Polyoxometalates on cationic silica
Highly selective and efficient O_2/air-based oxidation of 2-chloroethyl ethyl sulfide at ambient temperature

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Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

Abstract

Binary cupric nitrate and triflate systems catalyze the homogeneous air oxidation of the mustard (HD) simulant 2-chloroethyl ethyl sulfide (CEES) to the corresponding desired sulfoxide (CEESO) with effectively quantitative selectivity in acetonitrile under ambient conditions. This activity is enhanced when cationic silica nanoparticles coated with the anionic multi-iron polyoxometalates (POMs) are also present. The POM-coated nanoparticles are prepared by treatment of aqueous suspensions of Akzo Nobel Bindzil CAT® cationic silica nanoparticles with aqueous solutions of the POMs, $K_9[(Fe^{III}(OH_2)_2)_3(PW_9O_{34})_2]$ (K_9**4**) or $Na_{12}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]$ (Na_{12}**5**).

1. Introduction

The development of new materials to catalyze the selective aerobic oxidation of several classes of organic compounds, including thioethers, under ambient conditions (1 atm air/O_2 and 25 °C) is of both intellectual and practical interest (representative recent papers [1]). The ideal catalyst should not only be selective and reasonably rapid in the aerobic environment, but it should also be efficient in the solid state. While there are several dioxygenase enzymes that can selectively oxidize thioethers to sulfoxides using only air (or O_2 under ambient conditions) [2], the comparable situation is rare for abiological systems [1]. Synthetic catalysts for aerobic oxidation are typically only effective at higher temperatures (>60 °C), or they utilize radical chain mechanisms, which are inherently low in selectivity (representative work on autoxidation [3]).

Recently, we reported a series of early-transition-metal oxide anionic clusters (polyoxometalates or POMs) (recent reviews of POMs [4]) for the aerobic oxidation of aldehydes and sulfides, which are strongly activated as catalysts for this process upon binding to aluminum oxide-coated cationic silica nanoparticles (($Si/AlO_2)^{n+}$) [5]. The active catalyst is formed when anionic POMs exchange with Cl^- counterions. These materials combine the well-established homogeneous catalytic capabilities of POMs under ambient conditions (representative reviews on POMs in catalysis [6]) with the practical advantages of

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simple post-reaction work-up characteristic of heterogeneous catalysts. We now report the extremely selective O_2-based sulfoxidation of 2-chloroethyl ethyl sulfide (CEES, a common simulant for mustard gas, HD) using four representative POM-coated silica nanoparticle materials. The reaction requires the presence of a Cu-based co-catalyst in order to proceed at rapid rates under ambient conditions. This co-catalyst is a mixture of $Cu(OTf)_2$ and $Cu(NO_3)_2$ dissolved in acetonitrile. The system containing the cationic silica modified with the A-type sandwich POM $K_9[(Fe(OH_2)_2)_3(PW_9O_{34})_2]$ suspended in a solution of $Cu(OTf)_2$, and $Cu(NO_3)_2$ is the best catalyst reported to date for the selective air-based oxidation of CEES under ambient conditions.

2. Experimental

2.1. General methods and materials

$Na_6V_{10}O_{28}$ [7], $Na_5PV_2Mo_{10}O_{40}$ [8], $K_9[(Fe(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]$ [5], and $\alpha\beta\beta\alpha\text{-}Na_{12}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]$ [9] were prepared by the literature methods, and their purity was checked by infrared spectroscopy [10,11]. $Cu(NO_3)_2 \cdot 2.5H_2O$, $Cu(OTf)_2 \cdot 6H_2O$, CH_3CN (anhydrous), CEES, and 1,3-dichlorobenzene were purchased from Aldrich and used without further purification. The aqueous suspensions of cationic silica nanoparticles charge balanced with chloride anions (Bindzil CAT® from Akzo Nobel and henceforth designated "(Si/AlO_2)Cl") were used as received. The particle size distribution of the Bindzil CAT® was determined by photon correlation spectroscopy (PCS) using a Coulter N4 Plus instrument. All reagents except Bindzil CAT® were dried in vacuo overnight prior to use. The infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer, and ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer. Oxidation products were identified and quantified by gas chromatography (GC, Hewlett Packard 5890 series gas chromatograph equipped with a flame ionization detector, 5% phenyl methyl silicone capillary column, N_2 carrier gas, and a Hewlett Packard 3390A series integrator). Gas chromatography–mass spectrometry measurements were performed on a Hewlett Packard 5890 series II gas chromatograph connected to a Hewlett Packard 5971 mass selective detector. Elemental analyses were performed by Desert Analytics in Tucson, AZ.

2.2. Preparation of the catalyst materials

The preparation and characterization of the silica supported POM materials was recently reported [5]. In a typical preparation, a solution of the POM (0.25 g of $Na_6V_{10}O_{28}$, $Na_5PV_2Mo_{10}O_{40}$, $K_9[(Fe(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]$, or $\alpha\beta\beta\alpha\text{-}Na_{12}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]$ in 10 ml of de-ionized water) was added to a suspension of $(Si/AlO_2)Cl$ (Akzo Nobel Bindzil CAT®, 10 g). The resulting mixture was stirred for 3 h at 25 °C and then heated to 80 °C, until the water was completely evaporated. The resulting powder was dried at 120 °C for 1 h, washed with three 10-ml portions of acetonitrile (with no loss of POM after the first wash), and dried again at 120 °C for 1 h. The purity of the material was confirmed by elemental analysis, laser light scatttering measurements, and infrared spectroscopy.

2.3. Preparation and optimization of the catalytic activity of $Cu(OTf)_2/Cu(NO_3)_2$ solutions

A stock solution of 15 mM $Cu(NO_3)_2$ was prepared in 25-ml vials using anhydrous CH_3CN. The concentration of $Cu(OTf)_2$ was varied from 10 to 37.5 mM. The concentration of $Cu(NO_3)_2$ was kept constant in all reactions (15 mM). Aliquots (0.5 ml) of the $Cu(OTf)_2/Cu(NO_3)_2$ solution were placed in 20-ml vials and 0.876 mmol of 1,3-dichlorobenzene (GC internal standard) was added to each. The total volume of each solution was adjusted to 2.395 ml (four significant figures justified) by addition of anhydrous CH_3CN, and each vial was sealed and fitted with a PTFE septum. After stirring for 1–20 min, 0.100 ml of CEES was added via syringe. Air access during the reaction was provided through the needle in the cap. Each reaction was stirred continuously and monitored for 20–24 h, and aliquots were removed for GC analysis every 15 min. Importantly, the optimal ratio of $Cu(OTf)_2/Cu(NO_3)_2$ was subsequently used in all experiments. The $Cu(OTf)_2/Cu(NO_3)_2$ solution was evaluated for activity after catalysis (9 and 13 turnovers, respectively) and no change in activity was apparent. Blue-green crystals of $Cu(OTf)_2$ (identified

by X-ray crystallography) were re-isolated in high yield after catalysis (aerobic CEES oxidation).

2.4. Catalytic oxidation of 2-chloroethyl ethyl sulfide using POM-modified cationic silica nanoparticles

In a typical experiment, 15–25 mg of the POM-modified silica (POM/(Si/AlO$_2$)) was weighed out into 20-ml vials and suspended in 1.0 ml of CH$_3$CN. A 0.5-ml aliquot (37.5 mmol total Cu(II)) of the optimized Cu(OTf)$_2$/Cu(NO$_3$)$_2$ solution and 0.876 mmol of 1,3-dichlorobenzene (GC internal standard) were placed into the vial containing the POM/(Si/AlO$_2$). The total volume was adjusted to 2.395 ml, and the vial was sealed and fitted with a PTFE septum. After the solution was stirred for 1–20 min, 0.105 ml of CEES was added to initiate the reaction. Air access to the mixture was provided through a needle in the cap.

2.5. Initial rate determination and evaluation of the reaction kinetics

The reaction was monitored by GC to at least 10% conversion (consumption of CEES) because the oxidation product, CEESO, was confirmed to be stable under the reaction conditions. The kinetics data were evaluated, and the curves were fit using the Solver program in Microsoft Excel.

3. Results and discussion

Soluble binary cupric triflate and nitrate systems catalyze the air oxidation of the mustard (HD) analogue, 2-chloroethyl ethyl sulfide (CEES) to the corresponding desired sulfoxide (CEESO), with effectively quantitative selectivity in acetonitrile under ambient conditions (Eq. (1) and Table 1, row 1). This dioxygenase stoichiometry (Eq. (1)) has been noted in other recently reported catalytic O$_2$-based thioether oxidations [5,12–15]. Short of quantitative mineralization, which will be extremely difficult to realize at room temperature in the absence of light, the most effective catalytic decontamination of HD involves sulfoxidation:

$$RSR \text{ (e.g. CEES)} + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} RS(O)R \text{ (e.g. CEESO)}$$

$$(1)$$
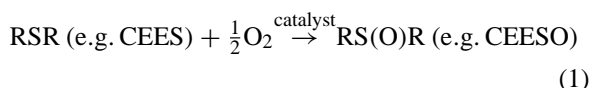
HDO (mustard sulfoxide) is far less toxic than the corresponding vesicant sulfone (HDO$_2$) and other products [16]. This Cu(NO$_3$)$_2$/Cu(OTf)$_2$ system (henceforth referred to as "Cu/Cu" for convenience) was determined to be optimal after examining several other Cu(II) salts alone, and in combinations. These optimization experiments indicated that both nitrate and an additional weakly binding counter anion such as trifluoromethane sulfonate (triflate or OTf$^-$) were required for optimal activity of the Cu(II)-based system. Isolation of high yields of blue-green crystals of Cu(OTf)$_2$ (characterized by X-ray diffraction) after 10 turnovers shows that this salt is not consumed significantly, if at all during catalytic turnover. However, based on the diminution of the intensity of the NO$_3^-$ peaks in the mid-infrared (826, 1380, 1790, and 2428 cm^{-1} after 13 turnovers) and the production of NO$_2$, nitrate is reduced during the reaction. Since each Cu(II) ion turns over many times (produces many equivalents of CEESO product per equivalent of Cu(II), as does each NO$_3^-$ ion) during reaction (see Table 1, row 1 and footnote h) and only one equivalent of nitrate is present, nitrate clearly is not the terminal oxidant. Significantly however, Kochi has clearly demonstrated that NO$_2$ can catalyze the aerobic oxidation of thioethers in dichloromethane solution under mild conditions [1a]. Thus, some CEESO production in the systems that we report here is no doubt taking place by NO$_2$ generated in situ and by the Cu(II) or Cu(II)/POM systems themselves. Significantly, when only Cu(NO$_3$)$_2$ was present under otherwise identical conditions, there was almost no production of CEESO. The experimental conditions make it very problematical to quantify how much CEESO is derived from the different catalytic processes taking place simultaneously. Fig. 1 indicates that the optimal ratio of nitrate to triflate for catalytic turnover is 1.5. Both anions clearly play roles in catalytic turnover. Triflate associates with the most active form(s) of the catalyst for selective sulfoxidation, but the nitrate dependence could derive solely from its role as a precursor for NO$_2$. The non-integer value of the optimal [OTf$^-$]/[NO$_3^-$] ratio is consistent with simultaneous sulfoxide production by a cupric triflate complex and by NO$_2$ generated in situ.

The acetonitrile-soluble tetra-*n*-butylammonium (TBA) salts of five polyoxometalates (POMs) from five representative families of POMs (Fig. 2), each with extensive and reversible redox chemistry, were

Table 1

Selective aerobic sulfoxidation of 2-chloroethyl ethyl sulfide (CEES) in acetonitrile by Cu(II) and/or polyoxometalate (POM)-based homogeneous and heterogeneous catalysts[a]

Catalyst[b]	POM (mmol)[c]	Percent conversion[d]	Percent yield[e]	TOF[f]	TON[g]
Homogeneous catalysts (catalysts in solution)					
$Cu(NO_3)_2/Cu(Otf)_2$ (Cu/Cu)[h]	0	56	56	–	–
$TBA_6V_{10}O_{28}$ (TBA$_6$**1**)[i]	0.003	0	0	0	0
$TBA_5PV_2Mo_{10}O_{40}$ (TBA$_5$**2**)[i]	0.0035	2.5	2.4	0.3	6
$TBA_6Fe_3PW_9O_{37}$ (TBA$_6$**3**)[i]	0.004	0	0	0	0
$TBA_9[Fe_3(A\text{-}PW_9O_{34})_2]$ (TBA$_9$**4**)[i]	0.004	0	0	0	0
$TBA_{12}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]$ (TBA$_{12}$**5**)[i]	0.002	0	0	0	0
Cu/Cu/TBA$_6$**1**	0.003	56	56	0	0
Cu/Cu/TBA$_5$**2**	0.0035	56	56	0	0
Cu/Cu/TBA$_6$**3**	0.004	81	81	2.7	54
Cu/Cu/TBA$_9$**4**	0.002	57	57	0	0
Cu/Cu/TBA$_{12}$**5**	0.0022	56	56	0	0
Heterogeneous catalysts (catalysts are partially or totally insoluble)					
$(Si/AlO_2)Cl$[j]	0	0	0	0	0
Na$_6$**1**	0.005	0	0	0	0
Na$_5$**2**	0.005	2	2	0.17	3.5
K$_6$**3**	0.004	0	0	0	0
K$_9$**4**	0.005	0	0	0	0
Na$_{12}$**5**	0.005	0	0	0	0
Cu/Cu/Na$_5$**1**/(Si/AlO$_2$)[k]	0.0009	59	58	0	0
Cu/Cu/Na$_4$**2**/(Si/AlO$_2$)[k]	0.0015	56	56	0	0
Cu/Cu/K$_5$**3**/(Si/AlO$_2$)[k]	0.0011	94	94	15	302
Cu/Cu/K$_8$**4**/(Si/AlO$_2$)[k]	0.0006	81	80.0	17.5	350
Cu/Cu/Na$_{11}$**5**/(Si/AlO$_2$)[k]	0.0004	56	56	0	0

[a] General conditions: 0.875 mmol (0.35 M) of CEES, catalyst (quantity given in column 2 or in footnote "h" for Cu(II) only reaction in the first row), 1 atm of air, 0.876 mmol (0.35 M) of 1,3-dichlorobenzene (internal standard) were stirred in 2.5 ml of acetonitrile at 25 °C for 20 h.

[b] No product was observed in the absence of POM, Si/AlO_2 or POM/(Si/AlO$_2$).

[c] Millimoles of total POM present in the catalyst during turnover.

[d] Percent conversion ((moles of CEES consumed/moles of initial CEES) × 100).

[e] Percent yield ((moles of CEESO/moles of initial CEES) × 100).

[f] Turnover frequency (turnovers/reaction time).

[g] Turnovers (moles of CEESO formed due to addition of POM to Cu/Cu/moles of POM, calculated as $\{C_{CEES}\times[(yield-56)/100]\}/C_{POM}$.

[h] (Cu/Cu) = 15 mM $Cu(NO_3)_2$ + 22.5 mM $Cu(OTf)_2$ (94 mmol of total Cu).

[i] $V_{10}O_{28}{}^{6-}$ (**1**); $PV_2Mo_{10}O_{40}{}^{5-}$ (**2**); $Fe_3PW_9O_{37}{}^{6-}$ (**3**); $[Fe^{III}(OH_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**4**); $[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{12-}$ (**5**).

[j] Cationic silica (Bindzil CAT®, 0.015 g suspended in solution).

[k] POM bound to $(Si/AlO_2)^{n+}$ (insoluble powder suspended in a solution of Cu/Cu).

also prepared and evaluated as catalysts for the aerobic sulfoxidation of CEES under ambient conditions (Table 1, rows 2–6). These include $V_{10}O_{28}{}^{6-}$ (**1**), an isopolyanion with little heretofore documented ability to catalyze effective homogeneous oxidations, $PV_2Mo_{10}O_{40}{}^{5-}$ (**2**), the mixed addenda heteropolyanion, a POM with considerable documented ability to catalyze homogeneous oxidations, including some by O_2, [6,12,13,17–19] the A-type sandwich POM $[(Fe(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (**4**), a POM recently prepared and showed to catalyze oxidations when bound to positive surfaces [5], and the conventional B-type Wells–Dawson sandwich POM, $\alpha\beta\beta\alpha\text{-}[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{12-}$ (**5**). In addition, a POM that appears to be a Keggin monomer and analyzes for $Fe_3PW_9O_{37}$ (**3**) but has thus far resisted characterization by X-ray crystallography was also evaluated. Four of the five complexes were effectively inactive, and **2** exhibited a quite low but reproducible activity.
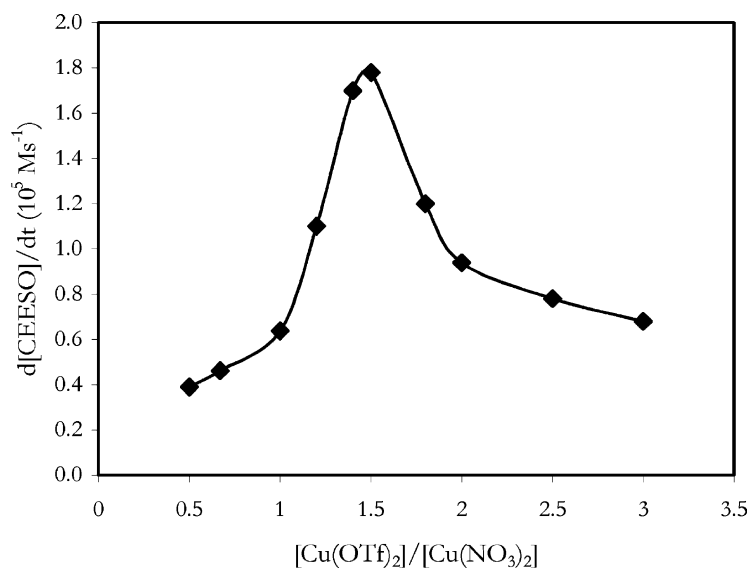
Fig. 1. Rate of CEESO formation as a function of ratio of $[Cu(OTf)_2]$ to $[Cu(NO_3)_2]$. Conditions: 1 atm of air, 25 °C; $[Cu(NO_3)_2] = 15$ mM in all reactions with $[Cu(OTf)_2]$ adjusted accordingly; $[CEES] = 0.35$ M for all reactions.
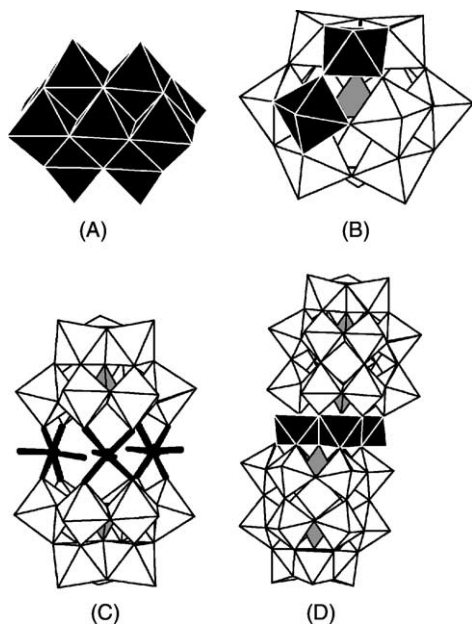

Fig. 2. Polyhedral structures of the four POMs used in this study. (A) A representative isopolyvanadate, $V_{10}O_{28}^{6-}$, (B) a representative mixed addenda Keggin heteropolyanion, $PV_2Mo_{10}O_{40}^{5-}$, (C) the A-type sandwich POM of formula $[(Fe(OH_2)_2)_3(A-\alpha-PW_9O_{34})_2]^{9-}$ (**4**), and (D) the B-type conventional Wells–Dawson sandwich POM of formula $\alpha\beta\beta\alpha-[(FeOH_2)_2Fe_2(P_2W_{15}O_{56})_2]^{12-}$.

Interestingly, when these five POMs were added to the optimized homogenous binary cupric system (Cu/Cu) (Table 1, rows 7–11), the activity of the later was basically unaffected. This is consistent, again, with all five POMs being inactive, but also not perturbing the Cu/Cu-based catalytic oxidations. This apparent minor impact of the POM on catalysis by the $Cu(NO_3)_2$-containing systems, indicates that the POM plays a minor role at best in producing NO_2 from reduction of NO_3^- in situ (via reaction of reduced POM + NO_3^-).

Significantly, however, when the insoluble POMs are supported on cationic silica and again suspended in the optimized Cu/Cu solution, there is a remarkable and reproducible increase in catalytic activity of two of the Fe-containing POMs, **3** and **4**. The cationic silica (Akzo Nobel Bindzil CAT®, or "(Si/AlO_2)Cl") is amorphous silica coated with a layer of cationic aluminum oxide, which is a charge balanced with chloride counterions. Upon treatment of this aqueous colloidal suspension with solutions of the anionic POMs, the chloride is displaced by the POMs, but the POMs retain most of their counter cations. In case of the potassium salt of **4**, recent laser light scattering experiments and elemental analyses are consistent with Eq. (2), as the POM support process (ion exchange
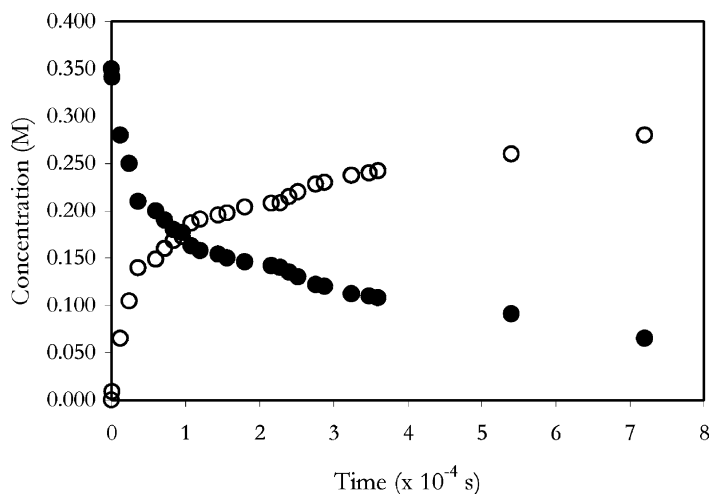
Fig. 3. Kinetics of aerobic CEES oxidation catalyzed by the Cu/Cu/K$_8$**4**/(Si/AlO$_2$) system. CEES consumption and CEESO formation as a function of time are indicated by symbols (●) and (○), respectively. Conditions: 25 °C; 1 atm of air; Cu/Cu: 15 mM Cu(NO$_3$)$_2$ + 22.5 mM Cu(OTf)$_2$; **4**: [(Fe(OH$_2$)$_2$)$_3$(A-α-PW$_9$O$_{34}$)$_2$]$^{9-}$, [K$_9$**4**] = 0.24 mM; [CEES] = 0.35 M for all reactions.
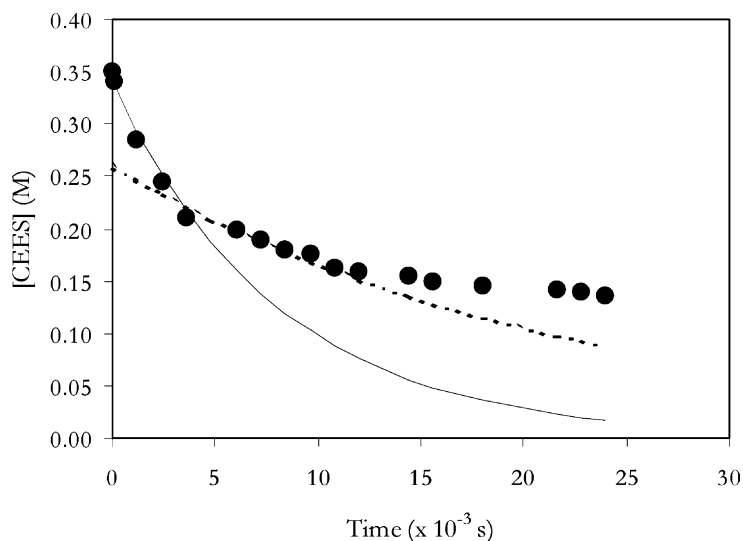

Fig. 4. Kinetics of aerobic CEES oxidation catalyzed by the highly active system comprised of K$_8$**4** electrostatically immobilized on the surface of cationic silica nanoparticles and these particles immersed in a solution of Cu/Cu (the Cu/Cu/K$_8$**4**/(Si/AlO$_2$) system). CEES consumption as a function of time is indicated by symbol (●). The solid line is an exponential fit of CEES consumption for the first five data points yielding a pseudo-first-order rate constant, k_{obs} = 12.5 × 10^{-5} s^{-1}. The dotted line is a second exponential fit of CEES consumption for data points 4–17 yielding a pseudo-first-order rate constant, k_{obs} = 4.5 × 10^{-5} s^{-1}. Conditions: 25 °C; 1 atm of air; Cu/Cu: 15 mM Cu(NO$_3$)$_2$ + 22.5 mM Cu(OTf)$_2$; **4**: [(Fe(OH$_2$)$_2$)$_3$(A-α-PW$_9$O$_{34}$)$_2$]$^{9-}$, [K$_9$**4**] = 0.24 mM, [CEES] = 0.35 M for all reactions.

and immobilization) [5].

$$\sim 58K_9\mathbf{4} + (Si/AlO_2)Cl$$
$$\Rightarrow (K_8\mathbf{4})_{\sim58}/(Si/AlO_2) + \sim 58KCl \qquad (2)$$
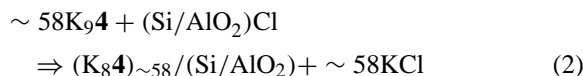
where $K_9\mathbf{4} = K_9[(Fe^{III}(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]$.

Fig. 3 shows the kinetic profile for the aerobic oxidation of CEES (and formation of CEESO) catalyzed by the system comprised of particles of $(K_8\mathbf{4})_{\sim58}/(Si/AlO_2)$ suspended in an acetonitrile solution of $Cu(NO_3)_2/Cu(OTf)_2$ (referred to henceforth and in the table as "$Cu/Cu/(K_8\mathbf{4})/(Si/AlO_2)$"). The kinetics are complex, but are fit relatively well by one dominant first-order process at low conversions and a second first-order process at high conversions (Fig. 4). The direct fit to these non-linearized first-order (exponential) rate expressions yields a pseudo-first-order rate constant, $k_{obs} = 12.5 \times 10^{-5}\,s^{-1}$ for the first five points, and a second pseudo-first-order rate constant, $k_{obs} = 4.5 \times 10^{-5}\,s^{-1}$ for points 4–17 as shown by the solid and dotted lines in Fig. 4, respectively. There is a small but marked retardation of the rate, partly as a result of mild inhibition of the reaction, Eq. (1), by the product CEESO. Because of this phenomenon and the multiple catalytic processes operating simultaneously, these pseudo-first-order fits are not significantly interpretable in a mechanistic context; they simply provide the speed of the chemistry.

Analysis of these composite catalyst systems in the presence of CEES by ^{13}C and ^1H NMR under anaerobic solutions indicates no appreciable change in the spectra of CEES. However, this does not necessarily rule out binding of CEES to the active form of the cupric catalyst. Clearly, the heterogeneity of the optimal catalytic systems, $Cu/Cu/(K_8\mathbf{4})/(Si/AlO_2)$ and $Cu/Cu/(K_{11}\mathbf{5})/(Si/AlO_2)$ (the last two rows in Table 1, respectively) and the complexity induced by intermediate NO_2, precludes a comprehensive kinetic analysis of these systems. Nevertheless, the sulfoxide selectivities and turnover rates in these systems are certainly noteworthy. They appear to be the most reactive potential catalysts yet for the catalytic decontamination of mustard without other requirements (no solvent, heat, light or additives needed but only air under ambient conditions).

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