Epoxidation of allyl alcohol to glycidol using titanium silicalite TS-1: effect of the reaction conditions and catalyst acidity

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The epoxidation of allyl alcohol to glycidol using the titanium silicalite TS-1 with hydrogen peroxide as the oxidant is described and discussed in detail. The reaction conditions (alcohol, solvent, temperature) required to obtain 100% selectivity to glycidol are described and this selectivity has been observed at conversions of allyl alcohol of up to 20%. Addition of excess hydrogen peroxide enhances conversion but does not appear to affect selectivity to glycidol deleteriously, whereas addition of hydrogen peroxide over an extended time period is not particularly beneficial. The major side reactions are the oxidation of the alcohol solvent and the ring opening solvolysis of the glycidol that leads to the formation of alkoxy diols. Base treatment of the TS-1 using sodium azide enhances the glycidol selectivity, whereas the incorporation of Brønsted acid sites by addition of aluminium into the framework structure of TS-1 enhances the selectivity to the products of solvolysis ring opening reactions.

Keywords: titanium silicalite TS-1; hydrogen peroxide as oxidant; allyl alcohol epoxidation; glycidol

1. Introduction

A number of studies have demonstrated that alkenes can be readily epoxidised by hydrogen peroxide using the titanium silicalite TS-1 [1–3]. However, it has been found that substitution of the alkene by electron withdrawing groups decreases significantly the reactivity of the carbon–carbon double bond since the decrease of the electron density renders it less susceptible to nucleophilic attack by the oxidant. This was recently illustrated by Clerici and Ingallina [4] when it was shown that the rates of epoxidation of allyl chloride and allyl alcohol were ca. 14 and 30 times slower respectively than the rate of 1-butene epoxidation. It is therefore of interest to determine how the epoxidation of allyl alcohol can be achieved and how the selectivity to the solvolysis ring opening reactions of the epoxide, which are noted to be the major route to by-product formation [4], can be controlled. In this paper we describe the reaction conditions required to achieve high selectivity to glycidol and demonstrate that the acidity of the TS-1 is a crucial controlling parameter for selectivity.

2. Experimental

2.1. Preparation of TS-1

Two samples of TS-1 were prepared for this study both with Si/Ti ratio of 25. The first was prepared using a variation on the original method of Taramasso et al. [5] using tetraethyl orthotitanate (TEOTi), tetraethyl orthosilicate (TEOSi) and water as reagents and tetrapropyl ammonium hydroxide (TPAOH) as the template. The detailed procedure has been described previously (catalyst 5 in ref. [6]). The second sample was prepared according to the method of Dwyer et al. [7] using ammonium fluoride, fumed silica, titanium trichloride and distilled water as reagents and tetrapropylammonium bromide (TPABr) as the template. The detailed procedure has been described previously (catalyst 9 in ref. [6]). Both samples were highly crystalline as determined by X-ray diffraction and electron microscopy. The first sample comprised orthorhombic crystallites ca. 0.3 μm in size and the second sample comprised larger monoclinic crystallites ca. 10 μm in size.

2.2. Preparation of Al-TS-1

Two samples of Al-TS-1 were prepared for this study. The first was prepared using a variation of the method of Qui et al. [8] and Dwyer et al. [7] using ammonium fluoride, fumed silica, titanium trichloride, aluminium chloride and distilled water as the reagents and tetrapropylammonium bromide (TPABr) as the template. Fumed silica (6.0 g, Scintron) was added to water (9.0 g) and mixed thoroughly to form a smooth paste. TPABr (13.3 g, Aldrich) dissolved in water (40.0 g) was added slowly with stirring to the silica paste to form a gel. A solution of ammonium fluoride (5.5 g) in water (15.0 g) was then added with stirring to the gel and subsequently titanium trichloride (1.1 g as a 30% solution in hydrochloric acid) and aluminium chloride (0.31 g as a 30% solution in hydrochloric acid) were added to give a Si/Ti ratio = 50 and a Si/Al ratio = 50. The gel was then aged for 24 h and was then placed in a static Teflon lined stainless steel autoclave and maintained at 175°C for 120 h. The product was then recovered by filtration, washed with distilled water, dried and calcined (6 h, 550°C).

The second sample of Al-TS-1 was prepared by a variation of the method of Thangaraj et al. [9] using tetrabutyl orthotitanate (TBOTi), TEOSi, aluminium isopropoxide and water as reagents and TPAOH as the template. TEOSi (45.0 g) was added slowly to TPAOH (80.0 g) and stirred for 30 min. To this solution TBOTi (2.25 g) dissolved in isopropyl alcohol (10.0 g) was slowly added with stirring at 60°C followed by the subsequent addition of aluminium isopropoxide (1.02 g) and stirred for 2 h to give a gel (Si/Ti = 33 and Si/Al = 43). Following the addition of deionised water (75 g) the gel was then heated at 160°C in a Teflon lined stainless steel autoclave for 72 h. The product was recovered by filtration, washed with distilled water, dried and calcined (6 h, 550°C).

2.3. Catalyst testing

The epoxidation reaction was carried out in a flask fitted with a stirrer, thermometer, a reflux condenser and a septum to enable samples to be withdrawn for analysis. In a typical experiment TS-1 (0.5 g) was stirred with allyl alcohol (0.1 mol), hydrogen peroxide (0.1 mol, 70%) in a solvent (45 ml) at a constant temperature for 24 h. The course of the reaction was monitored by GC and the final reaction products were analysed by GCMS and ^{13}C NMR spectroscopy.

Table 1
Epoxidation of allyl alcohol using TS-1

Solvent	Temp (°C)	Time (h)	Conv.[a] (%)	Product selectivity (mol%)			
				glycidol	3E12PD	2E13PD	glycerol
methanol	20	2	2.8	100	0	0	0
		4	4.2	100	0	0	0
		6	8.0	100	0	0	0
		24	20.2	97.5	2.5	0	0
	50	2	20.5	98.1	1.9	0	0
		4	25.8	96.0	4.0	0	0
		8	47.8	89.6	9.6	0.8	0
		24	58.1	71.4	25.9	2.7	0
	65	2	42.1	95.0	3.9	1.1	0
		4	52.1	87.1	10.9	2.0	0
		6	55.4	83.9	13.6	2.5	0
		24	75.3	62.0	30.0	7.0	1.0
ethanol	20	24	5.0	100	0	0	0
	50	2	15.0	100	0	0	0
		4	18.2	94.3	4.5	1.2	0
		6	20.0	86.7	10.8	2.5	0
		24	35.0	77.0	17.0	6.0	0
	65	2	46.6	64.4	28.1	7.5	0
		4	56.5	52.8	38.8	8.5	0
		8	57.4	36.0	48.0	14.8	1.0
		24	60.2	10.9	71.1	16.6	1.4
t-butanol	20	24	0	–	–	–	–
	50	24	0	–	–	–	–
	65	24	4.3	100	0	0	0

[a] Allyl alcohol conversion

3. Results

3.1. Effect of reaction conditions on allyl alcohol epoxidation

Allyl alcohol and hydrogen peroxide were reacted in a range of alcohol solvents and at three temperatures: 20, 50 and 65°C. The results, shown in table 1, indicate that the highest conversions and glycidol selectivities were obtained using methanol as solvent. In particular, 100% selectivity to glycidol can be achieved at 20% allyl alcohol conversion at 20°C. Increasing the carbon number of the alcohol solvent decreased the reactivity of allyl alcohol and for ethanol an increase in the products of the epoxide solvolysis ring opening was also observed. With *t*-butanol no reaction was observed at 20 and 50°C even after 24 h.

The effect of variation in the concentration of hydrogen peroxide was investigated for the reaction in ethanol at 65°C. For the reaction of equimolar concentrations of allyl alcohol and hydrogen peroxide, the conversion of allyl alcohol does not increase significantly after a reaction time of 4 h (table 1) indicating that the hydrogen peroxide was being rapidly consumed under these conditions. Addition of the same amount of hydrogen peroxide steadily over the first 4 h reaction period resulted initially in lower allyl alcohol conversion, as would be expected from the decreased hydrogen peroxide concentration, together with increased selectivity to glycidol (table 2). Stepwise addition of the hydrogen peroxide gave a slightly higher allyl alcohol conversion after 24 h reaction. Increasing the hydrogen peroxide concentration (2 mol/mol allyl alcohol) increased the allyl alcohol conversion markedly but resulted in lower glycidol selectivity (table 2).

As noted in previous studies [10] a possible side reaction involves the oxidation of the solvent catalysed by TS-1. In this study these side reactions were also observed but only to a minor extent. With methanol as the solvent low levels of formaldehyde and dimethoxy methane were observed. With ethanol as solvent at > 20°C these by-products comprised predominantly diethoxy ethane and acetaldehyde together with trace amounts of acetic acid.

3.2. Modification of TS-1 by base treatment

TS-1 was treated with sodium carbonate solution (0.1 mol ℓ^{-1}, 25°C) and this resulted in an almost total loss of catalytic activity although the only product formed was glycidol even though ethanol was used as solvent (table 3). TS-1 was then treated with sodium azide solutions with a range of concentrations (table 3) and although the reaction rate was decreased by this treatment, high selectivities to glycidol could be achieved.

3.3. Allyl alcohol epoxidation using Al-TS-1

Two samples of Al-TS-1, i.e. silicalite incorporating Ti and Al atoms within the framework, were prepared. The first sample, prepared according to the fluoride procedure, was found by X-ray diffraction to be well crystalline with the silicalite framework structure. Electron microscopy showed that the material comprised irregular monoclinic crystallites ca. 10 μm in size (fig. 1a). However, elemental analysis indicated that only trace levels of titanium had been incorporated into the structure. In addition, there was no band at 960 cm^{-1} in the infrared spectrum (fig. 2a). This material showed very little catalytic activity even at 65°C (table 4) and the products of the reaction of allyl alcohol were only the solvolysis products of glycidol, i.e. 3-ethoxy-1,2-propanediol (3E12PD) and 2-ethoxy-1,3-propanediol (2E13PD). This activity is much lower than that obtained for an equivalent preparation with the absence of Al (table 4).

A sample of Al-TS-1 was synthesised using the modi-

Table 2
Effect of hydrogen peroxide addition on allyl alcohol epoxidation using TS-1 [a]

Method [b]	Time (h)	Conv. [c] (%)	Product selectivity (mol%)			
			glycidol	3E12PD	2E13PD	glycerol
1	2	22.6	84.5	12.4	3.1	0
	4	30.7	83.7	12.7	3.6	0
	6	43.8	75.6	19.2	5.2	0
	24	67.3	43.4	47.7	8.9	0
2	2	81.7	50.4	40.5	9.9	0
	4	90.1	40.5	43.8	13.7	2.0
	8	96.7	18.2	61.0	17.6	3.2
	24	100	2.0	72.4	20.6	5.0

[a] Reaction at 65°C using ethanol solvent.
[b] Method 1: hydrogen peroxide (1 mol/mol allyl alcohol) added stepwise over initial 4 h; method 2: hydrogen peroxide (2 mol/mol allyl alcohol) added at the start of the reaction.
[c] Allyl alcohol conversion.

Table 3
Allyl alcohol epoxidation using modified TS-1 [a]

Treatment [b]	Time (h)	Conv. [c] (%)	Product selectivity (mol%)			
			glycidol	3E12PD	2E13PD	glycerol
0.1M Na_2CO_3	24	2.0	100	0	0	0
2.0 M NaN_3	2	0.5	100	0	0	0
	4	1.4	100	0	0	0
	6	2.7	100	0	0	0
	24	13.4	89.0	11.0	0	0
1.0 M NaN_3	2	1.5	100	0	0	0
	4	3.3	100	0	0	0
	6	5.7	100	0	0	0
	24	22.7	88.6	11.4	0	0
0.1 M NaN_3	2	3.8	100	0	0	0
	4	5.7	100	0	0	0
	6	9.3	96.7	3.3	0	0
	24	21.5	56.9	38.1	5.0	0

[a] Reaction at 65°C using ethanol solvent.
[b] TS-1 (1.0 g) was treated with the solution specified (50 ml) at 25°C, filtered, dried and calcined at 500°C.
[c] Allyl alcohol conversion.

fied Thangaraj procedure described previously. X-ray diffraction showed the material to be well crystalline with the silicalite structure. Electron microscopy showed the material to comprise regular orthorhombic crystallites ca. 0.3 μm in size (fig. 1b). Elemental analysis indicated that Al and Ti were both incorporated (Si/(Al + Ti) = 25, Al/Ti = 1) Al MAS NMR showed a single resonance at $\delta = 56$ ppm, relative to $Al(OH)_3$ as standard, which is indicative of Al in a tetrahedral environment. The infrared spectrum exhibited a band at 960 cm^{-1} (fig. 2a). As synthesised the material was in the potassium form and demonstrated < 1% allyl alcohol conversion at 65°C after 24 h reaction. After ion exchange with ammonium nitrate and calcination the Al-TS-1 was found to be an active catalyst (table 4) and the products derived from allyl alcohol were exclusively the solvolysis products 2E13PD and 3E12PD. Glycidol was not observed as a product even though it must have been formed initially within the microporous environment since the solvolysis products could not otherwise have been formed (fig. 3).

4. Discussion

Allyl alcohol represents a particularly difficult substrate for epoxidation since the hydroxyl substituent α to the carbon–carbon double bond withdraws electron density from the double bond rendering it less susceptible to epoxidation by an electrophilic oxidation reagent. Hence the conditions required for allyl alcohol epoxidation are more severe than substrates not containing such a substituent. This point was recently illustrated by Clerici and Ingallina [4] who noted that the relative rates of epoxidation of 1-butene, allyl chloride and allyl alcohol were 1 : 0.071 : 0.033 respectively. Under the more severe reaction conditions required for the epoxidation another problem is encountered in that the resultant epoxide is more susceptible to nucleophilic attack by the solvent, e.g. by water to form glycerol and alcohols to form ether diols. Indeed, the hydrolysis reaction dominated early attempts [5] at allyl alcohol epoxidation since only glycerol was obtained. However, the results of the present study show that under appropriate conditions high selectivities to either glycerol or the ether diol solvolysis products can be achieved for this reaction using TS-1 or a modified TS-1. Even though we specifically set out to reproduce the early studies using *t*-butanol [5], using our samples of TS-1, glycerol was not observed and even at 65°C glycidol was the only product from allyl alcohol although the conversion was only 4.3% after 24 h. The low reactivity of these studies using *t*-butanol can be explained by considering the stereochemistry of the intermediate involved in the epoxidation reaction. According to Clerici and Ingallina [4] the most probable active species involves an adduct between TS-1, hydrogen peroxide and the alcohol to form a cyclic species **I** (scheme 1). In this case the interaction of **I** with allyl alcohol in the required geometry to epoxidise the double bond would be expected to be sterically hindered in the channel structure of TS-1. Hence with *t*-butanol as solvent due to the steric restrictions it is anticipated that most of the reaction must occur on the external crystallite surface and not within the micropores. Van der Pol and van Hooff [11] have found that the use of large peroxides such as *t*-butyl hydroperoxide does not lead to hydroxylation of phenol in the presence of TS-1 due to steric constraints, which provides further support for this conclusion. In addition,

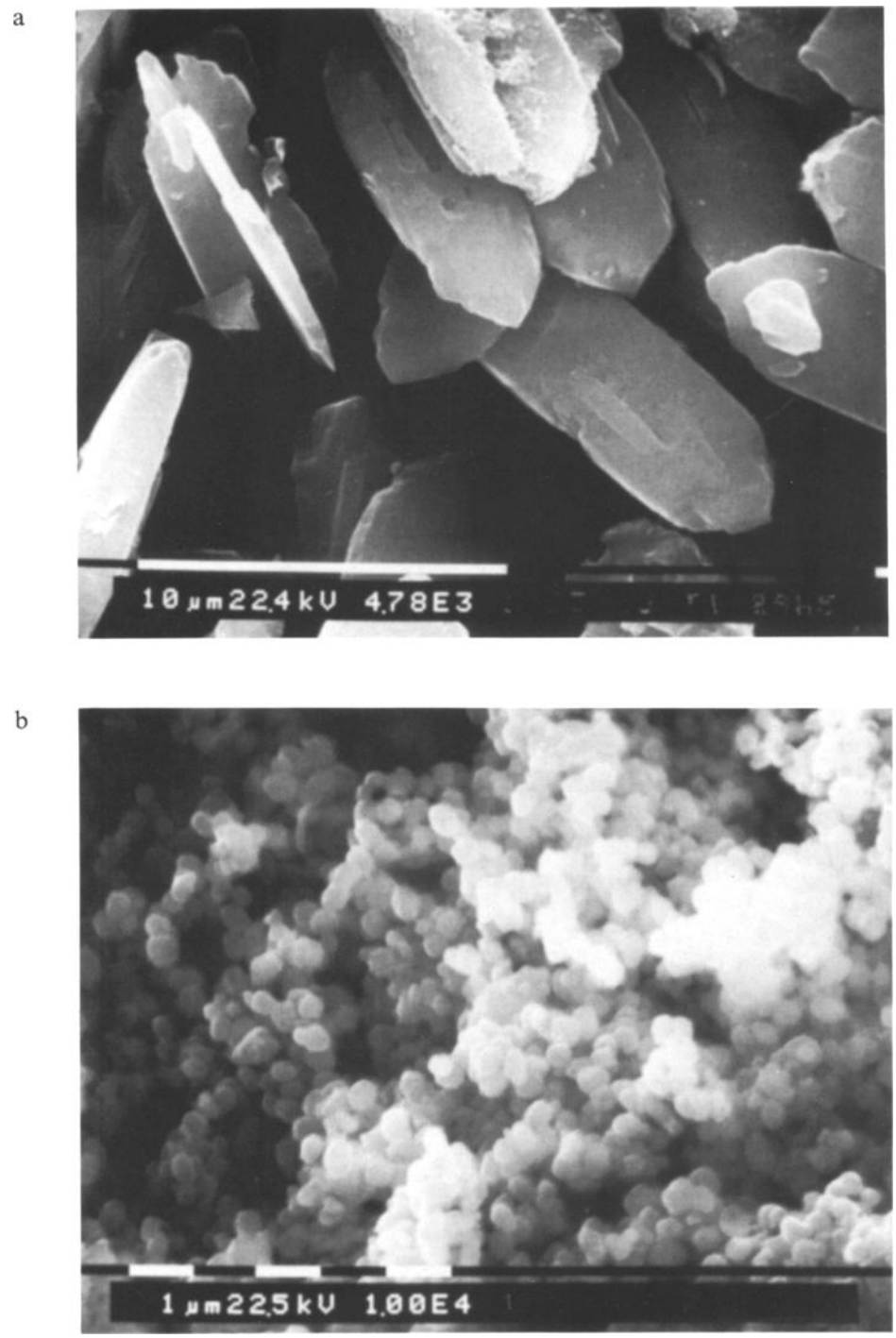


Fig. 1. Electron micrographs of Al-TS-1 (a) prepared by the fluoride method and (b) prepared by the modified Thangaraj method.

electronic factors may also play a role since the three methyl groups of the *t*-butanol would be expected to donate more electron density via the inductive effect in comparison to a primary alcohol, e.g. ethanol and methanol. This effect could reduce the electrophilicity of the catalytic species **I** leading to decreased reactivity for a substrate requiring a highly electrophilic oxidant.

Decreasing the carbon number of the alcohol resulted in a significant increase in the rate of allyl alcohol epoxidation. A low conversion of allyl alcohol to glycidol was noted at 20°C and significant conversions could be achieved at 50 and 65°C, although the ether diols became the dominant products. In general the relative rate of allyl alcohol epoxidation increased in the order

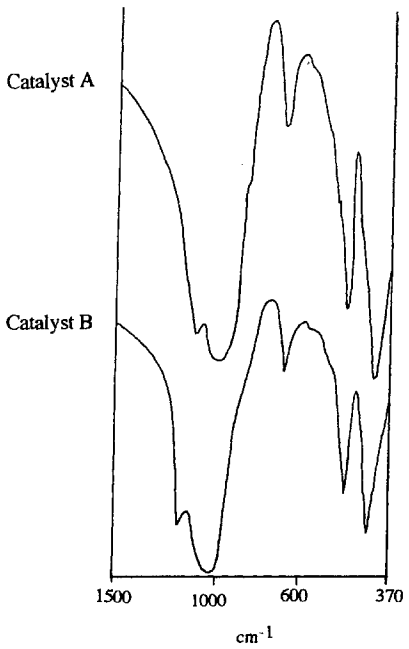


Fig. 2. Infrared spectra of Al-TS-1 (a) prepared by the fluoride method and (b) prepared by the modified Thangaraj method.

t-butanol < ethanol < methanol as solvent. This is in agreement with the steric factors discussed previously and with the results for the epoxidation of simpler substrates [4]. In addition the rate of ether diol formation increased in the order *t*-butanol < methanol < ethanol as solvent. For *t*-butanol lack of ether diol formation is due to steric factors whereas the difference in reactivity for methanol and ethanol is due the higher nucleophilicity of ethanol. In a separate experiment the addition of glycidol to ethanol at 65°C in the absence of TS-1 did not result in the formation of ether diols and hence the solvolysis reaction is catalysed by TS-1 possibly involving an acidic site created by the interaction of hydrogen peroxide with TS-1. Experiments where the concentration of hydrogen peroxide was increased indicate that the rates of both epoxidation and solvolysis were enhanced when ethanol was used as solvent. Such an effect is consistent with the formation of a five-membered ring intermediate **II** (scheme 2) formed between TiOOH and the solvent which could be expected to act as a Brønsted acid.

Further evidence for the importance of an acid site formed by TS-1 and hydrogen peroxide in the epoxidation reaction is obtained from the experiments involving the modification of TS-1 with sodium carbonate and sodium azide. This results in an enhancement in glycidol selectivity at the expense of the ether diol products, the magnitude of the effect being dependent on the concentration of the reagent.

The introduction of Brønsted acid sites by the addition of framework Al atoms into TS-1 also provides evidence on the role of acidity. For Al-TS-1, glycidol is not observed as a product and the ether diols are the exclusive products resulting from allyl alcohol epoxidation. This experiment demonstrates the usefulness of a bifunctional acidic oxidation catalyst since it permits the formation of the secondary reaction products. Hence, by controlling the concentration and nature of the acid sites in TS-1 it is possible to achieve control over the selectivity for both the exclusive formation of the primary epoxide product as well as the secondary solvolysis products. It is interesting to note that Al-TS-1 exhibits a lower overall rate of allyl alcohol epoxidation when

Table 4
Allyl alcohol epoxidation using Al-TS-1 [a]

	Size (μm)	Time (h)	Conv. [b] (%)	Product selectivity (mol%)			
				glycidol	3E12PD	2E13PD	glycerol
TS-1 [c]	10	2	3.4	100	0	0	0
Al-TS-1 [c]	10	24	28.3	27.9	54.5	17.6	0
		6	1.3	0	75.0	25.0	0
		12	1.8	0	68.4	31.6	0
		24	3.2	0	68.7	31.3	0
TS-1 [d]	0.3	2	23.7	87.3	12.7	0	0
		4	29.2	79.0	21.0	0	0
		8	33.8	68.9	31.3	0	0
		24	54.7	39.5	60.5	0	0
Al-TS-1 [d]	0.3	2	3.8	0	60.5	39.5	0
		6	25.0	0	59.7	40.3	0
		24	43.0	0	68.0	32.0	0

[a] Reaction in ethanol at 65°C.
[b] Allyl alcohol conversion.
[c] Prepared using the fluoride method.
[d] Prepared using a modification of the method of Thangaraj et al. [9].

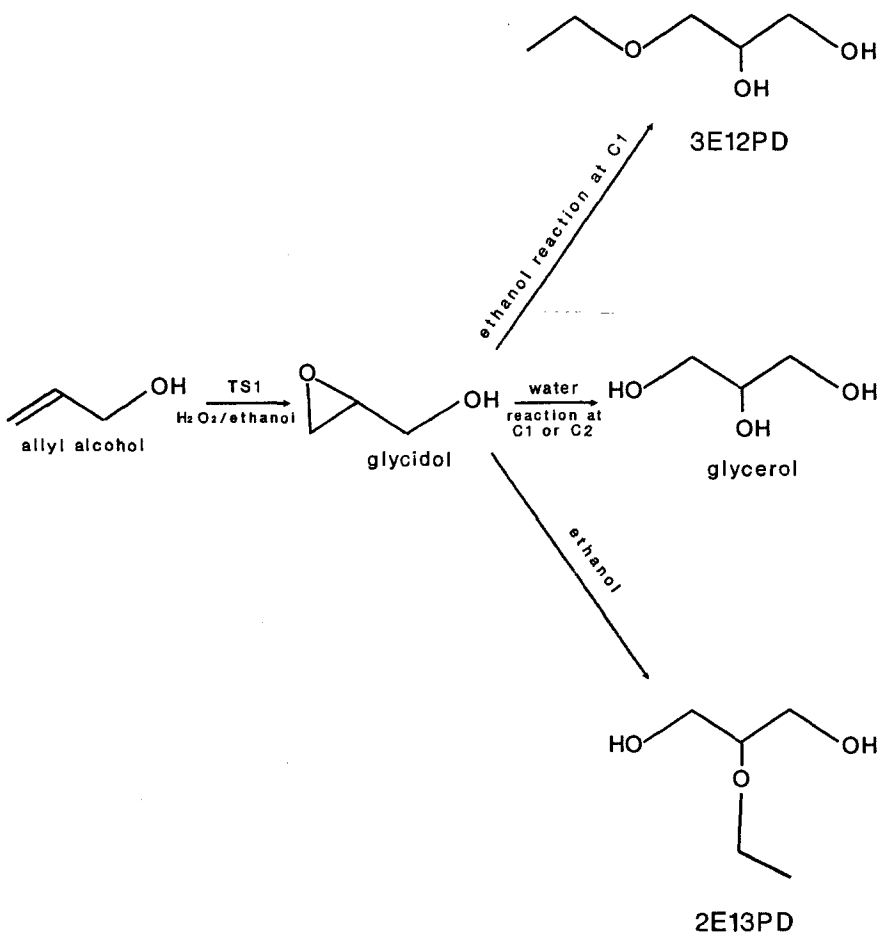
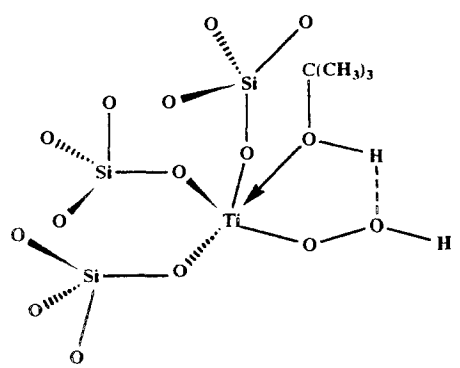


Fig. 3. Reaction scheme.

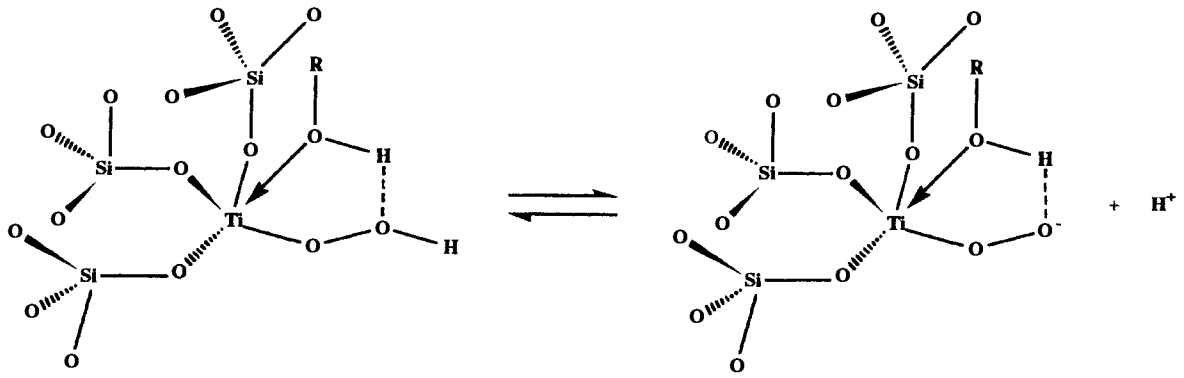
compared with TS-1 at the same reaction conditions. This effect is not due to a morphological effect since Al-TS-1 and TS-1 samples with the same morphologies have been examined, ca. 0.3 μm orthorhombic crystallites from the modified Thangaraj method and ca. 10 μm crystallites from the fluoride method, and a consistent decrease in reaction rate was observed. It is therefore clear that should the epoxide be required as the exclusive product at high reaction rate then Al should be rigorously excluded from the TS-1 synthesis. It is interesting to note that Clerici and Ingallina [4] showed an increase in the rate of epoxidation of alkenes occurred on addition of dilute hydrochloric acid. However, the origin of this rate enhancement must be related to a different effect than the action of Brønsted acid sites introduced via framework Al.



I

Scheme 1.

The position of the ring opening of the glycidol oxirane ring on solvolysis with ethanol is also dependent on the acidity of the TS-1. In the absence of TS-1 the solvolysis reaction under basic conditions would be expected to give 3E12PD whereas under acidic conditions the expected product is 2E13PD. In this study this is observed since the treatment of TS-1 with sodium azide does lead to an increase in the selectivity of 3E12PD relative to 2E13PD (table 3). In addition, the incorporation of Brønsted acid sites in Al-TS-1 leads to an enhancement in the formation of 2E13PD, as would be expected from the enhanced acidity (table 4). However, 2E13PD remains the minor solvolysis product relative to 3E12PD and this is considered to be a result of shape selectivity of the microporous catalyst. In the



II

Scheme 2.

0.55 nm channel structure of TS-1 and Al-TS-1 the formation of 2E13PD would be expected to be sterically hindered when compared with the linear 3E12PD molecule.

No attempt has been made in this study to optimise the yields of the products but it is apparent that by appropriate choice of reaction conditions, TS-1 morphology and modification procedures, allyl alcohol can be readily epoxidised using hydrogen peroxide as oxidant.

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