

# Epoxidation of $\beta$ -Isophorone over a Titania–Silica Aerogel: Effect of Catalyst Pretreatments with Bases

R. Hutter, T. Mallat, A. Peterhans, and A. Baiker<sup>1</sup>

Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

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The epoxidation of  $\beta$ -isophorone with TBHP and an amorphous mesoporous titania–silica aerogel, containing 20 wt% TiO<sub>2</sub>, has been investigated. The nature of side reactions and the possibility of suppressing them by modification of the catalyst with bases was studied. The as-synthesized (unmodified but calcined) aerogel afforded only moderate selectivity to epoxide (36–87%) in the temperature range of 343–373 K. 4-Hydroxy-isophorone and  $\alpha$ -isophorone were the major by-products, formed in isomerization reactions of product and reactant, respectively, and catalyzed by acidic sites present on titania–silica. The selectivity to epoxide could be improved by pretreatment of the aerogel with neutral or weakly basic alkali or alkaline earth metal salts. Treatment of the aerogel with aqueous NaOAc followed by recalcination at 873 K afforded 94% selectivity at 90% peroxide conversion. Application of stronger bases was detrimental to the epoxidation activity and selectivity.

We propose that the improved selectivity is due to ion exchange between the weakly basic additive and the surface Brønsted sites (silanol groups). Neutral salts are preferentially anchored to the polar (acidic) surface sites and reduce their accessibility for the more bulky and less polar reactant. The detrimental effect of strong bases is partly due to excess basicity of the catalyst after pretreatment, as the side reactions are also catalyzed by bases. Besides, prolonged treatment with NaOH partially hydrolyzed the Ti–O–Si bonds and restructured the material (titania microdomains in the silica matrix), as evidenced by FTIR and Uv-vis spectroscopy. The study of the epoxide ring opening reaction demonstrated the limited relevance of *ex situ* acidity measurements for predicting the role of acid sites in complex epoxidation reactions. © 1997 Academic Press

## INTRODUCTION

Ti- and Si-containing oxidic materials have attracted much attention in the past decades as solid oxidation catalysts. The development of an amorphous silica-supported titania catalyst (TiO<sub>2</sub>-on-SiO<sub>2</sub>) by Shell (1) and the discovery of the Ti-containing silicalite TS-1 by Enichem (2) represent two well-known, commercialized examples. TiO<sub>2</sub>-on-SiO<sub>2</sub> is active in epoxidation with alkylhydroperoxides as

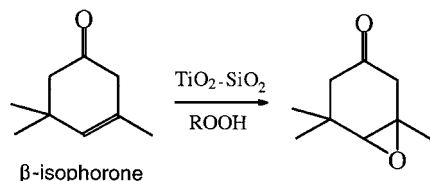
oxidant, whereas TS-1 possesses the advantage of using the cheap oxidant aqueous H<sub>2</sub>O<sub>2</sub> in a variety of oxidations, such as epoxidation, hydroxylation, and alkane oxygenation.

The outstanding properties of titania-on-silica and TS-1 have stimulated the research in this area. The large and ultra large pore Ti-containing molecular sieves, such as Ti- $\beta$  (3) or Ti-MCM-41 (4) have broadened the application range of molecular sieves to bulkier olefins. In parallel, new Ti- and Si-containing oxometal catalysts were developed and their properties tuned for the requirements of the epoxidation reaction (5, 6). A TiO<sub>2</sub>-on-SiO<sub>2</sub> catalyst prepared by grafting TiF<sub>4</sub> on an amorphous silica carrier was reported to be active with H<sub>2</sub>O<sub>2</sub> as oxidant (7). Grafting a bulky organic titanium complex on a mesoporous silica MCM-41 (8) resulted in a supported titania catalyst which was considerably more active than Ti-MCM-41.

The performance of microporous titania–silica mixed oxides prepared by the sol–gel method has also been improved (9, 10). It has been shown that the proper selection of preparation conditions results in catalytic properties comparable to those of crystalline Ti-containing molecular sieves (11). Even the hydrophobicity of the molecular sieves could be mimicked and the surface polarity of the sol–gel mixed oxide (xerogel) tuned in a broad range by using precursors containing non-hydrolyzable alkyl groups (beside the generally used alkoxy groups) (12).

Recently, we have shown that active and selective titania–silica aerogels can be prepared by the sol–gel method followed by semicontinuous extraction with supercritical CO<sub>2</sub> (13, 14). The controlled synthesis of amorphous titania–silica aerogels with a high density of heteronuclear Ti–O–Si connectivity and a mesoporous texture (15–17), providing accessibility for bulky olefins and organic hydroperoxides to the active sites, was shown to be crucial for obtaining active catalysts. A titania content of ca. 20 wt% proved to be very suitable for achieving these properties. Various cyclic olefins, including cyclododecene, norbornene, and limonene were epoxidized with selectivities up to 93% related to the peroxide and close to 100% related to the olefin (18). In the epoxidation of  $\alpha$ -isophorone, which represents an electron-deficient  $\alpha$ -keto olefin, these titania–silica

<sup>1</sup> To whom correspondence should be addressed. E-mail: Baiker@tech.chem.ethz.ch.



SCHEME 1. Epoxidation of β-isophorone.

aerogels provided excellent epoxide selectivity (98–100%) under mild conditions (19, 20). The electron-deficiency of the olefin influenced mainly the reaction rate, whereas the selectivity remained high.

Titania–silica binary oxides are also well-known solid acids, catalyzing various reactions including the isomerization of butenes (21), cumene dealkylation and propan-2-ol dehydration (22). Tanabe *et al.* proposed that the acidity is induced by a charge imbalance due to the difference in the coordination states of  $\text{Ti}^{4+}$  and  $\text{Si}^{4+}$  (23). The advantage of the combination of the oxidizing ability of Ti with the acidity of titania-silica materials was well demonstrated for the decomposition of 1,2-dichloroethane (24). On the other hand, the Brønsted and/or Lewis acidic sites in these materials, the presence of which has been verified for titania–silica mixed oxides (25–27), silica supported titania (28–30), and TS-1 (31, 32), may strongly influence the product selectivity in oxidation reaction (33). For example, ring opening of the epoxide to the corresponding derivatives was proposed to be a consequence of acidic sites present on the catalyst surface (32, 34–40). It has been reported for TS-1 that the selectivity to epoxide can be improved when the residual acidity of the catalysts is neutralized (34–40).

The aim of the present work was to study the efficiency of titania–silica aerogel in an epoxidation reaction, where the acidity of the catalyst can play a crucial role in determining the product composition. The epoxidation of β-isophorone was chosen as a model reaction (Scheme 1), using the 20 wt%  $\text{TiO}_2$ –80 wt%  $\text{SiO}_2$  aerogel and *t*-butylhydroperoxide as oxidizing agent.

## EXPERIMENTAL

### Materials

*t*-Butyl hydroperoxide (TBHP; ca. 1.24 M in isooctane; Fluka) was used as received. 3,5,5-Trimethyl-2-cyclohexene-1-one (α-Isophorone, >99%, Fluka), 3,5,5-trimethyl-3-cyclohexene-1-one (β-isophorone, >99.5%, F. Hoffmann-La Roche), 2,6,6-trimethyl-2-cyclohexene-1,4-dione (ketoisophorone, >99%; Aldrich), 3,5,5-trimethyl-2,3-epoxy-cyclohexanone (α-isophorone oxide, 99%; Aldrich), ethylbenzene (EtB), cumene (>99.5%), isopropylalcohol (i-PrOH, absolute) were distilled and stored under argon.

The synthesis of sol-gel derived titania–silica aerogel has been described in detail elsewhere (15, 18). The  $\text{H}_2\text{O}$ :alkoxide:acid moles + alia was 5:1:0.09. Distilled water after ion exchange and analytical or purum grade reagents were used. The Ti contents of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The catalyst samples were stored in closed vessels under argon.

The titania–silica aerogel 20LT (20 wt%  $\text{TiO}_2$ ) was prepared using the sol-gel method combined with ensuing extraction of the solvent with supercritical  $\text{CO}_2$  at 313 K and 24 MPa (low-temperature aerogel, LT). The raw aerogel (20LT<sub>raw</sub>) was calcined in a flow of dry air at 873 K. 20LT possessed a BET surface area of 648  $\text{m}^2/\text{g}$ , a pore volume  $V_{\text{p}(\text{N}_2)}$  of 2.9  $\text{cm}^3/\text{g}$ , and a mean pore diameter ( $d_p$ ) of 18 nm. More details on the characterization of sol-gel titania–silica by means of FTIR, UV-vis,  $\text{N}_2$ -physisorption, X-ray diffraction, TEM, and thermal analysis have been reported previously (15–18).

A silica-supported titania catalyst ( $\text{TiO}_2$ -on- $\text{SiO}_2$ , 2 wt%  $\text{TiO}_2$ ) was prepared by grafting tetraisopropoxytitanium(IV) on Aerosil 200 (Degussa,  $S_{\text{BET}} = 191 \text{ m}^2 \text{ g}^{-1}$ ,  $V_{\text{p}(\text{N}_2)} = 1.6 \text{ cm}^3/\text{g}$ ,  $d_p$  34 nm), followed by calcination at 873 K; details can be found elsewhere (18).

The catalyst treatment with metal acetates or other sodium compounds was performed by adding 1 g calcined aerogel to 25 ml 0.1 M aqueous solution of a metal salt or base. The slurry was stirred for 30 min at 353 K and then filtered. The solid was washed four times with boiling water (5 ml), dried in vacuum for 1 h at 373 K, and then calcined in an air flow for 3 h at 873 K. The catalyst samples were stored in closed vessels under argon.

### Epoxidation of β-Isophorone

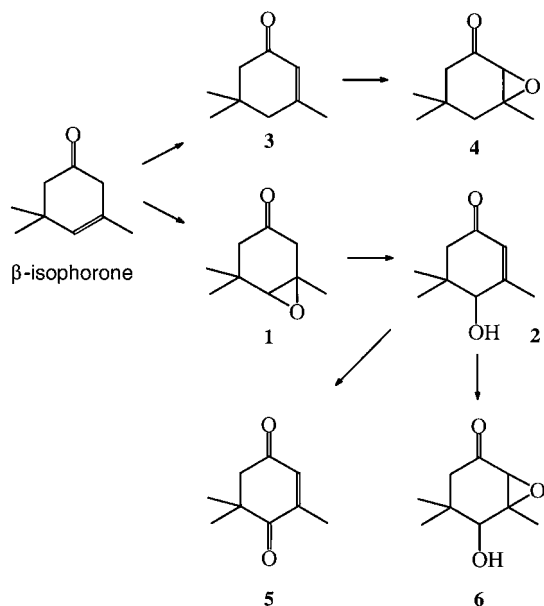
The catalytic runs were carried out batchwise in a glass reactor under argon (99.999%). In a typical run 20 ml EtB, 9 ml (61 mmol) β-isophorone, 1 ml (7.2 mmol) cumene and 4.5 ml (5.6 mmol) TBHP (1.24 M in isooctane) were introduced into the reactor in this order. The solution was heated to 353 K and the reaction was started by adding 200 mg catalyst to the vigorously stirred slurry. These standard conditions were used, if not otherwise stated.

The course of the reaction was monitored by gas chromatography and the products were identified by GC-MS and NMR spectroscopy. Cumene was used as internal standard for quantitative GC analysis. Resistance of solvent and cumene against oxidation was confirmed. The selectivities were calculated according to the subsequent definitions:

$$S_{\text{epoxide}}(\%) = 100 \cdot [\mathbf{1}] / ([\text{isophorone}]_0 - [\text{isophorone}]),$$

$$S_{\text{peroxide}}(\%) = 100 \cdot [\sum(\mathbf{1} + \mathbf{2} + \mathbf{5})] / ([\text{peroxide}]_0 - [\text{peroxide}]),$$

in which all concentrations are expressed on a molar



SCHEME 2. Dominant side reactions during the epoxidation of  $\beta$ -isophorone.

basis. The subscript  $_0$  stands for initial values. Peroxide selectivity was calculated for the sum of oxidation products { $\beta$ -isophorone oxide (**1**), 3,5,5-trimethyl-2-cyclohexene-4-hydroxide-1-one (**2**), and 2,6,6-trimethyl-2-cyclohexene-1,4-dione (**5**), as shown in Scheme 2}. Hydroperoxide conversion was followed by GC and quantitatively determined by iodometric titration.

The initial rate ( $r_0$ ) was defined as moles of  $\beta$ -isophorone converted to oxidation products (**1**, **2**, and **5**) in the first 120 sec.

#### Isomerization of $\beta$ -Isophorone Oxide to 4-Hydroxy-Isophorone

Into a 200 ml reactor were introduced 80 ml EtB, 36 ml (0.24 mol)  $\beta$ -isophorone, 18 ml (22.4 mmol) TBHP (1.24 M in isooctane), and 2 g catalyst. The solution was heated to 353 K. After 7 h the catalyst was filtered off. *t*-BuOH, isooctane, residual peroxide, EtB, and  $\beta$ -isophorone were separated from the reaction solution by distillation in vacuum. The remaining product mixture, which contained  $\beta$ -isophorone oxide as a major component (>95%), was used to study the presence of acidic sites on titania-silica aerogel.

In a typical procedure 0.5 ml of the reaction product (ca. 3.0 mmol epoxide), 20 ml EtB, 0.5 ml (3.6 mmol) cumene and 4.5 ml (5.6 mmol) TBHP (1.24 M in isooctane) were introduced into the reactor. The solution was heated to 333 K and the reaction was started by adding 200 mg catalyst to the vigorously stirred slurry.

#### Physico-Chemical Methods

Nitrogen physisorption was performed at 77 K on a Micromeritics ASAP 2000 instrument. All spectroscopic mea-

surements were made at room temperature. A Perkin Elmer 2000 FTIR unit was used for IR measurements 100 scans were accumulated for each spectrum at a spectral resolution of  $4\text{ cm}^{-1}$ . 1 mg sample in 100 mg dry KBr was compressed to a wafer and placed directly into the IR beam. The UV-vis diffuse reflectance spectra (DRS) of the powder samples were recorded on a Perkin Elmer Lambda 16 spectrophotometer equipped with a 76-mm integrating sphere (ambient conditions,  $\text{BaSO}_4$  as a reference). The XPS spectra were recorded with a Leybold-Heraeus LHS 11 instrument using  $\text{MgK}\alpha$  (1253.6 eV) radiation. The base pressure of the apparatus was lower than  $5 \times 10^{-10}$  mbar. The energy scale was calibrated using  $\text{Au } 4f_{7/2} = 84.0$  eV. Corrections of the energy shift, due to the steady-state charging effect, were accomplished by assuming the C 1s line of the adsorbed hydrocarbons as lying at 285.0 eV.

## RESULTS

### Product Composition as a Function of Temperature

The epoxidation of  $\beta$ -isophorone with the titania-silica aerogel 20LT and TBHP was investigated in the temperature range of 343–373 K. As shown in Table 1, the initial rate of oxidation increased with ascending temperature, but some catalyst deactivation was observed at high conversion, at 360 K or above. The loss of activity is likely due to undesired polymerization reactions of the products or the reactant olefin, as it was indicated by some unidentified high-molecular-weight by-products ( $M > 350$ ) in the GC-MS spectra. The monotonous decrease of the efficiency of peroxide consumption ( $S_{\text{peroxide}}$ ) with increasing reaction temperature is ascribed to the competing homolytic decomposition of the oxidant.

The side reactions and by-products of  $\beta$ -isophorone epoxidation are shown in Scheme 2. The product composition at 75% peroxide conversion as a function of reaction temperature is depicted in Fig. 1. In addition to the desired product  $\beta$ -isophorone oxide (**1**), 3,5,5-trimethyl-2-cyclohexene-4-hydroxide-1-one (**2**), 2,6,6-trimethyl-2-cyclohexene-1,4-dione (**5**), and  $\alpha$ -isophorone (**3**) were formed in significant amounts. The isomerization of  $\beta$ - to

TABLE 1  
Influence of Temperature on the Epoxidation of  $\beta$ -Isophorone<sup>a</sup>

<i>T</i> (K)	$r_0$ (mmol g <sup>-1</sup> min <sup>-1</sup> )	$t_{50\%}$ (min) <sup>b</sup>	$t_{75\%}$ (min) <sup>b</sup>	$t_{90\%}$ (min) <sup>b</sup>	$S_{\text{epoxide}}$ (%) <sup>c</sup>	$S_{\text{peroxide}}$ (%) <sup>c</sup>
343	0.7	70	390	930	87	91
353	1.4	30	180	400	83	90
363	2.4	17	90	>1400	51	78
373	3.7	10	90	>1400	36	63

<sup>a</sup> Reactions were carried out under standard conditions at 353 K.

<sup>b</sup> Time required for 50, 75, and 90% peroxide conversion, respectively.

<sup>c</sup> Selectivities are referred to 75% peroxide conversion.

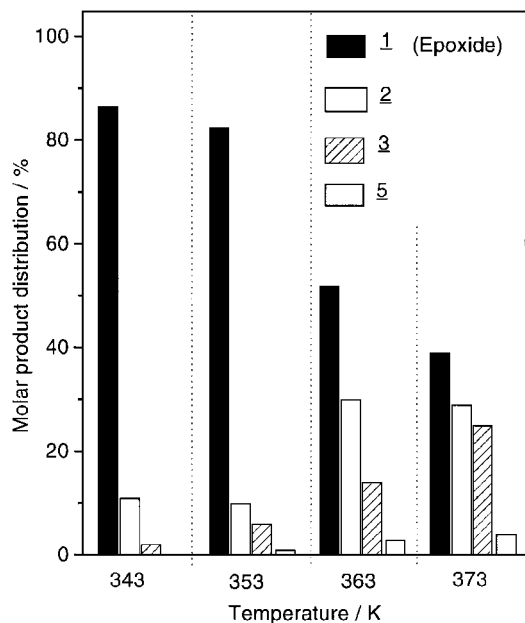


FIG. 1. Influence of reaction temperature on the molar product distribution according to Scheme 2, determined at 75% peroxide conversion (standard conditions).

$\alpha$ -isophorone and the opening of the epoxide ring, involving the acidic H-atom in  $\alpha$ -position to the carbonyl group, are the two dominant side reactions observed. Furthermore, the corresponding epoxides of  $\alpha$ -isophorone and 4-hydroxy-isophorone, i.e.,  $\alpha$ -isophorone oxide (**4**) and 4-hydroxy-isophorone oxide (**6**), were detected in the experiments conducted at 363 and 373 K. However, these compounds (**4** and **6**) never made up more than 0.5% of all products. At higher temperature some other unidentified organic compounds were detected in minor amounts (<0.5%).

Since both the epoxide ring opening reaction and the isomerization of  $\beta$ - to  $\alpha$ -isophorone are acid- or base-catalyzed (41, 42) low epoxide selectivity is suggested to be a consequence of the acidic properties of titania-silica mixed oxides (25–27). The formation of **4** and **6** was slow and only observed at higher reaction temperatures. This is attributed to the electron deficiency of the C=C double bonds in **2** and **3**, which have been found to be difficult to epoxidize by electrophilic metal catalyst/alkylhydroperoxide systems (20, 43).

#### Comparison of Raw and Calcined Aerogels to $\text{TiO}_2$ -on- $\text{SiO}_2$

The influence of calcination on the catalytic behavior of the aerogel is illustrated in Fig. 2. The reaction rate as well as the selectivity to epoxide were improved by thermal treatment of the catalyst in dry air at 873 K. This behavior is presumably due to the removal of water and organic residue which are present in the raw sample (20LT<sub>raw</sub>).

Note that these findings stand in contrast to the behavior of this catalyst in the epoxidation of cyclohexene (**18**) and  $\alpha$ -isophorone (**20**). In the latter two reactions calcination had a negative influence on activity and no influence on the selectivity (close to 100%).

In Fig. 2 the catalytic performance of 20LT is compared also to  $\text{TiO}_2$ -on- $\text{SiO}_2$  (Shell-type) catalyst calcined at 873 K. The initial rate and the selectivity to epoxide of the silica-supported titania was lower than those of 20LT and 20LT<sub>raw</sub> aerogels. Deactivation of  $\text{TiO}_2$ -on- $\text{SiO}_2$  catalyst was observed at peroxide conversions above ca. 50%. Moreover, the uncalcined (raw)  $\text{TiO}_2$ -on- $\text{SiO}_2$  (not shown in Fig. 2) was totally inactive, in agreement with earlier findings (18, 44). It is seen from Fig. 2 that  $\text{TiO}_2$ -on- $\text{SiO}_2$  catalyzes the same side reactions as titania-silica aerogel in the epoxidation of  $\beta$ -isophorone. It is supposed that this is likely to be a consequence of the acidic surface properties of these materials (25–30).

#### Effect of Catalyst Pretreatment with Alkali or Alkaline Earth Metal Acetates

The influence of catalyst pretreatment with aqueous solutions of alkali or alkaline earth metal acetates (followed by recalcination at 873 K) on the activity and selectivity of 20LT is illustrated in Table 2. In most cases an induction period of about 5 to 10 min due to pretreatment was observed, during which very slow product formation was measured, and consequently the initial rate was not calculated.

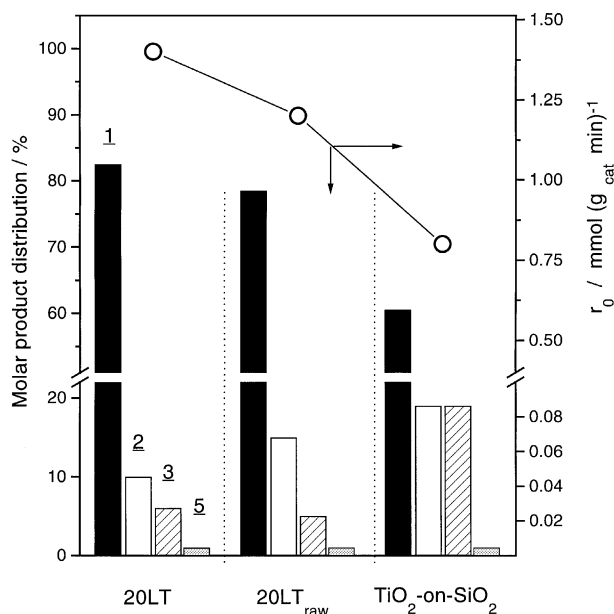


FIG. 2. Initial rates ( $r_0$ ) and product composition (at 75% peroxide conversion) in the epoxidation of  $\beta$ -isophorone at 353 K. Catalysts compared are the aerogel before and after calcination at 873 K (20LT<sub>raw</sub> and 20LT, respectively), and  $\text{TiO}_2$ -on- $\text{SiO}_2$  calcined at 873 K. The numbers stand for the designated compounds according to Scheme 2. Unidentified products: <0.5% (not shown).

TABLE 2

Performance of 20LT after Treatments with Basic Metal Acetates<sup>a</sup>

Treatment with <sup>b</sup>	$X_{\text{peroxide}}$ (%)	$S_{\text{peroxide}}$ (%)	Product composition (%)			
			1	2	3	5
No treatment	75	— <sup>c</sup>	83	10	6	1
No treatment	90	90	78	13	7	2
NaOAc	90	70	94	4	1	0.5
Mg(OAc) <sub>2</sub>	90	53	84	4	11	0.5
Ba(OAc) <sub>2</sub>	90	70	90.5	2	6.5	0.5

<sup>a</sup> The reactions were performed under standard conditions at 353 K.<sup>b</sup> For details of catalyst pretreatment see Experimental.<sup>c</sup> Not measured.

Both the isomerization from  $\beta$ - to  $\alpha$ -isophorone (**1**  $\rightarrow$  **3**) and the epoxide to an allylic alcohol (**1**  $\rightarrow$  **2**) by ring opening were suppressed by sodium acetate. Pretreatment with barium or magnesium acetate improved the epoxide (**1**) selectivity, but had no positive influence on the epoxide ring opening reaction. The superior behavior of aerogel treated with metal acetate is supposed to be a result of lower surface acidity of the catalyst due to exchange of acidic protons ( $\text{H}^+$ ) with  $\text{M}^{n+}$ , as it was proposed for Ti- $\beta$  and TS-1 (39, 45).

Unfortunately, NaOAc treatment resulted in a decrease of activity by 20% related to the untreated sample. Besides, the decomposition of TBHP was more favored after treatment of the catalyst with the weak bases and the efficiency of peroxide consumption decreased.  $\text{Mg}^{2+}$  containing samples accelerated the peroxide decomposition resulting in a significant drop of peroxide selectivity ( $S_{\text{peroxide}}$ ).

The catalytic data indicated and XPS analysis confirmed that the pretreatment procedure with metal salt solutions resulted in an uptake of the corresponding metal cations (ion exchange) on the surface of 20LT. Some representative data of XPS analysis are collected in Table 3. The alkali or alkaline earth metal concentrations were in the range of 0.8–1.0%. In case of the NaOAc-treated sample no loss of  $\text{Na}^+$  content could be detected after the epoxidation reaction. The Ti/Si atomic ratio was practically unaffected by the treatment with the weakly alkaline aqueous solution and by the epoxidation reaction.

TABLE 3

Surface Composition by XPS Analysis of 20LT before and after Pretreatments with Bases

Treatment with <sup>a</sup>	Ti/Si (atom/atom)	Na (atom-%)	Ba (atom-%)
No treatment	0.109	<0.1	<0.1
NaOAc	0.108	0.8	—
NaOAc <sup>b</sup>	0.103	0.8	—
$\text{NaN}_3$	0.110	1.0	—
$\text{Ba}(\text{OAc})_2$	0.105	—	1.0

<sup>a</sup> For details of catalyst pretreatment see Experimental.<sup>b</sup> Determined after use in the epoxidation reaction.

TABLE 4

Surface Area and Performance of 20LT after Treatments with Various Sodium Compounds<sup>a</sup>

Treatment with <sup>c</sup>	BET $\text{m}^2 \text{g}^{-1}$	$S_{\text{peroxide}}$ (%) <sup>b</sup>	$X_{\text{peroxide}}$ (%)	Product composition (%) <sup>b</sup>			
				1	2	3	Others
No treatment	648	— <sup>d</sup>	75	83	10	6	1
No treatment	648	90	90	78	13	7	2
NaOAc	565	70	90	94	4	1	1
$\text{NaN}_3$	— <sup>d</sup>	76	90	90	9	0	1
$\text{Na}_2\text{CO}_3$	— <sup>d</sup>	79	90	55	27	17	1
NaCl	518	80	90	93	6	0	1
NaOH	314	70	90	48	23	8	1

<sup>a</sup> The reactions were performed under standard conditions at 353 K.<sup>b</sup> Determined at 90% peroxide conversion, except for treatments with NaCl (66%) and NaOH (20%).<sup>c</sup> For details of catalyst pretreatment see Experimental.<sup>d</sup> Not measured.

### Effect of Catalyst Pretreatment with Various Sodium Compounds

As it is shown in Table 4, the catalytic behavior was considerably influenced by pretreating 20LT with aqueous sodium compound solutions followed by calcination at 873 K. Epoxide selectivity was significantly improved by neutral (NaCl) or slightly basic ( $\text{NaN}_3$ ) sodium compounds, but none of them surpassed the efficiency of NaOAc. Medium ( $\text{Na}_2\text{CO}_3$ ) or strong (NaOH) bases decreased the epoxide selectivity and favored the isomerization reactions (**1**  $\rightarrow$  **2** and **1**  $\rightarrow$  **3**), as compared to untreated 20LT. This is an indication that the isomerization reactions are catalyzed also by bases.

On the basis of peroxide conversion achieved in 2 h, the reaction rate was barely affected by  $\text{NaN}_3$  treatment, but other Na compounds diminished the activity by 15–30%. In case of NaOH the loss of activity amounted to 85%. In parallel, a decrease in BET surface area was observed. Thus, the drop in activity seems to be (at least partly) associated with the reduced surface area of the samples.

The marked decrease in surface area through NaOH treatment shows that the titania–silica aerogels are not stable under strongly basic pretreatment conditions. FTIR and UV analysis provided further support for this conclusion. FTIR spectroscopy revealed a substantial decrease of the relative intensity of the band at ca.  $950 \text{ cm}^{-1}$ , indicating a loss in Ti–O–Si connectivity (Fig. 3) (2). On the contrary, no significant change was observed after a pretreatment with aqueous NaOAc.

Furthermore, UV-vis spectroscopy in the DR mode showed a shift of the UV-adsorption edge to lower wave numbers after pretreatment with NaOH, indicating Ti agglomeration and formation of  $\text{TiO}_2$  microdomains (Fig. 4) (2). No loss of Ti after the NaOH treatment could be

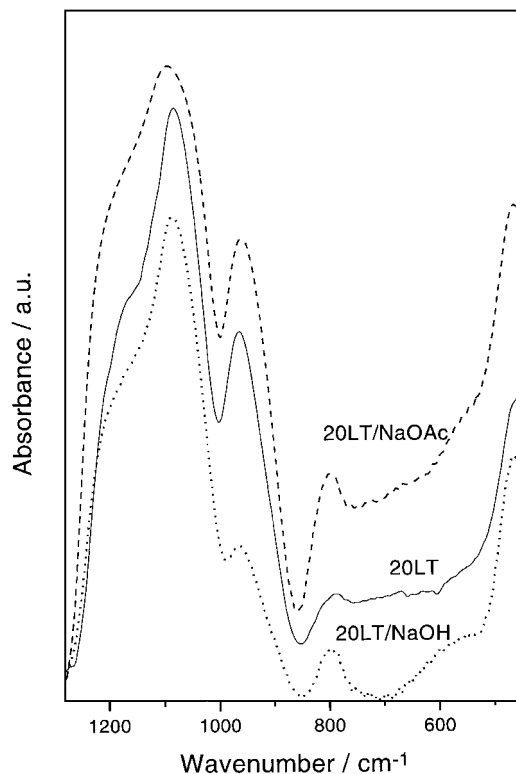


FIG. 3. FTIR spectra of the aerogel after calcination (20LT) and after pretreatments with aqueous NaOAc (20LT/NaOAc) and NaOH (20LT/NaOH) solutions, followed by recalcination at 873 K.

detected by ICP-AES analysis. For comparison, complete deactivation of TS-1 was observed after a treatment at room temperature with 1 M NaOH for 24 h (34) or with 0.1 M NaOH for 4 h (45). It has also been shown that NaOH can

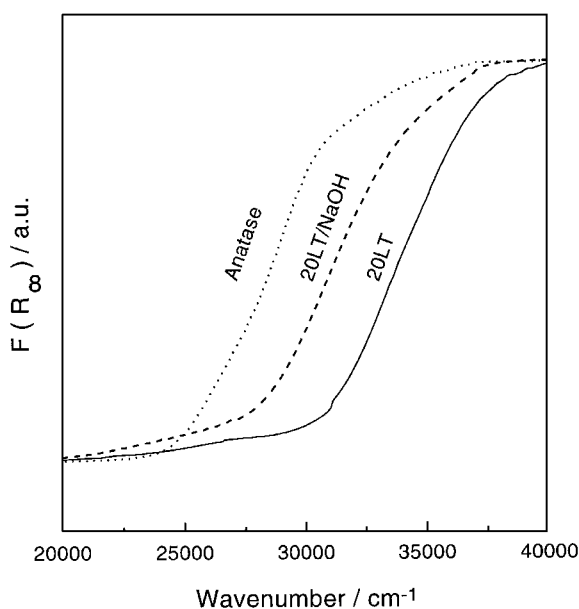


FIG. 4. Influence of catalyst pretreatment with NaOH on the diffuse reflectance spectra of 20LT aerogel.

be used to improve epoxide selectivity when the pretreatment procedure involves contacting TS-1 for a few minutes, but is detrimental when longer contact times are used (40).

#### Effect of Catalyst Pretreatment and TBHP on the Isomerization of $\beta$ -Isophorone Oxide

The presence of acidic sites on the titania-silica aerogel was studied using the acid-catalyzed isomerization of  $\beta$ -isophorone oxide (1) to 4-hydroxy-isophorone (2). In order to minimize the amount of TBHP consumed by side reactions, this reaction was performed at 333 K.

Figure 5 compares the reactivity for the epoxide ring opening in presence and absence of titania-silica catalyst. Although the oxirane ring may also be opened via an uncatalyzed way, the isomerization experiments demonstrate that this reaction is insignificant under the reaction conditions applied. Thus, opening of the oxirane ring during epoxidation of  $\beta$ -isophorone is mainly induced by titania-silica. Figure 5 also compares the reactivity of 20LT for the isomerization in the presence and absence of TBHP. The reaction is greatly accelerated by the presence of the organic hydroperoxide. Note that no change in the acidity of a titania-silica was observed in the solvolysis of *cis*-2,3-epoxybutane in the presence of TBHP (34). On the other hand, the rate of the acid-catalyzed reaction was greatly enhanced by the presence of H<sub>2</sub>O<sub>2</sub>, similarly to the behavior of TS-1.

The isomerization activity of differently pretreated catalysts is compared in Fig. 6. Treatment of 20LT with an aqueous NaN<sub>3</sub> solution followed by calcination at 873 K

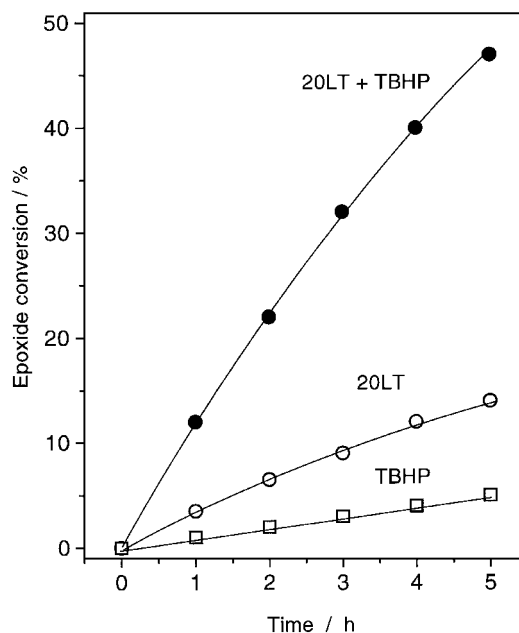


FIG. 5. Conversion of  $\beta$ -isophorone oxide (1) to 4-hydroxyisophorone (2) in the presence of 20LT or TBHP, and both of them (for conditions see Experimental).

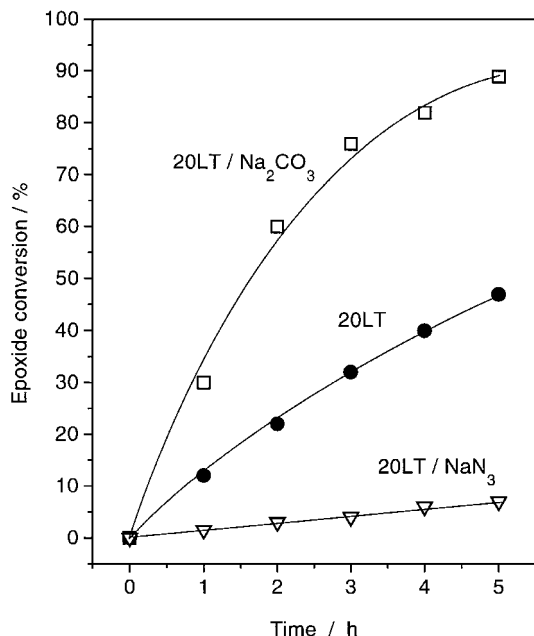


FIG. 6. Influence of catalyst pretreatment with sodium carbonate (20LT/Na<sub>2</sub>CO<sub>3</sub>) or sodium azide (20LT/NaN<sub>3</sub>) on the isomerization of  $\beta$ -isophorone oxide (**1**) to 4-hydroxy-isophorone (**2**) in the presence of 20LT and TBHP (for conditions see Experimental).

slows down the epoxide ring opening reaction compared to the untreated titania-silica. A similar procedure with aqueous Na<sub>2</sub>CO<sub>3</sub>, however, results in a faster formation of 4-hydroxy-isophorone. Thus, the remaining small amount of weak base NaN<sub>3</sub> inhibits the acid-catalyzed isomerization of the epoxide, Na<sub>2</sub>CO<sub>3</sub> is, however, too basic and promotes the reaction, as the epoxide ring opening reaction can also be catalyzed by bases.

## DISCUSSION

The 20 wt% TiO<sub>2</sub>-80 wt% SiO<sub>2</sub> aerogel has been found to be an active catalyst in the epoxidation of  $\beta$ -isophorone, using TBHP as oxygen source. After calcination at 873 K, the aerogel provided a maximum selectivity of 78% at 90% peroxide conversion at 353 K. Dominant side reactions were the acid/base catalyzed (41, 42, 46) isomerization of  $\beta$ -isophorone and the product epoxide, according to Scheme 2. By modifying the aerogel with neutral or weakly basic alkali or alkaline earth metal salts, epoxide selectivities up to 94% at 90% peroxide conversion were achieved. The suppressed activity in isomerization reactions indicates that the acidity of the aerogel was successfully reduced. Ba<sup>2+</sup> and Na<sup>+</sup> were found to be most suitable as metal cations for achieving high selectivity.

The role of acidity of titania-silica in the isomerization reactions and the influence of bases were demonstrated by the isomerization of  $\beta$ -isophorone oxide (**1**) to 4-hydroxy-isophorone (**2**). The results indicated that the Ti-peroxo

complex is considerably more acidic than titania-silica alone (i.e., in the absence of TBHP). In case of epoxidation with TS-1 and H<sub>2</sub>O<sub>2</sub>, the increase in acidity was attributed to the presence of a stable five-membered cyclic structure (35, 43). The influence of peroxide on the acidity of titania-silica aerogel differs from the findings reported previously for TiO<sub>2</sub>-SiO<sub>2</sub> coprecipitates (34). Based on solvolysis of *cis*-2,3-epoxybutane, it was proposed that TBHP (in contrast to aqueous H<sub>2</sub>O<sub>2</sub>) did not enhance the acidity of amorphous TiO<sub>2</sub>-SiO<sub>2</sub> coprecipitates. An explanation for this apparent contradiction may be the different solvent used for the solvolysis experiments. Whereas we used EtB, a solvent found to be very suitable for the titania-silica/TBHP system, Davis *et al.* (34) used MeOH. This strongly polar solvent is known to severely inhibit the epoxidation with alkylhydroperoxides. Thus, strong coordination of the solvent (MeOH) to the relatively hydrophilic TiO<sub>2</sub>-SiO<sub>2</sub> coprecipitate hinders the formation of the catalyst-hydroperoxide complex, which is assumed to be the reason for the enhanced acidity. Note that in the catalytic oxidations, where the TiO<sub>2</sub>-SiO<sub>2</sub> coprecipitate was found to be active, methyl ethyl ketone and not MeOH was used as solvent (34).

It has been shown that not only the metal cation, but also the corresponding anion has a great influence on the epoxidation reaction. Medium and strong bases, such as Na<sub>2</sub>CO<sub>3</sub>, had a negative influence on the epoxidation selectivity and the isomerization reactions were accelerated. This indicates that Na<sub>2</sub>CO<sub>3</sub> not only neutralizes the acidity of titania-silica aerogel but also induces some basicity. Similarly, treatment of TS-1 with sodium carbonate resulted in a reduced selectivity, and an almost complete loss of oxidation activity was observed (36).

It is assumed that the low activity of the sample treated with NaCl is partly due to a collapse in BET surface area. Additionally, it has to be assumed that chlorine anions can form stable complexes with Ti. The Cl<sup>-</sup> ligand might compete for coordination sites on titanium, thus preventing the formation of a Ti peroxo complex. Similarly, fluorides were found to be strong inhibitors of epoxidation and alkane oxidation using TS-1 as catalyst (35, 47). A detailed kinetic analysis of the epoxidation reaction over titania-silica aerogel, including the influence of bases and olefin conversion on the product composition will be published elsewhere (49).

Very recently (45), the improved selectivity of Ti-substituted molecular sieves after a treatment with weakly basic (NaOAc), neutral (Na<sub>2</sub>SO<sub>4</sub>) or even weakly acidic (NaH<sub>2</sub>PO<sub>4</sub>) inorganic compounds has been interpreted by an ion-exchange process between a surface silanol group (Brønsted site) and the additive. The loss of catalytic activity when applying a strong base has been attributed to the deprotonation of water coordinated to the active (and acidic) Ti site and to the formation of species inactive in epoxidation.

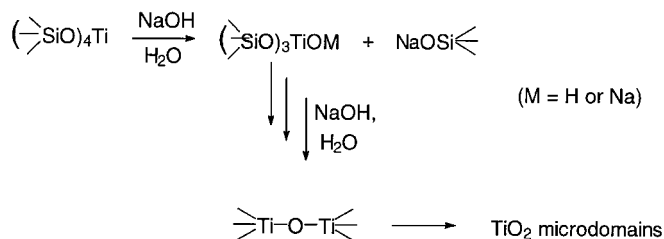


SCHEME 3. Ion exchange of surface silanol groups during catalyst pretreatment with aqueous basic solutions.

However, the suppression of acid-catalyzed side reactions by neutralizing the surface OH groups with  $\text{Na}_2\text{SO}_4$  (or  $\text{NaCl}$  in our experiment) is rather unlikely (Scheme 3). Titania–silica is one of the strongest acids among the mixed oxides, but it is still not a superacid. Its acid strength ( $H_0 \approx -8$  (48)) is well below that of sulphuric acid ( $H_0 = -12$ ). Moreover, sulphuric acid formed in this ion-exchange reaction would still be an excellent isomerization catalyst.

We propose that ion exchange is responsible for reducing surface acidity only when applying basic additives. In case of neutral or weakly acidic compounds used for catalyst pretreatment, the reduced activity of the catalyst in acid-catalyzed side reactions is rather due to a preferential adsorption (anchoring) of the inorganic salt at the acidic sites. These acidic sites are the most polar surface sites in the titania–silica. It is reasonable to assume that in the apolar medium applied for epoxidation, the strongly polar but neutral salt will be preferentially anchored to the polar surface sites. By this way the accessibility of these surface sites for the less polar and more bulky olefin or epoxide is substantially reduced, resulting in a suppression of acid-catalyzed side reactions. A neutral salt can also anchor strongly to the active Ti sites and reduce their accessibility for the reactant. This effect is similar to the retardation effect of a polar solvent, and can explain the reduced rate of the epoxidation reaction after treatment with neutral or weakly basic salts.

On the other hand, strong bases can destroy the structure of the catalyst, as evidenced by our FTIR and Uv-vis studies. The destruction of the titania–silica mixed oxide is assumed to proceed by alkaline hydrolysis of the Ti–O–Si structural parts. The complex hydrolysis and condensation processes result in the formation of titania microdomains surrounded by the silica matrix, as illustrated in Scheme 4. We propose that catalyst restructuring is the main reason



SCHEME 4. Restructuring of titania–silica during the pretreatment with aqueous NaOH, followed by washing and calcination. Note that several hydrolysis-condensation steps (indicated by multiple arrows) are necessary to build  $\text{TiO}_2$  microdomains.

for the detrimental effect of strong bases, rather than the deprotonation of the Ti-active site. In absence of restructuring the excess base could easily be removed and the activity of the aerogel restored during washing the pretreated catalyst with water. Note that in case of TS-1 the structural integrity of the catalyst after a prolonged treatment with strongly alkaline solutions has not been examined (34, 35, 40, 45). Our interpretation is supported by the former observation that only a prolonged treatment of TS-1 with aqueous NaOH resulted in catalyst deactivation (40).

## CONCLUSIONS

Amorphous titania–silica aerogels, derived by applying the sol–gel method with ensuing semicontinuous extraction of the solvent with supercritical  $\text{CO}_2$ , are active catalysts in the epoxidation of  $\beta$ -isophorone. Using a calcined aerogel with 20 wt%  $\text{TiO}_2$  and *t*-butyl hydroperoxide as oxidant, only moderate epoxide selectivities are achieved due to side reactions catalyzed by acidic sites present on the mixed oxide. Treatment of the catalyst with alkali or alkaline earth metal salts prior to the reaction improves the selectivity to epoxide up to 94% at 90% conversion. The selectivity improvement by 16% under comparable conditions is attributed to the suppression of acidity of the mixed oxide. The fact that both side reactions, the isomerization of the olefin and the epoxide ring opening reaction, can be catalyzed by acids or bases restricts the use of suitable compounds for neutralization of the catalyst to relatively weak bases. The selective transformation of  $\beta$ -isophorone to the corresponding oxirane illustrates that not only the choice of the proper synthesis conditions, but also the subsequent modification of aerogels are important tools in broadening the scope of successful applications of titania–silica mixed oxides as epoxidation catalysts.

Investigation of the epoxide ring opening reaction revealed that the acidity of the titania–silica aerogel is enhanced considerably (by a factor of about 3.5) by the addition of alkylhydroperoxide, due to the formation of the Ti-peroxo complex. This indicates that *ex situ* acidity measurements (e.g., adsorption of basic compounds) cannot be meaningfully correlated with the activity of titania–silica in acid-catalyzed reactions in the presence of a peroxide.

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