Thermal Restructuring of Silica-Grafted TiCl_x Species and Consequences for Epoxidation Catalysis

Philipp Mania, René Verel, Florian Jenny, Ceri Hammond, and Ive Hermans*^[a]

Abstract: TiCl₄ grafted to dehydrated silica is an industrially applied catalyst for the epoxidation of propylene. As with many heterogeneous catalysts, the precise nature of the surface species is not yet fully known, prohibiting reliable structure–activity correlations. In this study, the speciation and restructuring of site-isolated Ti^{IV} Lewis acid

centers was carefully investigated by using a variety of techniques. The initially formed ≡SiOTiCl₃ species were

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tripodal (\equiv SiO)₃TiCl species. The superior activity and stability of such tripodal species is demonstrated for catalytic olefin epoxidation under continuous flow conditions.

found to restructure upon heating

through the transfer of Cl ligands to

the silica surface, eventually leading to

Introduction

From a technological point of view, heterogeneous catalysts offer substantial advantages over the analogous homogeneous catalysts, especially for large-scale processes.^[1] Nevertheless, homogeneous catalysts are often molecularly defined species, facilitating mechanistic studies. Heterogeneous catalysts, on the other hand, contain a broad range of poorly defined surface-species with different degrees of activity and selectivity, complicating fundamental studies. Even for industrially applied catalysts, the precise surface speciation is often unknown. A key example of such a poorly understood workhorse catalyst is TiCl₄-grafted silica. This catalyst is used in the so-called styrene monomer/propylene oxide (SMPO) process for the epoxidation of propylene using ethylbenzene hydroperoxide as the oxidant.^[2-6] Despite decades of industrial and academic research, the precise nature of the active sites has still not been unambiguously established. Nevertheless, there seems to be a consensus that the most active titanium species is fourfold coordinated and in a tetrahedral geometry.^[7] During the operational lifetime of the catalyst, significant deactivation is observed and various analyses provide evidence for leaching, as well as agglomeration of highly dispersed Ti species. The latter would take place through the formation of soluble titanium complexes, which can be re-deposited to the silica and/or titanium species downstream in the catalyst bed.^[4,5] This process leads to a redistribution of the activity and the growth of TiO_x parti-

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Synthesis of the SMPO catalyst starts with the thermal dehydration of the silica support, followed by the anchoring of TiCl₄ in the gas phase. Although the formation of monopodal species (i.e., \equiv SiOTiCl₃, singly bonded to the surface) is often assumed, some reports claim the direct formation of multipodal species (i.e., two- or threefold-bonded to the surface).^[8] Furthermore, the effect of the beneficial thermal treatment on the nature and speciation of the Ti species is also not fully understood. Gaining fundamental insight into the molecular structure of such catalysts, and being able to improve the performance of the SMPO and related catalysts, is therefore a challenge of intellectual and practical relevance.

Results and Discussion

Grafting TiCl₄ to isolated silanol sites: Upon thermal pretreatment of silica, chemisorbed water is lost by the condensation of hydrogen-bonded silanol groups, without significant loss in surface area or porosity. This leads to non-interacting and statistically distributed silanol groups (=SiOH), characterized by a sharp IR signal at 3745 cm⁻¹. ¹H magic angle spinning (MAS) NMR spectroscopy, as well as IR spectroscopy, shows that the average silanol surface-density decreases from approximately 2.5 nm⁻² at 200 °C, to 0.7-0.9 nm⁻² at 700 °C.^[9] Such silica particles pretreated at 700 °C are well-exploited for the synthesis of single-site catalysts.^[1a,10] Although the (temperature-dependent) \equiv SiOH site-distribution is not yet fully established, there seems to be a consensus that most isolated silanol groups are attached to fairly unstrained SiO rings (i.e., 6-membered rings or larger).^[11] An appropriate cluster for the computational in-



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Figure 1. Small cluster used for the computational description of the \equiv SiOH sites.

vestigation of the reactivity of such single-site species must contain the inherent constrains of the surface species, however, they must also retain some flexibility associated with known physicochemical properties. The small cluster displayed in Figure 1 reduces the complex surface species to a manageable structure with a rigid tris(siloxide) assembly featuring a hydrogen-bonding network between the three siloxides. These interactions enforce Si–O–Si angles that are close to those expected for silica. Similar cluster calculations have successfully been used to model similar systems.^[12] The scaled harmonic O–H stretching frequency of 3750 cm⁻¹ is in excellent agreement with the experimental value of 3745 cm⁻¹.

Upon grafting of TiCl₄ (see the Experimental Section), the formation of HCl is observed with in situ gas phase IR spectroscopy through its characteristic rotational-vibrational manifold at 2900 cm⁻¹.^[13] This implies a reaction between the isolated \equiv SiOH and the TiCl₄. IR spectroscopy of the solid shows a nearly quantitative disappearance of the \equiv SiOH signal (Figure 2). Bulk analysis of the material (heated to 50 °C) reveals a Cl/Ti ratio of 3 ± 0.1 , in line with \equiv SiOTiCl₃ species.^[14]

The grafting reaction was computationally investigated and found to proceed through a prereactive complex between the TiCl₄ and the \equiv SiOH site (Figure 3), lowering the adiabatic barrier to only 6.0 kcal mol⁻¹. Initially, HCl forms



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Figure 3. Adiabatic potential energy surface for the grafting of $TiCl_4$ to an isolated \equiv SiOH site.

a postreactive hydrogen-bonded complex, before it is eliminated through a variational transition state (entropy driven). The average distance between the Ti species being more than one nm, lateral interactions between the surface species seem unlikely.

Based on these experimental observations and computational predictions, one can assume that TiCl₄-grafting results in the formation of isolated \equiv SiOTiCl₃ sites. This hypothesis is, however, in disagreement to a literature report claiming that TiCl₄-grafting would lead to multipodal sites, even at room temperature. The formation of isolated \equiv SiOTiCl₃ sites is also in disagreement to recent studies demonstrating that the grafting of trimethylrhenium^[16] and triethylaluminum^[17] can yield dinuclear species, grafted either through two terminal- or two bridged siloxy ligands. The formation of multipodal Ti species will be addressed below.

After room-temperature-grafting of TiCl₄, the SMPO catalyst is typically heated to improve its stability. The chemistry taking place during this thermal treatment is, however, also not yet understood. The results in Figure 4 show that the Ti-loading remains constant at around (1.15 ± 0.05) wt % up to 200 °C, but thereafter decreases rather rapidly to





Figure 2. Transmission IR spectra of silica pretreated at 700 °C: a) before, and b) after TiCl₄ grafting ($T_{\rm post}$ =50 °C).^[15]

Figure 4. Ti loading (*) and Cl/Ti ratio (\blacktriangle) as a function of the postgrafting thermal treatment temperature, T_{post} .

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 (0.75 ± 0.05) wt% at 500 °C. The Cl/Ti ratio qualitatively follows the same trend as the Ti loading, fluctuating around 3.0 ± 0.1 up to 250 °C, followed by a fast decrease to 2.0 ± 0.1 at 500 °C (Figure 4).

Above 200 °C, the formation of TiCl₄ can be observed in the gas phase by transmission IR spectroscopy (glass cell with KBr windows; see the Supporting Information). As well as accounting for the decrease in Ti content, the thermal elimination of TiCl₄ is remarkable given that the average distance between two Ti^{IV} sites is more than 1 nm. It seems indeed unlikely that two Ti species could directly interact and eliminate TiCl₄ without intermediate restructuring.

Spectroscopic and computational investigations: The coordination environment of the Ti^{IV} species was investigated with diffuse reflectance spectroscopy (DRS) in the UV/Vis region (Figure 5).^[18] Whereas the decrease in signal intensity



Figure 5. Diffuse reflectance UV/Vis spectra of the different Ti-SiO₂ materials, heated to: a) 50, b) 250, and c) 450 °C.

can be attributed to the decreasing Ti-loading, one also observes a clear shift of the peak maximum from 260 over 250 to 230 nm for samples treated at 50, 250, and 450 °C, respectively, indicating a significant change in the surface speciation; this observation requires additional investigation.

NMR spectroscopy is a powerful technique to discriminate the identity of molecular compounds.^[19–20] Figure 6 displays the static ³⁵Cl NMR powder spectra of TiCl₄-grafted samples, heated to different temperatures (see the Experimental Section). The spectrum of the sample heated to 50 °C (upper trace of Figure 6) shows the predominant contribution of a species that is characterized by a small quadrupole coupling constant (QCC) of \approx 4 MHz (based on a simulated fit of the powder spectrum). The spectrum of the sample post-treated at 250 °C (middle trace of Figure 6) contains contributions from an additional type of species featuring a significantly broader QCC in the order of 12.5 MHz. For the sample heated to 450 °C (lower trace of Figure 6), the narrow component is absent.

To gain a better insight in the possible surface species, quantum-chemical calculations were used to predict the QCC of monopodal, bipodal, and tripodal Ti^{IV} species



Figure 6. Static ^{35}Cl NMR spectra of materials treated at 50, 250, and 450°C ($T_{\rm pre}\!=\!700$ °C); recorded on a 500 MHz spectrometer.^[21]

(Figure 7 and the Supporting Information). Static QCCs of 13.7 (average of the three Cl atoms), 14.5 (average of the two Cl atoms), and 15.0 MHz were calculated for the mono-, bi-, and tripodal species, respectively.^[22] Unlike the bi- and tripodal species, the monopodal species can rotate round the Si–O–Ti bond, leading to a dynamically averaged QCC of 5.7 MHz. The assumption of a fast rotation, averaging out the quadrupolar tensor is justified as the rotational barrier is computationally predicted to be only 0.2 kcalmol⁻¹, that is,



Figure 7. B3LYP-DFT optimized models for \equiv SiOTiCl₃-, (\equiv SiO)₂TiCl₂-, and (\equiv SiO)₃TiCl surface species.

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 $\ll RT$. These predicted QCC values support our hypothesis that TiCl₄-grafting initially leads to freely rotating monopodal \equiv SiOTiCl₃ species. ³⁵Cl NMR spectroscopic measurements hence further disprove the literature claim that multipodal Ti species are formed in the reaction of TiCl₄ with dehydrated silica at room temperature.^[8] The significantly larger QCCs observed for samples treated at higher temperature suggest that the \equiv SiOTiCl₃ species are transformed into non-rotating, that is, more constrained, species.

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By using the time-dependent DFT method, the UV/Vis absorption spectra of the models depicted in Figure 7 were predicted (Figure 8). Comparing these predictions with the experimental spectra in Figure 5 suggests a gradual restruc-



Figure 8. Computationally predicted UV/Vis absorption spectra of: a) \equiv SiOTiCl₃, b) (\equiv SiO)₂TiCl₂, and c) (\equiv SiO)₃TiCl.

turing of the surface species from predominantly \equiv SiOTiCl₃ over (\equiv SiO)₂TiCl₂ to (\equiv SiO)₃TiCl. We emphasize that the UV/Vis extinction coefficients are predicted to increase in the order \equiv SiOTiCl₃ < (\equiv SiO)₂TiCl₂ < (\equiv SiO)₃TiCl, whereas the intensity of the experimental spectra decreases as a function of the post-treatment temperature. This observation is however in line with the decreasing Ti-loading observed in Figure 4.

Summarizing the observations made so far leads to the following intermediate conclusions: 1) TiCl₄-grafting initially forms monopodal \equiv SiOTiCl₃ species, which appear fairly stable up to 50 °C as demonstrated by ³⁵Cl NMR spectroscopy; 2) upon heating, significant restructuring takes place, leading to multipodal species featuring larger QCCs in the ³⁵Cl NMR spectra; 3) above 250 °C, TiCl₄ is eliminated, causing a loss in Ti-loading and further restructuring; 4) samples heated to 450 °C show no evidence for remaining monopodal species, based on ³⁵Cl NMR spectroscopy.

Unfortunately, ³⁵Cl NMR spectroscopy is not sensitive enough to distinguish between bi- and tripodal species. The nature of the surface species was therefore further investigated with the probe molecule N,N-bis-(trimethylsilyl)methylamine (denoted (TMS)₂NCH₃). After exposure of the materials to the amine probe (see the Experimental Section), the liquid-nitrogen-trapped effluent of the reactor was investigated by using ¹H NMR spectroscopy. For the materials heated to 50 and 250 °C, the formation of trimethylsilyl chloride (TMSCl) was observed, indicating a reaction between the Ti–Cl species and the amine probe, similar as we observed for CpTiCl₃ (Cp=cyclopentadienyl) dissolved in methanol. For the material heated to 450 °C, TMSCl was not detected, indicating that the species present in that material are unreactive towards the amine probe and hence significantly different.

The reaction between the TiCl_x surface species and the amine probe was computationally investigated and found to be fairly exothermic (Scheme 1), except for tripodal species in which $\Delta_r E$ was only -4.7 kcal mol⁻¹.



Scheme 1. Reaction of the $(TMS)_2NCH_3$ probe with the mono- and bipodal Ti^{IV} species; reaction energies and predicted ¹³C- and ¹H NMR chemical shifts for the methyl group in the probe.

The experimental ¹H NMR spectra of the various samples after amine grafting are displayed in Figure 9. We emphasize that the methyl proton-signals are split, due to scalar or Jcoupling with the ¹³C (see the Experimental Section). It is observed that the sample which was heated to only 50°C mainly features a signal around $\delta = 3.7$ ppm, with an additional minor contribution at $\delta = 3.5$ ppm. This observation is in line with the ³⁵Cl NMR spectrum of this material (top panel of Figure 6), mainly revealing a signal from freely rotating \equiv SiO-TiCl₃ species For the sample heated to 250°C, the contribution of the peak at $\delta = 3.5$ ppm significantly increased, whereas for the 450 °C sample both signals are absent. The latter observation is in line with the absence of TMSCl formation in the effluent (see above). In the ¹³C NMR spectra (see the Supporting Information), the samples heated to 50 and 250 °C feature a broad peak between $\delta = 33$ and 40 ppm; for the sample heated to 450 °C this



Figure 9. ¹H NMR spectra of the materials treated at: a) 50, b) 250, and c) 450 °C, after exposure to the $(TMS)_2N^{13}CH_3$ probe molecule.

signal is also absent. These observations confirm that the amine probe does not react with the species present after heating to 450 °C and hence confirm that those species are fundamentally different from those dominating at lower post-treatment temperatures.

Deconvolution and comparison of the experimental spectra with the predicted ¹H- and ¹³C NMR shifts for the monoand bipodal species (Scheme 1) confirms our hypothesis that the sample heated to 50 °C mainly contains monopodal \equiv SiOTiCl₃ species (\approx 85%) and only a minor amount of bipodal species (\approx 15%). The sample heated to 250 °C contains a significant amount of bipodal species, in line with the contribution of two compounds in the ³⁵Cl NMR spectrum (middle panel of Figure 6). These results can however not exclude the presence of tripodal species in the sample heated to 250 °C, but clearly indicate the absence of mono and bipodal species in the material heated to 450 °C. We indirectly interpret this as strong evidence for the exclusive presence of tripodal species in the latter sample.

Figure 10 displays the IR spectra before and after amineprobe grafting for the materials heated to 250 and 450 °C. Two characteristic TMS signals are visible in the range



Figure 10. IR spectra of the TiCl₄-grafted materials heated to 250 °C: a) before, and b) after grafting of (TMS)₂NCH₃; and of the material heated to 450 °C: c) before, and d) after probe grafting. e) The same sample as in spectrum d but after being heated at 230 °C, overnight.

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3000–2870 cm⁻¹. For the materials heated to 50 (not shown) and 250 °C, two additional –CH₃ vibrations are identified at 2830 and 2800 cm⁻¹ (indicated with # in Figure 10). If the CH₃ group in the probe is ¹³C labeled, those vibrations shift by -8 cm^{-1} , in line with the assignment. The 2800 cm⁻¹ signal corresponds to the symmetric –CH₃ stretch of the amine grafted to either mono- or bipodal Ti species (computationally predicted frequency of 2900 cm⁻¹). In NMR spectroscopy, those protons appear between $\delta = 3.4$ and 3.7 ppm (Figure 9) and the C atom between $\delta = 33$ and 40 ppm (see the Supporting Information). The signal at 2830 cm⁻¹ corresponds to the same –CH₃ vibration in the amine species that reacted with the siloxane bridges (Scheme 2).^[23] In the



Scheme 2. Reaction of the (TMS)₂NCH₃ probe with a siloxane bridge.^[23]

NMR spectra, those protons appear around $\delta = 2.5$ ppm and the carbon around $\delta = 27$ ppm (see the Supporting Information). Grafting of the amine probe to the sample heated to 450 °C also induces the appearance of the 2830 cm⁻¹ signal; the signal at 2800 cm⁻¹, however, remains absent. This observation is in line with our hypothesis that mono- and bipodal species are absent in the material heated to 450 °C.

Spectra b and d in Figure 10 show in addition a small peak at 3450 cm^{-1} (marked with *) that can be attributed to the N–H stretch in the {(TMS)₂N(CH₃)H}+Cl⁻salt, formed upon reaction of in situ formed HCl with the probe.^[24] In NMR spectroscopy, the CH₃ protons of this salt appear around $\delta = 2.5$ ppm and the carbon at around $\delta = 24$ ppm (see the Supporting Information). When the sample is heated to 230°C, overnight, in high vacuum, this signal disappears (see, for example, spectrum e in Figure 10), in line with the volatility of this compound.

We emphasize that the DRS UV/Vis, the ³⁵Cl NMR spectroscopy, and the amine-probe experiments are consistent and point towards a gradual restructuring of the Ti species from predominantly monopodal to tripodal upon heating.

Extended X-ray absorption Fourier-transformed spectroscopy (EXAFS) reveals two major scatterers for the material heated to 450 °C, arising from Cl- and O ligands (Figure 11, spectrum a). Comparing the EXAFS of fine anatase particles, previously reported by Fraile et al.,^[25] to spectrum a in Figure 11 clearly disproves their presence in our material. The first coordination shell of Ti was subsequently compared to that in TS-1, suggesting that the Ti is surrounded by more than 2 but less than 4 oxygen atoms, in line with our proposed tripodal site. We emphasize that no indication for a Ti–Ti pathway could be found,^[26] in line with our hypothesis of site-isolated species. Even though the number of adjustable parameters was close to the number of independent parameters,^[25] we attempted to fit the EXAFS spectrum.

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Figure 11. The k^3 -weighted *R*-space EXAFS spectra of the TiCl₄-grafted material: a) heated to 450 °C, b) TS-1, c) the grafted material after being washed with *tert*-butanol, and d) after a catalytic epoxidation experiment.

A reasonable fit was obtained for approximately three O atoms (at 1.8 Å) and one Cl atom (at 2.2 Å) in the first shell.^[26]

> Scheme 5. Transfer of a Cl ligand from Ti to Si for a slightly bigger surface model (see the Supporting Information for the full model).

Mechanistic proposal: Having ruled out the formation of a Tidimer species, we are left with

the question of how the TiCl₄ elimination (observed above 200 °C) takes place. Grafting CrO_2Cl_2 to silica pretreated at 800 °C, Scott et al. proposed the formation of the six-membered ring-structure shown in Scheme 3, through transfer of a Cl ligand from the Cr to the Si.^[27] Whereas there is no evi-



Scheme 3. Treatment of CrO_2Cl_2 with a hydroxyl-bearing strained siloxane ring.^[7]

dence for the significant abundance of the required strained hydroxyl-bearing siloxane rings at silica heated to 700°C, the Cl-transfer hypothesis deserves further investigation.

Starting from the unstrained monopodal \equiv SiO-TiCl₃, a transition state could be located for the Cl transfer to the geminal Si atom (Scheme 4). However, such a rearrangement faces a thermally inaccessible barrier of 63 kcalmol⁻¹, mainly due to ring strain.

Extending the model to a slightly bigger system (Scheme 5) helps to release the ring strain, bringing the barrier for Cl transfer down to $38.5 \text{ kcal mol}^{-1}$ (see the Supporting Information for the full model). Assuming a pre-exponential factor of 10^{14} s^{-1} , the half-lifetime of this rearrangement reaction can be estimated to be approximately

in the ³⁵Cl NMR spectrum upon heating (middle trace of Figure 6).

 $\Delta E^{act} = 63 \text{ kcal mol}^{-1}$

Scheme 4. Transfer of a Cl ligand from Ti to Si for a small model.

100 min at 200 °C. As a consequence of this reaction, the Cl

atom is transferred approximately 0.5 nm away from the original TiCl₃ group, and one creates a fairly unstrained bi-

podal (\equiv SiO)₂TiCl₂ site. This mechanism is consistent with

the appearance of an additional compound with high QCC

It is our hypothesis that this shifted Cl ligand can be picked up by a neighboring \equiv SiOTiCl₃ site, thus forming TiCl₄ and re-establishing a siloxane bridge (Scheme 6). The adiabatic barrier for this reaction is predicted to be 36.2 kcal mol⁻¹, that is, 2 kcalmol⁻¹ lower than the Cl-transfer step. This mechanism explains the elimination of TiCl₄, and hence the decrease in Cl/Ti ratio at higher temperatures, without the direct interaction of two \equiv SiOTiCl₃ sites. Consecutive



Scheme 6. Mechanism for the elimination of TiCl₄.

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transfer of a second Cl ligand to the silica surface would transfer the bipodal $(\equiv SiO)_2 TiCl_2$ species into tripodal $(\equiv SiO)_3 TiCl$ sites.

Providing direct experimental evidence for the formation of SiCl bonds proved to be a difficult task. Indeed, the signal-to-noise ratio of ²⁹Si MAS NMR spectroscopy is too low to observe small amounts of SiCl bonds. ³⁵Cl NMR was also found to be insensitive for chlorine bound to silica, as verified by model compounds. A possible reason could be that the quadrupolar coupling constant for SiCl groups is such that the efficiency of the adiabatic wideband uniform rate and smooth truncation (WURST) pulses for excitation and refocusing is very low. As a consequence, SiCl species could be virtually undetectable with this technique.

Although some evidence for Si–Cl vibrations could be obtained from IR spectroscopy (see the Supporting Information), we decided to use X-ray photoelectron spectroscopy (XPS). Indeed, earlier work had shown that the Cl 2p orbital energies are slightly shifted from 198.4 eV for TiCl species^[28] to 199.5 eV for SiCl species.^[29] The experimental spectra obtained for the thermally treated TiCl₄-grafted materials (Figure 12) clearly reveal a shift of the peak maxima



Figure 12. XPS spectra of the TiCl₄-grafted material after being heated to: a) 50, b) 250, and c) 450 °C; the dashed lines are the simulated spectra, based on two signals, positioned at 198.4 and 199.5 eV (see the Supporting Information).

to higher binding energy, associated with a significant broadening of the signal. The most plausible explanation for this is the formation of an additional Cl species with different binding energy. For the material heated to 50 °C, only the Cl–Ti signal at 198.4 eV was necessary to fit the experimental data (see the Supporting Information). No evidence for SiCl bonds could be obtained for this sample. However, the spectra of the materials heated to 250 and 450 °C could not be fitted with a single signal at 198.4 eV. Indeed, for those samples, a second signal centered at 199.5 eV becomes increasingly important, accounting for approximately 20 and 50% of the Cl 2p signal, respectively. These results support our Cl-transfer hypothesis and suggest that the 450 °C sample contains an equivalent amount of TiCl and SiCl bonds. Combining all experimental and computational information, the restructuring mechanism in Figure 13 can be proposed. A Cl ligand from a monopodal ≡SiOTiCl₃ species is



Figure 13. Proposed thermal restructuring mechanism leading to the tripodal Ti^{IV} species.

transferred to the silica surface, remote from the Ti site by opening a \equiv Si-O-Si \equiv siloxane bridge. This step leads to a non-strained bipodal (\equiv SiO)₂TiCl₂ species and \equiv Si-Cl bonds (Figure 13, step 1). Transfer of the surface-bound chlorine to a neighboring \equiv SiOTiCl₃ species establishes a new (lessstrained) siloxane bridge upon the elimination of TiCl₄ (Figure 13, step 2). In a subsequent step, one more Cl ligand from the bipodal Ti^{IV} site can be transferred to the surface. The last step establishes tripodal species, explaining the final Cl/Ti ratio of 2 (inductively coupled plasma optical emission spectrometry, ICP-OES) and the ratio of Ti-Cl to Si-Cl bonds of approximately 1 (XPS).

Catalytic epoxidation experiments: Acquiring fundamental insight into heterogeneous catalytic processes demands that one can correlate the nature of the catalytic sites with the observed activity. The catalytic performances of the TiCl₄grafted materials post-treated at 250 and 450 °C were compared with a catalyst prepared through impregnation with Ti(OiPr)₄ according to a benchmarked literature procedure^[30] (see the Supporting Information) in the solvent-free epoxidation of cyclooctene with tert-butyl hydroperoxide as a model reaction. Prior to exposing the catalyst to the olefin/peroxide mixture, the material was washed with tertbutyl alcohol to substitute the Cl ligand of the surface species by an alkoxyl ligand upon elimination of HCl, which is able to open epoxides and therewith lowering the selectivity. This ligand exchange can be observed with Raman spectroscopy (Figure 14), showing a disappearance of the Ti-Cl stretching vibration at 487 cm⁻¹ and a slight perturbation of the symmetric deformation of the Ti^{IV}-tetrahedron from 530 to 517 cm⁻¹. Also, bulk analysis ICP-OES and EXAFS spectroscopy (Figure 11, spectrum c) reveals the disappearance of a Cl ligand. The first coordination shell of the washed



Figure 14. Raman spectrum of the material heated to 450 °C, mainly containing (\equiv SiO)₃TiCl, before and after being washed with *tert*-butanol ((\equiv SiO)₃TiOR).

material has a higher coordination number than four, which is probably due to additional coordination of *t*BuOH (see also the additional features between 2.2 and 3.7 Å in spectrum c in Figure 11). This can also be seen from the decrease of the pre-edge feature (see the Supporting Information).

The epoxidation activity of the materials was compared by using 0.3 mg of Ti, taking into account the Ti loading of the various materials. The contact time of 2 min was chosen in such a way that the most active catalyst (i.e., the TiCl₄grafted material, which was heated to 450 °C) reached a conversion of 98% (i.e., the reactor effluent still contained 2% of the limiting reactant, that is, the peroxide). Several interesting observations can be made (Figure 15). First of all, the TiCl₄-grafted material that was heated to 450 °C is significantly more active than the material heated to only 250 °C. Furthermore, it can be observed that the latter material suffers from severe deactivation, losing nearly 90% of its activity over two weeks on-stream. ICP-OES analysis indicates a Ti loss of $\pm 95\%$ after two weeks on-stream. The material prepared by impregnation with Ti(O*i*Pr)₄ shows an inter-



Figure 15. Stability of various catalysts during the solvent-free epoxidation of cyclooctene with *tert*-butyl hydroperoxide (100 mM) at 80°C: TiCl₄-grafted materials heated to: a) 450°C, and b) 250°C, and c) a Ti(O*i*Pr)₄-impregnated catalyst.

mediate activity, but also suffers from deactivation due to leaching ($\pm 30\%$ Ti loss over two weeks on-stream). The catalytic data in Figure 14 demonstrate unambiguously that whatever the speciation for the impregnated catalyst looks like, the material is not as stable as the TiCl₄-grafted material, heated to 450 °C for which ample evidence was provided that the active sites are tripodal. No changes could be observed in X-ray absorption near-edge structure (XANES; not shown) or extended X-ray absorption fine structure (EXAFS; Figure 11, spectra c and d), indicating that the material is indeed stable under the reaction conditions.

Conclusion

The grafting of TiCl₄ to isolated silanol groups on dehydrated silica was investigated by using a variety of techniques. Initially, one forms site-isolated \equiv SiOTiCl₃ species, which can freely rotate around the Si-O-Ti axis, thereby giving rise to a narrow ³⁵Cl NMR powder spectrum. Upon heating, Cl transfer from those monopodal species to the silica surface leads to the formation of more rigid multipodal species. The reaction of such a transferred Cl ligand with a neighboring \equiv SiOTiCl₃ species leads to the elimination of TiCl₄ and explains the Ti loss at higher temperatures. Eventually, one ends up with a material with predominantly tripodal (=SiO)₃TiCl species. The corresponding (=SiO)₃TiOR species, obtained by washing the (=SiO)₃TiCl species with ROH, are shown to be very active and stable towards leaching in the solvent free epoxidation of olefins with tert-butyl hydroperoxide under continuous flow conditions.

Experimental Section

Material synthesis: Silica powder (Aerosil 200 from Degussa, specific surface area of 200 m²g⁻¹) was impregnated with water and dried, overnight, at 120 °C in a vacuum oven. Subsequently, the material was dehydrated at 700 °C ($T_{\rm pre}=700$ °C) under 5 µbar dynamic vacuum and stored in a glovebox (<1 ppm O₂ and H₂O) to avoid the re-adsorption of water. TiCl₄ (ACROS, three times distilled before use, colorless) was then deposited onto less than 400 mg of material at approximately 10 µbar static vacuum. A typical deposition cycle consisted of a transfer phase (5–10 min), a reaction phase (30 min), a desorption phase under dynamic vacuum to evaporate excess TiCl₄ (5–10 min), and finally a postgrafting heat treatment at 50 °C ≤ $T_{\rm post} \le 450$ °C (60 min).

Bulk analysis: Ti and Cl were quantified with ICP-OES (Ultima 2 from Horiba Jobin Yvon), after digestion with HF or H_2SO_4 (both methods give similar results). The Cl content was determined by precipitation of silver chloride (digestion with H_2SO_4). A known amount of catalyst was dissolved in an AgNO₃ solution (200 ppm) containing 1 M H_2SO_4 ; all of the remaining solid material was centrifuged off after 24 h. The chlorine content of the catalyst was obtained from the difference of silver concentration before and after addition of the catalyst.

Spectroscopic characterization methods: ¹H- and ¹³C NMR spectra were acquired on an Avance NMR spectrometer (Bruker, Karlsruhe, Germany) operating at a ¹H Larmor frequency of 700 MHz. The samples were spun around the Magic Angle with a rate of 12 kHz at room temperature by using a double resonance 4 mm probe (containing ± 40 mg sample). The probe was tuned to the resonance frequencies of ¹H (700.13 MHz) and ¹³C (176.06 MHz). The ppm scale of the spectra was calibrated by

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using the ¹³C signal of adamantane as an external secondary reference. In total three spectra were acquired on each of the samples. First, a ¹H spectrum was acquired using a single 90 degree pulse of 4.0 µs duration for excitation and a recycle delay of 2 s. Second, a 13C spectrum was acquired using a cross polarization (CP) sequence with a two-pulse phase-modulation (TPPM) decoupling of ¹H during acquisition. The initial 90 degree pulse was calibrated to 3.1 µs (81 kHz), the CP period with a duration of 1.5 ms employed a linear ramp from 70 to 100% and was experimentally optimized to give maximum intensity on ¹³C. The decoupling during acquisition employed the same radio-frequency (rf) field amplitude as the 90 degree pulse (81 kHz). The TPPM had a phase difference of 15 degrees between pulses and a duration of 6.5 µs per pulse. The acquisition time was 29.1 ms with 4096 point and a sweep-width of 400 ppm. A total of 4096 scans were added with a recycle delay of 2 s. The free induction decay signals (FID's) were processed by zero filling to 8k points and apodization with a 128 Hz Lorentzian prior to Fourier Transform and phasing.

The ³⁵Cl-NMR spectra were acquired on a Varian/Chemagnetics Infinity+spectrometer (Agilent, Palo Alto, USA) using a 6 mm DR MAS probe-head (containing ± 100 mg sample). The probe was tuned to the resonance frequency of ³⁵Cl (around 49 MHz) and the sample was not rotated and was packed in custom-made containers of polymethylmethacrylate (PMMA) with caps equipped with O-rings to ensure a gastight fit. The PMMA containers (instead of ZrO2 rotors) proved crucial to avoid a background signal of the satellite transitions of ⁹¹Zr. The samples were packed inside a glovebox and during the experiments a continuous flow of N₂(g) was maintained around the sample container. The spectra are skyline superpositions of a number of individual spectra with varying center frequencies. For each experiment the tuning and matching was optimized for the respective center frequency used. A quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) experiment was used to acquire the data according to the method of Schurko with identical WURST pulses for excitation and refocusing.^[19-20] The WURST pulses used an exponent of 80 and a symmetric frequency sweep from -400 to +400 kHz. The pulses had a duration of 50 µs with a maximum amplitude of the rf field of approximately 22 kHz. In addition to the rf amplitude, the delays τ_1 , τ_2 , and τ_3 were carefully adjusted by using a test sample of Cp₂TiCl₂ to values of 28.0, 3.0 and 10 µs. A total of 100 echoes were acquired per scan. Each of these was digitized in 100 points with a dwell time of 1.0 µs, leading to a spectral width of 1.0 MHz and 10000 acquired points per QCPMG echo train. Each of the echoes was apodized with a sine squared function centered at the echo maximum (not for Cp2TiCl2 and CpTiCl₃ samples). The whole echo train was then multiplied with a Gaussian function with a width of 512 Hz, zero filled to 16k points and Fourier transformed. Finally, the absolute mode was taken. The superposition of the spectra followed by a skyline projection produced the spectra as presented in the figures. The samples were independently measured twice to verify the reproducibility.

All IR measurements of the solid samples were performed in transmission mode, on a self-supporting wafer by using a Bruker ALPHA R instrument inside a glovebox. Time-resolved IR measurements were conducted on a Bruker VERTEX 70v in a homemade glass cell with KBr windows. Diffuse Reflectance UV/Vis spectra were recorded with a Maya 2000 spectrometer (Ocean optics) equipped with a UV/Vis deuterium/halogen light source (DH-2000-BAL from Mikropack) against a BaSO₄ background.

XPS analysis was performed by using a PhI5000 VersaProbe spectrometer (ULVAC-PHI, INC.) equipped with a 180° spherical capacitor energy analyzer and a multi-channel detection system with 16 channels. Spectra were acquired at a base pressure of 5×10^{-8} Pa by using a focused scanning monochromatic Al_{Ka} source (1486.6 eV) with a spot size of 200 µm. The instrument was run in the FAT analyzer mode with electrons emitted at 45° to the surface normal. Charge neutralization utilizing both a cool cathode electron flood source (1.2 eV) and very low energy Ar⁺ ions (10 eV) was applied throughout the analysis.

Raman measurements were performed with an in Via Raman microscope from Renishaw by using a 325 nm excitation laser.

XAS measurements at the Ti K-edge (E=4976 eV) were performed at the X10DA (SuperXAS) beamline at the Swiss Light Source (SLS), Villigen, Switzerland. Scans were performed with a Si(111) crystal monochromator, and were collected in fluorescence mode by using a germanium detector from 4.900 to 5.800 keV. In the EXAFS analysis of the spectra recorded, multiple scans were averaged to improve the signal-to-noise ratio and fitted to actual XAS-measured data of Ti foil. The raw XAS data were background corrected, and normalized by using the Athena software package. Shell fits were performed in *R*-space (0.5 < R < 3.0 Å) after Fourier transformation ($3 < k < 10 \text{ Å}^{-1}$) of k^3 -weighted spectrum.

Probing of the surface species: *N*,*N*-Bis(trimethylsilyl)methylamine (Sigma Aldrich, three times distilled before use) was contacted with the samples in the same way as TiCl₄, and heated from 50 to 250 °C at 5 µbar dynamic vacuum. *N*,*N*-bis(trimethylsilyl)methylamine with ¹³C-labeled methyl-group was synthesized by adding dry diethyl ether (32 mL) under an inert nitrogen atmosphere to lithium hexamethylsilizane (1.88 g), in a 2-neck-round-bottom-flask immersed in an ice bath. After 10 min, of ¹³C labeled methyl iodide (0.65 mL) was added. After 15 min, the milky-yellowish liquid was allowed to heat up to reflux temperature (35 °C) meanwhile turning transparent. The mixture was left reacting for 48 h, and the liquid phase was transferred into another flask through cold distillation. Finally the solvent was evaporated under vacuum.

Catalytic experiments: Continuous epoxidation experiments were performed in a flow reactor (internal diameter 1.5 mm) with catalyst particles sieved to 200–250 μ m to avoid back-mixing and a large pressuredrop. Products were quantified against a decane internal standard with GC (HP6890; HP-5 column, 30 m/0.32 mm/0.25 mm; flame ionization detector).

Computational methods: Quantum chemical calculations were performed with the Gaussian 09 software^[31] at the UB3LYP/6–311++G(df,pd)// UB3LYP/6–31G(d,p) level of theory,^[32] by using a LANL2DZ basis set with an additional *f*-polarization function for Ti.^[33] The reported relative energies of the stationary points on the potential energy surfaces (PESs, that is, the energy barriers E_b and reaction energies $\Delta_r H$) were corrected for zero-point-energy (ZPE) differences and are reported at 0 K (adiabatic PESs). Computed frequencies are scaled by a factor 0.9614.^[34] The polarizable continuum model (PCM),^[35] as implemented in Gaussian 09, was used to take into account solvent effects when necessary.

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