Supporting Information

A Heterogeneous Catalyst Grafted *in situ* for Selective Oxidation Based on Mn Triazacyclononane

Nicholas J. Schoenfeldt, Andrew W. Korinda, Justin M. Notestein[*]

Northwestern University, Department of Chemical and Biological Engineering, 2145 Sheridan Road, Technological Institute, Room E136, Evanston, Illinois 60208

Email: j-notestein@northwestern.edu

Supporting Information Index

Physical Measurements.

All solution phase ^{1}H NMR were recorded on an Inova 500 MHz NMR or an Oxford NMR AS400. Solid state [13]C

CP/MAS NMR was recorded on a Varian 400 MHz NMR after thorough drying of the solid samples at 120 °C to

minimize physisorbed water (Adamantane external standard). Electrospray ionization mass spectrometry (ESI-

MS) was performed on an Agilent 6210 TOF LCMS after dissolving samples in acetonitrile. Thermogravimetric

analysis (TGA) was recorded under N_2/O_2 atmosphere using a TA Instruments TGA Q500 in high resolution mode

with a 50 °C/min ramp rate from room temperature up to 800 °C. Solution phase UV-visible spectra were

recorded with a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Diffuse reflectance UV-visible (DR-UV-vis)

were recorded using a Harrick Praying Mantis attachment on the Shimadzu UV-3600. Gas chromatography (GC)

was done with a Shimadzu GC-2010 gas chromatograph with a flame ionization detector (FID) and a Thermo

Scientific TR-1 column (30m x 0.25mm ID x 0.25um). The He linear velocity was kept constant at 60 cm/sec, and

the column program began with a 3 min hold at 50 °C followed by a 50 °C/min ramp to 270 °C with another 2 min

hold. Products were identified by comparison to authentic standards and by gas chromatography mass

spectroscopy (GC-MS) with a Hewlett Packard HP 6890 Series GC system equipped with a HP 6890 Series Mass

Selective Detector.

Synthesis

All chemicals were used as received from Sigma-Aldrich unless otherwise noted.

Ligand synthesis:

N,N',N"-Tri(p-toluenesulfonyl)diethylenetriamine (Ts$_3$-dient) was prepared according to literature method by

dropwise addition of a p-toluenesulfonyl chloride (28.6 g, 0.15 mol) solution in ether (150 mL) to stirred solution of

diethylenetriamine (5.2 g, 0.05 mol) and NaOH (6.00 g, 0.15 mol) in water (50 mL). The solution was allowed to

stir for 1.5 h at room temperature after addition was complete. The product was filtered off and washed with cold

water, methanol, and ether. Re-crystallization from boiling methanol (400 mL) gave fine, white needles.[1] Yield:

16.75 g (60%).

1,2-Di(p-toluenesulfonyloxy)ethane (Ts$_2$-glycol) was prepared by adding solid portions of p-toluenesulfonyl

chloride (30.5 g, 0.16 mol) to a stirred solution of ethylene glycol (5.0 g, 0.08 mol) in dry pyridine at 0 °C over a 20

min period. The reaction mixture was allowed to stir at room temperature for 1 day. Crushed ice was then added

directly to the mixture, and it was placed in the refrigerator at 2-6 °C for 1 day. The white solid was then filtered and washed with cold water, ethanol, and ether. It was then re-crystallized from a minimum of hot acetone upon addition of ether.[1] Yield: 17.5 g (58%).

1,4,7-Tritosyl-1,4,7-triazacyclononane (Ts$_3$-Tacn) was prepared by adding Ts$_3$-dient (9.2 g, 16.2 mmol) to toluene (150 mL). The white slurry was stirred while adding NaOH (2.0 M, 18 mL, 2.2 eq) followed by tetrabutylammonium hydroxide (1.0 M, 1.6 mL, 0.1 eq) in water. A reflux condenser was attached, and the reaction mixture was heated to 90 °C with stirring for 0.5 h. Ts$_2$-glycol (6.0 g, 0.016 mol) was added scoop-wise to the mixture every eight minutes over a 5 h period (~0.15 g per addition). The mixture was allowed to react an additional 3 h at 90 °C, at which point it was cooled to room temperature and allowed to stir overnight. The white solid was filtered and washed with cold water, ethanol, and ether.[2] Yield: 7.8 g (81%)

1,4,7-Trimethyl-1,4,7-triazacyclononane (tmtacn) was prepared by dissolving Ts$_3$-Tacn (3.1 g, 5.2 mmol) in 5-7 mL concentrated sulfuric acid. The mixture was allowed to stir for 5-6 h at 140 °C. The mixture containing the de-protected triamine was neutralized to pH=7 with stirring upon slow addition of 5.0 M NaOH. Formaldehyde (7.0 mL, 18 eq) and formic acid (6.2 mL, 30 eq) were then added sequentially via syringe, CO$_2$ evolution was minimal. A reflux condenser was attached, and the mixture was allowed to stir at 101 °C for 12-15 h. The reaction mixture was cooled to room temperature then neutralized to pH=14 by slow addition of 5.0 M NaOH. The reaction mixture was stirred for 5-10 minutes in chloroform (20 mL). The mixture was then added to a seperatory funnel and extracted 10 times with 15 mL portions of chloroform. The organic layers were combined and dried over Na$_2$SO$_4$. The mixture was then filtered and the solution was evaporated down to isolate a viscous, light yellow oil, which was stored at 2-6 °C.[2] Yield: 0.9 g (99%). The ^{1}H and ^{13}C NMR spectra showed pure product and agreed with literature spectra.

Complex synthesis:

The manganese triazacyclononane dimer, **1**, $[Mn_2(Me_3\text{-}Tacn)_2(\mu\text{-}O)_3](PF_6)_2 \cdot H_2O$, was synthesized by dissolving tmtacn (0.68 g, 4.0 mmol) in 8 mL 2:1 EtOH/H_2O. $MnCl_2 \cdot 4H_2O$ (0.8 g, 1 eq), and KPF_6 (1.1 g, 1.5 eq) were then added simultaneously to the reaction mixture. Stirring at 50 °C for 20 minutes gave a creamy brown suspension. The mixture was cooled to 0 °C while stirring for 10 minutes, at which time 8.0 mL of a freshly prepared 1:1 H_2O_2 (1.5 M)/NaOH (1.0 M) solution was added drop-wise over 5-7 minutes via syringe. The mixture was allowed to stir an additional 15 minutes at 0 °C. The reaction solution was filtered and evaporated to dryness, then re-dissolved in MeCN. This process was repeated 3-4 times, until all remaining solids were completely soluble in MeCN. Large red crystals were obtained following crystallization from MeCN/EtOH. The product was filtered and washed with ethanol and ether.[3] Yield: 0.65 g (42%). Mass Spectrum (ESI$^+$, MeCN): m/z 645.17 ([M – PF_6]$^+$), 501.21 ([M – 2PF_6]$^+$). Elemental Analysis: (calc. $Mn_2C_{18}H_{44}N_6O_4P_2F_{12}$) C 26.9% (26.7), N 10.3% (10.4), Mn 13.0% (13.6).

The carboxylic acid bridged manganese triazacyclononane dimer, **2**, $[Mn_2(Me_3\text{-}Tacn)_2(\mu\text{-}O)(\mu\text{-}OOCCH_3)_2](PF_6)_2$, was synthesized by dissolving tmtacn (117.4 mg, 0.7 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (134.4 mg, 0.5 mmol), KPF_6 (116.6 mg, 0.6 mmol), CH_3COONa (102.8 mg, 1.25 mmol) and $NaHCO_3$ (104.9 mg, 1.25 mmol) in 7.5 mL de-gassed MeCN under Ar. The reaction mixture was stirred and the temperature was slowly increased to 55 °C. A color change from brown to brownish-purple was observed within minutes of reaching the desired temperature. After stirring for 3 h, the reaction mixture was cooled to R.T., filtered in air, and evaporated to dryness. The obtained solid, **2** (144.0 mg, 0.164 mmol, 65.7%), was washed with EtOH and Et_2O and stored under Ar.[3] ESI-MS and elemental analysis were consistent with the literature.

Support Functionalization

Mesoporous silica gel (Selecto Scientific, 32-63 μm particle size, BET surface area 500 m^2/g), fumed silica gel (Aeroperl, Evonik Degussa, BET surface area 300 m^2/g), and amorphous-alumina (Selecto Scientific, 63-150 μm particle size, BET surface area 165 m^2/g), unless otherwise noted, were treated at 120 °C under dynamic vacuum for 12-15 h prior to grafting. Acidic (A), neutral (N), and basic (B) grades of alumina were utilized – the neutral and acidic grades are manufactured with additional HCl to create pH = 2 and pH = 7 solutions, respectively, when the solids are immersed in water. 2-(carbomethoxy)-ethyltrimethoxysilane was used as obtained from Gelest, Inc.

Ester functionalized SiO$_2$, fumed SiO$_2$ (S-E, FS-E) and Al$_2$O$_3$ (A-E) were obtained by adding a desired quantity of dehydrated support to 50 mL anhydrous pyridine under inert atmosphere. The calculated quantity of 2-(carbomethoxy)ethyltrimethoxysilane was then injected into the reaction mixture via syringe. The mixture was heated to 125 °C and allowed to reflux 24 hours. The solids were then isolated by filtration on a glass frit, and were washed with pyridine (200 mL) and ether (50 mL). The ester functionalized material was then soxhlet extracted for 24 hours from benzene to ensure removal of any ungrafted ester precursor. The solids were again filtered, washed with toluene (200 mL) and ether (50 mL), and dried under vacuum. Presence of the surface ester was confirmed by ^{13}C CP/MAS NMR (Figure S1).[4] Surface densities of the ester functionalities (Figure S2) were calculated from TGA weight loss profiles (Figure S3), and were found to range from 0.14 – 0.92 mmol/g SiO$_2$.

Carboxylic acid functionalized SiO$_2$, and fumed SiO$_2$ (S-CA, FS-CA) and Al$_2$O$_3$ (A-CA) was obtained by refluxing S-E, FS-E or A-E in 25 mL 1.0 M HCl for 24 hours. The deprotected carboxylic acid functionalized solids were then washed with copious amounts of water (2 L) and ether (100 mL) to ensure removal of HCl. The solids were then dried under vacuum and stored in a desiccator until use. Presence of the deprotected surface carboxylic acid was confirmed by ^{13}C CP/MAS NMR (Figure S1).[4] Surface densities of the carboxylic acid functionalities (Figure S2) were calculated from TGA weight loss profiles (Figure S3), and were found to range from 0.06 – 0.66 mmol/g SiO$_2$. Some loss of weakly bound ester groups during acid deprotection resulted in carboxylic acid surface densities lower than the corresponding ester surface densities. The surface hydroxyl density of the functionalized supports was investigated by DR-UV-vis-NIR (Figure S4).

Cyclooctene Oxidation:

Cis-cyclooctene (Sigma-Aldrich) was distilled over powdered NaOH through a Vigreux column under inert atmosphere.[5] The freshly distilled cyclooctene was then passed through an activated neutral alumina column, and was then stored under nitrogen. All other chemicals were used as received from Sigma-Aldrich unless otherwise noted.

Batch reactions were carried out in Wheaton 3 mL conical reactor vials with Teflon caps. A desired amount of co-catalyst (often S-CA or A-CA), HPLC grade MeCN (2 mL), and **1** were then added to the reaction vial followed by o-dichlorobenzene (100 μL), and distilled cis-cyclooctene (50 μL). Spinvane conical stir bars were sealed into the reactor vials, and they were then placed inside a fabricated aluminum thermal block sitting on a Thermoelectrics Unlimited, Inc. cold-plate stirrer. The vial was allowed to stir until reaching thermal equilibrium at 0 °C. 30 wt.% aqueous hydrogen peroxide (130 μL) was then added via syringe, and the reaction mixture was allowed to stir for 3 hours at 0 °C. After reaction, excess PPh$_3$ was added and stirred with the reaction mixture for ~10 minutes to terminate the reaction prior to injection into the GC, thus preventing any remaining H$_2$O$_2$ from reacting with the reactants and/or products at high temperature inside the GC injector.[6] It must be noted that this step is critical to observe true selectivities. The reaction liquid was then filtered through a Whatman glass microfiber syringe filter and transferred to a GC vial for analysis.

Semi-batch reactions were carried out in a 100 mL 2-neck round bottom flask equipped with stir bar. A desired amount of co-catalyst (often S-CA or A-CA), HPLC grade MeCN (40 mL), and **1** were then added to the reaction flask followed by o-dichlorobenzene (2 mL), and distilled cis-cyclooctene (1.0 mL). The reaction mixture was then caped with a rubber septum and lowered into a 50% ethylene glycol/water bath, which was chilled using a VWR chiller. The system was allowed to equilibrate to 0 °C while stirring. Hydrogen peroxide (2.6 mL, 30%) was then slowly injected (0.44 mL/h) using a kd Scientific syringe pump and PE and PTFE syringe and transfer line. A portion (~0.4 mL) of the reaction mixture was removed at t=0, and following completion of H$_2$O$_2$ injection. The analyzed portion was allowed to soak for 10 minutes with excess PPh$_3$ reducing agent, which was used to terminate the reaction and prevent any remaining H$_2$O$_2$ from reacting with the reactants and/or products at high

temperature inside the GC injector.[6] The reaction liquid was the filtered through a Whatman glass microfiber syringe filter and transferred to a GC vial for analysis.

Co-catalyst Comparisons: A series of batch or semi-batch reactions were conducted under equivalent reaction conditions with varying types of co-catalyst; none, SiO_2 or S-CA, FS-CA, Al_2O_3 or A-CA (acidic, neutral, and basic), and homogeneous valeric acid. For batch reactions, the combination of S-CA and **1** yields substantially more total turnover numbers to diol and epoxide products than **1** alone or **1** with un-functionalized SiO_2 or Al_2O_3 (Table S1). As co-catalyst, A-CA does not increase total TON above that of **1** alone. Given the low productivity, no significant differences are abovseved when using the different Al_2O_3 supports. Notably, S-CA leads to around an order of magnitude higher total TON than its closest homogeneous analog, valeric acid, when similar concentrations of co-catalyst are present.

Decomposition of H_2O_2 catalyzed by **1** with and without CA co-catalyst was investigated by comparing the amount of H_2O_2 consumed in varying systems at 0 °C and room temperature. A control sample was made by dissolving 130 μL 30 wt.% H_2O_2 in 2.0 mL MeCN inside a 3 mL conical reactor vial with Teflon cap. A second reactor vial was dosed with 130 μL H_2O_2, 2 mL MeCN and 0.2 mg **1**. Finally, a third reactor vial was dosed with130 μL H_2O_2, 2 mL MeCN and 0.2 mg **1**, and 1.10 mg S-CA co-catalyst. The reactor vials were then stirred for 3 h at desired temperature, at which point the reaction solution was filtered. H_2O_2 concentration was then determined by Iodometric titration (Table S2).[7]

Catalyst leaching tests: Leaching tests were conducted to demonstrate the heterogeneity of all solid catalysts reported in this study. For leaching tests, a 2 hour control reaction was allowed to proceed at 0 °C with 10 mg of S-CA support material. This reaction demonstrates the total reactivity that all systems under equivalent conditions should be expected to exhibit over the course of a 2 hour reaction time. Trial A was set up at the same time and under equivalent conditions as the control. This reaction vial was allowed to react for one hour, at which time a small portion was removed and treated for GC analysis. Simultaneously, a 1.0 mL portion of the trial A reaction liquid, which still contained H_2O_2, was transferred without filtration to an empty vial at 0 °C. This sample was allowed to react for an additional 1 hour period, at which time it was processed for GC analysis. Trial B was

set up at the same time and under equivalent conditions as the control. This reaction vial was allowed to react for

one hour with H_2O_2 present, at which time a small portion was removed and treated for GC analysis.

Simultaneously, a 1.0 mL portion of the trial B reaction liquid was transferred without filtration to an empty vial at 0

°C. Additionally, a portion of fresh S-CA equal to the initial amount used (10 mg) was added to this transferred

solution. This sample was allowed to react for an additional 1 hour period, at which time it was processed for GC

analysis. Neither transferred sample from trial A nor B showed any additional catalytic activity once removed from

the self-assembled heterogeneous catalyst from the initial reaction vial (Figure S5).

High conversion conditions: A series of catalytic reactions were conducted to verify the ability of self-grafted **1** to

operate with near 100% conversion of cyclooctene (Table S3). This series of reactions was conducted identical

to previously described batch reactions, however the amount of 30 wt.% H_2O_2 was increased (0.5 mL) while the

amount of **1** was variably increased (0.5 – 1.5 mM). The quantity of supplied S-CA was also variably increased to

maintain a constant 2 mol CA / mol Mn ratio. Table S3 shows that 0.5 mM **1** with 0.5 mL 30 wt% H_2O_2 was

sufficient to convert 96% of the 0.17M cyclooctene. These conditions correspond to a 1:340:3700 ratio of

1:cyclooctene:H_2O_2.

Substrate Scope

Cyclohexene (Sigma-Aldrich) was passed through an activated neutral alumina column to remove oxidized

species prior to use. Cyclohexenone, norbornylene, 1-octene, styrene, α-methylstyrene, trans-β-methylstyrene,

and cis-stilbene were used as received from Sigma-Aldrich. All catalytic reactions were carried out in Wheaton 3

mL conical reactor vials with Teflon caps and batch addition of oxidant. A desired amount of S-CA co-catalyst

(~10 mg), HPLC grade MeCN (2 mL), and **1** (0.24 mg) were then added to the reaction vial followed by o-

dichlorobenzene (100 μL) or HPLC grade toluene (100 μL) as internal standard, and desired substrate (0.38

mmol). Spinvane conical stir bars were sealed into the reactor vials, and they were then placed inside a

fabricated aluminum thermal block sitting on a Thermoelectrics Unlimited, Inc. cold-plate stirrer. The vial was

allowed to stir until reaching thermal equilibrium at 0 °C. 30 wt.% aqueous hydrogen peroxide (130 μL) was then

added via syringe, and the reaction mixture was allowed to stir for 3 hours at 0 °C. After reaction, excess PPh_3

was added and stirred with the reaction mixture for ~10 minutes to terminate the reaction prior to injection into the

GC, thus preventing any remaining H_2O_2 from reacting with the reactants and/or products at high temperature inside the GC injector.[6] The reaction liquid was then filtered through a Whatman glass microfiber syringe filter and transferred to a GC vial for analysis. The GC retention times and response curves were calibrated with authentic samples (Sigma Aldrich) or epoxides generated from the reaction of the alkene and m-chloroperbenzoic acid. For determination of the amounts of unknown "others", the oxidized products were assumed to have the same response curves as the starting material. GC-FID response curves are primarily dependant on carbon number for a given family of compounds.

Adsorption and *in situ* grafting of 1 on Carboxylic Acid Functionalized Supports

Adsorption of **1** on S-CA or A-CA was achieved by stirring a portion of S-CA at a ratio of 1.5 CA/Mn in a homogeneous solution of **1** in MeCN or MeCN/H_2O mixtures; loss of solution phase **1** was observed via UV-visible spectroscopy (Figure S6 and S7). Disappearance from solution is accelerated in MeCN/H_2O_2 mixtures. Added H_2O_2 at the concentrations used in this study does not reduce peak intensity or change peak location for solution phase **1** with no co-catalyst present (Figure S6). S-CA or A-CA and **1** in MeCN, MeCN/H_2O, or MeCN/H_2O_2 were stirred for 3 hours, at which time the solids were filtered and washed with copious amounts of MeCN (200 mL) and ether (20 mL). The solids were dried under vacuum and investigated by DR-UV-vis (Figure S8). The spectra of S-CA-derived materials were comparable to those of **1** in solution. Reduced peak intensity or broadening of the peak at ~320 nm was observed following self-catalyzed grafting on S-CA from MeCN/H_2O_2 mixtures, which was comparable to the solution phase spectra of **2** (Figure 2). Although loss of solution phase **1** was also observed via UV-vis when A-CA was allowed to stir in MeCN, MeCN/H_2O, and MeCN/H_2O_2 solutions of **1** (Figure S7), the DR-UV-vis spectra are unstructured and much weaker than for adsorption onto S-CA (Figure S8).
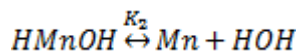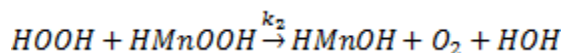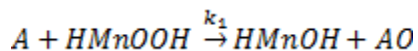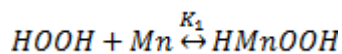
Determination of Mn content and reactivity following self-grafting of 1 on S-CA: A large scale reaction corresponding to 45x increase from previously described batch reactions was set-up by dissolving **1** (11.8 mg) in 100 mL of MeCN. The initial concentration of Mn in this solution was determined to be 0.26 mM by ICP-OES (Mn calibration performed with Mn ICP standards from Sigma-Aldrich). 90 mL of the stock catalyst solution (0.023 total mmol Mn obtained, 0.030 theoretical) was added to a 250 mL round bottom flask equipped with stir bar.

Distilled cis-cyclooctene (2.25 mL), o-dichlorobenzene (4.5 mL), and S-CA (91.3 mg, 2 mol CA / mol Mn) were then added to the reaction flask, which was lowered into a chilled ethylene glycol / H_2O bath at 0 °C. Once the reaction mixture had equilibrated to 0 °C with stirring, 30 wt.% H_2O_2 (5.85 mL) was added as a single injection. The solution was stirred 3 h at 0 °C, at which time a small portion of solution (2.25 mL) and worked up as described previously for GC analysis (reaction produced 280 total *TON* with 30 % selectivity to diol). The solids from the reaction flask were filtered on glass fiber filter paper, washed with 200-300 mL fresh MeCN, and dried under vacuum. 11.1 mg of the obtained solid was dissolved in aqueous nitric acid and analyzed for Mn content by ICP-OES (0.013 mmol Mn obtained, 57 % of Mn supplied during reaction was supported following catalysis and washing/drying of the solid). ICP-OES analysis of fresh S-CA displayed no Mn signal. Reuse of this solid in cyclooctene oxidation under identical conditions as above resulted in only 51 *TON*, demonstrating that the solid catalyst formed *in situ* is a reactive intermediate and distinct from the air stable Mn(IV-IV) complex 1.

The same procedure as above but without cyclooctene, grafts 80% of the Mn as determined by ICP-OES, but after recovery, this material performs only 13 *TON* for cyclooctene oxidation in subsequent reactions, further demonstrating that the most active catalyst is formed *in situ* and is distinct from an arbitrary Mn-loaded solid.

Relating total TON to relative rates of oxidation and H_2O_2 decomposition.

The following simplified mechanism is a representative example of alkene oxidation with simultaneous H_2O_2 decomposition. Critically, a single intermediate activated complex is specified for both reactions. The following discussion below is only intended to demonstrate how total productivity at 100% conversion of H_2O_2 is related to the relative rates of oxidation and peroxide decomposition and are not to be interpreted strictly. No attempt has been made to rigorously fit to all the observed reaction data.

$$HOOH + Mn \overset{K_1}{\leftrightarrow} HMnOOH$$

$$A + HMnOOH \overset{k_1}{\rightarrow} HMnOH + AO$$

$$HOOH + HMnOOH \overset{k_2}{\rightarrow} HMnOH + O_2 + HOH$$

$$HMnOH \overset{K_2}{\leftrightarrow} Mn + HOH$$

The nature of the activated complex HMnOOH remains equivocal for this system. AO represents all direct oxidation products including epoxide and *cis*-diol. Other studies have indicated that one oxygen originates from the oxidant and the other from solvent water, thus supporting this stoichiometry.

Using mass action kinetics,

Rate of oxidation $= r_{ox} = -\dfrac{d[A]}{dt}$

$$= -k_1[A][HMnOOH] = -\frac{k_1 K_1 [cat][A][HOOH]}{1 + K_1[HOOH]}$$

Rate of peroxide consumption $= r_{ox} + r_{decomp} = -\dfrac{d[HOOH]}{dt}$

$$= -k_1[A][HMnOOH] - k_2[HOOH][HMnOOH] = r_{ox}\left(1 + Z\frac{[HOOH]}{[A]}\right) = -\frac{d[A]}{dt}\left(1 + Z\frac{[HOOH]}{[A]}\right)$$

where $Z = k_2/k_1$, the relative rate constants for peroxide decomposition and oxidation respectively. The rate of oxidation is a composite of all possible oxidation events, primarily epoxidation and dihydroxylation.

A parametric expression relating alkene and hydrogen peroxide is written as:

$$\frac{d[HOOH]}{dt} = \frac{d[A]}{dt}\left(1 + Z\frac{[HOOH]}{[A]}\right)$$

$$\frac{d[HOOH]}{d[A]} = 1 + Z\frac{[HOOH]}{[A]}$$

Changing to conversion using $C(t) = C_0(1-X)$, gives:

$$\frac{dX_{HOOH}}{dX_A} = \frac{A_0}{HOOH_0} + Z\frac{1 - X_{HOOH}}{1 - X_A}$$

For an initial ratio of reactants $A_0/HOOH_0 = 0.35$, as employed in Table 1 of the manuscript, the relation between the two conversions can be numerically calculated for various values of Z. The conversion of alkene X_A at complete conversion of hydroperoxides, $X_{HOOH} = 1.0$ is the right intercept. These maximal values are directly comparable to total *TON* of the manuscript. Maximal conversion values of alkene for this starting reactant ratio are collected and plotted below. Using this graph, the rate constant ratio under this reaction scheme for the homogeneous catalyst **1** is ~100. The rate constant ratio for cyclooctene oxidation for the heterogeneous catalyst **2'** is ~6.5, giving a relative acceleration of ~15 times. Thus, for this reaction scheme, an order of magnitude increase in *TON* to oxidation products corresponds to an approximately order of magnitude increase in relative rate constants.
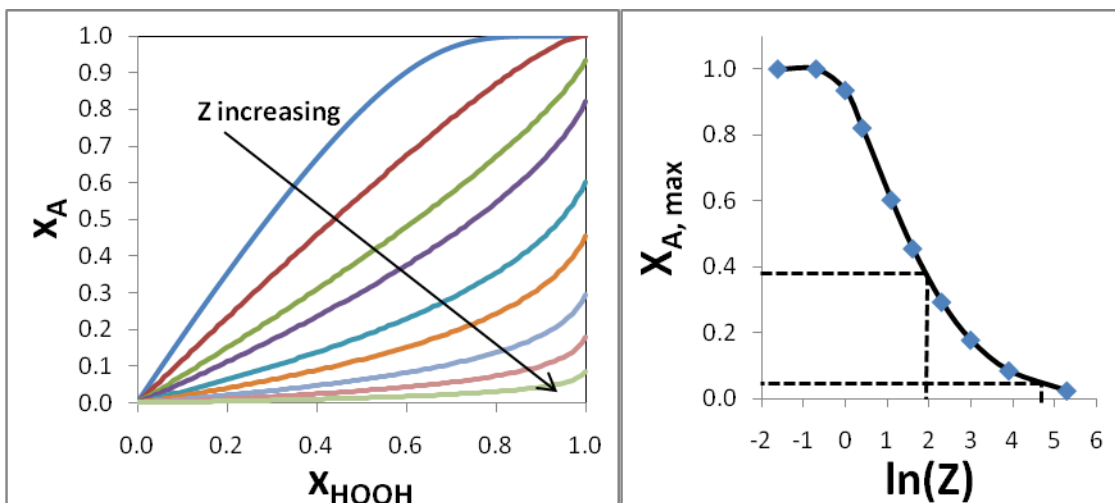
References

(1) Searle, G.H.; Geue, R.J. *Aust. J. Chem.* **1984**, 37, 959-970.

(2) Madison, S.A.; Batal, D.J. *Lever Brothers Co.* **1994**, U.S. Pat. 5,284,944.

(3) Koek, J.H.; Russell, S.W.; van der Wolf, L.; Hage, R.; Warnaar, J.B.; Spek, A.L.; Kerschner, J.; DelPizzo, L. *J. Chem. Soc. Dalton Trans.* **1996**, 353-362.

(4) McKeen, J.C.; Yan, Y.S.; Davis, M.E. *Chem. Mater.* **2008**, 20, 5122-5124.

(5) Armarego, W.L.F..; Chai, C.L.L. *Purification of Laboratory Chemicals: Fifth Ed.*; Elsevier: Great Britain, 2003.

(6) Shul'pin, G.B. *J. Mol. Catal. A: Chem.* **2002**, 189, 39-66.

(7) Gordon, G.; Cooper, W.J.; Rice, R.G.; Pacey, G.E. *Disinfectant Residual Measurement Methods: Second Ed.;* AWWARF and AWWA: Denver, CO.
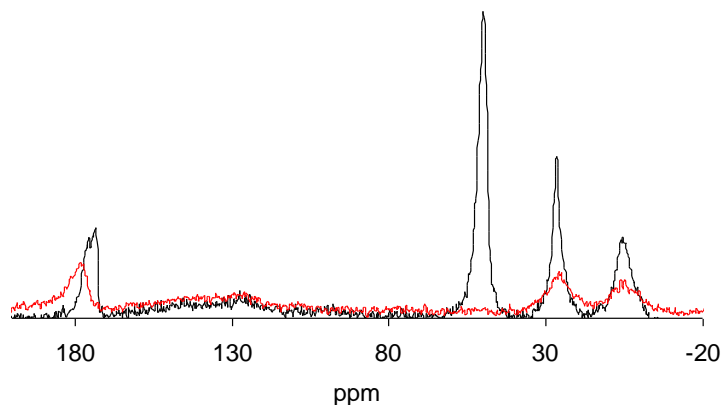
Supporting Figures

Figure S1. ^{13}C CPMAS NMR of the ester functionalized SiO_2 (S-E, black), and CA-functionalized SiO_2 (S-CA, red).
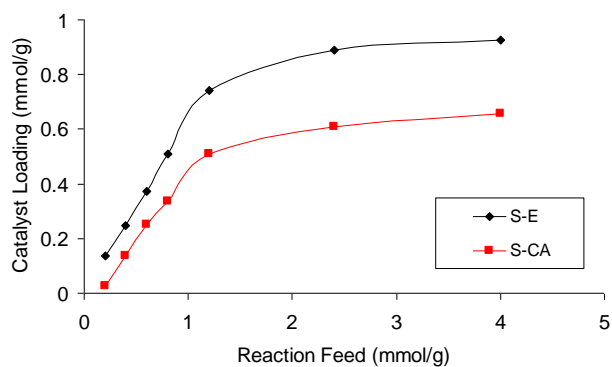

Figure S2. S-E and S-CA surface densities created by varying the amount of precursor in the grafting solution.
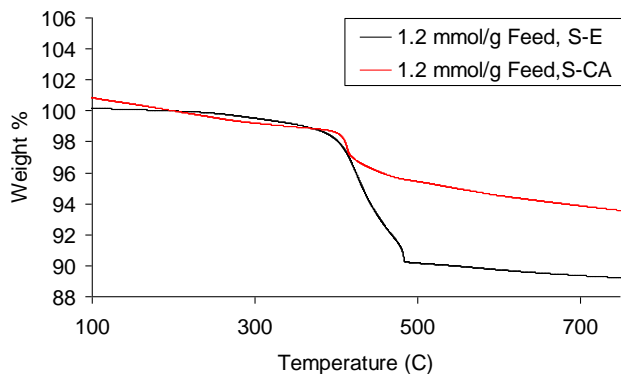

Figure S3. Characteristic TGA curves performed under N_2/O_2 for the methyl ester (S-E) and the de-protected carboxylic acid (S-CA). After normalization by the mass loss of silica due to Si-OH condensation, molar loadings are determined by assuming a combustible fragment of $C_3H_6COOCH_3$ for the methyl ester and C_3H_6COOH for the grafted carboxylic acid.
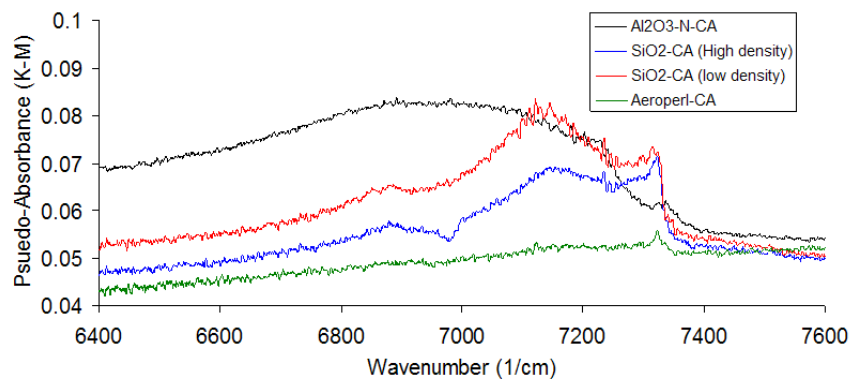
SI-14

Figure S4. Diffuse reflectance UV-visible-NIR of CA functionalized supports showing the second overtone of the OH stretching bands. Peaks near 7350 cm^{-1} are indicative of isolated silanols, broad peaks from 7000-7300 cm^{-1} indicate H-bonded silanols, and higher energy peaks are is indicative of surface bonded water. The overall density of surface hydroxyls increases A-CA > S-CA > FS-CA.

Table S1. Cyclooctene oxidation with Mn dimer and various co-catalysts under equivalent conditions[a].

Co-Catalyst	CA/Mn	Total TON	Diol Selectivity
None	0	4	13
SiO$_2$	0	3	24
S-CA	1	147	34
S-CA	10	465	39
S-CA[b]	2	455	45
FS-CA	1	198	42
Al$_2$O$_3$-A	0	5	27
Al$_2$O$_3$-A-CA	1	3	0
Al$_2$O$_3$-N	0	1	0
Al$_2$O$_3$-N-CA	1	2	0
Al$_2$O$_3$-B	0	1	24
Al$_2$O$_3$-B-CA	1	2	19
Al$_2$O$_3$-B-CA	10	3	43
Valeric	1	17	11
Valeric	10	53	49
Valeric/SiO$_2$	10	13	14
Valeric	500	644	61

[a]All reactions were performed in batch reactor (unless otherwise noted) at 0°C with 3h reaction time, 2.0 mL acetonitrile, 0.13 mM Mn dimer, 0.17 M cis-cyclooctene, and 130 μL 30wt.% H$_2$O$_2$.

[b]Semi-batch reactions were carried out at 0 °C, 40 mL acetonitrile, 0.13 mM Mn dimer, 0.17 M cis-cyclooctene, and 2.6 mL 30 wt.% H$_2$O$_2$ added slowly over 5.91 hours (0.44 mL/hr). Data were collected after 6 h.

Table S2. Catalase (decomposition of H_2O_2) activity of **1** with and without S-CA co-catalyst.

Sample	Temperature (°C)	$[H_2O_2]$ (M)	Catalase Activity (%)
Control	0	0.74	NA
	27	0.74	NA
MeCN/**1**	0	0.43	41.9
	27	0.26	64.9
MeCN/**1**/S-CA	0	0.49	33.8
	27	0.47	36.5

[a] All reactions were performed in batch reactor with 3h reaction time.

[b] Control sample contains 2.0 mL acetonitrile, and 130 μL 30wt.% H_2O_2.

[c] All other samples contain 0.1 mM dimer, 2.0 mL acetonitrile, and 130 μL 30wt.% H_2O_2

[d] MeCN/**1**/S-CA sample contains 1.22 ± 0.17 mg S-CA (0.59 mmol CA / g).
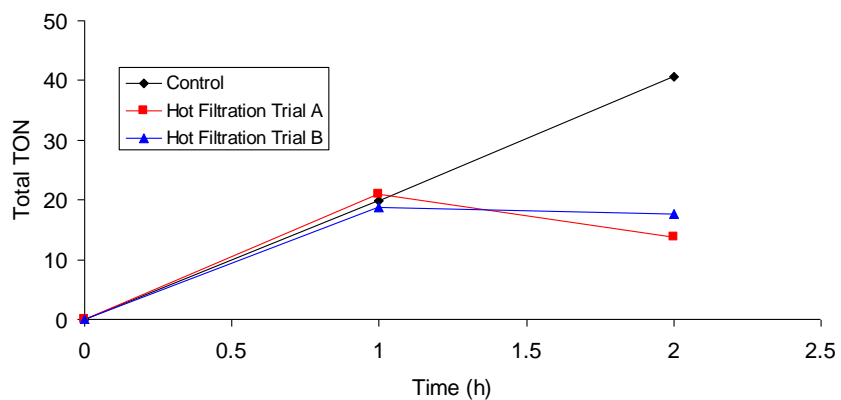

Figure S5. Leaching tests done to demonstrate heterogeneity of all catalyst activity reported in this study. The control reaction ran for 2 hours at 0 °C. Hot filtration trial A ran for one hour, at which point a sample was removed for GC analysis and simultaneously, a 1 mL portion was transferred to a new reaction vial and allowed to react an additional hour. Hot filtration trial B was run the same as trial A. except an additional fresh portion of S-CA was added to the transferred solution.

Table S3. Full conversion of cis-cyclooctene under equivalent conditions[a] with varying catalyst concentrations.

[dimer] (mM)	TON	Diol (%)	Conversion (%)
0.5	241	15	96
1.0	102	15	100
1.5	74	15	100

[a]All reactions were performed in batch reactor at 0°C with 3h reaction time, 2.0 mL acetonitrile, 0.17 M cis-cyclooctene, 100 μL dichlorobenzene and 500μL 30wt.% H_2O_2.
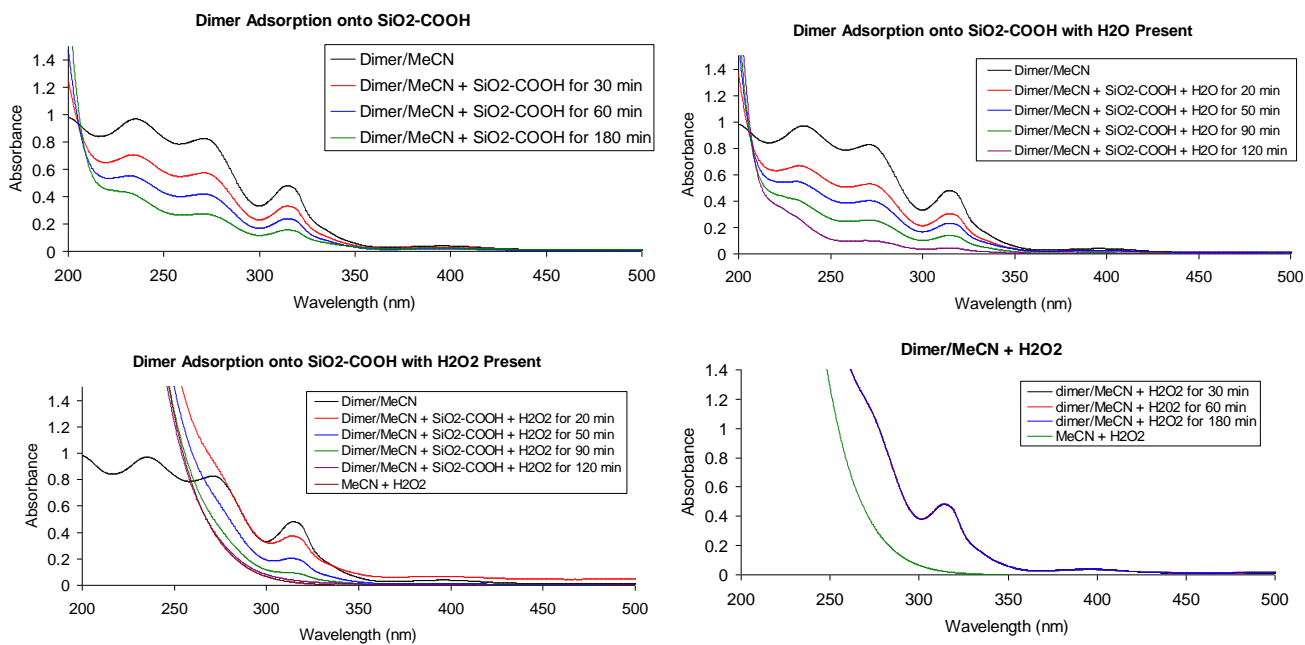

Figure S6. UV-vis solution structure of **1** in MeCN/H_2O/H_2O_2 with and without S-CA co-catalyst, demonstrating loss of solution species only as they adsorb on the co-catalyst surface
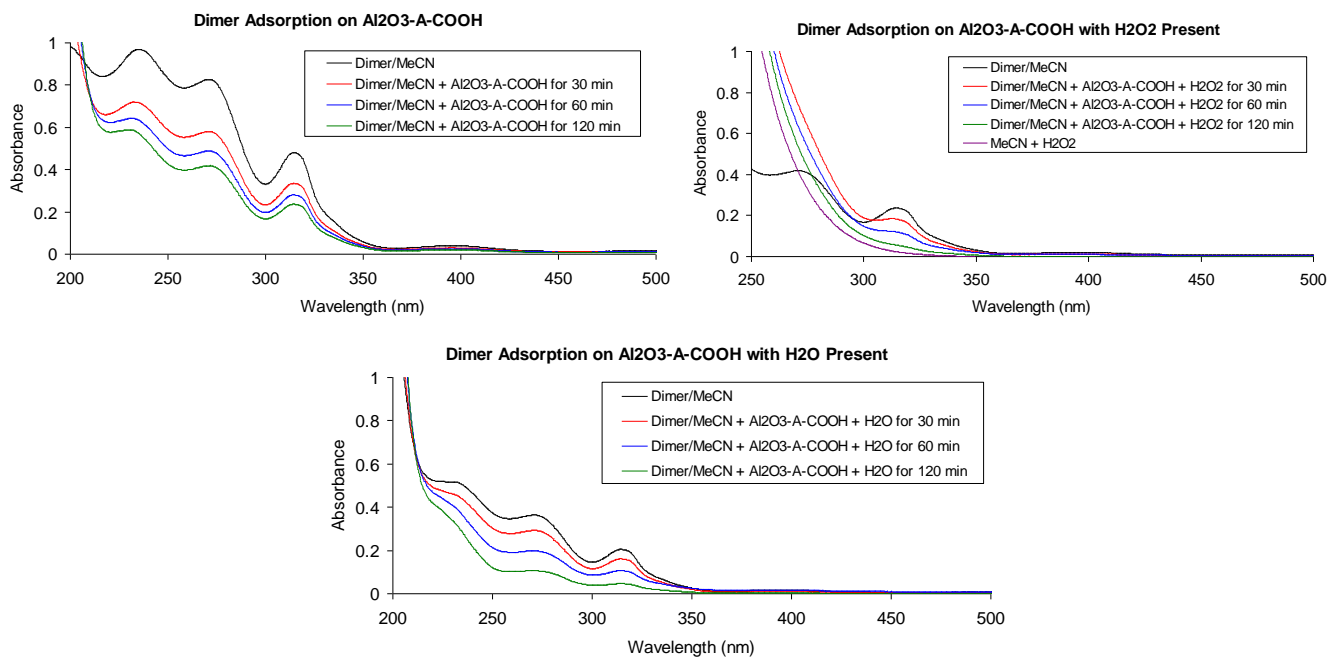
Figure S7. UV-vis solution structure of **1** in MeCN/H_2O/H_2O_2 with A-CA co-catalyst, demonstrating loss of solution species.
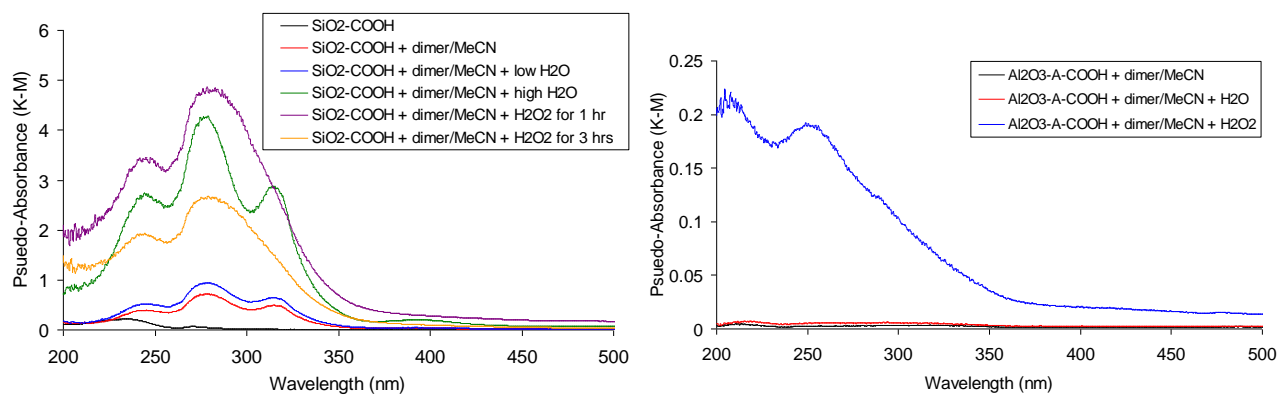

Figure S8. DR-UV-vis surface spectroscopic structure of **1** on S-CA (left) and A-CA (right) co-catalyst following various adsorption or self-catalyzed grafting techniques. Note greatly expanded scale on right.