

Parametric, mechanistic, and data-driven approaches to elucidate and control zeolite EMT crystallization

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ABSTRACT

Zeolites are often metastable in their native growth environments owing to similar energies of formation among open frameworks, which poses challenges for achieving pure crystalline phases without the assistance of an organic structure-directing agent. Syntheses where organics are substituted with inorganic structure-directing agents are more prone to the formation of polymorphs, with pure phases often confined to narrow growth conditions that also restrict control over their physicochemical properties. In this study, we establish a broad synthetic design space for crystallizing one of the most metastable zeolites, EMT, using parametric studies to identify growth conditions leading to pure zeolite products and establish a database for machine learning to assess parameter sensitivity. Our combined findings reveal that EMT synthesis is highly sensitive to changes in temperature and solution alkalinity. We show that the judicious selection of growth conditions can produce nanosized zeolite EMT crystals as well as intergrowths with zeolite FAU (faujasite), a structural analogue of EMT, without the aid of an organic template or unconventional synthesis protocols. In situ atomic force microscopy is used to probe the mechanism of EMT crystallization wherein we observe that surface growth occurs by two- and three-dimensional generation and spreading of islands at low and high supersaturation, respectively. These modes of growth do not extend beyond a single layer, suggesting bulk crystallization is dominated by the disorder-to-order transition of amorphous precursors, similar to recent findings for zeolite FAU. Collectively, this work highlights the sensitivity of zeolite EMT synthesis to changes in its growth environment. Techniques to expand the range of zeolite synthesis conditions, particularly for organic-free methods, are essential for the design of next-generation porous materials. Coupling these efforts with *in situ* measurements that resolve the complex mechanisms of zeolite growth provides a deeper understanding of nonclassical pathways wherein the observations for EMT align with a growing number of zeolite structures whose modes of crystallization are dominated by the reorganization of amorphous precursors rather than classical solution-mediated processes.

1. Introduction

One of the most common catalytic applications of aluminosilicate zeolites is fluid catalytic cracking (FCC). Approximately 14.5 million barrels of feedstock are treated every day in FCC units in over 300 oil refineries worldwide, with around 840,000 tons of FCC catalysts produced and used every year [1]. Faujasite (FAU) is a large-pore zeolite that has been a major component of FCC catalysts since 1964 [1,2]. The FCC process exposes these catalysts to severe conditions, causing zeolites to deactivate quickly, leading to the loss of framework integrity and the eventual collapse of structure. This motivates research efforts to optimize zeolite properties for improved catalytic on-stream lifetime and selectivity [1–3]. Examples include the design of hierarchical or

nanosized zeolites with reduced crystal size and/or introduced mesoporosity, or the identification of alternative structures to zeolite FAU that may possess superior properties for FCC processes [1,2,4].

Breck and coworkers first reported that the cubic FAU framework could support recurrent twinning on (111) planes to produce a hexagonal framework structure [5]. The structural commission of the International Zeolite Association assigned this twinned zeolite with the framework code EMT (Scheme 1) [6–8]. Both FAU and EMT zeolites have networks of three-dimensional large pores: zeolite FAU has a face centered cubic unit cell with space group $Fd\bar{3}m$ and unit cell parameters $a = 24.74 \text{ \AA}$; and EMT has a hexagonal unit cell with space group $P6_3/mmc$ and unit cell parameters $a = 17.45 \text{ \AA}$ and $c = 28.46 \text{ \AA}$ [9]. A key difference between these structures is that sodalite cages (i.e., truncated octahedra) in

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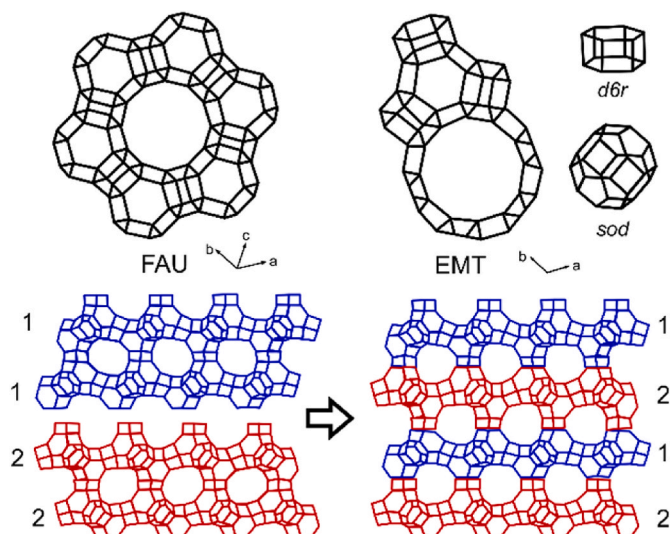
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Scheme 1. Structures of zeolites FAU and EMT with their composite building units, double-6-ring (*d6r*) and sodalite cage (*sod*), and the illustration of EMT constructed via the combination of one FAU segment (1, blue) with its mirror image (2, red) to create an alternating sequence (see Table S1 for crystal structure parameters).

FAU are connected through double-six rings (*d6r*) to give a zinc blende structure, whereas in EMT they are arranged in a wurtzite structure. The formation of EMT and FAU structures can be visualized in terms of the stacking of FAU segments [9]. Notably, the layers of FAU are stacked by a center of inversion whereas EMT exhibits a stacking sequence related by mirror symmetry. The distinct stacking of sheets results in pores being arranged in diagonal and zigzag configurations for FAU and EMT, respectively [10]. The pore structure of FAU contains a network of uniform supercages (1.12 nm diameter), whereas the presence of modified supercages, so-called *hypercages* (1.24 nm³) and *hypocages* (0.61 nm³), is characteristic of the EMT structure [11].

Zeolites FAU and EMT are typically prepared with sodium ions and do not require the use of an organic structure-directing agent (OSDA) [12]. Syntheses are performed at relatively low temperature (<70°C) to avoid interzeolite transformations [13,14]. Mintova and coworkers [14–17] have reported multiple studies on the synthesis of zeolite EMT, including the preparation of nano-sized EMT crystals in which nucleation is controlled by mixing and aging freshly prepared gel components at a temperature of 4°C prior to crystallization at 50°C for 45 h. Other studies have examined the role of OSDAs in EMT synthesis, particular with respect to their direction of EMT/FAU intergrowths [6–8]. For example, it has been reported that OSDAs methyltriethylammonium (E3M) and tetraethylammonium (TEA) can direct the formation of ECR-30 and ECR-35 (or ZSM-20), respectively, which are both EMT-dominant EMT/FAU intergrowths [18]. Inorganic additives can also be used to promote EMT/FAU intergrowths, as demonstrated by the use of Li⁺ to direct the synthesis of zeolites ZSM-2 and ZSM-3, and Cs⁺ to promote the formation of CSZ-1 and CSZ-3 [18,19]. Alternative additives include organosilanes, ionic liquids, and inorganic salts [10,20,21]. Prior studies have demonstrated that EMT/FAU intergrowths are promising catalysts and adsorbents for various applications. Li and coworkers [22] observed improved conversion of tri-isopropyl benzene (TIPB) by catalytic cracking over EMT/FAU intergrowths; and Kalia-guine and coworkers [23] showed improved CO₂ adsorption properties of intergrowths functionalized with aminosilanes. Xu and coworkers [24] used CoMo impregnated EMT/FAU intergrowths as multifunctional catalysts for hydroisomerization, aromatization, and hydrodesulfurization, and demonstrated their superiority over pure phases of FAU and EMT. Imbert and coworkers [25] proposed a similar methodology using Pt incorporation to achieve the highest initial conversion

and isopentane yield in the n-pentane hydroisomerization reaction.

In this study, we examine a broad parameter space for synthesizing pure zeolite EMT in organic-free media. The wide range of synthesis conditions include molar compositions, temperatures, supersaturation, and precursor selection. These studies elucidate conditions that favor zeolite EMT crystallization as well as the formation of EMT/FAU intergrowths without the use of organic or extraneous inorganic additives. Here, we also investigate EMT surface growth using *in situ* atomic force microscopy to probe dynamic events in real time. Our findings reveal a mode of growth that deemphasizes the role of soluble species (solution phase) in favor of growth from amorphous precursors (solid phase). Collectively, these studies expand the design space for synthesizing pure zeolite EMT, which is a promising material for processes that are essential to evolving energy and environmental applications.

2. Results and discussion

2.1. Stabilizing zeolite EMT in organic-free media

The synthesis of zeolites without the use of an organic structure-directing agent (OSDA) typically relies on an alkali metal functioning as an inorganic structure-directing agent (ISDA). The most common ISDA is Na⁺ where the final Na-zeolite crystal structure depends on synthesis composition and temperature spanning the following general ranges: 30 – 65°C for zeolites FAU, LTA, and EMT; 100°C for zeolites GIS, SOD, and MFI; and 180°C for zeolites ANA, CAN, and JBW [12]. Synthesis mixtures used to prepare Na-zeolites commonly have high concentrations of silica and alumina in strongly alkaline solutions (i.e., H₂O/NaOH ~ 20). The formation of zeolite polymorphs, often through interzeolite transformations [12,26], is pervasive in organic-free syntheses. One method of tracking zeolite crystal phases is through the construction of ternary (kinetic) phase diagrams (Fig. 1A) using three principal molar fractions of the synthesis mixture: Si, Al, and NaOH. All other variables such as time, temperature, and water content are fixed. The relative percentage of crystalline or amorphous phases in solids extracted from synthesis mixtures is estimated by powder X-ray diffraction (PXRD) using reference patterns obtained from the International Zeolite Association Structure Database (Fig. S1).

Prior literature reveals EMT to be one of the most metastable Na-zeolites with syntheses restricted to low temperatures (<40°C) [14,15,27] and relatively few studies rigorously exploring the phase space for its crystallization. Here, we selected the most commonly reported synthesis temperature [15] of 40°C to construct a ternary phase diagram (Fig. 1A, callout) using a molar composition $x \text{ Na}_2\text{O} : y \text{ Al}_2\text{O}_3 : z \text{ SiO}_2 : 450\text{H}_2\text{O}$ with a fixed synthesis time of 72 h. The composition of each growth mixture in the phase diagram accounts for additional alkali hydroxide (0.65y + 0.06z Na₂O) introduced with the silica (sodium silicate) and alumina (sodium aluminate) sources (see Methods for details). When comparing EMT synthesis at 40°C (Fig. 1, green shading) to that of its structural analogue FAU at 65°C (Fig. 1, blue shading), the region for pure EMT is substantially smaller and located in the corner of the phase diagram where silica and alumina concentrations are low and NaOH concentrations are high. The water content of EMT syntheses is nearly double that of FAU; however, the high concentration of caustic leads to a ratio of H₂O/NaOH ~ 10 that is lower than the corresponding value of 17 in FAU syntheses [12].

Similar to most Na-zeolites, the formation of EMT occurs in Si-rich growth media (2 < Si/Al < 9). As the Si/Al ratio of the growth mixture decreases, we observe a binary mixture of EMT and LTA, consistent with the LTA phase region being located within the Al-rich sector of the ternary diagram (Fig. 1A, red shading). Along the border of EMT and LTA regions, we observe trace quantities of zeolite RHO (Fig. S1), which shares a similar composite building unit (*lta* cage) with LTA (Table S5). Obtaining pure RHO in organic-free media typically requires higher temperatures (>90°C) and mixtures of ISDAs (e.g., Na⁺ and Cs⁺) [28,29]. Here we observe zeolite RHO at much lower

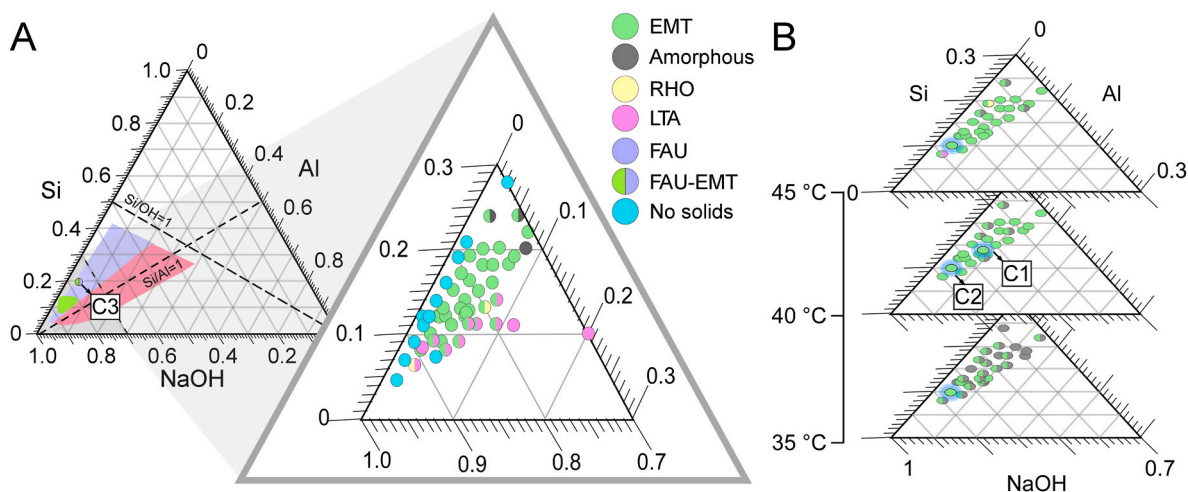


Fig. 1. (A) Kinetic (ternary) phase diagram of Na-EMT (green) superimposed on regions previously reported for zeolites Na-FAU (blue) and Na-LTA (red) at 65°C for 148 h [12]. All EMT syntheses were performed at 40°C for 72 h using molar compositions of $x \text{ Na}_2\text{O} : y \text{ Al}_2\text{O}_3 : z \text{ SiO}_2 : 450\text{H}_2\text{O}$ (see Table S2 for details). The axis “NaOH” accounts for the Na_2O contained within Si and Al sources. Callout: synthesis compositions resulting in zeolite EMT (green), amorphous (grey), zeolite RHO (yellow), and no apparent solids (aqua blue). Circles with split colors represent either incomplete crystallization or the presence of two zeolite phases, as determined by PXRD (Figs. S1 and S2). Concentration C3 leading to a FAU/EMT intergrowth material is highlighted (refer to Section 2.3). (B) Ternary diagrams plotted with temperature as a fourth-dimension spanning from 35 to 45°C with highlighted compositions C1 and C2.

temperature, but never as a pure phase. As the concentration of NaOH in the EMT growth mixture is decreased, shifting the synthesis towards the FAU region, crystallization is incomplete, i.e., there is residual amorphous material in the product, which we attribute to differences in the water content and temperature of FAU and EMT syntheses. The latter is prepared with a more dilute growth mixture and reduced synthesis temperature, which hinders zeolite FAU crystallization (*vide infra*).

One difference between EMT synthesis conditions in this study compared to those reported in literature is the temperature of pre-synthesis aging. Here, we prepared separate solutions of silica and alumina at room temperature prior to mixing, whereas Ng et al. [15] carried out these steps in an ice bath at 4°C. The effects of temperature on the formation of (alumino)silicate oligomers or amorphous precursors and subsequent nucleation and growth pathways of zeolites are not fully understood; however, we posit that the conditions used in our protocol lead to more soluble species prior to mixing. An advantage of room-temperature mixing is the ability to prolong synthesis times without observing interzeolite transformations, thereby minimizing the formation of impurities. For example, Mintova and coworkers [15] reported the onset of an impurity (zeolite SOD) when EMT syntheses exceeded 36 h of heating. On the contrary, we extended our synthesis time to 16 days (or 384 h) and did not observe an impurity phase (Fig. S2). This enhanced stabilization of zeolite EMT using room-temperature aging proved to be instrumental for parametric analyses, allowing a broader range of synthesis conditions to be assessed without significantly compromising zeolite phase purity.

We examined the impact of synthesis temperature (Fig. 1B) on EMT crystallization, keeping the heating time and solution compositions the same as those reported in Fig. 1A. The ternary phase diagram was extended in a fourth dimension to explore a relatively narrow range of temperatures (35, 40, and 45°C). When the temperature is lowered to 35°C, the crystallization of zeolite EMT is incomplete, leading to residual amorphous material in extracted solids (Fig. S3), indicating longer times are needed to achieve full crystallinity. When the temperature is increased to 45°C, the phase diagram is largely unchanged from that of 40°C, suggesting that zeolite EMT syntheses could be performed at even higher temperature, although the synthesis times may need to be reduced (<72 h) to avoid interzeolite transformation. For instance, we observed EMT formation at 50°C after 24 h (Fig. S4); and even higher temperatures were used to prepare EMT/FAU intergrowths (see Section 2.3). Mapping the EMT phase space over a much broader range of

synthesis conditions, however, would require an exhaustive combinatorial effort, which is outside the scope of this study.

2.2. Time-resolved analysis of EMT crystallization

Mintova and coworkers [14,15,17] reported the formation of EMT nanocrystals (5–20 nm) with a hexagonal morphology using a composition of $18.45 \text{ Na}_2\text{O} : 1 \text{ Al}_2\text{O}_3 : 5.15 \text{ SiO}_2 : 450\text{H}_2\text{O}$ (labelled C1 in Fig. 1B) with low-temperature (pre-)mixing. We reproduced their procedure and obtained similar EMT crystals (Fig. 2A). Interestingly, synthesis with a slightly altered composition of $18.45 \text{ Na}_2\text{O} : 0.5 \text{ Al}_2\text{O}_3 : 4 \text{ SiO}_2 : 450\text{H}_2\text{O}$ (labelled C2 in Fig. 1B) using room-temperature mixing and twice the synthesis time resulted in EMT nanocrystals (Fig. 2B and C) with slightly larger size. Electron diffraction patterns of EMT particles (Fig. 2D) confirmed a higher degree of crystallinity using room temperature (pre-) mixing compared to the low-temperature protocol (Fig. 2A, inset). Previous studies have reported that mixing reagents in an ice bath is essential to obtain EMT nanocrystals (~10 nm), positing that lower temperature facilitates the formation of small, isolated precursors [14]. A similar low-temperature mixing protocol was demonstrated for nanosized zeolite FAU [13]. High-resolution transmission electron microscopy (HR-TEM) images (Fig. 2C) show that room temperature (pre-) mixing leads to ultra-small EMT crystallites (20–40 nm), analogous to the outcome reported by Grand et al. [28] for the synthesis of nanosized zeolite RHO crystals (20–30 nm), but with a higher degree of aggregation that makes it challenging to observe isolated crystals. The collective results from studies of three Na-zeolites (EMT, FAU, RHO) suggest that multiple factors may be critical to achieve zeolite nanocrystals where the exact pathways leading to smaller crystal size is not fully understood.

The structural changes underpinning the amorphous-to-crystalline transition were evaluated using diffraction and pair distribution function (PDF) data collected for solids recovered at various times during the EMT synthesis. In the diffraction data (Fig. 2E), Bragg peaks in PXRD patterns are evident from 20 h onwards, with broad features evident at the same 2θ positions as early as 13.5 h. The PDFs extracted from the total X-ray scattering data provide insight into the local structure during the transformation as a weighted histogram of the atom-atom distances. The first 3 peaks in the PDF (Fig. 3A), at ~1.64, 2.66, and 3.09 Å, correspond to the T–O, O···O, and T···T distances within/between corner-shared TO_4 tetrahedra. The PDFs were weighted by r to amplify

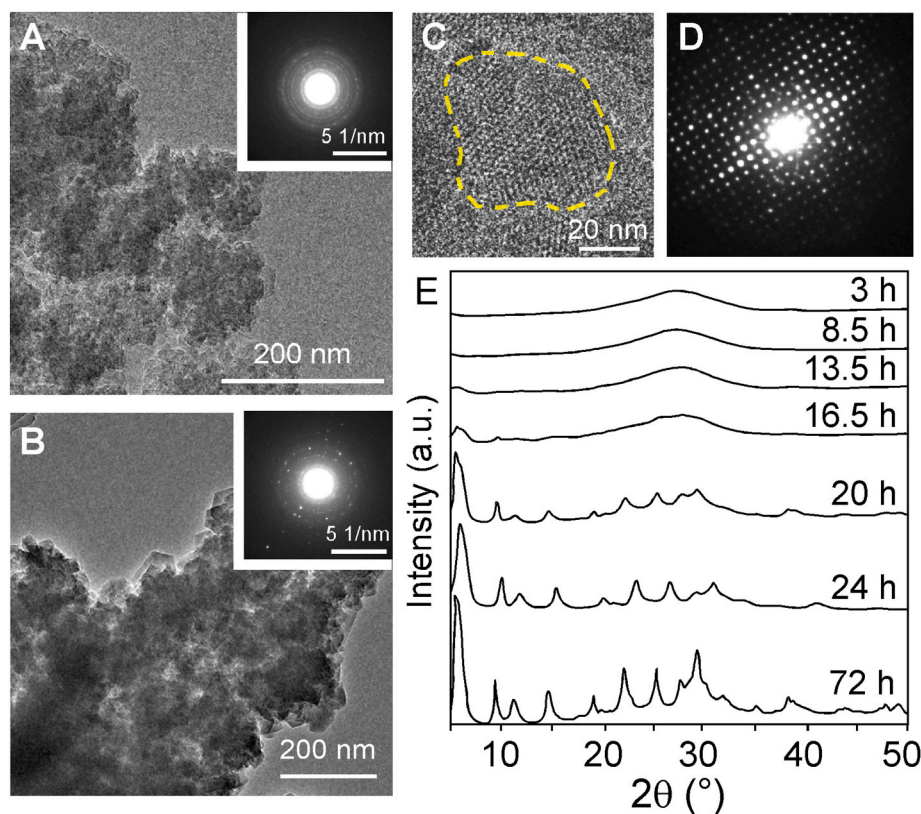


Fig. 2. (A and B) Transmission electron microscope (TEM) images of samples prepared with growth mixture compositions (A) C1 and (B) C2 using low- and room-temperature (pre-)mixing, respectively. Each composition is highlighted in Fig. 1B. Insets: selected area electron diffraction (SAED) patterns of the entire imaging regions. (C) HR-TEM image of an EMT nanocrystal prepared with composition C2. The dashed line outlines the contour of a single particle within a larger aggregate. (D) Electron diffraction pattern of an individual crystal from the sample in panel B. (E) PXRD patterns of solids extracted from an EMT synthesis at 40°C over a 72-h period using a growth mixture with composition C2.

and, thus, better visualize the features at longer distance.

In the initial amorphous state, there are no well-defined features in the PDF beyond ~ 11 Å, which indicates substantial disorder, either static or dynamic, on a nanometer scale (Fig. 3A). As the reaction progresses, the T...T peak sharpens, reflecting a reduced distribution in the T-O-T bond angle, and shifts to slightly higher r suggesting a more open, potentially more strained corner-shared geometry (Fig. 3B and C). Importantly, the second T-O correlation is broadly distributed between 3.60 and 3.80 Å in the amorphous state. This peak is associated with 4-rings (4R) that are prevalent in EMT. The initially broad feature suggests disorder (non-planarity) in the 4R (and perhaps, other 3/5 ring-sizes). This feature sharpens significantly during crystallization as a symmetric 4R becomes locked in. Initially broad peaks at ~ 4.33 Å correspond to T...O and T...T correlations in the 4- and 6-rings, respectively, sharpen and grow in their intensity. Linear combination analysis (LCA) of the PDF datasets confirms the transformation occurs directly between the amorphous (3 h) and crystalline (20 h) end members, without a significant intermediate state.

Aluminum speciation during zeolite EMT synthesis was characterized by solid-state ^{27}Al magic angle spinning (MAS) NMR. Analysis of the as-received starting reagent, NaAlO_2 , reveals a sharp peak at approximately 80 ppm (Fig. S6). After combining both alumina and silica sources at room temperature and heating the mixture for 3 h at 40°C, the ^{27}Al MAS NMR spectrum shows a single peak at around 60 ppm (Fig. 4). The peaks at 80 and 60 ppm in the ^{27}Al MAS NMR spectra for reagent and EMT precursors, respectively, correspond to a tetrahedral aluminum coordination, consistent with the chemical shifts of Al-O tetrahedra reported in literature [30]. The peak shift from 80 ppm in NaAlO_2 to 60 ppm in zeolite EMT amorphous precursors is attributed to the formation of Si-O-Al tetrahedra. When comparing PXRD patterns

(Fig. 2E) with ^{27}Al MAS NMR spectra (Fig. 4), the transition from amorphous to crystalline products has no apparent change in aluminum coordination, which suggests that most aluminum enter the EMT framework as tetrahedrally-coordinated species. During EMT crystallization, the intensity of the ^{27}Al MAS NMR peak at 60 ppm increases with a concomitant narrowing of its width; however, throughout the entire synthesis the extracted solids show no evidence of extra-framework Al, which would be detected around 0 ppm.

Nitrogen adsorption/desorption isotherms were obtained for solids extracted at various stages of zeolite EMT synthesis (Fig. S7) to monitor the temporal evolution of the Brunauer-Emmett-Teller (BET) surface area, S_A , and micropore volume, V_{micro} (Fig. 5A). Textural analysis is consistent with PXRD data showing that crystallization is nearly complete after 24 h of heating, although there is an apparent increase in relative crystallinity with additional heating, as indicated by the slight increase in V_{micro} (Fig. 5A) and PXRD peak intensity (Fig. 2E) after 72 h. This trend deviates from other zeolites reported in literature where textural properties often reach values approximately equal to those of the final crystalline product during the apparent induction period [26], indicating that amorphous precursors begin to develop structural features and pores that are characteristic of the zeolite product. Energy dispersive X-ray (EDX) spectroscopy reveals an approximately constant Si/Al ratio of extracted solids (Fig. 5B, squares) that is nearly identical to the final zeolite product (Si/Al = 1.1 at 72 h). Inductively coupled plasma (ICP) analysis of supernatant solutions (Fig. 5C, callout) shows a Si-rich medium (Si/Al ~ 15) where the Na^+ concentration monotonically decreases during the induction period (from 3 to 13.5 h), and then increases during crystallization (from 21 to 24 h) to a relatively constant value without noticeable changes in solution pH (Fig. 5B, circles). These collective observations suggest zeolite EMT crystallization is

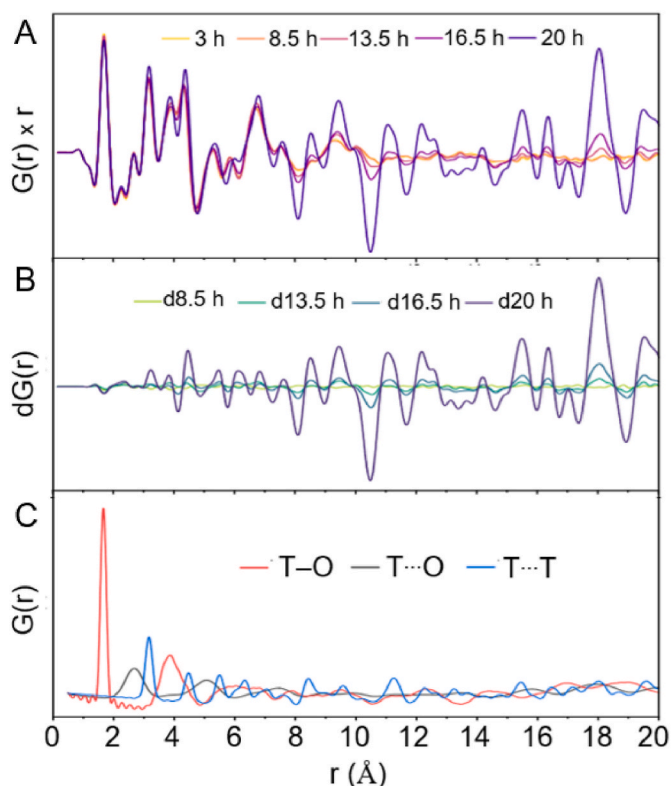


Fig. 3. Pair distribution function (PDF) analysis. (A) r -weighted PDF data for solids recovered at different times from a synthesis with composition C2 at 40°C. (B) r -weighted differential PDFs highlighting the changes following the sample at 3 h. (C) Simulated partial PDFs for the crystalline EMT product to help identify atom-atom pairs that contribute to the PDFs.

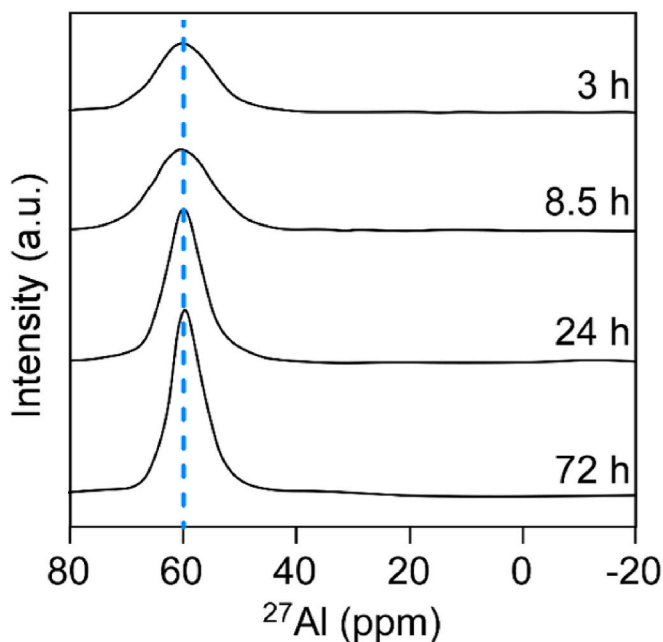


Fig. 4. Solid-state ^{27}Al MAS NMR spectra of samples extracted at various times during synthesis with composition C2 at 40°C. The only peak observed at 60 ppm (dashed line) corresponds to tetrahedral Al, while extra-framework Al (expected at 0 ppm) is not detected.

dominated by events taking place in the amorphous precursors by pathways that are elusive. The nonmonotonic evolution of supernatant composition is evidence that the solid and liquid states exchange species; however, the nearly constant Si/Al ratio of the solids would seem to suggest the aluminum consumed during crystal growth is predominantly coming from the amorphous precursors. This supports our hypothesis that zeolite EMT growth is dominated by solid-state processes that likely involve local dissolution and reprecipitation, similar to the mechanism proposed for zeolite FAU [31] and consistent with molecular simulations of nonclassical zeolite AFI crystallization reported by Molinero and co-workers [32] where barriers to nucleation are negligible and local order develops within different regions of amorphous precursors. This pathway can also explain why microporosity is often detected well before the onset of Bragg peaks in PXRD patterns [33].

Zeolite EMT synthesis was repeated with different silica sources to assess whether the proposed solid-mediated crystallization pathway is sensitive to the nature of amorphous precursors. All syntheses were carried out at 40°C using composition C2, but with the nominal silica source (sodium silicate) replaced with three alternatives: fumed silica, colloidal silica (LUDOX AS-40), and tetraethyl orthosilicate (TEOS). Switching silica sources introduced more amorphous particles in the initial synthesis mixture. We were careful to ensure all syntheses had the same overall composition, taking into account the additional Na_2O in sodium silicate by adding more NaOH to the gel mixtures prepared with other silica sources. Despite similarities in their overall molar composition, we observed subtle differences in supernatant pH after room temperature aging for sodium silicate (pH 13.46), fumed silica (pH 13.68), TEOS (pH 13.55), and LUDOX AS-40 (pH 13.68). We attribute these differences to the degree of silica dissolution and corresponding consumption of hydroxide ions. During early stages of synthesis the pH is approximately constant (Fig. 5B); however, at the end of synthesis (72 h) there are differences in pH for mixtures prepared with sodium silicate (pH 13.70), fumed silica (pH 13.33), TEOS (pH 13.32), and LUDOX AS-40 (pH 13.45).

Growth mixtures prepared with sodium silicate are initially clear (homogeneous) solutions that gradually become opaque with heating time (Fig. S8) as amorphous precursors are formed. For syntheses using all other silica sources, the initial mixtures are opaque immediately after room temperature mixing (Fig. S8), forming colloidal suspensions rather than viscous gels. One noticeable difference of replacing sodium silicate with an alternative silica source is the formation of impurities (e.g., zeolites RHO and LTA). In select cases, these impurities can be eliminated by adding an additional 20% NaOH (Fig. S9); however, the same outcome was not observed when adding 20% NaCl, indicating a higher alkalinity is essential to achieve pure EMT.

2.3. Intergrowths of EMT and FAU

The ability to synthesize hierarchical zeolites comprised of interconnected nanosheets is often associated with crystal structures capable of growing as thin layers or supporting branched architectures [4]. Previous studies have revealed that branching is prevalent in environments that promote epitaxial intergrowth of two structures with different symmetries, wherein the higher-symmetry structure serves as a bridge connecting the one with lower symmetry [34]. Several studies have reported hierarchical zeolites formed by intergrowths, which include FAU/EMT with FAU as the dominant phase [10,18,20], EMT/FAU with EMT as the dominant phase [24], CAN/SOD [35], and MFI/MEL with MFI as the dominant phase [34,36,37]. Tsapatsis and coworkers [20] reported the rotational intergrowth of a hierarchical EMT/FAU zeolite prepared with 3-(trimethoxysilyl) propyl octadecyl dimethyl ammonium chloride (TPOAC) as the OSDA, which promotes EMT nucleation close to the edge of FAU nanosheets on (111) and (11 $\bar{1}$) faces, followed by branching to generate interpenetrated sheets with a house-of-cards arrangement. Machine learning has recently been

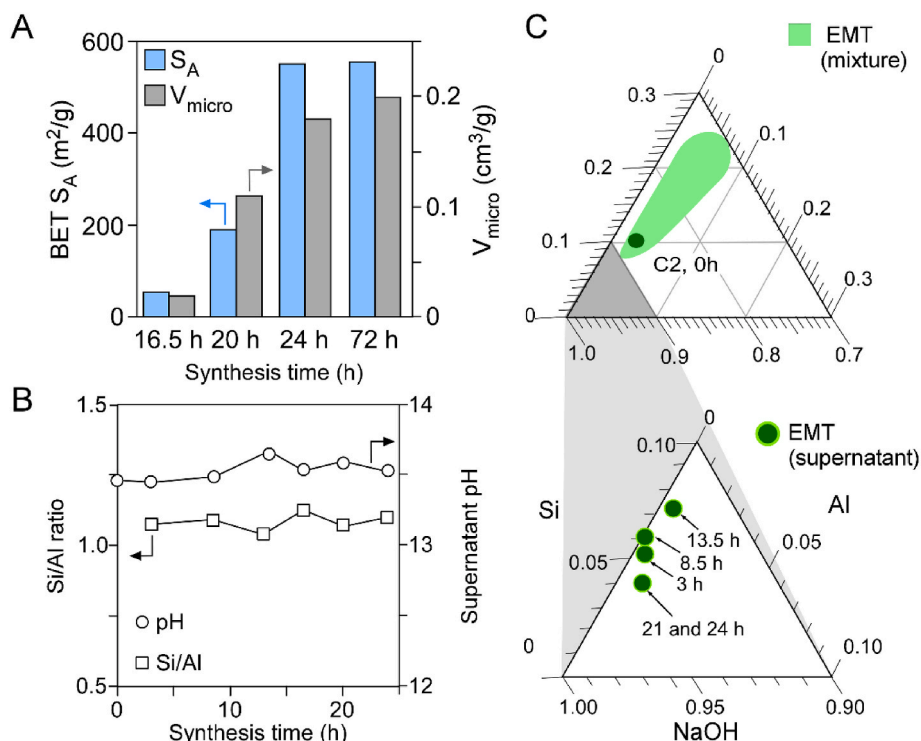


Fig. 5. (A) BET surface area S_A (blue, left y-axis) and micropore volume V_{micro} (grey, right y-axis) of solids extracted at periodic heating times (see Fig. S7 in the Supporting Information (SI) for the N_2 adsorption/desorption isotherms). (B) EDX analysis of Si/Al ratios (squares, left y-axis) and pH (circles, right y-axis) for solids and corresponding supernatant solutions, respectively. (C) The ternary phase diagram of zeolite EMT from Fig. 1A (green shading) where C2 indicates the overall composition (solids + supernatant) and the diagram in the bottom is an enlarged region of the shaded grey segment where symbols indicate time-elapsing changes in supernatant composition (green circles) determined by ICP elemental analysis. The silica content of supernatant solutions (Si/Al ~15) is much higher than those of amorphous precursors (Si/Al < 1.2) and zeolite EMT product (Si/Al = 1.1).

used to predict intergrowths between two zeolite structures [38]. It is also possible that rotational intergrowths or twinning within a single structure can lead to self-branched or pillared zeolite MFI [34,36,39], CHA [40], and MTW [41].

The majority of hierarchical zeolite syntheses require OSDAs; however, prior studies have shown that EMT/FAU intergrowths can be prepared in organic-free media [4]. Factors such as alkalinity, temperature, aging time, Si and Al source selections, and inorganic additives (e.g., alkali metals) impact intergrowth formation [18,42]. Here, we identified conditions leading to FAU/EMT intergrowths by modifying the pure EMT synthesis. Notably, we maintained the same protocol of dissolving Si and Al sources in separate solutions prior to mixing at room temperature, but we switched the Al source from sodium aluminate to aluminum hydroxide, used slightly reduced NaOH and water contents, and increased the synthesis temperature from 40 to 65°C. One of the molar fractions (Si/Al/NaOH) leading to an FAU/EMT intergrowth is labelled in Fig. 1A as composition C3, which lies outside the pure EMT region and within the pure FAU region [43]. The full set of synthesis conditions leading to FAU/EMT intergrowths are provided in Table S6 of the SI, along with PXRD patterns revealing a FAU-dominant composition (Fig. S10) and textural properties that indicate a hierarchical structure with both micro- and mesoporosity (Fig. S11). Scanning electron microscopy (SEM) images reveal a house-of-cards architecture for FAU/EMT intergrowth crystals (Fig. 6A) with an overall geometry that resembles pure FAU crystals (Fig. 6B). SEM images of solids extracted at different stages of synthesis (Fig. S10) show the emergence of the house-of-cards morphology with an interzeolite transformation to GIS that occurs after 7 days of heating. While this is consistent with a prior study of Na-zeolites showing a FAU-to-GIS transformation [44], here we observe this phenomenon at much lower temperature (65°C) compared to conventional GIS syntheses at 100°C [12]. A similar observation has been reported for MFI/MEL intergrowths (referred to as self-pillared

pentasils) that transform to Na-MOR (mordenite) with prolonged heating time [36].

2.4. *In situ* characterization of EMT surface growth

Mechanistic studies of Na-zeolite crystallization in organic-free media have revealed nonclassical routes involving two-step nucleation within amorphous precursors and growth from either the solid or solution phases [31]. For zeolite A (LTA), nucleation is believed to occur within the interior of the precursor [45], whereas for FAU, it is thought to take place on their exterior surfaces [46]. Solvent entrapped within the interior of FAU precursors can also facilitate nucleation via the dissolution or condensation of aluminosilicate species [47]. Growth processes also involve various nonclassical pathways, such as crystallization by particle attachment (CPA) and classical layer-by-layer surface growth via monomer addition [48,49]. Silicalite-1 (siliceous MFI) grows by a CPA process involving the addition and structural rearrangement of amorphous precursors [50]. Similar pathways have been posited for SSZ-13 (CHA) and other zeolites [51]. Recently, we used *in situ* atomic force microscopy (AFM) to show that zeolite LTA grows by multiple pathways depending on the supersaturation of the supernatant solution. In some cases, we find that supernatant solutions extracted at intermediate stages of synthesis, when used as media for seeded crystallization, do not result in surface growth. Examples include zeolite FAU where crystallization is seemingly dominated by processes occurring within the solid phase [31].

AFM is a powerful tool for examining dynamic processes of crystal surface growth with near-molecular resolution [52–53]. Here, we used AFM to track zeolite EMT surface growth in real time from its own supernatant solution. A prerequisite of AFM measurements is the preparation of large crystals as substrates. In our previous study of zeolite FAU, we used a reported protocol [7] with 15-crown-5 (Fig. 7A) as the

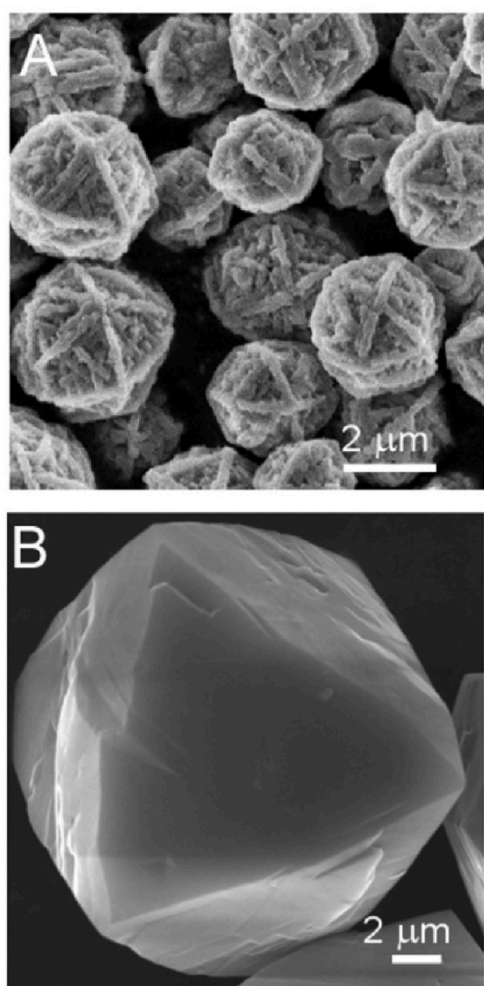


Fig. 6. Scanning electron micrographs of (A) FAU/EMT intergrowth crystals and (B) pure zeolite FAU. The FAU/EMT sample was prepared using a growth mixture with a molar composition of 2.5 SiO₂: 0.25 Al₂O₃: 5 Na₂O: 173H₂O (labelled as composition C3 in Fig. 1A) that was heated at 65°C for 4 days. The FAU sample was prepared using a growth mixture with composition 3.5 SiO₂: 1.0 Al₂O₃: 4.76 Na₂O: 8.0 TEA: 454H₂O that was heated at 100°C for 21 days.

OSDA to prepare large crystals. A similar approach was reported for EMT [8] using 18-crown-6 (Fig. 7B) as an OSDA to generate approximately 10-μm crystals. We reproduced this synthesis protocol to obtain large, hexagonal-shaped EMT platelets (Fig. 7C) as substrates for *in situ* measurements. AFM images of the as-synthesized EMT (100) surface reveal unfinished layers (Fig. 7D) with a combination of single steps and macrosteps. The presence of unfinished layers is a characteristic attribute of classical growth by monomer addition. Anderson and coworkers [54] have reported AFM images of similar features for a broad range of zeolite structures, suggesting classical pathways of growth. The birth and spreading mode of layered growth is prevalent at low supersaturation [48], which is associated with late-stage zeolite syntheses when amorphous precursors are largely consumed. In some instances (e.g., silicalite-1), it has been posited that classical growth is more prevalent at high synthesis temperature [50]. This may also be true for the EMT crystals in Fig. 7D, which were synthesized at 110°C and exhibit a surface topography that provides circumstantial evidence of layered growth.

Growth mixtures used to generate the zeolite EMT phase diagram in Fig. 1 are initially clear solutions, but become opaque when heated, which is not amenable for *in situ* AFM measurements. As an alternative, we used a similar molar composition (18.45 Na₂O: 0.25 Al₂O₃: *z* SiO₂:

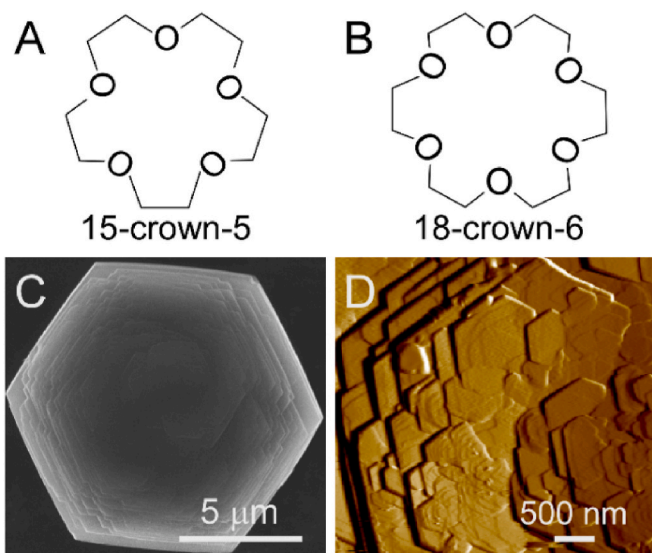


Fig. 7. (A and B) Molecular structures of OSDAs used to synthesize large crystals of (A) zeolite FAU (15-crown-5) and (B) zeolite EMT (18-crown-6). (C) Scanning electron micrograph of a large EMT crystal prepared from a synthesis at 110°C with 18-crown-6 as the OSDA. These crystals were used as substrates for *in situ* AFM measurements. (D) AFM amplitude-mode image in air of an as-synthesized EMT crystal substrate showing the layered topography of basal (100) surfaces.

450H₂O) with reduced silica and alumina concentrations. We tested two different silica concentrations (*z* = 2 and 3.5) wherein a fresh growth solution was continuously supplied by a syringe pump to the AFM liquid cell maintained at 45°C. Fig. 8A contains time-elapsd images extracted from Movie S1 showing an EMT (100) surface growing from the solution with lower silica concentration. The initial area selected for imaging had large terraces with single steps (arrow in Fig. 8A). Prior to imaging, the liquid cell was slowly heated to the set point temperature, allowing 140 min to reach steady state (i.e., equivalent to the average liquid residence time in the sample cell). Continuous AFM imaging after reaching steady state reveals the generation of islands (oval in Fig. 8A). These features have heights of ~1 nm, which is less than the unit cell dimension (*a* = 1.7 nm), suggesting they form by the addition of soluble species. The clear solutions used for AFM measurements remain visibly transparent after 3 h of heating; however, oblique illumination microscopy (OIM) measurements reveal particles with an average diameter of 100 ± 2 nm (Fig. S12) that grow in population with heating time (from 3.0 × 10⁷ to 5.6 × 10⁷ particles cm⁻³) without any change in particle size. Interestingly, we never observe surface features with heights of comparable size; hence, there is no evidence that these 100 nm particles participate in surface growth.

During continuous AFM imaging, the generation of new islands persists until the original terrace of the EMT (100) surface is completely covered, which occurs after ~80 min of imaging. There is no apparent critical 2D island size associated with classical nucleation since all features grow and none appear to dissolve. One island highlighted in Fig. 8A was tracked over time and the corresponding height profiles (Fig. 8B) show in-plane advancement, which is a signature of classical 2-dimensional (2D) surface growth (Fig. 8C). There is a distribution of island widths once the surface reaches full coverage wherein the islands retain their individual domains without coalescing into a uniform layer. This behavior is atypical of classical growth, including prior studies of zeolite LTA where 2D growth results in the merging of islands into a single layer. It is unclear why unfinished layers initially present on the substrate do not advance; and also why newly formed islands do not merge into a single layer. Once the surface reaches full coverage, growth seemingly ceases and there is no generation of new islands.

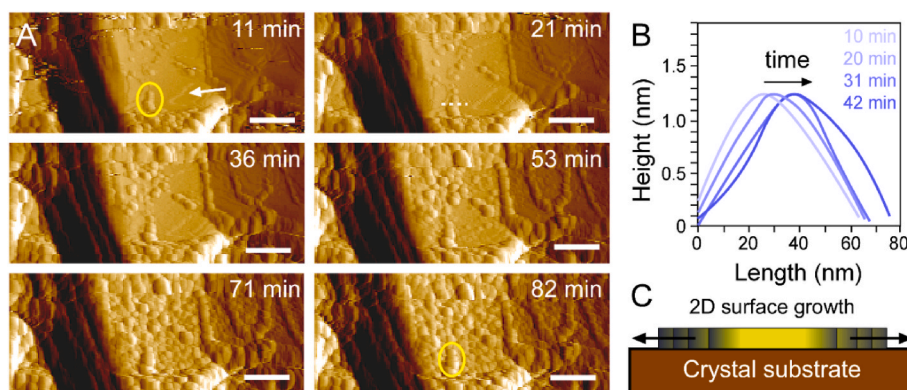


Fig. 8. (A) Time-elased AFM amplitude-mode images of an EMT (100) surface growing at 45°C in the solution with lower supersaturation (18.45 Na₂O: 0.25 Al₂O₃: 2 SiO₂: 450H₂O). The arrow indicates a single step. Images were extracted from Movie S1 with listed imaging times. All scale bars equal 200 nm. (B) Height profiles of the feature highlighted by the oval in panel A showing in-plane layer advancement with heating time. (C) Idealized scheme of classical 2-dimensional (2D) surface growth.

A second AFM experiment was carried out using a growth solution with 1.75-fold higher silica concentration. After reaching the set point temperature, the EMT (100) surface had a roughened interface from the start of imaging (Fig. 9A). The heights of these features are nearly an order of magnitude larger than those observed at lower silica concentration. Unlike the measurement at lower supersaturation, here we observe continued growth of surface features, even after reaching full coverage of islands. Time-resolved height profiles of a representative surface feature (green oval in Fig. 9A) show both in-plane and out-of-plane growth (Fig. 9B). The incremental change in width and height is suggestive of growth by soluble species; however, this occurs by a 3-dimensional (3D) process, which is uncommon for classical mechanisms but has been previously reported for zeolite FAU [31]. Similar to the dynamic series of events observed at lower supersaturation (Fig. 8A), islands do not merge into a single layer, but retain their rounded morphology during 3D growth. In both sets of *in situ* AFM experiments, surface growth produces topographies that differ from as-synthesized substrates. This is attributed in large part to differences in temperature for AFM measurements (45°C) and the synthesis of EMT crystal substrates (110°C), suggesting there is an activation barrier for 2D layer generation and spreading, analogous to the mechanism proposed for

silicalite-1 (MFI) surface growth [50].

2.5. Assessing EMT phase behavior sensitivity

We used machine learning (ML) to identify key synthesis parameters and propose combinations of synthesis conditions that lead to the formation of pure zeolite EMT. To achieve this, we developed XGBoost [55] classification ML models utilizing compositional parameters such as the molar fractions of Si, Al, and Na⁺, their stoichiometric ratios, and physical criteria such as temperature and synthesis time across 174 different attempts to prepare pure EMT in organic-free media. Our results suggest that temperature is the most impactful parameter (Fig. 10A), with values slightly higher than ambient (40–45°C) favoring pure-phase EMT zeolite, which agrees with previous reports [12,14] of organic-free syntheses of zeolite EMT. We also generated hypothetical zeolites by combining synthesis parameters both within and beyond the range of the original dataset. Using the ML classifier, we determined the probability with which each case would yield pure EMT. Our results show that when the synthesis parameters lie within or near the range of the original dataset, the ML model can successfully predict the formation of zeolite EMT. For example, five out of six proposed synthesis

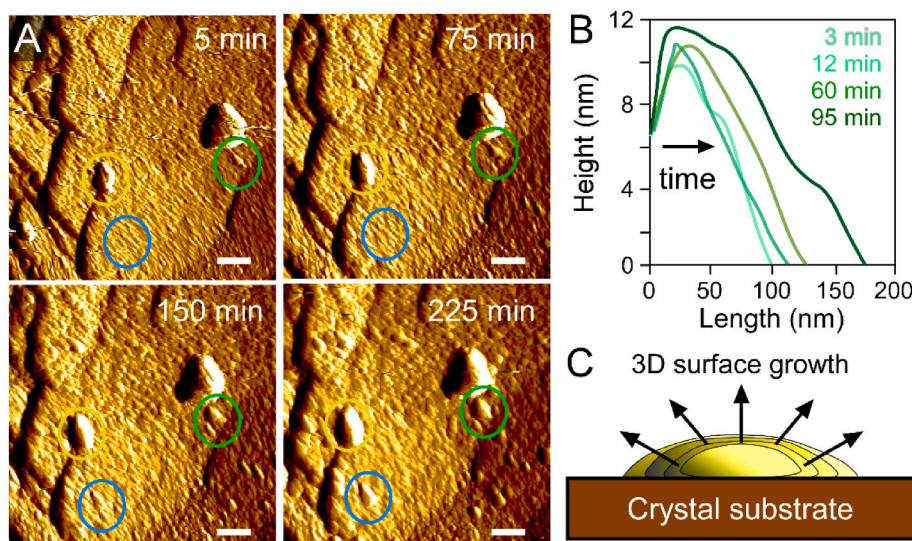


Fig. 9. (A) Time-elased AFM amplitude-mode images of an EMT (100) surface growing at 45°C in a solution with higher supersaturation (18.45 Na₂O: 0.25 Al₂O₃: 3.5 SiO₂: 450H₂O). The three ovals highlight different growing features (see Movie S2). All scale bars equal 500 nm. (B) Height profiles of the feature highlighted by the green oval in panel A showing both in-plane and out-of-plane advancement with heating time. (C) Idealized scheme of 3-dimensional (3D) surface growth by the addition of soluble species.

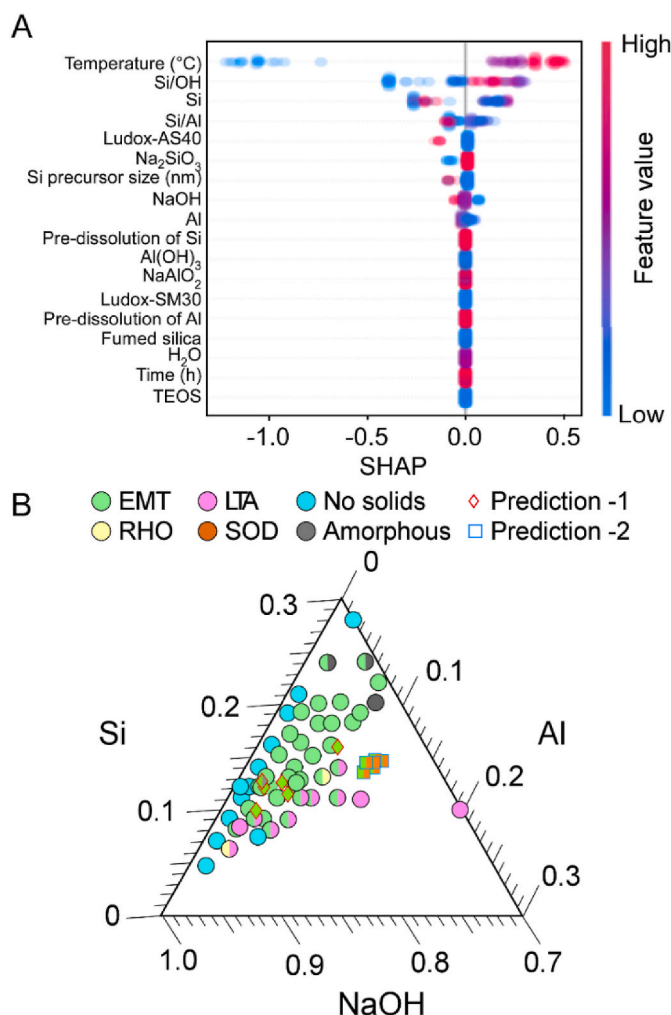


Fig. 10. Machine learning analysis of zeolite EMT phase behavior. (A) Importance of the synthesis parameters in controlling the formation of EMT, obtained via the SHAP (SHapley Additive exPlanations) analysis [57]. (B) Ternary phase diagram reproduced from Fig. 1A with new synthesis conditions proposed by machine learning where hypothetical zeolites were generated by combining synthesis parameters within (red highlighted diamonds) and beyond (blue highlighted squares) the range of the original dataset, which were then experimentally validated.

conditions in this domain resulted in the successful synthesis of pure EMT (red highlighted diamonds in Fig. 10B). In contrast, when exploring synthesis conditions away from the original dataset, corresponding to regions not previously probed, the model fails to make accurate predictions. None of the six proposed conditions in this unexplored domain produced pure EMT (blue highlighted squares in Fig. 10B).

These results indicate the limitations of ML – it is predictive within the original dataset range but not in unexplored synthesis regions where no training data exist; however, slightly beyond this range, the model demonstrates strong predictive power. Notably, the ML model correctly identified five out of six successful cases, including two with Si/Al ratios of 1.7 and 2.3, both below the 2.5 lower bound of the experimental dataset in Fig. 1A. This performance success rate of ~85% far exceeds the <33% success rate of our own domain-expertise-guided approaches in synthesizing pure zeolite EMT. A comprehensive analysis of the dataset, feature processing, and ML model comparisons is provided in a separate, ML-focused study [56] (see also the Methods section in the SI).

3. Conclusions

In summary, we used a combination of experimental design and machine learning to map the phase space of zeolite EMT and identify the most sensitive parameters influencing the synthesis of this highly metastable structure, respectively. The compositional range of organic-free media required to obtain pure zeolite EMT is significantly narrower than many other Na-zeolites. Here we showed that room temperature aging enables the preparation of zeolite EMT nanocrystals while also extending the timeframe for synthesis by reducing the rate of inter-zeolite transformation – an outcome that allows higher synthesis temperature to shorten crystallization times without sacrificing phase purity. This led to the identification of parameters that promote FAU/EMT intergrowths without the aid of an organic structure-directing agent. Moreover, the use of machine learning to expand the synthesis space of zeolite EMT highlighted the limitations of data analytics, which has become a major tool for the rational design of next-generation materials.

This study points to nonclassical pathways being the driving mechanisms for zeolite EMT crystallization through the formation of amorphous precursors, similar to processes observed for other zeolites. We leveraged unique high-temperature liquid AFM capabilities to explore EMT surface growth in supernatant solutions of varying silica supersaturation. Our findings revealed that surface growth occurs by the addition of soluble species, despite the presence of colloidal particles in the growth medium. Measurements at low and high supersaturation reveal the evolution of islands on EMT crystal surfaces by 2- and 3-dimensional spreading, respectively. Interestingly, the rates of island advancement do not lead to substantial out-of-plane (3D) growth, suggesting that the primary mode of EMT crystallization involves a disorder-to-order transition of amorphous precursors – notably, a process dominated by dynamic events in the solid state rather than the solution. This is consistent with elemental analysis showing that the overall composition of the supernatant solution is far from that of the final EMT crystalline product. This observation also aligns with growing evidence in the literature indicating that nonclassical nucleation and growth involving amorphous precursors are common pathways in zeolite syntheses.

Precisely controlling crystal growth mechanisms for the purpose of tailoring material properties is nontrivial, but does present opportunities to continue searching for versatile approaches to engineer zeolites for a broad range of commercial applications. For example, knowledge of nucleation pathways can be used to control key physicochemical properties, such as crystal size and morphology. Notably, the ultra-small crystal size of zeolite EMT makes this material a promising candidate for adsorption or catalytic applications, particularly in view of its similar topology to that of zeolite FAU, which is one of the most widely-used commercial catalysts. Analogous to zeolite FAU, conventional syntheses of zeolite EMT yield prohibitively low Si/Al ratios for their practical use as catalysts; thus, post-synthesis dealumination processes would be required to obtain more siliceous materials (with suitable hydrothermal stability) for catalytic applications, comparable to the protocols used to convert zeolite Y (FAU) into ultra-stable zeolite Y (USY), as a topic for future investigation.

CRedit authorship contribution statement

Zhiyin Niu: Writing – original draft, Investigation, Formal analysis, Conceptualization. **Emmanuel A. Olanrewaju:** Writing – original draft, Investigation, Data curation. **Taimin Yang:** Data curation. **Akhil Sree Kumar:** Writing – original draft, Investigation, Data curation. **Luke M. Tufaro:** Data curation. **Simon M. Vornholt:** Formal analysis, Data curation. **Chenfeng Huang:** Formal analysis, Data curation. **Jaeyul Kim:** Formal analysis, Data curation. **Santosh Adhikari:** Data curation. **Karena W. Chapman:** Writing – review & editing, Methodology, Formal analysis. **Jeremy C. Palmer:** Writing – review & editing,

Methodology. **Mingjian Wen:** Writing – review & editing, Supervision, Formal analysis. **Jeffrey D. Rimer:** Writing – original draft, Supervision, Resources, Project administration, Methodology, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2026.114399>.

Data availability

Data will be made available on request.

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