DEVELOPING ORGANIC FREE CRYSTALLIZATION PATHWAYS FOR THE OPTIMIZATION OF ZEOLITE CATALYSTS

by

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Dedicated to my babaji (wish you were here),

mummy and papa

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ABSTRACT

Zeolites are an essential class of crystalline porous materials with a wide range of applications. A core objective of optimizing zeolites is to produce materials with physicochemical properties and corresponding performances that exceed conventional counterparts. This places an impetus on elucidating and controlling processes of crystallization where one of the most critical design criteria is the ability to prepare zeolite crystals with ultrasmall dimensions to mitigate the deleterious effects of mass transport limitations. Zeolite crystallization predominantly occurs by nonclassical pathways involving the attachment of complex (alumino)silicate precursors to crystal surfaces, yet recurrent images of fully crystalline materials with layered surfaces comprised of nanometer-sized steps are evidence that growth also occurs by a classical route of molecule (monomer) attachment. Recent studies have shown that a controlled switch from nonclassical to classical pathways can alter the anisotropic rates of crystallization with concomitant impact on material properties that affect their performance in commercial applications; however, few studies identify conditions under which zeolites grow by a purely classical mechanism.

Seed-assisted approaches in zeolite synthesis differ from classical processes in that the seeds tend to dissolve, giving rise to an unknown memory of the parent crystal structure that facilitates the nucleation of the daughter. It has been hypothesized in literature that a shared structural feature, such as a composite building unit, between the parent and the crystals produced from a non-seeded growth solution results in identical parent-daughter framework types.

This Thesis focuses on how seed-assisted syntheses impact zeolite properties such as size, morphology, structure, and defects. We observe that the molar composition of the growth mixture and the properties of the seed crystals play a significant role in controlling the kinetics of nucleation and the trajectory of interzeolite transformations. Furthermore, we observe that seeds offer unique routes to achieve small crystal sizes and distinct morphologies in comparison to many conventional syntheses. Advantages of seeding include shorter synthesis time and the ability to reduce or eliminate the need for organic structure-directing agents, thereby providing a facile and efficient route to design zeolites for various industrial applications. The fundamental mechanisms underlying zeolite seed-assisted crystallization are complex and elusive; however, our study provides new insight into these processes and highlights the important role of kinetics in governing parent-daughter (or seed-product) relationships.

Furthermore, we use high temperature atomic force microscopy (AFM) to image zeolite crystal surface growth *in situ*. We report time-resolved images of 2-dimensional growth demonstrating layer generation by three distinct mechanisms, including nucleation from the edges of surface defects. Our findings reveal that silica nanoparticles in the growth medium incorporate into advancing steps on crystal surfaces to generate defects (i.e., amorphous silica occlusions) that largely go undetected in literature. *In situ* AFM measurements also show the dominance of gel mediated crystal growth in the case of faujasite zeolite syntheses.

Table of Contents

ACKNOWLEDGEMENTSi	v
ABSTRACT	V
List of Tables	X
List of Figuresx	i
Chapter 1 Prior work in zeolite crystal engineering	1
1.1 Introduction	1
1.2 Industrial applications of zeolites	2
1.2.1 Catalysis	4
1.2.2 Adsorption and separation	6
1.2.3 Ion exchange	7
1.3 Zeolite crystallization mechanisms: nucleation and crystal growth	7
1.3.1 Nucleation	8
1.3.2 Crystal growth	0
1.4 Synthetic chemistry of zeolites	2
1.5 Engineering porous architecture: hierarchical zeolites1	9
1.6 Dissertation outline	1
Chapter 2 Seed-assisted zeolite synthesis: the impact of seeding conditions and interzeolite transformations on crystal structure and morphology	4
2.1 Introduction2	4
2.2 Results and discussion2	8
2.2.1 Parent-daughter structural relationships2	8
2.2.2 Impact of seeds on crystal morphology	4
2.3 Conclusion	7
2.4 Experimental	8
2.4.1 Materials	8
2.4.2 Synthesis of seed crystals	9
2.4.3 Seeded zeolite synthesis	0
2.4.4 Characterization	0
Chapter 3 Organic-free interzeolite transformation in the absence of common building units4	1
3.1 Introduction4	1
3.2 Results and discussion	3
3.3 Conclusion	0
3.4 Experimental5	1
3.4.1 Materials	1

3.4.2 Zeolite crystallization	51
3.4.3 Materials characterization	52
Chapter 4 Spontaneous pillaring of pentasil zeolites	53
4.1 Introduction	53
4.2 Results and discussion	54
4.3 Conclusion	62
4.4 Experimental	63
4.4.1 Materials	63
4.4.2 Synthesis of seed crystals	63
4.4.3 Self-pillared pentasil synthesis	64
4.4.4 Synthesis of conventional ZSM-5 catalyst	64
4.4.5 Characterization	64
4.4.6 Catalytic measurements	66
Chapter 5 In situ imaging of 2-dimensional surface growth reveals the prevalence and defects in zeolite crystallization	1d role of 68
5.1 Introduction	68
5.2 Results and discussion	71
5.2.1 Conditions for layered surface growth	71
5.2.2 Role of surface defects in 2d layered growth	74
5.2.3 Conclusions	79
5.3 Experimental	80
5.3.1 Materials	80
5.3.2 Synthesis of zeolite substrates	81
5.3.3 Preparation of zeolite growth solutions	81
5.3.4 Atomic force microscopy	82
5.3.5 Nuclear magnetic resonance (NMR) spectroscopy	82
5.3.6 Additional characterization	83
Chapter 6 In situ investigation of FAU crystallization	84
6.1 Introduction	84
6.2 Results and discussion	86
6.2.1 Role of aluminum in FAU surface growth	90
6.2.2 Comparison using bulk syntheses	91
6.3 Conclusion	93
6.4 Experimental	94
6.4.1 Materials	94

6.4.2 Synthesis of zeolite substrates	94
6.4.3 Preparation of zeolite growth solutions	94
6.4.4 Atomic force microscopy	95
6.4.5 Additional characterization	96
Chapter 7 Summary and future outlook	97
References	
Appendix A	153
Appendix B	167
Appendix C	173
Appendix D	180
Appendix E	

List of Tables

Table 2.1 Molar composition of growth solutions and synthesis temperatures	29
Table 3.1 Synthesis compositions used in seeded and non-seeded protocols	44
Table 4.1 Physicochemical properties of H-form zeolite samples.	54
Table A.1 Synthesis parameters and references for the ternary (kinetic) phase diagram in	n Figure
S1	165
Table D.1 Elemental analysis of growth solutions using ICP-OES.	187

List of Figures

Figure 1.1 (A) LTA crystal structure with composite building units <i>sod</i> , <i>d4r</i> , <i>and lta</i> . (B) Representation of medium and large pores present in zeolite structures. (C) Examples of one- two- and three-dimensional zeolites
Figure 1.2 Zeolites used commercially are highlighted (adapted from Refs ^{24, 25}). Zeolites highlighted by blue are primarily used in catalytic applications, whereas zeolites highlighted by red mainly have applications in detergency or adsorption/ separation3
Figure 1.3 Applications of zeolitic materials in oil refining processes. Green color indicates zeolite- based processes. Adapted from Ref ²⁸
Figure 1.4 (A) General energetic landscape as a function of nucleation progress showing classical and nonclassical nucleation. (B) Potential pathways for zeolite nucleation. (C) Kossel model of a crystal surface. (D) Mechanisms of growth as a function of supersaturation.
Figure 1.5 Diverse modes of zeolite A crystallization involving nonclassical (top) and classical layered (bottom) growth pathways ¹⁰⁹
Figure 1.6 (A) Aspects of the synthetic transition of boron beta zeolite to B-SSZ-24 ²²¹ . (B) Impact of seed content on ZSM-5 product Si/Al ratio and crystal size ²⁰² . (C-D) Use of FAU in IZT for (C) metal encapsulation and (D) phosphorous insertion
Figure 1.7 (A) Effectiveness factor as a function of Thiele modulus. At low effectiveness factors only a small portion of the crystal is efficiently utilized during the reaction. (B) Schematic representation of different nanosized zeolites and hierarchical zeolites ²⁴⁷ 20
Figure 2.1 (A) Interzeolite transformations (B) Seeded growth. Comparisons of disparate parent- daughter structures can be made on the basis of shared composite building units or rings of the zeolite frameworks
Figure 2.2 (top) Comparison of four framework types with molar volumes V of 35.4, 32.7, 34.6, and 33.1 cm ³ mol ⁻¹ , respectively. (bottom) Composite building units (CBUs) with dashed boxes indicating commonalities among the four frameworks. Data from IZA ²²
Figure 2.3 Ternary (kinetic) phase diagram with growth solutions S1, S2 and S3 (grey circles). For more information refer Figure A .1 and Table A.1
 Figure 2.4 Products obtained using (A) MEL and (B) MFI seeds in growth solutions S1 (left) and S2 (right). (C and D) Time-elapsed PXRD patterns using (C) silicalite-2 (MEL, Si/Al = ∞) and (D) ZSM-5 (Si/Al = 14) seeds in growth solution S1 and S2 respectively32
Figure 2.5 Seed-assisted syntheses using ZSM-12 (MTW) seeds. (A) Time-elapsed PXRD patterns in growth solution S2. (B and C) SEM images of products obtained after (B) 1 day and (C) 10 days of synthesis (scale bars = 5 μm). (D) Products in solutions S1 (left) and S2 (right)
Figure 2.6 SEM images of (A – C) Mordenite and (D - F) ZSM-5 crystals prepared from solution S1 and S3 respectively (A, D) without seeds (B, E) with silicalite-2 (MEL) seeds (C, F) with mordenite (MOR) seeds
Figure 2.7 SEM images of ZSM-5 crystals prepared with (A) 2 wt% and (B) 13 wt% silicalite-2
seeds in solution S3 (scale bars = 2 μ m). Insets: high mag. images. (C) Average Si/Al ratio of products (blue circles), and the average crystal size (red diamonds)
Figure 3.1 Ternary (kinetic) phase diagram with organic-free growth mixtures S1 – S3 (yellow diamonds) corresponding to the compositions listed in Table 3.1 . Inset: Enlarged grey region with reported compositions for MFI (red) and MOR (blue) synthesis

Figure 3.2 Powder X-ray diffraction patterns of solids extracted from growth mixture S2 (prepared with USY) reveals the temporal evolution of amorphous and crystalline (MFI, MOR, and Figure 3.3 (top) Stages of zeolite phase transformation with increasing synthesis time. The molar volumes for each zeolite were obtained from the IZA²². (bottom) Composite building Figure 3.4 SEM images of (A) parent USY (CBV760) zeolite and solids extracted from growth mixture S2 (using USY as the sole source of Si and Al) at different time intervals. Three distinct morphologies in D are labelled as i - iii. Scale bars are equal to 5 μ m unless Figure 3.5 (A-C) TEM selected area electron diffraction patterns of crystals in a 48 h sample indexed to (A) MOR, (B) MFI, and (C) quartz (corresponding TEM images are provided Figure 3.6 SEM image of ZSM-5 crystals prepared from (A) a FAU-to-MFI IZT (B) colloidal silica and sodium aluminate (in replacement of USY) with intergrowths on (010) surfaces Figure 4.1 (A) Time-resolved PXRD patterns for the synthesis of SPP1 using silicalite-2 (MEL) seeds. SEM images of (B) silicalite-2 seeds and the (C) SPP1 product after 3 days of seeded growth. (D) High magnification of FE-SEM image of a SPP1 crystal......55 Figure 4.2 (A) TEM image revealing individual sheets of SPP1 with ED pattern (inset). (B) TEM image of ultra-microtomed SPP1 showing and (D) corresponding corresponding FFT ED pattern. (D) HRTEM image of the yellow box in F with an overlaid MFI structure.....55 Figure 4.3 (A - C) FE-SEM images of solids extracted from a SPP1 synthesis at the following times: (A) 1, (B, D, E) 2, and (C) 3 days. (F) Idealized schematic of heterogeneous Figure 4.4 (A) Percent crystallinity as a function of synthesis time measured from PXRD patterns. Figure 4.5 FE-SEM and TEM images from the (A-C) SPP2 synthesis using ZSM-11 seeds (D-F) SPP3 synthesis using silicalite-1 seeds (G-I) SPP4 synthesis using ZSM-5 seeds after 3 Figure 4.6 (A) Friedel craft alkylation reaction used as a model liquid phase reaction. (B) Benzyl alcohol conversion during Friedel craft alkylation reaction (C) Selectivity of the Figure 4.7 (A) Sub-complete methanol conversion in the MTH reaction at 350 °C. (B) Turnover number (histogram, left axis) estimated between 50 to 30% conversion and the ethene-Figure 5.1 (A) Diverse modes of zeolite A crystallization. (B) Structure and composite building units (CBUs) of zeolite A (LTA). (C-D) AFM images reveal three types of layers on crystal surfaces. (F and G) Time-elapsed AFM images in TMA⁺. All scale bars 400 nm. Figure 5.2 (A) Time-elapsed AFM images of layers advancing from a screw dislocation. Illustration of (B) spiral growth from a screw dislocation (C) 2D nucleation and spreading. (D - F)Time-elapsed AFM images showing 2D nucleation and layer propagation......74 Figure 5.3 (A) Low magnification AFM image showing multiple hillocks with type I defects at each apex (arrows). (B - E) Time-elapsed AFM images of the region in panel A (dashed white box) during zeolite A growth ($\sigma = 0.6$) with schematic below. Scale bars 500 nm.

Figure 5.4 (A) AFM image of zeolite A crystal surface during growth in a solution prepared with colloidal silica ($\sigma = 0.6$). Inset: high resolution image of a faceted type I protrusion. (B) Statistical analysis of the heights for type I and II features (blue and red, respectively).

Figure A.1 Ternary (kinetic) phase diagram of growth mixture compositions reported in literature for MEL, MFI, MOR, and MTW syntheses corresponding to the regions depicted in Figure 2.3. The numbers correspond to molar compositions provided in Table A.1..154
 Figure A.2 Powder X-ray diffraction (XRD) patterns for MEL seeds with Si/Al ratios of (A) ∞, (B)

- Figure A.5 (A C) Representative SEM images of MEL seeds with Si/Al ratios of (A) ∞, (B) 35, and (C) 16. (D) SEM image of MTW seeds. (E G) Representative SEM images of MFI seeds with Si/Al ratios of (E) ∞, (F) 40, and (G) 14. (H) SEM image of MOR seeds. 156
 Figure A.6 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-11 seeds (Si/Al ratio = 16) in MOR growth solutions (A) S1 and (B) S2.
 Figure A.7 Time-elapsed powder XRD patterns for the products obtained at different time intervals

Figure A.9 Time-elapsed powder XRD patterns for the products obtained at different time intervals
by introducing ZSM-5 seeds (Si/Al ratio 14) in MOR growth solution S1
Figure A.10 Time-elapsed powder XRD patterns for the products obtained at different time
intervals by introducing ZSM-5 seeds (Si/Al ratio = 40) in MOR growth solutions (A)
S1 and (B) S2
Figure A.11 Time-elapsed powder XRD patterns for the products obtained at different time
intervals by introducing silicalite-1 (MFI) seeds in MOR growth solutions (A) S1 and
(B) S2
Figure A.12 SEM images of products obtained from solution S1 with (A – D) ZSM-11 seeds (SAR
= 16) (E-H) ZSM-11 seeds (SAR = 35) (I-L) silicalite-2 seeds at synthesis times: (A.E.I)
1day, (B.F.J) 3 days, (C.G.K) 6 days, and (DH.L) 10 days,
Figure A.13 SEM images of products obtained from solution S2 with $(A - D)$ ZSM-11 seeds (SAR
= 16) (E-H) ZSM-11 seeds (SAR = 35) (I-L) silicalite-2 seeds at synthesis times: (A.E.I)
1 day, (B.F.J) 3 days, (C.G.K) 6 days, and (DH.L) 10 days,
Figure A 14 SEM images of products obtained from solution S1 with $(A - D)$ ZSM-5 seeds (SAR
= 14) (E-H) ZSM-5 seeds (SAR = 40) (I-L) silicalite-1 seeds at synthesis times: (A.E.I)
1 day, (B.F.J.) 3 days, (C.G.K.) 6 days, and (DH.L.) 10 days,
Figure A.15 SEM images of products obtained from solution S2 with $(A - D)$ ZSM-5 seeds (SAR
= 14 (F-H) ZSM-5 seeds (SAR = 40) (I-L) silicalite-1 seeds at synthesis times: (A E I)
1 (B, F,J) = 3 days. (C.G.K) 6 days, and (DH.L) 10 days
Figure A 16 Time-elapsed powder XRD patterns for the products obtained at different time
intervals by introducing ZSM-12 seeds (Si/Al = 30) in MOR growth solution S1 164
Figure A 17 Representative SEM images of products obtained with ZSM-12 seeds (SAR 30) in
MOR growth solution S1 (A B C D) and MOR growth solution S2 (E F G H) at the
following synthesis times (from left to right): 1 day 3 days 6 days and 10 days 164
Figure A 18 Time-elansed powder X-ray diffraction patterns for the product(s) obtained seeded
growth in solution S1 using silicalite-2 seeds at (A) 130°C and (B) 170°C 165
Figure B 1 Ternary (kinetic) phase diagram of growth mixture compositions reported in literature
for MFI and MOR syntheses corresponding to labelled points in the inset of Figure 3.1
in the manuscript. The numbers corresponding to incorrespond to compositions provided in Table A 1, 168
Figure B 2(A) PXRD patterns of solids extracted from the growth mixture S2 using USY as the
silica source (B) Reference powder XRD patterns for MFI and MOR obtained from the
IZA^{22} A reference pattern for quartz was obtained from RRUEE project database ³⁶⁹
169
Figure B 3 Powder X-ray diffraction (XRD) patterns of solids extracted from growth mixture \$2
using colloidal silica (SM30) as the silica source after 24 h 32 h 48 h 72 h and 8 d of
hydrotharmal tractment at 100%
Figure P 4 Identification of (A) more anite (P) 7SM 5 and (C) quest z in the solids extracted from
Figure D.4 Identification of (A) moldenite, (D) ZSM-5, and (C) quartz in the solids extracted from
growth mixture S2 (using US1 as the sole source of S1 and A1) after 48 if of hydrotherman
Figure 190°C by transmission electron microscopy
Figure B.5 Scanning electron micrograph of solids extracted from growth mixture S2 using USY
as the sole source of S1 and A1. This image corresponds to a sample heated for 16 h at
$\frac{190^{\circ}\text{U}}{1}$
Figure B.6 Identification of (A) mordenite (MOR), (B) ZSM-5 (MFI), and (C) quartz in the solids
extracted from growth mixture S2 (using USY as the sole source of S1 and AI) after 48 h
of hydrothermal treatment at 190°C by Raman spectroscopy

Figure B.7 Scanning electron micrograph of solids extracted from growth mixture S2 using colloidal silica (SM30) as the Si source. This image corresponds to a sample heated for Figure C.1 Ternary (kinetic) phase diagram with MOR growth solution (blue circle). The orange and blue shaded regions depict approximate compositional regions reported in literature for syntheses of pentasil zeolites......174 Figure C.2 Nitrogen adsorption/desorption isotherms at 77 K for SPP samples synthesized with different seeds (refer to Table 1) and conventional ZSM-5......174 Figure C.3 (A) PXRD pattern and (B) SEM image of the product obtained after 15 h of heating extracted from SPP1 growth mixture. TEM images of solids extracted from a (C) SPP1 Figure C.4 HRTEM image of the precursor extracted at 1 day of hydrothermal treatment from Figure C.5 TEM images for (A) SPP1 synthesis after 2 days of treatment; (B) SPP2 synthesis after 1 day; (C) SPP3 synthesis after 1 day; and (D) SPP4 synthesis after 3 days. Scale bars 500nm and 100 nm in the low and high mag respectively. (A1-D1) SAED analyses of Figure C.6 (A) PXRD patterns of the solids extracted at times spanning from 4 to 10 days. Peaks corresponding to zeolite MOR are marked with asterisks (*). (B and C) Representative SEM images of solids extracted after (B) 4 days and (C) 10 days.....177 Figure C.7 (A) Powder XRD pattern and (B) SEM image of mordenite crystals prepared using Figure C.8 Percent crystallinity as a function of synthesis time for SPP2 (solid circles) and SPP3 Figure C.9 FE-SEM images of SPP3 crystals showing the high degree of aggregation. Scale bar Figure C.10 (A) Average nanosheet thickness y and (B) average bulk crystal size x measured for 25 crystals in a single batch. Error bars span two standard deviations. Insets: schematics defining dimensions y and x.....179 Figure C.11(A) Powder XRD pattern and (B) SEM image of the conventional ZSM-5 catalyst Figure C.12 Selectivity of hydrocarbon products obtained in the MTH reaction (assessed at ca. 40% conversion) with different H-form SPP and conventional ZSM-5 catalysts......180 Figure D.1 Comparison of <100> step velocities during in situ measurements of layer advancement at 50 °C. The steps correspond to 2D layers, spiral dislocations, and hillocks emanating Figure D.2 Zeolite A growth in the presence of TMA⁺ ($\sigma = 2.7$). Time-elapsed AFM images after (A) 1 h and (B) 3 h (C) increased scan size after 3 h of growth showing the area of Figure D.3 (A) Liquid ²⁷Al NMR spectra of a zeolite A growth solution at various temperatures (20 -65 °C). (B) Comparison of monomer ($\delta = 80$ ppm) peak areas for the zeolite A growth solution with Na⁺ (blue circles), and a sodium aluminate as control (red squares).182 Figure D.4 Statistical analysis of 2D island radii that (A) dissolve and (B) grow during continuous imaging. From the assessment of AFM images, island dissolution and growth are both Figure D.5 AFM images in solution C2 ($\sigma = 0.6$) with sodium silicate as the silica source. Snapshots in selected areas A1, A2, and A3 highlight the dynamics of surface growth with

Figure D.6 AFM images in solution prepared with different silica sources: (A-C) Colloidal silica (D-F) TEOS and (G-H) Fumed silica. The solution with colloidal silica was prepared by dissolving colloidal silica in an alkaline solution prior to the addition of alumina.184

Figure D.7 AFM images in solution C2 (σ = 0.6) prepared with colloidal silica. Snapshots in selected areas A1, A2, and A3 highlight the dynamics of surface growth with increasing imaging time (total imaging time = 270 min). The scale bar equals 500 nm......185
Figure D.8 (A) PXRD pattern and (B) SEM image of solids extracted from a TMA⁺-containing

Figure E.1 Powder XRD patterns of parent FAAU crystals, crystals heated in solution 1 with Si/Al ratio 2 at 70°C for 3 hours, and solution heated at same conditions with FAU crystals. 188
Figure E.2 AFM images of crystal surface heated in solution (A-B) 1 and (C-D) 4 at 60°C. All scale

Chapter 1 Prior work in zeolite crystal engineering

1.1 Introduction

Zeolites are crystalline microporous materials with well-defined pore structures on the molecular scale¹. Zeolites were first described by Swedish chemist Axel Cronstedt in 1756^{2, 3} when he observed a mineral appear to be boiled on heating. Hence, he coined the term "zeolite" which means "boiling stone" in Greek^{4,5}. Two centuries later, the first synthetic zeolite was reported by Richard Barrer in 1940s. He utilized natural zeolites leucite and analcime to synthesize chabazite in the presence of barium chloride under hydrothermal conditions⁶. Later he reported zeolite synthesis directly from silica and alumina sources⁷. Later in the 1950s, researchers at Union Carbide began studies on zeolite synthesis from aluminosilicate gels. This led to the discovery of two of the most industrially important zeolites, LTA and FAU⁸⁻¹⁰. Zeolite A (LTA) was mainly utilized in ion exchange and gas separation while faujasite (FAU) with a higher Si/Al ratio was found to be an effective cracking catalyst for the conversion crude oil distillates to gasoline products¹¹⁻¹³. In subsequent discoveries organic molecules began to be utilized as structure-directing agents (SDAs) as a substitute for inorganics, which led to the discovery of high silica zeolites: beta (BEA)¹⁴ and ZSM-5 (MFI)¹⁵ using the organics tetraethylammonium (TEA⁺) and tetrapropylammonium (TPA^{+}) , respectively. Currently there are around 250 zeolite framework types that have been realized and utilized in different industrial applications as discussed later. In 1982, the synthesis of a new family of aluminophosphate molecular sieves, zeotypes designated as A1PO₄-n, was reported by Union Carbide¹⁶⁻¹⁸. The discovery of the aluminophosphate family of molecular sieves greatly expanded the structural diversity of zeolites and zeotypes. Not only that the main framework elements were not limited to A1 and Si atoms, and the upper limit of pore size exceeded the previous limit of 12 rings¹⁹⁻²¹. Each zeolite framework is assigned a three-letter code by international zeolite association (IZA)²².

The basic building units of zeolites are tetrahedra (TO₄, where T: Si, Al, B, Ga, Fe, Zn, Ge, P, etc.) which are connected through apical oxygens. Different arrangements of these tetrahedra in three-dimensional space leads to different zeolite frameworks. Zeolite crystal structures can be deconstructed into different building units at different levels. At a basic level are composite building units (CBUs) (Figure 1.1A). Many zeolite structures share the same set of CBUs. This has been basis of hypotheses to explain interzeolite transformations, as discussed in Chapter 2. Many CBUs are rings constructed by connecting multiple tetrahedra and defined by the number of tetrahedra units present (e.g., 4, 5, 6, 8,10, or 12 membered rings). Pore dimension is an essential property of zeolites and can be a deciding factor in industrial applications, such as separations and catalysis. Zeolites containing pores formed by 8-, 10-, and 12-membered rings are called small, medium, and large pores, respectively. Extra-large pores consist of rings with 14 or more T atoms or tetrahedral units (Figure 1.1B). Arrangement of these rings can lead to formation of cages whose larger rings are too narrow to allow transport of any molecule larger than water. Another polyhedral structure that can be formed is a cavity which, unlike cages, allows passage of molecules. Channels are pores that extend infinitely in one direction. Many zeolites consist of multi-dimensional channel systems, formed by the intersection of channels (Figure 1.1C).



Figure 1.1 (A) LTA crystal structure with composite building units *sod*, *d4r*, *and lta*. (B) Representation of medium and large pores present in zeolite structures. (C) Examples of one-, two-, and three-dimensional zeolites.

1.2 Industrial applications of zeolites

Ever since their discovery, zeolites have found different industrial applications. Some features of these microporous materials responsible for their widespread industrial application are:

(i) wide range of composition, (ii) tunable acidity/basicity, (ii) high thermal stability, (iii) multidimensional pore structure, (iv) high surface area, and (v) non-corrosive and non-toxic^{23, 24}.

Zeolites recognized by International Zeolite Association (IZA)											
ABW	ACO	AEI	AEL	AEN	AET	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFV	AFX	AFY	AHT	ANA	ANO	APC	APD	AST	ASV	ATN
ATO	ATS	ATT	ATV	AVE	AVL	AWO	AWW	BCT	BEA	BEC	BIK
BOF	BOG	BOZ	BPH	BRE	BSV	CAN	CAS	CDO	CFI	CGF	CGS
CGF	CGS	CHA	-CHI	-CLO	CON	CSV	CTH	CZP	DAC	DDR	DFO
DFT	DOH	DON	EAB	EDI	EEI	EMT	EON	EPI	ERI	ESV	ETL
ETR	ETV	EUO	EWO	EWS	-EWT	EZT	FAR	FAU	FER	FRA	GIS
GIU	GME	GON	G00	HEU	IFO	IFR	-IFT	-IFU	IFW	IFY	IHW
IMF	IRN	IRR	-IRY	ISV	ITE	ITG	ITH	-ITN	ITR	ITT	-ITV
ITW	IWR	IWS	IWV	IWW	JBW	JNT	JOZ	JRY	JSN	JSR	JST
JSW	KFI	LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTF	LTJ	LTL
LTN	MAR	MAZ	MEI	MEL	MEP	MER	MFI	MFS	MON	MOR	MOZ
MRE	MRT	MSE	MSO	MTF	MTN	MTT	MTW	MVY	MWF	MWW	NAB
NAT	NES	NON	NPO	NPT	NSI	OBW	OFF	ОКО	OSI	OSO	OWE
-PAR	PAU	PCR	PCS	PHI	PON	POR	POS	PSI	PTO	PTT	PTY
PUN	PWN	PWO	PWW	RHO	-RON	RRO	RSN	RTE	RTH	RUT	RWR
RWY	SAF	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SEW	SFE
SFF	SFG	SFH	SFN	SFO	SFS	SFV	SFW	SGT	SIV	SOD	SOF
SOR	SOS	SOV	SSF	-SSO	SSY	STF	STI	STO	STT	STW	-SVR
SVV	-SVY	SWY	-SYT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI
UFI	UOE	UOS	UOV	UOZ	USI	UTL	UWY	VET	VFI	VNI	VSV
WEI	-WEN	YFI	YUG	ZON							

Figure 1.2 Zeolites used commercially are highlighted (adapted from Refs ^{24, 25}). Zeolites highlighted by blue are primarily used in catalytic applications, whereas zeolites highlighted by red mainly have applications in detergency or adsorption/ separation.

The global market for synthetic zeolites is estimated at US\$4.5 billion in the year 2020 and is projected to reach US\$5.2 billion by 2026, growing at an annual rate of 2.7% over this period²⁶. Moreover, natural zeolites are also widely used but predominantly as commodities for low value/large scale applications and are used as animal feed, odor control, water purification, oil and grease absorbent, unclassified end uses, fertilizer carrier, gas absorbent (and air filtration), pet litter, desiccant, wastewater treatment, soil amendment, traction control (ice melt), synthetic turf, aquaculture, and fungicide or pesticide carrier²⁷. In the United States in 2017, sales of natural zeolites increased by 14% to 81,300 metric tons as compared to 71,300 metric tons in 2016, while worldwide production remained constant at around 1 million metric tons during the same time period²⁷. Out of the 250 frameworks synthesized, 17 are of commercial interest and only five of

these are produced in significant amounts for catalytic applications²⁸ (**Figure** 1.2). Their application can be broadly classified into three main categories: catalysis, adsorption and separation, and ion exchange.

1.2.1 Catalysis

In the global market of synthetic zeolites, catalysts hold the highest percentage (value basis). The majority of the base chemicals that constitute our daily consumer goods and energy carriers like transportation fuels have passed through these molecular sieves²⁹. Some zeolite structures, mainly MFI and FAU and to a minor extent MOR, are versatile materials, i.e., their properties can be tuned to the specific requirements of different industrial applications. **Figure 1**.3 highlights the processes in oil refineries that utilize zeolites as catalysts; however, the largest fraction of zeolite catalysts is used in fluid catalytic cracking (FCC) and hydrocracking (HDC)^{24, 30, 31}. FCC is mainly a gasoline making process, and HDC is mainly a middle distillate making process. Both processes utilize zeolite Y (FAU) as the main catalyst³²⁻³⁵. The economic impact of zeolite catalysts can be easily understood in view of their higher activity and selectivity towards gasoline as compared to previous generation catalysts (i.e., amorphous silica and alumina) that led to the increase in the gasoline yield while reduction in FCC units³⁶.



Figure 1.3 Applications of zeolitic materials in oil refining processes. Green color indicates zeolitebased processes. Adapted from Ref ²⁸.

Zeolites have also been utilized in methanol to olefin (MTO) and methanol to gasoline (MTG) processes for converting methanol directly to commercial chemical commodities³⁷. It is an essential process as the main raw material, methanol, can be produced from alternate carbon sources such as biomass, coal, and natural gas. The first MTG process was commercialized in 1985 by Mobil corporation³⁸. The world's first MTO unit was constructed, and operation started in August 2010 in Baotou, China. It was based on MTO technology developed at Dalian Institute of Chemical Physics (DICP), China^{39, 40}. This process utilized SAPO-34 (CHA) as a catalyst due to its small pore openings, medium acidity, and high thermal/hydrothermal stability^{41, 42}.

Zeolites have also been proposed as active catalysts in the removal of NOx from car exhaust gas using selective catalytic reduction in the presence of NH₃^{43, 44}. NOx causes acid rain and is a major component in highly toxic smog. To meet the current emission control requirements from governments around the world, zeolite catalysts are seemingly a viable option to replace outdated two-way exhaust catalysts consisting of metals such as platinum, palladium, and rhodium supported on a metal oxide⁴⁵. With initial research started on medium- and large-pore zeolites such

as ZSM-5 (MFI)⁴⁶⁻⁴⁹, mordenite (MOR)^{50, 51}, zeolite Y (FAU)⁵², and beta (BEA)⁵³, it was the smallpore chabazite (CHA) that was a breakthrough in obtaining high NOx reduction efficiency with excellent activity at low temperature and high durability to harsh hydrothermal conditions⁵⁴⁻⁵⁶.

1.2.2 Adsorption and separation

Zeolites are excellent adsorbents due to their inherent molecular sieving effect. They have found an important place in separation technologies due to their tunable pore architecture with different extra-framework species and crystal sizes^{57, 58}. They provide energy efficient options for separation and purification which are as less energy intensive as compared to traditional separation processes such as distillation, evaporation, and drying⁵⁹. Zeolites are used for O₂ and N₂ production from air, drying industrial gases, alcohol dehydration, hydrocarbon isomer separation, N₂/CH₄ separation, H₂ production from reforming and refinery off-gas, desalination, and water purification⁶⁰⁻⁶³.

Several zeolite frameworks have been tested for the fabrication of membranes including zeolite A, mordenite, ferrierite, ZSM-11, ZSM-5, SAPO-34, and chabazite, among others⁶⁴. To date only zeolite A membranes have been commercialized for the dehydration of solvents^{65, 66}. Recently, pure silica zeolite ITQ-55 showed high selectivity towards ethylene for its separation from ethane, owing to its distinctive pore topology with large heart-shaped cages and framework flexibility⁶⁷. It was projected to cut the amount of energy used to purify ethylene by 25%⁶⁸. Zeolites are also modified with different species such as Zeolitic imidazolate frameworks (ZIFs) and extra-framework species to improve upon their separation efficiency⁶⁹. MFI type zeolites have been well studied for the separation of xylene isomers, which is an important factor in the economics of p-xylene production. MFI nanosheets with few nanometers thickness have been fabricated and tested to exhibit high p-xylene selectivity⁷⁰⁻⁷². One of the remaining challenges in this area of research is to increase the mass transfer of xylenes while maintaining the selectivities.

1.2.3 Ion exchange

Zeolites are quintessential ion exchange materials. Owing to their negatively charged aluminosilicate framework, they can accommodate alkali and alkaline earth metals. Moreover, large molecules such as ammonia, water, and nitrate ions can reside inside the channels and cavities of zeolites⁷³. The largest percentage of zeolite applications is in detergency where they are used as water softeners to remove magnesium and calcium through ion exchange⁷⁴. They have emerged as ideal alternatives to phosphates used in detergent formulations wherein the environmentally safe attribute of zeolites is leading to their growing use in phosphate-free detergents. It is estimated that the global zeolite detergent market is valued at US\$ 1.8 billion in 2018 and is expected to reach US\$ 2 billion by 2028. Although several zeolite frameworks have been tested as water softeners, zeolite A (LTA) is typically used for commercial applications in conjunction with zeolite X (FAU). In the 1950s, natural zeolites such as clinoptilolite gained widespread attention in radioactive waste applications. It was shown to be effective in removing ⁹⁰Sr²⁺ and ¹³⁷Cs⁺ from process wastewaters^{75,} 76 . Due to their high selectivities, zeolites can adsorb radioactive cations from solutions even at lower concentration and in the presence of competing cationic species. Another major application of zeolites is the treatment of municipal and agricultural wastewater, wherein both natural and synthetic zeolites have been tested for the removal of ammonia and ammonium⁷⁷. Examples include zeolite W (MER), zeolite F (KFI), and clinoptilolite (HEU). Recent findings have shown that zeolites ion-exchanged with inexpensive transition metals are ideal materials for antimicrobial applications⁷⁸. Ion-exchange properties of zeolites can be exploited for a variety of biochemical processes and have the potential to facilitate significant advances in biology, medicine, and the pharmaceutical industry in the near future⁷⁹.

1.3 Zeolite crystallization mechanisms: nucleation and crystal growth

Zeolites are thermodynamically metastable phases relative to nonporous phases (e.g., quartz). Thus, progressive transformation to more stable phases often occurs with prolonged hydrothermal treatment⁸⁰. Calorimetric studies based on all silica zeolites have demonstrated that the enthalpies of formation ΔH_f for zeolites exhibit an approximately linear relationship with framework molar volume or framework density; however, there is very little difference in ΔH_f among framework types (i.e., values differ by less than 10 kJ/mol)^{81, 82}. Thus, kinetic factors are important when considering zeolite formation^{83, 84}. Indeed, the kinetics of crystallization determines the physicochemical properties of the final crystal product such as its structure (polymorph), crystal size, morphology, and composition⁸⁵⁻⁸⁸. Furthermore, there are hundreds of thousands of theoretically predicted zeolite structures that are thermodynamically possible⁸⁹; however, only ca. 250 structures have been synthetically realized. In that respect, it is essential to understand the underlying mechanisms and peer into the "black box" of zeolite crystallization to optimize the final zeolite crystals as well as bridge the gap between hypothetical and synthesized zeolite structures.

1.3.1 Nucleation

Nucleation is a complex phenomenon and probing atomistic level events at time scales under realistic experimental conditions for some systems remains a challenge⁹⁰. Complex systems such as proteins, colloids, biominerals and zeolites have been demonstrated to deviate from classical nucleation theory $(CNT)^{91, 92}$. According to CNT, crystal formation is driven by the difference in the Gibbs free energy which is dependent on the gain in the surface free energy (ΔG_s) and loss in the free energy (ΔG_v) by the formation of an initial crystal cluster (nucleus). Thus, for a growth to take place, clusters should have a critical radius (R_c), overcoming the energy barrier (ΔG_c) (**Figure** 1.4**A**). The major limitation of CNT is that it fails to describe or overestimates the nucleation rate in many cases. These limitations can be overcome by a two-step mechanism. According to this mechanism, small clusters first densify to form a metastable phase, which is followed by structural ordering and thus, the formation of a nucleus (**Figure** 1.4**A**)⁹³. Notably, the formation of initial clusters is considered stochastic by nature.



Figure 1.4 (A) General energetic landscape as a function of nucleation progress showing classical and nonclassical nucleation. (B) Potential pathways for zeolite nucleation. (C) Kossel model of a crystal surface. (D) Mechanisms of growth as a function of supersaturation.

Zeolite nucleation has been shown to occur through various mechanisms (**Figure 1.4B**)⁹⁴. ⁹⁵. Nucleation can occur through monomer addition followed by layer-by-layer growth; amorphous precursors can aggregate to form primary aggregates which densify further and result in secondary amorphous aggregates followed by crystallization to final zeolite structure;⁹⁶⁻⁹⁹ and alternatively, nucleation can occur by agglomeration of the initial amorphous precursors to small particles wherein nucleation occurs at either the interior or outer surface of these amorphous particles¹⁰⁰⁻¹⁰². For nucleation inside the gel, it has been observed to occur within gel cavities where a liquid phase is present followed by reorganization at the solid/liquid interface leading to zeolite crystallization¹⁰³. Furthermore, nucleation by aggregation of amorphous gel particles or nanoparticles has also been observed¹⁰⁴⁻¹⁰⁶. One reasoning for the nucleation to occur at the interface is the high density of these gels which hinder the material transport and thus nucleation can only take place either at the outer surface of these amorphous precursors (or in the voids present inside gel particles)¹⁰⁷. The major factors controlling these different pathways are still inconclusive.

A distinct feature of zeolite nucleation is the presence of diverse precursors in the growth solution such as monomers, oligomers, clusters/gels, and amorphous particles¹⁰⁸. The exact physical state of precursors in most zeolite syntheses is unknown. This is due to the fact that these precursors undergo compositional and structural changes during synthesis, which is oftentimes obscured by categorizing these precursors as generally "amorphous" without taking into account subtle differences in local order. Moreover, the nature of these precursors is highly dependent on the synthesis conditions such as sources of silica and alumina utilized^{109, 110}.

1.3.2 Crystal growth

Zeolite crystal growth has been shown to occur two pathways: classical and non-classical^{111,112}. In classical growth mechanism, growth occurs by the addition of monomers from solution to the crystal surface. Three common sites for monomer addition are illustrated by a Kossel crystal model system: kinks, steps, and terraces (**Figure 1.4C**)^{113,114}. Monomer incorporation into a kink site is the most energetically favorable due to the formation of three monomer–crystal bonds (compared to two bonds for steps and a single bond for terraces). Moreover, monomer attachment to a kink regenerates the kink, and does not change the surface free energy of the crystal. The classical growth can shift into three regimes based on the supersaturation, at lower supersaturation, growth occurs by birth and spread mechanism. With further increase in supersaturation, growth occurs by kinetic roughening (**Figure 1.4D**)¹¹⁵. Non-classical growth involves diverse range of precursors that can vary with respect to their microstructure (i.e., amorphous or crystalline), size and shape, and state of matter (i.e., solid or liquid-like)^{116, 117}. The advent of surface sensitive techniques such as atomic force microscopy (AFM), interferometry, and confocal microscopy has led to unique insights on the mechanism(s) of crystal growth for a number of zeolites and zeotypes

such as LTA^{100, 109, 118-123}, FAU¹²⁴⁻¹²⁶, LTL¹²⁷, MFI^{111, 128}, SAV¹²⁹, MER¹³⁰, and CHA¹³¹. Notably, Anderson and coworkers showed the formation of steps and terraces on fully crystalline LTA, MER, FAU, and MFI and concluded that birth and spread is the dominant pathway for zeolite growth^{119, 124, 128, 130}. The same group also reported that spiral growth is the preferential mode of growth for zeotypes such as STA-7¹²⁹ and zinc phosphate SOD¹³². It must be noted that most of the studies in the literature employ *ex situ* techniques to probe the crystallization mechanism of zeolites, which is subject to controversial interpretations since the mechanistic insights are limited when interpreting *ex situ* data. As such, if one wishes to obtain definitive evidence of crystallization pathway(s), techniques capable of investigating the dynamic sequence of events on crystal surfaces with molecular-level resolution are highly desired. To this end, Rimer and coworkers developed a unique *in situ* AFM tool to capture the zeolite surface growth in solvothermal conditions with exceptional spatiotemporal resolution^{109, 111, 118}.



Figure 1.5 Diverse modes of zeolite A crystallization involving nonclassical (top) and classical layered (bottom) growth pathways¹⁰⁹.

In situ AFM studies on silicalite-1 revealed that crystal growth occurs by both molecular addition and nanoparticle attachment¹¹¹. The first *in situ* demonstration of silicalite-1 surface

growth identified novel pathways of crystallization involving 3-dimensional nucleation and island growth. These findings were in direct contrast with the layer-by-layer growth mechanism proposed for other zeolites using *ex situ* data. Recently, Rimer and coworkers extended the applicability of the technique to a more challenging system: zeolite A (or LTA)^{109, 118}. The growth solutions of zeolite A are opaque due to the presence of bulk amorphous precursors. In the case of zeolite A, diverse precursors were identified contributing to surface growth ranging from monomers and oligomers to nanocrystals, gel-like islands and nanoparticles (**Figure 1**.5).

1.4 Synthetic chemistry of zeolites

Zeolites are generally prepared by hydrothermal synthesis in aqueous media where sources of T-elements (Si, Al, Ge, B, etc.) along with inorganic and/or organic cations are mixed together in basic or fluoride media. In the most cases, an organic compound acts as the SDA. Crystallization proceeds in a closed vessel (e.g. autoclave) at elevated temperature (usually 100 - 240 °C) under autogenous pressure for a period ranging from a few hours to several months¹³³.

The effect of growth mixture composition has been shown in numerous studies¹³⁴. For example, previous studies^{86, 135} have shown that FAU and LTA zeolites preferably nucleates in Siand Al-rich regions, respectively. The transition from pure LTA to pure FAU phase increases as gel Si/Al ratio increases (0.5 to 5). Similarly for ZSM-5 (MFI) and mordenite (MOR), ZSM-5 has been shown to be a preferred phase over mordenite at higher Si/Al ratio (>30) and lower Na/Si ratio^{136, 137}.

Numerous studies have shown that crystallization at low temperature generally leads to smaller sized crystals than those prepared at high temperature. It has been shown that low temperature favors nucleation over crystal growth. This leads to formation of a large number of nuclei which grow slowly to unform sizes¹²³. Furthermore, low temperature can also lead to the selective nucleation of a specific phase. Mintova and coworkers^{84, 87} synthesized nanosized EMT-type crystals by decreasing the crystallization temperature. The authors found that low temperature

favors nucleation of the EMT phase while precluding the formation of other completing zeolite phases such as FAU and SOD. Synthesis of nanosized FAU crystals by homogeneous distribution of species in the growth suspension was achieved by pre-dissolving silica in alkali solution prior to mixing it with an alkaline aluminate solution at low temperature to decrease the polymerization kinetics, thus leading to the formation of uniform amorphous particles that crystallized into nanosized FAU crystals⁸⁸. This example highlights the significance of the synthesis protocol in obtaining zeolites with specific properties.

Organic and inorganic structure-directing agents have also been shown to play an essential role in zeolite crystallization. Organic structure-directing agents (OSDAs) are molecules with shape and size commensurate with the channels and cages of the crystal¹³⁸. First reports of using OSDAs in zeolite crystallization date back to 1960, with the objective of obtaining high silica zeolites. Since then, OSDAs have been extensively utilized to discover new frameworks and/or improve the properties of known zeolites. OSDAs facilitate pore formation, alter the kinetics of crystallization, and can alter the aluminum distribution in the zeolite crystal¹³⁹⁻¹⁴⁵. Although organics are most notably discussed within the context of their structure-directing effects, it has also been demonstrated that they have diverse effects on solution properties and the modes of zeolite crystallization¹⁴⁶.

Inorganic SDAs (typically alkali and alkaline earth metals) act as extra-framework cations balancing the negative charge of Al sites in the crystal¹³⁸. Al-rich zeolites with low Si/Al ratios can be synthesized in purely inorganic systems^{147, 148}. Inorganic cations are also found in naturally occurring zeolites¹⁴⁹. Prior studies have categorized the effects of inorganic SDAs on the basis of their ability to either promote or disrupt hydrogen bonding of water molecules around the cation, with subsequent displacement by (alumino)silicate species leading to the formation of nuclei. Notably, Li and Na ions are referred to as structure formers, while K, Rb, and Cs are structure breakers owing to their large ionic radii^{150, 151}. In general, the rate of crystallization is reduced or enhanced in the presence of structure breakers or formers, respectively. Inorganic SDAs can also

promote specific zeolite phases. Okubo and coworkers have shown that potassium cation inhibits LTA nucleation leading to formation of low silica zeolite X (LSX)¹⁵². Alkali metals have effects on diverse length scales, from the molecular level (e.g., structuring of water), to the nanoscopic scale (e.g. zeolite structure direction), to the microscopic (e.g. gel/crystal dissolution)¹⁵³⁻¹⁵⁵.

Cooperative effects of organic and inorganic SDAs have also been investigated¹⁵⁶⁻¹⁶⁰. Rimer and coworkers demonstrated that the synergy between organic and inorganic structure-directing agents improved crystallization rates of ZSM-5 (MFI) zeolites¹⁵³. In similar investigations, Lobo and coworkers showed that the presence of Na⁺ decreases the nucleation rate of zeolite BEA* while increasing its growth rate owing to the competition between Na⁺ and TEA⁺ for surface adsorption sites and occlusion into the precursor particles⁹⁹. Furthermore, the effect of different combinations of SDAs on the final physicochemical properties has also been evaluated^{142, 161-164}. The charge density mismatch (CDM) approach utilizes cooperative templating between large organo-cations with low charge density and small organo-cations with high charge density and has enabled the synthesis of new zeolites such as UZM-4 (BPH), UZM-5 (UFI), and UZM-9 (LTA)¹⁶⁵⁻¹⁶⁹.

The properties of zeolite crystals are dependent upon the choice of the silica source. For instance, water soluble silica sources such as sodium silicate (also known as water glass) produce active silicate species at ambient temperature while water insoluble sources such as colloidal silica and fumed silica usually depolymerize in alkaline solutions under elevated temperatures^{108, 170}. Many studies have previously shown the effect of these different silica sources on the crystallization pathway and the physicochemical properties of the final product such as crystal size^{85, 110, 171-174}. Rimer and coworkers¹⁰⁹ recently utilized *in situ* atomic force microscopy (AFM) to show the incorporation of undissolved amorphous particles during the crystal growth of zeolite A in the presence of colloidal silica while substitution with sodium silicate resulted in clear solutions devoid of such particles. Inclusion of amorphous particles will lead to defects in the zeolite crystals and can have a detrimental effect on their performance in various applications.

Substitution of silicon with different heteroatoms also plays a significant role in zeolite crystallization. Previous studies have shown that zeolite MFI is predominately stable in high silica organic-free conditions (Si/Al>25, gel) while mordenite (MOR) is more stable in low-silica systems¹⁷⁵. Germanium introduction in the crystallization system has led to the formation of zeolites with open structures containing double four ring (d4r) and/or double three ring (d3r) units¹⁷⁶. Double four rings (d4Rs) are a common structural unit in most of the Ge-containing zeolites, due to the higher flexibility of Ge-O-Ge and Ge-O-Si bond angles compared to Si-O-Si²⁰. ¹⁷⁷⁻¹⁷⁹. Furthermore, the high lability of Ge-O bonds is a key factor for their hydrolysis, even under ambient conditions, which leads to the formation of individual silica-rich layers via the removal of mostly germanium containing d4r units¹⁸⁰. This chemically selective top-down disassembly (from 3D to 2D structures) is the key step of the ADOR process (Assembly-Disassembly-Organization-Reassembly), which often results in the synthesis of novel zeolites, including six new zeolites: IPC-2(OKO), IPC-4 (PCR), IPC-6 (*PCS), IPC-7, IPC-9 and IPC-10 synthesized from the UTL structure^{181, 182}.

Hydroxide ions (OH⁻) are common mineralizing agents in zeolite synthesis^{183, 184}. These ions facilitate dissolution and polymerization-depolymerization reactions of (alumino)silicates¹³³. Solution pH is commonly identified as a crucial parameter for controlling reaction kinetics, an outcome that is challenging to deconvolute from its effect on (alumino)silicate speciation and oligomerization because pH cannot be independently controlled without introducing additional counterions into the growth mixture^{141, 185, 186}. Fluoride ions (F⁻) have also been utilized as mineralizing agents¹⁸⁷. They were first used by Flanigen and coworkers in the synthesis of all silica zeolites¹⁸⁸. Due to the balance of positive charge of the SDAs by the occluded fluoride ions, there is a significant reduction in number of Si–O–…HO–Si hydrogen bonds. Thus, zeolites synthesized through this route show low density of defects^{189, 190}. Fluoride ions are also found to direct the formation of specific structures, including zeolite frameworks^{191, 192} such as MFI, FER, MTT, and TON and the incorporation of heteroatoms (B, Ga, Ti, and Fe)^{193, 194}.

One approach to control or alter the crystallization pathway is to introduce seeds of precrystallized zeolites into the growth solution to promote the formation of a desired framework¹⁹⁵⁻ ²⁰². Seeds can provide a source of nutrients (solute), a stable environment for heterogeneous nucleation, or a substrate for epitaxial growth, depending on the fate of seeds in the growth mixture²⁰³⁻²⁰⁶. Seed-assisted synthesis (SAS) leads to shorter crystallization times and reduces the formation of crystal impurities (or polymorphs). Furthermore, this methodology reduces the economical constraints and adverse environmental effects imposed by minimizing the requirement of expensive organics in the synthesis mixture²⁰⁷. Interzeolite transformation (IZT) can occur in SAS when using seeds of different structure than the one formed by the growth mixture in the absence of seeds. Alternatively, IZT can occur without seeds where an initial thermodynamically metastable framework undergoes a transformation involving the nucleation and growth of second framework that is putatively more thermodynamically stable^{141, 208-216}. This process can occur multiple times, with each step resulting in a product that is more stable than the previous one, seemingly in accordance with the Ostwald rule of stages⁸⁶. The overall impact of synthesis protocols utilizing IZT has been studied, but there remains a vast research space yet to be explored. In one study, Zones and coworkers have utilized FAU as a parent zeolite with different Si/Al ratios to synthesize a series of zeolite structures in the presence of an OSDA. Using Al-rich FAU, they synthesized a silica-rich version of CHA (SSZ-13), which exhibits exceptional catalytic activity in the NH₃-SCR reaction¹⁴¹. Using high-silica FAU, they also obtained SSZ-41 (VET)²¹⁷ and SSZ-98 (ERI)²¹⁸. Other groups have also reported the use of FAU as the sole or partial source of Si and Al atoms to synthesize other zeolite frameworks^{208, 211, 213, 219}. It can be easily observed that most of these studies involve dissolution of parent FAU crystals, but it remains unclear whether the seeds dissolve completely to supply Si and Al or partially dissolve to supply more complex precursors (e.g., CBUs). It has been suggested, however, that even X-ray amorphous intermediates possess local structure, which can markedly influence nucleation and growth mechanisms^{116, 220}.

Interzeolite transformations provide pathways to synthesize zeolites which would not be possible with conventional silica and alumina sources. For example, B-SSZ-24 (AFI) has been synthesized using a B-BEA precursor (**Figure 1.6A**). The presence of BEA crystals in the growth solution provides precursors with specific order and composition that drives the system towards the B-SSZ-24 crystallization which could not be achieved without zeolite seeds²²¹. Furthermore, this approach can be essential in synthesizing zeolite crystals with nanosized dimensions, which beneficially reduce diffusion limitations for catalytic applications^{205, 222}. Rimer and coworkers showed that final crystal sizes (red diamonds) are smaller when synthesis mixtures possess higher seed concentrations, with the overall Si/Al ratio (blue circles) of crystals being independent of seed content (**Figure 1.6B**)²⁰². The inset shows the SEM image of ZSM-5 crystals obtained with 13wt% seeds. Although these findings warrant further exploration, this is an interesting technique to engineer crystal size without affecting the final composition in an organic-free system, which is difficult to achieve otherwise.



Figure 1.6 (A) Aspects of the synthetic transition of boron beta zeolite to B-SSZ-24²²¹. (B) Impact of seed content on ZSM-5 product Si/Al ratio and crystal size²⁰². (C-D) Use of FAU in IZT for (C) metal encapsulation and (D) phosphorous insertion.

Another application of IZT is to obtain metal-containing zeolites, which are effective catalysts in alkane dehydrogenation, methane dehydroaromatization, and biomass valorization²²³. The main challenge in the direct synthesis of metal-containing zeolites is that hydrated metal precursors are too large to enter the zeolite pore channels during post-treatment, especially for small or medium pore zeolites, and precursors precipitate under highly alkaline hydrothermal synthesis conditions²²⁴. In this regard, zeolites (especially FAU) have been utilized as a carrier for metals for successful encapsulation based on the ship-in-a-bottle approach where a parent zeolite stabilizes the metal clusters or nanoparticles in the interior preventing metal precipitation during IZT to a daughter zeolite with high metal loading (**Figure** 1.6**C**)^{225, 226}. This approach was recently extended to the direct synthesis of phosphorous-containing AFX (**Figure** 1.6**D**)²²⁷. Phosphorous-modified zeolites with tunable Brønsted acidity have better selectivity and can thus more effectively suppress

undesired side reactions²²⁸⁻²³⁰. Apart from encapsulation, isomorphous substitution of metal ions in the zeolite framework at tetrahedral sites has also been achieved by IZT²³¹. Although literature about utilizing interzeolite transformations to create zeolites with different chemistry is relatively scarce, this method has the potential to open a new avenue in the future of zeolite synthesis.

1.5 Engineering porous architecture: hierarchical zeolites

The inherent micropores (typically < 1 nm) present in zeolite structures can provide excellent shape selectivity and confinement effects^{232, 233}. But these small pores also restrict the access of zeolite acid sites to large molecules and slow down the diffusion of molecules which are in comparable size to zeolite pores. This delayed transport allows further conversion of reactants and products into unwanted side products, which may also serve as coke precursors. This leads to faster deactivation of zeolite catalysts. Slow diffusion can also lead to poor utilization of overall zeolite catalysts²³⁴⁻²⁴⁵. In **Figure** 1.7**A**, the effectiveness factor, η (ratio of observed reaction rate to intrinsic reaction rate) is represented as a function of Thiele modulus (ϕ). In general Thiele modulus describes the relationship between diffusion and reaction rates in porous catalyst pellets and mathematically is given as ²⁴⁶

$$\phi = L \sqrt{\frac{K_m C_s^{n-1}}{D_{A,eff}}} \tag{1}$$

with K_m = rate constant of the reaction, C_s = concentration at the surface of the pellet, n = reaction order and $D_{A,eff}$ = effective diffusion coefficient.

In order to maximize the effectiveness factor, the Thiele modulus should be minimized which can be done by either increasing the diffusivity or by reducing the effective diffusion length²⁴⁷. In case of zeolite catalysts, effective diffusion path length can be reduced in different ways as shown in **Figure** 1.7**B**: (i) By introducing second order of porosity (mesopores or macropores)^{248, 249}. Zeolites with multiple order of porosity are referred to as hierarchical zeolites; (ii) By reducing the overall crystal size of zeolites, leading to formation of nanocrystals and

nanosheets^{205, 250-259}. Red arrows represent the characteristic diffusion length in a purely microporous crystal and green arrows show the reduced diffusion path lengths in nanosized or hierarchical systems



Figure 1.7 (A) Effectiveness factor as a function of Thiele modulus. At low effectiveness factors only a small portion of the crystal is efficiently utilized during the reaction. (B) Schematic representation of different nanosized zeolites and hierarchical zeolites²⁴⁷.

Many synthesis strategies have been developed in the past to synthesize hierarchical zeolites with both an abundant secondary porosity and full interconnected mesopores or macropores²⁶⁰⁻²⁶⁸. The synthesis methods can be broadly classified into two categories: post-synthetic treatments and *in situ* synthetic routes. The former is a destructive process involving either desilication or dealumination. It involves dissolving selective parts of zeolite crystals leading to meso- or microporosity. Dealumination, which involves the removal of Al from the zeolite framework with steam²⁶⁹⁻²⁷² or acid^{273, 274} treatment, is the most widely used post-synthetic method in industry. This treatment has been extensively utilized to produce ultra-stable Y (USY) with larger mesopore volume and a higher Si/Al ratio by steaming of pristine zeolite Y²⁷⁵. USY is the main component of FCC and hydrocracking catalysts. Desilication induces mesoporosity by selectively removing Si from the zeolite structure in alkaline solution²⁷⁶. It is suitable for zeolites with high Si/Al ratios (25-50)²⁷⁷. The most extensive investigations concerned with the influence of treatment parameters on the mesopore formation have been made for zeolite ZSM-5²⁷⁸. Besides, its
effectiveness has also been demonstrated for other zeolite framework structures, including MTW²⁷⁹, MOR²⁸⁰, BEA²⁸¹, AST²⁸², FER²⁸³, MWW²⁸⁴, IFR²⁸⁵, STF²⁸⁶, CHA²⁸⁷, FAU²⁸⁸, and TON²⁸⁹. Chemical etching in the fluoride medium has also been utilized where combination of HF and NH₄F leads to indiscriminatory etching of both Si and Al from the zeolite framework²⁹⁰⁻²⁹². Thus, hierarchical zeolites with similar composition as parent zeolites are obtained²⁹³.

Another post-synthetic treatment is based on a two-step approach consisting of partial-tototal dissolution of the zeolite in NaOH solution and the subsequent hydrothermal treatment with surfactants, such as cetyltrimethylammonium bromide or chloride (CTAB or CTAC). The introduction of well-controlled mesoporosity into zeolite crystals is based on a crystalrearrangement theory. Only when the Si–O–Si bonds were opened by a cationic surfactant in base condition and transformed into negatively charged Si–O– species can the structural reorganization be realized. This approach allows for the necessary interactions between the surfactant and the zeolite and avoids the dissolution of the crystals (i.e. all material is preserved)^{294, 295}.

In situ methods can also be used to incorporate mesoporsity. Hard templates with relatively rigid structure such as carbon materials, polymers, and biological materials can be used in zeolite synthesis. After the synthesis, the template is removed by calcination or dissolution, resulting in mesoporosity at the locations of occluded hard template²⁹⁶⁻³⁰⁰. Alternatively, soft templating can also be done by either using SDA as well as mesoporogens such as surfactants, organosilanes, or two-in-one templates consisting of hydrophobic alkyl chains on one side and hydrophilic quaternary ammonium groups on the other.

1.6 Dissertation outline

The physicochemical properties of zeolite catalysts such as acidity, porous architecture, crystal size, external surface roughness, and crystal morphology can significantly alter their performance for a wide variety of reactions. Fewer than 25 framework types are used in commercial applications. There are two major challenges associated with optimizing and/or expanding this list

of materials for industrial applications. The first is the development of more streamlined routes to reduce the cost of zeolite synthesis. The second one is the lack of fundamental knowledge regarding the crystallization mechanism(s) of zeolites which often prohibits the control of zeolite properties. This dissertation focuses on three critical elements of zeolite catalyst design: (i) investigating the role of different parameters in organic-free zeolite synthesis such as gel composition, crystallization temperature, seed properties on the crystallization pathway to control the zeolite phase, and the optimization of other physicochemical properties as mentioned above ; (ii) developing organic-free routes for the fabrication of hierarchical zeolites to improve the performance of zeolites particularly in stability, lifetime, and activity using an economically feasible seed-assisted approach; and (iii) establishing techniques that are capable of monitoring complex mechanism(s) of zeolite crystallization with sufficient spatiotemporal resolution.

In Chapters 2 and 3, we investigate a working hypothesis in seed-assisted approaches to synthesize zeolites based on shared structural features, such as a composite building unit, between the parent and the crystals produced from a non-seeded growth solution results in identical parent-daughter framework types. Our findings reveal that this scenario is true only in certain cases, but often the initial structure formed in seeded syntheses is metastable, resulting in interzeolite transformation(s) with prolonged hydrothermal treatment. In general, the trajectory tends to favor a final structure identical to that obtained by non-seeded growth under identical synthesis conditions. Furthermore, we explore how seed-assisted syntheses impact zeolite properties such as size, morphology, structure, and defects.

In Chapter 4, we present a facile, commercially viable method to develop self-pillared penatsil zeolites using MEL- or MFI-type zeolites as crystalline seeds, thus avoiding, for the first time, the use of any organic or branching templates in crystallization media. The resulting hierarchical materials consist of large external surface area and high percentages of external acid sites, which markedly improves their catalytic performance in reactions such as Friedel crafts alkylation and methanol to hydrocarbons. We further utilize time-resolved electron microscopy to

provide unprecedented evidence for the heterogeneous nucleation and growth of sequentially branched nanosheets on the surfaces of amorphous precursors.

In Chapters 5 and 6, we investigate the crystallization of LTA and FAU, respectively, using *in situ* atomic force microscopy with high spatiotemporal resolution. We show that for 2dimensional growth of LTA, layer nucleation from surface defects is the most common pathway. These defects are generated by the incorporation of undissolved silica nanoparticles into advancing steps on crystal surfaces that largely go undetected by conventional analytical techniques in the literature. Furthermore, we monitor FAU crystallization under different conditions and report that this particular zeolite framework predominately grows by nonclassical pathways in contrast to LTA and MFI (silicalite-1), which grow by a combination of classical and nonclassical pathways, as reported previously by our group.

Chapter 2

Seed-assisted zeolite synthesis: the impact of seeding conditions and interzeolite transformations on crystal structure and morphology

2.1 Introduction

The unique properties of zeolites, including their exceptional (hydro)thermal stability, tunable acidity, and diverse range of pore networks, enable their widespread use in industrial applications spanning adsorption and catalysis to ion exchange and separations^{233, 301, 302}. There are many approaches used to tailor the physicochemical properties of zeolites, such as their crystal structure (e.g., pore sizes and dimensions), chemical composition (e.g., Si/Al ratio), and mass transport properties (e.g., crystal size and mesoporosity). A common (and often required) technique in zeolite synthesis involves the incorporation of one or more organic molecules that function as structure-directing agents (SDAs). These species typically have a size and geometry that is commensurate with the channels and cages of the targeted zeolite framework¹³⁹. For instance, Choi et al. synthesized single unit cell ZSM-5 nanosheets using a di-quaternary ammonium-type surfactant and showed that these materials exhibit improved catalyst lifetime in the methanol to hydrocarbon reaction³⁰³. Recent examples have demonstrated the advantages of using computational models or machine learning to effectively screen potential SDAs³⁰⁴, while rational approaches using SDAs that mimic critical transition states in chemical reactions have been used to produce optimal (reaction-designed) zeolite catalysts³⁰⁵. Cooperative effects of multiple organic SDAs as well as mixtures of organic and inorganic SDAs have also been exploited for the purposes of tailoring crystal structure^{259, 306}, size^{307, 308}, and/or the number and distribution of aluminum sites within the framework^{153, 158}. Despite recent developments, the use of organics can impose commercial limitations owing to high economic and environmental costs. One approach to either reduce or eliminate organics in zeolite synthesis is the use of seed crystals, which can reduce the total synthesis time, eliminate impurities, and alter particle size^{95, 198}. This approach has been successfully utilized to synthesize various zeolite frameworks: *BEA³⁰⁹⁻³¹¹, MTW^{312, 313}, MFI^{257,}

³¹⁴, FER³¹⁵, MEL³¹⁶, LTA³¹⁷, MOR³¹⁸, RTH³¹⁹ and FAU³²⁰. It is also an integral component of multistep syntheses to produce zeolite membranes for gas separations³²¹.

In the classical sense of seed-assisted crystallization, the seeds undergo immediate growth to bypass the induction period or can provide interfaces for heterogeneous nucleation. Conversely, seed-assisted growth in zeolite synthesis is more complex due to the presence of numerous precursors that include (alumino)silicate monomers, oligomers, and amorphous particles or gels¹⁹⁶. There have been multiple mechanisms reported for seed-assisted zeolite synthesis. Xiao and coworkers proposed a core-shell growth mechanism in which the solute leads to overgrowth (shell) on the surface of seeds (core)³²². A more commonly observed phenomenon is one reported by Sano and coworkers who proposed a complete dissolution of seeds, giving rise to locally ordered aluminosilicates (oligomers or small particles) in the growth solution that recrystallize to the final zeolite product²⁰⁸. In general, the recrystallization of the parent zeolite (seed) into a daughter zeolite can be classified into two categories. The first refers to interzeolite transformations (Figure 2.1 A), which occur in media containing mainly zeolite seeds (parent) and few amorphous precursors. In these processes, dissolution-reprecipiation processes lead to the conversion of one zeolite (parent) into a different zeolite structure (daughter). The second mechanism is seeded growth (Figure 2.1 **B**) where a small amount of seeds (parent) is added to a growth mixture of predominately amorphous precursors, leading to the dissolution of seeds and recrystallization into a daughter zeolite with either the same or different structure as the original seed.

There is growing interest in seed-assisted zeolite synthesis. Okubo and coworkers proposed a working hypothesis based on empirical evidence positing that common composite building units (CBUs) between the seed and crystals obtained from non-seeded growth solutions will lead to identical parent-daughter crystal structures³²³. For example, ZSM-11 (MEL) seeds introduced in a mordenite (MOR) growth solution (both having one common CBU) yielded a ZSM-11(MEL) product. Additional examples were provided where the zeolite structure of the seed was retained when there was at least one common CBU between the seed and the zeolite obtained from the

starting synthesis gel in the absence of seeds. When considering interzeolite transformations, there are also examples where parent-daughter crystals share a common structural feature. Examples include transformations of LEV into CHA³²⁴, FAU into LEV³²⁵, FAU into CHA, and *BEA into MFI²¹¹ where each pair of structures share at least one common CBU.



Figure 2.1 (A) Interzeolite transformations (B) Seeded growth. Comparisons of disparate parentdaughter structures can be made on the basis of shared composite building units or rings of the zeolite frameworks.

As shown in (**Figure** 2.1), structural similarities could be extended to more basic subunits, such as n-rings. For instance, Sano et al.³²⁶ also reported transformations of FAU (d6r, sod) into *BEA (mor, bea, mtw) and MAZ (dsc, gme), i.e., frameworks that do not share any common CBU. In these cases, the authors attributed the transformations to common four-member rings in several CBUs (e.g., d6r, bea and gme). Goel et al.²¹¹ reported transformation of lower density frameworks (FAU or *BEA) into high density frameworks (MFI, CHA, STF and MTW). They also posited that the presence of a common CBU permits transformations without using seeds or an organic SDA. Muraoka et al. proposed that during FAU-to-CHA transformation, a specific rearrangement of aluminosilicates occurs rather than a simple transfer of their common CBU (double-6-membered ring) wherein the final atomic configuration of CHA is dependent on the parent FAU zeolite³²⁷.

However, examples of interzeolite transformations have been reported where both parent and daughter lack any common structural features. For instance, Qin et al. demonstrated the transformation of FAU into MFI in absence of seeds or organic SDAs²¹³. Kirschhock and coworkers²¹⁰ reported the transformation of FAU into a wide range of structures (e.g. ABW, MER, and ANA) that do not share any common CBU with FAU. Indeed, Schwalbe-Koda et al.³²⁸ used machine learning to discover that 65% of the interzeolite transformations reported in literature do not involve common CBUs. Thus, one of the prevailing questions is whether or not the criterion of shared structural features is essential for interzeolite transformations and seeded growth.

Interzeolite transformations and seed-assisted growth can provide pathways for the synthesis of zeolites with controlled elemental composition and crystal morphology^{317, 329, 330}. Iglesia and coworkers have utilized interzeolite transformations to control the encapsulation of large metal clusters in zeolite pores, which otherwise could not be achieved by post-synthesis ion exchange²²⁶. Despite numerous studies of interzeolite transformations, the mechanism and driving force for these processes are not well understood. Navrotsky and coworkers established a trend for purely siliceous zeolites where the enthalpy of formation is proportional to molar volume⁸², which can be used as a descriptor to rationalize many reported transformations. However, there are examples that seemingly defy this trend (e.g., MFI-to-MOR^{213, 331}), revealing that other factors such as elemental composition (the presence of Al or other heteroatoms) impact the enthalpy of formation^{81, 332} in ways that have yet to be quantified. To this end, a single (universal) descriptor is incapable of predicting interzeolite transformations. One complicating factor is that the chemical potential of the growth solution changes over the course of zeolite synthesis, reflecting the temporal changes in soluble species as precursors are consumed. This gives rise to metastable structures that can undergo a series of interzeolite transformations (akin to the Ostwald rule of stages) with prolonged hydrothermal treatment⁸⁶.

Herein, we explore the effect of parameters such as growth solution composition, seed properties, synthesis time, and temperature on the kinetics of nucleation and interzeolite transformations in seed-assisted zeolite synthesis. We examine the factors governing parentdaughter relationships by selecting zeolites with common structural features as well as those lacking structural similarity. Our findings expose several limitations to prevailing hypotheses of shared CBUs. Moreover, we explore the impact of seeds on crystal morphology and highlight the important role of kinetics in seeded growth. To this end, our findings provide insights into organicfree protocols to tailor the physicochemical properties of zeolite crystals.

2.2 Results and discussion

2.2.1 Parent-daughter structural relationships

Here we examine the impact of growth solution composition, seed structure and properties, and synthesis time on parent-daughter relationships in seeded growth experiments. As shown in Figure 2.2, we selected four commercially relevant zeolite frameworks types for analysis: MOR, MFI, MEL, and MTW. Among these zeolites, MFI and MEL share multiple common composite building units (CBUs). MOR shares a single CBU with MFI and MEL, whereas MTW only shares one CBU with MFI. The various combinations of shared structural entities provide an opportunity to test scenarios where the frameworks of the growth solution, parent crystal (seed), and daughter crystal (product) either exhibit similar structural features or lack any commonality. The molar volume of these frameworks varies (from high to low) as MOR \approx MEL > MTW \approx MFI. While interzeolite transformations tend to occur in order of decreasing molar volume⁸⁶, these trends are reported for purely siliceous zeolites⁸²; thus, differences in the framework composition (i.e. Si/Al ratio) of parent and daughter crystals makes it difficult to ascertain the thermodynamic driving force for processes observed in this study. For example, interzeolite transformations can occur in the order of decreasing framework density (e.g. MFI-to-MOR)²¹³, consistent with the recent study by Schwalbe-Koda et al.³²⁸ highlighting numerous examples of transformations occurring in sequences of increasing molar volume.



Figure 2.2 (top) Comparison of four framework types with molar volumes V of 35.4, 32.7, 34.6, and 33.1 cm³mol⁻¹, respectively. (bottom) Composite building units (CBUs) with dashed boxes indicating commonalities among the four frameworks. Data from IZA²².

Solution ^a	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O	T (°C) ^b
S 1	3.42	18	1	324	165
S 2	30	100	1	2000	150
S 3	9.6	60	1	2580	190

Table 2.1 Molar composition of growth solutions and synthesis temperatures

a. Compositions exclude the addition of seeds; b. Seeded syntheses were performed at 150 °C.

For this study we selected two growth solutions (**compositions S1 and S2 in Table** 2.1) that are commonly reported for mordenite synthesis^{312, 333}. The kinetic (ternary) phase diagram in **Figure** 2.3, which was constructed from a survey of literature (**Figure** A.1 **and Table** A.1), reveals a region of overlapping synthesis compositions between MOR and pentasil zeolites MFI and MEL, while the region for MTW is distinctly separated from that of MOR. The basis for selecting these

two growth solutions is that S1 lies within intersecting regions of MOR and MFI/MEL while S2 is within an isolated MOR region. Results of seeded growth reported by Itabashi et al.³²³ have shown that introduction of ZSM-11 (MEL) or ZSM-5 (MFI) seeds in a growth solution similar to S2 resulted in the generation of MEL and MFI products, respectively. This outcome of identical parent and daughter crystals aligned with their working hypothesis of common CBUs between the seed and the product of non-seeded growth (i.e. mordenite). It could be argued that this procedure would also be applicable to solution S1, which overlaps the MEL/MFI phase space. Therefore, we followed a similar protocol using ZSM-11 seeds (Si/A1 = 16) in a S1 solution and showed that after 6 days of synthesis, the final product is mordenite, which is contrary to the expected outcome based on the prevailing hypothesis of common CBUs. To ascertain the reason for this difference, we carried out time-elapsed studies in solutions S1 and S2 to observe the trajectory of seeded growth (including potential phase transformations) using a variety of parent crystals with different Si/A1 ratios and framework types.



Figure 2.3 Ternary (kinetic) phase diagram with growth solutions S1, S2 and S3 (grey circles). For more information refer **Figure** A.1 **and Table A.**1.

MEL-type crystals prepared with three compositions (Si/Al = 16, 35, and ∞) were used as seeds in solutions S1 and S2 (**Figure** 2.4**A**). For the synthesis employing silicalite-2 seeds (Si/Al = ∞) in growth solution S1, powder XRD patterns (**Figure** 2.4**C**) of the solids extracted after 1 day of heating reveal an amorphous product, suggesting the dissolution and/or significant disordering of seeds, which is a commonly observed phenomenon in seeded growth of zeolites³¹³. Alternatively, residual seed crystals (either pristine or partially disordered) may be present in quantities that are too small to detect by XRD. Additional synthesis time (e.g., 3 days) leads to the formation of pentasil zeolite. It should be noted that it is often difficult to distinguish between MEL and MFI phases in powder XRD patterns³³⁴; therefore, in cases where it is not evident which phase(s) is present, we denote the product(s) as a generic label of pentasil to indicate the presence of MEL and/or MFI. For experiments in S1 solutions, we never observed a pure pentasil product, but rather mixtures containing mordenite. As the silicon content of seeds increases, we observe that the time period for pentasil-to-mordenite transformation is extended to approximately 10 days (compared to 6 days for seeds with the lowest Si/Al ratio (Figure 2.4C and panels A of Figure A.6, Figure A.7). Interestingly, syntheses in growth solution S2 (i.e. the composition furthest from the penasil region in the phase diagram) yields fully crystalline penasil (or MFI) products within the first 3 days of synthesis (panels B of Figure A.6, Figure A.7, Figure A.8). In the case of seeds with Si/Al = 16, we did not observe the pentasil-to-mordenite transformation after 10 days of synthesis (Figure A.6 B). Contrary to seeded growth in solution S1, the timeframe for pentasil-to-mordenite transformation in solution S2 increases with decreasing Si/Al ratio, such that purely siliceous seeds (silicalite-2) yield fully crystalline mordenite within 6 days of synthesis. One of the primary differences between S1 and S2 is the gel Si/Al ratio for each solution (9 and 50, respectively). According to previous studies^{136, 175}, high Si/Al ratio (>30) of the growth solution is optimal for the crystallization of pentasil zeolites while low Si/Al ratio (<30) is optimal for the MOR crystallization. This offers a possible explanation for the promotion of pentasil structures in seeded growth using solution S2, despite the fact that its location is within the MOR region of the kinetic phase diagram.



Figure 2.4 Products obtained using (A) MEL and (B) MFI seeds in growth solutions S1 (left) and S2 (right). (C and D) Time-elapsed PXRD patterns using (C) silicalite-2 (MEL, Si/Al = ∞) and (D) ZSM-5 (Si/Al = 14) seeds in growth solution S1 and S2 respectively.

Repeating these experiments using MFI-type seeds of varying composition (Si/Al = 14, 40, and ∞) yielded less definitive trends with respect to seed Si/Al ratio (**Figure 2.4B**); however, we generally observed for solutions S1 and S2 that higher silicon content resulted in enhanced stability of MFI phases at earlier synthesis times. In the majority of cases, ZSM-5 (MFI) was the first crystalline phase to be detected (e.g., **Figure 2.4D**). In solution S2, all products within the first day of synthesis were pure ZSM-5 (**Figure 2.4D** and panels B of **Figure A.10** and **Figure A.11**). The most unusual observations involved ZSM-5 seeds with Si/Al = 40 where growth solution S1 resulted in a delayed induction period followed by the generation of pure mordenite (**Figure A.10A**), whereas growth solution S2 produced pure ZSM-5 over the course of 10 days (**Figure A.10B**). The findings from these experiments reveal that under certain circumstances, the working hypothesis of common CBUs reported by Okubo and coworkers³²³ is correct, in that identical parent-daughter relationships are achieved when the seed crystal shares at least one common CBU with the crystalline product obtained from the non-seeded growth solution (i.e. MOR in this study).

It should be noted, however, that this hypothesis is highly dependent upon the selection of growth solution composition and the Si/Al ratio of the parent (seed) zeolite. It is also anticipated that synthesis temperature is an important parameter given that higher temperature expedites interzeolite transformations, which we demonstrated in a previous study⁸⁶. Here, we observed in select cases that transformations at higher temperature (170°C) are faster than those at lower temperature (130°C), thus highlighting the important role of kinetics in determining parent-daughter relationships (**Figure** A.18).

To further examine the hypothesis of common CBUs in seeded growth we used ZSM-12 (MTW) seeds, which do not share any common structural feature with MOR and are synthesized in a different region of the kinetic phase diagram. Time-resolved studies reveal that seeded growth in both S1 and S2 solutions yields zeolite products counter to the working hypothesis. Notably, seeded growth in solution S2 results in a ZSM-12 product after 1 day of synthesis (Figure 2.5 A, B). This is particularly interesting given that this is an OSDA-free procedure, which is uncommon for ZSM-12 syntheses unless seeds are introduced in growth mixtures³¹². If the same synthesis is allowed to proceed for 3 days, we begin to detect mordenite in the product, while solids extracted over 10 days of synthesis continue to show a mixture of both MTW and MOR (Figure 2.5 C). In solution S1, the first phase detected is ZSM-5 (MFI), which shares one common CBU with MTW (Figure A.16). This is not entirely unexpected since solution S1 overlaps with the MFI region in the kinetic phase diagram (Figure 2.3); however, extended synthesis time leads to a MFI-to-MOR interzeolite transformation (Figure 2.5 D), indicative of the general trend for seeded growth in solutions S1 and S2 to transition to mordenite with prolonged synthesis time. Therefore, the sum of observations in the seeded growth study presented here seem to indicate that shared CBUs between the seed and crystals produced from the (non-seeded) growth solution is not the dominant factor governing parent-daughter structural relationships. Indeed, the driving force for crystallization is seemingly more nuanced. The fact that interzeolite transformations are frequently observed is an indication that many of the initial products formed at short synthesis times are

kinetically trapped. This may offer an explanation for discrepancies with Itabashi et al.^{312, 323}, whose results are reported for short synthesis times (i.e. less than 24 h) that can lead to the formation of metastable products. In our study, extended periods of hydrothermal treatment led to a progressive shift from the kinetically-trapped structure to a presumably more thermodynamically stable product that would otherwise be obtained in the absence of seeds. Collectively, these findings seem to indicate that the selection of synthesis conditions (e.g., growth medium composition, time, and temperature) are more influential than the structure and properties of seed crystals.



Figure 2.5 Seed-assisted syntheses using ZSM-12 (MTW) seeds. (A) Time-elapsed PXRD patterns in growth solution S2. (B and C) SEM images of products obtained after (B) 1 day and (C) 10 days of synthesis (scale bars = 5 μ m). (D) Products in solutions S1 (left) and S2 (right).

2.2.2 Impact of seeds on crystal morphology

It is well established that the use of seeds in zeolite synthesis can lead to products with dramatically different crystal size and shape compared to the original seeds and/or the product of synthesis in the absence of seeds. Here, we examine to what extent the selection of seeds impacts the physicochemical properties of the final product. The nominal mordenite crystals obtained from solution S1 (without seeds) have an ill-defined morphology with a polydisperse size distribution (**Figure** 2.6 **A**). The same synthesis using silicalite-2 seeds results in a bimodal population (**Figure** 2.6 **B**) of rod-like mordenite crystals (> 10 μ m in length) and much smaller crystals (ca. 1 μ m) with random (or less-defined) morphology. When using mordenite seeds (the same as those depicted in

Figure 2.6 **A**), the resulting mordenite product exhibits a thin disc-like shape (**Figure** 2.6 **C**) and an approximately uniform distribution of crystal size. Thus, it is evident that the morphology and size of mordenitecrystals can be modified by varying the seed (parent) crystal structure, although the exact mechanism for these changes is not well understood. These findings further confirm the benefits of seed-assisted synthesis as an efficient method to tailor crystal habit compared to alternative methods utilizing organics, such as zeolite growth modifiers (ZGMs)^{335, 336} or cooperative OSDAs^{337, 338}.



Figure 2.6 SEM images of (A – C) Mordenite and (D - F) ZSM-5 crystals prepared from solution S1 and S3 respectively (A, D) without seeds (B, E) with silicalite-2 (MEL) seeds (C, F) with mordenite (MOR) seeds

To further explore the ability of seed-assisted protocols to control crystal habit, we examined a third growth solution (S3 in Table 1) corresponding to a composition that is reported for OSDA-free synthesis of ZSM-5³³³. In the absence of seeds, this synthesis produces a relatively uniform size distribution of ZSM-5 crystals (ca. 4 μ m in the b-direction) with the traditional coffin-like morphology (**Figure** 2.6 **D**). When the synthesis is repeated using silicalite-2 (MEL) seeds, the product has a similar morphology (**Figure** 2.6 **E**), but dramatically reduced crystal size (ca. 200 nm in the b-direction). For the same synthesis using mordenite seeds, there is no marked change in crystal size (**Figure** 2.6 **F**); however, the product contains significantly more defects (i.e.

intergrowths). The latter is a commonly observed feature in syntheses of ZSM-5, but the exact origins of defect formation are not well understood. One possibility is that the dissolution of mordenite seeds results in a residual "memory" of the parent structure (e.g., oligomers, rings, CBUs)^{327, 339}; and that these species putatively play a role in the generation of defects.

All syntheses reported to this point used a constant seed content (10 wt%); however, we observed that the final crystal size is dependent upon the quantity of seeds added to the growth mixture. An example of these findings is reported here for ZSM-5 synthesis in solution S3 (gel Si/Al = 60) using silicalite-2 seeds (Si/Al = ∞). The nominal size of ZSM-5 crystals in the absence of seeds is ca. 4 µm. In the presence of only 2 wt% silicalite-2 seeds, the crystal size is reduced by more than 100 times to an average value of 342 nm (Figure 2.7 A). This general trend is consistent with prior studies of MFI-type zeolite synthesis using silicalite-1 seeds^{133, 257}. Systematic studies of seeded ZSM-5 synthesis with increasing seed content reveals a monotonic decrease in crystal size with increasing seed content (Figure 2.7 C) wherein the highest seed content evaluated (13 wt%) yields 146 nm crystals (Figure 2.7 B). The size of the crystals was measured along the b-direction, which corresponds to the direction of straight channels (i.e. the less tortuous channels that more prominently impact the internal mass transport properties of ZSM-5)³⁴⁰. It has been demonstrated in literature that a reduced path length along the straight channels in MFI leads to better catalytic activity^{341, 342} as well as improved performance in separations³⁴³. It is interesting to note that varying seed content had no significant impact on the composition of zeolite products (Figure 2.7 C), which maintain a constant Si/Al \approx 20, measured by EDX. Collectively, our findings indicate that for the synthesis conditions selected in this study, only a small quantity of seeds are required to impact crystal size without altering product Si/Al ratio. The latter point is of particular importance given that it is often challenging to independently vary one property (e.g., size) without altering in some way other properties (e.g., composition). Moreover, the ability to achieve this outcome in the absence of organics increases the commercial relevance of this synthesis approach.



Figure 2.7 SEM images of ZSM-5 crystals prepared with (A) 2 wt% and (B) 13 wt% silicalite-2 seeds in solution S3 (scale bars = 2 μ m). Insets: high mag. images. (C) Average Si/Al ratio of products (blue circles), and the average crystal size (red diamonds).

2.3 Conclusion

In summary, we have examined the relationships between parent and daughter crystals in seeded growth assays using a variety of seed properties and growth solution compositions. The factors governing these relationships appear to be more multifaceted than a comparison of underlying structural features, such as the similarity of composite building units. In many instances we observe that seeded growth results in interzeolite transformations where the timescales are dependent upon the conditions selected, and the rationale for the observed trajectory is not well understood or easily predictable. In general, our observations indicate that the growth solution, which has been largely overlooked in previous studies of seeded growth, plays an important role in controlling the kinetics of interzeolite transformations. The thermodynamic driving force for these transformations cannot be easily described by a single variable, such as molar volume. The dissolution of seeds presumably leads to species that initially facilitate the nucleation of an identical

structure; however, over the course of synthesis the composition of the growth solution changes, thereby altering the chemical potential (i.e., driving force), leading to the nucleation of a new phase. This highlights the importance of kinetics in seeded zeolite syntheses wherein the hypotheses of parent-daughter relationships in seed-assisted syntheses relative to non-seeded cases must take into account additional factors that include (but are not limited to) synthesis time, temperature, and the compositions of seeds and the growth medium. Although not explicitly examined in this study, it is possible that seed crystal size or the presence of defects in seeds (e.g., silanol nests, non-framework Al, etc.) can impact the kinetics of seeded growth synthesis and/or the properties of the final product.

Seed-assisted zeolite synthesis is a facile and economically viable approach to alter crystal habit. Our findings reveal that the nature of the seed has a significant impact on the final product; and that only a small quantify of seeds is needed to dramatically reduce crystal size without any unintended modification of framework composition (Si/Al ratio). This generalizable approach, while effective, is more of an art than a science given the unknown mechanisms of seeding. The proposed "memory" of dissolved seeds during the early stages of synthesis is not well understood and has not been experimentally verified; thus, the impact of residual seed species on processes of nucleation and growth is elusive. The ability of seeds to alter the pathways of zeolite crystallization, however, holds tremendous promise as a route to access properties that are otherwise unattainable by non-seeded growth. The findings presented here offer additional insight into seeded growth and the unintended interzeolite transformations that can occur during these predominantly organic-free syntheses.

2.4 Experimental

2.4.1 Materials

The following chemicals for zeolite synthesis were purchased from Sigma Aldrich: LUDOX AS-40 (40 wt% suspension in water), tetraethylorthosilicate (TEOS, \geq 99.5%), sodium aluminate

(57.1% Al2O3 and 37.2% Na2O), 1,8-diaminooctane (DAO, 98%), tetrapropylammonium bromide (TPABr, 98%) and tetraethylammonium bromide (TEABr, 98%). Additional chemicals purchased from Alfa Aesar included sodium hydroxide (98% pellets) and tetrabutylammonium hydroxide (TBAOH, 40%). All reagents were used as received without further purification. Deionized (DI) water used in all experiments was purified with an Aqua Solutions RODI-C-12A purification system (18.2 MΩ).

2.4.2 Synthesis of seed crystals

MEL seeds with Si/Al ratios of ∞ (silicalite-2) and 33 (ZSM-11) were synthesized with organic structure-directing agents (OSDAs) TBAOH and DAO, respectively, according to previously reported protocols^{316, 344}. For samples with a crystal Si/Al ratio of 16, the synthesis involved the addition of NaAlO₂ to a NaOH solution followed by additions of TEOS and TBAOH to obtain a final molar composition of 20 TBAOH: 4 Na₂O: 100 SiO₂: 2.5 Al₂O₃: 3000 H₂O. The solution was aged for 2 h at room temperature and transferred to a 23 mL Teflon-lined stainless steel acid digestion bomb (Parr Instruments), which was placed in a Thermo Scientific gravity convection oven and heated at 160°C for 1 day under static conditions.

MFI seed crystals with Si/Al ratios of ∞ (silicalite-1) and 14 (ZSM-5) were synthesized with TPABr and without OSDA, respectively, according to previously reported protocols^{345, 346}. For samples with a crystal Si/Al ratio of 40, seeds were purchased from Zeolyst (CBV 8014) and were calcined in a Thermo Fisher Lindberg Blue furnace at 550°C for 10 h (with temperature ramping rate of 1 °C min⁻¹) under the constant flow of compressed air (Matheson Tri-Gas) at 100 mL min⁻¹ before application. ZSM-12 (MTW) and mordenite (MOR) seed crystals were synthesized with TEABr and without an OSDA, respectively, according to previously reported protocols^{333, 347}. All of the seeds synthesized using an OSDA were calcined at 550°C for 10 h (according to the above procedure) prior to their addition to growth solutions.

2.4.3 Seeded zeolite synthesis

Seed-assisted syntheses were carried out by first adding sodium aluminate to an aqueous NaOH solution followed by the addition of LUDOX AS-40 to obtain the molar ratios listed in Table 1. To this solution was added the seeds in amounts spanning 2 to 13 wt% (calculated relative to the total silica in the growth solution). The nominal amount of seeds used in experiments was 10 wt% unless mentioned otherwise. The growth solution was aged at room temperature for ca. 24 h and subsequently transferred to a 23 mL acid digestion bomb. Hydrothermal treatment was carried out in an oven at temperatures spanning from 130 to 170°C under autogenous pressure. Solids extracted after select time intervals were isolated from the mother liquor by two cycles of centrifugation and washing with DI water, followed by drying in an oven at 60°C.

2.4.4 Characterization

Powder X-ray diffraction (XRD) patterns of dried solids were collected on a Rigaku SmartLab diffractometer with a Cu K α source (40kV, 30mA). Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 instrument equipped with FEG at 10 kV. All samples were carbon coated (layer thickness \approx 20 nm) prior to imaging to reduce charging. The size of the crystals was measured from multiple SEM images of a single batch. Elemental analysis was performed by electron dispersive X-ray (EDX) spectroscopy. EDX spectra were collected using a JEOL SM-31010/METEK EDAX system at 15kV and a 15mm working distance.

Chapter 3 Organic-free interzeolite transformation in the absence of common building units

3.1 Introduction

An underlying uncertainty in the field of zeolite crystallization is the relative roles of kinetics and thermodynamics in mediating nucleation (including polymorph selection)^{94, 348}, crystal growth^{118, 133}, and intercrystalline transformations^{86, 212}. The thermodynamics of zeolite formation and transformations has been examined using techniques such as calorimetry where examples, albeit few, indicate small differences in the heats of zeolite formation^{81, 349, 350}, while the heat of interzeolite transformation is reportedly undetectable³⁵¹, which seemingly places greater emphasis on controlling the kinetic pathways of these processes. This can be accomplished using an organic structure-directing agent (OSDA), which exhibits a size and shape commensurate to the channels and/or cages of zeolite structures, thus facilitating the formation of porous networks^{305, 352-354}. Approximately 30 of the reported 239 zeolite framework types have been prepared from organicfree media³⁵⁵. Economic and environmental factors motivate the elimination of organics from commercial synthesis; however, it is challenging to prepare zeolites with high silicon content or expand the list of synthetically-realized frameworks^{89, 356, 357} in the absence of OSDAs^{139, 144, 358}. Moreover, there have been many significant discoveries of novel OSDAs capable of tailoring zeolite morphology and size¹⁵³. Examples include the synthesis of 2-dimensional nanosheets with sizes on the order of several unit cells of the crystal structure (ca. 2 - 5 nm)^{303, 341, 359}. Numerous studies have shown that ultra-small zeolite crystals (or thin films) exhibit markedly improved performance relative to their commercial analogues in applications spanning from separations to catalysis^{61, 303}.

One method of minimizing or eliminating OSDAs in zeolite synthesis is the use of a parent crystal that undergoes an interzeolite transformation to a desired (daughter) structure^{212, 360}. This approach has been demonstrated for a range of metastable zeolites, such as faujasite (FAU) and

beta (BEA*)^{211, 226, 326}. For instance, Sano and coworkers synthesized high-silica AEI zeolites via interzeolite transformation of FAU parent crystals³⁶¹. Corma and coworkers employed a similar strategy to prepare high-silica chabasite (CHA), which could not be obtained using traditional silica and alumina sources²¹⁹. Both of these examples highlight the advantage of using interzeolite transformation to overcome the limitations of conventional protocols for achieving high Si/Al ratios; however, this approach has also proven to be an effective route to accelerate the rate of crystallization and improve product yields. For instance, Kubota and coworkers used FAU parent crystals to reduce the overall time of a MSE zeolite synthesis from 14 to 3 days³⁶².

In a majority of OSDA-free interzeolite transformations, the parent and daughter crystals exhibit some degree of structural similarity. Several groups have hypothesized that OSDA-free interzeolite transformations only occur when both parent and daughter share at least one common composite building unit (CBU)^{211, 212, 326}. Examples include (but are not limited to) the transformation of LEV to CHA (common CBU: d6r)³²⁴ and BEA* to MFI (common CBU: mor)²¹¹. There have been exemptions to this rule. For instance, the sequential interzeolite transformation of FAU-to-GIS-to-ANA⁸⁶ involves three structures lacking any common CBUs. Moreover, FAU can be converted to additional structures with disparate CBUs (i.e. ABW and MER)²¹⁰ through the judicious selection of alkali metals. In such cases, it appears that a parent crystal serves primarily as the source of Si and Al for zeolite synthesis. For most reported transformations where the parent and daughter lack structure similarity, it is necessary to use either an OSDA with specificity for the daughter zeolite or seeds of the target (daughter) zeolite^{211, 326}. Okubo and coworkers proposed a common parent-daughter CBU hypothesis in seeded zeolite synthesis in the absence of OSDAs³²³. They posited that a seed crystal will direct the growth of the same zeolite provided that the growth mixture selected for the synthesis (in the absence of seeds) yields a crystal structure with at least one common CBU. For example, ZSM-5 (MFI) seeds placed in a mordenite (MOR) growth mixture yields a ZSM-5 product owing to a shared CBU (mor oligomer) between MFI and MOR framework types.

Here, we demonstrate the direct transformation of USY (FAU) to ZSM-5 in the absence of organics and without the use of ZSM-5 seeds. This specific transformation involving two zeolites lacking a common CBU was previously deemed improbable^{211, 363}. The FAU-to-MFI interzeolite transformation is accomplished using a growth medium that favors OSDA-free ZSM-5 crystallization. A ternary (kinetic) phase diagram (Figure 1) indicates general regions where zeolite X and Y (FAU), mordenite, and ZSM-5 are synthesized in media using only Na+ as an inorganic structure-directing agent. The synthesis of FAU-type materials occurs under conditions of low H₂O content, high alkalinity, and low temperature $(25 - 80 \,^{\circ}\text{C})^{87, 135, 152, 364-367}$. Conversely, the synthesis of ZSM-5 requires more dilute growth mixtures with a disproportionally higher silica content and higher temperature. Mordenite is prepared under conditions that are similar to ZSM-5, with the exception that the former can be prepared at higher alumina concentration owing to its lower Si/Al (framework) ratio.

3.2 Results and discussion

The sol gel compositions used for zeolite synthesis and interzeolite transformation are listed in **Table** 3.1. Growth mixtures S1, S2, and S3 (plotted in **Figure** 3.1) are typical compositions for OSDA-free syntheses of zeolite Y, ZSM-5, and mordenite, respectively. Comparison of reported MFI and MOR syntheses in literature (**Figure** 3.1, inset) reveal that S2 and S3 are in an overlapping region of both structures, which suggests that subtle differences in synthesis conditions can lead to the formation of either zeolite structure (**Figure** B.1 and **Table** A.1). First, we focus on growth mixture S2 where the use of commercial zeolite USY (Zeolyst CBV760) as the sole source of Si and Al leads to the formation of ZSM-5. Iglesia, Zones and coworkers²¹¹ performed a similar synthesis with USY seeds using growth mixture S3 and reported an amorphous product. In their study, it was necessary to introduce tetrapropylammonium (a common OSDA for MFI-type zeolite) and ZSM-5 seeds to obtain a fully crystalline ZSM-5 product. Moreover, in order to achieve composition S3 with USY as the sole aluminosilicate source, they used commercial USY (Zeolyst CBV780) with a higher Si/Al ratio of 40.

Solution	Si source	T (°C)	Si	Ala	NaOH	H ₂ O	Time	Product
S 1	AS40 ^b	65	2.11	1.05	5.79	100	7 d	FAU
S2	SM30	190	2.18	0.7	0.7	100	32 h	MFI
S2	USY ^c	190	2.18	0.7	0.7	100	32 h	MFI
S 3	SM30	150	1.05	0.03	0.53	100	32 h	Am ^d
S 3	SM30	190	1.05	0.03	0.53	100	32 h	MFI
S 3	USY ^c	150	1.05	0.03	0.53	100	40 h	Am ^d

Table 3.1 Synthesis compositions used in seeded and non-seeded protocols

a. Sodium aluminate is used as Al source unless otherwise specified; b. Synthesis with SM 30 results in a partially amorphous product; c. No additional Al source is used for interzeolite transformations using USY (CBV760 and CBV780 for S2 and S3 respectively; d. Am = Amorphous



Figure 3.1 Ternary (kinetic) phase diagram with organic-free growth mixtures S1 – S3 (yellow diamonds) corresponding to the compositions listed in **Table** 3.1. Inset: Enlarged grey region with reported compositions for MFI (red) and MOR (blue) synthesis.

For comparison, we prepared growth mixture S3 wherein USY was replaced with different silica and aluminum sources: colloidal silica (SM30) and sodium aluminate. Interestingly, we observed that an increase in synthesis temperature from 150 to 190°C leads to the formation of fully crystalline ZSM-5. The same outcome was observed for growth solution S2 using USY (Zeolyst CBV760) or its replacement with the alternative aluminosilicate sources (**Table** 3.1).

These findings reveal that it is possible, under certain synthesis conditions, to directly transform parent USY to ZSM-5 without the use of OSDA or ZSM-5 seeds.

Using growth mixture S2 with USY, we examined powder X-ray diffraction (XRD) patterns of extracted solids at periodic times during hydrothermal treatment (**Figure** 3.2) to resolve the temporal evolution of crystal structure(s). Room temperature aging of the alkaline growth mixture (pH 11.1) results in loss of USY structure through either partial or complete dissolution, as evidenced by the appearance of an amorphous (broad) peak in the powder XRD pattern. The first appearance of Bragg peaks corresponding to ZSM-5 occurs around 24 h of hydrothermal treatment. Continued heating results in further crystallization of ZSM-5 followed by the emergence of both mordenite (MOR) and quartz peaks around 48 h. A MFI-to-MOR transition has been previously reported in literature³³¹. After 8 days of heating, there is a significant increase in the percentage of quartz product with residual mordenite and trace amounts of ZSM-5.



Figure 3.2 Powder X-ray diffraction patterns of solids extracted from growth mixture S2 (prepared with USY) reveals the temporal evolution of amorphous and crystalline (MFI, MOR, and quartz) products.

We previously reported⁸⁶ that one of the primary driving forces for interzeolite transformation is the sequential formation of zeolites with higher framework density, which is

qualitatively consistent with the Ostwald rule of stages that predicts the conversion of an initially metastable structure to ones that are more thermodynamically stable. The use of density gradients to rationalize the sequence of stages is based on calorimetry data^{81, 350} showing a relationship between molar volume and enthalpy of formation. As shown in Figure 3, the FAU-to-MFI transformation (from high to low molar volume) is consistent with this trend; however, the formation of MOR with higher molar volume is seemingly inconsistent with the expected sequence of stages, whereas quartz (being one of the most stable silicates) is compliant. Interestingly, the trajectory depicted in **Figure** 3.3 is independent of the silicon source. For instance, we followed the same synthesis protocol using growth mixture S2 where USY was replaced with colloidal silica and sodium aluminate. This modified protocol resulted in the same progression of stages (**Figure** B.3), with the only disparity being a lower percentage of mordenite in the final product.



Figure 3.3 (top) Stages of zeolite phase transformation with increasing synthesis time. The molar volumes for each zeolite were obtained from the IZA²². (bottom) Composite building units (CBUs) of all zeolite framework types used in this study.

The energetics and pathway(s) associated with the MFI-to-MOR transformation are not well understood; however, one could reasonably predict this phenomenon given that composition S2 is located in an overlapping MFI/MOR phase space within the ternary diagram (**Figure** 3.1, inset). When trying to explain interzeolite transformations by the relationship between molar volume and enthalpy of formation, as depicted in **Figure** 3.3, it is important to note that this general trend was derived for purely siliceous zeolites⁸². Given that the majority of zeolites (and zeotypes) contain aluminum and other heteroatoms, it is unreasonable to expect that a single discriptor (i.e. molar volume) is universally applicable. Indeed, Navrotsky and coworkers have demonstrated that variations in zeolite framework Si/Al ratio influences the enthalpy of formation⁸¹. Therefore, temporal changes in (alumino)silicate speciation and/or concentration over the course of zeolite growth can alter supersaturation (i.e. chemical potential), which can have a concomitant effect on the thermodynamic driving force for the nucleation and growth of new crystal structures.

Developing predictive models of interzeolite transformation is challenging since the correlations between free energy of formation and zeolite composition or crystal structure are not well understood. There are instances where both parent and daughter zeolites exhibit nearly identical composition, such as the transformation between FAU (Si/Al = 1.5 - 2.5) and GIS (Si/Al = 1.5 - 2.0)³⁶⁸. For the system in this study, the Al content of zeolites increases with each interzeolite transformation: USY (Si/Al = 30 - 40) to ZSM-5 (SI/Al = 16) to MOR (Si/Al = 6). There is a also stark difference in the elemental composition of mordenite (Si/Al = 6) and ZSM-5 (Si/Al = 16) obtained from growth mixtures S2 and S3. During the sequence of stages in **Figure** 3.3, the removal of Al from the growth mixture with each interzeolite transformation leads to a progressive accumulation of silica that seemingly promotes the formation of quartz (a common impurity in zeolite synthesis)¹³⁷. Unlike FAU and MFI framework types, which do not share a common building unit, there is one common CBU between MFI and MOR (**Figure** 3.3). It is uncertain, however, if this shared CBU is a causal or coincidental factor in the observed MFI-to-MOR transformation.



Figure 3.4 SEM images of (A) parent USY (CBV760) zeolite and solids extracted from growth mixture S2 (using USY as the sole source of Si and Al) at different time intervals. Three distinct morphologies in D are labelled as i – iii. Scale bars are equal to 5 μm unless otherwise labelled.



Figure 3.5 (A-C) TEM selected area electron diffraction patterns of crystals in a 48 h sample indexed to (A) MOR, (B) MFI, and (C) quartz (corresponding TEM images are provided in **Figure** B.4). Scale bars are equal to 2 nm⁻¹.

In the case of the FAU-to-MFI transformation, it is unclear if there is any molecular signature of the parent crystal (e.g., CBUs or oligomers) that remains after room temperature aging, although qualitative evidence points to the fact that there is some memory of the FAU structure. Scanning electron microscopy (SEM) images of samples extracted during early heating time show

what appears to be amorphous worm-like particles (**Figure** B.5), analogous to those reported for other zeolites¹¹⁷. Conversely, SEM images of as-received USY (**Figure** 3.4 **A**) show the presence of ca. 800 nm particles with ill-defined morphology. Micrographs of samples extracted after 24 h (**Figure** 3.4 **B**), corresponding to the first appearance of Bragg peaks in **Figure** 3.2, reveal the presence of ZSM-5 crystals (ca. $20x10x10 \ \mu\text{m}^3$) surrounded by what appears to be either amorphous precursors or residual (or partially dissolved) USY parent crystals. Samples extracted at a time corresponding to nearly complete FAU-to-MFI transformation show a population of ZSM-5 crystals (**Figure** 3.4 **C**) with the typical coffin-shape morphology (**Figure** 3.6 **A**) and residual smaller particles of unidentified structure. Preparation of ZSM-5 using colloidal silica and sodium aluminate as replacements for USY results in crystals with smaller size, a higher degree of faceting, and more intergrowths (i.e., defects) on basal (010) surfaces (arrows in **Figure** 3.6 **B**). A lower resolution image is provided in **Figure** B.7.



Figure 3.6 SEM image of ZSM-5 crystals prepared from (A) a FAU-to-MFI IZT (B) colloidal silica and sodium aluminate (in replacement of USY) with intergrowths on (010) surfaces (arrows). Scale bars are equal to 5 μm.

Distinct differences in the number of intergrowths on ZSM-5 crystals prepared with and without USY seems to indicate that the use of USY alters zeolite crystallization. This seems to suggest that the growth medium contains species (growth units) that are different, which can presumably alter the pathways of crystal formation; however, we observe that the time to reach fully crystalline ZSM-5 is unchanged, irrespective of the aluminosilicate source (**Figure B.2 and Figure B.3**). For syntheses employing USY as the only aluminosilicate source, SEM images of

samples extracted after 40 h of heating (**Figure** 3.4 **D**) reveal a heterogeneous distribution of particle size and shape, consistent with powder XRD patterns revealing the presence of three crystalline products, consistent with Raman spectroscopy (Figure S6). Energy-dispersive X-ray spectroscopy (EDX) analysis of this sample reveals a distribution of Si/Al ratio, while transmission electron microscopy selected area electron diffraction patterns of various morphologies confirm the presence of mordenite (**Figure** 3.5 **A**), ZSM-5 (**Figure** 3.5 **B**), and quartz (**Figure** 3.5 **C**).

3.3 Conclusion

In summary, we have shown that it is possible for a FAU-to-MFI interzeolite transformation to occur in the absence of an OSDA and/or ZSM-5 seeds. This example also indicates that heuristics based on the presumption that transformations occur between structures with common CBUs is not universally applicable to all zeolite syntheses. Overall, there are relatively few reported examples of intercrystalline transformations in literature, thus making it difficult to derive general hypotheses that are capable of explaining the factor(s) governing structural transitions. In this study, the thermodynamic driving force for ZSM-5 crystallization from faujasite is not well understood. It is apparent that the selection of synthesis composition within the ternary phase diagram, as well as other parameters (e.g., temperature), impacts zeolite structural transitions. Moreover, the observed MFI-to-MOR transformation highlights the inability to rely on a single physical property, such as molar volume, to predict the sequence of stages. Prior experiments have shown that differences in the enthalpy of parent and daughter zeolites are often too small to be detected by techniques such as calorimetry. This seems to suggest that thermodynamic factors driving structural transitions can be subtle, and thus may be difficult to measure and ultimately predict. It is evident that interzeolite transformations can be a facile and highly efficient method of tailoring the physicochemical properties of zeolites; however, more studies are clearly needed to elucidate the fundamental mechanisms of these processes in zeolite synthesis.

3.4 Experimental

3.4.1 Materials

The following reagents were purchased from Sigma-Aldrich: colloidal silica (LUDOX SM-30), sodium hydroxide solution (NaOH, 1 M). Sodium aluminate (NaAlO2, technical grade) was purchased from Alfa Aesar. USY zeolite (CBV760) was purchased from Zeolyst. Deionized (DI) water was produced with an Aqua Solutions RODI-C-12A purification system (18.2 M Ω). All reagents were used as received without further purification.

3.4.2 Zeolite crystallization

For synthesis with USY as the sole aluminosilicate source, USY (CBV760) was added to a solution of NaOH and DI water. For synthesis with colloidal silica (SM30) and NaAlO₂ as the silica source and alumina source, respectively, NaOH and NaAlO₂ were mixed with DI water followed by the addition of SM30 to yield a growth mixture with a molar composition of 0.35 Na₂O: 2.18 SiO₂: 0.035 Al₂O₃:100 H₂O (labelled as solution S2) or 0.265 Na₂O: 1.05 SiO₂: 0.015 Al₂O₃:100 H₂O (labelled as solution S3). The growth mixture was aged at room temperature for 1 h under continuous stirring and was then placed in a Teflon-lined stainless steel acid digestion bomb (Parr Instruments) and heated at either 150 or 190°C under autogenous pressure for 24 h - 8 d without rotation. For the synthesis of FAU, the alumina source (NaAlO₂) was added to solution of NaOH and DI water followed by the addition of the silica source (SM30) to obtain a growth mixture with a molar composition of 2.89 Na₂O: 2.11 SiO₂: 0.525 Al₂O₃:100 H₂O. The resulting mixture was aged at room temperature for 1 day followed by hydrothermal treatment at 65°C for 7 days under static conditions. After hydrothermal treatment, mixtures were removed from the oven and immediately cooled to room temperature by quenching. Crystals were isolated from the supernatant by three cycles of centrifugation (13,000 rpm) and washing. The resulting solid was dried at room temperature in air.

3.4.3 Materials characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku diffractometer using Cu K α radiation (40kV, 40 mA). Scanning electron microscopy (SEM) was conducted at the Methodist Hospital Research Institute in the Department of Nanomedicine SEM Core using a Nova NanoSEM 230 instrument with ultrahigh resolution FESEM (operated at 15 kV and a 5mm working distance). Energy dispersive X-ray spectroscopy (EDX) was performed using a JEOL SM-31010/METEK EDAX system at 15 kV and 15 mm working distance. X-ray photoelectron spectroscopy (XPS) analysis of samples was performed using a PHI 5800 ESCA (Physical Electronics) multitechnique system equipped with a standard a achromatic Al K α X-ray source (1486.6 eV) operating at 300 W (15 kV and 20 mA) and a concentric hemispherical analyzer. The equipment neutralizer component was utilized to prevent charging effects. All data were collected at a 45° takeoff angle. The Raman characterization was done on a confocal micro-Raman microscope Xplora, Horiba JY instrument using an excitation wavelength of 532 nm. The Raman results were further confirmed with the RRUFF database as well as the powder XRD diffraction patterns³⁶⁹. Transmission electron microscopy was carried out using a JEOL 2010FX instrument operated at 200 kV with 0.18 nm resolution, equipped with EELS and EDS and selected area electron diffraction pattern (SAEDP) analysis. The SAEDP were indexed following the standard procedures described by Williams and Carter³⁷⁰. The d-spacings were corroborated in the RRUFF database where the Crystallography Index Chart (CIF) was downloaded and the d-spacings were simulated using the Vesta Software.

Chapter 4 Spontaneous pillaring of pentasil zeolites

4.1 Introduction

The network of micropores in zeolite catalysts imposes diffusion limitations that can compromise their performance in numerous applications²³⁹. There have been many approaches used to improve mass transport in these porous aluminosilicates, which include the introduction of secondary pore structures (meso/macro) through post-synthesis desilication/dealumination^{278, 371,} ³⁷², surfactant treatments^{294, 373}, and templating^{249, 299, 303, 374, 375}, which generates hierarchical materials with a distribution of pores. It has been shown that hierarchical zeolites exhibit superior catalytic performance relative to conventional counterparts in various industrially-relevant chemical reactions^{233, 238, 247}, such as alkylation^{376, 377}, Fischer-Tropsch synthesis³⁷⁸⁻³⁸⁰, methanol/methane upgrading^{241, 381}, cracking²⁹⁴, and biomass conversion^{382, 383}. Alternative approaches to reduce internal diffusion constraints include the synthesis of nanosized zeolites^{87, 88,} ^{100, 259, 384}. Ryoo and coworkers introduced methods of preparing 2-dimensional (2D) MFI-type zeolites (uni- and multi-lamellar)^{303, 385, 386} with sizes on the order of several unit cells of the crystal structure. Tsapatsis and coworkers introduced a direct method of generating pillared nanosheets, referred to as self-pillared pentasil (SPP) zeolites, which improve mass transport by introducing meso/macropores with greater access to acid sites^{341, 387}. While these hierarchical zeolites markedly improve catalyst performance, their syntheses can often result in have several limitations that can include a limited range of zeolite acid concentration (i.e. higher Si/Al ratios), low products yield, multiple synthesis steps, or the required use of an organic structure-directing agent (OSDA), all of which impose restrictions for commercialization²⁰⁷. Here, we demonstrate an OSDA-free, seedassisted method of preparing SPP zeolites. To our knowledge, this is the first direct synthesis of pillared MFI-type zeolite nanosheets without the use of organics. Seed-assisted synthesis of SPP zeolites have the added benefits of producing large product yields and high acid site concentrations

that leads to enhanced catalytic performance in methanol to hydrocarbons (MTH) and Friedel-craft alkylation (FCA) reactions in comparison to conventional ZSM-5 catalysts.

4.2 Results and discussion

We selected an organic-free medium (Si/Al = 9) for crystallization with a composition that lies near the boundary of three zeolites (Figure C.1 and Table A.1): mordenite (MOR), ZSM-11 (MEL), and ZSM-5 (MFI). Seed-assisted synthesis was carried out by adding calcined crystals (10 % by mass) to this growth mixture. Four different batches of zeolites seeds (Table 4.1) were prepared according to reported protocols: silicalite-2 (siliceous isostructure of ZSM-11), ZSM-11 (Si/Al = 33), silicalite-1 (siliceous isostructure of ZSM-5), and ZSM-5 (Si/Al = 40). Focusing initially on seed-assisted syntheses using silicalite-2, powder X-ray diffraction (PXRD) patterns of solids extracted from syntheses at periodic times (Figure 4.1 A) reveal that MEL-type seeds dissolve within 1 day of hydrothermal treatment. Given that the sample is predominantly comprised of amorphous aluminosilicate precursors, it is difficult to ascertain if silicalite-2 seed crystals (Figure 4.1 B) fully or partially dissolve. After 2 days of synthesis, Bragg peaks corresponding to pentasil zeolite (MEL or MFI type) are detected in the PXRD pattern; and within 3 days crystallization is complete. Analysis of the final product reveals a predominantly MFI structure, although MEL-type zeolite may be present given the close similarity in PXRD patterns of the two zeolites^{70, 388, 389}. This sample has a high Al content (i.e. Si/Al = 8, nearly equivalent to the starting gel) with ca. 28% of all Brønsted acid sites located on external surfaces. Interestingly, scanning electron micrographs (Figure 4.1 C) reveal a hierarchical morphology resembling self-pillared pentasil (SPP) zeolites reported by Tsapatsis and coworkers³⁴¹. High magnification images of this sample, referred to herein as SPP1, show that pillared nanosheets are arranged in a "house of cards" configuration^{303, 359} with an average thickness of ca. 30 nm (Figure 4.1 D) and a distribution of both mesopores and macropores (marked as yellow circle) (Figure C.2).

Table 4.1 Physicochemical properties of H-form zeolite samples.

Sample ^a	Seed	BET SA b	External S _A ^b	V _{micro} ^b	Si/Al °	Cacid	Acid Type (%) ^e		Bext f	EFAl ^g
		(m²/g)	(m²/g)	(cm ³ /g)		(µmol/g) ^d	В	L	(%)	(%)
SPP1	Silicalite- 2	499	135	0.14	8	914	80	20	27	12
SPP2	ZSM-11	492	133	0.14	8	877	89	11	30	14
SPP3	Silicalite- 1	434	48	0.15	10	785	81	19	8	7
SPP4	ZSM-5	503	150	0.14	8	816	74	26	57	15
ZSM-5		420	43	0.15	18	782	87	13	6	9

(a) SPP = self-pillared pentasil; conventional ZSM-5 was synthesized by a reported protocol ³⁴²; (b) BET surface area (S_A) was obtained from N₂ adsorption/desorption with external S_A and microporous volume (V_{micro}) calculated by the t-plot method; (c) Si/Al ratio measured by EDX; (d) acid site density (C_{acid}) measured by NH₃ –TPD; (e) acid type measured by pyridine FTIR where B = Brønsted acid sites and L = Lewis acid sites; (f) B_{ext} = fraction of acid sites on external surfaces obtained from B_{diTPy}/B_{py}; (g) EFAl = extra-framework Al measured by ²⁷Al MAS NMR.



Figure 4.1 (A) Time-resolved PXRD patterns for the synthesis of SPP1 using silicalite-2 (MEL) seeds. SEM images of (B) silicalite-2 seeds and the (C) SPP1 product after 3 days of seeded growth. (D) High magnification of FE-SEM image of a SPP1 crystal.



Figure 4.2 (A) TEM image revealing individual sheets of SPP1 with ED pattern (inset). (B) TEM image of ultra-microtomed SPP1 showing and (D) corresponding corresponding FFT ED pattern. (D) HRTEM image of the yellow box in F with an overlaid MFI structure.

Previous syntheses of SPP and related 2-dimensional zeolites (e.g., multi-lamellar nanosheets)^{359, 374, 386} all required the use of OSDAs. The synthesis of SPP1 is the first OSDA-free, bottom-up route to achieve a hierarchical zeolite. The use of crystalline seeds is critical to achieving the pillared architecture. Tsapatsis and coworkers^{387, 390} demonstrated that nanosheets of SPP are mostly MFI zeolite, whereas they hypothesized the intersections (or junctions) between nanosheets are MEL zeolite, which acts as a four-fold symmetric connector. Transmission electron microscopy (TEM) images of SPP1 indicate the presence of numerous nanocrystalline subdomains (**Figure 4.2 A**) while the selected area electron diffraction (SAED) pattern of the entire particle reveals a single crystallographic registry, which was confirmed from TEM images of ultra-microtomed SPP1 (**Figure 4.2 B**) where the resulting thin slices reveal lattice fringes oriented parallel to each other throughout the cross-section. Diffraction of the entire area (**Figure 4.2 C**) confirms the single crystal nature, whereas a high-resolution image with an overlay of the MFI framework (**Figure 4.2 D**) clearly indicates nanosheets are oriented in the [010] direction (i.e. exposing straight channels on the large surface area facets).

Zeolite syntheses typically involve long induction periods followed by rapid crystallization that makes it challenging to visualize the early stages of nucleation^{95, 109}. It has long been postulated^{100, 391} that numerous zeolites, including ZSM-5, are formed via heterogeneous nucleation on (or within) amorphous precursors, although direct evidence is generally lacking. One unique aspect of SPP1 synthesis is a relatively slow rate of growth following nucleation that enables the direct visualization of crystallization at various stages. Solids extracted from growth mixtures at early times contain mostly amorphous precursors is observed after 1 day of heating (**Figure 4**.3 **A** and **Figure C**.4). Solids extracted after longer times (**Figure 4**.3 **B,D**) contain a population of SPP crystals on precursor surfaces. High resolution SEM images reveal spheroidal protrusions on the surfaces of nanosheets (**Figure 4**.3 **C**), which are signatures of a nonclassical growth
pathway^{118, 392}. Previous studies have shown that MFI-type zeolite grows by a combination of monomer addition (classical pathway) and amorphous particle attachment^{146, 335, 393} followed by disorder-to-order transitions that initiate 3-dimensional nucleation of new layers on zeolite surfaces¹⁰⁴. Here, heterogeneous nucleation of SPP crystals is directly visualized by electron microscopy to show with unprecedented resolution wherein pillars emerge emerging from amorphous particles (**Figure 4.3 E**) and branching into the larger hierarchical networks of intersecting nanosheets (illustrated in **Figure 4.3 F**). These observations defy conventional beliefs that organics are necessary in zeolite crystallization to generate nanosheets and/or facilitate pillaring.



Figure 4.3 (A – C) FE-SEM images of solids extracted from a SPP1 synthesis at the following times: (A) 1, (B, D, E) 2, and (C) 3 days. (F) Idealized schematic of heterogeneous nucleation and growth of SPP zeolites on amorphous interfaces.

The intermediates of the four systems studied (SPP1, SPP2, SPP3, and SPP4) were further analyzed by TEM and SAED (**Figure** C.5). In all cases, they comprised two different phases, a dark globular component (high contrast) from which a lighter structure (low contrast) emerges. The morphology of the later is consistent with the self-pillared architecture observed by SEM (**Figure** 4.3 **A-E and Figure** 4.4 **C-K**). At high magnification, this lighter phase shows protrusions, which are likely nuclei of SPP zeolites obtained at longer times (**Figure** 4.3 **C and Figure** 4.4 **C, F, I**). Analysis of this phase by SAED produced faint patterns (**Figure** C.5), which are consistent with the weak Bragg peaks in powder XRD patterns (**Figure** 4.1 **A, Figure** 4.4 **A, and Figure** C.7). This indicates that, at this intermediate stage, these materials have not yet fully crystallized.



Figure 4.4 (A) Percent crystallinity as a function of synthesis time measured from PXRD patterns. (B) IZT from pentasil-to-MOR on the further synthesis.



Figure 4.5 FE-SEM and TEM images from the (A-C) SPP2 synthesis using ZSM-11 seeds (D-F) SPP3 synthesis using silicalite-1 seeds (G-I) SPP4 synthesis using ZSM-5 seeds after 3 days of heating.

The exact mechanism of pillaring in the absence of an OSDA is unknown, but we speculate that growth mixtures prior to the onset of nucleation contain some "memory" of the dissolved silicalite-2 seeds^{202, 212}. The pillared architecture could be attributed to the remnants of seeds with

a MEL-type structure that putatively facilitate branching (i.e., nanosheet junctions, **Figure** 4.3 **F**). This hypothesis first proposed by Tsapatsis and coworkers³⁴¹ has yet to be confirmed; however, in a follow up study⁷⁰ they provided definitive evidence that MFI nanosheets are comprised of MEL intergrowths. This seemingly suggests that the MFI seeds used in this current study to prepare SPP3 and SPP4 likely contain a minor fraction of MEL, which may potentially contribute to the memory of dissolved seeds.

In the absence of seeds, the growth mixture selected for this study produces mordenite crystals lacking hierarchical structure (Figure C.7). Interestingly, time-resolved studies of seeded growth reveal that SPP1 is fully crystalline after 3 days of heating (Figure 4.4 A), which is approximately one-fourth the time required for non-seeded growth mixtures. Additional synthesis time results in an interzeolite transformation from SPP1 to mordenite (Figure 4.4 B) where the latter nucleates within the interior of SPP1 clusters (Figure C.6) and gradually consumes hierarchical zeolites with prolonged heating. The pillared architecture could be attributed to the remnants of seeds with a MEL-type structure that facilitates branching (i.e., nanosheet junctions, **Figure** 4.3 **F**). To test this point, we performed a similar synthesis using three different seeds: ZSM-11 (MEL), silicalite-1 (MFI), and ZSM-5 (MFI). All syntheses resulted in SPP zeolite (Table 4.1), referred to as samples SPP2, SPP3, and SPP4, respectively. The kinetics of SPP2 and SPP3 crystallization (Figure C.8) is similar to SPP1 (Figure 4.4 A), but SPP4 deviates from the others by reaching a maximum 80% crystallinity with residual ca. 20% amorphous material prior to the onset of the interzeolite transformation. Time-resolved SEM and TEM images of SPP2 (Figure 4.5 A-C), SPP3 (Figure 4.5 D-F), and SPP4 (Figure 4.5 G-I) samples at various stages of growth reveal similar mechanisms of heterogeneous nucleation from amorphous precursors. All SPP materials have similar hierarchical structure with varying degrees of branching, while the morphology of SPP3 (Figure 4.5 E) derived from silicalite-1 seeds exhibits a higher degree of aggregation (Figure C.9). This indicates that branching occurs irrespective of seed crystal structure. The use of MEL-type seeds results in higher surface area (Table 1), but its average nanosheet thickness (ca. 40 nm, Figure C.10) is comparable to other SPP materials (with the exception of SPP3, which is around 60 nm). All materials prepared by seeded growth (with the exception of SPP3) exhibit unusually high fractions of Brønsted acid sites on their exterior surfaces (**Table** 4.1), as high as 7-fold the value of conventional ZSM-5.



Figure 4.6 (A) Friedel craft alkylation reaction used as a model liquid phase reaction. (B) Benzyl alcohol conversion during Friedel craft alkylation reaction (C) Selectivity of the alkylated product (TMBB) at isoconversion (ca. 75 %).



Figure 4.7 (A) Sub-complete methanol conversion in the MTH reaction at 350 °C. (B) Turnover number (histogram, left axis) estimated between 50 to 30% conversion and the ethene-to-2MBu ratio (symbols, right axis) of all catalysts at ca. 40% conversion.

We tested the catalytic performance of all SPP samples with an overall particle size of 1.1 $-2.3 \mu m$, (**Figure** C.10) and compared the results to that of a conventional ZSM-5 catalyst with an overall crystal size of 300 nm (**Figure** C.11). All SPP samples were subjected to mild acid pre-treatment to remove any residual amorphous material, followed by ion exchange with NH₄⁺ and calcination to generate H-form catalysts. Elemental analysis of SPP and ZSM-5 samples revealed

similar acid concentration and distributions of Brønsted and Lewis acids (Table 4.1). We first tested the impact of two key features of SPP catalysts – large external acid site concentration and high surface area – using the Friedel craft alkylation (FCA) reaction of mesitylene with benzyl alcohol (Figure 4.6 A). This liquid-phase reaction predominantly occurs on exterior surfaces of the zeolite owing to the bulky size of mesitylene that cannot readily access interior channels of medium-pore zeolites (i.e. MFI and MEL)^{394, 395}. Comparison of all five catalysts reveal a significantly higher activity of SPP materials compared to ZSM-5 (Figure 4.6 B) with SPP2 exhibiting the most rapid increase in benzyl alcohol conversion. Interestingly, the selectivity of SPP catalysts for the desirable product, 2-benzyl-1,3,5-trimethylbenzene (TMBB), is ca. 2-fold higher than ZSM-5 (Figure 4.6 C). This improved performance is attributed to the unique physicochemical properties of the hierarchical zeolites; however, a signature of SPP zeolites prepared by seed-assisted synthesis is their unusually high aluminum content (Si/Al < 15, Table 4.1). There is a possibility that at such low Si/Al ratio, there are extraframework Al species³⁹⁶ present on the external surface. Nature of such species is currently unknown, and it might contribute to the difference in reactivities in different SPPs in FCA reaction. To our knowledge, SPP and other hierarchical MFI-type zeolites reported in literature have not been directly synthesized with Si/Al ratios less than 40, which is outside the range of most commercial ZSM-5 zeolites (i.e., Si/Al < 20).

Methanol-to-hydrocarbons (MTH) was used as a second reaction to assess the performance of hierarchical and conventional catalysts. Gas-phase reactions at sub-complete conversion (50 – 60 %) reveal that all SPP catalysts exhibit improved lifetime compared to conventional ZSM-5 (**Figure** 4.7 **A**). The performance of SPP catalysts can be grouped in two general categories: those with around 2-fold lower rates of deactivation (SPP2 and SPP3) and those with around 4-fold lower rates of deactivation (SPP1 and SPP4) compared to ZSM-5. These groupings also apply to the measured turnover number (TON), or moles of methanol converted per mole of Brønsted acid (**Figure** 4.7 **B**). The two groupings of SPP catalysts have TON values of around 900 and 450 mol MeOH/H⁺, respectively, which are significantly larger than that of conventional ZSM-5 (240 mol MeOH/H⁺). All five catalysts exhibit similar product selectivity (**Figure** C.12), which is evaluated using the ethene-to-2MBu ratio (**Figure** 4.7 **B**, symbols) where 2MBu refers to both 2-methylbutane and 2-methyl-2-butene. This ratio is a signature of the dominant MTH cycle (olefin vs. aromatic) with lower numbers indicating an enhanced propagation of the olefin cycle³⁹⁷. A slightly lower value of ethene/2MBu for SPP catalysts is qualitatively consistent with a previous study by Bhan and coworkers²⁴⁵ showing that ZSM-5 with reduced internal mass transport limitations (e.g. smaller crystal dimensions) promotes the olefin cycle. Overall, this study reveals that SPP zeolites prepared by seed-assisted synthesis exhibit improved catalytic performance (relative to conventional ZSM-5). Moreover, a qualitative comparison of SPP catalysts with hierarchical ZSM-5 reported in literature containing less aluminum content and thinner nanosheets (ca. 3 nm)³⁰³ indicates comparable performance, although previous studies report MTH reactions at 100% methanol conversion, which overestimates catalyst lifetime³⁹⁸.

4.3 Conclusion

In summary, self-pillared pentasil zeolites have been prepared by the use of either MEL or MFI seeds without the assistance of any organic structure-directing or branching agents. By timeresolved electron microscopy, we have been able visualize heterogeneous nucleation and capture the subsequent emergence of these hierarchical zeolites from the surfaces of amorphous precursors. From the onset of crystallization, the SPP zeolites present a clear pillared architecture that undergoes concerted growth and branching with reaction time. Although the exact mechanism of pillaring is unknown, we speculate that remnants from the dissolved seeds imprint some "memory" in the growth mixtures that facilitate the branching. This phenomenon occurs for both MEL- and MFI-type seeds, resulting in similar hierarchical structures with varying degrees of branching. These SPP zeolites present a large external surface area (almost triple that of conventional ZSM-5) and an exceptionally high percentage of external acid sites (up to 7-fold higher than conventional ZSM-5). These two key features significantly improve catalytic performance. The evaluation of SPP zeolites in the Friedel craft alkylation reaction of mesitylene with benzyl alcohol results in higher conversion and an approximate two-fold increase in the selectivity to the desirable product. Similarly, we observe in the MTH reaction that SPPs extend catalyst lifetime and markedly enhance turnovers (as much as 4-fold relative to conventional ZSM-5). These findings highlight the potential use of this facile, efficient method of seed-assisted synthesis towards the realization of commercial hierarchical zeolite catalysts.

4.4 Experimental

4.4.1 Materials

The following chemicals for zeolite synthesis were purchased from Sigma Aldrich: LUDOX AS-40 (40 wt% suspension in water), tetraethyl orthosilicate (TEOS, \geq 99.5%), sodium aluminate (57.1% Al₂O₃ and 37.2% Na₂O), 1,8-diaminooctane (DAO, 98%), and tetrapropylammonium bromide (TPABr, 98%). Additional chemicals purchased from Alfa Aesar included sodium hydroxide (98% pellets) and tetrabutylammonium hydroxide (TBAOH, 40%). All reagents were used as received without further purification. Deionized (DI) water used in all experiments was purified with an Aqua Solutions RODI-C-12A purification system (18.2 MΩ).

4.4.2 Synthesis of seed crystals

Seeds of MEL zeolite with Si/Al ratios of ∞ (silicalite-2) and 33 (ZSM-11) and the MFI seeds with a Si/Al ratio of ∞ (silicalite-1) were synthesized according to previously reported protocols²⁰². ZSM-5 seeds with a Si/Al ratio of 40 was purchased from Zeolyst (CBV 8014). All seeds were calcined in a Thermo Fisher Lindberg Blue furnace at 550 °C for 10 h (with temperature ramp rate of 1 °C min⁻¹) under the constant flow of compressed air (Matheson, 100 cm³ min⁻¹) before application.

4.4.3 Self-pillared pentasil synthesis

Seed-assisted syntheses were carried out by first adding sodium aluminate to an aqueous NaOH solution followed by the addition of LUDOX AS-40 to obtain the growth solution with a molar composition of 3.42 Na₂O: 18 SiO₂: 1 Al₂O₃: 324 H₂O. The nominal amount of calcined seeds used in experiments was 10 wt%. The growth solution was aged at room temperature for ca. 24 h and subsequently transferred to a 23 mL acid digestion bomb (Parr Instruments). Hydrothermal treatment was carried out in an oven at 150 °C under autogenous pressure without rotation. Solids extracted after select time intervals were isolated from the mother liquor by two cycles of centrifugation and washing with DI water, followed by drying in an oven at 60 °C. These samples were washed with 0.1M HCl in 3 wt% suspension at room temperature for 5 h to remove any remnants of amorphous material. As-synthesized samples were converted to proton form by ion exchange wherein the calcined zeolite was mixed with a 1.0 M NH₄NO₃ solution to obtain a 2 wt% suspension. This mixture was heated to 80 °C for 2 h and the process repeated three times with centrifugation/washing between each ion exchange cycle. The final NH₄-zeolite samples were calcined once again with the same conditions stated above to generate H-form zeolites.

4.4.4 Synthesis of conventional ZSM-5 catalyst

Conventional ZSM-5 catalyst was prepared according to previously reported protocol³¹⁶. The as-synthesized sample was converted to proton form by ion exchange followed by calcination through same protocols as above.

4.4.5 Characterization

Powder X-ray diffraction (PXRD) patterns of dried solids were collected on a Rigaku SmartLab diffractometer with a Cu K α source (40 kV, 30 mA). Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 instrument equipped with FEG at 10 kV. All samples were carbon coated (layer thickness ~ 30 nm) prior to imaging to reduce charging. The size of the crystals was measured from multiple SEM images of a single batch. Elemental analysis was performed by

electron dispersive X-ray (EDX) spectroscopy. EDX spectra were collected using a JEOL SM-31010/METEK EDAX system at 15 kV and a 15 mm working distance. The morphology of the crystals was also investigated by transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, 200 kV, 0.14 nm of resolution). Selected samples were embedded in a Spurr resin, cured, and cut into slices 80 nm thin using an RMC-MTXL ultramicrotome (Boeckeler Instruments, Tucson, AZ). These slices were then placed on a grid to study the interior of the zeolite crystals by TEM. Digital analysis of TEM micrographs was performed using Gatam DigitalMicrographTM 1.80.70 for GMS 1.8.

Textural analysis was performed with a Micromeritics 3flex instrument using N₂ as a probe gas for physisorption. Surface area was calculated from the BET isotherm and micropore volume was estimated by the t-plot method. Solid-state ²⁷Al NMR experiments were performed at 11.7 T on a JEOL ECA-500 spectrometer, equipped with a 3.2 mm field gradient magic angle spinning probe. The ²⁷Al MAS NMR data were obtained at a spinning frequency of 12.5 kHz with a $\pi/12$ pulse width of 1.25 µs and a recycle delay of 0.8 s. The number of scans was 4096 for all measurements. The total amount of acid sites was determined by temperature-programmed desorption of ammonia (NH₃-TPD). Prior to TPD, ca. 50 mg of catalyst was first outgassed in Ar (Matheson, 30 cm³ min⁻¹) for 4 h at 550 °C with a heating ramp of 2 °C min⁻¹. Ammonia was adsorbed at 150 °C until saturated, followed by flushing with Ar for 120 min at 150 °C. The ammonia desorption was

monitored using the quadrupole mass spectrometer (Cirrus 3-XRd, MKS Instruments) until 700 °C with a ramp of 5 °C min⁻¹. The fraction of acid site type (Brønsted vs. Lewis) and the fraction of acid sites present on external surfaces were estimated by FTIR spectroscopy with pyridine (Py) and 2,6-di-tert-butylpyridine (diTPy) as probe molecules, respectively. Infrared spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR spectrometer at 2 cm⁻¹ optical resolution. Prior to FTIR measurements, the catalysts were pressed in self-supporting discs and were pre-treated in the sample cell at 450 °C for 2 h in N₂ (Matheson, 50 cm³ min⁻¹). An excess of probe molecules was admitted by multiple pulse injections of 1.0 μ l into the FTIR sample cell. Physisorbed molecules

were subsequently removed by evacuation at the adsorption temperature. Difference spectra were obtained by subtracting the spectrum of the zeolite before probe molecule adsorption using the Thermo Scientific OMNIC series software. The amount of adsorbed probe molecule was determined by using the integrated area of a given band with the molar extinction coefficients provided in the literature^{399, 400}.

4.4.6 Catalytic measurements

Methanol-to-hydrocarbon (MTH) reaction was carried out in a ¹/₄ inch stainless steel tube installed in a resistively heated furnace (Model 3210, Applied Test Systems). The catalyst bed was supported between two plugs of quartz wool. A K-type thermocouple (Omega Engineering) was inserted into the stainless tube to measure the temperature of the catalyst bed. Prior to the reaction, the catalyst bed was pretreated *in situ* at 550°C for 3 h under the flow of dried air (6 cm³ min⁻¹ of O₂, 24 cm³ min⁻¹ of N₂). The catalyst bed was then cooled to the reaction temperature, 350°C. Methanol was fed by a syringe pump (Harvard Apparatus) at 7 μ L min⁻¹ into a heated inert gas stream of Ar (Matheson, 30 cm³ min⁻¹). Reaction effluent was evaluated using an on-stream gas chromatograph (Agilent 7890B) equipped with a flame ionization detector. To compare the deactivation rate of the catalysts, reactions were carried out at a sub complete methanol conversion, X, with the initial conversion regulated by adjusting the catalyst mass. Methanol conversion is defined as

$$X = \left[1 - \frac{c_{eff}}{c_{feed}}\right] * 100\% \tag{2}$$

where C_{eff} is the carbon-based molar concentration of both methanol and DME in the effluent and C_{feed} is the concentration of methanol in the feed. The selectivity S_i of hydrocarbon product *i* is defined as

$$S_i = \left[\frac{C_i}{C_{t,eff}}\right] * 100\% \tag{3}$$

where C_i is the carbon-based molar concentration of hydrocarbon *i* in the effluent and $C_{t,eff}$ is the total carbon-based molar concentration of hydrocarbons in the effluent.

To compare the deactivation rate between different catalyst samples, the turnover number (TON) is calculated for a selected span of time-on-stream (TOS) using a modified form of the equation reported by Bhan and coworkers⁴⁰¹

$$TON(t) = \frac{1}{[H]_0^+} \int_{t_1}^{t_2} F(\tau) d\tau$$
(4)

where $[H^+]_0$ is the total number of Brønsted acid sites, $F(\tau)$ is the molar flow rate of converted carbon (reacted methanol), and t is the TOS selected between times t_1 and t_2 corresponding to 50 and 30% methanol conversion, respectively.

Friedel–Crafts alkylation reaction of mesitylene with benzyl alcohol was carried out in a septumsealed, round-bottom flask (100 ml) with magnetic stirring. A fixed quantity of the catalyst (100 mg) was added to 190 mmol of mesitylene and the mixture heated at 120 °C for 15 min in an oil bath. After that, 2 mmol benzyl alcohol was injected into the mixture by using an elongated steel needle and this moment was labelled as initial reaction time. The samples were withdrawn at different time intervals and were filtered with 0.2 μ m filter. The filtered liquid samples were analyzed using a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector. Since mesitylene is present in excess, benzyl alcohol was considered as the main reactant, with the conversion (X_{BA}) and selectivity of alkylated product (S_{TMBB}) defined as

$$X_{BA} = \frac{N_{BA,0} - N_{BA}}{N_{BA,0}} = \frac{N_{TMBB} + N_{DBE}}{N_{TMBB} + N_{BA} + N_{DBE}}$$
(5)

and
$$S_{TMBB} = \left[\frac{N_{TMBB}}{N_{TMBB} + N_{DBE}}\right] * 100\%$$
 (6)

where $N_{BA,0}$ is the mole amount of benzyl alcohol in the feed and N_{BA} , N_{TMBB} , and N_{DBE} are the mole amounts of benzyl alcohol, alkylated product 2-benzyl-1,3,5-trimethylbenzene (TMBB), and ether product dibenzyl ether (DBE) in the reaction mixture.

Chapter 5 In situ imaging of 2-dimensional surface growth reveals the prevalence and role of defects in zeolite crystallization

5.1 Introduction

The growing demand for zeolites with tailored physicochemical properties has stimulated interest in understanding growth mechanisms to guide rational design of materials for diverse applications. Despite significant efforts to elucidate the fundamental pathways of zeolite nucleation and crystal growth^{87, 100, 104, 125, 167, 402-411}, these processes are not well understood owing in part to the inherent complexity of zeolite crystallization⁴¹²⁻⁴¹⁴. For instance, zeolites growth occurs by nonclassical pathways (**Figure 5.1 A**) involving the attachment of precursors ranging from oligomers to amorphous particles and small crystallites^{111, 131, 392, 415, 416}. These processes involve disorder-to-order transitions governed by dissolution and reprecipitation of amorphous precursors, which transpires in tandem with a classical pathway involving monomer addition.



Figure 5.1 (A) Diverse modes of zeolite A crystallization. (B) Structure and composite building units (CBUs) of zeolite A (LTA). (C-D) AFM images reveal three types of layers on crystal surfaces. (F and G) Time-elapsed AFM images in TMA⁺. All scale bars 400 nm.

During the early stages of zeolite synthesis, growth mixtures containing numerous amorphous precursors lead to crystallization by particle attachment, or CPA^{104, 123, 392, 417}. As the synthesis nears completion, the consumption of precursors results in growth solutions comprised

mostly of monomers where the predominant mode shifts to a classical mechanism; however, recent studies have shown that the use of organics as either structure-directing agents (SDAs)^{153, 308, 393} or zeolite growth modifiers (ZGMs)^{146, 416} can selectively switch the mode of growth between CPA and monomer addition. Prior studies of zeolite growth have largely focused on silicalite-1 (MFI) as a model system where it has been demonstrated that crystallization occurs by parallel pathways¹¹¹. The harsh conditions of zeolite synthesis (i.e., high pH and temperature) and the slow rates of crystallization pose difficulties for *in situ* tracking of nucleation and growth⁴¹⁸; thus, a majority of what is known about zeolite crystallization tends to be inferred from ex situ data^{168, 419,} ⁴²⁰. For instance, atomic force microscopy (AFM) images of fully crystalline zeolite samples extracted from synthesis mixtures provide insight into possible growth mechanisms¹²⁶. Anderson and coworkers have published AFM topographical images of numerous zeolite frameworks showing surfaces comprised of layers with heights equivalent to the unit cell dimensions of the crystal structure^{115, 119}. These features are characteristic of classical growth and, thus, are highly suggestive that new layers are created by 2-dimensional (2D) birth and spreading via the attachment of monomers^{90, 115}. The nucleation of 2D islands occurs at a critical radius, R_{crit}, as illustrated in **Figure** 5.1 **C**. As supersaturation decreases, the value of R_{crit} increases and 2D nucleation ceases in favor of layer generation from spiral dislocations (Figure 5.1 B), where each segment advances once reaching a critical length, L_{crit}, resulting in crystal interfaces comprised of stepped hillocks^{421,} 422

For this study we selected zeolite A (LTA) to investigate mechanisms of classical growth. Zeolite A is a natural mineral that is also produced synthetically at commercial scale for industrial processes involving adsorption and ion exchange^{302, 423, 424}. Zeolite A is a cubic crystal (Pm⁻ 3 m space group) with lta cages comprised of 8-membered ring windows (**Figure** 5.1 **B**) constructed from the interconnection of sod and d4R composite building units (CBUs). Zeolite A prepared in the absence of organics is enriched in aluminum (Si/Al = 1)⁴²⁵ with few exceptions^{167, 317, 426-428}. The silicon content can be increased using tetramethylammonium (TMA⁺) as an organic SDA⁴²⁸⁻⁴³⁰,

which is known to stabilize subunits of the crystal structure^{431, 432}. Numerous studies of zeolite A crystallization employ ex situ techniques, such as the work of Mintova and coworkers¹⁰⁰ who used transmission electron microscopy (TEM) to show that nucleation can occur inside amorphous gellike aggregates. Others have postulated that crystallization occurs via the attachment of CBUs (sod, lta, or d4R). Park et al.¹⁶⁷ proposed that growth of high silica zeolite A occurs by the formation of sodalite (sod) cages around lta cages. Analysis of zeolite A crystal surfaces by TEM has revealed the presence of incomplete sod cages⁴³³, whereas ex situ AFM images show evidence of growth via 2D nucleation and spreading of layers with step heights equal to ca. 1.2 nm (equivalent to one unit cell)¹¹⁹. Several groups have proposed that double-4-membered ring (d4R) species are putative growth units on the basis of microscopy data showing layered surfaces with step heights less than a unit cell (ca. a/2) or computational calculations indicating these groups lead to stable surface terminations¹²⁰. AFM images of fully-grown zeolite A crystals extracted at the end of a synthesis show different topological features, providing evidence of distinct modes of layered surface growth. These features include spiral dislocations, hillocks (i.e., pyramidal layers), or unknown protrusions on hillocks that are postulated to be foreign particles or twin crystals that can promote layer nucleation via a twin-plane re-entrant corner mechanism¹²¹.

In a previous study we reported the first *in situ* AFM measurements of zeolite A surface growth over a range of synthesis conditions¹¹⁸. Our findings revealed two mechanisms of nonclassical crystallization (**Figure 5.1 A**) at conditions of high supersaturation and/or temperature: formation of gel-like islands and (nearly)oriented attachment of nanocrystals. At moderate supersaturation we observed kinetic roughening involving the rapid nucleation of layers, which created irregular interfaces that were difficult to image in real time for the interpretation of dynamic events. In this study, we operate at lower supersaturation to examine 2D layered growth. Herein we show surface growth involves multiple pathways that either follow birth-spreading theory or deviate from conventional models, including identification of layer generation from

surface defects as a prominent mechanism. Moreover, the unparalleled spatiotemporal resolution of *in situ* AFM allowed for direct visualization of defect occlusion during layered growth.

5.2 Results and discussion

5.2.1 Conditions for layered surface growth

The growth of zeolite A surfaces was monitored in real time using AFM to track the generation and spreading of layers in various media at a fixed temperature of 50 °C. Measurements of assynthesized substrates reveal the presence of two types of growth hillocks on (100) surfaces: (i) layers advancing from screw dislocations (**Figure 5.1 C**) and (ii) layers emanating from protrusions located at the apex of the hillock (**Figure 5.1 D**). In both cases, the height of each layer is equivalent to the dimension of a single unit cell (ca. 1.2 nm). During *in situ* growth measurements, we also observed the nucleation of 2D islands (**Figure 5.1 E**) that are not evident on the surfaces of assynthesized crystals. Comparison of step velocities advancing from the three different sources of layer nucleation – screw dislocations, 2D islands, and protrusions – indicates similar rates (or kinetics) of layer advancement within the error of measurement (**Figure D.1**).

Growth solutions for AFM studies were prepared according to a reported method¹¹⁸ wherein mixtures containing (alumino)silicate colloidal precursors and soluble species were heated for a period of time before extracting the supernatant by centrifugation and filtration. The resulting clear solutions contain no evidence of residual particulates, as confirmed by dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS)¹¹⁸. Layered growth was only observed in solutions prepared with sodium ions as the SDA. Replacement with TMA+, an organic SDA used to prepare nanosized^{431, 432} or high-silica⁴³² zeolite A, resulted in a nonclassical mode of growth, analogous to our previous study¹¹⁸ showing what appears to be a gel-like coating on the crystal surface (**Figure** 5.1 **F**). Surface roughening is followed by the gradual smoothening of the interface with continuous AFM imaging (**Figure** 5.1 **G** and **Figure** D.2), a distinguishing attribute of gel-like deposits being removed by the rastering motion of the AFM tip. The presence of these features obscures

measurements of layered growth and dramatically reduces the rate of crystallization, consistent with prior studies⁴³⁴ reporting that zeolite A synthesis in the presence of TMA⁺ requires higher temperatures (e.g., 100 °C). Therefore, all experiments discussed herein were performed in organic-free media.

AFM studies were performed at relative supersaturation, σ , spanning from 0.6 to 2.7 using growth solutions prepared with colloidal silica unless otherwise specified (see the CHAPTER 1 - Chapter 1 - Appendix D - Supplementary Information Text for details of σ calculations). Evidence of monomeric alumina species in zeolite A growth solutions was gleaned from liquid ²⁷Al NMR analysis, which shows the presence of only aluminum monomer, Al(OH)₄, over a range of temperatures (Figure D.3). In situ AFM measurements at low supersaturation ($\sigma = 0.6$) revealed layer generation from screw dislocations (Figure 5.2 A) where time-elapsed images reveal the first turn in the spiral occurs once reaching a critical length, L_{crit} , of 25 – 40 nm (Figure 5.2 B) – a value in good agreement with estimates of $L_{crit} = 30 - 50$ nm reported by Sacco and coworkers¹²¹ from ex situ AFM images of as-synthesized zeolite A crystals. Studies by Anderson and coworkers409 have modelled zeolite A growth by screw dislocations assuming this to be a dominant mode of layer advancement. Indeed, one would expect the surfaces of as-synthesized crystals to be comprised almost solely of screw dislocations owing to the low supersaturation conditions during the final stages of crystallization, prior to solid extraction from the saturated supernatant; however, we find that dislocations are rarely observed in AFM images of substrates compared to growth hillocks (Figure 5.1 D), as discussed in the next section.



Figure 5.2 (A) Time-elapsed AFM images of layers advancing from a screw dislocation. Illustration of (B) spiral growth from a screw dislocation (C) 2D nucleation and spreading. (D – F) Time-elapsed AFM images showing 2D nucleation and layer propagation.

AFM studies performed at higher supersaturation ($\sigma = 2.7$) reveal growth by 2D layer generation and spreading (**Figure 5.2 C**). Time-resolved images extracted from Movie S3 reveal layer-by-layer growth (**Figure 5.2 D-F**) where a minor fraction of the layers dissolve (**Figure 5.2 D**, island III) in favor of a majority that grow (**Figure 5.2 D**, islands I and II) and eventually merge into a contiguous layer. In classical nucleation theory, the critical radius of 2D nucleation, R_{crit} , is defined as the size at which an island grows 50% of the time⁹⁰. Based on statistical analysis of sequential AFM images, we estimate Rcrit = 15 – 30 nm (**Figure D.4**) for the specific conditions (T = 50 °C and σ = 2.7) of these measurements.

5.2.2 Role of surface defects in 2d layered growth

The third and most prevalent mode of surface growth observed by in situ AFM is layer generation from protrusions (Figure 5.1 D). Here we refer to type I protrusions as large features on as-synthesized substrates located at the apex of hillocks on zeolite A crystal surfaces (Figure 5.3 A), similar to features observed in *ex situ* AFM images of other zeolite crystals (e.g. SSZ-13)¹³¹. AFM measurements of zeolite A surface growth captured layer generation and spreading from type I features. We selected a representative as-synthesized crystal substrate with a type I feature located at the apex of a hillock (Figure 5.3 A, dashed box). Focusing on an upper terrace of the hillock, continuous AFM imaging reveals the nucleation of a new layer emanating from one side of the protrusion (Figure 5.3 B-E). The new layer is comprised of steps oriented at a 45-degree angle relative to the pyramidal type I feature. The initial times of layer advancement result in the asymmetric growth of the new layer as it begins to encircle the type I feature (Figure 5.3 D). At later times, opposing edges of the new layer combine to fully surround the protrusion (Figure 5.3 E), leading to a more symmetric layer with a geometry that is commensurate with each underlying step of the hillock. Newly-generated layers are bounded by rounded edges that grow into faceted (100) steps with increased imaging time. Idealized schematics of layer generation and spreading (Figure 5.3 B-E) are provided below. This phenomenon is analogous to a recent study by Tsapatsis and coworkers⁶¹ who reported the anisotropic growth of micron-sized silicalite-1 (MFI) nanosheets around silicalite-1 seed crystals.



Figure 5.3 (A) Low magnification AFM image showing multiple hillocks with type I defects at each apex (arrows). (B – E) Time-elapsed AFM images of the region in panel A (dashed white box) during zeolite A growth ($\sigma = 0.6$) with schematic below. Scale bars 500 nm.

High resolution AFM images of type I protrusions reveal that these features tend to be faceted (inset of **Figure 5.4 A**). This observation suggests that the feature is crystalline, although its exact structure is unknown and difficult to identify by AFM or other techniques. It is possible that the pyramid-shaped feature is an intergrowth of zeolite A. Conversely, Burchart et al.⁴³⁵ reported that faujasite (FAU), which also has a cubic crystal structure (Fd⁻³ m space group), is capable of growing epitaxially on the surfaces of zeolite A crystals. Syntheses of LTA and FAU framework types are typically performed in Al- and Si-rich media, respectively¹⁰². Although *in situ* AFM measurements are performed in Al-rich growth solutions (Si/Al < 0.1), the protrusions are generated during the synthesis of substrates using growth solutions with Si/Al = 0.6 and the addition of an organic growth modifier, triethanolamine (TEA). The latter is known to sequester aluminates⁴³⁶⁻⁴³⁸, and can potentially generate a pseudo Si-rich environment for faujasite crystallization. As such, we cannot report with certainty the nature of type I features composition and structure.



Figure 5.4 (A) AFM image of zeolite A crystal surface during growth in a solution prepared with colloidal silica ($\sigma = 0.6$). Inset: high resolution image of a faceted type I protrusion. (B) Statistical analysis of the heights for type I and II features (blue and red, respectively).

A second type of protrusion corresponds to smaller features (**Figure 5.4 A**, type II) that only appear when imaging in growth solutions prepared with a colloidal silica source. The average size of type II adsorbates is nearly 3-4 times smaller than type I features (**Figure 5.4 B**). Type II features are evidence that a small population of amorphous silica particulates is present in the growth solution, at a concentration below the detection limit of scattering techniques such as DLS and SAXS. To confirm that type II features correlate with the silicon source, we conducted an alternative experiment where colloidal silica was replaced with sodium silicate. *In situ* AFM measurements of as-synthesized crystal substrates in this modified growth solution did not result in the deposition of type II features (**Figure D.5**). Likewise, if the growth solution is prepared directly (as opposed to the use of supernatant solutions after filtration of solids) by dissolving colloidal silica in an alkaline solution prior to the addition of alumina, we also do not observe type II features (**Figure D.6A-C**). Similarly, type II features were not observed in experiments using growth solutions prepared with tetraethyl orthosilicate (**Figure D.6D-F**) or furned silica (**Figure D.6G-H**), supporting the hypothesis that the presence of amorphous particulates depends upon the choice of silica source; however, the history of the growth solution also plays a role. For instance, each supernatant solution used for AFM experiments varied with respect to the number and size of type II features (0 – 8 nm, **Figure 5.4 B**). Such variance is expected for growth solutions at low supersaturation extracted at the end of zeolite crystallization once the majority of amorphous precursors have been consumed. We would expect a larger population of type II features at higher supersaturation (i.e. earlier crystallization times), which leaves open the possibility that these species may be present in solutions prepared with alternative silica sources. This hypothesis, however, cannot be confirmed by AFM given that high supersaturation leads to nonclassical growth (similar to **Figure 5.1 F**) that complicates the identification of type II features on zeolite A crystal surfaces.

During *in situ* measurements of surface growth, the height of type I features is approximately constant with few exceptions (i.e., in some instances we observe an increase in height with imaging time). Type II features, which are presumed to be undissolved remnants of the colloidal silica source, are populated on (100) terraces, but have no apparent impact on the velocity of advancing layers. Time-resolved imaging of surface growth shows steps advancing through and incorporating type II features into advancing layers (**Figure 5.5 A-C**). Here we highlight two different type II features initially positioned in front of an advancing layer (**Figure 5.5 A**, dashed circle) and in front of an advancing step bunch (**Figure 5.5 A**, arrow). High magnification images of the type II feature overcome by an advancing single layer (**Figure 5.5 D**) reveals that once the layer reaches the protrusion, which has a height approximately equal to that of the step (ca. 1 nm), it appears as though the entire feature is consumed within the advancing layer (**Figure 5.5 D**, t = 1 h); however, the feature reemerges at a later time (**Figure 5.5 D**, t = 2 h), but with a height that is nearly one-half of its original value (**Figure 5.5 E**). This suggests a fraction of the type II feature is occluded within one pass of an advancing single layer, which seems to indicate that the feature is partially raised from the surface.



Figure 5.5 (A – C) AFM images of growth showing layers advancing through type II features (dashed circle and white arrow). High-res images showing the (D) partial occlusion and (F) incorporation of a type II feature with corresponding (E, G) height profiles.

High magnification images of the protrusion overcome by an advancing step bunch (**Figure** 5.5 **F**) reveals that the type II feature is fully embedded within the hillock, thus generating an occluded defect site. This is evident when comparing sequential AFM images and corresponding height profiles at periodic imaging times. Overall, the data presented in **Figure** 5.5 indicate that step advancement on terraces with adsorbed type II features can lead to the occlusion of these amorphous silicates within the crystal. This outcome is analogous to crystallization by particle attachment leading to heterogeneous distributions of elements within crystals when there is disparate composition of the bulk and precursors incorporated at the surface³⁹². The observed source of defects in zeolite A is a potential consequence of employing colloidal silica as a starting reagent. Given the common use of colloidal silicates in zeolite synthesis, we speculate these defects may be a more general phenomenon. In a broader context, nanoparticle occlusion in crystals is an active field of research owing to frequent observations of nanocomposites in natural systems and

its widespread use in synthetic methodologies to design materials with unique properties⁴³⁹. For example, it has been demonstrated in numerous cases⁴⁴⁰⁻⁴⁴³ that zeolite syntheses employing metals or metal oxides nanoparticles (with sizes larger than zeolite pores) can lead to their incorporation within the crystal to generate bifunctional catalysts with improved performance. The occlusion of nanoparticles in nonporous inorganic materials has proved successful for engineering functional nanocomposites for semiconductors, solar cells, and other applications to impart enhanced properties unattainable by conventional methods⁴⁴⁴⁻⁴⁴⁶. Parallels can also be made with biominerals, such as calcium carbonates, where growth can lead to the occlusion of various species in the form of particulates (e.g. polymers)^{439, 447}, organic molecules (e.g. amino acids)^{448, 449}, or ions (e.g. $Mg^{2+})^{450, 451}$.

5.2.3 Conclusions

In summary, we used *in situ* AFM to identify multiple pathways of classical growth where the most common mode of layer generation stems from large (type I) protrusions, which are presumed to be defects located at the apex of hillocks. Secondary growth of these surfaces reveals continued generation of new layers from the edge of defects, leading to the sustained growth of hillocks. Direct observation of type II defects was enabled by the identification of conditions leading to 2D layered growth, which was only possible in organic-free media. Indeed, the substitution of Na⁺ with TMA⁺ leads to a nonclassical mode of growth that obscures defects via the formation of roughened crystal surfaces that do not appreciably grow within the times investigated (t < 12 h). We posit this marked change in growth kinetics is attributed to a gel-like nature of these features, which is distinctly different than layers generated in organic-free media.

Parametric analysis of growth conditions also reveals that the selection of the silicon source, most notably colloidal silica, is paramount in the generation of type II features, which are deemed to be the remnants of undissolved amorphous silicates. The occlusion of nanoparticles, which are seemingly too few in number to be detected by scattering techniques, has gone undetected in zeolite synthesis, and it remains to be determined how prevalent their incorporation in crystals would be during bulk crystallization. For example, AFM studies are performed under the slow, constant flow of growth solution to the liquid sample cell, which provides a continuous supply of fresh amorphous silica particulates. In zeolite synthesis under static conditions and constant volume, the solutions have not been filtered to remove the solids; therefore, the presence of amorphous precursors leads to the possibility of type II species being generated *in situ* throughout synthesis. The small size of these features, however, presumably make them difficult to detect by common analytical techniques. The ubiquitous observation of defects (types I and II) indicate their prevalent role in zeolite A crystallization. Moreover, the presence of type II defects has practical implications as they can reduce acid site concentration and/or restrict diffusion in nanopores, which would negatively affect their performance in applications of catalysis and adsorption (in stark contrast to the rational design of nanocomposites where particle occlusion can have a positive impact on performance, e.g., metal@zeolite bifunctional catalysts). Amorphous particle occlusion is ostensibly associated with media containing undissolved silica, which is common in zeolite synthesis. Although the observations reported here are specific to zeolite A, our findings are highly suggestive that this phenomenon may occur with other framework types prepared by similar sol gel methods.

5.3 Experimental

5.3.1 Materials

The following chemicals were used as reagents for zeolite synthesis: sodium hydroxide (98% pellets, MACRON Fine Chemicals), sodium aluminate (Al₂O₃·Na₂O or NaAlO₂, 54.41% Al₂O₃ and 41.02% Na₂O, Alfa Aesar), LUDOX AS-40 (40%, Sigma Aldrich), tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich, St. Louis, MO), sodium silicate (Na₂SiO₃, 29%, J.T. Baker), fumed silica (Cab-O-Sil, M-5, Spectrum Chemical), and triethanolamine (TEA, 100%, J.T. Baker).

Deionized (DI) water in all experiments was prepared using an Aqua Solutions RODI-C-12A purification system (18.2 M Ω). All reagents were used as received without further purification.

5.3.2 Synthesis of zeolite substrates

Large cubic crystals of zeolite A (LTA) were synthesized using a previously reported protocol¹²⁰. The synthesis mixture was prepared in a 125-mL polypropylene (PP) container with a molar composition of 1.23 SiO₂: 1 Al₂O₃: 2.71 Na₂O: 5.5 TEA: 288 H₂O. The solution was aged at room temperature for 4 h under continuous stirring. The PP container was heated in a Thermo-Fisher Precision Premium 3050 Series gravity oven at 85°C for 14 days and was quenched to room temperature. The zeolite crystals were recovered by vacuum filtration using a 1 µm GHP filter (Pall Corporation) and washed multiple times with DI water.

5.3.3 Preparation of zeolite growth solutions

Growth solutions for atomic force microscopy (AFM) experiments were prepared from a 90 g mixture with a molar composition of 1 SiO₂: 0.87 Al₂O₃: 11.2 NaOH: 190.6 H₂O. Colloidal silica (LUDOX AS-40) was used as the silica source unless otherwise stated. In a PP container, NaOH was added to degassed DI water with subsequent addition of sodium aluminate. The silica source was added to the resulting solution after 30 min of stirring. The mixture was left aging at room temperature for 48 h under continuous stirring. The growth solution was heated in an oven at 65°C for various times and quenched in an ice bath. The precipitate was removed by centrifuging the solution twice at 13,000 rpm for 45 min in a Beckman Coulter Avanti J-E instrument. The supernatant was decanted and filtered twice using a 25-mm syringe filter (0.20 μ m nylon membrane, VWR international). The resulting clear supernatant was used as a growth solution for *in situ* AFM measurements. Three solutions used in this study, referred to as C1 (high supersaturation), C2 (low supersaturation), and C_{eq} (solubility), were obtained after heating at 65 °C for 3.5, 4, and 24 h, respectively.

5.3.4 Atomic force microscopy

Zeolite A crystals used for substrates in AFM measurements were firmly placed on a 15-mm specimen disk (Ted Pella, Inc.) using quickset Loctite epoxy (Henkel Corporation) that was cured in an oven at 65°C for 12 h. The sample was then removed from the oven and cooled to room temperature in air. The sample was rinsed with DI water to remove loosely-bound crystals, and dried with N₂ gas. All AFM measurements were performed on an Asylum Research MFP-3D-SA instrument (Santa Barbara, CA) equipped with a custom liquid sample cell¹¹¹. The sample was placed in a closed AFM liquid cell. AFM images were collected using an uncoated silicon nitride cantilever (Olympus TR800PSA) with a spring constant of 0.60 N m⁻¹. The crystal substrate was first scanned in air to locate a desired imaging area. Growth solution was then introduced into the liquid cell by a syringe and the sample was left to equilibrate with the solution at room temperature for ca. 30 min. The temperature was then ramped to a set point (50 or 65°C) at a rate of 1°C min⁻¹. During AFM measurements, growth solution was continuously supplied to the liquid cell using a syringe pump (Razel Scientific Instruments, Model R100-E) at a rate of 1.2 cm³ h⁻¹. The sample cell was allowed to equilibrate for 1 h at the set point temperature before imaging in tapping mode at a scan rate of 1.2 Hz and 256 lines per scan.

5.3.5 Nuclear magnetic resonance (NMR) spectroscopy

All liquid ²⁷Al NMR measurements were performed on a JOEL ECA-600 NMR spectrometer operating at 600 MHz with 10 wt% deuterated water added to the solution for frequency lock. NMR measurements were carried out at room temperature as well as high temperature. The temperature was ramped to a pre-determined temperature at a constant rate of 1°C min⁻¹. The solution was allowed to equilibrate for 10 min before collecting a spectrum. It should be noted that the results of NMR were independent of growth solution preparation. Notably, the data presented in this study was gathered from the supernatant of zeolite A growth solutions; however, preparation of solutions with equivalent Si and Al content via the mixing of reagents without additional steps to isolate the solution from particulates resulted in identical NMR spectra. Moreover, AFM studies showed no

differences between the two methods of growth solution preparation. We also assessed solutions after different periods of room temperature aging and observed no differences with respect to (alumino)silicate speciation or modes of surface growth.

5.3.6 Additional characterization

Powder X-ray diffraction (XRD) patterns of dried solids were collected on a Rigaku SmartLab diffractometer with a Cu K α source (40kV, 30mA). Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 instrument equipped with FEG at 10 kV. All samples were carbon coated (layer thickness \approx 20 nm) prior to imaging to reduce charging. Samples analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) were sent to Galbraith Laboratories.

Chapter 6 In situ investigation of FAU crystallization

6.1 Introduction

Faujasite (FAU) is the most widely used zeolite framework in industry as a catalyst in cracking. It occurs naturally and was first synthetically realized by Union Carbide with Si/Al < 1.5 (zeolite X) and Si/Al > 1.5 (zeolite Y). Ultra-stable form (USY) was developed by dealumination of zeolite Y to improve its catalytic stability. With the changing chemical economy and the use of different feedstocks, it is essential to understand the crystallization mechanisms of these zeolites to more precisely tune the physicochemical properties of materials to match the needs of each application.

Zeolite crystallization mechanisms have been discussed in the introduction section of Chapter 5 and in section 1.3 of Chapter 1. Many research groups have studied the crystallization of FAU. Ginter et al.⁴⁵² studied the structural and compositional evolution of aluminosilicate precursors in zeolite Y (FAU) during the aging period using spectroscopic techniques (NMR, IR, and Raman) wherein it was concluded that the initial aluminosilicate precursor formed by the adsorption of aluminum on colloidal silica to produce amorphous solids with Si/Al = 1. After complete dissolution of colloidal silica, this amorphous aluminosilicate precursor rearranges by interacting with silicate anions in the solution leading to crystallization of zeolite Y. Similar studies were performed by Rimer and coworkers where they reported the formation of core-shell precursors where most of the silica source is isolated within the interior and is thus initially unavailable in growth solutions. At early stages of the synthesis, LTA first crystallizes in a pseudo-Al-rich environment followed by nucleation of FAU. Aging of FAU synthesis media was also investigated by Ogura et al., where they highlight the importance of aging for the formation of amorphous precursors as essential for FAU formation. Without aging, syntheses can result in the formation of SOD, ANA, or CHA⁴⁵³.

Anderson and coworkers have utilized *ex situ* atomic force microscopy (AFM) to speculate that zeolite Y grows by a layer-by-layer mechanism based on the presence of unfinished layers on fully crystalline zeolite Y surfaces¹²⁴. It should be noted that crystals utilized in their study were synthesized with crown ether as an OSDA, which can ultimately affect the crystallization mechanism. In later studies they supported their earlier observations using computer modelling⁴⁰⁹. Okubo and coworkers also also utilized *ex situ* AFM to investigate FAU crystallization. They found that crystal growth of faujasite proceeded via direct incorporation of soluble species. They observed that most of the top surface structures of the seed crystals were terminated by d6r units, while some were by complete or incomplete sodalite (sod) cages. These results showed that aluminosilicate species equal to or smaller than 6 rings contributed to crystal growth^{125, 126}.

Mintova and coworkers used electron microscopy to show that nucleation occurs on the outer surface of amorphous precursors¹⁰¹, consistent with Oleksiak et al.¹⁰², whereas Valtchev and coworkers posited nucleation occurs inside gels (i.e. within cavities at the interface of solid and liquid)⁹⁶. Fan et al. utilized *in situ* UV Raman spectroscopy to investigate zeolite X (FAU) crystallization⁴⁰⁵. They found that initially amorphous aluminosilicate species composed of predominately 4-rings are formed in the solid phase in the early stage of nucleation. These 4-membered rings are connected with each other via double 6-rings together with silica monomer in the liquid phase to form crystalline zeolite X. Lercher and coworkers used a combination of NMR and EXAFS to probe the nucleation and crystallization of FAU. They proposed that nucleation occur thought out the amorphous precursors rather than on just exterior surface. The structure directing action of Na⁺ leads to formation of sodalite-like units which rearrange further to form the FAU super cage⁴⁰⁸.

Here we use *in situ* atomic force microscopy to investigate FAU crystal growth and to deconvolute the role of different factors effecting the crystal growth mechanism.

6.2 Results and discussion

FAU crystal substrates utilized in this study are shown in **Figure** 6.1**A** with octahedral morphology comprised of (111) facets (**Figure** 6.1**B**,**D**). Unlike zeolite A (LTA) surfaces, which are ladened with hillocks, FAU surfaces do not have any distinct features (e.g., steps or hillocks) (**Figure** 6.2**C**).

FAU is known to co-crystallize with zeolite A (LTA)¹⁰². Both zeolite structures share a common CBU (i.e., *sod*). Here, we selected a composition from the FAU-LTA phase diagram that was previously reported by our group^{86, 102}. Based on parametric studies at various synthesis conditions, it was shown that FAU is more stable in the growth mixtures with high Si/Al ratios (>2.5) while LTA is stable in Al-rich media (gel Si/Al<1.5), with binary FAU-LTA products observed at intermediate Si/Al ratios^{86, 135}. Our group previously investigated LTA crystallization for the composition *a* in **Figure** 6.1**E** where the supernatant was extracted at different time intervals during crystallization and was used as a growth mixture for *in situ* AFM¹¹⁸. The composition of the supernatant was dependent upon the duration of heating and can lead to diverse crystallization modes. We also a similar approach of extracted supernatant at different synthesis times to show the incorporation of amorphous nanoparticles into the crystal surface during zeolite A growth (see Chapter 5)¹⁰⁹.



Figure 6.1 (A, B, D) SEM image of FAU crystals used as substrates for AFM with insets showing the idealized habit and (111) facets. (C) *Ex situ* AFM image of same substrate in air. (E) Kinetic ternary phase diagram showing different compositions used in this study (shaded regions are based on a previous study⁸⁶).

For the investigation of FAU crystallization, we selected composition 4 which lies in the FAU region of the phase diagram in **Figure** 6.1**E**. We extracted supernatants at different time intervals during crystallization (**Figure** 6.2**A**) and used these as the solutions for seeded growth in AFM measurements at 60°C. For the supernatant extracted at early stages of crystallization (5 h), gel-like features on the surface were removed by the continuous rastering of the AFM tip, analogous to the phenomenon previously observed for LTA¹¹⁸. This might be due to the high concentration of (alumino)silicate species in the supernatant solution that deposit on the FAU crystal surface and did not undergo a disorder-to-order transition to allow further crystallization. To resolve this, we extracted the supernatant at a later stage of crystallization (8 h), but this growth mixture was observed to be in close equilibrium with the crystal substrate with no further growth and minimal dissolution. At different time intervals, we did not observe layered growth of crystal surfaces, in stark contrast to observations of LTA surface growth. This seems to indicate that these two zeolites grow via distinct mechanisms.



Figure 6.2 (A) Elemental composition of supernatants and (B) PXRD of solids extracted at different time intervals during synthesis using growth mixture 4 (**Figure** 6.1**E**) (C) Time-elapsed AFM images under supernatant extracted at (C) 5 and (D) 8 hours.

We selected a different growth mixture (composition 1 in **Figure** 6.1**E**). This clear solution was prepared directly (i.e., without extraction of a supernatant) and is similar to the one used by Okubo and coworkers for the comparison of crystallization in FAU and LTA systems by *ex situ* AFM. Interestingly, AFM measurements with this growth mixture revealed three-dimensional surface growth. Snapshots from selected areas A1, A2, and A3 highlight the dynamics of surface growth (total imaging time = 120 min). The height profile (**Figure** 6.3**B**) of a surface feature indicated by the yellow arrow in **Figure** 6.3**A1** shows the height almost doubled within a timespan of one hour. This three-dimensional growth can be easily observed in other locations on the crystal surface, as indicated in panels A2 and A3 of **Figure** 6.3. Sequential AFM images can be used to measure step velocity, which is an essential parameter for quantifying crystallization kinetics. This is more challenging to measure when growth deviates from single step propagation; however, in **Figure** 6.3**C** the distance between two approaching surface features (shown by the double arrow in **Figure** 6.3**A**) is plotted as a function of imaging time. The velocity of the advancing front is the half of the slope of this curve and is estimated to be 0.75 nm min⁻¹. The velocity of advancing features is much lower than those obtained for zeolite A step advancement (3.6 nm min⁻¹)¹⁰⁹ showing slower crystallization kinetics for FAU as compared to LTA, although both experiments were conducted with disparate growth solutions.



Figure 6.3 (A) Three-dimensional growth of features on a FAU crystal surface using solution 1.(B) Height profile of the feature marked with a yellow arrow in A1. (C) Interstitial length between two advancing surface features (marked with yellow double headed arrow). All scale bars equal 500 nm.

6.2.1 Role of aluminum in FAU surface growth

Effect of different parameters such as molar composition and temperature can be easily investigated for growth composition 1 (**Figure** 6.1**E**) since it is directly prepared, in comparison to extracted supernatant solutions of composition 4 (shown by open blue circles in **Figure** 6.1**E**).

A major difference in the supernatant compositions for LTA (see Chapter 5) and FAU in this study is the limiting reagent. For LTA, supernatants used in AFM measurements were rich in Al, thus Si was the limiting limiting reagent. Since Si was in low concentrations compared to Al, it was mostly present as monomers based on liquid Al NMRanalysis¹⁰⁹. In our study, supernatant solutions used for AFM measurements are rich in Si (i.e., Al is the limiting reagent); thus, there is insufficient amount of Al to scavenge every Si in solution. Under these conditions it is more likely for silicates to form oligomers, although the concentration of Si is below the detection limit for NMR.

We tested the role of Al concentration for the growth mixture using composition 1 by increasing gel Si/Al ratio (i.e., reducing Al concentration) from 5 to 10. In AFM movies we observed very slow dissolution and no growth of FAU surfaces (**Figure** 6.4**A-C**). It is apparent that high Al content is essential for FAU growth. When decreasing the gel Si/Al ratio from 5 to 3.5, we observe gel-like features on the surface (**Figure** 6.4**D-F**). Excess Al in the growth mixture promotes the formation of gel-like layers on FAU crystal surfaces where the properties (composition and structure) of these features are unknown. Upon further reduction in the Si/Al ratio to 2, we observe protrusions on the surface (**Figure** 6.4**G-I**). The population of these protrusions increases with time, with no distinct change on the substrate surface itself.

To further investigate the nature of these protrusions, we performed an *ex situ* study using the same growth mixture composition and FAU crystal seeds. As can be seen in **Figure** E.1, the powder XRD pattern for crystals after 3 h of *ex situ* treatment shows peaks for the FAU framework along with some additional peaks with very low intensity. From SEM images, the crystal substrate is rough and covered with protrusions (**Figure** 6.5**B**). This phenomenon is similar to that observed

for finned zeolite growth that has been shown to be effective in reducing mass transport limitations in pentasil zeolites (MFI and MEL)²⁰⁴. The implications for rough features observed in FAU secondary growth and the exact nature of rough protrusions remain elusive. From XRD analysis it seems that these features may be associated with some form of sodium aluminate (non-zeolitic phase). It indicates a certain upper limit to the amount of Al in the growth solution, beyond which additional Al in the solution can potentially form sodium aluminate on crystal surfaces.



Figure 6.4 AFM images of a FAU crystal surface heated in solution 1 at 60°C with modified liquid Si/Al ratio (A-C) 10, (D-F) 3.5, and (G-H) 2. The total scanning time for each experiment is 90 min. All scale bars equal 500 nm.

6.2.2 Comparison using bulk syntheses

Compositions 1 and 4 used for *in situ* AFM measurements differ in synthesis protocol – notably the selection of (alumino)silicate sources and water content. As discussed in Chapter 1, these parameters can have notable effects on the crystallization mechanism. For equivalent comparison, we performed bulk synthesis using these growth solution compositions, but at different water
content while keeping all other conditions fixed. As shown in **Figure** 6.5**A**, we can clearly see the effect of water content: with an increase in water content, compositions 2-4 result in amorphous products. A potential explanation for these results can be made on the basis of supersaturation. For instance, with increased water content there is not a high enough supersaturation to drive nucleation. Composition 2 was selected to investigate the effect of two protocols from composition1 and 4. Both cases (**Figure** E.2), show similar growth dynamics.



Figure 6.5 (A) Kinetic ternary phase diagram expanding the compositions in **Figure** 6.1**E** with crystallization carried out at different water content. (B) SEM image of FAU crystals heated at 70°C for 3 h in solution 1 with a Si/Al_{sol} ratio of 2. Inset: high magnification image of a surface covered with protrusions.



Figure 6.6 Potential pathways of solute incorporation into growing zeolite cyrstals (purple): (i) growth from species in solution (blue); (ii) growth directly through the gel (solid) phase; and (iii) a local solution-mediated exchange between gel and crystal.

Overall, in FAU crystallization studies it appears that the supernatant plays a minor role in comparison to the gel (or solid amorphous) phase. Under most common conditions used for FAU

synthesis (e.g., compositions 3 and 4), AFM reveals no observable growth in the timeframes of analysis. For composition 1, which is abnormal for bulk FAU synthesis, the solution does lead to 3-dimensional growth of FAU crystal surfaces. This highlights the importance of solid/gel phase in the growth of FAU. As shown in **Figure** 6.6, if the growth is mediated by pathway *i*, then the supernatant will lead to the growth (similar to what is reported for zeolite LTA). On the other hand, if growth occurs through the gel (or amorphous solid) phase, as illustrated by pathway ii, or through local exchange between the gel(solid) and crystal (pathway *iii*), then the supernatant alone would not be able to facilitate crystal growth. As such, amorphous precursors are essential for FAU crystal growth which is in agreement with previous studies^{96, 454}. Valtchev and coworkers⁴⁵⁴ have shown that for FAU crystal growth, two mechanisms involving propagation through the gel network and solution can co-exist at the very beginning of the crystallization process. Still, they postulated solution mediated growth mechanism to be dominant. Although, this is not direct evidence of a solid-mediated crystallization mechanism, it clearly suggests FAU is unique in comparison to LTA.

6.3 Conclusion

In summary, faujasite surface growth has been investigated *in situ* with different growth solution compositions. The findings offer new insights into the sol-gel chemistry of FAU crystallization. The supernatant extracted at different time intervals did not lead to growth of the crystal substrate whereas direct clear solutions with abnormal composition do show three-dimensional growth. Furthermore, the effect of different parameters such as the limiting reagent (Si or Al), temperature, and water content were investigated. For the limiting reagent Al, there is an optimal molar ratio above which rough protrusions appear on the surface of FAU; and at lower limits of Al content, there is no observed surface growth. Difference in the growth dynamics between the supernatants and clear solution, indirectly suggests solid-mediated crystallization which has been proposed before in case of FAU.

6.4 Experimental

6.4.1 Materials

The following chemicals were used as reagents for zeolite synthesis: sodium hydroxide (98% pellets, MACRON Fine Chemicals), sodium aluminate ($Al_2O_3 \cdot Na_2O$ or $NaAlO_2$, 57.1% Al_2O_3 and 37.2% Na_2O , Alfa Aesar), LUDOX AS-40 (40%, Sigma Aldrich), sodium silicate (Na_2SiO_3 , 29%, Sigma Aldrich), and triethanolamine (TEA, 100%, J.T. Baker). Deionized (DI) water in all experiments was prepared using an Aqua Solutions RODI-C-12A purification system (18.2 M Ω). All reagents were used as received without further purification.

6.4.2 Synthesis of zeolite substrates

Large cubic crystals of faujasite (FAU) were synthesized using a previously reported protocol⁴⁵⁵. The synthesis mixture was prepared in a 125-mL polypropylene (PP) container with a molar composition of 3.50 SiO_2 : $1 \text{ Al}_2\text{O}_3$: $4.76 \text{ Na}_2\text{O}$: 8.0 TEA: $454 \text{ H}_2\text{O}$. The solution was aged at room temperature for 1 day under continuous stirring. The PP container was heated in a Thermo-Fisher Precision Premium 3050 Series gravity oven at 100°C for 21 days and was quenched to room temperature. The zeolite crystals were recovered by vacuum filtration using a 1 µm GHP filter (Pall Corporation) and washed multiple times with DI water.

6.4.3 Preparation of zeolite growth solutions

Growth solutions for atomic force microscopy (AFM) experiments were prepared through two different methods:

Method 1: From a 60 g mixture with a molar composition of 5 SiO₂: 1 Al₂O₃: 11 NaOH: 190 H_2O (composition 4 in Figure 6.1E). Colloidal silica (LUDOX AS-40) was used as the silica source unless otherwise stated. In a PP container, NaOH was added to degassed DI water with subsequent addition of sodium aluminate. The silica source was added to the resulting solution after 30 min of stirring. The mixture was left aging at room temperature for 48 h under continuous stirring. The

growth solution was heated in an oven at 65°C for various times and quenched in an ice bath. The precipitate was removed by centrifuging the solution in a Beckman Coulter Avanti J-E instrument. The supernatant was decanted and filtered twice using a 25-mm syringe filter (0.20 μ m nylon membrane, VWR international). The resulting clear supernatant was used as a growth solution for *in situ* AFM measurements.

Method 2: Growth mixture with a molar composition of 9 SiO₂: 1 Al₂O₃: 180 NaOH: 5760 H₂O (composition 1 in Figure 6.1E). Na₂SiO₃ was dissolved in water and kept at 80°C. Separately, Al(OH)₃ was dissolved in NaOH solution and stirred for 30 minutes at 80°C. After the aluminate solution became clear the latter solution and added to the former solution and stirred for 15 minutes at 80°C. The clear solution was filtered twice using a 25-mm syringe filter (0.20 μ m nylon membrane, VWR international). The resulting filtered solution was used as a growth solution for *in situ* AFM measurements.

6.4.4 Atomic force microscopy

FAU crystals used for substrates in AFM measurements were firmly placed on a 15-mm specimen disk (Ted Pella, Inc.) using quickset Loctite epoxy (Henkel Corporation) that was cured in an oven at 65°C for 12 h. The sample was then removed from the oven and cooled to room temperature in air. The sample was rinsed with DI water to remove loosely-bound crystals, and dried with N2 gas. All AFM measurements were performed on an Asylum Research MFP-3D-SA instrument (Santa Barbara, CA) equipped with a custom liquid sample cell. The sample was placed in a closed AFM liquid cell. AFM images were collected using an uncoated silicon nitride cantilever (Nano world PNP-TR) with a spring constant of 0.32 N m⁻¹. The crystal substrate was first scanned in air to locate a desired imaging area. Growth solution was then introduced into the liquid cell by a syringe and the sample was left to equilibrate with the solution at room temperature for ca. 30 min. The temperature was then ramped to a set point (65°C) at a rate of 1°C min⁻¹. During AFM measurements, growth solution was continuously supplied to the liquid cell using a syringe

pump (Razel Scientific Instruments, Model R100-E) at a rate of $1.2 \text{ cm}^3 \text{ h}^{-1}$. The sample cell was allowed to equilibrate for 1 h at the set point temperature before imaging in tapping mode at a scan rate of 1.2 Hz and 256 lines per scan.

6.4.5 Additional characterization

Powder X-ray diffraction (XRD) patterns of dried solids were collected on a Rigaku SmartLab diffractometer with a Cu K α source (40kV, 30mA). Scanning electron microscopy (SEM) images were obtained using a Zeiss Leo 1525 instrument equipped with FEG at 10 kV. All samples were carbon coated (layer thickness \approx 20 nm) prior to imaging to reduce charging.

Chapter 7 Summary and future outlook

The past twenty years has witnessed a resurgence in zeolite research owing to their role as catalysts in reactions such as emissions control,^{456, 457} C1 chemistry,⁴⁵⁸ biomass conversion,^{459, 460} and most recently polymer recycling,^{461, 462} which has expanded their utility beyond traditional applications as sorbents in ion-exchange and separations and as catalysts in the (petro)chemical industry.^{24, 28} In the coming decades, it is paramount that innovations in zeolite design meet the demands of a shifting energy economy. There are several approaches that can be taken to address these changes. One option is new materials discovery; however, the most expedient is the optimization of known structures towards achieving exceptional physicochemical properties. This objective is nontrivial owing to the complex growth media and multiple mechanisms involved in zeolite crystallization, many of which are not well understood, thereby complicating efforts to develop causal relationships between synthesis parameters and crystal properties. With each new breakthrough in zeolite synthesis the key findings are seemingly constrained to few zeolite crystal structures under limited synthesis conditions. Achieving this level of design for advanced zeolitic materials relies on knowledge of nucleation and growth pathways to inform new synthesis strategies. This dissertation focusses on tuning the physicochemical properties of zeolites such as structure, size, morphology, and pore architecture in organic free medium. Furthermore, it broadens the nanoscale understanding of crystal growth of commercial relevant zeolites LTA and FAU through the use of high temperature atomic force microscopy (AFM).

In Chapters 2-4, we focus on tailoring zeolite catalyst properties though seed assisted crystallization. We explored different seed assisted synthesis involving interzeolite transformations and tested previously reported hypothesis for the structure of the final zeolite product. We established an organic free pathway for the synthesis of self-pillared pentasil (SPP) zeolites. We further investigated the crystallization of SPPs using electron microscopy. These SPP zeolites present a large external surface area (almost triple that of conventional ZSM-5) and an

exceptionally high percentage of external acid sites (up to 7-fold higher than conventional ZSM-5). These two key features significantly improve catalytic performance. The evaluation of SPP zeolites in the Friedel craft alkylation reaction of mesitylene with benzyl alcohol results in higher conversion and an approximate two-fold increase in the selectivity to the desirable product. Similarly, we observe in the MTH reaction that SPPs extend catalyst lifetime and markedly enhance turnovers (as much as 4-fold relative to conventional ZSM-5). These findings highlight the potential use of this facile, efficient method of seed-assisted synthesis towards the realization of commercial hierarchical zeolite catalysts.

In Chapters 5-6, we utilize atomic force microscopy to investigate the crystallization of industrially relevant aluminosilicates (e.g., zeolite A and zeolite X) with high spatiotemporal resolution. We observe distinct growth regimes as a function of supersaturation and temperature. Interest in understanding zeolite A and X formation stems from their widespread use as a commercial molecular sieve as well as an active catalyst in industrial reactions. We show that in zeolite A crystallization at low supersaturation where layer growth occurs via three distinct regimes. Experiments performed in the presence of sodium ions (Na⁺) or tetramethylammonium cations (TMA⁺) (inorganic and organic structure-directing agents, respectively) reveal unique pathways of growth with markedly different kinetics. Furthermore, we also study zeolite X crystallization which shows a prevalence of gel mediated growth.

Future development of seed-assisted and other methods in zeolite synthesis would greatly benefit from more in-depth knowledge of fundamental mechanisms. This, in turn, places more emphasis on experimental studies to go beyond observational findings – where changes to a synthesis parameter is correlated to a modified property of the zeolite – towards efforts that address how changes to each synthesis parameter alter the physicochemical state of the system and its corresponding impact on nucleation and/or growth. Examples have already demonstrated how partial answers to these questions can be achieved from the synergy of combined experimental and computational efforts. Although machine learning especially in zeolite material synthesis is in very

initial state but the emergence of new tools such as these may prove instrumental for the translation of zeolite synthesis methods across a broad set of crystal structures and synthesis conditions. Similar approaches have been applied to other materials, such as polymers, metal organic frameworks (MOFs), and semiconductors.⁴⁶³⁻⁴⁶⁶

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Appendix A - Chapter 2 supporting information



Figure A.1 Ternary (kinetic) phase diagram of growth mixture compositions reported in literature for MEL, MFI, MOR, and MTW syntheses corresponding to the regions depicted in Figure 2.3. The numbers correspond to molar compositions provided in **Table** A.1.



Figure A.2 Powder X-ray diffraction (XRD) patterns for MEL seeds with Si/Al ratios of (A) ∞, (B) 35, and (C) 16.



Figure A.3 Powder XRD patterns for MFI seeds with Si/Al ratios of (A) ∞ , (B) 40, and (C) 14.



Figure A.4 Powder XRD patterns of (A) MOR and (B) MTW seeds prepared with Si/Al ratios of 8 and 30, respectively.



Figure A.5 (A – C) Representative SEM images of MEL seeds with Si/Al ratios of (A) ∞ , (B) 35, and (C) 16. (D) SEM image of MTW seeds. (E – G) Representative SEM images of MFI seeds with Si/Al ratios of (E) ∞ , (F) 40, and (G) 14. (H) SEM image of MOR seeds.



Figure A.6 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-11 seeds (Si/Al ratio = 16) in MOR growth solutions (A) S1 and (B) S2.



Figure A.7 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-11 seeds (Si/Al ratio = 35) in MOR growth solutions (A) S1 and (B) S2.



Figure A.8 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing silicalite-2 (MEL) seeds in MOR growth solution S2.



Figure A.9 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-5 seeds (Si/Al ratio 14) in MOR growth solution S1.



Figure A.10 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-5 seeds (Si/Al ratio = 40) in MOR growth solutions (A) S1 and (B) S2.



Figure A.11 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing silicalite-1 (MFI) seeds in MOR growth solutions (A) S1 and (B) S2.



Figure A.12 SEM images of products obtained from solution S1 with (A – D) ZSM-11 seeds (SAR = 16) (E-H) ZSM-11 seeds (SAR = 35) (I-L) silicalite-2 seeds at synthesis times: (A,E,I) 1day, (B,F,J) 3 days, (C,G,K) 6 days, and (DH,L) 10 days.



Figure A.13 SEM images of products obtained from solution S2 with (A – D) ZSM-11 seeds (SAR = 16) (E-H) ZSM-11 seeds (SAR = 35) (I-L) silicalite-2 seeds at synthesis times: (A,E,I) 1day, (B,F,J) 3 days, (C,G,K) 6 days, and (DH,L) 10 days.



Figure A.14 SEM images of products obtained from solution S1 with (A – D) ZSM-5 seeds (SAR = 14) (E-H) ZSM-5 seeds (SAR = 40) (I-L) silicalite-1 seeds at synthesis times: (A,E,I) 1day, (B,F,J) 3 days, (C,G,K) 6 days, and (DH,L) 10 days.



Figure A.15 SEM images of products obtained from solution S2 with (A – D) ZSM-5 seeds (SAR = 14) (E-H) ZSM-5 seeds (SAR = 40) (I-L) silicalite-1 seeds at synthesis times: (A,E,I) 1day, (B,F,J) 3 days, (C,G,K) 6 days, and (DH,L) 10 days.



Figure A.16 Time-elapsed powder XRD patterns for the products obtained at different time intervals by introducing ZSM-12 seeds (Si/Al = 30) in MOR growth solution S1.



Figure A.17 Representative SEM images of products obtained with ZSM-12 seeds (SAR 30) in MOR growth solution S1 (A, B, C, D) and MOR growth solution S2 (E, F, G, H) at the following synthesis times (from left to right): 1 day, 3 days, 6 days, and 10 days.


Figure A.18 Time-elapsed powder X-ray diffraction patterns for the product(s) obtained seeded growth in solution S1 using silicalite-2 seeds at (A) 130°C and (B) 170°C.

Table A.1 Synthesis parameters and references for the ternary (kinetic) phase diagram in Figure S1.

	References	Molar composition			Mole fraction			T	Time(h)	Phase	Alkali
		x Si	y Al	z H ₂ O	Si	Al	OH	(°C)			Cation
1	Golemme et al. (1991)	100	0.25	1250	0.91	0.00	0.09	170	24	MFI	Na ^{+[a]}
-		100	1.25	1250	0.90	0.01	0.09	170	20	MFI	Na ^{+ [a]}
2	Cizmek et al. (1995)	60	0	800	0.92	0.00	0.08	170	NA	MFI	Na ^{+[a]}
		60	2	800	0.90	0.03	0.07	170	NA	MFI	Na ^{+[a]}
		60	4	800	0.87	0.06	0.07	170	NA	MFI	Na ^{+[a]}
3	Mintova et al. (1998)	100	3	4000	0.63	0.02	0.35	180	21	MFI	Na ⁺
4	Machado et al. (1999)	18	2	324	0.76	0.08	0.15	165	48	MFI	Na ⁺
		40	2	1720	0.73	0.04	0.23	190	24	MFI	Na ⁺
		60	2	2580	0.74	0.02	0.24	190	24	MFI	Na ⁺
		80	2	3440	0.74	0.02	0.24	190	24	MFI	Na ⁺
		120	2	5160	0.75	0.01	0.24	190	24	MFI	Na ⁺
		18	2	324	0.67	0.07	0.25	165	48	MOR	Na ⁺
		10	2	180	0.71	0.14	0.14	165	48	MOR	Na ⁺
5	Houssin et al. (2003)	10	0	117	0.85	0.00	0.15	125	NA	MFI	Na ^{+ [a]}
6	Kim et al. (2004)	100	8	2250	0.78	0.06	0.16	190	NA	MFI	Na ⁺
		100	6	2500	0.75	0.04	0.21	190	NA	MFI	Na^+
		100	3	2500	0.76	0.02	0.21	190	NA	MFI	Na ⁺
7	Ren et al. (2012)	60	2	4000	0.69	0.02	0.29	170	21	MFI	Na ^{+ [a]}
8	Jablonski et al. (1986)	173.4	2	245	0.81	0.01	0.18	180	24	MFI/MEL	Na ^{+ [a]}
9	Castello et al. (2006)	19	2	293.6	0.64	0.07	0.29	175	120	MOR	Na^+
10	Lee et al. (2006)	1	0.07	45	0.73	0.05	0.22	150	336	MOR	$K^{+[a]}$
		1	0.06	32	0.58	0.03	0.39	150	336	MOR	Na ^{+ [a]}
11	Lv et al. (2011)	30	2	3300	0.78	0.05	0.16	170	72	MFI/MOR	Na ^{+ [a]}
		15	2	165	0.74	0.10	0.16	170	72	MOR	Na ^{+ [a]}
		20	2	220	0.71	0.07	0.22	170	72	MOR	Na ^{+ [a]}
12	Millini et al. (1998)	25	2	1125	0.68	0.05	0.27	170	336	MOR	Na ^{+ [a]}
13	Shaikh et al. (1993)	40	2	1500	0.62	0.03	0.35	150	40	MOR	Na ^{+ [a]}
14	Sun et al. (1995)	85	2	565	0.68	0.02	0.30	145	192	MOR	Na ⁺
		52	2	565	0.57	0.02	0.41	145	288	MOR	Na^+
		74	2	565	0.65	0.02	0.33	145	288	MOR	Na^+
		105	2	565	0.72	0.01	0.26	145	288	MOR	Na^+
		98	2	565	0.71	0.01	0.28	145	288	MOR	Na^+
15	Sharma et al. (2008)	10	2	48	0.71	0.14	0.14	175	24	MOR	Na^+
16	Shen et al. (2018)	90	2	3588	0.78	0.02	0.21	160	72	MEL	\mathbf{K}^+
17	Mintova et al. (2002)	1	0	12	0.77	0	0.23	90	72	MEL	-

...Table B1 (continued)

	References		Molar composition			Mole fraction			Time(h)	Phase	Alkali Cation
			y Al	z H ₂ O	Si	Al	OH	(-C)			Cation
18	Dong et al. (2003)	1	0	12	0.87	0	0.13	114	168	MEL	-
19	Gonazalez et al. (2009)	100	4	4200	0.81	0.03	0.16	150	72	MEL	Na ^{+ [a]}
		100	1	4200	0.83	0	0.17	150	72	MEL	Na ^{+[a]}
20	Piccione et al. (2001)	1	0	10	0.85	0	0.15	150	96	MEL	Na ^{+ [a]}
21	Kustova et al. (2004)	100	2	200	0.69	0.01	0.29	180	72	MEL	Na ^{+[a]}
22	Yoo et al. (2003)	80	2	995	0.9	0.02	0.08	160	120	MTW	Na ^{+[a]}
		60	2	750	0.88	0.03	0.09	160	120	MTW	Na ^{+[a]}
23	Iyoki et al. (2010)	80	2	1040	0.83	0.02	0.15	160	120	MTW	Na ^{+[a]}
24	Sanhoob et al. (2014)	1	0.004	12.574	0.87	0.01	0.12	145	120	MTW	Na ^{+ [a]}
25	Jegatheeswaran et al. (2015)	80	2	960	0.82	0.02	0.16	160	144	MTW	Na ^{+[a]}
26	Rosinski et al. (1983)	1	0.005	16.082	0.68	0.01	0.3	138	984	MTW	Na ^{+[a]}
27	Gopal et al. (2001)	80	2	1015	0.85	0.02	0.13	160	132	MTW	Na ^{+[a]}
		1	0.025	13	0.85	0.04	0.11	160	132	MTW	Na ^{+[a]}

[a] Synthesis mixtures contain an organic structure-directing agent

Appendix B - Chapter 3 supporting information



Figure B.1 Ternary (kinetic) phase diagram of growth mixture compositions reported in literature for MFI and MOR syntheses corresponding to labelled points in the inset of Figure 3.1 in the manuscript. The numbers correspond to compositions provided in Table A.1.



Figure B.2(A) PXRD patterns of solids extracted from the growth mixture S2 using USY as the silica source.(B) Reference powder XRD patterns for MFI and MOR obtained from the IZA²². A reference pattern for quartz was obtained from RRUFF project database³⁶⁹.



Figure B.3 Powder X-ray diffraction (XRD) patterns of solids extracted from growth mixture S2 using colloidal silica (SM30) as the silica source after 24 h, 32 h, 48 h, 72 h, and 8 d of hydrothermal treatment at 190°C.



Figure B.4 Identification of (A) mordenite, (B) ZSM-5, and (C) quartz in the solids extracted from growth mixture S2 (using USY as the sole source of Si and Al) after 48 h of hydrothermal treatment at 190°C by transmission electron microscopy.

The specific crystalline structure of the SiO₂ phase was identified as quartz (**Figure** 3.4**G**).³⁶⁹ The correlation to quartz (based on d-spacing) is approximately 0.41 nm. Furthermore, the other planes assigned to quartz match this phase while none correspond to the zeolites. The MFI-type zeolite is characterized by its regular geometry (orthorhombic) and the relatively large single and standalone coffin-shaped crystals, as observed in SEM and optical microscopy during Raman analysis. Due to the large size of ZSM-5 crystals, here we only see a small section of the entire crystal. The characteristic crystallographic data was also confirmed with reports in literature.^{308, 334} The lattice parameter along the "a-axis" is approximately 0.55 nm for the (022) plane along with the characteristic reflection at 0.89 nm corresponding to a (210) plane; however, this reflection is hidden under the beam stopper. To this end, we index the second order reflection, (420), having a

d-spacing of 0.45 nm. Nevertheless, one can observe the sequence of diffracted beams. The third reflection identified at 0.56 nm corresponds to the (131) plane. This combination of planes is characteristic of the [110] zone axis that represents the orientation of this crystal. Lastly, the MOR zeolite is polycrystalline, which is concluded on the basis of a ring-like selected area electron diffraction pattern (SAEDP). The main d-spacing of 0.68 nm corresponds to the (220) plane. Other characteristic d-spacings identified are 0.51 and 0.46 nm for the planes (040) and (400), respectively.



Figure B.5 Scanning electron micrograph of solids extracted from growth mixture S2 using USY as the sole source of Si and Al. This image corresponds to a sample heated for 16 h at 190°C.



Figure B.6 Identification of (A) mordenite (MOR), (B) ZSM-5 (MFI), and (C) quartz in the solids extracted from growth mixture S2 (using USY as the sole source of Si and Al) after 48 h of hydrothermal treatment at 190°C by Raman spectroscopy.

Insets: optical micrographs of each crystal analyzed. It has been demonstrated that Raman spectroscopy can be used to characterize the zeolite structure.⁴¹⁹ In the spectrum for MOR, the most intense band at 470 cm⁻¹ corresponds to bending modes of 4-membered rings.⁴¹⁹ For the spectrum of ZSM-5, the band at 380 cm⁻¹ with highest intensity corresponds to the bending mode of 5-membered rings and bands at 290 cm⁻¹ correspond to the bending mode of 6-membered rings. The bands at 440 cm⁻¹ and 470 cm⁻¹ correspond to 4-membered rings, whereas the band at 800 cm⁻¹ corresponds to the symmetric stretching of T-O bonds.⁴¹⁹ In the spectrum of quartz, the characteristic peaks align with reference spectra in literature.³⁶⁹ Collectively, the results in this figure are in agreement with powder XRD patterns showing the presence of three crystalline products (MOR, MFI, and quartz).



Figure B.7 Scanning electron micrograph of solids extracted from growth mixture S2 using colloidal silica (SM30) as the Si source. This image corresponds to a sample heated for 32 h at 190°C.

Appendix C - Chapter 4 supporting information



Figure C.1 Ternary (kinetic) phase diagram with MOR growth solution (blue circle). The orange and blue shaded regions depict approximate compositional regions reported in literature for syntheses of pentasil zeolites.



Figure C.2 Nitrogen adsorption/desorption isotherms at 77 K for SPP samples synthesized with different seeds (refer to Table 1) and conventional ZSM-5.



Figure C.3 (A) PXRD pattern and (B) SEM image of the product obtained after 15 h of heating extracted from SPP1 growth mixture. TEM images of solids extracted from a (C) SPP1 and (D) SPP2 growth mixture after aging at room temperature.



Figure C.4 HRTEM image of the precursor extracted at 1 day of hydrothermal treatment from growth solution with silicalite-1 seeds (i.e., SPP3 synthesis).



Figure C.5 TEM images for (A) SPP1 synthesis after 2 days of treatment; (B) SPP2 synthesis after 1 day; (C) SPP3 synthesis after 1 day; and (D) SPP4 synthesis after 3 days. Scale bars 500nm and 100 nm in the low and high mag respectively. (A1-D1) SAED analyses of selected regions of samples shown in (A-D), respectively.



Figure C.6 (A) PXRD patterns of the solids extracted at times spanning from 4 to 10 days. Peaks corresponding to zeolite MOR are marked with asterisks (*). (B and C) Representative SEM images of solids extracted after (B) 4 days and (C) 10 days.



Figure C.7 (A) Powder XRD pattern and (B) SEM image of mordenite crystals prepared using solution S1 containing no seeds.



Figure C.8 Percent crystallinity as a function of synthesis time for SPP2 (solid circles) and SPP3 (open squares) measured from powder XRD patterns.



Figure C.9 FE-SEM images of SPP3 crystals showing the high degree of aggregation. Scale bar equals to 500 nm.



Figure C.10 (A) Average nanosheet thickness y and (B) average bulk crystal size x measured for 25 crystals in a single batch. Error bars span two standard deviations. Insets: schematics defining dimensions y and x.



Figure C.11(A) Powder XRD pattern and (B) SEM image of the conventional ZSM-5 catalyst synthesized from a previously reported protocol.³⁴²



Figure C.12 Selectivity of hydrocarbon products obtained in the MTH reaction (assessed at ca. 40% conversion) with different H-form SPP and conventional ZSM-5 catalysts.

Appendix D - Chapter 5 supporting information



Figure D.1 Comparison of <100> step velocities during in situ measurements of layer advancement at 50 °C. The steps correspond to 2D layers, spiral dislocations , and hillocks emanating from type I defects. Error bars span two standard deviations.



Figure D.2 Zeolite A growth in the presence of TMA⁺ (σ = 2.7). Time-elapsed AFM images after (A) 1 h and (B) 3 h (C) increased scan size after 3 h of growth showing the area of continuous imaging (white dashed box). Scale bars equal 1 µm.



Figure D.3 (A) Liquid ²⁷Al NMR spectra of a zeolite A growth solution at various temperatures (20 -65 °C). (B) Comparison of monomer ($\delta = 80$ ppm) peak areas for the zeolite A growth solution with Na⁺ (blue circles), and a sodium aluminate as control (red squares).



Figure D.4 Statistical analysis of 2D island radii that (A) dissolve and (B) grow during continuous imaging. From the assessment of AFM images, island dissolution and growth are both observed within a similar range, $R_{crit} = 15 - 30$ nm.



Figure D.5 AFM images in solution C2 ($\sigma = 0.6$) with sodium silicate as the silica source. Snapshots in selected areas A1, A2, and A3 highlight the dynamics of surface growth with increasing imaging time from left to right (total imaging time = 360 min).



Figure D.6 AFM images in solution prepared with different silica sources: (A-C) Colloidal silica (D-F) TEOS and (G-H) Fumed silica. The solution with colloidal silica was prepared by dissolving colloidal silica in an alkaline solution prior to the addition of alumina.



Figure D.7 AFM images in solution C2 ($\sigma = 0.6$) prepared with colloidal silica. Snapshots in selected areas A1, A2, and A3 highlight the dynamics of surface growth with increasing imaging time (total imaging time = 270 min). The scale bar equals 500 nm.



Figure D.8 (A) PXRD pattern and (B) SEM image of solids extracted from a TMA⁺-containing growth solution (50/50 Na⁺/TMA⁺) after heating at 65 °C for 24 h. The crystalline structure of LTA was confirmed by comparing the experimental powder XRD pattern to a reference of zeolite A (LTA) provided by IZA²².



Figure D.9 AFM images after (A) 0 h and (B) 2 h of continuous scanning at higher temperature (65 °C) in a solution with TMA⁺. (C) Increased scan size after 2 h of continuous imaging (white dashed box). All scale bars equal 1 µm.



Figure D.10 (A) Liquid ²⁷Al NMR spectra of TMA⁺-containing growth solutions at various temperatures (listed). (B) Comparison of monomer ($\delta = 80$ ppm) peak areas growth solution with Na⁺ (blue circles), TMA⁺ (yellow triangles), and sodium aluminate as a control (red squares).

Solution ^a	Cor	G		
Solution	Si	Al	Na	0
C1	0.03	0.24	3.03	2.7
C2	0.01	0.24	2.97	0.6
Ceq	0.007	0.246	3.15	0.0

Table D.1 Elemental analysis of growth solutions using ICP-OES.

a: C1, C2, and Ceq represent compositions of solutions prepared with colloidal silica (LUDOX AS-40) leading to 2D layer growth, spiral growth, and equilibrium (solubility), respectively.





Figure E.1 Powder XRD patterns of parent FAAU crystals, crystals heated in solution 1 with Si/Al ratio 2 at 70°C for 3 hours, and solution heated at same conditions with FAU crystals.



Figure E.2 AFM images of crystal surface heated in solution (A-B) 1 and (C-D) 4 at 60°C. All scale bars equal to 500nm.