Synthesis of a family of peracid-silica materials and their use as alkene epoxidation reagents

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Graphical Abstract

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Abstract

Alkene epoxidation is an important process for the production of resin monomers and other chemical intermediates. The challenges of and high costs associated with purifying these reactive intermediates motivates the search for new reagents that can afford epoxides in high yields and selectivity with no soluble byproducts. Here, we synthesize a family of silica-supported peracids with variations in the peracid surface density and surface chemistry and describe their use as epoxidation reagents. Materials in this study were synthesized from either sol-gel co-condensation with cyanoalkylsilanes or by grafting of silyl esters to pre-formed silica, giving titrated peracid loadings from 0.3 to 1.5 mmol/g. At constant peracid:alkene ratios, epoxide yields increased monotonically with increasing surface density, up to 1.0 mmol/g for the highest loading materials. Mixed silica surfaces possessing both alkyl and peracid moieties gave, at similar peracid surface densities, 2-3-fold greater olefin conversion, and doubled epoxide selectivity from 45 to >95%, as compared to materials with peracids alone. Hydrophobic, mixed silane-supported peracids give unusual, high selectivity to dioxide syntheses from dienes even at low conversion, suggesting strong adsorption of reactive intermediates, which is not possible for soluble peracids. These experiments suggest tunable parameters that lead to improvements in selectivity and yields in epoxidation with these easily-handled, immobilized peracids.

KEYWORDS *epoxidation; peroxyacid; supported reagent; sol-gel*

Introduction

The synthesis of epoxides for use in glycols and epoxy resins is an important industrial process that motivates research in selective oxidation. In the year 2000, 430,000 metric tons of epoxy resins were consumed in the US alone.[1] Reaction selectivity is a primary challenge in epoxide synthesis, and various approaches aim to prevent oxidative side-products, ring-opening, and over-oxidation of the epoxide,[2-6] in order to minimize yield losses and challenging down-stream separations. Epoxides can be unstable at high temperatures and in the presence of many acids and bases, often making purification difficult. For that reason, many epoxides, and especially multifunctional epoxides for use in epoxy resins, are only available as technical-grade mixtures of several products. Syntheses which utilize stoichiometric oxidants or additives, such as O_2 with an aldehyde, H_2O_2 with alkaline acetonitrile, or peracids, are typically undesirable as they generate stoichiometric amounts of waste that then must also be removed from the crude reaction mixture.[7-9] As in Figure 1, peracids and alkenes react to form epoxides and carboxylic acids. In addition to the challenge of removing the co-product, carboxylic acids can catalyze undesired epoxide ring opening.[10-12] Immobilized peracids, which can be used in a packed bed, were developed in hopes of addressing these concerns. Initial reports of immobilized peracids used polymeric supports,[13, 14] and reported low epoxide selectivity and, in some cases, explosive decomposition of the materials.[15] Silica-supported peracids have been reported to yield high selectivity to certain epoxides,[16][17, 18] but prior studies have focused only on a single material. Here we report on the synthesis of a series of materials with systematic variation of the peracid surface density, chain length, and presence of other alkyl groups on the surface. The reactivity of these materials in cyclohexane, styrene, and divinylbenzene epoxidation is compared to their surface and bulk properties.

Experimental

Cyclohexene, styrene, divinylbenzene (DVB), tetraethyl orthosilicate, n-dodecylamine, sodium bicarbonate, 1% starch solution, sodium thiosulfate, potassium iodide and 30% H_2O_2 (aq.), were used as received from Sigma-Aldrich. Note that DVB is only available as a technical grade containing ~15%

ethylvinyl benzene and a mixture of divinylbenzene isomers. 3-cyanopropyltriethoxysilane, cyanoethyltriethoxysilane, n-propyltriethoxysilane, ethyltriethoxysilane, methyltriethoxysilane, and 2-(carbomethoxy)ethyltrimethoxysilane were used as received from Gelest Inc. Dichlorobenzene was used as received from Alfa Aesar. Concentrated sulfuric acid, ethanol, and silica gel (Selecto Scientific, 32-63 micron particle size, 650 m²/g N₂ BET surface area, 6 nm pore diameter) were used as received from VWR, unless otherwise noted. All water was purified to 18MΩ resistivity.

Grafting of Silanes. Silanes were grafted onto silica utilizing a previously reported method (Figure 2).[19-21] Silica (Selecto) was dehydrated overnight at 120°C under dynamic vacuum. 1–2 g dehydrated silica was added to 50 mL of anhydrous pyridine in a round bottom flask under N₂ with stirring, and 2-(carbomethoxy)-ethyltriethoxysilane was added at 1.0 mmol of silane per g of silica. The suspension was then heated to reflux for 24 to 48 hours, cooled to 60°C, and isolated by filtration. The silica was washed with 50 ml of pyridine, 50 ml of ether, and Soxhlet extracted for 12 to 48 hours with toluene. After extraction, samples were collected and dried under dynamic vacuum overnight. The ester-modified solids were converted to carboxylate-silica by refluxing for 12–24 h in 25 mL of 1.0 M HCl for every 2 g of solid. After hydrolysis, samples were collected and isolated via filtration, and Soxhlet extracted with water and dried under dynamic vacuum overnight.

Synthesis of Sol-Gel Materials. Silica materials were synthesized by adapting a previously reported sol-gel synthesis procedure (Figure 3).[16] In the base case, 6.6 g (36 mmol) of n-dodecylamine was dissolved in 69 mL of ethanol, 70 mL of water was added, then the solution sonicated until no visible crystals were present. The mixture was cooled to room temperature, and 13.5 g (65 mmol) of tetraethylorthosilicate (TEOS) and 65 mmol 3-cyanopropyl triethoxysilane (CPTS) were added in succession and mixed on a shaker plate for 21 h, yielding 10 g of 1:1 TEOS:CPTS nitrile-silica. Other materials were synthesized by replacing some of the CPTS with additional TEOS under identical synthesis conditions to produce 3:1 TEOS:CPTS, 5:1 TEOS:CPTS and TEOS-only control materials. Still other materials were prepared with cyanoethyltriethoxy silane (CETS) replacing CPTS in mixtures with n-

propyltriethoxy silane (nPTES), ethyltriethoxy silane (ETES), or methyltriethoxy silane (MTES), with molar ratios given in Table 1. All as-synthesized nitrile-silica samples were collected via vacuum filtration, washed with 100 ml of ethanol and air dried, then Soxhlet extracted in ethanol overnight to remove n-dodecylamine from the pores. The solids were then collected and dried under dynamic vacuum overnight.

Nitrile-silica was hydrolyzed in two ways. In method A, 10 mL of 50% aq. H_2SO_4 were added to every gram of nitrile-silica, and the suspension was stirred and heated to reflux for 3-6 hours, following literature precedent.[16-18, 22] [23, 24] The suspension was cooled to 70°C and solids were collected via filtration. Samples were then washed with acetonitrile and water until the water exhibited a neutral pH, collected, and dried overnight under dynamic vacuum. In method B, nitrile-silica samples were suspended in 50% aq. H_2SO_4 and stirred at 80°C for 72 hours to convert surface nitriles to carboxylates. Samples were washed with acetonitrile and water until the water exhibited a neutral pH, collected, and dried overnight under dynamic vacuum.

Synthesis of peracid-silica. Following Figure 1, to every gram of carboxylate-silica, regardless of original synthesis method, 3ml of 70% H_2SO_4 was added and stirred at 0°C in a polypropylene vessel.[17, 18] 30% aqueous H_2O_2 was added in a 10:1 ratio of H_2O_2 to carboxylic acid, and the suspension was stirred for 6 hours. The material was filtered and washed with acetonitrile, then dried under vacuum at room temperature for 3 hours. Peracid loadings were determined through iodometric titrations under inert atmosphere. It should be noted that peracid materials prepared in glass vials gave markedly lower iodometric titrations.[25] After synthesis, peracid-silica materials were stored at -4°C until use. No evidence of significant peracid decomposition was observed over the space of months.

Titant for iodometric titrations was prepared with distilled water, small amounts of sodium bicarbonate to suppress bacterial growth, and $\text{Na}_2\text{S}_2\text{O}_3$ dissolved to reach 20mM. 0.1 g of peracid-silica was added to 50-100 mL water in a round bottom flask, sonicated to disperse the silica, purged with N_2 and maintained under an inert atmosphere during titration. 10ml of 20% H_2SO_4 and 10 mL of 1% (w/v) aq. KI

was added to the suspension; yellow indicated peracids. Titrant was added drop-wise until the suspension was a faint yellow, and 2 mL of starch solution was added, dying the solution dark blue. Addition of the titrant continued until the blue faded. Reported peracid loadings are reproducible to ± 0.01 mmol/g.

Characterization of Silica Materials. Prior to any characterization, samples were dried overnight at ambient temperature under dynamic vacuum in order to remove water and trace solvents from the materials. Transmission and diffuse reflectance infrared Fourier-transform spectroscopy (FT-IR and DRIFTS, respectively) used a Thermo Nicolet Nexus 870 with the Tabletop Optics Module (TOM) and KBr as a reference material. Transmission samples were ground with KBr and formed into pellets. Solid-state ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (SS ^{13}C CP/MAS NMR) was conducted on a Varian 400 MHz NMR at a spin rate of 5 kHz using adamantane as an external standard. Thermogravimetric analysis (TGA) utilized a TA Instruments Q500 thermogravimetric analyzer. Materials were heated in 100 sccm of 90%/10% O_2/N_2 at $10^\circ\text{C}/\text{min}$ to 800°C . Surface area and pore size distributions were calculated via N_2 physisorption at its normal boiling point using a Micromeritics ASAP 2010. Samples were pretreated at <5 mtorr and 120°C overnight. Surface areas and pore distributions were determined from standard BET, BJH, and t-plot methods.

Epoxidation. Cyclohexene, styrene, and divinylbenzene epoxidations were carried out in acetonitrile with 30 mM alkene and 10 mM dichlorobenzene as an internal standard. The peracid was present in 100% excess vs. titrated groups and 200% excess for styrene; % excess was varied for divinylbenzene. The reaction vessel was continuously mixed on a shaker plate at ~ 300 rpm for 1 to 24 hours at room temperature. Product solutions were filtered through a Whatman GF/F $0.7\mu\text{m}$ glass fiber syringe filter, and product distributions and yields were determined by a Shimadzu 2010 GC-MS with a SHRXI-5MS column and a temperature ramp from 60°C to 260°C at $10^\circ\text{C}/\text{min}$ and calibrated against authentic standards for cyclohexene oxidation (cyclohexene oxide, cyclohexanediol, cyclohexenone, cyclohexenol) and for styrene oxidation (styrene oxide, styrene diol, benzaldehyde, benzoic acid, and phenylacetaldehyde;

the latter two not being detected in the reaction solutions). Divinylbenzene monoxide (DVBM) and divinylbenzene dioxide (DVBD) were identified by comparison of MS fragmentation patterns. Acetamide, an oxidation product of acetonitrile solvent, was not detected in any experiment. In some cases, spent peracid materials were recovered by filtration, washed with acetonitrile and water, and again subjected to peracid synthesis condition.

Results and Discussion

Materials Characterization. DRIFTS is consistent with the conversion of nitrile groups to acids then to peracids (Figure 4 and Supporting Information Figures 1 and 2). The as-synthesized materials show a prominent $\text{C}\equiv\text{N}$ stretch at 2250 cm^{-1} , which is completely replaced by a carbonyl stretch at 1725 cm^{-1} , suggesting complete oxidation of the nitriles. After treatment with $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, a new feature appears at 1575 cm^{-1} , while the feature at 1725 cm^{-1} is reduced to a shoulder, consistent with incomplete conversion to the peracid, as determined from iodometric titration.[26] DRIFTS also rules out the possibility of adsorbed sulfate species, expected as two sharp peaks at 1103 and 1249 cm^{-1} , [27] which could contribute to the formation of a sulfate-based oxidant.

SS ^{13}C CP/MAS NMR (Figure 5 and Supporting Information Figure 3) of carboxylate-silica shows resonances at 177 ppm , which are assigned to the carboxylate. Resonances between 7 and 30 ppm are consistent with the organosilane groups. No resonances are observed that would be consistent with residual nitrile (120 - 150 ppm). In most cases, no residual surface ethoxy (50 - 70 ppm) is observed.

TGA estimates the organic group loadings on the carboxylate-silica samples. Significant mass losses are observed between 300°C and 650°C corresponding to combustion of the organic content (Supporting Information Figure 4). Mass losses are very sharp in many cases, consistent with very high loadings of the organic groups. Functional group loadings are calculated assuming all ethoxy groups are hydrolyzed in the various workup steps, and that the mass loss represents complete combustion of organosilane. In

the case of mixed organosilanes, it is assumed that the mass loss arises from loss of functional groups in the same distribution as present in the synthesis mixture.

Table 1 shows that loadings range between 1.4 and 3.8 mmol carboxylates per g for the sol-gel derived carboxylate-silica. TGA of the nitrile-silica precursor from 1:1 TEOS:CPTS gives an organic loading of 4.2 mmol/g, only 10% higher than the eventual carboxylate loading, and within the accuracy of these measurements, indicating that the nitrile is cleanly converted into the supported carboxylate. The two grafted carboxylate-silica samples have loadings of 0.8 and 1.0 mmol/g.

BET surface areas (Table 1) for all sol-gel materials range from 500-800 m²/g, as expected for these types of materials.[26] As the TEOS:CPTS ratio increases, the surface areas of these materials tend to increase. In agreement with expectation, BJH pore distributions of samples 5:1 and 1:1 TEOS:CPTS show mesoporosity and no significant microporosity (3.0 and 3.9 nm surface area-weighted average pore diameters; Figure 6 and Supporting Information Figures 5-7). The 1:1 TEOS:CPTS material shows a wider pore size distribution; silicas synthesized with higher organosilane content are typically less ordered than their low-loading counterparts. The 3:1 TEOS:CPTS sample shows only microporosity (Supporting Information Figure 7). Residual ethoxy signals in the SS ¹³C CP/MAS NMR (Supporting Information Figure 3) suggest that this composition does not completely condense and open up the pore structure. Materials containing both alkyl and carboxylate moieties also show only microporosity, with the exception of the 2:1:1 TEOS:CPTS:MTES material, which shows a mixture of micropores and poorly-ordered mesopores, based on the shape of the isotherm, the absence of a peak in the BJH pore size distribution, and the t-plot (Supporting Information Figure 5-7). Others have reported that mixed organosilanes can significantly change pore size distributions from the base case.[28] The grafted carboxylate materials gave surface areas and pore diameters moderately lower than their parent silicas, consistent with even, sub-monolayer grafting.

Titration of peracid materials. Peracid loadings determined by iodometric titration are reported in Table 1 and increase with the loading of the carboxylate from synthesis. As a negative control, bare silica ma-

materials show no titratable peroxides. The efficiency of carboxylate-to-peracid conversion is generally 25-30% for the base case 1:1 TEOS:CPTS and other materials where the nitrile is hydrolyzed in refluxing H_2SO_4 , method A. This level of peracid conversion is expected from previous reports with similar synthesis conditions.[17, 18, 23, 24] Nitrile hydrolysis method B, at lower temperatures and longer time, ultimately gives materials with higher peracid loadings and efficiencies of peracid synthesis. Peracid syntheses are an equilibrium between added H_2O_2 , carboxylate, and water. This explains the relative consistency among sets of materials, and also suggests that the improved conversion from method B-hydrolyzed materials is related to a lesser amount of silica framework hydrolysis and thus lower amounts of water trapped in the silica structure. In all cases, the final amount of titratable peracid may be lower than that originally synthesized due to decomposition during washing and intervening storage, but this is essentially unquantifiable.

The grafted materials ultimately give very low levels of the final peracid, 0.02 to 0.03 mmol/g, in spite of high carboxylate loadings. Grafted materials are less robustly attached to the silica framework vs. their co-condensed counterparts, and these low loadings may be the result of cleaving the carboxylates from their supports after the strongly oxidizing H_2O_2 / H_2SO_4 treatment.[29-31] Additionally, materials grafted under these conditions retain a high density of SiOH groups and adsorbed water, which can catalyze the peracid decomposition to the carboxylate, or prevent its formation in the first place.[32]

Cyclohexene Epoxidation. Due to the low loadings of peracids on the grafted silica materials, an unfeasibly large amount of silica is required for alkene epoxidation. These materials were not investigated further. Table 2 summarizes the epoxidation of cyclohexene by sol-gel derived peracid- SiO_2 . All reactions are carried out at room temperature. Control samples of bare silica subjected to the peracid synthesis conditions (e.g. H_2SO_4 and H_2O_2) show no substrate conversion, ruling out oxidation by adsorbed H_2O_2 , peroxy sulfonates, or other mechanisms. Across sol-gel materials, as the titrated peracid surface density increases from 0.3 to 1.0 molecules/ nm^2 , the 1-hour conversion of cyclohexene dramatically increases from 10% to 95% conversion. The lowest surface density materials show cyclohexenol as a

product, suggesting that radical oxidation mechanisms initiated by peracid decomposition at the surface are at least partially responsible for oxidation over these materials. In contrast, the highest loaded 1:1 TEOS:CPTS material gives >95% conversion and >95% selectivity to the epoxide. The regenerated 1:1 TEOS:CPTS material show markedly lower product yields, in spite of similar peracid loadings to the virgin material. The loss in activity does not appear to be connected with irreversible decomposition of the functional groups, and is instead likely due to strongly adsorbed species that inhibit catalyst access by the alkene, or residual water from the washing steps, which leads to rapid decomposition of the peracid.

For all materials, no titratable peracid remains after 6 h under reaction conditions, and thus epoxide yields can be taken as a measure of selectivity between oxygen transfer and peracid decomposition. Overall, it is believed that effective materials synthesize epoxides through direct electrophilic oxygen transfer between the alkene and the supported peracid, which is the typical mechanism of soluble peracids, [3,4] and consistent with high selectivity to the epoxide for the high-yielding materials. On the other hand, poor yields are likely caused by competitive decomposition of the peracid. Radical decomposition leads to active OH radicals, which can form oxygenated products such as cyclohexenol. Competitive oxidation of the solvent to acetamide was not observed, and typically occurs under basic conditions.[8,9] Peracid decomposition can also occur by a 2-electron route catalyzed by the acidity of surface silanols and adsorbed water, giving only the parent carboxylate and O₂ and no oxygenated products. [32] Materials with a low surface density of peracids, and thus a higher surface SiOH:peracid ratio, would be expected to be more susceptible to decomposition, as observed. It also cannot be ruled out that poorly performing materials retain higher amounts of residual sulfuric acid solution from the peracid synthesis. This would accelerate peracid decomposition to the detriment of epoxide yields.

Further comparisons amongst the mixed organosilane materials (Table 2) reveal two interesting trends. First, at similar peracid surface densities, materials containing mixed organic layers give higher cyclohexene conversion. For example, 3:2:1 TEOS:CPTS:nPTES greatly outperforms 5:1 TEOS:CPTS, and

2:1:1 TEOS:CPTS:nPTES outperforms 3:1 TEOS:CPTS, despite their nearly identical peracid loadings. Secondly, the CPTS-derived materials outperform the shorter CETS-derived materials. Likewise, materials with the longer non-functional organosilane (nPTES), outperform the shorter ETES and, especially, MTES. In the latter materials, cyclohexenol products are evidence of the dominance of uncatalyzed radical oxidation reactions. The enhanced yields may be due either to improved stability of the peracids with respect to decomposition, or to enhanced reactivity with the alkenes. Silanols are known to decompose peracids, which would reduce yields and reduce selectivity to epoxides. [25] Thus, the higher yields and selectivities associated with higher peracid densities and with longer organosilanes are consistent with their physical blocking of surface silanols, ‘fencing-in’ the peracids, and preventing peracid decomposition.

Finally, it is noted that the extent of epoxide hydrolysis to the diol is highly variable from sample to sample. In particular, 3:2:1 TEOS:CPTS:nPTES and 2:1:1 TEOS:CETS:MTES give much greater extents of hydrolysis than materials without additional organosilanes. In contrast to classical epoxidations with H_2O_2 , which generate H_2O as a co-product, these ring-opened products arise from water present on the material before the alkene solution is added. Residual water appears to be strongly sensitive to synthesis conditions, and is present even in more ostensibly hydrophobic materials. Alternate drying methods and solvents may decrease this residual water.

Styrene Epoxidation. Table 3 reports the epoxidation of styrene by supported peracid materials. Bare silica treated with H_2O_2 and H_2SO_4 yields no oxidized products. Previous reports by others gave <10% yield of products of styrene oxidation over supported peracids, and gave predominantly overoxidation products. [17, 18, 33] In contrast, under the conditions of this study, the materials synthesized here are capable of 30-40% styrene conversion with 70-80% selectivity to epoxide, the remainder being benzaldehyde. These epoxide yields are much higher than in previous reports. Overall, reactivity pat-

terns generally follow those found with cyclohexene, and the lower yields are consistent with an electrophilic oxidant.

Divinylbenzene epoxidation. A subset of materials was tested in the epoxidation of divinylbenzene (DVB). Divinylbenzene dioxide (DVBDO) is an important potential epoxy resin and a challenging reaction target. 1:1 TEOS:CPTS, with its large pores and high peracid content, was chosen for initial scoping reactions. Table 4 shows the low DVB conversion (25%) over 1:1 TEOS:CPTS, even with 3-fold excess of peracid to double bonds. Conversion was relatively insensitive to added peracid, with stoichiometric peracid giving 20% conversion and very similar product distributions.

Technical grades of DVB contain ~15% ethylvinyl benzene, and 1:1 TEOS:CPTS appears to be a relatively indiscriminate oxidant under these conditions, equally oxidizing all of the double bonds present in solution. The dioxide product DVBDO is produced roughly in proportion to the amount of the monoxide generated as the initial product from DVB epoxidation. In contrast to styrene epoxidation, however, the epoxidation of DVB does not generate detectable aldehyde over-oxidation products. The three mixed organosilane materials with high peracid loading were also tested for DVB epoxidation, and all give 10-15% conversion after 24hr with an excess of the peracid. Unexpectedly, all of these materials give predominantly the bisepoxide DVBDO, with essentially no monoxide detected for the mixed-porosity 2:1:1 TEOS:CPTS:MTES sample. DVBDO is typically produced in series from the monoxide DVBMO, so high DVBDO selectivity at low DVB conversion is very unexpected. DVBDO is the desired product for use in epoxy materials, and it is extremely difficult to purify, especially from residual DVBMO. The origin of the unusual selectivity pattern is hypothesized to be due to strong reactant adsorption on the surface of the hydrophobic mixed silane materials, and as a result, the monoxide reacts again before it diffuses away, leading to high DVBDO selectivities. Modeling the adsorption of DVB and DVBMO on the proposed active site may provide better insight into this phenomenon.

Conclusion

A variety of peracid-silica materials were synthesized for the first time, showing promise of developing new classes of supported oxidants. Grafting of peracid precursors resulted in materials with very low peracid content that were not useful for epoxidation. The development of a more efficient peracid synthesis procedure may improve peracid loadings, allowing the study of these materials as supported oxidants.

In contrast, sol-gel based syntheses were used to synthesize a set of peracid-silica materials that were shown to be capable of significant amounts of alkene epoxidation with selectivity determined by the syntheses chosen. The series of materials synthesized indicated a great dependence on both the density and the environment of the peracid. High carboxylate densities led to higher peracid loadings, and doubling of peracid density increased the 1-hour conversion of cyclohexene by a factor of 3-4. Improvement of the peracid synthesis procedure may afford even higher peracid densities. Further, the peracid environment had a large role in the activity of these materials. Materials co-condensed with additional organosilane groups displayed higher cyclohexene epoxidation activity at a given peracid loadings. In an attempt to better understand this phenomenon, materials with varying alkyl lengths and peracid lengths were synthesized, and it was seen that as the relative length of the alkyl group to the peracid group increased, the activity of these materials increased, suggesting a mechanism by which the peracids are screened from the surface and each other.

In addition to cyclohexene oxidation, these materials were shown to give much higher yields of styrene oxide than previously reported materials, presumably due to the change in surface chemistry. It was shown that a slower, lower-temperature synthesis of the grafted carboxylate from the as-synthesized gel improved ultimate peracid loadings, and further control of the water present during peracid synthesis and epoxidation may further improve styrene oxidation activity. Finally, these materials have been shown to be capable of divinylbenzene epoxidation. The desired dioxide was increased from a minority product to the primary product by altering the non-functional organosilane incorporated during silica synthesis. While the peracid content of these materials is similar, the change in alkyl precursor appears

to alter the adsorption and reaction sites on these materials. These materials demonstrate that product selectivity and the oxidation activity of a solid oxidant can be readily tailored by environment on a materials surface.

Acknowledgment. The authors acknowledge The Dow Chemical Company for financial assistance, and Dr. Kurt Hirsekorn and Dr. Dario Prieto-Centurion for helpful discussions. SS ^{13}C CP/MAS NMR spectroscopy was performed at IMSERC, funded by NSF DMR-0521267. DRIFTS experiments were carried out at NUANCE with support from NSF-NSEC, NSF-MRSEC, Keck Foundation, the State of Illinois and Northwestern University.

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Table 1. Summary of Silica Materials

Material (hydrolysis method)	Surf. area, m ² /g (pore dia., nm) ^a	Loading, mmol/g (group/nm ²)		Peracid, % ^d
		all groups ^b	peracid ^c	
5:1 TEOS:CPTS (A)	770 (3.0)	1.4 (1.1)	0.35 (0.3)	25%
3:1 TEOS:CPTS (A)	550 (mp)	1.8 (1.9)	0.5 (0.55)	30%
1:1 TEOS:CPTS (A)	590 (3.9)	3.8 (3.8)	1.0 (1.0)	25%
	590 (3.9) ^e	4.0 (4.0) ^e	0.7 (0.7) ^e	15% ^e
3:2:1 TEOS:CPTS:nPTES (A)	490 (mp)	3.7 (4.4)	0.3 (0.35)	17%
2:1:1 TEOS:CPTS:nPTES (A)	450 (mp)	3.7 (4.3)	0.5 (0.65)	27%
2:1:1 TEOS:CPTS:ETES (B)	660 (mp)	3.7 (3.3)	1.26 (1.12)	67%
2:1:1 TEOS:CETS:MTES(B)	660 (mp)	3.7 (3.3)	1.45 (1.28)	77%
2:1:1 TEOS:CPTS:MTES(B)	470 (mp)	3.7 (4.6)	1.31 (1.63)	70%
Grafted Alkyl Acid (A)	690 (6.0)	1.0 (0.9)	0.03 (0.03)	<5%

^a Surface area calculated BET isotherm of N₂ physisorption. Average pore diameter calculated from the BJH method for mesoporous materials. ‘mp’ denotes predominantly or exclusively microporous materials with no maximum in the pore size distribution above 2 nm. See supporting information Figures 5-7 for isotherms, BJH pore size distributions, and t-plots.

^b Total organic loading determined from thermogravimetric analysis

^c Peracid loading determined from iodometric titration

^d Relative to total carboxylate content, +/- 5%. Carboxylate estimated from cyanosilane fraction in synthesis, e.g., of the total 3.7 mmol/g organic in 2:1:1 TEOS:CPTS:nPTES, carboxylate is 50%, or 1.8 groups/g.

^e used in cyclohexene epoxidation and regenerated

Table 2: Epoxidation of Cyclohexene

Material	Peracid, mmol/g (nm ⁻²) ^a	Product yield, ^b 1 hr, 6hr	Product Distribution			
			epox	diol	enol	enone
5:1 TEOS:CPTS	0.35	10%	45%	0%	55%	0%
	(0.3)	15%	40%	0%	60%	0%
3:1 TEOS:CPTS	0.50	25%	90%	10%	0%	0%
	(0.55)	70%	80%	10%	0%	10%
1:1 TEOS:CPTS	0.95	>95%	>95%	0%	0%	0%
	(0.95)	n/a				
1:1 TEOS:CPTS ^c	0.80	10%	>95%	0%	0%	0%
	(0.8)	25%				
3:2:1 TEOS:CPTS:nPTES	0.30	35%	~5%	85%	0%	0%
	(0.35)	70%	10%	80%	0%	0%
2:1:1 TEOS:CPTS:nPTES	0.50	30%	80%	20%	0%	0%
	(0.6)	80%	50%	35%	0%	15%
2:1:1 TEOS:CPTS:ETES	1.26	n/a	75%	25%	0%	0%
	(1.12)	60%				
2:1:1 TEOS:CETS:MTES	1.45	n/a	15%	80%	5%	0%
	(1.28)	45%				
2:1:1 TEOS:CPTS:MTES	1.31	n/a	80%	0%	20%	0%
	(1.63)	40%				

^a by iodometric titration. As in Table 1.^b 30 mM alkene, 10 mM dichlorobenzene internal standard in acetonitrile. 1-24hr shaking at room temperature. 100% excess of peracid per cyclohexene. Reaction products quantified by GC-MS.^c regenerated

Table 3: Epoxidation of Styrene

Material	Peracid, mmol/g (nm ⁻²) ^a	24h conv. ^b	epox. sel.
5:1 TEOS:CPTS	0.35 (0.3)	20%	80%
3:1 TEOS:CPTS	0.50 (0.55)	35%	75%
1:1 TEOS:CPTS	0.95 (0.95)	30%	75%
1:1 TEOS:CPTS ^c	0.8 (0.8)	35%	70%
3:2:1 TEOS:CPTS:nPTES	0.3 (0.35)	40%	75%
2:1:1 TEOS:CPTS:nPTES	0.50 (0.6)	35%	70%
2:1:1 TEOS:CPTS:ETES	1.26 (1.12)	20%	70%
2:1:1 TEOS:CETS:MTES	1.45 (1.28)	20%	90%
2:1:1 TEOS:CPTS:MTES	1.31 (1.63)	10%	80%

^a by iodometric titration.^b 30 mM alkene, 10 mM dichlorobenzene internal standard in acetonitrile. 24hr shaking at room temperature. 200% excess of peracid per double bond. Selectivity given as % of detected products. Reaction products quantified by GC-MS; remainder benzaldehyde.^c regenerated

Table 4: Epoxidation of Divinylbenzene

Material	Peracid, mmol/g (nm ⁻²) ^a	24h conv. ^b	ox. events, mmol	EVBM0	DVBMO	DVBDO (MO:DO)
1:1TEOS:CPTS ^c	0.95 (0.95)	25%	8.3	15%	75%	10% (7.5:1)
2:1:1 TEOS:CPTS:ETES	1.26 (1.12)	15%	5.4	70%	10%	20% (1:2)
2:1:1 TEOS:CETS:MTES	1.45 (1.28)	15%	5.9	60%	5%	35% (1:7)
2:1:1 TEOS:CPTS:MTES	1.31 (1.63)	10%	5.6	15%	0%	85% (<1:15)

^a by iodometric titration.

^b 30 mM alkene, 10 mM dichlorobenzene internal standard in acetonitrile. 24hr shaking at room temperature. 200% excess of peracid per double bond. Selectivity given as % of detected products. Reaction products quantified by GC-MS; ring-opened products of DVB oxidation cannot be readily detected. EVBM0 = ethylvinylbenzene monoxide, the epoxide of the 15% impurity in DVB. Oxidation events accounts for multiple double bonds in a molecule and = EVBM0 + DVBMO + 2*DVBDO.

^c material also tested with 0%, 50%, and 100% excess peracid, giving 20%, 25%, and 30% conversion, respectively, with no significant differences in product selectivity.

Figure 1: Generalized synthesis of peracids from the corresponding grafted carboxylate in $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ and their use, in a second step, as epoxidation agents for cyclohexene, styrene, or divinylbenzene.

Figure 2: Grafting 2-(carbomethoxy)-ethyltriethoxysilane in pyridine yields an immobilized ester, converted to the carboxylate in a second hydrolysis step. Carboxylate loadings are $\sim 1. \text{nm}^{-2}$ but gave inefficient conversion to the peracid.

Figure 3: Co-condensation of TEOS, cyanosilanes, and various alkyl silanes to yield solid particles. Nitriles are converted to carboxylates by, route A), reflux in H_2SO_4 for 3-6h, or heating in H_2SO_4 for 72h at 80°C . Total organic surface densities range from $1\text{-}5. \text{nm}^{-2}$, with up to 77% conversions to peracid.

Figure 4: DRIFTS shows the conversion of 1:1 TEOS:CPTS nitrile-silica (A) into carboxylate-silica (B), then peracid-silica (C) by DRIFTS for 1:1 TEOS:CPTS. The nitrile at $\sim 2250 \text{ cm}^{-1}$ is converted into a carbonyl at 1726 cm^{-1} and then a peracid carbonyl at 1676 cm^{-1} . Scale bar corresponds to 5% reflectance. Additional spectra can be found in the supporting information.

Figure 5: Solid-State CP/MAS ^{13}C NMR of representative carboxylate-silica samples A) 3:2:1 TEOS:CPTS:nPTS and B) 5:1 TEOS:CPTS. 5 kHz spin rate. Unlabeled resonances near 20 ppm corresponds to co-condensed *n*-propyl silane groups. Additional spectra can be found in the supporting information.

Figure 6: Pore size distribution and (inset) N_2 physisorption isotherms of representative carboxylate-silica samples. A) mesoporous 1:1 TEOS:CPTS and B) microporous 3:2:1 TEOS:CPTS:nPTS. Additional isotherms and distributions can be found in the supporting information.

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