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Titania–Silica Mixed Oxides: Influence of Reaction Additives on the Epoxidation of (*E*)-2-Hexen-1-ol

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The epoxidation of the allylic alcohol (*E*)-2-hexen-1-ol has been investigated using an amorphous titania–silica aerogel with a TiO_2 content of 20 wt%. The catalyst was prepared by the alkoxide–sol–gel route and the solvent was removed by semicontinuous extraction with supercritical CO_2 at 313 K. The epoxidation was carried out with *tert*.-butylhydroperoxide as oxygen source. Epoxide ring opening by the acid-catalyzed attack of (*E*)-2-hexen-1-ol and formation of high-molecular-weight by-products were observed as the main side reactions under optimized conditions the competitive oxidation of the alcoholic function was negligible. The rate and selectivity of the epoxidation reaction could significantly be improved by careful drying of the aerogel *in situ* at 473 K, by azeotropic distillation of toluene from the reaction mixture, and/or by addition of solid bases ($NaHCO_3$, zeolite 4A) to the reaction mixture. High epoxide selectivities up to 90–98% were obtained at 50–90% peroxide conversion within 5–60 min, using a catalyst/hexenol ratio of 3.3 wt%. The activity and selectivity of the aerogel is comparable to that of TS-1. The positive influence of solid bases was found to be due to their minor solubility in the weakly polar medium and to the neutralization of the acidic sites on the aerogel. Contrary to earlier observations, bases can increase or decrease the rate, depending on the water content of the system. Zeolite 4A acts as a base and a drying agent.

INTRODUCTION

The development of Ti- and Si-containing heterogeneous epoxidation catalysts has received considerable attention. The first truly heterogeneous and active catalyst was an amorphous silica-supported titania (0.5–5 wt%), which has been used for the manufacture of propylene oxide by Shell (1). The invention of Ti-substituted molecular sieves (TS-1, TS-2), which can use the environmentally friendly H_2O_2 as oxygen source, opened a new field in heterogeneously catalyzed oxidation reactions (2). The application of TS-1 is limited to relatively small reactants that are able to reach the active sites located in the microporous channels. This limitation has been overcome with large and ultralarge-pore Ti-containing zeolites isomorphous to zeolite β or MCM-41 (3), though their activity and selectivity to epoxide are not as outstanding as those of TS-1 (4).

Titania–silica mixed oxides derived by the solution sol–gel method have also been proposed for epoxidation. Xerogels with microporous structure revealed only low to moderate activity in the epoxidation of unfunctionalized olefins (5, 6). Amorphous microporous silicates with different Ti loadings were tested in 1-hexene and 1-octene epoxidation and the turnover frequency was found to be highest for silicates with low Ti content (4% TiO_2) (7). Ti-containing mesoporous silica was more active and selective than Ti-β and TS-1 in the epoxidation of cyclohexene using aqueous H_2O_2 as oxidant (8).

A catalyst, selective and active with aqueous H_2O_2, a peroxide that normally cannot be used with the rather hydrophilic titania–silica mixed oxides, was obtained by grafting TiF_4 on silica (9). On the other hand, incorporation of B^{3+} and Al^{3+} resulted in loss of activity and in diol formation (10).

Titania–silica mixed oxides with a Ti loading of 10–20 wt%, derived by the sol–gel method, provided good results in the epoxidation of 1-octene and cyclohexene using *tert.*-butylhydroperoxide (11). The best epoxide yield reported was 73.6% along with a peroxide selectivity of 76.3%. A titania–silica mixed oxide catalyst prepared by coprecipitation was also tested in the epoxidation of 1-hexene, using alkylhydroperoxides as well as H_2O_2 as oxygen source, but both reaction rate and selectivity were very low (12).

Recently, highly active and selective titania–silica has been prepared by the sol–gel method using tetramethoxysilicon and tetraisopropoxytitanium stabilized with acetyl acetone (13). Drying of the gel was found to be a crucial parameter for the catalytic activity of these mixed oxides. Removal of the solvent by semicontinuous extraction with supercritical CO_2 at low temperature preserved the high Ti dispersion in the silica matrix and the mesoporous structure of the aerogels. These catalysts proved to be superior to TiO_2-on-SiO_2, TS-1, and titania–silica xerogels in the epoxidation of cyclic olefins (14–17). Epoxide selectivities up to

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TABLE 1

Epoxidation of Allylic Alcohols with Ti- and Si-Containing Catalysts

Entry	Reactant	Product(s) (selectivity in %)	Peroxide	Temperature (K)	Olefin conversion (%)	Activity[a] [g/(g · h)]	Ref.
			TiO_2-on-SiO_2				
1	Cyclohexen-3-ol	Epoxide (85)	TBHP	383	ND	ND	1
2	Allyl alcohol	Epoxide (71)	TBHP	371	ND	ND	1
3[b]	2-Buten-1-ol	Epoxide (94)	TBHP	RT	ND	ND	20
			TS-1				
4	Allyl alcohol	Epoxide (100)	H_2O_2	323	15	0.87	21
5	Allyl alcohol	Epoxide (95) Acrolein (5)	H_2O_2	333	95	1.2	22
6	4-Methyl-3-penten-2-ol	Epoxide (>95)	H_2O_2	330	90	0.05	23
7	Geraniol	Epoxide (90) Aldehyde + acid (10)	H_2O_2	330	86	0.54	24
8	Nerol	Epoxide (90) Aldehyde + acid (10)	H_2O_2	330	85	0.53	24
9	Cyclohex-2-en-1-ol	Epoxide (80)	H_2O_2	330	85	0.53	24
			Ti-MCM-48				
10	2-Penten-1-ol	Epoxide (46) 2-Pentenal (54)	H_2O_2	323	ND	ND	25

[a] Amount of olefin converted in unit time using unit amount of catalyst.

[b] Catalyst obtained by treating silica with $Ti(OPr^i)_4$.

ND, no data available. RT, room temperature.

100% could be achieved in the oxidation of unfunctionalized olefins with alkylhydroperoxides. Even the electron-poor (deactivated) α,β-unsaturated ketone α-isophorone could be oxidized to the corresponding oxirane with a maximum selectivity of 98% (15).

The epoxidation of allylic alcohols with soluble Ti(IV), V(V), and Mo(VI) complexes has been thoroughly investigated (18, 19), but only a few papers deal with epoxidation over solid catalysts. The available data are collected in Table 1. In the case of allyl alcohol the solvolysis of glycidol could be suppressed in ethanol and 100% selectivity at 15% conversion was achieved with TS-1. Base treatment of TS-1 with sodium azide and sodium carbonate suppressed Brønsted acidity and the acid-catalyzed ring opening reaction, but also lowered the rate of epoxidation. In contrast, incorporation of aluminum into the TS-1 framework increased Brønsted acidity and the selectivity to solvolysis products (21).

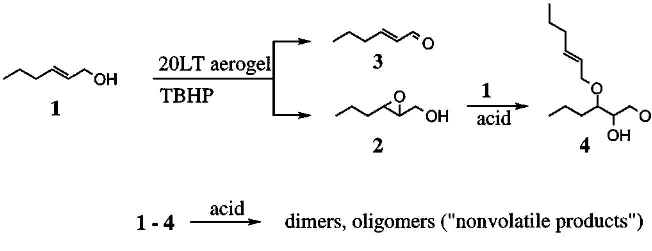
Alterations in reaction rate and selectivity in the epoxidation of various allylic alcohols were ascribed to their structure (22, 26). Allylic alcohols possessing a terminal double bond were epoxidized slowly but selectively. Reactants with an internal double bond were more reactive, but competitive oxidation of the alcoholic to a carbonyl functional group became a dominant side reaction.

In this paper we report the epoxidation of an allylic alcohol catalyzed by the mesoporous titania–silica aerogel containing 20% titania (20LT aerogel). This catalyst showed outstanding activity and selectivity in the epoxidation of simple cyclic alkenes and α-isophorone (27). It is therefore of interest to extend the application of the aerogel to the more complex oxidation of allylic alcohols. (*E*)-2-Hexen-1-ol (**1**) was chosen as a model reactant (Scheme 1) to investigate the rate and selectivity of epoxidation, compared with those of alcohol oxidation and acid-catalyzed side reactions.

EXPERIMENTAL

Materials

Distilled water (after ion exchange) and analytical-grade reagents were used for the catalyst synthesis and epoxidation reaction. *tert.*-Butylhydroperoxide (TBHP, Fluka, ca. 3 M solution in toluene, stored over molecular sieve 4A), *trans*-2-hexenal (Aldrich, 99%) and (2*R*,3*R*)-(+)-3-propyloxiranemethanol (Aldrich, 97%) were used without further purification. (*E*)-2-Hexen-1-ol (Aldrich, 96%) and cumene (Fluka, >98%) were distilled before use. Molecular sieve 4A pellets (Chemie Uetikon) and molecular sieve 4A



SCHEME 1

powder (Fluka) were activated overnight at 423 K *in vacuo*, if not otherwise stated.

For the preparation of H-exchanged zeolite 4A, 5 g molecular sieve 4A powder and 50 ml of 1 M aqueous NH_4NO_3 solution were stirred for 1 h at 363 K. Then the solid was filtered off and washed with water. This procedure was repeated twice. The zeolite was dried first *in vacuo* at 298 K, then in an oven at 393 K for 2 h and at 773 K for 4 h.

Catalyst Preparation

Detailed information on the synthesis of sol–gel titania–silica was published earlier (13). The same acronym for the sample is used in this paper: the number in 20LT indicates the Ti content expressed as weight percent TiO_2; the two capital letters indicate the drying method applied (low-temperature extraction with supercritical CO_2).

A modified titanium alkoxide precursor was synthesized; for this purpose two solutions were prepared: the first consisted of 2.81 g acetylacetone (acac, Fluka, >99.5%) in 2.8 ml isopropanol (*i*-PrOH, Riedel de Haen) and the second, of 8.0 g tetraisopropoxytitanium(IV) (TIPOT, Fluka) diluted in 8.45 ml *i*-PrOH (molar ratio of TIPOT : acac = 1 : 1). The two solutions were mixed and refluxed for 1 h, then *i*-PrOH was evaporated at 10 kPa for 16 h.

The sol–gel process was carried out at ambient temperature in a closed glass reactor in argon. Tetramethoxysilicon(IV) (TMOS, Fluka, 150 mmol, 22.77 g) and the modified TIPOT (28 mmol) were dissolved in 22 ml *i*-PrOH. The hydrolysant consisted of 15 ml water and 16 mmol HCL (37 wt%, Fluka) dissolved in 15 ml *i*-PrOH. The hydrolysant was added in 1 min to the alkoxide solution with vigorous stirring. After 5 min, 84 ml *i*-PrOH was introduced and stirring continued for 24 h.

The resulting gel was semicontinuously extracted with supercritical CO_2 in an autoclave. The extraction was completed in 1 h at 313 K and 24 MPa with a CO_2 flow of 20 g min^{-1}. Portions of the raw aerogel were heat treated in a tubular reactor. They were heated at 5 K min^{-1} up to 673 K in a nitrogen flow. After cooling to ca. 353 K, they were heated again at 5 K min^{-1} in air and kept for 5 h at 673 K.

The characterization of 20LT by N_2 physisorption, X-ray diffraction, thermal analysis, X-ray photoelectron spectroscopy (XPS), and vibrational spectroscopy has been published elsewhere (13, 14, 28, 29). The X-ray amorphous material possessed a good Ti dispersion, high surface area ($S_{BET} = 682$ m^2/g), and mesoporous structure (mean pore diameter $\langle d_p \rangle = 9$ nm, pore size maximum = 40 nm).

Epoxidation Procedure

The reactions were carried out batchwise in a mechanically stirred, closed 100-ml thermostated glass reactor fitted with thermometer, reflux condenser, septum for withdrawing samples, and dropping funnel for the addition of peroxide. All reactions were performed under argon to avoid the presence of oxygen and moisture. Before the catalytic run the glass was dried in an oven and allowed to cool under argon. In a standard procedure, 0.2 g aerogel 20LT was transferred under argon into the glass reactor. Sixty millimoles (6.01 g) (*E*)-2-hexen-1-ol, toluene (solvent), and 1 ml cumene (internal standard) were added. The dropping funnel was charged with 13.5 mmol TBHP as a 3 M solution in toluene. The total reaction volume was 21 ml. The solution was heated to the desired temperature and the reaction started by adding the peroxide to the vigorously stirred slurry (1000 rpm). Aliquots were removed at various time intervals, filtered, and analyzed by gas chromatography (HP 5890 equipped with a cool on-column inlet and a 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 epoxide (**2**) and 2-hexenal (**3**) products were identified by GC by comparison with authentic samples; the product (**4**) resulting from the opening of the epoxide ring was identified by ^{1}H-NMR, ^{13}C-NMR, and MS.

The following modifications of the standard procedure were applied to improve the performance of 20LT:

Method A. 20LT was heated *in situ* in the reactor before use in an argon flow at 473 K for 16 h, then the epoxidation was performed according to the standard procedure.

Method B. 20LT was dried according to method A. (*E*)-2-Hexen-1-ol and excess solvent (toluene) were added. About 30 ml toluene was then removed by (azeotropic) distillation. [The distillate contained some (*E*)-2-hexen-1-ol, which was taken into correction.] One milliliter of cumene was added and the method followed according to the standard procedure.

Method C. 20LT was dried according to method A. Four millimoles (0.336 g) of $NaHCO_3$ was added together with the reactants and the epoxidation performed according to the standard procedure.

Method D. 20LT was dried according to method A. One and one-half grams of activated molecular sieve 4A was added together with the reactants, and the epoxidation followed the standard procedure.

The selectivities (S) are calculated as follows:

Epoxide (**2**) selectivity related to the peroxide consumed: $S^*_2\ (\%) = 100 \cdot [\mathbf{2}]_f / ([\text{peroxide}]_i - [\text{peroxide}]_f)$.

Epoxide (**2**) related to hexenol (**1**) converted: $S_2\ (\%) = 100 \cdot [\mathbf{2}]_f / ([\mathbf{1}]_i - [\mathbf{1}]_f)$.

2-Hexenal (**3**) related to hexenol (**1**) converted: $S_3\ (\%) = 100 \cdot [\mathbf{3}]_f / ([\mathbf{1}]_i - [\mathbf{1}]_f)$.

Hydroxyether (**4**) related to hexenol (**1**) converted: $S_4\,(\%) = 100 \cdot [\mathbf{4}]_f/([\mathbf{1}]_i - [\mathbf{1}]_f)$.

Nonvolatile products (nv) related to hexenol (**1**) converted: $S_{nv}\,(\%) = 100 \cdot [nv]_f/([\mathbf{1}]_i - [\mathbf{1}]_f)$.

The subscripts i and f stand for initial and final values, respectively. The hexenol conversion is given in mole percent of the maximal attainable value.

For the study of the solubility of $NaHCO_3$, the standard reaction mixture except 20LT and TBHP was mixed with 0.34 g $NaHCO_3$ at 363 K for 1 h. The filtrate was mixed with an equal amount of water and the pH of the aqueous phase after separation was measured (pH 7.4). The experiment was repeated without addition of $NaHCO_3$, as a reference (pH 4.1).

RESULTS

Role of Catalyst Pretreatment and Reaction Additives

Preliminary experiments revealed that calcination of the titania–silica aerogel 20LT and storage in a closed vessel before use were not sufficient for the fast and selective epoxidation of (*E*)-2-hexen-1-ol. Further drying *in situ* in the reactor before the epoxidation reaction was necessary to activate the (hydrophilic) catalyst, as illustrated in Fig. 1a. Epoxidation over the aerogel, which was calcined at 673 K but not dried again before use, was slow and incomplete. Thermogravimetric analysis indicated that most of the physisorbed water is removed during heating of the catalyst to 473 K. *In situ* drying at 473 K (method A) or azeotropic distillation of traces of water (method B) increased the reaction rate considerably and 70% hexenol conversion was attained in 10–12 min, as compared with 60 min with the untreated 20LT (standard method). For comparison, a process similar to the standard procedure has been successfully applied for the epoxidation of simple cyclic olefins, such as cyclohexene (14). The influence of water adsorbed on the catalyst surface was minor, and 100% epoxide selectivity related to the olefin was achieved before or after calcination but without any further treatment of an aerogel containing 10 wt% TiO_2 (14).

With respect to the influence of additives under water-free conditions (Fig. 1a), the presence of the weak solid base $NaHCO_3$ (procedure C) retarded the reaction considerably, whereas another base, zeolite 4A (procedure D), had no significant influence on the rate of hexenol conversion.

The efficiency of peroxide consumption is illustrated by the epoxide selectivities related to the peroxide (S_2^*) in Fig. 1b. A rapid decrease in peroxide selectivity was observed in the reaction performed according to the standard procedure. There was a remarkable improvement after the aerogel was dried *in situ* by method A or B, and after 60 min (ca. 90% hexenol conversion) the selectivities were 85–86%. Method D, in the presence of molecular sieve 4A, provided the highest peroxide selectivity (91% at 96% hexenol conversion).

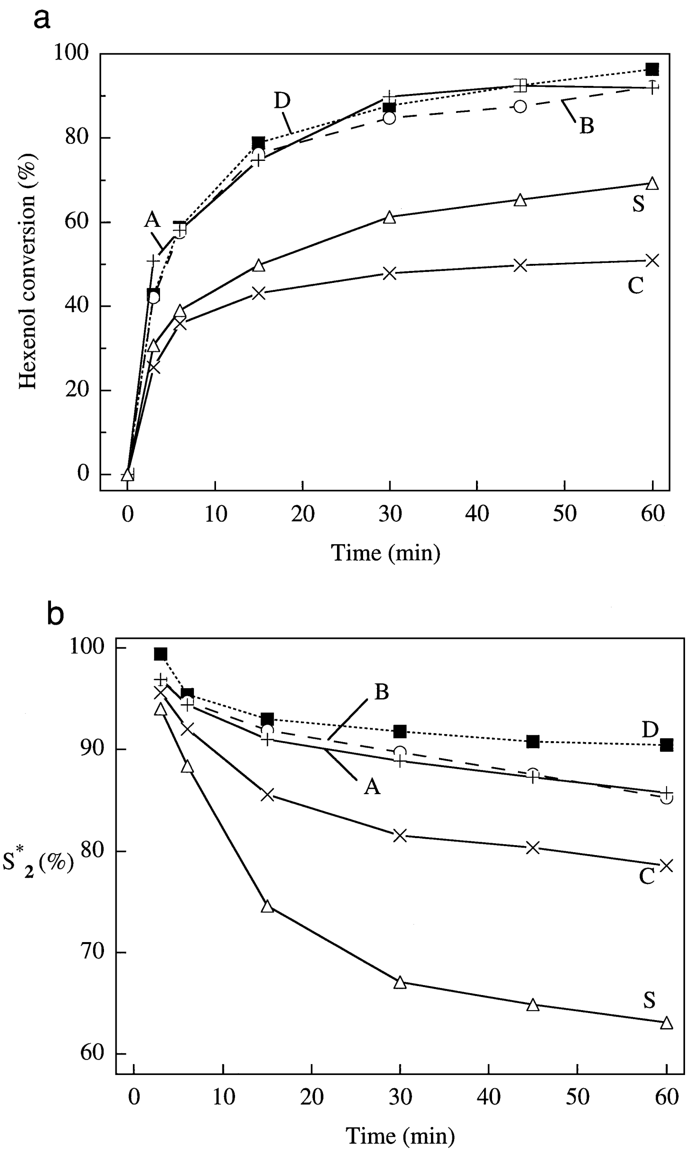


FIG. 1. Influence of catalyst pretreatment and additives on the epoxidation of (*E*)-2-hexen-1-ol: conversion versus time (a) and epoxide selectivity related to peroxide consumed, S_2^* (b). Standard reaction conditions, 363 K; for description of methods A–D and standard method see Experimental. Catalyst pretreatment method: (△) standard method (S); (+) A; (○) B; (×) C; (■) D.

The influence of catalyst pretreatment and reaction additives is rather similar when the epoxide selectivities are related to hexenol converted (S_2). The main difference is that the *in situ* drying in the absence of added base (method A) is less efficient in converting **1** to **2** than methods B–D. Methods B and D provide high selectivity (90–92%) and high conversion rate (85–90% hexenol conversion after 30 min). Selectivities to all products at 50 and 90% hexenol conversion are shown in Table 2.

TABLE 2

Influence of Catalyst Pretreatment and Additives on the Epoxidation of (*E*)-2-Hexen-1-ol (Standard Conditions[a])

Procedure[b]	Hexenol conversion (%)	Selectivity (%)			
		S_2	S_3	S_4	S_{nv}
Standard	50	67	7	8	18
A	50	97	0	3	0
	90	76	1	8.5	14.5
B	50	98	0	2	0
	90	87	1	10	2
C	50	87	11	1	1
D	50	98	1	1	0
	90	92	1	7	0

[a] Reaction temperature: 363 K.

[b] For the description of methods A–D and standard procedure, see Experimental.

From Fig. 1 and Table 2 we can conclude that the standard procedure, which was found to be very efficient in the epoxidation of unfunctionalized cyclic olefins (14), fails in the epoxidation of hexenol: the catalyst deactivates at around 50% conversion and one-third of the converted reactant is lost by side reactions (mainly by di- and oligomerization). Careful drying of the aerogel (A) improves the initial epoxide selectivity, but not sufficiently at high (90%) conversion. Interestingly, drying by azeotropic distillation (B) is considerably more efficient than *in situ* drying alone. Addition of solid bases after *in situ* drying (C, D) had contradictory effects, which will be discussed later.

Oxidation of (E)-2-Hexen-1-ol in the Absence of Aerogel

To reveal the role of basic additives in the epoxidation of (*E*)-2-hexen-1-ol, the reaction was repeated without the aerogel but in the presence of $NaHCO_3$ or zeolite 4A. The selectivity and rate data are collected in Table 3. The epoxidation reaction catalyzed by 20LT is shown as a reference. The rate of epoxide (**2**) formation, related to the amount of catalyst and/or additive, indicates that none of the additives possesses an inherent activity for the epoxidation of hexenol (**1**). The presence of 1.5 g zeolite 4A pellets increased the rate of epoxide formation by a factor of 24, as compared with the reaction performed in the absence of any solid material (blank reaction). Still, the zeolite was almost 500 times less active than the 20LT aerogel. Note that it has recently been proposed (30) that zeolite 4A is an efficient catalyst for the epoxidation of some allylic alcohols, including **1**.

When considering the product distribution, it is clear from Table 3 that mainly high-molecular-weight by-products are produced in the blank reaction or in the presence of $NaHCO_3$. However, zeolite 4A pellets provided an astonishingly good selectivity to epoxide (**2**), relative either to hexenol converted (61%) or to peroxide consumed (93%). It seems that the molecular sieve had a rather complex effect on the reaction by suppressing the peroxide decomposition and the formation of high-molecular-weight

TABLE 3

Epoxidation Activity and Selectivity of 20LT and 4A and of 20LT and the Reaction Additives Independently[a]

Catalyst	Additive (amount in g)	S_2^{*b} (%)	Product composition[c] (%)				Rate of formation of **2** and nv (mmol h^{-1} g^{-1})[d]		Rate of conversion of **1** (mmol $h^{-1}g^{-1}$)[e]
			2	**3**	**4**	nv	**2**	nv	
Aerogel 20LT[f]	4A pellets (1.5)	98	>99	<1	0	0	73	0	73
Aerogel 20LT[g]	—	96	97	0.5	1.5	0	748	0	771
	—	7	3	27	0	70	0.1[h]	2.6[h]	3.8[h]
	$NaHCO_3$ (0.34)	3	1.5	13.5	0	85	0.14	8.5	10
	4A powder (1.5)	70	26	6	0	68	0.8	2	2.9
	4A pellets (1.5)	93	61	10	0	29	1.6	0.8	2.6

[a] Reaction temperature: 363 K.

[b] At 40% peroxide conversion.

[c] At 40% hexenol conversion.

[d] Average rate of formation of epoxide (**2**) and nonvolatile products (nv), related to the amount of catalyst and/or additive; calculated at 40% hexenol (**1**) conversion.

[e] Average rate of conversion of **1**, related to the amount of catalyst and/or additive; calculated at 40% hexenol conversion.

[f] 0.2 g; pretreatment method D.

[g] 0.2 g; pretreatment method A.

[h] Reaction rate in mmol h^{-1}.

("nonvolatile") by-products and by increasing the rate of epoxide formation.

Influence of the Amount of Molecular Sieve 4A Used as Additive

To elucidate the role of molecular sieve 4A as an additive in the epoxidation of (*E*)-2-hexen-1-ol, various amounts of 4A pellets were added to 0.2 g of titania–silica aerogel 20LT dried *in situ* at 473 K (method D). Conversion of hexenol versus time at 333 K is plotted in Fig. 2a. The epoxidation with 20LT is shown as a reference. As compared with the reference reaction, addition of 1.5 g zeolite 4A resulted in a much higher rate of hexenol conversion, though the zeolite alone does not possess significant activity. Only a relatively large amount of zeolite provided significant rate enhancement.

TABLE 4

Influence of the Zeolite Amount on the Epoxidation of (*E*)-2-Hexen-1-ol (Method D, 333 K)

Zeolite amount (g)	Hexenol conversion (%)	Selectivity (%)			
		S_2	S_3	S_4	S_{nv}
—	50	71	1	9	19
0.05	50	89	2	8	1
	75	73	2	11.5	13.5
0.15	50	90	3	7	0
	75	79	3	9.5	8.5
1.50	50	92	1	2	5
	75	88	1	2	9

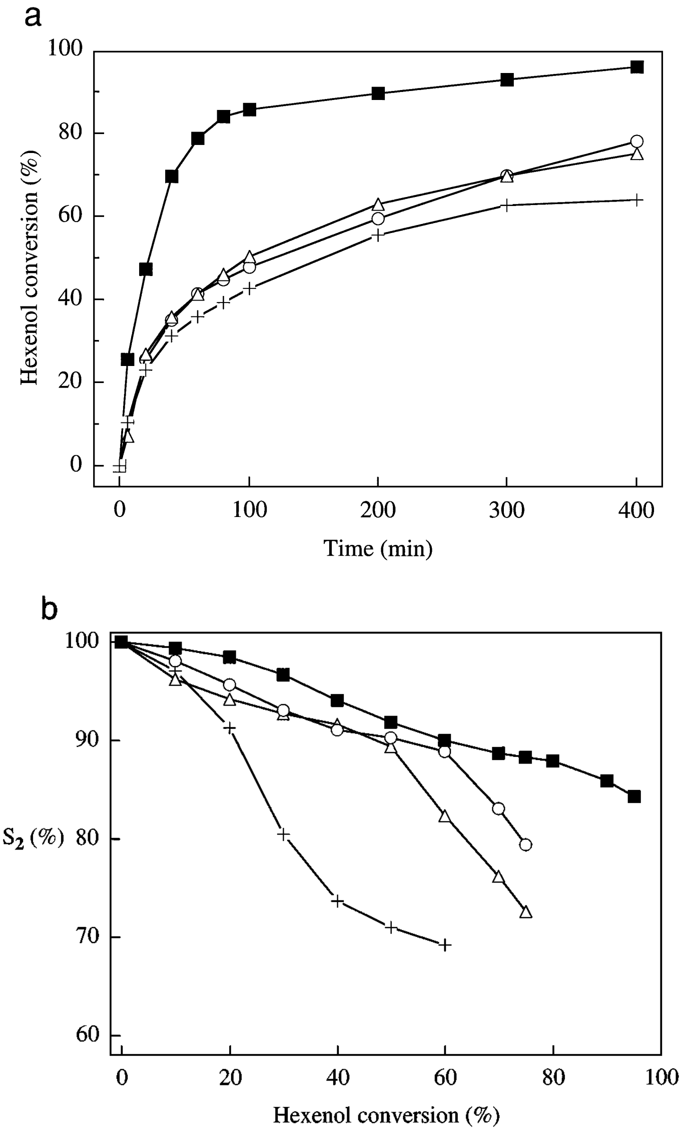


FIG. 2. Influence of the amount of molecular sieve 4A pellets on hexenol conversion (a) and on the selectivity to epoxide, S_2 (b) Method D and standard conditions, except the amount of 4A; temperature: 333 K. Amount of 4A: (+) none, (△) 0.05 g, (○) 0.15 g, (■) 1.5 g.

Epoxide selectivity S_2 as a function of hexenol conversion is plotted in Fig. 2b. In absence of zeolite 4A the selectivity dropped notably with increasing hexenol conversion. Formation of the hydroxyether **4** and di- and oligomers was the main reason for the decrease in selectivity, which is illustrated in Table 4. In contrast, the drop in epoxide selectivity was shifted to higher conversions even by the addition of small amounts of zeolite 4A. Addition of 1.5 g molecular sieve provided good selectivity up to high hexenol conversion, mainly by suppressing the further reaction of epoxide to the hydroxyether (**2** → **4**).

Comparison of Acidic and Basic Additives

The beneficial effect of molecular sieve 4A on both conversion and epoxide selectivity in the aerogel-catalyzed reaction was illustrated in the previous section. Molecular sieve 4A, used mainly as a drying agent, is a strong base: a mixture of 0.16 g molecular sieve pellets and 5 ml H_2O (0.2 M Na^+) provided a pH of 10.4 (11.0 for the 4A powder). To study the effect of this basic character, we prepared the H-exchanged form of the molecular sieve 4A powder, which represents a solid acid. $NaHCO_3$ was found to be a 125–500 times weaker base than zeolite 4A in the same aqueous solution.

Figure 3a represents hexenol conversion in the presence of basic and acidic additives. The highest rate was achieved with the 4A pellets as additive. The rate-accelerating effect ceased when $NaHCO_3$ was used together with the pellets. Note that the rate of hexenol epoxidation (method A) was lowered by the addition of $NaHCO_3$ (method C) as well (see Fig. 1a). Similarly, slower conversion of hexenol was observed with the H-exchanged form of the 4A powder, as compared with the basic form used as additive. This is an indication that the basicity of the unmodified molecular sieve is important in obtaining a higher rate. Note that

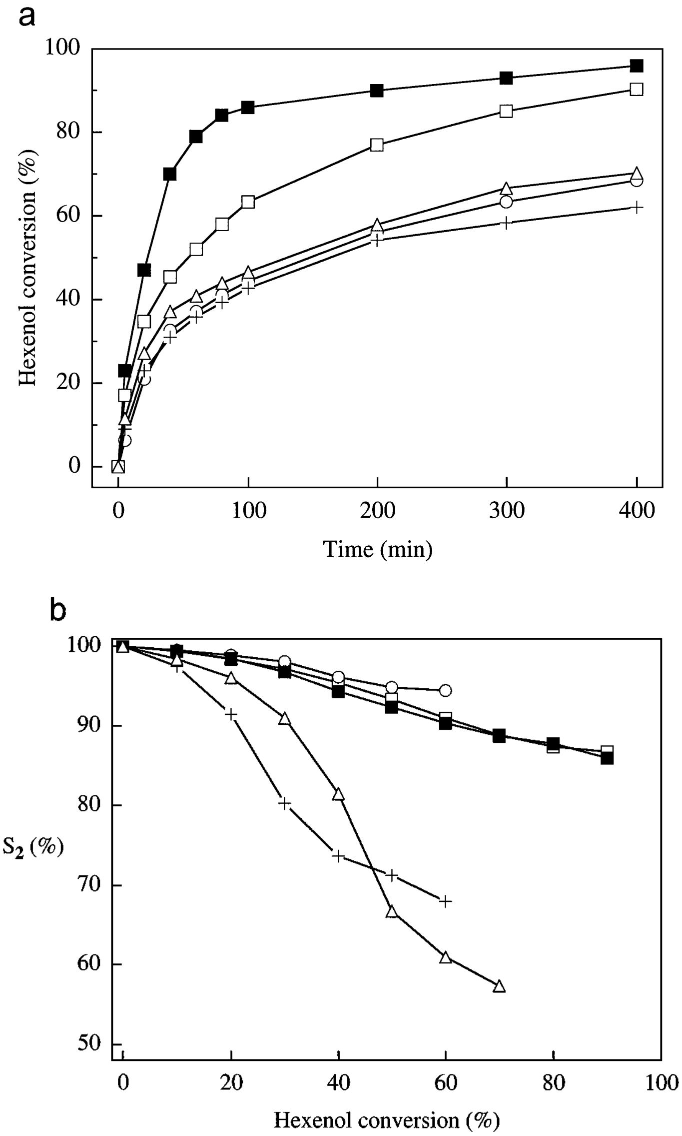


FIG. 3. Influence of acidic and basic additives on hexenol conversion (a) and on epoxide selectivity, S_2 (b). Method A and standard reaction conditions, except the additives; temperature: 333 K. Reaction additives: (+) no additive, (△) 1.5 g H-exchanged molecular sieve 4A powder; (■) 1.5.g molecular sieve 4A pellets; (□) 1.5 g molecular sieve 4A powder; (○) 1.5 g molecular sieve 4A pellets and 4 mmol $NaHCO_3$.

zeolite 4A provides very dry reaction conditions, which can also contribute to the high rate and selectivity (31).

Figure 3b shows epoxide selectivity as a function of hexenol conversion. Molecular sieve 4A powder and pellets as additives behaved equally. They provided high epoxide selectivities S_2 up to high hexenol conversions (>90%). The addition of both $NaHCO_3$ and zeolite 4A barely improved the selectivity. Again, the high selectivity must be attributed to the basicity of the molecular sieve (and $NaHCO_3$), because the substitution of the sodium ions by protons in the 4A powder resulted in a dramatic decrease in the selectivity. The initial selectivity was significantly higher than that of the reference reaction without any additive. This enhancement is likely due to elimination of water during reaction, as mentioned above. This positive effect was successively eliminated by the acid-catalyzed formation of **4** and the nonvolatile by-products, whose selectivities at 70% hexenol conversion amounted to 16% (S_4) and 24% (S_{nv}), respectively, along with an epoxide selectivity S_2 of 57%.

Figures 4a and 4b illustrate the actual amounts of **2** and **4** during reaction. Note that the reactant and the three

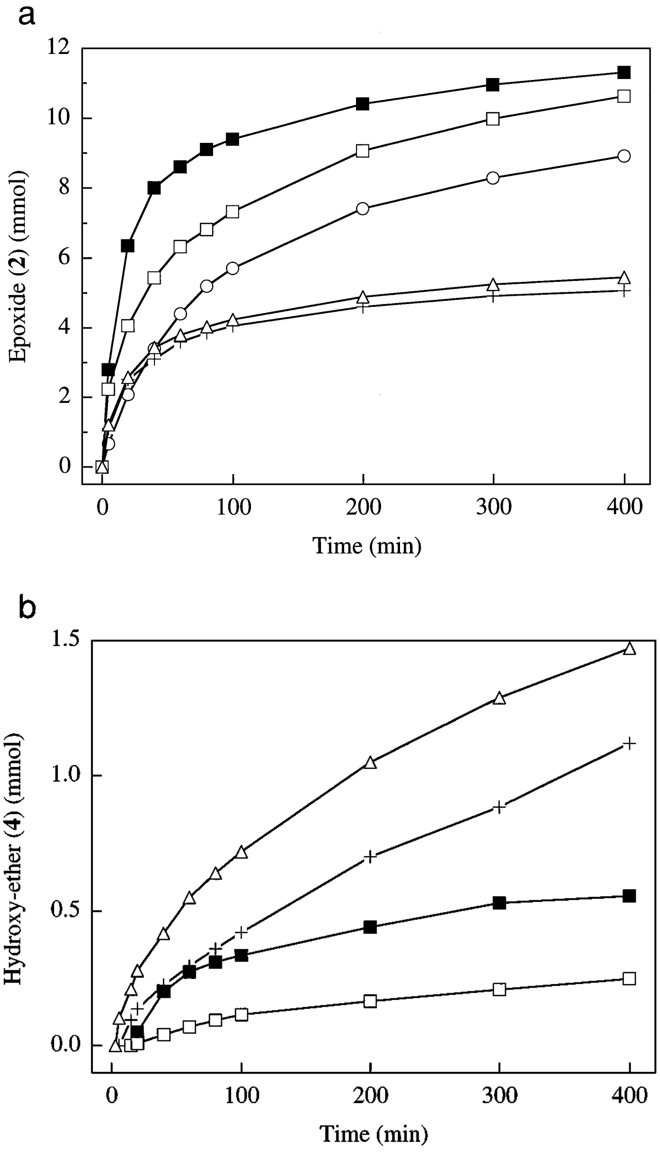


FIG. 4. Amounts of epoxide **2** (a) and hydroxyether **4** (b) as a function of time in the presence of reaction additives. Method A and standard reaction conditions, except the additives; temperature: 333 K. Reaction additives: (+) no additive, (△) 1.5 g H-exchanged molecular sieve 4A powder, (■) 1.5 g molecular sieve 4A pellets, (□) 1.5 g molecular sieve 4A powder, (○) 1.5 g molecular sieve 4A pellets and 4 mmol $NaHCO_3$.

identified products **2**–**4** are bi- or trifunctional compounds and all are able to produce dimers and oligomers, here termed nonvolatile (nv) products. Accordingly, the rates of formation of **2** and **4** can be determined from Figs. 4a and 4b only when S_{nv} is zero or close to it.

We can see from Fig. 4b that in the presence of the H-exchanged form of zeolite 4A powder the epoxide was further attacked by the reactant at the ring position to give **4**, the amount of which continuously increased with time. In contrast, the addition of basic 4A powder suppressed the formation of **4**. This result suggests that the ring opening of the epoxide is catalyzed mainly by acids. Interestingly, no ring opening of the epoxide was observed when $NaHCO_3$ was used as second additive together with the 4A pellets. This is the explanation for the outstanding epoxide selectivity with these additives (Fig. 3b).

In all reactions the amounts of hexenal (**3**) were rather small, only a few percent of the epoxide. The highest hexenal/epoxide molar ratio of about 0.05 was observed in the presence of H-exchanged 4A. Interestingly, not only acids but bases also favor the oxidation of the primary −OH group of **1**, but the aerogel itself is a poor catalyst for this reaction.

Temperature Dependence of the Epoxidation

Several reaction parameters can influence the rate and selectivity of hexenol epoxidation, including the chemical nature of the peroxide, the reactant/peroxide ratio, solvent, and temperature. Here only the influence of reaction temperature is shown as the role of additives has been investigated at 333 and 363 K.

The oxidation of (*E*)-2-hexen-1-ol at 333, 348, and 363 K is illustrated in Figs. 5a and 5b. In each case 4 mmol $NaHCO_3$ was added to the calcined but not redried catalyst (standard procedure). The rate of hexenol conversion increased when the reaction temperature was raised, but an optimum epoxide selectivity was achieved at 348 K (Fig. 5a). The selectivity to high-molecular-weight by-products, which mainly contributed to the decrease in S_2, is shown in Fig. 5b. At 333 K, the epoxidation became rather slow and the formation of dimers and oligomers became dominant.

Some interesting data from the experiments shown in Figs. 1 and 5 are collected in Table 5. Addition of $NaHCO_3$ to the reaction mixture (method C) decreases the rate and conversion achievable in 60 min only when the aerogel is redried *in situ* before reaction. Drying (method A) or addition of $NaHCO_3$ independently enhances the rate and epoxide selectivity considerably. At high conversion (92–93%) the basic additive is even more efficient in suppressing the acid-catalyzed side reactions than drying the aerogel before reaction (S_2 at 60 min).

Similarly, the rate-accelerating effect of zeolite 4A was a function of reaction temperature, as illustrated by the data in Table 6.

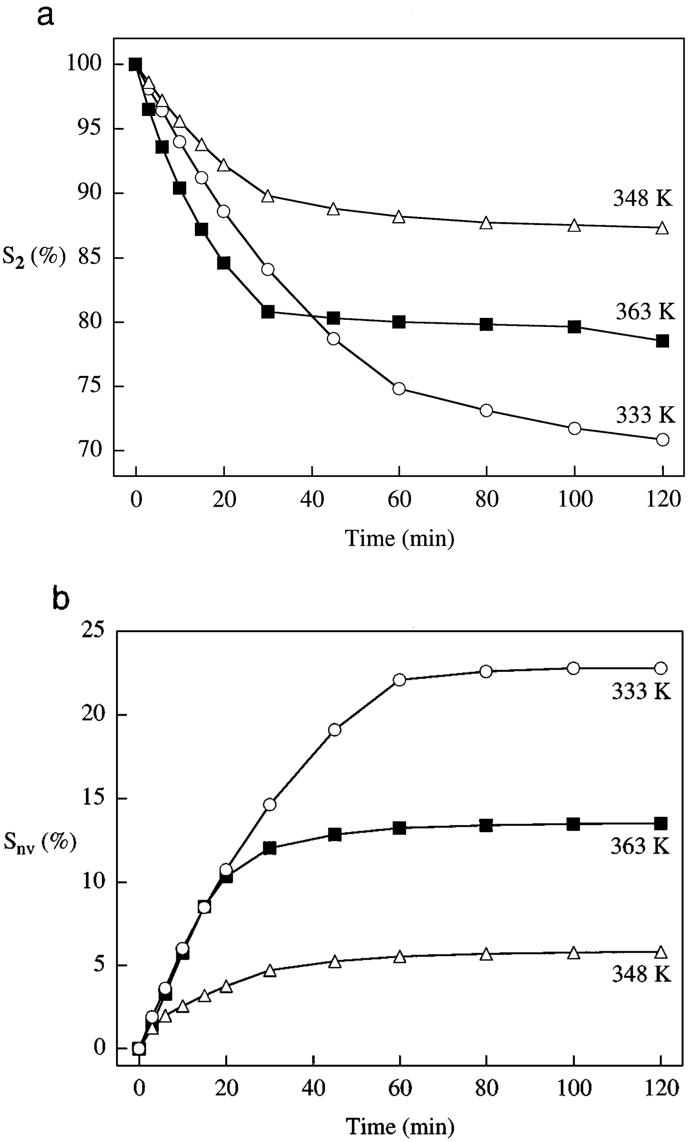


FIG. 5. Epoxide selectivity, S_2 (a), and selectivity of nonvolatile by-products, S_{nv} (b), at different reaction temperatures. Standard reaction conditions and 4 mmol $NaHCO_3$.

Homogeneous or Heterogeneous Catalysis?

To confirm that the titania–silica catalyst is truly heterogeneous and its activity is not due to soluble Ti(IV) complex formation, a set of experiments were performed. The reference experiment shown in Fig. 3 ("no additive") was repeated and after 8 min the warm reaction mixture was filtered and the reaction was continued without the aerogel. No further conversion could be detected in the absence of catalyst, which proves that no active soluble species were present in the filtrate. In addition, when the reference experiment was repeated with the catalyst already used for 8 min, the rate of epoxide formation was similar to that of the reference experiment.

TABLE 5

Conversions and Epoxide Selectivities (S_2) in the Epoxidation of Hexenol (1) with 20LT at 363 K (Data Collected from Figs. 1 and 5)

Catalyst pretreatment	Additive	Conversion at 60 min (%)	S_2 at 60 min (%)	S_2 at 50% conversion (%)	S_4 at 50% conversion (%)
Standard	—	69	58	66	8
Drying (method A)	—	92	75	97	3
Drying (method C)	$NaHCO_3$	51	87	87	1.3
Standard	$NaHCO_3$	93	80	96	1.6

These experiments demonstrate that the titania–silica aerogel is a really heterogeneous, recyclable catalyst.

DISCUSSION

Good selectivity in the epoxidation of (E)-2-hexen-1-ol (**1**) can be achieved only when the rate of epoxide (**2**) formation is considerably higher than the rates of various side reactions (Scheme 1).

As illustrated in Figs. 1 and 5 and Tables 2 and 5, careful removal of water and/or addition of a solid base to the reaction mixture resulted in a high rate of hexenol conversion at 348–363 K, together with epoxide selectivities up to 90–98%. For example, drying the aerogel *in situ* followed by distilling off toluene (method B) afforded about 90% conversion in 1 h. The calculated activity (i.e., amount of olefin converted by 1 g catalyst in 1 h) is 0.67. For comparison, only allyl alcohol could be epoxidized by TS-1 with higher activity (1.2); for other alkenols the activity of TS-1 was lower (0.05–0.54, Table 1). Unfortunately, the activity of other Ti- and Si-containing catalysts could not be calculated due to the incomplete description of the experiments.

The epoxidation of **1** was complicated by several side reactions (Scheme 1). Oxidation of the primary OH function to a carbonyl group (**3**) was a minor reaction, though both solid acids and bases favored the formation of **3** (Tables 2 and 3).

Dimerization and oligomerization of any of the bi- and trifunctional reactants and products and the epoxide ring opening reaction (**2** → **4**) are catalyzed by the acidic sites of the aerogel. Drying the catalyst or adding a solid base efficiently suppressed these reactions (Fig. 4b, Tables 2 and 4).

TABLE 6

Effect of Zeolite 4A Addition to the *in Situ* Dried Aerogel (Method A)

Zeolite added	Temperature (K)	Conversion (%)	
		30 min	60 min
−	333	28	36
+	333	60	79
−	363	90	92
+	363	88	96

Interestingly, drying of the aerogel before reaction or the presence of a base during reaction had rather similar effects on selectivity. Drying resulted in the condensation of some ≡Si−OH groups to ≡Si−OH−Si≡ connections (11). This process seems to be very important during drying by distilling off toluene (method B). There are two main sources of water formation during reaction: formation of hexenal **3** and the homolytic decomposition of the peroxide (32). Addition of water to the aerogel reverses the above condensation reaction of the surface silanol groups and produces Brønsted sites. Bases can neutralize these acidic sites and suppress the acid-catalyzed side reactions. The outstanding positive effect of zeolite 4A is attributed to its basicity and drying ability.

It is well known (21, 33, 34) that treatment of TS-1 or titania–silica with a weakly basic solution before use can significantly enhance epoxide selectivity. However, neutralization of the surface acidic sites can be achieved much more simply—by addition of solid base to the reaction mixture. At first sight it is astonishing that, e.g., $NaHCO_3$ can dissolve in the rather apolar reaction medium and migrate into the pores of the aerogel. The significant base concentration in the toluene–cumene–hexenol mixture was proved by control experiments (see Experimental). The presence of dissolved base was clearly detectable by the increase in pH by more than 3 units. Accordingly, the effect of solid base is due to the diffusion of dissolved base to the aerogel surface and neutralization of the acidic sites. A comparison of our method with the generally applied catalyst pretreatment with basic solutions, followed by drying and calcination (21, 33, 34), shows that addition of a solid base is simpler and there is no danger of overdosing the base.

A careful analysis of the data presented in the figures and tables indicates that a high rate of epoxide formation was always accompanied by the negligible formation of high-molecular-weight by-products ($S_{nv} \leq 1\%$). We propose that the main effect of catalyst drying and base additives on the rate of epoxide formation is the elimination or neutralization of the acidic sites. In this way the acid-catalyzed formation of oligomers and blocking of the catalyst pores are prevented.

There are several examples in the literature (21, 33, 34) that bases improve the epoxide selectivity of Ti- and Si-containing catalysts, but simultaneously decrease the reaction rate. The loss of activity was explained by the formation of stable Ti–peroxide complexes at higher pH that are inert to reactions with the olefin (32). However, our results (Tables 5 and 6) demonstrate that bases can exert positive, negative, and also negligible effects on the alkene conversion, depending on the presence of water and the reaction temperature. We propose that it is not the formation of an inactive Ti–peroxo complex, but rather the blocking of the active sites by high-molecular-weight, i.e., poorly dissolving and migrating, by-products that is responsible for the loss of activity.

CONCLUSIONS

This study demonstrated the good performance of 20 wt% TiO_2–80 wt% SiO_2 aerogel in the rather demanding epoxidation of 2-hexen-1-ol. Both reaction rate and epoxide selectivity could be improved by careful drying of the aerogel or by simple addition of a solid base ($NaHCO_3$ or zeolite 4A). A comparison with literature data indicates that the amorphous mesoporous aerogel is at least as active and selective as TS-1 in alkenol epoxidation, without any limitation concerning the size of the reactant.

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