Epoxidation with $Ti(OSiMe_3)_4$: a homogeneous model mimicking titania–silica mixed oxides?

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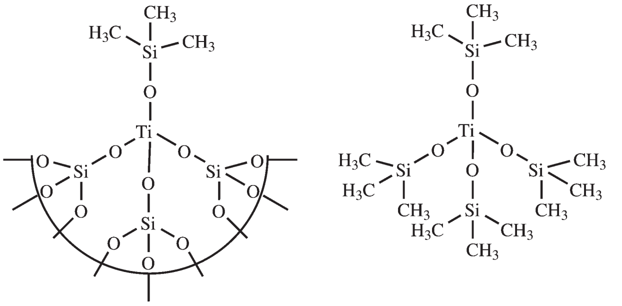
$Ti(OSiMe_3)_4$ is an active homogeneous catalyst for the epoxidation of allylic alcohols under mild conditions using *tert*-butyl hydroperoxide as oxidant in an apolar solvent. It affords an average turnover frequency of up to 1470 h^{-1} and 100% regioselectivity (geraniol) or 100% *cis*-selectivity (cyclohexenol). UV-Vis measurements indicate that the ability of substrates to coordinate to the catalyst determines the reaction rate and stereoselectivity. This is the likely explanation for the poor or completely missing reactivity of substrates possessing no OH function (cyclohexene, methoxycyclohexene) and also for the substrate-dependent effect of water in the system. $Ti(OSiMe_3)_4$ is suggested to be a good soluble homogeneous model catalyst mimicking the highly active isolated tetrahedral Ti sites in (silylated) titania–silica mixed oxides.

Introduction

Sol-gel titania–silica mixed oxides, either as mesoporous aerogels[1–4] or microporous xerogels,[5,6] are powerful epoxidation catalysts. Their activity is attributed to the high dispersion of Ti in the silica matrix (site isolation) and to a high surface area. A limitation to practical application is their strongly hydrophilic character, which necessitates the use of organic peroxides as the oxidant in non-aqueous medium. Silylation of the preformed mixed oxides improves the catalytic performance remarkably and diminishes the sensitivity towards water.[7–9] Upon silylation, a more hydrophobic surface is obtained by partial transformation of the surface silanol groups to trimethylsiloxy functions. In addition, the $(\equiv SiO)_3TiOH$ type active sites are transformed into $(\equiv SiO)_3TiOSiMe_3$ ones (Scheme 1). Another approach to synthesize hydrophobic mixed oxides is the partial replacement of the tetraalkoxysilane precursor by an alkyltrialkoxysilane in the sol-gel process. Introduction of surface methyl or phenyl groups afforded excellent catalysts for the epoxidation of olefins and allylic alcohols, even in the presence of water.[6,10–12]

For comparison, in the microporous crystalline titanium silicalite TS-1 the isolated Ti sites are located in hydrophobic channels or cavities of the molecular sieve and aqueous hydrogen peroxide can be used as oxidant.[13–15] The role of water in the formation of the active Ti sites and in the epoxidation mechanism has been addressed by several research groups.[16–19]


Scheme 1 Schematic representation of an isolated Ti site in silylated titania–silica (left) and of the homogeneous catalyst $Ti(OSiMe_3)_4$- (right).

Various titanium silasesquioxane complexes have been proposed as soluble models for the catalytically active centers in TS-1.[20–23] Interestingly, *tert*-butyl hydroperoxide (TBHP) was used as oxidant as none of these complexes were active with aqueous H_2O_2.[24] Grafting a titanium silasesquioxane onto a hydrophobic polysiloxane demonstrated that an ideal model for TS-1 should possess isolated $Ti(OSi\equiv)_n$ ($n = 3, 4$) sites in a hydrophobic environment.[24] Other limitations of titanium silasesquioxane complexes as soluble, homogeneous model catalysts are the presence of Ti–O–Ti bonds in the structure and slightly distorted tetrahedron bond angles.[21]

During the sol-gel synthesis of titania–silica aerogels various active sites may form, ranging from isolated Ti atoms surrounded by four siloxy groups (most active and selective) to titania nanodomains possessing mainly Ti–O–Ti linkages (barely active and selective).[25] This structural variety may well be tuned by the appropriate choice of catalyst precursors and preparation conditions but the synthesis of a uniform structure has not yet been achieved.[4,26,27] The presence of structurally different Ti sites in the amorphous silica matrix hampers the unambiguous interpretation of the catalytic properties and the development of a feasible mechanistic model. Hence, the importance of using a homogeneous model of the isolated Ti site in the silica matrix is obvious.

The aim of the present work was to test $Ti(OSiMe_3)_4$ as a simple and commercially available model compound for a stable and isolated tetrahedral Ti site surrounded by four siloxy groups. This compound seems to be a particularly attractive model of silylated titania–silica (Scheme 1). The catalytic performance of $Ti(OSiMe_3)_4$ has been investigated in the epoxidation of allylic alcohols, an allylic ether and cyclohexene (Scheme 2). Reaction rates, chemo- and stereoselectivities, and sensitivity to water are compared to the corresponding values typical for solid Ti- and Si-containing epoxidation catalysts.

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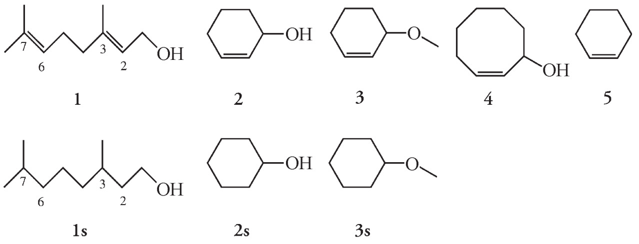

Scheme 2 Substrates used in the epoxidation reactions (**1**–**5**) and in the UV-Vis measurements (**1s**–**3s**).

Experimental

Materials

The following commercially available chemicals were used: toluene (Fluka, 99.5%, abs.), dodecane (Merck, 99%), *n*-hexane (Fluka, 99.7%, abs.), anisol (Fluka, 99%), geraniol (**1**, Aldrich, 98%), 2-cyclohexen-1-ol (**2**, Fluka, 97%), *tert*-butyl hydroperoxide (TBHP, Fluka, 5.5 N in nonane, additionally dried over freshly activated 4 Å molecular sieve), $Ti(OSiMe_3)_4$ (ABCR, 99.5%, stored under argon), $Si(OSiMe_3)_4$ (Acros, 98%), 3,7-dimethyloctan-1-ol (**1s**, Aldrich, 99%), cyclohexanol (**2s**, Fluka, 99%), cyclohexene (**5**, Merck, 99%).

Methoxycyclohexene (**3**, 97%)[28] and 2-cycloocten-1-ol (**4**, 97%)[29] were synthesized according to known procedures. Methoxycyclohexane (**3s**, 99.5%) was prepared as follows: 10 ml anisol was hydrogenated at 100 bar and room temperature with 75 mg catalyst (5 wt. % Rh/C, Engelhard) under vigorous stirring. After 17 h, the catalyst was filtered off, the filtrate distilled at 318 K (38 mbar) and the product identified with GC-MS ($m/z = 114$, 85, 82, 71, 67, 58, 55, 45, 41) and ^{1}H-NMR [$\delta = 1.27$ (m, 5H), 1.53 (m, 1H), 1.74 (m, 2H), 1.93 (m, 2H), 3.14 (m, 1H), 3.34 (s, 3H)].

The amorphous mesoporous titania–silica aerogel Ae-1 (1 wt. % TiO_2, 1060 m^2 g^{-1} BET surface area, 3.1 cm^3 g^{-1} pore volume) and the silylated aerogel Ae-1-sil (1 wt. % TiO_2, 750 m^2 g^{-1} BET surface area, 2.7 cm^3 g^{-1} pore volume) were prepared on the basis of a former recipe.[25] The high degree of dispersion of Ti in the silica matrix was confirmed by UV-Vis DRS, DRIFT, XPS[25] and XANES[30] methods.

Methods

UV-Vis measurements were performed on a Perkin Elmer Lambda 16 spectrometer and the spectra recorded above 210 nm. To solutions of $Ti(OSiMe_3)_4$ in dry *n*-hexane ($c = 0.356$ mmol l^{-1}) were added **1s**, **2s** or **3s** in 400-fold molar excess and TBHP in 100-fold molar excess. The solutions were freshly prepared and the same solutions but without $Ti(OSiMe_3)_4$ were used as reference. The experimental error is estimated to be less than 10% in absorption area.

All epoxidation reactions were conducted under argon to avoid the presence of oxygen and moisture. In the standard epoxidation procedure the reactor was pre-dried at 473 K in an argon flow for 1 h, than solvent, internal standard (dodecane) and 30 µl (0.067 mmol) $Ti(OSiMe_3)_4$ were added and the epoxidation was carried out at 333 K. When the reaction was catalyzed by an aerogel, 0.1 g (0.0125 mmol Ti) catalyst was pre-dried *in vivo* in the reactor at 473 K for 1 h in an argon flow. To the aerogel catalyst were then added solvent and 0.5 ml internal standard. This mixture was heated to the reaction temperature. Olefin (10 mmol) was added and the reaction started by adding 2.5 mmol TBHP in nonane (olefin : TBHP : $Ti(OSiMe_3)_4$ = 150 : 37.5 : 1). In some experiments up to 0.75 mmol H_2O was added (H_2O : $Ti(OSiMe_3)_4$ = 11 : 1). The total reaction volume was 10 ml.

The products were analyzed by an HP-6890 gas chromatograph equipped with a cool on-column inlet and an HP-FFAP column. The epoxides were identified by comparison with authentic samples and by GC-MS. The internal standard method was used for quantitative analysis. 100% yield could not be achieved due to various side reactions, including Lewis acid catalyzed and radical reactions. Taking the epoxidation of 2-cyclohexen-1-ol with titania–silica as an example, the following major products and by-products were detected: cyclohexanol oxide (epoxidation), cyclohexan-1-ol-3-one (rearranged epoxide), cyclohexenone, cyclohexanone oxide and 1,4-cyclohexene diol (allylic oxidation). Besides, the carbon balance indicated some oligomerization; these heavy products could not be detected by GC. More details of typical side reactions catalyzed by titania–silica have been published recently.[31] The same products as a result of Lewis acid catalyzed and radical reactions were identified from epoxidations with $Ti(OSiMe_3)_4$.

TBHP conversion was determined by iodometric titration using a Metrohm 686 Titroprocessor. Two different types of chemoselectivities are calculated: epoxide selectivity related to the reactant consumed:

$$S_{C=C}(\%) = 100 \cdot [\text{epoxide}]/([\text{reactant}]_0 - [\text{reactant}])$$

and epoxide selectivity related to the peroxide consumed:

$$S_{TBHP}(\%) = 100 \cdot [\text{epoxide}]/([\text{TBHP}]_0 - [\text{TBHP}]).$$

Epoxide yield and olefin conversion are related to the initial amount of TBHP (limiting component). The reaction rate is characterized by the turnover frequencies (mol epoxide × mol $Ti_{catalyst}{}^{-1}$ × h^{-1}): the average turnover frequency ($TOF_{50\%}$) denotes the rate of epoxide formation at 50% TBHP conversion and the initial TOF_0 is related to 2 min reaction time. Selectivities, conversions and yields are calculated at 50% TBHP conversion, where $t_{50\%}$ denotes the reaction time needed for 50% TBHP conversion.

Results and discussion

Effect of substrate structure on the epoxidation rate and selectivity

The catalytic performance of $Ti(OSiMe_3)_4$ has been tested in the epoxidation of some open chain and cyclic allylic alcohols [geraniol (**1**), cyclohexenol (**2**), cyclooctenol (**4**)] and a cyclic olefin (cyclohexene, **5**). Epoxide formation at 333 K is shown in Fig. 1 and the initial rates and selectivities are collected in Table 1. Clearly, $Ti(OSiMe_3)_4$ is an active and selective homogeneous epoxidation catalyst, providing high regio- and diastereoselectivities in the epoxidation of allylic alcohols.

The critical role of the allylic OH group in epoxide formation is demonstrated by the complete unreactivity of methoxycyclohexene (**3**). No epoxide was detected even at

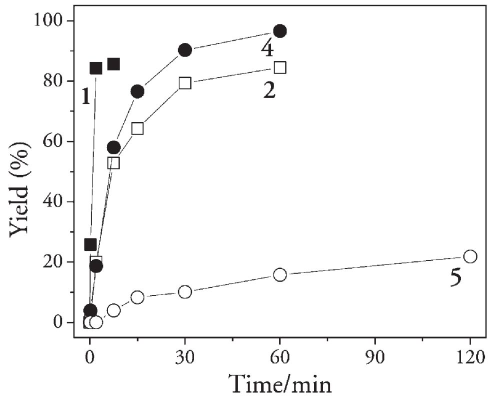

Fig. 1 Epoxidation of geraniol (**1**), 2-cyclohexen-1-ol (**2**), cyclooctenol (**4**) and cyclohexene (**5**); standard conditions.

Table 1 Epoxidations with $Ti(OSiMe_3)_4$ under dry conditions[a]

Substrate	$TOF_{50\%}$[b] / h^{-1}	$t_{50\%}$[c] / min	% $S_{C=C}$	% S_{TBHP}	% Yield	% RS/ DS[d]
1	1470	0.9	72	92	46	100
2	186	5	83.5	76	38	100
3	0	–	–	–	0	–
4	180	7	95	100	50	91.5
5	3.1	225	38	60	30	–

[a] Standard reaction conditions, $T = 333$ K. [b] Average TOF at 50% TBHP conversion. [c] Reaction time until 50% TBHP conversion. [d] Regioselectivity for 2,3-epoxide for geraniol (**1**), diastereoselectivity for *cis*-epoxide for cyclohexenol (**2**) and cyclooctenol (**4**).

363 K after 4 h reaction time. This shows the influence of decreased nucleophilicity when interaction *via* the alcoholic OH group is impossible, and also the effect of some steric hindrance by the –OMe group. For comparison, the epoxidation of cyclohexene (**5**) was also strongly retarded by the missing OH interaction. The initial rate was lower and the selectivities were poor, compared to those achieved in the epoxidation of cyclohexenol (**2**). Besides, epoxidation of cyclohexene was always accompanied by a short initial period of a few minutes, in which no epoxide was produced. To sum up, the epoxidation activity ($TOF_{50\%}$) of $Ti(OSiMe_3)_4$ decreases in the order: $\mathbf{1} \approx \mathbf{2} > \mathbf{4} > \mathbf{5} > \mathbf{3}\ (= 0)$.

A closely related catalyst, $Ti(OSiPh_3)_4$, was found to be almost inactive in the epoxidation of cyclohexene with TBHP.[22] The poor activity may be attributed to the increased steric demand of $OSiPh_3$ groups as compared to $OSiMe_3$ groups, or to the higher stability of Ti–O–Si bonds in $Ti(OSiPh_3)_4$ by electron orbital mixing, taking into account a probable epoxidation mechanism involving Ti–O–Si bond cleavage.

Geraniol (**1**), possessing two isolated C=C double bonds, represents a suitable structure to gain information about regioselectivity of the epoxidation reaction. Reaction at the double bond remote to the OH functional group would be favorable due to its enhanced nucleophilicity, whereas epoxidation of the allylic double bond is directed by interaction of the OH group with the Ti-hydroperoxy complex. In epoxidations with $Ti(OSiMe_3)_4$ the 2,3-epoxide is formed exclusively (Table 1).

Diastereoselectivity is another valuable source of information on the hydroxy-directing effect in epoxidation reactions. Epoxidation of cyclohexenol (**2**; dihedral angle of 139°)[32] yielded solely the *cis*-epoxide (Table 1). Cyclooctenol (**4**) with a dihedral angle of 199°[32] was epoxidized mainly to the *cis*-epoxide. It has been shown that diastereoselectivity in the epoxidation of cyclic allylic alcohols depends on steric and electronic factors, which are governed by the oxidizing agent and the ring size (dihedral angle, C=C–C–O).[32–34]

UV-Vis analysis of catalyst-substrate-oxidant interactions

Differences in the complexation behavior of the open chain allylic alcohol **1**, the cyclic allylic alcohol **2** and the cyclic allylic ether **3** were analyzed by UV-Vis spectroscopy. In these measurements the saturated forms of olefins **1**–**3** (denoted as **1s**–**3s**, Scheme 2) were used to mimic the catalyst-substrate interaction but minimize the UV absorption above 210 nm.

$Ti(OSiMe_3)_4$ showed an intense absorption in the range of 210–215 nm, absent from the spectrum of the corresponding silicon compound $Si(OSiMe_3)_4$. This band was assigned to a ligand-to-metal charge transfer (LMCT) transition of a fourfold coordinated Ti center.[35,36] Note that a change in the LMCT band can either occur due to additional coordination of the substrate directly to the Ti site or to H-bonding of the substrate to the O atom of an $–OSiMe_3$ ligand. Adsorption of the substrates and TBHP, present in high excess, decreased the intensity of the band at 210–215 nm and produced a new broad band in the range of 240–280 nm. The changes are illustrated by the difference spectra in Fig. 2. The absorption intensity of the $Ti(OSiMe_3)_4$ band at 210–215 nm decreases in the following order upon complexation: TBHP > 3,7-dimethyl-octane-1ol (**1s**) > cyclohexanol (**2s**) ≫ methoxycyclohexane (**3s**). The observed shift upon adding **3s** was minor and did not exceed the estimated experimental error. The complexation order is attributed to steric hindrance in **2s** relative to **1s** and to the missing OH function in **3s**. When the results are transferred from the hydrogenated model substrates **1s**–**3s** to the substrates **1**–**3**, this order corresponds well to the reactivity order observed in epoxidations with $Ti(OSiMe_3)_4$ (Table 1). Apparently, the ability of the substrate to coordinate to the catalyst determines the rate of the epoxidation reaction, assuming a similar epoxidation mechanism.

Catalyst stability—effect of water

As mentioned in the Introduction, the behavior of solid Ti- and Si-containing catalysts towards water is remarkably different. The hydrophylic sol-gel titania–silica mixed oxides hydrolyze and deactivate in the presence of water, while TS-1 is commonly used for epoxidation in aqueous medium and water is assumed to be a ligand in the active peroxo complex.[37,38] The best known homogeneous catalyst, $Ti(OPr\text{-}i)_4$ in the presence of alkyltartrates (Sharpless epoxidation) is retarded by water even at 253 K.[39,40] Clearly, interaction of $Ti(OSiMe_3)_4$ with water is important for understanding the characteristics of this catalyst.

The role of small amounts of water in the epoxidation of various substrates is illustrated in Figs. 3–5. In general, the faster the epoxidation under dry conditions, the smaller is the effect of water on the reaction rate and (stereo)selectivity. Using a $H_2O : Ti(OSiMe_3)_4 = 11 : 1$ molar ratio, in the epoxidation of geraniol (**1**) the initial rate decreased by only 16%, while the initial reaction rates were undetectably low in the epoxidation of cyclooctenol (**4**) and cyclohexene (**5**) (see Fig. 3). Considering the average reaction rate for up to 4 h reaction time, the slow epoxidation of **5** was retarded only slightly, compared to the reaction under dry conditions. The retarding effect of H_2O on the epoxidation of **4** as a function of water : catalyst ratio is shown in Fig. 4. Increasing water concentration led to a steady decrease of TOF [Fig. 4(a)].

In the epoxidation of **1** and **2** the high stereoselectivities remained unaffected in the presence of water. In contrast,

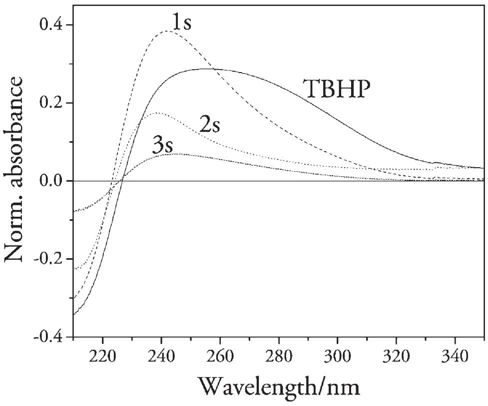

Fig. 2 UV-Vis analysis of the interaction of $Ti(OSiMe_3)_4$ with TBHP and the substrates **1** and **2**, mimicked by the use of their saturated forms: 3,7-dimethyloctan-1-ol (**1s**), cyclohexanol (**2s**) and methoxycyclohexene (**3**)s. The difference between the spectra obtained in the presence and absence of additive is shown to emphasize the changes. $Ti(OSiMe_3)_4$: substrate molar ratio = 1 : 400, $Ti(OSiMe_3)_4$: TBHP = 1 : 100.

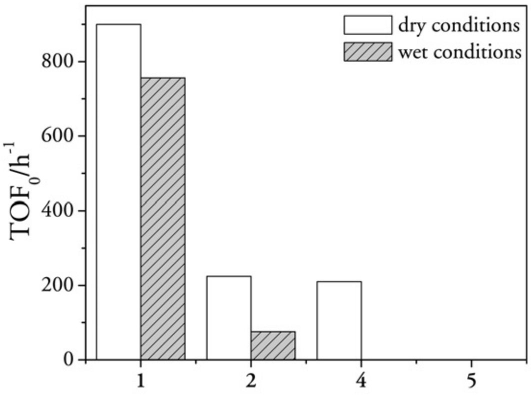

Fig. 3 Effect of water on the initial rate (TOF_0) in the epoxidation of geraniol (**1**), 2-cyclohexen-1-ol (**2**), cyclooctenol (**4**) and cyclohexene (**5**). H_2O : $Ti(OSiMe_3)_4$ molar ratio is 11; standard reaction conditions.

water had a dramatic influence on the epoxidation of **4** as shown in Fig. 4(b). Increasing the H_2O : $Ti(OSiMe_3)_4$ molar ratio from 0 to 11 successively lowered the fraction of *cis*-epoxide from 91% to 3.5%. Considering the initial selectivities, the effect of water is even more striking: 100% *cis*-epoxide under dry conditions after 2 min reaction time and 100% *trans*-epoxide with an eleven-fold excess of water after 7.5 min reaction time. All these observations point towards detrimental structural changes induced by hydrolysis, resulting in a loss of activity and selectivity.

In the above experiments water was added at zero time, together with TBHP. When the reaction mixture in the presence of water [H_2O : $Ti(OSiMe_3)_4 = 11 : 1$] was stirred for 7.5 min at 333 K ("prehydrolysis") before the addition of cyclooctenol (**4**), epoxidation was almost completely blocked as illustrated in Fig. 4(a) (bottom line). The similar influence of prehydrolysis of the catalyst in the absence of geraniol (**1**) is shown in Fig. 5. When water is added at zero time together with TBHP, the decrease in reaction rate was minor, compared to the reaction under dry conditions. However, prehydrolysis of the catalyst for 7.5 min at 333 K with only a small amount of water [H_2O : $Ti(OSiMe_3)_4 = 1$] before adding geraniol and TBHP lowered the reaction rate dramatically. One hundred percent conversion was achieved only after 4 h reaction time, though the regioselectivity to 2,3-epoxide was still excellent (99%). Apparently, strong complexation of the allylic alcohol substrate present in excess [olefin : $Ti(OSiMe_3)_4 = 150 : 1$] can retard hydrolysis of the catalyst. Note that different structures have been proposed for the "hydroxy-assisted" mechanism of allylic alcohol epoxidation over Ti- and Si-containing catalysts.[41,42]

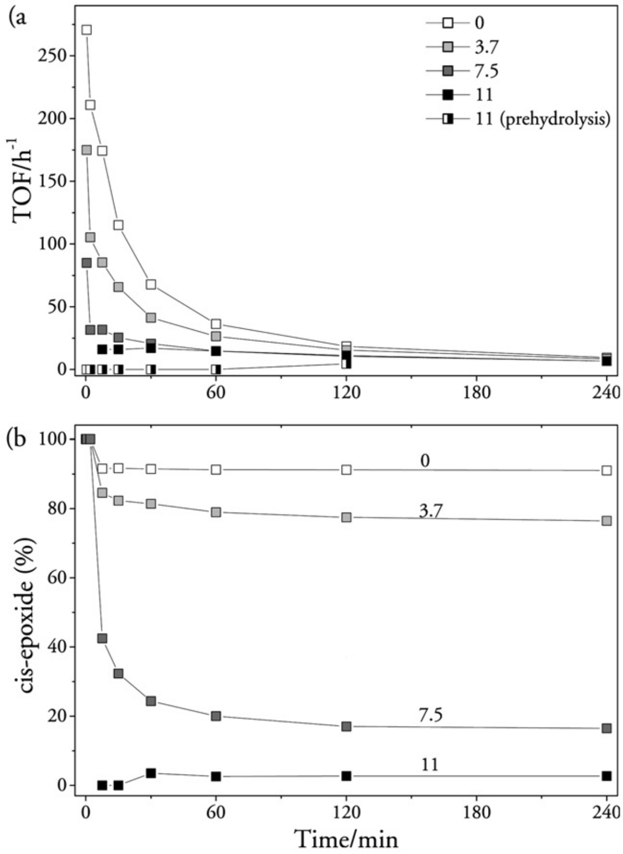

Fig. 4 Influence of water on the (a) reaction rate (TOF) and (b) stereoselectivity in the epoxidation of cyclooctenol (**4**). The H_2O : $Ti(OSiMe_3)_4$ molar ratios are 0, 3.7, 7.5 and 11. Water is added at zero time or else the catalyst is prehydrolyzed for 7.5 min in the absence of **4**, under otherwise standard reaction conditions.

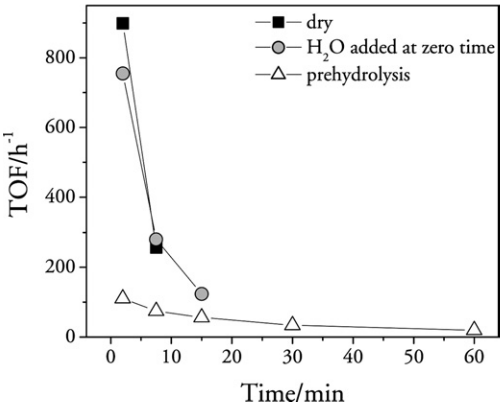

Fig. 5 Effect of water on the reaction rate (TOF) in the epoxidation of geraniol (**1**) under otherwise standard reaction conditions. (■) Dry conditions; (○) H_2O added together with TBHP at zero time, H_2O : $Ti(OSiMe_3)_4$ molar ratio is 11; (△) $Ti(OSiMe_3)_4$ prehydrolyzed for 7.5 min at 333 K before addition of TBHP and **1**, H_2O : $Ti(OSiMe_3)_4$ molar ratio is 1.

Comparison to other Ti- and Si-based catalysts

The performance of $Ti(OSiMe_3)_4$, Ae-1-sil, Ae-1 and TS-1 is compared in Table 2 for the epoxidation of 2-cyclohexene-1-ol (**2**), a commonly used test reaction. TS-1 and Ae-1 are the least active catalysts, though a reliable comparison is not possible due to the strikingly different reaction conditions. Silylation of the aerogel Ae-1 (to Ae-1-sil) increased the epoxide yield but barely influenced the diastereoselectivities. The beneficial influence of silylation of titania–silica mixed oxides has generally been attributed to the reduced hydrophylic character

Table 2 Comparison of various Ti- and Si-based catalysts in the epoxidation of 2-cyclohexen-1-ol (**2**)[a]

Catalysts	Peroxide	TOF_0[b] / h^{-1}	$t_{50\%}$[c] / min	% Yield at $t_{50\%}$	% *cis*:*trans* at $t_{50\%}$
$Ti(OSiMe_3)_4$ (0.067 mmol Ti)	TBHP	222	5	38	100 : 0[d]
Ae-1-sil (0.0125 mmol Ti)	TBHP	48	204	41	76 : 24
Ae-1 (0.0125 mmol Ti)	TBHP	50	240	33	79 : 21
TS-1[e] (0.11 mmol Ti)	Aq. H_2O_2	8	–	68	90 : 10

[a] Standard reaction conditions, $T = 333$ K. [b] Initial TOF_0 after 2 min reaction time. [c] Reaction time until 50% TBHP conversion. [d] *trans*-epoxide not detected. [e] 30% H_2O_2, acetone, 8 h reflux.[41]

of the surface.[7,9,25] Still, even Ae-1-sil is inferior to the homogeneous model catalyst Ti(OSiMe$_3$)$_4$ when considering either the initial reaction rate per Ti site or the diastereoselectivity to *cis*-cyclohexanol oxide. Ti(OSiMe$_3$)$_4$ shows the potential of a completely silylated aerogel possessing isolated tetrahedral Ti sites and a hydrophobic surface derived by protection of all Ti–OH and Si–OH groups.

The aerogel Ae-1 and the homogeneous model Ti(OSiMe$_3$)$_4$ were compared also in two other reactions, in the epoxidations of an open chain allylic alcohol (geraniol, **1**) and a cyclic olefin (cyclohexene, **5**) (see Table 3). Ti(OSiMe$_3$)$_4$ was superior in the epoxidation of **1** in which reaction the interaction of the allylic OH group with the active site likely plays a crucial role in the mechanism with both catalysts. In contrast, Ae-1 was far more active in the epoxidation of **5**. Note that epoxidation of cyclic olefins is the best catalytic use of titania–silica mixed oxides.[43] The low activity of Ti(OSiMe$_3$)$_4$ in the epoxidation of olefins without an OH group (such as **3** and **5**, Table 1) indicates that the use of this compound as a homogeneous model of titania–silica mixed oxides may be limited to the epoxidation of unsaturated alcohols.

The sensitivity of Ti(OSiMe$_3$)$_4$ to water is moderate, compared to other homogeneous Ti catalysts. For example, the Ti catalyzed asymmetric epoxidation of allylic alcohols in the presence of trace amounts of water (*i.e.*, when the reaction is carried out in the absence of a molecular sieve) affords low conversion and enantioselectivity.[39] Among the solid catalysts, titania–silica mixed oxides are rapidly deactivated by water but silylation diminishes this sensitivity.[11] Hence, in this respect Ti(OSiMe$_3$)$_4$ seems to be a good model for (silylated) titania–silica.

The main limitation of Ti(OSiMe$_3$)$_4$ as a homogeneous model is that it represents an ideal tetrahedral Ti site isolated by four –O–SiMe$_3$ ligands, instead of –O–Si(–O–Si≡)$_3$ ''ligands'' corresponding to the silica matrix in titania–silica (Scheme 1). It is very likely that this ligand effect also contributes to the excellent activity and selectivity of Ti(OSiMe$_3$)$_4$ as compared to that of Ae-1-sil. A logical conclusion is that Ti(OSiMe$_3$)$_4$ should be considered as a good homogeneous model for silylated titania–silica in which comparison the distorting effect of different ligands of the isolated Ti site is smaller. Besides, it is conceivable that not only the improved hydrophobicity but also the changes in the ligand environment of the Ti site contributes to the better catalytic performance of silylated titania–silica, as compared to the original mixed oxide.

Conclusions

Ti(OSiMe$_3$)$_4$ is a good homogeneous catalyst that is active and highly stereoselective in the epoxidation of open chain and cyclic allylic alcohols. Epoxidation of other substrates possessing no OH function is slow or shows no reaction at all. UV-Vis spectroscopy confirmed the importance of the substrate-catalyst interaction *via* the OH functional group and the role of steric restrictions in achieving a high rate. Though the catalyst is sensitive to water, a strongly coordinating reactant such as geraniol can retard hydrolysis and good yields and excellent stereoselectivities are obtained even in the presence of water.

We propose that Ti(OSiMe$_3$)$_4$ may be a suitable homogeneous model catalyst, mimicking the active sites in titania–silica mixed oxides, particularly silylated titania–silica, in the epoxidation of unsaturated alcohols. This soluble catalyst possesses a tetrahedral Ti site isolated by four siloxy groups, which seems to be structurally closely related to the most active Ti sites in the mixed oxides. The sensitivity to water is similar for the two catalysts. Application of Ti(OSiMe$_3$)$_4$ as a homogeneous model catalyst can promote theoretical calculation of the possible reaction mechanism in epoxidations with titania–silica. A limitation of Ti(OSiMe$_3$)$_4$ as a homogeneous model catalyst is the partly different ''ligand'' environment of Ti, that is OSiMe$_3$ groups in the soluble catalyst instead of OSi(OSi≡)$_3$ groups in the mixed oxide. This limitation is less important for silylated titania–silica mixed oxides with the general structure shown in Scheme 1.

Table 3 Comparison of Ti(OSiMe$_3$)$_4$ and Ae-1 in the epoxidation of geraniol (**1**) and cyclohexene (**5**)[a]

	Ti(OSiMe$_3$)$_4$		Ae-1	
Substrate	TOF[b] $_{50\%}$/h^{-1}	$t_{50\%}$[c] /min	TOF[b] $_{50\%}$/h^{-1}	$t_{50\%}$[c] /min
1	1470	0.9	42.5	96
5	3.1	225	98	57

[a] Standard reaction conditions, T = 333 K. [b] Average TOF at 50% TBHP conversion. [c] Reaction time till 50% TBHP conversion.

References

1 H. D. Gesser and P. C. Goswami, *Chem. Rev.*, 1989, **89**, 765.
2 M. Schneider and A. Baiker, *Catal Rev*, 1995, **37**, 515.
3 R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **153**, 177.
4 J. B. Miller, L. J. Mathers and E. I. Ko, *J. Mater. Chem.*, 1995, **5**, 1759.
5 M. A. Holland, D. M. Pickup, G. Mountjoy, E. S. C. Tsang, G. W. Wallidge, R. J. Newport and M. E. Smith, *J. Mater. Chem.*, 2000, **10**, 2495.
6 Y. Deng and W. F. Maier, *J. Catal.*, 2001, **199**, 115.
7 M. L. Pena, V. Dellarocca, F. Rey, A. Corma, S. Coluccia and L. Marchese, *Microporous Mesoporous Mater.*, 2001, **44**, 345.
8 J. Bu and H. K. Rhee, *Catal. Lett.*, 2000, **65**, 141.
9 A. Corma, M. Domine, J. A. Gaona, J. L. Jorda, M. T. Navarro, F. Rey, J. Perez-Pariente, J. Tsuji, B. McCulloch and L. T. Nemeth, *Chem. Commun.*, 1998, 2211.
10 H. Kochkar and F. Figueras, *J. Catal.*, 1997, **171**, 420.
11 F. Figueras and H. Kochkar, *Catal. Lett.*, 1999, **59**, 79.
12 C. A. Müller, R. Deck, T. Mallat and A. Baiker, *Top. Catal.*, 2000, **11/12**, 369.
13 B. Notari, *Adv. Catal.*, 1996, **41**, 253.
14 B. Notari, *Catal. Today*, 1993, **18**, 163.
15 C. B. Khouw, C. B. Dartt, J. A. Labinger and M. E. Davis, *J. Catal.*, 1994, **149**, 195.
16 A. Zecchina, S. Bordiga, C. Lamberti, G. Ricchiardi, D. Scarano, G. Petrini, G. Leofanti and M. Mantegazza, *Catal. Today*, 1996, **32**, 97.
17 P. E. Sinclair, G. Sankar, C. R. A. Catlow, J. M. Thomas and T. Maschmeyer, *J. Phys. Chem. B*, 1997, **101**, 4232.
18 C. M. Zicovich-Wilson, R. Dovesi and A. Corma, *J. Phys. Chem. B*, 1999, **103**, 988.
19 G. Ricchiardi, A. de Man and J. Sauer, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2195.
20 H. C. L. Abbenhuis, S. Krijnen and R. A. van Santen, *Chem. Commun.*, 1997, 331.
21 M. Crocker, R. H. M. Herold, A. G. Orpen and M. T. A. Overgaag, *J. Chem. Soc., Dalton Trans.*, 1999, 3791.
22 J. M. Thomas, G. Sankar, M. C. Klunduk, M. P. Attfield, T. Maschmeyer, B. F. G. Johnson and R. G. Bell, *J. Phys. Chem. B*, 1999, **103**, 8809.
23 M. C. Klunduk, T. Maschmeyer, J. M. Thomas and B. F. G. Johnson, *Chem.-Eur. J.*, 1999, **5**, 1481.
24 M. D. Skowronska-Ptasinska, M. L. W. Vortsenbosch, R. A. Van Santen and H. C. L. Abbenhuis, *Angew. Chem., Int. Ed.*, 2002, **41**, 637.
25 C. Beck, T. Mallat and A. Baiker, *J. Catal.*, 2001, **204**, 428.
26 G. Cerveau, R. J. P. Corriu and E. Framery, *J. Mater. Chem.*, 2000, **10**, 1617.
27 K. Kosuge and P. S. Singh, *J. Phys. Chem. B*, 1999, **103**, 3563.
28 J. Lessard, P. V. M. Tan, R. Martino and J. K. Saunders, *Can. J. Chem.*, 1977, **55**, 1015.
29 H. Meier, C. Antony-Mayer, C. Schulz-Popitz and G. Zerban, *Liebigs Ann. Chem.*, 1987, 1087.
30 J. D. Grunwaldt, C. Beck, W. Stark, A. Hagen and A. Baiker, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3514.

31 C. Beck, T. Mallat and A. Baiker, *Catal. Lett.*, 2001, **75**, 131.

32 W. Adam, C. M. Mitchell and C. R. Saha-Moller, *Eur. J. Org. Chem.*, 1999, 785.

33 T. Itoh, K. Jitsukawa, K. Kaneda and S. Teranishi, *J. Am. Chem. Soc.*, 1979, **101**, 159.

34 W. Adam and A. K. Smerz, *Tetrahedron*, 1995, **51**, 13 039.

35 C. K. Jørgensen, *Modern Aspects of Ligand Field Theory*, North-Holland, Amsterdam, 1971.

36 J. A. J. Duffy, *J. Chem. Soc., Dalton Trans.*, 1983, 1475.

37 W. Adam, A. Corma, A. Martinez, C. M. Mitchell, T. I. Reddy, M. Renz and A. K. Smerz, *J. Mol. Catal. A*, 1997, **117**, 357.

38 P. E. Sinclair and C. R. A. Catlow, *J. Phys. Chem. B*, 1999, **103**, 1084.

39 Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765.

40 M. G. Finn and K. B. Sharpless, *J. Am. Chem. Soc.*, 1991, **113**, 113.

41 R. Kumar, G. C. G. Pais, B. Pandey and P. Kumar, *J. Chem. Soc., Chem. Commun.*, 1995, 1315.

42 W. Adam, A. Corma, T. I. Reddy and M. Renz, *J. Org. Chem.*, 1997, **62**, 3631.

43 M. Dusi, T. Mallat and A. Baiker, *Catal. Rev. Sci. Eng.*, 2000, **42**, 213.