

Synthesis of High Silica Zeolites Using a Mixed Quaternary Ammonium Cation, Amine Approach: Discovery of Zeolite SSZ-47

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A zeolite synthesis system is described in which a minor amount of structure-directing agent is used to specify the nucleation product, and then a larger amount of an amine is used to provide both pore filling and basicity capacities in the synthesis. A number of syntheses of different zeolite products are described for reactions in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ range of 35, which are conditions which yield high silica zeolites but are toward the more catalytically active end of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ spectrum. There are a number of cost-saving benefits described for this synthesis route including reduced structure-directing agent cost, waste stream cleanup costs, and time in reactor and reagent flexibility. Some details of the reaction are shown for this route to zeolite SSZ-25. The reaction was also used as a way to screen a new structure-directing agent, and zeolite SSZ-47 was discovered in this manner. The surprisingly high inorganic cation uptake in some of the zeolite products also may indicate that they play an important role in the stabilization and growth of structure-directing agent determined nuclei, particularly in syntheses under low structure-directing agent concentrations.

Introduction

High silica zeolites remain important in the search for new process technology in heterogeneous catalysis. These materials offer the attraction of less corrosive solid acid catalysis as well as ease of separation of catalyst and product. So there is an incentive to find new zeolite structures that are capable of greater product selectivity. Many of the newer structures reported require organic molecules as guests toward an inorganic host, with the combination that develops a molecular assembly arrangement during the nucleation and crystallization stages of zeolite synthesis. While there is ample evidence that there is a very good correlation between the spatial geometry of the guest molecules and the resulting void regions of the high silica zeolite host lattice,^{1,2} the guest/host product does not appear to be simply a thermodynamic result. A variety of high silica zeolites do not seem to show great differences in their enthalpies of formation even though they are structurally dissimilar.³ Recent studies on the entropic contributions also continue this trend.⁴

To the extent that the zeolite-growing complex may arise from kinetic events, we have been interested in

changing the context in which our organo-cation guest molecules operate. In this regard, some new zeolite structures may be realized, as exemplified by the use of calcined boron beta zeolite as a synthesis source of both silica and boron.⁵

However, even as new structures are being discovered, the challenges in commercially producing them keep growing. This is in large part due to the combination of the need to fill void regions in the growing crystal, the necessity to use a larger amount of structure-directing agent (SDA) to also provide some of the OH contribution, and then the mass of the SDA providing the space-filling selectivities. Figure 1 gives a rough look at some of the increasingly larger SDAs used in the last few decades, resulting in the crystallization of novel and unusual phases such as SSZ-23 with 9 and 7 rings, SSZ-26 with both a 10- and 12-ring channel system, SSZ-35 with a 10-ring system opening into 18-ring cavities, and the new 14-ring structures (UTD-1 and CIT-5). All of these required some sizable SDAs in the success of their original crystallizations. Details about the structures of these and most other zeolites described in this paper can be found at: www.zeolites.ethz.ch/Zeolites/StdAtlas.htm.

Table 1 contrasts the amount of SDA used in preparations and the actual amount found in the products. Both numbers are relative to 5 equiv of SiO_2 . The examples are taken from the literature, which are

* To whom correspondence should be addressed.

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

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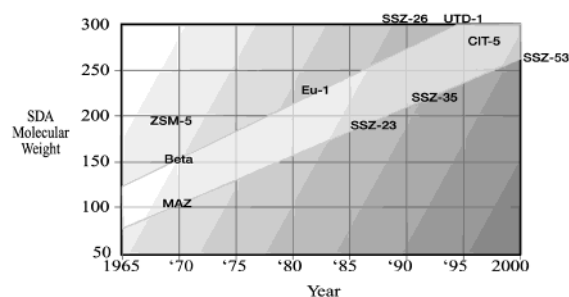


Figure 1. A representation of a general trend toward larger organo-cations (SDA) used in the discovery of new high silica zeolites. The first three materials listed in the vicinity of 1970 came from the commercially available tetramethyl, tetraethyl, and tetrapropylammonium cations, yielding TMA-omega, beta, and ZSM-5, respectively.

Table 1. Rough Calculations of SDA Use and Cost in Zeolite Synthesis

zeolites	reactants		product
ZSM-12	1 SDA	5 SiO ₂	0.25
ZSM-23	2.3	5 SiO ₂	0.25
MCM-22	2.5	5 SiO ₂	0.40
SSZ-25	1	5 SiO ₂	0.40
ZSM-22	1.5	5 SiO ₂	0.20
ECR-18	1.5	5 SiO ₂	0.15
EU-1	0.6	5 SiO ₂	0.30
SSZ-13	1	5 SiO ₂	0.50

Scheme 1. Rough Calculations of SDA Use and Cost in Zeolite Synthesis (Continued)

- ① SDA/SiO₂ = 0.20 is assumed from Table 1.
Yield Efficiency ~ 90%, experimentally observed and based upon SiO₂
- ② MW: SiO₂ = 60
SDA₁ = 100 (for Amines, TMA)
SDA₂ = 200 (for Diquats, Bigger Quat)
- ③ Reactant SDA/SiO₂ Mass Ratios: 0.33 to 0.66
lb/lb(SDA used/SiO₂ product) to Product: 0.37 to 0.73
- ④ Down-the-Line Factors Which Affect Zeolite Production Cost
 - Run Concentration • Run Time • Filtration
 - Ion-Exchange • Waste: Streams and Incineration

mostly from the International Zeolite Association publication from their Synthesis Commission, dealing with verified procedures for zeolite synthesis.⁶ Scheme 1 projects rough calculations as to how much SDA would be required to produce some of the sieves; these calculations are factored in by using a pound/pound comparison after yields and so on. It is easy to see that as much as 50% of the product's final mass might be required for the SDA, with only a tenth of that quantity appearing in the final product mass. Then, there would also be the additional cost of synthesizing some of these complex SDAs.

In this study, we explore the use of matching a small amount of our organo-cation with a much larger amount of a nonspecific amine. The concept used in this attempt was to have the SDA provide the initial nucleation selectivity and then hope that a cheaper, less selective molecule could provide the pore-filling aspect as the crystal continued to grow. The use of this new reaction system provides several features:

Table 2. Ratios Applied in Typical Inorganic Synthesis (with SiO₂ = 1)^a

Al/SiO ₂	0.06 ^b
amine/SiO ₂	0.22
KOH/SiO ₂	0.20
H ₂ O/SiO ₂	44
adamantyl/SiO ₂	0.06 (or less)

^a Conditions: temperature = 170 °C, rpm = 43. ^b Al source is Reheis F-2000 aluminum hydroxide gel (dried, 53 wt % Al₂O₃).

(1) There will be examples where the crystallization rate is accelerated.

(2) No organo-cation is wasted in the synthesis, thus providing commercial advantages.

(3) The amine can potentially be recovered, also offering commercial advantage.

(4) This reaction can even serve as a source for the discovery of new zeolites, and the synthesis and properties of SSZ-47 will be described.

Experimental Section

The zeolite synthesis reactions were carried out in 23 mL, Teflon-lined Parr reactors. These were loaded onto a spit built into a Blue M convection oven, heated at 170 °C. The reactors were tumbled at 43 rpm. The typical reaction ratios employed,⁷ on a molar basis (unless otherwise stated in the text), were as follows:

Organo-cation = 1, SiO₂ = 50, amine = 10, Al₂O₃ = 1.6, KOH = 10, and H₂O = 2000. In experiments where we have varied SDA/amine, the amine was held constant in the experiment, using the value shown here.

The source of silica was Cabosil M5, and aluminum was provided as hydrated aluminum hydroxide gel, Reheis F-2000 (53–56 wt % Al₂O₃). Table 2 shows the ratios relative to silica = 1, which is a mode more commonly seen in reports of zeolite syntheses. The details concerning how we have approached the characterization of the zeolite products have been described before.⁸

Results and Discussion

1. SSZ-25. We began by studying zeolite SSZ-25 (MWW type) which had originally been discovered in a synthesis where a quaternized aminoadamantane was the only organic molecule employed. Table 3 gives the results of varying the amine and the concentration of the organo-cation used in the study of the crystallization of SSZ-25. In some instances, the adamantyl-based organo-cation can even be replaced by using the free amine or the alcohol derivative of adamantane, and these structures are given in Figure 2. This can lead to an even cheaper synthesis of the desired product. It can be seen that in the absence of the adamantyl derivative, no SSZ-25 product is obtained; other zeolites are formed from the amine molecules that are present.

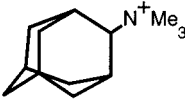
Table 3 also shows the results of experiments where different levels of quaternary organo-cation have been used, and there are also runs with and without seeding. These experiments reveal a surprising result that the synthesis actually proceeds faster with less of the organo-cation. On one hand, the synthesis requires the presence of the organo-cation to form the correct product, but less of it is better. This result was also observed

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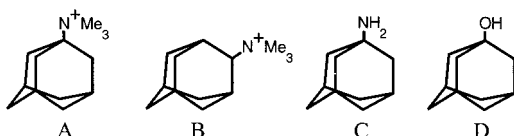
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(8) Chen, C. Y.; Finger, L. W.; Medrud, R. C.; Kibby, C. L.; Crozier, P. A.; Chan, I. Y.; Harris, T. V.; Beck, L. W.; Zones, S. I. *Chem.-Eur. J.* **1998**, *4*, 1312.

Table 3. Crystallization Rates for SSZ-25 Using Two Organic Components

				
component 1	component 2	seeds	days at temp.	product XRD
piperidine	none	no	6–7	ZSM-5
piperidine	B	no	5–6	SSZ-25
piperidine	B	yes	2–3	SSZ-25
cyclopentylamine	none	no	5–6	ZSM-5
cyclopentylamine	B	yes	3–4	SSZ-25
isobutylamine	none	no	7–10	SSZ-32 (Al-rich MTT)
isobutylamine	B	yes	2–3	SSZ-25
isobutylamine	B ^a	no	4–5	SSZ-25
isobutylamine	B ^b	no	6	SSZ-25
none	B	no	10	SSZ-25
none	B	yes	6	SSZ-25

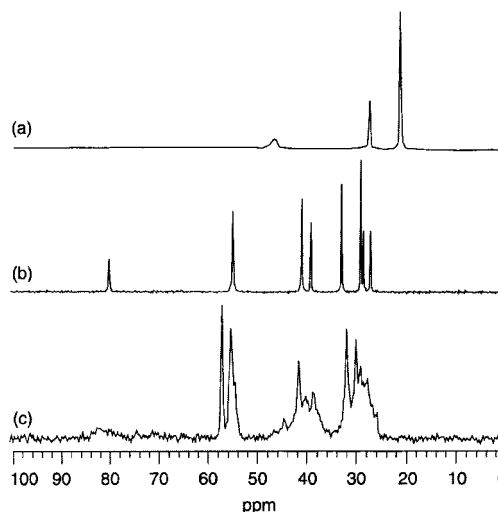
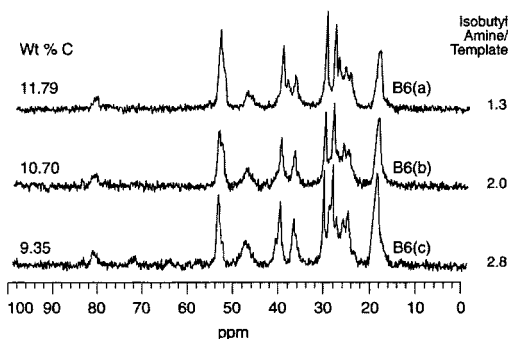
^a B/SiO₂ = 0.10. ^b B/SiO₂ = 0.20.

**Figure 2.** Adamantyl compounds A–D which can be used in the mixed template system to synthesize SSZ-25.

by Cambor and colleagues in the synthesis of the all-silica ITQ-1 using a mixture of adamantyl organo-cation and an amine.⁹ Does this indicate that even though the organo-cation is needed for nucleation (to specify the correct phase) it also ties up silicate in solution and may slow the transfer of the latter to a growing crystal? This needs to be explored. When a mixed template system (as we sometimes call this mixture of quaternized SDA and free amine combination) is being used, seeding the reaction with the desired zeolite product also helps the crystallization to occur more rapidly. The combination of using the mixed template system and seeding is shown to reduce the crystallization time, with the use of SDA B, by a factor of 3–4 times for the synthesis of SSZ-25. The replacement of SDA B with the aminoadamantane C renders the synthesis even less expensive.

We were interested in learning more of the details concerning the success of this mixed template approach and how the two organic components were being used. We decided to track their use by ¹³C MAS NMR. As a prelude, some experimental standards were gathered. Figure 3 shows NMR spectra for the quaternized isobutylamine in the solid state, the SDA B in the solid state, and spectra of B in the SSZ-25 zeolite from a synthesis where it is the only organic component employed. When the mixed template products are made, we'll need these three standards to sort out the observed spectra.

Figure 4 shows three NMR spectra for the SSZ-25 products where the amount of isobutylamine in the synthesis was kept constant but the amount of SDA B was varied. In looking at the spectra, as the amount of SDA B is decreased, one can clearly see the contribution of the isobutylamine growing larger in the recovered

**Figure 3.** ¹³C MAS NMR spectra for key compounds under study in the synthesis of SSZ-25: (a) The quaternized isobutylamine in the solid state (HCl salt). (b) The quaternized SDA B in the solid state. (c) The spectra of B within the SSZ-25 zeolite product when B is the only organic component in the synthesis.**Figure 4.** ¹³C MAS NMR spectra for a series of runs using B and isobutylamine. From B6(a) to B6(c) are runs with decreasing amounts of B in the synthesis. The ratios of isobutylamine (fixed concentration) to B are 2, 4, and 8 for a–c. The margins show the ratios of the two components in the product as determined by NMR. Also shown is the total C content for the sample.

product. On one margin of the spectra, we show the total carbon content of the products, which decreases with less SDA B in the synthesis. It can be noted that C/N⁺ is 13 for B but only 4 for the quaternized isobutylamine. On the other margin, we list the ratio of the two components as determined by integration values in these NMR spectra. Again, the increase in the isobutylamine contribution is verified.

Even though the amount of total SDA B decreases in some of the products in this trio of experiments, its representation greatly exceeds its presence in the initial synthesis. In Figure 5, a comparison of the synthesis reactant ratios of the two components and their presence in the products is made. The plotting of these sets of values, as the starting quantities are changed, nicely demonstrates the selective uptake of the SDA B. This is a trend which will be generally seen as we examine other zeolite systems. This result also is not entirely unexpected in the sense that in the limit of low SDA B (none) there is no longer a selectivity for SSZ-25 at all. So the necessity of having a small amount of SDA had been understood from results of the experiments shown

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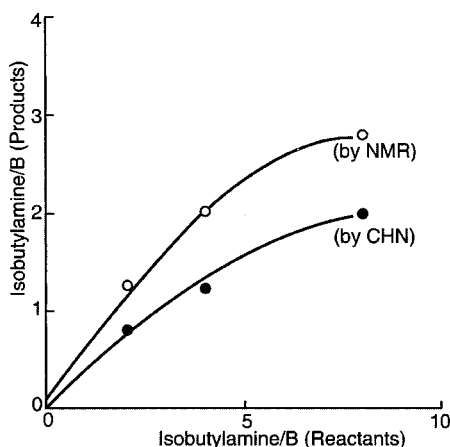
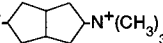
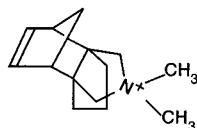

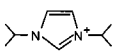
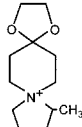
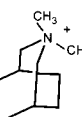


Figure 5. Plots of the results of the organic component analysis in the product vs the reactant ratios. Determinations were made by both NMR and deconvolution of C,H,N analyses. The data shows that the adamantyl compound B is preferentially incorporated into the product.

Table 4. Generalization of the Reaction

SDA	SDA/SiO ₂	Zeolite
$(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_6\text{N}^+(\text{CH}_3)_3$	0.04	EU-1
$(\text{CH}_3)_3\text{N}^+$  $\text{N}^+(\text{CH}_3)_3$	0.04	EU-1
	0.02	SSZ-35
	0.02	ZSM-11
	0.02	SSZ-32
	0.03	ZSM-12
	0.05	SSZ-28

in Table 3. Additional details concerning the synthesis of SSZ-25 from this mixed system have recently been described in another study.¹⁰

2. Flexibility of Amines and Organo-Cations Which Can Be Used. Table 4 lists a number of SDAs which were successfully employed in this mixed template synthesis. The ratio of SDA to SiO₂ can be seen to be as much as 10-fold less than those in the examples given in Table 1. The products of the reaction also show that additional pore filling would have had to occur in these syntheses, based upon a consideration of available void volumes and SDA/SiO₂ values that it translates to. This would be particularly true for the larger void volume materials such as SSZ-25, SSZ-35, and ZSM-11, all of which can be prepared via this route.

Table 5. SSZ-32 Produced Using Listed Amines

example no.	amine	amount of amine (g)
22	methylamine	0.5 ^a
23	NH ₄ OH	0.66 ^b
24	butylamine	0.20
25	<i>t</i> -butylamine	0.25
26	dipropylamine	0.22
27	isopropylamine	0.20
28	cyclopentylamine	0.26

^a 40% aqueous solution. ^b 30% aqueous solution.

¹³C MAS NMR of ZSM-11 (as made)

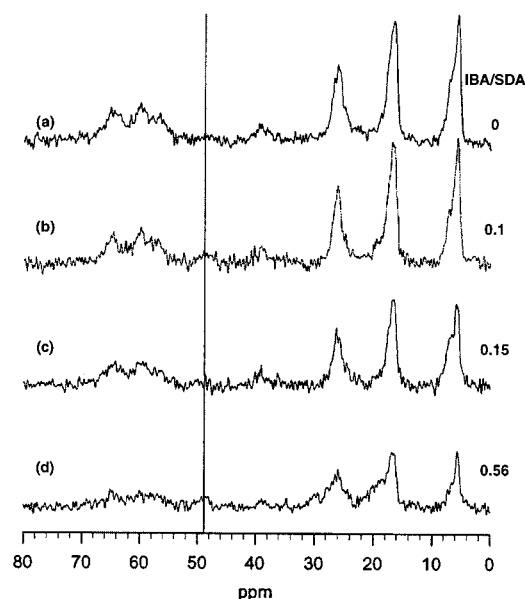


Figure 6. ¹³C MAS NMR spectra for a series of runs to make ZSM-11. The solid line is for the weak peak related to isobutylamine. The greatest to the least SDAs for a fixed isobutylamine concentration are indicated from the top to the bottom. Reactant IBA/SDA ratios are (a) 1.5, (b) 3.0, (c) 6.0, and (d) 9.0. Numbers on the right show ratio in product by NMR. IBA equals isobutylamine.

Table 5 shows that for a single system, like the synthesis of the aluminum-rich MTT zeolite SSZ-32,¹¹ a variety of amines will work as long as a small amount of the *N,N*-diisopropyl imidazolium cation is present. The flexibility concerning the amine can translate into savings in manufacture in terms of the cost and availability of the amine for use in the large scale preparations. What happens to the rest of the micropore volume? In the case of SSZ-32 crystallizing from a mixture of an organo-cation and isobutylamine, when the ratios of the two are varied, one sees an increasing amount of the amine in the product, but the SDA is still the preferred component. This can be shown by NMR or by analysis of the C/N⁺ values in the final product. If other systems are analyzed, it will be found that the organo-cation is used in the synthesis preferentially, beyond its relative concentration. Figures 6 and 7 show that there is considerably less isobutylamine found in the product system for zeolites EU-1 or ZSM-11 in comparison with the SSZ-25 reactions shown. Nonetheless, the greatest amount of isobutylamine is observed

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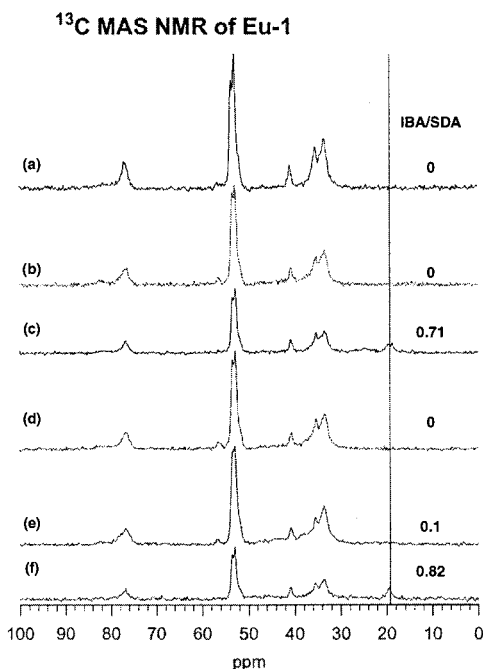


Figure 7. ^{13}C MAS NMR spectra for two different series in the production of EU-1. As in Figure 6, the SDA content decreases from the top to the bottom. The top three spectra are for a system that uses diisobutylamine as the free amine. The three spectra at the bottom are the analogous series for isobutylamine. A solid line represents methyl peak from either diisobutyl or isobutylamine. Reactant IBA/SDA ratios are (a) 1.5, (b) 3.0, (c) 6.0, (d) 1.5, (e) 3.0, and (f) 6.0. Numbers on the right are ratios in the product.

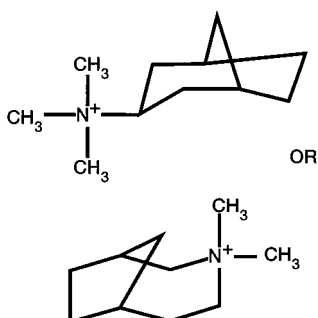


Figure 8. Two related organo-cations which produce zeolite SSZ-47 when used in conjunction with isobutylamine.


in the runs with the lowest amount of SDA in the initial synthesis mix.

3. New Zeolite SSZ-47. In the course of screening a variety of organo-cations in this particular synthesis context, a new material was discovered. It is termed SSZ-47, and it is made by using a high level of isobutylamine and a lower amount of one of a group of bicyclo-organocations.¹² One example is the organo-cation *N,N*-dimethyl-3-azoniabicyclo[4.2.1]nonane cation. This structure is shown in Figure 8 along with another SDA that can be used to make SSZ-47. It is easy to imagine that they might have similar space-filling behavior within the SSZ-47 product.

The new zeolite product, SSZ-47, can be contrasted with a sample of EU-1 also made in this synthesis approach. The X-ray powder pattern of SSZ-47 (Figure

Table 6. Characterization Data for SSZ-47

Micropore volume:	0.06	(0.15)*
$\text{SiO}_2/\text{Al}_2\text{O}_3$:	>20	(>40)*
Constraint Index (600°F):	1.33	(2.0)*

MTG (700°F)		Negligible*
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*EU-1 data

9) shows that it belongs in the structural group NES/EUO/NON, which previously had been elegantly described by the research group at ICI.¹³ The pattern of EU-1 is shown in Figure 10, and the similarities (and the few key differences in terms of absences of lines) can be seen. The properties of SSZ-47 seem to portray it as a larger pore material than EU-1. It is possible that it contains elements of an incompletely closed cavity system related to EU-1 (EUO) or NU-87 (NES). Some of the characterization comparisons to EU-1 are given in Table 6. The SSZ-47 has relatively low micropore volume, and this may be due to faulting or blocking of channels by intergrowth. The new phase can be typically more Al rich than EU-1, and from the two catalytic tests it is shown to be a larger pore zeolite than the EU-1. For example, the lower the value seen in the Constraint Index test¹⁴ the larger the pores of the zeolite. In the conversion of methanol to higher hydrocarbon products, SSZ-47 can yield a product as large as hexamethylbenzene;¹⁵ this product is not detected when EU-1 is the conversion catalyst. But again, this may be complicated by features of the actual structure. Further work is in progress to try to solve the structure of this new zeolite. Figure 11 shows that once again the isobutylamine incorporation can be seen at the lowest SDA levels used in the synthesis.

4. Role of Inorganic Cations in This Mixed Template System. Aside from the observation that both organic components can be observed within the zeolite product, we also examined the fate of the potassium cations in the system. Figure 12 shows that an inverse correlation can be found for the amount of N and K^+ found in the zeolite product for several of the zeolites studied in this reaction system. At first, it could be imagined that they each compete for aluminates sites within the framework of the zeolite. But the elemental analyses clearly show that there are examples where the amount of N/Al already exceeds 1, and that is in cases where there remains a net positive amount of K^+ as well. This could be such a case if some of the isobutylamine, found within the product, is not actually being used to charge-balance the framework sites.

In Figure 12, in the extreme point where a sample of ZSM-11 has an almost 1:1 ratio for K^+/Al , one can see that there is still a significant amount of N present (0.25 ratio). Recall that in Figure 6, even though isobutyl-

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(12) Lee, G. S.; Nakagawa, Y.; Zones, S. I. U.S. Patent 6,156,290, 2000.

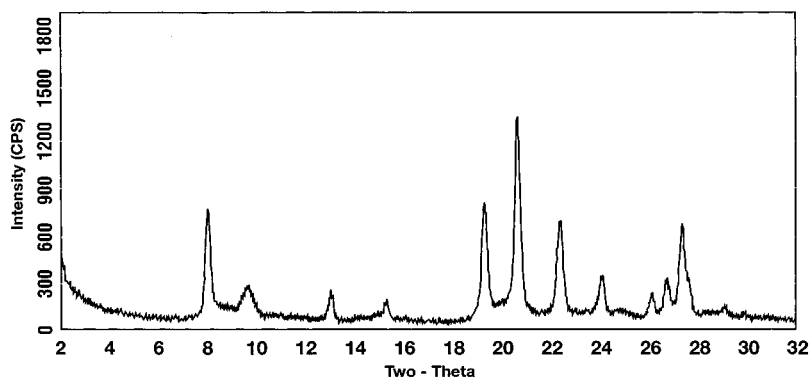


Figure 9. Powder XRD pattern for zeolite SSZ-47.

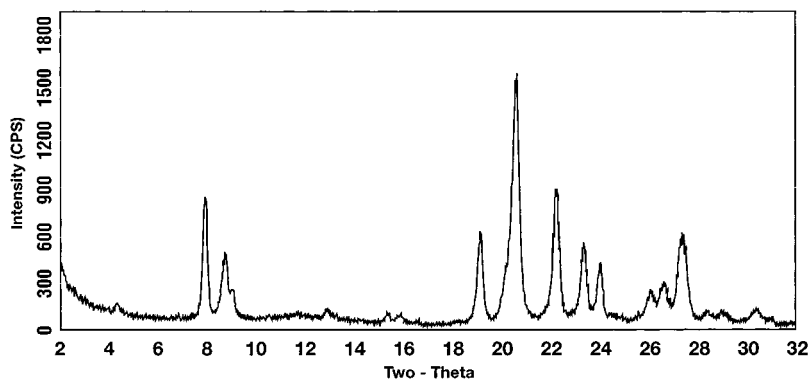


Figure 10. Powder XRD pattern for zeolite EU-1 synthesized under the same conditions as the SSZ-47, shown in Figure 9.

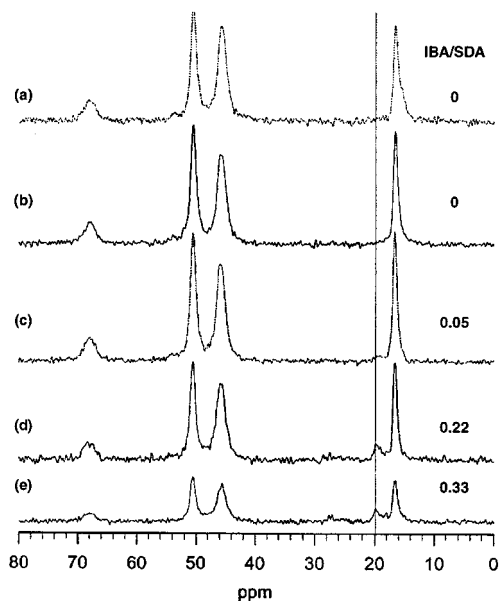


Figure 11. ^{13}C MAS NMR spectra for a series of SSZ-47 runs. Experiments are organized as in Figures 6 and 7. The solid line is for the methyl group in isobutylamine, and it disappears when enough SDA is present in the synthesis. Reactant IBA/SDA ratios are (a) 1.5, (b) 2.0, (c) 3.0, (d) 5.0, and (e) 10. Numbers on the right are ratios in the product. IBA equals isobutylamine.

amine is detectable in the NMR spectra for the reaction with the lowest amount of SDA, the signal strength is much less than that seen in Figure 4. The implication here is that the K^+ cations play a significant role on the growth of the ZSM-11 at low SDA concentrations. Figure 13 shows a generalization that the K^+ cation contents are higher in the zeolite products as the

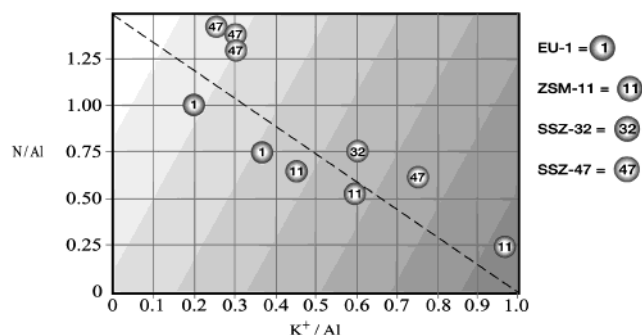


Figure 12. A plot of N^+/Al vs K^+/Al found in the zeolite products that use the mixed template synthesis route.

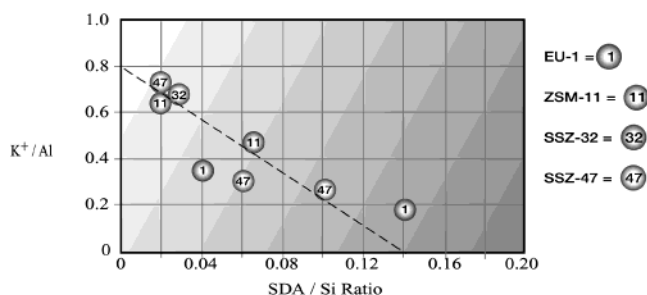


Figure 13. A plot of the same K^+/Al values vs the reactant SDA/SiO_2 ratios employed in the syntheses. Selected data from four zeolite series are shown.

starting SDA/Si ratio diminishes. Entirely SDA-free syntheses of high silica zeolite structures such as ZSM-5 have been seen before in sodium-rich synthesis contexts¹⁶ and within SAR ranges of 15–40, typically. Another concept to emerge is that if the cations also play

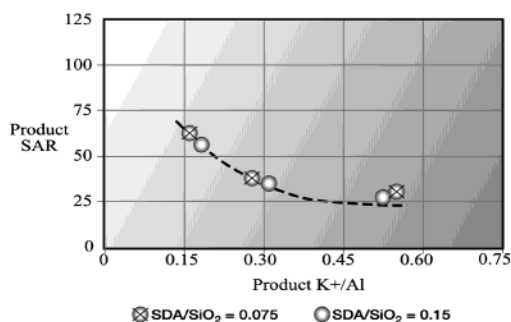


Figure 14. The SAR of the products, made in the same series of SSZ-32 runs as in Figure 15, vs product K^+/Al value. Symbols denote same series. Note that for this series (and those in Figure 15), there are two nitrogens per SDA, so $N/Al = 2$ could actually mean just a 1:1 correspondence.

an important lattice stabilization role during crystallization (if not nucleation as well, although we know that the SDA is really the key factor in the latter), then this type of synthesis may work best for high silica zeolites crystallizing in a range where Al is still part of the structure. So this reaction may not work as well at SAR of 100 or more.

Missing in Figures 12 and 13 are representatives from SSZ-25 syntheses. The values for the organic component and K^+ do not fit on these curves. Likewise, the isobutylamine content is much more pronounced in the SSZ-25 runs than in the four cases plotted in Figures 12 and 13 (see Figure 4 again for the contrast). The K^+ contents are much lower in the SSZ-25 products over the range of SDA/isobutylamine ratios explored. This difference for SSZ-25 may be related to its relatively unique zeolite structure. There are large cavities and an entirely separate 10-ring system which is more spatially hindered. It is easy to imagine the adamantyl derivatives residing in the large cavities but possibly not in the smaller channel pore filling. If that was the only role, however, our NMR spectra would always show a constant amount of isobutylamine in the product. But that is not observed, and the isobutylamine must also populate cavity regions when the SDA content is too low to account for complete pore filling of this feature in the zeolite (which accounts for about two-thirds of the total void volume). Whatever the reason, the K^+ cations seem to do a better job of crowding out isobutylamine in the other zeolite systems shown in any detail in this study (ZSM-11, EU-1, SSZ-32, SSZ-47).

What happens if we take a fixed ratio of SDA and isobutylamine and then change the Al content in the synthesis? Does this affect the role of the K^+ cations? Figure 14 shows how the K^+/Al values diminish as the product SAR value goes up for SSZ-32 (MTT) runs. In turn, the N/Al ratio continues to climb even higher (Figure 15) for these same runs (the experiments are actually for two different SDA/isobutylamine reactant values at each Al concentration run in the experiment). As the SAR value becomes higher, the SDA takes over the pore filling and its presence may even exceed the charge-balancing role needed for the framework Al.

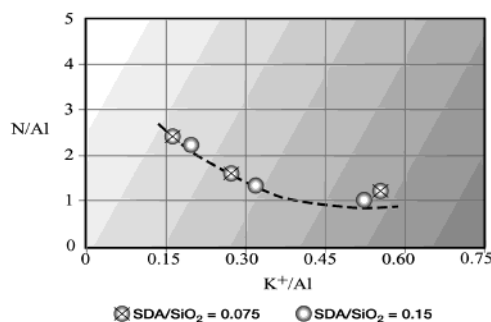


Figure 15. N/Al vs K^+/Al ratios for a series of runs to make SSZ-32 at different reactant SAR. Open circles are for $SDA/SiO_2 = 0.15$ and closed circles have the ratio at 0.075.

Conclusions

The mixed template route of zeolite synthesis, using a minor amount of the structure-specifying SDA and an excess of a smaller amine, has been shown to be a successful route toward making a number of aluminosilicate zeolites. In addition to reducing the amount of SDA required in the synthesis, which is often the most expensive component, this reaction was shown to accelerate crystallization, for example, in the synthesis of SSZ-25. Seeding further helped in the shortening of crystallization time.

The reaction system showed reagent flexibility. Specific examples discussed here were the use of nonquaternized, polar adamantyl compounds in the synthesis of SSZ-25. Different amines could be used as well. This benefits the zeolite manufacturer in terms of both cost and availability of large amounts of amine. A number of small amines including even ammonia and methylamine were shown to function in conjunction with the imidazole SDA to produce SSZ-32. The SDA is preferentially incorporated into the growing zeolite structure (as was demonstrated for SSZ-25), but this confers an additional advantage on the synthesis system as used for manufacture. The reaction can be tailored in such a way that the SDA concentration is sufficiently low so that it would be entirely used up in the growing zeolite and there would be none to treat in the reaction waste stream. The excess amine might be recycled by distillation.

An analysis of the formed zeolite product showed that there was a surprising amount of alkali cation present (potassium in these runs). There was generally an inverse function for potassium incorporation vs either of the nitrogen-containing components; ^{13}C MAS NMR experiments confirmed that at low SDA reagent levels, both organic nitrogen compounds are present in the products. The net nitrogen and potassium levels more than balance the charge requisite for aluminum in the framework. This indicates that some isobutylamine (for example) may be present playing more of a pore-filler role. To the extent that alkali cations may play any important role in the stabilization and crystal growth from nuclei in any of the zeolites studied, here, then the reaction may work best in a moderately high-silica mode. By that we mean the SiO_2/Al_2O_3 ranges of 15–100. Indeed, we have seen that this reaction allows us to produce some one-dimensional zeolites at the boundaries of their highest Al loading (e.g., MTT, TON, MTW, STF). This becomes a benefit in the attempt to produce the most catalytically active versions of these zeolites.

Finally, the reaction showed value as a screening reaction for looking at SDAs in the hopes of generating new zeolite materials. For the first time in this reaction, two SDAs were found to generate SSZ-47. This relatively Al-rich, high silica zeolite belongs in the same structural family as NES/EUO/NON, based upon a comparison of XRD data. The new material as catalyst was shown to have a larger pore behavior than EU-1, to which it seems closely related. Work continues toward solving the structure of SSZ-47.

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