Carbon Powder and Fiber-Supported Polyoxometalate Catalytic Materials. Preparation, Characterization, and Catalytic Oxidation of Dialkyl Sulfides as Mustard (HD) Analogues

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We report here a prototype material for the sustained catalytic decontamination of mustard analogues with the ultimate goal being the fabrication of self-decontaminating clothing. $H_5PV_2Mo_{10}O_{40}$ (**1**) can be supported on carbon cloths as well as powders, with **1**/Ambersorb 572 being the best material (high catalytic activity and low desorption of **1**). Evaluation of the desorption of **1** from six carbon supports indicates that the PPAN (pyrolyzed polyacrylonitrile) and Ambersorb 572 materials are highly effective at retaining the immobilized **1** even under catalytic conditions (oxidation of tetrahydrothiophene, THT, by *tert*-butyl hydroperoxide, TBHP). The products of THT oxidation, tetrahydrothiophene oxide (THTO) and *tert*-butyl alcohol (TBA), inhibit the reaction at high conversions; however, the catalytic activity can be restored by heating in a vacuum oven to 80 °C. The reactivity for oxidation of four different thioethers by TBHP catalyzed by **1** supported on hydrophobic (Ambersorb 563) and hydrophilic (Ambersorb 572) carbon powders indicates that while the steric and electronic characteristics of the thioether substrates are a factor in reactivity, the hydrophobicity of the carbon support is not.

Introduction

Effective matrixes (porous, robust, etc.) for immobilization of polyoxometalate catalysts are of considerable interest and potential value. The attractive properties of polyoxometalates (highly modifiable, robust, inexpensive, nontoxic, etc.)[1−3] have recently made them some of the most actively developed and commercialized catalysts in both homogeneous[3] and heterogeneous[4−6] modes. Heteropolyacids (HPAs) in particular have been employed extensively as both supported[2,7−10] and unsupported acid catalysts.[7,8,11,12] If better supports could be found for polyoxometalates, the catalytic applications could be extended considerably. Some careful and encouraging studies have been made of catalytic materials based on immobilized polyoxometalates. In 1981 Izumi and Urabe found that HPAs could be entrapped in active carbon.[13] They achieved liquid-phase etherization of butanol and *tert*-butyl alcohol, vapor-phase esterification of acetic acid with ethanol, alkylation of benzene, and the dehydration of 2-propanol.[13] In 1991 Neumann and Levin reported the selective oxidation of alcohols and amines catalyzed by 10 wt % $Na_5PV_2Mo_{10}O_{40}$ on activated carbon.[14] In 1994 Fujibayashi et al. supported a new mixed addenda heteropolyoxometalate, $(NH_4)_5H_4PV_6Mo_6O_{40}$, on active carbon that exhibited catalytic activity for the aerobic oxidation of phenols, hydroquinones, and benzyl alcohol,[15] and more recently, Dupont et al. studied HPAs on carbon as catalysts for the esterification of acrylic acid by butanol.[16] Despite these efforts, however, more basic research is needed with respect to materials for immobilization of polyoxometalates. Physical studies of HPAs on carbon include ^{31}P, ^{29}Si, and ^{17}O NMR, FT-IR and X-ray diffraction of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$[17] and the determination of the acidity of $H_3PW_{12}O_{40}$ by microcalorimetry and methanol dehydration.[18]

A significant and specific challenge that is addressed in this effort is the design and formulation of a material that is simultaneously effective for decontaminating chemical warfare (cw) agents, in particular mustard, $(ClCH_2CH_2)_2S$ (HD), and yet has the requisite properties to facilitate fabrication of clothing (fiberous, elastomeric, etc.). We report here the preparation and characteriza-

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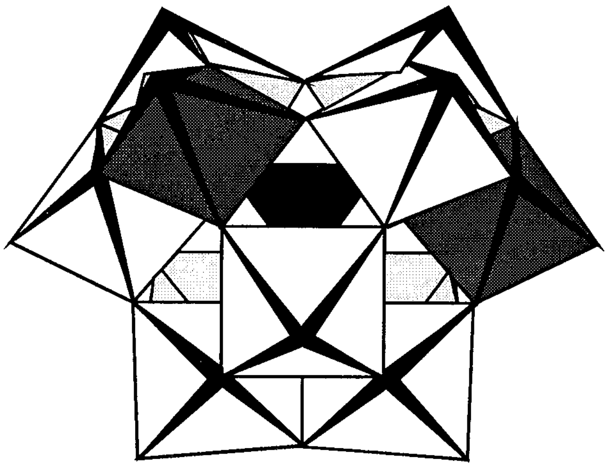

Figure 1. Polyhedral representation of the 1,6 isomer of $PV_2Mo_{10}O_{40}^{5-}$.

tion of such materials. Specifically we demonstrate the immobilization of $H_5PV_2Mo_{10}O_{40}$ (**1**; see Figure 1) on six different forms of carbon, including three carbon cloths, one of which is elastomeric. We furthermore examine both the effective oxidation of HD analogues including tetrahydrothiophene, THT, by the utilitarian (inexpensive and heavily used) oxidant *tert*-butyl hydroperoxide, TBHP,[19,20] catalyzed by these materials and the integrity of the polyoxometalate immobilization under various conditions.

Experimental Section

Methods and Materials. The Ambersorb materials, Maxsorb, and carbon black were powders, and the other three carbon materials were cloths. The stretchable carbon material is the Westvaco carbon impregnated in a matrix of elastomeric polyurethane material. The technical notes provided by Rohm and Haas Co. report the properties of the Ambersorb adsorbents to be extremely reproducible. Table 1 gives the pertinent information on the various carbons. The $H_5PV_2Mo_{10}O_{40}$ catalyst was prepared and purified by literature procedures.[21] All other reactants, solvents, internal standards, and products were obtained from Aldrich and had purities >98% by gas chromatography. The terminal oxidant, TBHP, was purchased as a solution in decane (4.52 M) to prevent solubility difficulties. Reactions were monitored on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 5% phenylmethylsilicone capillary column. Electronic absorption spectra were recorded from 190 nm to 820 nm using a Hewlett-Packard 8452A diode array spectrophotometer. Transmission electron microscopy was performed on a Hitachi HF-2000 field emission TEM by supporting the samples on Formvar-coated copper disks. The powder patterns were determined using an X_1 advanced diffraction system instrument made by Scintag (Cu Kα radiation).

Table 1. Characteristics of the Carbon Materials in This Study

carbon	manufacturer	surface area (m^2/g)	porosity (ml/g) (micro, meso)[a]
Ambersorb 572	Rohm & Haas	1100	0.41, 0.19
Ambersorb 563	Rohm & Haas	550	0.23, 0.14
Maxsorb AW30	Kansai Coke & Chem.	3100	1.5, 0.30
Carbon Black	Cabot	207	nonporous
G-16	Electrosynthesis	207	nonporous
PPAN[b]	Natick RD & E Center	690	−, 0.052; total pore volume = 0.41
TSA-14[c]	Westvaco	2102	0.55, 0.98

[a] Micropores <20 Å, Mesopores <50 Å. [b] Pyrolyzed polyacrylonitrile (PPAN). Experimental carbon (not commercially available). [c] The word "stretchable", in the text, refers to Westvaco's TSA-14 in a polyurethane matrix. U.S. Patent 5,416,056.

Synthesis of Carbon Supported $H_5PV_2Mo_{10}O_{40}$ Catalysts. The polyoxometalate **1** (0.3495 g) was dissolved in 50 mL of deionized water and added to 3.5000 g of the carbon material. The water was removed in vacuo at 80 °C overnight. The only exception to this procedure was that used for Ambersorb 572. The Ambersorb 572 adsorbed the polyoxometalate directly from solution. After stirring the mixture of Ambersorb 572 and **1** for 73 h at 25 °C, the **1**/Ambersorb 572 was filtered off and dried at 70 °C for 17 h. All **1**/carbons were then stored in an oven at 110 °C. The samples were analyzed by Natick RD & E Center for molybdenum and vanadium; carbon material (% molybdenum, % vanadium): PPAN (3.21, 0.30), G-16 (1.38, 0.21), Ambersorb 563 (3.51, 0.30), and Ambersorb 572 (2.77, 0.20).

Comparison of Catalysts and Substrates. In all reactions the toluene, TBHP, and carbon-supported catalysts were placed in a 10-mL round-bottom flask sealed with a Suba Seal septum stopper and taken through 3 degas/gas cycles with argon. Next, 20 μL of degassed internal standard (isooctane) was added. Injection of the degassed thioether substrate through the septum stopper initiated the reaction. The reactions were stirred at 700 rpm and ambient temperature. Aliquots were extracted at various times and analyzed by gas chromatography. The reaction aliquots (0.3 mL) were filtered with Rainin Nylon-66 syringe filter units (45-μm porosity) to remove carbon particles before analysis. The TBHP was quenched by addition of the reaction aliquot to 100 μL quantities of CH_3CN each containing approximately 1.2 equiv of tetrabutylammonium borohydride. This precluded assessing yields based on TBHP. Conversion was determined by following the loss of thioether. See tables and figure captions for exact concentration information in each experiment.

Strength of Immobilization. The **1**/carbon materials (0.1000 g) were each added to 2 mL of acetonitrile and 2 mL of water. They were filtered after 24 h at 25 °C, and the supernatant was analyzed by UV−vis spectrophotometry to determine the quantity of **1** that had desorbed from the carbon. The **1**/Ambersorb 572 and the **1**/PPAN carbon, which had not lost any **1**, were then kept at 40 °C for an additional 12 h and reanalyzed.

Results and Discussion

Immobilization Characteristics. Table 2 gives the quantities of **1** desorbed from the carbon supports in both polar protic (H_2O) and polar aprotic (CH_3CN) media. A requirement of any catalytically competent material used as part of a protective garment would be that the immobilized catalytic components not wash off in the rain. Virtually none (<1%) of the polyoxometa-

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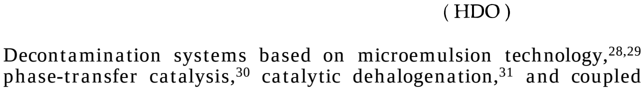
(19) The need for catalytic methods to selectively oxidize HD, has been well documented.[26] Selectivity is imperative because the corresponding sulfoxide, bis(2-chloroethyl) sulfoxide (HDO), is relatively nontoxic, whereas the corresponding sulfone is highly toxic:[27]



Decontamination systems based on microemulsion technology,[28,29] phase-transfer catalysis,[30] catalytic dehalogenation,[31] and coupled photochemical and thermal redox catalysis[32] have all been recently reported. There have also been reports of catalytic aerobic oxidations of thioethers.[33−36] These systems, however, employ high temperatures and pressures. Current work in our laboratory is geared toward developing polyoxometalate catalysts that will oxidize thioethers under ambient conditions.

(20) We recently demonstrated that **1** could be supported on carbon powders and used as a recoverable heterogeneous catalyst for the oxidation of THT.[24]

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Table 2. Assessment of the Desorption of $H_5PV_2Mo_{10}O_{40}$ (1) from the Carbon Supports in Water and Acetonitrile[a]

1/carbon	% of **1** desorbed into H_2O	% of **1** desorbed into CH_3CN
1/Ambersorb 563	b	b
1/Ambersorb 572	<1	<1
1/Ambersorb 572[c]	<1	<1
1/carbon black	52	52
1/G-16	100	100
1/stretchable	20	59
1/PPAN	< 1	<1
1/PPAN[c]	< 1	<1

[a] Conditions: The carbon (0.1000 g) was placed in 2.00 mL of the solvent for 24 h at 25 °C and filtered, and then the supernatant analyzed by UV−vis at 310 and 330 nm. HPA loadings are given in the Experimental Section. [b] Could not be determined as a chromophoric material from the Ambersorb 563 interfered with the electronic absorption spectrum of **1**. [c] After an additional 12 h at 40 °C.

Table 3. $H_5PV_2Mo_{10}O_{40}$ (1) Supported on Carbon Powders and Fibers as Catalysts for the Oxidation of a Representative Thioether, Tetrahydrothiophene (THT)[a]

1/carbon	% conversion of THT at 30 min[b]
A. Carbon Powders	
1. Ambersorb 563/**1**	23 ± 1.4
2. Ambersorb 572/**1**	52 ± 2.6
3. carbon black/**1**	35 ± 2.8
B. Carbon Fibers	
4. G-16/**1**	54 ± 4.2
5. stretchable/**1**	17 ± 1.4
6. PPAN/**1**	12 ± 2.1
C. Controls (No. 1)	
7. no carbon	0 (23 at 22 h)
8. Ambersorb 572	0 (8 at 3.8 h)
9. Stretchable	0 (11 at 3.8 h)

[a] Reaction conditions: 51 mM THT, 91 mM TBHP, 0.1000 g of **1**/carbon, 20 μL of isooctane (internal standard), 7.00 mL of toluene, 700 rpm, 25 °C, Ar atmosphere. HPA loadings are given in the Experimental Section. [b] Conversion = $(([THT]_o - [THT])/[THT]_o) \times 100$.

late was lost when **1**/PPAN or **1**/Ambersorb 572 was washed in either solvent, even after 12 h at 40 °C. G-16 had the lowest catalyst integrity as 100% of the polyoxometalate was desorbed in both H_2O and CH_3CN. In Table 3, the reactivities of the various **1**/carbons are evaluated using toluene as a solvent (**1** is not soluble in toluene) to circumvent having solubilized **1** adding to the catalysis. Electronic absorption spectra of the supernatant solutions showed that the polyoxometalate was not damaged from the immobilization and subsequent desorption processes where desorption was observed.

Transmission electron microscopy was attempted on Ambersorb 572 and **1**/Ambersorb 572, but clear images of the immobilized catalyst were not obtained. While there is a report in the literature of imaging discrete polyoxometalates, these complexes were polyoxotungstates with twice the electron density of **1**.[22] The electron beam diffraction patterns of the two samples were very different. The carbon material without supported catalyst gave a fuzzy pattern (significant scattering), whereas the **1**/Ambersorb 572 gave a sharp and symmetrical pattern. Unfortunately, the $H_5PV_2Mo_{10}O_{40}$ could not be detected in the X-ray diffraction powder pattern of the **1**/Ambersorb 572 due to strong background scattering by the carbon (supporting information, Figures S1−S3).

Catalytic Efficiencies. All the carbon supported polyoxometalate (**1**) materials catalyze the rapid and selective (no sulfone, detection limit = 3 mM) oxidation of thioether HD analogues by the stoichiometry given in eq 1. Previous flow microcalorimetric studies using

$$R_2S + t\text{-BuOOH} \xrightarrow[\text{Ar/room temperature}]{H_5PV_2Mo_{10}O_{40}/\text{carbon}} R_2SO + t\text{-BuOH} \qquad (1)$$

trichloroethylene as the adsorptive in measuring the heats of adsorption for the microporous carbons containing **1** indicated that the sorptive sites were not blocked.[23] However, recent preliminary work using toluene vapor in flow microcalorimetric studies show that **1** binds to a population of micropores in the test carbons. The overall results were that the carbons could adsorb the same amount of toluene with and without **1** adsorbed. However, there was a delay in the rise of the adsorption curve at early times due to blocking of the micropores. The micropores are <20 Å in diameter. The Keggin species is approximately 12 Å in diameter. This indicates that those carbons high in micropores would be more reactive because the microporous nature of the carbon leads to a higher percentage of monomeric (versus aggregated) polyoxometalate catalyst associated with the carbon. This fits with the order of reactivity we have observed.[24] Table 3 shows the reactivity of the various **1**/carbon materials for catalyzing the oxidation of THT by TBHP. Reproducibility of the data is indicated by the standard deviation as well as supplementary Figure S4. Comparison of reactions 1−6 with the control reactions 7−9 demonstrates the catalytic effect of the polyoxometalate, **1**. The G-16 and Ambersorb 572 based catalysts were the fastest. G-16, however, would not be a good choice for protective gear because **1** is completely desorbed from it in water. Although the PPAN material was very effective at immobilizing **1**, it too would be a less than optimal choice for protective wear based on its low reactivity. Of the carbons in Table 3, Ambersorb 572 optimizes the simultaneous attributes to effectively bind **1**, retain **1** in the presence of water (and acetonitrile), and catalyze the rapid oxidative degradation of the mustard analogue THT. The inferior reactivity of the Ambersorb 563 and carbon black based materials relative to the Ambersorb 572 based material likely results from the difference in pore volume as well as the difference in hydrophobicity. The Ambersorb 572 has almost twice the microprosity of the Ambersorb 563 (0.41 mL/g compared to 0.23 mL/g). Also, the Ambersorb 572 is much more hydrophilic than the Ambersorb 563, as will be discussed later in the text. The stretchable carbon (henceforth "Stretchable") is the Westvaco TSA-14 in a polyurethane matrix. This carbon has properties (surface area, pore volume, and CCl_4 adsorption isotherms) that are very similar to Maxsorb AW30. The surface area (m^2/g) of Maxsorb AW30 and TSA-14 is 3100 and 2102, respectively. The

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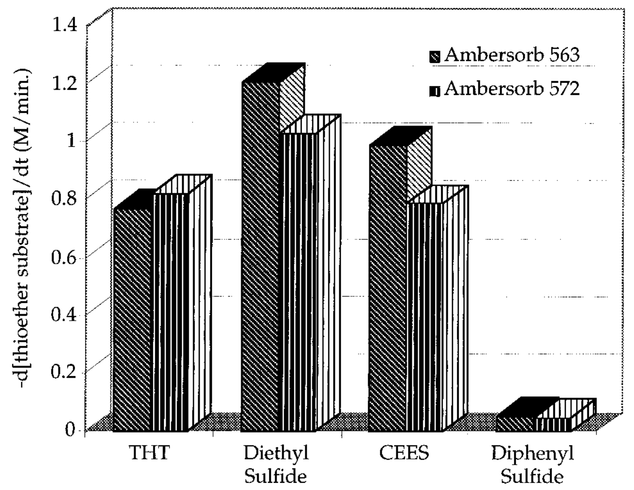

Figure 2. Comparison of the reactivity (rate of loss of thioether substrate) of **1** supported on a hydrophilic (Ambersorb 572) and a hydrophobic (Ambersorb 563) carbon material for oxidation of four representative thioethers. HPA loadings are given in the Experimental Section. R_2S (51 mM), TBHP (91 mM), **1**/Carbon (0.0500g), 20 μL of isooctane as internal standard, 700 rpm, 25 °C, toluene solvent.

adsorption of CCl_4 (g of CCl_4/g of carbon) for Maxsorb AW30 and TSA-14 is 1.0 and 1.1, respectively. Previous studies found **1**/Maxsorb AW30 powder to be a very effective catalyst under these conditions.[24] The rates of reaction for the oxidation of THT were 1.31 M min^{-1} for **1**/Maxsorb powder and 0.552 M min^{-1} for **1**/stretchable. Therefore, the polyurethane matrix inhibits the reactivity by only a factor of 2.4. This is fortunate because this stretchable carbon has already been used to make carbon based underwear and socks.

Effect of Carbon Hydrophobicity. The oxidation of four different thioethers by TBHP catalyzed by $H_5PV_2Mo_{10}O_{40}$, **1**, supported on two carbons of differing hydrophobicities was evaluated. The manufacturer, Rohm and Haas Co., reports that Ambersorb 572 is hydrophilic and will readily hydrate in water, whereas the Ambersorb 563 is more hydrophobic and takes several days to hydrate.[25] Water adsorption isotherms reported in the technical notes from Rohm and Haas Co. show that the adsorption capacity of Ambersorb 563 is 3 times lower than Ambersorb 572 at 100% humidity: 100 and 300 mg/g, respectively.[25] Figure 2 indicates that the carbon hydrophobicity has little or no effect on the reactivity of the **1**/carbon catalysts. For a given substrate, the rates are very similar for both the Ambersorb 563 and Ambersorb 572 (standard deviation of the experiments is ±5%). The steric bulk of the thioether substrates and to a lesser extent the electron density on the thioether sulfur atoms largely dictates the reactivity. The bulky diphenyl sulfide is less reactive than the three aliphatic thioethers THT, diethyl sulfide, and chloroethyl ethyl sulfide (CEES). One might expect the THT to react faster than the diethyl sulfide or CEES as the sulfur atom is less hindered in THT, but the rates are comparable. The slower than expected rate for THT derives in part from inhibition by the products of the reaction (see discussion below).

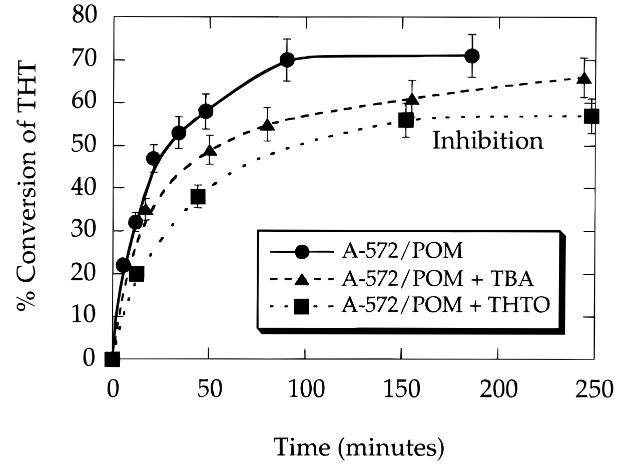

Figure 3. Inhibition of the reaction by the reaction products, tetrahydrothiophene oxide (THTO) and *tert*-butyl alcohol (TBA). THT (51 mM), TBHP (91 mM), **1**/Ambersorb 572 (0.1000g), 20 μL of isooctane as internal standard, 700 rpm, 25 °C, toluene solvent. (▲) 15 μL of TBA added before injection of the THT substrate; (■) 15 μL of THTO added before injection of the THT substrate.

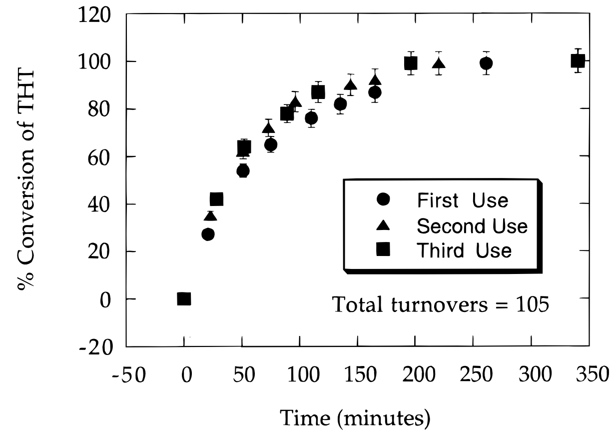

Figure 4. Evaluation of the reusability of a representative **1**/carbon cloth, "stretchable". THT (51 mM), TBHP (91 mM), **1**/carbon (0.2000g), 20 μL isooctane as internal standard, 700 rpm, 25 °C, toluene solvent.

Product Inhibition. Figure 3 shows three reaction profiles. The products of the THT reaction, THTO and TBA, were determined to be inhibiting the reaction at high conversions and causing the premature curvature seen in the profile defined by filled circles. In the other two reactions, TBA or THTO was added before injection of the THT substrate and, as seen in the figure, caused an even faster loss of activity. The **1**/carbon catalyst can; however, be reactivated by heating in a vacuum oven to 80 °C for approximately 17 h. It is interesting to note that inhibition is not observed during reaction of the other substrates: diethyl sulfide, diphenyl sulfide,

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or chloroethyl ethyl sulfide (CEES). The reactions of these three substrates approach 100% conversion and exhibit conventional kinetics (i.e., the rate of the reaction is fast at initial times and slows as the reaction nears completion). The reaction profiles are typical of first-order reactions. Only with THT does the reaction profile level off before complete conversion of the substrate. The likely explanation for the markedly more effective inhibition by THTO relative to the sulfoxide products of the other thioethers is that the lower steric bulk and greater basicity of THTO result in more effective binding to and kinetic saturation of the catalytic sites on the **1**/carbon material.

Reusability. Previous work has shown that the Ambersorb-572 powder is recoverable and reusable.[24] Figure 4 illustrates the reusability of the "stretchable" carbon cloth. The reactions were run as described in the Experimental Section. The **1**/carbon was recovered by filtering, rinsed with toluene, and then kept in a vacuum oven at 80 °C until the next use. The virtual overlap of the three reaction profiles indicates that the catalytic cloth is not damaged, and even after 105 turnovers it maintains its original reactivity.

Supporting Information Available: X-ray powder patterns and a reaction profile (5 pages). Ordering information is given on any current masthead page.

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