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Tripodal titanium silsesquioxane complexes immobilized in polydimethylsiloxane (PDMS) membrane: Selective catalysts for epoxidation of cyclohexene and 1-octene with aqueous hydrogen peroxide

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ABSTRACT

We investigated the activity, epoxide selectivity, H_2O_2 efficiency, and recyclability of heterogeneous alkene epoxidation catalysts prepared by encapsulation of tripodal Ti silsesquioxane complexes in polydimethylsiloxane (PDMS) membrane. We found that $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$/PDMS (**3**) and $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$/PDMS (**4**) displayed high activity, epoxide selectivity (⩾97%), and H_2O_2 efficiency (⩾97%) in cyclohexene- and 1-octene epoxidation with aqueous H_2O_2. Moreover, these catalysts were highly recyclable. The high H_2O_2 efficiency can be attributed to the uniformly non-polar environment provided about the Ti silsesquioxane complex in **3** and **4** by the PDMS membrane, which presumably results in low local water concentrations and higher [alkene]:$[H_2O_2]$ ratios at the Ti center than in the bulk reaction medium; both of these effects favor the epoxide selectivity and minimal leaching of titanium. Our study of the effect of solvent on catalyst activity revealed that acetonitrile is to be preferred as solvent, since methanol inhibits the epoxidation at long reaction times.

1. Introduction

Tripodal Ti silsesquioxane complexes have been found to display excellent activity and selectivity in catalytic epoxidation of unactivated alkenes with alkyl hydroperoxides [1–3]. Furthermore, while heterogeneous Ti-based catalysts, such as titania-on-silica [3,4], titania–silica mixed oxides [5], and titanium silicalite-1 (TS-1) [6,7], invariably contain a range of Ti site types [3,8–10], the available evidence indicates that the tripodal Ti site is most active and selective for alkene epoxidation [1–3]. Consequently, tripodal Ti silsesquioxane complexes are attractive precursors for the preparation of well-defined heterogeneous alkene epoxidation catalysts. In this context, there have been several reports concerning the immobilization of Ti silsesquioxane complexes. The impregnation of a tripodal Ti silsesquioxane complex into the pores of MCM-41, followed by silylation of the outer surface of the MCM-41 with a bulky silane to prevent leaching of the silsesquioxane complex, has been used to prepare a material that was active in the epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) [11]. Heterogeneous Ti silsesquioxane catalysts that showed activity toward epoxidation of alkenes with aqueous hydrogen peroxide (H_2O_2) have been prepared via immobilization of tripodal Ti vinyl-silsesquioxane complexes by in situ copolymerization on a mesoporous SBA-15-supported polystyrene polymer [12], or by grafting onto a siloxane copolymer (via hydrosilylation) followed by crosslinking of the resulting polymer with a vinyl-terminated siloxane polymer [13]. However, control of the three-dimensional structure of the polymer, necessary to ensure a hydrophobic environment around the Ti complex, appears difficult by this method. On the other hand, heterogeneous catalysts containing bipodal Ti sites (such as $(\equiv SiO)_2TiCp_2$ and $(\equiv SiO)_2Ti(OBu_2)$ [14,15] and gel catalysts containing tetrapodal Ti sites (i.e. $(\equiv SiO)_4Ti$) have been reported to display activity toward the epoxidation of alkenes with H_2O_2 [16]. However, bipodal and tetrapodal Ti sites are inherently less efficient in alkene epoxidation than tripodal Ti site, as previously mentioned [2]. Hence, improved methods for the immobilization of tripodal Ti silsesquioxane complexes remain a critical need.

Herein we describe a simple and effective method for the preparation of heterogeneous alkene epoxidation catalysts by encapsulation of tripodal Ti silsesquioxane complexes in polydimethylsiloxane (PDMS) membrane. This type of immobilization relies on the physical encapsulation of the catalyst. PDMS is an excellent choice in this regard because it is hydrophobic, chemically rather inert (and is particularly resistant to oxidation), and thermally stable to 250 °C. Moreover, it has been successfully applied to the immobilization of several types of oxidation catalysts, including Jacobsen's catalyst, metallo-porphyrins, and zeolites

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[17–19]. In this study, we describe the preparation of immobilized Ti silsesquioxane catalysts [Ti(NMe$_2$){(c-C_6H_{11})$_7$Si$_7$O$_{12}$}]/PDMS (**3**) and [Ti(NMe$_2$){(i-C_4H_9)$_7$Si$_7$O$_{12}$}]/PDMS (**4**), which display high activity toward the epoxidation of cyclohexene and 1-octene, as well as excellent H_2O_2 efficiency and epoxide selectivity.

2. Experimental

2.1. Methods and materials

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. glovebox. Solvents were dried and distilled by standard methods before use [20]. Following vacuum distillation from the appropriate drying agent, $CDCl_3$ was degassed by repeated freeze–pump–thaw cycles. All solvents were stored in a glovebox over 4 Å molecular sieves that had been dried in a vacuum oven at 150 °C for at least 48 h prior to use. Unless otherwise stated, all reagents were purchased from Aldrich Chemical Company. 1-Octene (>98%) and cyclohexene were dried over activated 4 Å molecular sieves prior to use. Uncross-linked PDMS (Sylgard184) was purchased from Dow Corning Corporation and H_2O_2 solution (30%) was purchased from Mallinckrodt Baker Inc. Incompletely condensed silsesquioxanes (trisilanolalkyl-POSS) $R_7Si_7O_9(OH)_3$ (R = i-C_4H_9 and c-C_6H_{11}) were purchased from Hybrid Plastics Inc. and dried overnight under vacuum at 50 °C prior to use. The compounds Ti(NMe$_2$)$_4$ [21] and [Ti(NMe$_2$){(c-C_6H_{11})$_7$Si$_7$O$_{12}$}] (**1**) [2] were prepared according to the literature methods.

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian Gemini-200 spectrometer or a Varian VXR-400 spectrometer at room temperature unless otherwise stated. All chemical shifts are reported in units of δ (downfield from tetramethylsilane) and ^{1}H and ^{13}C chemical shifts were referenced to residual solvent peaks. ^{29}Si NMR spectra were recorded with inverse-gated proton decoupling in order to increase resolution and minimize nuclear Overhauser enhancement effects. To ensure accurate integrated intensities, [Cr(acac)$_3$] (0.05 M) was added to ^{13}C and ^{29}Si NMR samples as a shiftless relaxation agent and a delay of at least 5 s was used between observation pulses for ^{13}C measurements and 10 s for ^{29}Si measurements. GC analyses were performed on a Shimadzu GC-17A instrument with flame ionization detection (FID), a 60 m × 0.32 mm (0.25 mm film thickness) Agilent JW Scientific DB-5 GC column, and helium as carrier gas. An injection temperature of 140 °C was employed, which was found to be sufficiently low to avoid the occurrence of secondary reactions in the injection port. UV–vis spectra were collected in the absorption mode on an Agilent 8453 spectrophotometer using a direct insertion method. Infrared spectra were obtained on a Mattson Galaxy Series FTIR 5000 spectrophotometer. Proton-induced X-ray emission (PIXE) analyses for Ti were performed by Elemental Analysis Inc., Lexington, KY. The analytical error is estimated at ±1% (relative). Elemental analysis for C, H, and N was performed by Complete Analysis Laboratories Inc., Parsippany, NJ.

2.1.1. Synthesis of [Ti(NMe$_2$){(i-C_4H_9)$_7$Si$_7$O$_{12}$}] (2)

Ti(NMe$_2$)$_4$ (0.200 g, 0.892 mmol) was added via syringe to a stirred solution of (i-C_4H_9)$_7$Si$_7$O$_9$(OH)$_3$ (0.68 g, 0.859 mmol) in diethyl ether (10 mL). Stirring the reaction mixture at room temperature for 18 h afforded a deep yellow mixture, which was filtered. The filtrate was reduced to dryness under vacuum and the residue was dissolved in toluene. Acetonitrile was added dropwise to precipitate **2** as a yellow microcrystalline solid, which was isolated by filtration, washed with acetonitrile (3 × 5 mL) and dried under vacuum. Yield: 0.732 g, 97%. ^{1}H NMR ($CDCl_3$): δ 3.19 (s, 6H, NMe$_2$), 1.84 (m, 7H, $CH_2CH(CH_3)_2$), 0.94 (br d, 42H, $CH_2CH(CH_3)_2$), 0.56 (br d, 14H, $CH_2CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 45.14 (s, NMe$_2$), 26.00, 25.92 (overlapping s, $CH_2CH(CH_3)_2$), 24.27, 24.16 (overlapping s, $CH_2CH(CH_3)_2$), 22.92, 22.81, 22.76 (s, 3:1:3 for $CH_2CH(CH_3)_2$). ^{29}Si NMR ($CDCl_3$): δ −65.23, −67.89, −68.96, (3:1:3). Anal. Calcd. for $C_{30}H_{69}NO_{12}Si_7Ti$: C, 40.93; H, 7.90. Found: C, 40.81; H, 8.01.

2.2. Incorporation of tripodal Ti silsesquioxane complexes into PDMS membranes

Sylgard184 is sold as two components, prepolymer (RTV 615A) and crosslinker (RTV 615B), that are mixed in a 10:1 ratio and heated to fully cure. The PDMS membrane was prepared by modification of a literature method [22]. The PDMS slabs were dried overnight at 65 °C. Each slab was cut into irregular pieces with dimensions ranging from 1 mm to 1 cm; these were later cut into smaller pieces for ease of handling.

2.2.1. [Ti(NMe$_2$){(c-C_6H_{11})$_7$Si$_7$O$_{12}$}]/PDMS (3)

A CH_2Cl_2 solution (0.8 mL) of [Ti(NMe$_2$){(c-C_6H_{11})$_7$Si$_7$O$_{12}$}] (**1**, 0.0530 g, 0.0496 mmol) was added to a Schlenk flask containing PDMS slabs (1.00 g) and allowed to stand under N_2 atmosphere with periodic shaking. After complete adsorption of CH_2Cl_2 into the PDMS slabs, they were placed under vacuum to remove the CH_2Cl_2; less solvent than the maximum that would swell into PDMS was used so that all of the CH_2Cl_2 containing **1** would adsorb into the slabs. The slabs were briefly rinsed with CH_2Cl_2 (3 mL) under N_2 atmosphere to remove any catalyst on the surface and dried again under vacuum. The slabs of **3** (5.03% by weight **1**) were stored in a glove box under N_2 at ambient temperature. UV–vis: λ_{max} = 230 nm. Anal. Calcd. for **3**: Ti, 0.23. Found: Ti, 0.27.

2.2.2. [Ti(NMe$_2$){(i-C_4H_9)$_7$Si$_7$O$_{12}$}]/PDMS (4)

Compound **4** was prepared from [Ti(NMe$_2$){(i-C_4H_9)$_7$Si$_7$O$_{12}$}] (**2**, 0.0530 g, 0.0598 mmol) using the method described for **3**. The slabs of **4** were stored in a glove box under N_2 at ambient temperature. UV–vis: λ_{max} = 235 nm.

A sample of **4** containing 7.62% by weight of **2** was analyzed by PIXE (proton induced X-ray emission). Anal. Calcd. for **4**: Ti, 0.41. Found: Ti, 0.38.

2.3. Procedure for catalytic alkene epoxidation

Epoxidation tests were performed in a magnetically stirred 50-mL three-necked flask, equipped with a condenser, thermometer probe and septum for withdrawing samples. In a typical reaction, solvent (CH_3CN or CH_3OH, 5 mL), toluene (30 mg, 0.3 mmol as internal standard), alkene (1-octene or cyclohexene, 0.5 mmol), a quantity of Ti/PDMS catalyst equivalent to 0.01 mmol of Ti (2 mol%), and a stirrer bar were placed in the flask. The mixture was heated to 60 °C and an equimolar or greater amount (relative to alkene) of aqueous H_2O_2 was added via syringe. A sample was immediately taken for analysis (GC and titration), and additional samples for analysis were taken at regular intervals. The H_2O_2 concentration was determined with aqueous Ce(SO$_4$)$_2$ (0.1 M) and ferroin indicator using the titration method. The selectivity to epoxide and H_2O_2 efficiency were determined as follows: epoxide selectivity = (mol. of epoxide formed/mol. of alkene consumed) × 100; and H_2O_2 efficiency = $\{[\text{epoxide}]/([H_2O_2]_0 - [H_2O_2]_t)\} \times 100$.

2.4. Ti silsesquioxane complex leaching studies

The experimental procedure is the same as described in Section 2.3 for catalytic alkene epoxidation with H_2O_2 at 60 °C. After the reaction had proceeded for a specified amount of time, a sample of the reaction mixture was taken for GC analysis. An aliquot (about half) of the reaction mixture was then transferred by canula into a three-necked Schlenk flask equipped with a thermometer and condenser. Both the original reaction mixture (containing immobilized catalyst) and the aliquot (absent immobilized catalyst) were heated as before for identical amounts of time. Samples were taken at regular intervals from each reaction mixture for GC analysis. Only the reaction mixture containing immobilized catalyst continued to form epoxide product. At completion, the catalyst was isolated by filtration, washed with acetonitrile (5 mL), and dried under vacuum for 2 h. The recovered catalyst was then analyzed for its Ti content by PIXE, as well as characterized by UV–vis spectroscopy (see Section 3).

2.5. Catalyst recyclability studies

The experimental procedure is the same as described in Section 2.3 for catalytic alkene epoxidation with H_2O_2 at 60 °C. After the alkene epoxidation had proceeded for a specified amount of time, the catalyst was removed by filtration, washed with acetonitrile (5 mL), and dried under vacuum for 2 h. The catalyst was then reused for alkene epoxidation as described in Section 2.3.

3. Results and discussion

3.1. Preparation and characterization of tripodal titanium complexes

One of us (MC) has previously reported the synthesis of a series of tripodal Ti silsesquioxane complexes, including $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ (**1**), as well as data for the epoxidation of 1-octene with *tert*-butyl hydroperoxide (TBHP) using tripodal Ti silsesquioxane complexes as catalysts [2]. In this study, we have similarly prepared $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$ (**2**) in excellent yield via protonolysis of $Ti(NMe_2)_4$ with one equivalent of $(i\text{-}C_4H_9)_7Si_7O_9(OH)_3$ (trisilanolisobutyl-POSS) in diethyl ether (Eq. (1)). The formulation and structure of **2** were established by microanalysis and solution (^1H, ^{13}C, and ^{29}Si) NMR data.

(1)

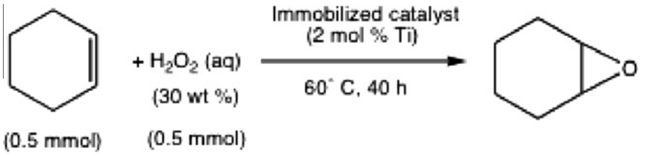
Consistent with the C_{3v} symmetry expected for tripodal $Ti(NMe_2)$silsesquioxane species, the ^{29}Si NMR spectrum of **2** showed three resonances at $\delta = -65.23$, -67.89, and -68.96 ppm for the silsesquioxane Si atoms in a 3:1:3 ratio. Moreover, consistent with previous observations for Ti silsesquioxane complexes [23,24], the resonance for the Si atoms bearing OH groups (at $\delta = -58$ ppm for trisilanolisobutyl-POSS) shifts upfield (by ca. 7 ppm) upon co-ordination of the oxygen with titanium. Analogous to $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ (**1**), compound **2** is an air- and moisture-sensitive yellow solid. It displays good solubility in polar hydrocarbon solvents, such as THF, diethyl ether, chloroform, and dichloromethane, as well as in aromatic hydrocarbon solvents, such as benzene and toluene, but shows poor solubility in acetonitrile.

3.2. Incorporation of tripodal Ti silsesquioxane complexes into PDMS membranes

Immobilized Ti silsesquioxane catalysts $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$/PDMS (**3**) and $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$/PDMS (**4**) were readily prepared by adding a CH_2Cl_2 solution of the appropriate tripodal Ti silsesquioxane complex (**1** and **2**, respectively) to the PDMS membrane under N_2 atmosphere. The PDMS membranes were swelled by CH_2Cl_2, which facilitated diffusion of the Ti silsesquioxane complex into the membranes. Removal of CH_2Cl_2 under vacuum, rinsing of the membranes with CH_2Cl_2, and drying again under vacuum afforded the catalysts. The compositions of **3** and **4** were confirmed by elemental analysis using proton-induced X-ray emission (PIXE); in each case, the weight percent of titanium found was in good agreement with the calculated value. UV–vis and IR spectroscopic methods were used to characterize the structure of immobilized catalysts **3** and **4**. The UV–vis data for **3** and **4** are consistent with the retention of a tetrahedral Ti site in the materials. Specifically, the UV–vis spectra of **3** and **4** contained an intense absorption at 230 and 235 nm, respectively (see Supplementary material); these absorptions are close to the range (212–228 nm) previously reported for Ti silsesquioxane complexes and assigned to a ligand to metal charge transfer transition involving four-coordinated titanium bearing oxygen ligands [2]. The absence of bands above 250 nm indicates that octahedral Ti sites and TiO_2 were negligible in the materials [25]. The IR spectra of **3** and **4** contained a partially obscured band of medium intensity falling in the range 940–960 cm^{-1}; a similar band in the range 930–970 cm^{-1} in the IR spectra of tripodal Ti silsesquioxane complexes [2], titanium silicates such as TS-1 and Ti-MCM-41 [26,27], and amorphous titania–silica mixed oxides [28] was convincingly assigned to a Si–O–Ti stretching vibration [2].

3.3. Alkene epoxidation activity

The catalytic activity of $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$/PDMS (**3**) and $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$/PDMS (**4**) toward the epoxidation of cyclohexene and 1-octene with H_2O_2 was investigated as a test of their epoxidation efficiency. At 60 °C in MeCN, reactions of cyclohexene or 1-octene with 1 equivalent of aqueous H_2O_2 in the presence of 2 mol% of catalyst **3** or **4** proceeded to high conversion with excellent H_2O_2 efficiency to selectively produce cyclohexene oxide or 1,2-epoxyoctane, respectively (Table 1, entries 1–4; Eqs. (2) and (3)). The highly efficient use of H_2O_2 by **3** and **4** is remarkable given that Ti silsesquioxane complexes are not active for epoxidation with H_2O_2 under homogeneous conditions, due most likely to excessive coordination of water to titanium. However, the PDMS membrane provides a uniformly non-polar environment about the Ti silsesquioxane complex in **3** and **4**, which presumably results in low local water concentrations, as well as higher [alkene]:$[H_2O_2]$ ratios at the Ti center than in the bulk reaction medium (such an effect has been verified for TS-1, the non-polar character of the zeolite resulting in a higher concentration of the alkene reactant in the zeolite relative to the bulk medium) [29,30]. A high alkene:H_2O_2 ratio is favorable for the epoxide selectivity, since the Ti-hydroperoxo intermediate (Ti-OOH) formed from reaction of the Ti complex with



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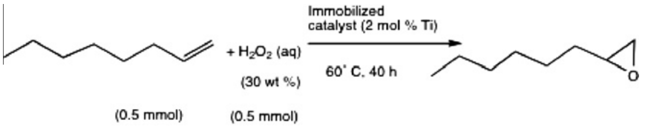


(3)

Table 1
Epoxidation of 1-octene ($1\text{-}C_8H_{14}$) and cyclohexene ($c\text{-}C_6H_{10}$) with H_2O_2 catalyzed by titanium silsesquioxane complexes immobilized in PDMS.

Entry	Catalyst	Substrate	Solvent	Conv. (%)	Epo. Sel.[j] (%)	Effi.[k] (%)	TON[l]	ref.
1	**3**	$1\text{-}C_8H_{14}$	MeCN	95.1[a]	99.2	98.1		
2	**4**	$1\text{-}C_8H_{14}$	MeCN	89.0[a]	99.0	99.0		
3	**3**	$c\text{-}C_6H_{10}$	MeCN	88.0[a]	99.1	98.3		
4	**4**	$c\text{-}C_6H_{10}$	MeCN	89.0[a]	99.0	98.2		
5	**3**	$1\text{-}C_8H_{14}$	MeOH	68.0[a]	98.4	97.1		
6	**4**	$1\text{-}C_8H_{14}$	MeOH	81.4[a]	97.3	97.0		
7	**4**	$1\text{-}C_8H_{14}$	MeCN	47.0[b]	99.0	99.0	470	
8	**4**	$1\text{-}C_8H_{14}$	MeOH	35.9[b]	99.0	98.0	359	
9	**4**	$c\text{-}C_6H_{10}$	MeCN	42.0[b]	99.0	99.0	420	
10	**4**	$c\text{-}C_6H_{10}$	MeOH	32.0[b]	99.0	99.0	320	
11	TS-1[d]	$1\text{-}C_6H_{12}$[g]	MeCN	14.5[c]	100	63.8	94.5	25
12	TS-1[d]	$1\text{-}C_6H_{12}$[g]	MeOH	21.2[c]	96.6	91	138.2	25
13	Ti-beta[e]	$1\text{-}C_6H_{12}$[g]	MeCN	17.7[c]	100	43.6	66.5	25
14	Ti-beta[e]	$1\text{-}C_6H_{12}$[g]	MeOH	8.7[c]	36.3	38.1	32.7	25
15	TS-1[f]	$c\text{-}C_6H_{10}$	MeCN	4.9[c]	–	–	36.1	25
16	TS-1[f]	$c\text{-}C_6H_{10}$	MeOH	0.9[c]	–	–	6.6	25
17	Ti-beta[e]	$c\text{-}C_6H_{10}$	MeCN	17.7[c]	80	52.2	66.5	25
18	Ti-beta[e]	$c\text{-}C_6H_{10}$	MeOH	40.4[c]	0.6	80.1	151.9	25
19	**4**	$1\text{-}C_8H_{14}$	MeCN	44.9[h]	99.0	99.0		
20	**4**	$1\text{-}C_8H_{14}$	MeCN	26.0[i]	99.0	99.0		

[a] Reaction conditions: 0.01 mmol of Ti, 0.5 mmol of alkene, 0.5 mmol of H_2O_2 (30% aqueous solution), 5 mL solvent, 60 °C, and 40 h.

[b] Reaction conditions: 0.01 mmol of Ti, 10 mmol of alkene, 10 mmol of H_2O_2 (30% aqueous solution), 10 mL solvent, 60 °C, and 2 h.

[c] Reaction conditions: 60 °C, 2 h (4 h for cyclohexene oxidation with TS-1), 10 mmol of alkene, 10 mmol of H_2O_2 (31% aqueous solution), 0.05 g of catalyst, and 10 mL solvent.

[d] Si/Ti = 53.

[e] Si/Ti = 30.

[f] Si/Ti = 60.

[g] $1\text{-}C_6H_{12}$ = 1-hexene.

[h] Reaction conditions are same as described for superscript *a* (above) except 5 mmol of H_2O_2 (30% aqueous solution) was used.

[i] Reaction conditions are same as described for superscript *a* (above) except 10 mmol of H_2O_2 (30% aqueous solution) was used.

[j] Epoxide selectivity = (mol of epoxide formed/mol of alkene consumed) × 100.

[k] H_2O_2 efficiency = $\{[\text{epoxide}]/([H_2O_2]_0 - [H_2O_2]_t)\} \times 100$.

[l] Turnover number: the mole of substrate converted per mole of Ti present in the catalysts.

the H_2O_2 can undergo two main processes: oxygen transfer to the alkene, resulting in formation of the epoxide or decomposition via homolytic fission of the Ti–OOH bond (in which case no oxygen transfer occurs) [2,31]. High alkene concentrations increase the probability that the Ti–OOH intermediate is intercepted by the alkene before decomposition can occur. Moreover, limiting the concentration of (acidic) H_2O_2 and H_2O at the Ti sites helps to reduce the occurrence of Ti leaching (*vide infra*). Thus, the hydrophobic environment provided by the PDMS membrane facilitates the efficient utilization of H_2O_2 for alkene epoxidation by Ti silsesquioxane catalysts.

The use of acetonitrile as solvent for alkene epoxidations with immobilized catalysts **3** and **4** is particularly suitable, since it is miscible with olefins and aqueous H_2O_2 in all proportions. Moreover, it does not swell PDMS to any appreciable extent (the swelling ratio, $S = D/D_0$, measured experimentally for MeCN at 25 °C is equal to 1.01, where D is the length of PDMS in the solvent and D_0 is the length of the dry PDMS) [32], and Ti silsesquioxane complexes are completely insoluble in it (thereby promoting retention of the Ti silsesquioxane complexes in the membrane). However, given that it has been shown that the nature of the solvent strongly influences the performance of titanosilicate catalysts in alkene epoxidation [7,25,33], we evaluated the effect of a protic solvent on the epoxidation efficiency of **3** and **4**. The protic solvent chosen was methanol because it has comparable polarity (dielectric constant = 32.6) to acetonitrile (dielectric constant = 37.5) and it has been found not to appreciably swell PDMS (S = 1.02 at 25 °C) [32]. The epoxidation of 1-octene with 1 equivalent of aqueous H_2O_2 was conducted in methanol at 60 °C in the presence of 2 mol% of immobilized catalyst **3** or **4** for 40 h. As shown in Table 1 (entries 5 and 6), both the H_2O_2 efficiency and the epoxide selectivity of **3** and **4** were excellent in methanol (and similar to those achieved in acetonitrile under similar conditions, Table 1, entries 1 and 2).

For both catalysts, $[\text{Ti}(\text{NMe}_2)\{(c\text{-}C_6H_{11})_7\text{Si}_7\text{O}_{12}\}]$/PDMS (**3**) and $[\text{Ti}(\text{NMe}_2)\{(i\text{-}C_4H_9)_7\text{Si}_7\text{O}_{12}\}]$/PDMS (**4**), the epoxidation of 1-octene with H_2O_2 to form 1,2-epoxyoctane proceeded to greater completion when acetonitrile was the solvent as opposed to methanol (Fig. 1, see also Table 1, entries 7–10). In this regard, we note that **3** displayed comparable catalytic activity in acetonitrile and methanol during the early stages of the epoxidation reaction (up to ~25% completion, Fig. 1). Similarly, the epoxidation activity of **4** was comparable in the two solvents, up to ~44% completion of the reaction (Fig. 1). In contrast, during the later stages of the reaction, the epoxidation activity of both catalysts decreased at a greater rate in methanol than in acetonitrile (Fig. 1). Catalysts **3** and **4** likely form different active species in the two solvents: the active intermediate in MeOH presumably possesses a stable five-membered ring structure formed by coordination of MeOH to Ti and

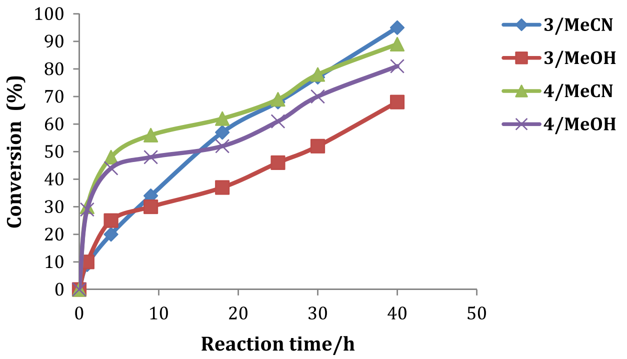
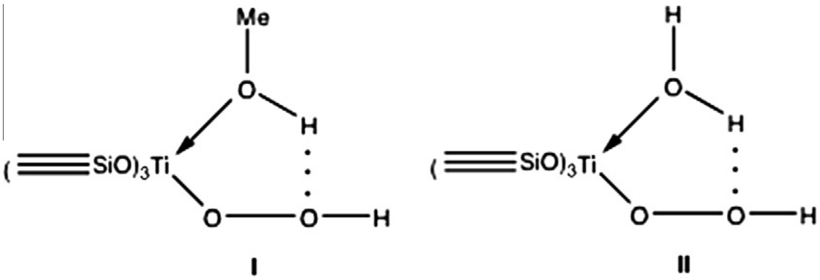


Fig. 1. Time profile of the epoxidation of 1-octene with H_2O_2 catalyzed by catalysts **3** and **4** (reaction conditions: 60 °C, 0.5 mmol of 1-octene, 0.5 mmol of H_2O_2 (30% aqueous solution), 0.01 mmol of Ti, and 5 mL solvent).



Scheme 1. Structures proposed intermediate Ti species.

hydrogen bonding to the Ti–OOH complex (**I**, Scheme 1). On the other hand, the active intermediate in acetonitrile is derived via coordination of water to Ti (**II**, Scheme 1). In this regard, the putative active species in TS-1-catalyzed alkene epoxidation in methanol is analogous to **I** [7,33], while a species equivalent to **II** is proposed to contribute in Ti-beta-catalyzed alkene epoxidation in acetonitrile [7,33]; and the fact that alkene epoxidation over TS-1 is more favorable in MeOH than in MeCN, while alkene epoxidation over Ti-beta is more favorable in MeCN than in MeOH (e.g. Table 1, entries 11–12 and 13–14) is widely accepted as resulting from the presence of these different active species [7,25,33]. Due to the lower donor properties of water, an active species similar to **II** (in which a water molecule is coordinated to Ti, Scheme 1) would possess greater electrophilic character and hence exhibit higher intrinsic epoxidation activity than an active species similar to **I** (in which an alcohol molecule is coordinated to Ti, Scheme 1), and could be stabilized in the hydrophilic pores of Ti-beta while the hydrophobic pores of TS-1 would be much less efficient for its formation. However, since our catalysts showed comparable 1-octene epoxidation activity in acetonitrile and methanol during early stages of the reaction (Fig. 1), we believe that in addition to the possible differences in 1-octene epoxidation activities of species **I** and **II**, inhibition of the reaction due to excessive coordination of MeOH to Ti contributes to reduced activity of our catalysts in methanol solvent. Consistent with this suggestion, it has been reported for a variety of homogeneous and heterogeneous titanium and vanadium catalysts that alkene epoxidation with alkyl hydroperoxide (ROOH) is inhibited by the alcohol (ROH) co-product [31]. The reason why the inhibition appears later in the reaction may be due to slight swelling of the PDMS at long reaction times (albeit not enough to cause significant leaching, see Section 3.3.1), thereby increasing the concentration of MeOH in the hydrophobic PDMS membrane. In both acetonitrile and methanol, $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$/PDMS (**4**) displayed greater catalytic activity than $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$/PDMS (**3**) early in the epoxidation of 1-octene with H_2O_2 (Fig. 1). Presumably, **4** is more active than **3** because active species derived from **4** possess a more open coordination environment about the Ti center (and hence are more reactive) than analogous species derived from **3**, given the reduced steric bulk of isobutyl group versus cyclohexyl group. Consistent with this explanation, it has previously been observed that cyclopentyl-substituted tripodal Ti silsesquioxane complexes are more active homogeneous epoxidation catalysts than their bulkier cyclohexyl-substituted analogs [2].

In order to assess the epoxidation efficiency of tripodal Ti silsesquioxane complexes encapsulated in PDMS membrane in relation to epoxidation efficiencies of much studied titanosilicate catalysts, such as TS-1 and Ti-beta, we carried out cyclohexene- and 1-octene epoxidation with H_2O_2 using **4** (0.01 mmol Ti) as catalyst in MeCN or MeOH under conditions analogous to those previously reported for 1-hexene- and cyclohexene epoxidation with H_2O_2 using TS-1 or Ti-beta as catalyst (10 mmol of alkene, 10 mmol of H_2O_2, 10 mL solvent, 60 °C, and 2 h) [25]. As shown in Table 1, **4** achieved higher turnover numbers for both cyclohexene- and 1-octene epoxidation with H_2O_2 (entries 7–10) than either TS-1 or Ti-beta (entries 11–18) under similar reaction conditions; conversion of cyclohexene over TS-1 was especially low due to the inability of cyclohexene to enter the TS-1 pore system (entries 15–16). The high epoxide selectivity ($\geqslant$97%) and outstanding H_2O_2 utilization efficiency ($\geqslant$97%) achieved for the epoxidation of 1-octene and cyclohexene with H_2O_2 in MeCN and MeOH using **3** or **4** as catalyst at 60 °C (Table 1, entries 1–10) are in contrast with typical results of alkene epoxidation with H_2O_2 using heterogeneous Ti-based catalysts. For example, 1-hexene epoxidation with H_2O_2 using TS-1 or Ti-beta as catalyst was found to occur with high epoxide selectivity but low H_2O_2 efficiency at 60 °C in MeCN (and in MeOH for Ti-beta) (Table 1, entries 11–14) [25]. And Ti-beta-catalyzed reaction of cyclohexene with H_2O_2 was found to occur with moderate epoxide selectivity and low H_2O_2 efficiency in MeCN, and with very poor epoxide selectivity in MeOH (Table 1, entries 17–18) [25].

As discussed earlier, we believe that the uniformly non-polar environment provided by the PDMS membrane limits the concentration of H_2O_2 and H_2O at the Ti sites in **3** and **4**, resulting in higher [alkene]:[H_2O_2] ratios at the Ti center than in the bulk reaction medium. In turn, this effect maintains the prevalence of tripodal Ti sites (see Section 3.2) in **3** and **4** throughout the course of the epoxidation reactions, which makes possible the excellent epoxidation efficiency of the catalysts. In this regard, based on steric and electronic arguments, tripodal complexes represent the best comprise between high Lewis acidity on the one hand, and steric accessibility of the Ti center on the other, and the available data strongly support the tripodal site being the most active and selective for epoxidation [1–3]. Consequently, tripodal Ti silsequioxane complexes are inherently more efficient than heterogeneous Ti-based epoxidation catalysts, since the latter inevitably contain a variety of Ti site types. For example, bipodal ($(\equiv SiO)_2Ti(OH)_2$), tripodal ($(\equiv SiO)_3Ti(OH)$), and tetrapodal ($(\equiv SiO)_4Ti$) sites are believed to exist in heterogeneous catalysts, such as titania-on-silica and TS-1 [2], while the presence of oligomeric Ti species has also been inferred [8,9], in addition to crystalline TiO_2 (anatase and rutile) [10]; all of these various Ti species show varying degree of activity in catalyzing alkene epoxidation and/or peroxide decomposition. Presumably, heterogeneous Ti silsesquioxane catalysts containing bipodal Ti sites [14,15] and gel catalysts containing tetrapodal Ti sites [16] display lower epoxide selectivity and alkene conversion profiles than $[Ti(NMe_2)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$/PDMS (**3**) and $[Ti(NMe_2)\{(i\text{-}C_4H_9)_7Si_7O_{12}\}]$/PDMS (**4**) due to the lower activity and selectivity of these sites. On the other hand, heterogeneous Ti silsesquioxane catalysts prepared by grafting of tripodal Ti vinyl-silsesquioxane complexes onto a polymeric matrix likely possess a less uniform hydrophobic environment around the tripodal Ti site, resulting in faster modification and/or deactivation of the catalyst, and hence

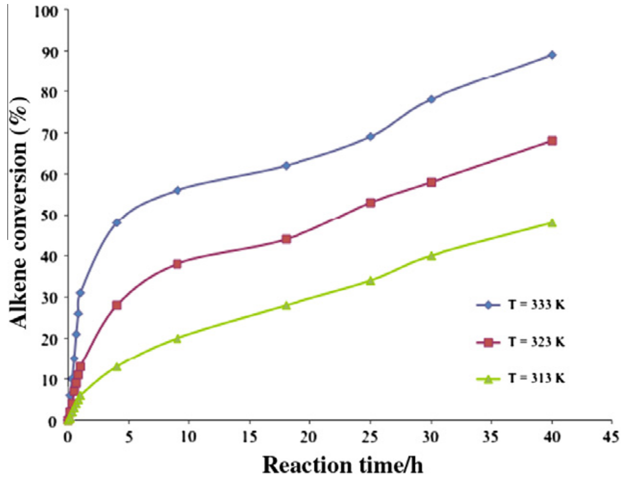


Fig. 2. Time profile of the epoxidation of 1-octene with H_2O_2 catalyzed by catalysts **3** at different temperatures (Reaction conditions: 0.5 mmol of 1-octene, 0.5 mmol of H_2O_2 (30% aqueous solution), 0.01 mmol of Ti, and 5 mL solvent).

Table 2
Catalyst recyclability studies.[a]

Solvent	Cat.	Substrate	Conversion (%) Epoxidation cycle[d]				
			1	2	3	4	5
MeCN	**3**	1-Octene[b]	15.1	14.4	14.1	14.1	14.0
MeCN	**4**	1-Octene[b]	43.0	42.9	42.5	42.0	42.0
MeOH	**3**	Cyclohexene[c]	63.4	62.9			

[a] Reaction conditions: 60 °C, 0.5 mmol of alkene, 0.5 mmol of H_2O_2 (30% aqueous solution), 0.01 mmol of Ti, and 5 mL solvent.
[b] Reaction time = 2 h.
[c] Reaction time = 20 h.
[d] Epoxide selectivity ⩾99% and H_2O_2 efficiency ⩾98%.

reduced epoxide selectivity and alkene conversion profiles [12] in comparison with **3** and **4**.

Detailed studies of the kinetics and mechanism of alkene epoxidation catalyzed by **3** or **4** are currently underway in our laboratory. However, our preliminary data indicate that the epoxidation reactions are not diffusion-controlled, as indicated by significant differences in the initial rate of alkene conversion in the temperature range 313–333 K (Fig. 2); a plot of ln k against $1/T$ afforded a straight line and a resulting apparent activation energy of 69 kJ/mol (not far from the 41 to 60 kJ/mol range reported for epoxidations with TBHP catalyzed by homogeneous tripodal Ti silsesquioxane catalysts). At 60 °C in MeCN, we found that reaction of 1-octene with 10 or 20 molar equivalents H_2O_2 (30% aqueous solution) in the presence of 2 mol% of catalyst **4** proceeded with considerably less conversion of 1-octene, albeit the selectivity for 1,2-epoxyoctane remains high (Table 1, entries 19–20). Evidently, low [alkene]:[water] ratio leads to significant catalyst deactivation, due presumably to excessive coordination of water to titanium, making it difficult to determine the dependence of alkene conversion rate on [H_2O_2].

3.3.1. *Studies of Ti silsesquioxane complex leaching and catalyst recyclability*

To establish that the Ti silsesquioxane catalyst remained encapsulated in the PDMS membrane and that the epoxidation reactions occurred in PDMS rather than in the solvents, we examined the catalytic properties of the reaction mixture and the catalyst recyclability. An aliquot (about half) of the reaction mixture was removed when the epoxidation of cyclohexene with H_2O_2 in MeCN at 60 °C and using **3** as catalyst was at approximately 63% completion (after 20 h). The aliquot was placed in a Schlenk flask under N_2 and heated as before for 20 h. The reaction did not proceed any further in this control experiment, while in the Schlenk flask containing **3**, conversion of cyclohexene into cyclohexene oxide grew to 88%, proving that leaching of the Ti silsesquioxane complex from PDMS membrane is minimal, if any. Using **4** as catalyst under similar reaction conditions as earlier, the epoxidation of cyclohexene with H_2O_2 in MeOH was at approximately 31% completion after 2 h. Again, removing an aliquot of the reaction mixture and heating it at 60 °C for 15 h did not result in further reaction. These control experiments were repeated multiple times with the same result each time: the solvent did not contain any appreciable amount of Ti silsesquioxane complex and the epoxidation reactions occurred in PDMS. Further support for the latter conclusion was obtained by isolating the catalyst (**3** or **4**) via filtration after completion of the epoxidation reaction, washing the recovered catalyst with acetonitrile, drying it under vacuum for 2 h, and then analyzing the recovered catalyst for its Ti content by PIXE. The Ti content found for used **3** was 0.32% in comparison with 0.27% found for pristine **3**, while the Ti content found for used **4** was 0.32% in comparison with 0.38% found for pristine **4**. These results are consistent with little loss of Ti from the catalysts under our epoxidation conditions; we presume the slight increase in Ti content found for used **3** is reflective of small variation in the Ti content from slab to slab of **3** and **4**. We also characterized the recovered catalysts by UV–vis spectroscopy. Consistent with prevalence of tetrahedral Ti sites in the materials (and analogous to the pristine catalysts), the UV–vis spectra of used **3** and **4** contained an intense absorption at 230 and 235 nm, respectively (see Supplementary material). In addition, neither spectrum contained a significant band above 250 nm, indicating that octahedral Ti sites and TiO_2 were negligible in the materials [25].

Consistent with retention of the tripodal Ti silsesquioxane complex in the PDMS membrane, the catalysts are recyclable (Table 2). When the epoxidation of 1-octene with H_2O_2 (1 equiv.) at 60 °C in MeCN using **3** as catalyst had proceeded for 2 h (to approximately 15% completion), the catalyst was removed by filtration, washed with acetonitrile, and dried under vacuum for 2 h. The catalyst was then reused for 1-octene epoxidation as before. As shown in Table 2 (entry 1), the activity (% alkene conversion), epoxide selectivity, and H_2O_2 efficiency of the catalyst were highly reproducible for the 5 cycles studied. Analogous recycling of **4** in catalytic epoxidation of 1-octene with H_2O_2 in MeCN furnished similar results: the activity, H_2O_2 efficiency, and epoxide selectivity of catalyst were highly reproducible for 5 cycles (Table 2, entry 2). Using **3** as catalyst for the epoxidation of cyclohexene with H_2O_2 in MeOH revealed that the catalyst can also be recycled in methanol; the conversion of cyclohexene to cyclohexene oxide and the H_2O_2 efficiency were comparable after two cycles (Table 2, entry 3). The aforementioned results clearly support minimal leaching of titanium from the catalyst, due presumably to limited concentration of (acidic) H_2O_2 and water (as well as methanol) at tripodal Ti sites inside the PDMS membrane.

4. Conclusions

The incorporation of Ti silsesquioxane complexes in a PDMS membrane furnished active heterogeneous catalysts, [Ti(NMe$_2$){(c-C_6H_{11})$_7Si_7O_{12}$}]/PDMS (**3**) and [Ti(NMe$_2$){(i-C_4H_9)$_7Si_7O_{12}$}]/PDMS (**4**), for the epoxidation of cyclohexene and 1-octene with aqueous H_2O_2. These catalysts displayed excellent H_2O_2 efficiency (⩾97%) and epoxide selectivity (⩾97%), and are highly recyclable. The high H_2O_2 efficiency can be attributed to the uniformly non-polar environment provided about the Ti silsesquioxane complex in **3** and **4** by the PDMS membrane, which presumably results in low local water concentrations, as well as higher [alkene]:[H_2O_2] ratios at the Ti center than in the bulk reaction medium; both of these effects favor the epoxide selectivity and minimal leaching of titanium. However, given that the principle deactivation pathway of Ti-based epoxidation catalysts is leaching of Ti into solution [34,35], some loss of Ti from immobilized tripodal Ti silsesquioxane epoxidation catalysts is likely upon extended use. If Ti leaching from were to occur, the tripodal sites could be easily regenerated by the addition of an appropriate Ti compound, either in situ [36] or ex situ. Since the incompletely condensed silsesquioxane contains three chemically identical silanol groups, the tripodal Ti site should be formed exclusively.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.05.003.

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