On the limited selectivity of silica-based epoxidation catalysts

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Epoxidation of 2-cyclohexen-1-ol with TBHP and TiO_2–SiO_2, Fe_2O_3–SiO_2 and SiO_2 aerogels has been studied. The influence of surface silanol groups and transition metal impurities in titania–silica on the product distribution has been analyzed. The results, supported by literature data, indicate that high surface area silica cannot generally be regarded as an inert matrix in epoxidation catalysts. Contribution of Ti-free silica limits the selectivity of Ti- and Si-containing catalysts in demanding epoxidation reactions. The activity of silica – together with the background oxidation of the olefin – may lead to overestimated intrinsic activities when the reaction rate is related to the Ti content of the catalyst.

KEY WORDS: epoxidation; titania–silica; aerogel; cyclohexenol; side reactions; impurities

1. Introduction

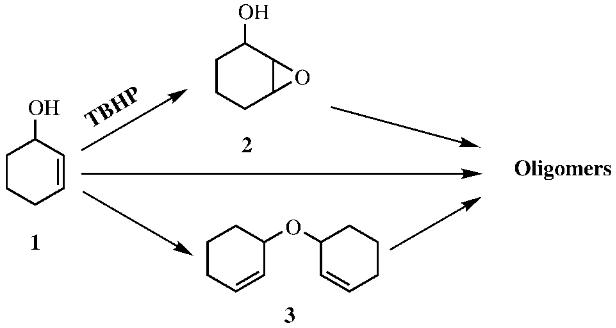
Epoxidation of functionalized olefins is an important transformation in synthetic chemistry [1]. The search for efficient alternatives to homogeneous catalysts led to the development of various heterogeneous catalysts [2–4]. Many of these solid catalysts contain Ti, V, Zr or Mo as the active site isolated by a silica matrix. The most studied examples are TS-1 and other isomorphously substituted molecular sieves, titania-on-silica and titania–silica mixed oxides. These catalysts show outstanding performance in the synthesis of simple aliphatic or cycloaliphatic oxiranes but they are less effective in the demanding epoxidation of allylic alcohols or α,β-unsaturated carbonyl compounds [5–9].

Various strategies have been proposed to overcome this limitation. Considering only titania–silica mixed oxides, efficient methods are the catalyst pretreatment with basic alkali metal salts [8], addition of an inorganic base or amine to the reaction mixture [10–12], and catalyst hydrophobization by refluxing in an apolar solvent [11]. More sophisticated techniques include the modification of the catalyst surface by silylation [13,14], and by introducing apolar or polar organic functional groups into the silica matrix [10,15,16].

Silica, the major component of these catalysts, has usually been regarded as inactive in epoxidation reactions and only poorly active in peroxide decomposition [17–20]. In contrast, Ti-free SiO_2 aerogels were astonishingly efficient in the epoxidation of cyclohexene with TBHP, though the nature of active sites remained unclear [10]. Zeolite 4A, which is widely used in the Ti-catalyzed asymmetric epoxidation of allylic alcohols to maintain anhydrous conditions [21], has been shown to effectively catalyze the regio- and stereoselective epoxidation of various allylic alcohols [22,23]. These striking observations led us to study the role of silica matrix in the epoxidation of 2-cyclohexen-1-ol (**1**). The product distribution in the complex reaction (scheme 1) is a sensitive indicator of various acidic sites on the catalyst surface which can catalyze epoxidation, ether formation and oligomerization [2,12].

2. Experimental

Amorphous mesoporous silica, titania–silica and iron–silica low temperature aerogels were prepared on the basis of former recipes [24,25]. Ti-containing aerogel: The Si/Ti molar ratio was 132/1, corresponding to *ca.* 1 wt% TiO_2 for a theoretical catalyst TiO_2–SiO_2. A solution consisting of 0.152 g titanium bisacetylacetonatediisopropoxide (Aldrich, 75 wt% in i-PrOH), 6.28 g tetramethoxysilane (Fluka, 99%) and 2.5 ml i-PrOH was prepared. The hydrolysant, consisting of 0.36 g HNO_3 (65%), 3.26 g H_2O and 10 ml i-PrOH was added under vigorous stirring. After 6 h, 1.54 g trihexylamine in 20.5 ml i-PrOH was added to the mixture. Gelation occurred within 1 h and the gel was aged for 6 days. Pure silica aerogels were prepared likewise without adding titanium bisacetylacetonatediisopropoxide.



Scheme 1. Reaction network in the epoxidation of 2-cyclohexen-1-ol (**1**).

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Fe-containing aerogel: A solution consisting of 47.42 g tetraethoxysilane (Fluka, 99%) and 60 ml EtOH (Fluka, 99.8%) was prepared. The hydrolysant aqueous HCl was added under vigorous stirring and the reaction mixture was heated to 323 K for 1.5 h. After cooling to room temperature, Fe(III) acetylacetonate (Fluka, 98%, for 2 wt% Fe_2O_3), 40 ml EtOH and 12 ml acetylacetonate (Fluka, 99%) were added and the mixture was aged for 1 h at 323 K and then for 14 h at room temperature (rt). Gelation occurred after addition of 12 ml $EtOH/NH_4OH$ (6 : 1 vol%). The total volume was 150 ml and the molar ratios of H_2O : alkoxide : acid were 2 : 1 : 0.01.

The sol–gel syntheses were carried out in a glass reactor at rt under Ar. The resulting gels were semicontinuously extracted with supercritical CO_2 in a glass liner to prevent contamination from the steel autoclave. The extraction with a CO_2 flow of 15 $g\,min^{-1}$ was completed within 5 h at 313 K and 200 bar. Portions of the raw aerogels were ground and heated in a tubular reactor in an upward air flow, at a rate of 5 $K\,min^{-1}$ up to 673 K (1173 K for "SiO_2-HT") and kept at this temperature for 4 h.

A SiO_2 aerogel calcined at 673 K was silylated as follows [26]: a solution of 0.6 g *N*-methyl-*N*-(trimethylsilyl) trifluoracetamide (Aldrich, 99%) in 6 g toluene was added to the *in situ* redried (1 h, 473 K, Ar flow) SiO_2 (0.3 g). The mixture was stirred at rt for 2 h, then the catalyst was filtered, washed with toluene and dried in air to give the sample "SiO_2-silylated."

For hydration (hydrophilization) of SiO_2 the calcined sample was kept in water-saturated air in a closed vessel for 20 h, then the physisorbed water was removed in high vacuum before the epoxidation reaction (SiO_2-hydrated).

Epoxidations were carried out under Ar in a mechanically stirred, 50 ml glass reactor. In a standard procedure, 100 mg aerogel was predried *in situ* in the reactor at 474 K for 1 h in an Ar flow. After cooling to rt, toluene (solvent) and 0.5 ml dodecane (internal standard) were added. The mixture was heated to 363 K, 10 mmol 2-cyclohexen-1-ol was added and the reaction started by introducing 2.5 mmol *tert*-butyl-hydroperoxide (TBHP, Fluka, *ca.* 5.5 M in nonane, stored over molecular sieve 4A) to the vigorously stirred slurry. The total reaction volume was 10 ml. Epoxidation of 10 mmol cyclohexene was carried out similarly, at 333 K. Conversion of the reactant is related to the amount of TBHP.

Products were analyzed gas chromatographically and identified by GC-MS and by comparison to authentic samples. TBHP conversion was determined by iodometric titration. The oxidation selectivities, related to the olefin and TBHP consumed, were calculated as follows:

$$S_{\text{olefin}}\ (\%) = \frac{[\text{epoxide}]}{[\text{olefin}]_0 - [\text{olefin}]} \times 100,$$

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

The specific surface areas (S_{BET}), mean pore diameters ($\langle d_p \rangle$) and specific desorption pore volumes ($V_p(N_2)$) were evaluated by the BJH method and determined by nitrogen physisorption at 77 K using a Micromeritics ASAP 2000 instrument. Before measurement, the samples were degassed at 373 K until a final pressure below 0.1 Pa was achieved.

Laser ablation inductively coupled plasma spectroscopy with mass spectrometric detection (LA-ICP-MS) was used for ultra trace element analysis. Usually 34 measurements have been performed for each metal (for Fe and Ni: 68) and the mean value was calculated.

3. Results

3.1. Catalyst characterization

The textural properties of all aerogels were characterized by N_2 physisorption (table 1). The aerogels calcined at 673 K possessed high surface area (>1000 $m^2\,g^{-1}$) and mesoporous structure. The mean pore diameters assuming cylindrical pores were 8 nm or above. Calcination at high temperature (1173 K) or silylation of SiO_2 diminished the surface area as expected, though the mesoporous structure was preserved.

3.2. Epoxidation of cyclohexenol – general features

The catalytic performance of the aerogels has been tested in the epoxidation of 2-cyclohexen-1-ol (**1**) with TBHP. Two representative runs over 1 wt% TiO_2–SiO_2 and SiO_2, and the blank experiment without catalyst, are shown in figure 1. At low conversion of **1** the reaction is very fast over the mixed oxide and slow on silica, but after 4 h the transformation of **1** is considerable also on silica. The product distribution after 4 h is shown in scheme 2. Over titania–silica the major products are the two stereoisomers of the epoxide (**4**/**5**) and non-volatile species (undetectable by GC). Formation of the latter species is deduced from the C-balance and attributed to acid-catalyzed oligomerization of **1** and **4**/**5**. Oligomers represent the dominant part of unidentified species in scheme 2. The non-oxidative transformation of **1** is responsible for the higher than 100% conversion related to the limiting reactant TBHP (molar ratio **1**/TBHP = 4). A typical feature of the epoxidation of **1** is the rapid loss of epoxide selectivity (S_{olefin}) in the first few minutes (figure 1(b)). We assume that successive blocking of a fraction of acidic sites by

Table 1
Physico-chemical characterization of the aerogels.

Catalyst	Calcination temperature (K)	S_{BET} ($m^2\,g^{-1}$)	$V_p(N_2)^a$ ($cm^3\,g^{-1}$)	$\langle d_p \rangle^b$ (nm)
1 wt% TiO_2–SiO_2	673	1056	3.06	11.6
SiO_2 (+ SiO_2-hydrated)	673	1102	3.77	13.7
SiO_2-HT	1173	651	2.39	14.7
SiO_2-silylated	673	703	2.76	15.7
2 wt% Fe_2O_3–SiO_2	673	1023	2.00	8.0

[a] Designates the BJH cumulative desorption pore volume of pores in the maximum range 1.7–300 nm diameter.

[b] Mean pore diameter $\langle d_p \rangle = 4V_p/S_{\text{BET}}$.

oligomers is responsible for retardation of the further loss of epoxide ("product-inhibited" reaction). Note that the addition of various amines to the reaction mixture can efficiently block these sites and improve the epoxide selectivity [2].

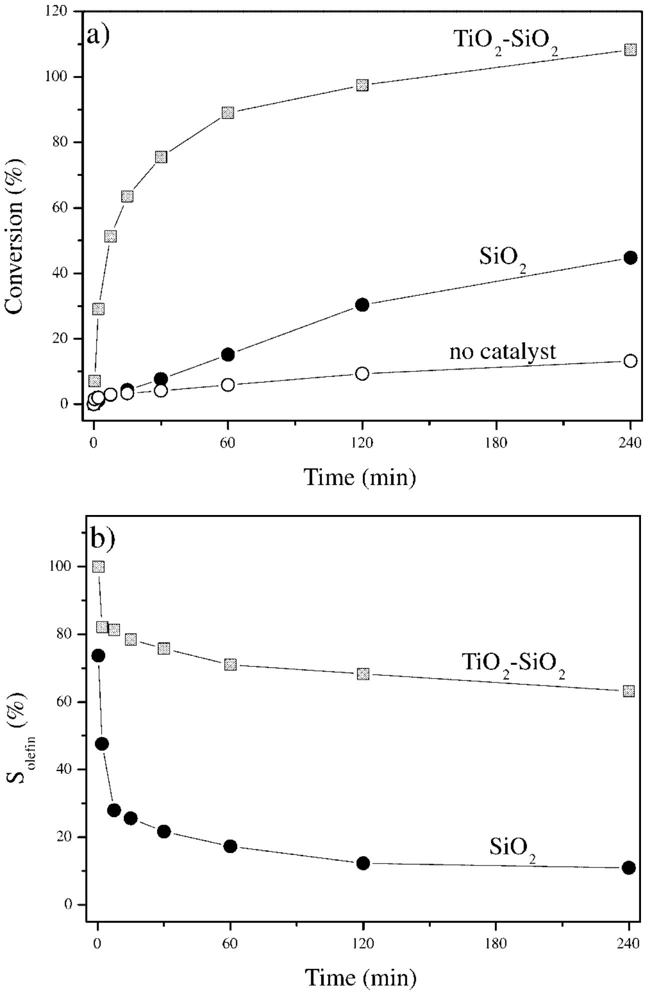


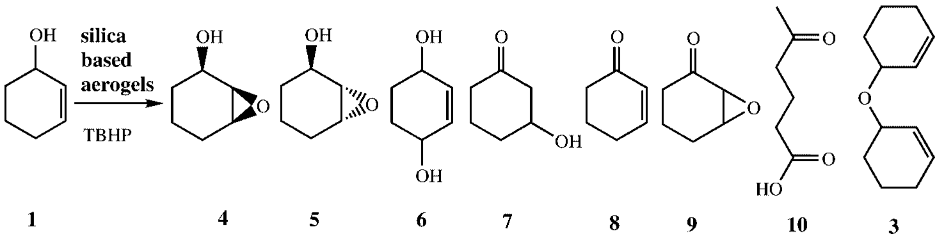
Figure 1. Epoxidation of 2-cyclohexen-1-ol (**1**) with TBHP over 1 wt% TiO_2–SiO_2 and SiO_2 aerogels and without catalyst under standard conditions: (a) conversion of **1** related to the limiting oxidant TBHP and (b) epoxide selectivity related to the olefin consumed (S_{olefin}).

In the presence of SiO_2 or without catalyst, allylic oxidation products and oligomers ("unidentified") were dominant (scheme 2). In the blank experiment mainly **8** formed *via* C–OH oxidation and the number of detectable side products remained small at the low olefin conversion. Addition of SiO_2 to the reaction mixture accelerated the conversion of **1**, and the formation of epoxide (**4**, **5**) and oligomers. Minor products were **6** *via* allylic oxidation, or epoxidation followed by rearrangement, **7** *via* epoxide isomerization, and **10** *via* epoxidation, C–C bond cleavage and hydration.

Partial oxidation of toluene and nonane (solvents) and dodecane (internal standard) during epoxidation of **1** was also detectable after 4 h reaction time (scheme 3). C–H oxidation of paraffins to the corresponding alcohols and ketones was clearly coupled with the background oxidation and remained unaffected by catalyst addition. The extent of these reactions is limited and destruction of the internal standard has only minor influence on the reliability of GC analysis. Allylic oxidation of toluene to benzylic alcohol and benzaldehyde was ten-fold enhanced (up to 0.5 mol% conversion) upon catalyst addition, indicating both uncatalyzed and catalyzed radical reactions. The significant transformation of aliphatic and aromatic hydrocarbons is attributed to the relatively high reaction temperature necessary to facilitate the epoxidation of **1**.

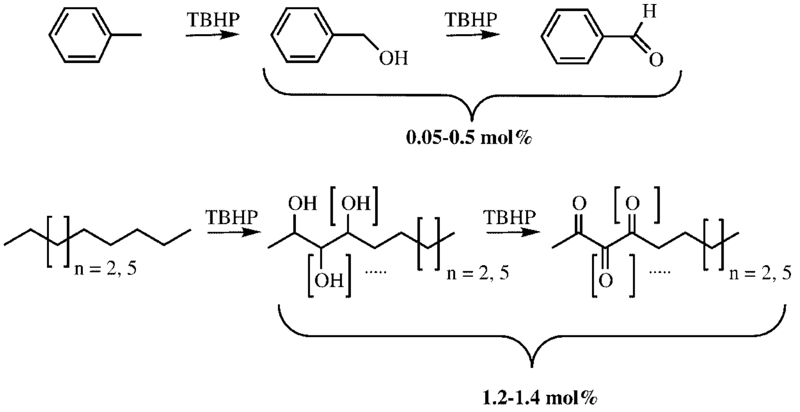
Literature data indicate that epoxide formation in the uncatalyzed (blank) experiment is usually minor [13,27,28]. An exception is the oxidation of cyclooctene where the uncatalyzed reaction with TBHP provided 14% epoxide yield at 333 K [29]. Similarly, silica has some activity in peroxide decomposition but the conversion of olefin to epoxide is mostly negligible [17,18,20]. In contrast, a Ti-free silica aerogel has been found astonishingly active and selective: 43% epoxide yield was obtained in the oxidation of cyclohexene with TBHP [10].

Direct comparison of our results to the literature data is not straightforward as the chemical structure of the reactant olefin should also play a role. This effect is illustrated by



Catalyst	Conversion (**1**)	Yields to major products (%)								
	(%)	4	5	6	7	8	9	10	3	Unid.*
No catalyst	13	0.05	0	0	0.05	10	0.4	0	0	2.5
SiO_2	44.5	4.0	0.9	1.3	0.22	19.1	3.9	0.22	0	14.9
TiO_2–SiO_2	108	52.6	15.6	0.7	0.22	3.8	1.0	0.22	0	33.9
Fe_2O_3–SiO_2	187	1.3	0.8	1.9	0.8	1.9	1.1	2.2	88.3	88.7

Scheme 2. Major products formed in the epoxidation of 2-cyclohexen-1-ol (**1**) in 4 h with various catalysts calcined at 673 K. Molar product distribution is related to the initial amount of TBHP (**1** : TBHP = 4 mol/mol); $*$ unidentified products, mainly non-volatile oligomers; detection limit *ca.* 0.01 mol%.



Scheme 3. Major products formed from the solvents (toluene and nonane) and internal standard (dodecane) during epoxidation **1** with or without catalyst. Molar product distribution is related to the solvent or internal standard converted in 4 h.

Table 2
Epoxidation of 2-cyclohexen-1-ol (**1**) and cyclohexene with various silica-based aerogels.[a]

Catalyst	Calcination temperature (K)	Rate of epoxide formation[b] (μmol h^{-1} m^{-2})	Rate of conversion[b] (μmol h^{-1} m^{-2})		S_{olefin} (%)	S_{TBHP} (%)	Epoxide yield (%)
			Olefin	TBHP			
		2-cyclohexen-1-ol (363 K)					
No catalyst	–	0	–	–	–	–	0
1 wt% TiO_2–SiO_2	673	1.49	2.11	1.86	71	80.5	63
SiO_2	673	0.059	0.34	0.19	17.5	31	2.5
SiO_2-HT	1173	0.067	0.46	0.22	14.5	30	1.5
SiO_2-hydrated	673	0.049	0.34	0.25	15	19.5	2.0
SiO_2-silylated	673	0.051	0.35	0.49	14.5	10.5	1.5
2 wt% Fe_2O_3–SiO_2	673	0.027	2.73	0.50	1.0	5.5	1.5
		Cyclohexene (333 K)					
SiO_2	673	0.1	0.58	0.23	17.5	44.5	4.5

[a] After 1 h reaction time, standard reaction conditions.

[b] Average specific rates in 1 h; not interpretable for the blank experiment (see also figure 1).

Table 3
LA-ICP-MS analysis of SiO_2 aerogel calcined at 973 K.

	Metal content (ppm)							
	Na	Al	Mn	Cr	Fe	Co	Ni	Cu
Average	40	6.2	2.1	18	57	0.3	8	3
Range	21–76	1.9–30	0.8–8.3	1.2–66	2.1–290	0.1–0.6	2.5–40	0.5–24

the epoxidation of cyclohexene over SiO_2 (table 2). Despite the lower reaction temperature by 30 K, the average rate of epoxide formation and the epoxide yield after 1 h was almost twice as high as in the epoxidation of **1**. The epoxide selectivity related to TBHP (S_{TBHP}) was also fairly high, 44.5%.

3.3. Epoxidation with silica – role of hydrophilicity and impurities

The specific activity of SiO_2 (related to unit surface area) was 25 times lower in epoxide formation and 6–10 times lower in converting **1** and TBHP, than that of 1 wt% TiO_2–SiO_2 (table 2). Four differently treated silicas were compared in the epoxidation of **1** to reveal the role of surface silanol groups in the activity of silica. Silylation with *N*-methyl-*N*-(trimethylsilyl)trifluoracetamide has been shown to effectively replace the hydrogen in the Si–OH groups and considerably increase hydrophobicity [26]. A similar effect is expected for calcination at high temperature (1173 K instead of 673 K), while hydration in humid air should increase the amount of Si–OH and the hydrophilicity of SiO_2. The results in table 2 show that these treatments had only small effects on the rate of olefin conversion and epoxide formation. The epoxide yield after 1 h was always in the range 2.0 ± 0.5% and the epoxide selectivity related to the olefin consumed (S_{olefin}) remained in the range 14.5–17.5%. Obviously, the surface concentration of Si–OH groups has only minor effect on the silica-catalyzed transformation of **1**. The differences are bigger in TBHP decomposition but no clear tendency can be seen.

Elemental analysis by LA-ICP-MS revealed that the most important impurities of the SiO_2 aerogel were Fe, Na and Cr, and the distribution of all metals was highly uneven (table 3). It is known that Fe cations, and even fine iron oxide particles, can promote the Fenton reaction with a radical decomposition of hydroperoxides *via* homolytic cleavage of the C–H bonds [30–32]. In a control experiment we used a 1 wt% Fe_2O_3–SiO_2 aerogel for the epoxidation of **1** (scheme 2). Although the conversion of **1** increased considerably mainly due to ether (**3**) formation and oligomerization, the rate of epoxide formation and the epoxide yield after 1 h were even lower than those values obtained with the original SiO_2 aerogel after any treatment (table 2). Hence, we have to rule out the importance of Fe as an active site for the epoxidation of **1**, but Fe, and presumably some other metal impurities in silica, may play a dominant role in the acid-catalyzed side reactions (ether formation, oligomerization) during epoxidation of **1**. Recently, Kochkar and Figueras [10] concluded the same concerning the epoxidation activity of Fe impurity in silica.

4. Discussion

A broad range of reactions has been detected during epoxidation of 2-cyclohexen-1-ol (**1**). These transformations are only partly catalyzed by the various silica-based aerogels and both homolytic and heterolytic decomposition of TBHP have been involved. A detailed analysis can help to understand the role of the components of Ti- and Si-containing epoxidation catalysts and the reasons for the limited selectivity in the epoxidation of allylic alcohols.

4.1. Epoxidation

It is generally accepted that in epoxidation reactions over Ti- and Si-containing solid catalysts the most active site is tetrahedral Ti isolated by siloxy groups [33,34]. However, the activity of high surface area silica is not negligible: in the epoxidation of **1** it contributes to about 4% of the total amount of epoxide formed over the 1 wt% TiO_2–SiO_2 aerogel and the rate of epoxide formation was even higher in cyclohexene oxidation (table 2). Under certain conditions the contribution of Ti-free silica to the total epoxide yield may be as high as around 50%, compared to that of titania–silica [10].

Application of differently pretreated SiO_2 aerogels revealed that the surface concentration of silanol groups, and thus the hydrophylic or hydrophobic character of silica, is not important in epoxide formation (table 2). Fe being present in silica as an impurity might be an active species [30,32,35], but control experiments with a 1 wt% Fe_2O_3–SiO_2 aerogel demonstrated that iron oxide was inactive in epoxidation. A feasible explanation for the epoxidation activity of high surface area silica is the leaching of other metal impurities, such as Cr or Co (table 3), and homogeneous catalysis. Note that the excellent epoxidation activity of chromium silicalite-2 has been attributed to homogeneous catalysis due to trace amounts of Cr leached from the isomorphously substituted zeolite [36]. Another indication for the importance of metal impurities in silica is the former observation that in the epoxidation of cyclohexene with a high purity SiO_2 (Degussa 200) and alkylhydroperoxides the epoxide formation was minor or not detectable at all [10,18].

Epoxide formation in the uncatalyzed reaction (scheme 2) was negligible, only 0.05%. Still, this possibility cannot be ruled out. In a more facile reaction such as the epoxidation of cyclooctene background oxidation provided 14% epoxide yield, despite the lower temperature of 333 K [29].

4.2. Non-oxidative transformations

The various silica-containing aerogels catalyze oligomerization of reactant and products though the uncatalyzed oligomerization is also significant at 363 K (scheme 2). The control experiment with a 1 wt% Fe_2O_3–SiO_2 aerogel suggests that metal impurities in the aerogels may play a role in ether formation (dimerization of **1** to **3**) and oligomerization reactions. Mainly these reactions are responsible for the rapid loss of epoxide selectivity in the first few minutes (figure 1) and likely contribute to catalyst deactivation by blocking a fraction of active sites. A further, less important acid-catalyzed transformation is epoxide rearrangement indicated by the formation of **7**.

4.3. Allylic oxidation

Allylic oxidation of **1** leading to diols and ketones (**6**, **8** and **9**, scheme 2) was substantial over Ti-free SiO_2 and in the uncatalyzed reaction. These radical reactions can occur *via* transition-metal-catalyzed oxidation and peroxide decomposition similar to the Fenton reaction [32] and are important at the relatively high reaction temperature (363 K). Sheldon *et al.* [36] found that homogeneous Cr and particularly Co catalysts were orders of magnitude more active than titania-on-silica in TBHP decomposition at 363 K in benzene.

4.4. Hydrocarbon oxidation

Oxygenation of aliphatic hydrocarbons used as solvent and internal standard were dominantly uncatalyzed reactions (scheme 3). Benzylic oxidation of toluene solvent was tenfold faster over silica-based aerogels than in the blank experiment, likely due to the catalytic effect of trace amounts of transition metal impurities in silica. The total amount of these oxygenated hydrocarbons was relatively small, but they may disturb the analysis and diminish the product quality.

5. Conclusions

On the basis of our results and literature data we can conclude that high surface area silica in silica-based epoxidation catalysts cannot be regarded as an inert matrix. The contribution of Ti-free silica may seriously distort (by a factor of up to 2 [10]) the turnover frequencies related to the Ti content of the catalyst. In facile epoxidations uncatalyzed reactions (background oxidation) are also not negligible [29].

Since silica is active but usually poorly selective to epoxide formation, epoxidation with titania–silica mixed oxides is limited to a certain degree of selectivity. In this respect the chemical nature of reactant and the reaction temperature are crucial. Epoxidation of simple aliphatic and cycloaliphatic olefins is possible with very high selectivities but for more demanding reactions the use of high purity catalyst precursors seems to be advantageous.

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