

Tailoring molecular sieve properties during SDA removal via solvent extraction

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Abstract

Pure-silica molecular sieves with the MFI topology and zincosilicates, aluminosilicates, borosilicates and pure silicates with the *BEA topology are synthesized and subjected to solvent extraction treatments in an effort to remove the organic structure-directing agents (SDAs) from the micropores. For both molecular sieve topologies, the amount of SDA that can be removed by extraction is found to be dependent on the size of the SDA and the strength of interaction of the SDA with the molecular sieve framework. Furthermore, the potential for extraction of SDAs from the micropores of the material is shown to correlate well with the temperature at which the SDA combusts in thermogravimetric analyses experiments. For materials with SDAs that are small relative to the size of the micropores, the fraction of SDA that can be removed is found to correlate well with the fraction of the SDA that decomposes below 400°C in the materials studied here. SDA that burns or decomposes at temperatures exceeding this value is strongly bound to the framework via ionic charge-balancing interactions. The ease of liberation of charge-balancing tetraethylammonium (TEA) cations from the various metallosilicates is shown to be $Zn > B > Al$, following the reverse trend of known Bronsted acidity of the various types of sites. It is shown that this tightly bound SDA is removed by extraction under conditions that simultaneously hydrolyze part of the framework. For example, TEA cations charge-balancing boron atoms in the silicate framework are removed with concomitant hydrolysis of the B–O–Si bonds, releasing the tightly bound TEA cation with subsequent desorption of the boron and TEA from the molecular sieve pores. A borosilicate with the *BEA topology synthesized with TEA fluoride as an SDA is shown to be a precursor to a variety of molecular sieves as was previously demonstrated for the zincosilicate with the *BEA topology, CIT-6. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most high-silica zeolites and molecular sieves require the use of an organic structure-directing agent (SDA) in their synthesis. From an economic standpoint, this organic SDA is often the most expensive component in the synthesis. For this reason, the vast majority of commercially available

zeolites are materials that can be synthesized in the absence of an SDA. In particular, all pure-silica molecular sieves prepared by direct synthesis require the use of an organic or organometallic SDA. This requirement limits the number of pure-silica, hydrophobic molecular sieves that are available commercially. Hydrophobic molecular sieves are sought after for their excellent adsorptive and catalytic properties (high-silica aluminosilicates and titanosilicates) as well as for their increased hydrothermal stability. Hence, synthetic routes that could significantly reduce the costs associated with the production of hydrophobic molecular sieves would be useful advances.

Typically, organic SDAs are combusted at high temperatures in air to remove them from the as-synthesized molecular sieves. Hence, a way of potentially reducing the cost of zeolites that require organic SDAs in their synthesis is to develop techniques that will remove the SDA by non-destructive means, thereby potentially allowing for the recovery and reuse of the expensive SDA. One method that appears to be promising for some molecular sieves is solvent extraction. Extraction techniques for the production of porosity in molecular sieves were first introduced in conjunction with the development of M41S mesoporous molecular sieves in the early 1990s [1,2]. Subsequently, new techniques have evolved and extraction is now one of the preferred methods for the removal of surfactant SDAs from mesoporous solids. Removal of organic SDAs from microporous materials, specifically zeolites, is markedly more difficult, as the size of the SDA is generally closely related to the size of the micropores and easy diffusion of the SDA out of the pores is therefore impeded. In addition, in many cases, the SDA interacts strongly with the silicate framework via charge-balancing ionic interactions. The destruction of this interaction is generally difficult to achieve by solvent extraction.

Solvent extraction was extended to microporous silicates with the extraction of tetraethylammonium hydroxide (TEAOH) and subsequent dealumination of zeolite beta with refluxing nitric acid solutions in 1993 by Fajula and coworkers [3]. Using this treatment, nearly complete removal of the organic SDA only occurred under the harshest

conditions, with concomitant formation of significant mesoporous volume and loss of some microporosity. Under these conditions, virtually all of the aluminum in the sample is removed and silanol nests are left in their place.

TEA-based SDAs are good candidates for extraction from molecular sieves of the *BEA topology because the size of the SDA is smaller than the size of the largest micropore of the solid. It was reasoned that a beta molecular sieve containing TEA weakly complexed to the solid in the form of tetraethylammonium fluoride (TEAF) might be easily removed from the molecular sieve by solvent extraction under mild conditions. Indeed, TEAF was extracted from organic-functionalized molecular sieves in 1998 [4]. Subsequently, the technique was applied to the removal of TEAOH from zirconosilicates with the *BEA structure [5,6]. In both of these cases, the SDA is smaller than the size of the micropores and the interaction of the SDA with the oxide framework is relatively weak.

In this work, we discuss the applicability of solvent extraction as a means to remove organic SDAs from pure silicates with the MFI topology and aluminosilicates, borosilicates, zirconosilicates and pure silicates with the *BEA topology. Furthermore, we highlight the ability to tailor the properties of the molecular sieve by varying the extraction conditions such as solvent, temperature and time.

2. Experimental section

2.1. Synthesis of molecular sieves

CIT-6 (*BEA topology) was synthesized as described previously [5,6]. First, 0.133 g zinc acetate dihydrate (Fisher) and 0.048 g of lithium hydroxide (Aldrich) were dissolved in 6.2 g water. To this, 3.49 g of a 30 wt.% colloidal silica solution in water (Nissan Chemical) was added under stirring. After several hours, this clear solution (composition: 1 SiO₂/0.65 TEAOH/30 H₂O/0.05 LiOH/0.03 ZnO) was next transferred into a Teflon-lined autoclave and heated for five days statically at 150°C. The synthesis was then quenched in a water bath and the solid products were recovered by filtration.

In a typical MFI synthesis, 14 g of a hexamethylenediamine/hydrofluoric acid (pH = 7.15, 2.14 mmol/g, HMDA/HF) aqueous solution were added to 6.38 g of tetraethylorthosilicate (TEOS) dropwise with stirring. The mixture was allowed to stir overnight at room temperature to get a white slurry. Ethanol generated by the hydrolysis of the ethoxysilanes was removed along with excess water by evaporation. The final gel composition was: 1 SiO₂/1 HMDA–HF/10 H₂O. The gel was transferred to a Teflon liner and then to an autoclave. The autoclave was heated at 135°C with rotation (~60 rpm) for 40 days. The autoclave was then removed from the oven and quenched in a water bath. The products were recovered by filtration and washed with water and acetone. This synthesis was adapted from Ref. [7,8]. The sample made via this method is referred to as Si–MFI–F. Si–MFI was also synthesized at 150°C in basic media using a gel of the composition: 1 Si/0.5 Piperizine/0.1 TPABr/50 H₂O. This sample is referred to as Si–MFI–OH.

Zeolite beta was synthesized in aluminosilicate [9,10], borosilicate [9] and pure-silica [9,11] form in fluoride media using TEAF as an organic SDA. For the aluminosilicate example, 2.25 g of aluminum nitrate non-hydrate and 12.16 g of TEAF were dissolved in 13.3 g of water. Subsequently, 25.5 g of TEOS was added and the mixture was allowed to stir overnight. After adding 0.04 g pure-silica beta seeds, the slurry was rotovapped to remove ethanol and excess water. The gel (1 SiO₂/0.05 AlO_{1.5}/0.55 TEAF/7.25 H₂O) was added to a Teflon-lined autoclave and heated at 140°C with rotation for nine days. The products were recovered by filtration and washed with water and acetone. Si-Beta (denoted Si-Beta–F–Meso) was also synthesized using Si–MCM-41 as a silica source via a method already described [9].

Pure-silica beta was synthesized in OH[−] media using two additional methods. The first route employed the use of piperidinium-based SDAs [12]. To a flask containing 1.3 g of water, 30.3 g of 4,4′-trimethylenebis(1-methyl-1-benzylpiperidinium) hydroxide solution (15% in water) was added and the mixture was stirred for 5 min. 10.63 g of TEOS was then added and the contents of the flask were allowed to stir overnight. After remo-

ving the ethanol by evaporation, the gel was added to a Teflon-lined autoclave and heated for several weeks at 150°C. The products were recovered by filtration and washed with water and acetone. This sample is referred to as Si-Beta–OH. The second route utilized calcined mesoporous MCM-41 as a silica source following a procedure described in detail previously [13]. This sample is labeled Si-Beta–OH–Meso.

2.2. Organic structure-directing agent removal

SDAs were removed from the micropores of molecular sieves by extraction with aqueous acetic acid unless otherwise noted. For extraction at low temperatures, approximately 0.4 g of as-synthesized sample was contacted with 150–200 ml of aqueous acetic acid (50% water) and heated in an oil bath at 80°C for 12–24 h. After filtration and washing with water, the process was repeated. At elevated temperatures, 0.2 g of sample were contacted with 35 g of extraction solution (10 g acetic acid 25 g water) and heated in a Teflon-lined autoclave in an oven with rotation (~60 rpm) for 48 h unless otherwise noted.

2.3. Analytical methods

Nitrogen adsorption isotherms were obtained at 77 K using an Omnisorp 100 sorption apparatus operating in static mode using fixed dosing. Prior to the adsorption experiment, samples were treated under vacuum at 175°C for at least 6 h. Nitrogen adsorption capacities are reported at $P/P_0 = 0.2$. Vapor phase water adsorption isotherms were obtained on a McBain–Bakr balance after pretreatment at 175–200°C in situ. ¹¹B and ²⁷Al NMR spectra were collected on a Bruker AM 300 spectrometer equipped with a cross-polarization magic angle spinning (MAS) accessory. Samples were packed in 4 mm zirconia rotors and spun in air. The ²⁷Al (78.2 MHz) and ¹¹B (96.3 MHz) NMR spectra were obtained at a spinning speed 12 kHz (using fully hydrated samples in the case of Al). All experiments were referenced externally. Thermogravimetric analyses (TGA) were performed on DuPont 951 thermogravimetric analyzer. Samples were heated in air at a rate of

10°C/min from room temperature to 800°C. Elemental analyses were performed at Galbraith Laboratories, Inc., Knoxville Tennessee. Calcination of samples was carried out by heating in flowing nitrogen to approximately 500°C, at which point the gas flow was changed to air.

3. Results and discussion

The potential to remove organic SDAs from as-synthesized, microporous molecular sieves is governed by at least two factors: (1) the size of the SDA relative to the size of the micropores of the solid and (2) the strength of the interaction between the solid and the SDA. To illustrate the first point, we considered two cases; (i) extraction of SDAs from medium pore molecular sieves with the MFI topology and (ii) from large pore molecular sieves with the *BEA topology. Extractive treatments with aqueous acetic acid (one of the most efficient SDA extraction solvents known to date [4,5]) did not remove any organic SDA from pure-silica *BEA containing the large bis-piperidinium-based SDA at temperatures below 100°C. At higher temperatures, structural collapse of the molecular sieve occurred. In contrast, TEA based SDAs, which are relatively small compared to the size of the largest pore in *BEA zeolites could be extracted from the molecular sieve micropores with this treatment [3,4]. Similarly, the linear SDA HMDA can be effectively removed from molecular sieves with the MFI topology (see Table 1)

Table 1
Extraction of HMDA/HF from as-synthesized Si-MFI-F^a

Solvents	SDA/UC	SDA% Ex- tracted ^b
– ^c	5.35	–
Pyridine/H ₂ O	2.97	45
Methanol/H ₂ O	1.60	70
Acetic acid/H ₂ O	0.59	89
Acetic acid/pyridine/H ₂ O	0.30	94
Dimethylformamide	5.95	0
Dimethylformamide/H ₂ O	2.64	51

^a Gel composition: 1 Si/1 HMDA/0.1 NaF/17 H₂O.

^b 48 h extraction, 50% water, 135°C in an autoclave.

^c As-synthesized.

whereas the large tetrapropylammonium-based SDAs cannot.

To probe the role of the interaction strength, we considered a series of molecular sieves with the *BEA topology: a pure silicate, a borosilicate and an aluminosilicate synthesized with TEAF as the SDA (Si-Beta-F, Al-Beta-F and B-Beta-F in Table 2) and a zincosilicate synthesized with TEAOH as an SDA (CIT-6 in Table 2). TEAF can be completely removed from the pores of the pure silicate, whereas some SDA remains in materials that contain boron or aluminum in the framework (Table 2). In the case of the borosilicate, 85% of the SDA and 60% of the boron are removed by extraction at 80°C as determined by TGA and elemental analysis. This result indicates that the interaction strength between the SDA and the borosilicate is stronger than in the pure silicate. Presumably, the TEA is weakly bound to five-coordinate silicon (Si(OSi)₄F) in the pores of the pure silicate [14], whereas some of the SDA must interact with Si(OSi)₃OB sites in the borosilicate. If the remaining organic is taken to be entirely TEA⁺, it corresponds to 0.24 mmol TEA⁺/g SiO₂. This agrees very closely with the amount of B in the sample as determined by elemental analysis (0.22 mmol B/g SiO₂). This result supports the notion that strong B-TEA interactions are responsible for the incomplete removal of the SDA by solvent extraction.

For the case of aluminosilicate beta, only a small fraction of the SDA can be removed by acetic acid treatment and this fraction does not depend on the extraction temperature (unlike in the case of the borosilicate). Extraction at 80°C or 160°C removes 49% of the SDA, giving 37.5% of the porosity of the calcined sample. This result indicates that the strength of the TEA–aluminosilicate interaction is significantly stronger than the interaction in the borosilicate or silicate, as expected based on the known Bronsted acid strengths of the different metasilicates. Similar to the borosilicate beta, the amount of organic that remains after extraction mirrors the aluminum content (TEA⁺/Al ratio = 1.07). ²⁷Al MAS NMR spectra of the extracted materials indicate that all of the aluminum remains tetrahedrally coordinated after the extraction treatment (52.0 ppm,

Table 2
Synthetic and physical parameters of samples

Sample	SDA	Si/X ^a	Si/X ^b	Si/X ^c	% Extracted ^d	Porosity ^e	TGA ^f	% Loss < 400°C ^g
CIT-6	TEAOH	33.3	22.1	>500	>99	0.233 (0.237)	575	61
Si-Beta-F	TEAF	–	–	–	>99	0.239 (0.237)	375	100
Al-Beta-F	TEAF	20.0	18.2	18	49	0.085 (0.233)	680	48
B-Beta-F	TEAF	40.0	29.2	74	85	0.222 (0.241)	455	79
Si-Beta-OH	bis-PIP	–	–	–	None	None	680	68
Al-Beta-OH ^h	TEAOH	ND	ND	ND	45	ND	680	45
B-Beta-OH ⁱ	TEAOH/ DABCO	ND	15.6	ND	75	0.099 (0.250)	640	61
Si-Beta-OH- Meso	TEAOH	–	–	–	>99	0.248 (0.242)	385	100
Si-Beta-F-Meso	TEAF	–	–	–	>99	0.193 (0.204)	385	100
Si-MFI-OH	TPABr	–	–	–	None	None	450	13
Si-MFI-F	HMDA/ HF	–	–	–	98 ^j	0.136 (0.146)	325	100

ND = not determined.

^a Gel composition.

^b As-synthesized composition, X = B, Al, or Zn.

^c Composition after extraction at 80°C.

^d As determined by TGA after extraction at 80°C.

^e Porosity after extraction; porosity of the calcined sample in parentheses in cc liquid N₂/g SiO₂; P/P₀ = 0.2.

^f Temperature (°C) at which weight loss in the TGA ceases.

^g % of mass loss *x*, where 200°C < *x* < 400°C, by TGA.

^h From Ref. [3].

ⁱ Sample provided by Chevron.

^j Extraction at 135°C for two days, extraction at 80°C for 16 h, 2x gave 85% extraction and 0.095 cm³/g.

spectra not shown). This observation is in agreement with results obtained for aluminum-containing CIT-6 [5].

Comparison of the ability to extract SDAs from as-synthesized molecular sieves with the temperatures at which the SDAs combust in TGA experiments yields some interesting information. A rough estimate of the strength of the interaction of the SDA with the solid material can be obtained by noting the temperatures at which the SDAs decompose upon heating in air. Data in Table 2 indicate that SDA combustion in TGA experiments at low temperatures is potentially a positive indication of the possibility of removal of that SDA by solvent extraction. An important temperature to note in TGA experiments is approximately 400°C. It is possible to essentially completely extract the SDA from as-synthesized molecular sieves in which the SDA is completely combusted (or decomposed) at 400°C or below in TGA experiments (Si-Beta-OH-Meso, Si-Beta-F-Meso, Si-Beta-F, Si-MFI-F). In contrast, mate-

rials where the SDA is decomposed to a large extent at temperatures higher than 400°C are not amenable to SDA removal by solvent extraction.

For the molecular sieves where only a fraction of the SDA can be removed, such as B-Beta-F, Al-Beta-F, B-Beta-OH and Al-Beta-OH, comparison of the percentage of the SDA that combusts below 400°C (Table 2) with the percentage of the SDA that is removed by extraction at 80°C (Table 2) shows that the amount of extracted SDA roughly equates with the amount of SDA that combusts below 400°C in TGA experiments. This is yet another indication that 400°C appears to be a useful marker to identify the potential for extraction of SDAs from these microporous molecular sieves. However, the presence of SDA that combusts at temperatures below 400°C is not an indication that the SDA *necessarily* can be extracted. Indeed, in samples where no extraction is possible, e.g. Si-MFI-OH and Si-Beta-OH, a portion of the SDA combusts below 400°C in TGA experiments. However, in these materials,

the SDA is too large to be removed from the micropores by non-destructive means and hence no extraction is possible. The 400°C level appears to be useful for estimation of the amount of SDA that can be removed if the SDA is small relative to the size of the micropores. Note that the threshold temperature of 400°C identified in this work can potentially be influenced by factors such as TGA heating rate, TGA atmosphere (air vs. inert), sample crystal size and sample pore size (topology). However, under the conditions used here, crystal size variations of approximately an order of magnitude (Si-Beta-F synthesized with rotation 1–5 µm; Si-Beta-F synthesized statically 10–30 µm) did not affect the SDA decomposition temperature significantly. In addition, the 400°C level holds for both the large pore *BEA samples as well as the medium pore MFI materials studied.

CIT-6 is an interesting material in that it is the only material in Table 2 where essentially 100% of the SDA can be extracted at 80°C but a significant portion of the SDA combusts at temperatures above 400°C in TGA experiments. The organic that combusts at high temperatures in this zincosilicate and also in the borosilicate and aluminosilicates with the *BEA topology is assigned to TEA⁺ cations balancing Si–O–M[–] sites in the material (where M = Al, B or Zn). In the aluminosilicate Al-Beta-F, this interaction can not be destroyed by extraction under the conditions used here and hence the SDA residing at this site is fixed

under these conditions. In contrast, the strength of the Zn–TEA interaction in the *BEA framework appears to be significantly weaker than the strength of the Al–TEA complex in the same framework. In CIT-6, the TEA cation can be readily exchanged for a proton, exposing the metal site to hydrolysis in the acidic media. It is noteworthy that in all cases (zincosilicate and borosilicate in this work; aluminosilicate in Ref. [3]), after TEA is removed from the charge-balancing site in acid media the majority of the M–O–Si bonds are also hydrolyzed and the metal atom is removed from the framework.

A number of different conditions were developed to extract TEAOH from the pores of CIT-6 [5]. Data describing the characteristics of CIT-6 samples extracted in different manners are contained in Table 3. Extraction at 80°C with 1 N NH₄NO₃ removed 58% of the TEAOH, leaving the zinc in the framework. As expected, the percentage of SDA that can be removed by this technique corresponds closely with the amount of SDA that combusts below 400°C (Table 2). Hence, under conditions that do not disrupt the integrity of the framework, only the SDA that is not associated with the anionic framework sites can be removed. Contacting the material with aqueous acetic acid at any temperature tested results in removal of zinc from the framework and nearly complete extraction of TEAOH from the micropores as reported previously [5]. In agreement with

Table 3
Characteristic of CIT-6 extracted under a variety of conditions

Solvent	Temperature (°C)	Time (h)	Si/Zn ^a	% SDA removed ^b	N ₂ capacity (cm ³ /g) ^c	H ₂ O capacity (cm ³ /g) ^c
None	550 (calcined)	–	22.1	100	0.237	0.076
1 N NH ₄ NO ₃	80	72 ^d	27.5	58	0.167	ND
Aqueous acetic acid ^e	60	18, 2x	697	>90	0.233	0.077
Aqueous acetic acid ^{e,f}	135	12, 2x	546	>99	0.233	0.015
Aqueous acetic acid ^{e,f}	135	24, 2x	ND	>99	0.226	0.012
Aqueous acetic acid ^{e,f}	135	48, 2x	ND	>99	0.222	0.013
Aqueous acetic acid ^{e,f}	185	48, 1x	ND	>99	0.192	ND

ND = not determined.

^a By elemental analysis.

^b By TGA.

^c At $P/P_0 = 0.2$.

^d 12, 12, 24, 24 h, each with fresh solution.

^e 10 g acetic acid, 25 g H₂O, 0.2 g sample.

^f Autoclave, rotating at 60 rpm in an oven.

Table 4
Extraction of SDAs from as-synthesized B-Beta-F

Temperature	Extraction solution	Time	Si/X ^a	% Extracted ^b	TEA/B ^c	Porosity ^d
–	As-synthesized	–	29.2	–	0.8 ^c	–
–	Calcined	–	ND	–	–	0.241
80°C	1N NH ₄ NO ₃	12 h, 3x	ND	76	ND	0.182
80°C	1N HCl/Pyridine	16 h, 2x	43.6	86	0.65	0.230
80°C	Aqueous acetic acid	16 h, 2x	74.3	85	1.11	0.222
135°C	Aqueous acetic acid	9.5 h	88.1	82	1.64	0.208
160°C	Aqueous acetic acid	144 h	587	96	2.08	0.168

ND = not determined.

^a As determined by elemental analysis.

^b As determined by TGA.

^c Organic/B ratio after extraction assuming all organic is TEA⁺.

^d Nitrogen adsorption ($P/P_0 = 0.2$).

^e Estimation of TEA fraction: large loss from ~370–450°C.

earlier results, extraction at 60°C leaves vacancies in the framework in positions zinc previously inhabited (as determined by ²⁹Si Bloch decay (BD) NMR, spectra not shown), leaving a hydrophilic material, whereas extraction at higher temperatures fills the defects with silica from other parts of the crystal, producing a hydrophobic material. As the data in Table 3 indicate, extraction at progressively higher temperatures results in more hydrophobic materials at the expense of a small amount of porosity loss.

In Ref. [5], it was demonstrated that the zincosilicate CIT-6 can be used as a precursor to a variety of molecular sieves simply by varying the conditions used for SDA extraction. Zincosilicates, pure silicates of varying hydrophobicity, and aluminosilicates were all synthesized from a single CIT-6 precursor by employing different extraction conditions. Similar principles can be applied to the borosilicate beta described here. Data concerning extraction of TEAF from B-Beta-F under a variety of conditions are given in Table 4. It is noteworthy that removal of boron from the framework occurs concomitantly with removal of the TEA⁺ that balances it. Furthermore, after extraction, all boron that remains in the sample is tetrahedrally coordinated, as determined by ¹¹B MAS NMR (single peak at –4.6 ppm, spectrum not shown). These observations imply that it might be possible to obtain a borosilicate with a variety of Si/B compositions by using various extraction treatments. Indeed, by varying extraction conditions

such as time and temperature, the sample B-Beta-F, which has a Si/B ratio of 29.2 in the as-synthesized form, can be transformed into a porous borosilicate with a Si/B ratio higher than this (74.3 by extraction at 80°C, or >585 by extraction at 160°C). Extended extraction at 160°C results in some loss of microporosity due to structure collapse, an observation seen before in beta OFMSs synthesized in fluoride media [9] and extracted under similar conditions. Use of 1 N NH₄NO₃ as extraction solvent at 80°C results in removal of 76% of the SDA from the pores, an indication that this extraction solvent behaves similarly when treating B-Beta-F and CIT-6.

These simple extraction treatments remove the vast majority of the organic SDA allowing for possible recovery and reuse of the organic. Additionally, the treatment leaves the remaining boron tetrahedrally coordinated in framework positions. Subsequent calcination to remove the last fraction of TEA gives the completely porous borosilicate in proton form. If this borosilicate is further extracted after calcination, all of the boron can be removed and the vacancies created are healed with silicon from other parts of the crystal to make a hydrophobic pure silicate.⁵ Hence, starting with a single borosilicate beta, beta materials can be

⁵ Acetic acid treatments of calcined silicates and borosilicates have been investigated in detail and the critical role of solvent pH and temperature have been elucidated. These results will be reported in detail elsewhere [15].

made with a variety of Si/B ratios greater than the value of the starting material. Additionally, aluminosilicate, gallosilicate and pure-silica beta materials can be synthesized from this single starting material via simple extraction treatments following the model developed for CIT-6 [5]. However, CIT-6 remains a more useful and versatile precursor in that all of the SDA can be removed by extraction, removing the need for a calcination step in the synthesis of metallosilicates from this precursor.

4. Conclusions

Solvent extraction is a useful tool for the generation of porosity for a variety of molecular sieves of the *BEA structure. The ability to extract SDAs from the micropores of molecular sieves depends on both the size of the SDA relative to the size of the micropore and the strength of the interaction between the SDA and the framework. In the case of all-silica beta synthesized with TEA-based SDAs, essentially complete SDA removal can be obtained with extraction with aqueous acetic acid. In the case of borosilicates and aluminosilicates, the SDA-framework interaction is markedly stronger and only a fraction of the SDA can be removed under most conditions. Similar to the zincosilicate CIT-6 [5], B-Beta that was synthesized using TEAF is shown to be useful precursor to a variety of molecular sieves with the *BEA structure.

The potential for removing SDAs by solvent extraction can be tracked by the temperature at which the SDA burns out of the molecular sieve in TGA experiments. Organic that combusts in TGA experiments below 400°C can be extracted from the micropores of sieves when the SDA is smaller than the micropore opening in the samples studied

here. Organic that combusts above this temperature is more strongly bonded to the framework through charge-balancing interactions at the heteroatom site (B, Al, Zn) and can only be removed with concomitant hydrolysis of the Si–O–M (where M = B, Al, Zn) bonds when in acidic media.

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