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Design Principles for the Synthesis of Self-Pillared ZSM-5 Zeolite Nanosheets

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ABSTRACT: The design of next-generation materials for emerging energy and environmental applications heavily relies on empirical approaches to direct nonclassical nucleation and crystal growth pathways, polymorphism, intercrystalline transformations, and seed-assisted growth processes. A long-standing obstacle to nanoporous materials design is the complexity of crystallization, which hinders the development of predictive models and/or physical descriptors that can guide their synthesis. In this study, we use a combination of state-of-the-art synthesis, characterization, and computational design to prepare hierarchical MFI-type zeolites, which we couple with benchmark catalytic testing to assess structure-property-performance relationships. These hierarchical materials are intergrowths of two commercially relevant zeolite frameworks, MFI and MEL, prepared as self-pillared pentasil (SPP) zeolites through seed-assisted, organic-free syntheses for which little theoretical guidance existed. By comparing a large library of zeolite seeds with different pore sizes, dimensions, and structural composite building units, we determined the relative impact of seed and silica source selection, among other synthesis variables. Combined experimental and computational studies are used to test several hypotheses in literature to rationalize the choice of seed structure and establish a more robust selection criteria for seed-assisted synthesis of zeolites. Specifically, we show that a data-driven approach to develop structural descriptors correlates to new, facile routes to rationally design SPP zeolites, addressing knowledge gaps in the fundamental understanding of (non)classical crystal growth mechanisms that are characteristic of nanoporous aluminosilicates.

INTRODUCTION

Since the pioneering work of Richard Barrer in the 1940s to produce synthetic zeolites, these materials have found commercial applications in diverse fields such as catalysis, ion exchange, and separations.^{1,2} Their versatility stems in large part from their robust physicochemical properties and well-defined porosity; however, the ability to control zeolite crystallization is nontrivial owing to their complex mechanisms of nucleation and growth.¹ The intrinsic micropores (< 1 nm) of commercial zeolites pose mass transfer limitations that compromise their performance in applications. Consequently, there is a need to develop more systematic approaches to synthesize zeolites with nano-sized or hierarchical architectures to enhance their internal diffusion properties for processes that can be leveraged to meet the demands of the evolving energy and environmental landscapes.

The rational design of hierarchical zeolite has garnered significant attention as an approach to introduce larger pore networks, such as mesopores and/or macropores. There have been many examples published over the past two decades demonstrating how hierarchical zeolites often exhibit superior performance compared to traditional zeolites in commercially relevant catalytic applications, such as Friedel-Crafts alkylation,³ Fischer-Tropsch synthesis,⁴ isomerization,⁵ methanol-to-olefins,⁶ and biomass conversion.⁷ The synthesis of hierarchical zeolites can be achieved through top-down and bottom-up methods. Typically, these approaches involve the use of expensive organic reagents, multi-step procedures, and/or conditions that result in low product yields and, therefore, are less feasible for industrial-scale processes.⁸⁻¹¹ One type of bot-

tom-up approach that is underexplored for engineering hierarchical materials is the use of zeolite crystals as seeds. Traditionally, seed-assisted syntheses are employed to lower induction and/or synthesis times, reduce the formation of impurities (i.e., polymorph control), or direct the formation of nano-sized zeolites.¹²⁻¹⁴ Seed-assisted synthesis often involves an inter-zeolite transformation (IZT) where an initial seed progressively disappears at the expense of a secondary (final) product. Although these processes have been employed for many years in zeolite science, the underlying mechanisms of IZT remain a subject of ongoing research.^{15,16}

Our group recently reported an organic-free, seed-assisted method of synthesizing self-pillared pentasil (SPP) zeolites using (alumino)silicate MFI and MEL seeds in a growth mixture that would otherwise produce Na-mordenite (MOR) without seeds.¹⁷ The SPP materials produced in organic-free media exhibit thicker (30 – 50 nm) nanosheets compared to those synthesized with a variety of quaternary ammonium-type organic structure-directing agents that yield ca. 3 nm thickness.^{9,18-22} Although the seed-assisted protocol results in larger ZSM-5 (MFI) crystals, there are three advantages of this synthetic approach: (i) avoidance of expensive organics, (ii) generation of high product yields, and (iii) higher aluminum content (Si/Al < 15) than a majority of MFI-type hierarchical materials reported in literature with Si/Al > 30. Zeolite composition is particularly important for catalytic applications where high acid site density is often advantageous. In our initial study,¹² we put forth a hypothesis that the successful seed-assisted synthesis of SPP is associated with shared composite building units (CBUs) between the parent (seed) and

daughter (product) zeolites. This is consistent with the hypothesis proposed by Okubo and coworkers²³ for IZT processes; however, it has also been demonstrated that IZT can occur without any common CBUs.²⁴ Furthermore, literature suggests that factors involved in seed-assisted and IZT processes are considerably more complex.^{1, 25} Schwalbe-Koda et al.^{26, 27} used a computational approach based on graph theory and structural representations to predict IZT parent/daughter relationships and intergrowths on the basis of their structural and topological similarity. Their study used a comprehensive literature analysis to demonstrate that zeolite pairs exhibiting specific IZT pathways or intergrowths shared either similar graph connectivity or atomic environments, including the pair of MFI and MEL that are critical to SPP synthesis. Others have used computational approaches to rationalize zeolite intergrowths on the basis of interfacial transition layers²⁸ and interfacial energies between two zeolitic phases²⁹.

Despite these hypotheses, there is very little evidence relating synthesis conditions to the degree to which intergrowths and pillaring are promoted in organic-free syntheses using zeolite crystals as seeds. For instance, it remains unclear whether SPP zeolites can be synthesized using alternative seeds, whether the common CBU hypothesis is valid for the identification of new seeds for hierarchical zeolite synthesis, and whether SPPs created from different seeds exhibit unique physicochemical properties. Herein, we investigate key factors influencing the degree of pillaring in SPP zeolites using a combination of experiments and data science to test the common CBU hypothesis and explore a broader design space for their synthesis. Among the variables we assess is the structure of zeolite crystal seeds, as well as the selection of the silica source. We show that the latter is critical to obtaining an amorphous precursor that is an appropriate substrate for heterogeneous nucleation of pillared MFI nanosheets. We also investigate potential correlations between MEL content and the morphology (i.e., degree of pillaring) for each set of SPP materials. Finally, we highlight the implications of these choices in the catalytic performance of the synthesized samples. One of the key findings of this study is the demonstration that structures with a high degree of pillaring can be achieved using computationally selected seeds, thus establishing an efficient framework for designing hierarchical zeolites.

RESULTS AND DISCUSSION

2.1 Structure and growth steps of SPP zeolite. Zeolite SPP is an intergrowth of two frameworks (Figure 1A): MFI (the predominant component) and MEL (the minor component). The self-pillared architecture of SPP is attributed to the higher symmetry of MEL (tetragonal space group) compared to that of MFI (orthorhombic space group).^{22, 30} Both zeolite framework types contain long chains of interconnected five-membered Si–O tetrahedral units, referred to as pentasil chains.³¹ The way in which these pentasil chains connect differs between MFI and MEL, resulting in distinct porous networks. Notably, MFI exhibits both sinusoidal channels along the *a*-direction and straight channels along the *b*-direction, whereas MEL possesses identical straight channels in both the *a*- and *b*-directions.^{31, 32} Tsapatsis and coworkers²² have hypothesized that MEL enables junctions for the branching of MFI nanosheets; however, the structure of intersections at an atomistic level is elusive. Nevertheless, synthesis of SPP can be achieved using either MFI or MEL seeds, which match the framework of the crystal or junction and thus are maximally similar to the targeted hierarchical structure.

In this study, pillaring was initially assessed by microscopy (qualitative screening) and subsequently more quantitatively by textural analysis. Evidence of pillaring is gleaned from the presence of multiple “cross-like” features (Figures 1A and S1A) in micrographs corresponding to intergrowths. These features are rectangular in shape and differ from rough or spheroidal protrusions (e.g., finned zeolites³³) or faceted single intergrowths often reported as defects on MFI (010) surfaces (Figure S1B).³⁴ The series of steps involved in the synthesis of zeolite SPP using a seed-assisted, organic-free protocol is illustrated in Figure 1B. Calcined zeolite seeds are added to a growth mixture containing amorphous aluminosilicate precursors. In the absence of seeds, the synthesis will produce Na-mordenite (MOR); however, in the presence of seeds, their dissolution at early synthesis times seemingly alters the growth environment in ways that are not well understood and promotes the nucleation of SPP. Nanosheets emerge from the surfaces of amorphous precursors, as idealized in Figure 1B(i), and naturally form pillared architectures. Multiple heterogeneous nucleation events occur on a single precursor, leading to aggregates of SPP particles, as illustrated in Figure 1B(ii). At longer synthesis times, there is an interzeolite transformation to zeolite MOR wherein we previously reported¹⁷ that nucleation originates from the center of SPP aggregates and leads to highly anisotropic rod-like crystals, as illustrated in Figure 1B(iii). Depending on the selection of seed crystals and synthesis conditions, zeolite MOR can nucleate prior to the

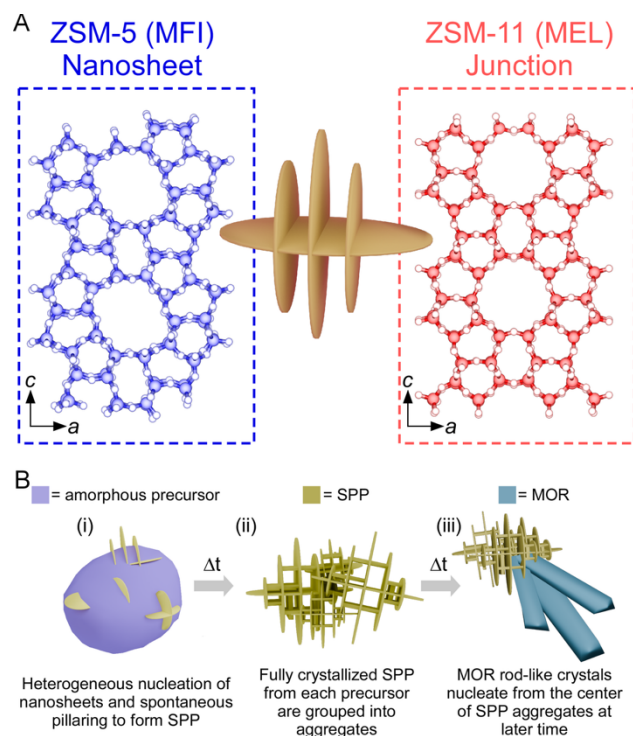


Figure 1. (A) Schematic of an idealized self-pillared pentasil (SPP) zeolite comprised of two primary components: ZSM-5 (MFI) enriched nanosheets and a minor fraction of ZSM-11 (MEL) intergrowth. The structures of MFI (blue) and MEL (red) shown in the dashed boxes are viewed along the *b* direction of each framework (i.e., parallel to their straight channels). (B) Sequential steps during the synthesis of zeolite SPP from an initial, organic-free mixture of amorphous aluminosilicate precursors and crystal zeolite seeds: (i) nanosheets of zeolite MFI nucleate heterogeneously on the surfaces of amorphous precursors and natu-

rally form pillars; (ii) multiple SPP crystals formed within the same precursor develop into aggregates; and (iii) longer synthesis time leads to the nucleation of zeolite MOR within the core of SPP aggregates wherein zeolite MOR growth leads to a concomitant disappearance of SPP (Figure S2).

completion of SPP crystallization. The mechanism of SPP formation involves the depletion of amorphous precursors from their exterior surfaces to interior cores¹⁷; therefore, the origin of MOR nucleation at the center of SPP aggregates suggests there may be residual amorphous material, which may not always be detected by powder X-ray diffraction (PXRD). The growth medium also contains a high concentration of Na⁺ ions, which are common inorganic structure-directing agents (ISDAs) that promote the nucleation of zeolite MOR at later synthesis times. In the following sections, we systematically investigate the impact of growth solution composition, silica source, and seed crystal structure on the degree of pillaring during zeolite SPP synthesis in organic-free media.

2.2 Sensitivity of SPP syntheses to growth mixture composition. In our initial study of seed-assisted organic-free SPP synthesis,¹⁷ we selected a single composition listed as Point 1 in Figure 2A and tested the use of four crystal seeds, choosing both the siliceous and aluminosilicate isostructures of MFI and MEL zeolites: ZSM-5 (MFI), silicalite-1 (i.e., siliceous MFI), ZSM-11 (MEL), and silicalite-2 (i.e., siliceous MEL). We showed that the highest degree of pillaring was achieved with silicalite-2 (MEL) seeds (Figure 2B), which is used in this study as the nominal case for assessing a broader range of synthesis conditions. The ternary phase diagram in Figure 2A shows that the compositions for organic-free (non-seeded) syntheses of pure Na-MOR (pink shading) and Na-MFI (blue shading) are in regions of high and low alkaline media, respectively, with a small degree of overlap.¹² In order to assess

electron microscopy (SEM) images of the SPP zeolites prepared with compositions corresponding to (B) Point 1 and (C) Point 7 in the ternary phase diagram. (D) SEM image of the same synthesis mixture in Point 1 where the silica-to-water molar composition is increased from 18 SiO₂: 324 H₂O (panel B) to 18 SiO₂: 600 H₂O (panel D).

the sensitivity of SPP synthesis to changes in growth mixture composition, we selected points in the phase diagram that include the regions of MFI/MOR overlap (Points 2, 5, and 6), pure MFI (Points 3 – 5), and pure MOR (Points 7 – 10). Surprisingly, only two additional compositions resulted in the formation of zeolite SPP: Point 2 (Figure S3) and Point 7 (Figure 2C). All other synthesis compositions resulted in non-pillared MFI (blue circles), with the exception of Points 8 and 9 that yielded MOR (purple circles) slightly outside the reported phase space of mordenite in literature (Figure S4).

A parametric analysis of all possible zeolite synthesis parameters requires a herculean effort that is outside the scope of this study; however, we did assess the effects of several key parameters that include synthesis temperature, water content, and silica source. Tsapatsis and coworkers showed that temperature is an important parameter for organic-assisted SPP synthesis.³⁰ Here, we made slight modifications to the nominal SPP synthesis (Point 1, 150 °C) to assess two different temperatures (130 and 170 °C) – neither of which resulted in high-quality SPP zeolites. At the lower temperature, PXRD patterns (Figure S5A) and SEM images (Figure S5B) of extracted solids reveal MOR nucleation well before the complete consumption of amorphous precursors. At the higher temperature, the same observation is made (Figure S5C), but with accelerated kinetics (i.e., a reduction from 7 to 2 days synthesis time). In addition to increased MOR impurity, changes in synthesis conditions can reduce the degree of pillaring. For example, altering the pre-synthesis aging protocol from room temperature to 50 °C accelerates SPP nucleation, but results in thicker nanosheets with reduced pillaring (Figure S6).

Water content is another important parameter in zeolite synthesis that influences many properties and processes, including the kinetics of MFI-type zeolite crystallization.^{20, 35} Tsapatsis and co-workers demonstrated that steam exposure transforms single-unit-cell MFI zeolite nanosheets into thicker, rougher crystallites while retaining their crystallinity and porosity.³⁶ Here, we performed syntheses by adjusting the nominal condition (Point 1, 324 H₂O) with two different water contents (224 and 600 H₂O) while keeping all other conditions constant. A previous study by Okubo, Tsapatsis, and coworkers²⁰ showed that increased water content in ZSM-5 syntheses containing diquatary ammonium organic structure-directing agents (OSDAs) leads to more intergrown crystals. Here, we observe similar trends wherein increased water content of the SPP synthesis resulted in apparent higher degree of pillaring in SEM images (Figure 2D) and a slightly larger overall crystal size. Conversely, our findings show that lower water content produces fewer pillars (Figure S7), but does accelerate the crystallization time (i.e., reducing the synthesis time from 72 to 24 hours).

The heterogenous nucleation of SPP on surfaces of amorphous precursors (Figure 3A) suggests that the properties of precursors can potentially impact this pathway. In general, it has been demonstrated that the choice of silica source can have a major impact on zeolite crystallization.^{37, 38} In this study, we assessed SPP synthesis using three different silicon sources: colloidal silica (Ludox AS-40), which is the source

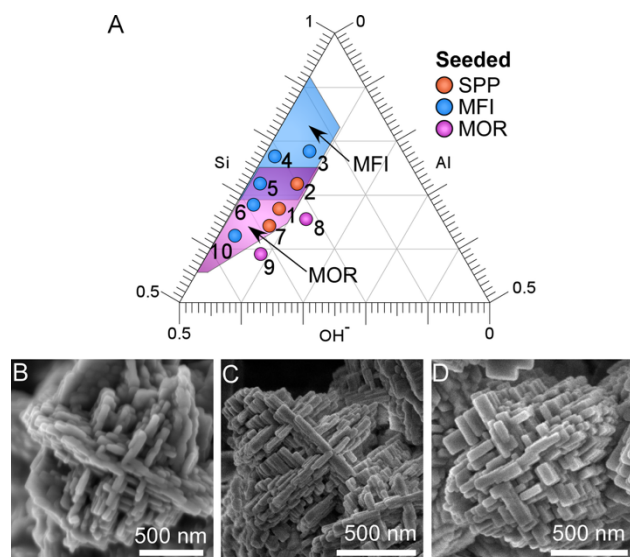


Figure 2. (A) Ternary phase diagram constructed from the molar fractions of Si, Al, and NaOH. Shaded regions indicate non-seeded syntheses of Na-MFI (blue) and Na-MOR (purple) from literature.¹² All symbols represent seed-assisted synthesis using growth mixtures prepared by the addition of 10 wt% siliceous MEL (silicalite-2) as seeds to a solution with a molar composition of 18 SiO₂: 1 Al₂O₃: 6.84 NaOH: 324 H₂O using colloidal silica and sodium aluminate as sources. The products obtained from seeded synthesis after heating at 150 °C for 1 – 10 days (see Figure S4) resulted in zeolite SPP (red circles: 1, 2, 7), MFI (blue circles: 3 – 6, 10), and MOR (purple circles: 8, 9). (B – D) Representative scanning

used for the nominal condition (Point 1, Figure 2A), tetraethyl orthosilicate (TEOS), and fumed silica. We previously reported that as-received silica sources can exhibit distinct silica connectivity, or microstructure.³⁹ In zeolite growth media, silica sources undergo a small degree of dissolution but also form larger aggregates.^{1, 39, 40} One exception is TEOS, which produces soluble species after hydrolysis that can self-assemble into small nanoparticles (3 – 6 nm).⁴¹ Our findings demonstrate that replacing colloidal silica with TEOS transforms the final morphology from a house-of-cards structure to a conventional coffin-shaped ZSM-5 crystal (Figure 3B). We also tested mixtures of TEOS and colloidal silica over a range of TEOS molar percentages: 80% (Figure 3C), 50% (Figure 3D), and 20% (Figure 3E). Although the addition of TEOS reduces the synthesis time to 1 day (Figure S8), our findings reveal that even a slight replacement of colloidal silica with TEOS dramatically reduces the degree of pillaring. A similar effect was observed when replacing colloidal silica with fumed silica (Figure 3F).

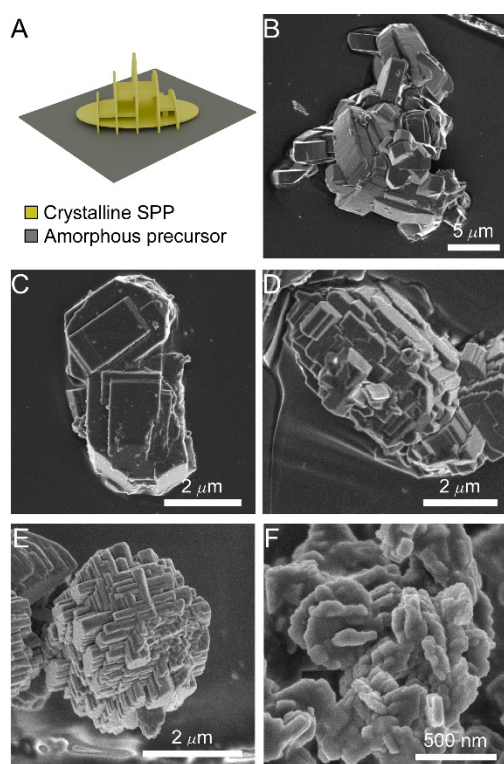


Figure 3. Impact of silicon source on SPP synthesis using siliceous MEL (silicalite-2) as seeds. (A) Illustration of heterogeneous nucleation of zeolite SPP (gold) on the surface of an amorphous precursor (grey). (B – E) SEM images of solids extracted from syntheses (Point 1, Figure 2) where the amorphous precursors were generated from two silicon sources, TEOS and Ludox AS-40, using the following percentages of TEOS: (B) 100, (C) 80, (D) 50, and (E) 20%. (F) Representative SEM image of solids extracted from a synthesis with fumed silica as the silicon source. See Figure S8 in the Supporting Information for time-elapsd SEM images of syntheses with different silicon sources. All syntheses produced ZSM-5 (MFI) products (Figure S9); and removal of ethanol from TEOS syntheses did not impact the final product (Figure S10). For studies with fumed silica, the synthesis procedure was slightly modified by increasing the water content to facilitate stirring during the aging process; and then after overnight aging, most of the water was removed by heating at 60 °C before hydrothermal synthesis.

For studies using different silica sources, we extracted samples at regular synthesis times and performed elemental

analysis using a combination of energy dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS) to extract Si/Al ratios of the entire sample and regions within the outer rim (5 – 8 nm depth), respectively.⁴² The combination of EDX and XPS (Figure S11) allows for the analysis of surface and bulk Al content (or $Al_{\text{surface}}/Al_{\text{bulk}}$ ratio), which is approximately equal to unity for homogeneously distributed aluminum in amorphous precursors or zeolites, and exhibits values above and below unity for Al- and Si-zoned materials, respectively.³⁴ For the nominal synthesis using colloidal silica, we observe a relatively uniform distribution of silica and alumina (i.e., $Al_{\text{surface}}/Al_{\text{bulk}} \approx 1$) throughout crystallization (Figure S12 and Table S1). In contrast, when TEOS and fumed silica are used as silica sources, there is a monotonic increase in $Al_{\text{surface}}/Al_{\text{bulk}}$ ratio (from ca. 0.25 to 0.80) with synthesis time. We posit the enhanced siliceous exterior surfaces of precursors under these conditions alters heterogeneous nucleation and the ability to form intergrowths that are integral to the generation of SPP materials. Collectively, these parametric analyses indicate a narrow window of seed-assisted, organic-free synthesis conditions leading to the formation of SPP zeolite when MEL or MFI are used as seeds. In the following sections, we explore the most critical synthesis parameter – the crystal framework of the zeolite seed.

2.3 Impact of seed crystal structure on selectivity of SPP synthesis. The synthesis of zeolite SPP requires the use of crystal seeds to bypass the initial growth of zeolite MOR. Here, we assessed SPP synthesis using a broad range of zeolites as seeds to determine what structural features are critical to promote pillaring. Our initial criterion for selecting seeds was to ensure that the zeolite structure contained at least one shared composite building unit (CBU) with the MFI framework of SPP zeolite. In literature, there are many hypotheses of zeolite crystallization that emphasize the role of CBUs as possible growth units⁴³ or as a basis for designing seed-assisted syntheses without OSDAs.²³ These empirical rules consider shared CBUs between the seed (parent) crystal and the products of either seeded (daughter) or non-seeded syntheses. Other studies, however, have demonstrated that common CBUs are not a universal predictor of parent – daughter relationships, suggesting more complex processes are involved in seed-assisted zeolite crystallization.⁴⁴

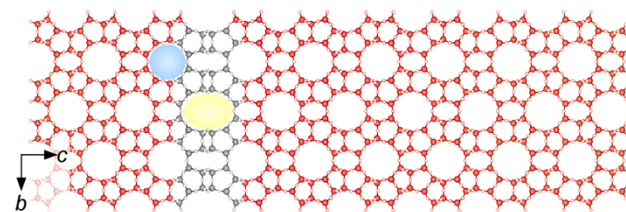


Figure 4. Unit cell of the SSZ-57 (SFV) structure (tetragonal) with unit cell parameters $a = 20.15$, $b = 20.15$, and $c = 109.76$ Å. The SFV structure is a member of the intergrowth family comprised of 10- and 12-membered rings (blue and yellow shading, respectively) with sections that exhibit similarities to zeolite MEL (highlighted in red) connected by junctions (grey).

Zeolites MEL and MFI, which were the only seeds tested in our previous study¹⁷, have identical CBUs. Considering the structural model of SPP is a majority of MFI with MEL intergrowth, an obvious choice would be to propose new seeds exhibiting maximal structural similarity to SPP and, consequently, to MEL or MFI. Thus, insight could potentially be gained from zeolites that have natural intergrowth structures,

such as zeolite SFV (SSZ-57)⁴⁵, which contains large sections of MEL (Figure 4). Zones and coworkers showed that SSZ-57 can be synthesized

Table 1. Composite building units (CBUs) of zeolites tested as potential seeds for zeolite self-pillared pentasil (SPP) synthesis.^a

	mor	cas	mfi	mel	d6r	bea	mtw	jbw	bik	cha	fer	pcr	lau	mso	sod	mtt	ton
MEL	■	■	■	■													
MFI	■	■	■	■													
MWW				■	■												
*BEA	■					■	■										
MTW		■					■	■	■								
CHA					■					■							
STT		■				■											
FER	■										■	■					
FAU					■										■		
MTT								■	■							■	■
TON								■	■							■	■

a. Red shading indicates SPP products; Red squares are common CBUs as the MFI and MEL components of SPP; Grey squares are CBUs not found in either MFI or MEL frameworks.

in hydroxide media using N-butyl-N-cyclohexylpyrrolidinium as an OSDA. Although it is structurally related to ZSM-11 (MEL), the framework of SSZ-57 exhibits a periodically modulated structure along the *c*-axis, forming a super-cell where isolated 12-ring features are embedded within a 10-ring channel system. These 12-ring features are not continuous but appear as spatially disordered, three-dimensional pockets distributed throughout the framework. Because of its distinct framework environments within a single crystallite, we hypothesized that SSZ-57 can serve as an effective seed for promoting the formation of SPP structures in our synthesis system.

Many zeolites are not structurally related to MEL or MFI; however, we were able to synthesize a library of 11 zeolite frameworks (Table 1) as potential seeds for SPP synthesis, which are divided into two categories: those sharing at least one common CBU with the desired SPP product (MEL, MFI, *SFV, MWW, *BEA, MTW, FER), and those lacking a common CBU (CHA, FAU, MTT, TON). With the exception of SSZ-57, the frameworks selected as seeds are readily synthesizable using commercial OSDAs, making them natural choices for this study. Later, we include one additional framework (STT) after uncovering design criteria using computational methods (see Section 3.4). Two seeds were obtained from commercial vendors (*BEA and FER), while all others were synthesized in house using protocols described in the Experimental Section along with corresponding PXRD, SEM and other characterizations (Figures S13 and S14; Table S2). All seeds were calcined prior to use in order to remove any occluded OSDAs. For all experiments reported herein, we selected Point 1 in Figure 3A for SPP syntheses since this was

identified as the most optimal synthesis composition. The initial screening to determine whether each seed produces SPP zeolite involved the visual inspection of scanning electron microscopy (SEM) images coupled with PXRD analysis to confirm the synthesis of MFI-type zeolite and textural analysis to assess total surface area.

Table 1 summarizes all seeds with 17 distinct CBUs, where those of MFI and MEL are highlighted with red squares. The red shading in Table 1 indicates the samples that showed some degree of pillaring in SEM images. Among the seeds having at least one shared CBU with MFI, six out of seven led to the formation of SPP-like materials. Similarly, three of the four lacking a common CBU produced dense (non-pillared) phases. At a cursory level, identifying potential seed crystals for SPP synthesis using the common CBU hypothesis appears promising; however, when we performed time-resolved *ex situ* PXRD analysis of solids extracted from seed-assisted syntheses (Figure S15) to determine the extent of SPP crystallization, we found that this criterion is less selective when considering the relative amounts of residual (unreacted) amorphous material or zeolite impurities. Figure 5A summarizes these results by subdividing the outcomes into syntheses employing seed crystals with shared CBUs (to the left of the dashed line) and those without shared CBUs, including the non-seeded control (to the right). These results show that, among the seeds listed in Table 1 sharing CBUs with MEL/MFI, only three of the eight produced fully crystalline SPP after 3 days of synthesis. These include MEL (Figure 2B), SFV (Figure 5B), MFI (Figure 5C), and STT (Figure 5D). Syntheses using seeds of zeolites MWW (Figure 5E), MTW (Figure 5F), and *BEA (Figure 5G) produced small

fractions of SPP (i.e., incomplete crystallization) with a significant amount of zeolite MOR formed as an impurity. For reference, we added SPP crystals to the list of seeds and observed the formation of a pure SPP product (Figure 5H) after 3 days of synthesis. The only seed lacking a common CBU to produce an SPP-like product was zeolite CHA (Figure 5I);

however, these crystals lack hierarchical meso-/macropores, consistent with textural analysis revealing low surface area (*vide infra*). Even though several seeds sharing CBUs with MEL and MFI are able to crystallize SPP, the nucleation kinetics, phase purity, and quality of the final crystal vary from seed to seed; thus, the nuances of SPP

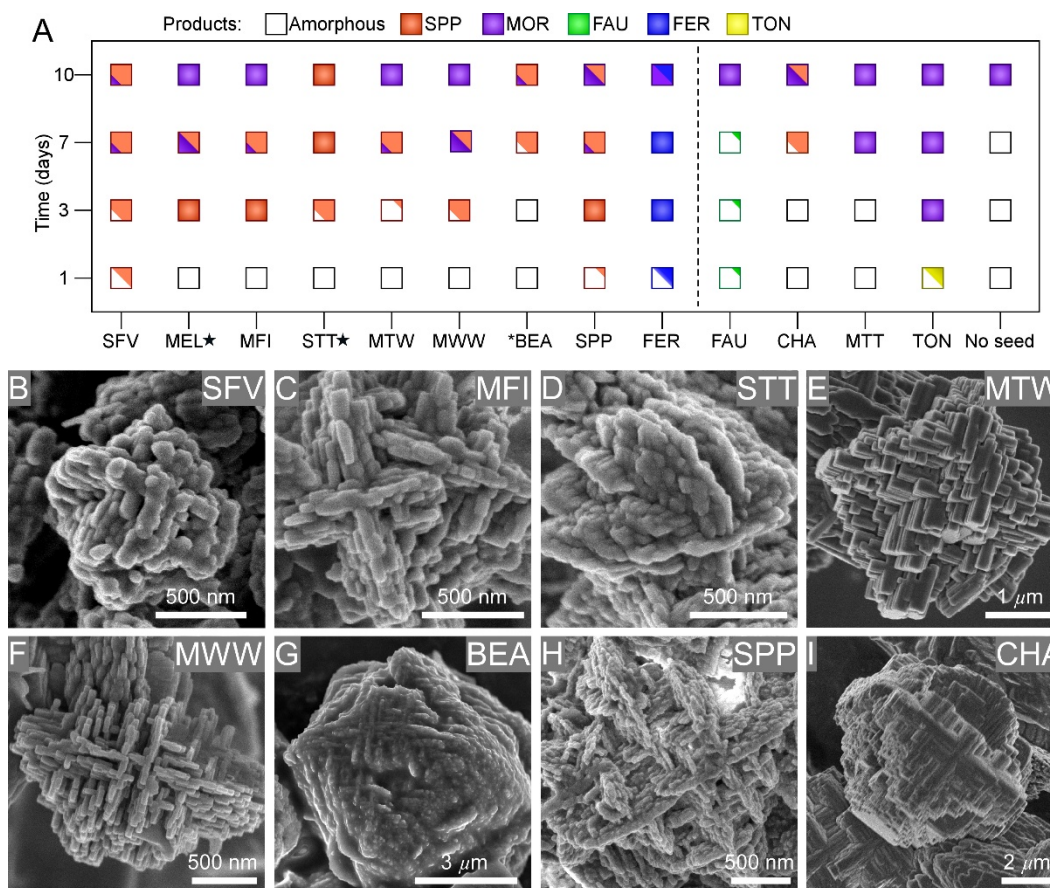


Figure 5. (A) Final products from seed-assisted SPP syntheses at various synthesis times using different zeolite seeds (x-axis) in growth mixtures with the same composition as Point 1 in Figure 2A (18 SiO₂: 1 Al₂O₃: 3.42 Na₂O: 324 H₂O) with corresponding PXRD patterns provided in Figure S15. The composition of zeolite crystals (colors) and residual amorphous phase (white) of each sample were estimated from PXRD patterns where mixtures are denoted as split squares (see Figure S9 in the SI). The dashed line separates seeds that share at least one common composite building unit (CBU) with zeolite MFI (left side) from those that share none (right side). The SPP phases (red) were identified by SEM images using the criterion in Figure S1A, and a non-seeded synthesis is shown for comparison (far right). (B – I) Representative SEM images of crystals with signatures of pillaring prepared with different zeolite seeds (frameworks labelled on each image). Solids were extracted from syntheses after heating each seeded growth solution at 150 °C for the following times: 3 days (C, F, H), 7 days (B, E, I) and 10 days (D, G). These syntheses used the following seeds: (B) SFV, (C) MFI, (D) STT, (E) MTW, (F) MWW, (G) *BEA, (H) SPP, and (I) CHA. Stars indicate purely siliceous seeds (Si/Al = ∞). Low-magnification SEM images are provided in Figure S16.

crystallization remain unexplained by the common CBU hypothesis.

2.4 MEL content and surface areas of SPP zeolites reveal a lack of trends across seeds. In our previous study, we proposed that the pillaring phenomenon occurred due to the retained "memory" of dissolving seeds, although the identities of these species are unknown.¹⁷ We also acknowledged that the disappearance of Bragg peaks for seeds in time-resolved PXRD patterns does not necessarily indicate complete dissolution of seeds prior to the onset of SPP nucleation (i.e., partial dissolution can lead to seed quantities below the detection limit of PXRD).¹⁷ Our previous study of the SPP growth mechanism¹⁷ reported time-elapsing electron micrographs and powder XRD patterns of extracted solids that lacked evidence of undissolved seeds, which we repeated in this study using

zeolite STT seeds (Figure S17). While these studies seem to indicate the seeds dissolve, it is possible that a small fraction remain (i.e., below the detection limit of PXRD). The only exception is the synthesis using zeolite FER seeds, which promote FER crystallization (Figures 5A and S15), where PXRD patterns always show peaks corresponding to zeolite FER within the first 10 days of synthesis, after which MOR impurities begin to appear.

The kinetics of SPP crystallization, however, are variable, with earlier nucleation observed when SFV, MTW, and SPP are used as seeds compared to MFI or MEL seeds. It is possible that dissolved species increase the number of junctions between branched nanosheets, in accordance with the structural model proposed by Tsapatsis and coworkers²² where the junctions are proposed to be MEL intergrowths in

MFI-rich SPP crystals. Molinero and coworkers¹⁵ suggested that intergrowths occur due to cross-nucleation between zeolites sharing a common crystal plane. Based on this hypothesis, we investigated whether the degree of pillaring within SPP zeolites is related to structural relationships between parent (seed) and daughter (SPP) structures.

At first, we selected the amount of MEL content present in zeolite SPP samples to determine whether this quantity is an accurate descriptor of the degree of pillaring. It is well established that the intensity and width of Bragg peaks is associated with several factors that include crystal size and its relative abundance (i.e., quantities >3 wt% of the sample). As illustrated in Figure 6A, the distribution of MEL intergrowth in MFI-rich SPP particles can either be larger (single) domains or smaller domains distributed throughout the nanosheets. The percentages of MEL and MFI in zeolite SPP samples was extracted from PXRD data using a calibration curve that was established from simulated patterns. The calibration curve, which was generated using the DIFFaX software (Figure S18), was used to approximate the percentage of MEL in each zeolite SPP sample (Figure 6B). The nominal sample prepared with MEL (silicalite-2) seeds contains ca. 3.3% MEL. Interestingly, the Brunauer–Emmett–Teller (BET) surface area obtained from nitrogen physisorption measurements does not correlate with the MEL content of the samples. Rather, the majority of samples spanning from the lowest to highest surface area (CHA and MEL seeds, respectively) contain less than 3% MEL, with the sole exception being the sample prepared with silicalite-1 (MFI) seeds. In general, the MEL phase fraction is commonly regarded as an indicator of the degree of MEL intergrowth²², which is expected to promote pillaring and increase the BET surface area; however, the absence of this trend in Figure 6B is counter to expectations, but may indicate that MEL is more aggregated into larger domains as compared to single unit cell domains observed previously (Figure 6A).³¹ To this end, domain size and connectivity may play a critical role in determining the extent and structural consequences of intergrowth beyond the limitations of PXRD to resolve. Furthermore, none of these quantities are able to explain the differences in SPP structures across seeds.

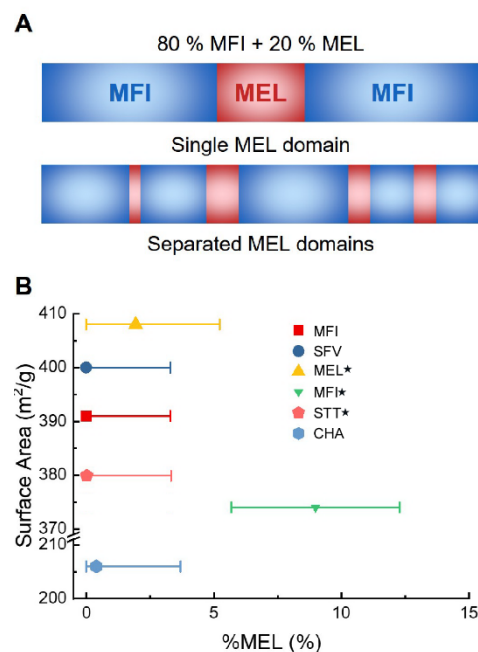


Figure 6. Quantification of MEL intergrowth percentages by powder X-ray diffraction (PXRD). (a) Idealized structural models showing potential MEL domain distribution modes within MFI crystals. (b) Comparison of total BET surface area as a function of MEL percentage determined from calibration curve developed from powder DIFFaX simulations (Figure S18). Pure MFI phase PXRD pattern yielded a MEL content of 3.3% according to our calibration curve, which is the maximum error calculated from different sources of errors, including baseline correction, peak integration, and curve fitting. This estimation method is valid for MEL content less than 30% and the powder sample being polycrystalline. The broad range of surface area corresponds to the hierarchical nature of samples ranging from highly pillared (e.g., MEL seeds) to samples with a low degree of pillaring (e.g., CHA seeds). Stars indicate purely siliceous seeds (Si/Al = ∞).

2.5 Rationalizing criteria for seed crystal selection with computation. Despite the qualitative success of the common CBU hypothesis in proposing seeds, it has practical limitations for more extensive validation studies based on the difficulties of synthesizing larger libraries of zeolites with shared CBUs. For instance, the International Zeolite Association structure database lists 68 frameworks with at least one common CBU as MFI (Table S3), but many of these zeolites require atypical synthesis conditions (e.g., noncommercial organics, fluoride media, etc.). Thus, from a data perspective, there is little information to support the *a priori* selection of one seed crystal over another using only the common CBU criterion.

Furthermore, the inability of common CBUs and MEL percentage to predict seed crystals for SPP synthesis motivated efforts to identify a descriptor based on data science. To rationalize why certain seeds can promote pillaring, we employed a computational approach to compare the structural similarity between the seeds and the final products (i.e., MFI and MEL) using inorganic synthesis maps developed by Schwalbe-Koda and coworkers.^{26, 27} This method builds on past work²⁶ by defining distances between zeolite frameworks according to their set of atom-centered representations, i.e., per-atom invariant vector representations that encode the neighborhood of each atom. This approach has previously been demonstrated to predict intergrowth among zeolite pairs and has demonstrated to correlate with similarity in inorganic

synthesis conditions.²⁷ Thus, we hypothesized that this continuous distance metric between discrete zeolite frameworks is a more nuanced seed selection method compared to the common CBU hypothesis.

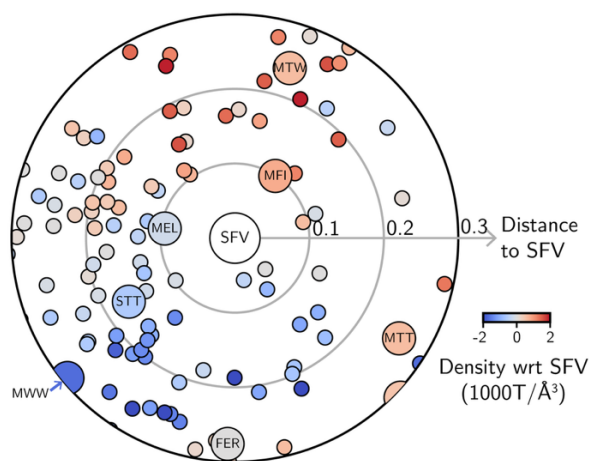


Figure 7. Computational model to predict parent-daughter pairings based on the structural distance of each zeolite to SFV according to the average minimum distance method.²⁷ The angles are optimized such that the distance between neighbors reflects their actual distance matrix, i.e., structurally similar zeolites tend to be clustered within the same angle. The color scale indicates framework densities with values equal to (white), less than (blue), and greater than (red) that of zeolite SFV (refer to Figure S19 in the SI for the full list of framework types).

In order to use this method to design zeolite seeds, we first proposed that ideal seeds maximize the similarity with the target framework. Since the SPP framework is a combination of MEL and MFI structures, we adopted the SFV framework (Figure 4) as the target reference structure against which distances are computed.⁴⁵ Figure 7 summarizes the distance between zeolite frameworks to SFV. In this radial plot, a shorter distance (smaller radius) implies greater similarity to SFV, which is hypothesized to increase the likelihood of intergrowth. The angle of each framework is obtained by bringing similar frameworks together and placing

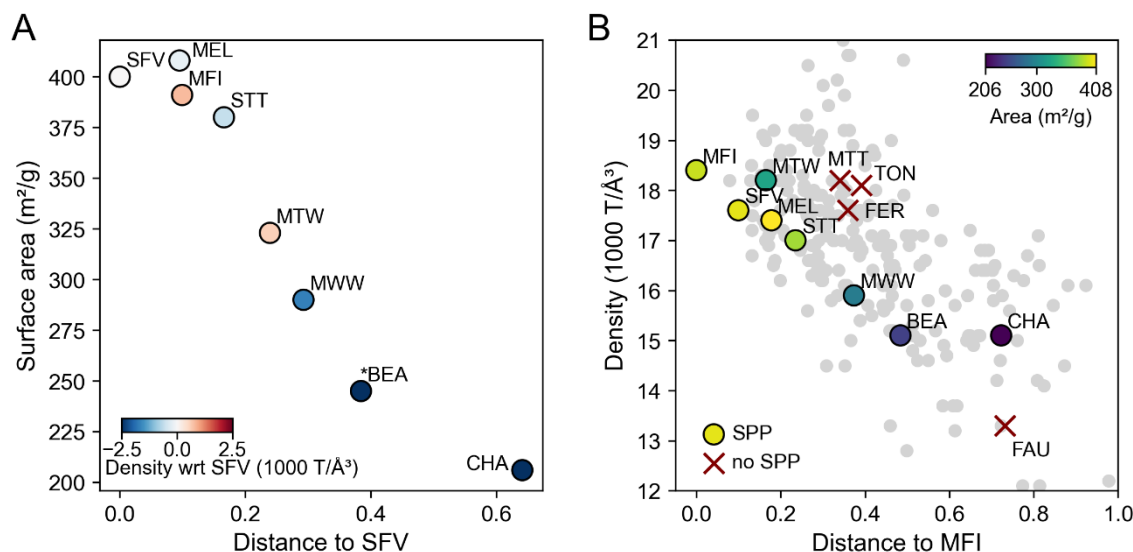


Figure 8. (A) Comparison of BET surface area (y-axis) for products of seed-assisted synthesis to the distance of each seed crystal to zeolite SFV (x-axis) provided in Figure 7. The symbols are color coded based on differences in density for each seed crystal to that of SFV. (B) Comparison of framework density for each seed crystal (y-axis) to the distance of each seed to zeolite MFI (x-axis). The color coding refers to the BET surface area from panel A that are indicative of zeolite products with a high degree of pillaring (yellow), moderate pillaring (green), and no SPP-like characteristics (× symbols). Based on these analyses, seed-assisted synthesis of SPP materials is generally correlated with seeds possessing shorter distances to SFV and lower framework density, which lead to products with a higher degree of pillaring (i.e., higher BET surface area). This is analogous to what we typically see in energy-density plots for hypothetical and known zeolites.⁴⁶ Lower densities may create competition in the recrystallization to SPP, whereas higher densities may reduce the driving force.

dissimilar frameworks far apart in a min-max optimization strategy. The color scale in Figure 7 is based on the difference in density (number of tetrahedral sites per volume) relative to SFV. This visualization allowed us to identify potential seeds for SPP synthesis. The full list of zeolites with short distances to SFV (Figure S19) contain many uncommon frameworks (e.g., OKO, TUN) that are nontrivial to synthesize; therefore, we worked only with those zeolites that could be prepared with commercially available OSDAs. First, we observed that MEL and MFI are indeed among the closest frameworks to

SFV, providing an initial validation to the method. Second, our initial screening of seeds in Table 1 did not include zeolites STT and SFV. The latter was used as the basis generating Figure 7 and the former (STT) was a non-intuitive structure identified from the computational method, which was later tested as a potential candidate for SPP synthesis.

Beyond the qualitative seed selection described above, our distance metric is able to rank the seeds according to the degree of pillaring of the resulting SPP zeolite. Nitrogen adsorption/desorption profiles of most pillared zeolites reveal

the presence of mesopores (Figure S22) while some have macropores that impact the total BET surface area. Figure 8A shows that when the total BET surface area of SPP syntheses is plotted against the distance to zeolite SFV for each listed seed crystal, the correlation is remarkably good. In general, we find that seeds with structure similarity to the idealized SPP (i.e., low distance to SFV) have higher surface areas, and thus produce higher quality SPP materials. In addition, seeds with densities closer to SFV, as indicated in Figure 8A with white or light shades of blue and red, produce the highest degree of pillaring. Given that density differences are known to influence recrystallization pathways in zeolites⁴⁷, this finding shows that, beyond the data-driven similarity, density is also a useful descriptor for seed selection. Figure 8B correlates both quantities in a single plot, where MFI (the primary structure that is crystallized) is chosen as the reference. These results highlight an interesting heuristic to the design of new seeds. Most successful seeds seem to lie in a region of low density, and low distance to MFI. Rules similar to this were previously observed in energy-density landscapes of zeolites and used to navigate the space of hypothetical frameworks.⁴⁸ This heuristic may explain why FER did not lead to the crystallization of SPP; when despite having density comparable with MEL and one common CBU with MEL/MFI, it has much higher distance to MFI/SFV for a zeolite with that range of

densities. In contrast, MWW also shares a single CBU with MEL/MFI and exhibits the same distance to MFI as FER (Figure 8B), but at a much smaller density. Chabazite (CHA) is the only exception to this rule, but it has been reported multiple times as an anomalous seed to ZSM-5 in other synthesis conditions.⁴⁹ According to this rule, we selected the STT framework as potential seed, as it lies in a range of low-density, low-distance towards MFI compared to its counterparts.

Time-elapsd analysis of SPP syntheses using zeolites STT and SFV as seeds revealed interesting trends. As shown in Figure 5A, zeolite STT seeds stabilized the formation of the SPP phase by preventing the formation of zeolite MOR within 10 days of synthesis. The use of SFV seeds accelerated nucleation (similar to the use of SPP seeds), but did not result in complete crystallization prior to the onset of zeolite MOR nucleation. These results further confirm that the computationally selected STT zeolite leads to high-quality SPP structures from a perspective of phase purity even when intuitively designed seeds such as SFV do not.

2.6 Impact of seed composition on SPP synthesis. One factor that may play an important role but is unaccounted for in this computational metric is the composition (i.e., Si/Al ratio) of seed crystals. In addition to silicalite-2, we also tested all-silica MFI (silicalite-1) and STT, whereas all other

Table 2. Properties and performance of H-form SPP zeolites with the highest degree of pillaring.

Zeolite Catalysts ^a	BET S _A ^b (m ² /g)	S _{ext} (m ² /g)	V _{micro} (cm ³ /g)	Si/Al	C _{acid} (μmol g ⁻¹)	TON ^c (mol/mol)
Seeds for SPP synthesis						
MEL*	408	68	0.15	9	444	7045
MFI	391	61	0.15	9	424	7452
MFI*	374	85	0.13	10	497	3307
STT*	380	120	0.13	9	464	3962
SFV	400	99	0.13	9	473	4025
MTW	323	30	0.12	9	465	3140
Reference (non-pillared)						
C-ZSM-5 ^d	435	113	0.14	20	278	2099

a. SPP zeolites were synthesized with the same conditions as Point 1 in Figure 2A (150 °C, 10 wt% seeds) for 3 days, with the exception of SFV (7 days) and STT (10 days), and asterisks indicate purely siliceous seeds (Si/Al = ∞); b. BET isotherm shown in Figure S22; c. Cumulative turnover number (TON) with units of mol_{MeOH}/mol_{H⁺} calculated in the range of methanol (MeOH) conversions of 50 – 30%; d. Conventional ZSM-5 (C-ZSM-5) catalyst was prepared according to a previous study.⁵⁰ Asterisks indicate siliceous seeds (Si/Al = ∞)

frameworks listed in Table 1 contain varying amounts of aluminum (see Table S2). In our previous study we showed that SPP materials could be produced using all-silica and aluminosilicate isostructures of zeolites MFI and MEL,¹⁷ where the least effective was ZSM-11 (MEL) and the most effective was silicalite-2 (MEL). Here, we assessed SPP synthesis using zeolite MFI seeds containing aluminum (ZSM-5) and those that are purely siliceous (silicalite-1). There are distinct differences in the kinetics of crystallization based on seed Si/Al ratio (Figure S20). The MFI seeds with high aluminum content (Si/Al = 12) lead to the appearance of an MOR phase at shorter synthesis times, resulting in the presence of impurity. A shift to MFI seeds with lower aluminum content (Si/Al = 40) or purely siliceous silicalite-1 (Si/Al = ∞) enables complete crystallization to zeolite SPP without the formation of MOR impurity. A similar trend was observed for zeolite STT when shifting from the all-silica seeds (Si/Al = ∞) used in Table 1 to an aluminosilicate isostructure (Si/Al = 30). The latter reduced the rate of SPP crystallization (Figure S21), resulting

in a partially crystalline product after 10 days of synthesis compared to fully crystalline product after 3 days using aluminosilicate STT seeds (Figure 5A). While we observe for select cases that more siliceous seeds enhance SPP formation, the exact role(s) of aluminum in seed-assisted synthesis, including its potential effects on crystal seed solubility, are unresolved subjects for future investigation.

2.7 Impact of seed selection on catalytic performance. To distinguish between the successful syntheses of zeolite SPP samples according to a new degree of freedom, we used catalyst performance as an additional metric. For catalytic testing we selected methanol to hydrocarbons (MTH) as a benchmark reaction and chose SPP materials screened in Figure 8A with the highest BET surface areas (374 to 408 m²/g). All as-synthesized materials were converted to proton-form catalysts (H-zeolites) using a reported ion-exchange and calcination procedure.¹⁷ The physicochemical properties of these materials are listed in Table 2. The total acid concentration (C_{acid}), measured by ammonia temperature-programmed desorption (NH₃-TPD), reveals approximately similar acidity

for all catalysts (Figure S23). Solid-state ^{27}Al magic-angle spinning (MAS) NMR spectra revealed similar results for all samples, which primarily contain framework aluminum and only a minor contribution of extra-framework species (Figure S22).

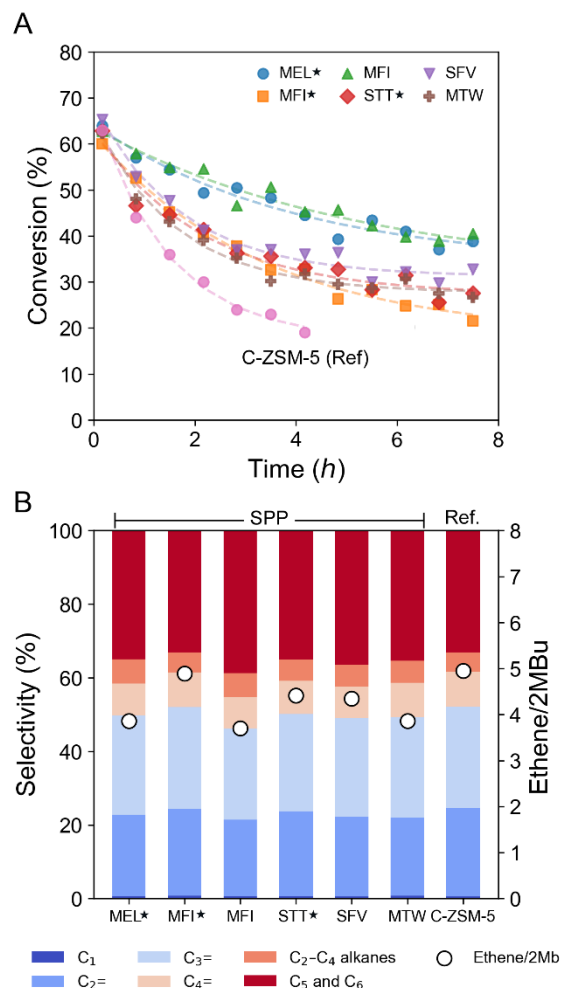


Figure 9. Methanol to hydrocarbon (MTH) reactions using H-form SPP zeolites (Table 2) at sub-complete conversion (methanol + dimethyl ether) in a packed bed reactor at 350 °C with a weight-hourly space velocity (WHSV) of 28 h⁻¹ (11.9 mg) for silicalite-2 and ZSM-5, 25 h⁻¹ (13.3 mg) for STT and silicalite-1, 26.8 h⁻¹ (12.4 mg) for SFV, 28.9 h⁻¹ (11.5 mg) for MTW, and 22.1 h⁻¹ (15 mg) for C-ZSM-5. All zeolites were synthesized for 3 days with the exception of SFV (7 days) and STT (10 days). A conventional non-pillared MFI sample, C-ZSM-5 (pink circles), is included as a reference (Ref) for comparison. Stars associated with zeolite frameworks indicate purely siliceous seeds (Si/Al = ∞) used to prepare SPP samples. (A) Time on stream (TOS) changes in conversion where dashed lines are interpolated to guide the eye. The cumulative turnover numbers (TON) assessed in the range of 50 to 30% conversion are provided in Table 2. (B) Product selectivities (histograms, left y-axis) and ethene-to-2MBu ratios (symbols, right y-axis) at early TOS (~50% conversion), where 2MBu refers to the sum of 2-methylbutane and 2-methyl-2-butene. The x-axis indicates seeds used to prepare each SPP catalyst along with the non-pillared MFI (C-ZSM-5) used as a reference.

Catalytic tests were performed in a packed-bed reactor with weight-hourly space velocities (WHSV = 22.1 – 28.9 h⁻¹) varied to achieve similar initial methanol conversions of ~65%. Time on stream (TOS) data for each catalyst (Figure

9A) and the corresponding cumulative turnover numbers (Table 2) reveal the following order of seed crystals from best to worst SPP catalysts: MFI (ZSM-5) ≈ MEL (silicalite-2) > STT ≈ SFV > MFI (silicalite-1) ≈ MTW > C-ZSM-5. Overall, these catalysts exhibit comparable performance with similar rates of deactivation (i.e., slopes of curves in Figure 9A) that outperform a conventional non-pillared MFI sample (C-ZSM-5). This latter serves as a reference and was intentionally selected from a reported protocol¹⁷ yielding similar-sized (ca. 300 nm, Figure S25) catalysts with less aluminum (Si/Al = 20), compared to syntheses of more aluminous ZSM-5 (Si/Al ≤ 12) that yield much larger particles (>1 μm) that rapidly deactivate in MTH reactions.³⁴

The SPP catalysts also exhibit similar product selectivities (Figure 9B, histograms) and nearly identical ethene-to-2MBu ratios (Figure 9B, symbols), where 2MBu refers to the sum of 2-methylbutane and 2-methyl-2-butene. This ratio has been used in literature⁵¹ as an indicator for the dominant reaction pathway in the MTH hydrocarbon pool (HCP) mechanism. Lower ethene/2MBu ratios refer to the enhanced propagation of the olefin-based cycle over the aromatic cycle in the HCP mechanism. All SPP catalysts exhibit relatively low ethene/2MBu ratios, consistent with previous findings¹⁷ showing their favorable mass transport properties that suggest these hierarchical structures operate as pseudo nanoparticles.

The trend in catalyst performance for seeds with the lowest distance to SFV does not exactly match the trend in Figure 8A for BET surface area; however, it should be noted that SPP crystallization is incomplete for several of the syntheses, which leads to slightly lower micropore volumes (Table 2) that likely impact catalyst performance. Nonetheless, the catalytic testing reveals a clear structure–function relationship, where the materials with highest degree of pillaring are those with the highest BET surface area and MTH catalyst performance. Interestingly, the SPP zeolite synthesized with the computationally designed STT seed exhibited performance equivalent to the SPP structure obtained using silicalite-1. As a reference, we include a conventional catalyst (C-ZSM-5) that exhibits faster deactivation (Figure 9A) compared to the SPP catalysts, resulting in the lowest turnover number (Table 2). SPP catalysts prepared with MWW and *BEA seeds could not be used as controls due to the presence of amorphous phases, similar to syntheses with the CHA seed. For example, we performed the MTH reaction using the catalyst prepared with CHA seeds; however, the performance was extremely poor (i.e., the catalyst was practically inactive with <15% conversion). This is attributed to the large fraction of residual amorphous material in this sample, consistent with its low micropore volume (0.09 cm³/g).

CONCLUSION

In summary, we have established robust selection criteria for seed-assisted, organic-free syntheses of SPP zeolites. We presented a data-driven approach to develop structural descriptors that are based on a model intergrowth zeolite (e.g., SFV with MEL segments) rather than using descriptors of either MEL or MFI frameworks, which are the two components of the zeolite SPP intergrowth structure. A computational model based on zeolite SFV as a reference was used to explain trends in surface area of the product SPP structures, and predicted zeolite STT as a viable seed structure. The STT seed was then experimentally tested and verified to produce zeolite

SPP with relatively high BET surface area. Several hypotheses in literature that are frequently used to rationalize seed-assisted zeolite synthesis or interzeolite transformations were found to be insufficient for predicting zeolite SPP synthesis. Among these include the selection of zeolites with common CBU(s) as well as evaluating the final products to assess trends in the percentage of MEL. The degree of pillaring, however, may still correlate with MEL content, but likely reflects the presence as ultrasmall intergrowth domains within SPP particles that are evasive to PXRD detection.

The parametric analysis of seed-assisted, organic-free synthesis of zeolite SPP in this study revealed a very limited window of growth solution compositions that can be used to generate highly pillared MFI-type crystals. We observed that there is a greater degree of flexibility in the selection of seed crystal structure compared to parameters such as the silica source, which is limited to colloidal silica. The high sensitivity to silica source selection indicates the resulting physicochemical properties of amorphous (alumino)silicate precursors is a critical variable for SPP crystallization. These collective findings generate new questions pertaining to the mechanism of heterogeneous SPP nucleation, while leaving open long-standing questions regarding the role of seed surfaces or species generated during seed dissolution (previously referred to as the seed “memory”) in the promotion of self-pillaring without assistance from organic structure-directing agents used in alternative approaches.

The steps taken in this study are directed toward recent efforts to address knowledge gaps in the fundamental understanding of (non)classical crystal growth mechanisms, which are characteristic of zeolites and related materials. These efforts can also potentially lead to the design of optimized catalysts for a broad range of applications where the enhanced mass transport properties of SPP zeolites provide materials with exceptional activity and stability relative to conventional ZSM-5 (MFI) catalysts.¹⁷ The overall performance of these materials depends on variables beyond their hierarchical structure. For example, zeolite SFV did not emerge as the best candidate owing to its lower crystallinity, which motivates future optimization of synthesis protocols to fully capitalize on the predictive capabilities of the data-driven model. Finally, the design principles proposed in this work can be extended to other framework topologies or intergrowth pairs. The continuous measure of distances between zeolites has already been proven to recognize synthesis similarities across the zeolite literature,²⁷ suggesting its generality beyond the MFI/MEL intergrowth. Future studies can test the universality of the seed selection strategy across frameworks and synthesis conditions.

EXPERIMENTAL SECTION

4.1 Materials. The following chemicals for zeolite synthesis were purchased from Sigma Aldrich: LUDOX AS-40 (40 wt% suspension in water), LUDOX AS-30 (30 wt% suspension in water), tetraethyl orthosilicate (TEOS, $\geq 99.5\%$), fumed silica, sodium aluminate (57.1% Al_2O_3 and 37.2% Na_2O), and sodium hydroxide solution (50 wt%). Additional chemicals purchased from Alfa Aesar included sodium hydroxide (98% pellets). Trimethyladamantylammonium hydroxide (TMAda, 20%) were purchased from SACHEM. 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 M Ω).

4.2 Preparation of seed crystals. The following seeds were purchased from Zeolyst: MFI (CBV8014 with Si/Al = 40 and CBV2314 with Si/Al = 11.5), *BEA (CBV814C with Si/Al = 19), and FER (CP914C with Si/Al = 10). Zeolites SFV (Si/Al = 25) and STT (Si/Al = 30) were provided by Dr. Stacey Zones (University of California, Berkeley). Seeds of MFI (Si/Al = ∞), MEL (Si/Al = ∞), MWW (Si/Al = 15), MTW (Si/Al = 50), MTT (Si/Al = 36), FAU (Si/Al = 2), CHA (Si/Al = 20), and TON (Si/Al = 45) were synthesized according to previous protocols.^{17, 52–58} The STT seed with Si/Al = ∞ was synthesized by adding 50 wt% NaOH solution into DI water followed by the addition of trimethyladamantylammonium hydroxide as the OSDA. To this solution, Ludox AS-30 was added to obtain a growth mixture with a molar composition of 0.05 NaOH:1 SiO_2 :0.1 OSDA: 20 H_2O . The growth solution was aged at room temperature for 24 hours and then transferred into a 23-mL digestion bomb (Parr Instruments) for 4 days at 160 °C with 30 rpm rotation. All seeds except FAU were calcined at 550 °C for 6 hours in a Thermo Scientific Linderberg Blue M box furnace.

4.3 Self-pillared pentasil zeolite synthesis. Seed-assisted syntheses were conducted by first adding sodium aluminate to an aqueous solution of sodium hydroxide. Next, LUDOX AS-40 was added to obtain a growth mixture with a molar composition of 3.42 Na_2O :18 SiO_2 :1 Al_2O_3 :324 H_2O with additional 10 wt% seed. The growth mixture was aged at room temperature for approximately 24 hours and then transferred to a 23-mL acid digestion bomb (Parr Instruments). Hydrothermal treatment was carried out in an oven at 150 °C under autogenous pressure. After a specific time interval, the solids extracted from the mother liquor were isolated by three cycles of centrifugation and washing with DI water. The resulting solids were then dried in an oven at 60 °C.

4.4 Materials characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku SmartLab diffractometer with a Cu K α source (40 kV, 40 mA). Field-emission scanning electron microscopy (FE-SEM) analyses were performed with a FEI Helios SEM/FIB working at 2 kV and 4–5 mm working distance. All samples were coated with a thin layer of carbon (layer thickness ≈ 30 nm) prior to imaging to reduce charging. Elemental analysis was performed by electron dispersive X-ray (EDX) spectroscopy. EDX spectra were collected using an Axia-ChemiSEM system at 15 kV and a 10 mm working distance. X-ray photoelectron spectroscopy (XPS) was performed on a PHI 5800 ESCA (Physical Electronics) system, which is equipped with a standard achromatic Al K α X-ray source (1486.6 eV) operating at 300 W (15 kV and 20 mA) and a concentric hemispherical analyzer. Since zeolites are insulating materials, the equipment neutralizer component was utilized to prevent charging effects. Textural analysis was performed with a Micromeritics 3Flex instrument using N_2 as a probe gas for physisorption. Solid-state 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. ^{27}Al MAS NMR spectra were obtained at a spinning frequency of 12.5 kHz, pulse of $\pi/12$, relaxation delay of 0.8 s, and 2 K scans. The ^{27}Al chemical shift was referenced using 1.0 M $\text{Al}(\text{NO}_3)_3$ aqueous solution.

4.5. Catalytic measurements. Methanol-to-hydrocarbon (MTH) reactions were carried out in a 1/4 inch glass 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 hours 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 μL 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:

$$X = \left[1 - \frac{C_{eff}}{C_{feed}} \right] \times 100\% \quad (1)$$

where C_{eff} is the carbon-based molar concentration of both methanol and dimethyl ether (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

$$S_i = \left[\frac{C_i}{C_{t,eff}} \right] \times 100\% \quad (2)$$

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 cumulative 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 coworkers⁵⁹

$$TON(t) = \frac{1}{[H^+]_0} \int_{t_1}^{t_2} F(\tau) d\tau \quad (3)$$

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. Conventional ZSM-5 (C-ZSM-5) was used as a reference for this catalytic study and was prepared according to a previous report.⁵⁰ Characterization details (BET, PXRD, and SEM) are shown in Table 2 and Figure S25.

4.6. Calculation of distances between zeolite structures for seed design. The distance between zeolite frameworks was obtained from a method reported by Schwalbe-Koda and coworkers.²⁷ In that work, each atom of the zeolite structure is represented by the sorted list of its distances to its *k* nearest neighbors. In an unweighted fashion, a structure with *n* atoms is thus represented by a matrix of size (*n*, *k*) and its lattice parameters. This representation was proven to resolve all ambiguities between periodic crystals in the Cambridge Structural Database despite its low computational cost. To compare different frameworks, we obtain the representation of an entire structure by taking the average vector across atoms, resulting in a single vector of length *k* per structure. The distance between two structures is thus defined as the L_∞ norm between two vectors. Structures and densities of zeolites were obtained from the International Zeolite Association structural database. The visualization from Figure 7 was produced by first considering the distance of each point to the origin as the distance of each zeolite structure towards SFV. Then, angles were obtained through an iterative optimization process where pair-

wise, two-dimensional distances on the radial plot should approximate the actual pairwise structural distances between zeolites (defined above). The optimization used the mean squared error between distances as loss function, the L-BFGS-B algorithm implemented in SciPy (v. 1.16.0), and a maximum of 100,000 iterations. Initial angles for zeolites were uniformly spaced in the range between 0 and 2π radians.

4.7. X-ray diffraction data analysis. To quantify the MEL content from PXRD data, a calibration curve was established based on simulated patterns generated using the DIF-FaX software, as shown in Figure S18. The experimentally synthesized pure phase MFI sample exhibited a peak intensity ratio (I_{102}/I_{101}) of 0.077, corresponding to an estimated MEL content of approximately 3.3% according to the calibration curve. Given that a pure MFI phase has mean 0% MEL content, 3.3% value also reflects the inherent quantification error of our method. Accordingly, the error bars shown in Figure 6B represent a uniform uncertainty of +/- 3.3% content for all samples, corresponding to the intrinsic quantification error of the DIFFaX-based calibration method, as determined from its application to the experimentally synthesized pure MFI reference.

ASSOCIATED CONTENT

SUPPORTING INFORMATION

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/jacs.xxxxxxx>.

Additional X-ray diffraction patterns and electron microscopy images, EDX and XPS characterizations, PXRD calibration curve, solid-state ²⁷Al NMR, structural distance of each zeolite to SFV, structural information and characterization of seeds used in this study and a full comparison of common building units across zeolite frameworks (PDF).

Data file containing all raw data for PXRD and nitrogen physisorption analyses of zeolite samples (Excel).

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Notes

JDR is an inventor on a provisional patent focused on the seeded synthesis of zeolite SPP (WO2022177935A1 and CA3208554A1). The authors declare no competing financial interest.

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