

Oxidation of 2-chloroethyl ethyl sulfide using V-APMS

Stephanie R. Livingston, Dharmesh Kumar¹, Christopher C. Landry*

Department of Chemistry, University of Vermont, 82 University Place, Burlington, VT 05405, United States

Received 6 August 2007; received in revised form 14 November 2007; accepted 14 November 2007

Available online 22 November 2007

Abstract

Vanadium-doped acid prepared mesoporous spheres (V-APMS) were prepared with vanadium loadings of 1–40 wt% using a wet-impregnation method. The effects of vanadium loading on the support were studied using N₂ physisorption and powder XRD. The pore volumes, surface areas, and pore diameters of the catalysts decreased as a function of vanadium loading and diffraction peaks corresponding to crystalline V₂O₅ were detected by XRD at an intermediate V loading, becoming more intense as the V content increased. These results indicate that at low V loadings, the vanadium oxide species were well-dispersed on the silica; however, at higher V loadings crystalline V₂O₅ was formed within the pores of the APMS. V-APMS was then studied as a heterogeneous catalyst for the oxidation of the chemical warfare agent stimulant 2-chloroethyl ethyl sulfide (CEES) using *tert*-butyl hydroperoxide (TBHP) as the oxidant. Kinetic studies at temperatures ranging from 0 to 50 °C showed that materials with low V loadings were the most effective catalysts for the reaction. The mechanism of the oxidation reaction appeared to be different for catalysts that were composed of well-dispersed vanadium oxide species than for catalysts containing microcrystalline or crystalline V₂O₅. Finally, a possible reaction scheme for the oxidation of CEES by V-APMS is discussed.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Mesoporous silica; Vanadium; Oxidation; Mustard gas; Heterogeneous catalysis

1. Introduction

The catalytic oxidation of bis(2-chloroethyl) sulfide, commonly known as the chemical warfare agent mustard gas, is a reaction of considerable interest as a means to chemically convert this toxic vesicant, or blistering agent, into a less harmful product. The partially oxidized product of mustard gas, bis(2-chloroethyl) sulfoxide, is not a vesicant and is significantly less toxic than the sulfide, but the fully oxidized product bis(2-chloroethyl) sulfone is also a toxic vesicant [1]. Therefore, it is desirable to develop a method by which bis(2-chloroethyl) sulfide is rapidly and selectively oxidized to its corresponding sulfoxide. Due to the toxic nature of mustard gas, the less toxic but structurally similar analogue 2-chloroethyl ethyl sulfide (CEES) is commonly used to study this reaction. Several heterogeneous and homogeneous catalysts that have been used to oxidize mustard gas and its analogues include titanium-containing zeolites

and molecular sieves [2,3], polyoxometalates [4–8], and various transition metal complexes [9–12]. The oxidants used in these reactions were hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP), and/or O₂. In particular, vanadium oxide catalysts, which are widely used in oxidative industrial processes such as the selective oxidation of hydrocarbons [13,14], the ammoxidation of aromatic hydrocarbons [15,16], and the manufacture of sulfuric acid [17,18], are also able to catalyze oxidations of sulfides [19,20]. In heterogeneous systems, the VO_x species are typically deposited as a thin layer onto an oxide support such as SiO₂, Al₂O₃, TiO₂, or ZrO₂ [20]. Numerous techniques have been employed to characterize supported VO_x catalysts including Raman, EXAFS, ⁵¹V NMR, IR, and UV–vis diffuse reflectance spectroscopy [13,21–23]. These techniques have shown that several different types of VO_x species can form on the support surface depending on the extent of V loading and dispersion of the V species. It is most commonly believed that at low vanadium loadings the vanadium oxide species exist as isolated VO₄ tetrahedra, consisting of a terminal V=O bond and oxygen bonds to the support [22]. As the vanadium loading increases, polymeric surface VO_x species form a monolayer on the support surface. Additional vanadium beyond monolayer coverage results in the formation of crystalline V₂O₅ [24]. The types

* Corresponding author. Tel.: +1 802 656 0270; fax: +1 802 656 8705.

E-mail address: christopher.landry@uvm.edu (C.C. Landry).

¹ Present address: RTI International, Center for Energy Technology, 3040 Cornwallis Road, Research Triangle Park, NC 27709, United States.

of vanadium species present on the support surface have been shown to affect the activity and selectivity of supported vanadium oxide catalysts in various oxidative processes [14,25,26].

Although a mechanism for the gas phase oxidation of various organic molecules using O_2 catalyzed by V_2O_5 and supported vanadium oxide species has been proposed [14,22,27], there is little information available regarding possible mechanisms for the oxidation of organic substrates by hydrogen peroxide or alkyl peroxides catalyzed by supported vanadium oxide species. Mechanisms have been proposed for the epoxidation of alcohols and the oxidation of alkenes, alcohols, hydrocarbons, and thioethers with peroxides, catalyzed by peroxovanadium complexes; however, these reactions occurred under homogeneous conditions [28,29]. A mechanism for the hydroxylation of benzene to phenol by VO_x supported on mesoporous silica has recently been proposed based upon the addition of hydrogen peroxide to the vanadium center to form peroxovanadium species that are believed to be the active intermediate in the generation of phenol [30]. This is similar to several mechanisms that have been proposed for homogeneous oxidations catalyzed by vanadium Schiff base complexes using hydrogen peroxide or TBHP as the oxidant [31–34].

Mesoporous silicas are particularly attractive catalytic supports due to their extremely large surface areas and pore volumes, which enable catalytic species to be dispersed on the silica at high loadings. Acid-prepared mesoporous spheres (“APMS”) are a type of mesoporous silica characterized by a spherical particle morphology and a disordered pore structure. We have recently reported that vanadium oxide species supported on APMS (“V-APMS”) are able to catalyze the oxidation of CEES using TBHP as the oxidant in dichloromethane [35]. The oxidation was found to be rapid, with complete conversion of CEES in less than 15 min for samples with a vanadium loading of at least 1 wt%. However, both the partially oxidized sulfoxide (CEESO) and the fully oxidized sulfone (CEESO₂) were produced. In this paper we describe the preparation and use of V-APMS with vanadium loadings of 1–40 wt% for the highly selective oxidation of CEES to CEESO by TBHP in MeCN. Kinetic studies were performed in order to investigate the relationship between the nature of the VO_x species and the ability of the catalyst to oxidize CEES. We also discuss a possible reaction schemes for the V-APMS-catalyzed oxidation of CEES by TBHP.

2. Experimental

2.1. Materials and methods

Powder X-ray diffraction experiments were performed using a Scintag X1 θ – θ diffractometer equipped with a Peltier (solid-state thermoelectrically cooled) detector using $Cu K\alpha$ radiation. N_2 physisorption isotherms were obtained on a Micromeritics TriStar 3000 instrument. Samples were heated at 150 °C under N_2 overnight prior to measurement. Surface areas and pore size distributions were calculated from the BET and the BJH methods, respectively [36,37]. Elemental analysis of V-APMS was performed by Robertson Microlit (Madison,

NJ) using ICP-AES to determine V loading concentrations. All chemicals were obtained by Sigma–Aldrich and used as received.

2.2. Synthesis of APMS

Cetyltrimethylammonium bromide (18 g, 0.040 mol) was dissolved in a solution of water (396.0 g), EtOH (100%, 111.0 g, 2.41 mol), and concentrated HCl (39.6 wt%, 44.5 g, 0.445 mol). Tetraethoxysilane (TEOS) (40.0 g, 192 mmol) was added and the solution was stirred for 5 min. NaF (47.6 g of a 0.5 M solution, 23.8 mmol) was then added and after approximately 80 s of stirring the solution turned opaque and was immediately transferred to a 1 L Teflon bottle. The mixture was then heated at 373 K for 60 min. After cooling to room temperature, the precipitate was collected by filtration, washed with distilled water and EtOH, and allowed to dry overnight. The APMS was then calcined in air using the following calcination profile: 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.

2.3. Synthesis of V-APMS

The vanadium-doped APMS samples were prepared by a wet-impregnation method. APMS (2.0 g) was added to aqueous solutions of NH_4VO_3 of various concentrations that would result in V-APMS samples containing 1–40 wt% vanadium. The mixture was stirred until dry and calcined using the calcination profile previously described, in order to ensure that the V was fully oxidized. The V-APMS samples were stored in a vacuum oven at 110 °C prior to use in the oxidation studies.

2.4. Catalytic oxidation of CEES

The liquid-phase oxidation of CEES was performed at atmospheric pressure at temperatures ranging from 0 to 50 °C. For each reaction CEES (5.0 μ L, 42.9 μ mol) and 1,2,4-trimethylbenzene (1.0 μ L, 7.5 μ mol), an internal standard, were added to a vial containing MeCN (3.0 mL). The solid catalyst or control solid (APMS, V_2O_5 , or V-APMS, 20 mg) was then added and the vials were placed in an ice or oil bath held at the appropriate temperature. After 30 min, TBHP (7.0 μ L, 6 M in decane determined by iodometric titration, 42 μ mol) was added. The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 μ m Millipore filter. The filtrate was analyzed by gas chromatography on a HP 5890 gas chromatograph equipped with an FID detector using a HP-5 column (J&W Scientific, 15 m \times 0.32 cm) to quantify the concentrations of the reactants and products by peak areas. The identity of the products was confirmed using an Agilent model 6890 gas chromatograph attached to an Agilent 5973 MS detector with a HP-5 column.

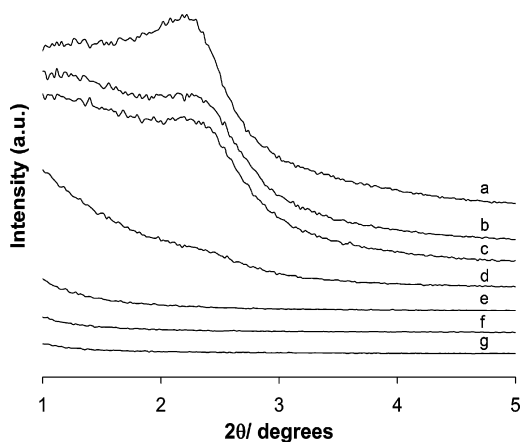


Fig. 1. Low-angle X-ray diffraction spectra of (a) APMS, (b) 1V-APMS, (c) 2V-APMS, (d) 7V-APMS, (e) 20V-APMS, (f) 40V-APMS, and (g) V_2O_5 .

2.5. Determination of the rate law and rate constants

The rate law was determined using the initial rates method and \ln - \ln plots [5]. The reactions were performed at 0°C and data points were collected at CEES conversions that did not exceed 15%. A typical set of experiments is described here. To determine the order of the reaction with respect to CEES, vials containing CH_3CN (3.0 mL), 1,2,4-trimethylbenzene ($1.0\ \mu\text{L}$, $7.5\ \mu\text{mol}$), 1V-APMS (20 mg), and varying amounts of CEES (1.5 – $6.0\ \mu\text{L}$, 12.9 – $51.5\ \mu\text{mol}$) were prepared. TBHP ($7\ \mu\text{L}$, 6 M in decane, $42\ \mu\text{mol}$) was added to each vial and the formation of CEESO was followed using the procedure previously described. The order with respect to TBHP was determined by a similar method, but the amount of CEES was held constant ($5.0\ \mu\text{L}$, $42.9\ \text{mmol}$) and the concentration of TBHP was varied (7.0 – $28.0\ \mu\text{L}$, 42 – $168\ \mu\text{mol}$). The order with respect the catalyst was determined by holding the concentrations of CEES ($5.0\ \mu\text{L}$, $42.9\ \mu\text{mol}$) and TBHP ($7.0\ \mu\text{L}$, 6 M in decane, $42\ \mu\text{mol}$) constant and varying the amount of catalyst used between 5 and 20 mg. Initial rates for the reactions were determined from a plot of [CEESO] versus time. The reaction orders were determined by plotting \ln of the concentration of CEES, TBHP, or moles of catalyst versus \ln of the initial rates and finding the slope of the line.

2.6. Catalyst stability

The initial rates for 1V-APMS catalyzed oxidation of CEES by TBHP were found at 0°C according to the reaction conditions described in Section 2.4. After the reaction reached comple-

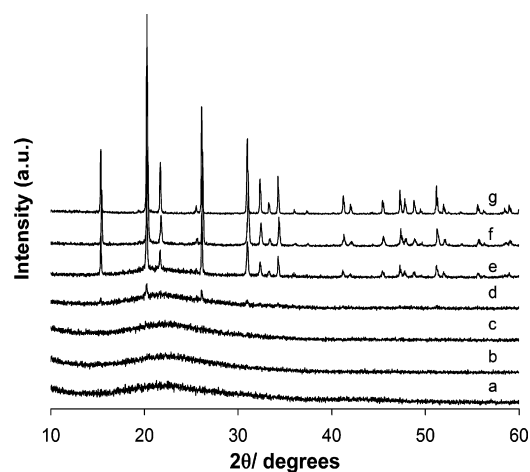


Fig. 2. High-angle X-ray diffraction spectra of (a) APMS, (b) 1V-APMS, (c) 2V-APMS, (d) 7V-APMS, (e) 20V-APMS, (f) 40V-APMS, and (g) V_2O_5 .

tion, the catalyst was recovered by filtration through a syringe equipped with a $0.22\ \mu\text{m}$ Millipore filter. The recovered catalyst was rinsed several times with acetonitrile, heated at 110°C in a vacuum oven overnight, and then reused in the oxidation of CEES under the same reaction conditions. This process was repeated twice.

3. Results and discussion

3.1. Physical characterization of V-APMS

V-doped APMS catalysts with vanadium loadings of 1–40 wt% were prepared using a wet-impregnation method, which involved the addition of APMS to an aqueous solution containing NH_4VO_3 , evaporation to dryness, and calcination of the resulting V-doped solid in order to immobilize the vanadium oxide species on the silica surface by an esterification reaction with the hydroxyl groups on the silica. The effects of this process on the type of V species present on the silica surface and the physical properties of the catalysts were determined by powder X-ray diffraction (XRD) and N_2 physisorption experiments. Materials are designated by $n\text{V-APMS}$, where n is the wt% of V loaded onto the support (chemical analysis indicated that the amount of V in the catalyst was approximately the same as the amount in the loading solution).

The XRD spectra of APMS, V-APMS, and V_2O_5 are shown in Figs. 1 and 2. The two notable features of the spectrum of undoped APMS are a broad peak in the low-angle region at $2\theta = 2.4^\circ$, which is indicative of a disordered mesoporous

Table 1
Vanadium content and physical properties of catalysts

| Catalyst | V content (wt%) | Surface area (m^2/g) | Pore volume (cm^3/g) | Pore diameter (\AA) |
|----------|-----------------|--|--|--------------------------------|
| APMS | – | 870 | 1.17 | 42 |
| 1V-APMS | 0.92 | 821 | 0.89 | 33 |
| 2V-APMS | 1.84 | 806 | 0.91 | 33 |
| 7V-APMS | 6.82 | 382 | 0.43 | 33 |
| 20V-APMS | 19.48 | 175 | 0.23 | – |
| 40V-APMS | 40.96 | 28 | 0.12 | – |

material, and another broad peak centered at $2\theta = 23^\circ$ which can be attributed to the amorphous nature of the silica support. The intensity of the low angle peak decreases with increasing vanadium loadings, resulting in complete loss of the peak in 20- and 40V-APMS. Similar reductions in peak intensity have been observed after the deposition of molecules inside the pores of mesoporous silica and have been attributed to the presence of scattering material in the pores, which reduces the scattering contrast between the pores and the pore wall and results in decreased peak intensities [38]. At low V loadings (less than 2 wt%), the XRD spectra of V-APMS samples were identical to undoped APMS in the high angle region, indicating that the V species were well dispersed on the support. However, several new peaks developed in the high angle region at V loadings of 7 wt%, which increased in intensity as a function of V loading. A comparison of the XRD spectra of V-APMS and V_2O_5 showed that the developing peaks corresponded to the formation of crystalline V_2O_5 . Consistent with our previous results [35], these XRD results indicate that well-dispersed VO_4 species were deposited on the pore walls of the silica at low vanadium loadings, but at higher loadings V_2O_5 was formed within the pores of APMS.

The results from N_2 physisorption experiments (Table 1) showed that the surface areas, pore volumes, and pore diameters of V-APMS decreased as a function of V loading. These changes can be attributed to three factors: (1) Si–O–Si bond cleavage and the formation of Si–OH groups at the pore surfaces when exposed to an aqueous solution, (2) anchoring of VO_x species to the pore walls, and (3) blockage or filling of the pores by the V species [25,35,39–42]. Although all three of these factors can contribute to a decrease in the surface area and pore volume of the catalysts, the extent to which they affect the physical properties of the catalysts differs greatly. For instance, although it has been shown that exposure to water results in a decrease in the pore volume and surface area of APMS [39], exposure to water cannot be the main source of the large decreases in pore volume and surface area that were observed as the V loading increased, since all of the catalysts were prepared by the same method of wet impregnation. Therefore, anchoring of VO_x species to the

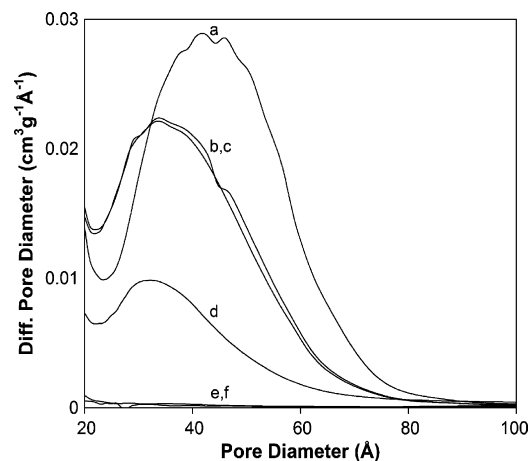


Fig. 3. Average pore size distributions of (a) APMS, (b) 1V-APMS, (c) 2V-APMS, (d) 7V-APMS, (e) 20V-APMS, and (f) 40V-APMS.

pore walls and the filling or blockage of the pore walls by the VO_x species must be the primary sources of the changes in physical properties. Further information regarding the sources of the physical changes that occur upon V loading can be observed in Fig. 3, which shows the effect of V loading on the average pore diameter, as well as the XRD results shown in Fig. 1. 1V-APMS and 2V-APMS had nearly identical physical properties and the surface areas and pore volumes of these catalysts were only slightly lower than the undoped material, providing support for the conclusion that the V in these solids is isolated on the silica surface. The large drop in surface area and pore volume that occurred at V loadings of 7 wt% and higher was most likely caused by blockage or filling of the pores of APMS by crystalline V_2O_5 , which was shown to be present by XRD. This is consistent with previous experiments on similar metal-doped mesoporous silica.

3.2. Catalytic oxidation of CEES

Fig. 4 shows the conversion of CEES to CEESO and CEESO₂ by TBHP in MeCN with various V-APMS species as the cata-

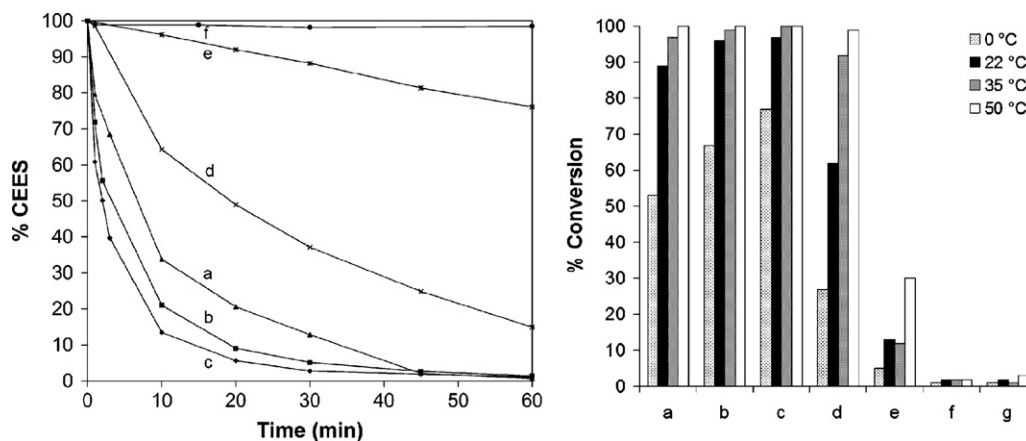


Fig. 4. Oxidation of CEES with TBHP using the catalysts (a) 1V-APMS, (b) 2V-APMS, (c) 7V-APMS, (d) 20V-APMS, (e) 40V-APMS, and (f) APMS. The left panel shows the conversion as a function of time at 22 °C. In the right panel, the conversion at 60 min is shown as a function of temperature for each catalyst, and the activity of V_2O_5 is included for comparison in the last series (g). All catalysts showed selectivities for CEESO of at least 96%. Reaction conditions: 0.0143 M CEES, 0.0025 M 1,2,4-trimethyl benzene, 0.014 M TBHP in MeCN.

lysts as a function of time. The V-APMS catalysts were found to be active and highly selective in the oxidation of CEES to CEESO at temperatures ranging 0–50 °C and formation of CEESO was nearly quantitative for all of the V-APMS catalysts. The oxidation did not occur to a significant extent with undoped APMS, with less than 7% CEES oxidized after 24 h at 22 °C. Therefore, the surface-bound vanadium oxide species must have been responsible for the observed catalytic activity of V-APMS. These results also showed that CEES was more rapidly oxidized as the V loading increased from 1 to 7 wt%, which is consistent with the idea that the number of catalytically active VO_x species increases as the vanadium loading increases, allowing the reaction to reach completion in less time. However, further increases in vanadium loadings from 7 to 40 wt% resulted in V-APMS catalysts that were less effective in the oxidation of CEES as a function of V loading. There are several factors that may contribute to the reaction becoming slower at high vanadium loadings. For example, the N_2 physisorption data revealed that the surface areas, pore volumes, and pore diameters decreased substantially as the V loading increased, due to filling of the pores of silica with VO_x species and ultimately V_2O_5 (Fig. 2). Although 20V- and 40V-APMS contained a higher percentage of vanadium by weight, some of the VO_x species were inaccessible to catalyze the reaction since they were located in the bulk of the V_2O_5 being formed, which ultimately resulted in fewer available catalytic active sites. Additionally, it has been reported that reaction rates and product selectivities are higher for supported vanadium oxide catalysts composed of dispersed VO_4 than V_2O_5 in some oxidative processes [43,44]. Thus, formation of V_2O_5 at high V loadings clearly had a detrimental effect on the oxidative capacity of the V-APMS catalysts in this reaction.

Estimated turnover numbers (TONs) and turnover frequencies (TOFs) for the various catalysts are given in Table 2. Care must be taken in the interpretation of these results, however, since these values were calculated from the total moles of vanadium in the catalyst and were based upon the assumption that all of the vanadium sites were accessible to catalyze the reaction. At low V loadings the vanadium oxide species appeared to be well-dispersed and the calculated TONs and TOFs may accurately reflect the true values. However, characterization of

Table 2
Estimated turnover numbers (TONs)^a and turnover frequencies (TOFs)^b for V-APMS

| Catalyst | TON ^a | TOF (h ⁻¹) ^b | | | |
|------------------------|------------------|-------------------------------------|----------|----------|----------|
| | | At 0 °C | At 22 °C | At 35 °C | At 50 °C |
| 1V-APMS | 12.0 | 6.3 | 10.6 | 11.5 | 11.9 |
| 2V-APMS | 6.0 | 4.0 | 5.7 | 5.8 | 5.9 |
| 7V-APMS | 1.6 | 1.2 | 1.6 | 1.6 | 1.6 |
| 20V-APMS | 0.6 | 0.2 | 0.3 | 0.5 | 0.6 |
| 40V-APMS | 0.3 | 0.01 | 0.03 | 0.03 | 0.08 |
| V_2O_5 | 0.2 | 0.002 | 0.004 | 0.002 | 0.006 |

^a Turnover numbers were calculated from the moles of CEES oxidized per mole of vanadium.

^b Turnover frequencies (TOFs) were calculated from the moles of CEES oxidized per moles of vanadium per hour.

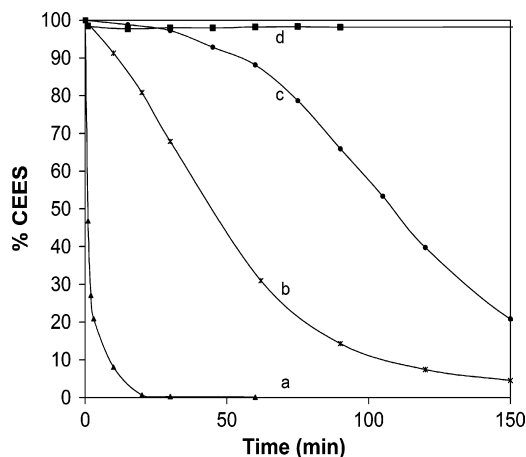


Fig. 5. Oxidation of CEES with TBHP at 50 °C with (a) 1V-APMS, (b) 40V-APMS, (c) V_2O_5 , and (d) APMS. Reaction conditions: 0.0143M CEES, 0.0025 M 1,2,4-trimethyl benzene, 0.014 M TBHP in MeCN, 20 mg catalyst.

the catalysts by N_2 physisorption and XRD revealed that the pores of the silica were blocked or filled by the vanadium oxide species as the vanadium loading increased and at V loadings of 7 wt% crystalline V_2O_5 clusters began to form. Therefore, it is clear that some of the V species were not accessible to catalyze the oxidation of CEES and the reported TONs and TOFs for the catalysts with higher vanadium loadings are underestimated.

Unsupported V_2O_5 was also investigated for its ability to catalyze the oxidation of CEES. After 60 min, it did not appear to be catalytically active. However, unlike undoped APMS, which was not able to oxidize CEES to a significant extent even over an extended period of time, 91% of the CEES was oxidized exclusively to CEESO after 24 h when V_2O_5 was added to the reaction mixture. A comparison of the oxidation of CEES by TBHP in the presence of APMS, V-APMS, and V_2O_5 at 50 °C (Fig. 5) revealed that after a brief induction period the rate of CEES oxidation gradually increased with time for both V_2O_5 and 40V-APMS before decreasing as the reaction reached completion, resulting in a sigmoidal curve. This type of curve is characteristic of oxidations involving free radical chain mechanisms [45,46]. The possibility of a free radical mechanism was investigated by the addition of 0.05 equivalents of hydroquinone, a free radical scavenger, to the reaction mixtures of 1V-APMS and V_2O_5 [47]. There was no effect on 1V-APMS catalyzed oxidation of CEES, but the induction period was increased to 240 min with V_2O_5 . These results suggest that when V_2O_5 is the catalyst, the reaction proceeds through a free radical mechanism, whereas when isolated VO_x species act as the catalyst a different process is in operation. The similarity of the plots for V_2O_5 and 40V-APMS suggest that the latter sample contains a significant amount of crystalline V_2O_5 , which is supported by the results of powder XRD experiments as well as EDAX studies.

One of the major advantages of heterogeneous catalysts is the ability to easily recover and reuse the catalyst. It is also important that the catalytic species resist leaching into the reaction mixture. The stability of 1V-APMS was studied by recovering the catalyst by filtration after the oxidation of CEES reached

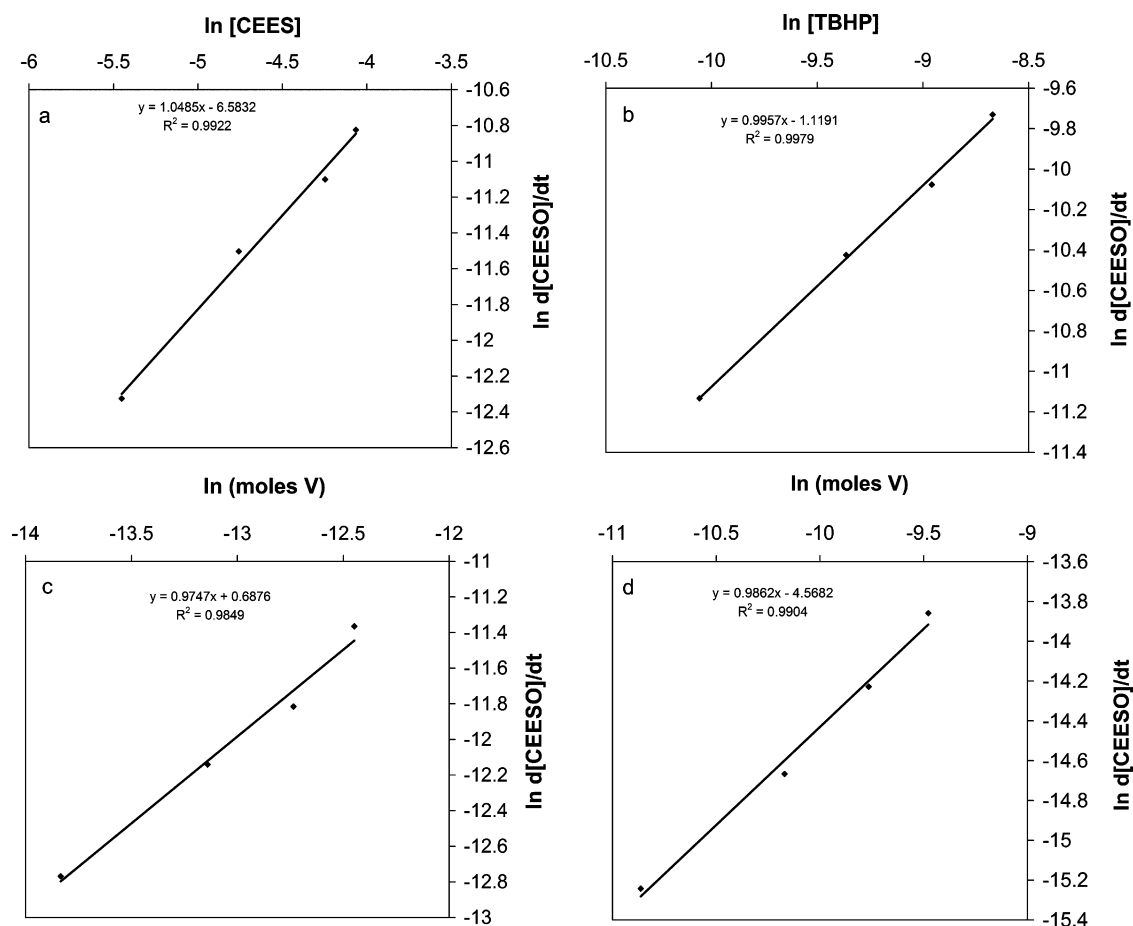


Fig. 6. \ln – \ln plots showing the initial rate of the oxidation of CEES as a function of (a) [CEES], (b) [TBHP], and moles of V when (c) 2V-APMS and (d) 20V-APMS were used as the catalysts.

completion, reusing the catalyst in two subsequent reactions, and determining the initial rates for the reaction for each run. The initial rates for CEES oxidation after the first, second, and third runs were $1.27 \pm 0.08 \times 10^{-5}$, $1.30 \pm 0.04 \times 10^{-5}$, and $1.21 \pm 0.06 \times 10^{-5} \text{ M s}^{-1}$. These values reveal that the reaction rate remained unchanged after three uses, which suggests that leaching of the catalytic species from the silica support did not occur. Under these reaction conditions, V-APMS was stable and could be used repeatedly without an adverse affect on the CEES oxidation rate.

3.3. Kinetic studies

In order to obtain kinetic information about the oxidation reaction, and to further compare the reaction when V-APMS with various V loadings were used as the catalyst, a series of reactions were performed using the same catalysts at various temperatures. The experimental rate law for oxidation of CEES by TBHP was determined by finding the order of the reaction with respect to CEES, TBHP, and V-APMS from \ln – \ln plots. The slopes of the linear regression lines of the \ln – \ln plots shown in Fig. 6 clearly show that the reaction was first order in both CEES and TBHP. The reaction order with respect to V was also determined for both 2V-APMS and 20V-APMS. Although it was

difficult to obtain accurate information regarding the reaction order for a heterogeneous catalyst using this method, the data strongly suggested that the reaction was also first order in V-APMS, which was in agreement with results obtained for the oxidation of CEES catalyzed by the phosphovanadomolybdate polyoxometalate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ supported on porous carbon [5]. These results led to the experimental rate law shown in the following equation:

$$\frac{d[\text{CEESO}]}{dt} = k[\text{CEES}][\text{TBHP}][\text{V-APMS}] \quad (1)$$

Since there was no evidence that V species were leaching from the solid during the reaction, the concentration of V-APMS was regarded as a constant for each reaction. This allowed the rate law to be further simplified to the pseudo-second-order expression shown in Eq. (2), where $k_{\text{obs}} = k[\text{V-APMS}]$.

$$\frac{d[\text{CEESO}]}{dt} = k_{\text{obs}}[\text{CEES}][\text{TBHP}] \quad (2)$$

The observed rate constants k_{obs} for V-APMS reported in Table 2 show that the reaction rate increased as a function of V loading up to 7 wt% V, after which it decreased. A comparison of k_{obs} for 1V-APMS and 2V-APMS revealed that the rate constants were directly proportional to the V loading, which was

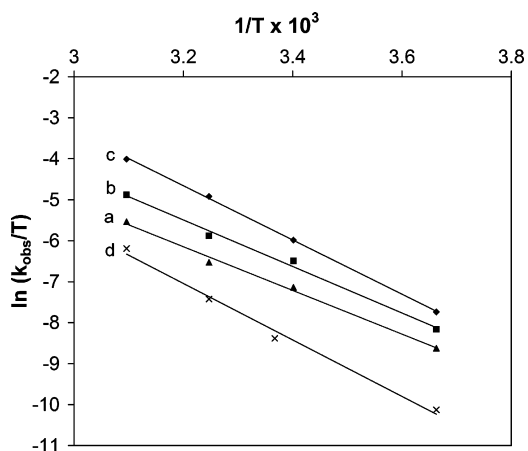


Fig. 7. Eyring plots for (a) 1V-APMS, (b) 2V-APMS, (c) 7V-APMS, and (d) 20V-APMS. Reaction conditions: 0.00429–0.0172 M CEES, 0.042–0.168 M TBHP, 5–20 mg V-APMS.

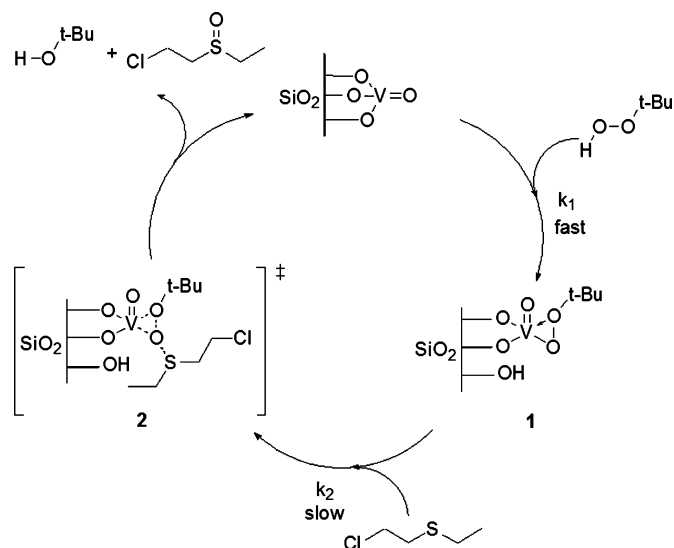
consistent with the formation of well-dispersed VO_4 species on APMS below monolayer surface coverage. At low loadings, isolated VO_4 species could form on the silica surface without the formation of V_2O_5 or significant blocking of the pores (which would render some of the V sites inaccessible), resulting in a value of k_{obs} for 2V-APMS that was approximately twice as large as that of 1V-APMS. At higher V loadings the observed rate constants were not proportional to the V loading, which could be attributed to a decrease in the number of accessible VO_4 active sites and the formation of catalytically less active crystalline V_2O_5 within the pores of the silica.

Eyring plots were prepared to determine activation parameters for the V-APMS catalysts (Fig. 7 and Table 3). The negative ΔS^\ddagger values for the catalysts indicate that the reaction passes through an ordered transition state. The activation enthalpies obtained from these plots further illustrate the relationship between the type of VO_x species present on the silica and the ability of V-APMS to catalyze the oxidation of CEES as the V species changed from isolated VO_4 to bulk V_2O_5 . The two catalysts with highly dispersed vanadyl species, 1V-APMS and 2V-APMS, had statistically indistinguishable enthalpies of activation ($\Delta H^\ddagger = 10.7 \pm 0.6$ and 11.1 ± 0.6 kcal mol $^{-1}$). This suggested that the reaction proceeded by the same mechanism for both of the catalysts and that the differences in the observed reaction rates was caused by the number of active sites available on the silica support. The enthalpies of activation were larger for the samples that contained V_2O_5 ($\Delta H^\ddagger = 13.2 \pm 0.5$ and 13.7 ± 0.4 kcal mol $^{-1}$ for 7V-APMS and 20V-APMS), sig-

Table 3
Observed rate constants and activation parameters for the oxidation of CEES using V-APMS catalysts^a

| Catalyst | k_{obs} (M $^{-1}$ s $^{-1}$) | | | | ΔH^\ddagger (kcal mol $^{-1}$) | ΔS^\ddagger (cal K $^{-1}$ mol $^{-1}$) |
|----------|---|---------------|---------------|---------------|---|--|
| | At 0 °C | At 22 °C | At 35 °C | At 50 °C | | |
| 1V-APMS | 0.049 ± 0.002 | 0.247 ± 0.018 | 0.451 ± 0.023 | 1.325 ± 0.069 | 10.7 ± 0.6 | −25.6 ± 2.3 |
| 2V-APMS | 0.078 ± 0.003 | 0.448 ± 0.020 | 0.863 ± 0.019 | 2.455 ± 0.202 | 11.1 ± 0.6 | −22.6 ± 1.4 |
| 7V-APMS | 0.120 ± 0.004 | 0.744 ± 0.018 | 2.253 ± 0.048 | 5.876 ± 0.071 | 13.2 ± 0.5 | −14.2 ± 0.7 |
| 20V-APMS | 0.011 ± 0.001 | 0.063 ± 0.004 | 0.184 ± 0.009 | 0.666 ± 0.070 | 13.7 ± 0.4 | −17.4 ± 1.1 |

^a Reaction conditions: [CEES] = 14.3 mM, [TBHP] = 14 mM, 2.5 mM 1,2,4-trimethyl benzene (internal standard), 20 mg catalyst.



Scheme 1. Possible reaction scheme for the catalytic oxidation of CEES by TBHP on V-APMS.

nifying that the decrease in k_{obs} values at high V loadings was not exclusively the result of fewer accessible active sites, but also involved a different type of catalytic species and reaction mechanism. The smaller ΔH^\ddagger for V-APMS with low V loadings also indicated that V-APMS with well-dispersed VO_4 species was better able to catalyze the oxidation of CEES than V-APMS containing V_2O_5 .

3.4. Mechanistic considerations

A possible reaction scheme for the oxidation of CEES by V-APMS with TBHP is shown in Scheme 1. Several mechanisms have been proposed for homogeneous catalytic sulfoxidations using vanadium Schiff base complexes that are based upon electrophilic activation of the peroxide followed by nucleophilic attack by the sulfur atom of the substrate [32,34]. A reaction scheme consistent with this type of peroxide activation begins with the formation of an electrophilically activated *t*-butyl peroxyvanadium species (1) as has been proposed by Lee for the hydroxylation of benzene by VO_x supported on silica [30]. Nucleophilic attack by the sulfur atom of CEES on the electrophilically activated oxygen results in the formation of the transition state 2 through which direct transfer of an oxygen atom from the coordinated *tert*-butyl hydroperoxy group to the sulfur atom of CEES can occur to yield CEESO and *tert*-butanol (TBA). This step would account for the negative ΔS^\ddagger values due

to the more highly ordered transition state **2**. The rate limiting step in this proposed mechanism is the second step in which **1** reacts with CEES. The overall rate of formation of CEESO is given by Eq. (3) and the concentration of **1** can be expressed by Eq. (4). Substitution of [1] into Eq. (3) results in the rate expression given in Eq. (5), which is consistent with the experimentally determined rate law (Eq. (1)):

$$\text{rate} = k_2[1][\text{CEES}] \quad (3)$$

$$[1] = k_1[\text{V-APMS}][\text{TBHP}] \quad (4)$$

$$\text{rate} = k_1k_2[\text{CEES}][\text{TBHP}][\text{V-APMS}] \quad (5)$$

4. Conclusions

The extent of V loading and therefore the nature of vanadium oxide species present in V-APMS was found to have a significant effect on both the physical properties of V-APMS and its ability to catalyze the oxidation of CEES by TBHP. At low V loadings, the vanadium was predominantly present as isolated VO₄ and the V-doped APMS catalysts retained much of the large surface area and pore volumes observed for the undoped substrate. At higher V loadings V₂O₅ was formed, filling the pores of the substrate and causing large decreases in the porosities of V-APMS. All of the catalysts were found to be highly selective in the partial oxidation of CEES to CEESO regardless of extent of V loading or reaction temperature. The stability of 1V-APMS was also studied and it was demonstrated that there was no change in the initial rate of the reaction after repeated use of the catalyst. The results of the kinetic studies showed that the activation parameters were different for samples containing bulk V₂O₅, which involves a free radical mechanism, and those with isolated VO₄ species, indicating that the reaction proceeded through different mechanisms for V-APMS with high and low V loadings. V-APMS samples with highly dispersed VO₄ species were more effective catalysts than V-APMS containing V₂O₅ for the oxidation of CEES, as indicated by their lower activation enthalpies. CEES oxidation by V₂O₅ appears to involve a radical chain mechanism, but CEES oxidation by V-APMS with lower V loadings does not seem to proceed through a radical process. A possible mechanism was proposed for the reaction catalyzed by isolated VO_x species.

Acknowledgement

This work was funded by the Army Research Office under grant number W911NF-06-1-0263.

References

- [1] J. Hirade, A. Ninomiya, J. Biochem. 37 (1950) 19–34.
- [2] V. Hulea, P. Moreau, F. Di Renzo, J. Mol. Catal. A: Chem. 111 (1996) 325–332.
- [3] V. Hulea, F. Fajula, J. Bousquet, J. Catal. 198 (2001) 179–186.
- [4] R.D. Gall, M. Faraj, C.L. Hill, Inorg. Chem. 33 (1994) 5015–5021.
- [5] R.D. Gall, C.L. Hill, J.E. Walker, J. Catal. 159 (1996) 473–478.
- [6] N.M. Okun, T.M. Anderson, C.L. Hill, J. Mol. Catal. A: Chem. 197 (2003) 283–290.
- [7] N.M. Okun, J.C. Tarr, D.A. Hilleshiem, L. Zhang, K.I. Hardcastle, C.L. Hill, J. Mol. Catal. A: Chem. 246 (2006) 11–17.
- [8] J.T. Rhule, W.A. Neiwert, K.I. Hardcastle, B.T. Do, C.L. Hill, J. Am. Chem. Soc. 123 (2001) 12101–12102.
- [9] D.P. Riley, M.R. Smith, P.E. Correa, J. Am. Chem. Soc. 110 (1988) 177–180.
- [10] S.E. Martin, L.I. Rossi, Tetrahedron Lett. 42 (2001) 7147–7151.
- [11] E. Boring, Y.V. Geletii, C.L. Hill, J. Mol. Catal. A: Chem. 176 (2001) 49–63.
- [12] A. Marques, M. Marin, M.-F. Ruasse, J. Org. Chem. 66 (2001) 7588–7595.
- [13] B. Grzybowska-Świerkosz, Top. Catal. 11/12 (2002) 23–42.
- [14] B.M. Weckhuysen, D.E. Keller, Catal. Today 78 (2003) 25–46.
- [15] H. Roussel, B. Mehlomakulu, F. Belhadj, E. Van Steen, J.M. Millet, J. Catal. 205 (2002) 97–106.
- [16] B. Lucke, K.V. Narayana, A. Martin, K. Jahnisch, Adv. Synth. Catal. 346 (2004) 1407–1424.
- [17] V.I. Pärvulescu, C. Paun, V. Pärvulescu, M. Alifanti, I. Giakoumelou, S. Boghosian, S.B. Rasmussen, K.M. Eriksen, R. Fehrmann, J. Catal. 225 (2004) 24–36.
- [18] O.B. Lapina, B.S. Bal'zhinimaeva, S. Boghosian, K.M. Eriksen, R. Fehrmann, Catal. Today 51 (1991) 469–479.
- [19] N. Moussa, J.M. Fraile, A. Ghorbel, J.A. Mayoral, J. Mol. Catal. A: Chem. 255 (2006) 62–68.
- [20] N.N. Trukhan, A.Y. Derevyankin, A.N. Shmakov, E.A. Paukshtis, O.A. Kholdeeva, V.N. Romannikov, Micropor. Mesopor. Mater. 44/45 (2001) 603–608.
- [21] G.C. Bond, S.F. Tahir, Appl. Catal. 71 (1991) 1–31.
- [22] I.E. Wachs, Catal. Today 100 (2005) 79–94.
- [23] H. Tian, E.I. Ross, I.E. Wachs, J. Phys. Chem. B 110 (2006) 9593–9600.
- [24] A.M. Turek, I.E. Wachs, E. Canio, J. Phys. Chem. 96 (1992) 5000–5007.
- [25] B. Solsona, T. Blasco, J.M. López Nieto, L.M. Peña, F. Rey, A. Vidal-Moya, J. Catal. 203 (2001) 443–542.
- [26] K. Lemke, H. Ehrlich, U. Lohse, H. Berndt, K. Jahnisch, Appl. Catal. A 243 (2003) 41–51.
- [27] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41–59.
- [28] V. Conte, F. Di Furia, G. Licini, Appl. Catal. A 157 (1997) 335–361.
- [29] A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 625–628.
- [30] C.-H. Lee, T.-S. Lin, C.-Y. Mou, J. Phys. Chem. C 111 (2007) 3873–3882.
- [31] J. Hartung, M. Greb, J. Organomet. Chem. 661 (2002) 67–84.
- [32] Q. Zeng, H. Wang, W. Weng, W. Lin, Y. Gao, X. Huang, Y. Zhao, N. J. Chem. 29 (2005) 1125–1127.
- [33] D.A. Cogan, G. Liu, K. Kim, B.J. Backes, J.A. Ellman, J. Am. Chem. Soc. 120 (1998) 8011–8019.
- [34] D. Balcells, F. Maseras, A. Lledos, J. Org. Chem. 68 (2003) 4265–4274.
- [35] C.R. Ringenbach, S.R. Livingston, D. Kumar, C.C. Landry, Chem. Mater. 17 (2005) 5580–5586.
- [36] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309–319.
- [37] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373–380.
- [38] M. Fröba, R. Köhn, G. Bouffaud, O. Richard, G. van Tendeloo, Chem. Mater. 11 (1999) 2858–2865.
- [39] A.C. Sorensen, B.L. Fuller, A.G. Eklund, C.C. Landry, Chem. Mater. 16 (2004) 2157–2164.
- [40] H. Berndt, A. Martin, A. Bruckner, E. Schreier, D. Muller, H. Kosslick, G.-U. Wolf, B. Lucke, J. Catal. 191 (2000) 384–400.
- [41] Y.-M. Liu, Y. Cao, N. Yi, W.-L. Feng, W.-L. Dai, S.-R. Yan, H.-Y. He, K.-N. Fan, J. Catal. 234 (2004) 417–428.
- [42] M. Morey, A. Davidson, H. Eckert, G. Stucky, Chem. Mater. 8 (1996) 486–492.
- [43] A. Khodakov, B. Olthof, A.T. Bell, E. Iglesia, J. Catal. 181 (1999) 205–216.
- [44] M.D. Argyle, K. Chen, A.T. Bell, E. Iglesia, J. Catal. 208 (2002) 139–145.
- [45] A. Sadana, J.R. Katzer, Ind. Eng. Chem. Fundam. 13 (1974) 127–134.
- [46] K. Yogish, N.V.S. Sastri, Ind. Eng. Chem. Res. 27 (1988) 909–915.
- [47] J.T. Thomas, R. Raja, G. Sankar, R.G. Bell, Nature 398 (1999) 227–230.