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Synthesis, Characterization, and Catalytic Application of a Cationic Metal−Organic Framework: $Ag_2(4,4'\text{-bipy})_2(O_3SCH_2CH_2SO_3)$

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We report a silver-based cationic metal−organic framework with two mixed organic linkers directing the structure. The structure consists of 1D Ag(4,4′-bipy) cationic chains arranged into close-packed layers. Weakly bound alkanedisulfonate anions charge-balance the layers, where only one oxygen of each sulfonate makes a long contact with the Ag. The unsaturated linear Ag centers likely allow the Lewis acidity displayed by the material for ketone protection as well as esterification. The material showed no reduction in yield after three catalytic runs with average 95% conversion yield for ketal formation and 57% for esterification without further water removal. In addition to hydrothermal conditions, the structure can be synthesized by reflux or room temperature, with almost identical catalytic ability. Other properties of this compound including chemical and thermal stability are also described.

Introduction

Hybrid inorganic−organic solid-state compounds are an emerging class of materials with exponential growth in recent years, especially metal−organic frameworks (MOFs).[1−3] Considering some retain a robust and geometrically defined structure at elevated conditions, this group of extended coordination frameworks have a wide range of application, such as catalysis,[4−6] gas storage,[7,8] gas absorption,[9] ion exchange,[10] and drug delivery.[11] Due to the great variety of metal units and organic linkers, these multifunctional materials have almost infinite possible combinations, and more recent efforts have been made to establish their structure−property relationships.

Heterogeneous catalysis using MOFs has attracted much effort due to increased environmental concerns, seeking stable and easily recoverable catalysts.[12] As yet, there are limited systematic reports concerning heterogeneous catalysis by porous coordination frameworks.[6,13] Microporous MOFs have been investigated recently and show that the active site is the Lewis acidic coordinatively unsaturated metal.[5,6,14,15]

Cationic metal−organic frameworks are a small subgroup of MOFs where the positive charge of the metals is stoichiometrically greater than the negative (or neutral) charge of organic linker. Charge-balancing extraframework anions function as structure directing agents (SDAs) and reside in the framework.[16−18] Positively charged MOFs may lead to a greater degree of coordinatively unsaturated metals owing to the weak electrostatic interaction between the metal and extraframework anions. Our group, among others, is taking the initial steps of applying cationic hybrid inorganic−organic frameworks to catalysis.[19] Nitrate, perchlorate, and ethanedisulfonate anions have been shown to direct the growth of cationic oxides and fluorides based on lower p-block elements. Hydrogen bonding and/or electrostatic interaction

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between the cationic host and SDA anion give rise to coordinatively unsaturated metal sites, thus yielding efficient Lewis acidity.[19−23]

A recent goal of our group is to isolate cationic extended frameworks based on transition metals which are thus more predictable in terms of coordination and properties. Aside from the well-established layered double hydroxides (LDHs)/hydrotalcite minerals, there are very few reports detailing cationic extended coordination polymers constructed from transition metals.[23,24] Silver(I), cadmium(II), and copper(I) are isoelectronic, with filled d^{10} shells that favor rigid, linear structures.[25] Several Ag(I) organosulfonate MOFs have been reported but are condensed neutral or open anionic frameworks.[26−29] Catalysis application of open cationic structures based on d^{10} shell metal ions remain largely unexplored and may form low-coordinate open metal sites for possible Lewis acidity.

Herein, we report a silver-based 1D cationic coordination polymer with 4,4′-bipyridine (4,4′-bipy) linker and templated by 1,2-ethanedisulfonate (EDS). The structure is a rare example employing mixed organic linkers to direct the cationic extended frameworks. Two different organic linkers support Ag(I) with enough openness to allow access by incoming guests. The synthesis, thermal properties, catalytic reactivity, and reusability are investigated in detail.

Experimental Section

Reagents. Silver nitrate ($AgNO_3$, Fisher ≥99.7%), 1,2-ethanedisulfonic acid (EDSA: $HO_3SCH_2CH_2SO_3H$, TCI Inc. 95%), and 4,4′-bipyridine [$(C_5H_4N)_2$, Acros Organics, 98%] were used as-received for the synthesis. 2-Butanone ($CH_3COCH_2CH_3$, Acros Organics, 99%), 2-pentanone (TCI America, 97%), ethylene glycol ($HOCH_2CH_2OH$, Acros Organics, 99%), acetic acid (glacial, CH_3COOH, MP Biomedicals, 99%), formic acid (Acros Organic, 99%), acetone (Fisher, 99.9%), and toluene ($C_6H_5CH_3$, Fisher, 99.7%) were used as-purchased for the catalytic studies.

Synthesis. Colorless crystals of $Ag_2(4,4'\text{-bipy})_2(O_3SCH_2CH_2SO_3)\cdot 4H_2O$ (which we denote as SLUG-21: University of California, Santa Cruz No. 21) was synthesized under hydrothermal conditions. A reactant solution with a molar ratio of 1:1:1:400 for $AgNO_3$:EDSA:4,4′-bpy:H_2O was stirred at room temperature for 10 min and then transferred to a 15 mL Teflon lined autoclave to 2/3 full. The autoclaves were heated at 150 °C for 5 days under autogenous pressure, during which the pH of the reactant solution increased from 1.8 to 2.2. Colorless large block crystals were isolated after filtration and rinsed by acetone (yield: 0.54 g, 98.7% based on silver nitrate). IR (KBr pellets): 3467s, 3050 m (O−H stretch); 1605s, 1535s, 1490s, 1418s (aromatic C−H stretch); 1328s (CH_2 stretch); 1200 m, 1070 m (SO_3^- stretch); 863s, 817s (aromatic C−H bending) (cm^{-1}).

Crystals of $Ag_2(4,4'\text{-bipy})_2(O_3SCH_2CH_2SO_3)\cdot 4H_2O$ can also be synthesized with no need for autoclaves by refluxing or stirring at room temperature. Reactions were carried out with the same ratio of reactants and crystals were filtrated after ca. 60 h (refluxing) and 5 days (stirring) reaction time. The yield is 74.1% (0.40 g) with refluxing and 83.3% (0.45 g) with stirring (both yields again based on silver nitrate).

Heterogeneous Catalysis. A 100 mg (0.13 mmol) portion of the as-synthesized crystal catalyst, 70 mmol of 2-butanone, and 70 mmol of ethylene glycol were introduced into 80 mmol of toluene, the latter was used as the solvent for a ketal formation reaction. The reaction was refluxed at 110 °C under Dean−Stark conditions for specified time intervals. The catalyst was isolated by filtration and reused on subsequent reactions without further treatment. A 100 mg portion of SLUG-21 was also applied for an esterification between 70 mmol acetic acid and 70 mmol ethanol in 8 mL toluene. The reactants were refluxed for 8 h without further methods for water removal. All product yields were determined by ^1H NMR (Supporting Information).

Instrumental Details. Samples for powder X-ray diffraction (PXRD) were measured on a Rigaku Americas Miniflex Plus diffractometer and were scanned from 2 to 60° (2θ) at a rate of 2° (2θ) per minute and 0.04° step size, under Cu−Kα radiation (λ = 1.5418 Å). Single-crystal X-ray diffraction data was obtained a Bruker SMART APEX II CCD area detector X-ray diffractometer under graphite monochromated Mo−Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using SADABS, and the structure was solved by direct method and refined with SHELXTL.[30] All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Crystal structure views were obtained using Diamond v3.2 and rendered by POV-Ray v3.6.

Thermogravimetric analysis (TGA) was performed using a TA Instruments 2050 TGA by heating from 25 to 600 °C under N_2 purge with a gradient of 15 °C/min. In-situ mass spectra coupled to the TGA were collected on a Pfeiffer Vacuum ThermoStar GSD 301 T3 mass spectrometer with a 70 eV ionization potential. Scanning electron micrographs (SEM) were collected on a Hitachi S-2700 SEM; ^1H NMR spectra were collected with a Varian Oxford 600 MHz spectrometer by dissolving the sample in 700 μL of deuterated choloroform with tetramethylsilane as the internal standard.

Results and Discussion

Crystals of SLUG-22 can be synthesized hydrothermally between 125 and 150 °C with reproducible crystal size and morphology (see optical micrographs in the Supporting Information, Figure S1). Reflux without applied pressure as well as stirring at room temperature may also be used. Micrographs (Figures 1 and S1) show that reflux also achieved high quality crystals with similar

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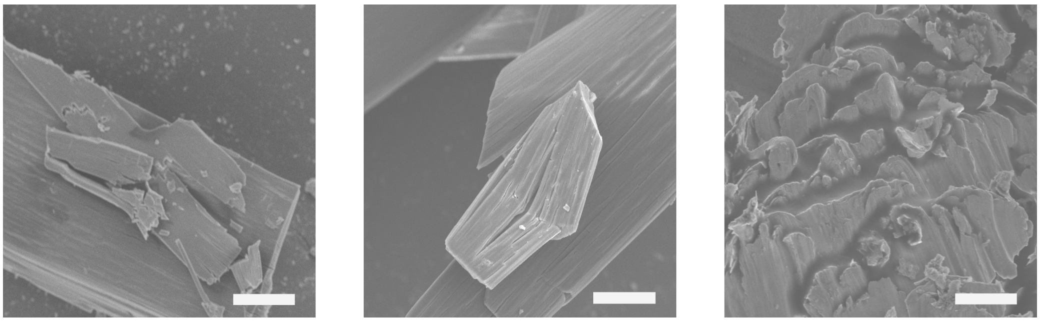

Figure 1. SEM images of SLUG-21 under hydrothermal conditions (left), refluxing (middle), and room temperature stirring (right). The scale bar is 40 μm for the left image, and 20 μm for both the middle and right images.

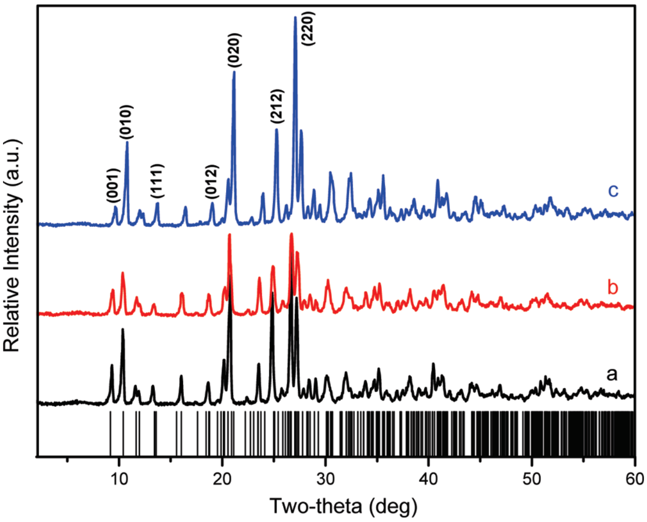

Figure 2. PXRD of as-synthesized SLUG-21 prepared from (a) hydrothermal methods, (b) refluxing, and (c) stirring. Theoretical data from the structure solved by single-crystal X-ray diffraction is shown at the bottom.

Table 1. Crystal Data and Structure Refinement of SLUG-21

empirical formula	$C_{22}H_{28}Ag_2N_4O_{10}S_2$
crystal system	triclinic
space group	$P\overline{1}$
formula weight (g/mol)	788.36
a (Å)	8.1174(17)
b (Å)	9.2860(19)
c (Å)	10.297(2)
α (deg)	71.589(2)
β (deg)	75.392(2)
γ (deg)	71.286(2)
volume (Å^3)	687.6(2)
Z	1
crystal size (mm^3)	0.06 × 0.05 × 0.03
color of crystal	colorless
goodness-of-fit on F^2	1.045
final R indices $I > 2\sigma(I)$	$R_1 = 0.0262$, $wR_2 = 0.0559$
R indices (all data)	$R_1 = 0.0288$, $wR_2 = 0.0569$

crystal morphology compared to the hydrothermal product. Room temperature stirring gave lower crystallinity but higher yield than reflux and larger specific surface area. PXRD of SLUG-21 prepared from the three methods confirms that the products give the identical phase and match the theoretical pattern based on the single crystal solution (Figure 2). SLUG-21 crystallizes in a triclinic crystal system with the $P\overline{1}$ space group (Table 1). All of the products are chemically stable in deionized water and organic solvents, including chloroform, toluene, and acetonitrile (Figure S6).

Single-crystal X-ray diffraction studies reveal that the structure of SLUG-21 is a cationic one-dimensional extended MOF of alternating Ag centers and 4,4′-bipy molecules bonded through Ag−N bonds (Figures 3 and 4). The chains are arranged into layers, with ethanedisulfonate (EDS) anions residing in the interlamellar space. The Ag-bipy layer is stabilized by 4,4′-bpy ligand $\pi-\pi$ stacking between adjacent 1D chains. Each end of the EDS molecule interacts electrostatically with adjacent cationic layers through one sulfonate oxygen, with Ag−O distances between 2.711(7) and 2.759(9) Å (Figure 4). The other two oxygens are involved in a hydrogen bonding network with interlamellar waters, which were resolved (Table 2). Silver(I) atoms with a full d shell form an almost linear geometry (two similar N−Ag−N angles of 171.5(3)° and 172.3(3)°], with Ag−N bond lengths in the range of 2.156(6)−2.170(7) Å. Two weak interactions occur between each Ag atom and the oxygen of the EDS anion, and the atom distances are between 2.711(7) and 2.759(9) Å. These distances are significantly longer than accepted Ag−O covalent bond lengths,[31] especially considering literature Ag(I) to sulfonate distances are in the range of 2.45−2.55 Å.[32−34] These values confirm that the EDS anions only interact electrostatically with the Ag(I)-bipy cationic extended framework.

Four crystallographically identified water molecules verify that SLUG-21 cannot be obtained under nonaqueous medium, as attempts to use dimethylformamide, pyridine, or 2-butanol as solvent were unsuccessful. The presence of hydrogen bonds between the EDS anion and intercalated water molecules (Figure 4 and Table 2) further stabilize the structure. Indeed, crystallinity was not lost after immersing SLUG-21 into unbuffered water or other common organic solvents for several weeks (Figure S6).

The thermal stability of SLUG-21 was also investigated in detail by TGA-MS under nitrogen flow and ex-situ

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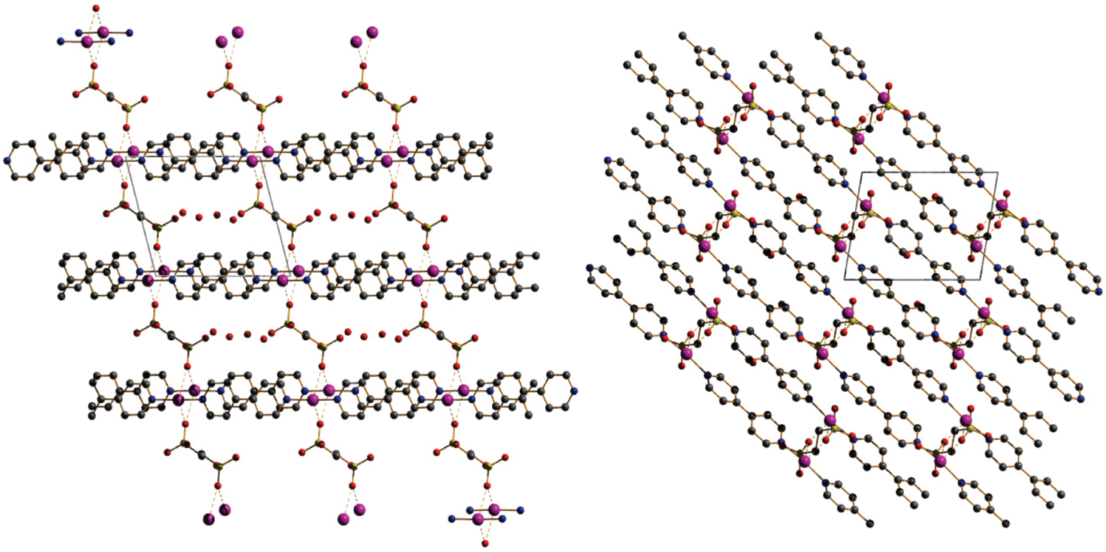

Figure 3. Crystallographic *a*-projection (left) and *b*-projection (right) of the structure with hydrogen atoms omitted for clarity (silver purple; carbon gray; sulfur yellow; oxygen red; nitrogen blue).

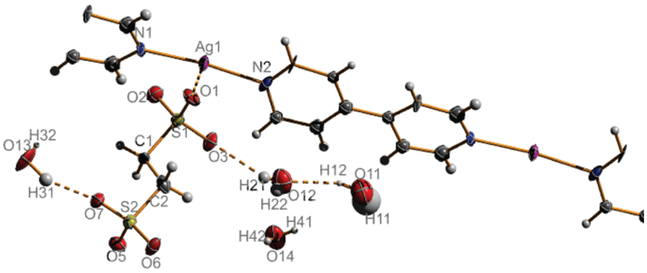

Figure 4. ORTEP diagram and atomic labeling of SLUG-21. Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Lengths, Angles, and Hydrogen Bonding in SLUG-21[a]

Ag(1)−N(1)	2.156(7)	Ag(1)−N(2)	2.171(7)
Ag(2)−N(3)	2.128(7)	Ag(2)−N(4)	2.156(7)
N(1)−Ag(1)−N(2)	171.5(3)	N(3)−Ag(2)−N(4)	172.3(3)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O(11)−H(12)···O(12)^{1}	0.81(4)	1.94(4)	2.711(15)	157(4);
O(14)−H(41)···O(13)^{2}	0.77(5)	2.27(5)	2.733(13)	119(4);
O(12)−H(21)···O(3)	0.61(7)	2.24(8)	2.784(13)	150(11);
O(13)−H(31)···O(7)	0.96(6)	1.89(7)	2.795(10)	158(5);
O(13)−H(32)···O(11)^{3}	0.76(6)	2.05(7)	2.724(13)	148(6);
O(11)−H(11)···O(6)	0.67(17)	2.31(16)	2.823(12)	135(17);
O(12)−H(22)···O(14)^{4}	0.74(9)	2.07(9)	2.751(12)	152(8);

[a] Symmetry transformations used to generate equivalent atoms: (1) x, y, $z - 1$; (2) x, y, $z + 1$; (3) $x + 1$, y, z; (4) $x - 1$, y, z.

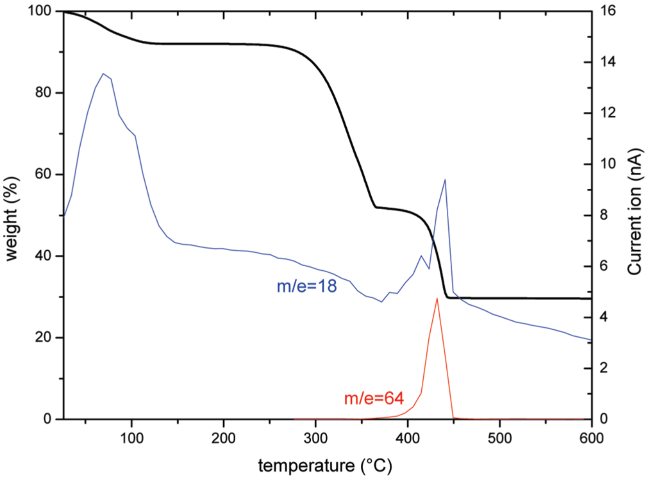

Figure 5. Thermogravimetric trace (black) and coupled mass spectra (blue and red for $m/e = 18$ and 64, respectively) of SLUG-21.

PXRD (Figures 5 and S2, Supporting Information, respectively). An 8.0% weight loss occurs after heating to 120 °C owing to the removal of most of the interlamellar water molecules (calculated: 9.13%). The increase in the $m/e = 18$ signal also supports the loss of water. Ex-situ PXRD shows reduction in crystallinity and slight phase transformation, but an open structure is retained. The higher temperature phase is stable up to ca. 300 °C, when the bipyridine decomposes by 350 °C (observed 40.2%, expected 39.6%). No major signal for either $m/e = 18$ or $m/e = 64$ also implies organic decomposition in this temperature range. The TGA trace is then stable state up to 400 °C, when another weight loss occurs. This event corresponds to loss of EDS anion (observed 27.6%, expected 29.2%), leaving a pure silver phase as confirmed by ex-situ PXRD after 450 °C (Figure S2). The coupled mass spectra at $m/e = 64$ appears to verify this decomposition step, with removal of an SO_2 fragment.

Considering Ag(I) is typically three to six coordinate among coordination polymers,[26−29,35−37] the two-coordinate Ag(I) sites in SLUG-21 are coordinatively unsaturated owing to the weak bonding by the EDS anions. In addition, the linear geometry metal sites are accessible by one-dimensional pores running along the *a*-axis (Figure 3). The lack of any metal hydroxyl groups and the observation of constant pH of 6.5 when SLUG-21 is placed in unbuffered deionized water indicates

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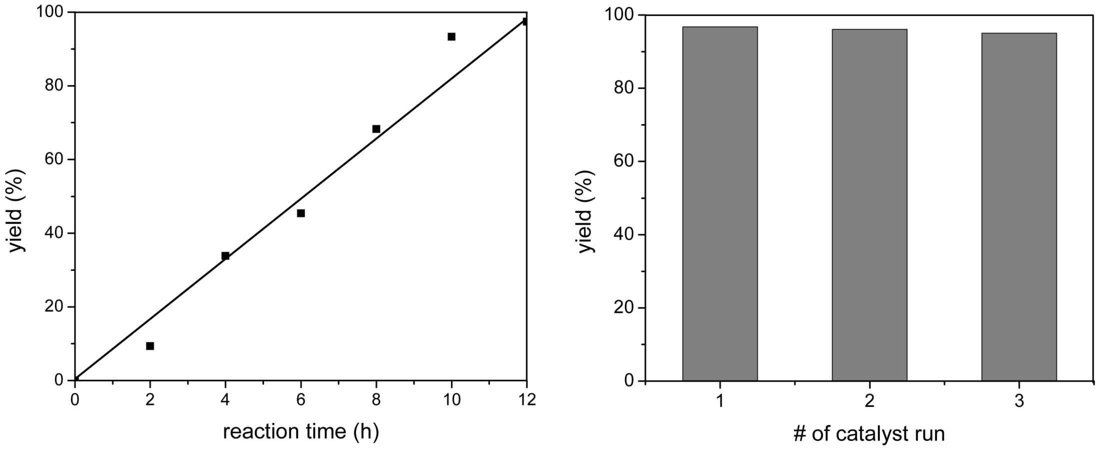
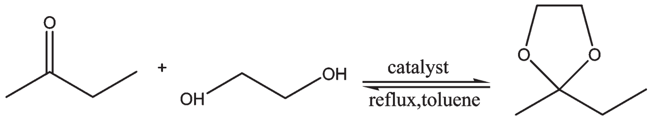


Figure 6. Yield for ketal formation by SLUG-21. (left) Yield vs time plot. (right) High conversion yield retained upon recycling the material.

Scheme 1. Acid Catalyzed Ketal Formation between 2-Butanone and Ethylene Glycol



the material is Lewis rather than Bronsted catalytic. Considering these factors, we investigated the Lewis acid catalytic activity of the compound.

Ketalization of aldehydes and ketones is important for the protection of carbonyl groups in preparative organic synthesis, especially drug design.[38] While toluenesulfonate is a standard catalyst, it is homogeneous and must be separated from the product by concentration under vacuum.[39] Recent heterogeneous catalysts such as tetrabutylammonium tribromide experience at least one of the following problems: (i) toxicity; (ii) high cost; (iii) difficulty in preparation; (iv) low yield for catalytic reaction.[40−42] The mechanism of the reaction requires the Lewis acid catalyst to activate the oxygen of the carbonyl group, allowing glycol to substitute for the ketone group. Our cationic silver-based compound was tested for ketal formation between 2-butanone and ethylene glycol (Scheme 1). The results reveal that SLUG-21 is a strongly active and reusable catalyst.

We used 0.127 mmol of SLUG-21 to catalyze a reaction between 70 mmol 2-butanone and 70 mmol ethylene glycol, for a catalytic ratio of 1 to 552. With a Dean–Stark trap to constantly remove the water, ketal product increases linearly until almost complete conversion after 12 h (Figure 6 left and Table 3). Compared with a blank experiment without catalyst under the same conditions and period of time, only negligible product formed (Table 3), confirming that SLUG-21 is an efficient Lewis acid catalyst.

Table 3. Conversion Yields for Catalytic Reactions

reaction	catalyst	time (h)	conv (%)[a]
ketalization	no catalyst	12	1
ketalization	hydrothermal SLUG-21	12	97
ketalization	reflux SLUG-21	12	96
ketalization	room-temp stirring SLUG-21	12	95
esterification	no catalyst	8	< 10
esterification	hydrothermal SLUG-21	8	57

[a] The conversion efficiency is determined by ^{1}H NMR.

Control experiments for the catalysis have been conducted by filtering off SLUG-21 after 6 h reaction time and then continuing the reaction for an additional 12 h. This study was conducted to determine whether the reaction is being catalyzed by the material or some other species present in the reaction solution. The additional 12 h led to less than 2% increase in ketal yield, proving that the SLUG-21 material is responsible for the catalytic activity. Negligible mass loss of SLUG-21 during the reaction further supports its inherent stability. In addition to ketalization of 2-butanone, different ketone precursors were studied, namely acetone and 2-pentanone. For acetone, the yield was ~90%, again with negligible yield in the absence of the catalyst (Figure S7, Supporting Information). The ketalization of 2-pentanone displayed slightly lower yield (87%, Figure S8, Supporting Information), possibly due to slower diffusion into the MOF pores by the more bulky precursor.

As previously mentioned, the structure is slightly transformed upon partial removal of intercalated water (Figure S2). There is lattice shrinkage along the *b*-axis, as evidenced by the shift of both (010) and (020) PXRD peaks to higher angle. This direction is to be expected since the EDS linker and intercalated water molecules reside in the interlamellar area, perpendicular to the layers as defined by the *b*-axis. The activated form is likely responsible for the catalysis. There is an ca. 10% mass loss of catalyst after the first cycle and negligible weight loss thereafter. The activated form of SLUG-21 is thus stable for this catalytic reaction and highly reusable, achieving similar yields through three cycles (Figures 6 and 7). We also tested the catalytic ability of SLUG-21

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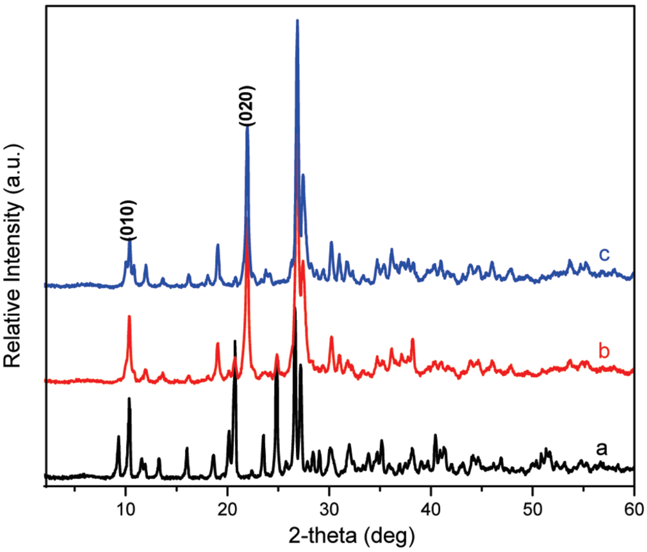
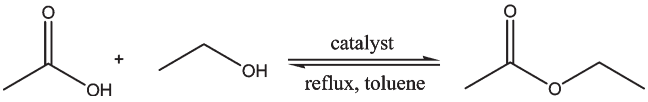


Figure 7. PXRD of (a) as-synthesized SLUG-21; postcatalysis after one (b) and three (c) catalytic cycles of ketal formation.

Scheme 2. Acid Catalyzed Esterification between Acetic Acid and Ethanol



prepared under ambient and reflux conditions and both showed similarly high yield (Table 3). All of the as-synthesized crystals thus have almost equivalent Lewis acid catalytic ability as well as reusability. Both ambient pressure routes also give the same activated form by TGA and ex-situ PXRD, achieving similar yields and reusability through at least three runs (Table S1, Supporting Information).

To further test the Ag(I) Lewis acid catalytic site activity, we also carried out an esterification reaction. This reaction has attracted increasing interest for potential application in biofuels. A stronger acid catalyst, however, is required to activate the carbonyl group of carboxylic acid, the conventional homogeneous catalyst being condensed sulfuric acid.[43] We carried out the esterification between acetic acid and ethanol with SLUG-21 as catalyst. 0.18 mol % of crystals (for a catalytic ratio of 556 to 1) gave a yield of 57% after 8 h reaction without taking further steps to remove the water byproduct (Table 3 and Scheme 2). Longer reaction time gave no improvement to the yield. An additional esterification experiment between formic acid and ethanol with SLUG-21 as catalyst reached over 70% yield (Figure S9, Supporting Information). The higher yield in formic acid is possibly due to the smaller precursor size, for greater diffusion into the extended framework. These satisfactory yields illustrate that SLUG-21 functions as an esterification catalyst.

Conclusions

The cationic Ag(I)−based MOF was isolated using a mixture of organic linker and anionic template. This strategy may lead to the discovery of other cationic extended frameworks with open metal sites for catalytic applications. The compound exhibits chemical stability in various solvents, as well as excellent Lewis acid catalytic ability by virtue of its coordinatively unsaturated metal sites. The catalyst can be continuously reused in the heterogeneous catalytic reaction without losing activity or significant mass. The material is synthesized in one step under ambient conditions, ideal for scale-up to industrial scale.

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Supporting Information Available: Optical micrographs, ex-situ PXRD, ^{1}H NMR spectra, and crystallographic information file (CIF) including refinement parameters and full bond distances. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Otera, J. *Esterification Methods, Reactions and applications*; Wiley VCH Verlag Gmbh and KgaA: Weinheim, Germany, 2003.