Experimental Procedures

General Procedures. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox, unless otherwise noted. Dry, oxygen–free solvents were used throughout. Tantalum(V) chloride was purchased from Strem Chemicals, Inc. and sublimed prior to use. \((N,N\text{-dimethylamino)}\text{trimethylsilane, (N,N-dimethylamino)butyldimethylsilane, and (N,N-dimethylamino)octyldimethylsilane were purchased from Gelest, Inc. and used without further purification. Acetonitrile was purchased from Aldrich and distilled from P\(_2\)O\(_5\) prior to use. Cyclohexene was purchased from Aldrich and dried over CaH\(_2\) prior to use. Aqueous hydrogen peroxide (30 %) was purchased from Aldrich and used as received. The following were prepared according to literature procedures: Ta(O\(_i\)Pr)\(_2\)[OSi(O\(_t\)Bu)\(_3\)]\(_3\) (I),\(^1\) SBA15,\(^2\) (BuO)\(_3\)SiOH,\(^3\) Ta(O\(_i\)Pr)\(_5\),\(^4\) and K\(_3\)Ta(O\(_2\))\(_4\).\(^5\)

Characterization. Benzene–\(d_6\) was purified and dried by vacuum distillation from sodium/potassium alloy. Solution \(^1\)H NMR spectra were recorded at 400 MHz using a Bruker AVB–400 spectrometer. Chemical shifts for \(^1\)H NMR spectra were referenced internally to the residual solvent proton signal relative to tetramethylsilane. Solid-state \(^{29}\)Si magic angle spinning (MAS) NMR spectra were recorded at 148.87 MHz using a Varian Inova 750 spectrometer. The spinning rate was 10 kHz and approximately 30000 scans were recorded for each sample. Nitrogen adsorption isotherms were obtained using a Quantachrome Autosorb 1, and samples were outgassed at 120 °C for at least 15 h prior to measurement. The Brunauer–Emmet–Teller (BET) method\(^6\) was used to determine surface areas, and the Barrett–Joyner–Halenda (BJH) method\(^7\) was used to
obtain pore size distributions. Thermal analyses were performed on a TA Instruments SDT 2960 Integrated TGA/DSC analyzer with a heating rate of 10 °C min\(^{-1}\) under a flow of nitrogen or oxygen. Calcinations were performed using a Lindberg 1200 °C three-zone furnace with a heating rate of 10 °C min\(^{-1}\) under a flow of air, and the temperature was held constant for 4 h. Carbon and hydrogen elemental analyses were performed by the College of Chemistry microanalytical laboratory at the University of California, Berkeley. Tantalum elemental analyses were performed at Galbraith Laboratories, Inc. (Knoxville, TN, USA) by means of inductively–coupled plasma (ICP) methods. Powder X–ray diffraction (PXRD) experiments were performed on a Siemens D5000 X–ray diffractometer using Cu K\(\alpha\) radiation. Samples for transmission electron microscopy (TEM) were prepared by depositing a hexanes suspension of the catalyst onto carbon–coated copper sample holders obtained from Ted Pella, Inc. Transmission electron microscopy was carried out on a Philips CM200 transmission electron microscope operating at 200 kV. Infrared spectra were recorded on a Nicolet Nexus 6700 FT-IR spectrometer with a liquid nitrogen cooled MCT-B detector. Measurements were made at a 4.0 cm\(^{-1}\) resolution. Gas chromatography (GC) analyses were performed with an HP 6890N system using a HP-5 phenyl methyl siloxane capillary (30.0 m \(\times\) 320 µm \(\times\) 0.25 µm nominal), and integration was performed relative to toluene. The mesoporous support, SBA15, was characterized by PXRD and \(\text{N}_2\) porosimetry prior to catalyst preparation (surface area, 585 m\(^2\) g\(^{-1}\); pore volume, 0.64 cc g\(^{-1}\); average pore radius, 3.3 nm). The hydroxyl group concentration of the SBA15 was determined to be 1.9(1) OH nm\(^{-2}\), via reaction of SBA15 with Mg(CH\(_2\)C\(_6\)H\(_5\))\(_2\) • 2 THF and quantification of the toluene evolved by \(^1\text{H}\) NMR spectroscopy.\(^8\)
TaSBA15 Preparation. The catalysts were prepared in a similar manner to those previously reported. The SBA15 was dried at 120 ºC in vacuo for 12 h and handled under a nitrogen atmosphere. A 0.50 g sample of SBA15 was suspended in pentane (30 mL) and a pentane solution (30 mL) of Ta(O\textit{iPr})\textsubscript{2}[OSi(O\textit{tBu})\textsubscript{3}]\textsubscript{3} (0.054 g, 0.050 mmol) was added at room temperature. The resulting mixture was stirred for 20 h and then filtered and washed with pentane (3 × 20 mL). The grafted material was dried in vacuo for 2 h prior to calcination at 200 ºC (10 ºC min\textsuperscript{-1}) under flowing air to yield a catalyst with 1.80 wt % Ta loading as determined by ICPAES.

Preparation of Surface-Modified TaSBA15 materials. A 0.250 g sample of the TaSBA15 catalyst was suspended in 20 mL of pentane. A 10 mL solution of RMe\textsubscript{2}Si(NMe\textsubscript{2}) in pentane (5 equiv based on surface silanol content) (R = Me, \textit{Bu, or \textit{Oc}) was added via cannula at room temperature. The suspension was stirred for 20 h at room temperature under flowing nitrogen. The solid was then filtered on a Büchner funnel and rinsed with pentane (3 × 10 mL). The resulting solid was dried in vacuo at 120 ºC for 12 h, and stored in a drybox.

Catalysis Procedure. A sample of catalyst (ca. 35 mg) was added to a 50 mL round-bottom flask fitted with a reflux condenser and a septum. Acetonitrile (5.0 mL) and cyclohexene (2.5 mL, 24.7 mmol) were added via syringe through the septum under a flow of nitrogen. Toluene (23 µL) was added as an internal standard. The mixture was allowed to equilibrate at the reaction temperature of 65 ºC for 10 min. Hydrogen peroxide (0.62 mL, 6.07 mmol) was added via syringe to the rapidly stirring solution. Aliquots (ca. 0.10 mL) were removed from the reaction mixture by syringe and then filtered and cooled. The filtrate was diluted with acetonitrile to 0.5 mL and analyzed by gas
chromatography (GC). Product assignments were made by comparison with the authentic samples analyzed under identical conditions.

**References**


Nitrogen porosimetry isotherms of a.) SBA15, b.) TaSBA15, c.) Me$_{\text{cap}}$TaSBA15, d.) Me$_{\text{uncap}}$TaSBA15, e.) Bu$_{\text{cap}}$TaSBA15, f.) Bu$_{\text{uncap}}$TaSBA15, g.) Oc$_{\text{cap}}$TaSBA15, and h.) Oc$_{\text{uncap}}$TaSBA15.
Representative pore size distribution plots determined from the adsorption branch of the nitrogen physisorption isotherm for a.) SBA15, b.) TaSBA15, c.) Me\textsubscript{cap}TaSBA15, and d.) Me\textsubscript{uncap}TaSBA15. Plots are offset for clarity.

Representative low angle PXRD patterns for a.) SBA15, b.) TaSBA15, c.) Me\textsubscript{cap}TaSBA15, and d.) Me\textsubscript{uncap}TaSBA15. Patterns are offset for clarity.
DSC traces with minima of endothermic transitions corresponding to H₂O desorption marked (+) at 68 ºC (TaSBA15), 51 ºC (Bu_{cap} and Oc_{cap}TaSBA15), and 50 ºC (Me_{cap}TaSBA15).

Solid-state $^{29}$Si MAS NMR spectra of a.) TaSBA15, b.) Bu_{uncap}TaSBA15, and c.) Bu_{cap}TaSBA15.
Yield of oxidation products relative to initial H₂O₂ concentration as a function of time during cyclohexene oxidation with (■) TaSBA15, (○) Me₅-cap-TaSBA15, (◆) Bu₅-cap-TaSBA15, and (▲) Oc₅-cap-TaSBA15.

Epoxide selectivity as a function of time during cyclohexene oxidation with aqueous H₂O₂, using (■) TaSBA15, (○) Me₅-cap-TaSBA15, (◆) Bu₅-cap-TaSBA15, and (▲) Oc₅-cap-TaSBA15.