Preparation of a silica-supported peroxycarboxylic acid and its use in the epoxidation of alkenes†

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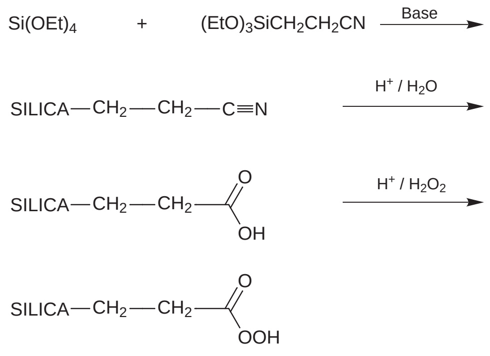
A new solid peroxyacid based on organically modified silica has been prepared and successfully applied to the epoxidation of alkenes.

Peroxyacids are active straightforward epoxidation reagents with wide application.[2] They do not require catalysts and are often excellent epoxidation reagents for unfunctionalised alkenes. Their use in epoxidation, however, is disputed because of the requirement of at least stoichiometric amounts in the reaction, resulting in the production of large amounts of acid waste. Although recycling of these acids to peroxyacids is possible by treatment with hydrogen peroxide in the presence of concentrated acids, this is normally not attractive for present-day homogeneous processes. An additional problem is that some types of the more active peroxyacids are not stable and therefore unsafe for use on a large scale. Because of these drawbacks the use of peroxyacids is not popular in industry.[3] The use of heterogeneous peroxyacids can deliver important improvements with respect to workup, recycling and stability. Heterogenisation of peroxyacids has, however, scarcely been studied and in the literature only a few examples are known where peroxyacids were supported on polystyrene resins.[4–8] Although these polymer-supported peroxyacids are active epoxidation reagents, their performance is poor due to the electron-releasing effect of the polymer backbone and their need for swelling. Furthermore, the close contact of easy oxidisable polymer backbones with strongly oxidative peroxyacids can potentially be dangerous (explosive). We now report a novel robust heterogeneous peroxyacid based on chemically modified silica, which is an active, selective and effective reagent for alkene epoxidation.

The preparation of the silica-supported peroxyacid is summarised in Scheme 1. The preparation of the cyanoethyl silica was partially based on a previously reported sol-gel method for MCM-type silicas.[9] Typically, tetraethyl orthosilicate (TEOS, 20.4 g, 98 mmol) and 2-cyanoethyltriethoxysilane (CETS, 21.3 g, 98 mmol) were added, separately, to a mechanically stirred mixture of ethanol (104 ml), water (106 ml) and *n*-dodecylamine (10 g, 54 mmol) at room temperature. A milky solution was rapidly formed, followed by precipitation. The stirring was continued for 21 h, yielding a thick white suspension. This was filtered and *n*-dodecylamine was removed by heating the solid at reflux in absolute ethanol (200 ml) for 3 h. This extraction was repeated three times. The solid was then dried in a vacuum oven at 95 °C for one night, yielding 15.2 g of a fine white solid (CN-silica). The CN-silica (10.0 g) was hydrolysed by heating it in 50% (v/v) aqueous sulfuric acid at 150 °C for 3 h. After cooling to room temperature, the silica was filtered and washed with an excess of water. Drying in a vacuum oven at 95 °C for one night afforded 10.3 g of COOH-silica. To 1 g of the COOH-silica were successively added methanesulfonic acid (3.0 g, 31 mmol) and hydrogen peroxide (70 wt% aqueous solution, 1.75 g, 36 mmol). This mixture was stirred at room temperature for 5 h. After this, the mixture was combined with 50 ml of water and filtered. The residue was thoroughly washed with an excess of water. The COOOH-silica (**1**) obtained was dried in a desiccator over KOH under vacuum for one night. Approximately 0.25 g of this desiccator-dried material was used to determine the number of peroxyacid groups by reductive titration with 0.1 M aq. $Na_2S_2O_3$ in the presence of I^-. Similarly prepared were **2** (ratio CETS:TEOS = 1:2) and **3** [3-cyanopropyltriethoxysilane (CPTS) instead of CETS, ratio CPTS:TEOS = 1:1].



Scheme 1

The epoxidation of *cis*-cyclooctene and cyclohexene to their corresponding oxides was carried out as follows. To a solution of the alkene (4 mmol) in 50 ml $CHCl_3$ was added the remaining part of the desiccator-dried COOOH-silica (0.75 g). This mixture was stirred at 30 °C for 24 h, after which it was filtered. The silica residue was washed with 25 ml $CHCl_3$. The combined filtrates were analysed by GC using 1,4-dichlorobenzene as an internal standard.

Table 1 shows that the treatment of the COOH-silicas with hydrogen peroxide in the presence of an acid resulted in materials containing peroxy groups. We confirmed that these were really supported peroxyacids by checking a blank silica. When a silica comprising TEOS only was treated in a similar way with hydrogen peroxide, no oxidation activity was found, which rules out the possibility of physically adsorbed hydrogen peroxide as the active reagent. Comparison of the peroxyacid loadings of **1** and **2** shows an interesting phenomenon. Despite the fact that the relative number of CETS groups in the synthesis of **2** was decreased by a factor 2 with respect to that of **1**, this resulted only in a reduction of the number of peroxyacid groups

Table 1 Epoxidation of *cis*-cyclooctene with silica-supported peroxyacids

Silica	1	2	3
Number peroxyacids/mmol g^{-1}	3.54	2.88	3.31
Specific surface area/m^2 g^{-1} [a]	426	1080	597
Conversion *cis*-cyclooctene (%)	55	57	62
Selectivity to cyclooctene oxide (%)	100	88	96
Efficiency of oxygen transfer (%)[b]	81	87	91

[a] Determined for the parent COOH–silica using the BET isotherm with dinitrogen as adsorbate. [b] 100 × (mmol epoxide formed)/(mmol COOOH groups per g dried silica × exact amount COOOH-silica).

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† See ref. 1

Table 2 Reagent recyclability in the epoxidation of cyclohexene with COOOH-silica **2**

Cycle	Number peroxyacids/mmol g^{-1}	Conversion (%)	Selectivity (%)	Efficiency of oxygen transfer (%)
0	2.95	57	77	81
1[a]	2.97	55	77	76

[a] The spent reagent of cycle 0 was removed by filtration, washed with $CHCl_3$, dried and subsequently regenerated. The amounts of reactant used in the regeneration process and epoxidation were adapted to the amount of spent reagent which remained after its recovery.

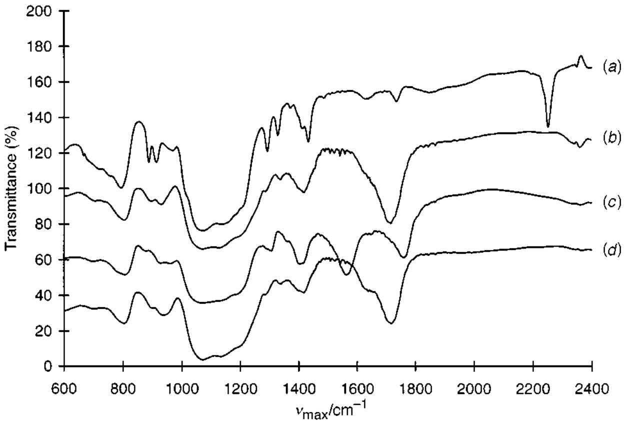

Fig. 1 DRIFT spectra of silica-supported peroxyacid **1** and its precursors: (*a*) CN-silica, (*b*) COOH-silica, (*c*) COOOH-silica **1** and (*d*) spent COOOH-silica.

in the final product by a factor of 1.2. This result may indicate a better accessibility of the carboxylic groups in the precursor of **2**, which is supported by its higher surface area.

Fig. 1 shows the DRIFT spectra of COOOH-silica **1** and its precursors. The precursors display the expected bands for CN (2252 cm^{-1}) and COOH (1715 cm^{-1}), respectively. Conversion of the COOH group into its corresponding peracid resulted, as expected,[2] in a shift of the band for the carbonyl group to higher frequencies (1760 cm^{-1}) and a spectrum consistent with that found for peracetic acid.[10] Interestingly, DRIFT also shows that the supported peroxyacid is converted into its parent acid during the epoxidation process (and neutralisation of the unreacted groups by reductive titration). This indicates that recycling is in principle possible.

Tables 1 and 2 show that the new COOOH-silicas were capable of epoxidising *cis*-cyclooctene and cyclohexene with high to excellent selectivities. In neither of the cases could by-products be detected by GC. Table 2 also shows that by giving spent COOOH-silica **2** another treatment with hydrogen peroxide/methanesulfonic acid, we managed to fully recycle the former number of peroxy groups, resulting in a silica which was still capable of epoxidising cyclohexene. Comparison of the oxygen transfer efficiencies of the silica materials with known polymer systems shows that the silica materials were much more effective in their transfer of oxygen to *cis*-cyclooctene. For example, Harrison and Hodge found for their polymer-supported peroxyacid (loading 3.5–4.0 mmol g^{-1}) a maximum efficiency of 48% only.[6] Despite the fact that we used an excess of alkene in our epoxidation experiments, the peroxy oxygens were not fully transferred to the substrate. Although decomposition of the supported peroxyacids may be responsible for the loss of oxygens (reminiscent of epoxidation with conventional peroxyacids[2]), we found in the case of **1**, by reductive titration of spent material, that the 'missing oxygens' could mainly be attributed to unreacted peroxyacid groups, indicating the presence of groups inaccessible to the alkene.

The new peroxyacid reagents have several important characteristics including loadings and activities which approach those found for conventional homogeneous peroxyacids (*e.g.* 70% MCPBA ≈ 4 mmol g^{-1}). Also, these materials appear to be stable under anhydrous conditions at room temperature (no loss in activity on drying and on storing the dry material over at least 24 h). We are currently optimising the performance of above mentioned supported peroxyacids. For this purpose, the effect of solvent and temperature will be studied in detail. Preliminary results show that epoxidation of a range of alkenes can be achieved using the new solid peroxyacid, that these materials are also effective in benign solvents such as EtOAc and that the oxygen transfer efficiencies can be further enhanced by fine-tuning of the silica synthesis and porosity.

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