

SSZ-42: the first high-silica large pore zeolite with an undulating, one-dimensional channel system

C. Y. Chen,^a L. W. Finger,^b R. C. Medrud,^a P. A. Crozier,^c I. Y. Chan,^a T. V. Harris^a and S. I. Zones^{*a}

^a Chevron Research & Technology Co., Richmond, CA 94802, USA

^b Carnegie Institution of Washington, Geophysical Laboratory, Washington, D.C. 20015, USA

^c Center for Solid State Science, Arizona State University, Tempe, AZ 85287, USA

The framework topology of the novel zeolite SSZ-42 is determined from single crystal data ($15 \times 15 \times 35 \mu\text{m}$) and refined from powder diffraction data; the crystalline architecture is characterized by an undulating, one-dimensional 12-membered ring channel system.

In this report we describe the structure of a novel zeolite designated as SSZ-42. The zeolite is synthesized using *N*-benzyl-1,4-diazabicyclo[2.2.2]octane cation as the template molecule.¹ In one synthesis batch we were fortunate to find single crystals of uniform size ($15 \times 15 \times 35 \mu\text{m}$) which were optically of very high quality, and which extinguished uniformly under crossed polarizers.

The framework arrangement of SSZ-42 was solved from single-crystal data collected with a CCD camera in the applications laboratory of Siemens Energy and Automation, Inc. in Madison, WI, using a crystal that still contained the occluded template molecules. Although the measurable intensity was obtained on only about half of the available reflections in a three-dimensional set of data and most of those reflections were weak, the data from this very small SSZ-42 crystal were sufficient to locate the framework atoms by using direct methods in SHELXTL (version 5.03) to generate a very good trial model, but not precise enough to get good bond distances. The crystal system is monoclinic. The symmetry of the silica framework can be described in space group $C2/m$. There are four topologically distinct T-atoms and 10 O-atoms.

Full powder patterns for both as-synthesized and calcined samples (crystal size 1–2 μm) were collected at high-resolution beamline X7A of the National Synchrotron Light Source, Brookhaven National Laboratory.[†] The calcined sample used for the powder diffraction was prepared by heating the calcined material at 350 °C for several hours in a glass capillary under vacuum, to remove as much of the adsorbed species as possible, and then sealing. The unit-cell parameters from the powder data are shown in Table 1. The framework atom parameters from the single-crystal data were used as a starting model to refine the powder data from the calcined sample, which contains only the framework atoms. Convergence was accomplished without difficulty using the program GSAS.² Difference electron density slices through the channel cross-section show no residual electron density. The refinement led to residuals of $wR_p = 0.066$, and $R_p = 0.050$ and $R_{\text{Bragg}} = 0.061$ with $\chi^2 = 1.02$. The Rietveld difference plot in Fig. 1 shows that the

Table 1 Unit-cell parameters for SSZ-42

Sample	As-synthesized	Calcined
$a/\text{\AA}$	18.6309(9)	18.4991(2)
$b/\text{\AA}$	13.3359(1)	13.4078(1)
$c/\text{\AA}$	7.61731(3)	7.57548(2)
$\beta/^\circ$	102.017(1)	101.471(1)
$V/\text{\AA}^3$	1851.12(1)	1841.49(2)

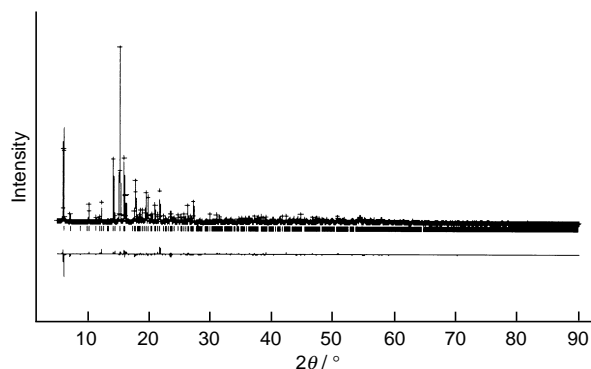


Fig. 1 Results of Rietveld refinement of a calcined SSZ-42 sample

observed and calculated powder patterns of the calcined sample agree very well.

The framework structure, viewed along the 12-MR channel (Fig. 2), is characterized by an undulating, one-dimensional channel system with pores comprised of 12 T-atoms. The framework density is 17.4 T/1000 \AA^3 . The pore diameter at the narrowest point in the XZ projection is 6.4 \AA . The cage at the widest point is *ca.* 10 \AA . As shown by the XZ projection in Fig. 3, the channel exhibits 'side pockets' which are reminiscent of those in SSZ-33³ and Beta⁴ zeolites formed by the intersection of channels. In SSZ-42, however, there are no intersecting channels. In the perpendicular projection (YZ) there are no undulations and the pore diameter is 6.7 \AA . It is apparent that the 12-membered ring is considerably distorted, giving the smaller than expected pore size.

The powder diffraction data from the as-synthesized sample displays considerable electron density in the channel. The template molecule must be disordered for the space group $C2/m$. Elemental analysis indicates two template molecules per unit cell. A possible location for the template molecule was generated by molecular modelling in the Insight computational environment (see Fig. 3).⁵ The template molecule spans the

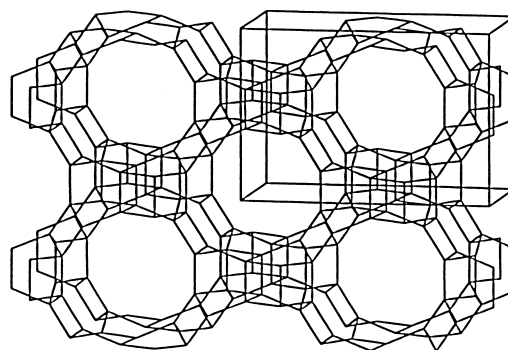


Fig. 2 The SSZ-42 framework viewed along [001]

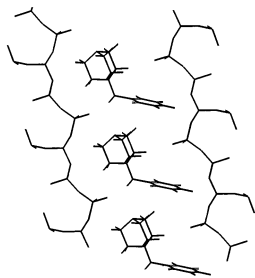


Fig. 3 XZ projection of the SSZ-42 framework showing minimized location of template molecules

volume from one side pocket diagonally to the next. The details of further structure refinement based on the as-synthesized synchrotron powder XRD pattern will be discussed at a later date.⁶ The atomic coordinates and selected bond distances and angles for the calcined form are listed in Tables 2 and 3, respectively. This structure does confirm once again the effective use of organocations as 'guest molecules' in developing the 'host' molecular sieve architecture.

Fig. 4 shows the experimental and simulated high-resolution electron micrograph (HREM) viewed along the [001] projection of SSZ-42. The experimental image is a spatially averaged image obtained with the low-dose method of Pan and Crozier.⁷ Initial analysis of the circumference of the main channel led us to the preliminary proposal of a 10-MR channel system but we were unable to come up with a structure that would yield a good

Table 2 Atomic coordinates for calcined SSZ-42

	<i>x</i>	<i>y</i>	<i>z</i>	$10^2 U_{iso}/\text{\AA}^2$
Si(1)	0.9876(3)	0.6151(4)	0.6972(7)	2.6(2)
Si(2)	0.1471(3)	0.6159(4)	0.9006(7)	3.0(2)
Si(3)	0.7516(3)	0.6122(4)	0.3779(8)	2.9(2)
Si(4)	0.8393(3)	0.7045(4)	0.7280(8)	3.2(2)
O(1)	0.0625(8)	0.6427(7)	0.8284(15)	3.9(4)
O(2)	0.9241(6)	0.6860(7)	0.7350(13)	1.9(3)
O(3)	0.1769(6)	0.6785(7)	0.0793(14)	2.6(4)
O(4)	0	0.6250(14)	0.5	6.5(7)
O(5)	0.7902(6)	0.6327(8)	0.5818(16)	4.1(4)
O(6)	0.1944(6)	0.6372(9)	0.7491(15)	6.3(5)
O(7)	0.9689(8)	0.5	0.7246(21)	4.1(6)
O(8)	0.6801(5)	0.6819(7)	0.3206(14)	2.1(3)
O(9)	0.1561(7)	0.5	0.9579(21)	5.8(7)
O(10)	0.7219(7)	0.5	0.3540(18)	2.8(5)

Table 3 Selected bond distances (Å) and angles (°) for calcined SSZ-42

Si(1)–O(1)	1.582(8)	Si(3)–O(5)	1.595(9)
–O(2)	1.583(8)	–O(6)	1.554(9)
–O(4)	1.562(4)	–O(8)	1.606(7)
–O(7)	1.606(5)	–O(10)	1.599(5)
Mean Si(1)–O	1.583	Mean Si(3)–O	1.588
Si(2)–O(1)	1.593(8)	Si(4)–O(2)	1.576(8)
–O(3)	1.597(8)	–O(3)	1.587(8)
–O(6)	1.602(9)	–O(5)	1.604(8)
–O(9)	1.614(4)	–O(8)	1.590(7)
Mean Si(2)–O	1.602	Mean Si(4)–O	1.589
Si(1)–O(1)–Si(2)	147.1(5)	Si(2)–O(6)–Si(3)	156.1(7)
Si(1)–O(2)–Si(4)	149.1(6)	Si(1)–O(7)–Si(1)	148.2(9)
Si(2)–O(3)–Si(4)	143.0(6)	Si(3)–O(8)–Si(4)	139.2(5)
Si(1)–O(4)–Si(1)	170.3(13)	Si(2)–O(9)–Si(3)	148.6(9)
Si(3)–O(5)–Si(4)	148.7(6)	Si(3)–O(10)–Si(3)	140.2(7)

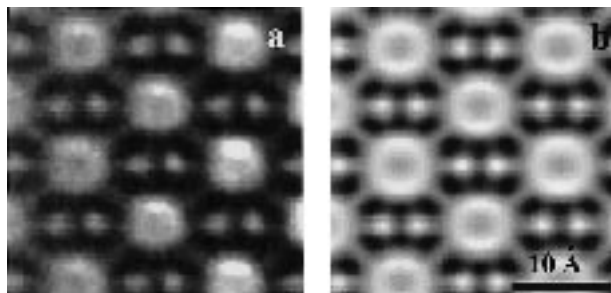


Fig. 4 (a) Spatially averaged experimental HREM image from [001] projection of SSZ-42 acquired with a JEOL 4000 EX operating at 400 kV. The image (showing point-to-point resolution of 2.2 Å) was recorded from a wedge-shaped crystal resulting in a gradation of the image intensity from left to right. (b) Simulated image of proposed SSZ-42 structure in the [001] projection. The image was calculated using multi-slice techniques for a crystal 40 Å in thickness and the objective lens set to Scherzer defocus (–490 Å).

fit between the simulated image and the experimental image. However, if we use the atomic coordinates derived from the XRD data we obtain an excellent match between the simulated and experimental HREM data [see Fig. 4(b)]. In this case, the unusual geometry causes the 12-MR to appear as a 10-MR ring in [001] projection. However, the comparison between the experimental and simulated images is clearly a stringent test of the accuracy of the proposed structure model.

The existence of large pores was also experimentally confirmed by the adsorption of a series of molecules with varying dimensions. N₂, *n*-hexane, 2,2-dimethylbutane and cyclohexane have a high adsorption capacity of *ca.* 0.20 ml g^{–1} in SSZ-42, which is closer to the adsorption data obtained in SSZ-33 and Beta, both possessing intersecting 10/12- or 12/12-MR channels. Based on these adsorption data, one could easily come to the incorrect conclusion that the framework architecture of this new material consists of an intersecting 10/12- or 12/12-MR channel system. In fact, the large adsorption capacity of SSZ-42 is due to large cages rather than to an intersecting channel system. The high adsorption capacity is exceptional for a large pore zeolite with a one-dimensional channel system.⁶

Footnote and References

† Supported by the US Department of Energy, Division of Material Sciences and Division of Chemical Sciences. We thank D. E. Cox, G. Zhang and G. Mondo for assistance in collecting the synchrotron data. We thank Chevron Research and Technology Company for support of zeolite research in the catalyst area and especially D. J. O'Rear and C. M. Detz.

- S. I. Zones and A. Rainis, *World Pat.*, 95/908793, 1995.
- A. C. Larson and R. B. Von Dreele, *GSAS—General Structure Analysis System*, Los Alamos National Laboratory Report LA-UR 86-748, 1986.
- R. F. Lobo, M. Pan, I. Y., Chan, H. X. Li, R. C. Medrud, S. I. Zones, P. A. Crozier and M. E. Davis, *Science*, 1993, **262**, 1543.
- J. M. Newsam, M. M. J., Treacy, W. T. Koetsier and C. B. deGruyter, *Proc. R. Soc. London, Ser. A*, 1988, **420**, 375.
- Template docking studies were done with the CVFF forcefield using Solids_Docking and Discover modules of computer software distributed by the Catalysis and Sorption Consortium of Molecular Simulations, Inc., San Diego, CA.
- C. Y. Chen, L. W. Finger, R. C. Medrud, P. A. Crozier, I. Y. Chan, T. V. Harris and S. I. Zones, in preparation.
- M. Pan and P. A. Crozier, *Ultramicroscopy*, 1993, **48**, 332.

Received in Columbia, MO, USA; 13th May 1997; 7/03323K