Microporous and Mesoporous Materials 202 (2015) 250–258

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis, characterization and structure solution of ULS-1 $|ETMA_8(H_2O)_{20}|[Si_{24}O_{48}(OH)_8]$, a layered silicate composed of half-sodalite cages

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ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 17 September 2014
Accepted 6 October 2014
Available online 16 October 2014

Keywords:
Ethyltrimethylammonium
Sodalite
Charge-density mismatch
Layered silicate

ABSTRACT

UOP layered silicate-1 (ULS-1), a highly siliceous layered silicate composed of $[4^26^2]$ half sodalite cages, has been synthesized hydrothermally at 100 °C from solutions containing ethyltrimethylammonium hydroxide and silica or aluminosilicate sources and the structure solved from powder XRD data in the Ibam spacegroup with $a = 28.909$ Å, $b = 8.380$ Å, $c = 11.569$ Å at room temperature. TGA/MS and NMR, Raman and IR spectroscopic characterization were utilized to examine the properties of ULS-1 and provide information for structure solution. ULS-1 contains the same silicate layer structure and stacking as that found in RUB-15 and DLM-2, but with ethyltrimethylammonium (ETMA) cations in place of tetramethylammonium stabilizing the half sodalite cages. The presence of ETMA increases the interlayer spacing to ~8.3 Å from the previously observed 8 Å, but also slightly increases the *c* unit cell constant in the layer direction.

1. Introduction

Layered silicates are an important class of materials which have been used as ion-exchange adsorbents, catalysts and scaffolds for biocomposites [1–3]. These materials tend to exist as thin silicate sheets of SiO_4 tetrahedral units extending in two dimensions with a surface comprising $SiOH/SiO^-$ groups, thereby generating an interlayer space of charge balancing cations and hydrogen bonded water which determine the layer spacing. Typically, these layers are impermeable; a rare example of a layered silicate containing pores through the layer is that of AMH-3 [4]. Many groups have used the exchangeability of the cations between the impenetrable layers to layer expand, exfoliate and otherwise chemically modify the silicate layers giving multiple new materials and uses from a single layered silicate starting material [1]. Both natural and synthetic layered silicates are known with the minerals magadiite [5,6], kenyaite [7,8], kanemite [9–11] and makatite [12] among the most well studied. Marler and Gies have recently written an excellent review and classification of the hydrous layer silicate field [13] and an entire issue of Dalton Transactions was devoted to layered inorganic solids and their uses [14].

A class of the large number of layered silicate materials is that comprising layers cut from the SOD zeolite structure. Both β-HLS [15] and HUS-1 [16] are made from layers cut from the [100] direction of SOD, albeit with different layer stackings, *ABAB* for β-HLS and *AA* for HUS-1. While these layers are cut from the SOD structure, condensation of the layers would lead to the AST structure, so they should be referred to as ast layers [13]. Interestingly, the precursor to HUS-1, HUS-5, has *ABAB* stacking of ast layers as does β-HLS, and is converted to the *AA* stacking of HUS-1 through no more than washing with H_2O [17]. Conversely, slicing along the [110] direction of SOD leads to sod layers composed of halved sodalite cages [16]. Multiple materials with this motif have been made from many different synthetic approaches, but which typically have tetramethylammonium (TMA^+) cations stabilizing the half sodalite cages, balancing the charge from the SiO^- groups and separating the silicate layers. RUB-15 [18] was synthesized from silicate solutions containing TMA hydroxide after a month at 120–140 °C while DLM-2 [19] crystallized after a failed synthesis starting from TMA^+ silsesquioxane (the well-known d4r zeolite building block), yet both preparations yielded the same TMA^+ stabilized half sodalite cage material. Recently, Gies and coworkers have shown in the preparation of RUB-51 the same sod layer structure, but with benzyltrimethylammonium ($BzTMA^+$) cations as the interlayer species [20]. In RUB-51, the layer stacking is *AA* rather than the *ABAB* observed for RUB-15 and DLM-2.

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http://dx.doi.org/10.1016/j.micromeso.2014.10.008
1387-1811/

At UOP, we have been working with ethyltrimethylammonium (ETMA) because it is a simple and readily available tetraalkylammonium available for use as a structure directing agent in zeolite synthesis. It is available as a solution in hydroxide form, allowing use as the hydroxide source to replace some or all of the traditionally utilized sodium in synthesis. While $ETMA^+$ has not been used with nearly the same frequency as TMA^+, the effect of $ETMA^+$ on zeolite crystallization has been extensively studied [21] by Lewis and coworkers. They have shown that while the structure directing effects of $ETMA^+$ tend to be similar to those of TMA^+ due to the structural similarity between them, unique products are obtained in syntheses using $ETMA^+$. In this manner, products such as the layered material UZM-17 [22,23], which condenses to UZM-25 (CDO framework) upon calcination, UZM-8 [24], and PKU-9 [25] are seen in syntheses where $ETMA^+$ has been used as a structure directing agent.

ETMA is of particular interest while using the charge density mismatch (CDM) synthesis technique. As shown by Lewis and Hong, CDM uses clear solutions containing silicon, aluminum and a large, low charge density tetraalkylammonium hydroxide [26]. These solutions are stable and do not crystallize. To crystallize a zeolite product, a solution containing a small, high charge density ion such as lithium, sodium or magnesium is introduced. The method has been successful in yielding microporous materials such as UZM-4 (BPH) [27], UZM-5 (UFI) [28], UZM-9 (LTA) [29], UZM-12(ERI) [30,31] and UZM-35 (MSE) [32]. Starting from either CDM-aluminosilicate solutions or all-silica solutions while using ETMA hydroxide as the structure directing agent, we have synthesized a novel layered silicate composed of $[4^26^2]$ half sodalite cages, named ULS-1, and report its structural characterization here.

2. Experimental

2.1. Synthesis

CDM preps were performed by making an aluminosilicate solution by dissolving $Al(OH)_3$ in ETMAOH. 1,4-Bismethylpyrrolidinium butane dibromide (C4P2 Br) and Ludox AS-40 were then added. To this solution, a solution of $Mg(OH)_2$ or LiOH was then added to form a solution of composition 100 Si:5 $Al(OH)_3$:80 ETMAOH:15 C4P2 Br:1.25 $Mg(OH)_2$:3566 H_2O or 100 Si:5 $Al(OH)_3$:60 ETMAOH:7.5 C4P2 Br:2.5 LiOH:2632 H_2O.

The resulting solution was then put into a Teflon bottle and kept at 100 °C statically for 5–7 months. By this time, white solid formed. The chunks of white solid were separated from any clear gel remaining and were worked up by washing and filtration followed by drying at 100 °C to yield a white powder. Other preps were loaded into 45 mL Teflon lined Parr bombs and kept in 125–175 °C ovens statically for times listed in Table 1.

Syntheses from all silica solutions were performed by combining solutions of ETMAOH and Ludox to yield solutions of composition 1 SiO_2:0.8 ETMAOH:28.7 H_2O. To these, $Mg(OH)_2$ or LiCl was sometimes added at 0.0125 mol ratio. These solutions were loaded into Teflon bottles and kept at 100 °C for 6 weeks to 3.5 months before workup by washing and filtration to yield a papery, white product.

Additionally, a preparation at 1 SiO_2:0.8 ETMAOH:18.7 H_2O:4 EtOH was performed by combining ETMA hydroxide and TEOS, mixing well and then loading into a Teflon bottle for 4 months at 100 °C.

2.2. Structure solution

The structure solution used X-ray diffraction data collected from laboratory and synchrotron radiation sources. Initial data were collected for samples packed in flat plates using Bragg–Brentano geometry on a Rigaku Ultima IV diffractometer equipped with a scintillation detector and diffracted beam monochromator or with a Detex silicon strip linear detector and a nickel filter. Materials were also packed into a 0.5 mm glass capillary and mounted on a Rigaku Ultima IV in parallel beam mode. The capillary was rotated at 60 rpm to obtain scans with minimal preferred orientation. Prior to several capillary experiments, the ULS-1 was dehydrated in-situ as described below. High resolution synchrotron powder diffraction data were collected at a temperature of 100 K using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413296 Å. Discrete detectors covering an angular range from -6 to 16° 2θ are scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and scan speed of 0.01°/s.

The 11-BM instrument uses X-ray optics with two platinum-striped mirrors and a double-crystal Si(1 1 1) monochromator, where the second crystal has an adjustable sagittal bend [33]. Ion chambers monitor incident flux. A vertical Huber 480 goniometer, equipped with a Heidenhain encoder, positions an analyzer system comprised of twelve perfect Si(1 1 1) analyzers and twelve Oxford-Danfysik $LaCl_3$ scintillators, with a spacing of 2° 2θ [34]. Analyzer orientation can be adjusted individually on two axes. A three-axis translation stage holds the sample mounting and allows it to be spun, typically at ~5400 RPM (90 Hz). A Mitsubishi robotic arm is used to mount and dismount samples on the diffractometer [35]. An Oxford Cryosystems Cryostream Plus device allows sample temperatures to be controlled over the range -193–227 °C when the robot is used.

The diffractometer is controlled via EPICS [36]. Data are collected while continually scanning the diffractometer 2θ arm. A mixture of NIST standard reference materials, Si (SRM 640*c*) and Al_2O_3 (SRM 676) is used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ.

Following XRD experiments, the extraction of the peak positions for structure solution and indexing was performed using the WinPLOTR program suite. Pattern indexing was carried out using DICVOL04 from twenty lines, with an absolute error on peak positions of 0.05° 2θ. The structure solution then followed from direct methods as described below.

2.3. Additional characterization

^{29}Si and ^{13}C MAS NMR were carried out at a frequency of 39.7491 and 50.3096 MHz (4.7 T), respectively. Samples were packed in zirconia rotors (7 mm o.d.) and spun at a frequency of 5 kHz. ^{29}Si CP MAS experiments were carried out using 3 ms

Table 1
Aluminosilicate synthesis conditions and products found.

CDM/Temp.	100 °C	125 °C	150 °C	160 °C	175 °C
Li	150 days ULS-1	Not performed	14 days UZM-15	6–11 days RUT/RTH	5 days RUT/RTH
Mg	150–210 days ULS-1	32 days amorph.	Up to 14 days largely amorph.	Up to 14 days largely amorph.	4 days largely amorph.