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# **Crystallization of Mordenite Platelets using Cooperative Organic Structure-directing Agents**

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ABSTRACT: 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 1-dimensional pores. These results are in excellent agreement with molecular dynamic 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 <sup>27</sup>Al {<sup>29</sup>Si}, <sup>27</sup>Al {<sup>1</sup>H}, and <sup>13</sup>C {<sup>1</sup>H} NMR correlation spectra, which establish the proximities and interactions of occluded OSDAs. A combination of high-resolution transmission electron microscopy and atomic force microscopy are used to quantify the size of the HOU-4 crystals, which exhibit a plate-like morphology, and to index the crystal facets. Our findings reveal that the combined OSDAs work in tandem to produce ultrathin, non-faulted HOU-4 crystals that exhibit improved catalytic activity for cumene cracking compared to mordenite crystals prepared via conventional syntheses. This unique demonstration of cooperativity highlights the potential possibilities for expanding the use of dual structure-directing agents in zeolite synthesis.

## 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 many physicochemical properties of zeolites, crystal size plays a significant role in mediating internal mass transport<sup>1-2</sup> wherein diffusion path lengths of less than 100 nm can markedly improve catalyst lifetime and alter product selectivity.<sup>3</sup> Various approaches have been explored to tune the anisotropic growth of zeolite crystals precisely, including the modification of synthesis conditions, introduction of growth modifiers,<sup>4</sup> design of new organic structure-directing agents (OSDAs),<sup>5-9</sup> and the use of crystalline seeds.<sup>10</sup> Achieving materials with well-controlled properties is often challenging, because the mechanisms of zeolite crystallization<sup>11-14</sup> are complex and poorly understood. Here, we combine state-ofthe-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),<sup>15</sup> which is difficult to prepare with sub-micron dimensions.<sup>16</sup>

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

is used as a commercial catalyst in reactions such as dehydration of alcohols to olefins,<sup>17</sup> oxidation of methane to methanol,<sup>18</sup> (hydro)isomerization,<sup>19</sup> cracking,<sup>20</sup> alkylation,<sup>21</sup> and carbonylation.<sup>22</sup> 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 shapeselective reactions; however, mordenite is highly susceptible to deactivation owing to mass transport limitations imposed by its 1-dimensional pores and large channels that facilitate the formation of polyaromatics (i.e., coke precursors). Reported syntheses of mordenite typically yield large crystallites with sizes that range from 5 to 20 µm and with stacking faults that alter the placement of 8-ring pockets within the channels.<sup>23-24</sup> Post-synthesis modification to introduce mesoporosity is one way of mitigating internal diffusion limitations.<sup>25</sup> Alternatively, the synthesis of crystallites with sub-micron dimensions of the [001] facet can extend catalyst lifetime. Suib and coworkers have reported sizes as small as 40 - 60 nm using complicated synthesis protocols that include the use of crystalline seeds,<sup>26</sup> alcohol additives, and/or microwave heating.27 Mordenite nanorods (ca.  $10 \times 100$  nm) have been synthesized using seeds or cationic gemini surfactants by Xiao<sup>28</sup> and Ryoo<sup>29</sup> and their coworkers, respectively. These syntheses have resulted in

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nanometer-sized domains within larger aggregates, which similarly involve limitations in internal mass transport.

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A combination of inorganic and organic structuredirecting agents are often used in zeolite syntheses to regulate the kinetics of crystallization.<sup>30</sup> 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.<sup>7</sup> OSDAs are occluded within the framework and are typically removed by post-synthesis 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.<sup>31-32</sup> 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.33 Combinations of OSDAs have also been used to prevent polymorphism in order to improve product purity.<sup>34</sup> Wright and coworkers have demonstrated for zeotypes, such as STA-20, that two organics may be necessary to achieve a desired crystalline phase.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 work synergistically to direct the mordenite framework structure. Parametric evaluation of synthesis conditions reveals that the judicious selection of OSDAs and growth media are critical to the formation of mordenite.

#### **RESULTS AND DISCUSSION**

Our findings have shown that two OSDAs, N,N,N-trimethyl-1-1-adamantammonium (TMAda+) and 1,2-hexanediol (D6<sub>1,2</sub>), work cooperatively to yield a MOR-type zeolite, referred to hereafter as HOU-4. TMAda+ is a welldocumented OSDA for commercial SSZ-13 (CHA) (Figure 1A). The same synthesis using only  $D6_{12}$  results in ZSM-5 (MFI) (Figure 1B), whereas an organic-free synthesis with Na<sup>+</sup> as an inorganic structure-directing agent also yields ZSM-5 (Figures S2 and S3). Interestingly, the combination of  $D6_{1,2}$ and TMAda<sup>+</sup> in solutions containing Na<sup>+</sup> produces HOU-4 (Figures 1C and S4). We observe that individual OSDAs and their binary combination generate three different zeolites (Figure 1D): ZSM-5 is a 3-dimensional medium-pore zeolite; SSZ-13 is a 3-dimensional small-pore zeolite; and mordenite is a 1-dimensional large-pore zeolite. The composite building units (CBUs)<sup>15</sup> of these three structures are vastly 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 crystal habit and quantity of occluded OSDA (Figure S7 and Table S3).



Figure 1. The OSDA(s), corresponding zeolite structure, and representative scanning electron micrograph for (A) SSZ-13 (CHA) prepared with TMAda<sup>+</sup>; (B) ZSM-5 (MFI) prepared with  $D6_{1,2}$  or Na<sup>+</sup> ions; and (C) HOU-4 (MOR) prepared with TMAda<sup>+</sup> and  $D6_{1,2}$ . Scale bars equal 1 µm. (D) X-ray powder diffraction patterns of the solid precipitates obtained after 6 days of hydrothermal treatment at 180°C (table S1) confirms 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 labelled 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).

SSZ-13 crystals have a spheroidal morphology with sizes of  $1 - 2 \mu m$  and 10 wt% organic (ca. 1.3 TMAda<sup>+</sup> per unit cell). ZSM-5 crystals exhibit an indistinct morphology with sub-micron dimensions, and contain 5 wt% organic (ca. 2.7 D6<sub>1,2</sub> per unit cell). HOU-4 crystallizes as thin plate-like particles that retain ca. 2  $D6_{1,2}$  and 2 TMAda<sup>+</sup> molecules per unit cell, as determined from synchrotron XPD data (Figure S8). All of the  $D6_{12}$  molecules are removed by post-synthetic washing with water (Figures S9 and S10), which establishes that D6<sub>12</sub> molecules are able to diffuse out of the mordenite nanochannels without appreciable restrictions. The mobility of D6<sub>1,2</sub> 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 post-synthesis 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



**Figure 2.** Indexing the habit of HOU-4 crystals. (A) HAADF STEM image of representative HOU-4 crystals taken in low magnification. (B) AFM amplitude mode image of a crystal in air. Inset: height profile measured along the dashed line. Scale bar equals 500 nm. (C) TEM image of a HOU-4 crystal with the [001] growth direction highlighted (arrow). (D) Indexed HOU-4 crystal with a (100) basal surface. (E) The selected area electron diffraction (SAED) pattern of the region in (C) marked by the dashed white circle. The zone axis is [100]. (F) Simulated SAED pattern from [100] based on the mordenite crystal structure (see Figure S12 for patterns of the [010] and [001] zone axes). (G) High-resolution TEM image of a HOU-4 crystal along the [100] zone axis. The black strips could be regarded as pore channels, with ca. 0.32 nm average width. (H) The HRTEM image in (G) after applying a Fourier filter, overlaid with the crystal structure model of mordenite along the [100] direction. Atoms are color coded as red (oxygen) and yellow (silicon or aluminum).

HOU-4 crystallites in the [010] direction can reach 1 µm 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 [100] direction 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 (Figures 2F and 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 2G), revealing an excellent match. Prior crystallographic analyses of synthetic mordenite commonly assign the 6-edged surface as the (001) face. <sup>24, 36-</sup> <sup>37</sup> 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<sup>+</sup> resides within the 12-ring channels (Figure 3B and D), Na<sup>+</sup> in the oval 8-ring channels, and D6<sub>1,2</sub> in the 8-ring side pockets (Figure 3C). Rietveld refinement of the framework structure with occluded structure-directing agents indicates that there are 2 Na<sup>+</sup>, 2 TMAda<sup>+</sup>, 2 D6<sub>1,2</sub> and 2 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



Figure 3. Rietveld refinement of HOU-4 using synchrotron powder diffraction data. (A) Measured (black), calculated (red) and difference profiles (blue) (table S4). Reflections from a quartz impurity are marked with a green asterisk. (B – D) An arrangement of the non-framework species within the channels of the **MOR** framework compatible with the

refined structure of HOU-4 (see also Figure S13): (B) viewed down the *c*-axis; (C) close-up of the 8-ring side pocket (highlighted in blue in (B)) showing the octahedral coordination of a Na<sup>+</sup> ion to 4 framework oxygen atoms, one water molecule and one D6<sub>1,2</sub> molecule; and (D) orthogonal view of the 12-ring channel (highlighted in pink in (B)) showing the arrangement of TMAda<sup>+</sup> ions along the channel. Atoms are color coded as grey (carbon), red (oxygen), blue (nitrogen), white (hydrogen), green (sodium), and yellow (T-sites occupied by silicon or aluminum).

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many mordenite syntheses. Quantitative solid-state onedimensional (1D) single-pulse <sup>13</sup>C and <sup>1</sup>H magic-anglespinning (MAS) NMR analyses (Figure S14) yield a larger estimated quantity of  $D6_{1,2}$  (6 – 13  $D6_{1,2}$ /TMAda<sup>+</sup>). 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<sup>+</sup> ions in mordenite. Models placing an increasing amount of alcohol within a single mordenite unit cell at fixed TMAda<sup>+</sup> loading (Figure 4A) show that alcohols stabilize the structure, leading to a minimum in the energy profile around 1.5 - 2.0 D6<sub>1,2</sub> molecule per unit cell. This indicates that the alcohol is not merely acting as a space filler,<sup>38</sup> but has a significant impact on the energetics of crystallization. As the quantity of TMAda<sup>+</sup> 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<sup>+</sup> within the large pores of HOU-4, MD simulations show that TMAda<sup>+</sup> is energetically favored to be within the 12-ring channels (Figure



**Figure 4.** Molecular simulations of organic occlusion in HOU-4 channels. (A) MD calculation of the stabilization energy for organics occluded in mordenite as a function of  $D6_{1,2}$  loading using a fixed 1.5 TMAda<sup>+</sup> per unit cell. Solid line is a guide for the eye. (B – D) MD simulation of OSDA molecules aligned within the 12-ring channel: (B) view along the c-direction; (C)  $D6_{1,2}$  aligned within the 8-ring pocket; and (D) TMAda<sup>+</sup> molecules arranged in the 12-ring channel. Images C and D contain 2 Na<sup>+</sup>, 2 TMAda<sup>+</sup>, and 2  $D6_{1,2}$  per unit cell. Atoms are color coded as grey (carbon), red (oxygen), blue (nitrogen), white (hydrogen), green (sodium), and yellow (T-sites occupied by silicon/aluminum).

4B and D) with the amine groups oriented in close proximity to the 8-ring pockets. At high TMAda<sup>+</sup> loading (2 per unit cell),  $D6_{1,2}$  molecules are oriented within the 8-ring pockets (Figure 4C), consistent with the XPD refinement. At lower TMAda<sup>+</sup> loadings,  $D6_{1,2}$  molecules are also observed to reside within the 12-ring channels between adjacent TMAda<sup>+</sup> molecules (Figure S16). Hence, both experiment and simulation suggest that the two OSDAs direct formation of mordenite in a synergistic fashion by stabilizing different features of the framework: TMAda<sup>+</sup> directs growth of the 12-ring channels, whereas  $D6_{1,2}$  predominately functions by stabilizing the 8ring pockets.

The site-specific interactions of different framework <sup>27</sup>Al species with OSDA molecules are established by solid-state HETeronuclear two-dimensional (2D) 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 corresponding 1H, 13C, 27Al, or 29Si species.<sup>39-40</sup> For example, covalent <sup>27</sup>Al-O-<sup>29</sup>Si bonds within the HOU-4 frameworks are unambiguously established by the 2D<sup>27</sup>Al<sup>29</sup>Si<sup>J</sup>-mediated NMR correlation spectrum (Figure 5A), which shows a distribution of correlated signal intensity at 54 ppm in the <sup>27</sup>Al dimension and -109 to -99 ppm in the <sup>29</sup>Si dimension arising from framework aluminum atoms bonded to fully- or partially-crosslinked  $^{29}\rm{Si}$  atoms. Previously, such 2D  $^{27}\rm{Al}\{^{29}\rm{Si}\}$  through-bond-mediated correlation spectra of aluminosilicate zeolites have been limited due in part to the low natural isotopic abundance of <sup>29</sup>Si (4.7%) and weak <sup>27</sup>Al-O-<sup>29</sup>Si J couplings (<20 Hz), but are enabled here by the improved sensitivity of lowtemperature measurement conditions. The <sup>27</sup>Al signals exhibit Czjzek lineshapes<sup>41</sup> that reflect an unbiased distribution of <sup>27</sup>Al heteroatom environments within the mordenite framework and among the four distinct tetrahedral (T) sites, corroborated by complementary <sup>27</sup>Al triple-quantum MAS NMR analyses (Figure S17). The relatively small percentage of partially-crosslinked <sup>29</sup>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 <sup>29</sup>Si MAS NMR is ca. 10 (Figure S18), which is consistent with values of ca. 10 and 13 measured by energydispersive X-ray spectroscopy (table S2) and estimated from synchrotron XPD refinement, respectively.

Different types of framework aluminum sites in HOU-4 are distinguished on the basis of their site-specific interactions with different OSDA molecules, which are established by the 2D  $^{27}$ Al{<sup>1</sup>H} (Figure 5B) and  $^{13}$ C{<sup>1</sup>H} HETCOR (Figure 5C) NMR spectra. The HETCOR spectra yield correlated  $^{13}$ C- or  $^{27}$ Al-<sup>1</sup>H signal intensities from  $^{13}$ C-<sup>1</sup>H or  $^{27}$ Al-<sup>1</sup>H nuclear spin pairs that are dipole-dipole-coupled through space over subnanometer distances. The different <sup>1</sup>H and  $^{13}$ C signals are assigned to <sup>1</sup>H and  $^{13}$ C moieties on D6<sub>1,2</sub> (green shaded regions) or TMAda<sup>+</sup> (red shaded regions) molecules by

analyses of complementary solid-state 1D and 2D <sup>13</sup>C{<sup>1</sup>H} NMR spectra (Figures S10 and S14) and solution state 1D <sup>13</sup>C NMR spectra of the zeolite synthesis effluent (Figure S19). The 2D <sup>27</sup>Al{<sup>1</sup>H} HETCOR spectrum (Figure 5B) resolves two <sup>27</sup>Al signals: one at 55 ppm, which is correlated to  ${}^{1}\text{H}$  signals at 2.2 to 3.6 ppm from TMAda<sup>+</sup> and D6<sub>1,2</sub>  ${}^{1}\text{H}$  moieties, and one at 53 ppm, which is correlated



**Figure 5.** (A) Solid-state 2D <sup>27</sup>Al{<sup>29</sup>Si} *J*-mediated NMR correlation spectrum acquired at 95 K, 9.4 T, and 10 kHz MAS. (B) Solid-state 2D <sup>27</sup>Al{<sup>1</sup>H} HETCOR spectrum acquired at 263 K, 18.8 T, 12.5 kHz MAS, and a <sup>27</sup>Al{<sup>1</sup>H} contact time of 0.5 ms. The ‡ symbol indicates a center-frequency artifact (for more details refer to the Supporting Information). (C) Solid-state 2D <sup>13</sup>C {<sup>1</sup>H} HETCOR spectrum acquired at 263 K, 11.7 T, 12.5 kHz MAS and with a <sup>13</sup>C {<sup>1</sup>H} contact time of 5 ms. All of the <sup>13</sup>C signals are assigned to <sup>13</sup>C molecules on the TMAda<sup>+</sup> and D6<sub>1,2</sub> molecules, as indicated in the inset molecular structures. 1D <sup>27</sup>Al, <sup>13</sup>C {<sup>1</sup>H}, or <sup>1</sup>H MAS NMR spectra acquired under the same conditions are shown along the corresponding <sup>27</sup>Al, <sup>13</sup>C, or <sup>1</sup>H axes for comparison with the 1D projections of the 2D spectra. (D) Idealized depiction of framework-OSDA and intermolecular interactions established by 2D NMR analyses. Green and red arrows indicate framework <sup>27</sup>Al interactions with D6<sub>1,2</sub> and TMAda<sup>+</sup> molecules, respectively; purple arrows indicate intermolecular interactions of commingled OSDA molecules.

only to the <sup>1</sup>H signal at 3.6 ppm from D6<sub>1,2</sub> alcohol headgroups coordinated to Na<sup>+</sup> cations.<sup>42</sup> These correlated signals evidence two different types of framework <sup>27</sup>Al species with either TMAda<sup>+</sup> or Na<sup>+</sup> cations charge-balancing the associated framework negative charges. As the TMAda<sup>+</sup> molecules are sterically hindered from entering the 8-ring mordenite channels, the framework <sup>27</sup>Al species proximate to TMAda<sup>+</sup> cations must be within the 12-ring channels. Those framework <sup>27</sup>Al species associated with charge-balancing Na<sup>+</sup> cations are likely located within the 8-ring pockets where the Na<sup>+</sup> species are positioned as determined by the synchrotron XPD analysis (Figure 3) and as corroborated by 2D 23Na<sup>{1</sup>H} HETCOR analyses (Figure S20). Furthermore, the different OSDA molecules are in close mutual proximities within the mordenite channels, as established by the 2D  ${}^{13}C{}^{1}H$ HETCOR spectrum of HOU-4 (Figure 5C). This spectrum shows correlated signals at 2.2-3.1 ppm in the <sup>1</sup>H dimension

and at <sup>13</sup>C shifts of 15, 24, 26, 34, 67, and 73 ppm (purple shaded regions) that arise from intermolecular interactions of <sup>1</sup>H environments in TMAda<sup>+</sup> molecules and the different <sup>13</sup>C environments in proximate (<1 nm) D6<sub>1,2</sub> molecules. Based on complementary 2D <sup>29</sup>Si{<sup>1</sup>H} 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 idealized 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 (Figure S22 – S25). The composition selected for this study (solution C1) falls within the range typically reported for organic-free ZSM-5.<sup>43</sup> 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<sup>+</sup> ions as the sole structure-directing agent, which leads to crystals with a large variance in size and shape (Figure 6). Introduction of D6<sub>1,2</sub> and/or TMAda<sup>+</sup> to conventional synthesis mixtures does not markedly reduce crystal size. Indeed, the growth mixture that generates HOU-4 is adopted from a SSZ-13 synthesis <sup>44</sup> where we have reported D6<sub>1,2</sub> to be an effective modifier of SSZ-13



**Figure 6.** Scanning electron micrograph of a conventional mordenite prepared by an organic-free synthesis using  $Na^+$  as an inorganic structuredirecting agent. The arrow highlights a 6-edged surface that is characteristic of many **MOR**-type crystals reported in literature. This surface is commonly indexed as the (001) face.

crystallization at low concentration (i.e., molar ratios less than 1.0  $D6_{1,2}$ : 1.0  $SiO_2$ ). Under such conditions, the diol reduces the size of SSZ-13 crystals by an order of magnitude; however, increased diol content (i.e., molar ratios in excess of 1.6  $D6_{1,2}$ : 1.0  $SiO_2$ ) shifts its role from that of crystal growth modifier to an OSDA that operates synergistically with TMAda<sup>+</sup> 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 is 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<sup>+</sup> with either 1,2-pentanediol (Figure 7A) or 1,2butanediol (Figure S25) lead to a SSZ-13 impurity, whereas 1,2-propanediol (Figure 7B) results in pure SSZ-13. Experiments 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<sup>+</sup> and diols of varying carbon length. At fixed TMAda<sup>+</sup> content and varying diol quantity, the minimum in the stabilization energy (Figure 7C) for D61,2 indicates the combination of this diol with TMAda<sup>+</sup> 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 8ring pockets and direct their growth.

It is not fully understood how the plate-like morphology of HOU-4 crystals is derived from the combined structuredirecting influences of TMAda<sup>+</sup> and  $D6_{1,2}$  molecules. The dual action of organics enhances growth along the direction of channels (c-direction) while hindering growth in the adirection. The role of cooperative OSDAs in HOU-4 crystallization is seemingly unrelated to that of a growth modifier that alters the crystal morphology in conventional mordenite synthesis, as neither organic produces solely thin crystals. In fact, the presence of  $D6_{1,2}$  has the opposite effect in conventional mordenite syntheses, where it increases crystal thickness in the absence of TMAda<sup>+</sup> (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



**Figure 7.** Scanning electron micrographs of the HOU-4 synthesis using a combination of TMAda<sup>+</sup> with (A) 1,2-pentanediol and (B) 1,2-propanediol. Crystals in (A) contain mixed phases of mordenite and SSZ-13 (isometric crystals) while those in (B) are pure SSZ-13 by XPD. (C) Stabilization energy from MD calculations as a function of *x* alcohols per unit cell (x = 0.5, 1.0, and 2.0) for a fixed loading of 1.5 TMAda<sup>+</sup> per unit cell. We find that D6<sub>1,2</sub> at a loading of 1.0 - 2.0 molecules per unit cell provides the greatest stabilization.

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**Figure 8.** Comparative catalytic performance of H-mordenite crystals (Si/Al = 8 by EDX) from a conventional synthesis and H-HOU-4 crystals (Si/Al = 9.5 by EDX). Cumene cracking was performed in a packed bed reactor at 450°C using a weight hourly space velocity (WHSV) of 2 h<sup>-1</sup>. The shaded regions were used to calculate catalyst turnover number using the density of acid sites as determined by NH<sub>3</sub>-TPD to account for the different number of active (Brønsted acid) sites for each catalyst.

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 dimension along the c-direction (parallel to the large-pore channels) is comparable, on the order of a micron; 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 NH<sub>3</sub> 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<sup>+</sup>) compared to conventional mordenite (10.3 mol cumene/mol H<sup>+</sup>) owing to the faster rate of H-mordenite deactivation. These results are qualitatively consistent with studies of nanosized zeolite catalysts in literature<sup>2, 45</sup> that generally report much longer lifetime 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 would influence the catalytic activity and stability. Rationalizing the differences in catalyst performance is outside the scope of this work, but 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, we are able to resolve the location 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 spatial distribution of organics within 12ring 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 more broadly 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 non-ionic 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<sup>+</sup> and TMAda<sup>+</sup> species to stabilize the different linear nanopore networks in mordenite.

The synthesis of non-faulted sub-micron mordenite crystals has been a significant challenge. The ability to generate materials with greater accessibility to acid sites and reduced internal mass transportations has implications for improving the design of commercial catalysts. Here, we show that the ability to prepare mordenite crystals with reduced stacking faults and high surface area improves catalyst lifetime fourfold relative to materials prepared by conventional methods. Collectively, the findings in this study 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-1-1adamantammonium hydroxide (TMAda-OH, 25 wt % in water, SACHEM Inc.), 1,2-hexanediol (D612, 98%), 1,2pentanediol (D51,2, 96% Aldrich), 1,2-butanediol (D41,2,  $\geq$ 98%,Sigma-Aldrich), 1,2-propanediol (D3<sub>1,2</sub>, ≥99.5%,Sigma-Aldrich), and aluminum hydroxide (80.3 wt % Al(OH)<sub>3</sub>, 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 Aqua Solutions RODI-C-12A purification system (18.2 M $\Omega$ ). All reagents were used as received without further purification.

Synthesis of mordenite. Mordenite (HOU-4) was synthesized with the OSDA N,N,N-trimethyl-1-1- adamantammonium hydroxide (TMAda-OH) and 1,2- hexanediol ( $D6_{1,2}$ ) using solutions with a molar composition of 0.052 Al(OH)<sub>3</sub>:1.0 SiO<sub>2</sub>:0.2 NaOH:44 H<sub>2</sub>O:0.1 TMAda-

OH:1.6 1,2-hexanediol. Sodium hydroxide (0.09 g, 0.0022 mol) was first dissolved in water (8.21 g, 0.4959 mol), followed by the addition of TMAda-OH (0.95 g, 0.0011 mol) and 1,2-hexanediol (2.17 g, 0.018 mol). This solution was stirred until clear (ca. 15 min). Aluminum hydroxide (0.06 g, 0.0005 mol) was added to the solution and left to stir 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 heated stirring was placed in a Teflon-lined stainless steel acid digestion bomb (Parr Instruments) and was heated under rotation ( $\sim$ 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 white powder (ca. 600 mg) by centrifuging the mother liquor (13,000 rpm for 45 min) for three cycles with DI water washes. Samples for microscopy were prepared by first redispersing 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.

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Conventional mordenite was synthesized using a growth solution with a molar composition of 1 Al<sub>2</sub>O<sub>3</sub>: 30 SiO<sub>2</sub>:5 Na<sub>2</sub>O:780 H<sub>2</sub>O.<sup>26, 46</sup> 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 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 0.45 µm membrane filter with copious amount of DI water washes. Samples for microscopy were prepared as described above.

37 Solid-state nuclear magnetic resonance (NMR). Solid-38 state 1D and 2D 1H, 13C, 27Al, and 29Si MAS NMR 39 spectroscopy was used to analyze the <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al, and <sup>29</sup>Si 40 environments in as-made ultrathin HOU-4 crystallites. The 41 2D <sup>27</sup>Al{<sup>29</sup>Si} J-mediated NMR correlation spectrum (Figure 42 3A) was acquired on a Bruker ASCEND 400 MHz (9.4 T) 43 DNP NMR spectrometer operating at Larmor frequencies of 44 400.203, 104.283, and 79.501 MHz for <sup>1</sup>H, <sup>27</sup>Al, and <sup>29</sup>Si nuclei, respectively. This instrument is equipped with a 3.2 45 mm triple-resonance HXY low-temperature MAS probehead. 46 Low-temperature measurement conditions of 95 K were used 47 for improved signal sensitivity. The spectrum was acquired 48 using a 2D Heteronuclear Multiple Quantum Correlation 49 (HMQC) pulse sequence<sup>47-48</sup> with an experimentally-50 optimized half-echo tau delay of 20 ms used to refocus the 51 weak (ca.  $1/(4\tau) = 12.5$  Hz) through-bond <sup>27</sup>Al-O-<sup>29</sup>Si J-52 couplings. The signal sensitivity was enhanced by applying a 53 1 ms <sup>27</sup>Al adiabatic double-frequency sweep pulse during the 54 preparation period to invert the <sup>27</sup>Al satellite transitions <sup>49</sup>. During the rotor-synchronized tau delay periods, 100 kHz of 55 continuous wave <sup>1</sup>H decoupling was applied. A recycle delay 56 time of 1 s was used with a rotor-synchronized  $t_1$  increment 57 step size of 100  $\mu$ s, 96  $t_1$  increments, and 256 transients for a 58

total acquisition time of 7 h. The 2D  $^{29}Si{^1H}$  and  $^{13}C{^1H}$ spectra were acquired on a Bruker AVANCE 500 MHz (11.7 T) wide-bore spectrometer operating at Larmor frequencies of 500.222, 125.789, and 99.369 MHz for <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si, respectively. Recycle delay times of 0.75 s were used with  $t_1$ increment step sizes of 128 µs. The 2D <sup>29</sup>Si{<sup>1</sup>H} HETCOR spectrum acquired at a short contact time (0.5 ms, Figure 3B)was acquired with 196  $t_1$  increments and 256 transients for a total acquisition time of 10.5 h. The 2D <sup>29</sup>Si{<sup>1</sup>H} HETCOR spectrum acquired at a longer contact time (5 ms, Figure S19) was acquired with 256  $t_1$  increments and 64 transients for a total acquisition time of 3.5 h. The 2D <sup>13</sup>C{<sup>1</sup>H} HETCOR spectra acquired with contact times of 0.5 and 5 ms (Figure S10) were acquired respectively with 250 and 430  $t_1$ increments and 512 and 128 transients for total acquisition times of 27 h and 11.5 h. The 2D <sup>27</sup>Al<sup>1</sup>H} (Figure 3C) and <sup>23</sup>Na<sup>{1</sup>H} (Fig. S20) HETCOR spectra were acquired on a Bruker AVANCE-III Ultrashield Plus 800 MHz (18.8 T) narrow-bore spectrometer operating at Larmor frequencies of 208.527, 211.681, and 800.242 MHz for <sup>27</sup>Al, <sup>23</sup>Na, and <sup>1</sup>H, respectively, and a Bruker 3.2 mm broadband doubleresonance HX probehead was used. The 2D <sup>27</sup>Al{<sup>1</sup>H} HETCOR spectrum was acquired with a repetition time of 1 s, 50  $t_1$  increments and 512 transients for a total acquisition time of 7 h. The 2D <sup>23</sup>Na{<sup>1</sup>H} HETCOR spectrum was acquired with a repetition time of 1 s, 32  $t_1$  increments and 1024 transients for a total acquisition time of 9 h. All of the 2D HETCOR spectra were acquired using homonuclear <sup>1</sup>H-<sup>1</sup>H eDUMBO- $\hat{1}_{22}$  decoupling <sup>50</sup> during the <sup>1</sup>H evolution periods to improve resolution in the <sup>1</sup>H dimensions. For the 2D  ${}^{29}Si{}^{1}H$ ,  ${}^{13}C{}^{1}H$ ,  ${}^{23}Na{}^{1}H$ , and  ${}^{27}Al{}^{1}H$  HECTOR experiments, a variable-temperature chiller unit was to cool 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-64 51 1H decoupling during the acquisition period.

Atomic force microscopy (AFM). AFM measurements were performed in air using an Asylum Research MFP-3D-SA instrument (Santa Barbara, CA). An aliquot of HOU-4 dispersed in water was placed on 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 inert Ar gas flow to remove loosely-bound crystals. AFM images were collected using a Cr/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.

**Electron microscopy.** Scanning electron microscopy (SEM) was performed with a FEI 235 dual-beam (focused ion-beam) system operated at 15 kV and a 5 mm working distance. All SEM samples were coated with a thin carbon layer (ca. 20 nm) prior to imaging. Transmission electron microscopy (TEM) was carried out for structural and morphology characterization using a Thermo Fischer (formerly FEI) 200 kV TitanX transmission electron microscope equipped with the windowless SDD Bruker EDS detector with fast processor.

**X-ray analysis.** Energy-dispersive X-ray spectroscopy (EDX) was performed using a JEOL JSM 6330F field emission SEM at 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 K $\alpha_1$  source (40 kV, 30 mA). For reference intensity ratio (RIR) analysis using

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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.<sup>15</sup> 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.<sup>52</sup> The wavelength was determined from a Si standard to be 0.7087Å. Additional details of XPD analysis are provided in the Supporting Information.

dvnamics (MD) simulations. Molecular MD simulations were performed with GROMACS 4.6.7.53 The MOR zeolite framework was modeled as an all silica structure using the ClayFF potential,<sup>54</sup> whereas the OSDAs (TMAda<sup>+</sup>, 1,2-pentanediol, 1,2-butanediol, 1-2-hexanediol, and 1-2heptanediol) were described using the generalized AMBER force field <sup>55</sup>. Atomic positions and lattice parameters for the mordenite framework were taken from the Database of Zeolite Structures. Na<sup>+</sup> ions were inserted into the 8-ring pockets, in the positions suggested by XRPD analysis (Figure S13). Although Na<sup>+</sup> 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<sup>+</sup> 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.<sup>56</sup> Van der Waals and realspace Coulombic interactions were truncated using a cutoff of 0.9 nm, and the particle mesh Ewald method <sup>56</sup> was used to treat long-range electrostatics, with parameters chosen to ensure a relative error of less than 10<sup>-4</sup> in the calculated energy. The equations of motion were propagated using a leapfrog integration scheme with a 2 fs time step.56 The temperature and pressure of the system were maintained using a Bussi-Parrinello velocity-rescaling thermostat57 and a Parrinello-Rahman barostat58, respectively. The relaxation time constants for both the thermostat and barostat were set to 2 ps.

Following our recent study of surfactant occlusion in zeolites,<sup>59</sup> energetically structured favorable MFI 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.,<sup>60</sup> 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 use to initialize a ns-long MD simulation at 300 K and 0 bar. Data from the last half of the MD trajectory were to evaluate the stabilization energy<sup>61-62</sup>  $E_s \equiv \langle U_{sys} \rangle - \langle U_{zeo} \rangle - \sum_i n_i \langle U_{SDA,i} \rangle$ , where  $\langle U_{sys} \rangle$  the average energy of the system,  $\langle U_{zeo} \rangle$  is the average energy of the empty zeolite framework,  $n_i$  is the number of inserted OSDA molecules of type *i*, and  $\langle U_{SDA,i} \rangle$  is the average energy computed for a single OSDA molecule in vacuum. The steps above were repeated to evaluate  $E_s$  for ~103 different conformations at each OSDA loading considered in the study. Conformations with low  $E_s$  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 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 (Brønsted acids) by ion exchange wherein calcined zeolite was mixed 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<sup>+</sup> with NH<sub>4</sub><sup>+</sup>. This process was performed three times with centrifugation/washing between each ion exchange cycle. The final NH<sub>4</sub>-zeolite samples were washed three times with DI water before they were calcined once again with the same conditions stated above, thus becoming H-form zeolite.

Cumene cracking over H-form catalysts was carried out in a <sup>1</sup>/<sub>4</sub> inch 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 flow of dried air (6 cm<sup>3</sup>/min of  $O_2$ , 24 cm<sup>3</sup>/min of  $N_2$ ). After this pretreatment, the catalyst bed was cooled down 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<sup>3</sup>/min), which resulted in a reactant flow with a weight hourly space velocity (WHSV) of 2 h<sup>-1</sup>. The cumene conversion is defined as the percentage of cumene reacted at the effluent of 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 coworkers,63

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

where  $[H^+]_0$  is the total number of Brønsted acid sites (obtained from the NH<sub>3</sub>-TPD data in Table S3),  $F(\tau)$  is the molar flow rate of converted carbon (reacted cumene), and *t* is TOS selected between times  $t_1$  and  $t_2$  corresponding to 85 and 70% cumene conversion (i.e., regions of nearly linear deactivation in Figure 4E).

Temperature-programed desorption of ammonia (NH<sub>3</sub>-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 out gassed in He for 1 h at 600°C with a heating ramp of 10°C min<sup>-1</sup>. Ammonia was adsorbed at 100°C until saturated, 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 with a ramp of 10°C min<sup>-1</sup>, using a flow of 25 mL min<sup>-1</sup>.

## ASSOCIATED CONTENT

## SUPPORTING INFORMATION

Additional details of materials characterization are provided, 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). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

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The authors declare no competing financial interests.

#### Author Contributions

All authors have given approval to the final version of the manuscript.

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# Table of Contents Graphic





Table of Content Graphic, Revised

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