

Polymethylated [4.1.1] Octanes Leading to Zeolite SSZ-50

Greg S. Lee and Stacey I. Zones¹

ChevronTexaco Research and Technology Center, 100 Chevron Way, Building 10, Room 2324, Richmond, 94802 California

Received October 19, 2001; in revised form February 14, 2002; accepted March 1, 2002

IN HONOR OF PROFESSOR GALEN STUCKY ON THE OCCASION OF HIS 65TH BIRTHDAY

In this communication, we report on the discovery of novel zeolite compositions, SSZ-50. The zeolite has the RTH topology but can be made over a large silica-to-alumina range including no aluminum at all. The surprising capability to produce a broad compositional range comes from the use of a single organo-cation guest molecule in the zeolite synthesis. The molecule is a specific derivative from within a family of 2-aza [4.1.1] bicyclo octanes that were prepared employing a sequence of organic synthesis steps from a starting ketone. Other cage-based zeolites like SSZ-35,-36,-39 and MTN arose from the use of the other derivatives in this series. We also comment on the tendency of a variety of polymethylated organo-cations to produce RTH, the closely related ITE, or the intergrowth structure, SSZ-36.

© 2002 Elsevier Science (USA)

INTRODUCTION

Professor Galen Stucky has been an important part of our zeolite chemical world at CRTC for over a decade. From time to time, we have had the pleasure of discussing our results on high silica aluminosilicate and boro silicate zeolites with him, either at UCSB or at technical meetings. We have always come away with some new relationships in inorganic chemistry to ponder. In our world of molecular sieve development for commercial applications in catalysis and adsorption, Prof. Stucky's group has provided a number of breakthroughs that have allowed us to reconsider what might be possible. From the earlier report that very open structures of zinc phosphates could be formed near the freezing point of water (1), through a range of mesoporous materials (2) and then on to materials developed around an important concept of "charge-balancing" (3), Galen's group has attempted to provide the greater community with not only new discoveries but the inorganic insights into how the chemistry comes about. In particular, for our research that has been actively engaged in the high silica spectrum, the lessons on charge balancing have been important. Novel materials in the gallium phosphate regime (4), to name one

¹To whom correspondence should be addressed. Fax: + 510-242-1599. E-mail: sizo@chevron.com.

area, have been successfully developed around the size and charge distribution of polyamines. In our work, we typically have many fewer charges residing in our eventual host structure, but the concept of where the counter cation charge resides remains an important one. In addition to this issue, we must also include entropy issues in organo-cation solvation (5) and favorable guest–host packing (6) as we move to the silica-rich regime for molecular sieves.

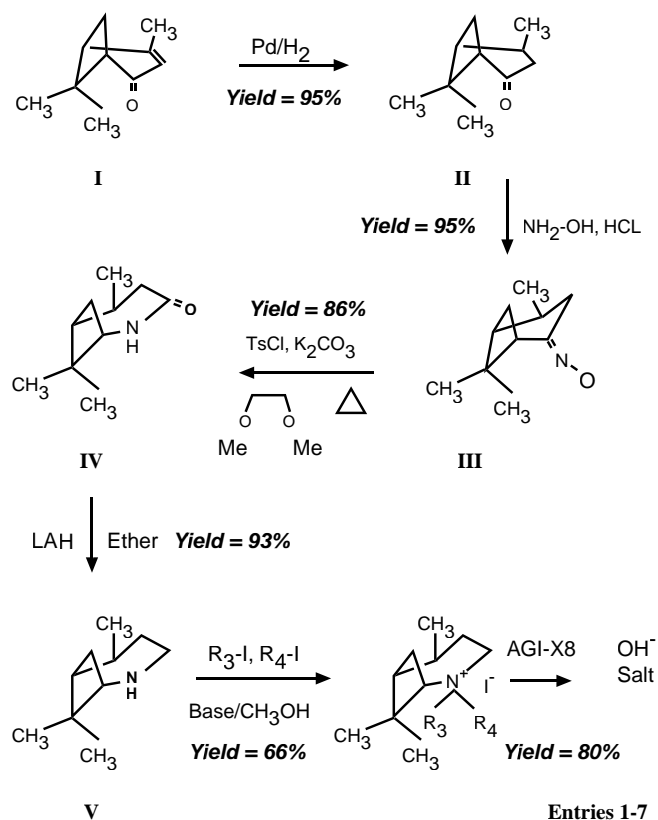
In this report, which we contribute in honoring Professor Stucky, we discuss our experimental work which has led to the discovery of a novel guest–host material, SSZ-50. We have found a particular organo-cation SDA (an abbreviation for structure-directing agent) that has a very high affinity for producing the RTH (7) structure over a large range of compositional variables. It is not at all unusual for the zeolite product to change in an experiment as the lattice substitution (for SiO₂) changes (8). So it is surprising when the experimentalist finds a guest molecule with selectivity for a single inorganic lattice structure. Professor Mark Davis had pointed out a few years ago that he believed this was the true "templating effect" in zeolite synthesis and it held for very few cases. Systems like ZSM-18 (9) and SSZ-26 (10) were produced by SDA which only crystallized these structures and no others. The great majority of organo-cations and amines can be found to produce more than one host structure as the synthesis variables are changed.

EXPERIMENTAL

Organic Chemistry

The synthesis of the organo-cation Entry 3 is outlined in Scheme 1. A number of other molecules used in the study follow a similar set of reaction steps. The molecules and their labels appear in Table 1. In general, we have made derivatives with and without a ring methyl substituent at position 5. Then for the ring nitrogen at position 2, the variations are for methyl, ethyl, mixtures or a cyclic pentamethylene as the alkylation groups produce a quaternized charge. A related derivative Entry 8, where the charged nitrogen is outside the ring, is also shown for comparison as its zeolite product selectivity is quite different.





Synthesis of N-ethyl-N-methyl-5, 7, 7-trimethyl-azonium bicyclo [4.1.1] Octane Cation (Entry 3)

Twenty grams of verbenone (Aldrich) are hydrogenated in a Parr hydrogenator to reduce the olefin. Two grams of Pd on charcoal are used as catalyst in 200 cm³ ethanol

TABLE 1
Organo-cation Used in the Study

Entry #	R ₁	R ₂	R ₃	R ₄
1.	H	H	CH ₃	CH ₃
2.	H	CH ₃	CH ₃	CH ₃
3.	H	CH ₃	CH ₃	CH ₃ CH ₂
4.	H	H	CH ₃ CH ₂	CH ₃ CH ₂
5.	H	CH ₃	CH ₃ CH ₂	CH ₃ CH ₂
6.	H	H	-(CH ₂) ₅ -	
7.	H	CH ₃	-(CH ₂) ₅ -	

(100%) and under 60 psig of hydrogen. After reaction, the mixture is passed through a short column of celite on silica, using ethanol for rinsing. Repeating this process yields additional quantities of the reduced bicyclo ketone. 72.9 g of the product is then combined with 40.34 g of hydroxylamine hydrochloride, 78.6 g of sodium acetate (tri-hydrate), 435 mL of ethanol (95%), and 218 g of water. This mixture is refluxed for 2 h. The cooled mixture is worked up by pouring into a brine solution and carrying out chloroform extractions (3 × 250 mL). The extracts are dried and stripped. Next, 88 g of this oxime is reacted with several components to yield a Beckmann rearranged product. The oxime is refluxed for 6 h (80°C) in a mixture of 153 g of tosyl chloride, 185 g of potassium carbonate, 768 mL of dimethoxy ethane, and 666 mL of water. The dimethoxy ethane is removed in a roto-evaporator. The remaining aqueous phase is extracted with chloroform (3 × 250 mL), and the latter is washed once with 300 mL of brine solution and then dried over sodium sulfate. Removing the dried solvent yields 76 g of oil, and a mixture of lactam products.

The desired product can be isolated by column separation using 2 kg of silica, slurried in *n*-hexane. The oil is loaded onto the column using 50 mL of methylene chloride. The column is run using 2% methanol in chloroform. 57.55 g of product is collected from fractions with the same TLC.

For reduction of the lactam, the following equipment is set up: a 3-neck round bottom with a cooling condenser, an addition funnel and a gas bubbler. A dry ice/acetone cold bath was used to control temperature during the reduction step. Under an inert atmosphere, 41.2 g of lithium aluminum hydride is added into 1030 mL anhydrous diethyl ether (cooled). Using the addition funnel, 57.5 g of lactam is added in 520 mL methylene chloride. The addition is intentionally slow to control heat evolution. Gradually, the reaction is allowed to take place at room temperature. Following TLC, the reaction is complete after overnight stirring at room temperature. Carefully, 41 mL of water is added with good stirring, and considerable gas evolution is seen via the bubbler. Next, 41 g of 15% NaOH is slowly added, and then finally 123.5 mL of water is added last and stirred for a while. The solids formed are collected by filtration and washed with additional methylene chloride. The combined organic washings are treated with an acidic aqueous solution to extract the protonated amines. Next, the aqueous solution is made basic and extracted with ether to collect the free amine.

12.80 g of the resulting amine is placed in an Erlenmeyer flask equipped with condenser. Eighty milliliters of methanol is used as solvent, and 19.12 g of ethyl iodide is the alkylating agent. The reaction mixture is refluxed for 48 h. The salt product is forced out with ether addition. The oil is taken up in 100 mL water, pH is adjusted to 12 and the free amine is extracted into methylene chloride. After drying and stripping, 11.14 g of monoethylated amine is recovered as

oil. This material is reacted in 60 mL of methanol with 17.56 g of methyl iodide to give the desired N, methyl, ethyl-quaternized product, Entry 3. Recrystallization from a solvent system consisting of the mixture of acetone, ethyl acetate and ether gives a solid with a melting point in the 215–220 range. The C and H NMR are correct for the desired product. The template is converted from the iodide form to the hydroxide form using BioRad AG1-X8 exchange resin. The reaction sequence is shown in Scheme 1.

Synthesis of Entry 8

Using the commercially available 2-keto, 4,4-dimethyl [3.1.1] bicycloheptane, a Leuckart reaction with dimethylformamide and formic acid can be run in a closed system at 185°C for 20 h. The reaction converts the keto group into dimethylamino functionality. The tertiary amine is recovered as oil from extraction with ether after making the reaction solution basic in water. The amine is quaternized with methyl iodide and then converted into the hydroxide salt with AG1-X8 resin (BioRad).

Zeolite Syntheses

In this study as in some of our recent studies for groups of organo-cations (11), we used a number of inorganic conditions designed to show how the SDA functioned as we changed the available amounts of aluminum or boron in the synthesis. This approach to screening is not as straightforward as asking the question about product formation as we only change the amount of a given Al source in the synthesis. Because the SDA are complex and expensive to prepare, we leverage their use by testing them in synthesis “reaction types” which have given us new chemistry in the past. Here are some of the examples of the reactions used, whose results are presented.

For SAR ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) = 10–20 2 mmol of the guest molecule as hydroxide is mixed with 0.20 g of 1 N NaOH solution and the total mass reaches 6 g with the addition of water. These mixtures are put together in the Teflon cup of a Parr 23 mL reactor. 2.5 g of Banco “N” silicate (a sodium silicate solution with 28 wt% SiO_2 and 8.9 wt% Na_2O) is added. 0.25 g of NH_4^+ Y zeolite is added as Al source. The reaction is then closed up and heated at 135°C, while being rotated on a spit in a convection-heated oven. The reactions are cooled every 3 days and checked for a pH jump (before crystallization about 11.80, increases to 12.50 or more with crystallization). Examination by SEM of the samples with pH jump are done, and if crystalline in appearance, the solid contents of the reactor are filtered and washed. The X-ray diffraction powder patterns are run to determine the phase(s).

For SAR = 30, 1 mmol of the organo-cation hydroxide is mixed with 3 g of 1N KOH solution and the total mass

reaches 11.4 g with H_2O addition. 0.088 g of Reheis F2000 aluminum hydroxide gel (53–56 wt% Al_2O_3) is dissolved in the basic solution. 0.90 g of Cabosil-M5-fumed silica (96 wt% SiO_2) is stirred. Lastly, 0.22 g of isobutylamine is added. The reactor configuration and ovens are the same as above. The reaction is heated at 170°C for 5–6 days and then followed by SEM. Studies on this type of reaction are described in Ref. [12].

For SAR = 40, 2.15 mmol of the organo-cation hydroxide is mixed with 1.43 g of 1 N NaOH solution and the total reaches 7.2 g with the addition of H_2O . The equipment is as above. 0.25 g of Na-Y zeolite is added as Al source and then 0.80 g of Cabosil M5 is blended into solution. The run conditions are 160°C and 43 RPM.

For SAR = 70, 3 mmol of organo-cation hydroxide is mixed with 0.76 g of 1 N NaOH solution and the total is brought to 7 g with H_2O . 0.25 g of Union Carbide’s LZ-210 Y zeolite (SAR = 13 and LOI is 18 wt% H_2O) and 0.75 g of Cabosil M5 are added. Reactions are run at 170°C and 43 RPM.

For SAR = 100, 2.15 mmol of organo-cation hydroxide, 1.5 g of 1 N NaOH and then H_2O reach a total mass of 11.75 g. 0.03 g of Reheis F2000 is dissolved and then 0.90 g of Cabosil M 5 is used. Reactions are carried out at 170°C and 43 RPM.

For $\text{SiO}_2/\text{B}_2\text{O}_3 = 30$, 2.25 mmol of organo-cation hydroxide reaches 4.35 g with H_2O addition. 0.095 g of sodium borate decahydrate is dissolved. 1.36 g of Dupont’s Ludox colloidal silica, AS-30 (30 wt% SiO_2) is added. The reaction is heated at 160°C without stirring.

Instrumental Analyses

The X-ray powder diffraction data were taken on a Siemens D-500 instrument. The SEM images were recorded on a Hitachi S-570 electron microscope. The NMR spectra (^1H and ^{13}C) for the organo-cations were recorded in CDCl_3 on a GE QE-300 instrument equipped with software to carry out DEPT analyses on the ^{13}C spectra. Wherever the molecular sieving or catalysis properties of SSZ-50 have been considered, the protocols used are those that we recently described for an extensive study on zeolite SSZ-42 (13).

Zeolite Structure Descriptions

A number of zeolite structures are mentioned in the text. They are mostly abbreviated by a 3-letter code assigned by the International Zeolite Association’s structure commission. The codes and framework model representations can be found at website: <http://www.iza-structure.org/databases/> 2001. We provide these framework structures in Appendix A so that the reader can refer to them during the discussion of zeolites made by various SDAs.

RESULTS AND DISCUSSION

[4.2.1] *Organo-cation (SDA) Systems*

The synthesis tactics displayed in Scheme 1 allow an entry into this rigid bicyclic family of SDA through manipulations of the ketones A and B, depending upon the presence or absence of the 5-methyl substituent. While the molecules are not large, they do provide conformational rigidity and a chance to assess the spatial contributions in building favorable guest/host nuclei en route to crystallizing molecular sieves. We have had past successes in permuting the substituent details in families of organo-cations. Previous studies have dealt with imidazoles (14), Diels-Alder products (15), ring-substituted piperidines (16), tri- and tetracyclic compounds producing zeolites SSZ-35 and 36 (11), and fused bicyclo structures (17).

The synthesis strategies have changed over time ranging from direct alkylation of basic nitrogen to conversion of cyclic ketones to basic nitrogen off the ring, to the reduction of Diels-Alder imides. In the most recent approaches, we have used the 3-sequence maneuver of converting cyclic ketones into oximes, rearrangement (Beckman) to lactams and then lithium aluminum hydride reduction to secondary amines within the ring. Finally, these are converted into quaternized compounds. In the [4.1.1] system, there may be some steric limits imposed upon which N-substituents can be obtained due to the crowding imposed by the gem dimethyls on the 4-ring part of the structure. In Table 1, we had listed a number of the SDA studied here. The resulting zeolite crystallization data are given in Table 2. The entries follow from the synthesis descriptions in the Experimental section. Some generalizations can be made about the results.

Starting with the smallest organo-cation, Entry 1, there is no 5-position methyl and both the nitrogen substituents are methyl. Looking across the entries in Table 2, most of the reaction conditions produce zeolite SSZ-35, a fascinating structure with 10-ring portals and shallow, 18-ring internal cavities leading back to the 10-ring portal. A representation

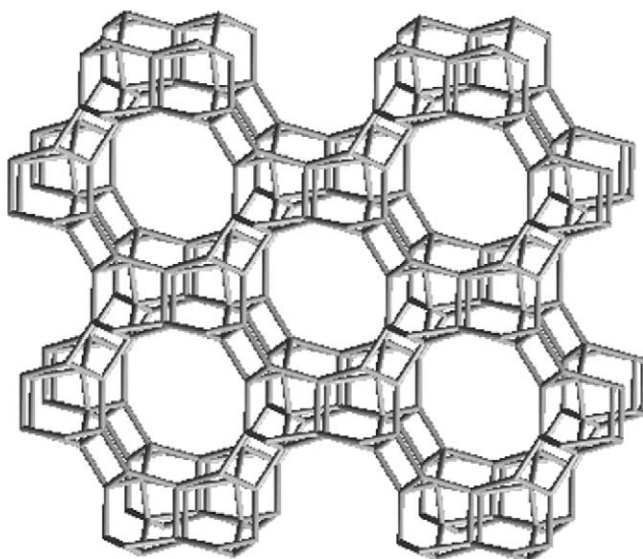


FIG. 1. Framework of STF.

of the structure is given in Fig. 1. The zeolite continues in an appropriate fashion with this type of one-dimensional channel. The structure has been described elsewhere (18). This is actually one of the larger pore products, we will see in this study, coming from the smallest SDA. A developing theme is that some of the larger SDA actually do a better job of stabilizing nuclei leading to big cavities and multi-dimensional, smaller portal entrances.

If a methyl group is now added to the 5-position of Entry 1, then SSZ-35 disappears as a crystallization product. The main product is now SSZ-36. SSZ-36 is a multi-dimensional 8-ring portal zeolite, that forms polymorphic mixtures of ITE and RTH phases (11). Figure 2 shows the relationship between the two pure polymorphs which form SSZ-36. As was the case for Entry 1, when the Al substitution is at its highest in the syntheses we show, SSZ-39 becomes the product. This latter zeolite is also what we call "cage-based" (11) and has 8-ring portals, leading to larger cavities.

TABLE 2
Zeolite Reaction Products from Entries 1-8

Entry #	SAR ^a = 10	30	40	70	100	SiO ₂ /B ₂ O ₃ = 40
1.	SSZ-39	Layer	SSZ-35	SSZ-35	SSZ-35	SSZ-35
2.	SSZ-39	No Product	SSZ-35	SSZ-35	SSZ-35	SSZ-35
3.	SSZ-50/ANA	SSZ-50	SSZ-50	SSZ-50	SSZ-50	RUB-13
4.	SSZ-13	SSZ-25	SSZ-36	SSZ-31	SSZ-31	No Product
5.	SSZ-36/ANA	No product	Layer	Amor.	Amor.	Layer
6.	Mordenite	Ferrierite	Beta	SSZ-31	Layer	Layer
7.	No product	Layer	Layer	Layer	Layer	No Product
8.	No product	Mordenite	ZSM-5	No Pr.	ZSM-39	ZSM-39

^aSAR = SiO₂/Al₂O₃.

Note. Amor. = Amorphous; No Pr. = No product.

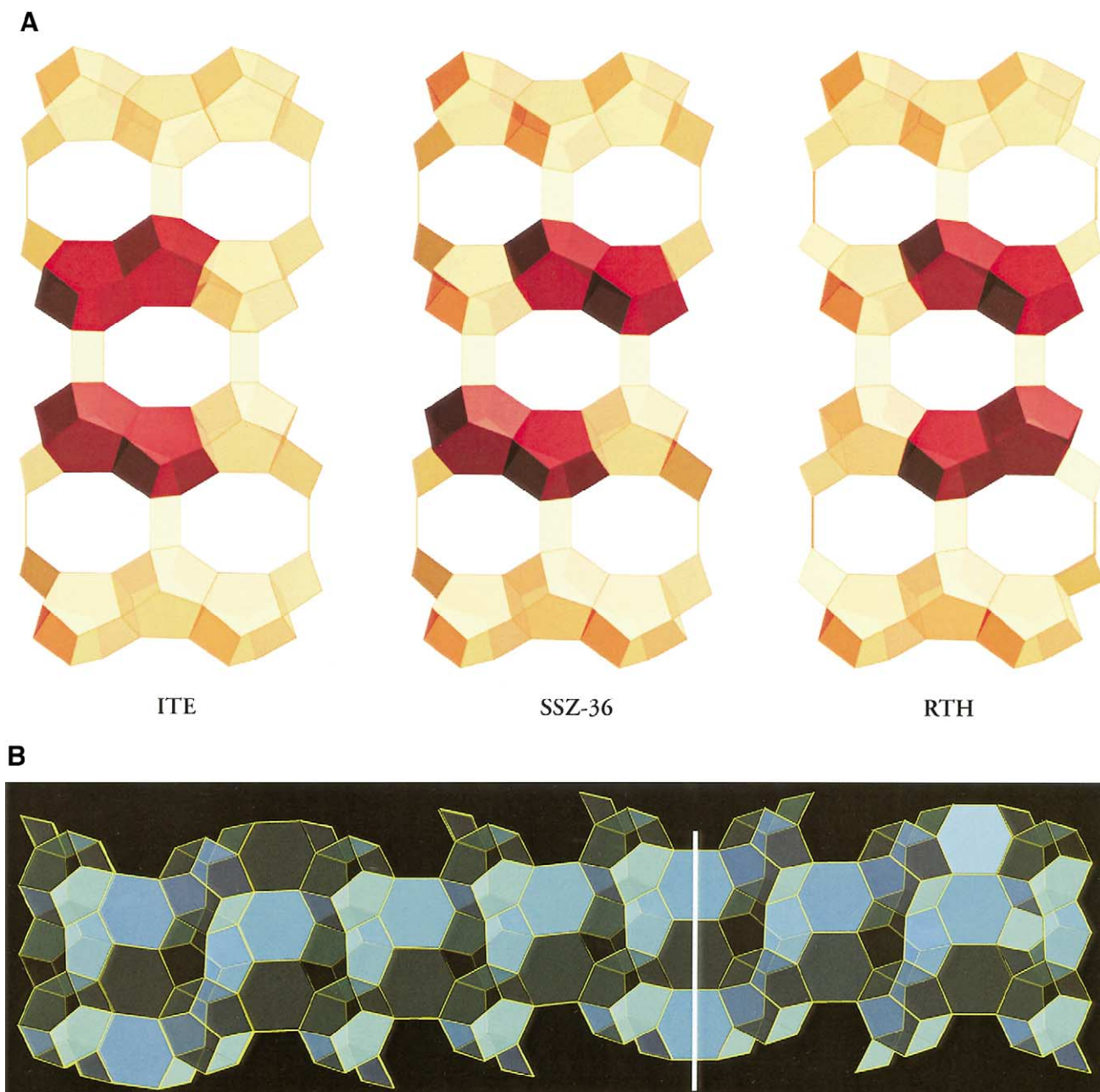


FIG. 2. (a) 3D representations of ITE, SSZ-36 and RTH highlighting difference in placement of common repeating subunits. (b) Interface of symmetry change in SSZ-36.

SSZ-39 is the aluminosilicate version of the AEI topology and as such has some relationship with chabazite-type zeolites.

Making the SDA only slightly larger than Entry 2, via introduction of an ethyl group at N + replacing a methyl, yields a very surprising SDA, capable of producing RTH with a high selectivity. A range of synthesis conditions, including borosilicate and all-silica, as well as those shown in Table 2, demonstrate the strong guest–host correlation for Entry 3 and RTH. Gies and co-workers first discovered

this topology using a mixture of a polymethylated piperidine and ethylenediamine in a borosilicate synthesis context (19). The complex amine used is shown in Fig. 3. We have patented the new compositions, resulting from the use of Entry 3, as SSZ-50 (20). The adsorption properties are the same as we had observed for the borosilicate, $0.22 \text{ cm}^3/\text{gm N}_2$, and the catalysis is selective for small-pore zeolite products (20). Even under our highest aluminum substitution reaction conditions, SSZ-50 is still crystallizing. Recall that for Entries 1 and 2, the product selectivity switched to

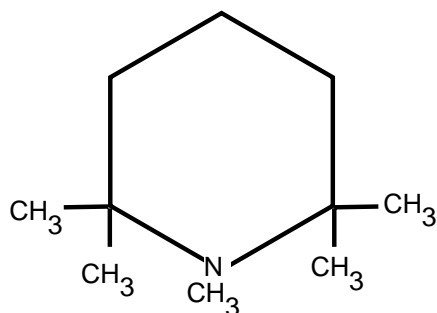


FIG. 3. Amine used in synthesizing RUB-13.

SSZ-39, which is not so here. This is another indication of the strong structure selectivity of this SDA.

At the other reaction extreme, the case with no lattice substitution, Entry 3 still has the capability to nucleate the RTH host, this time in the SiO_2/HF reaction system developed by Corma and Cambor (21). These reaction conditions typically utilize $\text{SiO}_2/\text{SDA}/\text{HF}$ ratios of 1/0.5/0.5 with $\text{H}_2\text{O}/\text{SiO}_2$ becoming one of the key reaction variables. The product selectivity can change over the range of ratios described from 3 to 20 or more. We found that Entry 3 once again had a high guest/host selectivity yielding RTH (SSZ-50) over the whole range of $\text{H}_2\text{O}/\text{SiO}_2$ values. The crystals produced are quite large and one is shown in Fig. 4. Figure 5 shows the aluminosilicate SSZ-50 for comparison. Figure 6 gives an XRD powder pattern taken at Brookhaven Beamline X7A for the all-silica

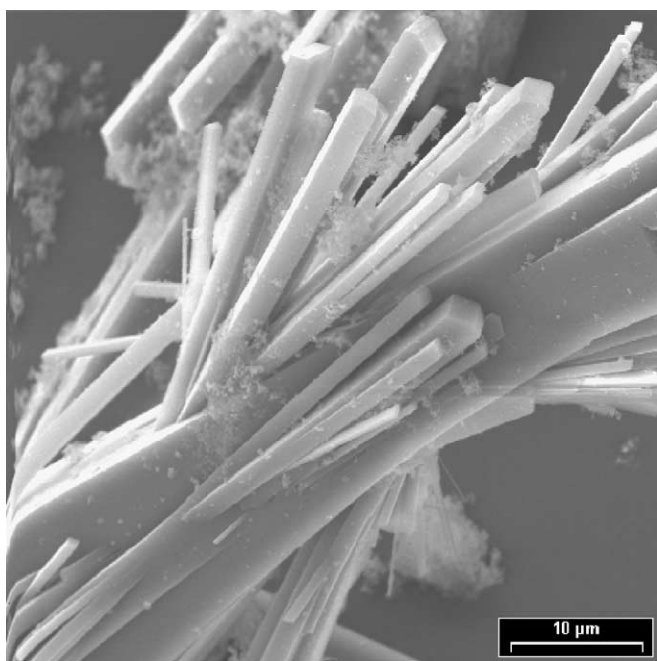


FIG. 4. SEM of all-silica SSZ-50.

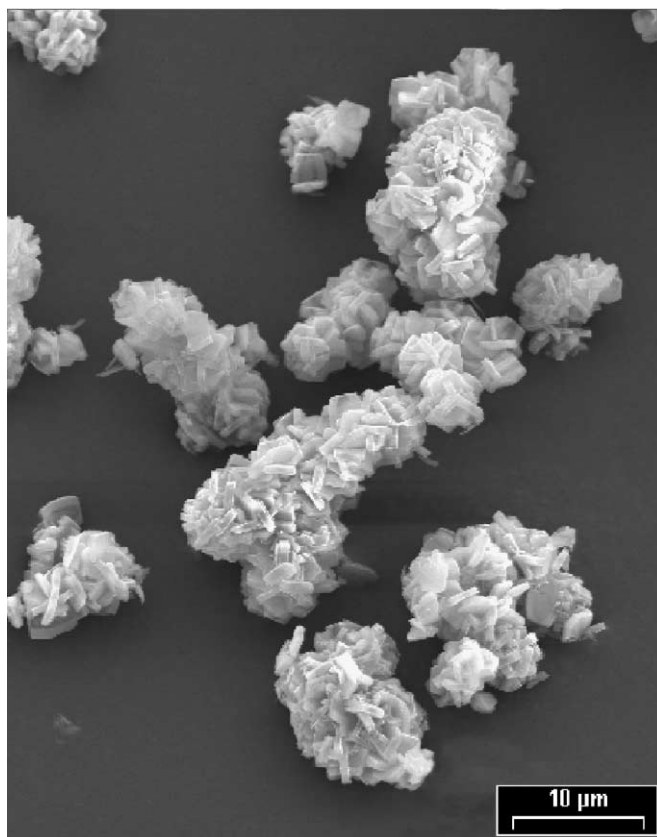


FIG. 5. SEM of aluminosilicate SSZ-50.

product, there is an evidence of the fluorine contributing to the stabilization of 5-coordinate silica (22). This type of inorganic chemical behavior has recently been demonstrated for several systems by Cambor and colleagues with preferential location of the fluorine atoms as part of 4-ring sub-units in the resulting zeolite structure (23).

Building up the size of the SDA by adding a second ethyl group, but eliminating the 5-methyl group gives Entry 4. In some sense, it is an isomeric configuration of three. Now, the selectivity for RTH is lost. In three instances, one begins to see an evidence of larger internal space available in the crystalline hosts. While one reaction yields SSZ-36 (Table 2), the less aluminum-rich reactions shift to a large pore zeolite SSZ-31 (24). This zeolite is one-dimensional with parallel apertures of $5.5 \times 8.8 \text{ \AA}$ and it is one of the few zeolites to be seen in this study which is not "cage-based" in its void volume characterization. Moving to more aluminum-rich synthesis contexts, zeolites SSZ-25 (MWW) and -13 (CHA) are then produced. These zeolites were among the first we discovered using adamantyl derivatives in high silica zeolite synthesis reactions (25,26). No product was recovered under borosilicate synthesis conditions.

A related SDA is Entry 5 where both N + substituents are ethyl and methyl, is once again present for the

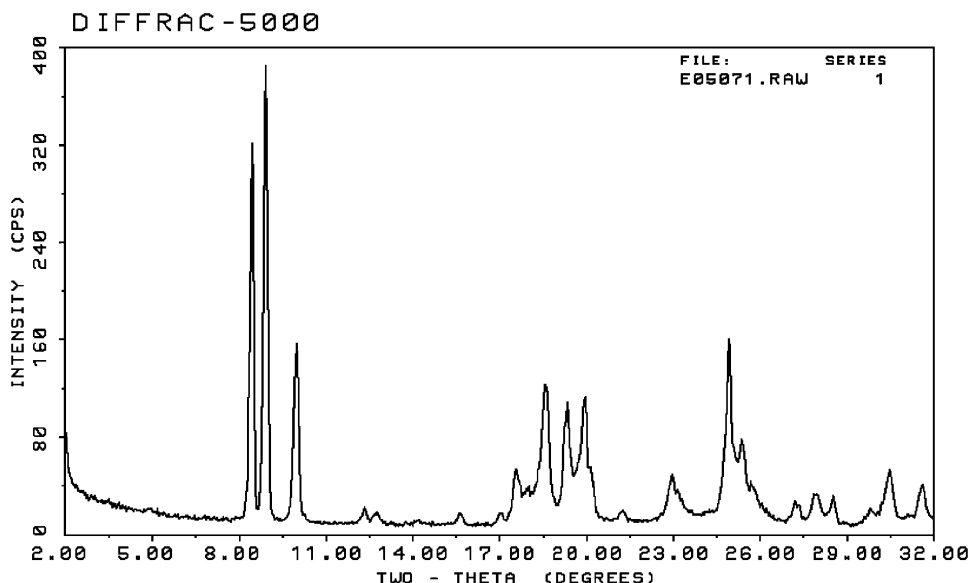


FIG. 6. XRD of SSZ-50 taken at Beamline X7A at Brookhaven National Laboratory.

position 5. The majority of the reactions we tried were unsuccessful with this SDA. At the high Al substitution, some SSZ-36 are crystallized along with analcime. The latter does not make use of the SDA. Entries 6 and 7 are the corresponding SDA, where the 2 ethyls are removed and replaced with a cyclic pentamethylene unit. Entry 6 has 5 = H and 7 has 5 = methyl. Entry 6 produces zeolite products completely unrelated to the rest of the study with zeolites like FER and MOR now being seen at the Al-rich end. These zeolites can form without a guest SDA. Beta zeolite (BEA) appears at moderate SAR values. It is usually expected to require a pore-filling guest for its formation. The slightly larger Entry 7 gives no product in any of our reaction attempts. Here, we may have a case of a molecule that is both too large and without much conformational flexibility as far as finding a good geometric fit into a potential host inorganic structure is concerned.

Entry 8 has some unusual features. Position 5 has both hydrogens replaced by methyl. The charged nitrogen is outside the ring and ring is one unit smaller. For the first time, MFI appears as a product. Also, at higher SAR, MTN crystallizes. At low SAR, MOR is found. All three events indicate likelihood for SDA decomposition during the reactions. The mordenite and MFI can form without organic guests under the conditions where they surface. The MTN is well specified by a molecule like trimethylamine. This component can easily arise from the parent Entry 8 with the loss of the group from position 2 as the SDA is heated over time. Further substantiation of SDA decomposition to yield trimethylamine, comes from the data that the final pH = 10.6; the same reaction using Entry 3 is completed at pH = 12.36.

Comparison of ITE, RTH and Guest Molecules

In the results reported in the previous section, we showed that some of the molecules studied in our derivatized [4.1.1] octane system could produce RTH (Entry 3) or SSZ-36, an intergrowth of RTH and ITE phases. None of the entries produced a pure ITE product. But we can note that the first report of ITE (ITQ-3) used a polymethylated bicyclooctane (27). This organo-cation, based upon a [3.2.1] octane is shown in Fig. 7. Distinct from ring atoms are 5 methyl substituents. Our successful candidate for producing SSZ-36 in this study is candidate 2. There are also 5 methyls. Entry 3 with 4 methyls and a single ethyl substituent gave SSZ-50 (RTH). Gies' original molecule, that produced RTH as RUB-13, contained 5 methyls (Fig. 3).

So, the question is do these polymethylated bicyclo organo-cations have a particular affinity for nucleating these closely related cavities, leading to either RTH or ITE. We have stressed the concept that van der Waals' interactions may be important in stabilizing guest/host interactions, particularly when the host is silicate and the guest possesses some inherent hydrophobicity (28). These polymethylated surfaces

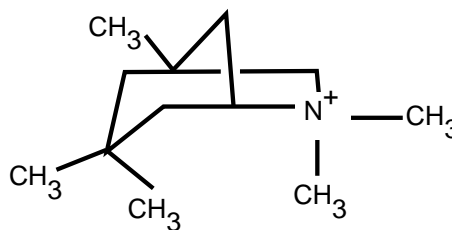


FIG. 7. [3.2.1] Octyl organo-cation used in synthesizing ITQ-3 (ITE).

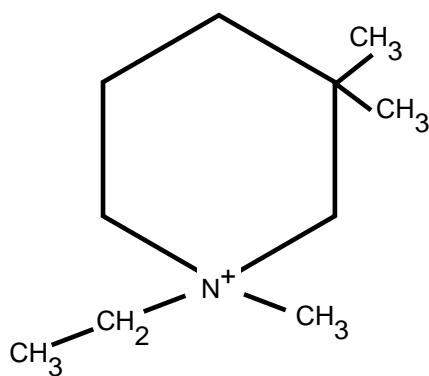


FIG. 8. Ring-methylated piperidine used in synthesizing SSZ-36.

certainly have the opportunity to provide some solvation hydrophobicity. These molecules also fall in the central region of the solvent transfer curve (water-to-chloroform) shown by Kubota and colleagues for organo-cations in high-silica zeolite synthesis (29). In that study, it was shown that a number of successful guest molecules, leading to new zeolite phases had a carbon-to-charged nitrogen ratio of 10–16. Smaller ratios did not transfer well from water and tended to stabilize less hydrophobic products like beta with high Al substitution. Molecules with values greater than 16 were almost entirely transferred to chloroform. At this point, in the zeolite synthesis, there is the possibility for a competing process: self-association of the organo-cations, leading to more likely formation of mesoporous products in crystallizing guest/host (silicate) structures. Interestingly, a number of monocyclic piperidines also worked in generating SSZ-36 (30). But again a number of these successful guest molecules had polymethylated surfaces. An example is given in Fig. 8.

Does this mean that to obtain these molecular sieve structures a polymethylated guest molecule is needed? While these types of molecules may stabilize these types of cavities well, through space filling and hydrophobicity, the answer is no. In the rather comprehensive study of molecules leading to either SSZ-35, -36 or -39, there were some derivatives, without much methylation and yet capable of making SSZ-36 (11). The C/N + ratios were probably in the

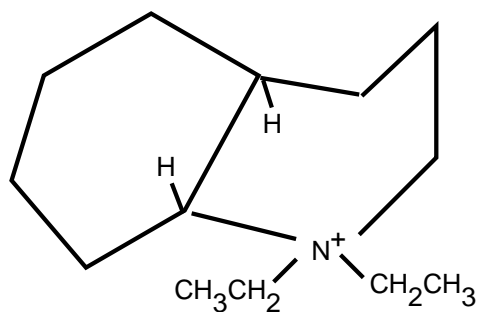


FIG. 9. [4.4.0] *trans*-decane organo-cation used in synthesizing SSZ-36.

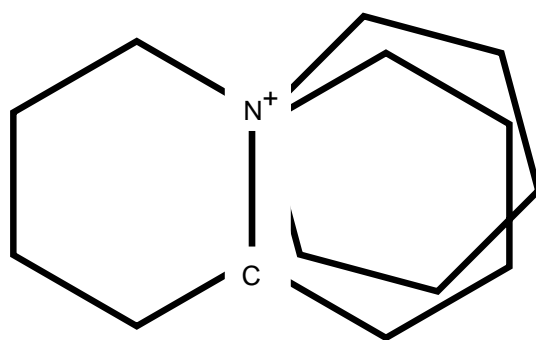


FIG. 10. [4.4.4.0] Tetradecane organo-cation used in synthesizing aluminosilicate MU-14 (ITE).

same range though the ring systems were larger than [4.1.1] octanes. Also, a bicyclo [4.4.0] decane showed a high selectivity for SSZ-36 (broad range for lattice substitution) depending upon the *cis-trans* conformation of the particular decane derivative. The successful molecule was the more successful *trans* configuration (see Fig. 9) (17). Finally, a pure-phase ITE can be made using a novel propellane (a [4.4.4.0] tetradecane) requiring no pendant nitrogen substituents. The molecule is shown in Fig. 10 and was used by the group in Mulhouse to make MU-14, a pure-phase ITE aluminosilicate (31). Under a different set of inorganic conditions, we had previously reported the ability of this propellane, but a smaller version ([3.3.3.0]), to make another cage-based product, Sigma-2 (32).

CONCLUSIONS

The use of partially hydrophobic organo-cations continues to lead to the discovery of new high silica zeolites. In this study, we show that a particular derivative of the [4.1.1] bicyclo octanes, leads to the crystallization of the zeolite with RTH topology over almost any lattice substitution range. The aluminosilicate (SSZ-50) and all-silica versions are reported for the first time. However, small changes in the organo-cation derivative lead to other zeolites being formed with SSZ-50 no longer seen, even as a minor product. We look forward to being able to demonstrate the unique fit of Entry 3 using molecular modeling approaches to assess van der Waals' interactions.

A closely related zeolite structure, ITE, can be formed as an intergrowth structure (generating SSZ-36) with RTH. A few of the derivatives in this [4.1.1] bicyclo octane show a good selectivity for producing the intergrowth structure. None were selective for the pure ITE phase. A generalized argument is made that polymethylated bicyclic organo-cations have particularly good nucleation selectivity for these "cage-based" zeolite types.

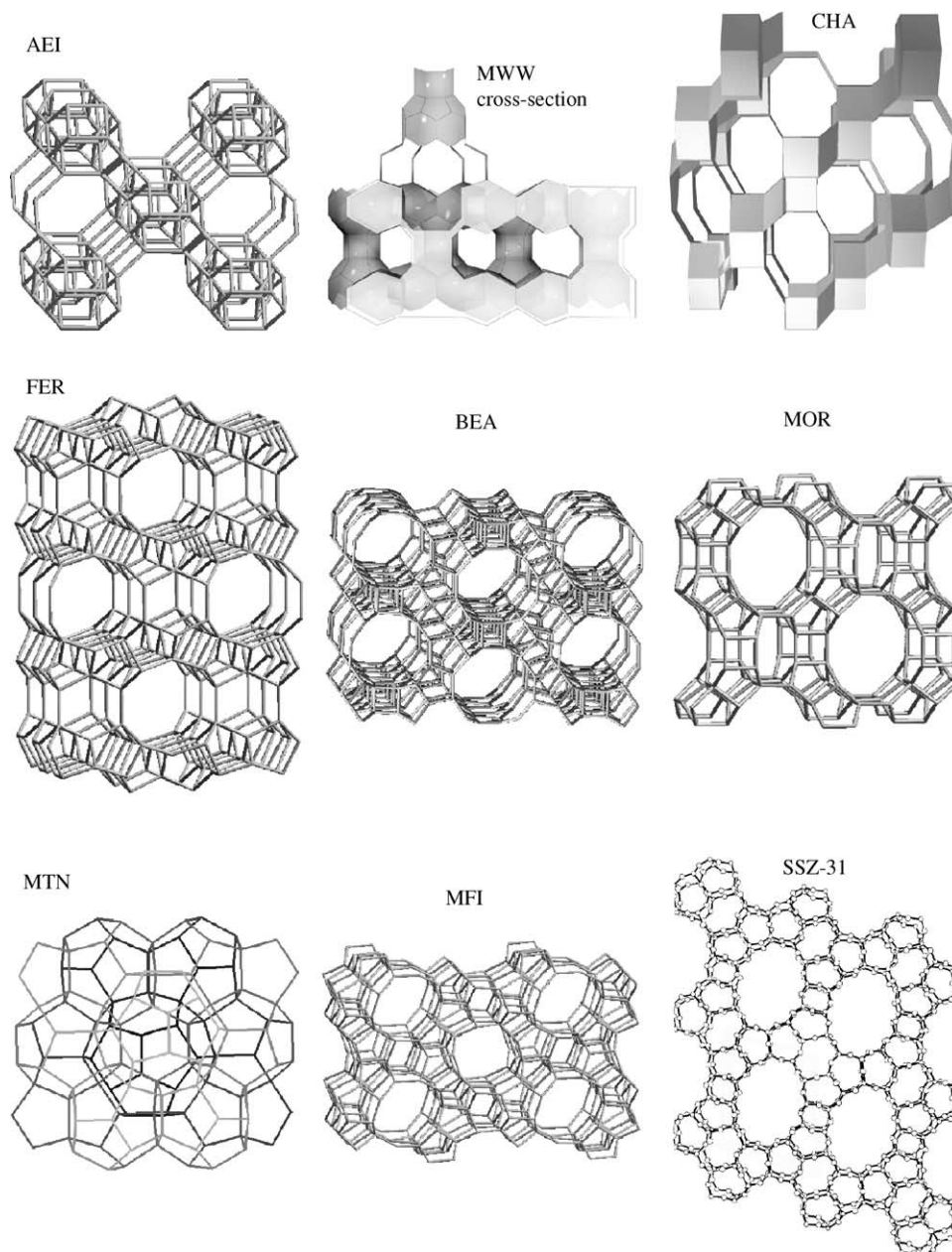
At high Al substitution conditions in the zeolite synthesis, another "cage-based" zeolite, SSZ-39, becomes a favorable product. This is the novel aluminosilicate analogue of the

previously discovered aluminum phosphate-based structure, ALPO-18 (AEI). SSZ-39 was specified by the smallest two derivatives in our [4.1.1] bicyclo octane series. It can also be made by other polymethylated bicyclo compounds like the [3.2.1] octane shown in Fig. 7.

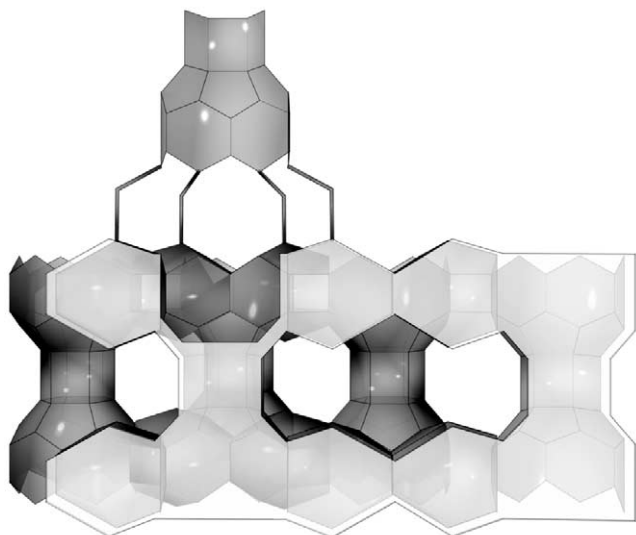
New zeolites will continue to be found by the trial-and-error application of new families of partially hydrophobic organo-cations introduced into high silica zeolite syntheses. A recent example is the description of the synthesis of new zeolites SSZ-53 and -55, reported by Elomari (33). On the other hand, the use of smaller, more hydrophilic guest

molecules will lead to a greater array of novel guest/host inorganic lattice structures. These systems will be more consistent with Stucky's charge-balancing approach to new material synthesis. The next challenge will be to remove the guest molecules in a manner leading to stable inorganic porous lattice structures. This problem will be complex due to the opportunity for many of the metal oxides employed to achieve coordination numbers higher than 4 in the initial crystallization.

APPENDIX A



APPENDIX A—Continued.



ACKNOWLEDGMENTS

We thank several members of the ChevronTexaco research staff at Richmond, CA for their contributions. The Brookhaven Beamline X7A data were collected and analyzed by Dr. R.C. Medrud and Mr. Ken Ong. Mr. Tom Rea and Mr. LunTeh Yuen collected the microscopy data. Prof. Herman Gies (Bochum University, Germany) was kind enough to look at the samples made from the all-silica HF route and communicate his preliminary NMR results to us. Kelly Harvey and Scott Harvey are thanked for the artistic rendering of the zeolite phases. Dr. Allen Burton also contributed in the SSZ-36 model representation.

REFERENCES

- W. T. A. Harrison, T. E. Gier, G. D. Stucky, R. W. Broach, and R. A. Bedard, *Chem. Mater.* **8**(1), 145 (1996).
- Y. Sakamoto, M. Kaneda, O. Terasaki, D. Y. Zhao, J. M. Kim, G. D. Stucky, H. J. Shin, and R. Ryoo, *Nature* **408**(6811), 449 (2000).
- P. Feng, X. Bu, and G. D. Stucky, *Nature* **338**(6644), 739 (1997).
- S. J. Weigel, S. C. Weston, A. K. Cheetham, and G. D. Stucky, *Chem. Mater.* **9**(6), 1293 (1997).
- P. Piccione, Ph.D. Thesis, Caltech, Department of Chemical Engineering, 2001.
- M. E. Davis and S. I. Zones, in "Synthesis of Porous Materials" (M. L. Occelli and H. Kessler, Eds.), pp. 1–34, Marcel Dekker, New York, 1997.
- S. Vortmans, B. Marler, H. Gies, P. Daniels, and I. Dierdorf, in "Zeolite Science 1994: Recent Progress and Discussions" (H. G. Karge and J. Weitkamp, Eds), 262pp. Elsevier, Amsterdam, 1995.
- S. I. Zones, Y. Nakagawa, Lun-Teh Yuen, and T. V. Harris, *J. Am. Chem. Soc.* **118**, 7558 (1996).
- K. D. Schmitt and G. J. Kennedy, *Zeolites* **14**, 635 (1994).
- S. I. Zones and D. S. Santilli in "Proceedings of the 9th International Zeolite Conference" (R. von Ballmoos, J. B. Higgins, and M. M. Treacy Eds), 177pp. Butterworths-Heinemann, London, 1993.
- P. Wagner, Y. Nakagawa, G. S. Lee, S.-J. Hwang, R. C. Medrud, M. E. Davis, and S. I. Zones, *J. Am. Chem. Soc.* **122**(2), 263 (2000).
- S. I. Zones and S.-J. Hwang, *Chem. Mater.* 313–321 (2002).
- C. Y. Chen, Larry W. Finger, R. C. Medrud, C. L. Kibby, P. A. Crozier, I. Y. Chan, T. V. Harris, L. W. Beck, and S. I. Zones, *Chem. Eur. J.* **4**(7), 1312–1323 (1998).
- S. I. Zones, *Zeolites* **9**, 458–467 (1989).
- Y. Nakagawa and S. I. Zones in "Molecular Sieves" (M. L. Occelli and H. Kessler, Eds), 222pp. Marcel Dekker, New York, 1992.
- Y. Nakagawa, G. S. Lee, T. V. Harris, Lun-Teh Yuen, and S. I. Zones, *Microporous Mesoporous Mater.* **22**, 69–85 (1998).
- G. S. Lee, S.-J. Hwang, Y. Nakagawa, M. E. Davis, P. Wagner, L. W. Beck, and S. I. Zones, *J. Am. Chem. Soc.* 2002, in press.
- P. Wagner, S. I. Zones, R. C. Medrud, and M. E. Davis, *Angew. Chem. Int. Ed. Engl.* **38**, 1269–1272 (1999).
- S. Vortmann S., B. Marler, H. Gies, and P. Daniels, *Microporous Mater.* **4**, 11–121 (1995).
- G. S. Lee and S. I. Zones, Eur. Pat Appl. # WO 01/44109 A1 6/2001.
- M. A. Cambor, A. Corma, and L. A. Villaescusa, *Chem. Commun.* 749 (1997).
- H. Gies, Personal communication based upon studies of the all-silica material described here.
- M. A. Cambor, P. A. Barrett, M. O. Diaz-Cabanas, L. A. Villaescusa, M. Puche, T. Boix, E. Perez, and H. Koller, *Microporous Mesoporous Mater.* **48**, 11–22 (2001).
- R. F. Lobo, M. Tsapatsis, C. C. Freyhardt, I. Y. Chan, C. Y. Chen, S. I. Zones, and M. E. Davis, *J. Am. Chem. Soc.* **119**, 3732–3744 (1997).
- S. I. Zones, Y. Nakagawa, G. S. Lee, C. Y. Chen, and Lun-Teh Yuen, *Microporous Mesoporous Mater.* **21**, 199–211 (1998).
- S. I. Zones, R. A. Van Nordstrand, D. S. Santilli, D. M. Wilson, Lun-Teh Yuen, and L. D. Scampavia, in "Zeolites: Facts Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds), 299pp. Elsevier, Amsterdam, 1989.
- M. A. Cambor, A. Corma, P. Lightfoot, L. A. Villaescusa, and P. A. Wright, *Angew. Chem. Int. Ed. Engl.* **36**, 2659 (1997).
- T. V. Harris and S. I. Zones, in "Zeolite Science 1994 and Beyond" (H. G. Karge and J. Weitkamp, Eds), Vol. A, pp. 29–36. Elsevier, Amsterdam, 1994.
- Y. Kubota, M. M. Helmkamp, S. I. Zones, and M. E. Davis, *Microporous Mater.* **6**, 213–229 (1996).
- Y. Nakagawa, G. S. Lee, S. D. Toto, and S. I. Zones, US patent 5,939,044, 1999.
- V. Valtchev, J.-L. Paillaud, T. Lefebvre, D. Le Nouen, and H. Kessler, *Microporous Mesoporous Mater.* **38**, 177–185 (2000).
- S. I. Zones, M. M. Olmstead, and D. S. Santilli, *J. Am. Chem. Soc.* **114**(11), 4195 (1992).
- S. Elomari and S. I. Zones, The Synthesis and Characterization of Novel Zeolites SSZ-53 and 55 in "Proceedings of the 13th International Zeolite Conference," Montpellier, (F. Fajula and F. DiRenzo Eds). Elsevier, Amsterdam, 2001.