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Synthesis of Propylene Oxide from Propylene and Hydrogen Peroxide Catalyzed by Titanium Silicalite

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The epoxidation of propylene with hydrogen peroxide in the liquid phase, in the presence of titanium silicalite catalyst (TS-1), is described. The best solvents are methanol and methanol/water mixtures. The temperature is normally between room temperature and 60°C. Under these conditions, reaction rates are fast, yields on H_2O_2 are quantitative, and selectivity to propylene oxide is very high. Propylene glycol and its monomethyl ethers and trace amounts of formaldehyde are the only by-products formed. Selectivity is further improved and the hydrolysis of the epoxide is almost suppressed when the residual acidity of the catalyst is completely neutralized. The activity of spent catalyst is recovered by calcining at 550°C or, more simply, by washing with solvents. Complete activity recovery shows that Ti is not removed from the crystalline framework during the epoxidation reactions.

INTRODUCTION

Metal-catalyzed epoxidations with hydrogen peroxide have not been as successful as with hydroperoxides, due to economics and to the lack of efficient catalysts. Group IV–VI metal oxides, and particularly MoO_3, V_2O_5, and WO_3, known to be good epoxidation catalysts with hydroperoxides, behave as hydroxylation catalysts with hydrogen peroxide. Thus they produce 1,2-glycols, as found by Milas as far back as the 1930s (*1, 2*). A few years later Mugdan and Young recognized that epoxides were most likely intermediates in the Milas reaction (*3*). They could not be isolated because hydrolysis, favored by water, high temperature, and low pH, converts them to glycols as soon as they are formed.

Epoxides were eventually obtained from simple unsubstituted olefins, when the contact time between the epoxides and water was minimized. This was achieved either by removing water during the reaction through azeotropic distillation (*4a*), or by using anhydrous hydrogen peroxide (*4b*), giving 85 and 35% yields, respectively. Yields of up to 85% have also been reported when reactions were carried out under phase-transfer conditions and metal oxides were replaced by a more active two-component catalyst WO_3/H_3PO_4 (*5*). However, it is unsafe to handle anhydrous or near-anhydrous organic solutions of hydrogen peroxide (*6*). Furthermore, the phase-transfer technique fails with lower olefins, because the latter yield water soluble epoxides.

More recently Renaud *et al.* (*7*) described catalysts based on Fe or Mn–porphyrin complexes, which catalyze the epoxidation of olefins in mild conditions. However the porphyrin ligand is unstable in the presence of oxidants. This is generally true for all catalysts based on metal complexes with organic ligands.

The discovery of titanium silicalite (TS-1) almost 10 years ago, opened up new opportunities (*8*). It was soon established that TS-1 was a very efficient catalyst for the epoxidation of various olefins with hydrogen peroxide under very mild conditions (*9*).

Reference (*10*) describes the structure

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and the overall reactivity of TS-1 in detail. In this paper we describe the epoxidation of propylene with H_2O_2 catalyzed by TS-1.

EXPERIMENTAL

X-ray powder diffraction analyses (XRD) were performed on a Philips diffractometer equipped with a pulse height analyzer, using Cu$K\bar{\alpha}$ radiation (λ = 0.154178 nm). FT–IR spectra were collected on a Perkin–Elmer 1730 spectrometer using the KBr wafer technique.

Materials

Methanol (C. Erba, RPE-ACS), 33% (C. Erba) and 60% (Interox) hydrogen peroxide, tetraethyl silicate (Dynasil A by Dynamit Nobel), tetraethyl titanate, 1,2-dimethoxyethane (Fluka, purum), and tetrapropylammonium hydroxide (Enichem Synthesis) were used as received. Ethanol, *t*-butyl alcohol, acetonitrile, ethyl acetate (all from C. Erba) were purified by distillation prior to use. Authentic samples of 1-methoxy-2-propanol and 2-methoxy-1-propanol were prepared according to Ref. (*11*). 1,2-Dimethoxyethane, propylene oxide (Fluka), propylene glycol (C. Erba), and their monomethyl ethers, for GLC calibration, were distilled prior to use.

Synthesis of Titanium Silicalite

We prepared TS-1 according to Ref. (*8a*). A solution of 1.5 g tetraethyltitanate in 45 g of tetraethylsilicate was added to 100 ml of a 20 wt% aqueous solution of tetrapropylammonium hydroxide (TPAOH) free from alkali metals, with magnetic stirring. The resulting mixture was kept at 60°C for 3 h. Occasionally we added distilled water to compensate for evaporation. Molar ratios in the final solution were: SiO_2/TiO_2 = 32.7, $TPAOH/SiO_2$ = 0.46, H_2O/SiO_2 = 35. The mixture was transferred to a 260-ml stainless-steel autoclave and heated in an oven at 175°C, under autogenous pressure, without stirring, for 24 h. After cooling to room temperature, the crystalline product was separated from the liquid by filtration, washed several times with water, dried for 2 h at 100°C, and finally calcined for 5 h at 550°C in air (TiO_2 = 2.8 wt%, SiO_2/TiO_2 molar ratio 46, crystallite size 0.1–0.3 μm). IR and XRD spectra of the product were in agreement with literature data (*10d*).

Synthesis of TS-1/SiO₂ (8c)

Tetraethylsilicate (1346 g) was added to 1437 g of a 12 wt% aqueous solution of tetrapropylammonium hydroxide, under vigorous stirring. The mixture was heated at 60°C for 1 h and subsequently diluted with 5890 g of water.

Titanium silicalite was prepared according to the procedure previously described, omitting the calcination step. An amount of 3500 g of TS-1 was filtered from the mother liquor, washed with water, and added with stirring to the solution of silica. The slurry was spray dried and then heated under nitrogen 2 h at 550°C. Calcination at this temperature was continued for 2 h in air (TiO_2 2.6 wt%, SiO_2/TiO_2 molar ratio 51, particle size 20 μm).

Pretreatment of TS-1/SiO₂ with Sodium Acetate (9d)

TS-1/SiO_2 (100 g) was added to 500 ml of a 0.5% aqueous solution of sodium acetate. The slurry was heated 10 min at 100°C with stirring and then filtered. This treatment with sodium acetate solution was repeated twice. The product was subsequently washed four times with boiling water (500 ml each time) and then twice with methanol at room temperature. It was dried for 2 h at 550°C (TiO_2 2.6 wt%, SiO_2/TiO_2 molar ratio 50, Na = 0.14%).

Epoxidation Procedure in Methanol/Water Solvent

Experimental apparatus. The epoxidation of propylene is a fast and highly exothermic reaction. It is, therefore, difficult to maintain a constant temperature using only a simple thermostatic bath. This is particularly true at the very beginning of the reaction. Figure 1 shows the apparatus we used

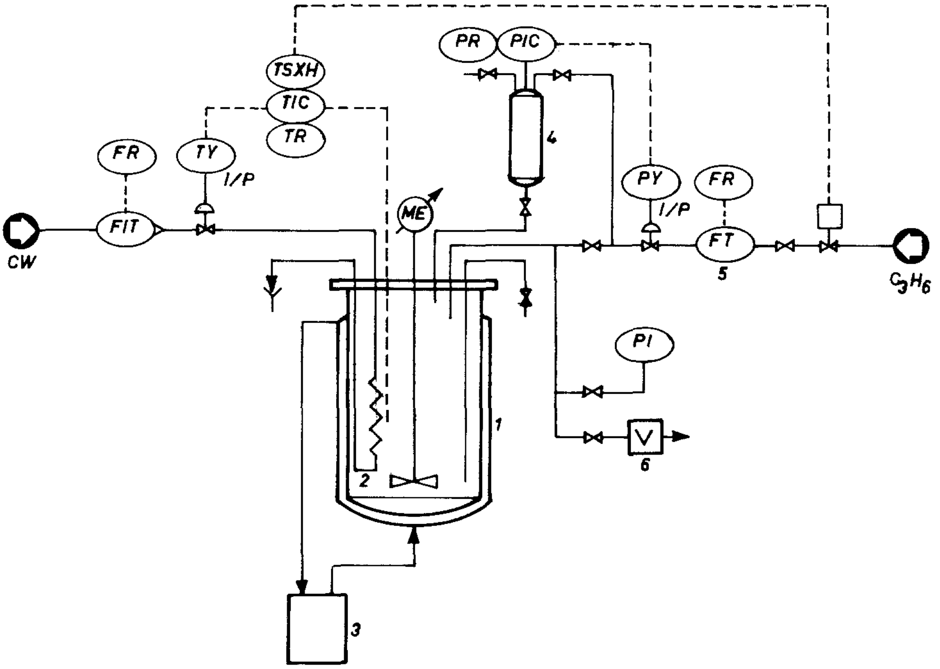


FIG. 1. Experimental apparatus for the epoxidation of propylene in methanol and methanol/water solvents. (1) Autoclave, (2) cooling coil, (3) thermostat, (4) hydrogen peroxide tank, (5) mass flow meter, (6) vacuum pump. (FIT) flow indicator-transmitter. (FR) Flow recorder. (I/P) Current to pressure converter. (TIC) Temperature indicator-controller. (TR) Temperature recorder. (TSXH) Temperature high switch interlocked to C_3H_6 feed solenoid valve. (PIC) Pressure-indicator controller. (PR) Pressure recorder. (FT) Flow transmitter. (PI) Pressure indicator. (ME) Magnetically driven stirrer. Dotted lines indicate electrical connections.

in this work. Because it is potentially dangerous to handle hydrogen peroxide solutions (*6*), we placed the reaction vessel in a barricaded area. We set up the equipment so that we could start the reaction, take samples, and terminate the experiment by remote control from outside the barricade. The reactor consisted of a 1-liter capacity autoclave (304 stainless steel), equipped with a magnetically driven stirrer, a thermocouple, an inlet for liquid reagents, a second inlet connected to the hydrogen peroxide tank, a third inlet for the gaseous propylene supply, an outlet for sampling, and a cooling coil. An outer jacket was provided in the reactor through which water at constant temperature could be circulated. The reaction temperature was maintained constant within ±0.2°C by removing excess heat with cold water (13°C). The flow rate of the latter in the cooling coil was regulated by a control valve. Propylene was supplied through a line equipped with a solenoid valve, a mass flow meter, and a control valve. The solenoid valve was aimed at stopping the gas supply if temperature increased beyond safety levels. Gaseous propylene was fed into the autoclave by the control valve at the same rate as it was consumed. Thus the pressure was maintained constant.

Epoxidation of propylene. In a typical run air was removed from the system by means of a nitrogen cylinder and a vacuum pump. An amount of 31 g of 60 wt% aqueous hydrogen peroxide, 23 g of water, and 10 g of methanol were charged in the hydrogen peroxide tank. An amount of 490 g of methanol, 6.6 g of *t*-butyl methyl ether, and 2.24 g of TS-1 were added to the reactor. The slurry was heated at 40°C under pressure

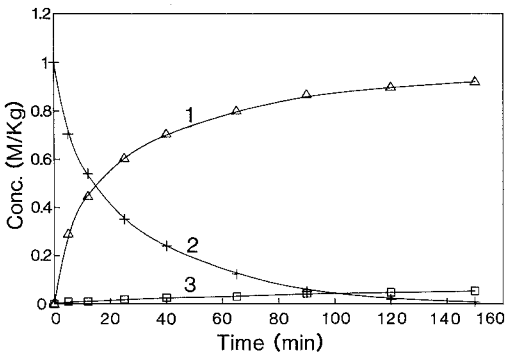


FIG. 2. Epoxidation of propylene with H_2O_2 in methanol/water at 40°C. Reaction conditions: CH_3OH 92 wt%, TS-1 0.4 wt%, $P_{C_3H_6}$ = 4 atm. (1) Propylene oxide, (2) hydrogen peroxide, (3) propylene glycol, 1-methoxy-2-propanol, and 2-methoxy-1-propanol.

of propylene (4.0 atm) and with vigorous stirring. We started the reaction by adding the aqueous hydrogen peroxide solution. Aliquots were removed at various time intervals and analyzed by gas chromatography and iodometric titration. GLC analyses were performed on a Hewlett–Packard HP 5880 gas chromatograph, using a flame ionization detector and a glass column (2.4 m × 4 mm) containing Porapak PS as the stationary phase. Results are shown in Fig. 2. Results listed in Tables 1 and 3 were similarly obtained.

Aging tests were carried out by using the same catalyst in a series of experiments. The catalyst was recovered from the previous run by centrifugation, washed only once with the minimum amount of methanol at room temperature, and used again without drying. Results are illustrated in Fig. 4.

We generally used 30–35% H_2O_2 concentration. All the water present at the end of the reaction was taken into account to calculate the methanol/water composition. The concentration of titanium silicalite is referred to liquid reagents present at beginning of the reaction, before the propylene was charged in. Selectivity and yields are always based on hydrogen peroxide.

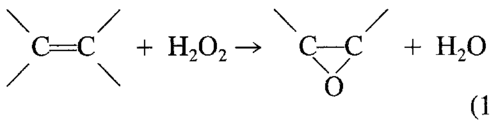
Epoxidation Procedure in Ethanol, t-Butanol, Acetonitrile, Methyl Acetate

In most organic solvents the reaction is slower than in methanol. Thus the temperature can be kept constant simply by an external thermostatic bath. In this case, our reactor was a 300-ml volume glass pressure vessel, equipped with an inlet for gaseous propylene, an outlet for liquid sampling, and a thermocouple.

In a typical run, 40 g of a mixture containing known amounts of solvent, hydrogen peroxide, titanium silicalite, and an internal standard (*t*-butyl methyl ether for reactions in methanol, methyl acetate, acetonitrile, and *t*-butanol, 1,2-dimethoxyethane for those in ethanol) was heated at 40°C. Then propylene was charged at constant pressure. Aliquots were removed at time intervals and analyzed as described above. A glass column (1.5 m × 2 mm) containing LAC 728 (15% on Chromosorb W) stationary phase was also used for GLC analysis, in addition to the Porapak column mentioned above.

RESULTS

Reaction (1) shows the epoxidation of olefinic double bonds:



(1)

Reaction (1) is quite general. Ethylene, propylene, butenes, longer chain olefins, allyl alcohol, allyl chloride, and olefins with other functional groups have been epoxidized under mild conditions (*9*). The main limitations to (1) come from the molecular size of both the olefinic reagents and their epoxide derivatives. These must be small enough to diffuse in and out the channels of TS-1, where the catalytic sites are located. Figure 2 shows the epoxidation of propylene in methanol/water solution at 40°C. Under these conditions, the reaction is fast and very selective. After 90 min, 95% of the hydrogen peroxide is consumed, with 90% selectivity

TABLE 1[a]

Epoxidation of Propylene in CH_3OH/H_2O Solvents

N	T (°C)	H_2O_2 (M/Kg)	TS-1 (g/Kg)	t (min)	CH_3OH (wt%)	C_3H_6 (atm)	Selectivity to C_3H_6O (%)	Selectivity to Glycols (%)
1	40	0.99	4.02	72	92	4	94	4
2	40	0.99	6.00	34	92	4	95	5
3	40	0.99	8.00	22	92	4	95	4
4	40	0.99	12.00	11	92	4	93	6
5	40	0.50	7.95	18	92	4	96	3
6	40	1.75	7.95	60	92	4	90	8
7	20	0.99	7.90	50	92	4	97	2
8	60	0.99	7.90	11	92	4	88	10
9	40	0.99	8.00	33	92	4	[b]	
10	40	0.99	8.00	56	52	4	90	9
11	50	0.99	8.00	30	52	6	90	8
12	50	0.99	8.00	22	52	8	89	9
13	50	0.99	8.00	120	25	8	75	

[a] See experimental section for reaction conditions. Selectivity and reaction times are referred to 90% H_2O_2 conversion.

[b] Propylene oxide, 0.75 *M*/kg, is added since the beginning of the reaction.

to propylene oxide. Propylene glycol and its monomethyl ethers are the main by-products, in addition to small amounts of formaldehyde. The latter comes from the oxidation of methanol solvent. We did not detect other by-products which may have come from the allylic oxidation of propylene. The decomposition of hydrogen peroxide to oxygen is also negligibly small. This result is significant, because metal-catalyzed epoxidations are often accompanied by radical decomposition of the peroxide reagent, forming oxygen and a variety of organic by-products (*12*).

The epoxidation reaction is best carried out in solvents which are able to dissolve both propylene and hydrogen peroxide. Examples are lower alcohols, ketones, esters, acetonitrile, and their mixture with water. The solvent has an important effect on the outcome of the reaction, i.e., on yields, by-product formation, and reaction kinetics (Fig. 3).

Precautions should be taken with acetone and other ketones because they can quite easily form hazardous peroxides with hydrogen peroxide (*13*). In competition with the epoxidation of C_3H_6, partial oxidation may convert primary and secondary alcohols to their corresponding aldehydes and ketones, (*10b, 10f, 14*). The extent of these

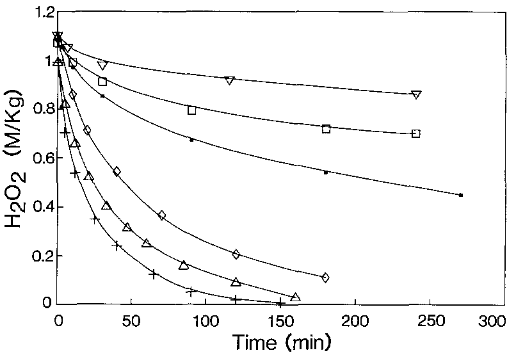


FIG. 3. Epoxidation of propylene in organic solvent/water mixtures. Hydrogen peroxide concentration is plotted against time. Reaction conditions: T = 40°C, TS-1 0.4 wt%, $P_{C_3H_6}$ = 4 atm. (+) CH_3OH 92 wt%, (△) CH_3OH 52 wt%, (◇) ethanol 88 wt%, (■) methyl acetate 90 wt%, (□) acetonitrile 88 wt%, (▽) *t*-butyl alcohol 88 wt%. In ethyl alcohol considerable amounts of acetaldehyde are formed in addition to propylene oxide.

reactions depends on the nature of the alcohol and on the reaction conditions. Reaction kinetics make unattractive acetonitrile, water, *t*-butanol, and methyl acetate solvents (Fig. 3).

Methanol is the best reaction medium for the epoxidation of propylene. The reagents and the products are very soluble, the main reaction is fast, and only negligible amounts of formaldehyde are produced. However, for practical reasons we have normally used aqueous methanol. Water is both added with the hydrogen peroxide solution and formed during the reaction. Furthermore, small amounts of H_2O have only minor effects on the epoxidation reaction (Table 1, Fig. 3). The rate of the reaction decreases considerably only above 50 wt% water concentration (Table 1, experiments 3, 10 and 12, 13). Nevertheless, the epoxidation of propylene proceeds, at a low rate, even in aqueous solutions of hydrogen peroxide (3–7 wt%), as long as the slurry is efficiently stirred to facilitate gas–liquid contact.

Comparison of the activities of homogeneous and heterogeneous catalysts is difficult because the number of active sites and their specific activities are not so well defined for the latter. Moreover, reaction conditions are generally different. However TS-1 appears to have a higher activity than other oxidation catalysts. The epoxidation of propylene proceeds faster and at lower temperatures with TS-1 and hydrogen peroxide (Table 1, Fig. 2) than with Mo or TiO_2/SiO_2 and hydroperoxides (*16*). Under the conditions of experiment 4 (Table 1), the initial rate of reaction is such that 1.7 mol of H_2O_2 are converted per gram of catalyst per hour.

It is not necessary to use concentrated solutions of hydrogen peroxide, as with metal oxide-based catalysts (*4*). With TS-1 the epoxidation of propylene is fast even in dilute solutions. Concentrations of H_2O_2 as low as 1% have been satisfactorily used (Table 1). Preliminary data suggest a reaction order between zero and unity in hydrogen peroxide, approaching zeroth order at the highest H_2O_2 concentrations.

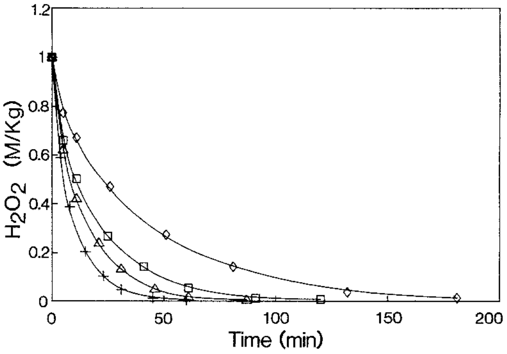


FIG. 4. Catalyst deactivation as a result of epoxidation of propylene with H_2O_2 in methanol/water solution. Hydrogen peroxide concentration is plotted against time. Reaction conditions: CH_3OH 92 wt%, TS-1 0,8 wt%, $T = 40$°C, $P_{C_3H_6} = 4$ atm. (+) Fresh catalyst, (△) 1st recycle, (□) 2nd recycle, (◇) 5th recycle.

Aging tests on TS-1 were carried out with repeated batch experiments. We used the same catalyst batch over and over again, without regeneration (Fig. 4). The catalytic activity decreases with time on stream, while product distribution and yields change only little. Calcining at 550°C restores the initial catalytic activity. TS-1 may also be regenerated by washing with solvents, somewhat above reaction temperature. This can be done either with methanol or with the solvent which is used in the reaction. Fresh and recovered catalysts have similar activity and physical-chemical properties, i.e., XRD pattern, IR spectra, and chemical composition. This means that titanium loss from the crystalline framework during the reaction and/or during the 550°C calcination is unlikely.

We believe that the most likely cause of deactivation is the deposition of slowly diffusing organic by-products inside TS-1 channels. This explains why high-temperature washings with solvents are sufficient to regenerate the catalyst. The nature of such compounds is not known. However, the epoxidation of 1-butene catalyzed by acid Al-TS-1, Ga-TS-1, and Fe-TS-1 shows that H_2O_2 conversion rate decreases as hydrolysis increases (*17*). In our case, polyethers may be formed from propylene oxide, in addition to propylene glycols. It is likely that they diffuse slowly out of TS-1 and hinder the reagents from reaching the catalytic sites.

We have also investigated whether any of the main reaction products inhibits the epoxidation of propylene. Propylene glycol and its monomethyl ethers have no effect on the course of the reaction, while propylene oxide reduces the rate of epoxidation somewhat (Table 1, experiments 3, 9). Thus to maintain a high reaction rate, propylene oxide, which is the second lowest boiling compound in the reaction mixture after propylene, should be removed. After propylene oxide has been removed, the solvent may be recycled several times without further purification.

TS-1 pretreatment

Binding TS-1 crystals with an inert material forms a catalyst with improved physical and mechanical properties. Silica, which is obtained from the hydrolysis of $Si(OEt)_4$ in the presence of tetrapropyl ammonium hydroxide, is best suited for this purpose. A catalyst prepared from 10% silica and 90% titanium silicalite has the required physical and mechanical properties (*8c*). The binder does not affect the catalytic activity of TS-1. The rate of the reaction remains the same if the amount of TS-1 is the same in pure and bound TS-1 samples (Table 3).

In addition to its outstanding properties in oxidation reactions, TS-1 is also a weak acid. It can hydrolyze propylene oxide in methanol/water solutions to propylene glycol, 1-methoxy-2-propanol, 2-methoxy-1-propanol (Table 2). The oxirane ring may also be cleaved through an uncatalyzed mechanism. However, literature data (*18*) and our work (Table 2) show that this hydrolysis pathway is unimportant below 60°C.

TABLE 2

Spontaneous and Catalyzed Hydrolysis of Propylene Oxide in CH_3OH/H_2O Solutions

T (°C)	$10^5.k^a$ (H_2O 100%)	$10^5.k^a$ (H_2O 23.5%)	$10^5.k^a$ (H_2O 7.5%)	$10^5.k^b$ (H_2O 7.5%)
30	0.114^c	0.024^d	0.016^d	0.049^d
60	2.11^e	0.269^d	0.166^d	—

[a] Rate constants are expressed as s^{-1}.

[b] Rate constants are expressed as liter · $g^{-1} \cdot s^{-1}$. The catalyst is TS-1.

[c] Extrapolated from Refs. (*18*).

[d] Unpublished results of M. G. Clerici.

[e] Reference (*18b*).

The solvolysis of the oxirane ring during the epoxidation of propylene is mainly due to this TS-1 catalyzed side reaction. For this reason, selectivities between 85 and 87% at 96% H_2O_2 conversion level are observed with TS-1 or TS-1/SiO_2 catalysts, and 15–17% of product is lost through hydrolysis reactions (Table 3). We have improved propylene oxide yields by treating TS-1 or TS-1/SiO_2 with dilute solutions of a basic compound, e.g., sodium acetate. After this pretreatment, selectivities to propylene oxide up to 97% have been reached at 97% H_2O_2 conversion level (Table 3). The exact role of sodium ions or other basic compounds is not known here. One possible explanation is the neutralization of weakly acidic Si–OH groups (*16*), present on defective TS-1 sites.

TABLE 3[a]

Epoxidation of Propylene in CH_3OH/H_2O 52% and Effect of TS-1 Pretreatment

t (min)	H_2O_2 (Conv.%)	Selectivity to	
		C_3H_6O (%)	Glycols (%)
70^b	96	87	11
70^c	96	85	13
70^c	97	97	3

[a] $T = 50°C$, $P_{C_3H_6} = 8$ atm, H_2O_2 0.99 M/kg, TS-1 8.2 g/kg.

[b] TS-1.

[c] TS-1/SiO_2 90%.

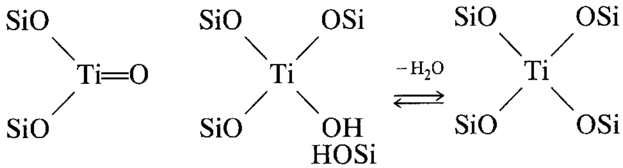
[d] TS-1/SiO_2 90% pretreated with sodium acetate.

DISCUSSION

The catalytic performance of titanium silicalite in epoxidation reactions differs from that of other catalysts based on Group IV–VI metal oxides. Polar solvents, particularly water and alcohols, compete for the active coordination sites of the latter. Therefore they should be avoided. The reaction is usually carried out above 80°C and *t*-butyl hydroperoxide (TBHP) is the oxidant of choice (*12, 16a*).

With TS-1, however, methanol and methanol/water mixtures are the solvents of choice, and the reaction is performed near room temperature. The best oxidant is hydrogen peroxide while TBHP is almost unreactive. Note that the TiO_2/SiO_2 Shell catalyst which is active for the epoxidation of propylene with hydroperoxides (*16a, 16b*), behaves more like the Group IV–VI oxide catalysts and not like TS-1.

TBHP is probably uneffective in TS-1 because it is too large to react in its less than 0.6-nm pores. Notari (*10e*) and Boccuti *et al.* (*19*) have suggested that TS-1 has structures (I)–(III), while Sheldon proposed structure (I) for TiO_2/SiO_2 (*16*).



(I) (II) (III)

In the absence of steric hindrance any of these Ti structures would coordinate TBHP molecules. The resulting Ti(TBHP) intermediate should be able to react with the olefin in the epoxidation step. This kind of mechanism is well established for Group IV–VI metal oxide-based catalysts, including TiO_2/SiO_2 (*20*). However, in TS-1 the Ti is located in channels with an average diameter of 0.55 nm. It is thus unlikely that a Ti(TBHP) species could be formed in TS-1. Furthermore, there is no space inside the channels to form the transition state complex between Ti–OOR and the olefin.

It is not easy to understand why TS-1 is so active in methanol/water, a solvent otherwise known to inhibit metal oxide catalysts. Two hypotheses can be made.

(1) Because of its organophilic character, TS-1 preferentially adsorbs the less polar H_2O_2 and olefin molecules. This decreases competition from water and methanol.

(2) The $Ti(H_2O_2)$ species has a different and more reactive structure on TS-1 than on TiO_2/SiO_2 or with soluble metal complexes. This might arise through interactions of $Ti(H_2O_2)$ complex with a solvent molecule and lattice SiO-bonds. Preliminary results show that a titanium hydroperoxo species is most likely formed in methanol solutions of hydrogen peroxide.

A study is in progress on the interactions between lattice Ti, H_2O_2, and the solvent, from which a better understanding of the catalytic properties of TS-1 is expected.

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