

## Supporting Information

### Evaluation of nanostructured vanadium (V) oxide in catalytic oxidations

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**General.** Solvents, reagents, starting materials, and product GC standards were purchased from commercial sources and used without purification. Conventional vanadium (V) oxide for comparison studies was purchased from Sigma-Aldrich (USA) (cat. #: 204854, Lot #: MKBH8550V). Gas Chromatograph (GC) analyses were conducted using an Agilent Technologies 7890A GC equipped with an Agilent

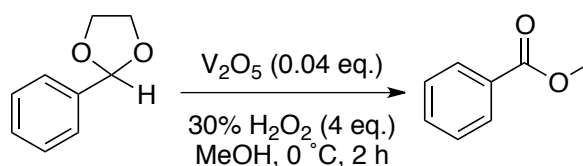
Technologies G4513A autosampler and a Flame Ionization Detector (FID). The GC was equipped with a 30 m x 0.32 mm x 0.25  $\mu\text{m}$  Agilent J&W GC column with an HP-5 stationary phase (cat. #: 19091J-413). GC analyses were carried out within the following parameters: inlet temperature: 250  $^{\circ}\text{C}$ ; 20:1 split at 130 mL/min; column flow: 6.5 mL/min, constant pressure; carrier gas: helium; FID temperature: 300  $^{\circ}\text{C}$ ; temperature program: 100  $^{\circ}\text{C}$  for 3 min, 50  $^{\circ}\text{C}/\text{min}$  ramp to 300  $^{\circ}\text{C}$ . Scanning electron microscopy images were taken using an Hitachi HD2000 STEM. Samples were prepared for imaging in solution, and a drop was placed onto a carbon formvar coated grid. Procedures for the assay of test reactions followed published protocols with minor alterations described below. The substrate for the oxidative deprotection of dithianes<sup>1</sup> (*i.e.* **S1**, *vide infra*) was prepared as described previously.<sup>2</sup>

**Preparation of nanostructured  $\text{V}_2\text{O}_5$  samples.**<sup>3</sup> Vanadium foils (0.25 mm, 99.8%, Advent Materials) were ground to a mirror finish before using as substrates, followed by rinsing with ethanol. Electrochemical anodization was carried out at room temperature in a solution of ethylene glycol (EG, Riedel-de Haën, 99.5%) with 7 mM  $(\text{NH}_4)_2\text{TiF}_6$  (Sigma-Aldrich, 99.99%) in 0.1 M HF (40 vol%, Merck). The anodization was conducted at 60 V for 120 minutes to grow porous  $\text{V}_2\text{O}_5$  layers with average diameter of 20 nm using a conventional two-electrode configuration with platinum gauze as a counter electrode. After anodization, the samples were rinsed with ethanol followed by thermal treatments at 250  $^{\circ}\text{C}$  for 3 h in air. A field-emission scanning electron microscope (Hitachi FE-SEM S4800) was used to investigate the morphologies and compositions of

the nanopores. The  $V_2O_5$  material was then cleaned from the vanadium foil substrate by gentle mechanical stripping with a knife.

**General Procedure for Preparation of GC Standard Curves.** Stock solutions (1M) of desired products and internal standard (ISTD, tetraglyme) were prepared in dichloromethane. Varying amounts of desired product (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.10 mmol) and a constant 0.05 mmol aliquot of ISTD were added to 1 mL volumetric flasks. The final volume was taken to 1 mL. These samples were injected into the GC, and the peak area ratio ( $[\text{product area}]/[\text{ISTD area}]$ ) was calculated. This ratio was plotted versus the concentration of the desired product to yield a linear relationship ( $r^2$  values greater than 0.998). In this manner, GC chromatogram peak areas were correlated to concentration.

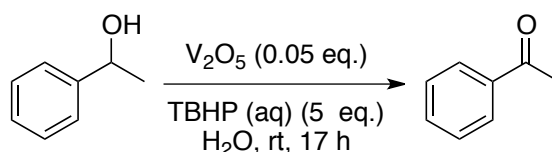
**General Procedure for Oxidative Deprotection of Acetals.<sup>4</sup>**



Vanadium pentoxide (7.24 mg, 0.04 mmol) was added to a 30% solution of hydrogen peroxide (0.45 mL, 4 mmol) and stirred at 0 °C until the vanadium pentoxide was dissolved and the solution was a reddish brown color. This solution was added to an ice-cold, stirred solution of 2-phenyl-1,3-dioxolane (136  $\mu$ L, 1 mmol) in methanol (3 mL). The reaction was quenched by the addition of a saturated aqueous sodium metabisulfite solution after 2 hours. The mixture was diluted with 10 mL of water and poured into a 60 mL separatory funnel. The mixture was extracted with dichloromethane (2 X 10 mL).

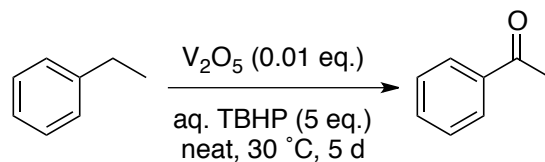
The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated by rotary evaporation. Tetraglyme (110  $\mu\text{L}$ , 0.5 mmol) was added to the crude product residue, and the mixture was reconstituted in 10 mL of DCM. A 1 mL aliquot of this solution was removed for GC analysis. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated.

**General Procedure for the Oxidation of Alcohols to Ketones with  $\text{V}_2\text{O}_5$ /TBHP.<sup>5</sup>**



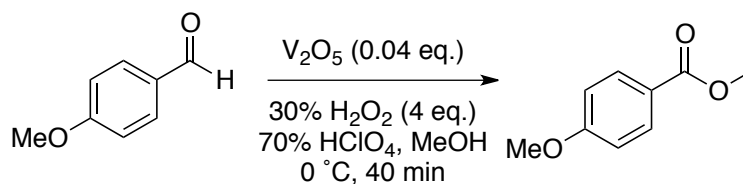
A mixture of vanadium pentoxide (9 mg, 0.05 mmol) and 1-phenylethanol (121  $\mu\text{L}$ , 1 mmol) was stirred in water (3 mL). *Tert*-butyl hydroperoxide (685  $\mu\text{L}$ , 5 mmol) was added, and the mixture was stirred at room temperature. The reaction was quenched by the addition of a saturated aqueous sodium metabisulfite solution after 17 hours. The mixture was diluted with 10 mL of water and poured into a 60 mL separatory funnel. The mixture was extracted with dichloromethane (2 X 10 mL). The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated by rotary evaporation. Tetraglyme (110  $\mu\text{L}$ , 0.5 mmol) was added to the crude product residue, and the mixture was reconstituted in 10 mL of DCM. A 1 mL aliquot of this solution was removed for GC analysis. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated.

### General Procedure for the C-H Oxidation of Ethyl Benzene with $V_2O_5$ /TBHP.<sup>6</sup>



Vanadium pentoxide (2 mg, 0.01 mmol) and ethylbenzene (123  $\mu$ L, 1 mmol) were suspended in aqueous *tert*-butyl hydroperoxide (685  $\mu$ L, 5 mmol) and stirred at 30 °C (oil bath). The reaction was quenched by the addition of a saturated aqueous sodium metabisulfite solution after 5 days. The mixture was diluted with 10 mL of water and poured into a 60 mL separatory funnel. The mixture was extracted with dichloromethane (2 X 10 mL). The combined organics were dried ( $Na_2SO_4$ ) and concentrated by rotary evaporation. Tetraglyme (110  $\mu$ L, 0.5 mmol) was added to the crude product residue, and the mixture was reconstituted in 10 mL of DCM. A 1 mL aliquot of this solution was removed for GC analysis. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated.

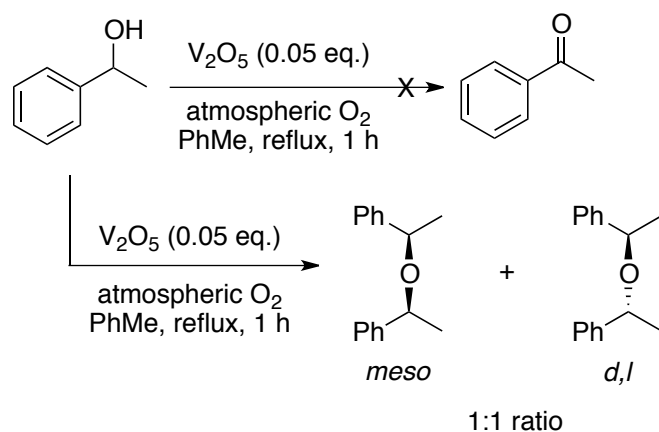
### General Procedure for the Oxidative Esterification of Aldehydes with $V_2O_5/H_2O_2$ .<sup>7</sup>



Vanadium pentoxide (7 mg, 0.04 mmol) was added to a 30% solution of hydrogen peroxide (0.45 mL, 4 mmol) and left to stir at 4 °C until the vanadium pentoxide was dissolved and the solution was a reddish brown color. This solution was added to an ice-cold, stirred solution of *p*-anisaldehyde (122  $\mu$ L, 1mmol) and perchloric acid (70%

aqueous solution, 0.5 mL) in methanol (5 mL). The reaction was stirred at 4 °C (ice bath) for 40 min. The reaction was quenched by the addition of a saturated aqueous sodium metabisulfite solution. The mixture was diluted with 10 mL of water and poured into a 60 mL separatory funnel. The mixture was extracted with dichloromethane (2 X 10 mL). The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated by rotary evaporation. Tetraglyme (110  $\mu\text{L}$ , 0.5 mmol) was added to the crude product residue, and the mixture was reconstituted in 10 mL of DCM. A 1 mL aliquot of this solution was removed for GC analysis. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated.

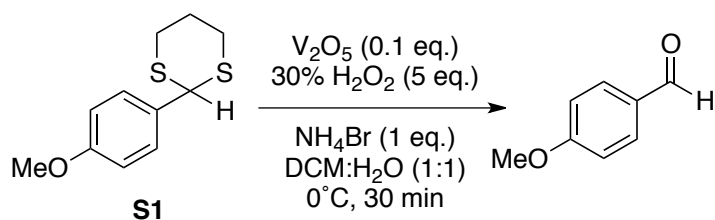
### General Procedure for the Oxidation of Alcohols Mediated by $\text{V}_2\text{O}_5/\text{air}$ .<sup>8</sup>



A mixture of vanadium pentoxide (9 mg, 0.05 mmol) and toluene (1.5 mL) was stirred and heated to 100 °C (oil bath). The 1-phenylethanol (121  $\mu\text{L}$ , 1 mmol) was added to the 100 °C solution and the flask was equipped with a reflux condenser. The mixture was heated at 100 °C (oil bath) open to air for 1 hour. The reaction was quenched by the addition of a saturated aqueous sodium metabisulfite solution. The mixture was diluted

with 10 mL of water and poured into a 60 mL separatory funnel. The mixture was extracted with dichloromethane (2 X 10 mL). The combined organics were dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated by rotary evaporation. Tetraglyme (110  $\mu\text{L}$ , 0.5 mmol) was added to the crude product residue, and the mixture was reconstituted in 10 mL of DCM. A 1 mL aliquot of this solution was removed for GC analysis. Yield of the 1:1 mixture of *meso*- and *d,l*-ethers was calculated based on the disappearance of starting 1-phenylethanol. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated. The identity of the *meso*- and *d,l*-ethers was confirmed by isolation and purification via column chromatography and characterization by GC-MS and  $^1\text{H}$  NMR spectroscopy. The inseparable mixture of *meso*- and *d,l*-ethers returned an  $^1\text{H}$  NMR spectrum identical to that published previously.<sup>9</sup>

### General Procedure for the Oxidative Deprotection of Dithianes with $\text{V}_2\text{O}_5/\text{NH}_4\text{Br}/\text{H}_2\text{O}_2$ .<sup>1</sup>



Ammonium bromide (10 mg, 1.0 mmol) was added to a 3 mL screw-top vial equipped with a stir bar and dissolved in 0.1 mL of deionized water. This solution was cooled to  $4^\circ\text{C}$  on an ice bath and vanadium pentoxide (2 mg, 0.1 mmol) and 30% hydrogen peroxide (60  $\mu\text{L}$ , 5 mmol) was added. The resulting solution was stirred at  $4^\circ\text{C}$  for 5 minutes. Next, a solution of dithiane **S1** (23 mg, 0.1 mmol) in dichloromethane (0.5 mL) was

added and the mixture was stirred at 4 °C for 30 minutes. The reaction was then quenched by the addition of 1 mL of a saturated aqueous sodium metabisulfite solution. The mixture was diluted with 0.5 mL of DCM. The DCM layer (1 mL) was removed and spiked with tetraglyme (11 µL, 0.05 mmol) and subjected to GC analysis. Reactions with conventional and nanostructured vanadium (V) oxides were conducted in triplicate. GC yields were averaged and standard deviations were calculated.

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