

## On the Role of Small Amines in Zeolite Synthesis

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A crystallization study was undertaken to relate the structure of small amines to the zeolite product obtained. At  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ , certain noncyclic amines (some not previously recognized) were specific for the formation of 10-ring zeolites, e.g., ZSM-22 and ZSM-23. For example, ethylmethylamine and diethylamine yielded highly crystalline ZSM-22, while ethylamine and isopropylamine yielded ZSM-23. Consistent with their larger size, cyclic amines such as piperazine produced the 12-ring pore system, ZSM-12. At lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (40), a different set of zeolites was obtained, as expected, ZSM-35 and MCM-22. Again, a specific relationship was observed between the amine employed and the zeolite obtained. In both  $\text{SiO}_2/\text{Al}_2\text{O}_3$  regimes, several amines played non-structure-specific pore- and pH-stabilizing roles and yielded ZSM-5. With relatively few exceptions, the zeolite products were fully porefilled with amine and low in Na ( $\text{Na}/\text{Al} < 1$ ). Computer simulations confirmed a pore-stabilizing role for both structure-specific and non-structure-specific amines. At the same time, among structure-specific ("structure-directing") amines, they showed that the interaction energy differences between alternative amine–pore combinations were often quite small (0.5–2.0 kcal/mol, for example). Nevertheless, the changes in amine–pore interaction energies for this group of amines consistently tracked the changes in zeolite products observed.

### Introduction

In the crystallization of siliceous zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio  $\geq 10$ ) and porous silicas, strong evidence exists for a structure-directing and, in some cases, "templating" role on the part of quaternary ammonium cations (quaternaries),<sup>1</sup> and much recent synthesis work has been devoted to a variety of increasingly large and often relatively exotic organic cations.<sup>2–6</sup> The result has been a continuing stream of new molecular sieve frameworks, e.g., VPI-8,<sup>7</sup> SSZ-31,<sup>8</sup> ITQ-4/MCM-58/SSZ-42,<sup>9–11</sup> ZSM-57,<sup>12</sup> ITQ-9,<sup>13</sup> UTD-1,<sup>14</sup> and CIT-5<sup>15</sup> and a frequently distinctive relationship between the framework obtained and the structure of the organic cation present in the reaction mixture.

The case of amines is very different. Despite the facts that they too have yielded recent new zeolite frameworks, e.g., PSH-3/MCM-22,<sup>16,17</sup> MCM-35,<sup>18</sup> and MCM-49<sup>19</sup> and that they have been studied in considerable detail,<sup>20–23</sup> particularly with respect to their ability to form clathrasils,<sup>5,24</sup> they command much less attention in the literature and their role in the chemistry of zeolite crystallization has never been adequately explained.

Reasons for the relative lack of attention to amines are probably four-fold: (a) quaternaries and other cations are often retained in a zeolite cavity, either due to their large size in relation to an exit pore or to the need to balance the charge associated with framework aluminum; (b) many of the amines used in zeolite crystallization are rather small and should be able to move in and out of a catalytically interesting zeolite pore at various stages in a crystallization process; (c) zeolite synthesis is often conducted at very basic pH ( $\text{pH} \geq 12$ ), where most amines would be largely unprotonated and presumably less powerful than quaternaries in their influence on a crystal-

lization process; (d) some researchers find troublesome the seemingly nonspecific relationship between amine molecular structure and product zeolite. Take, for example, the comment of Davis and Lobo<sup>25</sup> that "at least 22 and 13 different organic molecules can be used to synthesize ZSM-5 and ZSM-48, respectively." (It now appears that the ZSM-5 framework, though exceedingly rare, can occur in nature,<sup>26</sup> in the presumed absence of amine and/or quaternary, i.e., in the absence of any "template.")

Given the importance of amines in many zeolite crystallization processes and the lack of understanding with respect to their role in these processes, the following experiments were undertaken. The focus was on small amines (molecular weight generally  $\leq$  ca. 100), on siliceous zeolites ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  between about 20 and 2000), and on open, 10- and 12-ring pore structures, i.e., structures whose pores are circumscribed by 10 or 12  $\text{SiO}_4$  (and/or  $\text{AlO}_4$ ) tetrahedra, respectively. In every case studied,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, pH, and caustic (NaOH) and amine concentration were important variables. The approach was guided by the early observation<sup>27</sup> that  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio often determines the candidate frameworks in exploratory zeolite crystallization, while the cations present (to include amines, in this case) determine which of the competing frameworks is actually formed. To reduce concern that the details of initial gel formulation might unknowingly determine the product obtained, a solid silica source was chosen for the present experiments, such that silica dissolution and polysilicate (or polyaluminosilicate) equilibration would be requisite parts of every crystallization sequence.

### Experimental Section

The silica source for all crystallizations was Ultrasil VN3SP (Degussa, 92%  $\text{SiO}_2$ , 0.1%  $\text{Al}_2\text{O}_3$ , and 0.4%  $\text{Na}_2\text{O}$ ); the alumina

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source was NaAlO<sub>2</sub> solution (Nalco, 25.5% Al<sub>2</sub>O<sub>3</sub>, 19.5% Na<sub>2</sub>O, 53% H<sub>2</sub>O). Amines were obtained from Aldrich or Fisher Scientific. In a typical preparation, Ultrasil and then amine was added to a stirred solution of NaOH and NaAlO<sub>2</sub>, and crystallizations were conducted for 65 h at 160 °C, with stirring (200 rpm). The unlined autoclaves were cleaned with 10% KOH at 160 °C prior to each experiment, to avoid adventitious seeding. Products were filtered, water washed, and then air-dried 1–2 h at 120 °C.

Unless otherwise indicated, all zeolites discussed and analyzed had a nominal 100% crystallinity, as judged by the absence of an amorphous “halo” in the X-ray diffraction (XRD) pattern, by XRD comparison with appropriate laboratory reference samples, by scanning electron micrographs (SEM's), by ion exchange, and/or by *n*-hexane sorption measurements. Materials which were only partially crystalline have been placed in parentheses in the tables. (These detailed Tables are provided as Supporting Information with this manuscript.)

With most amines, successful crystallization of pure, single-phase zeolite required optimization of time, caustic, and amine level. Thus, most sets of experiments detailed in the Supporting Information tables extend from a low caustic/low amine experiment which produced either amorphous material or only partially crystalline zeolite through a series of successful crystallizations to a high caustic/high amine limit where dense phases such as  $\alpha$ -cristobalite ( $\alpha$ C) or  $\alpha$ -quartz ( $\alpha$ Q) began to appear.

Computer simulation results were obtained using the Sorption Module in MSI's Cerius<sup>2</sup>® software (versions 3.5 and 3.8) and MSI's COMPASS force field.<sup>28</sup> Within the Sorption Module, the Grand Canonical Monte Carlo option was used, to randomly insert, remove, rotate, and translate a rigid, uncharged sorbate within the zeolite pore space and to calculate a Lennard-Jones based van der Waals interaction energy. Electrostatic interactions were not included. Zeolite unit cell (uc) parameters for the studies were taken, where available, from the original references listed in the International Zeolite Association (IZA) tabulation,<sup>29</sup> with the exception of ferrierite (FER/ZSM-35). The original FER structure solution<sup>30</sup> included a symmetry-imposed, but improbable 180° T–O–T (T = Si, Al) bond angle, and uc parameters and atomic coordinates from a recently refined crystal structure were used instead.<sup>31</sup> Values used for frameworks not in the IZA publication were as follows: SSZ-24 (as-synthesized),<sup>32</sup> ZSM-48 (UDUD-*Imma*),<sup>33</sup> and SSZ-31 (polymorph A).<sup>8</sup>

The <sup>13</sup>C CP/MAS NMR spectra were recorded on a Bruker AMX-200 spectrometer. Magic-angle spin rates of 3.5 kHz and variable contact times of 0.1, 0.4, 0.8, 1.0, 1.5, 3.0, 5.0, and 10 ms were used for the relaxation time studies. Solution state <sup>13</sup>C NMR spectra were recorded with composite pulse decoupling on 20% (v/v) solutions of the amines in D<sub>2</sub>O on a Bruker AMX-360 spectrometer. All chemical shifts were referenced to TMS at 0.0 ppm.

## Results and Discussion

**Crystallizations at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 200 with Small, Noncyclic Amines.** For the base-case experiments, a sufficiently high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio was chosen such that aluminum in the reaction mixture or in the resultant zeolite might be considered simply a defect. Specifically, it was desired that all aluminum be in solution and monomeric, even at pH 11,<sup>34</sup> and that the aluminum, if incorporated into a zeolite framework, would represent less than one Al/uc. Thus, the reaction mixtures were relatively dilute, and the amine concentrations were high (generally 1–4 M, with R/SiO<sub>2</sub> ratios  $\geq$  0.3, where R = amine).

**TABLE 1: Products and Product Compositions Observed in the Presence of Noncyclic Small Amines, in Crystallizations at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 200**

amine	zeolite	Al/uc <sup>a</sup>	Na/uc <sup>b</sup>	R/uc
ethylamine (EA)	ZSM-23	0.3	0.2	1.2
isopropylamine (iPA)	ZSM-23	0.3	0.1	0.9
ethylmethylaniline (EMA)	ZSM-22	0.3	0.1	0.9
diethylamine (DEA)	ZSM-22	0.3	0.2	0.9
<i>n</i> -propylamine (nPA)	ZSM-5	1.1	0.9	7.0
ethylenediamine (en)	ZSM-22/-23 <sup>c</sup>	0.3	0.5	1.6
en, at high concentration	ZSM-48	0.5	0.2	2.4

<sup>a</sup> The ZSM-22 and ZSM-23 unit cells both contain 24 SiO<sub>4</sub> (and/or AlO<sub>4</sub>) tetrahedra, that of ZSM-48, 48, and that of ZSM-5, 96. <sup>b</sup> A Na/Al ratio less than 1.0 suggests that some portion of the amine is protonated. <sup>c</sup> A unit cell of 24 T atoms was assumed for “ZSM-22/-23.”

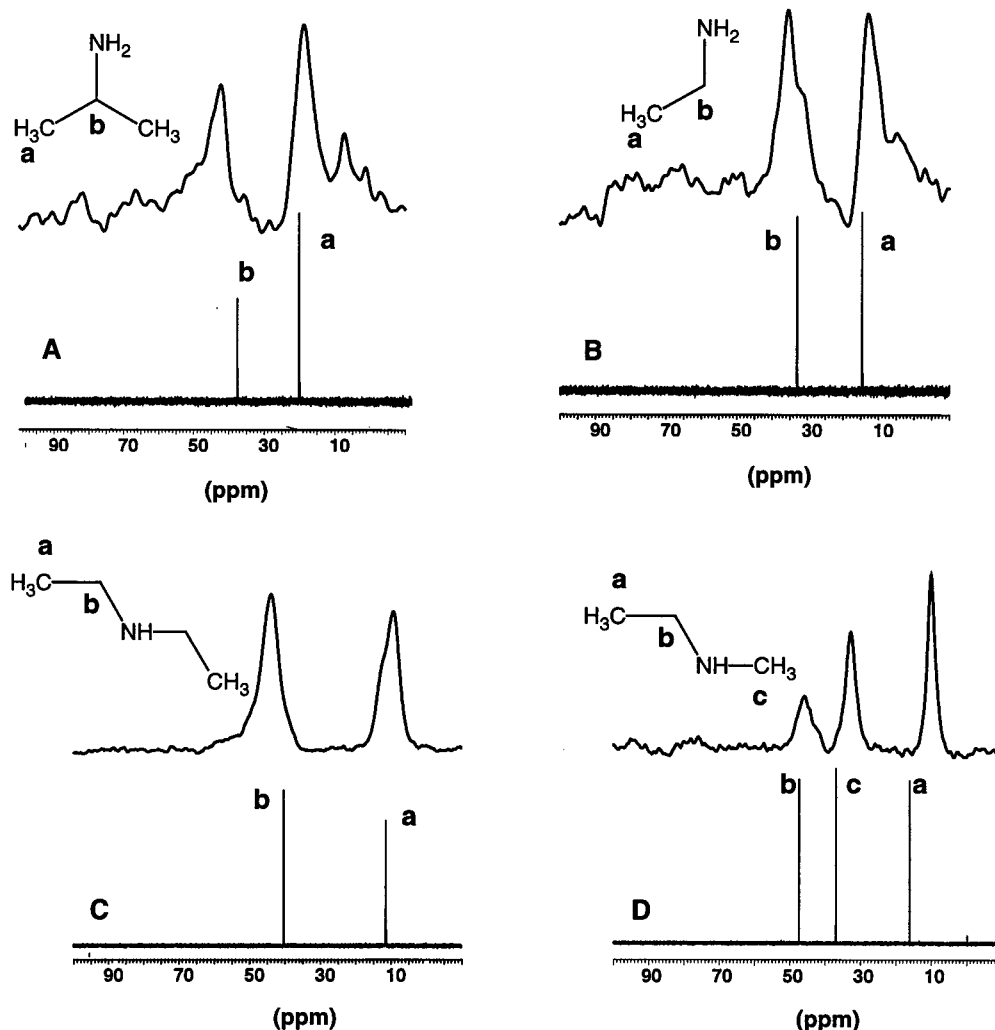
Conditions were also chosen such that the blanks (crystallizations in the absence of amine) yielded neither zeolite nor clathrasil. Accordingly, the base-case range of reaction mixture compositions was as follows: SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 200; R/SiO<sub>2</sub> = 0.3–4.0; H<sub>2</sub>O/SiO<sub>2</sub> = 30; Na<sup>+</sup>/SiO<sub>2</sub> = 0.02–0.2; OH<sup>−</sup>/SiO<sub>2</sub> = 0.002–0.2.

Out of 20–25 noncyclic small amines tested, four showed exceptional ability to produce highly crystalline ZSM-22 or ZSM-23, and one, depending on amine concentration, yielded either ZSM-48 or an intergrowth (or mixture) of ZSM-22 and ZSM-23 (“ZSM-22/-23”), as described in Table 1. Of the others, several yielded ZSM-5, and the example of *n*-propylamine is included in Table 1 for comparison. The bulkiest and most hydrophobic of the small amines, *tert*-butylamine (tBA), yielded clathrasil. Note that, in every case but one, the Na/Al ratio in the product zeolite was substantially less than 1.0. (A detailed tabulation of the analytical results is included in the Supporting Information, Table S-1. Example XRD patterns for the ZSM-22 and ZSM-23 products are similarly available, in Figure S-1 of the Supporting Information.)

While the summary in Table 1 identifies new routes to ZSM-22 and ZSM-23, most important is the observation that, when three different C<sub>3</sub> amines were used in a crystallization mixture under otherwise identical conditions, three different zeolites were formed. iPA yielded ZSM-23, EMA yielded ZSM-22, and nPA yielded ZSM-5. That ZSM-23 (aka. KZ-1) can be formed with iPA has been reported previously,<sup>21</sup> but its synthesis with EA appears to be new. Similarly, DEA is known<sup>21</sup> to yield ZSM-22 (aka KZ-2, Theta-1, and NU-10)<sup>35</sup> under certain conditions, but the use of EMA in synthesizing ZSM-22 is believed to be novel. The ability of nPA to yield ZSM-5 is of course long known.<sup>36</sup> (The special case of en in ZSM-22/-23 and ZSM-48 synthesis will be discussed below.)

The reason that three different zeolite products were obtained with the three different C<sub>3</sub> amines is believed to be the shape of the amine molecule and not the fact that one of the three is a secondary as opposed to a primary amine or that the three amines have slightly different basicities. As detailed in Table S-1 of the Supporting Information, each of the three zeolites was obtained over a range of caustic and amine concentrations, i.e., pH. Moreover, it is known that ZSM-22 can be prepared with a primary amine such as *n*-butylamine (nBA).<sup>21</sup>

Each of the amines was held tenaciously inside its respective zeolite, as evidenced first by a consideration of boiling points. All zeolites were dried at 120 °C, but EA boils at 17 °C, EMA at 37 °C, iPA at 34 °C, and nPA at 48 °C. The tenacity with which the amines were held was confirmed by <sup>13</sup>C NMR. As shown by the spectra in Figure 1, EA, iPA, EMA, and DEA were all intact and tightly bound within their respective ZSM-



**Figure 1.**  $^{13}\text{C}$  NMR Spectra of iPA ZSM-23 (A), EA ZSM-23 (B), DEA ZSM-22 (C), and EMA ZSM-22 (D). In each case, the solid state spectrum of the synthetic zeolite is on top and the solution NMR spectrum of the amine used in the synthesis is on the bottom.

23 and ZSM-22 pores. Both the differences in chemical shift and in line width between amine inside the zeolite and amine in solution were strong evidence of restricted motion in the pore. If an amine were free to rotate inside a pore, the line width would be narrower and the chemical shift closer to the solution value. (A certain ambiguity should be noted in the chemical shift comparison, since a portion of the amine is protonated.)

Rigidity of the amines inside the zeolite pores was also demonstrated by cross-polarization efficiency. (Cross-polarization transfers magnetization from protons to carbons in a molecule and is dependent on dipolar coupling. Molecular motion attenuates dipolar interactions, making cross-polarization times longer for mobile species; that is, the more rigid a molecule, the stronger the dipolar coupling, the more efficient the cross-polarization process, and the shorter the requisite cross-polarization time.) Cross-polarization times for carbons in the rigidly held amines in iPA ZSM-23, EA ZSM-23, EMA ZSM-22, and DEA ZSM-22 ranged from 250 to 900  $\mu\text{s}$ , as compared with 1400 to 2500  $\mu\text{s}$  for a sample of EMA ZSM-5, where a relatively large "cavity" exists in the framework and where the amine presumably has more freedom to rotate. No such cavity exists in the ZSM-22 and ZSM-23 pore systems. (The synthesis of ZSM-5 in the presence of EMA was achieved by increasing the amount of Al in the reaction mixture. This EMA ZSM-5 sample had a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 72.)

Similarly, NMR relaxation times indicated molecular rigidity. More rigid species relax more efficiently, i.e., more quickly. In

the EMA and DEA ZSM-22 and the EA and iPA ZSM-23 samples, relaxation times for the amines were in the 2–4 ms range, as compared with 9–14 ms in the EMA ZSM-5 sample. Although activation energies for the motion of the amines were not determined, the data unambiguously showed that the amines were rigidly held, i.e., that they fit tightly in their respective zeolite pores.

Computer simulation offered possible insight into the role of these amines in the crystallization process, through its potential ability to calculate the relative "goodness-of-fit" for an individual amine inside the pore of its respective zeolite product. Namely, if an amine molecule were to exert an effective structure-directing influence on a nascent zeolite pore, then a favorable interaction energy should exist for that specific amine–pore combination, relative to the energies calculated for other amine–pore combinations.

The first test of computer simulation was its ability to calculate the amount of amine held in the pores of a product zeolite. As shown in Table 2, that test was passed adequately, recognizing that water and sodium ion were also present in the pores of each zeolite, that some portion of the amine was no doubt lost on drying, and that some was presumably protonated (to achieve charge balance on the framework aluminum). (The Sorption Module in MSI's Cerius<sup>2</sup> software does not recognize charge on a sorbate, nor does it energy-minimize sorbate conformations inside a pore.) The "rigid sorbate" aspect of the software led to some arbitrariness in the choice of amine



**TABLE 2: Observed Amine Content vs the Computer-Calculated Maximum Loading for the Zeolites Obtained at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 200**

amine	zeolite	R/uc (observed)	R/uc (calcd) <sup>a</sup>
EA	ZSM-23	1.2	1.9
iPA	ZSM-23	0.9	1.7
EMA	ZSM-22	0.9	1.4
DEA	ZSM-22	0.9	1.3
nPA	ZSM-5	6.9	10.1

<sup>a</sup> Interaction cutoff distance (ICO) = 8.0 Å.**TABLE 3: Interaction Energies Calculated for Fully Loaded Noncyclic Amine–Zeolite Pairs (kcal/mol)<sup>a</sup>**

amine	ZSM23	ZSM-22	ZSM-48	ZSM-12	SSZ-31	SSZ-24
EA	<b>-11.1</b>	-10.8	-10.7	-9.6	-8.5	-8.0
EA-H <sup>+</sup>	<b>-8.7</b>	-8.4	-8.5	-7.5	-6.6	-6.1
iPA	<b>-14.0</b>	-13.0	-13.4	-12.2	-11.0	-10.4
iPA-H <sup>+</sup>	<b>-11.8</b>	-11.0	-11.3	-10.3	-9.2	-8.6
EMA	-13.1	<b>-14.1</b>	-13.5	-12.5	-11.2	-10.6
EMA-H <sup>+</sup>	-11.9	<b>-12.7</b>	-12.2	-11.1	-10.1	-9.4

<sup>a</sup> Effective amine–zeolite combinations, as observed experimentally, are shown in boldface type.

conformation, despite the fact that the molecules simulated were relatively small. Specifically, in Table 2, energy-minimized but extended conformers were chosen for EMA and DEA, while a similarly minimized, but coiled structure was used for nPA.

Initial “goodness-of-fit” calculations for amine and pore were limited to the simplest and smallest of the amines, EA, iPA, and EMA, given the uncertainty associated with conformational issues. They were also limited, initially, to two sets of very similar pore geometries, namely, to zeolites having only nonintersecting, unidimensional pores, but with two basically different pore sizes. Six zeolites were chosen for comparison, ZSM-23, ZSM-22, ZSM-48, ZSM-12, SSZ-31A, and SSZ-24, the first three having unidimensional 10-ring and the last three having unidimensional 12-ring pores. All pore diameters were 5–7 Å, and that dimension dictated the choice of interaction cutoff distance (ICO) used in the calculations. The question was the role of amine, if any, in the formation of a single, nascent pore, and the focus was on the interaction energy associated with that amine molecule and its immediate pore wall. (A neighboring pore presumably did not yet exist.) Thus, a relatively short ICO (8.0 Å) was used in all calculations cited. (The same trends were obtained when the ICO was varied, e.g., to ICO = 15.0 Å, when an alternative force field<sup>37</sup> was chosen, also at varied ICO, and when a single sorbate molecule, rather than a “porefill” complement, was used in the calculation.) The results are shown in Table 3 for both protonated and unprotonated amine.

The EA, iPA, and EMA computer results were clearly not definitive, being quite small, but the trends did agree with observation in multiple respects. First, the synthetically effective amine–zeolite combinations were those showing the most favorable interaction energies, i.e., the “best fit” of amine and pore. Second, that calculated energy differences among the various amine–zeolite combinations were quite small was very consistent with the fact that optimization of time, caustic, and amine concentration was required in order to obtain a pure zeolite. Third, the interaction energies for all three 12-ring structures (ZSM-12, SSZ-31, and SSZ-24) were notably less favorable than for those having 10-ring pores, i.e., these small amines should not (and generally do not) yield 12-ring zeolites. (Implicit in the suggestion that interaction energy differences may be a significant factor in the crystallization of these siliceous

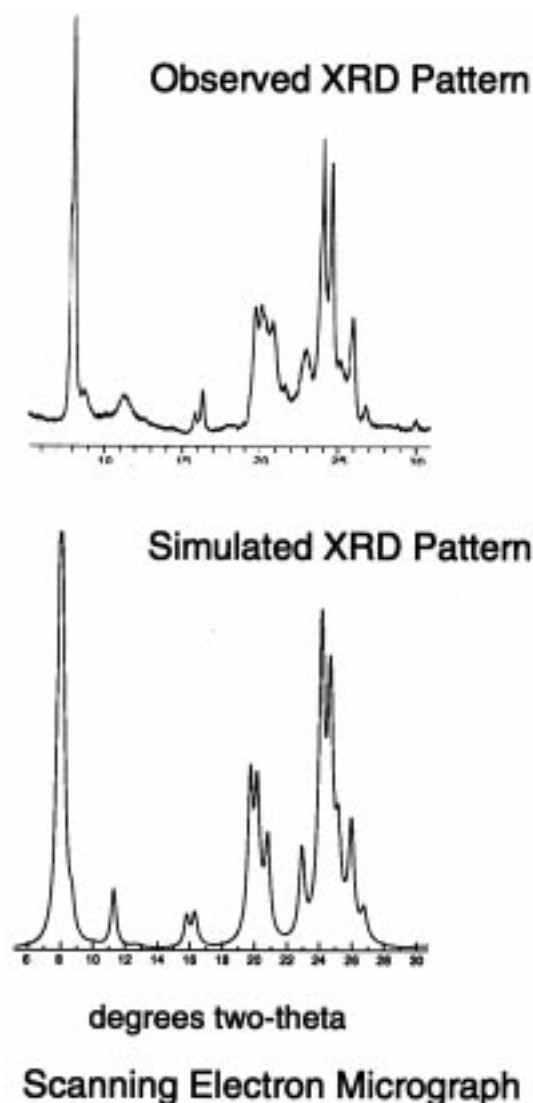
structures is the assumption that the basic frameworks all have very similar energies. Standard molar enthalpies of formation have been measured for several zeolitic silicas, namely, for ZSM-5, ZSM-11, ZSM-12, and SSZ-24, and all were found to be indistinguishable, to within experimental accuracy.<sup>38</sup>)

The behavior of en was more complex. At “low” concentration (en/SiO<sub>2</sub> = 0.3–2.0), it yielded what is believed to be an intergrowth of ZSM-22 and ZSM-23 (designated “ZSM-22/-23”). At higher en/SiO<sub>2</sub> (2.5–4.0), the product was ZSM-48. That ZSM-22 and ZSM-23 should be able to intergrow was reported earlier;<sup>40</sup> that they do so in the presence of en was suggested by the SEM in Figure 2. The SEM showed uniform needlelike crystals, as opposed to a mixture. Also shown in Figure 2, however, is an XRD pattern for the “ZSM-22/-23” product, together with a simulated XRD pattern for a mixture of ZSM-23 and ZSM-22. The two are quite similar. In the experiments, the degree of intergrowth and/or mixing varied with the specific reaction mixture composition and was most evident in the intensity of the XRD peak for ZSM-22 at 20.0–20.5° 2θ. (Although not observed in the present experiments, the synthesis of ZSM-22, i.e., NU-10, with en has been reported by others.<sup>41</sup>) Given the product shift with increasing en concentration, the present experiments suggested that the “preferred” product with en was ZSM-48. As will be seen below, when no aluminum was added to the en-containing reaction mixtures, only ZSM-48 (aka, EU-2<sup>42</sup>) was observed, and no “ZSM-22/-23.”

That ZSM-5, rather than ZSM-22, -23, or -48, should form at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ≥ 100 in the presence of nPA and several other amines was attributed to the larger size of these amines (conformational uncertainty precluded credible computer simulation). That ZSM-5 should form, rather than the dense layer structures noted in the blanks in Tables S-1 and S-2 of the Supporting Information, was attributed to the general, strong affinity of siliceous zeolitic pores for amine (often independent of the specific structure of that amine) and to yet another, quite different role for the amine, namely, a “pH-stabilizing” role. The former is a general, nonspecific pore-stabilizing role for amine in the crystallization of siliceous zeolites. The latter is believed to reflect both the basicity of the amine and the presumed interaction between amine and surface silanol, to free up caustic for participation in the crystallization process. In the absence of amine (in the blanks), caustic was consumed by the solid silica, and the pH dropped, from 13 and above to 12 and below. Crystallization slowed dramatically. In the presence of amine, at the same Na<sup>+</sup>/SiO<sub>2</sub> and OH<sup>-</sup>/SiO<sub>2</sub> ratio, the drop was much less precipitous. It is known that ZSM-5 can be prepared in the absence of any amine,<sup>39</sup> but in these experiments, at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios above 100, pure ZSM-5 was never observed.

The importance of amine size was further highlighted by the shift from ZSM-5 to ZSM-11 as the *n*-alkyl group on a primary amine grew longer, namely, from nPA to *n*-octylamine (nOA).<sup>36</sup> A coiled nOA would be consistent with the larger cavity formed by the intersection of pores in ZSM-11 vs ZSM-5. As shown by the detail in Table S-1 of the Supporting Information, the product ZSM-11 contained 4.5 nOA molecules per uc (vs 4.0 cavities/uc), and it had a Na/Al ratio of 0.2.

**Crystallization with Noncyclic Amines: Sensitivity to Aluminum.** Before addressing larger (cyclic) amines, it was important to note the effects which even a small variation in added aluminum could have on the course of crystallization. First, NaAlO<sub>2</sub> was eliminated from the experiments, such that the reaction mixtures contained only adventitious aluminum (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ≥ 1000); then, the amount of Al was doubled,



**Figure 2.** XRD and SEM characterization of "ZSM-22/-23." The simulated pattern is a nominal 80/20 mixture of ZSM-23 and ZSM-22, respectively.

reducing the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 200 to 100, while still using EA, iPA, EMA, DEA, nPA, and en (details are in Table S-2 of the Supporting Information).

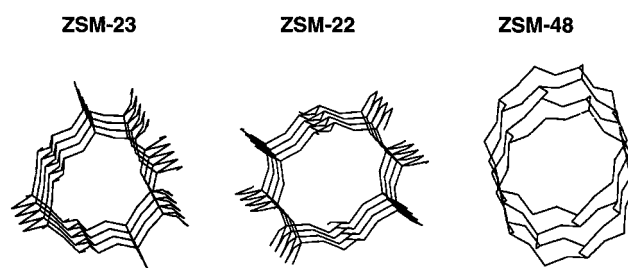
EMA and DEA proved to be very effective in these experiments. Namely, they produced ZSM-22 repeatedly and

**TABLE 4: ZSM-22 and ZSM-48 Product Compositions from Crystallizations Designed to Probe the Minimum and Maximum Zeolitic Aluminum Content with Selected Amines**

amine	zeolite	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Al/uc	Na/uc	R/uc
EMA	ZSM-22	1500 <sup>a</sup>	0.02	0.2	1.8
		100 <sup>b</sup>	0.5	0.1	0.9
DEA	ZSM-22	1500 <sup>a</sup>	0.03	0.3	1.0
		160 <sup>c</sup>	0.3	0.2	0.9
nPA	ZSM-48	1500 <sup>a</sup>	0.05	0.6	2.2
en	ZSM-48	1500 <sup>a</sup>	0.06	0.3	2.1

<sup>a</sup> Crystallization in the presence of only adventitious aluminum.

<sup>b</sup> Crystallization at gel  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 120$ . <sup>c</sup> Crystallization at gel  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ .



**Figure 3.** The distinctly different pore shapes of three 10-ring zeolites.

with varied Al content, as shown in Table 4. By contrast, when the Al level was varied only rather modestly, EA and iPA no longer produced ZSM-23. At  $\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 100$ , for example, EA and iPA commonly yielded ZSM-5. With nPA and en, on the other hand, in the absence of Al, the product was ZSM-48 and not ZSM-5. These product differences, summarized below, are all believed due to the effect of aluminum on the poly-(alumino)silicate structures present in the crystallizing reaction mixture, with the amine playing a more secondary role. Supporting this view was the fact that the 10-ring channel in ZSM-48<sup>33</sup> is circumscribed by a very uniform, interlinked, repetitive net of six-membered rings of  $\text{SiO}_4$  tetrahedra, analogous to but one ring smaller than the nets of six-rings which define the pores of SSZ-24<sup>32</sup> and SSZ-31.<sup>8</sup> The striking uniformity of these nets, contrasted with the pores of ZSM-23 and ZSM-22 in Figure 3, was consistent with the relative ease of ZSM-48 formation at very high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. Aluminum is believed to be the cause of the disorder common to samples of ZSM-48.

Table 4 again shows that, when the samples contained significant Al, the Na content of the products was not sufficient to balance the framework charge, and some portion of the intracrystalline amine (EMA, DEA) was presumably protonated.

**Crystallizations at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  Ratio = 200 with Cyclic Amines.** If EMA, DEA, iPA, and other small amines played a "porefill," structure-directing role in the crystallization of these various 10-ring zeolites, then larger amines might be expected to yield alternative, larger-pore frameworks, namely, 12-ring structures. (Recall, however, that a bulky amine such as tBA favored clathrasil, as opposed to open-pore zeolite formation.)

The formation of a large-pore zeolite, ZSM-12, did indeed occur when a cyclic was substituted for a noncyclic amine, in otherwise identical experiments, as shown in Table 5. As the size of the amine ring was increased from five to six to seven members and as the amine was made more hydrophilic (by using di- rather than monoamines), the product shifted from ZSM-5 and/or clathrasil to ZSM-12, as shown below. Moreover, as the size of the amine increased, e.g., from piperazine (pipz) to homopiperazine (homopipz) and *trans*-1,4-diaminocyclohexane (14DAC6), the amine content of the product ZSM-12 unit cell

**TABLE 5: Products and Product Compositions Observed in the Presence of Cyclic Amines, in Crystallizations at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 200**

cyclic amine	product	Al/uc <sup>a</sup>	Na/uc	R/uc
pyrrolidine (pyrr)	ZSM-39	1.4	0.5	4.5
	ZSM-5	1.0	2.2	9.8
piperidine (pipd)	ZSM-39	1.8	1.9	5.0
hmi	ZSM-12	0.6	0.7	1.5
	MCM-35	0.5	0.2	1.4
pipz	ZSM-12	0.4	0.6	1.9
homopipz	ZSM-12	0.4	0.4	1.3
14DAC6	ZSM-12	0.4	0.7	1.0
4AMpipd	ZSM-12	0.3	0.3	1.3
Dabco	ZSM-12	0.3	1.9	1.8

<sup>a</sup> The ZSM-12 and ZSM-39 unit cells contain 28 and 136 SiO<sub>4</sub> (and/or AlO<sub>4</sub>) tetrahedra, respectively. That of MCM-35 was assumed to contain 28 T atoms, for ease of comparison with ZSM-12.

**TABLE 6: Interaction Energies Calculated for Fully Loaded Cyclic Amine–Zeolite Pairs, for Zeolites Obtained at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 200 (kcal/mol)<sup>a</sup>**

amine	ZSM-23	ZSM-22	ZSM-48	ZSM-12	ZSM-5
pyrr	−14.8	−14.9	<b>−14.8</b>	−13.5	<b>−14.0</b>
pipz	−14.6	−16.4	−16.6	<b>−16.3</b>	−15.6
homopipz	<i>b</i>	−15.6	−16.4	<b>−18.7</b>	−16.8
Dabco	<i>b</i>	<i>b</i>	−15.4	<b>−18.8</b>	−17.7

<sup>a</sup> Effective amine–zeolite combinations are in boldface type. With pyrr, ZSM-5 was produced at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 200; ZSM-48, in the absence of Al. <sup>b</sup> The zeolite did not “sorb” the amine.

declined. The ZSM-12 pore was simply full, as supported by the results with 4-(aminomethyl)piperidine (4AMpipd) and 1,4-diazabicyclo[2.2.2]octane (Dabco). Also obtained under certain conditions with hexamethylenimine (hmi) was MCM-35, a zeolite which reportedly sorbs *n*- and perhaps cyclohexane.<sup>18</sup> Since its structure has not been published, MCM-35 was not included in the computer simulations below and will not be discussed further. (Full synthesis and analytical details are in Supporting Information Table S-3.)

Computer simulation supported the suggestion that increasing the size of the amine might shift the product from 10- to 12-ring zeolite, as shown in Table 6. Although conformational uncertainty again clouded the analysis (but to a lesser extent than with many of the noncyclic amines), interaction energies favored 10-ring zeolites with pyrr, a five-membered ring amine; they showed that ZSM-12 might well compete with ZSM-22 and ZSM-48 when a six-ring amine, e.g., pipz, was used (and that ZSM-23 should no longer be a product); and they showed that ZSM-12 should clearly prevail with seven-ring or bicyclic amines, e.g., homopipz and Dabco, respectively. “Predicted” behavior matched observation quite well. Regarding novelty, the synthesis of ZSM-12 has been reported using hmi<sup>43</sup> and probably using pipz (aka. NU-1344), but most current synthesis approaches favor the use of quaternary ammonium cations.<sup>45,46</sup>

It should be noted, however, that the computer simulations were suggestive, as opposed to definitive. The smallest of the cyclic amines, pyrr, is known to yield ZSM-23 and ZSM-48 under certain conditions and with certain reaction mixture compositions.<sup>23</sup> No similar claim has been found for ZSM-22, nor does there appear to be a successful synthesis as yet of ZSM-22 or ZSM-48 aided by pipz. No explanation is available as yet, but treating an amine molecule as a unreactive sorbate, in the presence of potentially reactive silanol groups, appears to be yet another necessary but unsatisfactory simplification in these modeling studies. (It is noteworthy that, in SiO<sub>2</sub>-only gels, pipz can yield a novel nonzeolitic layered material, EU-19. The

**TABLE 7: Products and Product Compositions Observed in the Presence of Cyclic Amines, in Crystallizations at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 40**

amine	product	Al/uc <sup>a</sup>	Na/uc <sup>a</sup>	R/uc <sup>a</sup>
pyrr	ZSM-35	2.2	0.3	4.5
pipd	ZSM-35	2.2	0.3	4.2
pipz	ZSM-35	2.0	0.9	3.9
hmi	MCM-22	4.1	0.9	9.8
homopipz	MCM-22	3.6	4.2	9.1

<sup>a</sup> The ZSM-35 unit cell contains 36 T atoms; that of MCM-22, 72.

layers contain surface silanols and are bridged by H-bonded pipz molecules.<sup>47</sup>)

**Crystallizations at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio = 40 with Cyclic Amines.** At very high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios, the switch from small (noncyclic) to larger (cyclic) amine brought a marked change in the zeolite produced, from a 10- to a 12-ring pore system, and the change was reflected in the interaction energies calculated for the competing amine–pore combinations. If that change was in fact due to “goodness-of-fit” on the part of the amine, then similar effects should be seen at other SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios, e.g., at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40, where a different set of frameworks compete in the crystallization process. Since ZSM-5 was known to form at these SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios with<sup>25</sup> (and without<sup>39</sup>) a variety of small, “pore- and pH-stabilizing” amines, the focus was on larger, cyclic amines.

At SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40, with these cyclic amines, the zeolite products were ZSM-35, MCM-22, and, in one instance (although never fully pure), ZSM-12. (The designation “MCM-22” was used in these pages to indicate both a member of the MCM-22 family of structures<sup>17,48</sup> and the formal MWW framework.)

The synthesis of ZSM-35 and MCM-22 with these amines was not surprising.<sup>49</sup> Unexpected was the formation of ZSM-12 in the presence of homopipz (see Table S-4 of the Supporting Information), since ZSM-12 usually prefers a much higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. Its formation may have been an artifact of aluminum removal early in the crystallization process by MCM-22 or ZSM-35, with subsequent formation of more siliceous ZSM-12. Interestingly, but not unexpectedly, ZSM-5 was the product in the absence of amine. The composition data in Table 7 showed again that all but one of the zeolites had a Na/Al ratio below 1, presumably indicating protonated amine.

The amine content of the ZSM-35 samples had special significance in that all samples contained essentially four amines per unit cell, a number consistent with the existence of four sites in the FER structure. As highlighted in molecular docking calculations with pipd,<sup>50</sup> the four sites allow for two amine molecules in the 10-ring channels of the zeolite and two in the energetically more favorable cavities which bridge those channels. Thus, all sites in the above as-synthesized ZSM-35 samples were filled with amine. Access to the bridging cavities in ZSM-35 is defined by restrictive eight-ring pores, however, indicating that the amine molecules in these positions must have been present when the cavity was formed. Thermogravimetric analysis (TGA) in flowing He supported that assertion and showed two very different types of pyrr. Two of the four pyrr molecules per unit cell were driven off between 125 and 300 °C; the other two were eliminated between 400 and 500 °C. (Sites for amine molecules in both ZSM-35 and MCM-22 are shown in Figure 4.)

Amine–pore interaction energies calculated for the four competing zeolites observed in these experiments were in perfect agreement with observation. With pyrr, pipd, and pipz, as shown in Table 8, the energies were most favorable for ZSM-35; with hmi and homopipz, MCM-22 and ZSM-12. Note that the



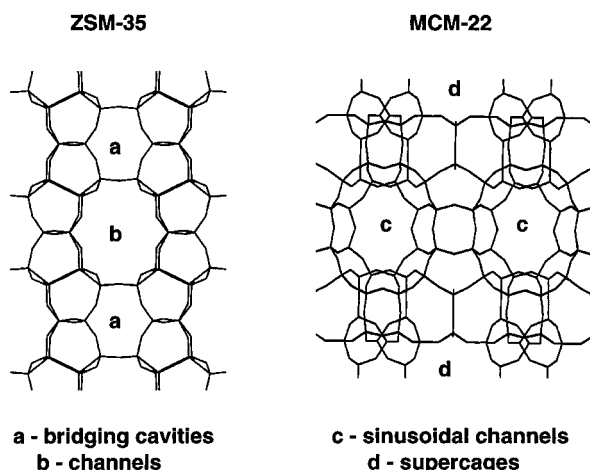


Figure 4. Sites for amine molecules in ZSM-35 and in MCM-22.

TABLE 8: Interaction Energies Calculated for Fully Loaded Cyclic Amine–Zeolite Pairs, for Zeolites Obtained at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  Ratio = 40 (kcal/mol)<sup>a</sup>

amine	ZSM35	MCM-22	ZSM-5	ZSM-12
pyrr	<b>−15.3</b>	−13.5	−14.0	−13.5
pyrr-H <sup>+</sup>	<b>−14.4</b>	−12.6	−12.6	−12.4
pipd	<b>−17.6</b>	−16.6	−14.9	−16.2
pipd-H <sup>+</sup>	<b>−15.9</b>	−15.4	−13.9	−15.1
pipz	<b>−18.1</b>	−16.4	−15.6	−16.3
hmi	−17.5	<b>−18.7<sup>b</sup></b>	−17.4	<b>−18.5<sup>b</sup></b>
hmi-H <sup>+</sup>	−16.0 <sup>c</sup>	<b>−17.7<sup>b</sup></b>	−16.4	<b>−17.3<sup>b</sup></b>
homopipz	−18.4	<b>−18.7<sup>b</sup></b>	−16.8	<b>−18.7<sup>b</sup></b>

<sup>a</sup> Effective amine–zeolite combinations are shown in boldface type.

<sup>b</sup> Product shifts from MCM-22 to ZSM-12 as  $\text{SiO}_2/\text{Al}_2\text{O}_3$  increases.

<sup>c</sup> ZSM-35 accepted hmi-H<sup>+</sup> only into its bridging cavities (2/uc).

interaction energies were those of a fully loaded pore system. With ZSM-35, for example, the energy calculated for pyrr in a bridging cavity was 3–4 kcal/mol more favorable than that for pyrr in the channel. It is tempting to suggest that a pyrr-encapsulating bridging cavity is the initial nucleus in ZSM-35 crystallization. More probably, however, the first recognizable entity in ZSM-35 crystallization is the PRE-FER sheet,<sup>51</sup> and the favorable energetics of the pyrr–cavity combination aid in the bonding together of such sheets to form a three-dimensional ZSM-35 framework. No evidence of a PRE-FER sheet was observed in the products of these experiments.

The pore system of MCM-22 is similarly complex and contains two general locations for hmi molecules. One is the 12-ring supercage; the other is the two-dimensional system of sinusoidal channels.<sup>17</sup> These two pore systems are independent and accessible through 10-ring pores. Computer calculation showed that interaction energies for the two hmi locations in MCM-22 differed by 3–4 kcal/mol, with the sinusoidal system being the more stable. Thus, as in the case of ZSM-35, one might suggest that this energetically favored, two-dimensional layer containing the sinusoidal channel system would be the initial nucleus of MCM-22.

Simulation results for hmi in MCM-22 were even more interesting when amine content and the known propensity of MCM-22 to crystallize in varyingly delaminated (“precursor”) forms<sup>48</sup> were considered. As noted earlier, the present MCM-22 products contained 9 to 10 hmi molecules per unit cell. (The precise, intracrystalline number was uncertain, since hmi boils slightly above the product drying temperature. TGA did not clarify the issue, showing a relatively steady weight loss between about 150 and 500 °C. A modest inflection point at 175 °C

could have indicated loosely bound excess hmi, however, as discussed below.)

Computer simulation showed that MCM-22 should accept only about seven hmi’s per uc, roughly half in the supercage and half in the sinusoidal channel system, with the latter being energetically favored, as noted earlier. The strong binding for hmi in the sinusoidal channel system, with relatively weak siting in the supercages, was very consistent with the partial delamination sometimes observed in MCM-22 “precursor” samples. It was also consistent with evidence for “pockets” (open supercages) on the external surface of MCM-22 crystals.<sup>48</sup> The presence of these “incomplete” surfaces would be consistent with product analyses, which showed the presence of hmi in some excess to what could be accommodated inside the MCM-22 framework. Moreover, such a surface would have a relative abundance of silanol groups, which would bond loosely to hmi molecules.

Protonated as well as unprotonated amines were simulated, in view of the low Na/Al ratios observed in both ZSM-35 and MCM-22 products, and are included in Table 8. As shown, interaction energies for protonated amine perfectly matched the observed crystallization behavior. Particularly noteworthy was the fact that the ZSM-35 framework readily accepted hmi-H<sup>+</sup> only in its bridging cavities and not in its channels. Presumably hmi-H<sup>+</sup>, if present in a reaction mixture, could actually impede the crystallization of ZSM-35, by making channel formation difficult. (Recall, however, that conformer choice was an inherent weakness in these computer simulations.)

## Conclusions

Substantial variety exists in the organics reportedly effective for synthesizing the frameworks discussed in this study. Thus, before closing, the crystallization-directing behavior of the present small amines should be placed in context with earlier reports. In addition, the very simple “sorption” approach used in this study to assess the ability of an amine to direct crystallization to one framework, rather than another, should be placed in context with the considerable number of more sophisticated computer “docking” studies. With regard to the former, it will be seen that consistency based on shape and size exists between the behavior of these small amines and that of other organics known to yield the same zeolite frameworks. Concerning the latter, it is believed that the present, simple approach to modeling has highlighted the very small differences in energy which exist between competing nascent pore systems and that it has shown the frequently overriding role which factors such as Al and caustic can play in defining the products obtained.

Regarding unidimensional 10-ring zeolites (ZSM-23, ZSM-22, and ZSM-48), the size and shape of the organic and the Al content of the reaction mixture were critically important. Both sensitivities were consistent with extensive literature, in that all three zeolites are known to form most readily from very siliceous reaction mixtures, e.g.,  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio  $\geq 100$ , and all exist in a  $\text{SiO}_2$ -only form. The size and shape contrast between ZSM-23 and ZSM-22 formation with small amines (branched vs linear, i.e., iPA vs EMA, respectively) finds parallel in more conventional synthesis reports. For example, the “branched” diquatery,  $(\text{CH}_3)_3\text{N}^+-\text{C}_7\text{H}_{14}-\text{N}^+(\text{CH}_3)_3$ , is a known route to ZSM-23,<sup>52–54</sup> while the analogous “unbranched” diamine,  $\text{NH}_2-\text{C}_7\text{H}_{14}-\text{NH}_2$ , reportedly yields ZSM-22.<sup>55</sup> Computer calculations showed that the interaction energy for a combination of the ZSM-23 pore and tetramethylammonium ion ( $\text{TMA}^+$ ), a conformationally ideal model for the above

diquaternary, was much more favorable than that for TMA<sup>+</sup> and ZSM-22. A favorable interaction energy was also calculated for ZSM-48, in keeping with its known ability to form in the presence of TMA<sup>+</sup>.<sup>33</sup>

Similarly, sensitivity to Al in the reaction mixture is a known characteristic of these zeolites. For example, ZSM-22 (aka NU-10) was the reported product with NH<sub>2</sub>-C<sub>6</sub>H<sub>12</sub>-NH<sub>2</sub> at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 170, while ZSM-48 was produced, under apparently the same reaction conditions, when no Al was present.<sup>41</sup> (The above-mentioned synthesis of ZSM-48 in the presence of TMA<sup>+</sup> was also in the absence of Al.<sup>33</sup>)

The case of very siliceous 12-ring zeolites, i.e., ZSM-12, SSZ-24, SSZ-31, VPI-8, and beta, deserves special comment, in that only ZSM-12 was observed in these high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> experiments. A comparison of interaction energies for these pore systems with one of the cyclic amines, Dabco, provided a possible explanation, namely, that porefilled ZSM-12 was the most energetically favored. (Dabco was chosen because it was the least susceptible of the cyclic amines to conformational ambiguity.) With Dabco, calculated energies for the above pore systems were -18.8 for ZSM-12, vs -17.4 to -18.3 kcal/mol for the others. Thus, even the largest of these cyclic amines should not (and, in these experiments, did not) generate a structure such as SSZ-24, and Dabco and similarly sized cyclic amines would certainly not be favored to yield an even larger 14-ring pore system such as CIT-5 or UTD-1 (calculated energies of 16.4 and 13.5 kcal/mol, respectively).

The present approach, calculating a Lennard-Jones "goodness-of-fit" for specific amine-pore combinations, was an attempt to distinguish quantitatively between the various roles a small molecule might play in zeolite crystallization, e.g., a structure-directing role, a general and nonspecific pore-stabilizing role, and a pH-stabilizing role. With the exception of energy minimization of the "sorbed" amine molecule, the present calculations were very similar to those reported by others for species such as TMA, tetraethyl- (TEA), tetrapropyl- (TPA), and tetrabutylammonium ions in ZSM-5, ZSM-11, and beta.<sup>56-59</sup> Those calculations<sup>56</sup> also ignored charge and correctly indicated that TEA ion "should" yield beta, while TBA ion "should" yield ZSM-11, as in fact both were known to do. Single-ion "docking" was not as successful for TPA in ZSM-5, but the issue was resolved by multi-ion simulations.<sup>57-59</sup> Importantly, the goal of those ongoing simulation efforts is much more ambitious than that of the present study. Those efforts seek to develop a truly predictive capability for "templating" in zeolite synthesis. That they may succeed was suggested by the recent use of molecular modeling to design a template to induce the formation of zeolite ZSM-18.<sup>60</sup> The present effort sought simply to explain the observed shift from one zeolite to another, within a relatively limited set of known competitor frameworks, when one amine was replaced by another.

## Summary

A broad, systematic crystallization program was undertaken using small amines in an effort to identify the correlation, if any, between amine structure and zeolite obtained. Both at very high and at more modest SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (200 and 40, respectively), it was found that the zeolite products were, with very few exceptions, fully porefilled with amine and low in Na (Na/Al < 1).

At very high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, several noncyclic amines (some not previously recognized) were specific for the formation of 10-ring zeolites, e.g., ZSM-22 and ZSM-23. EMA and DEA yielded highly crystalline ZSM-22, while EA and iPA yielded

ZSM-23. In keeping with their larger size, cyclic amines (pipz, homopipz, etc.) yielded a larger pore, 12-ring zeolite, ZSM-12.

At SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40, a different set of zeolites was obtained, ZSM-35 and MCM-22. Again, a specific relationship was observed between amine employed and zeolite obtained. In both SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> regimes, several amines played nonspecific but nonetheless important pore- and pH-stabilizing roles and yielded ZSM-5. Notably, ZSM-5 was the product even in the absence of amine at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 40.

Computer simulations confirmed a pore-stabilizing role for the amines. At the same time, they showed that the energy differences between alternative amine-pore combinations were often quite small. Nevertheless, changes in amine-pore interaction energies consistently tracked the changes in zeolite products observed. While the present computer modeling effort sought simply to explain observed behavior, it is believed that the approach can usefully rank-order candidate "templates" in an exploratory program to synthesize hypothetical new zeolite frameworks.

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**Supporting Information Available:** XRD patterns for iPA ZSM-23 and EMA ZSM-22 and detailed crystallization and product analysis results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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