Control of Product Selectivity for the Epoxidation of Allyl Alcohol by Variation of the Acidity of the Catalyst TS-1

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The acidity of TS-1 controls the product selectivity for the epoxidation of allyl alcohol with H_2O_2; base treatment of TS-1 enhances the selectivity to glycidol whereas incorporation of Brønsted acid sites enhances the selectivity to the products of solvolysis ring opening reactions.

The microporous titanium silicalite TS-1 has attracted considerable research attention since it was found to be an effective epoxidation catalyst when used with hydrogen peroxide as oxidant.[1] Initial studies showed that propene could be converted almost quantitatively to propene oxide at near ambient temperature and with dilute solutions of hydrogen peroxide.[2] Subsequently TS-1 has been found to be active for a range of oxidation reactions, *e.g.* the hydroxylation of phenol[3] and the ammoxidation of cyclohexanone.[4] Recently Tatsumi *et al.*[5] have shown that the incorporation of palladium into TS-1 permits the use of hydrogen–oxygen mixtures as the oxidant, presumably by the *in situ* formation of hydrogen peroxide as has been previously disclosed by Gosser.[6] Interestingly, although the epoxidation of a broad range of alkenes and substituted alkenes was described in the early work, the epoxidation of allyl alcohol to glycidol was not discussed. Clerici and Ingallina[7] have recently described a detailed study of the epoxidation of lower alkenes and have demonstrated that allyl alcohol epoxidation to glycidol was also possible, but at much lower selectivity and conversion when compared with other epoxidations. In general the presence of electron withdrawing substituents decreases the yield of the epoxide and the epoxidation of allyl alcohol therefore represents one of the most demanding reactions attempted with TS-1. Hence it is of interest to discover how this difficult epoxidation can be achieved at high selectivity and the secondary solvolysis reactions, which are noted to be the major route to byproduct formation,[7] can be controlled. We have now successfully addressed this problem and in this communication we demonstrate that the acidity of the TS-1 is a crucial controlling parameter that enables high product selectivity to be achieved.

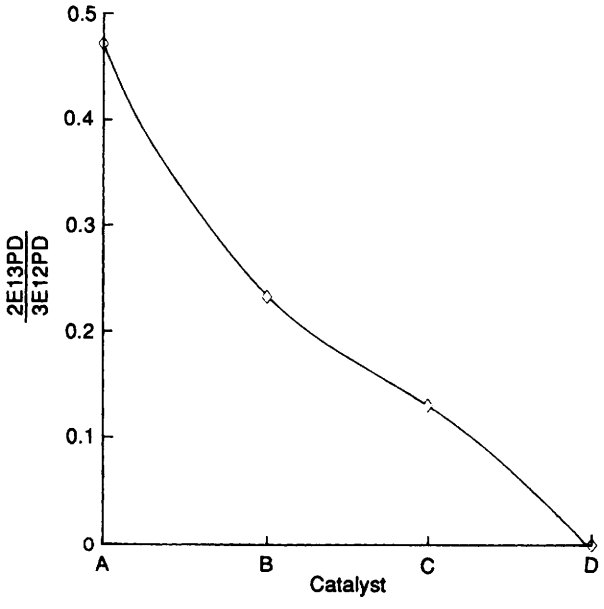
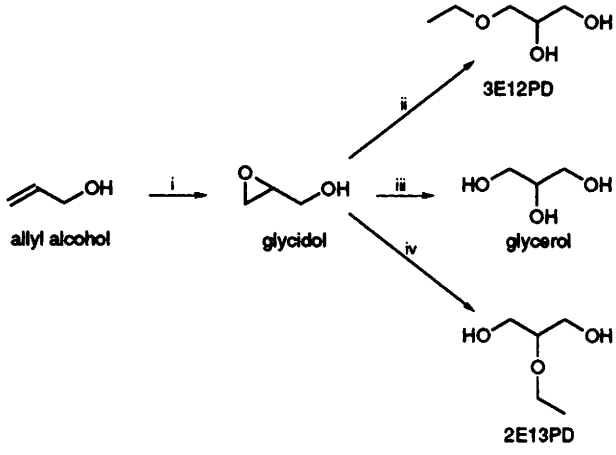


Fig. 1 Selectivity of the solvolysis products at 65 °C using ethanol as solvent, reaction time 24 h. Catalyst key: A Al-TS-1; B TS-1; C TS-1 treated with 0.1 mol l^{-1} NaN_3; D TS-1 treated with 1.0 mol l^{-1} NaN_3.

TS-1 was prepared according to the method of Notari *et al.*[8] with the ratio Si:Ti = 25. The TS-1 was found to be highly crystalline by powder X-ray diffraction and electron microscopy showed the material comprised uniform monoclinic 0.3–0.4 μ crystals. The effect of the reaction conditions on allyl alcohol epoxidation were initially investigated with this



Scheme 1 *Reagents and Conditions*: i, TS-1, H_2O_2/ethanol, ii, ethanol (reaction at C-1); iii, water (reaction at C-1 or C-2); iv, ethanol (reaction at C-2)

Table 1 Epoxidation of allyl alcohol using TS-1[a]

			Product Selectivity/mol%[c]		
T/°C	*t*/h	Conversion[b] (%)	Glycidol	3E12PD	2E13PD
20	2	2.8	100	0	0
	4	4.2	100	0	0
	6	8.0	100	0	0
	24	20.2	97.5	2.5	0
50	2	20.5	98.1	1.9	0
	4	25.8	96.0	4.0	0
	8	47.8	89.6	9.6	0.8
	24	58.1	71.4	25.9	2.7
65	2	42.1	95.0	3.9	1.1
	4	52.1	87.1	10.9	2.0
	6	55.4	83.9	13.6	2.5
	24	75.3[d]	62.0	30.0	7.0
50[e]	2	15.0	100	0	0
	4	18.2	94.3	4.5	1.2
	6	20.0	86.7	10.8	2.5
	24	35.0	77.0	17.0	6.0
65[e]	2	46.6	64.4	28.1	7.5
	24	60.2[f]	10.9	71.1	16.6
20[g]	24	0	—	—	—
50[g]	24	0	—	—	—
65[g]	24	4.3	100	0	0

[a] Solvent used MeOH unless stated otherwise. [b] Allyl alcohol conversion. [c] Product selectivity (PS) for glycerol = 0 mol% unless stated otherwise. [d] PS for glycerol = 1.0 mol%. [e] Solvent used EtOH. [f] PS for glycerol = 1.4 mol%. [g] Solvent used Bu^{t}OH.

sample of TS-1. In a typical experiment allyl alcohol (5.8 g) was added to a solution of hydrogen peroxide (70%, 4.9 g) in solvent (60 g). TS-1 (1.0 g) was then added and the mixture was stirred for 24 h at the required temperature. The course of the reaction was monitored using gas chromatography and the final products were also analysed using GCMS and NMR spectroscopy. The results, Table 1, indicate that at low temperature and using methanol as solvent 100% selectivity to glycidol can be achieved. As the temperature and reaction time is increased or the carbon number of the alcohol solvent is increased the formation of the products of glycidol solvolysis becomes apparent and with ethanol as solvent at 65 °C 3-ethoxy-propane-1,2-diol (3E12PD) and 2-ethoxy-propane-1,3-diol (2E13PD) are the major products. Glycerol, the product of glycidol hydrolysis, is only formed in very low yields at the highest temperature investigated. See Scheme 1.

Earlier, Clerici and Ingallina[7] demonstrated that the addition of hydrochloric acid enhanced the reaction rate of but-1-ene epoxidation but they observed that addition of sodium nitrate had no significant effect. Therefore we decided to investigate the effect of base treatment of TS-1 (Table 2). Treatment of TS-1 with sodium carbonate (0.1 mol l^{-1}, 25 °C) resulted in an almost total loss of catalytic activity. At 65 °C using ethanol as solvent the allyl alcohol conversion was only 2% after 24 h although the only product detected was glycidol. This indicates that TS-1 contains a site that can be poisoned by sodium carbonate. This site, which is important for the epoxidation reaction, is probably a weak Brønsted acid site. Two further experiments were carried out in which TS-1 was pre-treated with sodium azide and, although the reaction rate was decreased when compared with TS-1 that had not been pre-treated, high glycidol selectivity could be achieved with this solvent and temperature. In particular, relative to 2E13PD, the selectivity to 3E12PD was also enhanced and it could be obtained as an exclusive by-product.

To investigate the effects of acidity further on the reactivity of TS-1 a sample of Al-TS-1 (Ti + Al = 25, Ti/Al = 1) was prepared by the method of Thangaraj *et al.*[9] Powder X-ray diffraction showed the characteristic diffraction pattern of TS-1 and by electron microscopy the Al-TS-1 was found to comprise uniform monoclinic 0.3–0.4 μ crystals. The ^{27}Al MAS NMR spectrum showed a single sharp signal at δ 51.7 indicating that the Al atoms had been incorporated into the tetrahedral sites in the MFI structure.[10] Hence compared with TS-1, Al-TS-1 contains additional Brønsted acid sites that are associated with the hydroxyl groups adjacent to a framework Al atom. At the same reaction conditions described previously Al-TS-1 was found to give only the solvolysis products 3E12PD and 2E13PD (Table 2). Glycidol was not observed as a reaction product, although it is evident that it must have been formed initially within the microporous environment since the solvolysis product could not otherwise have been formed. This experiment demonstrates the usefulness of bifunctional acidic oxidation catalysts since it permits the exclusive formation of the secondary reaction products of the epoxidation reaction.

It is interesting to note that the position of 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, under basic conditions the solvolysis reaction would be expected to give 3E12PD, whereas under acidic conditions the major product would be expected to be 2E13PD. In this study, base treatment of TS-1 does lead to an increase in the selectivity of 3E12PD relative to 2E13PD as compared to the untreated TS-1 (Fig. 1). In addition, the incorporation of the Brønsted acid sites in Al-TS-1 leads to an enhancement in the formation of 2E13PD, as would be expected from the increased acidity. However, 2E13PD remains the minor by-product and this must be a result of the shape selectivity of the microporous catalyst. The pore size of the MFI structure is *ca.* 0.55 nm and the formation of the branched 2E13PD would be expected to be sterically hindered when compared to the linear 3E12PD molecule.

Although no attempt has been made to optimise the catalytic performance, the results of this study clearly show that the acidity of TS-1 needs careful control if the required product selectivity is to be achieved. In particular, the presence of acid sites promotes the solvolysis reactions and hence to achieve high yields of glycidol from the epoxidation of allyl alcohol such sites must be absent.

Table 2 Allyl alcohol epoxidation at 65 °C using ethanol as solvent[a]

Catalyst	*t*/h	Conversion[c] (%)	Product selectivity/mol%[b] Glycidol	3E12PD	2E13PD
TS-1[d]	24	2.0	100	0	0
TS-1[e]	2	1.5	100	0	0
	4	3.3	100	0	0
	6	5.7	100	0	0
	24	22.7	88.6	11.4	0
TS-1[f]	2	3.8	100	0	0
	4	5.7	100	0	0
	6	9.3	96.7	3.3	0
	24	21.5	56.9	38.1	5.0
TS-1[g]	2	46.6	64.4	28.1	7.5
	4	56.5	52.8	38.8	8.5
	8	57.4[h]	36.0	48.0	14.8
	24	60.2[i]	10.9	71.1	16.6
Al-TS-1[g]	2	3.8	0	60.5	39.5
	6	25.0	0	59.7	40.3
	24	43.0	0	68.0	32.0

[a] TS-1 (1.0 g) was treated with the solution specified (50 ml) at 25 °C, filtered, dried and calcined at 500 °C. [b] PS for glycerol = 0 mol% unless stated otherwise. [c] Allyl alcohol conversion. [d] Treatment: Na_2CO_3 (0.1 mol dm^{-3}). [e] Treatment: NaN_3 (1 mol dm^{-3}). [f] Treatment: NaN_3 (0.1 mol dm^{-3}). [g] No treatment. [h] PS for glycerol = 1.0 mol%. [i] PS for glycerol = 1.4 mol%.

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References

1 C. Neri, B. Anfossi, A. Esposito and F. Buonomo, Eur. Patent 100119, 1984.
2 M. G. Clerici and U. Romano, Eur Patent 100625, 1984.
3 A. Esposito, M. Taramasso, C. Neri and F. Buonomo, UK Patent 2116974, 1985.
4 P. Roffia, M. Padovan, E. Morelti and G. De Alberti, Eur. Patent 208311, 1985.
5 H. Tatsumi, K. Yuasa and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1992, 1446.
6 L. W. Gosser, US Patent 4681751, 1987.
7 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
8 M. Taramasso, G. Perego and B. Notari, US Patent 4410501, 1983.
9 A. Thangaraj, R. Kumar and S. Sivasanker, *Zeolites*, 1992, **12**, 135.
10 R. H. Meinhold and D. M. Bibby, *Zeolites*, 1990, **10**, 74.