

Synthesis and Structure Solution of UOP Layered Silicate-1 (ULS-1) with a Layer Comprising [4²⁶2] Half-Sodalite Cages

C.P. Nicholas,¹ M.A. Miller,¹ S.R. Miller,¹ R.W. Broach,² M.M. Galey,¹ S.Prabhakar, B. Lyons,²
and C.L. Nicholas^{2,*}

Collette.Nicholas@Honeywell.com

¹ *Exploratory Materials and Catalysis Research, Honeywell UOP, United States*

² *Advanced Characterization, Honeywell UOP, United States*

Introduction

Many natural and synthetic layered silicates are known. Among these are the well-studied minerals magadiite, kenyaite, and kanemite. Recently, Marler and Gies wrote an excellent review and classification of the hydrous layer silicate field¹ and an entire issue of Dalton Transactions was devoted to layered inorganic solids and their uses.² In working with high silica zeolites, we discovered and published the synthesis and structure solution of UOP Layered Silicate-1 (ULS-1), a highly siliceous layered silicate with a sod layer comprising [4²⁶2] half sodalite cages.³ ULS-1 was synthesized hydrothermally at 100°C from solutions containing ethyltrimethylammonium hydroxide and silica or aluminosilicate sources.

Experimental

Syntheses from all silica solutions were performed by combining solutions of ETMAOH and Ludox to yield solutions of composition 1 SiO₂ : 0.8 ETMAOH : 28.7 H₂O. To these, Mg(OH)₂ or LiCl was sometimes added at 0.0125 mole 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 SiO₂ : 0.8 ETMAOH : 18.7 H₂O : 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.

Results and Discussion

To arrive at the structure solution, numerous laboratory and synchrotron radiation XRD methods and instruments were utilized. The ULS-1 structure was solved from powder XRD data in the Ibam spacegroup with $a = 28.909 \text{ \AA}$, $b = 8.380 \text{ \AA}$, $c = 11.569 \text{ \AA}$ at room temperature.³ 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 sod 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 ~8.3Å from the previously observed 8Å, but also slightly increases the c unit cell constant in the layer direction. As can be seen from the ab plane shown in Figure 2, the layer stacking for ULS-1 is ABAB, the same as that observed in RUB-15 and DLS-2, synthesized with TMA⁺ as the cation, contrasting to RUB-51, synthesized using benzyltrimethylammonium (BzTMA), which has AA stacking.

In the ULS-1 structure, one methyl group of the ETMA⁺ is directed into each halved sodalite cage of the layer with the ethyl group (disordered over two positions) directed into the interlayer space. As a silicate, we were hopeful the material was thermally stable. Unfortunately, the material is unstable to elevated temperature, yielding a relatively amorphous XRD pattern upon calcination at 550°C. Two distinct weight losses observed by TGA comprising almost 15% of the sample occur prior to 100°C and have been identified by mass-spec analysis as water. A large mass loss then occurs, centered around 215°C, giving a total loss on ignition of 50%. This mass loss coincides with loss of crystallinity, indicating that template decomposition causes framework destruction.

Conclusions

The novel layered silicate ULS-1 crystallizes in the presence of ETMA⁺. Layer spacing and a unit cell constant for ULS-1 expands versus the related TMA⁺ directed materials RUB-15 and DLM-2. However, these values are smaller than those exhibited by RUB-51, templated by the even larger cation BzTMA⁺. We report the structure solution in orthorhombic Ibam space group with $a=28.909\text{\AA}$, $b=8.380\text{\AA}$, $c=11.569\text{\AA}$.

References

1. B. Marler, H. Gies, *Eur. J. Mineral.* **24**, 405-28 (2012).
2. J. Cejka, R.E. Morris, P. Nachtigall, W.J. Roth, eds. *Dalton Trans.* **43**(27) (2014) 10274-5.
3. M.A. Miller, S.R. Miller, R.W. Broach, M.M. Galey, S. Prabhakar, B. Lyons, C.L. Nicholas, C.P. Nicholas, *Micro. Meso. Mater.* **202**, 250-8 (2015).