INTRODUCTION

The demand for more efficient zeolite catalysts creates a need to develop new synthesis approaches capable of tailoring crystal properties for optimal performance. Among the many physicochemical properties of zeolites, crystal size plays a significant role in mediating internal mass transport, wherein diffusion path lengths of less than 100 nm can markedly improve catalyst lifetime and alter product selectivity. Various approaches have been explored to tune the anisotropic growth of zeolite crystals precisely, including the modification of synthesis conditions, the introduction of growth modifiers, the design of new organic structure-directing agents (OSDAs), and the use of crystalline seeds. Achieving materials with well-controlled properties is often challenging, because the mechanisms of zeolite crystallization are complex and poorly understood. Here, we combine state of the art X-ray powder diffraction (XPD) and solid-state NMR characterization techniques with computer modeling to examine the role of OSDAs in the formation of the mordenite framework type (MOR), which is difficult to prepare with submicrometer dimensions.

Mordenite is a large-pore zeolite (pore diameter ca. 0.7 nm) with unidirectional channels aligned along the c axis that is difficult to prepare with submicrometer dimensions.

Organic structure-directing agents (OSDAs) are exploited in the crystallization of microporous materials to tailor the physicochemical properties of the resulting zeolite for applications ranging from separations to catalysis. The rational design of these OSDAs often entails the identification of molecules with a geometry that is commensurate with the channels and cages of the target zeolite structure. Syntheses tend to employ only a single OSDA, but there are a few examples where two or more organics operate synergistically to yield a desired product. Using a combination of state-of-the-art characterization techniques and molecular modeling, we show that the coupling of \( N,N,N \)-trimethyl-1,1-adamantammonium and 1,2-hexanediol, each yielding distinct zeolites when used alone, results in the cooperative direction of a third structure, HOU-4, with the mordenite framework type (MOR). Rietveld refinement using synchrotron X-ray diffraction data reveals the spatial arrangement of the organics in the HOU-4 crystals, with amines located in the large channels and alcohols oriented in the side pockets lining the one-dimensional pores. These results are in excellent agreement with molecular dynamics calculations, which predict similar spatial distributions of organics with an energetically favorable packing density that agrees with experimental measurements of OSDA loading, as well as with solid-state two-dimensional \( ^{27}\text{Al}^{}\left\{^{29}\text{Si}\right\}, \quad ^{27}\text{Al}^{}\left\{^1\text{H}\right\}, \quad \text{and} \quad ^{13}\text{C}^{}\left\{^1\text{H}\right\} \) NMR correlation spectra, which establish the proximities and interactions of occluded OSDAs. A combination of high-resolution transmission electron microscopy and atomic force microscopy is used to quantify the size of the HOU-4 crystals, which exhibit a platelike morphology, and to index the crystal facets. Our findings reveal that the combined OSDAs work in tandem to produce ultrathin, nonfaulted HOU-4 crystals that exhibit improved catalytic activity for cumene cracking in comparison to mordenite crystals prepared via conventional syntheses. This novel demonstration of cooperativity highlights the potential possibilities for expanding the use of dual structure-directing agents in zeolite synthesis.
(hydro)isomerization,\textsuperscript{19} cracking,\textsuperscript{20} alkylation,\textsuperscript{21} and carbonylation.\textsuperscript{22} Prior studies have attributed the catalytic activity of mordenite to the intersection of 12-ring channels with 8-ring side pockets (Figure S1) that facilitate shape-selective reactions; however, mordenite is highly susceptible to deactivation owing to mass transport limitations imposed by its one-dimensional pores and large channels that facilitate the formation of polyaromatics (i.e., coke precursors). The reported syntheses of mordenite typically yield large crystallites with sizes that range from 5 to 20 \( \mu \text{m} \) and with stacking faults that alter the placement of 8-ring pockets within the channels.\textsuperscript{23,24} Postsynthesis modification to introduce mesoporosity is one way of mitigating internal diffusion limitations.\textsuperscript{25} Alternatively, the synthesis of crystallites with submicrometer dimensions of the [001] facet can extend the catalyst lifetime. Suib and co-workers have reported sizes as small as 40–60 nm using complicated synthesis protocols that include the use of crystalline seeds,\textsuperscript{26} alcohol additives, and/or microwave heating.\textsuperscript{27} Mordenite nanorods (ca. 10 \( \times \) 100 nm) have been synthesized using seeds or cationic gemini surfactants by Xiao\textsuperscript{28} and Ryoo\textsuperscript{29} and their co-workers, respectively. These syntheses have resulted in nanometer-sized domains within larger aggregates, which similarly involve limitations in internal mass transport.

A combination of inorganic and organic structure-directing agents are often used in zeolite syntheses to regulate the kinetics of crystallization.\textsuperscript{30} The synthesis of most zeolites requires the use of OSDA molecules with sizes and shapes that are commensurate with the cages/channels of the target zeolite, thereby facilitating the generation of the desired porous structure. OSDAs are occluded within the framework and are typically removed by postsynthesis calcination. It is common practice to use a single OSDA. In select cases, OSDAs can form clusters (e.g., dimers or aggregates) to stabilize the framework.\textsuperscript{31,32} Few syntheses employ two or more different OSDAs. Examples often involve scenarios where only one organic functions as the OSDA and the other alters properties such as crystal size or habit but is a bystander for structure direction.\textsuperscript{33} Combinations of OSDAs have also been used to prevent polymorphism in order to improve product purity.\textsuperscript{34} Wright and co-workers have demonstrated for zeotypes, such as STA-20, that two organics may be necessary to achieve a desired crystalline phase.\textsuperscript{35} In such cases, the OSDAs act cooperatively to produce a product that could not be achieved with either one alone.

Herein, we demonstrate how two OSDAs (one bearing a quaternary amine group and the other an alcohol) cooperatively direct the formation of mordenite crystals with an ultrathin platelet morphology unlike that obtained with conventional methods. The synthesis condition selected for this study produces two different framework types (MFI- or CHA-type zeolites) when each OSDA is used separately; however, the combination of organics yields mordenite. In order to elucidate the spatial distribution of organics within the channels and side pockets of the mordenite crystals, we used a combination of high-resolution electron microscopy, spectroscopy, and diffraction techniques coupled with molecular modeling to show how the distinct combination of OSDAs works synergistically to direct the mordenite framework structure. A parametric evaluation of synthesis conditions reveals that the judicious selection of OSDAs and growth media and conditions is critical to the formation of mordenite.

Figure 1. OSDA(s), corresponding zeolite structure, and representative scanning electron micrograph for (A) SSZ-13 (CHA) prepared with TMAda\textsuperscript{+} (B) ZSM-5 (MFI) prepared with D61,2 or Na\textsuperscript{+} ions, and (C) HOU-4 (MOR) prepared with TMAda\textsuperscript{+} and D61,2. Scale bars equal 1 \( \mu \text{m} \). (D) X-ray powder diffraction patterns of the solid precipitates obtained after 6 days of hydrothermal treatment at 180 \( ^\circ \text{C} \) (Table S1) confirming the formation of SSZ-13 (blue), ZSM-5 (green), and HOU-4 (red). The structure of HOU-4 was confirmed using a reference pattern for mordenite (black). Reflections corresponding to a quartz impurity in the HOU-4 sample (Figure S6) are labeled with diamonds. The presence of quartz is attributed to excess silica in the reaction mixture. Parametric studies reduced the quantity of quartz but were unable to eliminate the impurity entirely (see the Supporting Information for more details).

Our findings have shown that two OSDAs, \( \text{N,N,N,trimethyl-1,1-adamantanammonium (TMAda}^+ \) \) and 1,2-hexanediol (D61,2), work cooperatively to yield a MOR-type zeolite, referred to hereafter as HOU-4. TMAda\textsuperscript{+} is a well-documented OSDA for commercial SSZ-13 (CHA) (Figure 1A). The same synthesis using only D61,2 results in ZSM-5 (MFI) (Figure 1B), whereas an organic-free synthesis with Na\textsuperscript{+} as an inorganic structure-directing agent also yields ZSM-5 (Figures S2 and S3). Interestingly, the combination of D61,2 and TMAda\textsuperscript{+} in solutions containing Na\textsuperscript{+} produces HOU-4 (Figure 1C and Figure S4). Thus, we observe that individual OSDAs and their binary combination generate three different zeolites (Figure 1D): ZSM-5 is a three-dimensional medium-pore zeolite, SSZ-13 is a three-dimensional small-pore zeolite, and mordenite is a one-dimensional large-pore zeolite. The
composite building units (CBUs)\(^{15}\) of these three structures are different, with the exception of mor being shared by both MFI and MOR framework types (Figure S5). The three zeolites have similar elemental compositions (Table S2) but differ with respect to the crystal habit and quantity of occluded OSDA (Figure S7 and Table S3).

SSZ-13 crystals have a spheroidal morphology with sizes of 1–2 \(\mu\)m and 10 wt % organic (ca. 1.3 TMAda\(^+\) per unit cell). ZSM-5 crystals exhibit an indistinct morphology with submicrometer dimensions and contain 5 wt % organic (ca. 2.7 D61,2 per unit cell). HOU-4 crystallizes as thin platelike particles that retain ca. 2 D61,2 and 2 TMAda\(^+\) molecules per unit cell, as determined from synchrotron XPD data (Figure S8). All of the D6,1,2 molecules are removed by postsynthetic washing with water (Figures S9 and S10), which establishes that D6,1,2 molecules are able to diffuse out of the mordenite nanochannels without appreciable restrictions. The mobility of D6,1,2 within the large pore channels of mordenite was corroborated by molecular dynamics (MD) simulations (Movie S1). Facile extraction of the diol molecules from zeolite frameworks without the need for postsynthesis calcination is uncommon; therefore, the synthesis of HOU-4 offers a unique route to recover and potentially recycle the OSDAs.

Comparison of transmission electron micrographs from multiple batches (Figure 2A,C,D) show that the width of the HOU-4 crystallites in the [010] direction can reach 1 \(\mu\)m with an average length to width (or [001]/[010]) aspect ratio of 4.0 \pm 0.7. Atomic force microscopy (AFM) topographical images of HOU-4 crystals (Figure 2B) reveal an ultrathin habit wherein the analysis of numerous crystals shows a distribution of thicknesses in the [010] direction of around 80 nm (see Figure S11). Selected-area electron diffraction patterns (Figure 2E) were compared against simulated patterns for mordenite along the three principal crystallographic directions (Figure 2F and Figure S12). These comparisons confirm that the basal surface of HOU-4 is the (100) face. High-resolution TEM (HRTEM, Figure 2G) and the corresponding Fourier filtered image (Figure 2H) show that the 1D channels are oriented parallel to the longest dimension of the HOU-4 crystals. The indexing was further corroborated by overlaying the framework structure of mordenite along the [100] direction on the filtered HRTEM image (Figure 2H), revealing an excellent match. Prior crystallographic analyses of synthetic mordenite commonly assign the six-edged surface as the (001) face.\(^{24,36,37}\) Indeed, this general morphology is characteristic of most mordenite crystals prepared in the absence of organics (for example, see Figure 6). Assuming that the indexing of the facets of conventional mordenite crystals is correct, it appears that the cooperativity of OSDAs dramatically alters the HOU-4 crystal habit in ways that are neither predictable nor fully understood.

In order to ascertain the spatial arrangement of OSDAs within the zeolite channels, we analyzed an unwashed HOU-4 sample using synchrotron XPD data (Figure 3A) and confirmed that TMAda\(^+\) resides within the 12-ring channels (Figure 3B,D), Na\(^+\) in the oval 8-ring channels, and D6,1,2 in the 8-ring side pockets (Figure 3C). Rietveld refinement of the framework structure with occluded structure-directing agents indicates that there are two Na\(^+\), two TMAda\(^+\), two D6,1,2, and two water molecules per unit cell. No evidence of crystallite shape anisotropy or stacking faults was apparent in the peakshape profiles or in the structure refinement. HOU-4 appears to be free of the stacking disorder along the c direction that is present in many mordenite syntheses. Quantitative solid-state one-dimensional (1D) single-pulse \(^{13}\)C and \(^1\)H magic-angle-spinning (MAS) NMR analyses (Figure S14) yield a much larger quantity of D6,1,2 (∼10 D6,1,2/TMAda\(^+\)). This suggests that unwashed samples probably retain significant quantities of diol molecules on the particle surfaces, and this is in agreement
with thermogravimetric analysis of unwashed HOU-4 showing 37 wt% mass loss, consistent with the desorption of surface-adsorbed diol molecules (Figure S7C).

To further understand the role of occluded organics in HOU-4, we performed MD simulations of both OSDAs and Na⁺ ions in mordenite. Models placing an increasing amount of alcohol within a single mordenite unit cell at fixed TMAda⁺ loading (Figure 4A) show that alcohols stabilize the structure, leading to a minimum in the energy profile at around 1.5–2.0 D61,2 molecules per unit cell. This indicates that the alcohol is not merely acting as a space filler but has a significant effect on the energetics of crystallization. As the quantity of TMAda⁺ per unit cell is increased, less alcohol is required to minimize the energy (Figure S15). In agreement with XPD data revealing the presence of TMAda⁺ within the large pores of HOU-4, MD simulations show that TMAda⁺ is energetically favored to be within the 12-ring channels (Figure 4B,D) with the amine groups oriented in close proximity to the 8-ring pockets. At high TMAda⁺ loading (two per unit cell), D61,2 molecules are oriented within the 8-ring pockets (Figure 4C), consistent with the XPD refinement. At lower TMAda⁺ loadings, D61,2 molecules are also observed to reside within the 12-ring channels between adjacent TMAda⁺ molecules (Figure S16). Hence, both experiment and simulation suggest that the two OSDAs direct the formation of mordenite in a synergistic fashion by stabilizing different features of the framework: TMAda⁺ directs growth of the 12-ring channels, whereas D61,2 predominantly functions by stabilizing the 8-ring pockets.

The site-specific interactions of different framework 27Al species with OSDA molecules are established by solid-state two-dimensional (2D) heteronuclear correlation (HETCOR) NMR spectra of HOU-4 (Figure 5). The 2D NMR correlation spectra exploit internuclear dipole–dipole (through-space) or J (through-covalent-bond) couplings and are plotted as 2D contour plots, where correlated signal intensities manifest the mutual proximities or covalent connectivities of the corre-
sponding \(^{1}\)H, \(^{13}\)C, \(^{27}\)Al, or \(^{29}\)Si species.\(^{39,40}\) For example, covalent \(^{27}\)Al−O−\(^{29}\)Si bonds within the HOU-4 frameworks are unambiguously established by the 2D \(^{27}\)Al\{\(^{29}\)Si\} \(J\)-mediated NMR correlation spectrum (Figure 5A), which shows a distribution of correlated signal intensity at 54 ppm in the \(^{27}\)Al dimension and −109 to −99 ppm in the \(^{29}\)Si dimension arising from framework aluminum atoms bonded to fully or partially cross-linked \(^{29}\)Si atoms. Previously, such 2D \(^{27}\)Al\{\(^{29}\)Si\} through-bond-mediated correlation spectra of aluminosilicate zeolites have been limited due in part to the low natural isotopic abundance of \(^{29}\)Si (4.7%) and weak \(^{27}\)Al−O−\(^{29}\)Si \(J\) couplings (<20 Hz) but are enabled here by the improved sensitivity of low-temperature measurement conditions. The \(^{27}\)Al signals exhibit Czjzek lineshapes\(^{41}\) that reflect a distribution of \(^{27}\)Al heteroatom environments within the mordenite framework and among the four distinct tetrahedral (T) sites, corroborated by complementary \(^{27}\)Al triple-quantum MAS NMR analyses (Figure S17). The relatively small percentage of partially cross-linked \(^{29}\)Si species (ca. 2%, Figure S18) are probably associated with defect sites at the exterior of the particle surfaces. The Si/Al ratio of HOU-4 estimated by quantitative \(^{29}\)Si MAS NMR is ca. 10 (Figure S18), which is consistent with values of ca. 10 and 13 measured by energy-dispersive X-ray spectroscopy (Table S2) and estimated from synchrotron XPD refinement, respectively.

Different types of framework aluminum sites in as-made HOU-4 are distinguished on the basis of their site-specific interactions with different OSDA molecules, which are established by the 2D \(^{27}\)Al\{\(^{1}\)H\} \(J\)-mediated HETCOR (Figure 5B) and \(^{13}\)C\{\(^{1}\)H\} HETCOR (Figure 5C) NMR spectra. The HETCOR spectra yield correlated \(^{13}\)C−\(^{1}\)H or \(^{27}\)Al−\(^{1}\)H signal intensities from \(^{13}\)C−\(^{1}\)H or \(^{27}\)Al−\(^{1}\)H nuclear spin pairs that are dipole–dipole-coupled through space over subnanometer distances. The different \(^{1}\)H and \(^{13}\)C signals are assigned to \(^{1}\)H and \(^{13}\)C moieties on D6\(_{1,2}\) (green shaded regions) or TMAda\(^{\dagger}\) (red shaded regions) molecules by analyses of complementary solid-state 1D and 2D \(^{13}\)C\{\(^{1}\)H\} NMR spectra (Figures S10 and S14) and solution-state 1D \(^{13}\)C NMR spectra of the zeolite synthesis effluent (Figure S19). The 2D \(^{27}\)Al\{\(^{1}\)H\} HETCOR spectrum (Figure 5B) resolves two \(^{27}\)Al signals: one at 55 ppm,
which is correlated to \(^1H\) signals at 2.2 to 3.6 ppm from TMAda\(^+\) and D\(\text{O}_{1,2}\) \(^1H\) moieties, and one at 53 ppm, which is correlated only to the \(^1H\) signal at 3.6 ppm from D\(\text{O}_{1,2}\) alcohol headgroups coordinated to Na\(^+\) cations.\(^{42}\) These correlated signals evidence two different types of framework \(^{27}\text{Al}\) species with either TMAda\(^+\) or Na\(^+\) cations charge-balancing the associated framework negative charges. As the TMAda\(^+\) molecules are sterically hindered from entering the 8-ring mordenite channels, the framework \(^{27}\text{Al}\) species proximate to TMAda\(^+\) cations are expected to be within the 12-ring channels. Those framework \(^{27}\text{Al}\) species associated with charge-balancing Na\(^+\) cations are likely located within the 8-ring pockets where the Na\(^+\) species are positioned, as determined by the synchrotron XPD analysis (Figure 3) and as corroborated by 2D \(^{23}\text{Na}\{^1H\}\) HETCOR analyses (Figure S20).

Furthermore, the different OSDA molecules are in close mutual proximities within the mordenite channels, as established by the 2D \(^{13}\text{C}\{^1H\}\) HETCOR spectrum of HOU-4 (Figure 5C). This spectrum shows correlated signals at 2.2−3.1 ppm in the \(^1H\) dimension and at \(^{13}\text{C}\) shifts of 15, 24, 28, 34, 67, and 73 ppm (purple shaded regions) that arise from intermolecular interactions of \(^1H\) environments in TMAda\(^+\) molecules and the different \(^{13}\text{C}\) environments in proximate (<1 nm) D\(\text{O}_{1,2}\) molecules. On the basis of complementary 2D \(^{29}\text{Si}\{^1H\}\) HETCOR spectra (Figure S21) and the synchrotron XPD analyses, we conclude that the different OSDA molecules are intimately commingled within the zeolite pores and act cooperatively (as schematically shown in Figure 5D) during the hydrothermal syntheses of HOU-4 to direct the formation of the mordenite framework and the distribution of Al heteroatoms within both the linear 12-ring channels and the 8-ring pockets.

Parametric studies of HOU-4 synthesis reveal a sensitivity to growth mixture composition (Figures S22–S25). The composition selected for this study (solution C1) falls within the range typically reported for organic-free ZSM-5.\(^{43}\) Attempts to prepare HOU-4 in growth mixtures more commonly reported for mordenite (i.e., solution C5 with both OSDAs) at higher aluminum content resulted in much larger crystals. Mordenite is typically synthesized using Na\(^+\) ions as the sole structure-directing agent, which leads to crystals with a large variance in size and shape (Figure 6). Introduction of D\(\text{O}_{1,2}\) and/or TMAda\(^+\) to conventional synthesis mixtures does not markedly reduce the crystal size. Indeed, the growth mixture that generates HOU-4 is adopted from a SSZ-13 synthesis,\(^{44}\) where we have reported D\(\text{O}_{1,2}\) to be an effective modifier of SSZ-13 crystallization at low concentration (i.e., molar ratios less than 1.0 D\(\text{O}_{1,2}\) to 1.0 SiO\(_2\)). Under such conditions, the diol reduces the size of SSZ-13 crystals by 1 order of magnitude; however, increased diol content (i.e., molar ratios in excess of 1.6 D\(\text{O}_{1,2}\) to 1.0 SiO\(_2\)) shifts its role from that of crystal growth modifier to an OSDA that operates synergistically with TMAda\(^+\) to direct the formation of ultrathin mordenite crystals. This reveals that HOU-4 requires a threshold amount of diol and growth mixtures with much higher silicon content than are typically required for conventional mordenite synthesis.

The formation of HOU-4 and its purity are sensitive to the carbon length of the diol. For example, combinations of TMAda\(^+\) with either 1,2-pentanediol (Figure 7A) or 1,2-butandiol (Figure S25) lead to a SSZ-13 impurity, whereas 1,2-propanediol (Figure 7B) results in pure SSZ-13. Diols with carbon lengths in excess of six were not tested owing to their immiscibility in water. The results of diol substitution are consistent with MD simulations of mordenite with TMAda\(^+\) and diols of varying carbon length. At a fixed TMAda\(^+\) content and varying diol quantities, the minimum in the stabilization energy (Figure 7C) for D\(\text{O}_{1,2}\) indicates that the combination of this diol with TMAda\(^+\) is an energetically favorable pairing for
HOU-4 synthesis, consistent with experimental observations. Thus, both experiment and simulation suggest that D61,2 is optimal in size to span the 8-ring pockets and direct their growth.

It is not fully understood how the platelike morphology of HOU-4 crystals is derived from the combined structure-directing influences of TMAda+ and D61,2 molecules. The dual action of organics enhances growth along the direction of channels (c direction) while hindering growth in the a direction. The role of cooperative OSDAs in HOU-4 crystallization is seemingly unrelated to that of a growth modifier which alters the crystal morphology in conventional mordenite synthesis, as neither organic solely produces thin crystals. In fact, the presence of D61,2 has the opposite effect in conventional mordenite syntheses, where it increases crystal thickness in the absence of TMAda+ (Figure S26) relative to the control (Figure 6). The ability to prepare nanosized crystals has significant implications for catalytic applications. Zeolite catalysts with restricted mass transport, such as mordenite and other one-dimensional framework types, are the most susceptible to rapid deactivation by coking. Comparisons between HOU-4 and conventional mordenite crystals reveal that the crystal dimensions along the c direction (parallel to the large-pore channels) are comparable, on the order of a micrometer; however, the generation of ultrathin platelets leads to higher specific surface area, which can influence catalytic performance. To illustrate this point, we prepared acid forms of the platelets (H- Hou-4) and conventional crystals (H-mordenite). For catalytic testing we selected a reaction where shape selectivity was not critical in order to assess differences in catalyst activity. To this end, we used cumene cracking as a model reaction to evaluate time-on-stream lifetime. The total number of acid sites on each sample was quantified by NH3 temperature-programmed desorption (TPD). Tests in a packed-bed reactor at 450 °C reveal that the turnover number (evaluated in the shaded regions of Figure 8) is much larger for H-HOU-4 (38.7 mol cumene/mol H+) in comparison to conventional mordenite (10.3 mol cumene/mol H+) owing to the faster rate of H-mordenite deactivation. These results are qualitatively consistent with studies of nanosized zeolite catalysts in the literature that generally report much longer lifetimes owing to reduced mass transport limitations. For the study reported here, external acid sites probably play a role in the observed differences; however, it remains to be determined if the lack of stacking faults in HOU-4 improves internal mass transport and contributes to its improved lifetime. The different synthesis conditions may also yield distinct distributions of framework Al heteroatoms and associated Brønsted acid sites in H-mordenite and H-HOU-4, which influence the catalytic activity and stability. Rationalizing the differences in catalyst performance is a topic of ongoing investigation.

CONCLUSION

The generation of HOU-4 crystallites using a combination of two organics is one of only a few reported cases where multiple OSDAs work cooperatively to direct zeolite crystallization and structure. Using a collection of high-resolution characterization and modeling techniques, we are able to resolve the locations of both OSDAs in the pores of HOU-4. Combined synchrotron XPD, 2D solid-state NMR, HRTEM, and molecular modeling analyses reveal the framework structure and local compositions, types of framework–organic interactions, and relative distributions of organics within the 12-ring channels and 8-ring pockets of mordenite. The combination of these complementary techniques offers unparalleled insight into the roles of different OSDAs in directing zeolite crystallization to achieve distinct properties. We expect that the methods and analyses reported here can be extended to ascertain how SDAs tailor zeolite crystal size, shape, and composition. Indeed, one challenge in zeolite synthesis is determining how multiple organic and inorganic structure-directing species function in a concerted manner to influence the physicochemical properties of zeolites and control crystal polymorphism a priori. A unique aspect of HOU-4 crystallization is the role of nonionic alcohols, which interact relatively weakly with crystallizing zeolite frameworks and are rarely employed as OSDAs in zeolite syntheses. Here, diol molecules work in tandem with cationic Na+ and TMAda+ species to stabilize the different linear nanopore networks in mordenite.

The synthesis of nonfaulted submicrometer mordenite crystals has been a significant challenge. In this study, we have shown that the ability to prepare mordenite crystals with reduced stacking faults and high surface area improves the catalyst lifetime 4-fold relative to materials prepared by conventional methods. Collectively, our findings suggest that further exploration into the use of cooperative organics in zeolite syntheses holds considerable promise for the engineering and optimization of microporous materials.

EXPERIMENTAL SECTION

Materials. The following chemicals were used as reagents: Cab-O-Sil (M-5, Spectrum Chemical), silica gel (91%, Sigma-Aldrich), sodium hydroxide (98% pellets, MACRON Fine Chemicals), N,N,N-trimethyl-1,1-adamantanammonium hydroxide (TMAda-OH, 25 wt % in water, SACHEM Inc.), 1,2-hexanediol (D61,2, 98%), 1,2-
pentanediol (D$_5$1,2, 96% Aldrich), 1,2-butanediol (D$_4$1,2, 298%, Sigma-Aldrich), 1,2-propanediol (D$_3$1,2, ≥99.5%, Sigma-Aldrich), and aluminum hydroxide (80.3 wt % Al(OH)$_3$, SPI0250 hydrogel). It should be noted that the IUPAC names for the two OSDAs used in this study are hexane-1,2-diol and 1-adamantyl(trimethyl)azanium. Ion exchange was performed using ammonium nitrate (ACS reagent ≥98%, Sigma-Aldrich). Deionized (DI) water used in all experiments was purified with an Agua Solutions RODI-C-12A purification system (18.2 MΩ). All reagents were used as received without further purification.

**Synthesis of Mordenite.** Mordenite (HOU-4) was synthesized with the OSDA N$_3$N-trimethyl-1,1-adamantanammonium hydroxide (TMAda-OH) and 1,2-hexanediol (D$_6$1,2) using solutions with a molar composition of 0.052 Al(OH)$_3$ / 0.1003 g / 0.00061 mol). The solution was stirred until it was clear (ca. 15 min). Hydrogen peroxide (25% w/v) was added to the solution, and this mixture was stirred for another 15 min at room temperature. To this clear solution was added the silica source (0.67 g, 0.0112 mol), and the resulting mixture was first manually stirred with a plastic rod for ca. 15 min, followed by continuous stirring using a stir bar (400 rpm) for 4 h at 80 °C in a mineral oil bath. Approximately 10 g of growth solution after 4 h of heating stirring was placed in a Teflon-lined stainless steel acid digestion bomb (Parr Instruments) and was heated under rotation (~30 rpm) and autogenous pressure in a Thermo-Fisher Precision Premium 3050 Series gravity oven. The nominal time and temperature for HOU-4 synthesis was 6 days at 180 °C. The products of all syntheses were isolated as a white powder (ca. 600 mg) by centrifuging the mother liquor (13000 rpm for 45 min) for three cycles with DI water washes. Samples for microscopy were prepared by first dispersing a small amount of powder (ca. 5 mg) in DI water. An aliquot of this solution was placed on a glass slide and dried overnight. Crystals were transferred to metal sample disks for microscopy studies by contacting the glass slide with carbon tape for SEM.

Conventional mordenite mordenite was synthesized using a growth solution with a molar composition of Al$_2$O$_3$ / 30 SiO$_2$ / 5 Na$_2$O / 780 H$_2$O. Sodium hydroxide (0.25 g, 0.0061 mol) was first dissolved in water (8.437 g, 0.468 mol), followed by the addition of sodium aluminate (0.1003 g, 0.00061 mol). The solution was stirred until it was clear (ca. 15 min), followed by the addition of silica gel (1.212 g, 0.0183 mol), and the resulting mixture was stirred at 400 rpm for 4 h. Approximately 10 g of the growth mixture was placed in a Teflon-lined stainless steel acid digestion bomb and was heated under static and autogenous pressure. The nominal time and temperature for synthesis was 4 days and 170 °C, respectively. The products of all syntheses were isolated from mother liquor using vacuum filtration and a 0.45 μm membrane filter with copious amounts of DI water washes. Samples for microscopy were prepared as described above.

**Solid-State Nuclear Magnetic Resonance (NMR).** Solid-state 1D and 2D H, 13C, 29Si, and 27Al NMR spectroscopy was used to analyze the H, 13C, 29Si, and 27Al environments in as-synthesized HOU-4 crystallites. The 2D 29Si{27Al} J-mediated NMR correlation spectrum (Figure 3A) was acquired on a Bruker ASCEND 400 MHz (9.4 T) DNP NMR spectrometer operating at Larmor frequencies of 400.203, 104.283, and 79.501 MHz for 1H, 27Al, and 29Si nuclei, respectively. This instrument is equipped with a 3.2 mm triple-resonance HXY low-temperature MAS probehead. Low-temperature measurement conditions of 95 K were used for improved signal sensitivity. The spectrum was acquired using a 2D heteronuclear multiple quantum correlation (HMQC) pulse sequence with an experimentally optimized half-echo τ delay of 20 ms used to refocus the weak (ca. 1/4(τ) = 12.5 Hz) through-bond 27Al–O–29Si J couplings. The signal sensitivity was enhanced by applying a 1 ms 27Al adiabatic double-frequency sweep pulse during the preparation period to invert the 27Al satellite transitions. During the rotor-synchronized τ delay periods, 100 kHz of continuous wave 1H decoupling was applied. A recycle delay time of 1 s was used with a rotor-synchronized τ increment step size of 100 μs τ increments, and 256 transients for a total acquisition time of 7 h. The 2D 29Si{1H} and 1H{1H} spectra were acquired on a Bruker AVANCE III UltraShield Plus 800 MHz (18.8 T) wide-bore spectrometer operating at Larmor frequencies of 208.527, 211.681, and 800.242 MHz for 27Al, 23Na, and 1H, respectively. Recycle delay times of 0.75 s were used with τ increment step sizes of 128 μs. The 2D 31P{1H} HETCOR spectrum acquired at a short contact time (0.5 ms, Figure S11) was acquired with 196 transients and 256 transients for a total acquisition time of 10.5 h. The 2D 29Si{1H} HETCOR spectrum acquired at a longer contact time (5 ms, Figure S19) was acquired with 256 τ increments and 64 transients for a total acquisition time of 3.5 h. The 2D 13C{1H} HETCOR spectra acquired with contact times of 5 and 5 ms (Figure S10) were acquired respectively with 250 and 430 τ increments and 512 and 128 transients for total acquisition times of 27 and 11.5 h. The 2D 27Al{1H} (Figure 3C) and 23Na{1H} (Figure S20) HETCOR spectra were acquired on a Bruker AVANCE-III Ultrasil 800 MHz (9.4 T) spectrometer operating at Larmor frequencies of 400.203, 211.681, and 800.242 MHz for 27Al, 23Na, and 1H, respectively. The spectrum was acquired with a repetition time of 1 s, 50 τ increments, and 128 transients for a total acquisition time of 7 h. The 2D 27Al{1H} HETCOR spectrum was acquired with a repetition time of 1 s, 32 τ increments, and 1024 transients for a total acquisition time of 9 h. All of the 2D HETCOR spectra were acquired using homonuclear 1H–1H EDUMBO-121 decoupling during the 1H evolution periods to improve resolution in the 1H dimensions. For the 2D 29Si{1H}, 13C{1H}, 23Na{1H}, and 27Al{1H} HETCOR experiments, a variable-temperature chilling unit was to lower the sample temperature to approximately 263 K to reduce the mobility of the OSDA species and improve cross-polarization signal sensitivity. All of the 1D and 2D spectra were acquired with 100 kHz heteronuclear SPINAL-6411H decoupling during the acquisition period.

**Atomic Force Microscopy (AFM).** AFM measurements were performed using a Nanoscope X3D-3A microscope (Santa Barbara, CA). An aliquot of HOU-4 dispersed in water was placed on a silicon wafer and was allowed to dry at room temperature. The silicon wafer was calcined at 500 °C for 5 h, followed by cleaning under an Ar gas flow to remove loosely bound crystals. AFM images were collected using a C/Au-coated silicon nitride cantilever (Olympus RC800PB with a spring constant of 0.82 N/m) in contact mode at a scan rate of 1.2 Hz and 256 lines/scan.

**X-ray Analysis.** Energy-dispersive X-ray spectroscopy (EDX) was performed using a JEOI JSM 6330F field emission SEM at a working distance of 15 mm and voltage of 15 kV and 12 mA. X-ray powder diffraction (XPD) patterns of as-made zeolite samples were collected on a Siemens D5000 X-ray diffractometer using a Cu Kα source (40 kV, 30 mA). For reference intensity ratio (RIR) analysis using mordenite–quartz mixtures, a Rigaku SmartLab diffractometer (40 kV, 44 mA) was used. The MOR-type framework was confirmed using a reference pattern from the Database of Zeolite Structures. Synchrotron powder diffraction data were collected on an unwashed sample of HOU-4 in a 0.5 mm glass capillary on the Materials Science Beamline at the Swiss Light Source (SLS) in Villigen, Switzerland. The wavelength was determined from a Si standard to be 0.7087 Å. Additional details of XPD analysis are provided in the Supporting Information.
Molecular Dynamics (MD) Simulations. MD simulations were performed with GROMACS 4.6.7. The MOR zeolite framework was modeled as an all-silica structure using the ClayFF potential, whereas the OSDAs (TMAda, 1,2-pentanediol, 1,2-butanediol, 1,2-hexanediol, and 1,2-heptanediol) were described using the generalized AMBER force field. Atomic positions and lattice parameters for the mordenite framework were taken from the Database of Zeolite Structures. Na+ ions were inserted into the 8-ring pockets, in the positions suggested by XRPD analysis (Figure S13). Although Na+ ions stabilize Al in the framework, the positions of the Al sites are not precisely known. Consequently, Al was implicitly modeled by smearing a negative charge over the oxygens in the 8-ring pockets to counterbalance the Na+ ions and ensure electroneutrality. Potential parameters for describing van der Waals interactions between the OSDAs and zeolite framework atoms were evaluated using standard Lorentz–Berthelot combining rules. van der Waals and real-space Coulombic interactions were truncated using a cutoff of 0.9 nm, and the particle mesh Ewald method was used to treat long-range electrostatics, with parameters chosen to ensure a relative error of less than 10^-4 in the calculated energy. The equations of motion were propagated using a leapfrog integration scheme with a 2 fs time step. The temperature and pressure of the system were maintained using a Bussi–Parrinello velocity-rescaling thermostat and a Parrinello–Rahman barostat, respectively. The relaxation time constants for both the thermostat and barostat were set to 2 ps.

Following our recent study of surfactant occlusion in MFI structured zeolites, energetically favorable conformations for the OSDAs in mordenite were sampled using a three-step procedure. First, the OSDAs were gradually inserted into the zeolite framework using the alchemical transformation procedure described by Kim et al., whereby the OSDAs were converted from an ideal gas to fully interacting molecules over the course of a short MD simulation (500 ps) at ambient temperature. This gradual insertion step ensured that the system did not become trapped in unphysical, high-energy conformations. Next, the conjugate gradient algorithm was used to minimize the configurational energy of the system. Finally, the configuration from the energy minimization step was used to initialize a nanosecond-long MD simulation at 300 K and 0 bar. Data from the last half of the MD trajectory were used to evaluate the stabilization energy, where the average energy of the system, is the average energy of the empty zeolite framework, is the number of inserted OSDA molecules, and is the average energy computed for a single OSDA molecule under vacuum. The steps above were repeated to evaluate for ~10^3 different conformations at each OSDA loading considered in the study. Conformations with low values (lowest 10%) were saved for subsequent analysis.

Catalyst Preparation and Testing. Samples for catalysis were calcined in a Thermo Fisher Lindberg Blue furnace under a constant flow of 100 sccm dried air (Matheson Tri-Gas) at 550 °C for 5 h with a temperature ramping/cooling rate of 1 °C/min. These samples were converted to an acid form (Bromsted acids) by ion exchange, wherein the calcined zeolite was immersed with 1.0 M ammonium nitrate solution to obtain a 2 wt% suspension. This mixture was heated to 80 °C for 2 h to allow the exchange of Na+ with NH4+. This process was performed three times with centrifugation/washing between each ion exchange cycle. The final NH4+–zeolite samples were washed three times with DI water before they were calcined once again under the same conditions stated above, thus becoming H-form zeolite.

Cumene cracking over H-form catalysts was carried out in a 1/4 in. stainless steel tube installed in a Thermo Scientific Lindberg Blue M furnace. The catalyst bed was supported between two plugs of quartz wool, and 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 a flow of dry air (6 cm^3/min of O2, 24 cm^3/min of N2). After this pretreatment, the catalyst bed was cooled to the reaction temperature: i.e., 450 °C. Cumene (98%, Sigma-Aldrich) was fed by a syringe pump (Harvard Apparatus) at 2 μL/min into a heated inert gas stream of Ar (50 cm^3/min), which resulted in a reactant flow with a weight hourly space velocity (WHSV) of 2 h⁻¹. The cumene conversion is defined as the percentage of cumene reacted at the effluent of the catalyst bed. 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 co-workers:

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

where is the total number of Brønsted acid sites (obtained from the NH3-TPD data in Table S3), is the molar flow rate of converted carbon (reacted cumene), and is the TOS selected between times and corresponding to 85 and 70% cumene conversion, respectively (i.e., regions of nearly linear deactivation in Figure 8).

Temperature-Programmed Desorption of Ammonia (NH3-TPD). Temperature-programmed desorption of ammonia was performed by the Bhan group (University of Minnesota) on a Micromeritics Autochem II 2920 equipped with a TCD detector. Prior to TPD, ca. 100 mg of catalyst was first outgassed in He for 1 h at 600 °C with a heating ramp of 10 °C min⁻¹. Ammonia was adsorbed at 100 °C until saturation, followed by flushing with He for 120 min at 100 °C. The ammonia desorption was monitored using a TCD detector until an upper temperature of 600 °C was reached with a ramp of 10 °C min⁻¹, using a flow of 25 mL min⁻¹.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b09697.

Additional details of materials characterization, including XRD patterns, SEM and TEM images, TGA profiles, elemental analysis, solid-state NMR, AFM images and height profiles, details of molecular modeling, and examples of alternative synthesis conditions employing variants of OSDAs and the addition of modifiers (PDF) Molecular dynamics simulations (MP4)

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Notes
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C. Synthesis and structural characterization of MWW type zeolite


