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Vanadium-Doped Acid-Prepared Mesoporous Silica: Synthesis, Characterization, and Catalytic Studies on the Oxidation of a Mustard Gas Analogue

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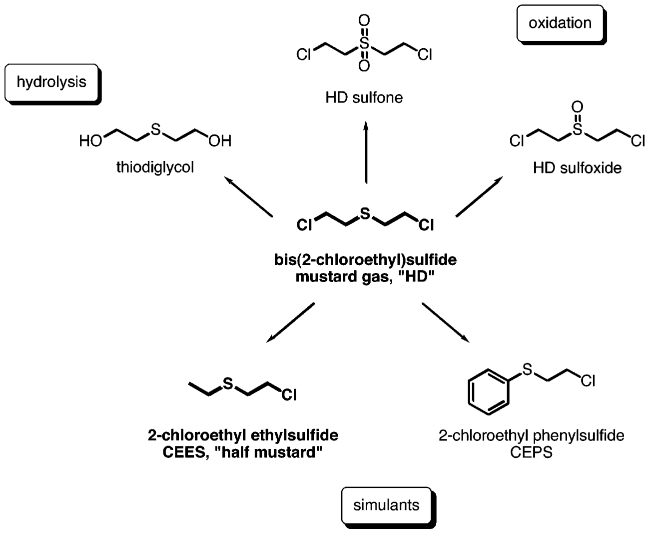
The room temperature, liquid-phase oxidation of 2-chloroethyl ethyl sulfide (CEES), an analogue of mustard gas, was investigated using vanadium-doped acid-prepared mesoporous silica ("V−APMS") as a solid catalyst. The V−APMS samples were prepared by wet impregnation with NH_4VO_3, followed by calcination. XRD, N_2 physisorption, SEM, and EPR were used to characterize the solid products. Samples with lower V contents (0.1−10 wt %) were found to contain isolated vanadyl species and were highly effective for oxidation of CEES to the corresponding sulfoxide and sulfone using *tert*-butyl hydroperoxide (TBHP) as the oxidant. Surface area and pore volume decreased significantly at higher loadings of V due to formation of V_2O_5 within the pores of the solid. The mechanistic route involved V^{5+}/V^{4+} redox cycles during the catalysis process, as revealed by EPR studies.

Introduction

Bis(2-chloroethyl) sulfide, commonly called mustard gas, is a highly toxic chemical warfare agent, due to its high reactivity toward proteins and DNA, and it acts by inducing biochemical and morphological changes in tissues.[1] Chemical reactions to convert mustard gas to more benign compounds are currently of much interest, since international treaties not only prohibit further production of this compound but also require the destruction of current military stockpiles of it in the next few years.[2] The usual method of large-scale destruction is incineration; however, generation of secondary pollutants such as CO and the fully oxidized oxidation product bis(2-chloroethyl) sulfone (Scheme 1) is also a problem due to their toxic nature. Interestingly, the partially oxidized product bis(2-chloroethyl) sulfoxide and the hydrolysis product thiodiglycol are relatively harmless, and formation of these compounds is usually the goal in the chemical detoxification of mustard.

Scheme 1. Examples of Oxidation and Hydrolysis Products of Mustards Gas, Bis(2-chloroethyl) Sulfide, and Two Commonly Used Mustard Gas Simulants



Since mustard gas is so toxic, research studies are usually carried out with less toxic structural analogues such as 2-chloroethyl ethyl sulfide (CEES), 2-chloroethyl phenyl sulfide, dimethyl sulfide, or other related compounds. Notable research progress has been made in the past few years to study the destruction and decontamination of mustard analogues. There are reports on oxidation and decontamination of thioether systems based on microemulsion processes, catalytic dehalogenation, phase transfer catalysis, photocatalysis, and redox catalysis reactions.[3−7] Among these, the oxidation of thioethers with oxidants such as H_2O_2, *tert*-butyl hydroperoxide (TBHP), and even O_2 has been extensively investigated using a variety of catalysts, including heteropolyacids,[8] Ru-based systems,[9−11] Ce^{4+} compounds,[12] benzyl

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trimethylammonium tribromide,[13] and complexes of Cr, Au, Fe, Mn, and Cu.[14−17] Several types of polyoxometalates[18] have shown good catalytic activity and selectivity for formation of sulfoxides.

Solids containing transition metals ("metal-doped" solids) have also been studied for thioether oxidation. Of the metal-based oxidation catalysts, vanadium-doped solids have been extensively tested and studied for a number of oxidation reactions. The interest in vanadium chemistry has been promoted in part by its ability to catalyze oxidations and oxo transfer reactions in biological systems.[19] Vanadium oxides and mixed oxides, heteropolyvanadates, vanadium alkoxides, vanadium acetylacetonate, and V complexes have been tested and employed as effective catalysts in dehydrogenation/oxidation of organic substrates,[20−23] where the vanadate and/or vanadyl species acts as an active center of catalysis.

V-exchanged, -substituted, -doped, and -grafted zeolites, mesoporous molecular sieves, and other supports, such as TiO_2, SnO_2, Al_2O_3, and SiO_2, are particularly attractive materials for use as catalysts for emission abatement and oxidation reactions. It is known that the activity and selectivity of supported vanadium oxide catalysts is dependent on the V content of the supports.[24] Depending upon the loading, the V species can be present as (i) isolated monovanadate species containing terminal vanadyl (V═O) groups with the V atom in tetrahedral coordination with oxygen ligands and (ii) as polyvanadate polymeric species, formed at higher loading of vanadium in the catalyst. The presence of the latter species has been found to affect the selectivity of the reaction and also has a negative effect on the catalyst due to creation of bulk, inaccessible V atoms. In addition, the coordination environment and the oxidation state of V were found to be influenced by the method of preparation and the nature of the solid support. Thus, studies have been performed on V-doped samples using EPR, NMR, and absorption techniques to find the effect of loading and local electronic and ligand environment on the coordination of V species and their catalytic behavior.[25−29]

Reduction of thioethers can also be used as a model for the conversion of mustard gas to less harmful compounds. Recently, our research group reported on the reduction of thiophene and CEES by hydrodesulfurization with H_2, using Mo-doped mesoporous SiO_2 as the solid catalyst.[30,31] Mesoporous solids have particular promise as substrates in solid-phase catalysis because they have unusually large surface areas (routinely in excess of 1000 m^2/g), large internal pore volumes, and narrow pore size distributions. Our studies have mainly focused on acid-prepared mesoporous silica (APMS), which has several additional advantages, since they have a spherical particle morphology with a controllable particle size between 1 and 10 μm, depending on synthesis conditions, and they may be synthesized in less than 2 h by a simple procedure. Spherical particle morphologies often play an important role in catalytic processes, helping to control the overall mass transfer kinetics and thus the rate and selectivity of heterogeneous reactions. This lends APMS an advantage over ordinary powders as a catalyst support. In addition, as with many mesoporous materials, the pore sizes of APMS may also be controlled either through modification of synthesis conditions or by postsynthetic treatments.[32−34] Although Mo−APMS is an effective hydrodesulfurization catalyst (indeed, more effective than Mo−MCM-41 or Mo−MCM-48), reduction of thioethers requires moderately high temperatures (at least 200 °C), making reduction of mustard gas impractical for military field use. Therefore, we have shifted our focus to oxidative catalysis using V−APMS. In this report, we describe the synthesis and characterization of V-doped APMS materials. We also continue our studies in this field by reporting on the oxidation of CEES with TBHP using V−APMS as a catalyst.

Experimental Section

Materials and Methods. Powder X-ray diffraction experiments were performed using a Scintag ×1 $\theta-\theta$ diffractometer equipped with a Peltier (solid-state thermoelectrically cooled) detector using Cu Kα radiation. N_2 adsorption and desorption isotherms were obtained on a Micrometrics ASAP 2010 instrument. Samples were degassed at 473 K under vacuum overnight prior to measurement. Surface areas and pore size distributions were calculated from the BET and the BJH methods, respectively. Elemental analyses (Si and V) were performed by Robertson Microlit (Madison, NJ) using ICP-AES for detection of V concentrations and ICP-microwave acid digestion for identification of Si concentrations. A Bruker ESP 300E EPR spectrometer was used for obtaining EPR spectra. All

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chemicals were obtained from Sigma-Aldrich and were used as received.

Synthesis of APMS. This procedure was modified from a previously published synthesis of APMS.[35] Cetyltrimethylammonium bromide (1.8 g, 4.9 mmol) was suspended in a solution of EtOH (100%, 11.1 g, 0.24 mol) and H_2O (39.7 g) in a 125-mL Teflon bottle. Concentrated HCl (36.9%, 4.4 g, 44.5 mmol) was added and the mixture was stirred until the surfactant was fully dissolved and the solution was clear. Tetraethoxysilane (TEOS) (4.0 g, 19.2 mmol) was then added, and the resulting solution was stirred for 10 s. At this point, NaF (4.76 g of a 0.5 M solution, 2.38 mmol) was added. After 90 s, the solution turned opaque. This mixture was then heated at 373 K for 40 min. The resulting white precipitate was captured by filtration, washed five times with distilled H_2O and once with 99.9% EtOH, dried, and then calcined in air. The following calcination profile was followed: from 298 to 723 K, the sample was heated at a rate of 2 K/min, followed by a 240 min hold at 723 K and then a 10 K/min ramp to 823 K and a hold time of 480 min at 823 K before cooling to room temperature.

Synthesis of V−APMS. In a typical synthesis, APMS (3.0 g) was suspended in 10 mL of an aqueous solution of NH_4VO_3 (0.294 M, 2.94 mmol). The mixture was stirred to dryness at room temperature and then calcined. Other V-doped samples were prepared by varying the concentration of V and by using V(O)(acac)$_2$ or $VOSO_4$ as the vanadium source.

Functionalization of APMS with Amino Groups (APMS−NH$_2$). APMS (3.0 g) and (3-aminopropyl)trimethoxysilane (3.5 g, 19.5 mmol) was added to toluene (100 mL) and the mixture was refluxed for 24 h. After cooling to room temperature, the solid was filtered, washed with toluene and acetone, and dried at 373 K in air.

Synthesis of V−APMS−NH$_2$. In a typical synthesis, APMS−NH$_2$ (1.50 g) was vacuum-dried at 373 K and then added to a solution of $VOSO_4$ (0.048 g, 29.4 mmol) in EtOH (100%, 10 mL). The solution was then stirred for 3 h, and then the solid was filtered, washed with EtOH, and dried at 373 K in air. VO(acac)$_2$ was also used as the vanadium source.

Electron Paramagnetic Resonance (EPR) studies. EPR spectra were obtained either at room temperature or at 77 K, using the X-band frequency of 9.46 GHz at a power of 1.00 mW. The center field used was 3500.00 G with a sweep width of 1800.00 G. All spectra were reported as first derivatives of absorption. EPR tubes were either 5 mm (for room temperature experiments) or 4 mm (for experiments at 77 K). To study changes in the oxidation state of V upon contact with CEES, 2-chloroethyl ethyl sulfide (0.100 mL, 0.107 g, 0.859 mmol) was added to a vial containing V−APMS (0.25 g). This mixture was then stirred and dried overnight. The percentage of V in each sample was variable; details are included in the text. Zeeman and hyperfine coupling constants were measured directly from the spectra; several spectra were also simulated to ensure consistency.

Catalytic Activity Studies. The oxidation of CEES was carried out in the liquid phase and at atmospheric pressure, using various V-doped APMS samples. In a typical experiment, a mixture containing 2-chloroethyl ethyl sulfide (0.0054 g, 42.9 μmol) in 3 mL of CH_2Cl_2 was placed in a vial and stirred. V−APMS (20 mg) and *tert*-butyl hydroperoxide (5.5 M in decane, 7 μL, 38.5 μmol) were then added and the resulting mixture was then stirred constantly for time periods varying between 30 s and 24 h. At various time intervals, aliquots from the reaction mixture were removed and filtered through a syringe with a 0.22 μm Millipore filter. The filtrate was then analyzed by GC−MS on an Agilent model 6890 gas chromatograph−mass spectrometer using a HP-5MS column (J&W Scientific, 15 m × 0.32 cm). CEES conversions were calculated based upon the total consumption of TBHP to produce 38.5 μmol of the oxidized products.

Table 1. N_2 Physisorption Properties and V Contents of V-Doped APMS Samples

sample	wt % V added	wt % V actual	surface area (m^2/g)	pore volume (cm^3/g)	pore diameter (Å)
APMS (no V)	−	−	870	0.75	36
5%[a] V−APMS	5	4.93	565	0.47	35
10% V−APMS	10	7.97	322	0.38	36
15% V−APMS	15	11.3	304	0.34	36
20% V−APMS	20	16.4	300	0.29	33
30% V−APMS	30	23.1	223	0.26	33
40%V−APMS	40	23.7	109	0.22	33

[a] Weight percent of V from doping solution.

Results and Discussion

Powder X-ray Diffraction (XRD) and N_2 Physisorption. In previous work, we prepared Mo-doped APMS by adding a Mo source, $(NH_4)_6Mo_7O_{24}$, directly to the APMS synthesis mixture.[30] This method took advantage of the fact that Mo forms anionic oxide clusters even at very low pH values (less than 2). In strongly acidic solutions, mesoporous silica such as APMS forms through the self-assembly of cationic silicate colloids in the presence of surfactants.[36] The repulsive interaction between the cationic colloids and cationic surfactants such as cetyltrimethylammonium bromide (CTAB) is mediated by chloride ions from HCl. Polyoxomolybdate anions are easily incorporated into the growing APMS structure through electrostatic interactions, in essentially quantitative yield. Unfortunately, although polyoxovanadates are well-known in aqueous solution, the dominant V species below pH 2 is VO_2^+. Therefore, we used a wet doping technique to disperse V in our samples. In this method, the calcined mesoporous silica, APMS was suspended in a solution of NH_4VO_3, which was then evaporated to dryness. A variety of V loadings were attempted by this method. The V-doped material was then recalcined to ensure that the metal was fully oxidized. The N_2 physisorption data for these samples are presented in Table 1. All samples showed type IV isotherms (Figure 1), which are characteristic of mesoporous materials. At higher loadings, a region of hysteresis was observed at higher partial pressures, which corresponds to the presence of textural porosity within the pores. It may also indicate that some structural breakdown has occurred in the materials, consistent with our previous results for samples exposed to postsynthetic treatments.[30] A decrease in the surface area and pore volume as a function of loading was observed for all samples. One source of such changes in the physical properties of the porous materials is the breaking of Si−O−Si bonds and re-forming of Si−OH groups at the pore surfaces upon exposure to aqueous

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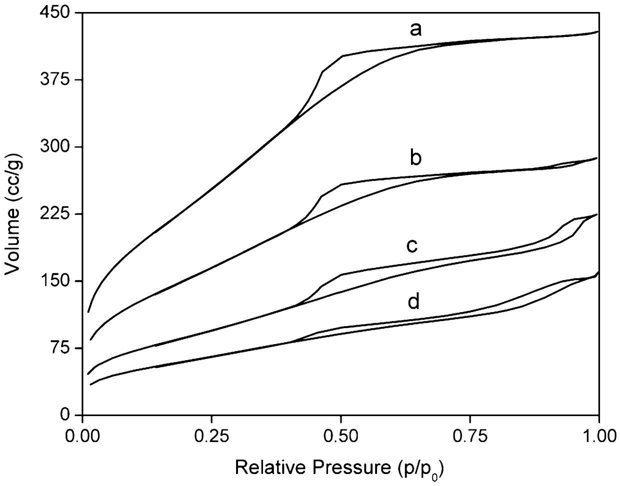

Figure 1. Nitrogen physisorption isotherms of APMS and V−APMS samples with several V loadings. The isotherm of pure APMS is shown in part a. V−APMS samples were identified by the weight percent of V in their doping solutions: (b) 5%, (c) 10%, and (d) 30%.

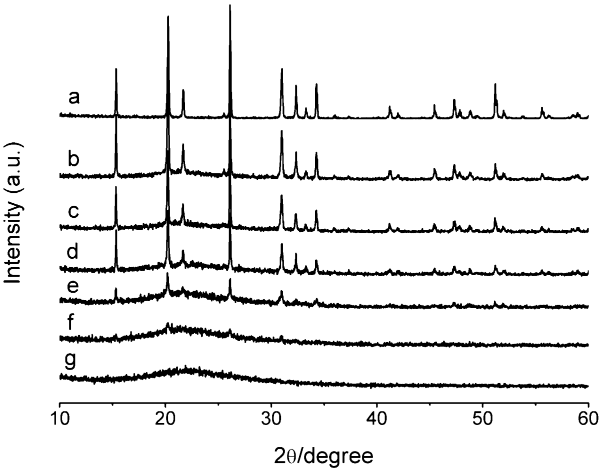

Figure 2. XRD spectra of V−APMS samples for several V loadings. Weight percent of V in the doping solution: (a) 100% V_2O_5, (b) 40%, (c) 30%, (d) 20%, (e) 15%, (f) 10%, (g) 5%.

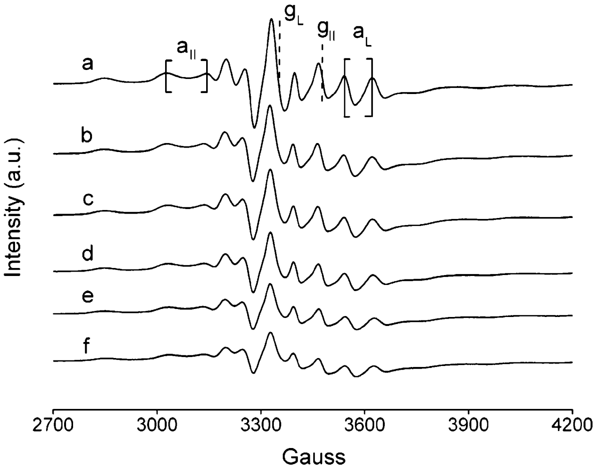

Figure 3. EPR spectra of V−APMS samples (5−40 wt % V) after exposure to CEES. Weight percent V in the doping solution: (a) 5%, (b) 10%, (c) 15%, (d) 20%, (e) 30%, (f) 40%.

solutions, as previously reported in our earlier work.[30] More importantly, such features are indicative of filling of the pores of the host APMS material with vanadium oxide species, as confirmed by XRD (see below).

Powder X-ray diffraction patterns of these samples for various loading levels are presented in Figure 2. The existence of broad XRD features at approximately 25° for samples with loadings of 0.1 to 10 wt % V are indicative of well-dispersed V, either as isolated, monomeric vanadyl species or as small clusters below the resolution of the XRD experiment.[29] With increasing V loading, however, strong and prominent XRD peaks corresponding to V_2O_5 species were observed. This indicates that at higher loadings, the isolated vanadyl species agglomerate together to form polymeric V_2O_5 species. Such behavior has been reported earlier by other researchers, where the extent of V loading was found to affect the nature of the vanadium species, changing from isolated, monomeric VO^{3+} species to polymeric V_2O_5.[29] It is also important to note the difference between the amount of V present in the impregnation solution and the amount that ended up in the solid. This difference increased as the amount of V in the impregnation solution increased. It appears that the material reaches a level at which no further V_2O_5 can be formed within the pores; beyond this point, any additional V is removed during calcination, which was evident from the presence of increasing amounts of V_2O_5 on the inside of the box furnace as the amount of V increased.

Electron Paramagnetic Resonance (EPR). Several sets of EPR experiments were performed in order to determine the effect of contacting V−APMS samples with CEES. These samples did not show any EPR signal prior to contact with CEES, indicating the presence of V in a fully oxidized +5, d^0 state (EPR silent), regardless of the doping level. As expected, EPR of “blank” (undoped) APMS and also bulk V_2O_5 exposed to CEES showed no signal. However, after contact with CEES, the V−APMS samples showed strong and prominent EPR signals with eight-line hyperfine patterns observed in the EPR spectrum (Figure 3). These spectra are characteristic of a V^{4+} species, indicating that upon exposure to CEES, the V^{5+} species in V−APMS are reduced to V^{4+}. These reduced V^{4+} species were in an anisotropic axial environment, as shown by the presence of two sets of EPR parameters in the spectra ($g_{\parallel}$ and $g_{\perp}$). The similarity between these spectra and those found for related V-doped silica materials leads to the conclusion that the bonding geometry of the V ion is C_{3v} or pseudo-C_{3v}, with a vanadyl (V=O) group bound to the silica surface through silanol linkages.[25,28,37]

The EPR spectra of V−APMS samples with varying V loadings (5−25 wt %) after exposure to CEES are remarkably similar, regardless of the amount of V present (Figure 3). Zeeman and hyperfine constants did not change as the concentration of V was increased, although some broadening in the peak width and decrease in intensity of the EPR signals was observed as the concentration increased. The absence of any additional splittings or new features in the EPR spectra of V−APMS samples can be used to draw conclusions about the proximity of the V ions to each other. In related experiments by other researchers, bond distances for vanadium−oxygen bonds in $[\{Cu(phen)_2\}_2V_4O_{12}]\cdot H_2O$ were found to be, on average, 1.80 Å for single bonds and 1.65 Å

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[37] Whittington, B. I.; Anderson, J. R. *J. Phys. Chem.* **1993**, *97*, 1032.

for double bonds, with a V−O−V angle of approximately 110°.[38] This led to a calculated separation of approximately 2.95 Å between vanadium centers bridged by an oxygen atom. Similar V species could be expected to form as precursors to V_2O_5 within APMS materials. However, to have neighboring nucleus interactions, the separation between V ions must be between 6 and 9 Å.[39] Line broadening becomes too severe when interactions occur at a distance of 2−4 Å and there are no detectable interactions when separation increases above 10 Å.[40] Thus, the vanadyl species in V−APMS must either be isolated on the pore surfaces (>10 Å) or involved in the formation of V_2O_5 clusters (∼3 Å). Since the data show that V_2O_5 exposed to CEES is EPR silent, and XRD spectra show no evidence of V_2O_5 in V−APMS with V loading of 5% or less, it can be concluded that the active species for this reaction are likely VO^{3+} species. Also, the decrease in the intensity of the EPR signal with increasing vanadium concentration in V−APMS can be attributed to an increase in V_2O_5 as the isolated vanadyl species polymerize.

For comparison, V^{4+}-doped APMS was prepared directly by wet impregnation with $V(O)(acac)_2$ rather than through reduction of V^{5+}. The concentration of V was kept at 5 wt % in the impregnation solution, and the samples were not calcined in order to avoid V oxidation. EPR of this sample is shown in Figure 4a. The characteristic eight-line vanadyl spectrum is somewhat similar to the V−APMS samples that had been reduced with CEES. However, the peaks are comparatively broad, indicating the presence of a wider variety of V environments in the material. Similar features were also observed by Van Doorslaer et al. for a $V(O)(acac)_2$−SBA-15 system, where they were attributed to interaction of VO^{2+} with the framework of the host material as well as to the possibility of formation of VO-hydrated species, in which the acetylacetonate ligands were replaced by water.[25] The spectrum also shows a very broad underlying single line with no hyperfine splitting and a Zeeman constant of 1.965. As explained above, this can be attributed to vanadium centers separated by distances between 6 and 9 Å.

In catalytic reactions (see below), leaching of V species was observed from the $VO(acac)_2$-doped APMS solid, as indicated by the growth in intensity of a blue color in the reaction solution. We therefore attempted to increase the retention of V within the solid by immobilizing it on an amine-terminated surface. Figure 4b,c shows EPR spectra of APMS samples that were treated with (aminopropyl)triethoxysilane (APTES) to afford an amine-terminated surface (APMS−NH_2) and then wet impregnated (1 wt % V) with $V(O)(acac)_2$ or $VOSO_4$. Both V^{4+} doping sources show spectra that are very similar to the CEES-reduced samples, without the broad features observed when unmodified APMS was used for $V(O)(acac)_2$ loading. These well-resolved hyperfine EPR patterns indicate the presence of VO^{2+} species in these samples in a well dispersed form, bonded to the amino groups, forming a distorted octahedral complex, as reported by Lee et al.[28] Table 2 lists the Zeeman and hyperfine constants for the spectra shown in Figure 4. The hyperfine constants for the amine-bridged vanadyl groups are higher than the vanadyl groups bound directly to the silica, indicating that the paramagnetic electron is more associated with the ligands for the amine-bridged vanadyl groups due to the stronger electron density withdrawing characteristics of the amines as opposed to the silica.

Table 2. EPR Parameters of V^{4+}-Doped APMS (compared to free electron, $g = 2.0023$)[a,b]

sample	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}$	$a_{\perp}$
1% $VO(acac)_2$, APMS-NH_2	1.945	2.015	173.0	73.5
1% $VOSO_4$, APMS-NH_2	1.943	2.019	177.6	67.4
5% $VO(acac)_2$, APMS	1.949	2.012	166.5	66.0
V^{4+} interactions[c]	1.965			
5% NH_4VO_3, APMS (V^{5+}, for comparison)	1.941	2.014	168.3	66.9

[a] $a_{\parallel}$ and $a_{\perp}$ are in units of 10^{-4} cm^{-1}. [b] Measurements taken on unevacuated, hydrated samples. [c] For Figure 4a only.

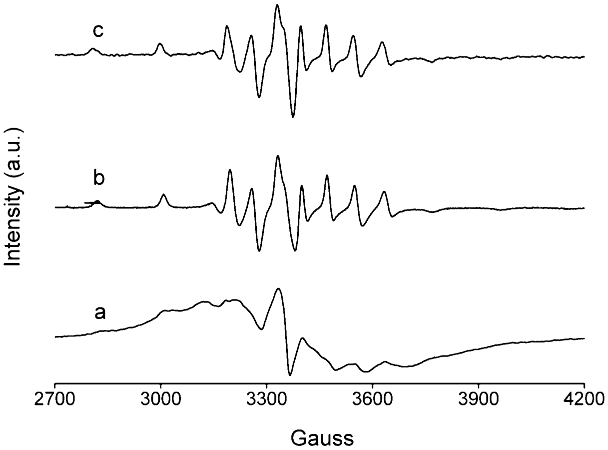

Figure 4. EPR spectra of V−APMS prepared with V^{4+} sources. Samples were not calcined prior to catalysis, to prevent oxidation to V^{5+}. (a) $VO(acac)_2$ source, unmodified APMS surface; (b) $VO(acac)_2$ source, amine-modified APMS surface; and (c) $VOSO_4$ source, amine-modified APMS surface.

Catalytic Oxidation of 2-Chloroethyl Ethyl Sulfide. The oxidation of thioethers to sulfoxides and sulfones is a thermodynamically favored reaction in the presence of oxidants such as oxygen, hydrogen peroxide, and organic peroxides, but in most cases the reaction rates are slow and the process does not reach completion, even after long reaction times. However, this reaction is easily catalyzed. Among the various catalysts used for oxidation of sulfides, the V-based catalysts, particularly the vanadium Schiff bases, have been found to be efficient catalysts for oxidation of R−S−R compounds, where R can be an alkyl or an aryl group.[41,42]

Oxidation of CEES to its oxidized products, the sulfoxide (CEESO) and sulfone ($CEESO_2$), was performed using the vanadium-doped APMS materials described above as catalysts. Figure 5 presents the results of oxidation of CEES with

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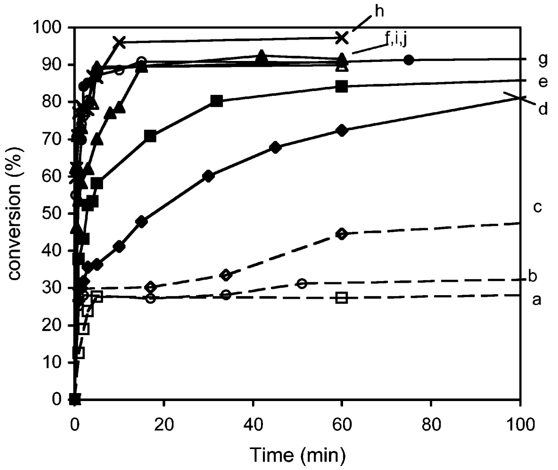

Figure 5. Percent conversion of CEES as a function of time during the oxidation of CEES by TBHP. Weight percent of V that was present in the doping solution of each sample: (d) 0.1%, (e) 0.5%, (f) 1.0%, (g) 5.0%, (h) 10%, (i) 15%, (j) 20%. Results for the uncatalyzed process (TBHP only) (a) and the reaction in the presence of undoped APMS (b) and V_2O_5 (c) are also shown.

Table 3. Comparison of Total CEES Conversion and Selectivity for V−APMS Samples

catalyst	% conversion after 1 h	CEESO/ $CEESO_2$
no solid	32	4.3
APMS only	32	5.9
V_2O_5	44	6.4
0.1%[a] V−APMS	69	4.4
0.5% V−APMS	91	3.5
1% V−APMS	94	3.2
5% V−APMS	95	2.8
10% V−APMS	97	3.1
15% V−APMS	90	4.6
20% V−APMS	91	4.3
$V(O)(acac)_2$ (soln)	67	11

[a] Weight percent of V from doping solution.

various V−APMS samples as a function of time, and a direct comparison of the results is found in Table 3. Also shown in the figure are activity plots for the "blank" APMS (no V) and V_2O_5. The rate of reaction is significantly slower when undoped APMS is present or in the absence of APMS than when the V−APMS is present, indicating the catalytic effect of V doping. On blank APMS, the reaction reaches a saturation stage after about 10−15 min and a maximum conversion of about only 29% of sulfide was achieved. On V_2O_5, the reaction rate was only slightly higher than that of the blank APMS. In the presence of V−APMS catalysts, the reaction proceeds at faster initial rates and shows higher conversions (69−97%), even for catalysts with V loadings as low as 0.1 and 0.5 wt %. The rate and the total conversion for the process was found to increase as a function of metal content in the V−APMS samples for a loading of V from 0.1 to 10 wt %. As the loading of V increased above 10 wt %, total conversions of CEES were found to decrease slightly with increased loadings. The decrease in catalyst activity coincides with the formation of V_2O_5 agglomerates in APMS samples, as observed in the XRD spectra. On the basis of these results, the higher activity of V−APMS samples with low V content (0.1−10 wt %) can be attributed to the presence of monomeric isolated vanadyl groups acting as active sites for the reaction. With increasing V loadings, polymeric V_2O_5 species are formed (Figure 2) which are less efficient as catalysts for oxidation of CEES, and this leads to the overall decrease in the activity of V−APMS samples with higher V loading (>10 wt %). Table 3 also shows the selectivity of various V-doped APMS samples. All catalysts show a selectivity for the sulfoxide over the sulfone, although the selectivity varies somewhat with the V content of the materials. The trend in selectivity is opposite to that of V content between 0.1 and 5 wt %. However, the selectivity begins to increase again as the V content increases between 5 and 20 wt %. The selectivity is inversely related to the CEES conversion, indicating that the strongest oxidation catalysts are those with intermediate V loadings. These trends are likely related to the V species present in the samples. At the lower V concentrations, the isolated vanadyl species in V−APMS samples are quite active for oxidation and more of the fully oxidized product is formed as the V content increases. Above 10 wt %, V_2O_5 clusters are observable by XRD. These clusters are less active but more selective for the partially oxidized product, and the selectivity begins to approach the values given for bulk V_2O_5.

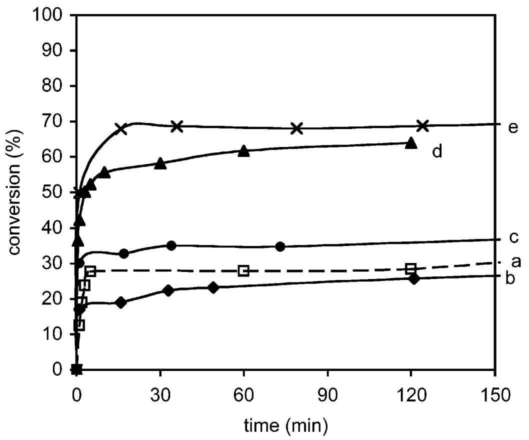

Figure 6. Percent conversion of CEES as a function of time during the oxidation of CEES by TBHP: (a) uncatalyzed reaction, (b) V−APMS−NH_2 (V source = $VO(acac)_2$, 5 wt % V) added to the reaction, (c) V−APMS−NH_2 (V source = $VOSO_4$, amine-modified APMS surface, 5 wt % V) added to the reaction, (d) V−APMS (V source = $VO(acac)_2$; 5 wt % V) added to the reaction, and (e) $VO(acac)_2$ dissolved in the reaction solution.

In addition to the above experiments on V^{5+}-doped APMS, catalytic studies of the oxidation of CEES were also carried out using V^{4+}-doped APMS. For comparison, homogeneous catalysis was also performed in solutions of V^{4+} complexes or salts, such as vanadyl bis(acetylacetonate) [$VO(acac)_2$] and $VOSO_4$. The total conversion and selectivity results for oxidation of CEES with TBHP in $VO(acac)_2$ solution are given in Table 3. The catalyst shows a conversion of about 67%, which is lower than the conversion observed for the V^{5+}-doped samples, but the selectivity for formation of sulfoxide was much higher. Encouraged by the high selectivity for the sulfoxide, attempts were made to immobilize V^{4+} on calcined APMS using the method of wet impregnation (Figure 6). However, a problem with this method was that a substantial amount of V leached from the solid into the solution, as determined by the appearance of a blue color in the reaction solution. The fact that this sample shows a total conversion similar to the homogeneous system (Figure 6d,e) is further indirect evidence that catalysis is taking place in solution, not at the surface of the solid. In an effort to trap the V^{4+} on the surface more effectively, the APMS surface was modified with $(MeO)_3Si(CH_2)_3NH_2$ prior to wet impregnation. It was hoped that the amine-terminated surface would be able to bind the vanadyl species more effectively, and indeed, there was less leaching of V from this material into the reaction solution. However, the total conversion of CEES was much lower than for free $VO(acac)_2$. Although the reasons for this low conversion are unclear, it may indicate that the V^{4+}/V^{5+} redox cycle is less efficient when the V^{4+} is immobilized on the surface. Further studies to probe the oxidation state and local environment of the metal in the V^{4+}−APMS samples are currently being performed.

Conclusions.

V^{5+}-doped APMS solids with low concentrations of V can effectively be used as active catalysts for oxidation of CEES with TBHP to give the sulfoxide, CEESO, as the major product. The sulfone, $CEESO_2$, is also observed to a certain extent. At these low loadings, V is present mainly as isolated, monomeric vanadyl groups. The loading of V in the APMS sample was found to affect both the total conversion and selectivity for CEESO versus $CEESO_2$. EPR studies performed on V-doped samples before and after exposure to CEES showed the reduction of V^{5+} to V^{4+} upon contact with CEES, indicating the role of a V^{5+}/V^{4+} redox cycle in sulfide catalysis. Studies with V^{4+} complexes and salts showed them to be active for CEES oxidation in homogeneous reactions, with higher selectivity for formation of CEESO than was found for the V^{5+} species. However, the V^{4+} species introduced by wet impregnation onto APMS leached into the reaction solution. V^{4+} species could be immobilized onto an amine-modified APMS surface, but these species were not found to be active for catalysis. These studies highlight the role of V^{5+} in APMS samples to act as efficient catalysts for oxidation of CEES.

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