

SSZ-60: a new large-pore zeolite related to ZSM-23†

Allen Burton* and Saleh Elomari

ChevronTexaco Energy Research Company, 100 Chevron Way, Richmond, CA, USA.

E-mail: buaw@chevrontexaco.com; elom@chevrontexaco.com; Fax: +1 510-242-1599;

Tel: +1 510-242-1810

Received (in Cambridge, UK) 2nd July 2004, Accepted 25th August 2004

First published as an Advance Article on the web 4th October 2004

SSZ-60 is a new borosilicate zeolite that may be prepared using *N*-ethyl-*N*-(2,4,4-trimethylcyclopentyl)pyrrolidinium or *N*-ethyl-*N*-(3,3,5-trimethylcyclohexyl)pyrrolidinium as a structure directing agent; the framework of SSZ-60 was determined by the FOCUS Fourier recycling method, its structure refined in space group $P2_1nm$ and found to possess a one-dimensional channel system with pores delimited by twelve-rings; the topological structure of SSZ-60 may be derived from a sigma-expansion of the framework of ZSM-23 (MTT).

Many novel high-silica zeolites have been prepared by using organic structure directing agents (SDAs) in their synthesis gels. These SDAs are usually water soluble species such as crown ethers,¹ transition metal complexes,² amines, or tetraalkylammonium cations. The latter class of molecules has yielded the greatest number of new high-silica zeolites as they provide the richest variability in terms of molecular design. Since many derivatives of readily available amines have been examined as SDAs, future advances in the synthesis of high-silica zeolites will require investigators to employ more sophisticated schemes to synthesize novel SDAs.

SSZ-60³ is a novel zeolite that can be prepared in the presence of either the *N*-ethyl-*N*-(2,4,4-trimethylcyclopentyl)pyrrolidinium cation or the *N*-ethyl-*N*-(3,3,5-trimethylcyclohexyl) pyrrolidinium cation (Fig. 1).^{4,5} These molecules belong to a class of organic SDAs derived from enamine intermediates. Ref. 5 describes such a family of molecules synthesized by the reaction of pyrrolidine with various cyclic ketones. Using this chemistry, our research group has prepared SDAs that promote crystallization of zeolites beta, ZSM-11, ZSM-12, SSZ-55⁶ as well as the novel zeolites SSZ-57,⁷ SSZ-58,⁸ and SSZ-63.⁹ Sastre *et al.* have also used this chemistry to examine the structure directing effects of cyclohexylpyrrolidinium derivatives.¹⁰

The zeolite is typically made directly as a borosilicate in a gel with an oxide ratio composition $1.0\text{SiO}_2 : 0.04\text{Na}_2\text{O} : 0.10\text{SDA}_2\text{O} : 0.021\text{B}_2\text{O}_3 : 42\text{H}_2\text{O}$. In a representative synthesis, 5.93 g of a 0.5 M aqueous solution of *N*-ethyl-*N*-(3,3,5-trimethylcyclohexyl)pyrrolidinium hydroxide, 1.2 g of 1 M NaOH, and 4.9 g of deionized water are mixed together in a 23 mL Teflon cup. Then 0.06 g sodium tetraborate decahydrate is dissolved in the mixture, 0.9 g of Cabosil M-5 added and the resultant gel is thoroughly mixed. The Teflon cup is capped off, placed in a steel Parr autoclave, and then

heated in an oven at 160 °C while tumbling at 43 rpm. After about 12 days, the reaction mixture is filtered to remove the solid products. The solids are washed with 1 L deionized water and then dried in an oven at 120 °C. The occluded organic molecules are removed by calcining samples in a shallow bed to 595 °C in an atmosphere of nitrogen containing 2% oxygen. Scanning electron microscopy indicates the crystallites of SSZ-60 are thin needles or laths about 3 µm in length. This morphology is often observed in zeolites with one-dimensional channels.

The structure solution and powder indexing were performed using data obtained with a Siemens D500 X-ray powder diffractometer (Cu K α radiation). The structure solution was carried out with FOCUS¹¹ in space group $Pnmm$, the topological symmetry of SSZ-60. Subsequent Rietveld refinements were carried out with GSAS.¹² Fig. 2 shows the framework of SSZ-60, a one-dimensional 12-ring zeolite. The micropore volumes determined by argon (0.13 mL g⁻¹) and nitrogen (0.14 mL g⁻¹) adsorption are consistent with those measured for other one-dimensional 12-ring zeolites. The structure of SSZ-60 may be derived from a modification of the MTT¹³ framework (ZSM-23), which possesses one-dimensional 10-ring pores. In fact, the *a* and *c* unit cell parameters are approximately equal to the dimensions found in the unit cell of ZSM-23. If the four-rings are removed from the projection along the *a*-axis and the neighboring five-rings are then fused together at the common edges shared with the four-ring, the MTT topology is obtained. A different hypothetical 12-ring structure¹⁴ can be derived from the MTT framework by performing an expansion along the *c*-axis instead of the *b*-axis.

Although the periodicity along the pore axis is only 5 Å, the channels of SSZ-60 possess large corrugations, or troughs, which almost completely surround the 12-ring windows. The dimensions of the 12-ring windows are 7.6 × 5.1 Å. However, the corrugations make the internal dimensions of the zeolite larger than the limiting dimensions of the windows. These corrugations are especially important in stabilizing branched chains or ring features in SDA molecules. Other notable examples of one-dimensional pore zeolites with unusually large corrugations include ZSM-23,¹⁵ SSZ-53,¹⁶ and SSZ-55.¹⁷

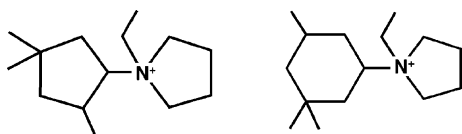


Fig. 1 The structure directing agents (SDAs) used to prepare SSZ-60.

† Electronic supplementary information (ESI) available: scanning electron microscopy images, synchrotron data collection conditions, refined atomic coordinates, refined bond distances and angles, and coordinates of hypothetical twelve-ring structure derived from the MTT framework. See <http://www.rsc.org/suppdata/cc/b4/b410010g/>

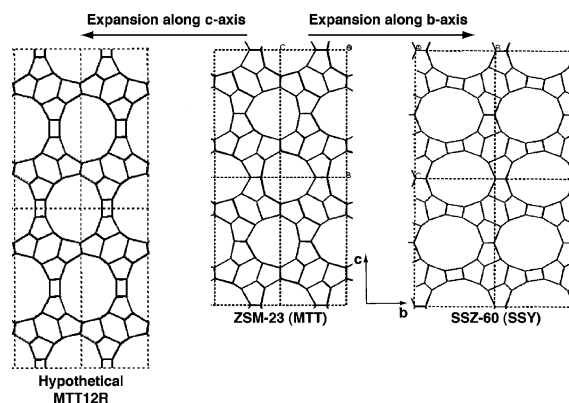


Fig. 2 Frameworks derived from alternate expansions of MTT along the *b*- and *c*-axis.

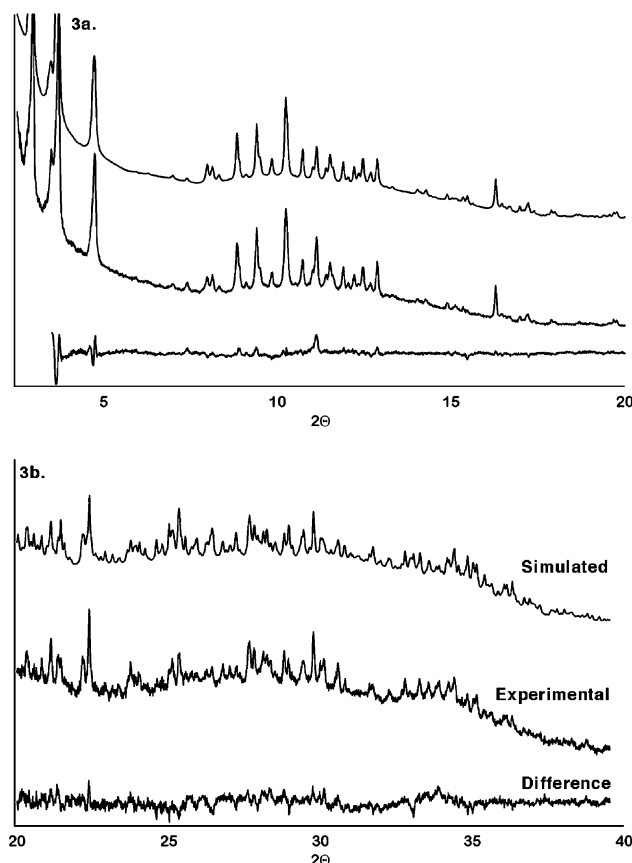


Fig. 3 Simulated, experimental, and difference profiles for the Rietveld refinement for calcined SSZ-60 (wavelength of 0.7102 Å).

Elemental analyses of the as-made zeolite indicate mole ratios of 15.0C : 1N : 30.4H (expected $C_{15}NH_{30}$) and Si/B = 44. The total mass loss by thermogravimetric analysis (12.3%) is close to that expected from the total C : H : N content measured by chemical analyses (12.1%). There is approximately 1 SDA molecule per 28 tetrahedral atoms or about 1 SDA per unit cell. The organic content of the as-made zeolite as well as the energy optimization of the organic material within the zeolite framework indicate that the SDA molecule prefers to reside with its long axis approximately parallel to the zeolite pore axis. These energy optimization calculations will be discussed at length in a future publication.

The structure of SSZ-60 was initially refined in space group $Pmnm$. However, with distance restraints, the refined Si–O distances and tetrahedral angles were outside the normal range of values observed for silica structures. There were significant disparities in the simulated and experimental intensities in several regions of the powder profile. In space group $Pmnm$, many of the framework atoms are constrained to reside within mirror planes perpendicular to the a -axis. Removal of this mirror plane (space group $P2_1nm$) allows the framework atoms to relax to a more energetically favorable structure. The resulting unit cell possesses the same number of tetrahedral atoms in the asymmetric unit. Rietveld refinement in this space group yielded excellent agreement between the experimental and simulated profiles of the synchrotron X-ray diffraction data (Fig. 3). The first two low-angle peaks were

excluded from the refinement due to problems with the high background and peak shape.

In their investigation of ZSM-23, Marler and co-workers concluded from solid-state ^{29}Si MAS NMR and powder diffraction experiments that the framework of ZSM-23 possesses space group symmetry $P2_1$.¹⁸ Although this space group is consistent with the removal of the mirror plane perpendicular to the pore axes, this symmetry is lower than the $P2_1nm$ symmetry we concluded for the framework of SSZ-60. It would not be surprising that ZSM-23 and SSZ-60 might possess similar framework symmetries. We repeated the refinement of SSZ-60 in space group $P2_1$, but this reduction in symmetry did not yield any improvement in the refinement. The $P2_1nm$ space group is consistent with the symmetry chosen by Schlenker, Higgins, and Cox for ZSM-23 [www.iza-structure.org/databases/].

This work was supported by ChevronTexaco Energy Research and Technology Company. Research was carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the US Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. We would like to thank Yongjae Lee and Ken Ong for their assistance in collecting the data for the synchrotron X-ray diffraction experiment. We are also grateful to Steve Trumbell for his assistance in the organic and zeolite syntheses. We also acknowledge G. E. Scheuerman, C. R. Wilson, and M. J. Riddle for their support of the new materials research program at ChevronTexaco.

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