Epoxidation of allylic alcohols with TiO$_2$–SiO$_2$: hydroxy-assisted mechanism and dynamic structural changes during reaction

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Epoxidation of allylic alcohols and cyclohexene with TBHP and titania–silica aerogels containing 1 and 5 wt% TiO$_2$ has been studied. For the oxidation of geraniol and cyclohexenol, the regio- and diastereoselectivities and kinetic data indicate an OH-assisted mechanism involving a dative bond between the OH group and the Ti site. This mechanism is disabled in the oxidation of cyclooctenol due to steric hindrance. The moderate regio- and diastereoselectivities of the aerogels, compared with those of TS-1 and the homogeneous model Ti(OSiMe$_3$)$_4$, are attributed to the presence of non-isolated Ti sites and to a "silanol-assisted" mechanism, according to which model the allylic alcohol is anchored to a neighboring SiOH group instead of the Ti-peroxo complex. Kinetic analysis of the initial transient period revealed rapid catalyst restructuring during the first few turnovers. A feasible explanation is the breaking of Si–O–Ti linkages of the carefully predried aerogels by water or TBHP, resulting in active Ti sites with remarkably different catalytic properties.

KEY WORDS: titania-silica; allylic alcohols; epoxidation; "silanol-assisted" mechanism; restructuring; induction period.

1. Introduction

Epoxidation of functionalized olefins, particularly allylic alcohols, by Ti- and Si-containing solid catalysts has received considerable attention in the past years [1–13]. Several different structures of the active Ti-peroxo complex have been proposed to interpret the excellent activity and (stereo)selectivity. In a recent quantum chemical study, Sinclair *et al.* [14] suggested a Ti(η^2-OOR$'$) structure as the active oxygen-donating species in the epoxidation of alkenes with titanosilicate catalysts (scheme 1(a)). They concluded that H$_2$O or alcohols competitively coordinate to Ti sites. For the epoxidation of allylic alcohols, Kumar *et al.* [15] assumed a transition state involving coordination of the –OH group of the reactant to the Ti active site via a dative bond (scheme 1(b)). On the basis of a comparative study of various catalysts and peroxides, Adam *et al.* [16] deduced a transition-state structure analogous to that of peracid epoxidations, involving interaction of the OH group with the peroxo oxygen atom via H-bonding (scheme 1(c)).

In the enantioselective epoxidation of allylic alcohols with a homogeneous Ti complex–alkyltartrate–*tert*-butylhydroperoxide (TBHP) system (Sharpless epoxidation, scheme 1(d), simplified), the most probable transition-state structure is a metal-alkylperoxo complex with hexacoordinated Ti, involving coordination of the allylic alcohol via a metal–alcoholate bond [17]. Note that even traces of water deactivate this catalyst [18].

To our knowledge, the mechanism of the epoxidation of allylic alcohols on titania–silica mixed or supported oxides has not been addressed yet. All models developed for TS-1 (scheme 1(a)–(c)) assume isolated, tetrahedral Ti surrounded by SiO groups as the active site that can expand the coordination number up to six during interaction with the solvent, the peroxide and the reactant. This structure and the hydrophobic proximity allowing the use of aqueous H$_2$O$_2$ as oxidant are typical for TS-1. In contrast, several types of active sites may exist in the strongly hydrophilic titania–silica mixed oxides [19]. We have shown recently that in sol–gel titania–silica, the isolated, tetrahedral Ti sites may be dominant but, owing to kinetic effects, it is difficult to achieve complete site isolation even at low titania contents [20]. The highest epoxidation activity related to catalyst mass was observed at 10 wt% TiO$_2$, indicating that complete site isolation is not a necessary requirement for mixed oxides [19,21].

A further point to be considered in a mechanistic study is the high abundance of SiOH groups in hydrophilic titania–silica in the vicinity of Ti sites. These SiOH groups may compete with the reactant, analogously to the effect of chelating ligands in homogeneous catalysis, and represent an interacting site for the reactant. Cleavage of a Ti–O–Si bond by water produces further SiOH groups and Ti sites with tripodal geometry (scheme 2). The latter structure has been denoted as the active site in amorphous titania-on-silica epoxidation catalysts [22–27]. Successive hydrolysis of Ti–O–Si bonds of closed lattice Ti sites resulting in tripodal and bipodal sites has been evidenced also for TS-1 [28–30].

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a) [14]   b) [15]

c) [16]   d) [17]
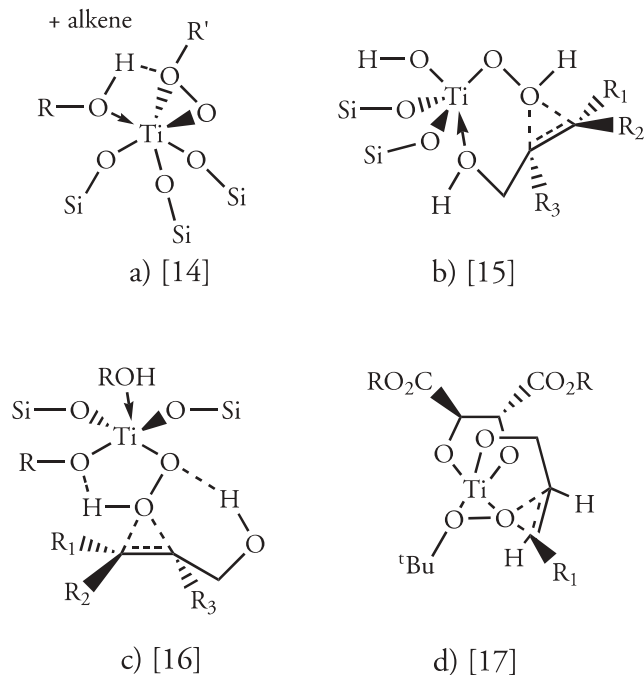
Scheme 1. Proposed transition-state structures in epoxidations with titanium containing heterogeneous and homogeneous catalysts.

Scheme 2. Addition of water or TBHP to an isolated, tetrahedral Ti site yielding a tripodal Ti site and a neighboring SiOH (R = H or ^tBuO).
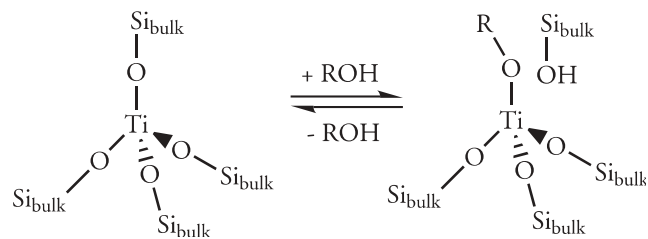
The aim of the present study was to clarify the nature of allylic alcohol–Ti site interaction during epoxidation with titania–silica aerogels and *tert*-butylhydroperoxide (TBHP). Epoxidation of some linear and cyclic allylic alcohols, and cyclohexene for comparison, have been chosen as test reactions (scheme 3). Besides, we report unusual variations in rate and stereoselectivity in the early stage of the reactions that are attributed to catalyst restructuring.

(S_{BET} 1060 m^2 g^{-1}, $V_{p(N2)}$ 3.1 cm^3 g^{-1}) and 25.3 for Ae-5 (S_{BET} 960 m^2 g^{-1}, $V_{p(N2)}$ 2.9 cm^3 g^{-1}), corresponding to 1 and 5 wt% TiO_2, respectively, for a theoretical catalyst TiO_2–SiO_2. A solution consisting of titanium-bisacetylacetonate-diisopropoxide (Aldrich, 75 wt% in isopropanol), tetramethoxysilane (Fluka, 99%) and 2.5 ml isopropanol was prepared (for 2.5 g mixed oxide). The hydrolysant, consisting of 0.36 g HNO_3 (65 wt%, 3.75 mmol), 3.26 g H_2O and 10 ml isopropanol, was added under vigorous stirring at room temperature. After 6 h, 1.51 g trihexylamine (5.63 mmol) in 20.5 ml isopropanol was added to the mixture. Gelation occurred within 1–8 h and the gel was aged for 6 days. The solvent was semicontinuously extracted with super-critical CO_2 at 313 K and 24 MPa. The raw aerogel was calcined in air at 673 K for 5 h.

Detailed description of the synthesis and characterization of the aerogels by N_2-physisorption, X-ray diffraction, thermal analysis, XPS, UV-Vis and DRIFT spectroscopy, and ^{29}Si-MAS NMR have been published earlier [19,20,33]. The degree of Ti dispersion in the silica matrix was confirmed by UV-vis DRS, DRIFT, XPS [20] and EXAFS [34] methods.

2. Experimental

2.1. Materials

The following commercially available chemicals were used: toluene (Fluka, 99.5%, abs.), dodecane (Merck, 99%), geraniol (**1**, Acros, 99%), 2-cyclohexen-1-ol (**2**, Fluka, 97%), cyclohexene (**4**, Merck, 99%), TBHP (Fluka, 5.5 N in nonane, additionaly dried over freshly activated molecular sieve 4 Å). Cyclooctenol (**3**, 97%) was prepared according to a known procedure [31].

Amorphous mesoporous titania–silica aerogels (Ae-X) were prepared on the basis of a former recipe [32]. The Si/Ti molar ratio was 132 for Ae-1

2.2. Methods

All *epoxidation reactions* were carried under Ar to avoid the presence of oxygen and moisture. In the standard epoxidation procedure ("dry" conditions), 0.1-g catalyst was dried in the reactor by heating to 473 K for 1 h in an Ar flow. Then, solvent (toluene) and 0.5 ml internal standard (dodecane) were added and the slurry was heated to 333 K. During heating up, 10 mmol of olefin was added and the reaction started by introducing 2.5 mmol TBHP in nonane ([olefin]$_0$: [TBHP]$_0$ = 4 : 1). In some reactions, activated molecular sieve 4 Å (50 mg) was also added to the reaction mixture. For

1   2   3   4
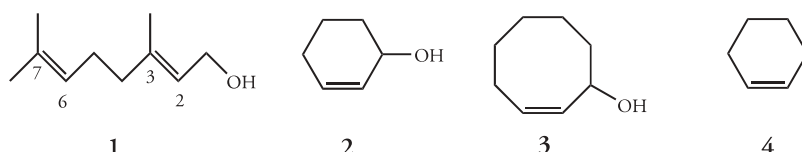
Scheme 3. Reactants used in epoxidation reactions.

"wet" conditions, an aqueous TBHP solution (H_2O/TBHP = 0.3) was used. The total reaction volume was 10 ml.

Samples were taken after 20 s, 2, 7.5, 15, 30, 60, 120 and 240 min. Sampling and filtering off the catalyst took about 6 s, so the real initial turnover frequency (TOF_0) values may be lower by up to 25%. As the sample preparation was uniform, the relative amounts of epoxide or the TOF_0 values provide a good semiquantitative measure of the initial reaction rate.

The products were analyzed by an HP-6890 gas chromatograph equipped with a cool on-column inlet and an HP-FFAP capillary column. The epoxides were identified by comparison with authentic samples and by GC-MS. The internal standard method was used for quantitative analysis. Hydroperoxide conversion was determined by iodometric titration using a Metrohm 686 Titroprocessor. Two different types of selectivities were calculated: epoxide selectivity (epoxide formed, related to the reactant consumed):

$S_{C=C}$ (%) = 100 · [epoxide]/([reactant]$_0$)-[reactant]), and peroxide selectivity (epoxide formed, related to the peroxide consumed):

S_{TBHP} (%) = 100 · [epoxide]/([TBHP]$_0$−[TBHP]).

Selectivities, conversions and yields are usually given at 50% TBHP conversion, where $t_{50\%}$ denotes the reaction time needed for 50% TBHP conversion in minutes. The epoxide yield and the olefin conversion are related to the initial amount of TBHP (limiting component). The turnover frequency (TOF) is related to the total amount of Ti present in the catalyst (mol epoxide formed per hour and mol Ti). $TOF_{50\%}$ denotes the rate of epoxide formation at 50% TBHP conversion and TOF_0 at 20 s reaction time.

3. Results and discussion

The feasibility of an OH-assisted reaction mechanism was investigated in the epoxidation of geraniol, cyclohexenol and cyclooctenol with the aerogels Ae-1 and Ae-5 using TBHP as the oxidant. The regioselective epoxidation of geraniol possessing two isolated C=C double bonds reflects the extent of coordination of the allylic OH group to the Ti-peroxo complex. Reaction at the double bond remote to the OH group would be favorable due to its enhanced nucleophilicity, whereas epoxidation of the allylic double bond is directed by interaction with the Ti site. The diastereoselectivity in the epoxidation of cyclohexenol and cyclooctenol indicates the steric demand of coordination of the reactant to the Ti complex [35].

The optimum conditions for epoxidation with titania–silica aerogels include a relatively high temperature (around 360 K) and high titania content (10–20 wt%) [19,21]. Here, we used a lower temperature of 333 K to allow an accurate kinetic analysis and low

titania content (1 and 5 wt%) in order to minimize the contribution of non-isolated Ti sites and avoid Brønsted acidity typical for aerogels containing 10 wt% or more titania.

3.1. OH-assisted epoxidation mechanism

Some important characteristics of the epoxidation of the allylic alcohol reactants are collected in table 1. The order of epoxidation activity, characterized by the time required to achieve 50% peroxide conversion, was: cyclooctenol > geraniol > cyclohexenol. The chemoselectivity followed the same trend and the sequence was independent of the Ti content of the catalysts. In contrast, epoxidation of cyclooctenol was the least stereoselective reaction, affording only 15% *cis*-epoxide under standard conditions. The pronounced regioselectivity in the epoxidation of geraniol and *cis*-epoxide selectivity in the oxidation of cyclohexenol reveal an OH-assisted reaction mechanism, *i.e.*, an interaction between the allylic hydroxyl group and the Ti-peroxo complex.

An intriguing question is the real nature of the reactant–Ti-peroxo complex interaction. Commonly, the stereochemical outcome of the epoxidation of allylic alcohols is used to speculate about the nature of the transition state. Kumar *et al.* [15] reported that the TS-1–aqueous H_2O_2 system epoxidized geraniol and nerol (*trans*- and *cis*-1-hydroxy-3,7-dimethylocta-2,6-diene, respectively) exclusively at the 2,3-position and produced preferentially (90%) the *cis*-epoxides in the oxidation of 2-cyclopenten-1-ol and 2-cyclohexen-1-ol. The high diastereoselectivity was ascribed to a transition

Table 1
Epoxidation of allylic alcohols with the aerogels Ae-1 and Ae-5, and the homogeneous reference catalyst Ti(OSiMe₃)₄. The rate and selectivities were determined at 50% TBHP conversion; standard reaction conditions

Substrate	$t_{50\%}$[a] (min)	$S_{C=C}$ (%)	S_{TBHP} (%)	RS or DS[b] (%)
		Ae-1		
Geraniol	96	67.5	68	75.5
Cyclohexenol	240	58	66	79
Cyclooctenol	54	82	95.5	15
		Ae-5		
Geraniol	21	57	57.5	75
Cyclohexenol	56	40.5	45.5	82.5
Cyclooctenol	8	91	98.5	14.5
		Ti(OSiMe₃)₄[c]		
Geraniol	0.9	72	92	100
Cyclohexenol	5	83.5	76	100
Cyclooctenol	7	95	100	91.5

[a]Reaction time till 50% TBHP conversion.
[b]Regioselectivity to 2,3-epoxide (geraniol), or diastereoselectivity to *cis*-epoxide for cyclohexenol and cyclooctenol.
[c]30 µL Ti(OSiMe₃)₄, epoxidation procedure, see experimental section.

state involving coordination of the allylic OH group to the Ti site via a dative bond (scheme 1(b)).

Adam *and* coworkers [16,36] compared the diastereoselectivities obtained in the epoxidation of open-chain allylic alcohols with TS-1 and Ti-β, and some homogeneous catalysts and stoichiometric oxidants. On this basis, a transition state analogous to the structure of peracid epoxidations was suggested, involving a H-bond interaction (scheme 1(c)). It has been shown, however, that beside the disregard of the pronounced dependence of epoxidations on the nature of solvent and peroxide, the model is limited to the use of H_2O_2 [14]. Epoxidation with alkylhydroperoxides, such as TBHP, would require the transfer of a bulky alkyl group instead of H, and the approach of the reactant to the sterically hindered O atom.

Using these models as analogies for the interpretation of epoxidations with titania–silica, the stereoselective epoxidation of geraniol and cyclohexenol strongly support an OH-assisted mechanism. The lower reaction rates measured in these reactions, compared to the barely stereoselective epoxidation of cyclooctenol, may indicate a transition state involving a dative bond between the OH group and the Ti site (scheme 1(b)). This model is in agreement with the well-known retarding effect of coordinating solvents or reaction products [37–39]. In the epoxidation of cyclooctenol, mainly the *trans*-epoxide is formed (table 1). The disfavored OH-assisted mechanism in this reaction is attributed to an increased steric hindrance, as compared to the epoxidation of cyclohexenol (different dihedral angles [35]). The weaker coordination of cyclooctenol to Ti leads to an acceleration of the reaction since most of the Ti sites are not blocked with the reactant.

Although the aerogels Ae-1 and Ae-5 provided the *cis*- and 2,3-epoxides of cyclohexenol and geraniol, respectively, with at least 75% selectivity (see table 1), these values remain well below the stereoselectivities of TS-1 (90% [15]) and the homogeneous complex Ti(OSiMe₃)₄ (91.5–100%, see table 1). We assume that two major effects can account for the inferior selectivity of aerogels. On the one hand, the hydrophobic TS-1 and the homogeneous catalyst Ti(OSiMe₃)₄ contain only isolated, tetrahedral Ti sites surrounded by SiO groups. In contrast, even Ae-1 with only 1 wt% TiO2 possesses mainly but not exclusively isolated Ti sites. As mentioned in the introduction, complete site isolation has not yet been possible to achieve with the sol–gel technique [2,20,40]. Various Ti sites with increasing fraction of Ti–O–Ti connectivity may be present in the aerogels even at low Ti content, and the stereoselectivity of these non-isolated Ti sites is assumed to be moderate.

Besides, surface silanol groups typical for hydrophilic titania–silica mixed oxides may also reduce the regio- and diastereoselectivities. This "silanol-assisted" epoxidation mechanism would allow geraniol to adsorb via H-bonding at a silanol group in the proximity of a Ti site and be epoxidized at the electronically favored 6,7-double bond, as depicted in scheme 4. Similarly, interaction of cyclohexenol with a Si–OH group in the vicinity of a Ti site may provide preferentially the *trans*-epoxide. A strong support to this model is the observation that the more hydrated the catalyst surface, the lower the stereoselectivity as shown in figure 1, which will be discussed below.

3.2. Kinetic analysis: Ti site restructuring by TBHP and water

A detailed kinetic analysis of the epoxidation of all four reactants revealed some unusual behavior of the aerogels in the very early stage of the reactions. Figure 1 shows the changes in rate and regio- and diastereoselectivities using the aerogel Ae-1. The most striking observation is that no epoxide could be detected after 20 s in the oxidation of cyclohexenol and cyclohexene under carefully dried conditions, and the TOF values reached their sharp maxima after 7.5 and 2 min, respectively. The reactions were repeated with the simultaneous addition of water and TBHP. Under these "wet" conditions, the kinetic curves changed to a "normal" behavior in both reactions, *i.e.*, the highest TOF was observed at 20 s (earliest sampling). Considering all four reactions, the effect of water addition on the reaction rate strongly depended on the reaction studied: it was negligible in the epoxidation of cyclooctenol, but it resulted in serious catalyst deactivation in the oxidation of geraniol, and also in the epoxidation of cyclohexene after a striking initial rate enhancement. The effect of water on the diastereo- and regioselectivities was always negative, independent of the reactant structure. As already mentioned, the loss of stereoselectivity is attributed to an increased surface SiOH concentration and a more dominant contribution of the silanol-assisted epoxidation route.
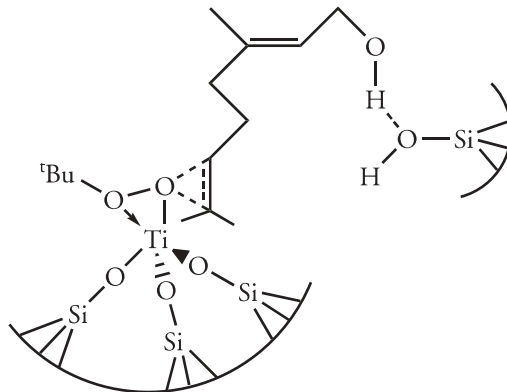
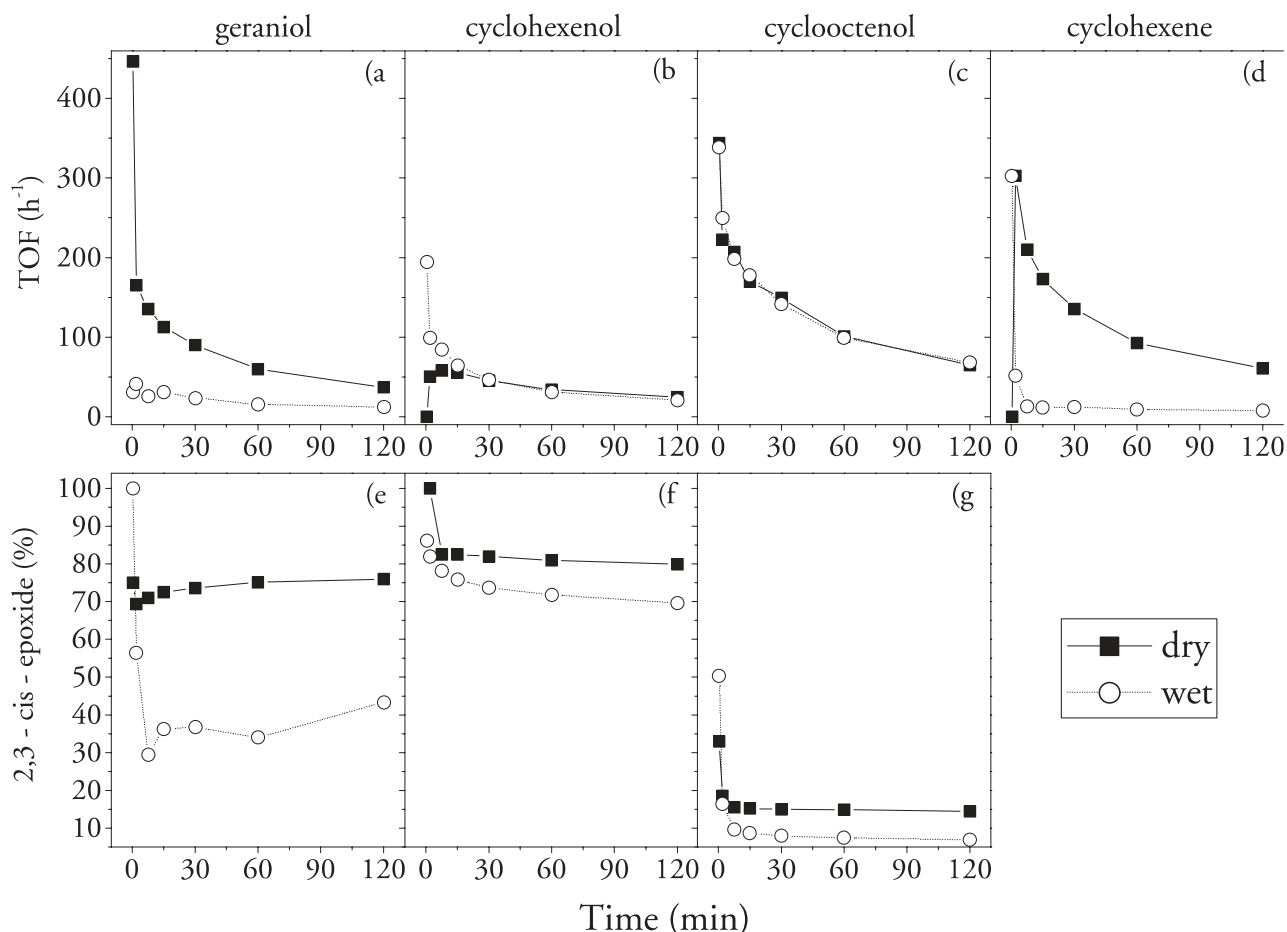Scheme 4. Silanol group-assisted epoxidation of geraniol, affording the 6,7-epoxide.

Figure 1. Kinetic analysis of the epoxidation of (a) geraniol, (b) cyclohexenol, (c) cyclooctenol and (d) cyclohexene with Ae-1 under dry (■) and wet (○) conditions. Under wet conditions, an aqueous peroxide solution was used (H$_2$O/TBHP/Ti molar ratio: 0.3/1/0.005). Changes in regioselectivity for (e) geraniol and in diastereoselectivity to the *cis*-epoxide in the epoxidation of (f) cyclohexenol and (g) cyclooctenol are also shown.

The zero initial TOF values in the epoxidation of cyclohexenol and cyclohexene may indicate only that the amount of epoxide desorbed from the catalyst surface after 20 s was below the detection limit. Even in this case, however, both reactions started at very low rates and they accelerated with time or by addition of water. This behavior is probably an indication to catalyst restructuring in the early stage of the reactions. The restructuring may proceed via Ti–O–Si cleavage either by H$_2$O or by TBHP, as shown in scheme 2. The initially formed tripodal site Ti(OSi)$_3$OH can further react with water or TBHP. The reverse process, the extensive dehydration of Ae-1 aerogel, has been shown recently by XANES studies [34]. Hence, we speculate that the aerogel predried *in situ* in the reactor before epoxidation contains Ti(OSi)$_4$ and Ti(OSi)$_3$OH as the dominant initial active sites. Reaction of these Ti sites with TBHP may result in the formation of the same Ti site Ti(OSi)$_3$OO^{t}Bu since cleavage of Ti–OH or Ti–O–Si bonds was calculated to occur with approximately the same activation barrier [14]. This Ti-peroxo complex is assumed to be the dominant active site in the epoxida-

tion of geraniol and cyclooctenol, but it requires a subsequent activation by the cleavage of a further Ti–O–Si bond for the efficient epoxidation of cyclohexenol and cyclohexene. Addition of trace amounts of water accelerates this transformation. The amount of water applied in the reactions under "wet" conditions (figure 1) was apparently too high and resulted in a subsequent catalyst deactivation. Note that there is a wealth of data demonstrating the poor performance of sol–gel titania–silica mixed oxides in the presence of considerable amount of water [41–44].

A further point to be considered is the decomposition of peroxides [45] and side reactions of allylic alcohols (e.g. dimerization [46]) and possibly the condensation of silanol groups in the apolar reaction medium. All these reactions afford water as a coproduct. In order to prove this assumption, we repeated the epoxidation of cyclohexenol (figure 1(b), dry conditions), and beside predrying the catalyst *in situ* at 473 K, the reaction was carried out in the presence of molecular sieve 4 Å. As a result, the initial induction period, in which no epoxide could be detected, was extended from 20 s to 2 min (not

shown). After this induction period, the TOF was considerably higher in the presence of molecular sieve 4 Å throughout the reaction, in agreement with earlier observations [44]. This experiment indicates that the lower the amount of water in the system, the slower is the restructuring of Ti sites and the formation of new, active Ti sites.

The timescale of Ti-site restructuring is illustrated in table 2, where the turnover numbers (TON), calculated from the amount of epoxides detectable in solution, are shown. In the first 20 s, the highest TON was 1.8 for both catalysts, *i.e.*, up to two epoxidation cycles occurred at the very early stage of the reaction. The exceptions were the oxidation of cyclohexenol and cyclohexene with the aerogel Ae-1, affording no detectable amount of epoxide. This catalyst is characterized by a high degree of Ti-site isolation [20] and, apparently, these isolated tetrahedral Ti sites are inactive in the epoxidation of cyclohexenol and cyclohexene, but during reaction they were converted into active Ti sites. Applying the aerogel Ae-5, the initial

induction period was missing or it was very short. It has been shown recently by XPS, UV-Vis and DRIFT spectroscopy that in catalysts containing more than 1 wt% TiO₂, the concentration of isolated tetrahedral Ti sites was considerably lower than that in Ae-1 [20]. Apparently, the additional sites possessing also Ti–O–Ti linkages produced some epoxide at the very beginning of the reaction. The role of site isolation is confirmed by the kinetic curves in figure 2, where the influence of Ti content of the aerogels on the epoxidation of cyclohexenol and cyclohexene is shown. (Note that the TOF values for Ae-1 are shown also in figure 1.) Clearly, the effect of Ti-site restructuring was less pronounced (figure 2(a)) or not detectable (figure 2(b)) with Ae-5.

4. Conclusions

Epoxidation of geraniol, cyclohexenol, cyclooctenol and cyclohexene has been studied using TBHP as oxidant and titania–silica aerogel catalysts containing 1 and 5 wt% TiO₂ (Ae-1 and Ae-5, respectively). The observed regio- and diasteroselectivities reveal an OH-assisted mechanism for geraniol and cyclohexenol. We assume a mechanism analogous to Kumar's model suggested for the epoxidation of allylic alcohols with TS-1 and H₂O₂ [15]. This model involving a dative bonding between alcohol and Ti (scheme 1(b)) fits best to our kinetic data and the well-known retarding effect of coordinating solvents on Ti^{IV}-silica epoxidation catalysts [13,29,37,39]. The low *cis*-epoxide selectivity and the enhanced reaction rate in the oxidation of cyclooctenol compared to those of cyclohexenol oxidation are attributed to steric hindrance by the bulkier cycloalkene ring that disfavors the OH-assisted mechanism.
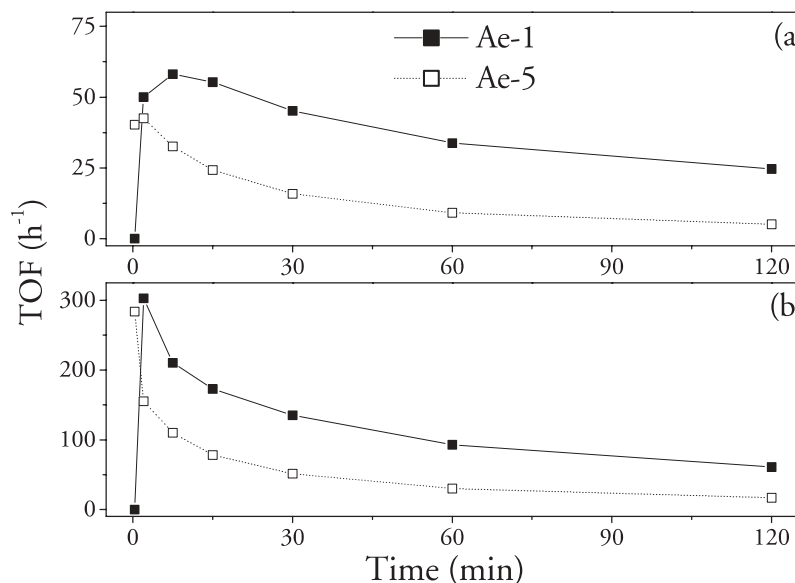
Table 2
Turnover numbers (TON) as a function of reaction time in the epoxidation of (**1**) geraniol, (**2**) cyclohexenol, (**3**) cyclooctenol and (**4**) cyclohexene with catalysts Ae-1 and Ae-5; standard reaction conditions

Time (s)	Ton[a]							
	Ae-1				Ae-5			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
20	1.8	0	1.8	0	1.3	0.2	1.8	1.6
120	3.8	1.6	7.2	10.1	4.2	1.4	7.2	5.2
7200	56	48.8	129.6	121.6	16.2	10.2	39.5	33.6

[a]Turnover number ({mol epoxide}/{mol Ti}); full conversion of TBHP corresponds to 200 and 40 TON for Ae-1 and Ae-5, respectively.

Figure 2. The effect of titania content of the aerogels on the initial transient period, as illustrated by the turnover frequencies in the epoxidation of (a) cyclohexenol and (b) cyclohexene with the catalysts Ae-1 (■) and Ae-5 (□) under dry conditions.

A final assessment of the reaction mechanism requires consideration of the following complicating factors:

(i) In contrast to TS-1 and the homogeneous model Ti(OSiMe₃)₄, complete site isolation has not been possible yet in sol–gel titania–silica mixed oxides. Depending on the synthesis method and Ti content, various Ti sites may be present covering the whole range from tetrahedral Ti surrounded by only SiO groups to octahedral Ti surrounded by TiO groups in titania nanodomains. It has been shown recently [20] that the fraction of isolated tetrahedral Ti sites in Ae-1 is high, approaching that of TS-1. Still, the lower regio- and diastereoselectivities of Ae-1, compared to those of TS-1 and Ti(OSiMe₃)₄, indicate significant differences. It has been demonstrated that, for example, a Ti site possessing three SiO and a TiO "ligands" is an active epoxidation catalyst [23], though its activity, selectivity and also the reaction mechanism may be different from those of a completely isolated Ti site.

(ii) The striking changes in rate and stereoselectivity in the initial transient period of the oxidation of allylic alcohols and cyclohexene (figure 1) are attributed to catalyst restructuring. This restructuring occurred during the first few turnover cycles and presumably involved the breaking of one or two Si–O–Ti connectivities by water or TBHP (scheme 2). The process was strongly accelerated by the presence of water, and led to sometimes spectacular rate enhancements, though it always lowered the stereoselectivity, independent of the reactant structure.

(iii) A major difference between TS-1 and Ti(OSiMe₃)₄, and sol–gel titania–silica is the strongly hydrophilic character of the latter materials. The high concentration of surface silanol groups may be the major reason for the lower stereoselectivity. We propose a "silanol-assisted" epoxidation mechanism, according to which the OH group of the reactant allylic alcohol interacts via H-bonding with a neighboring SiOH group, instead of the Ti-peroxo complex (scheme 4). This interaction is expected to diminish the stereoselectivity of allylic alcohol epoxidation and interprets the detrimental effect of water.

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