Methyltrioxorhenium supported on silica tethered with polyethers as catalyst for the epoxidation of alkenes with hydrogen peroxide

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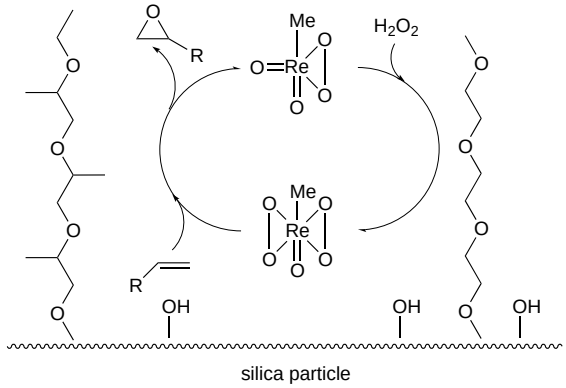
Methyltrioxorhenium has been supported on silica functionalized with polyether tethers; in the absence of an organic solvent, this catalytic assembly catalysed the epoxidation of alkenes with 30% aqueous H_2O_2 in high selectivity compared to the ring opening products observed in homogeneous media.

Simplification of catalyst recovery procedures by immobilizing selective and highly active homogeneous catalysts on a insoluble support is an ongoing endeavour designed to increase the use of catalysis in industrial settings.[1] The most common method of covalent attachment of a catalyst to an insoluble support usually yields a catalytic assembly of reduced selectivity and activity. The method of supported liquid or aqueous phase catalysis, where a film of solvent containing the catalyst is adsorbed on an insoluble particle such as silica, is an important improvement because reactions occur at a liquid–liquid interface, somewhat reducing the mass transfer limitations.[2] However, leaching of the solvent and thus catalyst still remains an important concern in such systems. We recently improved this technique of supported liquid phase catalysis by covalently attaching polyethers to a silicate particle using sol-gel procedures.[3] The attached polyether phase acted as the solvent for the catalyst (polyoxometalate) and allowed contact with one or more substrate phases.

Here we extend this concept on the use of silica with polyether tethers to a different catalytic oxidation reaction, the supported methyltrioxorhenium (MTO) catalysed epoxidation of alkenes with 30% aqueous H_2O_2. MTO has been shown to be an excellent epoxidation catalyst, with the shortcoming that the use of the necessary protic solvent leads to ring-opened products rather than epoxides.[4] Here we show that the use of methyltrioxorhenium supported on silica tethered with polyethers gives epoxides in high yields by tailoring the hydrophilic–hydrophobic balance of the polyether phase. As represented in the schematic drawing, (Scheme 1), the hydrophobic poly(propylene oxide) (PPO) units may increase the solubility of the alkene substrate in the solvent anchored phase, whereas the poly(ethylene oxide) (PEO) units serve to dissolve the aqueous hydrogen peroxide oxidant and stabilize the peroxo intermediate responsible for catalytic activity.[5]



Scheme 1

The silica particles with tethered polyether units were prepared in two steps. First, the relevant trialkoxysilanes **1**, with the appropriate polyethers groups, $(MeO)_3SiC_6H_4$-$CH_2O(CH_2CHRO)_nMe$ (R = H, Me), were prepared.† Second, the funtionalized xerogels were prepared by copolymerizing the appropriate amount of the monomer **1** and the non-functionalized monomer, $Si(OEt)_4$.‡ Typical epoxidation reactions were carried out by mixing functionalized silica, 30% H_2O_2 and MTO in small magnetically stirred vials. After stirring vigorously for about 5 min, the alkene substrates were added. The reactions were quenched by adding either CH_2Cl_2 or Et_2O to extract the substrate and products for GC and GC–MS analysis.

In order to probe the effect of the polyether tethers in the heterogeneous assembly, cyclohexene (which is known[4] to give *trans*-cyclohexane-1,2-diol as product in the homogenous aqueous–*tert*-butyl alcohol solvent system) was selected as model substrate in the current catalytic system. The results as presented in Table 1 show that MTO supported on non-functionalized silica demonstrated essentially no catalytic activity. MTO immobilized on polyether tethered silica showed several trends. Functionalization with only PEO showed increased conversion as a function of the amount of PEO, but low selectivities to epoxide. The low selectivity can be explained by the highly hydrophilic nature of the only-PEO assembly, which is similar to the homogeneous system. Use of only small amounts of PPO gave high yields but only moderate selectivities. Increased amounts of PPO without PEO reduced the conversion considerably, apparently due to the lower accessibility of the oxidant to the catalytic site. A balanced amount of both PEO and PPO gave the best results with almost quantitative (99.9%) conversion and high (86.4%) epoxide selectivity. The PPO is clearly shown to contribute to the

Table 1 Epoxidation of cyclohexene catalysed by methyltrioxorhenium supported on polyether tethered silica[a]

Polyether tether[b]	Conversion (mol%)	Selectivity (mol%)[c]
0%[d]	0.8	—
5% PEO	10.3	12.0
10% PEO	69.9	0
20% PEO	78.9	8.6
10% PEO, 5% PPO	81.6	57.2
10% PEO, 10% PPO	99.9	86.4
10% PEO, 20% PPO	33.1	84.9
4% PPO	92.4	55.9
10% PPO	19.6	64.4
20% PPO	1.0	—

[a] Reaction conditions: cyclohexene (1 mmol), 30% H_2O_2 (2 mmol), MTO (0.02 mmol) and polyether tethered silica (100 mg), room temp. 3 h. [b] The amount of polyether is the mol% of the relevant monomer used in the preparation of the silica, as described in footnote.‡ [c] Selectivity to the epoxide product; the only other product was *trans*-cyclohexane-1,2-diol. [d] Non-functionalized silica prepared by the sol-gel method.

selectivity of the reaction whereas the PEO contributes to the conversion and thus a careful balance of hydrophobic–hydrophilic characteristics§ of a silica particle can be uniquely used to maximize both the activity and selectivity of a supported catalyst. Although the effect of the polyether composition on activity and selectivity clearly indicated that the reaction was occuring in the polyether phase, additional verification showing that MTO was not dissolved in either of the reactants was possible by mixing 10% PEO, 10% PPO-SiO_2, 30% H_2O_2 and MTO for 10 min. After filtration, the filtrate (30% H_2O_2) showed no catalytic activity upon addition of cyclohexene. Similarly, mixing 10% PEO, 10% PPO-SiO_2, cyclohexene and MTO for 10 min, followed by filtration and addition of 30% H_2O_2 to the filtrate, showed no cyclohexene conversion.

In order to demonstrate the generality of this reaction, the oxidation of various other alkenes using the optimal heterogeneous system (MTO on 10% PEO–10% PPO-SiO_2) was compared to a typical homogeneous reaction using MeOH as solvent, (Table 2). Compared to the homogeneous standard, where quantitative conversions were the norm, the polyether tethered silica support showed somewhat lower activity even with more oxidant (three-fold excess) but very considerable selectivity to the epoxide, even in the case of indene whose epoxide is believed unstable under acidic conditions.[6] Oxidation of styrene also yielded benzaldehyde, the product of carbon–carbon bond cleavage. The homogeneous reaction system gave almost exclusively the ring opened products which were identified by GC–MS, except in the case of norbornene where epoxide was also observed. Finally, initial experiments were carried out to test the possibility of catalyst recycling. At the end of each reaction period the catalytic assembly was filtered under vacuum and washed with 1 ml of cold Et_2O, followed by addition of more substrate and oxidant. For four cycles the catalytic activity (85 ± 7 mol% conversion) and selectivity (89 ± 6 mol% epoxide) remained high, although there were rather considerable fluctuations. From the fifth cycle onward, both conversion and selectivity dropped considerably. Analysis by GC–MS of the reaction mixture after each cycle showed some polyether remnants, indicating that deactivation was by polyether detachment from the silica particle.

MTO supported on silica particles with polyether tethers is an effective catalytic assembly for the epoxidation of alkenes with H_2O_2 under environmentally benign conditions, *i.e.* no organic solvent. The ability to design and control the hydrophobic–hydrophilic balance of the attached polyether phase holds much promise for the development of new heterogeneous catalytic systems, especially where reactants are immiscible.

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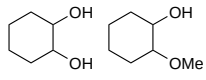
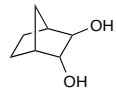
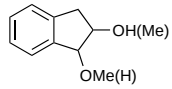
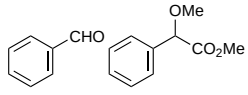
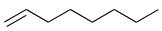
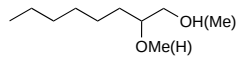
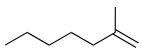
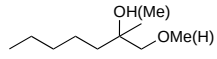
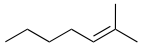
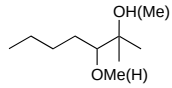
Table 2 Comparative oxidation of alkenes catalysed by methyltrioxorhenium supported on 10% PEO–10% PPO-SiO_2 *vs.* a homogeneous reaction[a]

Substrate	Conversion (mol%)[b]	Selectivity (mol%)[c]	Other products (mol%)
	99.9 (100)	86.4 (0)	 13.6 (7.9) 0 (92.1)
	94.2 (100)	71.0 (28.0)	 24.2 (64.4)
	88.5 (100)	94.3 (0)	 5.7 (100)
	83.8 (100)	33.8 (0)	 66.2 (0) 0 (100)
	62.7 (100)	100 (62.9)	 0 (37.1)
	80.2 (100)	79.4 (0)	 20.6 (100)
	72.8 (100)	93.2 (0)	 6.8 (100)

[a] Reaction conditions (heterogeneous): alkene (1 mmol), 30% H_2O_2 (3 mmol), MTO (0.02 mmol) on 10% PEO–10% PPO-SiO_2 (100 mg); (homogeneous): alkene (1 mmol), 30% H_2O_2 (2 mmol), MTO (0.02 mmol), MeOH (1 ml); 25 °C, 3 h. Values given in parentheses are for the homogeneous reaction. [b] Alkene conversion. [c] Selectivity to the epoxide product.

Footnotes and References

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† $(MeO)_3SiC_6H_4CH_2Cl$ (50 mmol) was reacted with poly(ethylene glycol) monomethyl ether (PEGME, MW = 350) (50 mmol) or poly(propylene glycol) monomethyl ether (PPGME, MW = 200) (50 mmol) in acetone (200 ml) in the presence of solid K_2CO_3 (250 mmol) at reflux for 18 h to form $(MeO)_3SiC_6H_4CH_2O(CH_2CHRO)Me$ **1a** (R = H) and **1b** (R = Me).

‡ A mixture of **1** and $Si(OEt)_4$ (total 10 mmol), water (100 mmol) and dibutyltin dilaurate (0.1 mmol) (polymerization catalyst) in acetone (40 ml) were heated at 60 °C for 3 h. The solution was kept in a beaker and the volatile organics were left to slowly evaporate over a period of two days at ambient temperature. The functionalized silica was then carefully washed twice with water and EtOH and dried *in vacuo*. Polymerization was quantitative (> 99%) as determined by microanalysis. The polymerization technique used is generally assumed to lead to a random (mixed) polymer (ref. 7). A detailed kinetic investigation of the rates of hydrolysis and self- and cross-condensation of **1** and $Si(OEt)_4$ would be required to verify this assumption and to exclude the formation of PEO and/or PPO enriched domains.

§ A wetting angle of 55° was measured for a 10% PEO–10% PPO-SiO_2 film. This wetting angle is indeed intermediate between hydrophilic (15–25°) and hydrophobic (80–100°).

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