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# Silsesquioxanes as molecular analogues of single-site heterogeneous catalysts

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We discuss herein selected examples of metal complexes of polyhedral oligosilsesquioxanes (POSSs) as models of single-site heterogeneous surface catalysts. The utility of these compounds as such models is illustrated when employed as analogues of single-site titanium species supported on a silica surface. Deep insights into structure–functionality relationships can be gained. In particular, it was possible to probe the relationship between accessibility of the reactive centre and turnover frequencies in a manner that is impossible for a purely heterogeneous catalyst. We also report that the partially dehydroxylated SiO<sub>2</sub> surface alone is an effective radical polymerization initiation catalyst. This surface reactivity is modelled by the solution reactions between the olefin substrate and two POSSs, the completely condensed trigonal prism, Si<sub>6</sub>Cy<sub>6</sub>O<sub>9</sub> (*a6b0*, Cy = Cyclohexyl, C<sub>6</sub>H<sub>11</sub>), and the incompletely condensed partial cube, Si<sub>7</sub>Cy<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> (*a7b3*). The former, with six-membered Si<sub>3</sub>O<sub>3</sub> rings, is a catalyst. The latter, without this feature, is not. Similar reactivity discrimination is observed in the gas phase reactions of these POSSs with the olefin substrate, examined using atmospheric pressure chemical ionization- and collision-induced decomposition spectroscopies. Silsesquioxane *a6b0*, containing Si<sub>3</sub>O<sub>3</sub> rings, reacts with the olefin, forming grafted olefin monomers and dimers, while this reactivity is not observed with silsesquioxane *a7b3*.

**Keywords:** silsesquioxane; catalyst; surface; titanium; radical; model

## 1. Introduction

Our understanding of catalytic sites has increased exponentially over the last three decades. It is now possible to speak of ‘designing’ a catalytic single-site without exaggeration, even in the field of heterogeneous catalysis (Thomas 2012). Stunning advances in the experimental and theoretical arsenal have made this possible, e.g. *operando* techniques (Beale *et al.* 2010) or the sheer computational power available, already in the humble desktop computer (Norskov *et al.* 2009).

Homogeneous catalysts are more easily studied than their heterogeneous counterparts, for the obvious reason that they are single-site catalysts dissolved in a well-defined reaction medium. Spectroscopic responses of active sites in

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One contribution of 14 to a Special feature ‘Recent advances in single-site heterogeneous catalysis’.

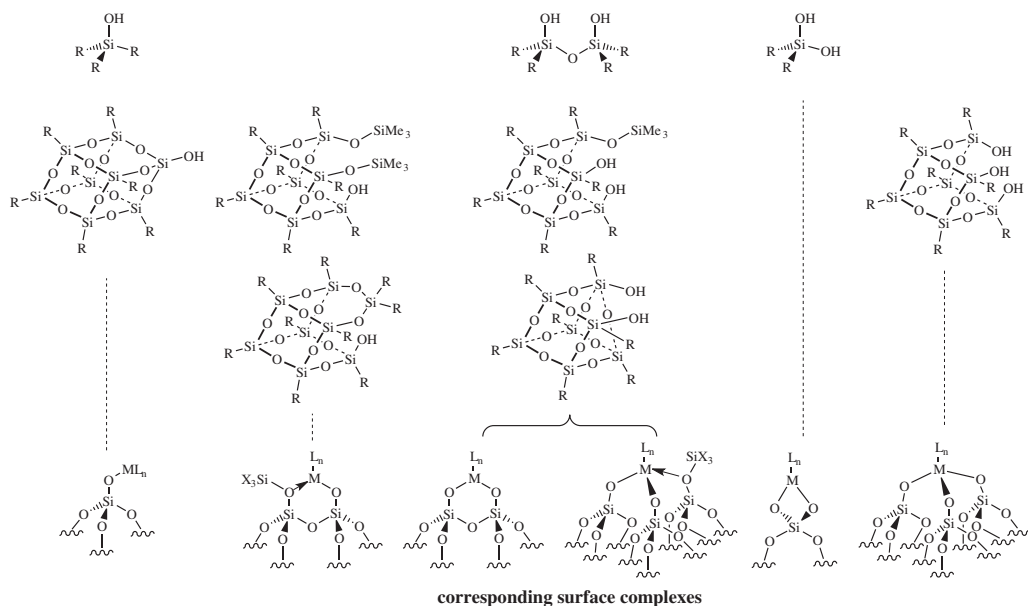


Figure 1. Molecular models that mimic the various types of silanol groups of a silica surface. Modified from Copéret *et al.* (2003).

heterogeneous catalysts are often masked by the response of the bulk material, and it is very difficult to tease out structural information of the active site, even before catalysis, let alone during catalysis—particularly, if the support is amorphous and/or if the active sites are not crystallographically distinct.

One approach to mitigating this difficulty is to use model compounds that are thought to represent the surface species envisaged. Here, soluble molecular analogues of silica surfaces, polyhedral oligosilsesquioxanes (POSS) have been used extensively, along with alkylsilanols, to mimic the structure and chemistry of silica surfaces (figure 1). Structures of the silsesquioxane family represent the best molecular equivalents of the silica surface as they mimic the environments of the different types of silanol groups (isolated, vicinal or geminal), the dispositions of near-surface silicon and oxygen atoms, and have  $pK_a$  values for  $\geq\text{SiOH}$  units that are close to that of silica (Ward *et al.* 2011). In addition, pure silica surfaces, particularly those containing grafted metal complexes, have also been successfully investigated. Important characteristics that can be replicated in silsesquioxane chemistry include electron-withdrawing bonding sites (Feher & Tajima 1994) and interactions with adjacent oxygen donors (Herrmann *et al.* 1994), which both contribute to the stability of grafted metal complexes (Liu *et al.* 1990; Abbenhuis 2000). Thus, silsesquioxane-based homogeneous models for single-site heterogeneous catalysts offer a unique opportunity to understand heterogeneous catalysis on a molecular level.

In this contribution, we will discuss two different types of POSS modelling behaviour. The first and more conventional is where the silsesquioxane acts simply as a ligand. This mode of action will be illustrated by reviewing titanium complexes of incompletely condensed POSS. The second mode of action is where

the silsesquioxane can model activity associated with the non-derivatized silica surface itself. Here, we will not discuss the well-established reactivity associated with silanol groups (e.g. very mild acidity, reversible condensation, etc.), but we will introduce a new discovery, i.e. a system in which the dehydrated silica surface can act as a radical polymerization initiator and where these single sites can be modelled qualitatively using silsesquioxanes.

## 2. Titanium–silsesquioxanes

In the mid-1990s, the preparation of isolated titanium species, supported by silica was a topic of great interest, in part, owing to the development of zeolite TS-1 (an MFI structure with framework-substituted isolated titanium atoms). Ti ions incorporated into the framework sites of silicalite I and II (i.e. TS1 and TS2, respectively, introduced by the Enichem Company; Perego *et al.* 1980) as well as into the framework sites of ZSM-12 (Tuel 1995), ZSM-48 (Serrano *et al.* 1992; Reddy *et al.* 1994), zeolite  $\beta$  (Cambor *et al.* 1993) and analogous microporous alumino- (and silico-) phosphates such as ALPO-5, ALPO-11 and SAPO-5 all show remarkable catalytic properties (Tuel & Taarit 1994; Ulagappan & Krishnasamy 1995).

However, one disadvantage of these titano-microporous catalysts was, and is, that their pore dimensions are too small to allow access to bulky reactants of the kind that dominate most of the chemical transformations which are of central importance in the fine-chemical and pharmaceutical industries. A significant step forward was reported (Corma *et al.* 1994; Tanev *et al.* 1994) with the preparation and use of Ti-MCM-41 in which the Ti is incorporated (during synthesis) in the framework of mesoporous silica having a pore diameter of *ca* 30 Å.

It appeared that either titanol or titanyl species were the active sites, but it was difficult to prepare them with confidence. By extending the concepts of what has come to be known as interfacial coordination chemistry (Scott & Basset 1994) and of surface organometallic chemistry (Wilkinson *et al.* 1982; Zecchina & Otero Areán 1993), titanocene dichloride was grafted onto the totally accessible inner surfaces of siliceous MCM-41 in presence of a base, as schematized in figures 2 and 3.

The resulting material, with well-separated, well-defined, high surface concentrations of Ti-containing active sites, exhibited very high catalytic performance compared with other heterogeneous Ti–silica catalysts.

By using such a well-defined organometallic precursor, it was possible (i) to predict what would happen chemically during the grafting process and (ii) to design the system in such a way that one was confident of having isolated sites which could then be interrogated with the synchrotron radiation technique extended X-ray absorption fine structure (EXAFS) to determine the nature of the site unequivocally. In fact, this paper demonstrates an up to that time unprecedented level of detail in structural characterization. It was possible to structurally follow not only the synthesis of the surface-grafted active catalyst from its precursor half-sandwich complex, but also to ascertain that the original four-coordinated active site becomes six-coordinated under reaction conditions, and to watch the activity being lost by water uptake and then to follow the reactivation of the catalyst subsequent to water removal, effectively identifying

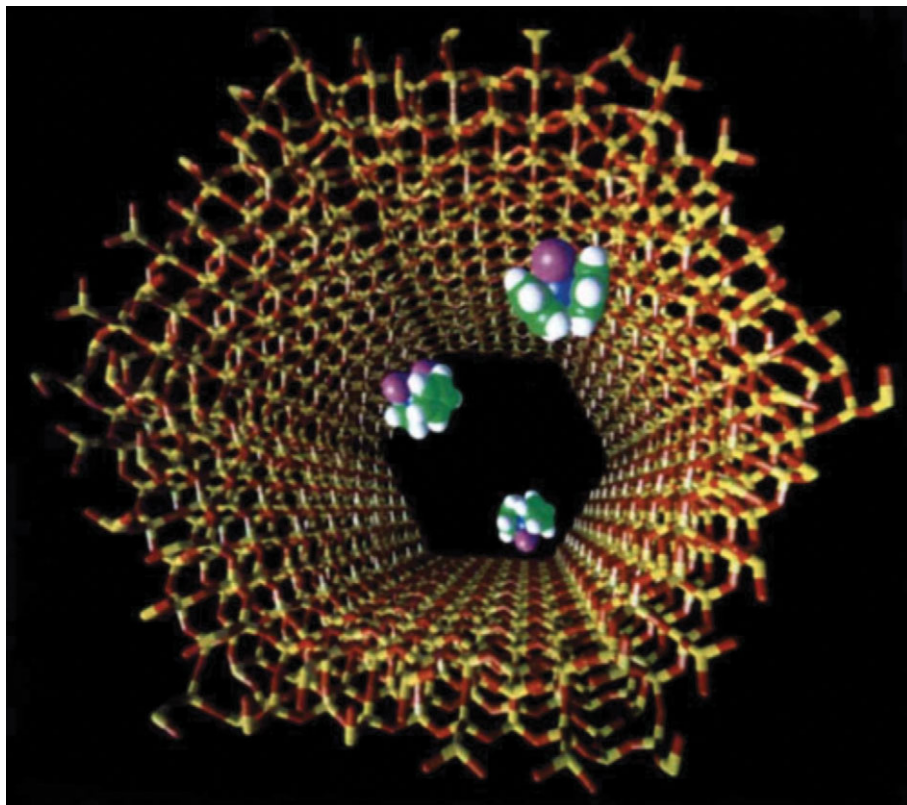


Figure 2. Illustration of titanocene dichloride diffusing into a channel of MCM-41 (Maschmeyer *et al.* 1995). (Online version in colour.)

the ‘pre-natal, post-natal, dead and resurrected’ states of the catalyst. From these studies, it was clear that the active sites are atomically dispersed titanol centres (Marchese *et al.* 1997, 1999; Sinclair *et al.* 1997; Thomas *et al.* 1999).

To investigate whether it was indeed possible to prepare the postulated intermediate half-sandwich titanocene complex and whether isolated titanols are, in fact, active catalytic centres, a number of studies were reported which sought to answer these questions using titanium complexes of silsesquioxanes as model compounds.

(a) *Half-sandwich complexes of titanium(IV) silsesquioxanes*

The first half-sandwich silsesquioxane complex was the pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) derivative, prepared by the reaction of  $\text{Cp}^*\text{TiCl}_3$  with  $(c\text{-C}_6\text{H}_{10})_7\text{Si}_7\text{O}_9(\text{OH})_3$  in the presence of  $\text{NEt}_3$  as previously described by Maschmeyer and co-workers (Hambley *et al.* 1992; Buys *et al.* 1994). This type of compound can also be synthesized by the reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3$  with  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OSbMe}_4)_3$  (figure 4; Feher *et al.* 1992). The latter method proves to be efficient for the synthesis of substituted-cyclopentadienyl–titanium–silsesquioxane complexes, such as  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{Ti}(\eta^5\text{-C}_5\text{Ph}_5)\}$

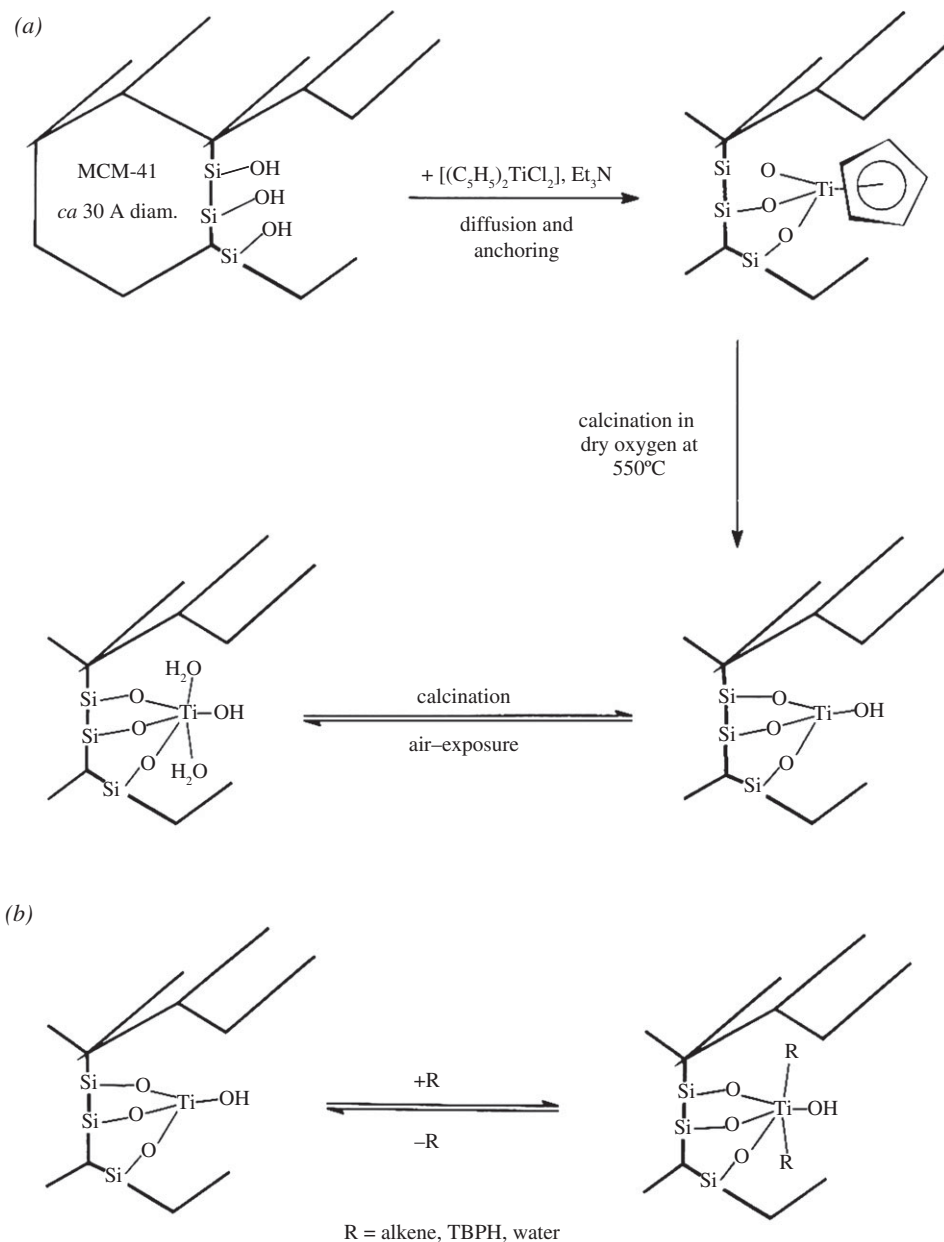


Figure 3. Illustration of the surface reactions associated with the grafting of titanocene dichloride (Maschmeyer *et al.* 1995). (a) Anchoring of half-sandwich complex, (b) calcination to prepare atomically dispersed Ti-centres.

(Field *et al.* 1994). This cp-titanium-silsesquioxane complex is an efficient and robust epoxidation catalyst (50°C, hexane, substrate: Ti, approx. 100:1) for oct-1-ene, cyclohexene and norbornylene (Abbenhuis *et al.* 1997). In the case of cyclohexene and norbornylene, conversions of 90 per cent and selectivities of greater than 95 per cent were obtained in 3 h.



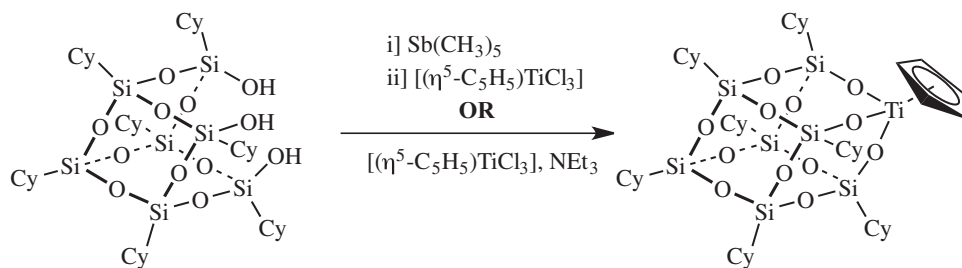


Figure 4. Synthetic route to the titanium(IV) silsesquioxane complex  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\}$ .

The stability of  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{Ti}(\eta^5\text{-C}_5\text{Ph}_5)\}$  under the catalytic conditions employed led van Santen and co-workers to immobilize the complex in the mesoporous silica MCM-41 (with Si/Al ratios of 42, 125 and  $\infty$ ; Krijnen *et al.* 1999). The adsorption was performed simply and quantitatively by stirring a hexane solution of the complex with the MCM-41. The adsorption kinetics for the complex were typical for ‘single-file diffusion’, which indicated that the adsorption occurred within the channels of the silica. The presence of aluminium in the silica resulted in a reduction in activity of the catalysts, and, under the conditions employed, the catalyst was leached quantitatively from the silica. For the aluminium-containing catalysts, the leaching was completely stopped by treating the silica with the silylating agent  $\text{Ph}_2\text{SiCl}_2$  prior to catalysis (Krijnen *et al.* 1998). In addition, when a conventional silica gel was used to adsorb the titanium complex, a significant degree of leaching was observed during catalysis. This indicated that channel-type aluminium-free pores were required for irreversible adsorption.

(b) *Modelling the active site after calcination with a  $(\equiv\text{SiO})_3\text{Ti}(\text{OR})$  silsesquioxane environment*

The reaction of the cubic trisilanol  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_3$  and  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$  with  $\text{Ti}(\text{O}^i\text{Pr})_4$  in tetrahydrofuran affords the titanosilsesquioxanes  $\{[(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9]\text{Ti}(\text{O}^i\text{Pr})\}_n$  (Tang *et al.* 2006) (**1a**) and  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_8\text{O}_9]\text{Ti}(\text{O}^i\text{Pr})\}_n$  (**1b**), respectively (figure 5; Maschmeyer *et al.* 1997).

Nuclear magnetic resonance (NMR) studies show that these compounds are in equilibrium between the four-coordinate monomer (**1<sub>M</sub>**) and a five-coordinate dimer (**1<sub>D</sub>**) with a relative monomer–dimer ratio of *ca* 2 : 1. Addition of methanol to a solution of (**1**) led to the rapid and exclusive formation of the six-coordinate dimer ( $\text{R} = c\text{-C}_5\text{H}_9$  (**2a**),  $c\text{-C}_6\text{H}_{11}$  (**2b**)). A single crystal suitable for X-ray diffraction studies was obtained for (**2b**). Compound (**1a**) displayed catalytic activity for the epoxidation of cyclohexene ( $40^\circ\text{C}$ ,  $\text{CHCl}_3$ , catalyst : tert-butylOOH : substrate = 0.05 : 1 : 12), achieving 13 per cent conversion after 1 h, 98 per cent selectivity to the epoxide and a turnover frequency (TOF) of  $0.7 \text{ mmol}(\text{product}) (\text{g Ti})^{-1} \text{ min}^{-1}$ . Under identical conditions, (**2b**) achieved a conversion of 93 per cent in 1 h with 98 per cent selectivity to the epoxide with a TOF of  $4.8 \text{ mmol}(\text{product}) (\text{g Ti})^{-1} \text{ min}^{-1}$ . As these complexes were prepared as model compounds for the grafted Ti heterogeneous catalyst system  $\text{Ti} \uparrow \text{MCM-41}$

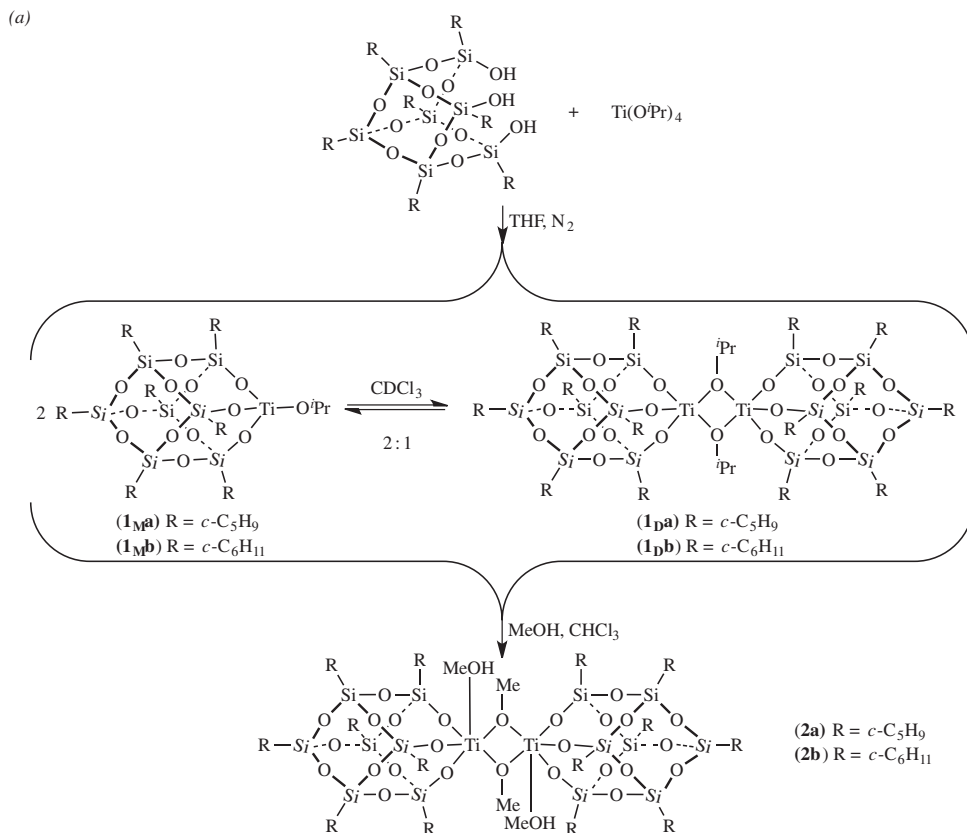
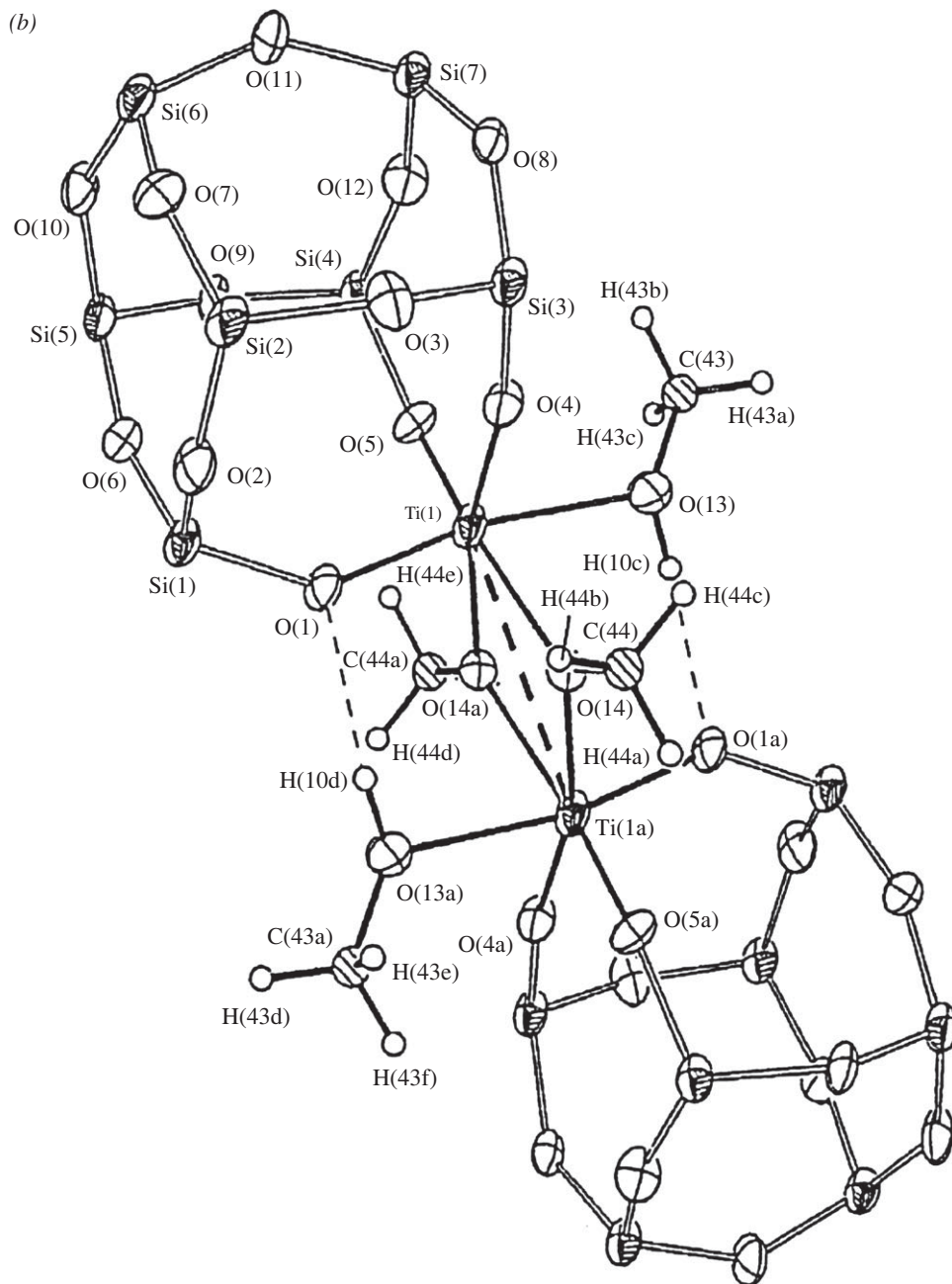


Figure 5. (a) Synthesis of the titanasilsesquioxanes (**1**) and (**2**) (redrawn from Maschmeyer *et al.* (1997)). (b) Crystal structure of (**2b**).

(Maschmeyer *et al.* 1995), it is instructive to compare the TOFs observed with those achieved by the grafted Ti catalyst. The heterogeneous case achieves a TOF of  $3 \text{ mmol}(\text{product})(\text{g Ti})^{-1} \text{ min}^{-1}$  for the epoxidation of cyclohexene under identical conditions to those employed for (**1a**) and (**2b**). This comparison of the TOFs shows that the dimer, (**2b**), displays the greatest activity of all three catalysts. This result initially seems to contradict the idea that the four-coordinated titanium would give rise to the greatest activity, i.e. it would be expected that monomer (**1a**) is most reactive (owing to the greater number of available coordination sites relative to the dimer). However, testing the nature of the group in the fourth coordination site of the dimer revealed that the reactivity of the catalyst was dependent upon the alkoxy group (in order of decreasing reactivity: OMe > O<sup>*t*</sup>Bu  $\gg$  O<sup>*i*</sup>Pr). Therefore, access to the four-coordinated site is very important—hence, when the fourth coordination site is occupied by a hydroxyl group, as on the actual surface, the accessibility is maximized. Although some reduction of the TOF in the heterogeneous system has to be allowed for due to diffusion barriers associated with its channels and pores.

To compare the activity of sol-gel prepared Ti-MCM-41 with silsesquioxanes other studies built on the insights above. Crocker *et al.* investigated the reaction of a series of homoleptic titanium(IV) complexes [TiL<sub>4</sub>] with the



Figure 5. (*Continued.*)

incompletely condensed silsesquioxane  $(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$ , affording the titanium–silsesquioxane complexes  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{TiL}\}$  ( $\text{L} = \text{CH}_2\text{Ph}$  (**3a**),  $\text{NMe}_2$  (**3b**),  $\text{OSiMe}_3$  (**3c**),  $\text{O}^i\text{Pr}$  (**3d**)) via a protonolysis reaction (Crocker & Herold 1997; Crocker *et al.* 1997). The tripodal  $\text{TiL}(\text{silsesquioxane})$  species formed were monomeric when freshly prepared, but when  $\text{L} = \text{O}^i\text{Pr}$ , dimerization

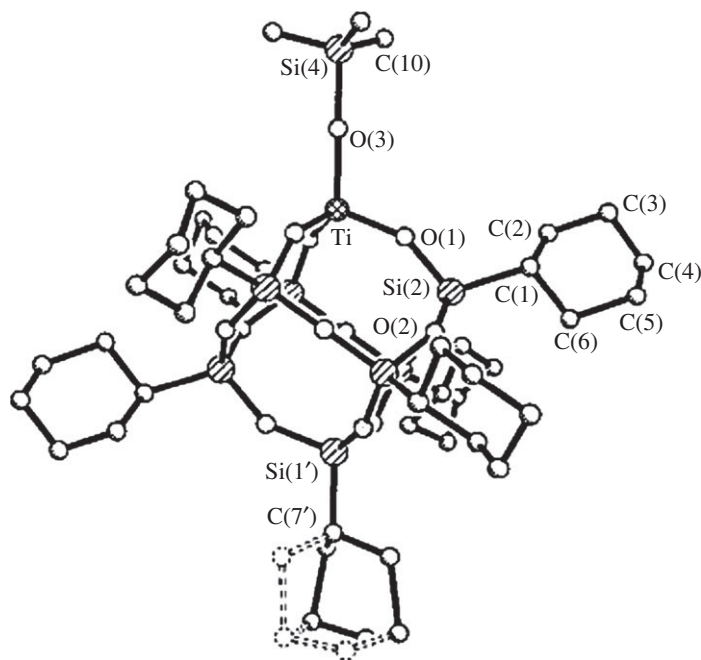


Figure 6. Molecular structure of  $\{[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}]\text{TiO}^i\text{Pr}\}$  (**3d**) (Crocker *et al.* 1997).

occurred on standing (affording a monomer : dimer ratio of *ca* 5 : 2; Maschmeyer *et al.* 1997). In the case of  $\text{L} = \text{OSiMe}_3$  (**3c**), the monomeric nature of the titanasilisequioxane species was confirmed by single crystal X-ray diffraction. The titanium centre in (**3c**) has pseudo-tetrahedral geometry and is coordinated to one tridentate silsesquioxane ligand and one siloxy ligand, such that the molecule has exact  $\text{C}_3$  symmetry (figure 6). Reaction of the disilanol silsesquioxane  $(c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9(\text{OH})_2(\text{OSiMe}_3)$  with half an equivalent of  $\text{TiCl}_4$  afforded the bis(silsesquioxane) complex  $\{[c\text{-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)_2\text{Ti}\}$  (**3d**). The epoxidation of oct-1-ene with  $t\text{BuOOH}$  was chosen as a test of catalytic activity for the complexes (**3a–d**) ( $80^\circ\text{C}$ , neat, substrate : Ti = 3342 : 1). The second-order rate constants for the epoxidation were found to be 1.23 (**3a**), 0.63 (**3b**), 0.97 (**3c**) and 1.49 (**3d**)  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  for the complexes. The selectivity of the reaction for all catalysts was greater than 93 per cent. The rate constant for the dimer (**3d**) ( $0.047 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) was an order of magnitude less than those of the other complexes tested with a selectivity of 83 per cent. Comparison with Ti-MCM-41 under the same reaction conditions revealed that the silsesquioxane-based catalysts were an order of magnitude more active based on the rate constants. Hence, the authors concluded that the most active sites in the heterogeneous materials (i.e. Ti-MCM-41) were the tripodal, open-lattice titanium sites. These results suggest that the lower activity of the Ti-MCM-41, prepared by sol-gel means, can be ascribed to the fact that only a small fraction of the surface titanium sites possesses the correct coordination environment for catalysis.

### 3. Silsesquioxane analogues of strained surface siloxanes

Although silica materials and silica-supported catalysts are ubiquitous (Min *et al.* 2003; Quignard & Choplin 2003; Severn *et al.* 2005; Corma & Garcia 2006), the synthetically meaningful radical chemistry that can be induced by their surfaces has largely been overlooked.

Silica surfaces are composed of rings of siloxane bridges ( $\equiv\text{Si-O-Si}\equiv$ ) and silanol groups ( $\equiv\text{Si-OH}$ ). The concentrations and types of these surface functionalities depend on a range of parameters, including the silica synthesis method (sol-gel, flame pyrolysis), the heating regimes to which the surface has been exposed in terms of temperature, length of time and the presence or exclusion of water/water vapour (Ravve 2000).

Siloxane bridges are characterized by their ring size (i.e. four- $(\text{Si}_2\text{O}_2)$ , six- $(\text{Si}_3\text{O}_3)$ , eight- $(\text{Si}_4\text{O}_4)$ , etc. membered rings), while the silanol groups are either isolated, geminal or vicinal and can occur around defects as so-called silanol 'nests' (Bordiga *et al.* 2000, 2001). When silica is exposed to high temperatures, some of the silanol groups condense to eliminate water and to produce siloxane rings, with the proportion of strained siloxane rings increasing with time and temperature (Iler 1979; Barrer 1982; Feher *et al.* 1989). At very high temperatures the siloxane rings can relax as the surface is close to melting, a process which decreases the number of strained surface species and, when occurring extensively, the surface area. Typically, silica heated above 250°C has no adsorbed water, and the number of Si-OH groups decreases from six OH/100 Å<sup>2</sup> initially to two OH/100 Å<sup>2</sup> at 500°C, then to one OH/100 Å<sup>2</sup> at 800°C (Griscom 2000).

Classically, only Si-OH groups were thought to be synthetically reactive and that hydrolysis of a siloxane to generate two Si-OH groups was needed to activate siloxanes. However, in this contribution we contend that strained six-membered surface siloxanes can also react by forming surface radicals and serve as synthetically useful radical initiators. Our hypothesis that relatively stable surface radicals can be generated is based on various electron paramagnetic resonance (EPR) investigations published over the last four decades involving silica-alumina and probe molecules (Rooney & Pink 1961, 1962; Hall 1962).

Using anthracene as an EPR probe of a calcined amorphous pure silica surface (600°C for 20 h under a stream of dry nitrogen), denoted as SiO<sub>2(600)</sub>, a strong signal was observed in the EPR spectrum recorded at 170 K (figure 7*a*). However, no signal was observed when anthracene was loaded onto uncalcined silica (figure 7*b*).

This shows that for radical formation to occur on silica no heteroatoms, such as aluminium, are necessary, and that silica surface species on their own are sufficient.

Therefore, calcined silica should be able to initiate various radical reactions such as free-radical polymerizations. This type of polymerization is commonly initiated/co-initiated by the decomposition of highly reactive and unstable species, such as azo-compounds (e.g. azobisisobutyronitrile), peroxides (e.g. di-*tert*-butyl peroxide; Perkins 1994) or various metallocenes, either as homogeneous (Cunningham & Fassihi 2005; Sánchez-Nieves & Royo 2007) or immobilized species (Tudor & O'Hare 1997; Choi *et al.* 2005). However, these catalysts are often expensive as well as non-trivial to synthesize and handle.

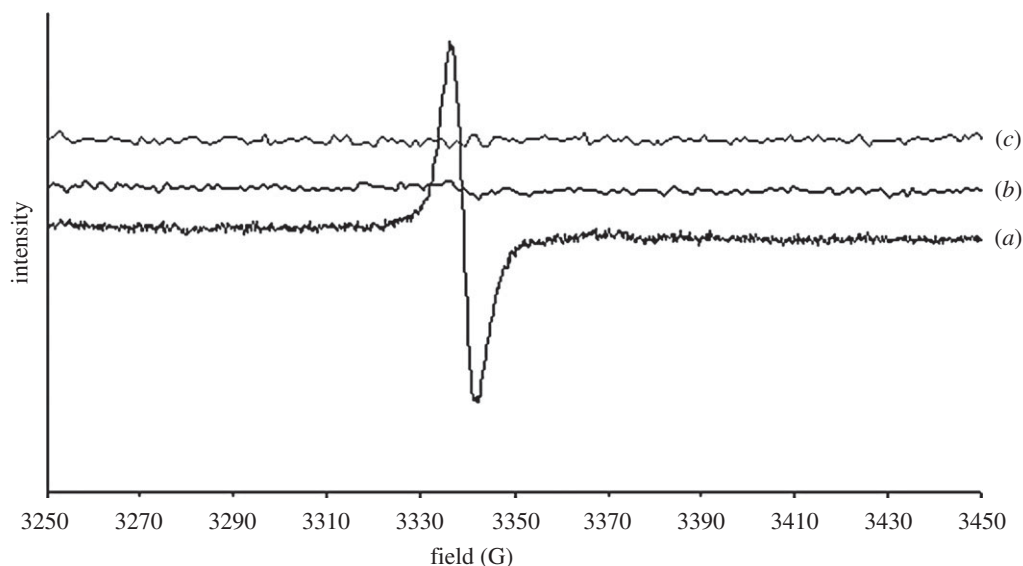


Figure 7. EPR spectra of (a)  $\text{SiO}_{2(600)}$ -anthracene, (b) uncalcined silica-anthracene, and (c) an empty EPR tube. All samples were prepared as neat solids and the spectra recorded at 170 K.

Significant implications for supported catalysts, active in reactions where radicals can influence observed reactivities and selectivities, would result if  $\text{SiO}_{2(600)}$  were, indeed, an active catalyst for, e.g. the radical polymerization of methyl acrylate. Table 1 summarizes the data of the relevant polymerization experiments in refluxing hexane.

Consistent with what is generally observed in radical methyl acrylate polymerizations, there is a degree of thermally induced ‘background’ polymerization (entry 1). Addition of uncalcined silica (postulated to have no active radical surface species) does not lead to higher than background conversions (entry 2). However, use of the  $\text{SiO}_{2(600)}$  catalyst increases the polymer yield to 77 per cent, generating a high-quality poly(methyl acrylate) with a polydispersity index (PDI) that is very close to the theoretically ideal value of 1.2 (entry 3; Rosen 2000; Stepto 2009). Addition of a common radical trap, 2,6-di-*tert*-butylphenol, reduces the yield to below background, as expected, showing that the action of the  $\text{SiO}_{2(600)}$  is of radical nature (entry 4). The performance of the  $\text{SiO}_{2(600)}$  catalyst when compared with standard literature methods (entries 5 and 6) compares very well in terms of PDI and  $M_n$  as well as  $M_w$ . The low PDI would be consistent with anchoring of growing polymer chains on the surface, decreasing the probability of chain branching during the polymerization.

Furthermore, when the activated  $\text{SiO}_{2(600)}$  catalyst is left in air it becomes inactive, but even after several months a simple re-calcination regenerates that activity to the extent that the catalytic activity is indistinguishable from the original sample. This is consistent with no trace metal contamination being responsible for the observed activity.

However, to further test whether the observed activity is, indeed, due to strained surface species and to absolutely rule out any metal contamination at ppm/ppb level providing the activity, molecular models of silanols ( $\text{Si-OH}$ ),

Table 1. Polymerization data of methyl acrylate in hexane using silica initiators.<sup>a</sup>

entry	catalyst	solvent	temperature (°C)	time (h)	yield (%)	$M_n$	$M_w$	PDI
1	—	hexane	70	24	22	2600	12 000	4.6
2	uncalcined SiO <sub>2</sub>	hexane	70	24	20	—	—	—
3	SiO <sub>2</sub> (600)	hexane	70	24	77	20 000	27 000	1.35
4	SiO <sub>2</sub> (600)/radical trap	hexane	70	24	13	—	—	—
5	CpTiCl <sub>3</sub> /MAO (Cunningham & Fassihi 2005)	toluene	50	4	51	7800	15 000	1.90
6	[(CuBr/TPEN/EBiB)] (Tang <i>et al.</i> 2006)	—	80	1.5	80	7800	9000	1.15
7	[(CySi) <sub>7</sub> (OH) <sub>3</sub> ], <i>a7b3</i>	hexane	70	24	21	2700	11 000	4.1
8	[(CySi) <sub>6</sub> ] <sub>9</sub> , <i>a6b0</i>	hexane	70	24	53	3600	14 000	3.9

<sup>a</sup>The selected silica source (0.0400 g) and methyl acrylate (8 ml) were heated under reflux in hexane (30 ml) for 24 h. The reaction mixture was cooled to room temperature and the hexane removed *in vacuo* to afford poly(methyl acrylate) as a highly viscous gel.

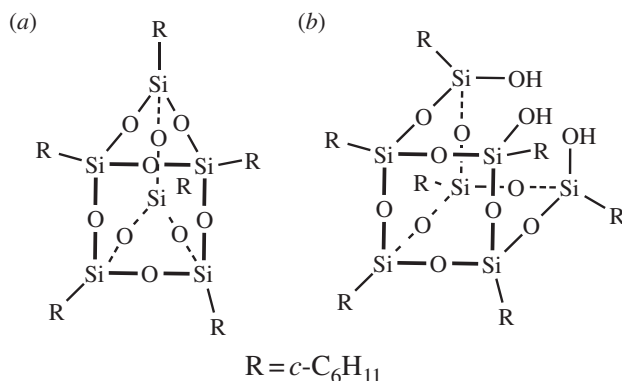


Figure 8. The silsesquioxanes (a) *a6b0* and (b) *a7b3* which were prepared following the procedure outlined by Pescarmona *et al.* (2004).

unstrained (eight-membered rings,  $\text{Si}_4\text{O}_4$ ) and strained (six-membered rings,  $\text{Si}_3\text{O}_3$ ) siloxanes (figure 8) were reacted with methyl acrylate analogously to the polymerizations involving  $\text{SiO}_{2(600)}$ .

For the model, *a6b0*, containing the strained siloxane rings a distinct increase in yield over the background reaction could be observed (entry 7), whereas from model compound *a7b3*, containing both silanol and unstrained siloxanes, no such additional activity resulted (entry 8).

These observations clearly and unequivocally prove that (i) no metal contamination was responsible for the silica reactivity, (ii) strained siloxanes are responsible for the observed radical chemistry and (iii) silanols have a negligible effect on the polymerization.

Based on the above, we propose a homolytic cleavage of a strained Si–O bond which gives rise to two radical species as the main radical formation and polymerization initiation reaction. Once the radicals have been generated they are free to react with suitable substrates, in this case the activated alkene in methyl acrylate. Indeed, high-resolution mass spectral studies (ESI+,  $\text{CH}_2\text{Cl}_2$ ) of the silsesquioxane *a6b0*, when injected in the presence of methyl acrylate, revealed the presence of ions at approximately  $m/z$  811, 856, 897 and 955, the first one being the parent ion of the unreacted silsesquioxane and the other three all consistent with a reaction between the methyl acrylate and the silsesquioxane. Structural interpretations of these precise masses are shown in figure 9. Therefore, we interpret the interactions as having arisen from homolytic cleavage of a relatively strained silsesquioxane Si–O bond, since this is consistent with the proposed mechanism and, because notably, such interactions are completely absent when using the more relaxed and incompletely condensed silsesquioxane *a7b3*.

Thus, the radical pre-cursor surface sites, postulated to be strained siloxane rings, such as, e.g.  $\text{Si}_3\text{O}_3$ , are successfully modelled by similar rings present in molecular analogues, i.e. the POSS [(cySi) $_6\text{O}_9$ ]. A related molecular species containing no such rings, but only  $\text{Si}_4\text{O}_4$  rings and silanols, displays no polymerization activity.

These results clearly show the necessity for careful assessment of the potential influence of the calcination history of supporting silica surfaces in catalytic reactions that are susceptible to influence by radical chemistry, particularly,

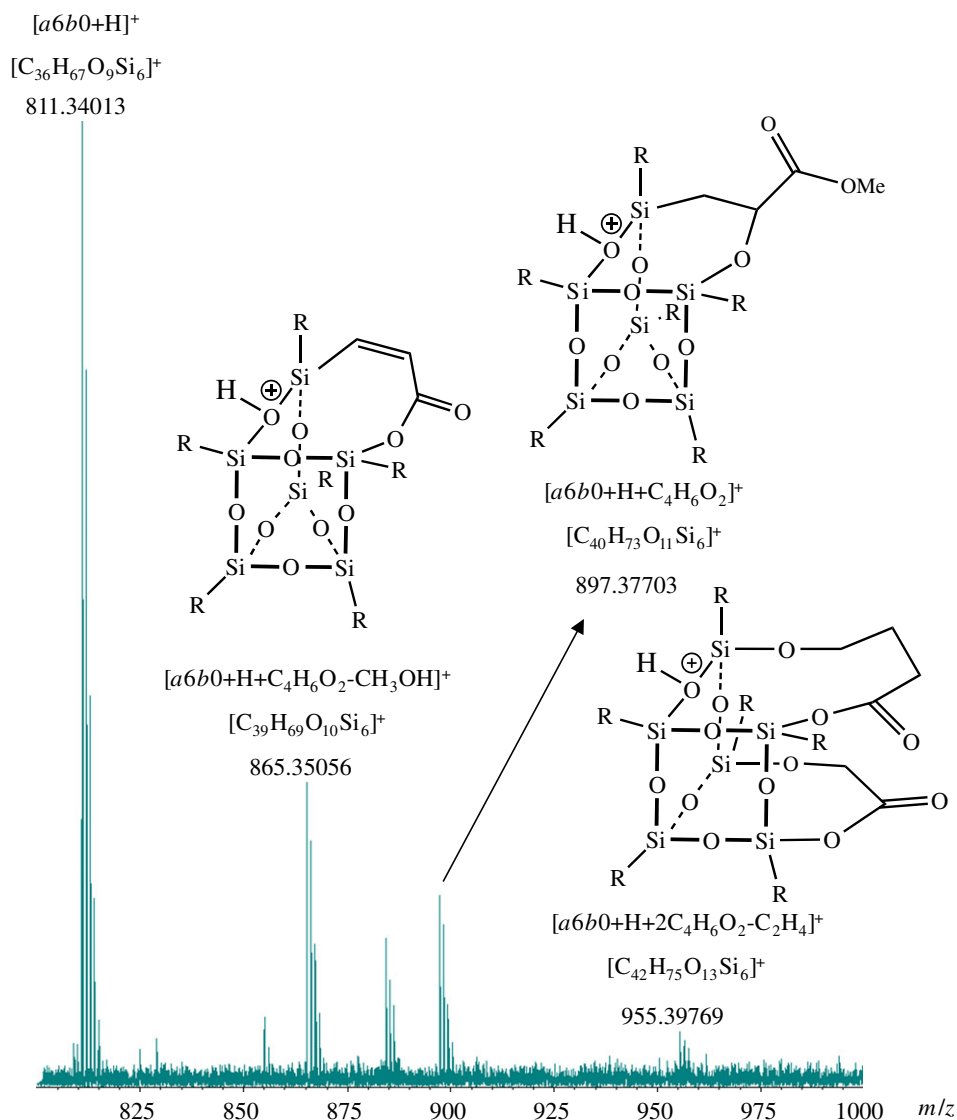


Figure 9. Mass spectrum (ESI+, CH<sub>2</sub>Cl<sub>2</sub>) of the completely condensed silsesquioxane *a6b0* when injected with methyl acrylate, with structural interpretations of the molecular formula obtained. (Online version in colour.)

when executing the design of single-site heterogeneous catalysts. The support surfaces may themselves act as single-site radical initiators in parallel to the desired chemistry.

#### 4. Conclusions

Overall, the insights into catalytic structure–functionality relationships, gained via chemical modelling using silsesquioxanes are unique, are unobtainable with



any other technique and have been tremendously valuable. As heterogeneous catalysts are increasingly used in fine chemistry applications as well—where even greater insight into their mode of action is needed—we predict a rich future for research into silsesquioxanes as catalyst models and catalyst precursors.

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