

On the Role of Small Amines in Zeolite Synthesis. 2

L. Deane Rollmann,^{*,†} John L. Schlenker,[†] Carrie L. Kennedy,[†] Gordon J. Kennedy,[†] and Douglas J. Doren[‡]

Mobil Technology Company, Strategic Research Center, P.O. Box 480, Paulsboro, New Jersey 08066, and University of Delaware, Department of Chemistry and Biochemistry, Newark, Delaware 19716

Received: October 5, 1999

A systematic study explored the ability of small amines to control the zeolites obtained at the high-pH levels typical of crystallizations at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 20 and 40. Experiments in the absence of amine showed that mordenite (MOR) was the preferred product at the lowest ratio, and ZSM-5 was the preferred product at the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. However, the addition of C_2 -, C_3 -, and C_4 -alkylamines changed the product dramatically. On addition of ethylamine, ZSM-5 was produced at the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and ZSM-35 was the preferred product with C_3 - and C_4 -amines. On addition of the largest of the group, *tert*-butylamine, the product reverted to MOR. With polyamines such as diethylenetriamine and triethylenetetramine, ZSM-5 samples were produced having framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios below 20. The hexane cracking activity of these samples was consistent with their exceptionally high Al content. The cyclic C_4 - to C_6 -amines, at both $\text{SiO}_2/\text{Al}_2\text{O}_3$ extremes, yielded ZSM-35 and MCM-22. Again, with the largest of this amine group, 1,4-diazabicyclo[2.2.2]octane, the product reverted to mordenite (and ZSM-5). Despite the very high pH of the crystallizations, all of the ZSM-5, ZSM-35, and MCM-22 samples contained charge-balancing protonated amines and were low in Na; that is, they had Na/Al ratios well below unity. The MOR samples were similarly pore-filled with amine, but their Na/Al ratios did not indicate substantial amine protonation, which is consistent with mordenite being the limiting high-pH product in these experiments. Computer simulation was helpful in distinguishing, on the part of amine, between a generally beneficial but structurally nonspecific “pore-fill” role and a structurally specific, “pore-directing” role, the latter leading to preferred crystallization among alternative zeolite frameworks.

Introduction

Complementing earlier reviews,^{1–7} an experimental study of the crystallization of siliceous zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 40–1000) showed the strong but distinctive pore-fill and pore-directing roles of small amines, together with an unclearly defined “pH-stabilizing” role.⁸ The pore-fill and pH-stabilizing roles appeared to be general characteristics largely independent of the detailed molecular size and shape of the amine. The pore-directing role, on the other hand, was very specific to a particular amine (or a closely related group of amines), and computer simulation suggested a correlation between the goodness-of-fit of such an amine inside a nascent pore and the zeolite framework that was produced. Only van der Waals forces were used in the calculations.

At the same time, it was shown that groups of candidate or “competitor” zeolite frameworks differed, depending on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the gel.^{8,9} At gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios above about 100, small amines, such as C_2 - and C_3 -alkylamines, yielded ZSM-5,¹⁰ ZSM-22 (also known as KZ-2, Theta-1),^{11–14} ZSM-23 (also known as KZ-1),⁴ and ZSM-48 (also known as EU-2).¹⁵ The product depended on the choice of amine and the reaction mixture composition. Larger, cyclic amines, such as pyrrolidine (pyrr), piperidine (pipd), hexamethylenimine (hmi), and 1,4-diazabicyclo[2.2.2]octane (dabco) yielded ZSM-5, ZSM-12,¹⁶ and MCM-35,¹⁷ along with, in the case of pipd, a non-open-pore, clathrasil structure, ZSM-39.⁶

At $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$, the commonly encountered competitor frameworks were ZSM-5, ZSM-35,^{18,19} MCM-22/PSH-3,^{20,21} and mordenite (MOR). In the case of the cyclic amines, the product again shifted with the amine, from ZSM-35 with pyrr to MCM-22 with hmi, a shift which was matched by the computer-calculated fit. (The designation “MCM-22” is used in this work to indicate both a member of the MCM-22 family of structures, including precursors and the formal, fully-linked, three-dimensional MCM-22 framework.^{22,23}) With smaller, acyclic amines, at $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 40 and 100, the usual product was ZSM-5, a framework obtained even in the absence of amine.

Decreases in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of a series of zeolite crystallization experiments, that is, increases in the desired amount of aluminum in a framework change not only the competitor frameworks but also the reaction mixture constraints (most notably, the requisite amount of caustic). Increased caustic is required for Al solubility; it is also required because the frameworks of lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ zeolites often contain relatively small, distinctive polyhedra or “secondary building units.”^{24,25} Inherent in the formation of many of these small polyhedra is a relatively low molecular weight on the part of the polysilicates (or aluminopolysilicates) that comprise the crystallizing reaction mixture. That molecular weight is largely controlled by pH, that is, caustic.

One expected consequence of increased caustic might be a decreased role for amines in the crystallization of less-siliceous zeolites, that is, zeolites having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between

[†] Mobil Technology Company.

[‡] University of Delaware.

approximately 15 and 40. At higher pH, little or no protonated amine would be expected in a crystallizing reaction mixture, and the amine might thus be ineffective in any pore-directing role. In addition, the pH-stabilizing role, noted earlier, could be absent in such circumstances (although the possible interaction of amine with compounds like gel-phase silanols cannot be excluded). Thus, the earlier experiments with amines were extended into a new, lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ (and higher pH) regime. To reduce concern that the details of initial gel formulation might unknowingly determine the product obtained, a solid silica source was chosen for the experiments, as had been done previously, 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% SiO_2 , 0.1% Al_2O_3 , and 0.4% Na_2O); the alumina source was NaAlO_2 solution (Nalco, 25.5% Al_2O_3 , 19.5% Na_2O , 53% H_2O). The amines were obtained from Aldrich and Fisher Scientific. A typical preparation occurs as follows: To a stirred solution of NaOH and NaAlO_2 were added Ultrasil and then amine, 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. The products were filtered, water washed, and then air-dried for 1–2 h at 120 °C.

Unless otherwise indicated, all of the 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, XRD comparison with appropriate laboratory reference samples, scanning electron micrographs (SEM's), ion exchange, and/or *n*-hexane sorption measurements. Prior to the *n*-hexane cracking activity measurements, all of the samples were converted to the H form, by ion exchange with 2 M NH_4NO_3 and air-calcination at 538 °C. If the samples contained organic material, they were heated for 1 h at 350 °C in N_2 and calcined for 2 h at 538 °C in air, prior to ion exchange. (Detailed Tables describing the crystallizations and the products are provided as Supporting Information.)

With or without the amines, successful crystallization of pure, single-phase zeolite required optimizations of time, caustic, and (where applicable) amine level. Thus, most sets of experiments detailed in the Supporting Information Tables extend from a low caustic/low amine experiment that yielded amorphous material, to a high caustic/high amine limit, at which it was clear that its behavior had been defined. Specifically, the experiments formed three groups, having gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios = 20, 26, and 40. Other mole ratios of reaction ingredients were in the ranges $\text{Na}^+/\text{SiO}_2 = 0.1\text{--}0.3$, $\text{amine}/\text{SiO}_2 = 0.5\text{--}4.0$ (when amine was present), $\text{OH}^-/\text{SiO}_2 = 0.03\text{--}0.3$, and $\text{H}_2\text{O}/\text{SiO}_2 = 30$.

Computer simulation results were obtained using the Sorption Module in MSI's Cerius² software (Version 3.8) and MSI's COMPASS force field.²⁶ 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. The electrostatic interactions were not included. The zeolite unit cell (uc) parameters for the studies were taken, where available, from the original references listed in the International Zeolite Association (IZA) tabulation,²⁷ with the exception of ferrierite (FER/ZSM-35). The original FER structure solution²⁸ included a symmetry-imposed, but improb-

TABLE 1: Products and Product Compositions Observed in the Absence of Amine

gel $\text{SiO}_2/\text{Al}_2\text{O}_3$	20	26	40
zeolite obtained	MOR	ZSM-5	ZSM-5
product $\text{SiO}_2/\text{Al}_2\text{O}_3$	15	24	33
product Na/Al	1.0	1.0	1.0
product Al/uc^a	5.6	7.4	5.5

^a The MOR unit cell (uc) contains 48 SiO_4 and AlO_4 tetrahedra; the ZSM-5 unit cell contains 96 SiO_4 and AlO_4 tetrahedra.

able, 180° T–O–T (T = Si, Al) bond angle; the uc parameters and atomic coordinates from a recently refined crystal structure were used instead.²⁹

Confirmation that the amines had not been degraded, by either strong caustic or elevated temperature, and that they were intact inside the product zeolites was achieved by ¹³C CP/MAS NMR spectra, recorded on a Bruker AMX-200 spectrometer.

Results and Discussion

Crystallizations without Amine. It was originally assumed that the reference point for distinguishing between pore-fill, pore-directing, and pH-stabilizing roles on the part of an amine (if such effects were to exist in these high-pH crystallizations) would be the blanks, namely, the product or products obtained in the absence of amine. Although ZSM-5 had been obtained readily and reproducibly without amine at $\text{SiO}_2/\text{Al}_2\text{O}_3$ gel ratios of 26 and 40 (see the tables in the Supporting Information), the blanks at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$ showed extreme sensitivity to the caustic level, yielding ZSM-5, ZSM-35, and MOR, the first two most commonly found only partially crystallized or in mixtures. Only MOR was comfortably reproducible at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$, the highest caustic levels examined. Analysis of the pure zeolites obtained in the absence of amine is shown in Table 1.

The most important characteristic to note in the products crystallized in the absence of amine (Table 1) was the invariant 1.0 Na/Al ratio, an indication that all of the aluminum was in the zeolite framework. Also noteworthy was the fact that MOR, and not ZSM-5, was obtained from the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ gels, additional evidence that competitor frameworks in crystallization experiments often change with changing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. (Complementing the change in gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was the fact that increased caustic in a homologous series of crystallization experiments yielded zeolites of decreasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio because of the higher solubility of SiO_2 versus Al_2O_3 .)

Crystallization in the Presence of Small, Acyclic Amines. Upon addition of small amounts of amine, the crystallization behavior changed remarkably. In particular, at the lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, (a) ZSM-5 was formed reproducibly (with ethylamine, EA) from gels having the uncommonly low (for this zeolite) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 20, and (b) ZSM-35 became an easily accessible, reproducible product, generally insensitive to modest changes in gel pH (and OH^-/SiO_2). The results are summarized in Table 2.

For the monoamines, not only were certain aspects of their products remarkable, but also their form inside the pores of those products was remarkable. Despite the fact that both initial and final pH values for the reaction mixtures were over 13 (vs amine pK_a 's of 10.5–11.0), the amine inside the zeolite was substantially protonated, as evidenced by the consistently low Na/Al ratios (except for MOR) shown in Table 3, at gel $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$. All of the ratios were less than or equal to 0.5.

From the data, two questions arise: What is the role of the amine in “directing” crystallization to ZSM-35, rather than MOR or ZSM-5? What occurs in the special case of low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ZSM-5? The first question was addressed on the basis of

TABLE 2: Products Obtained in the Presence of Acyclic Amines

amine	gel SiO ₂ /Al ₂ O ₃ ratio		
	20	26	40
ethylamine (EA)	ZSM-5	ZSM-5	ZSM-5
<i>n</i> -propylamine (nPA)	ZSM-35	ZSM-5	ZSM-5
<i>i</i> -propylamine (iPA)	ZSM-35	^a	ZSM-5
<i>n</i> -butylamine (nBA)	ZSM-35	ZSM-35	ZSM-5
<i>s</i> -butylamine (sBA)	ZSM-35	ZSM-35	ZSM-5
<i>i</i> -butylamine (iBA)	ZSM-35	ZSM-35	ZSM-35
<i>tert</i> -butylamine (tBA)	MOR	MOR	ZSM-5
ethylenediamine (en)	ZSM-35	ZSM-3, ZSM-5 ^b	ZSM-35, ZSM-5 ^b
diethylenetriamine (dien)	ZSM-5	ZSM-5	ZSM-5
triethylenetetramine (trien)	ZSM-5	ZSM-5	ZSM-5
tris(2-aminoethyl)amine (tren)	ZSM-5	ZSM-5	ZSM-5
dabco	MOR	MOR	ZSM-5

^a Mixtures of ZSM-5, ZSM-35, and, at higher NaOH/SiO₂ ratios, MOR. ^b Either zeolite could be obtained as a single, pure product, depending on the reaction mixture composition.

TABLE 3: Product Compositions Observed with C₂- to C₄-Amines, at a Gel SiO₂/Al₂O₃ Ratio of 20

amine zeolite	SiO ₂ /Al ₂ O ₃	Al/uc ^a	Na/uc ^a	R/uc ^a	Na/Al
EA ZSM-5	19	9.2	3.6	10.5	0.4
nPA ZSM-35	17	3.7	0.8	3.6	0.2
iPA ZSM-35	19	3.5	1.7	2.8	0.5
nBA ZSM-35	18	3.6	1.3	2.9	0.4
sBA ZSM-35	18	3.6	1.1	2.9	0.3
iBA ZSM-35	18	3.6	1.4	2.7	0.4
tBA MOR	18	4.9	4.0	1.4	0.8

^a The ZSM-35 unit cell contains 36 tetrahedra. R = amine.

computer simulation; the second, by a combination of ²⁷Al NMR, XRD analysis, sorptive measurements, and catalytic behavior. The reversion of the product to MOR (the blank) with tBA was attributed to the fact that tBA was the bulkiest of the amines, but this assertion was addressed by computer simulation as well, with interesting results.

Regarding the first question, note that, as the size of the amine was increased from EA to C₃- and C₄-alkylamine (except for tBA), the product shifted from ZSM-5 to ZSM-35. Note also that all ZSM-35 samples contained roughly 3–4 amine molecules per uc. The ZSM-35 framework contains two bridging cavities per uc and a straight channel, capable of holding 1–2 small amines (on the basis of computer simulation). Computer simulation predicted a ZSM-5 capacity of ~12 EAs/uc, versus an observed loading of 10–11, which is in good agreement. The fact that both the ZSM-35 and the ZSM-5 pores were substantially filled with amine was evidence of the general pore-fill ability of amines even at a gel pH above 13. (Recall that all of the samples were dried at 120 °C, and yet the ZSM-5 sample contained roughly 10 EAs/uc; the boiling point for EA is 17 °C.) The fact that ZSM-5 could be reproducibly synthesized with EA at gel SiO₂/Al₂O₃ = 20 may also indicate a pH-stabilizing role for this amine, despite the strong alkalinity of the reaction mixtures.

Computer simulation also suggested an increasingly more favorable fit for amine in ZSM-35, compared with ZSM-5, as the size of the amine was increased from C₂- to C₃- and C₄-alkyl groups. (Only amines with backbones extending no more than two atoms from a terminal or a branch point C- or N-atom were simulated because the configuration of the amine molecule in Cerius² Sorption must be defined by the user. Assigning a

TABLE 4: Interaction Energies Calculated for Fully Loaded Acyclic Amine–Zeolite Pairs (kcal/mol)^a

amine	ZSM-5	ZSM-35	MOR	ZSM-35 – ZSM-5
EA	−10.4	−11.4	−9.6	−1.0
EA-H ⁺	−8.1	−9.3	−6.6	−1.2
iPA	−12.4	−14.6	−10.6	−2.2
iPA-H ⁺	−10.5	−12.3	−9.0	−1.8
sBA	−13.9	−16.8	−13.1	−2.9
sBA-H ⁺	−13.5	−15.2	−11.4	−2.7
iBA	−14.0	−16.5	−13.0	−2.5
iBA-H ⁺	−12.0	−14.5	−11.2	−2.5
tBA	−12.4	−15.8 ^b	−13.2	
tBA-H ⁺	−11.6	^b	−11.5	

^a Effective amine–zeolite combinations, as observed experimentally, are shown in bold-face type. An interaction cutoff distance of 8.0 Å was used in all energy calculations. ^b ZSM-35 readily accepted tBA and tBA-H⁺ only in its bridging cavities.

TABLE 5: Products and Product Compositions Observed with Polyamines, at a Gel SiO₂/Al₂O₃ Ratio of 20

amine zeolite	SiO ₂ /Al ₂ O ₃	Al/uc	Na/uc	R/uc	Na/Al
en ZSM-35	19	3.5	0.4	3.1	0.1
dien ZSM-5	18	9.6	2.1	7.2	0.2
trien ZSM-5	20	8.9	1.9	5.6	0.2
tren ZSM-5	19	9.3	4.4	3.7	0.5

configuration to a molecule affords the opportunity for inadvertent prejudice in the results.) The increasingly favorable fit of amines in ZSM-35, versus ZSM-5 (and the eventual shift to MOR), is shown for both protonated and unprotonated amine by the simulation results in Table 4. That exception of EA was attributed to its multimolecular sorptive capacity in ZSM-5. (It is important to note again that these rudimentary computer calculations did not include electrostatic effects, nor did they include Na ion. Note also that the energy differences were small, generally no more than 2–3 kcal/mol.)

The Special Case of Low SiO₂/Al₂O₃ ZSM-5. Although mutinaite, a rare, naturally occurring zeolite, reportedly has ZSM-5 topology and a SiO₂/Al₂O₃ ratio of 16,³¹ relatively few synthetic samples of ZSM-5 have been reported as having this composition.^{32,33} One reason is believed to be the historically strong focus on synthesis with tetrapropylammonium (TPA) ion,³⁵ a large, spatially demanding cation. One TPA ion per ZSM-5 cavity (4/uc) would balance the charge on a framework having a SiO₂/Al₂O₃ ratio no lower than 46. Another reason might be a consideration of the fact that, if Al atoms were located only in four-ring frameworks, then the SiO₂/Al₂O₃ ratio could not be below 22. A literature analysis found no such exclusive siting.³⁴ (Examples of ZSM-5 synthesis with TPA ion are included in the Supporting Information, as reference points.)

The present results indicate that either a very small amine (e.g., EA) or, preferably, a polyamine can provide the positive charge necessary to balance the abundant negative charge on a ZSM-5 framework having more than 8 Al's per uc, that is, on samples having SiO₂/Al₂O₃ ratios below 22. Three such polyamine products are shown in Table 5, with dien, trien, and tren (together with comparative data for en ZSM-35).

Although en yielded ZSM-35 (just as had been the case with the similarly sized nPA), the larger polyamines, dien, trien, and tren all yielded ZSM-5, and every ZSM-5 product had a Na/Al ratio well below unity, indicating protonated amine. Most importantly, ²⁷Al NMR spectroscopy detected only tetrahedral Al, and the strength of the signal corresponded to a SiO₂/Al₂O₃ ratio less than 20. For example, the NMR spectrum of the sample of tren ZSM-5 in Table 5 corresponded to a framework SiO₂/Al₂O₃ ratio of 17. The XRD pattern of this sample is shown

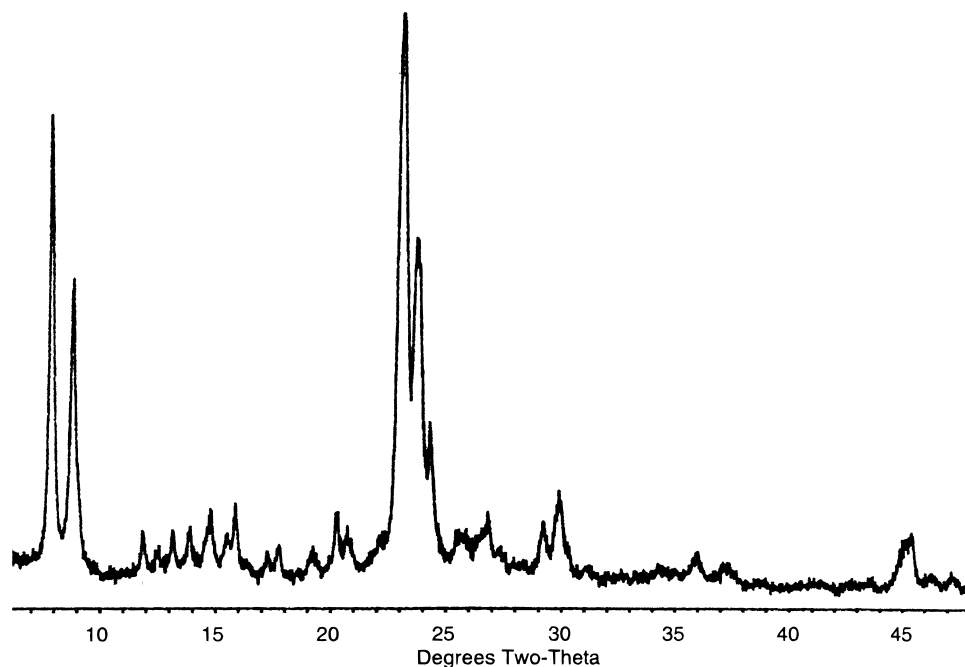


Figure 1. XRD pattern for ZSM-5, synthesized with tren at gel $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$.

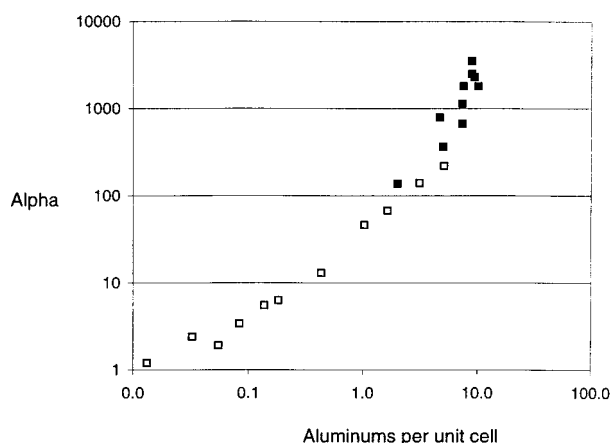


Figure 2. α activity vs ZSM-5 aluminum content. Filled squares are present results; open squares are taken from ref 36.

in Figure 1. In the H-form, it sorbed 12.3 wt % *n*-hexane or 8.2 molecules/uc, indicating a fully open pore system (25 °C, $p/p_0 = 0.1$).³³ (It is believed to be significant that all tren ZSM-5 samples showed a higher Na/Al ratio than did the dien or trien ZSM-5 samples. The higher ratio is attributed to diminished flexibility on the part of tren, versus dien and trien, making tren less able to satisfy framework charge.)

Catalytic activity was also consistent with the high framework Al content, as indicated by *n*-hexane cracking (" α ") activity. Earlier publications have shown a direct correlation between α activity and the framework Al content of a variety of ZSM-5 samples, extending up to ~ 5 Al's/uc ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 36$).³⁶ As shown in Figure 2, all of the samples generated and tested in this study exhibited α activity consistent with their purported framework Al content. For example, the sample of tren ZSM-5, in its H form, had an α of 2500. (Mild steaming is known to generate exceptionally high α activity.³⁷ None of the present samples had been steamed.)

Crystallization in the Presence of Cyclic Amines. As had been seen earlier at very high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios,⁸ the change from small, acyclic amines to larger, cyclic amines brought changes in the zeolites produced. Similar changes were observed

TABLE 6: Products Obtained in the Presence of Cyclic Amines

amine	Gel $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio		
	20	26	40
pyrr	ZSM-35	ZSM-35	ZSM-35
pipd	ZSM-35	ZSM-35	ZSM-35
hmi	^a	MCM-22	MCM-22
dabco	MOR	MOR	ZSM-5

^a MCM-22, ZSM-35, and MOR could all be obtained by varying the crystallization detail.

at the present, lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Namely, the products were ZSM-35, MCM-22, and MOR, as shown in Table 6. Interestingly, ZSM-5 was not observed (with one exception), even though ZSM-5 was the common product at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$ and 40, in the absence of amine.

Just as was the case with the acyclic amines, all zeolites except hmi MOR exhibited a Na/Al ratio substantially below unity, as shown in Table 7. Note that the R/uc content of a particular zeolite was constrained by the pore space of that zeolite and was largely invariant. As framework Al increased (as $\text{SiO}_2/\text{Al}_2\text{O}_3$ decreased), the additional charge on the framework required the presence of additional Na ions. Both Na/uc and Na/Al values increased steadily with the increasing product Al/uc (decreasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio). Despite a pH typically above 13, with the exception of the MOR samples, the product zeolites all contained substantial protonated amine. The computer simulation was consistent with the observed, distinct correlation between zeolite framework and amine content, that is, the invariant product R/uc values. With pyrr and pipd (and with hmi at $\text{SiO}_2/\text{Al}_2\text{O}_3 = 18$), all ZSM-35 products contained 3–4 amines per uc, a value matched by computer simulation. With MOR, the simulation predicted ~ 2.5 dabco molecules/uc, versus the 2.8 molecules/uc observed. Moreover, note that the observed R/uc content decreased as the size of the amine increased for the series of ZSM-35 samples, a further indication of pore filling by the amines.

That pyrr, pipd, and hmi also played a pore-directing role in the respective formation of ZSM-35 and MCM-22, that is, a role specific to the fit of their individual molecular shapes within

TABLE 7: Products and Product Compositions Observed with Cyclic Amines

amine zeolite	SiO ₂ /Al ₂ O ₃	Al/uc ^a	Na/uc ^a	R/uc ^a	Na/Al
gel SiO ₂ /Al ₂ O ₃ ratio = 20					
pyrr ZSM-35	18	3.6	0.9	4.5	0.2
pipd ZSM-35	18	3.6	0.8	3.4	0.2
hmi ZSM-35	18	3.6	1.8	3.3	0.5
hmi MCM-22	18	7.3	3.6	6.5	0.5
hmi MOR	16	5.4	4.1	2.2	0.8
dabco MOR	19	4.7	4.7	2.5	1.0
gel SiO ₂ /Al ₂ O ₃ ratio = 26					
pyrr ZSM-35	24	2.8	0.4	4.4	0.1
pipd ZSM-35	21	3.1	0.6	3.5	0.2
hmi MCM-22	22	6.1	1.0	8.3	0.2
dabco MOR	21	4.2	3.4	2.8	0.8
gel SiO ₂ /Al ₂ O ₃ ratio = 40					
pyrr ZSM-35	32	2.1	0.3	4.5	0.1
pipd ZSM-35	34	2.0	0.2	3.8	0.1
hmi MCM-22	34	4.0	0.3	9.4	0.1
dabco ZSM-5	33	5.5	2.7	4.4	0.5

^a The MCM-22 unit cell contains 72 tetrahedra.

TABLE 8: Interaction Energies Calculated for Fully Loaded Cyclic Amine–Zeolite Pairs (kcal/mol)^a

amine	ZSM-35	MCM-22	ZSM-5	MOR
pyrr	−15.3	−13.5	−14.0	−12.2
pyrr-H ⁺	−14.4	−12.6	−12.6	−11.1
pipd	−17.6	−16.6	−14.9	−14.8
pipd-H ⁺	−15.9	−15.4	−13.9	−13.7
hmi	−17.5	−18.7^b	−17.4	−16.6
hmi-H ⁺	−16.0	−17.7^b	−17.4	−15.6
dabco	−16.7	−19.0	−17.7^c	−17.4^c

^a Effective amine–zeolite combinations are shown in bold-face type.

^b The product was MCM-22 at SiO₂/Al₂O₃ = 26 and 40, but it could be shifted from MCM-22 to ZSM-35 and MOR at SiO₂/Al₂O₃ = 20.

^c The product shifted to MOR at SiO₂/Al₂O₃ = 26 and 20.

the pores of these zeolites (vs those of the ZSM-5 and MOR competitor phases), was supported by calculating individual amine–pore interaction energies. As shown in Table 8, the most favorable interaction energy, that is, the best fit for these amines, was in the pores of ZSM-35 and MCM-22, and that best fit shifted from ZSM-35 to MCM-22 as the size of the amine was increased, from a six- to a seven-membered ring.

The case of hmi in the computer simulations requires special comment because of the unusual crystallization behavior observed in many MCM-22 preparations. The crystallization of MCM-22 is typically believed to be a stepwise process characterized by varying cross-linked lamellae or “precursor” phases.^{22,23} When a fully cross-linked model of MCM-22 was used in the calculations, computer simulation predicted a capacity of ~7 hmi molecules per uc. In fact, it was common for water-washed, as-synthesized MCM-22 samples to contain as many as 10 hmi molecules per uc, a fact earlier discussed⁸ and consistent with partial delamination and the existence of “pockets” (open supercages) on the external surface of MCM-22 crystals. When only the sinusoidal channel system of a fully delaminated MCM-22 was considered, computer simulation with hmi yielded an interaction energy of 21.3 kcal/mol, which is very significantly greater than the values seen above for hmi in ZSM-35.

The simulation results with dabco also require comment, in that they highlight the limitations of these very rudimentary calculations. The product was not MCM-22, but rather ZSM-5 (or MOR, depending on the SiO₂/Al₂O₃ gel ratio). Modeling

with Cerius² Sorption does not address any chemistry aspects of the crystallization process, such as potential interaction with and bridging of silanol groups in a crystallizing reaction mixture.

Conclusions and Summary

Perhaps most striking in this systematic survey of the effects of amines on high-pH zeolite crystallization was the exceptionally strong affinity of the ZSM-5, ZSM-35, and MCM-22 frameworks for small amines. In literally every case, the product contained protonated amine (despite a gel pH often above 13) and a Na/Al ratio substantially below unity. The results, even for the MOR samples, clearly demonstrated a general, beneficial pore-fill role for amines in many zeolite crystallizations, independent of the specific molecular size and shape of the amine (so long as the amine could be accommodated within the zeolite pore space). This effect, along with pH stabilization, was probably responsible for the reproducible formation of ZSM-5 with EA at SiO₂/Al₂O₃ = 20, and it was no doubt an important contributing factor in most of the crystallization processes.

At the same time, a structure-specific, pore-directing role was shown in several instances, an effect specific to the molecular structure of the amine. It was most apparent when the substitution of one amine for another was accompanied by a change in the zeolite produced, as was observed when hmi was substituted for pyrr or pipd, producing MCM-22 in place of ZSM-35. This role was also believed to be present in more subtle shifts in product, such as when the product shifted from ZSM-5 to ZSM-35 on addition of a number of small C₃- and C₄-alkylamines, in place of EA.

Computer simulation was quite helpful in understanding crystallization behavior, by affording a comparative goodness-of-fit for an amine molecule within the pores of alternative or competitor zeolite frameworks. In fact, simulation was almost considered a prerequisite to the assertion of any pore-directing role on the part of those amines. However, the rigid sorbate aspect of the software did not allow credible simulation of larger molecules, such as dien, trien, or tren. It was clear that they were important in the synthesis of ZSM-5 at SiO₂/Al₂O₃ ratio = 20 and that they provided a pore-fill and charge-balance function. It is surmised that, because of their size, they also played a negative pore-directing role. They were simply too large to allow the pore of ZSM-35 to form.

Acknowledgment. The excellent technical assistance, input, and advice of E. J. Sockwell, E. A. Moy, D. F. Colmyer, C. E. Chase, S. E. Schramm, and Jim Gligor of Mobil Technology Co. was much appreciated. This manuscript is dedicated to the memory of Steve Lawton, a valued contributor and co-worker in these experiments.

Supporting Information Available: Detailed crystallization and product analysis results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Lok, B. M.; Cannan, T. R.; Messina, C. A. *Zeolites* **1987**, 7, 282.
- (2) Franklin, K. R.; Lowe, B. M. *Stud. Surf. Sci. Catal.* **1989**, 49A, 179.
- (3) Moretti, E.; Contessa, S.; Padovan, M. *Chim. Ind.* **1985**, 67, 21.
- (4) Parker, L. M.; Bibby, D. M. *Zeolites* **1983**, 3, 8.
- (5) Gunawardane, R. P.; Gies, H.; Marler, B. *Zeolites* **1988**, 8, 127.
- (6) Gies, H.; Marler, B. *Zeolites* **1992**, 12, 42.
- (7) Gies, H.; Marler, B.; Werthmann, U. *Molecular Sieves*; Springer-Verlag: New York, 1998; Vol. 1, pp 35–64.

- (8) Rollmann, L. D.; Schlenker, J. L.; Lawton, S. L.; Kennedy, C. L.; Kennedy, G. J.; Doren, D. J. *J. Phys. Chem. B* **1999**, *103*, 7175.
- (9) Rollmann, L. D. In *Zeolites: Science and Technology*; Nijhoff, M., Ribeiro, F. R., Rodrigues, A. E., Rollmann, L. D., Naccache, C., Eds.; Series E-80; NATO Advanced Studies Institute: The Hague, 1984; pp 109–126.
- (10) Rubin, M. K.; Rosinski, E. J.; Plank, C. J. U.S. Patent 4,151,189, 1979.
- (11) Fyfe, C. A.; Kokotailo, G. T.; Strobl, H.; Pasztor, C. S.; Barlow, G.; Bradley, S. *Zeolites* **1989**, *9*, 531.
- (12) Araya, A.; Lowe, B. M. *Zeolites* **1984**, *4*, 280.
- (13) le Febvre, R. A.; Kouwenhoven, H. W.; van Bakkum, H. *Zeolites* **1988**, *8*, 60.
- (14) Ernst, S.; Weitkamp, J.; Martens, J. A.; Jacobs, P. A. *Appl. Catal.* **1989**, *48*, 137.
- (15) Baki-Borodov, E. L.; Kozlova, N. I. *Chem. Abstr.* **1992**, *116*: 109532.
- (16) Rubin, M. K. U. S. Patent 5,021,141, 1991.
- (17) Rubin, M. K. U. S. Patent 4,981,663, 1991.
- (18) Plank, C. J.; Rosinski, E. J.; Rubin, M. K. U. S. Patent 4,016,245, 1977.
- (19) Jacobs, P. A.; Martens, J. A. *Stud. Surf. Sci. Catal.* **1987**, *33*, 217.
- (20) Puppe, L.; Weisser, J. U. S. Patent 4,439,409, 1984.
- (21) Leonowicz, M. E.; Lawton, J. A.; Lawton, S. L.; Rubin, M. K. *Science* **1994**, *264*, 1910.
- (22) Kennedy, G. J.; Lawton, S. L.; Rubin, M. K. *J. Am. Chem. Soc.* **1994**, *116*, 11000.
- (23) Lawton, S. L.; Leonowicz, M. E.; Partridge, R. D.; Chu, P.; Rubin, M. K. *Micropor. Mesopor. Mat.* **1998**, *23*, 109.
- (24) Meier, W. M. *Molecular Sieves*; Society of Chemical Industry: London, 1968; p 10.
- (25) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.
- (26) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338.
- (27) Treacy, M. M. J.; Higgins, J. B.; von Ballmoos, R. *Zeolites* **1996**, *16*, 323.
- (28) Vaughan, P. A. *Acta Crystallogr.* **1966**, *21*, 983.
- (29) Morris, R. E.; Weigel, S. J.; Henson, N. J.; Bull, L. M.; Janicke, M. T.; Chmelka, B. F.; Cheetham, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 11849.
- (30) Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974; p 636.
- (31) Galli, E.; Vezzalini, G.; Quartieri, S.; Alberti, A.; Franzini, M. *Zeolites* **1997**, *19*, 318.
- (32) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1984**, *88*, 3248.
- (33) Szostak, R. *Handbook of Molecular Sieves*; Van Nostrand Reinhold: New York, 1992; pp 518–527.
- (34) Newsam, J. M. *Stud. Surf. Sci. Catal.* **1996**, *102*, 231.
- (35) Argauer, R. J.; Landolt, G. R. U. S. Patent 3,702,886, **1972**.
- (36) Haag, W. O.; Lago, R. M.; Weisz, P. B. *Nature* **1984**, *309*, 589.
- (37) Lago, R. M.; Haag, W. O.; Mikovsky, R. J.; Olson, D. H.; Hellring, S. D.; Schmitt, K. D.; Kerr, G. T. *Stud. Surf. Sci. Catal.* **1986**, *28*, 677.