significantly different from those on pure-silicate cages (Fig. 4.6(b)). Although the smallest (trigonal) cage is endergonic (K^+ and Ca^{2+}) or nearly thermoneutral (Na^+) in formation with an internal cation, tetragonal prisms with an internal cation show the same exergonicity as cation-free cages, and larger cages show significantly more exergonic formation energies. For pentagonal prisms and larger cages, there is no noticeable difference between the net effects of internal vs. external cations.

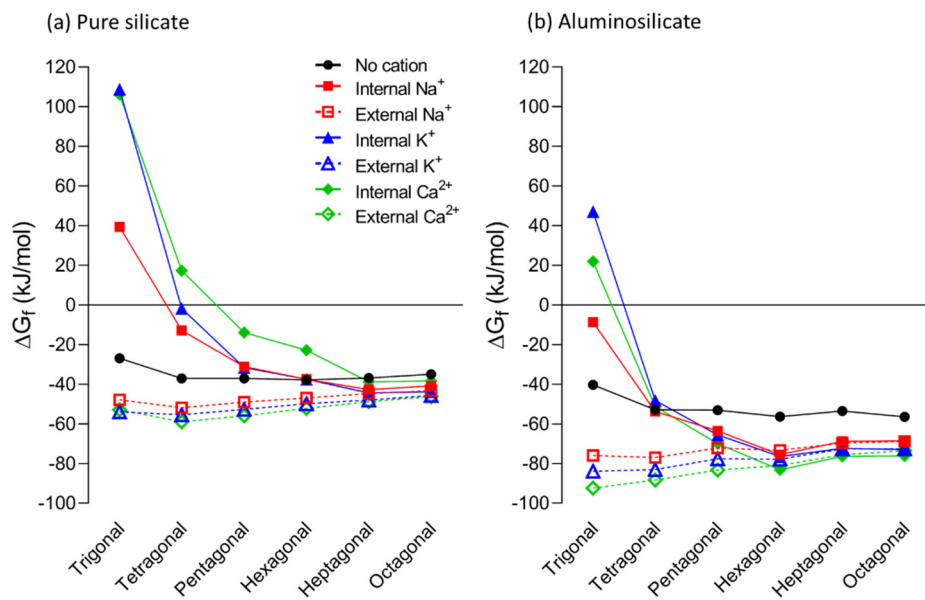


Fig. 4.6. Normalized formation Gibbs free energies (ΔG_f) of (a) silicate and (b) aluminosilicate ($\text{Si}/\text{Al} \approx 1$) cages with and without an alkali or alkaline metal cation (Na^+ , K^+ , or Ca^{2+}) at internal and external positions. The external cations are located at positions that exhibit the most exergonic formation energy (see Fig. 4.4). The Gibbs free energies are determined at 100 °C.

The observations described above clearly demonstrate the interplay of electrostatic interactions and steric effects between the different cages and cations. As discussed, a cation can have attractive interactions with framework oxygen atoms because of their negative charge. The cages that are optimized in the presence of cations at the external top surface position can provide the optimal distance information between cation and framework oxygen since there are no confinement effects. Fig. 4.7 shows the cage radii, which are determined as average Euclidean distances from the geometric center of framework oxygen atoms to each oxygen in the optimized cation-free cages. Also, average distances between the cation at the top surface and framework oxygen atoms that attractively interact with each cation are shown for comparison (dashed and dotted lines in Fig. 4.7, for pure-silicates and aluminosilicates, respectively). The stable cation-framework oxygen distances are longer than the radius of the trigonal prisms, which indicates that the trigonal prisms impose strong steric hindrances and are thus destabilized. Pure-silicate tetragonal prisms also do not have sufficient space to confine potassium, while the radius of the aluminosilicate tetragonal prism is comparable to the potassium-oxygen distance. Therefore, all cages larger than a tetragonal prism are not likely to impose steric hindrance to any internal cation, which is the case for the aluminosilicate systems, as seen in Fig. 4.6(b). In contrast, there are many pure-silicate cages that do not confine cations with strong favorability despite their sufficiently large space (i.e., pentagonal and hexagonal prisms for all cations, and heptagonal prism for calcium), and this can be attributed to the weak attractive interactions between the cage body and the cation (compared to aluminosilicate species). The discussion herein is clearly displayed in the charge density and optimized geometry of pentagonal prisms confining calcium, as shown in Fig. 4.8. The electrostatic cation-cage interactions are stronger in the presence of aluminum due to the more negatively charged oxygen atoms, which is reflected in the shorter cation-oxygen distances (Figs. 4.7(a) and 4.8). These differences lead to the opposite effects from calcium confinement on the formation of the pure-silicate and aluminosilicate pentagonal cages, which are destabilizing and stabilizing, respectively (Fig. 4.6).

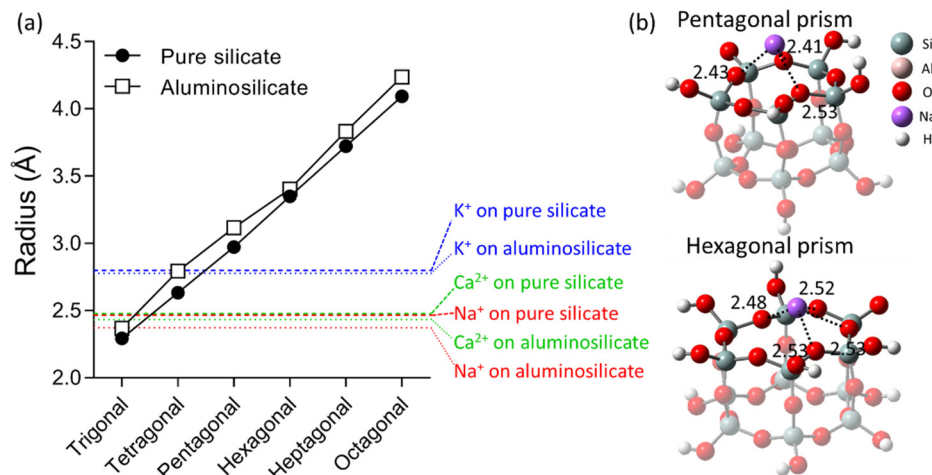


Fig. 4.7. (a) Radii of pure-silicate and aluminosilicate ($\text{Si}/\text{Al} \approx 1$) cages (solid lines with symbols) and optimal distances between (external) cation and framework oxygens (dashed lines for pure-silicates and dotted lines for aluminosilicates) (both in Å). On a cation-free cage, a geometric center between the framework oxygens is defined, with the average distance from the center to the framework oxygens defining the cage radius. The optimal cation-framework oxygen distances are determined on the cages optimized in the presence of a cation at the top surface position. The framework oxygens that are closely bound to the cation are selected, and the distances between the cation and framework oxygens are averaged. (b) Optimized molecular structures of pure-silicate cages in the presence of sodium on the top surface, along with the distances between sodium and the selected framework oxygens (in Å).

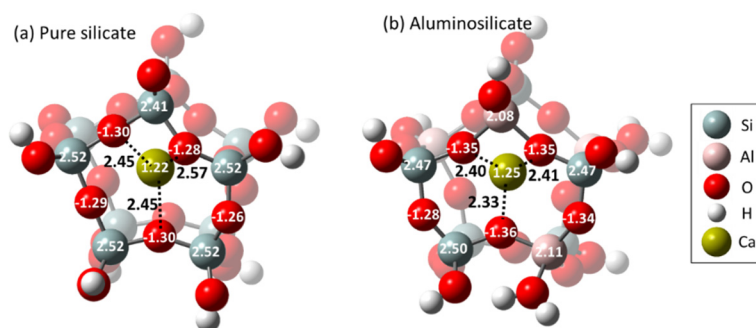


Fig. 4.8. Charge of framework atoms on a base of (a) pure-silicate and (b) aluminosilicate pentagonal prisms that confine calcium cation, as well as distances between cation and framework oxygen atoms (in Å). Atomic charges are calculated by Natural Bond Orbital analysis.

The thermodynamic understanding of the relationship between cage and cation reveals potential roles and limitations of cations in zeolite formation chemistry. We show that pure-silicate cages interact with alkali or alkaline earth metal cations primarily at external vertex/edge positions unless the cage is sufficiently large ($>$ hexagonal prism) to allow framework oxygen to confine cations. Moreover, the cations at an external location consistently show stronger stabilizing effects to pure-silicate cages compared to internal cations. These indicate that attractive interactions between pure-silicate cages and small inorganic cations (compared with bulky OSDAs) are extremely localized, which may adversely affect the stability of cages. This supports the experimental observation that the presence of alkali metal cations (Na^+) changes the stabilization of silicate cage species in solution²⁰⁰. On the other hand, aluminosilicate cages are shown to attractively interact with the cations, as seen by equally exergonic cage formation with internal and external cations (for cages $>$ tetragonal prism). These results corroborate the fact that the formation of pure-silicate species is only viable with bulky, hydrophobic, organic cations (e.g., tetraethylammonium cation (TEA^+)).

and tetramethylammonium cation (TMA^+)¹⁹⁹), whereas aluminosilicate zeolites can be synthesized in the presence of alkali metal cations¹⁶⁴. For the crystallization of siliceous zeolites, the role of alkali metal cations has been limited to facilitating the reaction in the presence of OSDAs²⁴⁴ or seed crystals²⁴⁵. Our results demonstrate that the key of OSDA-free synthesis of siliceous zeolites lies in enhancing attractive electrostatic interactions between the framework atoms and cation (for example, by introducing heteroatoms into the framework) or exploring bulkier inorganic cations (i.e., less charge density). Further, we posit that novel combinations of OSDAs and inorganic cations can be used to synthesize novel zeolite frameworks by stabilizing cages and structures that are not energetically favorable in conventional zeolite syntheses. Of more than 300,000 theoretically predicted zeolite frameworks²⁴⁶, only a small number (~250) have been realized experimentally, and it has been suggested that unique cation pairings are one method for designing previously unrealized architectures²⁴⁷.

Conclusions

In this work, we studied the formation thermodynamics of a wide range of zeolitic precursor species by applying density functional theory calculations. For purely siliceous and aluminosilicate ($\text{Si}/\text{Al} \approx 1$) complexes, we systematically investigated the dependence of formation energy on structure type, structure size, temperature, and the presence of alkali or alkaline earth metal cations (Na^+ , K^+ , and Ca^{2+}). It was found that the most condensed form of pure-silicate species, i.e., prismatic cages, show the highest exergonic formation, followed by multicyclic structures (linked 4-membered rings) and monocyclic structures (simple rings), since the higher degree of condensation favors entropic contributions, leading to more negative formation Gibbs free energy (i.e., more exergonic). As the entropic contribution to the Gibbs free energy is proportional to temperature, the formation preference of condensed structures increases with temperature. Conversely, investigation of aluminum-rich structures reveals significantly different trends. The thermodynamic preference among the three types of species almost vanishes with temperature (50-150 °C), imposing the formation of complexes with high structural diversity, while a size-dependence appears, favoring larger structures. At the same time, it was found that the formation Gibbs free energy of aluminosilicate structures is significantly more exergonic than pure-silicates. These findings consistently support the abundance of aluminum-rich natural and synthetic zeolites.

The effects of cations on formation thermodynamics of cages were found to depend highly on cation charge and size, cage size, and the presence of aluminum, which alters electrostatic interactions. In the case of pure-silicate cages, a terminal oxygen atom (resulting from the proton on terminal hydroxyl group being exchanged with cation) is more negatively charged than framework oxygens, so that the optimal location of a cation is an external vertex or edge, instead of being in proximity of framework atoms (i.e., surfaces) or inside cages. In contrast, framework aluminum and oxygen atoms in aluminosilicate cages (with high aluminum content) are less positively and more negatively charged, respectively, compared to silicon and oxygen in the pure-silicate cages. Therefore, for aluminosilicates, cations can strongly interact with the cage body (at surface or inside of cage) only if cages are sufficiently large to overcome steric hindrance. This supports experimental observations that alkali metal cations can direct growth of many aluminosilicate zeolites, whereas highly siliceous zeolites require the use of bulky organic cations or seed crystals.

Overall, the formation thermodynamics provided herein can potentially guide experimental efforts for discovering more effective synthetic methods of zeolite crystals. Moreover, our detailed study of structurally diverse zeolitic oligomers can provide insights into controlling specific zeolite synthesis pathways, including prenucleation pathways and interzeolite transformations. At the same time, a further theoretical investigation is required to address the effects of experimental factors that are omitted in the current work, e.g., alkaline pH conditions, explicit solvent, kinetics, and types of raw materials, for a more accurate description of zeolitic species growth. In particular, efforts using explicit solvation environments to more precisely capture cation effects on zeolite crystallization processes, as well as the role of water molecules on the reaction kinetics can be instrumental to unravel zeolite growth.

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