

Oxidation of a Mustard Gas Analogue Using an Aldehyde/O₂ System Catalyzed by V-doped Mesoporous Silica

Stephanie R. Livingston and Christopher C. Landry

*Department of Chemistry, 82 University Place
University of Vermont, Burlington, VT 05405*

Materials and Methods. Powder X-ray diffraction experiments were performed using a Scintag X1 $\theta - \theta$ diffractometer equipped with a Peltier (solid-state thermoelectrically cooled) detector using Cu K α radiation. N₂ physisorption isotherms were obtained on a Micromeritics TriStar 3000 instrument. Samples were heated at 150 °C under N₂ overnight prior to measurement. Surface areas and pore size distributions were calculated from the BET and the BJH methods, respectively [36,37]. All chemicals, with the exception of HFE-7100 (3M Corporation), were obtained from Sigma Aldrich and used as received. All reactions were performed at room temperature, 21 °C, and the reaction progress was measured using an Agilent model 6890 gas chromatograph attached to Agilent 5973 MS detector using a HP-5 column (J&W Scientific, 15 m x 0.32 cm). Elemental analysis for vanadium content was performed by Robertson Microlit Laboratories (Madison, NJ) using ICP-OES to determine V loading.

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 10 minutes. NaF (47.6 g of a 0.5 M solution, 23.8 mmol) was then added and after approximately 80 seconds of stirring the solution turned opaque and was immediately transferred to a 1 L Teflon bottle. The mixture was then heated at 100 °C for 60 min. After cooling for 30 minutes, 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 10K/min ramp to 823 K and a hold time of 480 min at 823 K before cooling to room temperature.

Synthesis of APMS doped with 0.6 wt% V (I). Vanadium-doped APMS was prepared by a wet impregnation method. APMS (1.0 g) was added to aqueous solutions of NH₄VO₃ that would correspond to V-APMS with final vanadium loadings of approximately 1 wt%. The mixture was stirred until dry and calcined using the calcination profile previously described. The product was heated overnight in a vacuum oven at 110 °C prior to use in the oxidation studies.

Oxidation of CEES in neat aldehydes. CEES (5.0 μ L, 42.9 μ mol) and 1,2,4-trimethylbenzene (1.0 μ L, 2.5 μ mol), an internal standard, were added to a vial containing acetaldehyde, propionaldehyde, or

trimethylacetaldehyde (3.0 mL). For the oxidation catalyzed by **1**, 20 mg of **1** was added to the solution. The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter and the filtrate was analyzed by GC-MS.

Oxidation of CEES in HFE-7100. CEES (5.0 µL, 42.9 µmol) and 1,2,4-trimethylbenzene (1.0 µL, 2.5 µmol) were added to a vial containing HFE-7100 (3.0 mL). 20 mg of the solid (either APMS or **1**) was added to the solution. The reaction was initiated by the addition of the aldehyde (429 or 858 µmol) to the vial. The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter and the filtrate was analyzed by GC-MS.

Oxidation of CEES in the presence of hydroquinone. CEES (5.0 µL, 42.9 µmol) 1,2,4-trimethylbenzene (1.0 µL, 2.5 µmol), hydroquinone (0.85 and 2.1 µmol) and 20 mg **1** were added to a vial containing acetonitrile (3.0 mL). The reaction was initiated by the addition of propionaldehyde (78.8 µL, 1.073 mmol) to the solution. The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter and the filtrate was analyzed by GC-MS.

Oxidation of propionaldehyde in the presence of hydroquinone. Propionaldehyde (31.5 µL, 429 µmol), 1,2,4-trimethylbenzene (1.0 µL, 2.5 µmol), and hydroquinone (0.85 and 2.1 µmol) were added to a vial containing acetonitrile (3.0 mL). 20 mg of **1** was added to the vial, the resulting mixture was stirred, aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter, and the filtrate was analyzed by GC-MS.

Oxidation of propionaldehyde. (31.5 µL, 429 µmol) and 1,2,4-trimethylbenzene (1.0 µL, 2.5 µmol) were added to a vial containing HFE-7100 (3.0 mL). 20 mg of **1** was then added to the solution followed by propionaldehyde (31.5 µL, 429 µmol). The resulting mixture was stirred and aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter and the filtrate was analyzed by GC-MS. The reaction was also performed in the absence of **1**.

Oxidation of CEES by peracetic acid. CEES (5.0 µL, 42.9 µmol), 1,2,4-trimethylbenzene (1.0 µL, 2.5 µmol), (0.85 and 2.1 µmol) and **1** (20 mg) were added to a vial containing HFE-7100 (3.0 mL). Peracetic acid (42.9 µmol) was added to the reaction mixture and stirred. Aliquots were removed and filtered through a syringe equipped with a 0.22 µm Millipore filter and the filtrate was analyzed by GC-MS. The reaction was also performed in the absence of **1**.

V Leaching Studies. 0.6V-APMS (40 mg) was stirred in a vial containing 6.0 mL of acetaldehyde, propionaldehyde, or trimethylacetaldehyde for 1 hr. The solid was then collected by filtration, dried, and sent for analysis by ICP-OES. Similarly, **1** (40 mg) was stirred in a vial containing 6.0 mL of HFE and 858 µmol of acetaldehyde, propionaldehyde, or trimethylacetaldehyde for 1 hr followed by filtration, drying, and ICP-OES analysis.

Table S1. Physical properties of catalyst

Catalyst	V Content (wt%)	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (Å)
APMS	0	888	0.91	30
0.6V-APMS	0.64	794	0.78	29

Table S2. Vanadium content of **1** after leaching tests

Solvent	% V $\pm$ 0.04%
As synthesized	0.64
Neat acetaldehyde	0.61
Neat trimethylacetaldehyde	0.38
Neat propionaldehyde	0.46
Acetaldehyde/HFE	0.61
Trimethylacetaldehyde/HFE	0.59
Propionaldehyde/HFE	0.59

Figure S1. Powder X-ray diffraction patterns for: (a) APMS, (b) **1**, and (c) V_2O_5 .

