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

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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.

1. 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 Fig. 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 [16–18], 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.

2. Experimental

Cyclohexene, styrene, divinylbenzene (DVB), tetraethyl orthosilicate, n-dodecylamine, sodium bicarbonate, 1% starch solution,

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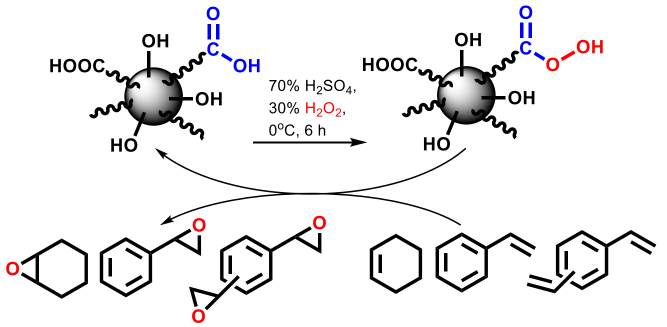

Fig. 1. Generalized synthesis of peracids from the corresponding grafted carboxylate in H_2O_2/H_2SO_4 and their use, in a second step, as epoxidation agents for cyclohexene, styrene, or divinylbenzene.

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-cyanopropyl triethoxysilane, 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 m^2/g N_2 BET surface area, 6 nm pore diameter) were used as received from VWR, unless otherwise noted. All water was purified to 18 MΩ resistivity.

2.1. Grafting of silanes

Silanes were grafted onto silica utilizing a previously reported method (Fig. 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 N_2 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 24–48 h, 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 12–48 h 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.

2.2. Synthesis of sol–gel materials

Silica materials were synthesized by adapting a previously reported sol–gel synthesis procedure (Fig. 3) [16]. In the base case, 6.6 g (36 mmol) of n-dodecylamine was dissolved in 69 mL of ethanol, then 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 tetraethyl orthosilicate (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.

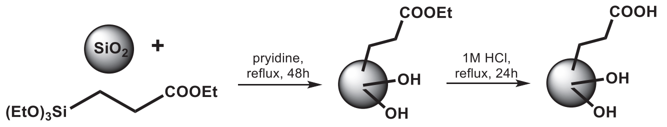

Fig. 2. Grafting 2-(carbomethoxy)-ethyltriethoxysilane in pyridine yields an immobilized ester, converted to the carboxylate in a second hydrolysis step. Carboxylate loadings are ~1 nm^{-2} but gave inefficient conversion to the peracid.

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 h, following literature precedent [16–18,22–24]. 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 h 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.

2.3. Synthesis of peracid-silica

Following Fig. 1, to every gram of carboxylate-silica, regardless of original synthesis method, 3 mL 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 h. The material was filtered and washed with acetonitrile, then dried under vacuum at room temperature for 3 h. 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.

Titrant for iodometric titrations was prepared with distilled water, small amounts of sodium bicarbonate to suppress bacterial growth, and $Na_2S_2O_3$ dissolved to reach 20 mM. 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. 10 mL of 20% H_2SO_4 and

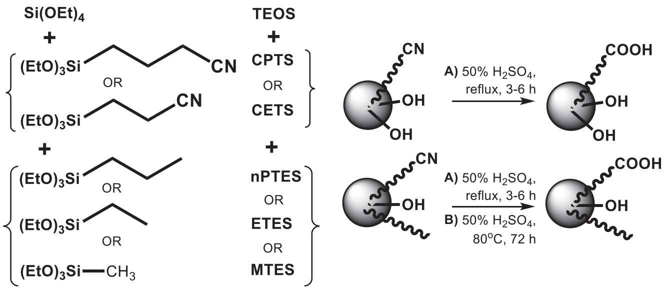

Fig. 3. Co-condensation of TEOS, cyanosilanes, and various alkyl silanes to yield solid particles. Nitriles are converted to carboxylates by, route A), reflux in H_2SO_4 for 3–6 h, or, route B), heating in H_2SO_4 for 72 h at 80 °C. Total organic surface densities range from 1 to 5 nm^{-2}, with up to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