Structure Analysis of New Porous Lithosilicate [Li-Si-O]-MFI

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Introduction

Recently we have reported several new microporous lithosilicate materials showing a high ion-exchange capacity and cationic conductivity.[1] The materials often display new topology mainly due to the presence of lithium cations incorporating into 3-dimensional four-connected silicate frameworks. The observation could be plausibly explained by understanding characteristics of geometrically more flexible [LiO4]-tetrahedra in silicate networks, comparing to well-known framework cations, such as silicon and aluminum.[2]

To test the generality of Li substitution in high silica frameworks, we chose silicalite (the pure silica form of aluminosilicate ZSM-5 with the MFI topology) as a potential substrate for new substantial frameworks of [(Li,Si)O4]-tetrahedra.[3] The structure contains two different channel systems: straight- and sinusoidal channels bounded by 10 rings of corner-connected SiO_4-tetrahedra. The successful incorporation of various cations such, as Al, As, B, Fe, Ga, and Ti, into the thermally stable MFI framework preserved a wide range of catalytic applications of the MFI family member.[4] Here we report the structure of the first example of Li substitution into the MFI framework to form the new ZSM-5 family member [Li-Si-O]-MFI.[5]

Methods and Materials

The starting mixture gel was prepared in system 0.5LiOH: $1SiO_2$: 1TPAOH: $44H_2O$. The pure sample of [Li-Si-O]-MFI was obtained under static hydrothermal conditions by heating at 175ºC for 7 days.

A twin crystal of [Li-Si-O]-MFI (10 x 5 x 2 μm^3) was used for the data collection at the GEOCARS beamline of the APS (λ = 0.689 Å). We measured 46004 reflections on 1530 frames in the $\omega/2\theta$ scan mode (θmax = 31°) at a counting time of 2 s per frame. The number of symmetrically nonequivalent reflections is 6605 obtained in a selected Laue roup mmm (R_{ini} = 0.06).

The crystal structure was determined by direct methods, Fourier calculations and refinement strategies, which are part of the SHELXL program package distributed by Bruker Analytical.[6]

Results

The two individuals of the twin crystal are rotated 90º about their shared c-axis, i.e., the applied twin matrix is (0 –1 0 / 1 0 0 / 0 0 1). Systematic extinctions uniquely identify the space group as $P2_12_12_1$, and lattice parameters are a = 19.793(4) Å, b = 19.766(4) Å, c = 13.266(3) Å.

The structure analysis showed a static disorder of silicon and lithium cations over the [Li-Si-O]-MFI framework sites. Four nitrogen cations, eight nonframework Li^+ cations, and some of the disordered carbon sites associated with the tetrapropylammonium (TPA) cations were located in subsequent Fourier difference calculations. Isotropic displacement parameters were assumed for all sites. After refining the occupancy parameters for C atoms without restrains, the final R_1-value converged to 0.07 ($R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$) for 5537 reflections [$|F_o| > 4\sigma(|F_o|)$].

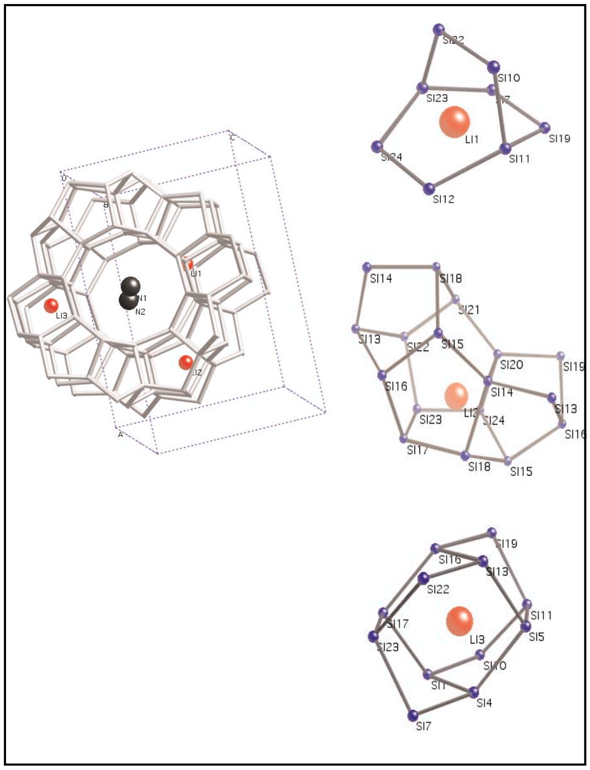

FIG. 1. (Left side): Partial structure of [Li-Si-O]-MFI. Extra framework lithium cations are occluded in narrow pore voids (medium circles) while the large TPA⁺ cations are present in the 10MR channels (dark, large circles). (Right side): Magnified features of encapsulated extra framework lithium cations, Li1, Li2, and Li3. Silicon and lithium atoms are statically disordered in the framework (small circles).

The structure determination gave an idealized formula $TPA^+{}_4Li^+{}_8[Li_4Si_{92}O_{192}]$ for as-synthesized [Li-Si-O]-MFI. This is also consistent with results from chemical analysis and ^{29}Si MAS NMR experiments.[5]

Discussion

Within the [Li-Si-O]-MFI framework, the bonding distances and occupancies on T sites show no sign of ordering of framework Li cations. Therefore, the reduction in symmetry of the orthorhombic framework from Pnma to $P2_12_12_1$ is most likely due to the presence of extra framework lithium cations. Non-framework lithium cations are occluded in three different sites within narrow cage-like voids outlined by the double 5MR (membered-rings) or 6MR. The 10MR channels are occupied exclusively by the two TPA^+ cations per unit cell (Fig. 1).

Having established the presence of both framework and extra framework Li in [Li-Si-O]-MFI, we expect the insights obtained thus far from the MFI system to be applicable to a wide range of high-silica zeolites. Work on complex Li-bearing zeolithic materials crystallizing as small single crystals will require the continued access to APS-style beamline facilities.

Acknowledgments

This work was performed at GeoSoilEnviroCARS (GSECARS), Sector 13, Advanced Photon Source at Argonne National Laboratory. We acknowledge financial support from the NSF and the DOE via DMR-0095633. Special thanks to Dr. Peter J. Eng and Dr. Joe. J. Pluth (GSECARS, University of Chicago, Chicago, IL 60637 U.S.A.) for helpful discussion and data collection.Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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