# Advances in Homogeneous and Heterogeneous Catalysis with Metal-Containing Silsesquioxanes

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**Abstract:** Metal-containing silsesquioxane derivatives provide new catalysts with both homogeneous and heterogeneous applicability. The steric and electronic properties of silsesquioxane silanolate ligands render metal centers more Lewis acidic than conventional alkoxide or siloxide ligands do. This concept has been exploited in newly developed catalysts for alkene metathesis, polymerization, epoxidation, and Diels-Alder reactions of enones. Other applications are envisioned in the near future.

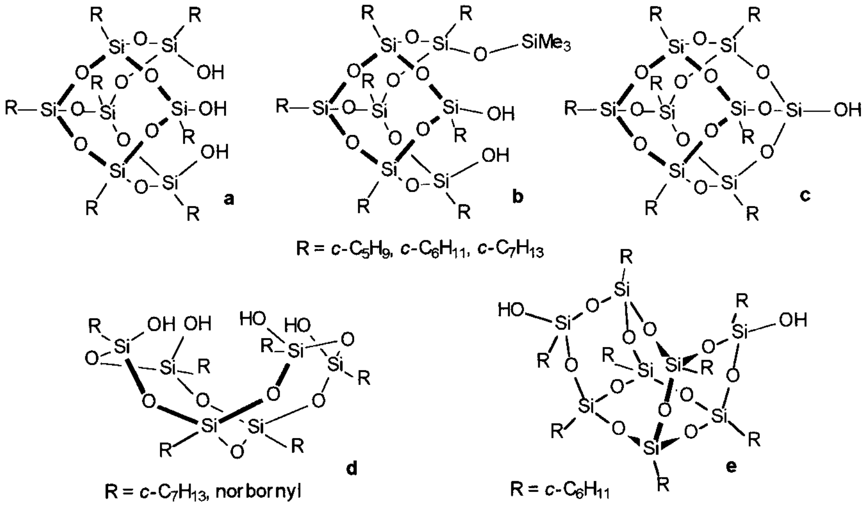
**Keywords:** catalysts • epoxidations • heterogeneous catalysis • silicon

## Introduction

Silsesquioxanes can be considered as small soluble chunks of silica, their degree of oligomerization is sufficient to result in Si/O cage structures that resemble crystalline forms of silica such as *β*-cristobalite and *β*-tridymite.[1] Moreover, incompletely condensed silsesquioxanes are suitable models for a variety of silanol sites that occur on silica surfaces (Scheme 1).[2, 3]

Over the last decade, many main group and transition metal complexes have been reported that contain silsesquioxane silanolate ligands. Some good reviews on silsesquioxanes and complexes derived therefrom are known.[1, 5] It is now evident that these complexes are capable of mimicking essential features of heterogeneous silica-supported transition metal catalysts. Important characteristics that can be replicated in silsesquioxane chemistry include electron-withdrawing bonding sites,[6] interactions with adjacent oxygen donors[7] which contribute to the stability of clusters grafted onto surfaces,[8] and a defined orientation of surface hydroxy groups which can dictate the selectivity by which reagents react with the surface. For example, the considerably enhanced alkene metathesis activity of surface carbene complexes over those of their homogeneous analogues has been similarly exhibited in silsesquioxane chemistry.[6]

Metal-containing silsesquioxane derivatives are increasingly being studied with their direct application as catalysts in mind. Herein are described such catalytic applications, a rapidly developing area of interest that already provides examples in both homogeneous and heterogeneous catalysis. Silsesquioxane-based homogeneous models for heterogeneous catalysts not only offer an unique opportunity to reach a molecular level understanding of heterogeneous catalysts, they are well underway to becoming applicable catalysts themselves! Some of these models exhibit activities that are comparable, or even better, to those of commercially used heterogeneous silica-supported catalysts.[9]



Scheme 1. Incompletely condensed silsesquioxanes.

Synthetic methods for silsesquioxane metal derivatives are well-documented and have been reviewed by Feher and

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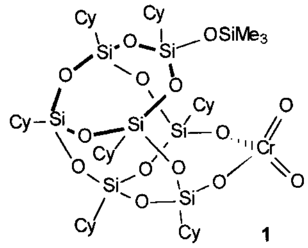
Budzichowski.[5] A brief discussion, however, is justified on the synthesis and availability of the incompletely condensed silsesquioxanes themselves. Completely new synthetic methodologies are emerging now that are likely to make these compounds better accessible.[4] Classically, the method of choice for the synthesis of the incompletely condensed silsesquioxanes involves the hydrolytic condensation of $RSiCl_3$.[1–3] Although the synthetic procedures are straightforward, they may involve an inconvenient gestation period before synthetically useful quantities of the silsesquioxane silanols can be isolated. For instance, for silsesquioxane **e** (Scheme 1) this period can be as long as nine months,[2] while a good yield of silsesquioxane **a** ($R = c\text{-}C_5H_9$) can be obtained in as little as about four days.[3a] A breakthrough in synthetic methodology is under development by the Feher group which gives fast access to incompletly condensed silsesquioxanes by the selective cleavage of one Si-O-Si linkage in readily available $R_8Si_8O_{12}$ cubo-octameric silsesquioxanes.[4] As a result, a much faster, though somewhat elaborate, alternative route to silsesquioxane **e** has already become available,[4c] together with fast routes to completely new, unexplored silsesquioxanes. In addition, one should note that several of the incompletely condensed silsesquioxanes discussed here have become commercially available since 1999 which may reflect improvements in synthesis methods.

## Discussion

**Alkene polymerization**: Several metallasilsesquioxanes have been reported to be active in the polymerization of ethene. Compound **1** represents a polymerization catalyst based on chromium. The reaction of the silsesquioxane disilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ with $CrO_3$ in the presence of the dehydration agent $MgSO_4$ gives a quantitative yield of the chromate ester $[(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(O_2CrO_2)]$ (**1**) that contains an $CrO_4$ unit with a nearly tetrahedral geometry.[10] This chromium compound is a catalyst precursor for ethene polymerization that can be activated with trimethylaluminum. At room temperature, ethene polymerization typically proceeded for several hundred to more than 3200 turnovers (≈3 h) before gelation occurred. Polymer characteristics were in the range: $M_n = 8890-61400$, $M_w = 60680-376500$, $M_w/M_n$ 3.45–6.13, $T_m = 130.7-132.1\,°C$. Although the polydispersity of the higher molecular weight polyethylene was high, this does not necessarily imply that a non single-site catalyst is involved. In this experiment, the polymerization was run till complete solidification of the reaction mixture occurred which is likely to result in a higher $M_w/M_n$ value.



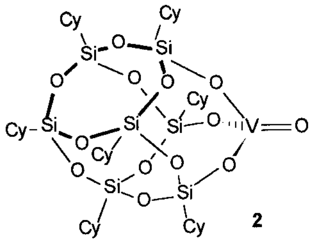
**1**

Phillips type polyethylenes:

$M_n = 8\,890\text{-}61\,400$
$M_W = 60\,680\text{-}376\,500$
$M_W/M_n = 3.45\text{-}6.13$

Chromium supported on silica is being used as a catalyst for the coordinative polymerization of ethene.[11] Well-known examples of industrially used systems are the Phillips catalyst, essentially $CrO_3$ on $SiO_2$ or $Al_2O_3$, and the Union Carbide system which is prepared from $[(\eta^5\text{-}C_5H_5)_2Cr^{II}]$ and $SiO_2$ (UNIPOL Catalyst).[12] Although the chromate compound **1** was described as a model for the Phillips catalyst, no further insight was obtained on the nature of the actual catalytic species nor on its presumed reduction by the alkylating agent. In general, the 'activation' of metal-oxo precatalysts remains elusive.[13] Interestingly, the polyethene produced by **1** is similar to that obtained from Phillips-type catalysts.

Vanadium silsesquioxane complexes have been reported that are suitable precatalysts for ethene polymerization. Monomeric and dimeric $[(c\text{-}C_6H_{11})_7Si_7O_9O_3V{=}O]$ (**2**) were obtained by the reaction of $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ with $(n\text{-}PrO)_3V{=}O$,[14] and used for ethene polymerization after activation with trimethylaluminum or $Al(CH_2SiMe_3)_3$. Polymerization activity was ascribed to the monomeric complex, the dimer being a precursor to the monomer.



**2**

Polyethylene:

$M_n = 21\,000$
$M_W = 47\,900$
$M_W/M_n = 2.28$

Single-site catalyst!

In the presence of $AlMe_3$ (1–5 equiv), solutions of the monomeric silsesquioxane complex **2** in benzene or hexane readily polymerize ethene. At 25 °C, ethene pressures of 1 bar, and relatively high vanadium concentrations of 3 mM, ethylene polymerization typically proceeded for 1000–1500 turnovers before gelation of the solution prevented further uptake of ethene. Typical $M_n$ and $M_w$ values were 21000 and 47900, respectively; the polydispersity is only 2.28. Interestingly, in this case the system can be described as a single-site catalyst. A survey of the catalyst's reactivity indicated that to a limited degree other alkenes could also be polymerized or copolymerized. Activity for propene was low, 125 turnovers, (25 °C, 8 bar, 3 h) occurred, rendering atactic polymer (MW< 10000). Copolymerization of ethene (1%) in neat propene produced small amounts (≈350 turnovers) of copolymer containing 5–10% propene. 1,3-Butadiene was polymerized well, the resulting product is >95% *trans*-1,4-polybutadiene.[15]

Based on spectroscopic analysis of low-temperature mixtures of **2** with the activating agent $Al(CH_2SiMe_3)_3$ a reaction sequence involving successive alkyl transfers and coordination of the vanadium oxo bond to the Lewis acidic aluminum sites was implicated as leading to the active catalyst [Eq. (1)]. The reaction sequence also accounts for the observed dependence of catalyst activity on the $AlR_3$ reagent, which reaches a maximum when about two equivalents of alkylaluminum agent are added. Larger amounts of $AlR_3$ result in reduction and deactivation of the metal centers, while fewer equivalents are not sufficient to result in complete catalyst activation.[16] A

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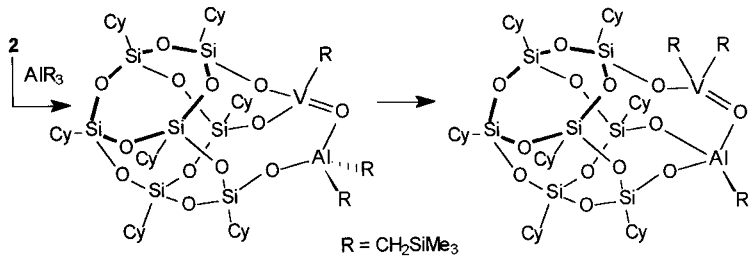


(1)

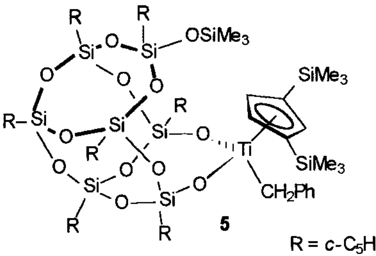
similar dependence of catalytic activity on the amount of the activating aluminum reagent was found for the silsesquioxane chromate **1**.[10]

In contrast to the activity exhibited by **1**/AlMe$_3$ or **2**/AlMe$_3$, simple siloxy analogues such as $(Ph_3SiO)_3V{=}O$,[17] $(Ph_3SiO)_2CrO_2$ or $[Cr({=}O)_2\{(OSiPh)_2O\}]_2$[18] show little or no activity towards ethene polymerization under identical conditions. This has been particularly well investigated for a series of vanadium complexes of formula $(Ph_3SiO)_{3-n}(CH_2SiMe_3)_nV{=}O$ that were found to likewise react with $Al(CH_2SiMe_3)_3$ to form Lewis adducts derived from coordination of Al to the terminus of the V=O group.[17] None of the resulting adducts, however, were particularly active in ethene polymerization: all are quickly deactivated and none appeared to be as active as the $[(c\text{-}C_6H_{11})_7Si_7O_{12}V{=}O]/AlR_3$ systems.

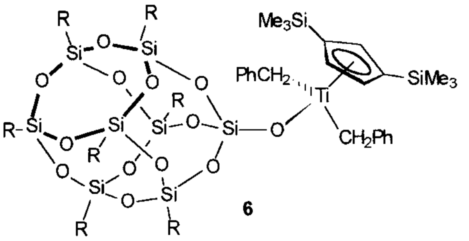
Interesting silsesquioxane-based Ziegler–Natta type catalysts were recently reported to result from the reaction of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)O_2Mg]_n$ ($n = 1$ or 2) with $TiCl_4$. The resulting bimetallic system $[(c\text{-}C_6H_{11})_7Si_7O_{12}MgTiCl_3]_n$ ($n = 1$ (**3**) or 2 (**4**)) could be activated with $AlEt_3$ and subsequently used for ethene polymerization.[9]

The polymerization of ethene could be catalyzed with an activity of 110.8 kgPE (g[Ti] h)$^{-1}$ which was higher than the activity of 60.0 kgPE (g[Ti] h)$^{-1}$ obtained for a commercial Ti/Mg/SiO$_2$ silica-supported catalyst with the same bimetallic content under similar reaction conditions. Gel permeation chromatography (GPC) analysis of the polyethene indicated $M_n = 26000$, $M_w = 140000$; the polydispersity of the resulting polymer was substantial: 5.5. On the basis of the analogy in synthesis, structural characteristics, and polymerization behavior, the silsesquioxane system employed may have potential as a bonding model for Ti/Mg-containing bimetallic silica-supported catalysts.

Heterogenization of well-defined homogeneous alkene polymerization catalysts is becoming an increasingly important topic since this provides the opportunity to combine the advantages of both supported and homogeneous catalysts such as morphology control combined with the presence of single active sites.[19] The most common method to immobilize, for instance, metallocene complexes consists of adsorption of the catalyst on a support that is pretreated with methylalumoxane (MAO) or other cocatalysts.[20] In view of catalytic alkene polymerization, silica-grafted Group 4 metal complexes of the type $[SiO]M(Cp)X_2$ ($X = Cl$, alkyl) are of interest. Using silsesquioxanes as silica mimics, such systems are currently being modeled and **5**–**7** serve as representative examples.[21]



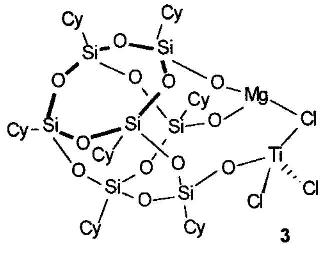
**5** / $B(C_6F_5)_3$/ ethene: no activity



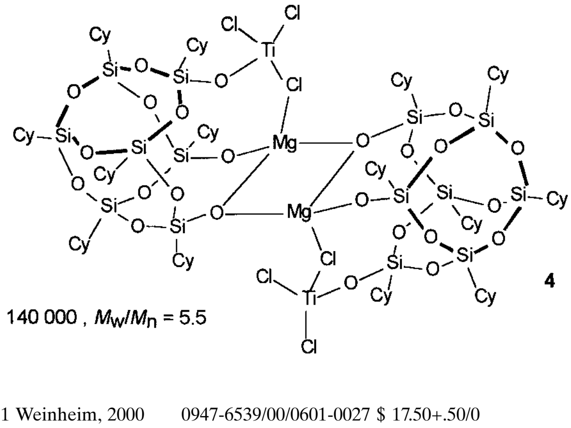
R = $c\text{-}C_5H_9$, $c\text{-}C_6H_{11}$

**6** / MAO: polyethylene:
$M_n$ = 125 000, $M_w$ = 890 000,
$M_w/M_n$ = 7.2

These, and related compounds, were subjected to catalytic ethene polymerization using a catalyst/MAO ratio of about 1000. A noteworthy finding was that although virtually all silsesquioxane complexes exhibited catalytic activity, (see complex **6**) the active catalyst invariably resulted from a series of transmetalation reactions with the methylalumoxane that induced cleavage of the silsesquioxane from the transition metal moiety. Since silsesquioxanes were used that model a variety of silanol sites present on silica, particularly with regard to the dentacity of the siloxy chelation, it might be

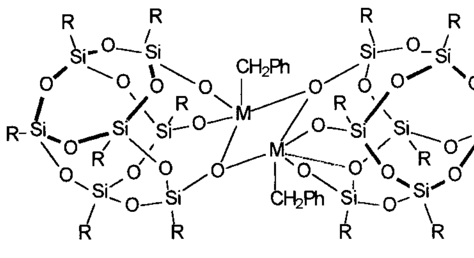


**3**



**4**

polyethylene: $M_n$ = 26 000, $M_w$ = 140 000, $M_w/M_n$ = 5.5



**7**

R = c-$C_5H_9$, M = Zr, Hf

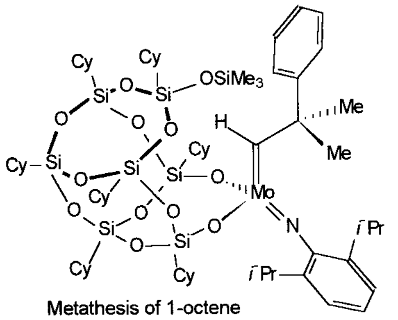
**7** (M = Zr)/ $B(C_6F_5)_3$: polyethylene:
$M_W$ = 15 180,
$M_W/M_n$ = 2.3
Activity: 2 400 kg /mol **7**.bar.h

**7** (M = Hf)/ $B(C_6F_5)_3$: polyethylene:
$M_W$ = 82 000,
$M_W/M_n$ = 3.2
Activity: 4 800 kg /mol **7**.bar.h

concluded that many grafted polymerization catalysts will leach upon activation by methylalumoxane. Obviously this should be kept in mind!

Several of the new silsesquioxane alkyl metal compounds could, however, be activated for ethene polymerization with $B(C_6F_5)_3$. With this milder reagent, no leaching takes places (thus **5** is not active) and moderate to excellent polymerization activity resulted, up to 4800 kgPE(molhbar)$^{-1}$ for **7** An interesting finding was that the dimeric Zr and Hf compounds already showed some polymerization activity without the use of any cocatalyst.

**Alkene metathesis**: Activity for catalyzing alkene metathesis reactions is well-documented for molybdenum and tungsten complexes and, in the absence of differential steric effects, tends to correlate with the electron-withdrawing ability of ancillary alkoxide ligands. With these observations in mind, the electron-withdrawing properties exhibited by silsesquioxanes have been applied to the field of alkene metathesis. The preparation of suitable Mo or W alkylidene complexes presented a significant synthetic challenge which was solved by application of a suitable transmetallating agent, $[(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OTl)_2]$. A resulting silsesquioxane alkylidene complex **8** turned out to be an excellent catalyst for alkene metathesis.[6]



Metathesis of 1-octene
TOF ~ 27 000 h

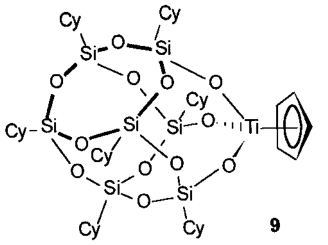
**8**

For instance, when 4800 equivalents of 1-octene are added to a catalytic amount of the alkylidene complex, 150 turnovers occurred within 20 s of mixing. Furthermore, while ethene accumulation slows down the productive metathesis reaction to 7-tetradecene, purging the system allowed this reaction to be run to completion. Similar results were obtained for 1- and 2-pentenes as well as *cis*-2-octene. In sealed tube reactions where ethene was not purged, the system remained active for about 1.5 days. Some catalytic applications involving functionalized alkenes were reported as well but the susceptibility of the alkylidene toward hydrolysis required the substrates to be nonprotic and strictly anhydrous.

Recently, silsesquioxane tungsten catalysts were reported that are active in the living ring-opening methathesis polymerization (ROMP) of norbornene. The low polydispersity (1.1 to 1.5) of the polymer is indicative for living polymerization. The actual catalysts, however, were not well-described but claimed to result from the reaction of $WCl_6$ with either $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ or $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ followed by reaction with $MgClCH_2Si(CH_3)_3$.[22]

**Alkene epoxidation**: Metallasilsesquioxanes have now been reported to be active in epoxidation of alkenes and several groups are currently working on this topic. Although one might expect titanium silsesquioxanes to be of interest for alkene polymerization, virtually all of the complexes involved here do not polymerize alkenes or, at least, their catalytic potential for alkene polymerization has not been investigated yet.

The first report on catalytic alkene epoxidation involved the known silsesquioxane titanium complex $[Ti(\eta^5\text{-}C_5H_5)(c\text{-}C_6H_{11})_7Si_7O_{12})]$ (**9**),[23] for which no catalysis was reported for a period of five years after its discovery! This compound



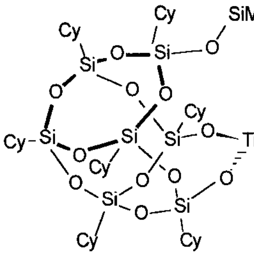
**9**

was found to catalyze alkene epoxidations using *tert*-butyl hydroperoxide (TBHP) as the oxidizing agent.[24] The catalyst is effective at low concentration and selectively produces alkene oxides in high yield with good peroxide economy. 'Easy' substrates such as cyclooctene and norbornene were virtually quantitatively epoxidized within 3 h using 1 mol% of the catalyst and equimolar amounts of alkene and epoxide at 50 °C. Also the somewhat difficult epoxidation of 1-octene was catalyzed efficiently (80% conversion, 80% selectivity after 24 h). In addition, the catalyst resists hydrolysis and is even stable in 1M aqueous HCl! This stability is remarkable, especially when taken into account that the related vanadium complex **2** is rapidly decomposed by protic reagents (e.g. hydroperoxides, alcohols) to give the trisilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ and complex mixtures of vanadium-containing products.

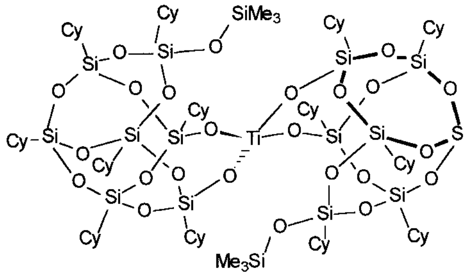
The synthesis of other tripodal species $[TiR\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ (R = $CH_2Ph$, $NMe_2$, $OSiMe_3$, O-*i*Pr) was achieved through the reaction of the appropriate homoleptic titanium(IV) complex $TiR_4$ and the silsesquioxane trisilanol

($c$-$C_6H_{11}$)$_7Si_7O_9(OH)_3$.[25] These, and related titanium silsesquioxanes of formula [TiR{($c$-R′)$_7Si_7O_{12}$}] (R = alkyl, cycloalkyl, alkylaryl, alkoxy, aryloxy, siloxy, amido, and OH; R′ = cyclopentyl, cyclohexyl, cycloheptyl) are also claimed in a recent Shell patent and were similarly applied to alkene epoxidation.[26] The reported catalytic activities of these complexes for the epoxidation of 1-octene using TBHP as the oxidant are supposed to be more or less similar to that of the cyclopentadienyl complex [Ti($\eta^5$-$C_5H_5$)($c$-$C_6H_{11}$)$_7Si_7O_{12}$)]; the exact catalytic conditions were somewhat remarkable: a 50-fold excess of 1-octene to TBHP was used, leading to very low alkene conversion.

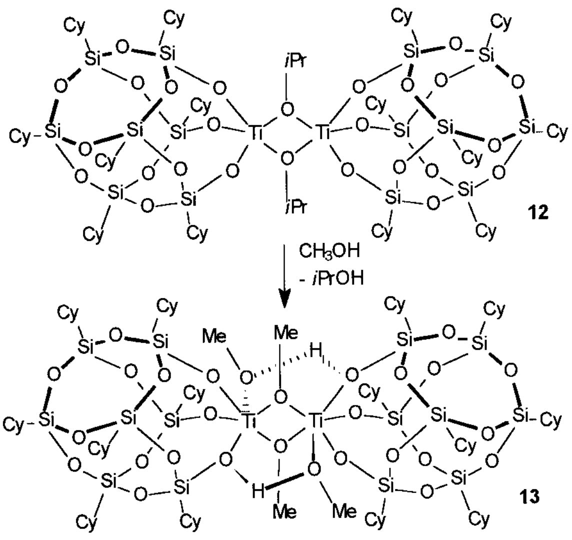
In addition, silsesquioxane titanium complexes **10** and **11** with bidentate siloxy coordination were reported that are derived from the silsesquioxane disilanol ($c$-$C_6H_{11}$)$_7Si_7O_9$(OSiMe$_3$)(OH)$_2$.[25] These complexes also are catalytically active in the epoxidation of 1-octene with TBHP although the activity is about an order of magnitude less than that of the tripodal species. Interestingly, there seems to be a relation between the dentactity of silsesquioxane coordination with respect to hydrolysis of the titanium sites: bidentate complexes are hydrolyzed by aqueous hydrogen peroxide, while terdentate derivatives do not, or very slowly, hydrolyze. Materials with monodentate silsesquioxane siloxy coordination were found to not only hydrolyze quickly but to already decompose in organic media containing anhydrous TBHP (vide infra).[24]



**10**



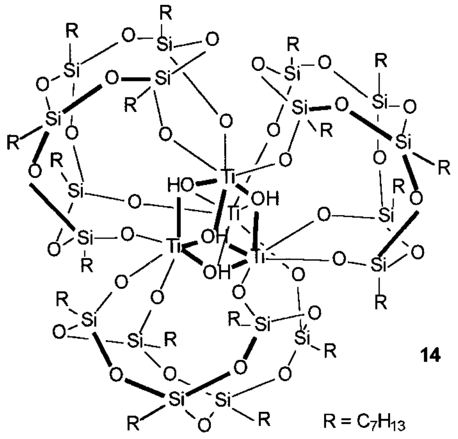
**11**



Scheme 2.

Dimeric tripodal titanium silsesquioxanes of formula [Ti(O-$i$Pr){($c$-$C_5H_9$)$_7Si_7O_{12}$}]$_2$·THF (**12**) and [Ti(OMe){($c$-$C_5H_9$)$_7Si_7O_{12}$}(MeOH)]$_2$ (**13**) were reported to result from the reaction of the trisilanol ($c$-$C_5H_9$)$_7Si_7O_9(OH)_3$ and titanium tetraisopropylate (→**12**) and the following substitution reaction using methanol (→**13**) (Scheme 2).[27] The isopropoxy compound **12** displays epoxidation activity which compares well with that from earlier studies: after 1 h at 50 °C, 48 % conversion was achieved for the epoxidation of cyclohexene with TBHP in $CDCl_3$ using a catalyst substrate ratio of 1:70:70 with 98 % selectivity towards the epoxide. The methoxide complex **13** exhibited much higher catalytic activity (93 % conversion after 1 h).

So far, all homogeneous epoxidation catalysts reported were exclusively active in combination with an organic peroxide. Catalysis involving the use of aqueous hydrogen peroxide proved to be impossible with these systems. This is a drawback when one considers that a procedure for the epoxidation of alkenes using environmentally friendly oxidants like $O_2$ and $H_2O_2$ is an important industrial and synthetic goal. As such, a breakthrough in this field may be the synthesis of the polyoxotitanate **14**, for which a cluster type structure was revealed by X-ray analysis.[28]



**14**

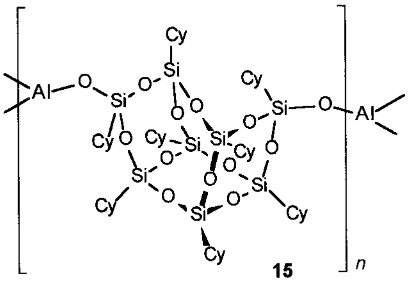
Reaction of the tetrasilanol ($c$-$C_7H_{13}$)$_6Si_6O_7(OH)_4$[3a] with titanium tetrachloride followed by reaction with water leads to clean formation of the polyoxotitanate [($c$-$C_7H_{13}$)$_7Si_6O_{11}$]$_3$[TiOH]$_4$ (**14**), a water-stable complex that only starts to thermally decompose at about 250 °C in air. The polyoxotitanate was found to be not only stable in protic oxidizing media but also to efficiently catalyze alkene epoxidations including those which use aqueous hydrogen peroxide as the oxidizing agent. For example, cyclooctene could be epoxidized with selectivities and conversions higher than 90 %; catalytic conditions: cyclooctene/TBHP=1, 0.3 mol % of catalyst, 24 h at 50 °C, 64 % conversion, >95 % selectivity to the epoxide; cyclooctene/$H_2O_2 = 50$, 1.4 mol % of catalyst compared to oxidant, 1 h at 80 °C, 100 % conversion of $H_2O_2$, >90 % selectivity to the epoxide.

Finally, silsesquioxanes containing a much higher titanium content have been reported to result from a one-step procedure by reaction of substituted silane triols with titanium tetraisopropylate in a 1:1 ratio. To date, the ability of these cluster compounds to catalyze either alkene epoxidations or polymerizations has not been reported.[29]

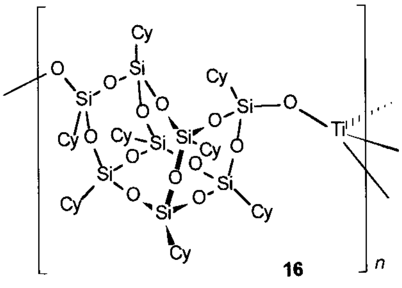
**Oligometallasilsesquioxanes as heterogeneous catalysts**: Over the last two years, several silsesquioxane-based approaches to heterogeneous catalysts have been reported. These involve the construction of insoluble silsesquioxane metal gels, phase immobilization of sufficiently robust silsesquioxane complexes, and the use of silsesquioxane metal complexes as precursors for porous oxide catalysts.

Past developments in silsesquioxane chemistry that could be regarded as promising for forthcoming applications in the field of heterogeneous catalysis included porous materials that were synthesized from silsesquioxane cage precursors,[30] and metal-containing polymeric derivatives.[31] Although these findings did initially not involve applications in actual catalysis, they provided a good indication that silsesquioxane chemistry was maturing to the extent where applications to *heterogeneous* catalysis would become feasible.

The silsesquioxane disilanol $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ has been used as a bifunctional building block for the construction of organosilicious polymeric materials. Because of the spatial restrictions of the silsesquioxane skeleton, silanol-centered reactions of $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ with bifunctional and multifunctional organometallic compounds are likely to give polymeric complexes through formation of bridging metal siloxy units.[30, 31] The silsesquioxane disilanol could be easily functionalized with trimethylaluminum, resulting in concomitant formation of methane and a colorless aluminosilsesquioxane gel **15** that contains a silsesquioxane cage framework similar to that present in its precursor.[32] In a typical gel-forming reaction, more than 80 % of the silanol units of the starting material were functionalized. The actual coordination environment of the aluminum sites present in the polymer is likely to be complicated. For instance, the 104.2 MHz $^{27}$Al MAS NMR spectrum of the gel consists of three, partially resolved resonances at $\delta = 50.0$, 29.9, and $-1.7$ ($\omega_{1/2} \approx 2500$ Hz), characteristic of four, five, and six-coordinate aluminum siloxy units, respectively.

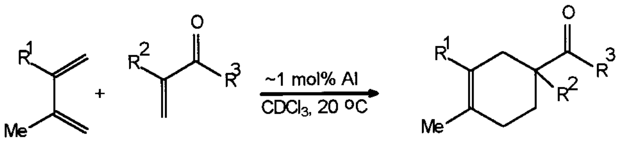


**15**



**16**

The aluminosilsesquioxane gel was found to accelerate Diels–Alder reactions of enones with several orders of magnitude over the thermal reaction [Eq. (2)]. The heterogeneity of the catalyst was proven by filtration experiments: upon filtration of the catalyst when reactions had reached about 50 % conversion, the reaction rate decreased to the thermal rate.

 (2)

$R^{1\text{-}3}$: any combination of H and Me
90% conversion in 1.5 - 20h

In a somewhat ambitious attempt to contribute to recent developments in heterogeneous oxidation catalysis,[33] the reaction of the silsesquioxane disilanol $(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2$ with $TiCl_4$ or $Ti(CH_2Ph)_4$ was performed and found to lead to the formation of a titanium-containing silsesquioxane gel **16**, similar as for $AlMe_3$ leading to **15** (vide supra). An essential feature is that during gel formation, titanium siloxy units (Ti-O-Si) result from functionalization of *isolated* silanol groups, the silsesquioxane being a bifunctional *monodentate* ligand. Gel **16** effectively catalyzes the epoxidation of alkenes by TBHP under mild conditions.[24] Though for the reactions studied, **16** is a reasonable to good precatalyst, attempts to filter off the gel during epoxidation, and thus to stop the reaction, met with complications. NMR studies showed that during epoxidation, rapid hydrolysis of **16** by TBHP occurs resulting in the *quantitative* reformation of the silsesquioxane disilanol and concomitant formation of non-siloxy titanium species that are catalytically active.

An essential feature of several of the proposed mechanisms of alkene epoxidation by titanium silicalites involves hydrolysis of a titanium siloxy function in a tetracoordinated active site.[34] For the titanium gel **16**, such a hydrolysis step would lead to rapid degeneration of the material since the titanium siloxy units (Ti-O-Si) here result from functionalization of *isolated* silanol groups; the silsesquioxane is a bifunctional *monodentate* ligand.

In full agreement with this hypothesis, the titanium(IV) silsesquioxane **9** was reported to be an active and *robust homogeneous catalyst* for alkene epoxidation that did not leach titanium under the catalytic conditions.[24] As such, the complex is an attractive candidate for heterogenization. It was reported that **9** could be immobilized in an MCM-41 molecular sieve,[35] exploiting its strong adsorption in the MCM-41 channel (Figure 1). The titanium-silsesquioxane-immobilized materials efficiently catalyzed (i.e. >95 % selectivity) the epoxidation of cyclooctene under mild conditions using *tert*-butyl hydroperoxide as the oxidant. The presence of aluminum in the MCM-41 should be avoided since this has an impeding effect on the

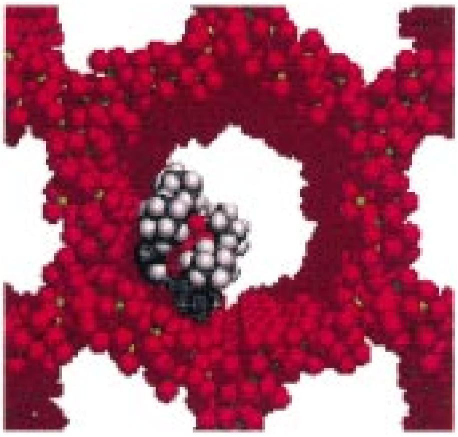


Figure 1. Graphical representation of the adsorption of **9** in the ≈30 Å pores of all-silica MCM-41.

performance of the catalyst and induces leaching of the silsesquioxane catalyst. Leaching of **9** could be completely blocked when the MCM-41 materials were treated with a silylating agent such as $SiCl_2Ph_2$ or $SiCl_2Me_2$ prior to catalysis. All heterogeneous catalysts could be easily recovered by filtration; an all-silica catalyst could even be re-used for at least three times without an apparent loss of activity. The use of MCM-41 type materials proved to be essential for successful catalyst immobilization.

The vanadium compound **2** has been well-described as a precatalyst for alkene polymerization. Its closely related cyclopentyl analogue $[(c\text{-}C_5H_9)_7Si_7O_9O_3V{=}O]$ was claimed to exhibit fair to excellent activity for the photooxidation of benzene and cyclohexane,[36] indicating its ability as a homogeneous analogue of silica-supported catalysts. The analogy may well be valid since only highly dispersed, isolated tetrahedral $VO_4$ species were considered to be active species. The claimed catalytic activity, however, is unlikely to result from the silsesquioxane complex itself. For the cyclohexyl analogue **2**, it was succinctly stated that it did not show any promise as an oxidation catalyst. For **2**, drastic conditions ($T > 250\,^{\circ}C$) were required for any observable reaction to occur with $PMe_3$, $PPh_3$, norbornene, CO, or $\alpha$-methylstyrene. These reactions, however, appeared to result from decomposition of **2**, rather than from reaction between **2** and the substrate. For substrates that were kinetically stable toward dioxygen under 200 °C (e.g. CO, norbornene, toluene) the presence of added oxygen had no effect.[14]

In addition, the vanadium complex $[(c\text{-}C_5H_9)_7Si_7O_9O_3V{=}O]$ has been used as a precursor to heterogeneous catalysts for the selective photoassisted oxidation of methane into methanal.[37] Silica-supported catalysts were prepared by incipient wetness impregnation of a pentane solution of the silsesquioxane on silica followed by air-flow pyrolysis at 523 or 723 K. The supported catalysts showed fair to excellent activities in the photooxidation, the activity of a catalyst that was subjected to air-flow treatment at 723 K was reported to have the highest turnover frequency (TOF): $9\,h^{-1}$. X-ray photoelectron spectroscopic (XPS) analysis showed that this catalyst no longer contained the original silsesquioxane species, since only trace amounts of carbonaceous materials were detected on its surface. Alltogether, this study indicates the possibility of using oligometallasilsesquioxanes as excellent precursors for porous oxide catalysts.

## Conclusion

Incompletely condensed silsesquioxanes have emerged as very interesting ligands that should no longer be regarded as chemical curiosities. Coordination of ($d^0$) metals to a silsesquioxane framework tends to generate electrophilic metal centers: the silsesquioxane framework is approximately as electron-withdrawing as a $CF_3$ group.[6] This property is likely to increase the catalytic activity of silsesquioxane complexes when compared with that of related compounds having conventional alkoxide or siloxide ligands. In applications involving alkene polymerization and metathesis, silsesquioxane ligands beautifully mimicked the considerably enhanced activity of surface alkyl and alkylidene species.[9, 12, 15]

In oxidation catalysis, silsesquioxanes have appeared as rigid, chemically inert ligands that displayed a rich coordination chemistry. Efficient catalysts for alkene epoxidation with organic peroxide have resulted,[24–27] and a new exiting field is emerging that uses silsesquioxanes for the construction of polyoxometalates.[28] Silsesquioxane-supported polyoxometalates might be further developed to catalyze oxidation processes that use environmentally friendly oxidizing agents such as $O_2$ and $H_2O_2$.

The use of Lewis acidic silsesquioxane-based derivatives will undoubtedly be further explored, their use in promoting Diels–Alder reactions should be regarded as a first demonstration of their catalytic potential.[32] Other Lewis acid catalyzed reactions, like Oppenauer oxidations or Meerwein–Pondorf–Verley reductions are likely to be reported in the near future, together with examples of enantioselective catalysis.

The field of catalysis by silsesquioxane metal complexes will profit further from new synthetic methodologies for both existing and novel incompletely condensed silsesquioxanes.[4] Ongoing developments in the field of silsesquioxane-based network solids and hybrid inorganic–organic materials will further pave the way for applications in the field of (heterogeneous) catalysis.[30–32, 39]

## Acknowledgement

The research of H.C.L.A. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences.

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Received: August 7, 1998
Revised version: June 15, 1999 [C1290]