Modelling the active sites of heterogeneous titanium-centred epoxidation catalysts with soluble silsesquioxane analogues

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By synthesising and structurally characterising new soluble titanosilsesquioxanes, and by following the dynamics of epoxidation of cyclohexene in their presence, the tripodally anchored Ti[IV] active sites in Ti–SiO$_2$ heterogeneous catalysts are modelled structurally and catalytically.

There is a growing family of titanosilicates (*e.g.* titano-zeolite β,[1] TS-1,[2] TS-2,[3] ETS-10,[4] JDF-L1[5] and Ti-MCM41[6–8]) which are particularly good catalysts for the selective oxidation of organic molecules. Of these, Ti ↑ MCM41 (in which isolated, accessible Ti[IV] ions are grafted to the inner surface of the mesoporous silica MCM41 using titanocene dichloride as precursor) exhibits high performance in the epoxidation of alkenes under mild conditions.[9,10]

As direct studies of the active site in heterogeneous systems are difficult, modelling studies, by either chemical or computational methods,[11] are essential in any attempts to elucidate the full characteristics of the active site(s). It is therefore desirable to prepare soluble molecular titanosilicates, especially since previously a similar strategy has proved helpful in the elucidation of the nature of the active site in Os- and Cr-containing silicas.[12]

We extend earlier modelling studies[13,14] by going beyond the simulation of just the first step of anchoring titanocene dichloride to the silica surface; the coordination environment after removal of the cyclopentadienyl ligand is modelled by reacting the well characterised cubic trisilanols [(c-pentyl)$_7$-Si$_7$O$_9$(OH)$_3$], **1a**, and [(c-hexyl)$_7$Si$_7$O$_9$(OH)$_3$], **1b**, with titanium tetra(isopropoxide) in tetrahydrofuran (THF) (Scheme 1).†

Three of the four titanium isopropoxide ligands of the trisilanols were substituted yielding titanosilsesquioxane **2** of

formula [(c-pentyl)$_7$Si$_7$O$_9$Ti(OPr^i)]$_n$·THF with loosely coordinated THF molecules. On extraction in hexane and recrystallisation from chloroform it is possible to displace the THF molecules and obtain pure **2**.‡ Studies of the ^{13}C NMR spectrum of this compound in CDCl$_3$ show an equilibrium between the four-coordinate monomer **2a** and five-coordinate dimer **2b**. A related dimeric Ti[III] silsesquioxane without additional alkoxide ligands has been observed previously.[15] These monomeric and dimeric forms are easily identified on the basis of their cycloalkyl *ipso*-carbon resonances.[16] In addition, bridging[17] and terminal[18] isopropoxide ligands have been identified, by both ^{1}H and ^{13}C NMR spectroscopy, the relative ratios of which indicate a monomer–dimer ratio of *ca.* 2 : 1 in CDCl$_3$ at room temp.[17]

Addition of methanol to a solution of **2** in CDCl$_3$ leads to fast ligand exchange and the almost exclusive formation of the six-coordinate dimer, titanosilsesquioxane **3**. Interestingly, no monomeric species could be observed in solution by NMR spectroscopy.[17] By switching from trisilanol **1a** to **1b** it has been possible to isolate a single crystal of **3** suitable for X-ray diffractive analysis and to establish its molecular structure (Fig. 1).§
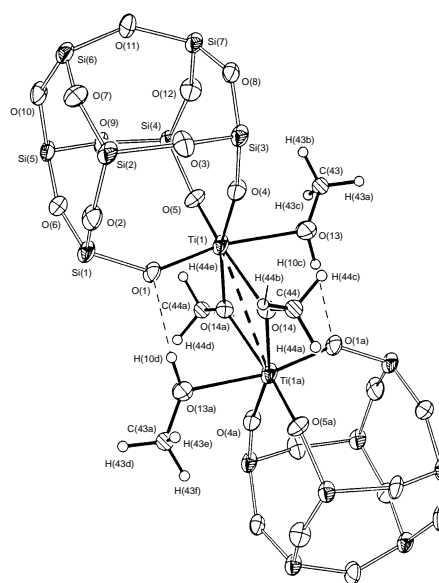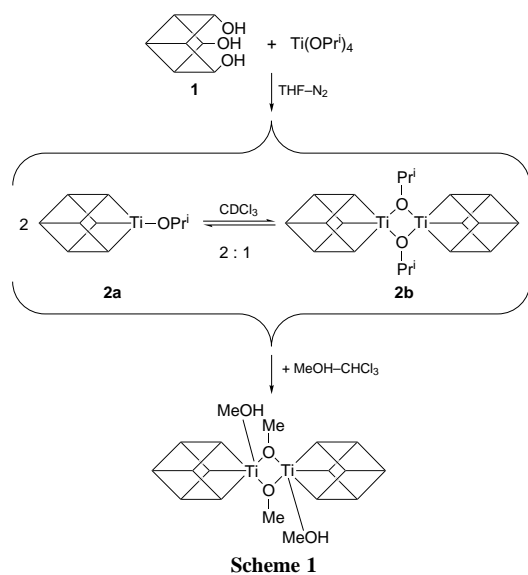

Fig. 1 Molecular structure of **3**, showing the atomic labelling scheme and H-bonding interactions in the dimer. Principal bond distances (Å) and angles (°): Ti(1)–O(1) 1.837(7), Ti(1)–O(13) 2.210(7), Ti(1)–O(14) 2.004(7), Ti(1)–O(14a) 2.022(7), Ti(1)···Ti(1a) 3.253(4), mean Si–O 1.619(8); O(1)–Ti(1)–O(4) 98.4(3), O(1)–Ti(1)–O(5) 100.6(3), O(1)–Ti(1)–O(13) 168.8(3); H(10d)–O(1) 1.985 Å shows directionality w.r.t the O(1) lone pair, O(13a)-H(10d)-O(1) 147.6, C$_6$H$_{11}$ groups are omitted for clarity. Symmetry operation: −x, −y, −z.

Scheme 1

The molecule is composed of two quasi-cubic silsesquioxanes related by a centre of inversion which lies between the two titanium atoms. These in turn are linked by two bridging methoxy groups with a mean Ti–O bond distance of 2.014(7) Å. The sixth position in the coordination sphere around the titanium is occupied by a datively bonded methanol group. The mean Ti–O silsesquioxane bond distance of 1.826(7) Å corresponds closely to that of grafted Ti ↑ MCM41 determined by EXAFS spectroscopy and calculational studies (1.81 Å and 1.82 Å, respectively).[9,11] The Ti–O distance of the datively coordinated methanol group [2.213(7) Å] corresponds closely to that observed for the Ti–substrate interaction (2.25 Å), observed for Ti ↑ MCM41 in its reactive state. This suggests a similar dative bonding of the substrate (most likely the peroxide, *cf.* Ti–O bonding distance of 2.26 Å in a *tert*-butylperoxotitanium complex[19]) to the titanium centre of the heterogeneous catalyst.

Dimer **2b** provides one free coordination site per titanium centre and the monomer **2a** two, allowing interactions with substrate molecules. Reactions with various peroxides showed that yellow peroxide complexes were readily formed, λ_{max} = 320 nm, indicative of η^2-coordinated peroxide.[20]

Monomer **2a**, with its readily available second free coordination site on the same titanium centre, makes this a close model for the postulated tripodally surface-anchored titanium monohydroxide proposed for grafted Ti ↑ MCM41.

Model compound **2** displays catalytic activity which compares well with earlier studies† in that after 1 h at 50 °C, 48% conversion was achieved for the epoxidation of cyclohexene with tetrabutylperoxyhydroxide (TBPH) in CDCl₃ using a catalyst–substrate ratio of 1 : 70 : 70 with 98% selectivity towards the epoxide. When comparing its turnover frequency (TOF) with that of the actual grafted Ti ↑ MCM41 catalyst (3 mmol cyclohexene g cat⁻¹ min⁻¹) under identical conditions,¶ a TOF of 0.7 mmol g cat⁻¹ min⁻¹ was observed, resulting in 13% conversion after 1 h. Interestingly, the titanosilsesquioxane **3** exhibited a much higher TOF (4.8 mmol cyclohexene g cat⁻¹ min⁻¹) resulting in 93% conversion after 1 h. Importantly, the catalytic conversion of cyclohexene to the epoxide is highly selective (98%) for both catalysts.

The lower performance of titanosilsesquioxane **2** relative to **3** runs counter to simple expectation as **3** is coordinatively saturated and the dimer–monomer equilibrium established for **2** shows it has free coordination sites. This result might be taken to imply a synergistic effect of the two titanium centres being in close proximity. However, such an effect has not been claimed for the Sharpless catalyst [Ti(tartrate)(OR)₂]₂ which is structurally related to **3**,[21] nor is there any evidence for it in heterogeneous catalysts, where it is well established that the TOF per titanium centre increases with their increased dispersion and isolation

Therefore, we have also prepared a series of titanosilsesquioxanes, encompassing methoxy, butoxy and isopropoxy groups at the fourth coordination site and find that the reactivity of these catalysts is indeed dependent upon the nature of the alkoxy group (in the order of decreasing activity : MeO > OBuᵗ ≫ OPrⁱ). The longer, but linear, butoxy group allows better access to the titanium centre than the shorter, but non-linear, isopropoxy group, further suggesting that accessibility to the tetrahedral Tiᴵⱽ centre is the main parameter controlling reactivity.

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Footnotes and References

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† Typical yield over 90% based on the silsesquioxane.

‡ *Selected spectroscopic data* for **2** (mixture of **2a** and **2b**): ¹H NMR (CDCl₃, 400 MHz, 295 K) δ 0.97 (m, 7 H, *ipso*-H), 1.21 [d, 4.3 H, terminal OC*H*(CH₃)₂], 1.18 [d, 2.1 H, bridging OC*H*(CH₃)₂], 1.52 (m, 36 H), 1.73 (m, 20 H), 4.00 [m, OC*H*(CH₃)₂] 3.93 [m, OC*H*(CH₃)₂]; ¹³C{¹H} NMR

(CDCl₃, 400 MHz, 295 K) δ 21.98, 22.08, 22.20 [s, 1 : 3 : 3, CH, *ipso*-C (monomer)], 21.52, 22.54, 22.62, 22.65, 22.67; [1 : 2 : 1 : 2 : 1, s, CH, *ipso*-C(dimer)], 25.30 [s, CH₃, bridging OCH(C*H₃*)₂], 25.71 [s, CH₃, terminal OCH(C*H₃*)₂], 26.59, 26.81, 26.83, 26.87, 26.94, 26.97, 27.03, 27.09, 27.16, 27.20, 27.27, 27.29, 27.33, 27.34, 27.36 (s, CH₂, unassignable), 72.20 [s, CH, terminal OC*H*(CH₃)₂]; *m/z* (FAB⁺): 919 (M − OPrⁱ), 876 [(M + 2H₂O)⁺ − 2C₅H₉], 858 [(M + 2H₂O)⁺ − 2C₅H₉], 840 (M⁺ − 2C₅H₉); UV–VIS (THF) λ/nm (λ_{max}/nm): 210–340 (260) (2 only), 210–500 (260, 320) (pre-catalysis), 210–370 (260) (post-catalysis).

For **3**: ¹H NMR (CDCl₃, 400 MHz, 295 K) δ 0.63, 0.73 (br m, 13 H, *ipso*-H), 1.19, 1.20 (br m, 71 H, cyclohexyl C*H₂*), 1.63, 1.69, 1.72 (br m, 73 H, cyclohexyl CH₂ and *H*OCH₃), 3.48 (br s, 6.3 H, HOC*H₃*), 4.05 (br s, 3.3 H, bridging OC*H₃*); ¹³C{¹H} NMR (CDCl₃, 400 MHz, 295 K) δ 23.22, 23.49 (br s, 5 : 2, *ipso*-C), 26.67, 26.76, 26.90, 26.97, 27.55, 27.67 (s, cyclohexyl CH₂, unassignable), 51.2 (br s, bridging OC*H₃*). Satisfactory elemental analyses obtained.

§ *Crystal data* for **3**: C₈₈H₁₆₈O₂₈Si₁₄Ti₂, 0.40 × 0.30 × 0.12 mm, T = 150 K, M = 2163.28, triclinic, space group $P\bar{1}$ (no. 2), a = 15.748(5), b = 16.911(7), c = 11.742(2) Å, α = 106.88(2), β = 96.78(2), γ = 101.40(3)°, U = 2882(2) Å³, Z = 1, D_c = 1.247 Mg m⁻³, λ = 0.71069 Å, $F(000)$ = 1160, R_1 = 0.0826 [3029 reflections with $I > 2\sigma(I)$], wR_2 = 0.2235 for 5354 independent reflections corrected for adsorption [μ(Mo-Kα) = 0.350 mm⁻¹] and 370 parameters [Ti, Si and O atoms anisotropic, except O(14)]. Structure solved by direct methods.[22] Refinement and all other calculations performed using SHELXL 93.[23] CCDC 182/569.

¶ The catalytic oxidation reactions of cyclohexene with tetrabutylperoxyhydroxide (TBPH) were performed analogously to the procedure outlined in ref. 9, *i.e.* under argon following standard procedures, at 40 °C with a ratio of 1 : 12 cyclohexene–TBPH and a cyclohexene–catalyst ratio of 1 : 0.05 by mass, using an 8% solution of cyclohexene in dry chloroform.

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