Synthesis and Rietveld Refinement of the Small-Pore Zeolite SSZ-16

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Recent research efforts invested in the synthesis of new high-silica zeolites have yielded several novel materials with medium (~5.6 Å) and large (~7.2 Å) pores.[1] Examples include new zeolites with intersecting 10 and 12 member rings—i.e., pores bounded by 10 and 12 tetrahedral (T) atoms respectively—like SSZ-26,[2] NU-87,[3] SSZ-37,[4] SSZ-25,[5] MCM-22,[6] CIT-1[7] (CON), and the aluminophosphate-based DAF-1 (DFO).[8] However, except for the zeolites SSZ-28[9] (DDR) and SSZ-13[10] (CHA), to the best of our knowledge, no new high-silica zeolites with small pores have been reported. High-silica small-pore zeolites could be potentially useful for several catalytic reactions including the synthesis of dimethylamine,[11] the reduction of NO_x from combustion gases[12] and the dewaxing of fuels for octane upgrading.[1] We present here the synthesis and structural characterization using Rietveld refinement of synchrotron X-ray powder diffraction data of the zeolite SSZ-16.

SSZ-16 was first reported as being crystallized in the presence of a diquaternary ammonium compound, derived from connecting two quinuclidine units together with a polymethylene bridge (see Figure 1, molecule I).[13] A typical synthesis is carried out dissolving 1.89 g of 1,4-bis(1-azoniabicyclo[2.2.2]octane)butyl dibromide in 6 mL of H_2O and mixing with 5 g of sodium silicate solution (Banco 38.3% solids, SiO_2:Na_2O = 3.22) in a Teflon-lined Parr autoclave. A second solution containing 0.25 g of $Al_2(SO_4)_3$·18 H_2O and 0.67 g of concentrated NaOH dissolved in 6 mL of H_2O is prepared. After mixing the two solutions, the autoclave is sealed and heated statically under autogenous pressure for 6 days at 140 °C. The product is collected by filtration and

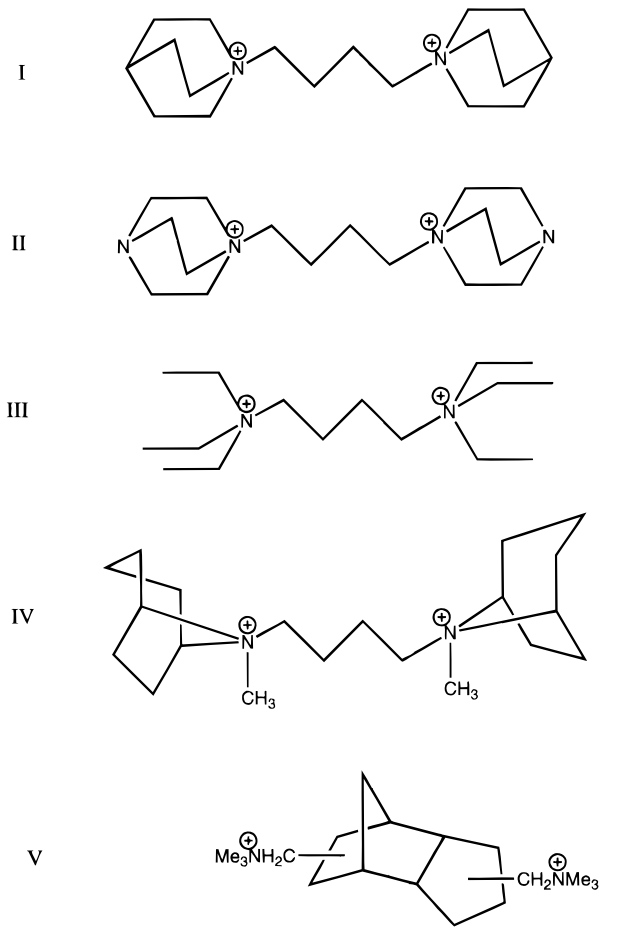

Figure 1. Structure-directing agents used for the synthesis of SSZ-16.

washed. To remove the occluded structure-directing agent, the sample was heated stepwise at 93 °C (2 h), 204 °C (2 h), 316 °C (2 h), 427 °C (2 h), and 528 °C (3 h) in a mixture of N_2/air. Chemical analysis of the calcined zeolite yields a composition of Si = 32%, Al = 5.2% and Na = 2.8% (w/w) for a Si/Al ratio near 6. Nitrogen adsorption isotherms (77 K) indicate that the product is microporous with an accessible void volume of ~0.22 cm^3g^{-1}.[13] Santilli has shown that the acid form of SSZ-16 is a very active catalyst for cracking reactions of linear hydrocarbons.[14]

The initial synthesis required a high hydroxide over silica ratio to guarantee that the SiO_2/Al_2O_3 ratio would not become too high and that other high-silica zeolites would not cocrystallize from the gel.[13] This material can be only synthesized in a restricted range of SiO_2/Al_2O_3 ratios. Lower values of OH/SiO_2 can be used if the synthesis involves the transformation of cubic P zeolite in the presence of a diquaternary ammonium compound and additional silica.[15]

Since the initial discovery of SSZ-16, several other diquaternary ammonium compounds have been found to be structure-directing agents[16,17] for the synthesis of

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this material.[18] Almost all the structure-directing agents have similar geometries and are formed of two large organic groups connected by a tetramethylene unit (see Figure 1). The optimum bridge length is four methylene units, but the material can also be synthesized using three and five methylene units. The similarity of molecules I−IV suggests that there is an optimum size of the structure-directing agent for the synthesis of SSZ-16 (vide infra).

The in-house X-ray powder diffraction (XRD) data of a calcined (i.e., organic removed) sample of SSZ-16 can be indexed using an hexagonal unit cell with approximate lattice constants $a = b = 13.6$ Å and $c = 19.7$ Å. The hexagonal symmetry and the similarity of the *a* and *b* parameters to several ABC... type zeolites (ERI, GME, OFF, CHA, etc.) suggested that this material could be part of this family of zeolites. On the basis of the similarity of the unit-cell parameters and the XRD pattern of SSZ-16 to the ones of SAPO-56[19] (AFX), it was concluded that SSZ-16 was possibly isotypic with this material. The adsorption capacity of SSZ-16, similar to the adsorption capacity of multidimensional small-pore zeolites, is also in agreement with the AFX framework topology (see below); as it is the observed catalytic properties, typical of small-pore zeolites. Systematic absences of the XRD data are in agreement with space group $P6_3/mmc$ (No. 194) which is the highest topological symmetry of SAPO-56. This result suggests, as expected, that the Al atoms are randomly distributed among the different T sites in the structure. The structure-directing agent for the synthesis of SAPO-56 (*N*,*N*,*N*′,*N*′-tetramethyl-1,6-hexanediamine) is approximately of the same dimensions than the organic molecules used for the synthesis of SSZ-16, although it can also be used for the synthesis of materials with smaller cages such as MAPSO-34 (CHA).[19]

A starting model for the Rietveld refinement[20−22] was obtained from distance−least-squares optimization (DLS-76)[23] of the atomic positions of the original model of SAPO-56, optimized using space group $P6_3/mmc$. After refinement of the background, scale factors, lattice and peak shape function parameters, atomic positions for the tetrahedral (modeled as 85% Si and 15% Al according to the chemical analysis), and oxygen atoms were then optimized. Soft geometrical constraints between tetrahedral and oxygen atoms were used at all times. Isotropic thermal parameters for the two tetrahedral (refined jointly) and seven oxygen atoms (also refined jointly) were subsequently refined. Analysis of the Fourier difference map showed a broad peak at the center of the 8-ring pores (special position $^1/_2$, $^1/_2$, $^1/_2$). Since the sample contains sodium cations occluded inside the zeolite pores, sodium cations were placed in this position and the isotropic and fractional occupancies were refined in the final stage of the refinement. The analysis of the Fourier difference map now shows a small amount of scattering density (0.44 e Å^{-3}) at the center of the double-six rings of the zeolite, and smaller residual electron density inside the gmelinite cage of the material (vide infra). However, attempts to refine additional sodium cations in these positions did not improve the residuals. In the final stage of the refinement, these sodium cations were left out of the model. The final amount of sodium found in the refinement corresponds to 72% of the amount obtained by chemical analysis, which is considered acceptable due to the small amount of sodium occluded in the sample.

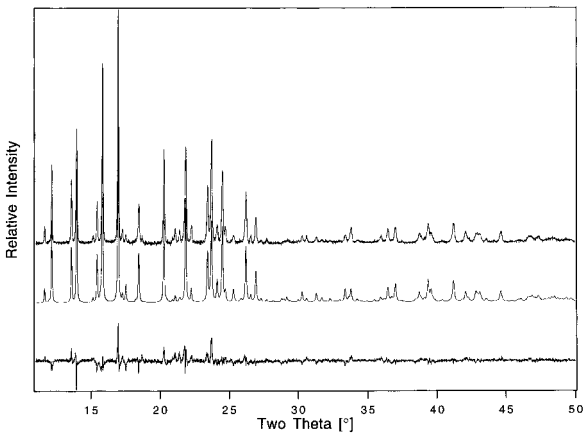

Figure 2. Observed, calculated and difference profiles (from top to bottom) of SSZ-16, $\lambda = 1.1997$ Å.

Although the residuals are low ($R_P = 7.9\%$ and $R_{WP} = 10.2\%$),[22] there is still some disagreement between the calculated XRD and the experimental pattern (in particular at 20.5, 23, and 23.5° 2θ, see Figure 2). This is probably due to the disorder of the Si/Al atoms in the tetrahedral sites and the presence of sodium cations in other positions in the crystal pores.[24] The final atomic positions and thermal parameters are presented in Table 1, and selected bond lengths and angles are presented in Table 2. All bond lengths and bond angles are within 2σ of the expected values. The unit-cell composition of SSZ-16, based on the chemical analysis,

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(21) The sample used for synchrotron XRD was treated as follows: the as-synthesized SSZ-16 was heated in air at 540 °C to remove the organic structure-directing agent occluded in the pores and was later dried at 350 °C under vacuum in a glass capillary which was then sealed. The synchrotron X-ray powder data were collected at the X7A beam line at the Synchrotron Light Source, Brookhaven National Laboratory, from 2 to 50° 2θ, using a wavelength $\lambda = 1.1997$ Å. The General Structure Analysis System (GSAS)[20] suite of programs was used for the Rietveld refinement of the synchrotron XRD data. No additional phases were detected in the XRD data, and all the peaks could be accounted for using the space group $P6_3/mmc$.

(22) Crystallographic data, details of data collection, and Rietveld refinement of SSZ-16: chemical formula $Na_{4.3}H_{2.7}[Al_{6.9}Si_{41.1}O_{96}]$; crystal system, hexagonal; space group $P6_3/mmc$, (No. 194); cell parameters $a = b = 13.6447(2)$ Å, $c = 19.7293(3)$ Å; unit-cell volume 3181 Å^3; framework density 15.1 T-atoms/1000 Å^3; data collection temperature 298 K; wavelength $\lambda = 1.1997$ Å, 2θ range 11−50°; step scan increment 0.01°, number of observations 3898, number of contributing reflections 280, number of structural parameters 24, number of profile parameters 9, $R_{WP} = 10.2\%$ and $R_P = 7.9\%$.

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(24) The large temperature factor for Na1 (Table 1) is probably due to disorder. Since there are only one or two aluminum atoms in 8-rings, it is likely that the equilibrium position for sodium is off-center. In addition, analysis of the difference pattern (Figure 2) suggests that some reflections are broader than others. A possible cause for this anisotropic broadening is the presence of faults in the structure, very common in other ABC... type zeolites. Further investigation, using electron diffraction for example, is necessary to clarify this point. Although the effect of anisotropic broadening has not been included in the refinement, the conclusion derived in this paper is not modified by this effect. Faulting in SSZ-16 seems to be much less frequent than in SAPO-56.[19] The normal probability plots of the refinement show a slope of one and an intercept of zero.

Table 1. Positional Parameters of Calcined SSZ-16 (with Standard Deviation in Parentheses)

atom[a]	site symmetry	*x*	*y*	*z*	multiplicity and Wickoff letter	occupancy factor
T1[b]	1	0.0005(31)	0.2296(4)	0.0768(3)	24*l*	1
T2[b]	1	0.3341(4)	0.4404(5)	0.1727(2)	24*l*	1
O1a	m	0.0972(6)	0.1944(12)	0.0809(8)	12*k*	1
O1b	2	0	0.2647(11)	0	12*i*	1
O1c	m	0.8723(6)	0.1277(6)	0.0898(8)	12*k*	1
O12	1	0.0193(7)	0.3313(10)	0.1277(8)	24*l*	1
O2a	m	0.3280(10)	0.4018(11)	0.25	12*j*	1
O2b	m	0.4475(6)	0.5525(6)	0.1445(7)	12*k*	1
O2c	m	0.2378(6)	0.4757(12)	0.1645(9)	12*k*	1
Na1	2/m	0.5	0.5	0.5	6*g*	0.51

[a] Isotropic temperature factors U_{iso} (Å^2): T = 0.0083(9), O = 0.0133(15), Na = 0.119 (25). [b] T = tetrahedral, Si 85% and Al 15%.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of SSZ-16

T1−O1a	1.617(3)	T2−O2a	1.603(2)
T1−O1b	1.590(3)	T2−O2b	1.636(2)
T1−O1c	1.621(3)	T2−O2c	1.617(3)
T1−O12	1.626(3)	T2−O12	1.626(2)
⟨T1−O⟩	1.614	⟨T2−O⟩	1.620
T1−O1a−T1	149.6(9)	Na1−O1b	3.19(1)
T1−O1b−T1	144.7(1)	Na1−O2b	3.11(1)
T1−O1c−T1	151.2(1)		
T1−O12−T2	148.1(6)		
T2−O2a−T2	144.3(1)		
T2−O2b−T2	140.3(1)		
T2−O2c−T2	147.9(1)		
⟨T−O−T⟩	146.6		

is $Na_{4.3}H_{2.7}[Si_{41.1}Al_{6.9}O_{96}]$ and the calculated framework density is 15.1 T-atoms nm^{-3}.

SSZ-16 is a member of the ABC... type of zeolites with the eight-layer sequence AABBCCBB.... SSZ-16 is isotypic with the aluminophosphate SAPO-56 (AFX) and the pore structure of this material is formed by two types of cages: the gmelinite cage and the large cage of $AlPO_4$-52 (AFT).[25] This cavity will be denoted AFT-cage and is illustrated in Figure 3. A series of stacked gmelinite cages run along the [0 0 1] axis of SSZ-16 and are formed by groups of layers in the pattern ·BAAB·BCCB·BAAB..., etc. These gmelinite cages are related by a 6_3-fold rotation axes along (0 0 *z*). The AFT cages are oriented along the *c* axis of the hexagonal crystal system, stacked one on top of one another and centered along the ($^1/_3$ $^2/_3$ *z*) and ($^2/_3$ $^1/_3$ *z*) axis. The cavities are formed between the layers ·ABBCCBBA· and the layers ·CBBAABBC·. Each large cavity contains nine 8-ring windows: the three top and three bottom windows are shared between the large AFT cages and the middle 8-ring windows are shared with the gmelinite-type cages. Preliminary energy minimization calculations of the structure-directing agents in the AFT cages of SSZ-16 indicate that there is a very good fit between the size of all the organic compounds of Figure 1 and the size of the cage. These calculations also show that the gmelinite cage is too small to host any of the structure-directing agents.

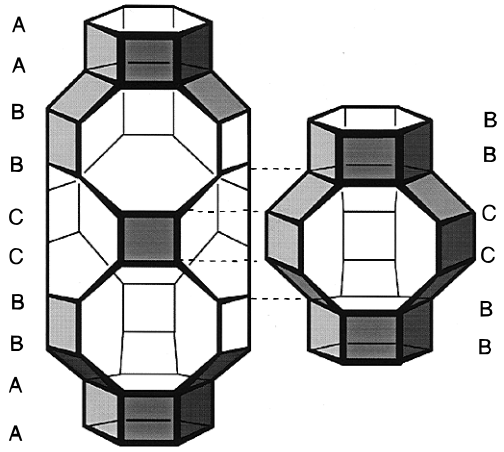

Figure 3. Illustration of the cages and framework topology of SSZ-16. Oxygen atoms have been omitted for simplicity. The large cage (AFT-cage) is formed between the AA...AA layers and the small cage (gmelinite cage) is formed between the BBCCBB layers. The dotted lines indicate the conectivity between the two different cages.

It is remarkable to notice that this layer sequence was first proposed as a hypothetical structure by Kokotailo and Lawton in 1964.[26] This AABBCCBB... type of zeolite have been systematically catalogued by Smith and Bennet as net #144.[27]

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