Control of acidity and selectivity of titania–silica aerogel for the epoxidation of β-isophorone

R. Hutter, T. Mallat, A. Peterhans, A. Baiker *

Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

Abstract

The epoxidation of β-isophorone (3,5,5-trimethyl-3-cyclohexene-1-one) with an amorphous mesoporous titania–silica aerogel and *t*-butyl hydroperoxide has been investigated. Dominant side reactions were the acid/base catalyzed isomerizations of β-isophorone to α-isophorone and of the product epoxide to 4-hydroxy-isophorone. The acidity of the aerogel was characterized by the epoxide ring opening reaction (to 4-hydroxy-isophorone). Two methods were shown to be efficient in tuning the acidity and the hydrophilic–hydrophobic character of the aerogel, and controlling the product distribution. A catalyst pretreatment in ethyl benzene afforded 98.5 and 93% epoxide selectivities at 75 and 90% peroxide conversions, respectively, without any influence on the oxidation rate. A simple addition of a weak inorganic base (such as $NaHCO_3$ or Na_2HPO_4) to the reaction mixture and carrying out the reaction in the presence of two solids in an apolar solvent was even more efficient: epoxide selectivities up to 95% were achieved at 90% conversion, with only small changes in reaction time and peroxide selectivity. Moreover, applying other bases the product composition could be varied in a very broad range. 4-Hydroxy-isophorone was the major product with Na_2CO_3 (65% selectivity at 90% conversion), while α-isophorone was formed almost exclusively in the presence of $BaCO_3$ or NaOH. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sol–gel derived titania–silica mixed oxides as catalysts have attracted growing interest in the past years due to the great versatility of the preparation technique [1–4]. Among other applications, the proper selection of the precursors and preparation conditions can result in excellent epoxidation catalysts [5–12]. Titania–silica aerogels provided outstanding activity and selectivity in the epoxidation of bulky olefins with alkyl hydroperoxides, when compared to the performance of large and ultra-large pore Ti-substituted molecular sieves [13–15]. The amorphous mesoporous aerogels were prepared by the sol–gel method followed by the extraction of the solvent with supercritical CO_2. Titania–silica mixed oxides and Ti-substituted molecular sieves possess rather different structural characteristics (e.g., crystallinity, pore structure, hydrophilic–hydrophobic character), but for both classes of materials the epoxidation activity is attributed to the presence of Ti–O–Si linkages (isolated Ti species in the silica matrix) [15,16]. High selectivities up to 95–100% have been reported in the epoxidation of simple alkenes

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* Corresponding author. E-mail: baiker@tech.chem.ethz.ch

and cycloalkenes with titania–silica. However, in case of functionalized and less reactive olefins acid-catalyzed side reactions can be important. The Lewis and Brønsted acidity of titania–silica mixed oxides have been thoroughly investigated [5–7,17,18]. It is known that the efficient epoxidation catalysts are strong Lewis acids [19]. Moreover, the Ti-peroxo complex in both TS-1 and titania–silica aerogel has been found to be considerably more acidic than the original Ti-site in the absence of peroxide [20–22]. Thus the redox and acidic properties are strongly interrelated and the acidity of titania–silica has to be tuned to the specific requirements of the reaction.

In epoxidations catalyzed by TS-1 in aqueous-organic medium, the acid-catalyzed side reactions could be suppressed by pretreatments of TS-1 with weak inorganic bases [22–27]. We have reported recently a similar observation using a 20 wt.% TiO_2–80 wt.% SiO_2 aerogel and TBHP [20,28]. The epoxidation of β-isophorone (3,5,5-trimethyl-3-cyclohexene-1-one) was competed by the acid-catalyzed isomerizations of the reactant to α-isophorone (3,5,5-trimethyl-2-cyclohexene-1-one, **3**), and the epoxide to 4-hydroxy-isophorone (3,5,5-trimethyl-2-cyclohexene-4-hydroxy-1-one, **2**), according to Scheme 1. A pretreatment of the catalyst with a weakly

alkaline aqueous solution followed by recalcination of the aerogel was efficient in minimizing the acid-catalyzed side reactions. In the best case 94% epoxide selectivity at 90% conversion of TBHP was achieved, though the rate of epoxidation decreased significantly after the basic treatment of the catalyst. The aim of the present work was to search for other possibilities for controlling the selectivity of titania–silica in this complex reaction.

2. Experimental

2.1. Catalyst

An amorphous mesoporous titania–silica aerogel containing 20 wt.% TiO_2 and 80 wt.% SiO_2 was prepared using the sol–gel method [14]. Distilled water after ion exchange and analytical or purum grade reagents were used. The acidic hydrolysant was added to an isopropanolic solution of tetraisopropoxytitanium-(IV) modified with acetylacetone (molar ratio alkoxide:acetylacetone = 1:1) and tetramethoxysilicon(IV). The water:alkoxide:acid molar ratio was 5:1:0.09. The resulting gel was dried by semicontinuous extraction with supercritical CO_2 at 40°C and 240 bar, and stored in a closed vessel under Ar. After calcination in flowing air at 600°C, the aerogel possessed a BET surface area of 650 m^2 g^{-1}, a pore volume of 2.9 cm^3 g^{-1}, and a mean pore diameter of 18 nm. Details on the synthesis and characterization of the sol–gel titania–silica have been reported previously [14,29,30].

Pretreatment in ethylbenzene (EtB): 1 g calcined aerogel was stirred in 100 ml EtB for 30 min at 50°C. The liquid was then removed in vacuum at 100°C. This treatment was repeated twice.

Pretreatment in water: 1 g calcined aerogel in 25 ml water was stirred for 30 min at 80°C, then filtered. The solid was dried in vacuum for 1 h at 100°C, and calcined at 600°C for 3 h.
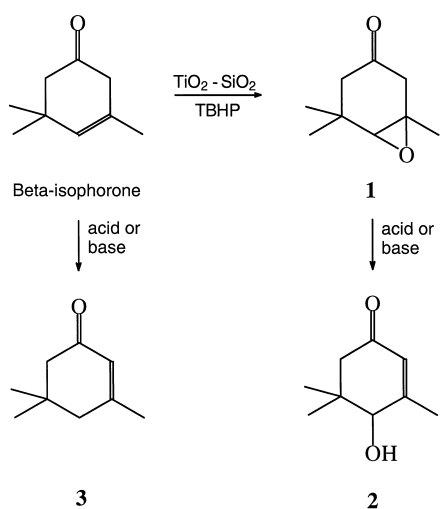
Scheme 1.

Pretreatment in acetic acid (AcOH): 1 g calcined aerogel in 25 ml 0.1 M aqueous AcOH solution was stirred at 80°C for 30 min, then filtered. The solid was washed four times with boiling water (4 × 5 ml), and dried and calcined as above.

2.2. Epoxidation procedure

The epoxidation reactions were performed in a glass reactor under Ar (99.999%) to avoid the presence of oxygen and moisture. An amount of 20 ml EtB (≥ 99.5%, Fluka), 9 ml (61 mmol) β-isophorone (> 99.5%; F. Hoffmann-La Roche, redistilled before use), 1 ml (7.2 mmol) cumene (≥ 99.5%, Fluka, internal standard for quantitative GC analysis) and 4.5 ml (5.6 mmol) t-butyl hydroperoxide (TBHP; ca. 1.24 M in isooctane, stored over zeolite 4A, Fluka) were introduced into the reactor. The mixture was heated to 80°C and the reaction was started by adding 0.2 g catalyst to the vigorously stirred slurry.

Epoxidation of β-isophorone in the presence of added water was performed according to the above standard procedure, except that some water was introduced in the reaction mixture by a syringe before the reaction mixture was heated to the reaction temperature.

The course of the reaction was monitored by gas chromatography and the products were identified by GC–MS and NMR spectroscopy. TBHP conversion was determined by iodometric titration. The oxidation selectivity, related to the peroxide consumed, was calculated for the sum of oxidation products according to the subsequent definition:

$$S_{peroxide}(\%) = 100[\Sigma(\mathbf{1} + \mathbf{2})]/([peroxide]_o$$
$$- [peroxide]).$$

The subscript o stands for initial values and all concentrations are expressed on a molar basis.

The initial rate of β-isophorone oxidation (r_2) was defined as the sum of oxidation products (**1** and **2**, according to Scheme 1) formed in

the first 2 min. After pretreatments with water, NaOAc or AcOH, induction periods of about 5 min were observed. In these cases the average rate was defined similarly but using a longer period of 120 min reaction time (r_{120}). The rate of reaction was also characterized by the time required for 50 or 90% TBHP conversion ($t_{50\%}$ and $t_{90\%}$, respectively).

2.3. Epoxide isomerization

An amount of 80 ml EtB, 36 ml (0.24 mol) β-isophorone, 18 ml (22.4 mmol) TBHP (1.24 M in isooctane) and 2 g titania–silica aerogel were introduced into a 200-ml reactor. The solution was heated to 80°C and mixed vigorously. After 7 h the catalyst was filtered off. t-BuOH, isooctane, residual peroxide, EtB and β-isophorone were separated from the reaction solution and the product β-isophorone oxide (**1**) was enriched by distillation in vacuum.

The isomerization of **1** and **2** was performed in the same reactor which was used for epoxidation. An amount of 0.5 ml (ca. 3.0 mmol epoxide) β-isophorone oxide (> 95%), 20 ml EtB, 0.5 ml (3.6 mmol) cumene (internal standard) and 4.5 ml (5.6 mmol) TBHP (1.24 M in isooctane) were introduced into the reactor. The solution was heated to 60°C and the reaction was started by adding 0.2 g catalyst to the vigorously stirred slurry.

3. Results and discussion

We have shown recently [20,28] that three major products are formed during the oxidation of β-isophorone with a titania–silica aerogel and TBHP. Beside the epoxide (**1**), α-isophorone (**3**) and 4-hydroxy-isophorone (**2**) were also produced by acid/base-catalyzed rearrangements of β-isophorone and the epoxide, respectively (see Scheme 1) [31]. Epoxidation of byproducts **2** and **3** were minor side reactions due to the electron deficiency of the C=C double bonds in α position to the carbonyl groups

[32,33]. Hydroxy-ether formation from the epoxide and the by-product *t*-butanol was negligible due to steric hindrance by the bulky *t*-butyl group [34,35].

In the following, two simple methods will be shown which are efficient in tuning the acidity of the aerogel and controlling the product distribution.

3.1. Hydrophilic–hydrophobic effects

The hydrophilic–hydrophobic character of the titania–silica aerogel was modified by pretreatments with ethyl benzene, water and AcOH. The rate and selectivity of β-isophorone oxidation before and after pretreatments are illustrated in Table 1. After the treatment with EtB the selectivity to the epoxide (**1**) increased remarkably at the expense of acid-catalyzed side reactions. Water and especially AcOH had the opposite effect on the product composition. It is important that none of these treatments significantly changed the oxidation rate and the peroxide selectivity. The pretreatment in EtB provided about the same positive effect on the product composition as the formerly suggested treatment with the solution of a weak base [20], such as NaOAc (Table 1, last entry), with the advantage that the oxidation rate was not diminished after hydrophobisation in the aromatic solvent.

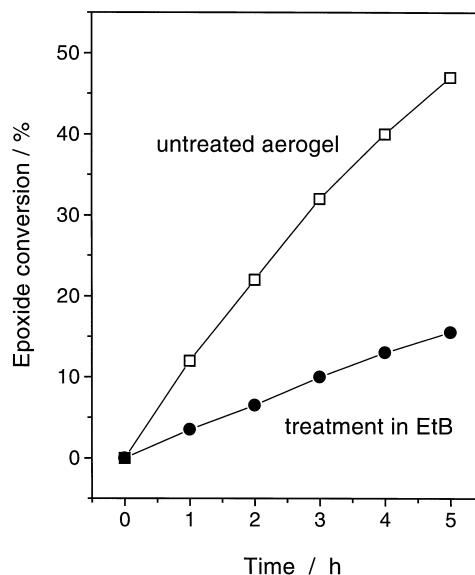The acidity of the aerogel was characterized by the epoxide ring opening reaction (**1** → **2**) in

Fig. 1. Influence of catalyst pretreatment on the isomerization of β-isophorone oxide (**1**) to 4-hydroxy-isophorone (**2**), according to Scheme 1.

the presence of TBHP. The rate of this acid-catalyzed side reaction decreased by a factor of about three after treatment of the aerogel in EtB (Fig. 1). Note that, contrary to the usual ex situ spectroscopic or chemisorption techniques, this test reaction indicates the real acidity of the aerogel under reaction conditions. In presence of the peroxide the rate of epoxide isomerization is influenced also by the Ti-peroxo complex, which is considerably more acidic than the original Ti species in the silica matrix [20–22].

In order to test the influence of water formed during reaction, the catalyst was wetted with

Table 1
Influence of pretreatments on the performance of titania–silica aerogel

| Treatment with	Rate[a] (mmol g^{-1} min^{-1})		$S_{peroxide}^{b}$ (%)	Product composition[b] (%)			
	r_2	r_{120}		**1**	**2**	**3**	others
no treatment	1.4	0.14	90	78	13	7	2
EtB	1.4	–[c]	–[c]	93	4	2.5	0.5
H$_2$O	–[c]	0.13	86	34	34	31	1
HOAc	–[c]	0.15	88	25	33	41	1
NaOAc	–[c]	0.09	70	94	4	1	1

[a]Average rate of oxidation determined after 2 (r_2) and 120 (r_{120}) min, respectively.
[b]Determined at 90% peroxide conversion.
[c]Not measured.

some water in situ in the reaction mixture before the oxidation of β-isophorone. The negative effect of water on the activity and selectivity is illustrated in Table 2. The aerogel pretreated in EtB was significantly less sensitive to water than the untreated (but calcined) aerogel. After addition of 20 mg water (10 wt.% of the catalyst) to the aerogel pretreated in EtB, the epoxide selectivity was still higher than in the run using the untreated catalyst without added water. This is an indication that EtB turns the titania–silica aerogel more hydrophobic. Note that the loss of activity and selectivity by the impact of water during reaction is an important problem in the epoxidation of allylic alcohols, where water is produced not only by decomposition of the peroxide but also by the oxidation of the OH functional group to a carbonyl group.

A simple explanation for the influence of pretreatments with water and AcOH is the partial hydrolysis of Si–O–Si and Si–O–Ti bonds (Scheme 2), and the reverse process can be expected during the treatment with EtB (azeotropic distillation). This type of hydrolysis–dehydration process was found to be completely reversible for TS-1 [16], and irreversible for titania–silica xerogels [36]. In the latter case the dissociation of Ti–O–Si bonds in humid air and formation of Ti–O–Ti bonds (titania domains) were observed at 80°C or above. The changes in product distribution (Table 2) indicate that the restructuring of our titania–silica aerogel in protic polar solvents is not completely reversible. Even after recalcination at 600°C the original
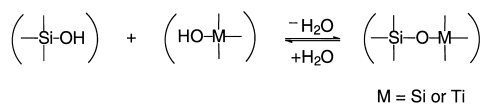
Scheme 2.

selectivity of the catalyst could not be regenerated. On the other hand, the oxidation activity of the aerogel remained unaltered after the treatments, indicating that none of these solvents were detrimental to the Ti–O–Si connectivity. (The good performance of titania–silica aerogels is attributed to the high abundance of Ti–O–Si connectivity; titania microdomains possess significantly lower epoxidation activity and selectivity [15].) Similarly, the structural changes during the pretreatment in EtB are not completely reversible, as indicated by the improved epoxidation selectivity even after water addition, but the activity of the catalyst was unaffected.

3.2. Influence of basic reaction additives

It is now well-established that the surface acidic sites on TS-1 or titania–silica can be neutralized and the acid-catalyzed side reactions during epoxidation suppressed by pretreatment of the catalyst with weak bases [22–28]. But there is a more attractive way to control the product distribution: the simple addition of a poorly soluble, weak inorganic base can provide a similar improvement in epoxide selectivity without the tedious pretreatment and recalcina-

Table 2
Influence of catalyst pretreatment and water addition on the product composition

Treatment of aerogel with	Added water (mg)	r_2^a (mmol g^{-1} min^{-1})	Product composition[b] (%)			
			1	**2**	**3**	others
no treatment	0	1.4	83	10	6	1
no treatment	18	0.5	69	21	9	1
EtB	0	1.4	98.5	1	0.5	0
EtB	2	1.1	94	4	1.5	0.5
EtB	20	0.8	91	6	2.5	0.5

[a] Initial (average) rate of oxidation determined after 2 min reaction time.
[b] Determined at 75% peroxide conversion.

tion procedures [35]. The product composition in the epoxidation of β-isophorone with titania–silica and various bases is illustrated in Fig. 2. No detectable amount of α-isophorone was formed in the presence of $NaHCO_3$ or Na_2HPO_4 and the epoxide selectivity at 90% peroxide conversion increased up to 95 and 94%, respectively. What is even more interesting, the proper choice of base could completely change the product distribution. For example, $BaCO_3$ and NaOH ceased the epoxidation reaction and α-isophorone was the main product with 99% selectivity. Na_2CO_3 increased the rate of oxirane ring opening reaction, as compared to the reaction with the aerogel alone, and 4-hydroxy-isophorone (**3**) was produced with 65% selectivity.

The reaction rates, characterized by the initial oxidation rate and the time required for 50 or 90% peroxide conversion, are collected in Table 3. All bases tested decreased the rate of epoxidation at low conversions, but in some cases
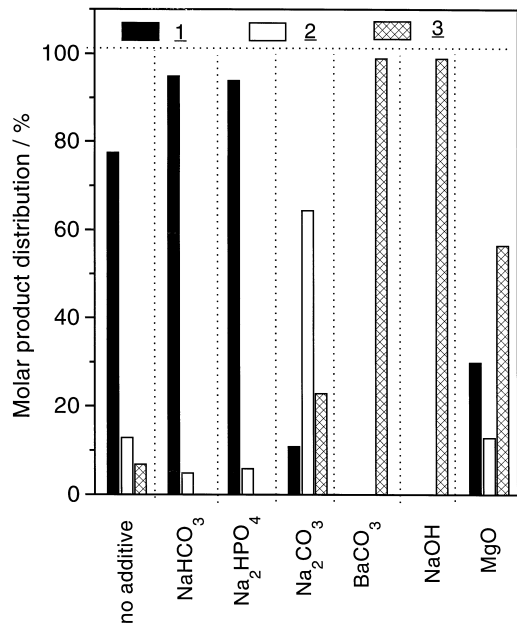
Table 3
Influence of reaction additives on the epoxidation of β-isophorone (4 mmol additive in each case)

Additive	r_2^a (mmol g^{-1} min^{-1})	$t_{50\%}^b$ (min)	$t_{90\%}^b$ (min)	$S_{peroxide}^c$ %
no additive	1.4	30	400	90
$NaHCO_3$	1.0	45	430	84
Na_2HPO_4	1.1	40	300	87
Na_2CO_3	0.5	65	> 1400	78[d]
$BaCO_3$	–[e]	> 1400	–	–[e]
NaOH	–[e]	30	78	–[e]
MgO	0.6	55	330	75

[a]Initial (average) rate of oxidation determined after 2 min reaction time.
[b]Time required for 50% and 90% peroxide conversion, respectively.
[c]Determined at 90% peroxide conversion.
[d]Due to the low reaction rate, selectivity is determined at 400 min.
[e]No oxidation products were found.

this effect was compensated by the smaller extent of catalyst deactivation at high conversions ($t_{90\%} < 400$ min). The oxidation selectivities related to the peroxide consumed are also smaller in the presence of both titania–silica and a base, as compared to the reaction with the aerogel alone.

The positive effect of bases on the epoxide selectivity has been shown to be due to the very low but significant solubility of the base, its migration to the pores of the aerogel and neutralization of the acidic sites [35]. The solubility of the base in the weakly polar medium is not a necessary requirement in cases where the rate of isomerization reaction was enhanced by the base. The formation of both **2** and **3** could occur on the surface of the base, without any contribution of the aerogel catalyst.

4. Conclusions

The amorphous mesoporous titania–silica aerogel containing 20 wt.% TiO_2 was prepared using the sol–gel method followed by semicontinuous extraction of the solvent with supercritical CO_2. This catalyst possessed good activity but only moderate selectivity in the epoxidation of β-isophorone. The major side reactions, the

Fig. 2. Influence of basic reaction additives on the product distribution determined at 90% peroxide conversion (for Na_2CO_3 and $BaCO_3$ at 400 min reaction time). The numbers stand for the designated compounds according to Scheme 1; unidentified products < 0.5% (not shown).

isomerization of the reactant and the product, were catalyzed by the acidic sites of the aerogel. Two methods have been shown to be efficient in enhancing the epoxide selectivity up to 95% at almost full conversion. Mixing in ethyl benzene followed by azeotropic distillation of the solvent turned the catalyst more hydrophobic and significantly less acidic. An even simpler modification of the usual epoxidation procedure included the addition of a poorly soluble weak inorganic base to the reaction mixture. In this case the positive effect on the product distribution is attributed to the neutralization of the surface silanol groups (Brønsted sites).

The idea of using two solids, catalyst and 'co-catalyst', for controlling the product distribution during epoxidation can be extended and applied in a more general way. The 'co-catalyst' can act as a catalyst accelerating the consecutive transformation of the primary product epoxide. The feasibility of this strategy has been demonstrated by using titania–silica and Na_2CO_3, and producing 4-hydroxy-isophorone from β-isophorone via the epoxide in one step. Note that the oxidation of the hydroxyl functional group of 4-hydroxy-isophorone results in ketoisophorone, a demanded intermediate in fine chemistry. It is likely that the application of titania–silica and a properly chosen solid base or acid can afford the one-step synthesis of other valuable products from olefins via the epoxide.

Acknowledgements

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