$Ag_5PV_2Mo_{10}O_{40}$, a Heterogeneous Catalyst for Air-Based Selective Oxidation at Ambient Temperature

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The development of molecules or materials that catalyze the selective oxidation of organic compounds using only air (or O_2) under ambient conditions is as potentially important technologically as it is challenging to achieve.[1−3] Solid-state catalysts with such activity could be utilized for purifying air by the selective oxidation of the toxic agents therein, including sulfur compounds (thioethers, thiols, H_2S)[4,5] and others. Unfortunately, the ability to catalyze selective (nonradical-chain) organic oxidations by O_2 without the consumption of a reducing agent is difficult.[6] With one exception,[7] the few homogeneous species that catalyze nonradical chain, reductant-free, O_2-based organic oxidations are all documented to proceed under conditions well above those in the ambient environment.[8−12] The additional requirement of effective operation as a solid makes the task of catalyst development more problematic still.[13] We report here the preparation, structure, and properties of a material, $Ag_5PV_2Mo_{10}O_{40}$ (Ag_5**1**), that catalyzes selective O_2 sulfoxidation of 2-chloroethyl ethyl sulfide (CEES, a common simulant for mustard gas) to its corresponding, far less toxic, sulfoxide (CEESO) when present simply as a low-surface-area powder using the ambient environment (room temperature and 1.0 atm of air).

Ag_5**1**, a salt of the redox active polyoxometalate (POM), $PV_2Mo_{10}O_{40}^{5-}$ (**1**),[14] and a redox active d-block cation, Ag(I), is made by a simple metathesis precipitation between $Na_5PV_2Mo_{10}O_{40}$ and $AgNO_3$ in water.[15] Two other Ag salts of POMs have been recently reported.[16,17] Thermogravimetric analysis of Ag_5**1** indicates it is stable up to 830 °C. Water molecules of solvation (11 per POM, ~8.4% weight loss) are evolved from 36 to 450 °C. Ag_5**1** is more stable than the precursor, $Na_5PV_2Mo_{10}O_{40}$ (830 °C versus 780 °C). While the solubility of Ag_5**1** is too low to facilitate acquisition of NMR spectra, it is sufficiently soluble in acetonitrile for diffraction quality crystals to be grown.[18]

The dominant structural feature of Ag_5**1** (Figure 1) recrystallized from MeCN and Et_2O involves two $PV_2Mo_{10}O_{40}^{5-}$ units bridged by two Ag(I) ions (Ag(7) and Ag(8)), each of which bonds to both bridging and terminal oxygens of the POM units. Each POM has, in addition, two nonbridging Ag(I) ions. All the Ag(I) centers are four-coordinate, with terminally coordinated acetonitrile molecules (one each for the POM-bridging Ag centers and two each for the nonbridging Ag centers).

Figure 2 shows the selective oxidation of CEES to the corresponding sulfoxide, CEESO, in 2,2,2-trifluoroethanol (TFE) catalyzed by Ag_5**1** using the ambient environment. TFE was used as the solvent because it assured that CEES and CEESO were soluble but that the catalyst, Ag_5**1**, was completely insoluble (see below). Furthermore, fluorinated media are attractive for protective applications against toxic agents.[19] Mass balance determinations indicated that the stoichiometry was CEES + 1/2 $O_2 \rightarrow$ CEESO (O_2 consumption was quantified by manometry, while CEES and CEESO were quantified by GC). The complete lack of products of oxidation at the α carbon atoms and the lack of a significant effect of even large quantities of 2,6-di-*tert*-butyl-4-methylphenol (BHT; see Supporting Information, (SI)) on the reactions are consistent with a dominant, if not exclusive, heterolytic mechanism.

Significantly, ~2300 mol of CEESO are produced per mol of surface accessible Ag_5**1** (based on a ~1.2-nm^2 cross-sectional area for Ag_5**1** derived from the X-ray structure and a five-point BET-determined surface area of 0.93 m^2 g^{-1} which is unchanged after 7.1 days of reaction, see SI). There is inhibition of the reaction by the CEESO product that is observable in Figure 2 (see also the SI). Furthermore, CEES binds to the catalyst (1.6 mol of CEES per mol of catalyst after 8.4 h) prior to oxidation to CEESO (Figure 1).

Significantly, there is no reaction in the absence of catalyst or in the presence of the POM precursor $Na_5PV_2Mo_{10}O_{40}$ (soluble), AgCl (insoluble), or both $Na_5PV_2Mo_{10}O_{40}$ and AgCl together, Na_3VO_4 (insoluble), $Na_2MoO_4 \cdot 2H_2O$ (insoluble), or a combination of Na_3VO_4 and Na_2MoO_4 under otherwise identical conditions.

To our surprise, $AgNO_3$ also proved to have detectable activity for aerobic CEES oxidation under ambient conditions. However, a comparison between the $AgNO_3$, which is soluble, and Ag_5**1**, which is insoluble, is not meaningful. $NaNO_3$ alone is inactive, indicating that NO_3^- is not the catalyst. Interestingly, the corresponding tungsten analogue of Ag_5**1**, $Ag_5PV_2W_{10}O_{40}$, and the Wells−Dawson complex, $Ag_9P_2V_3W_{15}O_{62}$, are both inactive under ambient conditions. Clearly, there is a synergistic effect between the Ag(I) cationic centers and the redox active V(V)

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(13) Recently discovered Au-based catalysts for selective air-based oxidation of thioethers turnover rapidly under ambient conditions but only in solution.[7]

(14) In all the many papers based on $PV_2Mo_{10}O_{40}$,$^{5-}$ this POM has been present as a mixture of five, as yet unseparable, labile positional isomers.

(15) To 40 mL of 0.214 M aqueous $Na_5PV_2Mo_{10}O_{40}$ (8.55 mmol) (Pettersson, L.; Andersson, I.; Selling, A.; Grate, G. H. *Inorg. Chem.* **1994**, *33*, 982−993) at 25 °C was added $AgNO_3$ (7.26 g, 42.7 mmol). The resulting red-orange amorphous powder was washed three times with water (25 °C) and three times with ether and dried to afford 5.07 g, (26.1% yield based on $Na_5PV_2Mo_{10}O_{40}$). Anal. Calcd (found) for $Ag_5PV_2Mo_{10}O_{40} \cdot 11H_2O$ Ag, 23.74 (23.99); Mo, 42.82 (43.30); P, 1.25 (1.29); V, 4.50 (4.60). FTIR (KBr, 1100−400 cm^{-1}): 1073 (sh), 1062 (m), 1048 (m), 946 (s), 863 (m), 777 (vs) cm^{-1}.

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(18) Orange crystals of Ag_5**1** (acetonitrile solvate) ($C_{34.6}$ $Ag_{10.4}$ Mo_{20} $N_{17.7}$ $O_{82.7}$ P_2 V_4, FW = 5293.07) were grown by slow diffusion of diethyl ether into an acetonitrile solution of Ag_5**1** at 25 °C. Diffraction intensities were measured on a Bruker D8 diffractometer equipped with a SMART APEX CCD detector at 100 K using Mo Kα (0.71073 Å) radiation. The crystal system is triclinic, space group P-1, $Z = 2$, $\rho = 2.936$ Mg/m^3, $a = 13.038(5)$ Å, $b = 21.175(8)$ Å, $c = 22.353(8)$ Å, $\alpha = 85.966(7)°$, $\beta = 83.556(7)°$, $\gamma = 77.854(7)°$. The final statistics based on F^2 are GOF 1.032, $R_1 = 0.0937$ and $wR_2 = 0.1731$ for $I > 2\sigma(I)$. Additional details are available as Supporting Information.

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10.1021/ja015812p CCC: $20.00

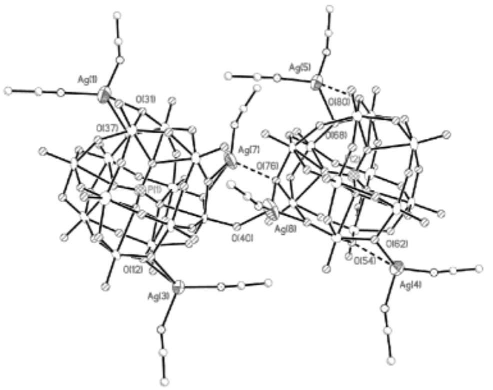

Figure 1. Structure of Ag_5**1** crystallized from MeCN and Et_2O (formula: $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}\cdot(MeCN)_{17.3}\cdot(H_2O)_{1.5}$). Each metal position on the POM has 1/6 V character and ca. 5/6 Mo character. Selected average bond lengths (Å) and angles (deg): $Ag-O_t$, 2.40; $Ag-O_b$, 2.49; $Ag-N_s$, 2.24; $P-O_c$, 1.53; $Mo-O_t$, 1.68; $Mo-O_b$, 1.96; O_c-Mo, 2.42; O_b-Ag-O_b, 62.9; $Mo-O-Mo$, 89.0; O_c-P-O_c, 109.4; where O_t = terminal oxygen, $O_b = \mu_2$-oxo, $O_c = \mu_3$-oxo, N_s = acetonitrile (solvent) nitrogen. Solvent (MeCN and H_2O) and silver ions not bound to the POM units have been omitted for clarity.

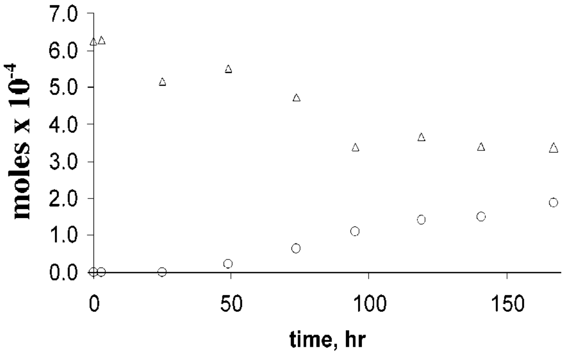

Figure 2. The heterogeneous, ambient-temperature air oxidation of $CH_3CH_2SCH_2CH_2Cl$ (CEES; △) to $CH_3CH_2S(O)CH_2CH_2Cl$, (CEESO; ○) catalyzed by Ag_5**1** powder under ambient conditions (rt and 1.0 atm air). CEES (0.275 M) and Ag_5**1** in 2,2,2-trifluoroethanol with 1,3-dichlorobenzene (internal standard) were stirred at 400 rpm in 18-mL glass vials fitted with Teflon septa. CEES and CEESO were quantified by GC.

centers inside a fairly labile **1** (polymolybdates such as **1** are far more labile than their polytungstate counterparts). Removal of half the waters of hydration of Ag_5**1** in vacuo results in effectively no change in catalytic activity, implying that H_2O is not involved in the rate-limiting step. Unfortunately, the heterogeneity of the insoluble catalyst Ag_5**1** precludes a meaningful assessment of the full rate law to clarify the reactive species.[20] However, Ag_5**1** was isolated and characterized after ∼2300 turnovers per surface exposed Ag_5**1** by four techniques: elemental analysis, FTIR (bands at 3300 cm^{-1} and a band at 1100 cm^{-1} consistent with S=O arise), solid-state ^{31}P NMR (a slight change in the chemical shift is observed), and X-ray crystallography. Data from the four techniques collectively confirm the presence of CEESO proximal to the Ag in the recovered catalyst after this number of turnovers (see SI). In addition, the characteristic dark green-blue color of the one-electron-reduced form of **1**, $PV_2Mo_{10}O_{40}^{6-}$, forms rapidly in the presence of CEES, indicating that catalytic turnover likely involves the reduction of the d^0 V(V) center, followed by reoxidation, a process observed in other thioether oxidations catalyzed by vanadium-containing POMs.[21−23]

A key concern regarding heterogeneous catalysts for liquid-phase reactions is whether the observed reactivity derives from the actual insoluble solid catalyst or from a small quantity of dissolved catalyst. Two related experiments indicate that it is the actual Ag_5**1** powder that accounts for the catalysis. First, Ag_5**1** is extremely insoluble in the catalytic medium (2.0 mL of TFE, 0.257 M in CEES; 1.0 atm of air). This was determined by stirring the same sample of Ag_5**1** 11 consecutive times in this medium, filtering each, concentrating the combined supernatants to 3.0 mL, and examining this solution by FTIR, UV−vis, and ^{51}V NMR spectroscopy. No Ag_5**1** was detectable. Second, Ag_5**1** was used in catalysis (see Figure 2 caption for conditions) and filtered. The catalytic activity of both the separated solid and the supernatant were then evaluated by product distribution analysis (only CEESO present) and early reaction kinetics. This was done twice, and the recovered Ag_5**1** powder had the same catalytic activity after one and two recoveries. In contrast, the supernatants were all catalytically inactive. These combined results argue strongly that the solid Ag_5**1** is the actual catalyst and that catalysis is not due to the dissolution and reactivity of any Ag_5**1** or any soluble $AgNO_3$ impurity (details in SI).

In summary, a salt between a d-electron transition metal cation and a polyoxometalate, both redox active, has unprecedented activity for catalyzing selective oxidation using the ambient environment.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles for $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}\cdot(MeCN)_{17.3}\cdot(H_2O)_{1.5}$, synthesis, characterization, and detailed experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] While rate laws have been reported for insoluble catalysts of liquid-phase reactions, this practice should be avoided unless accurate assessment of the active surface of the catalyst can be measured for every reaction.

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