

# Polyoxometalate-Modified Fabrics: New Catalytic Materials for Low-Temperature Aerobic Oxidation

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The polyoxometalate  $H_5PV_2Mo_{10}O_{40}$  (1) is deposited on cotton cloth, polyacrylic fiber, nylon fiber, carbon powder (Ambersorb 572), and the Japanese “self-deodorizing” fabric Smoklin by immersion of these materials in aqueous solutions of 1 followed by evaporation of the water. DRIFT spectra and chemical reactivity indicate that 1 is not damaged during deposition on the materials. More significantly, they catalyze  $O_2$ -based oxidations of two representative and common toxics in air, acetaldehyde and 1-propanethiol, in addition to a representative thioether, tetrahydrothiophene. These aerobic oxidations proceed heterogeneously with the substrates in the liquid phase and under unusually mild conditions (mostly ambient temperature and pressure). One representative reaction,  $CH_3CHO + O_2 \rightarrow CH_3COOH$ , catalyzed by several 1-fabric materials is examined in some detail. Kinetics, radical scavenging, and other experiments are consistent with the 1-fabric functioning primarily as a radical chain initiator. Surface area measurements and scanning electron microscopy of two representative materials, 1-polyacrylic and 1-Smoklin, before and after deposition of 1 and after catalysis indicate that the fibers are not demonstrably altered by deposition of 1, and that the 1-fabric catalysts are not significantly deactivated by use. In all cases, the surface areas are  $<0.5 \text{ m}^2/\text{g}$  by BET  $N_2$  adsorption, and the deposition morphology is clumps of 1 microcrystals covering  $<5\%$  of the fiber/cloth surface. Smoklin, designed and specified to be effective at removing the toxic and/or odorous molecules at ambient temperature, does not exhibit significant activity for catalytic  $O_2$  oxidations in our evaluations. In contrast, 1-Smoklin is quite active for all these processes. © 2000

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**Key Words:** polyoxometalate; fabrics; self-deodorizing; aerobic oxidation; acetaldehyde; tetrahydrothiophene (THT); methyl mercaptan; liquid-phase reactions; gas-phase reactions.

## INTRODUCTION

This paper reports the preparation and properties of new catalytic cloth materials to address a wide-spread and significant environmental problem, the destruction of air pollutants under ambient conditions. In one country, Japan, the growing desire to eliminate toxic and/or odorous molecules in air such as those emanating from exhaust

gases, sweat, rotten food, and cigarette smoke, has spawned a new industry—the manufacture of fabrics that destroy such molecules in indoor air under ambient conditions. The remarkable growth of this industry since its inception a few years ago (current revenues estimated to be over one billion U.S. dollars per year) testifies to the popularity of fabrics (clothing, upholstery, curtains, etc.) that would reduce air pollution in the home, work-place, car, and other environments. Fabrics with low activity for the degradation of offending gaseous molecules would be “self deodorizing,” the current stated thrust of this new Japanese industry, while those with high activity should purify air. Examination of the meager literature on these “self-decontaminating” fabrics indicates a serious shortcoming for most of them; namely they are effective through stoichiometric physisorption or chemisorption processes based on acid–base, ion pairing (salt formation) and/or oxidation–reduction reactions (1–6). Because this technology is stoichiometric and not catalytic, it is not very promising. If these fabrics are to avoid irreversible inactivation, the active groups on the fiber surfaces must be regenerable. In other words, a catalytic capability for destroying many toxic and/or odorous molecules in the gas phase at ambient temperatures is required.

Some of the most deleterious and/or foul-smelling compounds in indoor air include acetaldehyde, formaldehyde, hydrogen sulfide, methyl mercaptan, ammonia, trimethylamine, and nicotine. These suggest the optimally effective protective fabric materials would catalyze oxidative reactions, ideally air ( $O_2$ )-based oxidations, and to a lesser extent hydrolytic reactions. The major difficulty here is that while there are a myriad of literature reports of catalysis of  $O_2$ -based oxidations, there are only a few that function at lower temperatures ( $<60^\circ\text{C}$ ) and effectively none that are efficient under ambient conditions (7–9). In addition, these few systems that operate under such mild conditions require either an additional energy source such as light (i.e., photocatalysis (10)) or ultrasound (11) or the consumption of a stoichiometric reagent. The most prevalent example of the latter is the use of aldehydes in the presence of  $O_2$  and radical initiators to form reactive peracids *in situ* via autoxidation (12). The formidable challenge is to formulate a

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material that will catalyze the effective and rapid O<sub>2</sub>-based decomposition of the above species and others at ambient temperature and pressure.

We turned to polyoxometalates (POMs) for this initial effort to develop fabrics with catalytic activity for ambient temperature degradation reactions for several reasons. POMs have acidities, redox potentials, polarities, solubilities, and other molecular properties impacting catalytic activity that can be systemically altered (13). POMs catalyze a range of reactions under either homogeneous or heterogeneous conditions (14), and some have been recently commercialized. Heterogeneous POM catalysts can operate in supported (15) or bulk (16–18) modes. In addition, POMs are robust and inexpensive. Furthermore, extensive biological evaluations indicate that a majority of POMs are effectively nontoxic in cell culture (13c). The choice of H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**) as a catalyst for ambient temperature aerobic oxidation followed from extensive studies of POM-catalyzed aerobic oxidations of organic substrates in homogeneous solution under mild conditions (14, 18, 19) and studies of low-temperature liquid-phase peroxide-based oxidations catalyzed by **1** supported on carbon powders and cloths (20–22).

There are three other documented issues that relate to the new catalysts and catalysis reported here. First, there are approximately 10 reports, all patents, that address the effect of POMs on fabric dyes. Most of these involve the use of POMs as counteranions for cationic dyes (23). Second, there are reports of POMs catalyzing aerobic oxidation of acetaldehyde (16, 24), hydrogen sulfide (17), and alkyl mercaptans and thioethers (organic sulfides) such as tetrahydrothiophene (THT) (18), but all of these reactions are at temperatures well above ambient or in the liquid phase. Third, there is one report of POM-based fixed-bed catalytic reactor for the purification of gas in vents or passages. This reactor involves a POM (H<sub>3</sub>PMo<sub>6</sub>W<sub>6</sub>O<sub>40</sub>) immobilized on a porous support (25).

We report here the facile incorporation of the mixed-addenda POM, H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**) and some Co-substituted POMs into one representative Japanese “self-deodorizing” fabric, Smoklin, into other cloth materials and fibers, and into carbon powder (Ambersorb 572). The resulting “**1**-fabrics” and **1**-carbon catalyze facile O<sub>2</sub> oxidations of representative sulfur compounds and aldehydes and do so at ambient temperature.

## EXPERIMENTAL

**Materials.** The polyoxometalates H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**) (26), Na<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**3**) (26), H<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> (**2**) (27a), Na<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> (**4**) (27a), and K<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**8**) (27c) were synthesized following the literature procedures. Na<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**5**) was prepared by ion exchange of K<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**8**) using the sodium form of Amberlite

IR-120. K<sub>7</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**7**) and K<sub>8</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**6**) were prepared as in Refs. (27d) and (27e). K<sub>6</sub>SiCoW<sub>11</sub>O<sub>39</sub> (**9**) was synthesized by Michael Wemple in Hill's group. POM purity was checked by <sup>51</sup>V, <sup>31</sup>P, and <sup>183</sup>W NMR and elemental analysis. The samples of Smoklin cloth and acid-dyeable polyacrylic fiber were gifts from Walt Zybko of Malden Mills Industries, Inc., MA. The Smoklin cloth, a product manufactured by Asahi Chemical Industry Co. in Japan, is made from polyacrylic yarn. The acid-dyeable polyacrylic fiber, manufactured by Japan Exlan Company, Ltd., is a copolymer of acrylonitrile, vinyl acetate, and dimethylaminoethyl methacrylate, with the exact composition (monomer abundance) and molecular weight not available in the open literature. The “deep-dye” nylon fiber, obtained from DuPont, contains terminal NH<sub>2</sub> groups. The samples of cotton cloth were cut from a 100% cotton T-shirt after laundering. The Ambersorb 572 carbon powder was provided by Rohm & Haas Company. All samples were submitted to vacuum and then heated, or washed, submitted to vacuum, and then heated before use. All solvents were from Fisher or Burdick & Jackson company and had purities of >99%. The liquid phase internal standards and reagents were obtained from Aldrich and exhibited purities of >99%. All gases (O<sub>2</sub>, Ar, He) were from Specialty Gases and had purities of >99%. All reagents were used as received, except acetaldehyde, which was protected under Ar in the freezer to minimize adventitious autoxidation (radical chain oxidation by O<sub>2</sub>) or other possible reactions.

**Instrumentation.** All reactions involving CH<sub>3</sub>CHO, C<sub>3</sub>H<sub>7</sub>SH, and THT were monitored using a Hewlett-Packard 5890 or a 6890 gas chromatograph equipped with flame ionization detectors and capillary columns: HP-5 (5% phenylmethylsilicon) for THT and C<sub>3</sub>H<sub>7</sub>SH oxidation reactions and HP-FFAP (polyethylene glycol-TPA modified) for the liquid CH<sub>3</sub>CHO oxidation reactions. An HP-8451A diode array spectrometer was used to assess the concentration of **1** in supernatant solutions after catalysis or in suspension during the oxidation of liquid CH<sub>3</sub>CHO. <sup>51</sup>V, <sup>31</sup>P, and <sup>183</sup>W NMR measurements were carried out on a 500-MHz General Electric GN500, a 400-MHz Varian Inova 400, and a Varian Unity 400 spectrometer, respectively. Elemental analyses were conducted by E + R Microanalytical Laboratory, Inc. The diffuse-reflectance-infrared-fourier-transform (DRIFT) measurements on powdered **1** and the fabrics were obtained using a Nicolet 510 FT-IR spectrometer. The scanning electron microscopy (SEM) experiments were carried out on a *ISIDS-130/LaB<sub>6</sub>* instrument. The BET surface area measurements from nitrogen adsorption were made on a Micromeritics (Norcross, GA) Gemini porosimeter.

**Preparation of materials with supported POMs.** H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**), H<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> (**2**), Na<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**3**), Na<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> (**4**), Na<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**5**), K<sub>8</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**6**), and K<sub>7</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**7**). Carbon with supported **1**

(1-carbon) was synthesized following the literature procedure (20). POM-Smoklin and POM-cotton cloth were prepared as follows: 2 g of cloth was immersed in aqueous solutions of varying POM concentration at room temperature. After 24 h, the cloth was dried at room temperature, first in the air, and then *in vacuo* for 2 days. Preparation of POM-acrylic and POM-nylon fibers: the nylon and acrylic fibers were washed in boiling 2-propanol for 4 h and then dried *in vacuo* at 323 K before use. Representative 2-g samples were then immersed in aqueous solutions of varying POM concentration at 353 K for 2 h and then at ambient temperature for 1 day. Most of the water or excess solution was removed by rotary evaporation or by filtration at room temperature. The POM-nylon and POM-acrylic samples were then dried at room temperature, first in the air overnight and then *in vacuo* for 2 days. The percentages of POM on the cloth or fibers were determined by both weight difference and elemental analysis.

**General reaction conditions.** In all reactions, powdered **1**, the unmodified fabric, or the **1**-modified fabric was placed in a flask (25-ml schlenk flask for THT oxidation and 500-ml round-bottom flask for  $\text{CH}_3\text{CHO}$  oxidation) or a 20-ml vial (for  $\text{C}_3\text{H}_7\text{SH}$  oxidation), sealed with a septum stopper or screw cap, taken through three degas/gas cycles with He or Ar, and then purged and placed under 1 atm of  $\text{O}_2$ . Next, reagent solutions were added to this  $\text{O}_2$ -filled flask to initiate the reactions. The exact concentrations and amounts of the reagents for each reaction are given in the table captions (Results and Discussion). Appropriate control reactions in the form of flasks covered with aluminum foil indicated that the effect of the ambient laboratory light on these reactions was minimal. All materials were insoluble in the reagent solutions. The reactions were stirred using a digital stirrer at 400 to 800 rpm as indicated. Most of the reactions were run at ambient temperature; while some  $\text{C}_3\text{H}_7\text{SH}$  or THT oxidation reactions were run at 333 or 388 K. Some reactions involving fabrics were shaken gently at about 100 rpm on a Hoefer Red Rotor shaker. During the ambient temperature reactions, aliquots were extracted at various times and analyzed by GC. For reactions conducted above ambient temperature, the flasks or vials were cooled in an ice bath before aliquots were extracted and analyzed by GC. Rainin Nylon-66 syringe filter units (45  $\mu\text{m}$  porosity) were used to remove particles from aliquots before analysis. Blank control reactions with the powdered **1** or the fabric materials absent from the otherwise identical reaction systems were run at the same time. During some reactions such as the  $\text{O}_2$  oxidation of  $\text{CH}_3\text{CHO}$  catalyzed by the **1**-Smoklin and the **1**-acrylic (both showed high activity) and the oxidation of  $\text{C}_3\text{H}_7\text{SH}$ , electronic adsorption spectra were taken after a certain reaction time to assess the presence of POM in the supernatant solution or in suspension. If any **1** was detected, the POM-support material

was washed in boiling solvent and then allowed to react with a new substrate solution under the same reaction conditions. The detection, washing, and reaction procedures were repeated until no POM was found in the supernatant solution. The reported results in the tables and Fig. 4 are for the reactions that exhibited no detectable POM in the supernatant solution. All reactions were run in duplicate to assess reproducibility and the averages reported.

**Evaluation of acid catalysis in the aerobic oxidation of  $\text{CH}_3\text{CHO}$ .** The catalytic activity of representative acids,  $\text{CF}_3\text{COOH}$  and  $\text{CF}_3\text{SO}_3\text{H}$ , the latter of comparable or greater strength than **1**, was evaluated in place of **1** alone, unmodified fabric alone, or **1**-modified fabrics for the aerobic oxidation of  $\text{CH}_3\text{CHO}$ . The same procedure as described above was followed, except that the acid catalyst was dissolved in the reagent solution that was then immediately injected into the  $\text{O}_2$  filled flask to initiate the reaction. All reactions were run in duplicate to assess reproducibility and the averages reported.

**Assessment of inhibition in the aerobic oxidation of  $\text{CH}_3\text{CHO}$ .** In the reaction, a typical inhibitor (galvinoxyl or BHT = 2,6-di-*t*-butyl-*p*-cresol) was dissolved in the reagent solution that was then injected into the reaction system containing powdered **1** (prepared as described above). The mole ratio of inhibitor to **1** was 1.4 : 1. All reactions were run in duplicate to assess reproducibility and the averages reported.

**Evaluation of product ( $\text{CH}_3\text{COOH}$ ) inhibition in the aerobic oxidation of  $\text{CH}_3\text{CHO}$ .** The effect of the main product, acetic acid, was evaluated in reactions with no **1**, reactions with unmodified fabrics alone, or reactions with **1**-modified fabrics under otherwise identical conditions. All reactions were run in duplicate to assess reproducibility and the averages reported.

**Assessment of catalysis by insoluble POM materials.** The catalytic activity of several POM materials was evaluated under conditions where no POM was in solution. In a representative reaction,  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (**1**) powder was first stirred in chlorobenzene containing substrate (e.g., 1-propanethiol), a solution in which the POM has no detectable solubility. Aliquots were extracted at various times and filtered with Rainin Nylon-66 syringe filter units (45  $\mu\text{m}$  porosity) to remove particles before analysis by GC. After the above reaction, a glass frit (medium) was then used to remove POM by filtration and the supernatant thereof was analyzed by UV-vis to check the concentration of POM in the reagent solution before more substrate was added to the filtrate to continue the reaction under otherwise identical conditions. The filtered POM was washed with chlorobenzene, collected, and dried, first under an air flow and then under a 10-Torr vacuum at room temperature. The POM was then analyzed by IR and reused for the reaction under otherwise identical conditions. POM was also stirred

in solvent only under otherwise identical conditions and the supernatant thereof was analyzed by UV-vis to check the solubility of POM in the solvent. All reactions were run in duplicate to assess reproducibility and the averages reported.

*NMR measurements assessing protonation of  $C_3H_7SH$  and  $C_3H_7SSC_3H_7$  by **1**.*  $^1H$  NMR spectra of  $CD_3CN$  solutions of  $C_3H_7SH$  or  $C_3H_7SSC_3H_7$  with and without **1** and with and without one equivalent of  $CF_3SO_3H$  were compared.

## RESULTS AND DISCUSSION

*General.* A representative POM,  $H_5PV_2Mo_{10}O_{40}$  (**1**), with physical and catalytic properties thoroughly investigated by our group and many others (18, 20, 21, 28–30) is readily deposited on to representative fabrics and fibers imparting a range of catalytic activities to the resulting “**1**-fabrics.” The **1**-fabrics catalyze reactions at ambient temperature in the liquid phase. The subsequent sections address the preparation and characterization of the **1**-fabrics and catalysis of liquid phase redox reactions by the **1**-fabrics, in that order.

*Preparation and characterization.* The sources and basic compositions of the support materials and the details of the deposition of **1** from aqueous solution onto these unconventional catalyst supports are given in the Experimental. DRIFT spectra of **1**-modified Smoklin, cotton cloth, acrylic fiber, and nylon fiber are very similar to that of the unsupported **1** powder in the infrared range ( $600\text{--}1200\text{ cm}^{-1}$ ) where nearly all absorbances characteristic of POMs occur. The spectrum of an exemplary sample (5 wt% **1**-acrylic fiber) is shown in Fig. 1. The four principal peaks associated with the Keggin polyanion,

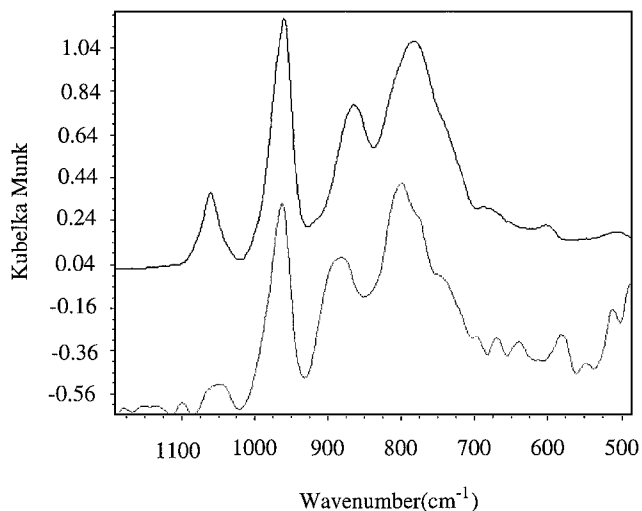


FIG. 1. The DRIFT spectra of unsupported  $H_5PV_2Mo_{10}O_{40}$  (**1**) powder (top) and **1**-acrylic (5 wt% of **1**; bottom).

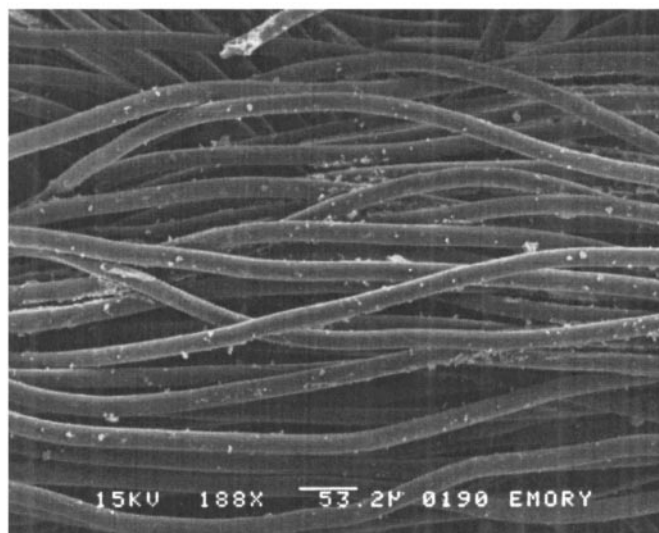
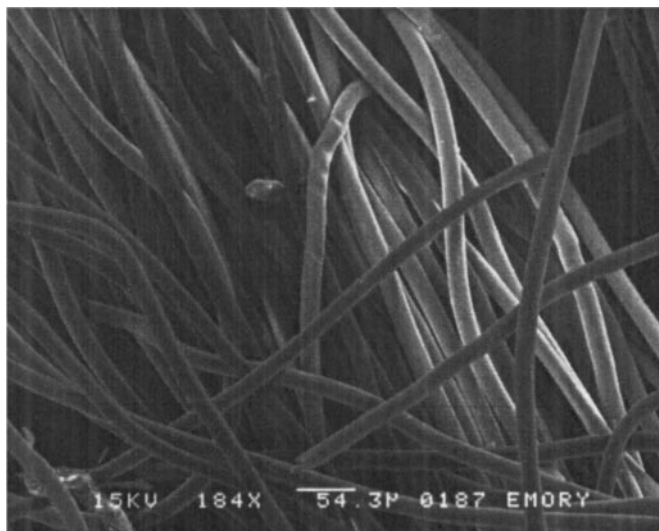


FIG. 2. The SEM pictures of acrylic (top) and **1**-acrylic (5 wt% of **1**; bottom).

$PV_2Mo_{10}O_{40}^{5-}$ , while shifted in the deposited **1** relative to **1** alone, are all present and present in the approximately the same ratios as in **1** alone. Shifts of metal–oxygen infrared stretching frequencies in Keggin complexes on changing the environment, including the counter cations, are well documented. While small quantities of other POMs may be formed upon adsorption of the POM on the fabrics, the spectra are consistent with a great majority of the deposited POM being unchanged  $PV_2Mo_{10}O_{40}^{5-}$ . SEM demonstrates that **1** is present as clumps of microcrystals unevenly distributed on the surface of the fabrics in the case of both **1**-acrylic and **1**-Smoklin (both 5 wt% **1**). Nearly all the clusters of **1** are in the  $1\text{--}5\ \mu\text{m}$  range for both **1**-fabrics. Figure 2 is the SEM picture of **1**-acrylic (5 wt%). The BET surface areas of fabrics (Smoklin and acrylic fiber) and **1**-fabrics (5 wt%) before and after the gas phase reactions

TABLE 1

Aerobic Oxidation of THT by Ambersorb 572 and H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (1)-Ambersorb 572<sup>a</sup>

	<b>1</b> (mmol)	% Conversion of THT <sup>b</sup>	% Yield of THTO <sup>c</sup>	Turnovers <sup>d</sup>
No catalyst	0	5	1	—
Ambersorb 572 <sup>e</sup>	0	22	8	—
<b>1</b> -Ambersorb 572 <sup>e</sup>	0.0078	74	25	23

<sup>a</sup> Reaction conditions: 0.704 mmol (0.64 M) THT and decane (internal standard) were stirred in 1.1 ml of chlorobenzene under 25 ml (1.02 mmol) of O<sub>2</sub> at 388 K for 45 h. All values are averages of two parallel experiments.

<sup>b</sup> % Conversion = (moles of THT consumed/moles of initial THT) × 100.

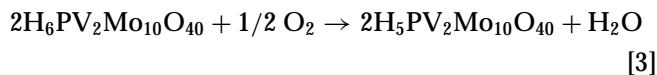
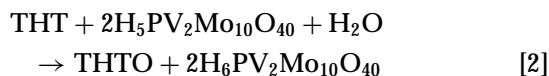
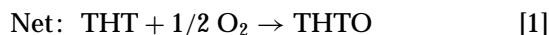
<sup>c</sup> % Yield = (Moles of THTO/moles of initial THT) × 100.

<sup>d</sup> Turnovers = Moles of THTO/moles of **1**.

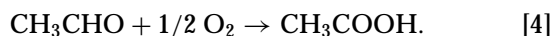
<sup>e</sup> 0.15 g, suspended in solution.

are all at or just below 0.5 m<sup>2</sup>/g, the quantitation limit of the equipment.

*Aerobic oxidation of tetrahydrothiophene (THT).* Table 1 summarizes the reaction conditions and results. The **1**-Ambersorb 572 is highly effective in retaining the immobilized **1** even under catalytic conditions (20). Tetrahydrothiophene oxide (THTO) is the main product of aerobic THT oxidation for the highly active catalyst, **1**-Ambersorb 572, the less active Ambersorb 572 without **1** (the control), and the reaction in the absence of the above two materials (the blank). The low product balances in Table 1 result, in part, from the adsorption of THT and THTO on the carbon powder. The high mole ratio of THT to **1** and the turnovers (see Table 1) indicate that the reaction is catalytic in **1**-Ambersorb 572. This is consistent with the chemistry documented for the oxidation of THT catalyzed by **1** in solution (18, 20, 21), namely that the net reaction, Eq. [1], proceeds by two general steps, Eqs. [2] and [3]. There is sufficient H<sub>2</sub>O initially in the undried chlorobenzene solvent to account for the oxygen in the initial sulfoxide product. Note that for the net reaction, the H<sub>2</sub>O consumed in Eq. [2] is regenerated in Eq. [3].



*Aerobic oxidation of CH<sub>3</sub>CHO.* The next reaction chosen to assess the effect of the **1**-fabrics on ambient temperature aerobic oxidation processes is



This reaction was chosen for three reasons: (i) it is well studied and practically significant (9, 29, 31–35); (ii) it usually proceeds by a radical chain mechanism (9) which,

if true in the case of the **1**-fabrics, would be distinct from the 2-step mechanism operable in most redox reactions catalyzed by POMs such as **1** (28, 29, 36); and (iii) acetaldehyde is one of the agents of greatest concern in household air and can be converted via Eq. [4] to the significantly less toxic acetic acid.

Table 2 summarizes the activity of powdered **1** alone and different **1**-modified materials as catalysts for the oxidation of acetaldehyde. CH<sub>3</sub>COOH is the major product in these liquid-phase reactions. In every reaction system involving **1** (either in supported or unsupported mode), the ratio of CH<sub>3</sub>CHO to **1** is higher than 50, consistent with **1** functioning as a catalyst or catalytic initiator. The **1** alone is definitely a good heterogeneous catalyst for the reaction, showing high turnover (36) and selectivity (76%). Comparison of **1** alone with the materials containing **1** are clearly not quantitatively meaningful, as the activity of heterogeneous catalysts depends on their surface area which is variable and hard to quantify in all cases. The data in Table 2 indicate that O<sub>2</sub> is the terminal oxidant in the reaction; no CH<sub>3</sub>COOH is produced when no O<sub>2</sub> is present. More promisingly, when **1** is supported on Smoklin or acrylic fiber, significantly higher conversions of CH<sub>3</sub>CHO and yields of CH<sub>3</sub>COOH are obtained relative to the Smoklin or acrylic alone (both

TABLE 2

Aerobic Oxidation of CH<sub>3</sub>CHO Catalyzed by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**) and Cloth Materials<sup>a</sup>

	<b>1</b> (mmol)	O <sub>2</sub> (mmol)	CH <sub>3</sub> CHO % Conversion <sup>b</sup>	Yield of CH <sub>3</sub> COOH Y% (Y%, T) <sup>c</sup>
No catalyst	0	0 <sup>d</sup>	19	0 (0, —)
No catalyst	0	20.5	28	0 (0, —)
<b>1</b> <sup>e</sup>	0.026	20.5	92	70 (76, 36)
<b>1</b> <sup>e</sup>	0.026	0 <sup>d</sup>	19	0.4 (2, 0.2)
Smoklin <sup>f</sup>	0	20.5	28	0 (0, —)
<b>1</b> -Smoklin <sup>f</sup>	0.013	20.5	65	52 (80, 53)
Acrylic <sup>f</sup>	0	20.5	16	0 (0, —)
<b>1</b> -Acrylic <sup>f</sup>	0.018	20.5	71	50 (70, 37)
Nylon <sup>f</sup>	0	20.5	8	0 (0, —)
<b>1</b> -Nylon <sup>f</sup>	0.024	20.5	24	0 (0, 0)

<sup>a</sup> Reaction conditions: 1.33 mmol (0.089 M) CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>COOH (internal standard) were stirred in 15 ml of 1,2-dichloroethane under 500 ml of O<sub>2</sub> (1 atm) at ambient temperature for 20 h. All values are averages of two parallel experiments.

<sup>b</sup> Conversion % = (moles of CH<sub>3</sub>CHO consumed/moles of initial CH<sub>3</sub>CHO) × 100.

<sup>c</sup> Y% = (moles of CH<sub>3</sub>COOH produced/moles of initial CH<sub>3</sub>CHO) × 100. Y% = (moles of CH<sub>3</sub>COOH produced/moles of CH<sub>3</sub>CHO consumed) × 100. T = moles of CH<sub>3</sub>COOH/moles of **1**.

<sup>d</sup> An anaerobic reaction, under 1 atm helium.

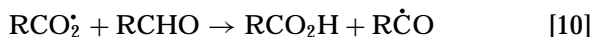
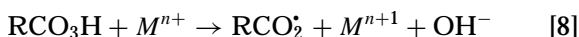
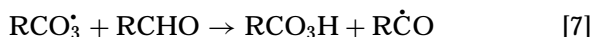
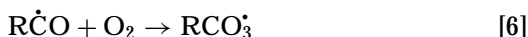
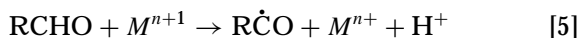
<sup>e</sup> Only powdered **1** (suspended in the solution).

<sup>f</sup> Cloth materials cut into pieces and suspended in the reagent solution.

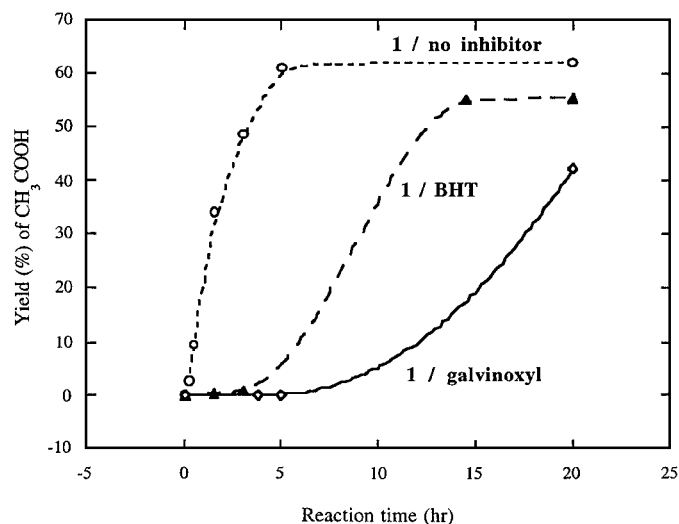
The average results for **1**-acrylic and **1**-Smoklin are from the third run (see Experimental) in which no detectable **1** was present in the supernatant solution or in suspension; while all others are the averages from the first run.

effectively inactive). The **1**-Smoklin (2.5 wt%) and **1**-acrylic (5 wt%) result in 53 and 37 turnovers, respectively. In contrast, the **1**-nylon (15 wt%) is marginally more effective than the nylon alone, most likely as a consequence of the inhibitory effect of the nylon itself (*vide infra*). In some experiments, CH<sub>3</sub>CHO is consumed, but no CH<sub>3</sub>COOH is formed because some CH<sub>3</sub>CHO is adsorbed on the **1**-fabrics and some partitions to the gas phase where it is quantified by gas chromatography.

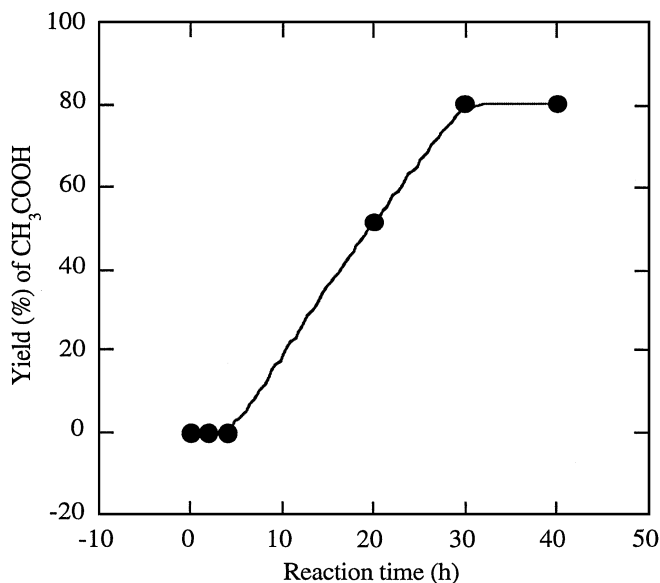
**Mechanism of Eq. [4] catalyzed by 1-fabrics.** Four lines of evidence make a very strong case that the aerobic oxidation of acetaldehyde catalyzed by these new POM-modified materials proceeds by a radical chain mechanism:



where  $\text{M}^{n+1} = \text{PV}_2\text{Mo}_{10}\text{O}_{40}^{5-}$  and  $\text{M}^{n+} = \text{PV}_2\text{Mo}_{10}\text{O}_{40}^{6-}$ . First, Eq. [4] is inhibited by two typical radical scavengers, galvinoxyl (2,6-di-*t*-butyl- $\alpha$ -(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyl-oxo, free radical) and BHT (2,6-di-*t*-butyl-*p*-cresol). See the Experimental for details. The CH<sub>3</sub>COOH yield versus time is shown in Fig. 3 for



**FIG. 3.** Inhibition of the aerobic oxidation of liquid CH<sub>3</sub>CHO in the presence of **1**, Eq. [4], by BHT and Galvinoxyl. Reaction conditions: 0.089 M CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>COOH (internal standard) were stirred in 15 ml of 1,2-dichloroethane under 500 ml of O<sub>2</sub> (1 atm) at ambient temperature for 20 h. The mole ratio of inhibitor to **1** was 1.4 : 1.



**FIG. 4.** Aerobic oxidation of liquid CH<sub>3</sub>CHO catalyzed by **1**-Smoklin. Reaction conditions: 0.089 M CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>COOH (internal standard) were stirred in 15 ml of 1,2-dichloroethane under 500 ml of O<sub>2</sub> (1 atm) at ambient temperature for 40 h.

regular and inhibited reactions. Second, Eq. [4] shows an induction period (see Fig. 4 for exemplary reactions). Induction periods can indicate autocatalysis as well as radical chain character. However, the CH<sub>3</sub>COOH product has very low catalytic activity (10% yield of CH<sub>3</sub>COOH in 47 h reaction). Third, both CH<sub>4</sub> and CO are present in the gas phase. Both products are well known to derive from radical intermediates: decarbonylation of CH<sub>3</sub>CO $\dot{\text{O}}$  forms CO and CH<sub>3</sub>, and the latter subsequently abstracts hydrogen from substrate or solvent (37).

Fourth, there is no acid catalysis of Eq. [4]. POMs including heteropoly acids are well documented to be highly effective acid catalysts and some processes have been recently commercialized (38–41). When two acid catalysts, CF<sub>3</sub>COOH and CF<sub>3</sub>SO<sub>3</sub>H, even at 10-fold higher concentrations than **1** were evaluated in place of **1**, there was very little activity (Table 3). While **1**, and hence the **1**-fabrics, are acidic, clearly the ability to catalyze Eq. [4] derives principally from the redox chemistry rather than acid chemistry of **1**. The high (80%) conversion of CH<sub>3</sub>CHO in the CF<sub>3</sub>SO<sub>3</sub>H reaction without producing a significant quantity of CH<sub>3</sub>COOH is more than likely due to acid catalyzed aldol condensation. In a control reaction **1**-Smoklin was added to neat acetaldehyde and an exothermic aldol condensation proceeded immediately.

The most likely function of **1**, either alone or supported on cloth or fiber, is as a redox based initiator via Eq. [5] (29b). Equation [5] has been proposed in other organic oxidation reactions catalyzed by redox active POMs in solution (31, 32) and specifically documented recently by Khenkin *et al.* for aldehyde oxidations (29b). There is ample

TABLE 3

Aerobic Oxidation of CH<sub>3</sub>CHO Catalyzed by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (1) and Acids<sup>a</sup>

	Catalyst (mmol)	CH <sub>3</sub> CHO % Conversion <sup>b</sup>	Yield of CH <sub>3</sub> COOH	
			Y%	(Y%, T) <sup>c</sup>
<b>1</b> <sup>d</sup>	0.026	92	70	(76, 36)
CF <sub>3</sub> COOH	0.32	27	7	(25, 0.3)
CF <sub>3</sub> SO <sub>3</sub> H	0.28	80	0.6	(0.8, 0.03)

<sup>a</sup> Reaction conditions: 1.33 mmol (0.089 M) CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>COOH (internal standard) were stirred in 15 ml of 1,2-dichloroethane under 500 ml (20.5 mmol) of O<sub>2</sub> (1 atm) at ambient temperature for 20 h. All values are averages of two parallel experiments.

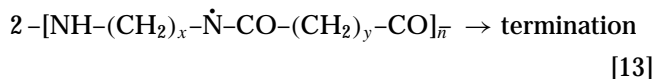
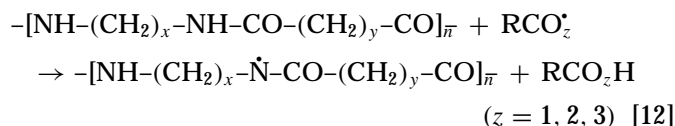
<sup>b</sup> Conversion % = (moles of CH<sub>3</sub>CHO consumed/moles of initial CH<sub>3</sub>CHO) × 100.

<sup>c</sup> Y% = (moles of CH<sub>3</sub>COOH produced/moles of initial CH<sub>3</sub>CHO) × 100. Y' % = (moles of CH<sub>3</sub>COOH produced/moles of CH<sub>3</sub>CHO consumed) × 100. T = moles of CH<sub>3</sub>COOH/moles of catalyst.

<sup>d</sup> Only powdered **1** (suspended in the solution).

evidence for Eqs. [6]–[11] from a host of other investigations (9).

The low activity of **1**–nylon for Eq. [4] is explained by reaction of the chain carrying or other key radical intermediates with the weak α N–H bonds in nylon, e.g.,



The resulting resonance delocalized amidoyl radicals are not sufficiently reactive to propagate the chain.

*Aerobic oxidation of CH<sub>3</sub>CHO catalyzed by other POMs.* Three cobalt-containing POMs, Na<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**5**), K<sub>8</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**6**), and K<sub>7</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**7**), were not effective catalysts for the aerobic oxidation of thioethers (e.g., Eq. [1]). However, all three of these POMs were far more effective than **1** as catalysts for the aerobic oxidation of CH<sub>3</sub>CHO to CH<sub>3</sub>COOH (Eq. [4]; Table 4). This constitutes a fifth line of indirect evidence for Eqs. [5]–[11] because Co(III/II) salts are usually the most effective catalysts for this general homolytic oxidation mechanism. The Co-containing POMs were active when present either as low-surface-area (~0.5 m<sup>2</sup>/g) powders or as 5 wt% loadings on fabrics. Like the reactions catalyzed by **1**, the reactions catalyzed by **5**, **6**, and **7** were significantly retarded by the presence of the radical inhibitor 2,6-di-*t*-butyl-*p*-cresol (BHT).

*Aerobic oxidation of 1-propanethiol.* 1-Propanethiol is chosen as the model for mercaptan contaminants in the en-

TABLE 4

Aerobic Oxidation of CH<sub>3</sub>CHO Catalyzed by POMs<sup>a</sup>

Catalyst	Time (h)	CH <sub>3</sub> CHO : POM <sup>b</sup>	CH <sub>3</sub> CHO % Conversion <sup>c</sup>	% Yield of CH <sub>3</sub> COOH <sup>d</sup>	Turnovers <sup>e</sup>
Blank	24	—	8	0	—
<b>5</b>	24	1538 : 1	98	67	1033
<b>6</b>	24	1521 : 1	96	60	916
<b>7</b>	24	1483 : 1	92	56	827
Blank	28.5	—	37	10	—
<b>5</b>	28.5	3075 : 1	80	70	2163
<b>6</b>	28.5	3041 : 1	72	59	1806
<b>7</b>	28.5	2966 : 1	73	62	1852
<b>5</b> +BHT	24	1538 : 1	22	18	180
Cotton	24	—	29	19	—
<b>5</b> -Cotton	24	1538 : 1	98	66	1006
<b>6</b> -Cotton	24	1521 : 1	90	50	759

<sup>a</sup> Reaction conditions: in a 20-mL vial, 0.0020 g of POM (Na<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**5**), K<sub>8</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**6**), or K<sub>7</sub>SiCoVW<sub>10</sub>O<sub>39</sub> (**7**)) was suspended in 2 mL of chlorobenzene. The vial was purged with O<sub>2</sub> for 2 min after which 0.481 mmol (0.055 mL) of pentane was added as an internal standard for GC analysis. The vial was wrapped with aluminum foil to prevent light exposure, and 0.961 mmol (0.054 mL) of CH<sub>3</sub>CHO were added. The reactions were run at ambient temperature for the indicated times. For the cloth samples, the POM (5 wt%) was deposited from aqueous solution and subsequently dried. 2,6-Di-*t*-butyl-*p*-cresol (BHT) was used as a radical inhibitor in a 1.2 : 1 ratio to POM. All values are averages of two experiments.

<sup>b</sup> Moles of CH<sub>3</sub>CHO/moles of POM. For the last three reactions (entries), another 0.961 mmol CH<sub>3</sub>CHO was added after 24 h, and the suspension was stirred for an additional 4.5 h.

<sup>c</sup> (Moles of CH<sub>3</sub>CHO consumed/moles of initial CH<sub>3</sub>CHO) × 100.

<sup>d</sup> (Moles of CH<sub>3</sub>COOH/moles of initial CH<sub>3</sub>CHO) × 100.

<sup>e</sup> Moles of CH<sub>3</sub>COOH/moles of POM.

vironment such as methyl mercaptan. Table 5 demonstrates that **1** is an effective catalyst for the aerobic oxidation of 1-propanethiol at ambient temperature and 1 atm O<sub>2</sub>. After 3 weeks, the turnover exceeds 100, although the reaction is rather slow. Other POMs were also evaluated as catalysts

TABLE 5

Aerobic Oxidation of C<sub>3</sub>H<sub>7</sub>SH Catalyzed by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (1) Powder<sup>a</sup>

	C <sub>3</sub> H <sub>7</sub> SH : O <sub>2</sub> : POM <sup>b</sup>	Time (day)	Yield% <sup>c</sup>	Turnovers <sup>d</sup>
Blank <sup>e</sup>	1 : 1 : 0	5	0.1	—
		14	0.1	—
		21	0.1	—
<b>1</b>	393 : 393 : 1	5	10	39
		14	24	94
		21	34	134

<sup>a</sup> Reaction conditions: 8.2 × 10<sup>-4</sup> mol of CH<sub>3</sub>SH dissolved in 2 mL of chlorobenzene and **1** powder were stirred at 500 rpm in 20-mL vials under 1 atm O<sub>2</sub> at ambient temperature.

<sup>b</sup> Mole ratios.

<sup>c</sup> Moles of RSSR/half the moles of initial RSH.

<sup>d</sup> (Moles of RSSR/moles of POM) × 2.

<sup>e</sup> No catalyst.

TABLE 6

Aerobic Oxidation of C<sub>3</sub>H<sub>7</sub>SH Catalyzed by POMs<sup>a</sup>

	[CH <sub>3</sub> SH] (M)	C <sub>3</sub> H <sub>7</sub> SH:O <sub>2</sub> : POM <sup>b</sup>	Time (h)	Yield% <sup>c</sup>	Turnover <sup>d</sup>
H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub> ( <b>1</b> )	0.59	393:393:1	42	9	34
K <sub>8</sub> Co <sub>2</sub> W <sub>11</sub> O <sub>39</sub> ( <b>8</b> )	0.59	431:393:1	42	13	58
K <sub>6</sub> SiCoW <sub>11</sub> O <sub>39</sub> ( <b>9</b> ) <sup>e</sup>	0.59	431:393:1	45	35	149
H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub> ( <b>1</b> )	0.76	292:157:1	46	13	37
K <sub>8</sub> Co <sub>2</sub> W <sub>11</sub> O <sub>39</sub> ( <b>8</b> )	0.76	298:157:1	46	22	67
K <sub>6</sub> SiCoW <sub>11</sub> O <sub>39</sub> ( <b>9</b> ) <sup>e</sup>	0.76	298:157:1	46	23	70

<sup>a</sup> Reaction conditions: CH<sub>3</sub>SH dissolved in 2 mL of chlorobenzene and POM powder were stirred at 500 rpm in 20-mL vials under 1 atm O<sub>2</sub> at room temperature.

<sup>b</sup> Mole ratios.

<sup>c</sup> Moles of RSSR/half the moles of initial RSH.

<sup>d</sup> (Moles of RSSR/moles of POM) × 2.

<sup>e</sup> The POM was slightly soluble in the reaction medium.

for the same reaction (Table 6). Both K<sub>8</sub>Co<sub>2</sub>W<sub>11</sub>O<sub>39</sub> (**8**) and K<sub>6</sub>SiCoW<sub>11</sub>O<sub>39</sub> (**9**) also exhibited some catalytic activity for this reaction. However, **9** was partially dissolved during the reaction, so the documented activity in this case can't be unequivocally attributed to either soluble **9** only or insoluble **9** only. POM-modified fabrics were also assessed for the reaction. Results in Table 7 demonstrate that **1**-Smoklin is a better catalyst for the reaction than **1**-cotton. In all these reactions, the main product is C<sub>3</sub>H<sub>7</sub>SSC<sub>3</sub>H<sub>7</sub>, and the overall stoichiometry is 2C<sub>3</sub>H<sub>7</sub>SH + 1/2 O<sub>2</sub> → C<sub>3</sub>H<sub>7</sub>SSC<sub>3</sub>H<sub>7</sub> + H<sub>2</sub>O.

TABLE 7

Aerobic Oxidation of C<sub>3</sub>H<sub>7</sub>SH Catalyzed by 10 wt% H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**)-Cloth<sup>a</sup>

	C <sub>3</sub> H <sub>7</sub> SH:O <sub>2</sub> :POM <sup>b</sup>	Reaction time (days)	Yield% <sup>c</sup>	Turnovers <sup>d</sup>
Blank <sup>e</sup>	1.4:1:0	6	0.1	—
Cotton	1.4:1:0	1	0	—
		6	0.2	—
<b>1</b> -Cotton	438:303:1	13	0.1	—
		1	0.4	2
		6	2	8
Smoklin	1.4:1:0	13	3	13
		1	0	—
		6	0.1	—
<b>1</b> -Smoklin	408:282:1	13	0.1	—
		1	3	13
		6	10	42
		13	17	68

<sup>a</sup> Reaction conditions: the fabric materials were placed in 2 mL of a 0.59 M chlorobenzene solution of C<sub>3</sub>H<sub>7</sub>SH and were shaken gently in 20-mL vials under 1 atm of O<sub>2</sub> at room temperature in the dark.

<sup>b</sup> Mole ratios.

<sup>c</sup> Moles of RSSR/half the moles of initial RSH.

<sup>d</sup> (Moles of RSSR/moles of POM) × 2.

<sup>e</sup> No catalyst.

TABLE 8

Aerobic Oxidation of C<sub>3</sub>H<sub>7</sub>SH Catalyzed by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**) Powder at 333 K<sup>a</sup>

	C <sub>3</sub> H <sub>7</sub> SH:O <sub>2</sub> :POM <sup>b</sup>	Time (h)	Yield% <sup>c</sup>	Turnover <sup>d</sup>
Blank <sup>e</sup>	1:2.2:0	20	0.1	—
<b>1</b> <sup>f</sup>	393:881:1	40	0.2	—
		20	25	98
Filtrate <sup>g</sup>	393:881:1	40*	76	299
		20*	1	—
Re-used <b>1</b> powder <sup>h</sup>	524:1175:1	40*	0	—
		20	8	42
		40	33	173

<sup>a</sup> Reaction conditions: 4.1 mmol C<sub>3</sub>H<sub>7</sub>SH in 10 mL of chlorobenzene and POM powder was stirred at 500 rpm in 250-mL flasks under 1 atm of O<sub>2</sub> at 333 K in the dark.

<sup>b</sup> Mole ratios.

<sup>c</sup> Moles of RSSR/half the moles of initial RSH.

<sup>d</sup> (Moles of RSSR/moles of POM) × 2.

<sup>e</sup> No catalyst.

<sup>f</sup> POM: 20 mg.

<sup>g</sup> After the above reaction involving POM, the POM was removed by filtration and more substrate was added to the filtrate to continue the reaction under otherwise identical conditions.

<sup>h</sup> The filtered POM was collected, dried, and 15 mg was reused for the same reaction starting with fresh reactants under otherwise identical conditions.

*Proof of catalysis by insoluble POM materials.* The experimental evidence establishes that totally insoluble POM materials are effective heterogeneous catalysts in liquid phase reactions under mild conditions. POM **1** was stirred in solvent heated up to 333 K overnight. The UV-vis spectrum of the supernatant taken afterward indicates that no POM dissolves in the solvent. Furthermore, both the fresh and reused POMs demonstrate significantly higher reactivity than the blank or the filtrate (supernatant) (Table 8). The decreased reactivity observed for the reused POM derives from its partial reduction during the first reaction run. This can be avoided if conditions are used under which the POM is fully reoxidized before reuse. In addition, the powder collected after the first run (Experimental) shows a very similar IR spectrum to that of the fresh **1**.

*Proof that 1-propanethiol reactant and dipropyl disulfide product are not protonated by H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (**1**).* The <sup>1</sup>H NMR spectra of C<sub>3</sub>H<sub>7</sub>SH in CD<sub>3</sub>CN with and without **1**, and C<sub>3</sub>H<sub>7</sub>SSC<sub>3</sub>H<sub>7</sub> in CD<sub>3</sub>CN with and without **1**, were compared with the spectra of both C<sub>3</sub>H<sub>7</sub>SH and C<sub>3</sub>H<sub>7</sub>SSC<sub>3</sub>H<sub>7</sub> in CD<sub>3</sub>CN but in the presence of a stoichiometric amount of CF<sub>3</sub>SO<sub>3</sub>H (triflic acid). It is clear from these collective spectra that **1** does not protonate either C<sub>3</sub>H<sub>7</sub>SH or C<sub>3</sub>H<sub>7</sub>SSC<sub>3</sub>H<sub>7</sub> significantly. The protonated species [C<sub>3</sub>H<sub>7</sub>SH<sub>2</sub>]<sup>+</sup> and [C<sub>3</sub>H<sub>7</sub>SHSC<sub>3</sub>H<sub>7</sub>]<sup>+</sup> formed upon addition of the very strong acid, CF<sub>3</sub>SO<sub>3</sub>H, give distinct peaks



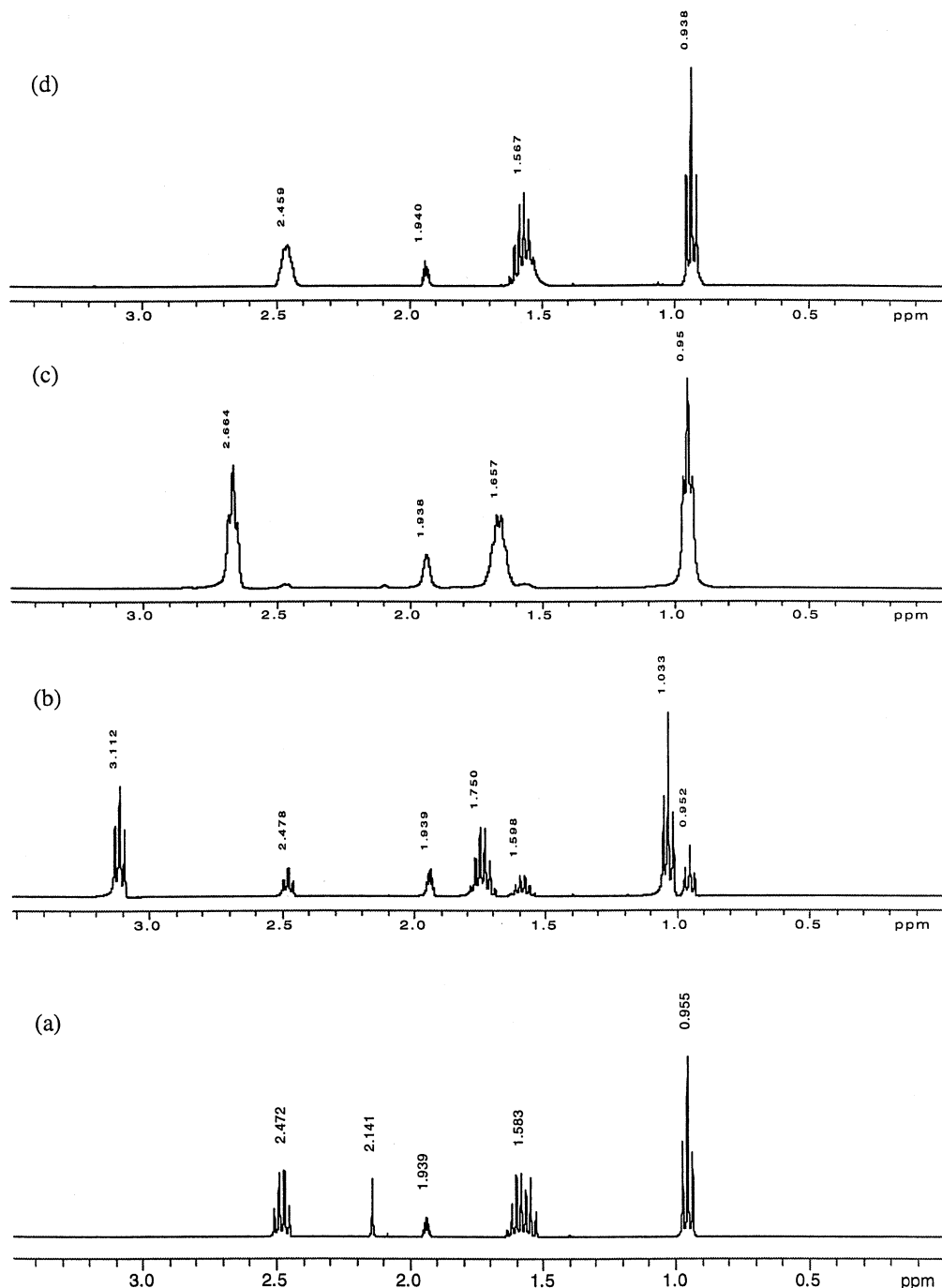


FIG. 5.  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{CN}$ : (a)  $\text{C}_3\text{H}_7\text{SH}$ , (b)  $\text{C}_3\text{H}_7\text{SH}$  and  $\text{CF}_3\text{SO}_3\text{H}$ , (c)  $\text{C}_3\text{H}_7\text{SH}$  and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (**1**) (showing peaks of unprotonated  $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$  product), (d)  $\text{C}_3\text{H}_7\text{SH}$  and  $\text{H}_5\text{AlW}_{12}\text{O}_{40}$  (**2**).

in the  $^1\text{H}$  NMR, while the spectra of both thiol reactant and disulfide product are minimally perturbed by the presence of a stoichiometric amount of **1** (Figs. 5 and 6). The new peaks appearing after addition of **1** to a  $\text{CD}_3\text{CN}$  solution of  $\text{C}_3\text{H}_7\text{SH}$ , not surprisingly, are those of unprotonated  $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$  (Fig. 5c) indicating oxidation of  $\text{C}_3\text{H}_7\text{SH}$  by **1**.  $\text{H}_5\text{AlW}_{12}\text{O}_{40}$  (**2**), a POM of comparable acidity to **1** but one with a far lower redox potential, neither oxidizes

nor protonates  $\text{C}_3\text{H}_7\text{SH}$  when added to a solution of this thiol.

## CONCLUSIONS

(1) A representative redox and catalytically active heteropolyacid polyoxometalate (POM),  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (**1**), is readily deposited on a variety of fiber and fabric materials

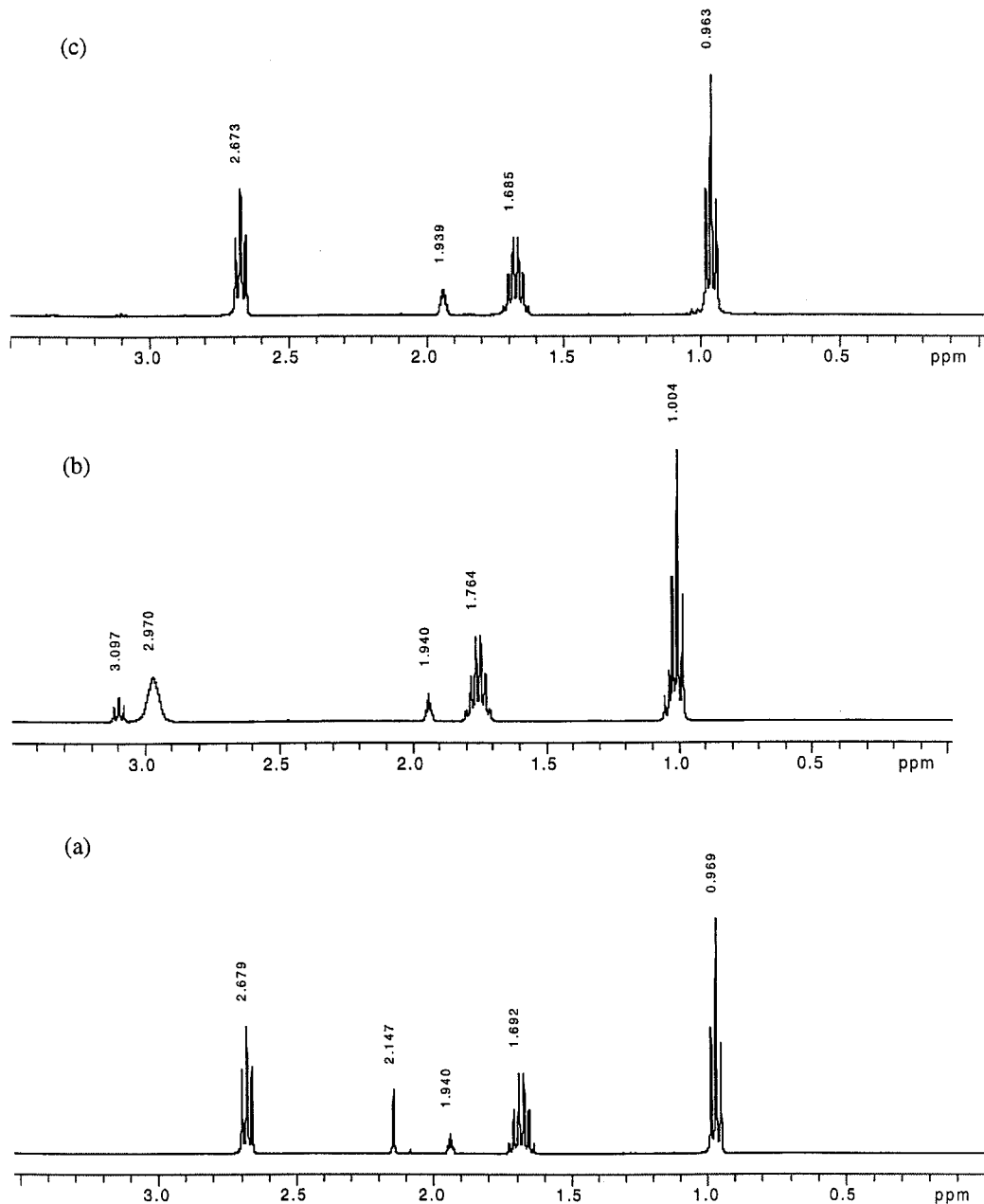


FIG. 6.  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{CN}$ : (a)  $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$ , (b)  $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$  and  $\text{CF}_3\text{SO}_3\text{H}$ , (c)  $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$  and  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  (**1**).

which imparts the catalytic properties of **1** to these materials (**1**-fabrics).

(2) The **1**-fabrics, including **1**-Smoklin ( $\geq 5$  wt%), **1**-acrylic ( $\geq 5$  wt%), and **1**-cotton cloth ( $\geq 15$  wt%), catalyze several aerobic ( $\text{O}_2$ -based) reactions in the liquid phase *under ambient conditions*. These include a representative classical radical chain autoxidation,  $\text{CH}_3\text{CHO} + 1/2 \text{O}_2 \rightarrow \text{CH}_3\text{COOH}$  (Eq. [4]), a reaction catalyzed even more effectively by 3 Co(II)-substituted POMs, and nonchain processes (oxidations of thioethers and thiols). Importantly, the *POM-free* fabrics including Smoklin, a new type of fabric designed and stated to be active for removing acetaldehyde,

thiols, and other air pollutants, show little or no activity under these very mild conditions.

(3) High turnovers can be obtained by varying POM and temperature.

(4) Experimental evidence establishes that totally insoluble POM materials such as **1** are effective heterogenous catalysts for liquid phase reactions.

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