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ScienceDirect
Journal of Molecular Catalysis A: Chemical 283 (2008) 52–59
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Oxidation of 2-chloroethyl ethyl sulfide using V-APMS

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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 N_2 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 V_2O_5 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 V_2O_5 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 V_2O_5. Finally, a possible reaction scheme for the oxidation of CEES by V-APMS is discussed.

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 O_2. 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 SiO_2, Al_2O_3, TiO_2, or ZrO_2 [20]. Numerous techniques have been employed to characterize supported VO_x catalysts including Raman, EXAFS, ^{51}V 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 VO_4 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 V_2O_5 [24]. The types

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doi:10.1016/j.molcata.2007.11.010

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 peroxovandium 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 ($CEESO_2$) 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 Kα 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 μL, 42.9 μmol) and 1,2,4-trimethylbenzene (1.0 μL, 7.5 μmol), 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 μL, 6 M in decane determined by iodometric titration, 42 μmol) was added. The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 μm 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 × 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.