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Solid Cocatalysts for Activating Manganese Triazacyclononane Oxidation Catalysts

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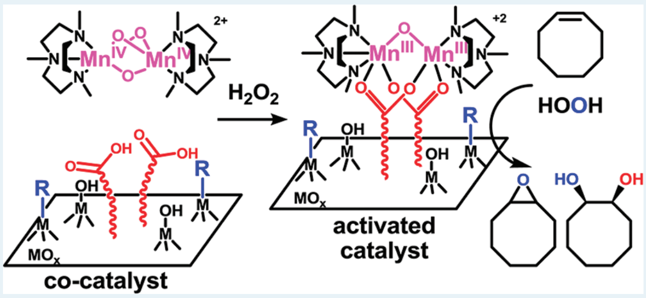
Supporting Information



ABSTRACT: Immobilizing a homogeneous catalyst provides obvious handling benefits, but ideally can also enhance catalyst productivity or selectivity because of beneficial interactions between the surface and the active site. Here, Mn 1,4,7-trimethyl-1,4,7-triazacyclononane dimers (**1**) are activated by carboxylate-containing solids for cyclooctene epoxidation/dihydroxylation with H_2O_2 at 0 °C. The productivity (TON, moles per mole **1**) and selectivity (to *cis*-diol) of cyclooctene oxidation by **1** are known to be tuned by choice of soluble carboxylate cocatalyst, and this concept is extended here to solid carboxylate cocatalysts. These solid cocatalysts are synthesized by covalently grafting benzoate and propanoate silanes to SiO_2 or allowing terephthalic acid or dihydroxyhydrocinnamic acid to chemisorb on oxides. Comparing analogous structures, SiO_2-grafted carboxylates outperform soluble benzoic acid (275 vs 25 TON at 2 equiv), hydrocinnamic acid (150 vs 40 TON at 2 equiv), and valeric acid (675 vs 70 TON at 10 equiv). Of the oxides tested as modifiers for carboxylate cocatalysts, TiO_2 leads to the largest improvements in oxidation productivity, boosting productivity to 300 TON when combined with 2 equiv of benzoic acid and to 425 TON when combined with ditopic terephthalic acid. The latter enhancement may be due to both a buffering effect and a high surface concentration of chemisorbed species that encourages formation of the presumed carboxylate-bridged active state of the catalyst. Dihydroxylation selectivities are a function of the carboxylate employed as well as the nature of the other groups on the solid cocatalyst surface. SiO_2 grafted with propionate groups gives ~50% *cis*-diol selectivity, but further modification with alkyl or perfluoroalkyl silanes increase *cis*-diol selectivity up to ~60%. Dihydroxylation selectivity is also ~60% for SiO_2 grafted with benzoate or ~70% for terephthalic acid chemisorbed on TiO_2. These solid cocatalysts introduce a number of additional tunable parameters that lead to enhanced productivity or selectivity for molecular oxidation catalysts like **1** that are activated by carboxylates.

KEYWORDS: epoxidation, cis-dihydroxylation, H_2O_2, hydrogen peroxide, heterogeneous, low-temperature, self-assembled, single site, grafted, grafting

1. INTRODUCTION

Dimeric manganese complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane, **1**, were first synthesized in the late 1980s and initially gained attention as model complexes for nonheme metalloenzyme active sites such as in catalase or the water-oxidizing center in photosystem II.[1−10] Complex **1** achieved industrial relevance when it was found to successfully bleach stains and lignin with H_2O_2 at ambient temperatures with short reaction times in both aqueous and nonaqueous media.[11−13] The complex was patented for use in wash detergents, but was ultimately removed from the market.[14,15] Subsequent investigations on **1** toward alcohol oxidation,[16−19] sulfoxidation,[20,21] and alkene epoxidation and *cis*-dihydroxylation[13,22,23] demonstrated its versatility, especially when carboxylate cocatalysts were employed. These cocatalysts increased productivity by limiting consumption of H_2O_2 (catalase activity) and helped to prevent catalyst deactivation.[17,24−28] Later it was shown that the cocatalysts form bridging carboxylates that replace μ-oxo bridges in **1**, forming reduced metal complexes such as **2′** during induction periods prior to substrate oxidation.[29−31] Varying the carboxylate cocatalyst changes activity and selectivity, especially for epoxidation and *cis*-dihydroxylation, with more electron-withdrawing carboxylates increasing productivity and bulky carboxylates increasing diol selectivity.[22−31] Due in part to the importance of assembly between the Mn complex and the carboxylate cocatalysts, the homogeneous catalyst system shows a strong dependence on solvent, residual H_2O, and pH.[11−31]

Immobilized molecular catalysts have a number of practical advantages, including ease of catalyst removal and the ability to use alternate solvents or operating conditions,[32−34] and a number of routes toward immobilizing **1** have been reported. These routes include encapsulation in zeolites[35] and covalent attachment of 1,4,7-triazacyclononane ligands onto SiO_2.[36] Recently,

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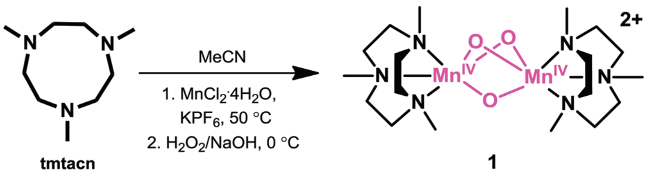
we reported that complex **1** assembles on propionate-functionalized SiO_2 under oxidation reaction conditions, forming **2** by analogy to structures formed from soluble carboxylic acids,[37] and further confirmed with X-ray absorption spectroscopy.[38] The solid cocatalyst can be used exactly like its soluble analogues without any modification of the amine ligand, and in this case, the grafted carboxylates serve both as cocatalysts and tethering moieties. The immobilized catalyst requires fewer equivalents of carboxylate and does not require slow addition of oxidant for good yields,[37,38] simplifying subsequent purification of products and improving reactor utilization. Significant changes in the reactivity of a homogeneous catalyst can occur when it is deposited on a surface. These can arise from a number of effects,[39−47] including changes to the solvent pH or polarity near the surface, or changes to the sterics and electronics at the catalytic metal because of tethering groups, nearby surface species, or the surface itself. Here, we present additional results on the role of the solid cocatalyst, carboxylate structure, and modification method in controlling total productivity and *cis*-diol versus epoxide selectivity.

2. EXPERIMENTAL SECTION

2.1. Physical Measurements. Solid state ^{13}C CP/MAS NMR spectra were recorded on a Varian 400 MHz NMR following a 120 °C sample drying period to minimize the effect of physisorbed water (adamantane external standard). An Agilent 6210 TOF LCMS was used to perform electrospray ionization mass spectrometry (ESI-MS) on samples dissolved in acetonitrile (MeCN). A TA Instruments TGA Q500 with a 10 °C/min ramp rate from room temperature to 800 °C under N_2/O_2 atmosphere was used for thermogravimetric analysis (TGA). Diffuse reflectance UV−visible (DR-UV) spectra were recorded with a Shimadzu UV-3600 UV−vis−NIR spectrophotometer using a Harrick Praying Mantis attachment. Gas chromatography (GC) was done with a Shimadzu GC-2010 gas chromatograph equipped with a Thermo Scientific TR-1 column (30 m × 0.25 mm ID × 0.25 μm) and a flame ionization detector (FID). The column oven temperature 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 at high temperature; He linear velocity was kept constant at 60 cm/s. Epoxide and diol products were identified by comparison to authentic standards and by gas chromatography mass spectroscopy (GC-MS) with a Hewlett-Packard HP 6890 Series gas chromatograph equipped with a HP 5972 Series Mass Selective Detector.

2.2. Synthesis. *2.2.1. Complex Synthesis.* All chemicals were used as received from Sigma-Aldrich unless otherwise noted. The 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) ligand can be obtained commercially (e.g., TCI America) or synthesized by established literature methods.[37,48,49] Mn tmtacn dimer, **1**, $[Mn_2(tmtacn)_2(\mu\text{-}O)_3](PF_6)_2\ H_2O$, was synthesized according to literature method (Scheme 1) by dissolving tmtacn (0.68 g, 4.0 mmol) in 8 mL of 2:1 $EtOH/H_2O$, followed by addition of $MnCl_2 \cdot 4H_2O$ (0.8 g, 1 equiv) and KPF_6 (1.1 g, 1.5 equiv).[48−50] The reaction mixture was stirred at 50 °C for 20 min, then cooled to 0 °C while stirring for 10−15 min in an ice bath. A gradual color change from creamy brown to dark brownish-red was observed upon slow addition of 8.0 mL of freshly prepared 1:1 H_2O_2 (1.5 M)/NaOH (1.0 M) solution. Red crystals of **1** were obtained following crystallization from MeCN/EtOH mixtures. The product was filtered, washed with ethanol and ether, then dried under vacuum and stored in a desiccator. Yield: 0.65 g (42%).

Scheme 1. Synthesis of the Manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (tmtacn) Dimeric Complex, 1[a]



[a] Counteranions not shown.

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).

2.2.2. Cocatalytic Solid Synthesis. Select starting properties of the solids (SiO_2, Al_2O_3, SiO_2-Al_2O_3, CeO_2, ZrO_2, MgO, TiO_2, Ti-SiO_2, and carbon) investigated in this study are given in Table 1. All oxides, unless otherwise noted, are fully hydroxylated as received and were dehydrated at 150 °C under dynamic vacuum for 12−15 h prior to subsequent modification. While not explicitly measured, surface hydroxyl densities are expected to be well in excess of the levels of carboxylate grafting. In some cases, SiO_2 was partially dehydroxylated by further heating under dynamic vacuum to 300 or 700 °C for 24 h. Various loadings of Ti supported on SiO_2 were synthesized by adding 1−2 g dehydrated SiO_2 to titanocene dichloride (Cp_2TiCl_2, 2.0−200.0 mM) in 35 mL of $CHCl_3$ with 3 equiv of triethylamine, washing, then heating to 600 °C for 2 h in air.[51] Additional details are found in the Supporting Information. Carbon (1−2 g) was ground in a mortar and pestle, transferred to filter paper packets, and Soxhlet extracted with 2.0 M HCl for 24 h. The solids were filtered, washed with 18 MΩ H_2O, EtOH, and Et_2O, and dried under dynamic vacuum. Some of these washed solids were transferred to a round-bottom flask containing 5.0 M HNO_3 (40−50 mL), and the mixture was heated at 110 °C for 24 h. This activated carbon was filtered, washed with 18 MΩ H_2O until the filtrate reached a pH > 6, dried under dynamic vacuum, and stored in a desiccator until use.

Grafted Carboxylates and Alkyl Chains. Propyltriethoxysilane (propyl), *n*-octyltrimethoxysilane (octyl), 80% perfluorododecyl-1*H*,1*H*,2*H*,2*H*-triethoxysilane/perfluoro-tetradecyl-1*H*,1*H*,2*H*,2*H*-triethoxysilane mixture (perfluoro), 1,1,1,3,3,3−hexamethyldisilazane+trimethylchlorosilane+pyridine (Sylon HTP, Sigma-Aldrich, “trimethyl”), ethyl 4-(triethoxysilyl)benzoate, and 2-(carbomethoxy)ethyltrimethoxysilane were used as obtained from Gelest, Inc. unless otherwise noted. Silanes and dehydrated/dehydroxylated oxide surfaces were handled under typical Schlenk-line conditions under N_2.

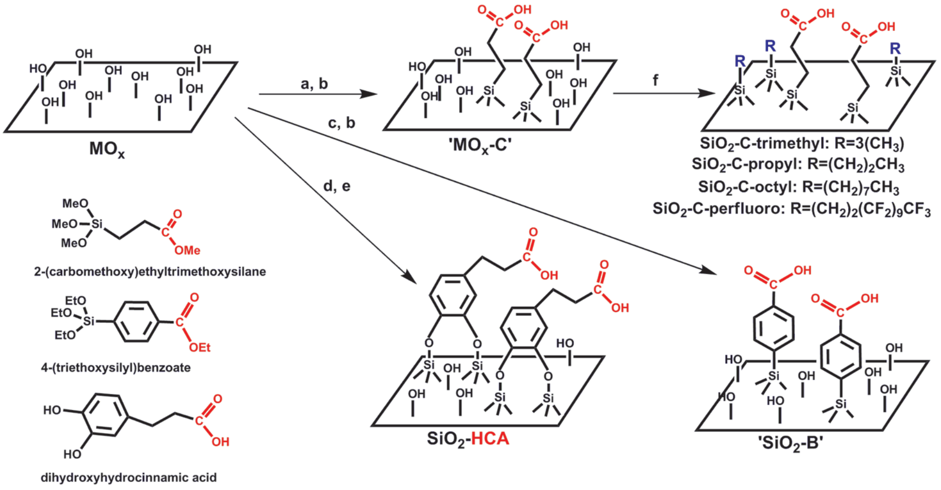
Carboxylates were grafted by adding 1−2 g dehydrated or dehydroxylated oxide (SiO_2, various Al_2O_3, Ti-SiO_2, or SiO_2-Al_2O_3) to 50 mL of anhydrous pyridine under N_2 with stirring (Scheme 2). The silane esters 2-(carbomethoxy)ethyltrimethoxysilane or ethyl 4-(triethoxysilyl)benzoate were added, typically at ~1.0 mmol silane per g oxide, and the suspension heated to reflux 24 h. The solids were isolated by filtration, washed with pyridine and ether, dried under vacuum, and Soxhlet extracted for 24 h with benzene to ensure complete removal of any ungrafted precursor. Following extraction, the solids were again filtered, washed with ether, and dried under dynamic vacuum. The ester-modified solids were converted to the carboxylic acid by refluxing for 12−24 h in 25 mL of 1.0 M HCl followed by

Table 1. Physical Properties of Solids Used in This Study

solid	grade	supplier	BET surface area (m^2 g^{-1})	particle size (μm)	suspension pH[a]
SiO_2	gel	Selecto Scientific	630	32−63	6.9
Ti-SiO_2	supported	in house	510−560[b]	32−63	5.0
Al_2O_3	γ	SASOL	200	100−250	7.2
Al_2O_3	acidic (a)	Selecto Scientific	165	53−150	4.1
Al_2O_3	neutral (n)	Selecto Scientific	165	53−150	7.1
Al_2O_3	basic (b)	Selecto Scientific	165	53−150	9.6
SiO_2-Al_2O_3 (0.3−1.3% Al)	Fumed Aerosil MOX 170	Evonik Degussa	170	<5	4.1
CeO_2	nanopowder	Sigma-Aldrich	15	<5	6.2
ZrO_2	nanopowder	Sigma-Aldrich	110	<5	7.0
MgO	nanopowder	Sigma-Aldrich	5	<5	10.5
TiO_2	Fumed Aeroxide P25	Evonik Degussa	50	<5	4.2
carbon	F600	Calgon	1700	400−1700	n/a

[a] Of 10 mL of H_2O with ~100 m^2 sample. [b] Several samples of different Ti content.

Scheme 2. Generalized Synthesis of Covalently-Modified Oxides (SiO_2-C, SiO_2-Al_2O_3-C, Ti-SiO_2-C, SiO_2-B, Al_2O_3-C, Al_2O_3-B, and SiO_2-HCA)



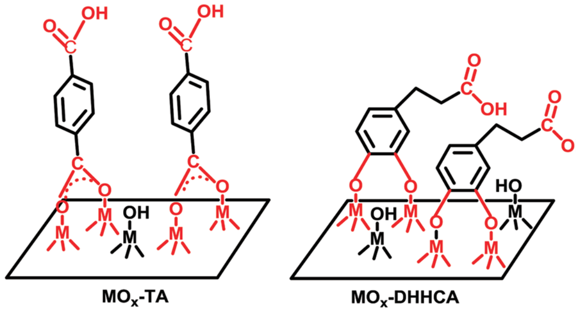
[a] 2-(carbomethoxy)ethyltrimethoxysilane in pyridine, reflux, wash; [b] HCl(aq), 100 °C; [c] 4-(triethoxysilyl)benzoate in pyridine, reflux, wash; [d] $SiCl_4$ in dichloromethane, $N(Et)_3$, stir, evaporate to dryness; [e] dihydroxyhydrocinnamic acid in pyridine, reflux, wash. Initial attachment through the carboxylate rather than the catechol is also possible, but would be unstable under washing conditions; [f] alkylsilane in pyridine, reflux, wash.

Soxhlet extraction with 18 MΩ H_2O, and drying under dynamic vacuum. [52] Materials synthesized this way are identified as the metal oxide "-C" to denote surface carboxylates synthesized from 2-(carbomethoxy)ethyltrimethoxysilane or "-B" to denote surface carboxylates synthesized from 4-(triethoxysilyl)benzoate (e.g., SiO_2-C, Al_2O_3-B, etc.). Some samples of SiO_2-C were added to an excess amount of the alkyl silanes listed above (typically 2.0 mmol silane per g SiO_2-C) in anhydrous pyridine and refluxed under N_2 for 24 h (Scheme 2). Following grafting, the solids were filtered, Soxhlet extracted with benzene for 24 h, washed with toluene and diethyl ether, and dried under dynamic vacuum. The resulting materials are denoted SiO_2-C-trimethyl, SiO_2-C-propyl, SiO_2-C-octyl, and SiO_2-C-perfluoro.

SiO_2 was also covalently modified with 3,4-dihydroxyhydrocinnamic acid (DHHCA) via a chlorinated SiO_2 surface (Scheme 2).[53,54] Dehydrated SiO_2 (1−2 g) was added to a reaction flask under N_2, $SiCl_4$ in CH_2Cl_2 (1.0 M, 4.5−9.0 mL) was added, followed by 1.0−2.0 mL of freshly distilled triethylamine, and the solution was stirred 3 h at room temperature. All volatiles were evaporated under dynamic vacuum for 12 h at 70 °C. The chlorinated SiO_2 was then added to a reaction flask containing excess DHHCA dissolved in 25 mL of anhydrous pyridine, and the mixture was refluxed for 12−24 h. The resulting material (SiO_2-HCA) was isolated by filtration, washed with acetonitrile, methanol, and 18 MΩ H_2O, then Soxhlet extracted with acetonitrile for 24 h, washed with methanol, 18 MΩ H_2O and diethyl ether, and dried under vacuum.

Chemisorbed Carboxylates. Terephthalic acid (20 mg, TA) was added to a borosilicate vial, covered with a layer of glass wool, followed by a layer of the as-received oxide (TiO_2, CeO_2, ZrO_2, SiO_2-Al_2O_3, Al_2O_3, SiO_2, Ti-SiO_2, and MgO) and a final layer of glass wool. The vial was inserted in a Schlenk tube, evacuated, sealed, and heated in a tube furnace from room temperature to 420 at 10 °C/min and held for 5 min, at which point the entire tube was removed from the furnace and allowed to cool to room temperature. Excess TA deposited outside the vial containing the

Scheme 3. Surface Structures Following Terephthalic Acid (TA) Sublimation (Left) and Dihydroxyhydrocinnamic Acid (DHHCA) in Situ Assembly (Right) on Generalized MO_x[a]



[a] Although depicted as covalent bonds, association with the surface will have a large degree of H-bond character with the surface hydroxyl groups. MO_x-DHHCA is depicted as attached through the catechol group, but it may be partially coordinated to the surface through the carboxylate, which would reduce its availability towards coordination with **1**.

now-modified solid. The vial was removed from the Schlenk tube, and the functionalized oxide was isolated (Scheme 3).[55] Materials synthesized this way are denoted as the metal oxide type followed by "-TA" (e.g., SiO_2-TA. TiO_2-TA, etc.).

Alternately, DHHCA was allowed to adsorb on oxide surfaces during reaction conditions.[56−59] Following the procedures in Section 2.3 and the ratios given in Table 5, complex **1**, DHHCA, and various oxides were suspended in MeCN. *cis*-Cyclooctene reactant, *o*-dichlorobenzene internal standard, and aqueous H_2O_2 were added to initiate the reaction. Samples for spectroscopy were isolated by filtration before addition of reactants or internal standard.

2.3. Cyclooctene Oxidation.

All chemicals were used as received from Sigma-Aldrich unless otherwise noted. *cis*-Cyclooctene was purified by distillation over powdered NaOH through a Vigreux column under N_2 atmosphere, then filtered through an activated neutral alumina column prior to use.[60]

Catalytic oxidation was carried out in Wheaton 3 mL conical reactor vials with vented Teflon caps. A desired amount of cocatalyst (oxides and/or soluble carboxylic acids), HPLC-grade MeCN (2.22 mL), and **1** (typically 0.27 mg, 0.34 μmol) were added to the reaction vial followed by distilled *cis*-cyclooctene (50 μL) and *o*-dichlorobenzene (100 μL) as internal standard. The vials were stirred and thermally equilibrated at 0 °C on a cold plate stirrer. H_2O_2 (130 μL, 30 wt % aqueous) was added, and the vial was stirred, generally for 5 h at 0 °C. A small amount of Ag powder was added at this time to terminate the reaction by decomposing remaining H_2O_2—a necessary step to eliminate olefin oxidation and product overoxidation during GC analysis. Control reactions indicated that the Ag powder did not react with or adsorb any of the reactants or products. The reaction mixture was then filtered through a Whatman GF/F syringe filter and was transferred to a GC vial for analysis. Epoxide and *cis*-diol products were compared to authentic samples by GC and GC-MS and accounted for the vast majority of the conversion. Mass balance (mmol oxidation product formed/mmol cyclooctene reacted) was found to be ≥85% for all reactions, excluding those with activated carbon cocatalysts. Turnovers (TON = mols oxidation product/mol **1**) are given ±5 TON or ±10% at higher conversion. Selectivities are ±5% absolute. No *trans*-diol product was detected in the reaction product or after deliberate reaction of epoxide with **2** under conditions equivalent to cyclooctene oxidation, demonstrating that neither acid-catalyzed ring-opening nor free radical oxidation were significant. Typically <10% of total productivity is observed as overoxidation products, principally the α-hydroxy ketone, and it is difficult to ascertain whether this overoxidation is a result of catalytic oxidation of the *cis*-diol or reaction between the *cis*-diol product and trace H_2O_2 during exposure to high temperatures in the gas chromatograph inlet.[37,38] For the purposes of this study, all overoxidation products observed were included in the *cis*-diol totals.

Table 2. Surface Loadings for Modified Oxides Used in This Study

cocatalyst	carboxylate loading (surface density) mmol g^{-1} (nm^{-2})
SiO_2-C	0.4 (0.5)
SiO_2-300-C	0.4 (0.5)
SiO_2-700-C	0.3 (0.4)
SiO_2-Al_2O_3-C	0.4 (0.5)
Al_2O_3-C	0.2 (0.8)
2.4 wt % Ti-SiO_2-C	0.7 (0.8)
SiO_2-B	0.3 (0.4)
Al_2O_3-B	0.7 (2.2)
SiO_2-HCA	0.1 (0.1)
TiO_2-TA	0.2 (2.7)
CeO_2-TA	0.1 (5.3)[a]
ZrO_2-TA	0.6 (3.3)
SiO_2-Al_2O_3-TA	0.4 (1.5)
γ-Al_2O_3-TA	0.6 (1.8)
a-Al_2O_3-TA	0.6 (2.3)
n-Al_2O_3-TA	0.9 (3.3)
b-Al_2O_3-TA	0.8 (3.0)
SiO_2-TA	0.6 (0.7)
Ti-SiO_2-TA	0.6 (0.7)
MgO-TA	0.5 (64.0)[a]

[a] High apparent surface densities indicate the presence of bulk TA crystallites, which can contribute, in principle, to oxidation reactions as soluble species.

3. RESULTS AND DISCUSSION

3.1. Materials Synthesis and Characterization.

Scheme 2 illustrates the synthetic strategy for the covalent grafting of carboxylates and alkyl chains from commercially available precursors. In all cases, the extent of grafting was estimated by quantitative O_2-TGA, normalized relative to the unfunctionalized oxide and assuming complete combustion of the organic fragment shown. These structures implicitly assume complete loss of any organosilane alkoxy groups after grafting and HCl treatment to generate the final carboxylic acid. Representative TGA curves are given in Supporting Information, Figure S3. By the described method, surface loadings of 0.4−0.6 mmol carboxylate (g SiO_2)$^{-1}$ were synthesized (Table 2). Some samples of SiO_2 were treated at 300−700 °C prior to grafting 2-(carbomethoxy)ethyltrimethoxysilane, which led to moderately reduced surface loadings for SiO_2-C materials, since surface dehydroxylation left fewer grafting points for the silanes. Other routes to materials containing covalently attached carboxylates, such as via co-condensation,[61−65]

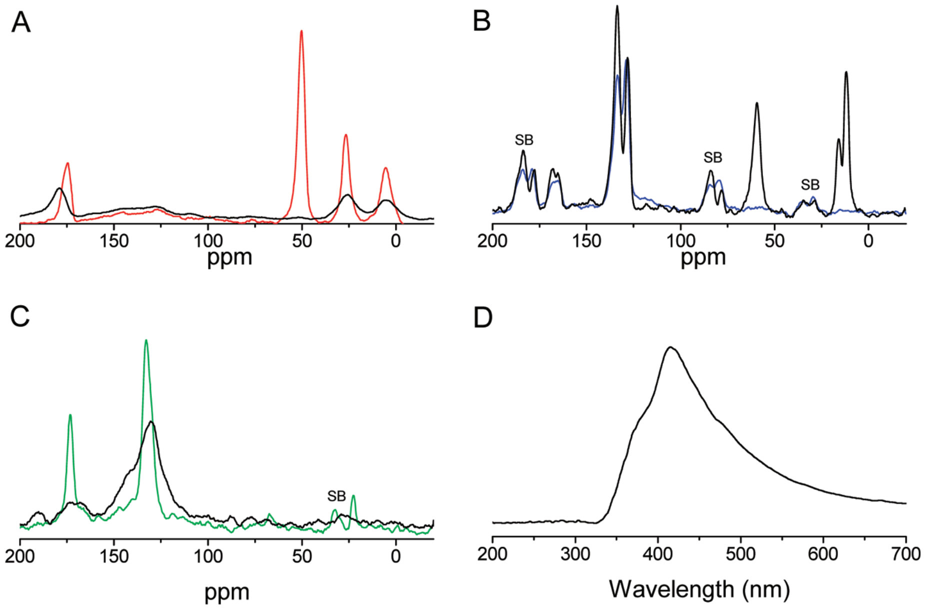


Figure 1. ^{13}C CPMAS NMR (A−C) of SiO_2 following grafting with (A) 2-(Carbomethoxy)ethytrimethoxysilane (ester, red), and the same material following deprotection to the carboxylic acid (SiO_2-C, black). (B) Ethyl 4-(triethoxysilyl)benzoate (ester, black), and the same material following deprotection to the carboxylic acid (SiO_2-B, blue). (C) Terephthalic acid modified TiO_2 (TiO_2-TA, black) and SiO_2 (SiO_2-TA, green). For all spectra "sb" denotes spinning side bands where present. For A and B sample spin rate was 5 kHz, for C spin rate was increased to 10 kHz. (D) DR-UV difference spectrum for TiO_2-DHHCA material isolated prior to substrate addition, relative to unmodified TiO_2, which reflects no light below ~350 nm. DHHCA alone or physically adsorbed on SiO_2 only show features at ~300 nm due to intrinsic $\pi-\pi^*$ transitions.

are certainly possible. In the case of sequentially modified materials (e.g., SiO_2-C-propyl), loading of the modifier was calculated similarly by normalizing against the mass loss of SiO_2-C alone (see Table 4). Scheme 3 illustrates possible structures for carboxylate-containing materials created by sublimation of TA or coordination of DHHCA onto various oxides. Loadings of TA (Table 2) were calculated from TGA weight loss profiles (Supporting Information, Figure S4) assuming complete combustion of the organic acid. The extent of DHHCA surface adsorption under reaction conditions was not quantified, and is expected to be low.

Grafting was verified by ^{13}C CP/MAS SS NMR following extensive sample washing (Figure 1A, B). SiO_2-grafted esters from 2-(carbomethoxy)ethyltrimethoxysilane show resonances at 5 and 25 ($-CH_2-$), 50 ($-OCH_3$), and 175 ($-COOR$) ppm respectively, while SiO_2-grafted esters from ethyl 4-(triethoxysilyl)benzoate show resonances at 12 and 15 ($-COO$-$CH_2\underline{C}H_3$ and residual -$SiOCH_2\underline{C}H_3$), 60 ($-COO\underline{C}H_2CH_3$ and residual -$SiO\underline{C}H_2CH_3$), 128 and 133 (aromatic), and 165 ($-COOR$) ppm, respectively. Complete conversion to the corresponding carboxylic acid (SiO_2-C and SiO_2-B) was confirmed by loss of the resonances at 50 ppm for SiO_2-C and 12, 15, and 60 ppm for SiO_2-B (residual SiOEt also removed).[52] Alkyl silanes grafted onto SiO_2-C (to form SiO_2-C-trimethyl, etc.) retain the characteristic peaks of SiO_2-C described previously, and show additional strong resonances between 0 and 35 ppm consistent with the presence of new $-CH_2-$ and $-CH_3$ groups (Figure 2). SiO_2-perfluoro also contains a broad peak centered at 114 ppm consistent with the presence of $-CF_2$- and $-CF_3$ (Figure 2D). For SiO_2-TA, (Figure 1C), a broad carboxylate resonance was observed centered at 172 ppm with aromatic resonances centered at 132 ppm. For TiO_2−TA, the characteristic resonances described for SiO_2-TA were reproduced and a new carboxylate resonance centered at 188 ppm was observed. Downfield shifts of carboxylate carbon resonance have been previously observed following complexation of carbonyl compounds with Ti (e.g., $TiCl_4$).[66] Attachment of DHHCA on TiO_2, isolated prior to substrate addition, was verified by the appearance of a catechol-to-Ti charge transfer band in the DR-UV centered at 417 nm. This band is diagnostic for direct coordination of phenolic groups to TiO_2 (Figure 1D).[67]

3.2. Epoxidation Activity and Selectivity. Previous work by others has shown that total productivity and selectivity of **1** is controlled by the structure and concentration of the carboxylic acid cocatalyst. The presumed active species is **2′**, in which two of the μ-oxo bridges of complex **1** are replaced by μ-carboxylato groups as in Scheme 4, concomitant with formal two electron reduction of the $Mn_2^{IV/IV}$ complex. The formal reduction requires that H_2O_2 be oxidized to O_2 or a reducing acid such as oxalic or citric be used. Productivity has been observed to increase with carboxylate concentration and increasing electron-withdrawing character of the bridging carboxylate; this may be due to an increase in the fraction of Mn present as **2′** instead of the relatively inert **1** or a deactivated structure that only decomposes H_2O_2. *cis*-Diol selectivity has been shown to increase with increasing bulk of the carboxylate cocatalyst,[29,30] as the transition state for dihydroxylation is apparently less constrained than that for epoxidation.

We previously reported that SiO_2 modified with propanoate groups (equivalent to SiO_2-C) serves as a cocatalyst and support for **1**, synthesizing surface structure **2** under reaction conditions (Scheme 4).[37,38] The surface structure was assigned based on spectroscopic comparisons to **2′**, similar selectivity as **2′**, and a maximum in H_2O_2 utilization at a 2/1 ratio of carboxylate/**1**. As confirmed here, the supported catalyst **2** based on SiO_2-C is much more active than **1** combined with soluble carboxylates of

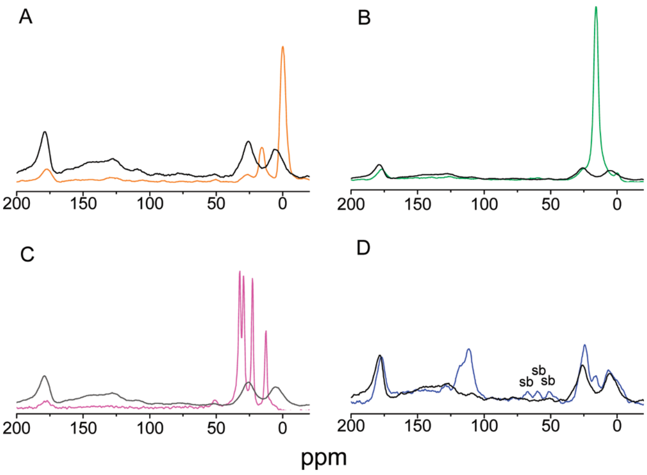
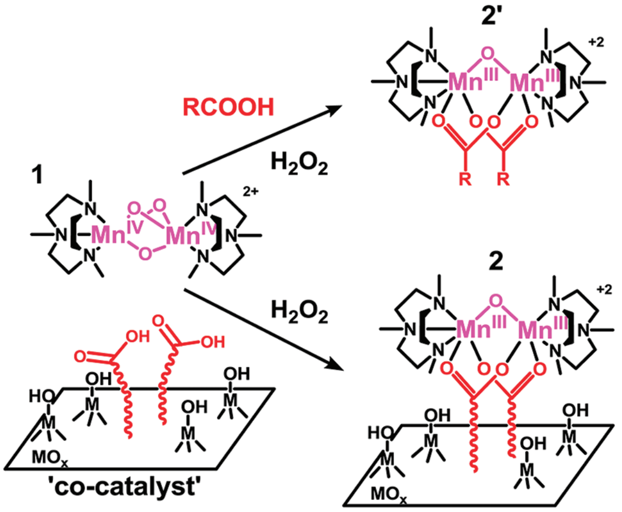


Figure 2. ^{13}C CPMAS NMR of SiO_2-C (black in each graph) following surface modification with various grafted alkyl chain silanes: (A) SiO_2-C-trimethyl, (B) SiO_2-C-propyl, (C) SiO_2-C-octyl and (D) SiO_2-C-perfluoro ("sb" denotes spinning side bands). All spectra were recorded using a sample spin rate of 5 kHz.

Scheme 4. Generalized Active Structures of the Soluble (2′) or Supported Catalyst (2) Formed from the Mn Dimer 1



analogous structure, (Figure 3, Table 3), and no evidence has been seen for significant conversion in the solution above solid SiO_2-C. (Supporting Information, Table S1). In general, SiO_2-C was shown to be a good epoxidation/dihydroxylation catalyst requiring fewer equivalents of carboxylate cocatalyst than the homogeneous system, having broad substrate scope, and negligible epoxide ring-opening for most substrates. A key question remaining was whether the selectivity and productivity could be controlled by choice of solid cocatalyst, as it can be in solution. Increased productivity is obviously desirable, as it decreases the cost of catalyst in the specialty chemicals applications where such a species would be most useful, and increased selectivity to *cis*-diols would be desired, as there are relatively few solid catalysts for this transformation, and many of those rely on precious or toxic metals.[68−73]

3.3. Grafted Carboxylates. Oxidation with **1** alone results in a total productivity of 15 TON over 5 h. As well documented in the literature, catalyst deactivation and subsequent H_2O_2 decomposition dominate over substrate oxidation when no carboxylic acid cocatalyst is present.[11−13,17,22−31,37,38] For all oxide and modified oxide cocatalysts in this paper, productivity is reported after 5 h, since all moderately productive systems have reached completion at or before that time. Some less-productive catalysts are not necessarily complete, but their slow kinetics would discourage utilization. Cocatalysts for **1** include simple carboxylic acids such as alkanoic acids like acetic or valeric acid (pentanoic acid), or benzoic acid. Here, 1−10 equiv of valeric or benzoic acid increase productivity up to ~10-fold (150 TON for 10 equiv of benzoic acid, Figure 3, Table 3). The total selectivity to *cis*-cyclooctanediol typically exceeds 60% and is higher for benzoic acid than valeric acid, consistent with a hypothesis developed for the homogeneous catalyst that steric bulk increases *cis*-diol selectivity.[29,30]

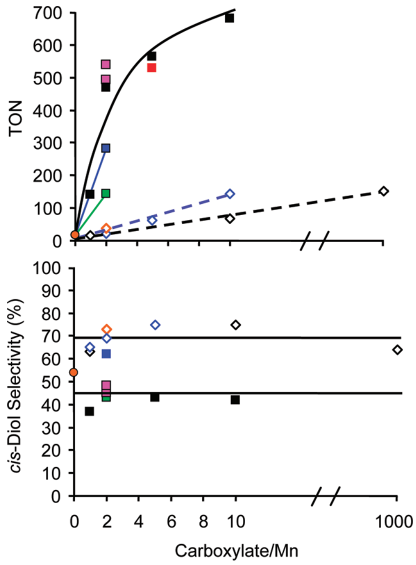


Figure 3. Catalyst productivity (above) and *cis*-diol selectivity (below) of **1** for the oxidation of *cis*-cyclooctene with solid cocatalytic solid modified with various grafted carboxylates or with soluble carboxylate cocatalysts. Lines are added as a guide to the eye. Solid black: SiO_2-C, solid pink: SiO_2-300-C and SiO_2-700-C, solid red: SiO_2-Al_2O_3-C, solid blue: SiO_2-B, solid green: SiO_2-HCA, open black: valeric acid, open blue: benzoic acid, open orange: HCA, solid orange circle: **1** alone.

More pronounced enhancements in productivity are noticed when carboxylates covalently grafted to SiO_2 (SiO_2-C, SiO $_2$-B, or SiO_2-HCA) are used as cocatalysts. As with the soluble cocatalysts, productivity increases with increasing carboxylate/Mn ratio (Figure 3, Table 3), but productivity with the solid cocatalyst always exceeds that of the analogous soluble carboxylate by as much as a factor of 10. For example, 1 equiv of grafted carboxylate results in similar productivity as 1000 equiv of valeric acid (140 and 150 TON, respectively). We assign the increased productivity to the effect of high local concentrations when carboxylates are grafted to the oxide surface.[37,38] Following the data in Table 3, these improvements cannot be replicated by simply mixing carboxylate, **1**, and SiO_2; adding SiO_2 is in fact detrimental. As for the soluble carbocylates, SiO_2-B gives higher *cis*-diol selectivity (~60%) than the alkanoic SiO_2-C or SiO_2-HCA, which we again ascribe to increased steric congestion at the coordinated Mn cluster. At the same carboxylate/Mn ratio, total productivity

Table 3. ***cis*-Cyclooctene Oxidation with 1 and Grafted Carboxylate Cocatalysts or Mixtures of Solids with Analogous Soluble Carboxylic Acids**[a]

cocatalyst	carboxylate/Mn	total TON	*cis*-diol (%)
none	0	15	55
valeric acid	1	15	65
valeric acid	10	65	75
valeric acid	1000	150	65
SiO_2 + valeric acid	10	5	50
SiO_2-C	1	140	40
SiO_2-C	2	475	45
SiO_2-300-C[b]	2	550	45
SiO_2-700-C[b]	2	500	50
SiO_2-C	5	575	45
SiO_2-C	10	675	40
SiO_2-Al_2O_3-C	5	525	45
Al_2O_3-C	2	<5	30
Al_2O_3-C	10	<5	45
HCA	2	40	75
SiO_2 + HCA	2	25	60
SiO_2-DHHCA	2	150	45
benzoic acid	2	25	70
benzoic acid	10	150	75
SiO_2 + benzoic acid	10	100	70
SiO_2-B	2	275	60
Al_2O_3-B	2	5	30
carbon[c]	n/d	55/210	50/60
activated carbon[c]	n/d	100/240	55/60

[a] Conditions: 5 h, 0 °C, MeCN, 0.14 mM 1, 0.15 M *cis*-cyclooctene, 0.51 M H_2O_2 (from 30 wt % H_2O_2). TON ± 5 or ±10%, selectivity ±5%. [b] SiO_2 treated at 300 and 700 °C, as labeled, before silane grafting. [c] 3 and 22 h reaction time. 2.0 mg added. Other reaction conditions identical.

follows SiO_2-C > SiO_2-B > SiO_2-HCA, increasing with decreasing steric bulk, which should encourage formation of the proposed active site **2** with multiple μ-carboxylato bridges. For SiO_2-C materials, productivity is minimally dependent on specific carboxylate loading, as controlled by SiO_2 dehydroxylation before grafting (Figure 3, Table 3) or by different concentrations present during synthesis. Average surface densities above 0.4 nm^{-2} (average separation less than 1.5 nm between the flexible carboxylates) appear to be sufficient to allow formation of the presumed active catalyst **2**.

The effect of further modification of the solid surface was examined with SiO_2-C-trimethyl, SiO_2-C-propyl, SiO_2-C-octyl and SiO_2-C-perfluoro. (Scheme 2, Table 4). These modified cocatalysts exhibited lower total productivities but higher *cis*-diol selectivities than SiO_2-C at similar carboxylate/Mn ratios and carboxylate surface loadings (e.g., 475 TON and 45% selectivity vs 325 TON and 60% selectivity for SiO_2-C vs SiO_2-C-trimethyl). The decreased productivity and increased selectivity are both consistent with increasing steric congestion at the surface that may not allow as many of the Mn complexes to adopt the catalytically active form, but those that do are more hindered and thus favor the *cis*-diol. The higher loading of the trimethylsilyl modification may be responsible for increasing selectivity more than for the other surface modifications.

Table 4. ***cis*-Cyclooctene Oxidation with 1 and Alkyl-Modified SiO_2-C Solid Co-Catalysts**[a]

cocatalyst	alkyl loading (surface density) mmol g^{-1} (nm^{-2})	total TON	*cis*-diol (%)
SiO_2-C		475	45
SiO_2-C-trimethyl	1.4 (1.7)	325	60
SiO_2-C-propyl	0.7 (0.8)	250	55
SiO_2-C-octyl	0.8 (1.0)	325	50
SiO_2-C-perfluoro	0.3 (0.4)	375	55

[a] Conditions: 5 h, 0 °C, MeCN, 0.14 mM **1**, 0.15 M *cis*-cyclooctene, 0.51 M H_2O_2 (from 30 wt % H_2O_2), carboxylate/Mn = 2. TON ± 5 or ±10%, selectivity ±5%.

SiO_2-Al_2O_3-C (Figure 3, Table 3) and all Ti-SiO_2-C (Supporting Information, Table S2) display productivity within 10% of SiO_2-C, suggesting that the SiO_2-based solids all have similar surface chemistry after grafting carboxylates. In contrast, all Al_2O_3-C and Al_2O_3-B cocatalysts were generally unproductive (Table 3). The apparent carboxylate surface densities on Al_2O_3-C and Al_2O_3-B were actually greater than those for SiO_2-C and SiO_2-B (Table 2), suggesting that the carboxylates on Al_2O_3 were unable to coordinate **1**, perhaps because of interactions with Lewis acidic or positively charged regions on the Al_2O_3 surface.

A special case included with this group of materials is the use of carbons, because they naturally possess carboxylate functionality. As seen in Table 3, the 22 h productivity of **1** + carbon lies between that of the soluble carboxylates and that of SiO_2-C or SiO_2-B. Activating the carbon in HNO_3 increases productivity, presumably because of an increase in the number of accessible carboxylates. Activation has a more pronounced effect at short time. The *cis*-diol selectivity of ~60% over the carbons resembles that of SiO_2-B, consistent with the activated carbon possessing benzoic acid functionality. These microporous materials have a significant drawback of long reaction times and poor mass balance (50%-60%), both of which are presumably due to diffusion and adsorption within the carbon particle. In principle however, activated carbons or glassy carbons may allow these catalysts to be used in conditions not suitable for oxides, such as in electrochemical applications.

3.4. Solid Co-Catalysts via Chemisorption on Oxides. In examining the cocatalytic role of carboxylates immobilized on oxides via chemisorption (Scheme 3), the oxidation of *cis*-cyclooctene was first carried out by **1** physically mixed with the unmodified oxide powders. Physical mixtures with oxides (SiO_2, ZrO_2, MgO, Al_2O_3) that are considered unreducible also result in negligible productivity (Table 5). In many cases, the combination of **1** and these oxides is actually detrimental to productivity relative to the oxide or **1** alone, likely because of enhanced catalyst deactivation and decomposition of H_2O_2. Selectivity to *cis*-diol is also reduced by 20−40% upon combination of these oxides with **1**. In contrast, others have observed enhancement in the productivity and *cis*-diol selectivity of Mn triazacyclononane catalysts when the ligand is covalently attached to SiO_2 but without externally added carboxylate.[36] Data in Table 5 argue that any enhancement observed in that case was due to the particular structure of the tethering group or to a change in the Mn complex nuclearity, rather than a property of the SiO_2. In contrast, for physical mixtures with TiO_2, CeO_2, SiO_2-Al_2O_3 and 2.4 wt % Ti-SiO_2, moderate synergistic behavior is seen. These oxides are negligibly catalytic on their own but enhance the productivity of

Table 5. *cis*-**Cyclooctene Oxidation by 1 in the Presence of Bare Oxides, MOx-TA, MOx-DHHCA, and Relevant Controls**[a]

		MOx + 1		MOx-TA + 1		MOx-DHHCA + 1[b]	
oxide	eq. TON w/o 1[c]	TON	*cis*-diol %	TON	*cis*-diol %	TON	*cis*-diol %
none		15	55	20 (25)[d]	30 (70)[d]	450 (--)[e] (40)[f]	60 (--)[e] (75)[f]
TiO_2	<5	55	55	425 (300)[d]	70 (70)[d]	650 (150)[e] (200)[f]	60 (70)[e] (75)[f]
CeO_2	10	30	35	300 (200)[d]	75 (70)[d]	500 (65)[e] (125)[f]	60 (60)[e] (65)[f]
ZrO_2	<5	15	30	200	75	130	60
SiO_2-Al_2O_3	5	30	40	225	66	325	60
γ-Al_2O_3	<5	5	35	110	70	250	60
a-Al_2O_3	<5	5	35	90	70	10	30
n-Al_2O_3	<5	5	35	70	65	425	60
b-Al_2O_3	<5	5	25	55	65	350	50
SiO_2	<5	<5	nd	30	50	350	50
2.4 wt % Ti-SiO_2	<5	100	55	125	65	325	55
MgO	20	10	40	10	nd	75	60

[a] Unless noted, 5 h, 0 °C, MeCN, 0.14 mM **1**, 0.15 M *cis*-cyclooctene, 0.51 M H_2O_2 (130 μL of 30 wt % H_2O_2). carboxylate/Mn = 2. TON ± 5 or ±10%, selectivity ±5% See Supporting Information, Table S3 for mass loadings of solids used. [b] Solid amounts chosen to provide similar surface area for all reactions (0.35−0.75 m^2 total). [c] Assuming an equivalent amount of **1** (0.14 mM) had been used in the reaction. [d] Physically mixed with 2 equiv of benzoic acid. [e] Physically mixed with 2 equiv of valeric acid. [f] Physically mixed with 2 equiv of HCA.

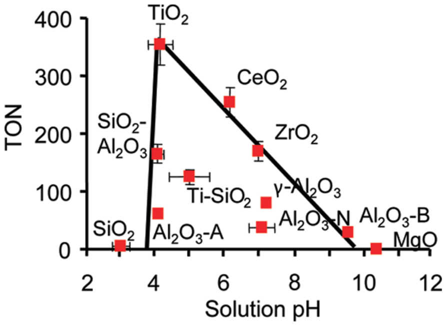


Figure 4. Observed trend between pH of H_2O suspensions of oxides (or tabulated PZC for SiO_2) and total productivity of MO_x-TA cocatalysts. After modification, the suspension pH is between 3.9 and 4.1 for all MO_x-TA cocatalysts, with the exception of MgO-TA, which remains strongly basic, and CeO_2-TA, which has a pH of 5.5. Data as given in Table 5.

1 by as much as 6-fold (2.4 wt % Ti-SiO_2). These four oxides are moderately acidic, and the productivity enhancement may be due to stabilization of a mixed oxidation state species derived from **1** that is active in epoxidation/dihydroxylation and is a poor H_2O_2 decomposition catalyst.[1] This effect must outweigh any enhancement in the background H_2O_2 decomposition under moderately acidic conditions.

The known, strong coordination of benzoates and catechols on many oxides as a way to present functional groups on surfaces not able to be modified by silane chemistry, like TiO_2 or CeO_2 (Scheme 3).[55−59] Terephthalic acid (TA) and dihydroxyhydrocinnamic acid (DHHCA) were ditopic molecules chosen for this purpose; one functional group can coordinate to the surface while the other is free to coordinate to **1**. This method of supporting carboxylates is rapid, inexpensive, and applicable to many oxides. As such, it is potentially amenable to library screening that can help discover novel reactivity. TA was thus directly sublimed onto TiO_2, CeO_2, ZrO_2, SiO_2-Al_2O_3, Al_2O_3, Ti-SiO_2, SiO_2, and MgO, and the resulting solids were used as cocatalysts with **1** for *cis*-cyclooctene oxidation (Table 4) at a constant carboxylate/Mn ratio of 2. SiO_2-TA, Ti-SiO_2-TA, and MgO-TA were not significantly more productive than what could be expected from the oxide and TA acting independently. The remaining oxides showed synergistic increases in productivity, following the trend $TiO_2 > CeO_2 > ZrO_2 \sim SiO_2\text{-}Al_2O_3 > Al_2O_3$. Many properties of the oxide surface can potentially contribute to the observed enhancements of productivity, such as the electronegativity of the metals, the charge on the oxide surface and its buffering capacity, and the TA surface density or other physical effects conducive to formation of the active catalyst **2**. Although soluble electron-withdrawing carboxylates are known to enhance productivity, metal electronegativity[74] in the various oxides is expected to only have minimal effects transmitted through the conjugated terephthalate. As evidence of this, Al_2O_3 is more electronegative than TiO_2, but Al_2O_3-TA is substantially less productive than TiO_2-TA. Carboxylate surface density, which should be high to maximize formation of **2**, also does not appear to be the deciding factor since TiO_2-TA and Al_2O_3-TA have similar TA surface densities (Table 2).

Total productivity generally appears to increase for oxides that create moderately acidic suspensions (Figure 4). Increasing acidity will weaken coordination of TA to the surface and to **1**, but will also help to activate H_2O_2. The latter effect apparently dominates, and total productivity reaches a maximum with TiO_2, whose suspensions buffer the solution near the pK_a of benzoic acid or the second pK_a of terephthalic acid. This match will stabilize the acid and conjugate base form of the TA, both of which are required in the proposed catalytic cycle.[29,30] SiO_2-Al_2O_3 and a-Al_2O_3 (which is treated with HCl during its manufacture) have strong Brønsted acid sites, which will disfavor strong coordination to the surface. SiO_2 has a low buffering capacity, and its surface is expected to be negatively charged under these conditions, again disfavoring formation of tightly coordinated surface complexes. Although the suspension pH of Ti-SiO_2 falls in an apparently ideal range, the few surface Lewis acid sites may be mostly titrated away by coordinated TA. The net effect is a proposed "volcano plot" with optimal productivity for TiO_2 and a rapid drop-off for surfaces that disfavor surface coordination because of strong acid sites or persistent negative charge (Figure 4).

The relative importance of having the carboxylates strongly coordinated to the oxide surface is seen by comparing (Table 5) cocatalysts consisting of benzoic acid (25 TON), TiO_2 (55 TON), benzoic acid + TiO_2 (300 TON), and TiO_2-TA (425 TON). As discussed above, the TiO_2 surface alone does enhance productivity of the homogeneous catalyst, perhaps by a buffering effect as proposed for other systems,[75] but using TA arranged at high density on TiO_2 further increases productivity, similar to what was seen for carboxylates covalently attached to SiO_2. These productivity enhancements demonstrate that the observed catalysis cannot be due to a soluble species, but more explicit tests of leaching will be required if this system is to be applied in flow chemistries or to renormalize turnover numbers to the number of adsorbed Mn complexes, rather than the total number of complexes. Regardless of the mechanism of productivity enhancement, TiO_2-TA, CeO_2-TA, ZrO_2-TA, and Al_2O_3-TA cocatalysts each achieved *cis*-diol selectivities of 71−74%. High selectivities to *cis*-diol are useful as there are few catalysts not requiring precious metals or toxic species (e.g., Ru or OsO_4).[66−78]

Simplifying the catalyst synthesis one step further, **1**, DHHCA, and various oxides were allowed to assemble under reaction conditions (e.g., in the presence of aqueous H_2O_2, *o*-dichlorobenzene internal standard, and *cis*-cyclooctene substrate in MeCN solution). DHHCA, like other catechols, is known to adsorb strongly to oxides such as TiO_2 and CeO_2 (Scheme 3).[56−59] As seen in Table 5 and Supporting Information, Table S4, soluble DHHCA is quite effective as a cocatalyst, and it is substantially more effective than hydrocinnamic acid (HCA). The role of the catechol OH groups may be to encourage strong association among DHHCA molecules in solution or perhaps to directly coordinate to **1**; this cocatalyst ought to be explored further on its own merits. CeO_2-DHHCA and TiO_2-DHHCA cocatalysts led to the largest total productivities, although only TiO_2-DHHCA exhibited productivities substantially larger than 2 equiv of DHHCA alone. (Table 5) The negligible or detrimental effects of the other supports presumably arise because they did not strongly adsorb the DHHCA, they adsorb DHHCA in such a way as to make the carboxylate unavailable for coordination with **1**, or they contributed significantly to undesired H_2O_2 decomposition. For most solid cocatalysts, observed *cis*-diol selectivities were generally as for the soluble DHHCA.

Similar to the other systems described above, HCA and valeric acid (as the soluble carboxylate or physically mixed with SiO_2) are ineffective cocatalysts, HCA and valeric acid physically mixed with TiO_2 or CeO_2 are improved, but TiO_2-DHHCA and CeO_2-DHHCA are the most effective cocatalysts. These comparisons demonstrate that the nature of the oxide and the coordination of the carboxylate to the oxide surface are both important to achieve high catalyst productivity.

4. CONCLUSIONS

Previous reports on the productivity and selectivity of **1** toward alkene oxidation indicated that pH buffering and high concentrations of electron-withdrawing carboxylate cocatalysts, which replace μ-oxo bridges in **1** under oxidizing conditions, generally lead to higher productivity, while carboxylates that add steric hindrance at the active site can alter the selectivity to favor *cis*-diol products over epoxides. Following our report on immobilization and activation of **1** on solid cocatalytic supports consisting of propanoate moieties grafted on SiO_2, we have expanded this behavior to alkyl and aromatic carboxylates, different oxides, and covalent grafting or chemisorption/self-assembly.

Two roles of the surface have been proposed. First, the oxide is proposed to buffer the solution near the surface, stabilizing the acid and conjugate base of the carboxylate and the active forms of the Mn complex. Second, the oxide is proposed to adsorb ditopic molecules such as DHHCA or terephthalic acid on moderately acidic oxides like CeO_2 and TiO_2 while maintaining an available carboxylate for interaction with **1**. Assembly of the carboxylates on the oxide surface creates high local concentrations and eliminates the entropic penalty to forming the catalytic assembly from **1** and two equiv of carboxylate. This in turn is proposed to place a larger fraction of the Mn catalyst in its active, carboxylate-bridged form. The importance of surface coordination is seen by the improved performance of SiO_2-C versus SiO_2 + valeric acid, TiO_2-TA versus TiO_2 + benzoic acid, or TiO_2-DHHCA versus TiO_2 + HCA. In each pair, the former carboxylate is present as high concentrations on a surface leading to high productivity, while the latter can, at most, physisorb complexes of **2** that have already formed. A number of commercially available carboxylate-containing solids (e.g., activated carbon) can also be used to activate **1**; however, the use of polymeric catalyst supports has been shown to cause difficulty in product quantification, and great care must be undertaken to ensure acceptable recovery and mass balance.

Increased selectivity to dihydroxylation is also an important finding since relatively few solid catalysts exist for this transformation. Immobilized benzoates (e.g., SiO_2-B or TiO_2-TA) are more selective than the immobilized straight chain acids (SiO_2-C or SiO_2-HCA). In particular, TiO_2-TA increased *cis*-diol selectivities to ∼70% at high productivity. Finally, this study demonstrates a number of new parameters that can be tuned without onerous ligand syntheses to give improved productivity and selectivity. Simple mixing of a ditopic molecule like DHHCA or TA, moderately acidic oxides like TiO_2 or CeO_2, and members of the large family of nonheme metalloenzyme mimics,[76−81] may allow rapid library screening for new or enhanced oxidation catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed synthetic protocols for ligand synthesis and SiO_2 functionalization with TiO_2, a description of catalyst leaching and oxide pH determination studies, as well as data from oxide characterization including TGA and DR-UV, and detailed experimental results for *cis*-cyclooctene oxidation data in support of paper figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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