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Diquaternary Ammonium Compounds in Zeolite Synthesis: Cyclic and Polycyclic *N*-Heterocycles Connected by Methylene Chains

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Abstract: An additional dimension has been added to our long-standing studies in high silica zeolite synthesis via a guest/host synergism. We have created and studied the impact of making symmetric diquaternary ammonium compounds, by varying the chain length between nitrogen charge centers, and the heterocycle size and geometry containing the nitrogen. This allows the introduction of a second spatial parameter in the use of the charged organo-cation guest in the zeolite synthesis. The series of 15 diquaternary ammonium compounds (5 heterocycles synthesized onto chain lengths of C4−C6) were tested in a total of 135 zeolite syntheses reactions. Nine screening reactions were employed for each guest molecule, and the conditions built upon past successes in finding novel high silica zeolites via introduction of boron, aluminum, or germanium as substituting tetrahedral framework atoms for silicon. Eighteen different zeolite structures emerged from the studies. The use of specific chain lengths for derivatives of the pyrrolidine ring system produced novel zeolite materials SSZ-74 and 75.

Introduction

Zeolite materials have a large impact on the applied sciences. Traditionally used as catalysts[1−4] and water softeners via ion exchange,[5] there has been a continued effort to branch into other areas as the chemical compositions and the three-dimensional architectures of the 4-connected inorganic oxides expand. Recent breakthroughs include the development of the zeolites as membranes grown with specific orientations,[6] membrane materials with novel features,[7] and zeolite development as chip technology components, valued for their structural integrity coupled with low dielectric *k* values.[8] An exciting emergence is the application and considerations for zeolite material in environmental control technologies.[9,10]

The availability of new materials for testing comes from advances made in the synthesis area. This can be principally the discovery of new structures and compositions, but equally important are the breakthroughs in lowering the cost of the zeolite materials.[11] Recently, some surprising advances had been made in discovering new zeolite structures that contained 10-rings, which run in more than one direction. The use of available materials of this type has long been dominated by ZSM-5 (IZA code **MFI**), a pioneer material having mostly SiO_2 composition, good resistance to fouling, and high temperature stability. With low Al substitution, the material is even hydrophobic. Representations of the **MFI** structure are given in Figure 1a. The range of catalytic uses for the material is so wide that an entire monograph was dedicated to describing the technologies emerging from the Mobil laboratories for the use of this material.[12] Its use has been a great commercial success.

When we speak of advances in this area, while there are upward of 180 novel zeolite structures,[13] only a few in recent years have been described as multidimensional 10-ring, after zeolites ZSM-5 (**MFI**) and -11 (**MEL**) discovered over 30 years ago. By using new synthesis approaches and new types of guest organo-cations (referred to in the zeolite literature as templates and then more recently as structure-directing agents, SDA; we will use the latter term[14]), these breakthroughs have been made. New SDA types produced zeolites SSZ-57[15] and 58.[16] The

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(1) Venuto, P. B. *Microporous Mater.* **1994**, *2*, 297.
(2) Corma, A. *J. Catal.* **2003**, *216*, 298–312.
(3) Degnan, T. Zeolites to MOF Mateials-40th Anniversary of the International Zeolite Conference; In *Studies in Surface Science and Catalysis*; Xu, R., Gao, Z., Chen, C., Yan, Y., Eds.; Elsevier: New York, 2007; Vol. 170.
(4) Smit, B.; Maesen, T. L. M. *Nature* **2008**, 671.
(5) Breck, D. W. *Zeolite Molecular Sieves*; Krieger Publ.: Malabar, FL, 1974.
(6) Choi, J.; Ghosh, J.; Lai, Z.; Tsapatsis, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7053.
(7) McKeen, J. C.; Yan, Y. S.; Davis, M. E. *Chem. Mater.* **2008**, *20*, 3791–3793.
(8) Li, Z.; Lew, C. M.; Li, S.; Medina, D. I.; Yan, Y. *J. Phys. Chem. B* **2005**, *109*, 8652–58.
(9) Elangovan, S. P.; Ogura, M.; Davis, M. E.; Okubo, T. *J. Phys. Chem. B* **2004**, *108*, 13059–13061.
(10) http://www.catalysts.basf.com/Main/mobile_emissions/mobile_sources/automotive_emissions/air_intake.be.
(11) Zones, S. I. In *Proceeding of the 3rd International Zeolite Symposium*; Cejka, J., Ed.; Studies in Surface Science and Catalysis Series; Elsevier Science: Amsterdam, 2005; pp 1−10.
(12) Chen, N. Y.; Garwood, W. E.; Dwyer, F. G. *Shape-Selective Catalysis in Industrial Applications*; Marcel Dekker: New York, 1996.
(13) http://www.iza-structure.org/databases/.
(14) Burkett, S. L.; Davis, M. E. *Chem. Mater.* **1995**, *7*, 920–928.

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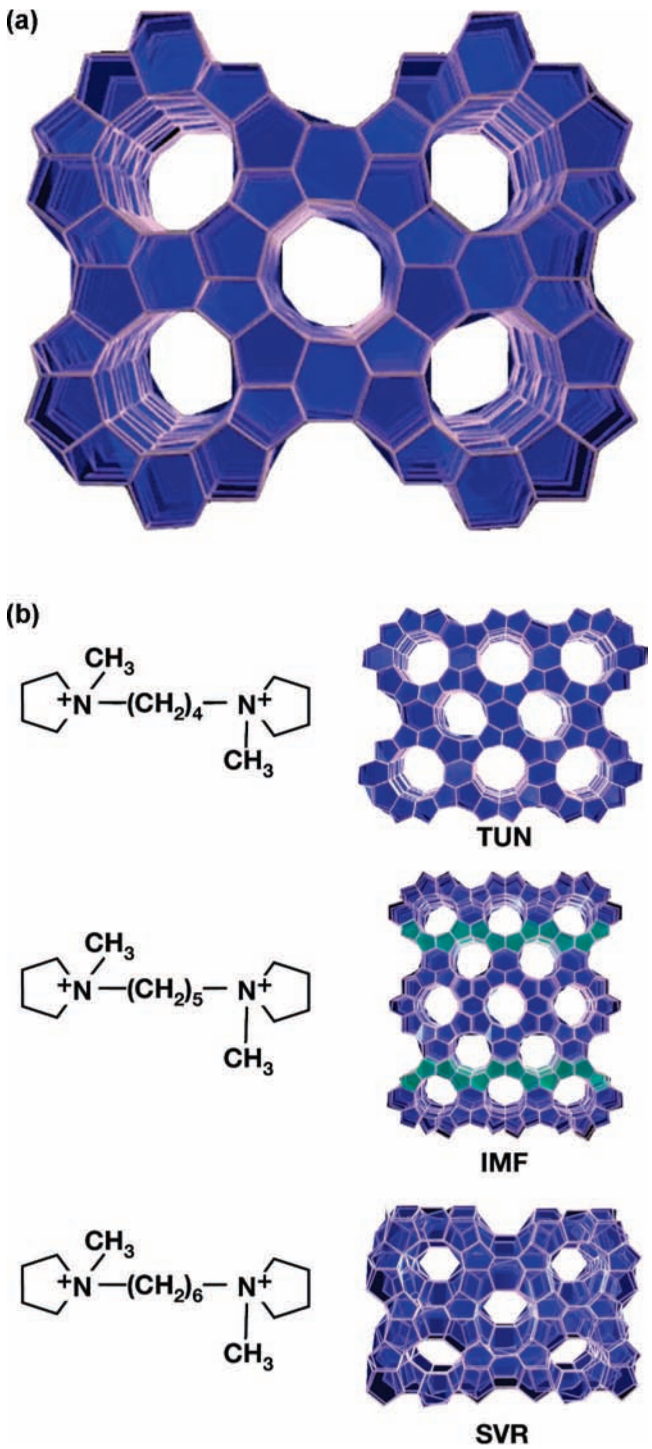

Figure 1. (a) Representation of the crystal structure of zeolite ZSM-5 (code = **MFI**). The intersection points represent sites for tetrahedral (termed T-atoms) atoms like silicon. The oxygens would reside near the midpoint of any line. The pore opening is about 5.5 Å. (b) Representations of three new 10-ring pore zeolites where the channels run in more than one dimension. Each is made with a guest molecule from *N*-methyl-pyrrolidine (PYR in Table 1) where the chain lengths vary. C4 yields TNU-9 (**TUN**), C5 yields IM-5 (**IMF**), and C6 yields SSZ-74 (**SVR**). While the details of the three zeolites have many similarities to **MFI**, the pore sizes are slightly different and appear larger in all three of these new zeolites.

introduction of fluoride ion, by Camblor and Corma,[17,18] greatly changed the chemistry of the synthesis system, allowing new structures to emerge under all-SiO_2 conditions but with high void volumes. ITQ-13 (**ITH**)[19] was found as a multidimensional 10-ring material via this route. Later, even more structures were found by the substitution of Ge for Si into these syntheses, again by the Corma laboratories.[20]

Recently zeolites IM-5 (**IMF**)[21] and TNU-9 (**TUN**)[22] were discovered using diquaternary ammonium SDA built from *N*-methyl pyrrolidine heterocycles connected by chain lengths of 5 and 4, respectively. These structures are shown in Figure 1b along with the zeolites they make. More recently, the zeolite SSZ-74[23] was discovered using the fluoride chemistry described above by Corma et al.[18] The structures of **IMF** and **TUN**, very complex zeolite structures (large number of T-atoms in the asymmetric unit), were recently solved using some elegant analytical diffraction and analysis techniques developed in the laboratories of Baerlocher and McCusker in Zurich and Terasaki et al. in Stockholm.[24−26] Importantly, the catalytic properties of these materials have been shown to differ from those of ZSM-5, making the discovery worthwhile.[27−29] We were surprised to see the discovery of IM-5 and then TNU-9 under very narrow restricted synthesis conditions (silica-to-alumina, termed SAR, is very narrow, and Na content is high), that we thought would likely avoid the use of the guest SDA and make mordenite zeolite instead. These concerns[30] are borne out in some of our studies below.

Seeing the success of these diquaternary compounds with varying chain lengths (Figure 1) in producing these multidimensional 10-ring zeolites (we show the ring sizes of the portals in Table 1), we were impressed that these guest molecules could produce new zeolites of this type. To get a better view of the three-dimensional aspects of the zeolite channels, you are encouraged to see the database on the website of the International Zeolite Association, which allows one to view these structures and rotate them. We wondered what might happen if we changed the chemical details of the heterocycles connecting the chain lengths. We created five different types of symmetric

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(15) Elomari, S. U.S. Patent 6,555,089, 2003.
(16) Elomari, S. U.S. Patent 6,544,495, 2003.
(17) Camblor, M. A.; Villaescusa, L. A.; diaz-Cabana, M. J. *Top. Catal.* **1999**, *9*, 59.
(18) Corma, A. *Proceedings of the 14th Int'l Zeolite Association*; Elsevier: Amsterdam, 2004; p 1.
(19) Corma, A.; Puche, M.; Rey, F.; Sankar, G.; Teat, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1156–59.
(20) Sastre, G.; Vidal-Moya, J. A.; Blasco, T.; Rius, J.; Jorda, J. L.; Navarro, M. T.; Rey, F.; Corma, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4722–4726.
(21) Benassi, E.; Guth, J. L.; Rouleau, L. WO 98/17581, 1998.
(22) Hong, S. B. Zeolites to MOF Materials-40th Anniversary of the International Zeolite Conference; In *Studies in Surface Science and Catalysis*; Xu, R., Gao, Z., Chen, C., Yan, Y., Eds.; Elsevier: New York, 2007; Vol. 170.
(23) Burton, A. W.; Zones, S. I.; Elomari, S.; Chan, I. Y.; Chen, C.-Y.; Hwang, S.-J.; Ong, K. K. Zeolites to MOF Materials-40th Anniversary of the International Zeolite Conference; In *Studies in Surface Science and Catalysis*; Xu, R., Gao, Z., Chen, C., Yan, Y., Eds.; Elsevier: New York, 2007; Vol. 170.
(24) Baerlocher, Ch.; Gramm, F.; Massueger, L.; McCusker, L. B.; He, Z. B.; Hovmoller, S.; Zou, X. D. *Science* **2007**, *315*, 1113–16.
(25) Gramm, F.; Baerlocher, Ch.; McCusker, L. B.; Warrender, S. J.; Wright, P. A.; Han, B.; Hong, S. B.; Liu, Z.; Ohsuna, T.; Terasaki, O. *Nature* **2006**, *444*, 79.
(26) Xie, D.; McCusker, L. B.; Baerlocher, C.; Burton, A. W.; Hwang, S.-J.; Rea, T.; Ong, K.; Zones, S. I. *Nat. Mater.* **2008**, *7*, 631–635.
(27) Corma, A.; Martinez-Triguero, J.; Valencia, S.; Benazzi, E.; Lacombe, S. *J. Catal.* **2002**, *206*, 125–133.
(28) Zones, S. I.; Chen, C. Y.; Corma, A.; Cheng, M. T.; Kibby, C. L.; Chan, I. Y.; Burton, A. W. *J. Catal.* **2007**, *250*, 41–54.
(29) (a) Zones, S. I.; Burton, A. W. U.S. Patent 7357904, April 15, 2008. (b) Zones, S. I.; Burton, A. W. U.S. Patent 7378295, March 25, 2008.
(30) Zones, S. I.; Nakagawa, Y.; Yuen, L. T.; Harris, T. V. *J. Am. Chem. Soc.* **1996**, *118*, 7558–67.

Table 1. Pore Size Data for Zeolites Made with Diquaternary Compounds Discussed

TUN 2 channels along [010]; both 10-ring; 5.6 Å × 5.5 Å 5.4 Å × 5.5 Å	**IMF** 5 channels; all 10-ring; along [010]; 5.3 Å × 5.9 Å; long [001]; 5.5 Å × 5.6Å 4.6 Å × 5.4 Å along [100]; 5.3 Å × 5.4 Å 5.1 Å × 5.3 Å	**STI** 2 channels; all 10-ring; along [100]; 4.7 Å × 5.0 Å; an 8-ring; along [001]; 2.7 Å × 5.6 Å
MTW 1 channel along [010]; a 12-ring; 5.6Å × 6.0Å	**BEA** 2 channels both 12-ring; along [100]; 6.6 Å × 6.7 Å along [001]; 5.6 Å × 5.6 Å	**BEC** 2 channels both 12-ring; along [100]; 6.0 Å × 6.9 Å along [001]; 6.3 Å × 7.5 Å
MFI 2 channels both 10-ring; along [100]; 5.1 Å × 5.5 Å along [010]; 5.3 Å × 5.6 Å	**MOR** 2 channels along [001]; a 12-ring; 6.5 Å × 7.0 Å an 8-ring; 2.6 Å × 5.7 Å	**RUT** 0 channels; apertures formed by 6-rings only
IWW 3 channels along [010]; a 12-ring; 6.0 Å × 6.7 Å; a 10-ring; 4.9 Å × 4.9 Å; an 8-ring; 3.3 Å × 4.6 Å	**STF** 1 channel along [001]; a 10-ring; 5.4 Å × 5.7 Å	**STO** channel system of this disordered polymorph is one-dimensional; ring sizes (no. of T-atoms): 12, 6, 5, 4
SSY 1 channel along [001]; a 12-ring; 5.0 Å × 7.6 Å	**AST** 0 channels; apertures formed by 6-rings only	**NON** 0 channels; apertures formed by 6-rings only
DOH 0 channels; apertures formed by 6-rings only	**AFX** 1 channel along [001]; an 8-ring; 3.4 Å × 3.6 Å	**SVR** 2 channels both 10-rings

diquaternary compounds for connection with methylene chain lengths of C4, C5, and C6. The heterocycles are shown in Table 2. We abbreviate the groups as PYR (*N*-methyl pyrrolidine), PIP (*N*-methyl piperidine), HOMO (*N*-methyl homopiperidine), TRO (*N*-methyl tropane), and QUIN (quinuclidine). The first three groups are ring expansions of the heterocycle. We will show that this change already produces great changes in product selectivity. The latter two are larger heterocycles and introduce more rigidity into the ends of the SDA diquaternaries.

We had previously studied a series of singly charged *N*-heterocycle SDA built around the piperidine ring structure and used in the fluoride-influenced reaction conditions.[31] Like Camblor and Corma, we found that the water content (H_2O/SiO_2 ratio) greatly affects the product outcome in syntheses where all other conditions are held constant. Results nicely showed that highly concentrated systems almost always produced frameworks of lower density with high internal void volumes (once the guest SDA is removed). Conversely, as the reactions became more dilute, higher framework density products dominated with the opposite characteristics. So we included these three water concentrations ($H_2O/SiO_2 = 3.5, 7.0, 14.0$) as a synthesis screen for the 15 SDA we created (five heterocycles with three chain lengths for each). Next, we expanded our synthesis field for the 15 SDA by providing six other synthesis regimes for each (90 more synthesis reactions).

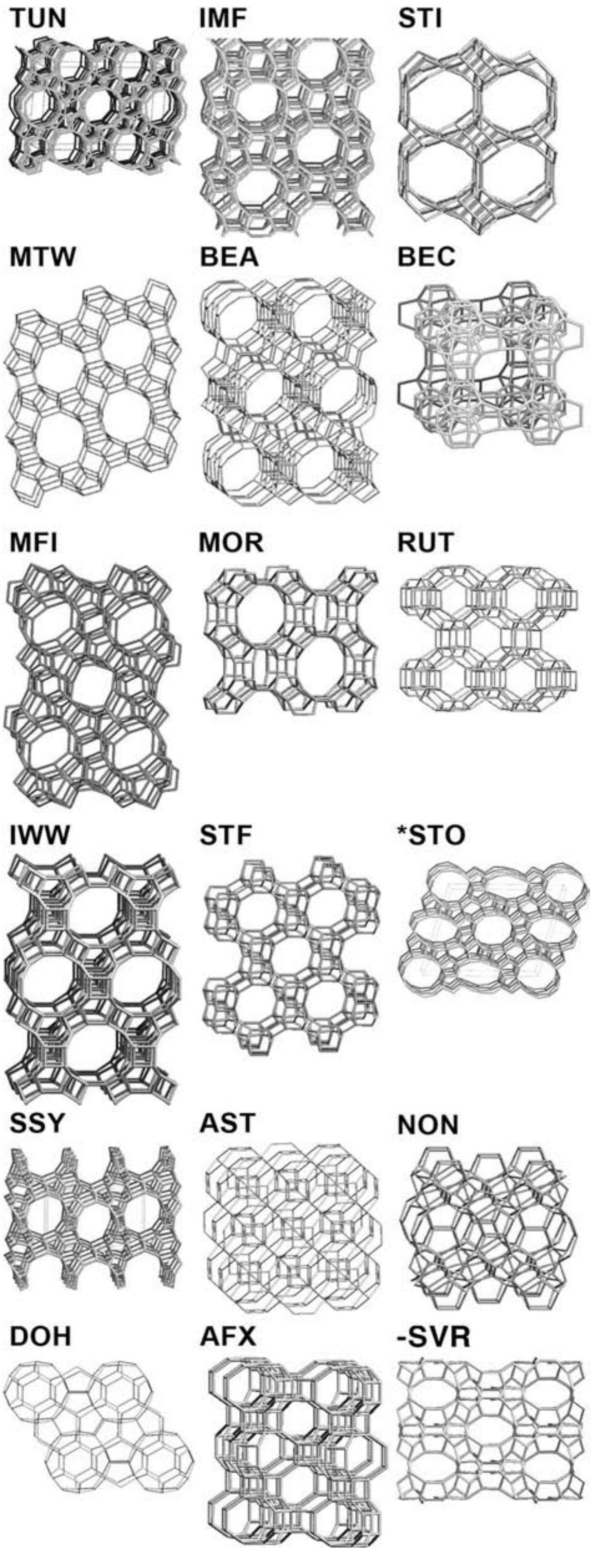

Figure 2. Framework structures of zeolites produced with discussed diquaternary compounds.

We added the following reaction types: (1) The first is a reaction where Ge is introduced at Si/Ge = 9. As mentioned above, the use of Ge can alter the reaction products.[20] (2) The second is a reaction where the SDA is used, but a second SDA, the smaller tetramethyl ammonium (TMA+), is introduced. This had been a recent feature in building great breakthrough products like

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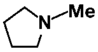
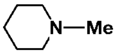
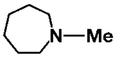
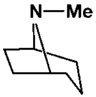
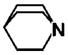
(31) Zones, S. I.; Lee, G. S.; Burton, A. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 9066–79.

Table 2. Various Heterocyclic End-Groups Used To Construct Diquaternary Ammonium Compounds of Chain Lengths C_4-C_6

Group	Common Name	Abbrev.
	N-methylpyrrolidine	(PYR)
	N-methylpiperidine	(PIP)
	N-methyl homopiperidine	(HOMO)
	N-methyl tropane	(TRO)
	Quinuclidine	(QUIN)

ITQ-29, an all-SiO_2 zeolite (**LTA**) structure.[32] (3) We ran the high Na cation reaction used to find IM-5 and TNU-9. (4) We screened a borosilicate synthesis based upon conditions in the discovery of SSZ-33 zeolite.[33] (5) We tried an aluminosilicate synthesis experiment, differing from (3) in that the Na content is kept low and the SDA provides the majority of the OH^- needed. This had been a good way to synthesize zeolite SSZ-26.[34] (6) We used reagent conditions similar to those in (5) but used a very high silica faujasite zeolite (TOSOH's 390 HUA product) to provide all of the SiO_2 and Al_2O_3 reagent. This gives a material with SAR > 200 and is a relatively reactive reagent. In essence, this is close to an all-SiO_2 screening of the SDA performance, and this was successfully used in making a catalytically active **VET** zeolite (SSZ-41).[35] The framework structures made with the discussed diquaternary compounds can be seen in Figure 2. For the nine reactions surveyed, we ran each type at a single temperature, using the conditions initially found to be successful in the discovery reactions we used as models. While it is true that product selectivity can change with temperature increase, we did recently find in a study of more than 20 piperidinium derivatives, in the HF type reactions, that the product at 150 and 170 °C remained the same for more than 70% of the SDA tested.[31]

Experimental Section

SDA Synthesis. A description of the SDA syntheses is given in a recent work.[36] Generally, the compounds were made by reacting tertiary amines with dihalides in methanol. The reactions were followed by thin-layer chromatography (methanol/chloroform), and when there seemed to be a major conversion to product (usually several days at room temperature) then the solvent was stripped off and the remaining solids recrystallized from a minimum of hot methanol. Tables for the calculated and determined C, H, and N elemental analyses are in ref 36. ^{13}C and ^1H NMR were taken for all 15 compounds to verify correct products and structures. Figure 3 is a comparative set of ^1H NMR spectra for all five compounds with a chain length of C5, demonstrating some features that should be present in all five compounds, even with the terminal tertiary amine substituents differing.

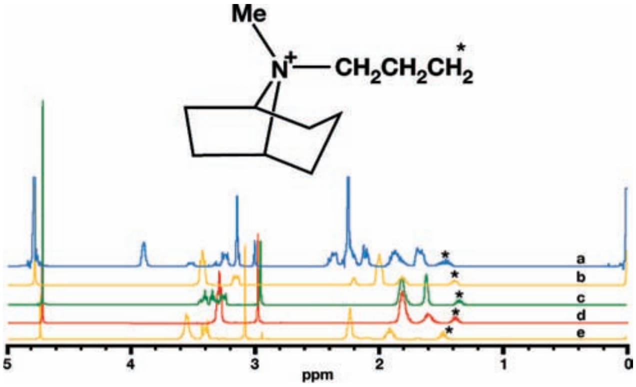


Figure 3. A comparative set of ^1H NMR spectra for the whole series of diquaternaries with C5 chain length. (a) Tropane (TRO), which is also pictured for half of the molecule; (b) quinuclidine (QUIN); (c) hompiperidine (HOMO); (d) piperidine (PIP); (e) pyrrolidine (PYR). The asterisk in each spectra is the position where the middle CH_2 unit in the C_5 chain appears. This is common to all five compounds.

Zeolite Synthesis. For the nine types of zeolite synthesis reaction investigated, the model systems reference products were described above.[31-35] All reactions, except the one based upon IM-5 synthesis, used the SDA as the OH^- compound (from resin exchange of the halide salts with BioRad AG1-X8). Reactions were run in 23 mL Parr 4345 reactors that contain Teflon cups. These reactors are loaded onto spits built into Blue M convection heating ovens. Reactions were rotated on the spits within the ovens at 43 rpm. For the first three HF reactions, runs were at 150 °C. The reactions with Si/Ge = 9, and the ones with TMA+ added, were run at 170 °C. The borosilicate reaction and the three reactions using various Al sources were run at 160 °C, except the IM-5 type reaction that is run at 170 °C.

Initially, reactions were run for 6 days and then removed from the oven and cooled. Once opened, a small representative sample was diluted into a larger amount of water in a 15 mL vial. Scanning electron micrographs were taken (JEOL JSM-6700F instrument) to determine if there was crystalline material present. If not, or if there was still sizable noncrystalline material, then the reaction was reheated for another 5 days. This procedure was repeated until the field was virtually all-crystalline material. At that time, a trial sample of solids was removed from the reactor and the X-ray diffraction pattern run to determine the phase(s) present and whether continued heating was warranted. In some instances, the synthesis was repeated because another sample of the product was desired. Running the subsequent reaction, unopened after cooling and then reheating, over a 2−3 week period still produced the same zeolite product as in the earlier case.

In some instances, there was a crystalline pattern, but because the pattern contained very strong, low angle ($2\theta < 6°$) peaks, it was considered that the product might be a layered product. In this case, the reaction was also reheated. In the tables that follow, if a product is labeled as "layered", this indicates that the pattern persisted for 40−50 days of reaction. There are some examples in the tables of zeolite products (i.e., SSZ-60; **SSY**) that were preceded by a layered product. This comparison is discussed in the next section. Aside from zeolitic or layered product designations, we included a third SDA/silicate product description. Some results are labeled as unknowns. Unlike the layered products, (a) we did not see platy, leafy morphology in the scanning electron microscope analyses (SEM), and (b) the X-ray diffraction pattern did not become mostly lost on calcination. These unknowns were not identified to us as known zeolites, but also some had sufficiently altered X-ray patterns and low porosity that we were uncertain as to the nature of the structural changes going from the as-made to the calcined material. We are continuing to study these unknown materials.

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(32) Corma, A.; Rey, F.; Rius, J.; Sabater, M. J.; Valencia, S. *Nature* **2004**, *431*, 287–290.
(33) Lobo, R. F.; Pan, M.; Chan, I.; Li, H. X.; Medrud, R. C.; Zones, S. I.; Crozier, P. A.; Davis, M. E. *Science* **1993**, *262*, 1543.
(34) Zones, S. I.; Santilli, D. S.; Olmstead, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 4195.
(35) Zones, S. I. U.S. Patent 5,591,421, 1997.
(36) Jackowski, A.; Zones, S. I.; Burton, A. W. *Zeolites and Related Materials: Trends Targets and Challenges(SET), Volume 174: 4th International FEZA Conference, 2−6 September 2008, Paris, France*; Elsevier: Amsterdam, 2008; pp 111−116.

Table 3. Products from Synthesis under HF Reaction Conditions with Variable H_2O/SiO_2

		H_2O/SiO_2		
		3.5	7.0	14.0
PYR	C_4	STI	STI	MTW
	C_5	DOH	MTW	MFI
	C_6	SSZ-74	SSZ-74	MFI
PIP	C_4	MTW	MTW	MTW
	C_5	BEA	BEA	MTW
	C_6	BEA	BEA	MFI
H0M0	C_4	MTW	MTW	MTW
	C_5	BEA	BEA	MTW
	C_6	BEA	MTW>BEA	MTW
TR0	C_4	LAYER	STF	STF
	C_5	MFI	MFI	SSZ-31
	C_6	MFI	MFI	MFI/BEA
QUIN	C_4	LAYER	MTW	MTW
	C_5	BEA	BEA	MTW
	C_6	BEA	BEA	MFI+?

Table 4. Products from Synthesis with Al^{+3} and OH^- Conditions for Selected Reactions

			reacton SAR	
		35[a]	40[b]	250[c]
PYR	C_4	TUN	MTW+	unknown
	C_5	BEA	MTW+	unknown
	C_6	BEA	BEA	SSZ-74
PIP	C_4	AFX	MTW+	MTW
	C_5	AFX	MTW+	MTW
	C_6	MOR	unknown	MTW/MFI
H0M0	C_4	MOR	unknown	unknown
	C_5	MOR	MTW>BEA	MTW
	C_6	MOR	BEA	MTW
TR0	C_4	MOR	LAYER	unknown
	C_5	MOR	SSZ-31	SSZ-31
	C_6	MOR	MFI	MFI
QUIN	C_4	MOR	LAYER	LAYER
	C_5	MOR	LAYER[d]	LAYER
	C_6	MOR	BEA/MFI	MFI

[a] IM-5 type reaction Na/Si = 0.70. [b] SSZ-26 type reaction Na/Si = 0.18. [c] SSZ-41 type reaction Na/Si = 0.10. [d] After several weeks of heating, this layered material converted over to a solid whose X-ray diffraction pattern shows a relationship to NU-88.

Table 5. Products Formed under Hydroxide Conditions and with Elements Other than Al Added into the System[a]

		Si/Ge = 9	B[b]	Me_4N^{+c}
PYR	C_4	IWW	unknown	AST
	C_5	IWW	MTW	AST
	C_6	unknown	MTW	RUT
PIP	C_4	IWW	MTW	NON
	C_5	IWW	MTW	RUT
	C_6	BEA/BEC	BTW	RUT
H0M0	C_4	MTW+	unknown	NON
	C_5	BEC	MTW	NON
	C_6	BEA	MTW	RUT
TR0	C_4	unknown	unknown	AST
	C_5	unknown	SSY	AST
	C_6	BEA/BEC	MFI	RUT
QUIN	C_4	unknown	LAYER	RUT
	C_5	LAYER/BEC	MTW	AST
	C_6	BEA/BEC	BEA	RUT

[a] Ge and B can be lattice substituents. Tetramethyl ammonium (TMA+) is a second SDA in the synthesis. [b] SSZ-33 type reaction. [c] Diquat N^+/TMA^+ = 1.5.

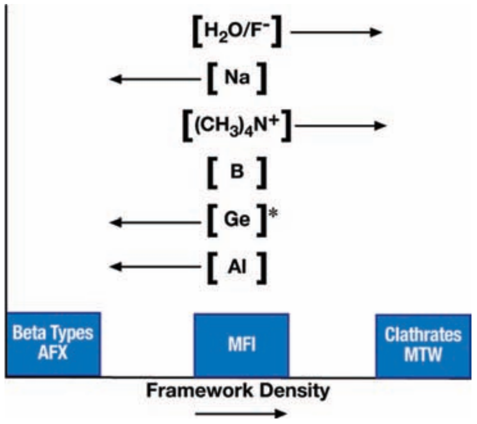

Figure 4. Product trends in the inorganic parameters. *Ge contributes by largely favoring 4-rings in the structure construction, leading to more open frameworks of lower density.

Characterization. The X-ray diffraction data (XRD) were taken on a laboratory Siemens D-500 instrument after the sample had been washed and dried. The SEM images are from a JEOL JSM-6700F instrument. The ^{13}C CPMAS NMR spectra were taken using a Bruker Avance 500 instrument.

Results and Discussion

Overview of Results and Chain Length Impact. The results for our trials are tabulated in Tables 3–5. Table 3 is for the 15 compounds run in the three HF reactions (three ratios of H_2O to SiO_2). Table 4 is for the reactions where the system is under OH^- control and some Al is used. Three reactions were explored for each SDA. In the reaction type (3), the conditions for IM-5 or TNU-9 synthesis were used. These reactions have OH^-/SiO_2 of above 0.60, and Na/SiO_2 is higher still. The reactions produce products that have SiO_2/Al_2O_3 ratios (termed SAR) in the 25–30 range. These tend to be very active zeolite catalysts with a high concentration of strong acid sites. A similar reaction (type 5) has about the same ratio of reactant SAR, but now the OH^-/SiO_2 is reduced to closer to 0.35 and the alkali content is lowered below a ratio of $Na/SiO_2 = 0.20$. We had good success in using this reaction to make zeolite SSZ-26. The third reaction keeps these OH and Na variables low and uses a form of Y zeolite (**FAU**) that has been removed of almost all Al content. It is a product from TOSOH (Japan) and allows us to make materials in an environment that behaves as all-silica, and yet we get products with low amounts of Al, which can then be used to give us information about the pore size influence in a catalytic (albeit lower conversion) reaction. Table 5 shows single reactions for the introduction of Ge into an all-SiO_2 system, and the impact on product formation will be apparent. There is another column for reactions with boron and then a third reaction where the SDA is supplemented by the addition of TMA cations. The secondary SDA (so to speak) comes about as a result of the two SDA system used recently by Corma's group in the discovery of ITQ-29, all-silica **LTA**, a remarkable discovery.[32] We also had an interest in this reaction because of our findings that a new phase, SSZ-77, was being generated by a smaller fragment from the original SDA in the synthesis.[37] Figure 4 gives a schematic of how the inorganic factors affect the probability of either open, low framework density products, or those with high density such as clathrates and one-dimensional channel zeolites. Per discussion of the impact coming from the

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(37) Earl, D. J.; Burton, A. W.; Rea, T.; Ong, K.; Deem, M. W.; Hwang, S.-J.; Zones, S. I. *J. Phys. Chem. C* **2008**, *112*, 9099–9015.

(38) (a) Hong, S. B.; Min, H.-K.; Shin, C.-H.; Cox, P. A.; Warrender, S. J.; Paul, A. W. *J. Am. Chem. Soc.* **2007**, *129*, 10870–10885. (b) Hong, S. B. *Catal. Surv. Asia (Springer)* **2008**, *12*, 131–44.

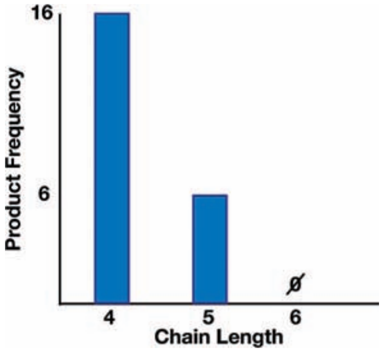

Figure 5. A histogram showing the frequency of layered products and the use of C_4−C_6 chains of any of the diquaternary compounds. Note that the C_6 chain lengths are not producing any layered products.

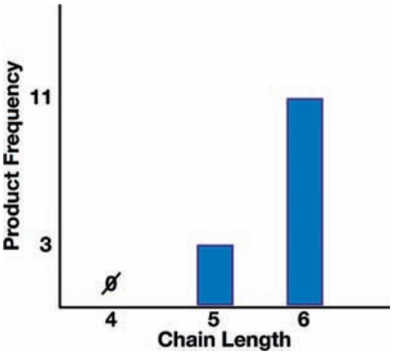

Figure 6. A histogram showing the frequency of **MFI** products and the use of C_4−C_6 chains of any of the diquaternary compounds. In contrast to Figure 5, the C_4 chains make no **MFI**, and the C_6 compounds are quite good at it.

15 SDA, we then provide interesting examples of the competition for control of nucleation selectivity between SDA and inorganic reaction context. We will see examples where each is dominant.

A number of trends can be seen for the SDA that emphasize the potential contributions of all three factors at work here: the length of the chain between charges, the size of the heterocycle connected to the charged nitrogen, and the inorganic context surrounding the use of the SDA. In every product made in the study, the SDA is part of the structure. While it can be the case that in reactions exhibiting low product diversity (type 2, here, with TMA+ cations, and type 3 with high Na+ concentrations) the structural details of the SDA employed may not have had much influence, they are still incorporated as guest molecules. Stabilization of silica-rich products in reaction media, featuring anions that attack Si−O bonds like OH^- and F^-, and elevated temperatures will necessitate pore-filling guest molecules. These greatly limit back-reactions to dissolution. This probably has the largest impact as we will see in examples where only Ge is leading to certain zeolite products. Similarly, only in high Na do we encounter phases like **MOR**.

Figure 5 shows the frequency of layered phase formation. It is not favored by the C6 chain. Yet the C6 chain, interestingly, is very hospitable for the formation of **MFI**. This is shown in Figure 6 and may explain why the layered materials do not form. An unusual feature in the formation of layered phases using chains of C4, and C5 to a lesser degree, is that they can be seen as metastable phases in some instances. While they persist for several weeks at times, they can occasionally be converted to the more stable three-dimensional zeolite. A recent study from Hong et al. shows how the novel multidimensional 10-ring zeolite TNU-9 can be preceded in the synthesis by the more layer-like **MWW**, an interesting material in its own right.[38] In the tables, if LAYERED is indicated, we do not know the actual details of the atomic structure. In a few instances, a material like MCM-47 (from the C4 chain) is found as the product. The research groups of Lobo and Deem determined its layered structure.[39] In one of our experiments here (see Table 5), the SDA with tropane as headgroup and a C5 chain produced what appeared to be a layered material (by both SEM images and XRD patterns) for several weeks. Suddenly, during one of the reheatings, the material was transformed into a rod-like product. The SEM images for the layered material, and then the eventual zeolite product, **SSY**, are shown in Figure 7a and b. The **SSY** phase, a one-dimensional 12-ring zeolite,[40] had never been made with this SDA before. Figure 8 shows the NMR of the as-made zeolite product, and the ^{13}C CPMAS NMR spectra indicate the tropane headgroup and the methylene chains are both observed

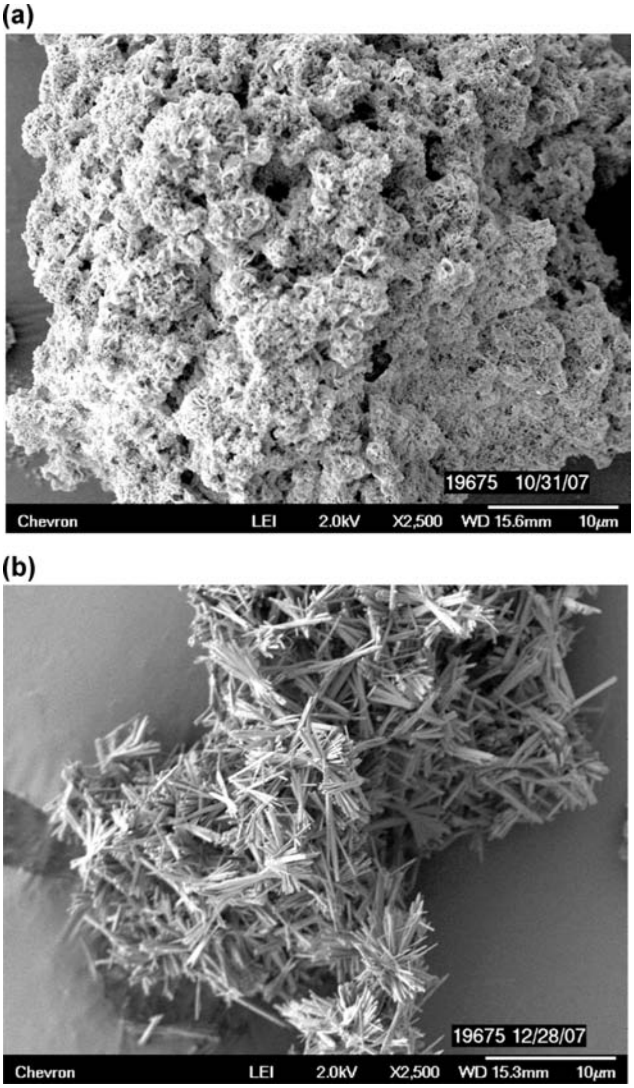

Figure 7. Scanning electron micrographs for the solids obtained for the synthesis with boron and the use of TRO−C_5−TRO. (a) Product (layered by XRD) at 3 weeks of run time and (b) product (**SSY**) now having formed after about 5−6 weeks, and the layered precursor having disappeared.

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(39) Burton, A. W.; Accardi, R. J.; Lobo, R. F.; Falcioni, M.; Deem, M. W. *Chem. Mater.* **2000**, *12*, 2936–42.

(40) Burton, A. W.; Elomari, S. *Chem. Commun.* **2004**, *22*, 2618–9.

Table 6. A List of the Fifteen Products for the Reaction Type with High Na Content, Modelled after IMF Discovery[a]

heterocycle	chain	zeolite
pyrrolidine	C_4	TUN
	C_5	IMF
	C_6	BEA
piperidine	C_4	AFX
	C_5	AFX
	C_6	mordenite
homopiperidine	C_4	mordenite
	C_5	mordenite
	C_6	mordenite
tropane	C_4	mordenite
	C_5	mordenite
	C_6	mordenite
quinuclidine	C_4	mordenite
	C_5	mordenite
	C_6	mordenite

[a] This table illustrates the point also made in Figure 8 for the effect of higher Na and OH^- values. The larger end groups on the diquaternaries all lead to mordenite.

in the zeolite product. As we have indicated already, chain length is a key parameter because only the C5 derivative in this series yields **SSY**. The headgroup is important as only tropane (of the five candidates) yields this product. Also, this zeolite is forming in reactions with boron present, but not Al, Ge, or a lack of any substituting T atom. So all three factors we have described have a role in the nucleation selectivity for the formation of this unusual zeolite product. Another factor we should note is that, given the NMR data, the SDA also has to have the ability to remain stable over long periods of reaction for the eventual nucleation to occur. It would be interesting to know if the SDA is stabilized from breakdown while embedded in the layers of the precursor guest/host product of the reaction.

Effect from High Sodium Content. Table 6 combines the reactions where we attempted to look at the 15 SDA in the reaction where IM-5 and TNU-9 had first emerged from the use of C5 and C4 diquaternaries for the *N*-methyl pyrrolidine (PYR) ring system. One can see that these were the only products we observed other than **BEA** and **AFX** for the C6 chains of the smallest head groups (PYR and PIP). The remaining nine reactions for the three larger head groups all produced **MOR** in this reaction. Elemental analysis for a few selected products did show that there was SDA in the **MOR**, but it is our belief that the high Na^+ and OH^- contents in the reaction favor the nucleation of **MOR**. Figure 9 restates a relationship we noted in early studies with variations in SDA and Na^+ providing the OH^-, which helps to drive the nucleation and crystallization. The general trend was that sufficient quantities of Na^+ favored **MOR** if the OH^- was commensurate or layered phases like magadiite if the OH^- was decreased.[41] For this reason, we moved to a system where the SDA provided much of the OH^- and the emergence of novel phases was helped. A nice example is seen in our borosilicate study for SSZ-33 (**CON**) and **BEA** in using two different polycyclic SDA isomers and varying Na content.[42]

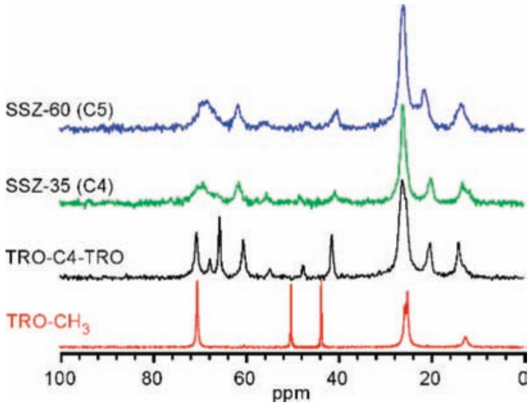

Figure 8. ^{13}C CPMAS NMR spectra of SDA in both SSZ-35 and SSZ-60 showing no indication of decomposition of SDA or inclusion of unchained tropane (TRO−CH_3). In comparison, ^{13}C CPMAS NMR spectra of two pure organic compounds (C4-tropane SDA and unchained tropane) are plotted at the bottom. Methylene (−CH_2−) carbons in the chain are seen well separately from those in the tropane head. Carbons attached to the positive nitrogen (−N^+−) are seen at chemical shifts over 40 ppm.

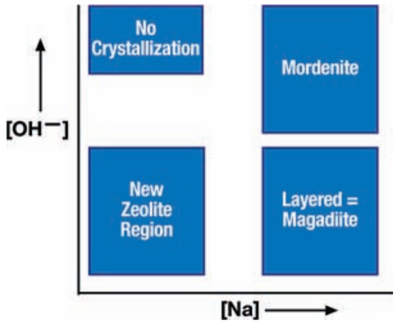

Figure 9. A diagram of how the use of sodium cations and hydroxide anions affects probabilities for crystallization products. High values of both favor mordenite formation with the guest organo-cation frequently not being included in the product. Lower values of each have favored the discovery of a number of high silica zeolite products, typically with ratios higher than mordenite products.

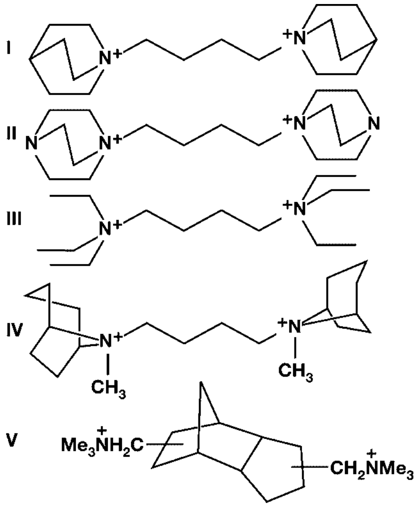

Figure 10. Structure-directing agents (SDA) used for the formation of SSZ-16 (**AFX**) from a past study (see ref 43). Note that two of them are part of this study, QUIN−C_4−QUIN and TRO−C_4−TRO.

We were not too surprised to see **AFX** emerge from the high alkali content reactions as it was discovered in this domain. Interestingly, Figure 10 shows, from our earlier work on this novel zeolite, that the tropane and quinuclidine candidates should be capable of making **AFX** as well, and perhaps some fine-tuning of the synthesis conditions here is needed to make them.[43] **AFX** was initially favored in these high NaOH conditions in

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(41) Davis, M. E.; Zones, S. I. In *Synthesis of Porous Materials*; Occelli, M. L., Kessler, H., Eds.; Marcel Dekker: New York, 1997; pp 1−37.

(42) Zones, S. I. *Microporous Mater.* **1994**, *2*, 281–287.

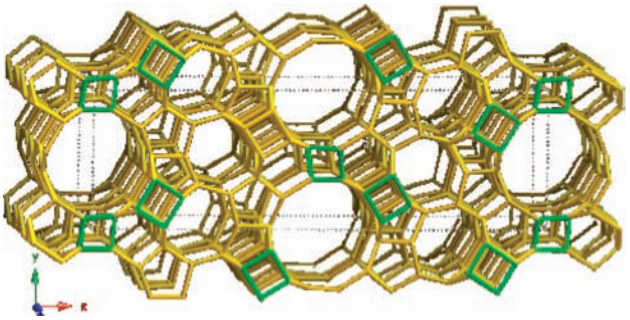

Figure 11. A model of **IWW** highlighting the double 4-rings.

reactions with temperatures near 135 °C. In this study, all reactions were modeled after other successful zeolites syntheses for certain discoveries and were run at 150, 160, or 170 °C. Perhaps this favors **MOR** over the formation of phases like **AFX**, and this variable should be re-examined for this reaction type 3.

Effect of Ge and B. The introduction of Ge into the system changes our product selectivities, and these are the instances where we see ITQ-22 (**IWW**) and ITQ-17 (**BEC**). Both of these materials have a greater population of double-4 rings within the zeolite structure, and Ge is said to favor the formation of these double 4-rings.[44] A model of **IWW** is shown in Figure 11. It is apparent from looking at the 15 reactions for the use of Ge that some products do not form. In that sense, the Ge presence serves as something of an inhibitor. In some past work concerning the discovery of VPI-8 (**VET**), a point was made that perhaps a good way to understand the influence of Zn in the formation of VPI-8 was to also understand what an inhibitor it seemed to be for another phase. Here, with Ge, no **MFI** is observed. If we compare with boron in the same table, more than half of the SDA lead to **MTW**, and only one out of 15 in the case of Ge. So Ge, perhaps in its desirability to be in 4-rings, makes it difficult for phases forming with mostly 5 and 6 rings (e.g., **MFI** and **MTW**). On the other hand, products like **IWW** and **BEC** with double 4-rings are not unusual at all. The introduction of TMA+ as a second cation overrides the synthesis system so that only clathrates (using the TMA+) are formed. The other diquat SDA, in the 15 different reactions, become irrelevant spectators under these reaction conditions.

Lack of Product Diversity for Homopiperidine Derivatives. We had noted at the outset that these reaction studies had produced 18 different zeolite structures (including the clathrate products arising from use of TMA+ cations). In making and studying the three homopiperidine derivatives in the nine synthesis reactions given to each SDA, only two zeolite products were found. Reactions produced **MTW** or **BEA**, and the occasional layered or unknown (and likely layered) result. If we remove the TMA+ reaction from consideration, then for the 24 remaining reactions, **MTW** appears as product in 12 of them and **BEA** in 7 (**BEC** is found in one of the Ge reactions, and **MOR** is the only product in all three reactions with high Na^+ content). In an earlier study, we had shown the transition from **BEA** to **MTW** as the lattice substitution diminished.[42] There was some indication that **MTW** may have been growing from a **BEA** crystal. The pore down **MTW** axis *c* (and there is only one pore) is the same as one of the pores found in **BEA**. In this study, the **MTW** is more likely in the less substituted reactions (like the near all-silica reaction in Table 4). Consistent with the earlier HF studies and effect of water contribution, the most dilute series in Table 3 also gives only **MTW**. The near all-silica reaction in Table 4, when considered on the whole, gives a range of zeolites but never **BEA** under these substitution-lean conditions.

Tropane SDA and Some Interesting Selectivities. Tropane can be thought of as also containing a seven-membered ring like homopiperidine. As part of a [3.2.1] octane ring system, the former is rigid however. There are some interesting contrasts for the two ring systems. An unusually narrow product selectivity was noted in the previous section for the use of the homopiperidine SDA. It is the only heterocycle that does not produce **MFI**, even though it is not the largest group. For some reason, it is easier for it to nucleate **MTW** and then **BEA** under other conditions. All other heterocycles have some conditions where **MFI** is the product, and, in fact, the tropane series is the best for producing **MFI** products. Clearly, the more rigid polycyclic heterocycle sits well in the cavities of **MFI** created where the channels cross. Again, in contrast to homopiperidine SDA, tropanes are the only ones that do not yield **MTW** in any reactions. Also, for a series of 27 reactions, **BEA** only appears once as a minor product. The tropane group must not fit well into the **MTW** channel, likely being slightly too large. On the other hand, the tropane SDA produced the larger 12-ring one-dimensional zeolite SSZ-31 in three reactions. Zeolite SSZ-60 (one-dimensional was also found) and SSZ-35 with large cavities were found as a product. So these other zeolites are all materials with room for the tropane SDA.

Generality of Various Zeolite Phase Formation. Another way to look at our product diversity is to capture a view of where the various zeolites are forming. Table 7 attempts to do this by contrasting the 18 zeolite products with their frequency of formation for the nine synthesis reactions studied for the 15 SDA. We have already mentioned some of the anomalies of different heterocycles not forming certain zeolite products in the preceding sections. Here, there is an effort to easily show how the inorganic chemistry can control the products. As

Table 7. A Matrix of Zeolite Formation and Reaction Type[a]

	HF reactions						ΔSi/Al		
	low H_2O	med	high	Ge added	TMA added	B added	low	med	high
TUN							•		
IMF							•		
SSZ-74	•	•					•		
STI	•	•							
MTW	•	•	•			•		•	•
BEA	•	•		•		•	•	•	
BEC				•					
MFI	•	•	•			•			•
MOR							•		
RUT					•				
IWW				•					
STF	•	•							
STO			•					•	•
SSY						•			
AST					•				
NON					•				
DOH	•								
AFX								•	

[a] For the 18 phases we encountered, some are very general (BEA and MTW can be found in six of the nine reaction types). Others are very selective to one reaction; IWW formation in Si/Ge chemistry is an example.

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(43) Lobo, R. F.; Zones, S. I.; Medrud, R. C. *Chem. Mater.* **1996**, *8*, 2409.

(44) Blasco, T.; Corma, A.; Diaz-Cabanas, M. J.; Rey, F.; Vidal-Moya, J. A.; Zicovich-Wilson, C. M. *J. Phys. Chem. B* **2002**, *106*, 2634–2642.

discussed above, for example, **IWW** and **BEC** only appear in the reaction series with Ge (reactant Si/Ge = 9). The clathrates only appear in the TMA+ series (except for the **DOH** result). Well-known zeolite phases like **MTW**, **MFI**, and **BEA** dominate the landscape of possible reaction conditions. **MTW** disappears for only the Al series with high Na content of Table 4. **BEA** appears in all reactions except the two most favoring high framework density products. **MFI** also can be found across the table, except for this same high Na^+ reaction and those with Ge. As mentioned before, the use of the C6 chain particularly favors the formation of **MFI**, but **BEA** and **BEC** replace **MFI** for the reaction with C6 chains once Ge is introduced.

Issues Concerning the SDA Orientation as Guest Molecules. It is easy to see the diquaternary ammonium compounds as extended along a chain with a predominant linear axis. In one of our earlier studies where we created SDA based upon imidazolium end groups, we did see most of the products made as one-dimensional pore host lattices. An interesting exception was the C6 diquats again making **MFI** products.[45] We actually have two issues to consider though. (1) Does the end group rotate off the linear axis in filling the zeolite pores? Casci and Shannon had argued that this occurred for the PYR-C5-PYR SDA in the **NES** (NU-87) zeolite product made in a gallosilicate synthesis. In NU-87, the larger regions are orthogonally arranged relative to 10-ring pore.[46]

(2) For all but our quinuclidine derivatives here (QUIN), there is also an issue of the orientation of the N^+−methyl substituent. Does it influence ring conformation for the monocyclic rings? Is its orientation the same for both N^+−Me groups? The work by Hong et al. in understanding the formation of **TUN**[22] seemed to indicate that these factors were important in understanding the guest fit into the multidimensional 10-ring product. Similarly, the structure solution for the novel multidimensional 10-ring zeolite SSZ-74 seems to show that the unusual vacancies, which are part of the structure, may have a specific interaction with N−Me PYR end groups, which interact with these periodic vacancies in the fluoride-facilitated synthesis of this new material.[26] A similar issue may be at work in stabilizing some aspects of the F anions in the structure of SSZ-75 (**STI**) described in this Article. Work is currently underway to rationalize some of the NMR and crystallographic features of this novel all-silica material. These issues of substituent orientation may emerge as important features in understanding the zeolite host selectivity during nucleation. Indeed, we have argued here the unlikely prospects of finding a structure like **TUN** or **IMF** in such high alkali cation environments. Yet they do form.

Conclusions

This study has attempted to examine the interplay of three variables in zeolite synthesis. For the SDA in diquaternary compounds, we examined the effect of charge separation by methylene chain length (C4−C6) and the effect of size and geometric constraints of the heterocyclic end groups containing charged nitrogen. The studies sought understanding of what further opportunities might be found, after the discoveries of three novel multidimensional 10-ring (intermediate pore) zeolites using diquaternaries built upon the *N*-methy pyrrolidine (PYR, here) heterocyclic end group. The zeolites TNU-9, IM-5, and SSZ-74 had all been found with chain lengths of C4−6, respectively. The PYR was the smallest heterocycle employed. Increasing the size of head groups did not result in the finding of other novel zeolite structures, although some new synthesis conditions of interest were found (**SSY**).

The third variable in the study was the inorganic context in which the trial use of the SDA took place. We chose nine reactions where some novelty of zeolite discovery had been found in the past. These conditions could hardly be considered all inclusive as each of the nine reactions could obviously contain extensions of other variables to be tried. The proof of this assertion was demonstrated within the study where **AFX** was found in high Na^+ reactions for the PIP derivatives, but not the rigid heterocycle SDA based upon C4 tropane or quinuclidine. Yet these other two SDA had been found to be able to make this zeolite under high Na^+ conditions, albeit at lower temperatures and slightly higher hydroxide contents. So further changes in these singular synthesis conditions, against the backdrop of type and chain length of heterocycle charged nitrogen, could yield additional product diversity. A good place to start might be the experiments where layered products (which we can consider as metastable, that is, on the way to making zeolites) were collected after weeks of reactions.

Finally, some surprises were encountered as far as the effects of SDA heterocycle comparison on product diversity. We saw some interesting barriers in that homopiperidine SDA did not make any **MFI** products. Conversely, tropane SDA were quite good at producing **MFI** but did not make any **MTW**, which was heavily favored in syntheses with homopiperidine SDA. The tropane SDA did make two other one-dimensional 12-ring zeolites, with larger apertures than **MTW**, leading to the consideration that the tropane heterocycle is too large for **MTW**. These unusual zeolite selectivities for certain SDA give us hope that these results can be used to better design future diquaternary SDA for the discovery of novel high silica zeolites.

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(45) Zones, S. I.; Burton, A. W. *J. Mater. Chem.* **2005**, *15*, 4215–23.

(46) Shannon, M.; Casci, J.; Cox, P. *Proceedings of the 14th International Zeolite Conf.*; Elsevier: Amsterdam, 2004; pp 110−117.