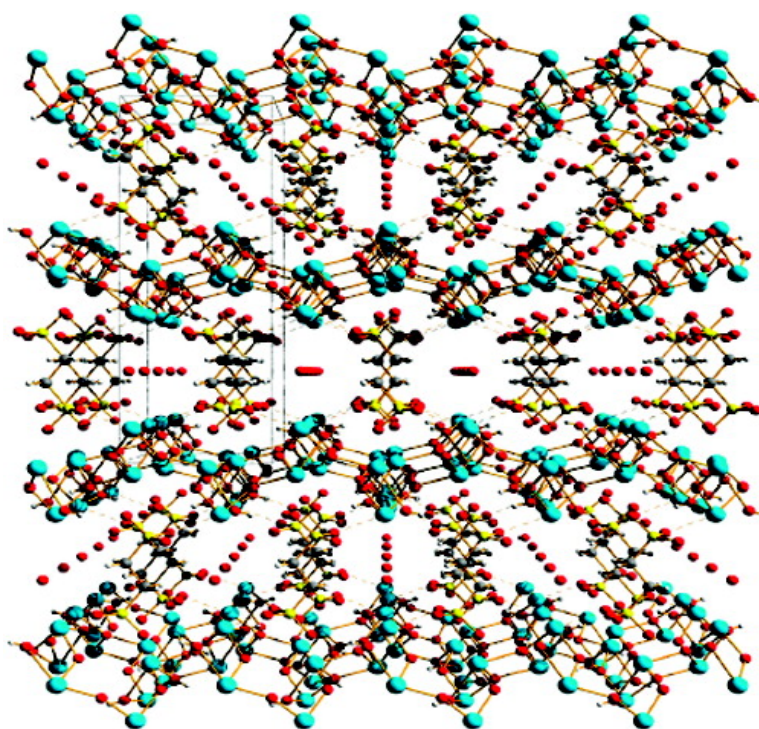


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Antimony Oxide Hydroxide Ethanedisulfonate: a Cationic Layered Metal Oxide for Lewis Acid Applications

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Abstract: We have discovered a rare example of a cationically charged inorganic material. The layered structure is an example outside the extensively studied isostructural set of anionic clays/layered double hydroxides and our previously reported lead fluoride nitrate. For the present compound, the antimony oxide hydroxide layers are positively charged and are templated by anionic alkylenedisulfonate. The organic molecules are only bonded electrostatically to the layers with sulfonate oxygen to antimony distances beyond the covalent range. The material catalyzes a ketal formation reaction as a Lewis acid without the need for drying the solvent before the reaction or a nonaqueous medium such as toluene. The catalyst is heterogeneous and is completely recovered after the catalysis for reapplication.

Introduction

Layered double hydroxides (LDHs) occur naturally as hydrotalcites and can also be synthesized in the laboratory.¹ Applications of as-synthesized LDHs and postsynthetic derivatives are based on their interlamellar anions and include anion exchange, base catalysis, drug delivery, polymerization supports, and photo- and electrochemistry.^{2–4} These materials remain the only well-studied class of purely inorganic compounds that possess anionic guests and a cationic charge on the host.^{5,6} The structure is based on brucite, Mg(OH)₂, where magnesium ions are octahedrally coordinated by six hydroxide ions and where the polyhedra edge-share into an extended layer. Partial substitution of M²⁺ for M³⁺ introduces positive charge and allows anions, for example, carbonate, to reside in the interlamellar space. The general formula for an LDH is [M²⁺_{1-x}M³⁺_x(OH)₂]Aⁿ⁻_{x/n}·mH₂O, where M²⁺ and M³⁺ can be a range of different metals and Aⁿ⁻ represents the guest anion. The anion can be inorganic, for example, nitrate or carbonate, or organic such as benzoate.³

A second example of a cationic extended inorganic material was previously reported by our research group, lead(II) fluoride nitrate, BING-5.⁷ The lead(II) fluoride layers with nitrate in the interlamellar space is the first example of a cationic inorganic material of its kind beyond LDHs and related oxides. The two-

dimensional lead(II) fluoride architecture consists of an inner neutral layer capped by two outer cationic layers. The material is synthesized hydrothermally at 150 °C, has the ability to exchange its interlamellar nitrates for inorganic anions such as dichromate,⁷ and offers high-temperature stability.

Cationic extended metal and semimetal oxides with elements such as lead and antimony are the target of our research. Antimony(III) forms trigonal pyramidal SbO₃ moieties possessing a lone pair suggesting that inorganic cationic layers are possible. Antimony oxides are of interest as fire retardants^{8,9} and are also used as catalysts,^{10–13} for example, for the polycondensation of poly(ethylene terephthalate)^{14–16} and the oxidation of phthalic anhydride to *o*-xylene.¹² A layered antimony oxide hydroxide with nitrate residing in the interlamellar space and low thermal stability was reported by Bovin in 1974.¹⁷ Thermogravimetric analysis (TGA) determined the solid to have a thermal stability to 175 °C, which is likely the reason that its catalytic and fire retardant properties have not been investigated.¹⁸ This example led us to investigate templating of antimony oxides/hydroxides with other inorganic or

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organic anions for new materials with properties of thermal stability and cationic character for applications as fire retardants and catalysts.

Hybrid inorganic–organic materials have advanced enormously in recent years as can be seen in the review from Cheetham et al.^{19–21} Applications are far-ranging, including catalysis, gas storage, separation, and purification.^{22,23} The structure of hybrid inorganic–organic materials consists either of a metal–ligand or metal–oxygen extended framework. Coté and Shimizu reviewed extended solids of organosulfonates which coordinate to silver or barium.²⁴ One example consists of barium layers with 4,5-dihydroxybenzene-1,3-disulfonate forming a pillared 3D metal sulfonate network that absorbs hydrogen sulfide. 1,3,5-Tris-(sulfomethyl)-benzene also coordinates with barium to give a three-dimensional extended network. Several recently discovered barium^{25–28} and silver²⁹ sulfonates also exist where the metal centers are connected by bridging sulfonates. In the case of silver, several sulfonates form extended networks, such as trifluoromethanesulfonate or phenylsulfonate.²⁴ Some reports have used ethanedisulfonate (EDS) as a template for inorganic–organic layered hybrids. All examples have the anion covalently bonded to the metal oxide layer^{30–33} and are therefore described as metal–organic frameworks (MOFs) such as those of Pb,³⁰ Cu,^{31,32} and Co.³³ The latter has cobalt hydroxide layers connected by EDS and displays ferromagnetic coupling between the sheets. We recently described an MOF where lead(II) fluoride layers are connected by EDS.³⁰ A copper hydrate example from Charbonnier et al. shows EDS can also form a metal–hydrate–alkanedisulfonate framework.^{31,32}

We present here a rare example of a two-dimensional cationic metal oxide hydroxide material that is not an LDH with only long contact between the layers and structure-directing anion. The material shows high thermal stability up to ca. 350 °C as well as catalytic activity. As an initial example, ketal formation is described, which is one of many Lewis acid reactions used in organic synthesis.^{34,35}

Experimental Section

Synthesis. Antimony(III) acetate [Sb(OOCCH₃)₃, Alfa Aesar, 97%] and 1,2-ethanedisulfonic acid [HO₃SC₂H₄SO₃H•H₂O, TCI Inc., 95%] were used as received. Crystals of [Sb₄O₄(OH)₂](O₃SCH₂CH₂SO₃)•H₂O were prepared by hydrothermal synthesis with a molar ratio of 100:1:5 for H₂O:Sb(OOCCH₃)₃:HO₃SCH₂CH₂SO₃H. The reagents were added sequentially, were thoroughly mixed, and were loaded into a 15 mL capacity autoclave to ca. 50% filling. The autoclave was heated statically for 3 days

at 150 °C during which the pH decreased from 3.5 to 2.5. Colorless crystals of [Sb₄O₄(OH)₂](O₃SCH₂CH₂SO₃)•H₂O (which we denote for simplification as SLUG-5 for University of California, Santa Cruz, Structure No. 5) remained after vacuum filtration and rinsing with ethanol [yield is based on antimony(III) acetate: 97.4%].

Catalysis. The following general procedure of ketal formation was used to characterize the performance of SLUG-5 as a Lewis acid catalyst. First, 3.10 μmol (2.5 mg) of catalyst was added to a round-bottom flask (capacity 50 mL). Then, 70 mmol of 2-butanone [CH₃COCH₂CH₃, Acros Organics, 99%] and 70 mmol of ethylene glycol [C₂H₄(OH)₂, Acros Organic, 99%] were added. All reactants were used as received. The reaction was refluxed for various time intervals under Dean–Stark conditions to continuously remove water. After the reaction, the catalyst was removed by filtration and the filtrate was dried with anhydrous magnesium sulfate. The product was isolated from ethylene glycol using a separatory funnel. Structure and yield were determined by ¹H NMR.³⁶

Instrumental. The material was initially characterized by powder X-ray diffraction (PXRD) with a Rigaku Americas Miniflex Plus powder diffractometer. Diffraction patterns were recorded from 2 to 60° 2θ with a step size of 0.04° at 1°/min. Single-crystal X-ray diffraction was obtained on a Bruker APEX II CCD area detector X-ray diffractometer. Data was collected with 2θ_{max} of 56.60°, λ(Mo Kα) 0.71073 Å, μ(Mo Kα) 8.053 mm⁻¹. The observed data, [I > 2σ(I)] 1731, were integrated by the program SAINT and analyzed for agreement and possible absorption using XPREP. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS. The structure was solved by direct methods and was refined by full-matrix least-squares analysis of F² against all reflections. The programs used include Bruker APEX-2 v2.1, Bruker SHELXTL-suite (v6.14), and Diamond v3.1e (Crystal Impact, 2007).

Thermogravimetric analysis (TGA) was measured on a TA Instruments 2050 TGA with nitrogen purge heating from 30° to 800 at 10 °C/min and coupled to a mass spectrometer (Pfeiffer Vacuum, ThermoStar, GSD 301 T3) with a 70 eV ionizing potential. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920 using aluminum sample pans and a heating rate of 5 °C/min from 30 to 500 °C. Elemental analysis was performed by Quantitative Technologies, Inc. (Whitehouse, NJ). NMR spectroscopy was carried out with a 600 MHz 5 mm indirect detection probe and PFG (pulse field gradients). Scanning electron microscope (SEM) images were collected on an SEM Hitachi S-2700.

Results and Discussion

[Sb₄O₄(OH)₂](O₃SCH₂CH₂SO₃)•H₂O is synthesized with simple techniques and at a low pH of 1.8. Water or 2-butanol (in equal volume) can be used as solvent. The resultant material is stable in a buffered aqueous solution in a pH range of 4–10 decomposing to Sb₂O₃ outside this range. The yield is highly reproducible with nearly complete conversion of antimony(III)

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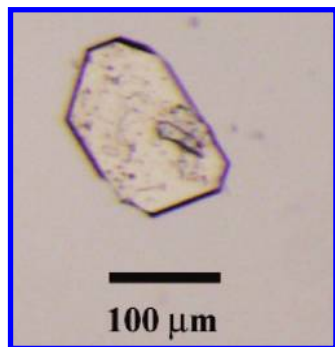


Figure 1. Optical micrograph of $[\text{Sb}_4\text{O}_4(\text{OH})_2](\text{O}_3\text{SCH}_2\text{CH}_2\text{SO}_3)\cdot\text{H}_2\text{O}$ in bifocused light.

acetate starting material after 3d reaction time. Figure 1 shows an optical micrograph of SLUG-5, and crystallographic data can be found in Table 1.

Table 1. Crystal Data and Structure Refinement for SLUG-5

empirical formula	$\text{C}_2\text{H}_{7.50}\text{O}_{12.50}\text{S}_2\text{Sb}_4$
formula weight [$\text{g}\cdot\text{mol}^{-1}$]	782.70
crystal system	orthorhombic
space group	$Pccn$
color of crystal	colorless
a [\AA]	21.8217(9)
b [\AA]	7.2520(3)
c [\AA]	8.7815(4)
V [\AA^3]	1389.68(10)
Z	4
temperature [K]	150(2)
$R_1[I > 2\sigma(I)]$	0.0188
wR_2 (all data)	0.0407
goodness of fit F^2	1.430
CCDC #	656220

SLUG-5 forms a two-dimensionally extended inorganic network with concomitant high thermal stability and electrostatic interaction between alkanedisulfonate anions and inorganic layers. The antimony(III) oxide hydroxide layers form an infinite network of Sb–O–Sb covalent bonds where pyramidal SbO_3 centers possess a free electron pair pointing into the interlamellar space (Figures 2–4). The $[\text{Sb}_4\text{O}_4(\text{OH})_2]^{2+}$ asymmetric unit defines the inorganic charged layer. The antimony is coordinated by three oxygen atoms with Sb–O bond lengths ranging from 1.952(2) to 2.078(2) \AA . The SbO_3 polyhedra connect into a chain along the c -axis (via O2 and O3). These chains are also linked by O3 along the b -axis to define the layer (Figure 3). Thus, O3 is triply bridging to metal centers (as for LDHs), while the other two oxygen atoms (O1 and O2) are doubly bridging. In addition, one oxygen atom (O1) is protonated as for LDHs. These similarities to LDHs likely aid in the formation of the cationic charge on SLUG-5.

1,2-Ethanedisulfonate (EDS) anions balance the charge of the cationic layers (Figure 4). The EDS anion is only electrostatically bonded to the layer. There is a long contact from the coordinatively unsaturated side of the Sb to one oxygen atom (O4) of the EDS. The $\text{Sb}\cdots\text{OS}$ contact distance of 2.451(2) \AA is well outside the accepted range for a covalent bond, which is generally between 1.9 \AA and 2.2 \AA . It also exceeds the sum of the atomic radii for covalent bond formation meaning that this structure is indeed a 2D cationic inorganic material.³⁷ The directionality of the long contact indicates a weak electrostatic interaction. A further indication that the layers are not covalently

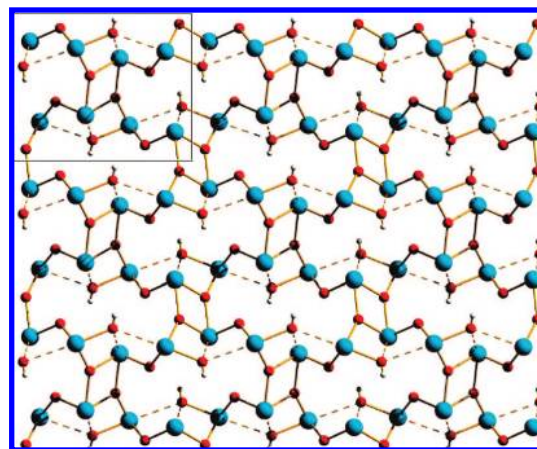


Figure 2. a -Projection of one layer of the structure (blue: antimony, red: oxygen, white: hydrogen); the dashed lines show long intralayer contacts between antimony and oxygen.

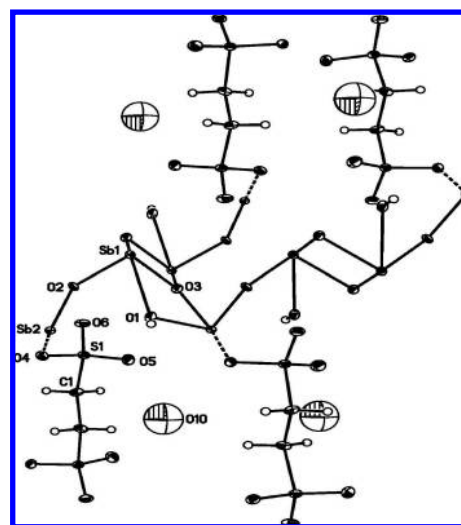


Figure 3. ORTEP diagram and atom-labeling scheme of SLUG-5.

bonded to the EDS anion is the decomposition of SLUG-5 when immersed in unbuffered water. The pH falls rapidly from 5.5 to 3.7, and antimony(III) oxide is formed. Hydrogen bonding between the hydroxyl group of the layer and one of the sulfonate oxygen atoms (O6) [2.726(3) \AA], however, stabilizes the material in nonaqueous solvents. The sulfonate oxygen atoms also define hydrophilic channels down the c -axis in which water molecules were observed from the crystallographic data (Figure 4). The hydrogen atoms on the water molecule could not be located and are presumably disordered. The closest contact from the water oxygen is 2.975(2) \AA to the nearby sulfonate oxygen, which is well within normal hydrogen-bonding contacts.

Various analytical techniques were used to characterize the material. PXRD was carried out for phase identification and to compare to theoretical data (Figure 5, i) derived from the subsequent single-crystal X-ray diffraction data. Elemental analysis of the as-synthesized product (3.14% C, 0.74% H) agrees well with the expected values on the basis of the stoichiometric formula (3.10% C, 0.78% H). Thermogravimetric analysis indicates two major weight losses (Figure 6). The first weight loss starting at ca. 350 $^{\circ}\text{C}$ corresponds to decomposition of the structure and accounts for the loss of EDS and crystalline water (experimental: 19.5%; theoretical: 20.2%). The resultant structure from powder X-ray analysis is valentinite, Sb_2O_3 (Figure 5, iii). There is negligible

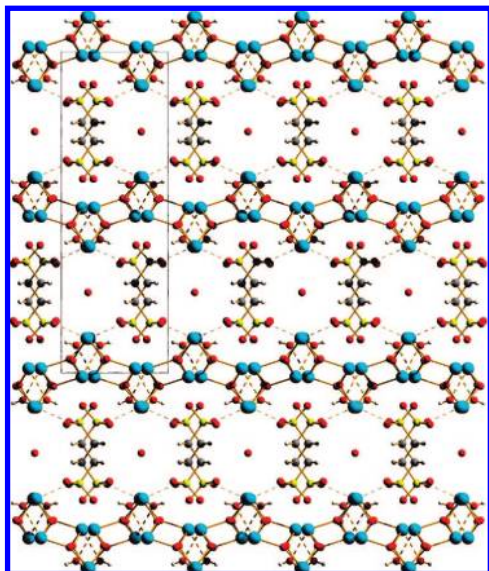


Figure 4. *b*-Projection perpendicular to the layers with water-filled channels along the *c*-axis (yellow: sulfur, gray: carbon).

physisorbed water, however, with no significant weight loss or structural rearrangement before this first decomposition step (Figure 5, ii). The crystallographically observed water therefore supports the stability of the structure. The second weight loss at ca. 600 °C of 71.7% gives rise to the formation of cervantite, Sb_2O_4 (Figure 5, iv). This transition corresponds to a partial loss of antimony oxide by sublimation known to occur at high temperature for the oxides of this element.³⁸ Both decomposition steps were confirmed with a mass spectrometer coupled to the TGA. DSC shows that the first weight loss is an endothermic reaction ($140 \text{ J} \cdot \text{g}^{-1}$). In addition, the crystal surface prior to catalytic studies was characterized by SEM (Figure 7).

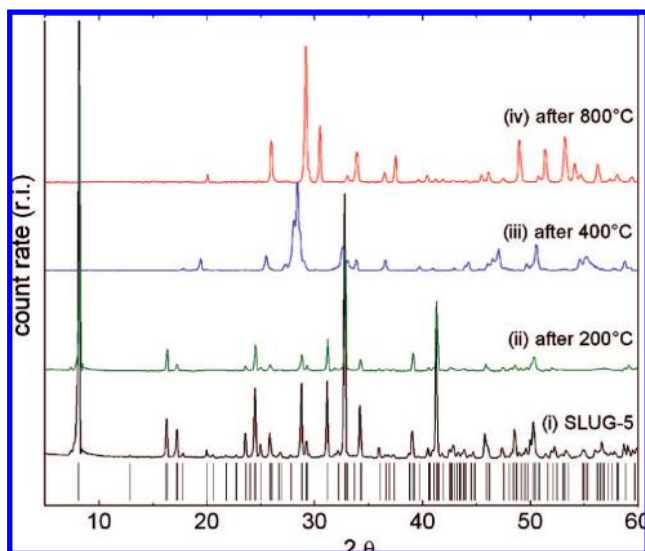


Figure 5. (i) PXRD of the as-prepared material (theoretical data from single-crystal X-ray data shown at bottom) and ex-situ measurements after heating to 200 °C (ii), 400 °C (iii), and 800 °C (iv).

The cationic character of the material was probed by anion exchange, exfoliation, high-pressure behavior, and catalytic studies. Initial attempts to exfoliate the layers or to exchange the EDS molecules for various anions such as nitrate, chromate, and 1,3-

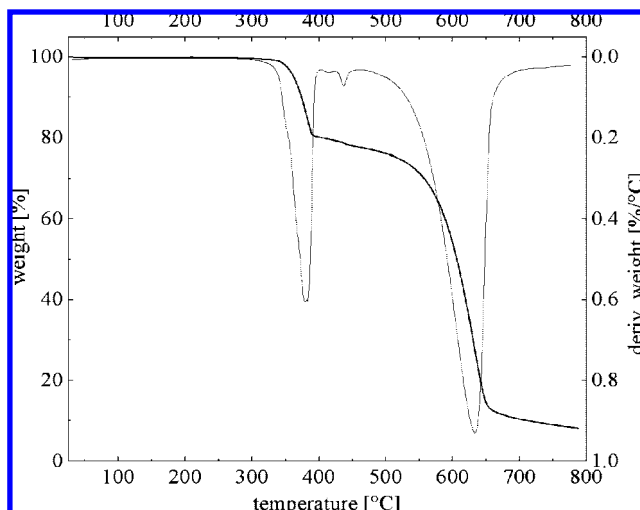


Figure 6. Thermogravimetric analysis of SLUG-5 in the range of 30–800 °C indicates that the material is thermally stable to ca. 350 °C.

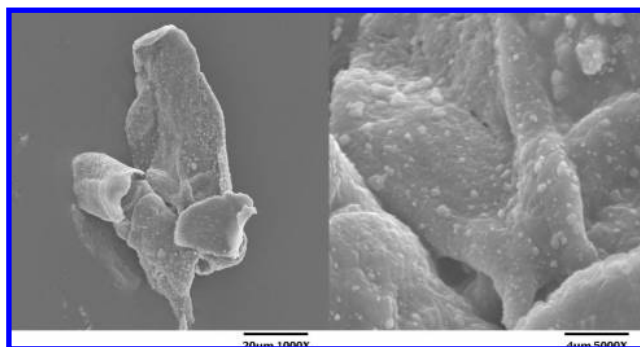


Figure 7. SEM micrographs of the crystal surface of powdered material.

propanedisulfonate were not successful. The hydrogen bonding likely forms a strong network and prevents exchange. Application of 15,000 lbs on a powdered sample in a dye press resulted in the decrease of all peaks along the *a*-axis by ca. 0.02 Å (Figure 8). Repeated experiments verified the slight compression.

Further experiments were performed to test the catalytic activity of SLUG-5, and they showed success for ketal forma-

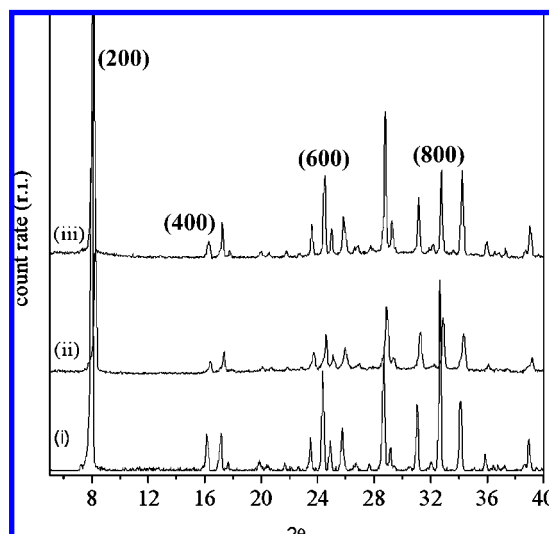
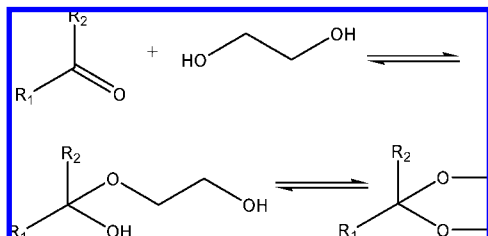


Figure 8. Powder X-ray measurement of SLUG-5 (i); after applying 15,000 lbs pressure (ii); after catalysis (iii).

tion. To test the catalytic activity, a sample was first exposed to water, and the pH decreased implying acidic character at room temperature and atmospheric conditions. This gained insight of SLUG-5's acidic behavior suggests Lewis acid catalysis as a possible application. We studied the material for activity of ketal formation from a ketone.

Ketal formation consists of two mechanistic steps. First, the ketone reacts with an alcohol to give a hemiketal through nucleophilic addition (Scheme 1).

Scheme 1. Ketal formation from ketone with 1,2-ethanediol



In the second step, the hemiketal undergoes a nucleophilic substitution to form a ketal. One example of a ketal formation catalyst is zeolites (microporous aluminosilicates), but such materials demand lengthy preparation and conversion procedures.³⁹ SLUG-5 can be used as synthesized with no drying or ion exchange needed prior to reaction. The alcohol in Scheme 1 is a special case of diol to dioxolane. This form of ketone reaction is common in organic synthesis to protect the carbonyl group of ketones.³⁵ Ketones are generally less reactive to form ketals than their acetal analogues. A catalyst is needed to polarize the bond and to create a better OH leaving group.

The reaction of 2-butanone with 1,2-ethanediol to 2-ethyl-2-methyl-[1,3]-dioxolane was tested with SLUG-5 as a heterogeneous catalyst. A 0.007% molar ratio of catalyst brought the reaction to 53% conversion of 2-butanone (Figure 9, Table 2)

Table 2. Yields for Ketal Formation

material	time	yield
no catalyst	3.0 h	0%
Sb ₂ O ₃	3.0 h	<2%
SLUG-5	3.0 h	53%

and was confirmed by ¹H NMR. To confirm that these properties were unique to SLUG-5, we tested antimony(III) oxide. The yield of the product was less than 2%. Figure 8i and iii illustrates that SLUG-5 is still present after performing the catalysis. The catalyst is not deactivated in the presence of water, that is, the solvent does not need to be dried prior to reaction. Recovered

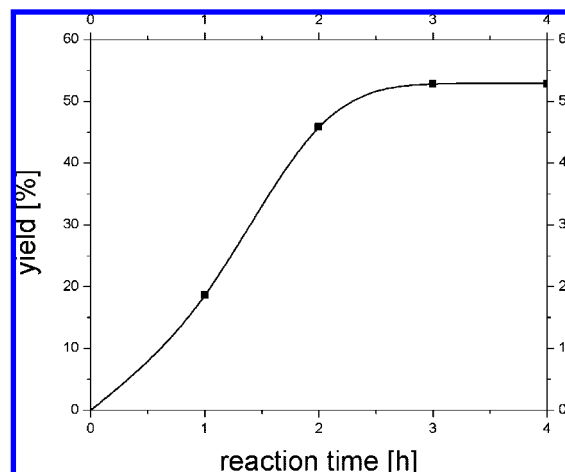


Figure 9. Yield–time plot for the reaction of 2-butanone with 1,2-ethanediol.

SLUG-5 material can be used again for the same catalytic reaction and gave identical reaction yields.

Conclusions

We have demonstrated a rare example of a cationic metal oxide hydroxide with high thermal stability and Lewis acid catalytic activity. SLUG-5 presents a new Lewis acid with properties of a green catalyst since toxic nonaqueous solvents such as toluene are not required nor do the ketone or glycol need to be dried before the reaction. The material is water stable and can be readily recovered after the reaction for additional catalysis. The material shows high potential for other acid-catalyzed organic reactions, which we are currently studying.

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Supporting Information Available: Crystallographic information file (CIF) available containing refinement parameters, fractional atomic coordinates, and bond lengths and angles. CCDS 656220. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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