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Citation for published version (APA):

Abbenhuis, H. C. L., Krijnen, S., & Santen, van, R. A. (1997). Modelling the active sites of heterogeneous titanium epoxidation catalysts using titanium silasesquioxanes: insight into specific factors that determine leaching in liquid-phase processes. *Chemical Communications, ChemComm*, 1997(3), 331-332.
<https://doi.org/10.1039/a607935k>

DOI:

[10.1039/a607935k](https://doi.org/10.1039/a607935k)

Document status and date:

Published: 01/01/1997

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Modelling the active sites of heterogeneous titanium epoxidation catalysts using titanium silasesquioxanes: insight into specific factors that determine leaching in liquid-phase processes

Hendrikus C. L. Abbenhuis,* Simon Krijnen and Rutger A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

Active catalysts for the epoxidation of alkenes by *tert*-butyl hydroperoxide are provided by silasesquioxane titanium(IV) derivatives; a non-leaching catalyst, not prone to irreversible protic cleavage of its siloxy functions by the oxidizing agent, contains a terdentate silasesquioxane ligand.

In the current search for non-leaching heterogeneous liquid-phase oxidation catalysts detailed studies of how the catalytically active metal species are bonded to the support are rare. Often, more attention is paid to the performance of the catalyst, rather than to the fundamental question whether the catalyst is truly heterogeneous or not. In order to approach this problem at a molecular level, we report here on epoxidations catalysed by titanium silasesquioxanes. In these silasesquioxanes, the titanium is incorporated *via* spatially oriented siloxy bonds (Ti–O–Si) which structurally resemble surface sites that have been purportedly identified on silica surfaces.

Heterogeneous titanium catalysts are very important in oxidation processes but at the same time have been reported to undergo some leaching in liquid-phase applications. For instance, the highly active Shell titanium/silica epoxidation catalyst^{1,2} becomes only truly heterogeneous after a certain time on stream.³ Similar materials, that are currently being reported as the result of grafting silica⁴ or MCM-41 mesoporous silica⁵ with titanium derivatives, or even novel titanosilicates,⁶ might therefore be only partially heterogeneous when applied in liquid-phase oxidation reactions.

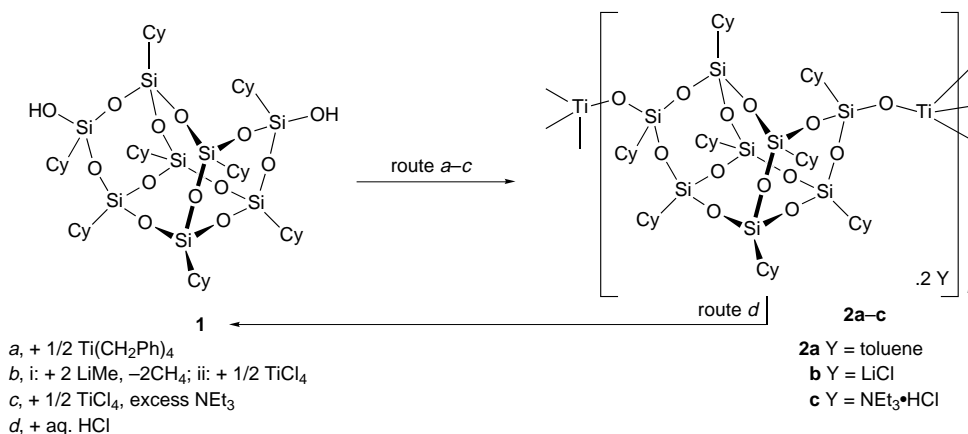
The silasesquioxane **1** (Scheme 1) possesses a well defined structure which includes two reactive, isolated hydroxy groups that occupy 'exo' positions above nearby Si₄O₄ rings, that are part of an interdigitated Si₈O₁₁ skeleton. Several functionalizations of **1** have already been achieved *via* clean silanol centred reactions and were in most cases reported to leave the silasesquioxane skeleton intact.^{7–9} Recently, we reported on the construction of a very active, truly heterogeneous catalyst from **1** for Diels–Alder reactions of enones.¹⁰

We found that, in toluene, the silanol groups present in **1** easily react with tetrabenzyltitanium (Scheme 1, route *a*), resulting in concomitant formation of toluene and a pale yellow titaniumsilasesquioxane gel **2a** that occludes the entire volume of the solvent used. When subjected to prolonged centrifugation (20 min at 900 g), the gel releases toluene until a toluene/silasesquioxane mass ratio of *ca.* 18 is reached. Upon drying *in vacuo*, the gel collapses into a powder, yielding **2a** free of solvent in 90% yield. The swelling capacity of the dried titaniumsilasesquioxane gel **2a** for toluene is reduced to approximately 0.5 ml g⁻¹.

Related titaniumsilasesquioxane gels were also prepared from the building block **1** involving reactions with titanium tetrachloride and a base (Scheme 1, routes *b* and *c*). As a result of these synthetic methods, the gels obtained contain enclosed lithium chloride or [NHEt₃]Cl.

The silanol-mediated functionalizations that lead to the formation of the silasesquioxane gels **2** are straightforward and find precedent in the well exploited silanol-centred reactivity of the related silasesquioxane (C₆H₁₁)₇Si₇O₉(OH)₃.¹¹ Powder reflection UV–VIS measurements on **2a–c** show the onset of significant UV absorption only below 350 nm, with a maximum at 220–240 nm. This indicates that in **2a–c** the titanium centres exist as four-coordinate titanium(IV) siloxy units.

Analysis of the titaniumsilasesquioxane gels **2** by single-pulse 79.5 MHz ²⁹Si MAS NMR provides a method to establish the degree of silanol functionalization during their formation. Upon substitution, the originally lower field resonance of the silanol silicon atoms at δ –58.9 shifts towards the higher field part of the spectrum where the other silasesquioxane silicon resonances are already found (δ –65 to –75). Comparison of the integrals over the two distinct parts of the spectra indicates that the fraction of remaining silanol units in the titanium gels **2a–c** is, typically, 0.05 (*cf.* 0.25 in the silasesquioxane **1**), *i.e.* *ca.* 80% of the silanol units of the starting material **1** have been functionalized in the gel-forming process.



Scheme 1 Synthetic routes to the titaniumsilasesquioxane gels **2a–c** (Cy = cyclohexyl)

Interestingly, when any of the gels **2** are subjected to acid hydrolysis followed by organic work-up, the silasesquioxane **1** can be recovered in near to quantitative yield (Scheme 1, route *d*). From this observation, it can be concluded that the silanol deprotonations involved in the formation of the gels **2** do not induce any change in the silasesquioxane framework.

The titanium silasesquioxane gels **2** efficiently catalyse the epoxidation of alkenes under mild conditions (see Table 1). In a typical reaction equimolar amounts of alkene and *tert*-butyl hydroperoxide (TBHP) were reacted over the catalyst (*ca.* 1 mol% Ti with respect to the substrates) in hexane at 50 °C. Though for the reactions studied, the silasesquioxane gels **2** were reasonable to good catalysts, attempts to filter the catalyst off during epoxidation, and thus to stop the reaction, met with complications which were indicative of severe leaching of catalytically active species from the titanium gels. Interestingly, NMR studies showed that during epoxidation, rapid hydrolysis of the gel by TBHP occurs resulting in the quantitative reformation of the silasesquioxane **1** and concomitant formation of non-siloxy titanium species that are catalytically active.

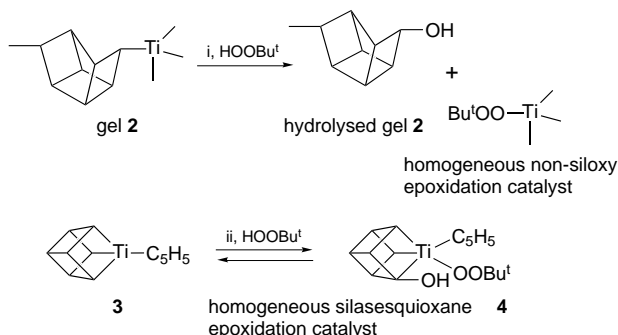
An essential feature of several of the proposed mechanisms of alkene epoxidation by titanium silicalites involves hydrolysis of a titanium siloxy function in a four-coordinate active site.^{12–15} For the titanium gel **2**, such a hydrolysis step would lead to rapid degeneration of the material since the titanium siloxy units (Ti–O–Si) result here from functionalization of isolated silanol groups, the silasesquioxane being a bifunctional monodentate ligand (Scheme 2, route *i*). This would therefore imply that silasesquioxane titanium species where the silasesquioxane can bind to titanium as a multidentate ligand are more robust epoxidation catalysts.

In order to verify this hypothesis, we have tested the activity of the known silasesquioxane complex **3**, that has a terdentate

Table 1 Epoxidation of alkenes with TBHP catalysed titanasilasesquioxanes^a

Catalyst	Alkene	<i>t</i> /h	Conv. (%)	Selectivity in alkene (%)
2a	Oct-1-ene	24	15	60
2b	Oct-1-ene	24	25	60
3	Oct-1-ene	24	80	80
2a	Cyclooctene	4	50	> 95
2b	Cyclooctene	4	90	> 95
3	Cyclooctene	3	90	> 95
2a	Norbornylene	4	60	> 95
2b	Norbornylene	3.5	90	> 95
3	Norbornylene	3	90	> 95

^a All reactions were performed using equimolar amounts (1.6 mmol) of alkene and dried *tert*-butyl hydrogen peroxide (1.6 mmol) in hexane (1.0 ml). Reactions were performed at 50 °C in sealed vials that were magnetically stirred using 25 mg of catalyst. Conversions and yields were determined by ¹H NMR spectroscopy.



Scheme 2 Schematic representation of the reaction of silasesquioxane titanium species with TBHP rendering species capable of alkene epoxidation: *i*, the irreversible hydrolysis of the silasesquioxane gels **2** and *ii*, the reversible hydrolysis of a silasesquioxane complex (the lines in the cube-type ligands represent Si–O–Si, with cyclohexyl units at the corners)

silasesquioxane ligand,^{8,16} for similar alkene epoxidations (Table 1). Interestingly, complex **3** turned out to be an epoxidation catalyst that is effective at low concentration and which selectively produces alkene oxides in high yield with good peroxide economy. Especially the somewhat difficult epoxidation of oct-1-ene is catalysed more effectively by **3**. The same catalytic performance was found for **3** that was repeatedly recrystallized from toluene–acetonitrile, which seems to exclude the possibility that undetected trace impurities in **3** are responsible for the observed catalytic activity. It is likely that due to multidentate silasesquioxane coordination, **3** does not hydrolyse irreversibly during epoxidation reactions (Scheme 2, route *ii*); in fact, the complex is even stable in 1 *m* aq. HCl! Under catalytic conditions, complex **3** can be easily monitored by ¹H and ¹³C NMR, its cyclopentadienyl unit providing a convenient and sensitive NMR probe. From these NMR experiments it could be concluded that after *ca.* 100 turnovers, complex **3** is still the only observable silasesquioxane species present and that it does not lose the cyclopentadienyl ligand during epoxidation catalysis. These findings are consistent with a mechanism for alkene epoxidation in which reversible hydrolysis of a titanium siloxy function occurs. In our opinion, these observations support the mechanism of heterogeneous alkene epoxidation by titanium silicalites proposed by Clerici, Ingallina, Sheldon and Van Doorn.^{12–15}

In conclusion, we have shown that new titanium-containing silasesquioxane gels effectively catalyse the epoxidation of alkenes by TBHP under mild conditions. The active catalyst, however, is a soluble, non-siloxy titanium species. Alternatively, the titanium complex **3**, that contains a terdentate silasesquioxane ligand, has excellent performance in the same epoxidations. In this case, the catalysis occurs exclusively through titanium siloxy complexes. As such, liquid-phase, silica-supported titanium epoxidation catalysts are predicted to be accessible and active in many cases but will be truly heterogeneous only when stringent conditions are met. More work on the structural characterization of the titanasilasesquioxane gels as well on their use in catalysis is currently in progress together with experimental work on the heterogenization of complex **3**.

The research of H. C. L. A. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW). S. K. thanks the Netherlands Institute for Catalysis Research (NIOK) for financial support.

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Received, 22nd November 1996; Com. 6/07935K