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[20] Alcohols (*R*)- and (*S*)-**2a** were converted into the corresponding *E*- and *Z* allylic alcohols by using Red-Al or Lindlar catalyst, respectively. The olefinic products were obtained in high yield, without racemization (*ee* >99 %) and excellent *E*/*Z* ratios (Red-Al: *E*/*Z* 100:0; Lindlar catalyst: *E*/*Z* 5:95). Thus, another class of hardly known highly functionalized synthetic intermediates is easily accessible; T. Schubert, M. Müller, unpublished results.

[21] The *ee* values were determined by conversion of epoxide (*S*)-**3a** and rac-**3a** into the terminal nitrile, by treatment with a threefold excess of KCN in ethanol/water (4:1) at 50 °C for 4 h. The nitrile obtained was separated by means of HPLC on a Chiralcel OB column (20 °C, 0.5 mL min^{-1}, 'Iso-hexane'/2-propanol 95:5), $R_t = 68.6$ min ((*R*)-**3a**), 79.3 min ((*S*)-**3a**).

Titanium Silsesquioxanes Grafted on Three-Dimensionally Netted Polysiloxanes: Catalytic Ensembles for Epoxidation of Alkenes with Aqueous Hydrogen Peroxide[**]

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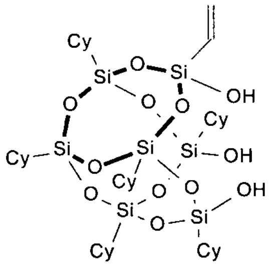
Few catalysts have been truly efficient in alkene epoxidation with aqueous hydrogen peroxide. Development of such catalysts is an important goal since with regard to desirability, this oxidant comes only second to oxygen itself.[1] Currently, the best catalyst in this field is the synthetic titanium-containing zeolite, titanium silicalite-1 (TS-1),[2] which is active for a wide range of oxidation reactions, including epoxidation.[3] For TS-1, activity seems to originate from a *combination* of a robust active Ti(OSi≡)$_n$ site ($n = 3, 4$),[4] and its location in a hydrophobic channel or cavity in the MFI (ZSM-5) structure.[5] The resulting catalytic ensemble prevents poisoning of the active site by water as well as unproductive decomposition of the oxidant. A series of titanium silsesquioxane complexes with structural elements that are very similar to the active TS-1 site have been reported to function as homogeneous catalysts.[6] Although some of these complexes are stable in aqueous media,[7] none could perform alkene epoxidation with hydrogen peroxide. It is tempting to ascribe this to the lack of a combination of the active titanium site with a suitable hydrophobic environment. The same phenomenon can acount for the lack of catalytic activity in a study by Sherrington and Alder on Ti^{IV}-grafted polysiloxane networks prepared from silanol-rich supports. These materials, showed no activity in alkene epoxidation with 30 % aqueous H_2O_2.[8] This can be ascribed to either the presence of residual silanol groups that make the materials more hydrophilic thus rendering unsuitable catalytic ensembles or to the presence of Ti centers with inappropriate structures.

Herein, epoxidation catalysts are reported that, like TS-1, epoxidize 1-octene but also substrates that are too large for TS-1 such as cyclooctene and cyclododecene. In this approach, ensembles are made from robust titanium silsesquioxane complexes. These are grafted on commercially available linear methylhydrosiloxane – dimethylsiloxane copolymers and then cross-linked by reaction with vinyl-terminated polydimethylsiloxanes. The resulting titanium polysiloxane materials are hydrophobic, three-dimensionally netted polymers that enclose the titanium sites in cavities that can, in principle, be varied according to the choice of the starting materials. Since titanium polysiloxanes are found to epoxidize alkenes with *aqueous* hydrogen peroxide, while titanium silsesquioxane complexes alone do not have this ability, we demonstrate the need for catalytic ensembles in this area of science.

Vinyl silsesquioxane trisilanol [$(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$] (**1**)[9] can be easily converted to new titanium silsesquioxane complexes [$(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_{12}TiX$] (**2a**, X = η^5-C_5H_5 (Cp), **2b**, X = O*i*Pr) by reaction with [Cl_3TiCp] or [Ti(O*i*Pr)$_4$], respectively. These reactions are similar to those previously described for the related, unfunctionalized silsesquioxane trisilanol [$(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$].[6b, 10] For both new complexes, the ^{13}C NMR spectra (400 MHz, $CDCl_3$) are particularly informative, showing four peaks for the cyclohexyl methine carbon atoms (ratio 2:1:1:2 for **2a** and 1:1:2:2 for **2b**) characteristic for C_2-symmetric, monomeric silsesquioxane titanium species. Attempts to obtain crystals of **2** suitable for X-ray analysis were unsuccessful thus far.



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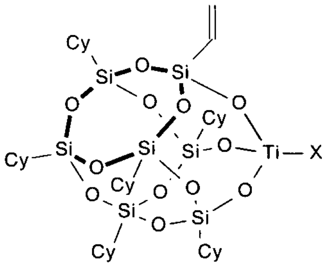

2a, X = η^5-C_5H_5
2b, X = O*i*Pr

Vinyl-bearing metallosilsesquioxanes readily undergo platinum-catalyzed hydrosilylation,[11] thus for the immobilization

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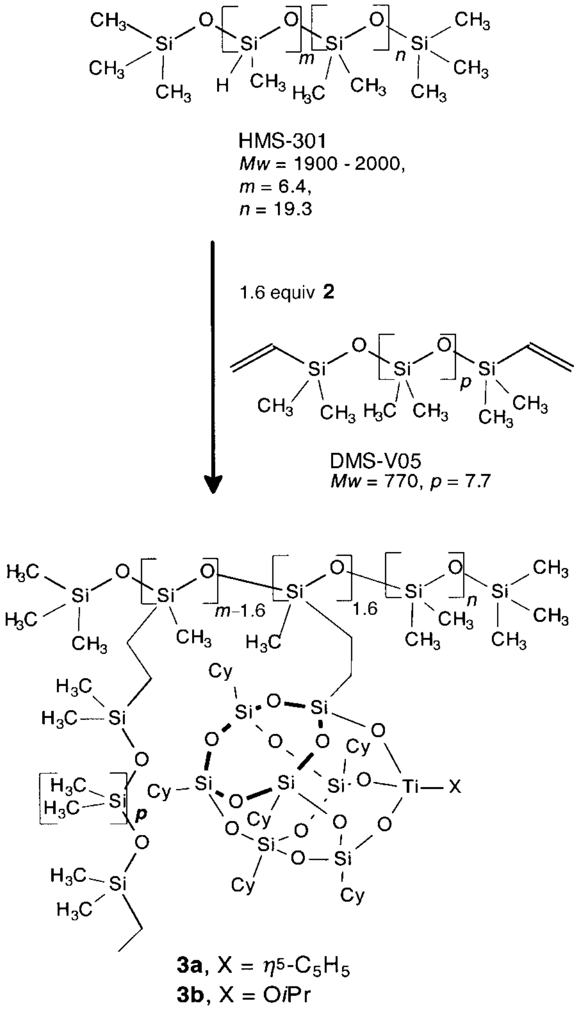
of **2**, linear methylhydrosiloxane dimethylsiloxane copolymers were chosen as a support. These copolymers are commercially available over a wide range of molecular weight and reactive silane content. Both **2a** and **2b** can be smoothly grafted on these copolymers, followed by cross-linking with the vinyl-terminated polydimethylsiloxanes DMS-V05, also conveniently available (Scheme 1), to form brittle organosiliceous materials **3**.



Scheme 1. Synthesis of three-dimensionally netted polymeric catalysts **3**.

The first step of the hydrosilylation of **2** with the methylhydrosiloxane – dimethylsiloxane copolymer HMS-301 can be monitored by ^{1} H NMR and ^{13}C NMR spectroscopy. Already half an hour after addition of the Pt hydrosilylation catalyst (ppm amounts) to the reaction mixture of **2** and HMS-301 in deuterated benzene (at the concentrations applied for polymer preparation), resonances assignable to vinyl groups have disappeared in both ^{1}H NMR and ^{13}C NMR spectra, and simultaneous changes of the cyclohexyl methine carbon pattern of the silsesquioxanes have taken place as observed by ^{13}C NMR spectroscopy.

Catalytic activity of materials **3** was first studied in the epoxidation of cyclooctene with equimolar amounts of *tert*-butylhydroperoxide (TBHP, 1.8 M in isooctane, 0.33 mol% Ti, 50 °C). From these experiments, it is clear that only grafted titanium derivatives yield truly heterogeneous catalysts. After reaction times of 24 h, 73 and 55 % conversion of cyclooctene to cyclooctene epoxide was found for **3a** and **3b**, respectively, with > 95 % selectivity. For comparison, a material **4b** related to **3b** resulting from a known, non-vinyl derivative [(c-$C_6H_{11})_7Si_7O_{12}$TiO*i*Pr],[6b] that is only physically "trapped" in the polysiloxane, was prepared by using the same polymerization procedure as for **3b**. For the system **4b**, using the same conditions as above, 61 % conversion of cyclooctene to cyclooctene epoxide was observed after 24 h. Hot filtration experiments, however, reveal that only materials **3** are truly heterogeneous catalysts, as the epoxidation stops when the polymer is filtered out of the reaction mixture. In the case of **4b** epoxidation proceeds further after filtration, due to leaching of [(c-$C_6H_{11})_7Si_7O_{12}$TiO*i*Pr] from the polymer.

Materials **3** were subsequently tested in the catalytic epoxidation of neat cyclooctene with 35 % aqueous hydrogen peroxide (H_2O_2/alkene = 1:4, 0.33 mol% Ti, 50 °C); the results are presented in Figure 1. Epoxide yields are based on the amount of peroxide used. From these experiments, it is clear that only grafted-titanium derivatives yield active catalysts in application with aqueous hydrogen peroxide. Material **4b** is less active than its fully heterogeneous analogue **3b**, despite having at least the same Ti content as **3b** (Figure 1). The lower catalytic activity of **4b** can be easily explained by leaching of [(c-$C_6H_{11})_7Si_7O_{12}$TiO*i*Pr] from the polymer, the unsupported complex being inactive in epoxidation with H_2O_2.

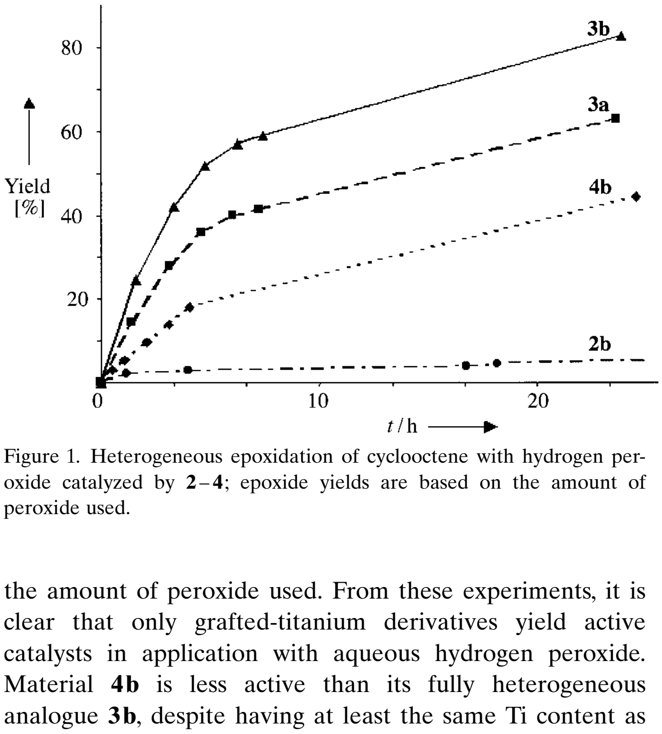


Figure 1. Heterogeneous epoxidation of cyclooctene with hydrogen peroxide catalyzed by **2**–**4**; epoxide yields are based on the amount of peroxide used.

The reaction scope of the most active catalyst **3b** was found to cover *n*-alkenes and large cyclic alkenes. For cyclododecene (H_2O_2/alkene = 1:4, 0.33 mol% Ti, 50 °C) a maximum epoxide yield of 45 % was reached; the remaining portion of the peroxide decomposed unproductively to O_2. Catalytic epoxidation with **3b** of 1-octene was optimized to give the epoxide in 62 % yield in 1.5 h (H_2O_2/alkene = 1:12, 2 mol% Ti, 80 °C); this is equivalent to a turnover frequency of about 20 h^{-1}. Reported turnover frequencies for 1-octene epoxidation by TS-1 vary from 4 to about 80 h^{-1} and generally increase significantly with increasing alkene/H_2O_2 ratios.[12] This is also valid for our systems. Since the synthesis of catalysts **3** allows an interesting degree of freedom with regard to support properties, such as tether length and the nature of the immobilized silsesquioxane complex, more active catalysts may result from further optimization. Such work is currently in progress together with comparative experiments using EURO TS-1.[12]

The results presented demonstrate that grafting of functionalized titanium silsesquioxanes on polysiloxanes provides a way to realize the formation of a catalytic ensemble that is capable of performing epoxidation with aqueous hydrogen peroxide. Clearly, the entire system is capable of outperforming the sum of its parts; it is the synergy between active site *and* its environment that allows the catalysts presented here, and likewise TS-1, or even metalloenzymes[13] to achieve their desirable performances.

Experimental Section

Synthesis of $[(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp]$ (**2a**): $[CpTiCl_3]$ (0.658 g) was added to $[(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3]$ (2.75 g, 3.00 mmol) in toluene (35 mL). Then an excess of dry pyridine (1.5 mL) was added to the mixture, which was stirred for 1 h at room temperature, filtered, and the filtrate was concentrated to about 10 mL. After addition of acetonitrile (10 mL), **2a** (2.35 g, 76% yield) was isolated as white crystals. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 6.53$ (s, 5H; C_5H_5), 6.0 (m, 3H; $CH_2{=}CH$-), 1.75 (m, 30H; CH_2-C_6H_{11}), 1.26 (m, 30H; CH_2-C_6H_{11}), 0.76 (m, 6H; CH-C_6H_{11}); ^{13}C NMR ($CDCl_3$): $\delta = 134.89$ (CH_2-vinyl), 130.97 (s, CH-vinyl), 116.26 (s, CH-Cp), 27.64, 27.57, 27.55, 27.52, 27.11, 27.01, 26.93, 26.89, 26.83, 26.77, 26.65 (s, CH_2-C_6H_{11}), 23.43, 23.22, 23.20, 23.15 (s, CH-C_6H_{11}, ratio 2:1:1:2); ^{29}Si NMR ($CDCl_3$): $\delta = -66.14$, -68.69, -69.33, -69.52 (s, *Si*-CH, 2:1:2:1 ratio), 78.01 (s, *Si*-vinyl); elemental analysis calcd (%) for $C_{43}H_{74}O_{12}Si_7Ti$: C 50.26, H 7.26; found: C 50.19, H 7.37.

Synthesis of $[(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_{12}TiO\mathit{i}Pr]$ (**2b**): $[Ti(O\mathit{i}Pr)_4]$ (0.91 mL, 3.00 mmol)) was added to $[(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3]$ (2.75 g, 3.00 mmol) in hexane (25 mL). The mixture was stirred at 50 °C for 1.5 h and the solvent was evaporated in vacuo to yield **2b** (3.03 g) as a crude white powder. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 6.06$ (m, 2H; $CH_2{=}$), 5.89 (m, 1H; $CH{=}$), 4.62 (m, 1H; $CH(CH_3)_2$), 1.77 (br m, 30H; CH_2-C_6H_{11}), 1.27 (m, 36H; CH_2-C_6H_{11} and CH_3-O*i*Pr), 0.81 (m, 6H; CH-C_6H_{11}); ^{13}C NMR ($CDCl_3$): $\delta = 135.69$ (s, CH_2-vinyl), 130.03 (s, CH-vinyl), 79.51 (s, $CH(CH_3)_2$), 27.52, 26.88, 26.83, 26.75, 26.70, 26.66 (s, CH_2), 25.65 (s, CH_3, O*i*Pr), 23.22, 23.19, 23.14, 23.09 (s, CH, 1:1:2:2 ratio); ^{29}Si NMR ($CDCl_3$): $\delta = -67.20$, -68.60, -69.36, -69.53 (s, *Si*-CH, 2:1:2:1 ratio), -78.96 (s, *Si*-vinyl); elemental analysis calcd for $C_{41}H_{76}O_{13}Si_7Ti$: C 48.21, H 7.50; found: C 49.05, H 7.82.

Immobilization of **2a** and **2b** in polysiloxane (**3**): Compound **1a** (726.9 mg) dissolved in toluene (3 mL) was added to methylhydrosiloxane–dimethylsiloxane copolymer (3.0 g; HMS-301, Gelest) diluted with toluene (4 mL) and platinum divinyltetramethyldisiloxane complex in xylene (20 mg; Gelest). The mixture was stirred at room temperature for 0.5 h, and then the Pt catalyst (20 mg) and vinyl-terminated polydimethylsiloxane DMS-V05 (2.40 g) dliuted in hexane (3 mL) was added. The reaction mixture was stirred for additional 15 min, poured into a Petri plate to evaporate the solvent and cured at 80 °C overnight. The brittle polymer was ground, and continuously extracted with diethyl ether for two days to remove ungrafted titanium. After filtration and drying polymer **3a** (5.1 g) was obtained. Elemental analysis: calcd: Ti 5.5; found: Ti 5.1 mg g^{-1}. The same procedure was applied using **2b** (720 mg) to achieve the same initial Ti content (5.5 mg Ti g^{-1} of reacting components) to give the polymer **3b** (4.8 g).

Alkene epoxidation: The epoxidation tests were carried out in 2 mL stirred batch reactors by using **3** (ca. 60 mg). For epoxidation with TBHP, TBHP (1.8 mmol) and cyclooctene (1.8 mmol) in isooctane were used. Epoxidation with aqueous H_2O_2 was carried out using H_2O_2 (35% aqueous solution) and neat alkene in the molecular ratios specified above. Excess of alkene is used here to suppress unproductive decomposition of H_2O_2 to O_2. Samples taken from the reaction mixtures were analyzed by GC analysis using a Carlo Erba GC6000 Vega Series apparatus equipped with a capillary DB-1 collumn and a FID (flame ionisation detector). For this purpose all samples contained 1,3,5-trimethylbenzene (25 μL; >98%, Merck) as GC internal standard. Epoxide yields are based on the amount of peroxide used.

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