

Control of Morphology and Catalytic Activity of a Cationic Layered Material

Claudia H. Swanson, Harris A. Shaikh, Yashar Abdollahian, Jesse L. Hauser, Mariko Ikehata, and Scott R. J. Oliver*

University of California, Santa Cruz, Department of Chemistry and Biochemistry, 1156 High Street, Santa Cruz, California 95064, United States

ABSTRACT: We have discovered three new synthetic pathways to our two-dimensional cationic inorganic material, antimony oxide hydroxide ethanedisulfonate, $[Sb_4O_4(OH)_2]$ - $(O_3SCH_2CH_2SO_3)$ ·H₂O. These new methods include room temperature conditions and allow control of crystal size and morphology for improved catalytic performance of the material. As a benchmark reaction, we studied ketalization of 2-butanone with 1,2-ethanediol, a common step for carbonyl



group protection. Our material is easily recovered for reuse and gives a higher yield and turnover rates than the typical iodine or toluenesulfonate homogeneous catalyst. The yield ranged between 79 and 92%, with the crystals from reflux conditions giving the highest yield when used as-synthesized. The morphology and properties for each crystal growth method are described in detail. A repeated catalysis study with powdered samples increases the yield to ca. 97%.

1. INTRODUCTION

Layered inorganic materials have broad application in ionexchange,¹ exfoliation,² drug delivery systems, and catalysis.^{3,4} New synthetic methods such as self-assembly, modular nanobuilding blocks, and polymer intercalation have given rise to a wide range of inorganic-organic hybrids and metalorganic frameworks (MOFs). These materials display potential applications such as improvement in strength and toughness, electrical resistance, and lower thermal expansion.⁵ Naturally occurring clays,³ particularly montmorillonite, kaolinite, and hydrotalcites (also known as layered double hydroxides), continue to be extensively explored as heterogeneous catalysts. Montmorillonite, $(Na,Ca)_{0:33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$, is a layered aluminosilicate anionic clay with intercalated sodium and calcium cations as well as water molecules. It has been proven to be an effective Lewis as well as Brønsted acid.⁶ The cations provide Lewis acidity, while the hydroxy groups of the aluminosilicate layers provide Brønsted acidity.⁷ In addition to clays,³ rare-earth metal triflates^{8,9} have been extensively studied for their homogeneous Lewis acid catalytic properties. Heterogeneous solid catalysts, however, can be easily separated from reaction products, also allowing for possible reuse and may operate without the need for a solvent.^{10,11} In general, Lewis acids catalyze a wide variety of significant reactions including Friedel-Crafts,¹² Diels-Alder,¹³ C-C bond formation, esterification, and ketalization.^{14,15}

Though excellent catalysts, clays have two major drawbacks: (i) they have to undergo postsynthetic calcination and in many cases cation exchange in order to be catalytically active;⁶ (ii) the layers are known to swell when exposed to water.⁷ This expansion is advantageous if larger cations need to be intercalated, but the catalytic performance significantly declines if there is water present in the reaction. Several traditional Lewis acids such as AlCl₃ and FeCl₃ also have inherent disadvantages, including reactivity with moisture as well as the necessity of stoichiometric equivalents in order for catalysis to occur. Other catalysts require inert conditions and/or calcination.^{3,16}

Recently, we reported the hydrothermal synthesis of a cationic layered antimony oxide hydroxide ethanedisulfonate, $[Sb_4O_4(OH)_2](O_3SCH_2CH_2SO_3) \cdot H_2O$ (denoted SLUG-5 for University of California, Santa Cruz, structure No. 5).^{17,18} We provided initial examples of its catalytic activity as a heterogeneous Lewis acid. The layered structure of SLUG-5 is defined by antimony oxide templated by ethanedisulfonate anions (Figure 1). The bonding between the layers is electrostatic, with only a long contact between one sulfonate oxygen on each end and the antimony centers. Water molecules residing between the ethanedisulfonate anions increase the stability of the structure via strong hydrogen bonding. The anionic moieties necessitate a positive charge on the material for electroneutrality. The material is thermally stable up to ca. 350 °C under atmospheric conditions, stable in aqueous medium and can be used as prepared.

Here, we report the controlled synthesis of SLUG-5 by several new synthetic methods, allowing us to tune the morphology and average particle size, ranging from 0.1 to 0.7 mm. The relationship between size and morphology of the crystals and their reactivity toward ketalization catalysis is

```
Received:June 30, 2011Revised:November 28, 2011Published:November 29, 2011
```



Figure 1. Space-filling view of SLUG-5 emphasizing the surface of the antimonate layers. The cylindrical ethanedisulfonate (bottom) templates the antimony oxide hydroxide into a 2D layer (top). The template is negatively charged and the surface has a positive charge, held together by electrostatic forces. Color coding: antimony (blue), sulfur (yellow), oxygen (red), carbon (gray), and hydrogen (white).

discussed. The thicker, more defined morphology from reflux conditions gave the strongest performance.

2. EXPERIMENTAL SECTION

2.1. Crystal Synthesis Methods. *2.1.1.* Hydrothermal Synthesis of SLUG-5 (I). Starting reagents antimony(III) acetate [Sb-(OOCCH₃)₃, Alfa Aesar, 97%] and 1,2-ethanedisulfonic acid (HO₃SC₂H₄SO₃H·H₂O, TCI Inc., 95%) were used as received, without further purification. Crystals of $[Sb_4O_4(OH)_2]$ -(O₃SCH₂CH₂SO₃)·H₂O were hydrothermally synthesized as reported previously,¹⁷ with a molar ratio of 100:1:5 for H₂O:Sb-(OOCCH₃)₃:HO₃SCH₂CH₂SO₃H. The autoclave was heated stat-

ically for 3 days at 150 °C. Colorless crystals were obtained after filtering and rinsing with ethanol [yield based on antimony(III) acetate: 97.4%]. Denoted as SLUG-5 (I).

2.1.2. Stirring-Induced Crystallization of SLUG-5 (II). Antimony-(III) acetate, 1,2-ethanedisulfonic acid, and water were added into a vial in a molar ratio of 1:5:100. The mixture was sealed and mechanically stirred for 4 days at ambient temperature. The product was recovered by filtration and rinsed with ethanol [yield based on antimony(III) acetate: 89.5%]. Denoted as SLUG-5 (II).

2.1.3. Reflux-Induced Crystallization of SLUG-5 (III). Antimony-(III) acetate, 1,2-ethanedisulfonic acid, and water were added into a round-bottom flask in a molar ratio of 1:5:100. The mixture was mechanically stirred and refluxed for 4 days. The product was filtered and rinsed with ethanol [yield based on antimony(III) acetate: 81.6%]. Denoted as SLUG-5 (III).

2.1.4. Evaporation-Induced Crystallization of SLUG-5 (IV). Antimony(III) acetate, 1,2-ethanedisulfonic acid, and water were added into a 10 mL beaker. The beaker was covered with a watch glass and allowed to evaporate at room temperature and pressure for 10 weeks. The product was filtered and rinsed with ethanol [yield based on antimony(III) acetate: 64.0%]. Denoted as SLUG-5 (IV).

2.2. Catalytic Reactions. The following general procedure of ketal formation was used to characterize the performance of SLUG-5 as a Lewis acid catalyst: first, 3.10 μ mol (2.5 mg) of catalyst was added to a round-bottomed glass reactor (capacity 50 mL). A 70 mmol portion of 2-butanone (methyl ethyl ketone, CH₃COCH₂CH₃, Acros Organics, 99%) and 70 mmol of ethylene glycol (HOC₂H₄OH, Acros Organics, 99%) were then added. Toluene (C₆H₅CH₃, EM Science, 99.5%) was used as solvent. The reactants were used as received, with no further treatment. The reaction mixture was refluxed for various time intervals under Dean-Stark conditions, which continuously removed evolved water. The catalyst was recovered by filtration after the desired reaction time and left overnight to air-dry. The product was separated from ethylene glycol using a separatory funnel, and the final product was obtained by fractional distillation. Structure and yield were determined by integrated ¹H NMR peak areas of the ketal product (2-ethyl-2-methyl-[1,3]-dioxolane, δ 3.93–4.00, m, 4H) versus 2-butanone and ethylene glycol (δ 3.73–3.78, m, 4H).



Figure 2. PXRD confirms that all synthesis methods gave rise to the SLUG-5 material: (I) hydrothermal synthesis, light green; (II) stirring-induced crystallization, dark green; (III) reflux-induced crystallization, blue; (IV) evaporation, red. Inset: an expansion of the low-angle majority peak.

2.3. Instrumental. All materials were first characterized by powder X-ray diffraction (PXRD) with a Rigaku Americas Miniflex Plus powder diffractometer equipped with $Cu-K\alpha$ radiation. Diffraction patterns were recorded from 2 to $60^{\circ} 2\theta$, with a step size of 0.04° at 1°/min. Thermogravimetric analysis (TGA) was measured on a TA Instruments 2050 TGA with nitrogen purge, heated from 30 to 800 °C at 10 °C/min and coupled to a mass spectrometer (Pfeiffer Vacuum, ThermoStar, GSD 301 T3) with a 70 eV ionizing potential. ¹H NMR spectroscopy was carried out with a 600 MHz 5 mm Indirect Detection Probe with PFG (Pulse Field Gradients) at 298 K. Scanning electron microscope (SEM) images were collected on an SEM Hitachi S-2700. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrophotometer. The scan range was from 400 to 4000 cm⁻¹ at a resolution of 1 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1. Characterization of Morphologies. The PXRD pattern for all samples I-IV are almost identical, confirming that the same product and crystallinity was obtained for all synthetic methods (Figure 2). The structure of SLUG-5 was previously determined by single crystal X-ray dffraction.¹⁷ The characteristic low angle peak at 8.37 2θ ($d \sim 10.50$ Å, which is the strongest reflection) indicates the layer-to-layer distance. The slight shift in the higher angle peaks and a change in intensity are likely due to preferred orientation, a consequence of the different morphologies (vide infra). The crystal growth is affected by several factors such as crystallization period (evaporation rate, cooling temperature) and stirring speed, with varying degree of preferred orientation for each morphology. For example, the (h00) peaks for SLUG-5 (II) are lowest intensity of the four methods and shifted to slightly lower d-spacing (Figure 2, inset). SLUG-5 (IV) displays the strongest intensity (200) peak. During the SLUG-5 (II) crystallization, the agitation by the stir bar likely interferes with and limits the degree of crystallization.

FT-IR spectra were also obtained to confirm the presence of the ethanedisulfonate template between the layers (Figure 3). Sharp bands observed between 1020 and 1013 cm^{-1} are



Figure 3. FT-IR spectra of the different morphologies confirm the presence of interlayer EDS anions: (I) hydrothermal synthesis, (II) stirring-induced crystallization, (III) reflux-induced crystallization, and (IV) evaporation.

ascribed to S–O stretching in the ethanedisulfonate. Peaks between 1139 and 1129 cm^{-1} represent sulfonate peaks¹⁹ and occur for all four morphologies, indicating a similar degree of interaction with the layers. The strong band between approximately 3200 and 3600 cm⁻¹, for each morphology, is due to hydrogen bonding.

Thermogravimetric analysis shows that morphologies II, III, and IV have an almost identical thermal stability (Figure 4). Weight loss starting at ca. 350 °C corresponds to the



Figure 4. Thermogravimetric analysis shows similar traces for all four synthesis methods: (I) hydrothermal, (II) stirring-induced, (III) reflux-induced, and (IV) evaporation.

decomposition of the structure and accounts for the loss of the ethanedisulfonate template (experimental: 18.0%; theoretical: 17.9%) and crystalline water (experimental: 2.0%; theoretical: 2.3%). The hydrothermal product (I) has a slightly higher thermal stability, presumably due to a more ordered lattice.¹⁷ In all cases, PXRD after heating to 600 °C indicates collapse to valentinite, Sb₂O₃ (ICDD #11-689). SLUG-5 (II, stirring) and (IV, evaporation) show a slight mass loss of ~2% around 280 °C, likely due to additional interlayer chemisorbed water.

After it was confirmed that the three new morphologies are the same as our crystal structure reported from hydrothermal synthesis, the size and morphology were investigated by SEM. Although the powder patterns are similar, the particle size and morphology greatly depend on the synthetic method. Hydrothermal crystals (I) are up to several millimeters in size with an uneven surface (Figure 5-I). Stirring-induced crystals (II) are very thin platelets, $1-5 \ \mu m$ in width (Figure 5-II). Refluxinduced crystals (III) are significantly larger and thicker, with a much greater size distribution of ~1 to 20 μ m (Figure 5-III). Evaporation-induced crystals (IV) display the most homogeneous morphology and smallest particle size (Figure 5-IV). As observed for other materials such as zirconium phosphates,²⁰ reflux conditions often give rise to smaller particles than hydrothermal conditions. The static conditions of hydrothermal (I) and evaporation (IV) led to a narrower particle size distribution.

Clearly, the size of the crystals can be effectively controlled by the synthetic technique. A given method affects the solubility of the precursors and thus supersaturation level and

Crystal Growth & Design



Figure 5. SEM of SLUG-5 synthesized by each method: (I) hydrothermal yields a rough surface and large particle size; (II) stirring-induced crystallization leads to thin platelets; (III) reflux-induced crystallization gave thicker crystals ranging from 1 to 20 μ m in size. The crystal edges are much sharper than for the other methods; (IV) evaporation-induced crystallization results in evenly shaped nanoplatelets, the smallest particles of the four methods.

rate of crystal growth. Hydrothermal conditions (higher temperature, autogenous pressure created in the autoclave) generally leads to larger crystals than reflux conditions due to the elevated pressure and reduced supersaturation, as well as the ripening effect due to greater temperature fluctuation and thermal gradients. Reflux gives rise to a higher level of supersaturation, for rapid growth of smaller crystals, with the agitation caused by stirring and boiling further limiting crystal size. Stirring and evaporation occurred under ambient conditions and hence formed smaller particles. While particle size is inversely proportional to specific surface area, the crystallinity and morphology are known be equally important in determining catalytic properties.

3.2. Catalytic Activity. As a benchmark reaction to compare the four morphologies, ketal formation from 2-butanone (methyl ethyl ketone, MEK) using 1,2-ethanediol (ethylene glycol) was studied. Generally, this step serves as protection of a carbonyl group from undesired side reaction (Scheme 1). The reaction was performed for 4 h (Experimental Section 2.2).

The morphology has a significant impact on the performance of the catalyst. The most efficient was catalyst (III), with a

maximum yield of 92%, followed by (I), (II), and (IV) (80– 84%, Table 1). The yield profile over 4 h is plotted in Figure 6. No reaction occurred in the absence of the catalyst or with EDSA only. It is unlikely any species including EDS are

 Table 1. Ketal Formation Yield for the Four Morphologies

 after 4 h Reaction Time

crystallization method	abbreviation	catalytic yield [%]
hydrothermal	Ι	83.9
stirring-induced	II	82.5
reflux-induced	III	92.3
evaporation	IV	79.6



Figure 6. Percent conversion of methyl ethyl ketone to ketal with different morphologies of SLUG-5 [hydrothermal (I), stirring-induced (II), reflux-induced (III), evaporation (IV)], as well as antimony oxide (V, square symbol at 4 h) and with no solid catalyst present (VI, triangle symbol at 4 h).

catalyzing homogeneously. We have published several related cationic inorganic materials that contain interlamellar EDS anions.^{21–23} In all cases, we removed the solid catalyst after several hours and allowed the reaction to continue. No additional ketal formed, while ¹H NMR showed that no EDS was present in any of the reaction mixtures. Antimony(III) oxide as catalyst resulted in a finite but very low yield of 3.0%, underscoring the activity of SLUG-5.

One possible explanation of the enhanced catalytic properties of the reflux-induced SLUG-5 (III) is the well-defined surfaces of the polygonal crystals. The crystals are larger than the rounded disk-like morphologies from stirring-induced (II) and evaporation (IV). Another possible explanation for the enhanced performance of (III) is the sharp crystal edges of the material. Such areas are known to have more defects as well as adsorb reactants onto the catalyst surface.^{24,25} This explanation would account for the lower performance by the

Scheme 1. Ketal Formation from 2-Butanone and 1,2-Ethanediol Results in a Protective Group for the Carbonyl Group^a



"Water is formed as a side product and removed during the reaction in order to shift the equilibrium to the right.

Crystal Growth & Design

Article



Figure 7. Percent ketal conversion by powdered (A) and preheated-powdered (B) SLUG-5 for the different synthesis methods [hydrothermal (I), stirring-induced (II), reflux-induced (III), and evaporation (IV)].

rounded morphology of evaporation (IV). Indeed, the rough edges of hydrothermal (I) and reflux (III) likely give higher ketal formation than the much smaller crystals of stirring (II) and evaporation (IV). The lack of porosity of SLUG-5 implies that the reactions are occurring on the surface of the particles and thus are sensitive to the surface morphology.

Another possible reason for the varying yields, however, is the structurally contained water. Water reduces the speed of the reaction by shifting the equilibrium toward the reactants and needs to be constantly removed from the system. Indeed, TGA below 250 °C (Figure 4) indicates a greater amount of physiand chemisorbed water in SLUG-5 (I, II, and III). We therefore further examined all four morphologies by repeating the catalysis in both powdered and preheated-powdered forms. To remove extra water from the surface of the latter, the samples were kept at 125 °C for 30 min. The conversion yield for the catalysis using all four SLUG-5 morphologies is ca. 97% after 4 h (Figure 7). Clearly, powdering increased specific surface area and in turn conversion yield. The powdered-preheated samples showed no increase in final yield as compared to the powdered SLUG-5 morphologies. Table 2 compares the conversion yields of as-synthesized, powdered and powdered-preheated SLUG-5.

Table 2. Comparison of Ketal Yield for the FourMorphologies after 4 h Reaction Time

		catalytic yield [%]			
crystallization me	thod	as-synthesized	powdered	preheated	
hydrothermal	Ι	83.9	96.3	98.4	
stirring-induced	II	82.5	97.3	95.4	
reflux-induced	III	92.3	96.6	97.7	
evaporation	IV	79.6	96.9	96.1	

4. CONCLUSIONS

Several new synthetic pathways to SLUG-5 requiring only ambient conditions have led to increased catalytic performance. The crystalline structure of SLUG-5 via hydrothermal (I), stirring (II), reflux (III), and evaporation (IV) are identical, yet their morphology influences the catalytic behavior. Reflux (III) gave the strongest catalytic yield with reactivity greater than that of hydrothermal (I) but with a far simpler, cost-effective synthetic method. Furthermore, the catalytic yield for all four forms of SLUG-5 increased to 97% when the samples were powdered. We are also investigating other reactions for SLUG-5 including Diels—Alder, esterification, and Friedel—Crafts alkylation. The cationic charge of the layers coupled with morphological control provides SLUG-5 a significant advantage over traditional catalysts. The material can be easily recovered by filtration for reuse, making it an attractive choice over homogeneous toluenesulfonate, the standard ketalization catalyst.

AUTHOR INFORMATION

Corresponding Author

*E-mail: soliver@chemistry.ucsc.edu.

REFERENCES

- (1) Tran, D. T.; Zavalij, P. Y.; Oliver, S. R. J. J. Am. Chem. Soc. 2002, 124, 3966–3969.
- (2) Ma, R.; Liu, Z.; Takada, K.; Iyi, N.; Bando, Y.; Sasaki, T. J. Am. Chem. Soc. 2007, 129, 5257–5263.
- (3) Centi, G.; Perathoner, S. Microporous Mesoporous Mater. 2008, 107, 3-15.
- (4) Tagusagawa, C.; Takagaki, A.; Hayashi, S.; Domen, K. J. Am. Chem. Soc. 2008, 130, 7230-7231.
- (5) Sanchez, C. A.; Crump, K. S.; Krieger, R. I.; Khandaker, N. R.; Gibbs, J. P. *Environ. Sci. Technol.* **2005**, *39*, 9391–9397.
- (6) Hawxwell, S. M.; Adams, H.; Brammer, L. Acta Crystallogr. Sect. B 2006, 62, 808–814.
- (7) Vaccari, A. Appl. Clay Sci. 1999, 14, 161-198.
- (8) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W. L. Chem. Rev. 2002, 102, 2227–2302.
- (9) Longbottom, D. Synlett 1999, 2023.
- (10) Forster, P. M.; Cheetham, A. K. Top. Catal. 2003, 24, 79-86.
- (11) Corma, A.; Garcia, H. Chem. Rev. 2003, 103, 4307-4366.
- (12) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S.-i. J. Org. Chem. **1997**, 62, 6997–7005.
- (13) Kobayashi, S.; Hachiya, I.; Araki, M.; Ishitani, H. Tetrahedron Lett. **1993**, 34, 3755–3758.
- (14) Patel, S. M.; Chudasama, U. V.; Ganeshpure, P. A. J. Mol. Catal A: Chem. 2003, 194, 267–271.
- (15) Banik, B. K.; Chapa, M.; Marquez, J.; Cardona, M. Tetrahedron Lett. 2005, 46, 2341–2343.

(16) Kobayashi, S.; Manabe, K. Pure Appl. Chem. 2000, 72, 1373–1380.

97

(17) Swanson, C. H.; Shaikh, H. A.; Rogow, D. L.; Oliver, A. G.; Campana, C. F.; Oliver, S. R. J. J. Am. Chem. Soc. 2008, 130, 11737–11741.

(18) Oliver, S. R. J. Chem. Soc. Rev. 2009, 38, 1868-1881.

(19) Fadini, A.; Schnepel, F. M. Schwingungsspektroskopie: Methoden und Anwendung; Thieme: Stuttgart, 1985.

(20) Kaschak, D. M.; Johnson, S. A.; Hooks, D. E.; Kim, H. N.; Ward, M. D.; Mallouk, T. E. J. Am. Chem. Soc. **1998**, 120, 10887–10894.

(21) Rogow, D. L.; Fei, H. H.; Brennan, D. P.; Ikehata, M.; Zavalij, P. Y.; Oliver, A. G.; Oliver, S. R. J. *Inorg. Chem.* **2010**, *49*, 5619–5624.

(22) Fei, H. H.; Paw, L.; Rogow, D. L.; Bresler, M. R.; Abdollahian, Y. A.; Oliver, S. R. J. Chem. Mater. **2010**, 22, 2027–2032.

(23) Fei, H. H.; Rogow, D. L.; Oliver, S. R. J. J. Am. Chem. Soc. 2010, 132, 7202-7209.

(24) Marra, G. L.; Tozzola, G.; Leofanti, G.; Padovan, M.; Petrini, G.; Genoni, F.; Venturelli, B.; Zecchina, A.; Bordiga, S.; Ricchiardi, G. *Stud. Surf. Sci. Catal.* **1994**, *84*, 559–566.

(25) Roeffaers, M. B. J.; Sels, B. F.; Uji-i, H.; De Schryver, F. C.; Jacobs, P. A.; De Vos, D. E.; Hofkens, J. *Nature* **2006**, 439, 572–575.