

Chemo- and diastereoselective epoxidation of allylic alcohols with a titania–silica aerogel

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Abstract

An amorphous mesoporous titania–silica aerogel (20 wt.% TiO_2 –80 wt.% SiO_2) and *tert*-butylhydroperoxide have been used for the epoxidation of various allylic alcohols. Cyclic allylic alcohols and alkenols possessing an internal double bond were more reactive than the allylic alcohols with a terminal C=C bond. Epoxide selectivities could be improved by catalyst pre-drying and hydrophobisation in toluene, as well as by the addition of (basic) zeolite 4Å and NaHCO_3 to the reaction mixture. Diastereoselective epoxidation of cyclic allylic alcohols yielded preferentially the *cis*-epoxides. The performance of the titania–silica aerogel in the epoxidation of allylic alcohols and α - β -unsaturated carbonyl compounds was compared to those of titania-on-silica and TS-1. Interestingly, titania-on-silica and TS-1 were inactive in the epoxidation of α - β -unsaturated carbonyl compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Allylic alcohols; Epoxidation; Titania–silica aerogel

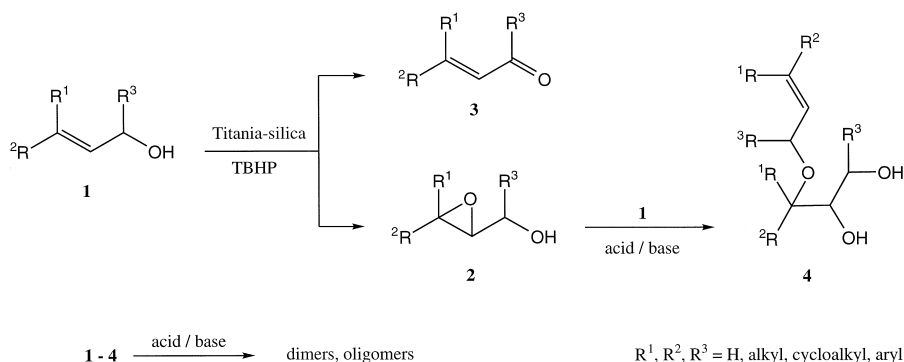
1. Introduction

Epoxides are desirable as useful intermediates, as well as target molecules. In the past years, considerable effort has been spent on substituting homogeneous transition metal catalysts by solids [1]. The development of an amorphous silica-supported titania by Shell researchers [2] represented a major breakthrough in the heterogeneously catalyzed epoxidations. The supported oxide was prepared by impregnating a silica carrier with a Ti^{IV} precursor, such as TiCl_4 or an organic titanium compound, followed by calcination. This catalyst has found

industrial application in propylene epoxidation, and has been shown to be active and selective also in the epoxidation of allyl alcohol and cyclohexenol [2].

The idea of preparing well-dispersed titania-on-silica by reacting a Ti-precursor with the surface silanol groups has been applied also by some other groups, as an example, silica gel treated with $\text{Ti}(\text{O}^i\text{Pr})_4$ was used in the epoxidation of unsubstituted alkenes, dienes and allylic alcohols with *tert*-butylhydroperoxide (TBHP) [3]. However, a relatively large amount of catalyst was required and secondary allylic alcohols were converted exclusively to the corresponding unsaturated ketones. Interestingly, a titania–silica mixed oxide obtained by supporting $\text{Ti}(\text{O}^i\text{Pr})_4$ on silica by a CVD method showed

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Scheme 1.

no activity at all in the epoxidation of allyl alcohol with TBHP or H_2O_2 [4].

An amorphous $\text{TiO}_2\text{-SiO}_2$, prepared by hydrolysis of tetraethoxytitanium and tetraethoxysilicon, was tested in the epoxidation of 2-buten-1-ol and 3-methyl-2-buten-1-ol (prenol) with aqueous H_2O_2 [5]. The activity and selectivity of this catalyst were rather low, and the oxidation of the alcoholic group was an important side reaction. Another sol-gel derived titania-silica mixed oxide with a Ti:Si ratio of 10:90 was not able to epoxidize allyl alcohol using either TBHP or H_2O_2 [4].

The poor performance of the above sol-gel mixed oxides is seemingly due to the inappropriate selection of synthesis conditions. There is a wealth of data available now which demonstrate that the nanoscale engineering of titania-silica xerogels and aerogels can provide outstanding epoxidation catalysts [6–10]. Even bulky cyclic olefins and α -isophorone, possessing an electron deficient $\text{C}=\text{C}$ double bond, could be epoxidized with high rate and selectivity using alkylhydroperoxides and an aerogel containing 20 wt.% TiO_2 [11,12]. The same catalyst afforded 87% yield in the epoxidation of *trans*-2-hexen-1-ol [13]. The reaction was carried out with TBHP and the in situ dried aerogel. Water, formed in small amount during the reaction, was eliminated by some zeolite 4A additive. It has been shown that the activity of titania-silica aerogel in the epoxidation of cyclic

olefins is two to three orders of magnitude higher than those of Ti- β and Ti-MCM-41 [10].

The aim of the present work was to extend the application range of our titania-silica aerogel and study the epoxidation of various allylic alcohols possessing a terminal or an internal double bond, as well as cycloalkenols, according to Scheme 1.

2. Experimental

2.1. Materials

Trans-2-hexen-1-ol (Aldrich, 96%), *cis*-2-hexen-1-ol (Aldrich, 95%), *cis*-2-penten-1-ol (Aldrich, 95%), 3-methyl-2-buten-1-ol (Fluka, > 98%), cinnamyl alcohol (Fluka, > 97%), 3-buten-2-ol (Fluka, > 97%), 1-hexen-3-ol (Acros, 98%), 1-octen-3-ol (Fluka, > 98%), 2-cyclohexen-1-ol (Fluka, ca. 97%), 3-methyl-2-cyclohexen-1-ol (Aldrich, 96%), 3,5,5-trimethyl-2-cyclohexen-1-ol (Fluka, > 95%), 2-cyclohexen-1-one (Fluka, > 95%) and cyclohexene (Fluka, > 99.5%) were distilled prior to use. Ethylbenzene (Fluka, > 99%), cumene (Fluka, > 98%) and toluene (Riedel-de Haën, > 99.7%) were distilled and stored over molecular sieve 4Å.

Cinnamaldehyde (Fluka, > 98%), 7-oxabicyclo[4.1.0]heptan-2-one (Aldrich, 98%), (2*R*,3*R*)-(+)-propyloxiranemethanol (Aldrich,

97%), (2*R*,3*R*)-*trans*-3-phenyloxirane-2-methanol (Fluka, > 99%), cyclohexenoxide (Fluka, ca. 99%), NaHCO₃ (Merck, > 99.5%) and *tert*-butylhydroperoxide (TBHP, ca. 5.5 M solution in nonane, over molecular sieve 4Å) were used without further purification.

Epoxides of the allylic alcohols that were not commercially available were prepared with *m*-CPBA [14] and identified by ¹H-NMR and ¹³C-NMR.

Molecular sieve 4Å (Chemie Uetikon) was activated overnight at 473 K in vacuum.

2.2. Catalyst preparation

The titania–silica aerogel containing 20 wt.% TiO₂ was prepared using the sol–gel method. The solvent was semicontinuously extracted with supercritical CO₂ at 313 K and 24 MPa (low-temperature aerogel). The raw aerogel was calcined in a flow of dry air at 673 K for 5 h. A detailed study on the synthesis of sol–gel derived titania–silica aerogels and their characterization by N₂-physisorption, X-ray diffraction, thermal analysis, XPS and vibrational spectroscopy has been published elsewhere [9,11,15,16]. The X-ray amorphous material possessed a good Ti dispersion, high surface area ($S_{\text{BET}} = 680 \text{ m}^2/\text{g}$) and mesoporous structure (mean pore diameter = 9 nm; maximum pore size = 40 nm).

2.3. Epoxidation procedure

All reactions were carried out under argon to avoid the presence of oxygen and moisture. Detailed reaction conditions will be provided in the tables. In the standard epoxidation procedure, the catalyst was transferred to a 50-ml glass reactor fitted with magnetic stirring, thermometer and reflux condenser, and heated in an argon flow to 473 K for 16 h. Olefin, an internal standard (ethylbenzene or cumene), and toluene (solvent) were added to the in situ dried catalyst. A dropping funnel was charged with TBHP as a 5.5 M solution in nonane (the olefin:TBHP

ratio was usually 4:1). The solution was then heated to the reaction temperature, and the reaction started by adding the peroxide to the stirred slurry. In some cases, the dry aerogel was further treated in the solvent: the olefin and excess toluene were added, and a fraction of toluene was then removed by azeotropic distillation. Depending on the method, activated molecular sieve 4Å and/or NaHCO₃ were used as additives. An aliquot was removed after the reaction time indicated in the tables, was filtered, and was analyzed by gas chromatography (HP 5890 equipped with a cool on-column inlet and an HP-FFAP capillary column). The internal standard method was used for quantitative analysis. Hydroperoxide conversion was determined by iodometric titration using a Metrohm 686 Titroprocessor.

The selectivities were calculated in the following way.

- Selectivity of the epoxide related to the olefin converted = $100 \frac{[\text{epoxide}]_f}{[\text{olefin}]_i - [\text{olefin}]_f}$
- Selectivity of the epoxide related to the peroxide consumed = $100 \frac{[\text{epoxide}]_f}{[\text{TBHP}]_i - [\text{TBHP}]_f}$
- Selectivity of the aldehyde related to the olefin converted = $100 \frac{[\text{aldehyde}]_f}{[\text{olefin}]_i - [\text{olefin}]_f}$
- Selectivity of the aldehyde related to the peroxide consumed = $100 \frac{[\text{aldehyde}]_f}{[\text{TBHP}]_i - [\text{TBHP}]_f}$

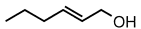
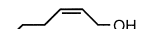
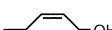



The subscripts *i* and *f* stand for initial and final values, respectively. The olefin conversion is given in mol% of the maximal attainable value.

3. Results

3.1. Oxidation of open chain primary allylic alcohols

In a previous study, the oxidation of *trans*-2-hexen-1-ol was achieved with high reaction rate and epoxide selectivity (Table 1, entry 1) [13]. The dominant side reaction was the acid-/base-catalyzed ring opening of the epoxide by the reactant alcohol to give a hydroxy-ether

Table 1
Epoxidation of open chain allylic alcohols^a

Entry	Reactant	Additive(s) (g)	Temp. (K)	Olefin conversion ^b (%)	Epoxide selectivity (%) related to	
					Olefin	Peroxide
1		4Å (0.5)	363	96	91	91
2		4Å (0.5)	363	82	80	75
3		4Å (0.5)	363	70	97	86
4		4Å (0.5)	363	109	34	43
5		4Å (1.5) NaHCO ₃ (0.34)	363	97	86	n.d. ^d
6		4Å (1.5) NaHCO ₃ (0.34)	333	32	94	n.d. ^d

^aReaction conditions: 70 mg catalyst (dried in situ at 473 K), 20 mmol olefin, 5 mmol TBHP, 0.5 ml ethylbenzene (internal standard), toluene (solvent); total volume = 6 ml; reaction time = 1 h.

^bOlefin conversion is related to TBHP (olefin:TBHP = 4:1).

^cReaction conditions: 200 mg catalyst (dried in situ at 473 K), 60 mmol olefin, 13.5 mmol TBHP, 1 ml cumene (internal standard), toluene (solvent); total volume = 21 ml; reaction time = 1 h.

^dNot determined.

(8%), whereas oxidation of the –OH function to a carbonyl group was minor (1%) (Scheme 1). Some other alkyl-substituted, open chain allylic alcohols have been epoxidized under the same conditions. The important conversion and selectivity data are collected in Table 1. High conversions were achieved in 1 h at 363 K. The prenenol conversion over 100% (entry 4) was due to considerable oligomerization of the olefin. (The olefin conversion is related to the peroxide, and the olefin:peroxide molar ratio was 4:1.) Seemingly, the conditions applied were good for the epoxidation of hexenols and pentenol, but not suitable for prenenol possessing a trisubstituted double bond. In the latter case, the epoxide was only a minor product (34%), and hydroxy-ether (13%) and unsaturated aldehyde (5%) were also formed.

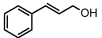
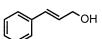
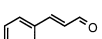
Lower reaction rates (based on conversion) were achieved for *cis*-allylic alcohols (entries 2

and 3) as compared to *trans*-hexenol. In the case of *cis*-pentenol (entry 3), epoxide ring opening was a minor reaction (ca. 3%), and no oxidation of the –OH function to a carbonyl group was observed. It is noteworthy that the *cis* and *trans* isomers of the reactants retained their stereospecificity in the products.

3.2. Influence of reaction conditions on the oxidation of acyclic primary allylic alcohols

The role of reaction additive and catalyst pretreatment is illustrated by two examples. The most important characteristics of the epoxidation of cinnamyl alcohol are collected in Table 2. Drying the aerogel in situ and addition of zeolite 4Å (standard procedure + addition of 4Å) was not efficient in achieving high conversion and selectivity, and the peroxide decomposed to a great extent, indicated by the low selectivity

Table 2
Epoxidation of cinnamyl alcohol and cinnamaldehyde

Reactant	Procedure ^a	t (h)	Olefin conversion (%)	TBHP conversion (%)	Epoxide selectivity (%) related to		Cinnamaldehyde selectivity (%) related to	
					Olefin	TBHP	Olefin	TBHP
	Standard + addition of 4Å	1	42	71	25	15	14	8
	Catalyst treatment in toluene	1	57	56	55	57	18	19
	Standard + addition of 4Å	5	15	n.d. ^b	43	n.d. ^b	—	—

^aStandard procedure + addition of 4Å: 70 mg catalyst (dried in situ at 473 K), 0.5 g activated zeolite 4Å, 20 mmol olefin, 5 mmol TBHP, 0.5 ml ethylbenzene (internal standard), toluene (solvent); total volume = 6 ml; $T = 363$ K. Catalyst treatment in toluene: 200 mg catalyst (dried in situ at 473 K followed by azeotropic distillation of a fraction of toluene), 60 mmol olefin, 13.5 mmol TBHP, 1 ml cumene (internal standard); total volume = 25 ml; $T = 363$ K.

^bNot determined.

based on TBHP. The aerogel that was dried in situ at 473 K and subsequently by azeotropic distillation (catalyst treatment in toluene, without addition of 4Å) was more active and remarkably more selective. Regardless of the conditions applied, cinnamyl alcohol was oxidized in a considerable extent to cinnamaldehyde.

The other example is the oxidation of prenol. The remarkable effect of NaHCO_3 additive (besides zeolite 4Å) is shown in Table 1 (entries 4–6). NaHCO_3 suppressed oligomerization and increased the epoxide selectivity by a factor of 2.5, under otherwise identical conditions. A similar striking effect of various basic additives on the product composition has been observed recently in the epoxidation of β -isophorone [17].

The kinetics of the reaction, using the standard procedure and either zeolite 4Å or 4Å and NaHCO_3 together as additives, is shown in Fig. 1. In the presence of zeolite 4Å only, the reaction was very fast at low conversion, but after ca. 30 min, the decomposition of the epoxide (mainly by hydroxy-ether formation) became faster than its formation. Oxidation in the presence of both zeolite 4Å and NaHCO_3 suppressed the hydroxy-ether formation substantially, and the epoxide was obtained with good

selectivity. Note that a similar rapid formation of the epoxide, followed by its decomposition, was observed in the oxidation of cinnamyl alcohol, when applying the standard conditions.

The influence of reaction additives and catalyst pretreatment on the rate and selectivity of allylic alcohol oxidation can be interpreted on the basis of our former detailed study of hexenol oxidation [13]. A careful pre-drying of the aerogel in situ at 473 K (standard procedure) and especially the subsequent hydrophobisation in toluene [17] eliminated a part of surface silanol groups (by condensation to Si–O–Si groups) and provided an active catalyst. However, water forms also during oxidation by the oxidative dehydrogenation of the –OH group and by the decomposition of the peroxide [1]. Zeolite 4Å can eliminate this water from the reaction mixture and maintain dry conditions, affording excellent performance of the aerogel in the oxidation of hexenols and pentenol. However, in the oxidation of some allylic alcohols, the Na form of zeolite 4Å seemingly acted as a catalyst of the ring opening and oligomerization side reactions (Scheme 1). In these instances, the addition of some weakly basic NaHCO_3 afforded higher epoxide selectivities, as illustrated in

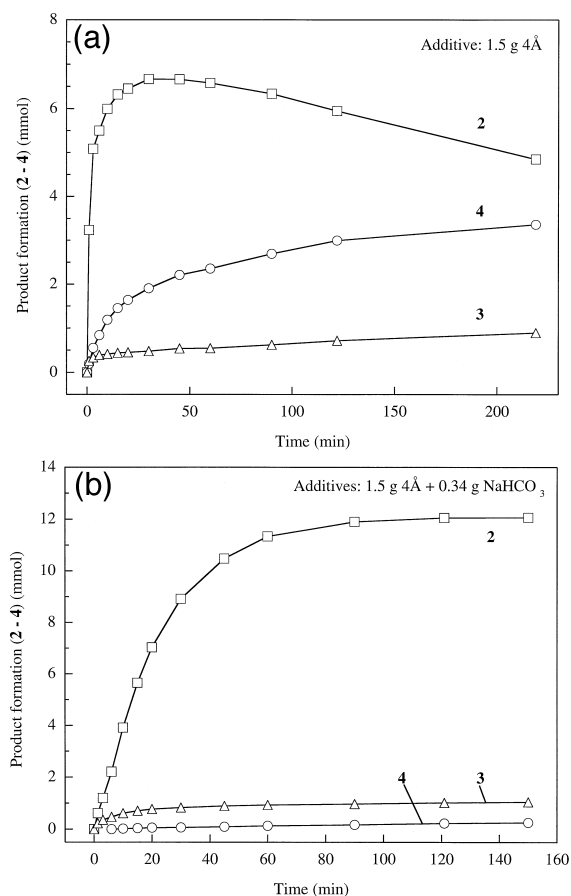


Fig. 1. Time-resolved product formation in the oxidation of prenol using 1.5 g zeolite 4Å (a) or 1.5 g zeolite 4Å and 4 mmol NaHCO₃ (b) as additives. Standard epoxidation procedure: 0.2 g aerogel (dried in situ at 473 K), 60 mmol prenol, 13.5 mmol TBHP, 1 ml cumene (internal standard), toluene (solvent); total volume = 21 ml; $T = 363$ K. (□) Epoxide (2); (Δ) unsaturated aldehyde (3); (○) hydroxy-ether (4).

Fig. 1. Note that the positive effect of a poorly soluble inorganic base additive has been shown to be due to its very low but significant solubility in the rather apolar medium, and to the neutralization of the surface acidic sites (Si–OH) formed by water [13].

3.3. Diastereoselective epoxidation of open chain and cyclic alcohols

The data in Table 3 (entries 1–3) illustrate that under standard conditions, the conversion

of open chain alcohols having a terminal double bond required longer reaction times, as compared to allylic alcohols with an internal double bond (Table 1) or cyclohexenols (Table 3, entries 4–6). The higher reactivity of allylic alcohols possessing an internal C=C double bond is likely due to the higher electron density resulting from the electron-releasing effect of the alkyl group. For comparison, the same titania–silica catalyst epoxidized 2-hexene three times faster than 1-hexene, under otherwise identical conditions.


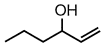
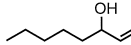




The highest epoxide selectivity was obtained with hexen-3-ol (entry 2), which had the lowest reactivity. No diastereoselectivity (buten-3-ol: 49/51) or only poor *threo*-selectivity (hexen-3-ol: 45/55) was observed. Note that in the metal-catalyzed epoxidation of acyclic allylic alcohols possessing a terminal or a *trans*-substituted double bond, 1,2- and 1,3-allylic strains are weak and the otherwise subordinate steric and electronic factors lead to *erythro*-selectivity [18,19]. However, the moderate *threo*-selectivity in the TS-1-catalyzed epoxidation of this type of allylic alcohols has been attributed to a transition state structure similar to that which had been established for peracid epoxidations [20].

Cyclic alcohols were much more reactive under the conditions applied, but reasonable epoxide selectivities were achieved only in the case of cyclohexenol (Table 3, entries 4–6). The *cis*-epoxides were produced preferentially for both 2-cyclohexen-1-ol and 3-methyl-2-cyclohexen-1-ol. In the latter case and also in the oxidation of isophorol (entries 5 and 6), the very low epoxide selectivities and conversion above 100% were due to numerous side reactions (oligomerization, epoxide ring opening, etc.).

The stereochemical outcome of the epoxidation of cyclic allylic alcohols with Ti-substituted zeolites TS-1 and Ti-β has been explained by the interaction of the –OH functional group with the active site or the epoxidizing agent in the transition state [20–22].

Table 3

Diastereoselective epoxidation of open chain and cyclic allylic alcohols catalyzed by titania–silica in the presence of zeolite 4Å^a

Entry	Reactant	t (h)	Olefin conversion ^b (%)	Epoxide selectivity (%)		Diastereomeric ratio
				Olefin	Peroxide	
1		5	95	37	65	49 : 51 (erythro : threo)
2		5	60	83	77	45 : 55 (erythro : threo)
3		5	74	71	67	— ^c
4		1	85	65	67	70 : 30 (cis : trans)
5		1	270	2.4	11	85 : 15 (cis : trans)
6		1	221	10	30	— ^c
7		4	30	81	nd	—

^aReaction conditions: 70 mg catalyst (dried in situ at 473 K), 0.5 g activated zeolite 4Å, 20 mmol olefin, 5 mmol TBHP, 0.5 ml ethylbenzene (internal standard), toluene (solvent); total volume = 6 ml; $T = 363$ K.

^bThe olefin conversion is related to TBHP (olefin:TBHP = 4:1).

^cThe diastereomers could not be separated by the gas-chromatographic method.

3.4. Influence of zeolite 4Å on the epoxidation of cyclohexenol

The role of zeolite 4Å in the epoxidation of 2-cyclohexen-1-ol is illustrated in Table 4. There was no detectable cyclohexenol conversion when using zeolite 4Å alone. On the other hand,

zeolite 4Å had a remarkable synergic effect on the rate of epoxide formation (indicated by the epoxide yield achieved in 1 h), and on the epoxide selectivity. The likely reason of the positive effect of zeolite 4Å on the epoxidation catalyzed by titania–silica has been discussed above.

Table 4

Synergic effect of zeolite 4Å in the diastereoselective epoxidation of 2-cyclohexen-1-ol catalyzed by the titania–silica aerogel^a

Entry	Aerogel (g)	Zeolite 4Å (g)	Cyclohexenol conversion (%)	TBHP conversion (%)	Epoxide selectivity (%)		Epoxide yield (%)	Diastereomeric ratio (cis:trans)
					Cyclohexenol	TBHP		
1	—	0.5	0	7	—	—	0	—
2	0.07	—	92	68	43	59	40	68:32
3	0.07	0.5	85	83	65	67	56	70:30

^aReaction conditions: catalyst (dried in situ at 473 K), activated zeolite 4Å (according to the table), 20 mmol olefin, 5 mmol TBHP, 0.5 ml ethylbenzene (internal standard), toluene (solvent); total volume = 6 ml; $T = 363$ K; reaction time = 1 h.

A similar positive influence of zeolite 4Å has been observed recently [13] in the oxidation of (*E*)-2-hexen-1-ol. In this reaction, zeolite 4Å produced some epoxide, but the average rate of epoxide formation over the titania–silica aerogel was more than two orders of magnitude higher than the rate over the zeolite. Besides, the epoxide selectivity was also rather moderate when using zeolite 4Å alone.

Interestingly, it has been proposed that zeolite 4Å would be an efficient catalyst for the epoxidation of allylic alcohols [19,23]. The epoxide yields were medium to excellent, but the reaction times required for reasonable conversions were rather high (24–144 h), despite of the unusually high catalyst loading (around 200–500 wt.%).

4. Discussion



Allylic alcohols could only be efficiently epoxidized by the titania–silica aerogel when the reaction conditions were properly chosen. A careful in situ pre-drying of the catalyst provided high rate and selectivity in the oxidation of open chain, unbranched allylic alcohols. It has been shown for prenil and cinnamyl alcohol that the catalyst pretreatment procedures and the presence of zeolite 4Å and NaHCO₃ additives have a substantial influence on the reaction rate and product distribution. The positive influence of solid bases is attributed to their minor solubility in the reaction medium and to the neutralization of the acidic sites on the aerogel. Removal of acidic sites by condensation of –Si–OH to Si–O–Si connections has been reported [17,24] and is supposed to play an important role during catalyst drying and catalyst hydrophobisation in toluene.

In homogeneous metal-catalyzed epoxidations, introducing an allylic hydroxyl group can result in a rate enhancement by a factor of > 200 [18]. On the contrary, the alcoholic function has a major negative impact on the olefin reactivity in the aerogel-catalyzed epoxidations.

The effect of an allylic hydroxyl group is shown in the comparison of cyclohexene and cyclohexenol epoxidation in Table 5.

Cinnamyl alcohol represents an allylic alcohol which is converted by the aerogel with low rate and selectivity to the epoxide under the standard conditions, as compared to other primary allylic alcohols. Under optimized conditions (catalyst treatment in toluene), this catalyst is still ca. 900 times more active (average rate of TBHP conversion related to the amount of catalyst and time) than silica gel treated with Ti(O^{*i*}Pr)₄ and only slightly less selective [3]. Prenol epoxidation is another example of a demanding epoxidation reaction. The formation of side products could be minimized by the addition of NaHCO₃, and 86% epoxide selectivity was obtained at 97% conversion. In contrast, TS-1 catalyzed preferentially the oxidation of the –OH function of prenil to form the unsaturated aldehyde [5]. In general, the activity of the titania–silica aerogel is rather low in the oxidation of alcohols. Accordingly, the competing formation of carbonyl compounds from allylic alcohols is usually a minor side reaction, and the corresponding epoxy alcohols can be synthesized with good selectivity. On the contrary, due to the high activity of TS-1 in the oxidation of various functional groups, the selective formation of epoxy alcohols is limited to the oxidation of some unsaturated alcohols possessing a terminal C=C bond [5,25].

Table 5
Influence of the alcoholic function on the epoxidation of olefins^a

Reactant	Catalyst (mg)	Rate ^b (mmol g ⁻¹ h ⁻¹)	Olefin conv. (%)	Selectivity (%)
	100	411	79	ca. 100
	200	43	52	31

^aThe aerogel was calcined but not dried in situ prior to use. Other reaction conditions: 60 mmol olefin, 13.5 mmol TBHP, 2 ml cumene (internal standard), ethylbenzene (solvent); *T* = 363 K; reaction time = 15 min.

^bAverage rate of epoxide formation, related to the amount of catalyst.

Another important difference between titania–silica aerogel and TS-1 is their reactivity in the epoxidation of α - β -unsaturated ketones and aldehydes. The aerogel-catalyzed epoxidation of cinnamaldehyde and 2-cyclohexenone was significantly slower than the oxidation of the corresponding allylic alcohols (Table 2, entries 1 and 3 and Table 3, entries 4 and 7, respectively). On the contrary, TS-1 [21] and also titania-on-silica [3] were totally inactive in the epoxidation of the electron-poor C=C bonds in α - β -unsaturated carbonyl compounds, including 2-cyclohexenone.

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