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Epoxidation of allyl alcohol to glycidol using titanium silicalite TS-1: effect of the method of preparation

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The epoxidation of allyl alcohol with hydrogen peroxide catalysed by the microporous titanium silicalite TS-1 has been investigated with respect to the effect of the method of catalyst preparation. Three methods of TS-1 synthesis have been studied using the standard tetrapropylammonium cation as template (i) using tetraethyl orthosilicate, tetraethyl orthotitanate as reagents, (ii) using a fluoride method and (iii) using tetrabutyl orthotitanate as the titanium source. The TS-1 samples were characterised by electron microscopy, X-ray diffraction and infrared spectroscopy. The method of preparation controlled the morphology of the TS-1 crystals and in particular the crystallisation time was found to be an important parameter. Data are presented that correlate the activity for the epoxidation of allyl alcohol with the morphology of TS-1. In addition it is found that the catalytic activity of TS-1 for this reaction is not related to the intensity or presence of the infrared absorption band at ca. 960 cm^{-1}.

Keywords: titanium silicalite TS-1 preparation; titanium silicalite TS-1 characterisation; allyl alcohol epoxidation; glycidol

1. Introduction

The microporous titanium silicalite TS-1 has been found to be an effective oxidation catalyst for a range of reactions of interest for the manufacture of fine chemicals. In general, hydrogen peroxide is used as oxidant, and the initial studies [1] showed that propene could be epoxidised by TS-1 with dilute solutions of hydrogen peroxide at near ambient temperature. Subsequently TS-1 has been found to be active for a range of oxidation reactions, e.g. the epoxidation of alkenes [2,3], the

hydroxylation of phenol [4] and the ammoxidation of cyclohexanone [5]. Recently Tatsumi et al. [6] have shown that the incorporation of palladium into TS-1 permits the use of hydrogen/oxygen mixtures as the oxidant.

TS-1 has the MFI structure and is structurally related to silicalite and H-ZSM-5. However, the incorporation of aluminium and titanium into the silicalite framework require different experimental approaches. This is because the basic conditions used in the preparation of silicalite and H-ZSM-5 lead to the formation of insoluble TiO_2 and hence titanium cannot be incorporated using an analogous procedure. A number of methods for the preparation of TS-1 have been described. The most successful of these are described as primary synthesis routes in which the titanium is incorporated directly into the lattice in contrast to secondary synthesis routes when the titanium is introduced at a subsequent stage following the initial synthesis of an MFI structure [7]. The synthesis of TS-1 was first described by Taramasso et al. [8] using tetraethyl orthotitanate as the titanium source. Many modifications of this procedure have been published and these include the use of tetrabutyl orthotitanate, which is claimed by Thangaraj et al. [9] to enable the incorporation of very high concentrations of titanium, up to a molar ratio of Si/Ti = 10, to be achieved. In addition, the fluoride procedures initially developed for the synthesis of MFI zeolites [10] have also been used successfully for the synthesis of TS-1 by Qui et al. [11], Dwyer et al. [12] and Tavolaro et al. [13]. Recently, van der Pol and van Hooff [14] compared a number of different preparation methods for TS-1. In a detailed study they identified a number of preparative parameters that were required for the synthesis of small crystals which were found to be the most active for the hydroxylation of phenol. In this paper we extend these earlier studies and examine the synthesis conditions required to obtain TS-1 in a form effective for the epoxidation of allyl alcohol to from glycidol; this reaction is considered to be one of the most demanding to be demonstrated to date for this material [15].

2. Experimental

2.1. PREPARATION OF TS-1

2.1.1. Preparation using tetraethyl orthotitanate

Catalysts 1–7 were prepared using a variation on the original method of Taramasso et al. [8] using tetraethyl orthotitanate (TEOTi), tetraethyl ortho silicate (TEOSi) and water as reagents and tetrapropyl ammonium hydroxide (TPAOH) as the template. The range of catalysts were prepared by variation in the Si/Ti ratio, crystallisation time and source of the template. The full range of TS-1 preparations is summarised in table 1.

In a typical procedure catalyst 1 was prepared as follows. TEOTi (0.75 g) was added with stirring to TEOSi (22.5 g) and the resulting green solution was aged at

Table 1
Catalyst preparation conditions

Catalyst	Si	Reagents [a] Ti	Template	Gel Si/Ti	Room temp aging (h)	Temp. (°C)	Crystallisation	
							time (h)	stirred
1	TEOSi	TEOTi	TPAOH(S)	40	24	175	24	no
2	TEOSi	TEOTi	TPAOH(S)	40	24	175	55	no
3	TEOSi	TEOTi	TPAOH(S)	40	24	175	240	no
4	TEOSi	TEOTi	TPAOH(A)	40	24	175	55	no
5	TEOSi	TEOTi	TPAOH(S)	25	24	175	55	no
6	TEOSi	TEOTi	TPAOH(S)	20	24	175	55	no
7	TEOSi	TEOTi	TPAOH(S)	16.5	24	175	55	no
8	Si	$TiCl_3$	TPABr(A)	25	24	175	120	no
9	Si	$TiCl_3$	TPABr(A)	25	24	175	120	yes
10	TEOSi	TBOTi	TPAOH(S)	25	0	160	72	no

[a] TEOSi = tetraethyl orthosilicate; TEOTi = tetraethyl orthotitanate; TBOTi = tetrabutyl orthotitanate; Si = fumed silica; TPAOH = tetrapropyl ammonium hydroxide; (S) = Sigma; (A) = Aldrich; TPABr = tetrapropyl ammonium bromide.

ambient temperature for 2 h. The aged solution was added slowly to TPAOH (50 ml, Sigma, 20% aqueous solution) with vigorous stirring at 60°C, the addition being carried out in 1 h to form a clear gel (mol ratio Si/Ti = 40). The gel was stirred at 60°C for 2 h to aid hydrolysis and to evaporate the alcohol produced. Water (40 ml, deionised) was added to the gel and it was aged at ambient temperature for 24 h. The aged gel was then placed in a Teflon lined stainless steel autoclave and maintained at 175°C for 24 h to enable the product to crystallise. The product was recovered by filtration, washed with water, dried and calcined (6 h, 550°C). The variations on this procedure were: catalyst 2 (55 h crystallisation time), catalyst 3 (240 h crystallisation time), catalyst 4 (TPAOH, Aldrich, containing 3.4% K), catalyst 5 (Si/Ti ratio 25), catalyst 6 (Si/Ti ratio 20), catalyst 7 (Si/Ti ratio 16.5), for catalysts 5–7 the variation in Si/Ti ratio was obtained by increasing the mass of TEOTi used.

2.1.2. Fluoride method

Catalysts 8 and 9 were prepared according to the method of Dwyer et al. [12] using ammonium fluoride, fumed silica, titanium trichloride 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 (2.1 g, 30% in hydrochloric acid) was added to give a Si/Ti ratio = 25. The gel was then aged for 24 h. Half of the aged gel was then placed in a static Teflon lined stainless steel autoclave and maintained at 175°C for 120 h (catalyst 8). The remaining portion of the aged gel was placed in a Teflon lined stainless steel autoclave, stirred at 100 rpm and maintained at 175°C for 120 h (catalyst 9). The products of both preparations were then recovered by filtration, washed with water, dried and calcined (6 h, 550°C).

2.1.3. Preparation using tetrabutyl orthotitanate

Catalyst 10 was prepared according to the method of Thangaraj et al. [9] using tetrabutyl orthotitanate (TBOTi), TEOSi and water as reagents and TPAOH as the template.

TEOSi (50.0 g) was added slowly to TPAOH (70.0 g) and stirred for 30 min. To this solution TBOTi (3.5 g) dissolved in isopropyl alcohol (7.0 g) was slowly added at 60°C and stirred for 2 h to give a gel (Si/Ti = 25). 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 water, dried and calcined (6 h, 550°C).

2.1.4. Silica/titania co-gels

Silica/titania co-gels were obtained as commercial samples (EP50 and ES70,

Crosfield Group). EP50 contained 2.5% Ti and was calcined at 500°C, while ES70 contained 4% Ti and was calcined at 870°C.

2.2. CHARACTERISATION OF TS-1

The as-synthesised and calcined samples of TS-1 were characterised by powder X-ray diffraction using Cu Kα radiation. The calcined samples were also investigated using infrared spectroscopy and in this case the samples were examined as standard KBr discs. Chemical analysis was carried out using atomic absorption spectroscopy and energy dispersive X-ray analysis. Surface areas were determined by nitrogen adsorption according to the BET method and were all found to be in the range 420–440 $m^2\ g^{-1}$.

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 NMR spectroscopy.

3. Results

3.1. PREPARATION OF TS-1 USING TETRAETHYL ORTHOTITANATE

Samples of TS-1 were prepared using a variation on the original method of Taramasso et al. [8] using gels prepared from tetraethyl orthotitanate (TEOTi), tetraethyl orthosilicate (TEOSi), water and tetrapropyl ammonium hydroxide (TPAOH) (table 1).

3.1.1. Effect of crystallisation time

The effect of crystallisation time at 175°C was investigated for a gel (Si/Ti = 40) that had been aged for 24 h. Catalysts 1–3 were prepared after crystallisation for 24, 55 and 240 h respectively, all other experimental parameters were the same (table 1). The calcined materials were characterised by powder X-ray diffraction; there were no significant differences observed for these samples and the diffraction patterns were found to be consistent with that expected for TS-1 [8] (fig. 1). The morphology of the three samples was examined using scanning electron microscopy (fig. 2). It is apparent that this method produces uniform orthorhombic crystallites of TS-1 ca. 0.3 μm in size for crystallisation times of 24 and 55 h (figs. 2a, 2b). In addition it was apparent that a few larger crystallites (ca. 0.5–

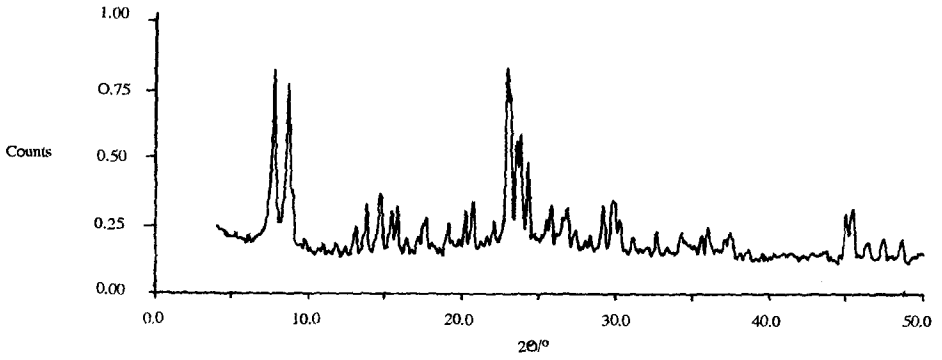


Fig. 1. Powder X-ray diffraction pattern of catalyst 1.

1.0 μm) were also formed in similar amounts in both preparations. The Si/Ti ratio of these two materials was similar (Si/Ti = 24) and the only significant difference was that the sample of TS-1 prepared using 55 h crystallisation time was much easier to filter and therefore recover from the synthesis mixture. The longer crystallisation time also produced mainly uniform orthorhombic crystallites of TS-1 ca. 0.3 μm in size but significant quantities of larger monoclinic crystallites (ca. 1 μm) were also formed (fig. 2c). In addition the incorporation of Ti was much lower for catalyst 3 (Si/Ti = 57.5). It is important to note that no significant amorphous material was detected either by scanning electron microscopy or baseline shift in the powder X-ray diffraction patterns. Based on these initial studies the crystallisation time was standardised at 55 h in all subsequent preparations for this method.

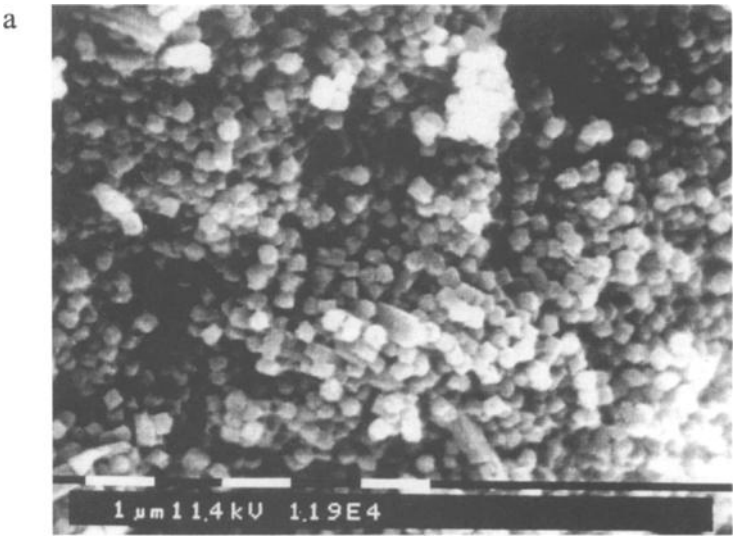
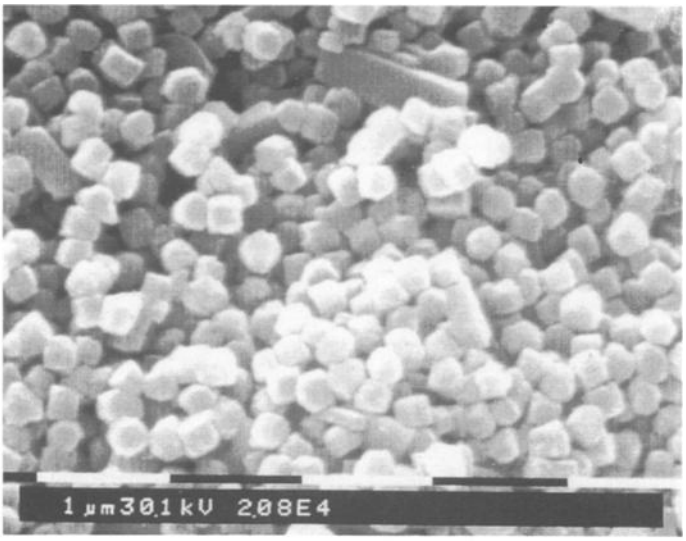


Fig. 2. Electron micrographs of TS-1 (a) catalyst 1, (b) catalyst 2, (c) catalyst 3.

b



c

Fig. 2. (Continued.)

3.1.2. Effect of addition of K^+

A sample of TS-1 (catalyst 4) was synthesised using the same method as for catalyst 2 except that the TPAOH template used contained 0.6% K^+ (table 1). Characterisation of catalyst 4 by powder X-ray diffraction gave the patterns of TS-1 and by elemental analysis the catalyst was found to contain 3.5% K^+ with Si/Ti = 40. Examination by scanning electron microscopy showed that catalyst 4

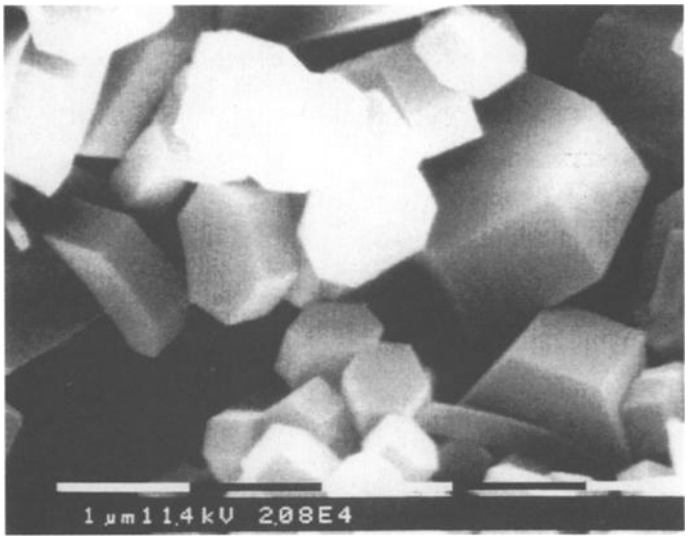


Fig. 3. Electron micrographs of catalyst 4.

comprised much larger crystallites when compared to catalyst 2, typically >1 µm with a fairly broad size distribution (fig. 3).

3.1.3. Effect of variation of gel Si/Ti ratio

Samples of TS-1 were prepared under identical conditions except that the Si/Ti

a

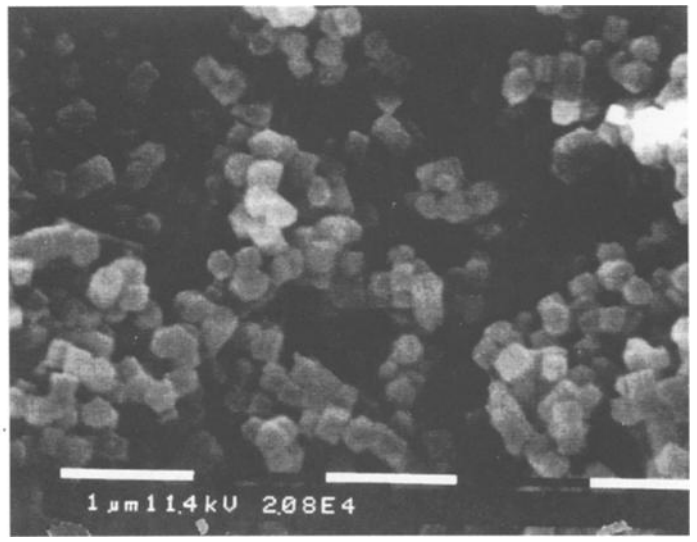
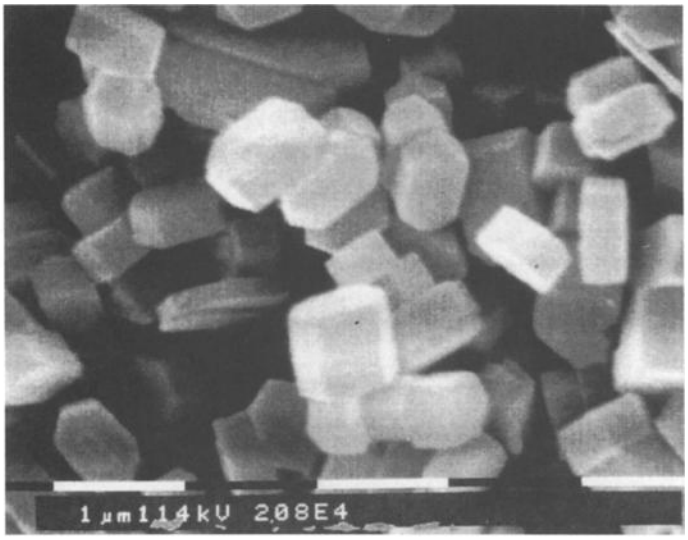


Fig. 4. Electron micrographs of TS-1 (a) catalyst 5, (b) catalyst 6, (c) catalyst 7.

b



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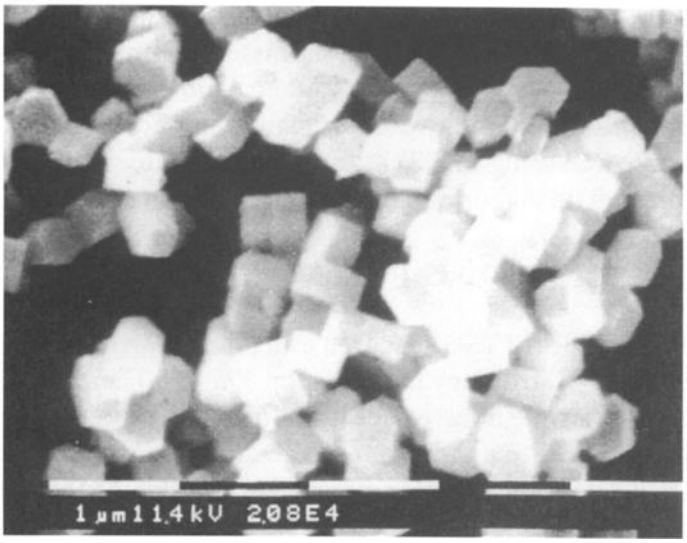

Fig. 4. (Continued.)

ratio of the gel varied (table 1): Si/Ti = 40 (catalyst 2), 25 (catalyst 5), 20 (catalyst 6), 16.7 (catalyst 7). X-ray diffraction patterns for all samples were consistent with TS-1 being the only crystalline phase. Elemental analysis indicated similar Si/Ti ratios in the calcined TS-1: 24 (catalyst 2), 29 (catalyst 5), 27 (catalyst 6), 25 (catalyst 7). Scanning electron microscopy indicated the samples contained crystallites of similar size and morphology (fig. 4).

3.2. PREPARATION OF TS-1 FLUORIDE ROUTE

Two samples of TS-1 were prepared from a gel containing fluoride ions (table 1) using identical conditions either without (catalyst 8) or with stirring (catalyst 9). X-ray powder diffraction showed both samples were well crystalline samples of TS-1. Elemental analysis showed that both samples had very similar Si/Ti ratios (Si/Ti = 27). Analysis using scanning electron microscopy indicated that the two samples exhibited very different morphology (fig. 5). Catalyst 8, prepared under static conditions, comprised uniform monoclinic crystallites with length >35 μm, but significant amounts of amorphous material were also present. Catalyst 9, prepared with stirring, also comprised uniform monoclinic crystallites but much smaller, ca. 10 μm in length, and no amorphous material was present.

3.3. PREPARATION OF TS-1 USING TETRABUTYL ORTHOTITANATE

A sample of TS-1 (catalyst 10) was prepared using the method of Thangaraj et al. [9] using a gel prepared from tetrabutyl orthotitanate (TBOTi), TEOSi, water and TPAOH (table 1). The sample was found to be crystalline using X-ray powder diffraction and the Si/Ti ratio of the calcined TS-1 was similar to that of the gel. Scanning electron microscopy showed that the material comprised uniform crystallites ca. 0.3 μm in diameter and no large monoclinic crystallites were observed (fig. 6). The crystallites were, however, less regular in shape when compared with the crystallites prepared using TEOTi as the titanium source and some amorphous material was apparent on the surface of the small crystallites.

3.4. CHARACTERISATION OF TS-1 BY INFRARED SPECTROSCOPY

Representative samples of TS-1 prepared using the different methods were characterised by infrared spectroscopy in the region 375–1500 cm^{-1} (fig. 7). Previous studies have shown that the infrared spectrum of TS-1 is similar to the iso-structural titanium-free silicalite except that a new absorption band is observed at 960 cm^{-1} for TS-1 [8,16]. This has been assigned to a stretching frequency of a TiO_4 unit [17] and is therefore indicative of titanium incorporation into the silicalite lattice. It is apparent that the strength of the absorption at 960 cm^{-1} varies considerably for the different samples. In particular, the band at 960 cm^{-1} is almost absent in the large crystallite samples (catalysts 4, 8 and 9) and is most intense in the small crystallite samples (catalyst 5). For comparison the infrared spectra of the silica/titania co-gels are also shown and both are observed to exhibit an absorption band at 960 cm^{-1}, but the intensity was not correlated with the titanium content of these materials. This demonstrates structures containing Ti, Si and O other than TS-1 can also give this characteristic absorption band.

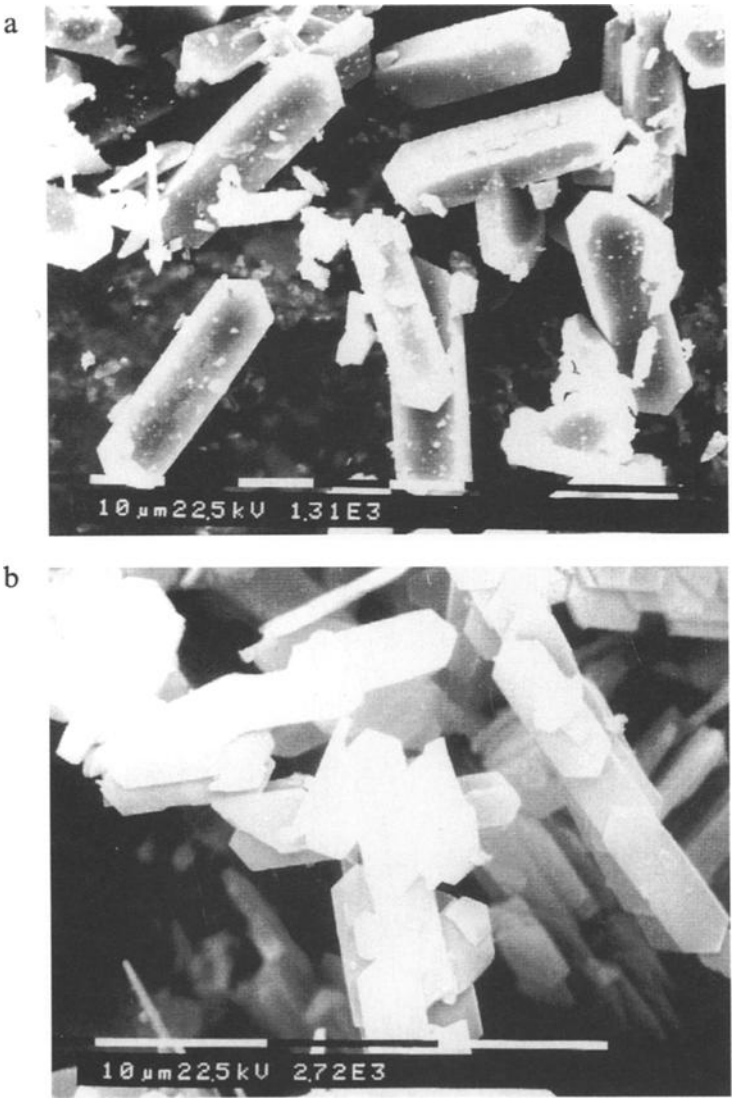

Fig. 5. Electron micrographs of TS-1 (a) catalyst 8, (b) catalyst 9.

3.5. EPOXIDATION OF ALLYL ALCOHOL

Representative samples of TS-1 (catalysts 5, 9 and 10), prepared using the three different methods discussed previously, were used as catalysts for the epoxidation of ally alcohol using hydrogen peroxide as oxidant at 65°C in ethanol as solvent (table 2). In addition the reaction was also tested with catalyst 4, TS-1 prepared using TPAOH template with a significant K^+ content, and this was found to be totally inactive. The products are mainly glycidol, 3-ethoxy-1,2-propanediol

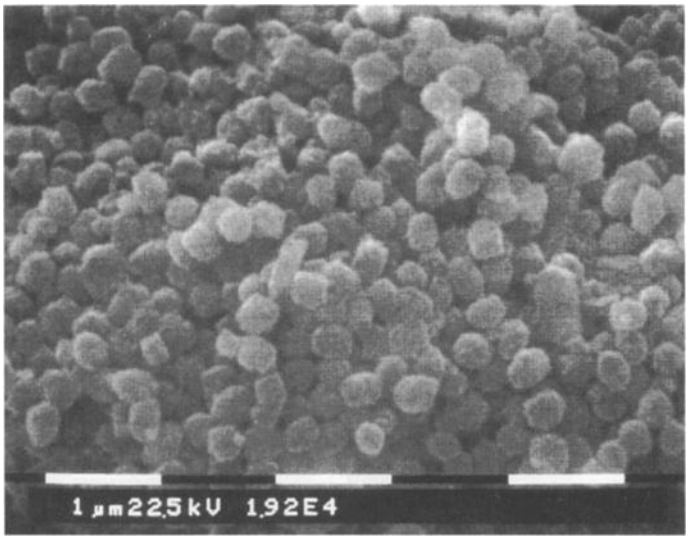

Fig. 6. Electron micrographs of catalyst 10.

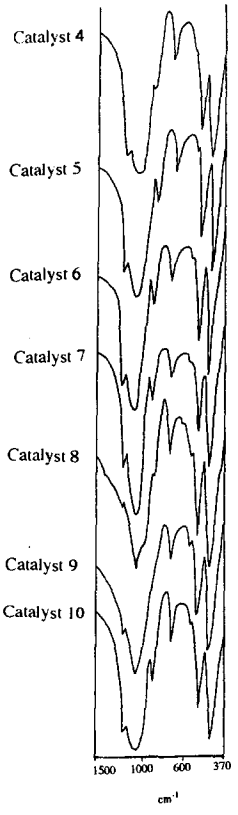

Fig. 7. Infrared spectra of catalysts 4–10

Table 2
Allyl alcohol epoxidation [a]

Catalyst	Size (μm)	Time (h)	Conv. [b] (%)	Product selectivity (mol%)			
				glycidol	3E12PD [c]	2E13PD [d]	glycerol
5	0.3	2	46.6	64.4	28.1	7.5	0
		4	56.6	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
9	10	2	3.4	100	0	0	0
		4	7.2	85.1	10.5	4.4	0
		6	9.7	68.7	21.3	10.0	0
		24	28.3	27.9	54.5	17.6	0
10	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

[a] TS-1 (1.0 g), allyl alcohol (5.8 g), ethanol (55.0 g) and hydrogen peroxide (70%, 5.0 g), 65°C.
[b] Allyl alcohol conversion.
[c] 3E12PD: 3-ethyl-1,2-propanediol.
[d] 2E13PD: 2-ethyl-1,3-propanediol.

(3E12PD) and 2-ethoxy-1,2-propanediol (2E13PD), although at long reaction times a low selectivity to glycerol is observed. It is apparent that the small crystallite samples of TS-1 (catalysts 5 and 10) were considerably more active than the larger crystallite sample (catalyst 9). In addition the silica/titania co-gels were examined as catalysts for this reaction using the same conditions. Both EP50 and ES70 were found to give very low conversion (0.1%) after 24 h reaction and glycidol was the only detected product.

4. Discussion

4.1. CONTROL OF TS-1 MORPHOLOGY

In this study three different synthesis methods for TS-1 have been investigated and these have resulted in materials with distinctly different morphologies. The major part of the work concentrated on variations on the original method described by Taramasso et al. [8] using TEOTi as the titanium source. The initial work of Taramasso et al. [8] used synthesis times of 6–30 days but a subsequent study by Clerici et al. [1] indicated that shorter times could also be used. Hence the crystallisation time was taken as the initial variable for the present work. The crystallite size is clearly a function of the crystallisation time since the material synthesised for

240 h exhibited significant amounts of large monoclinic crystallites in addition to the smaller crystallites that were dominant for the shorter synthesis times. In addition the materials prepared for 24 and 55 h were found to be very similar using the characterisation techniques employed, however, the material prepared for 55 h was easier to recover by filtration and this implies a slight increase in crystallite size for this material. Under static preparation conditions employed in this study the crystallisation time is therefore an important parameter controlling crystallite size. This is contrast to the findings of van der Pol and van Hooff [14] that indicated that crystallisation time did not have a significant effect on the crystallite size. However, in their studies the synthesis mixture was stirred and hence these findings may serve to indicate the differences that can be expected from static and stirred conditions. We compared static and stirred conditions for the fluoride method and it was found that the crystallite size formed under stirred conditions was considerably smaller than those prepared without stirring. These results indicate an interplay between stirring rate and crystallisation time could be used to obtain control over the morphology of the TS-1 crystallites.

Variation of the Si/Ti ratio in the gel or using TBOTi as titanium source based on the method of Thangaraj et al. [9] did not markedly affect the Si/Ti ratio of the TS-1. All these synthesis mixtures gave very similar materials. The only significant difference observed was that the TS-1 crystallites prepared from TBOTi appeared to have amorphous material coating their surface.

The TS-1 prepared using a TPAOH template contaminated with K^+ comprised large crystallites with a fairly broad size range. This finding is similar to that observed by van der Pol and van Hooff [14] for the influence of added alkali metal cations which at high concentrations also resulted in the formation of larger crystallites. The band at 960 cm^{-1} was almost absent in catalyst 4 and this effect has also been noted by Bittar et al. [18] when sodium impurities were added to the synthesis mixture of the analogous TS-2. It is considered that this results from the hydrolysis of the TEOTi under the alkaline conditions to give TiO_2 that is insoluble in the reaction mixture and eventually remains as amorphous TiO_2 in the prepared TS-1. The gel formed during the synthesis of catalyst 4 was noted to be white in colour which would be consistent with the formation of TiO_2, and this colouration was not observed for the gels for the analogous preparations of catalysts 1–3 and 5–7.

TS-1 prepared from the fluoride method comprised much larger crystallites, especially when the synthesis mixture was not stirred. The crystallites were also significantly different being *monoclinic* in morphology. The fluoride synthesis method was initially developed by Guth et al. [10] and it is known to be a procedure of choice if large crystals are required. A recent molecular modelling study by de Vos Burchart et al. [19] has addressed the orthorhombic/monoclinic transition and shown that it is influenced by increased temperature, being facile at 67°C, and additives to the synthesis mixture. The larger crystallite size of the TS-1 prepared by the fluoride method has been explained by Qui et al. [11] to result from the low

solubility of the silicon containing reagent resulting in slow nucleation and crystallisation rates. Stirring during the crystallisation process could increase the nucleation rate and therefore lead to more crystallites of smaller size, and this is consistent with the results of this study.

4.2. ALLYL ALCOHOL EPOXIDATION

It is clear from the preceding discussion that careful control of the conditions can lead to the synthesis of TS-1 samples which exhibit a range of morphologies. In a previous study van der Pol and van Hooff [14] showed that the morphology was a major parameter controlling the reactivity of TS-1 for the hydroxylation of phenol. In this study the effect of this parameter on the more demanding epoxidation of allyl alcohol was examined. The results (table 2) indicated that at low conversion and using ethanol as solvent 100% selectivity to glycidol can be achieved. As the reaction time is increased the formation of the products of glycidol solvolysis becomes apparent and 3E12PD and 2E13PD are the major products. These products are formed by ring opening reaction of the glycidol epoxide with the ethanol solvent. Glycerol, the product of glycidol hydrolysis, is only formed in very low yields at the highest temperature investigated. The observation of significant amounts of glycidol is in contrast to the early work of Taramasso et al. [8] in which it was shown that with dilute hydrogen peroxide solutions (5% in water) only glycerol was observed. However, recent studies by Clerici and Ingallina [15] have indicated that glycidol can be formed at higher hydrogen peroxide concentrations and this is consistent with our results. Although the morphology of TS-1 does not affect the products formed from the epoxidation of allyl alcohol, it is apparent that the crystallite size largely controls the activity of the sample. Hence the large crystallite material prepared by the fluoride method has low activity for the epoxidation reaction. The smaller crystallites of catalysts 5 and 10 give significantly higher conversions and hence the results are in agreement with the work of van der Pol and van Hooff [14]. It is interesting to note that the samples prepared from TEOTi (catalyst 5) and TBOTi (catalyst 10) have similar particle sizes, X-ray diffraction pattern and infrared spectra and yet catalyst 5 is significantly more active, particularly at shorter reaction times. It is possible that amorphous material associated with the TS-1 crystallites of catalyst 10 may be deleterious to the reactivity of this material.

The infrared band at 960 cm^{-1} has been shown in early studies [8] to increase in intensity with increasing titanium content of the TS-1. It has therefore been used as an indicator of the potential reactivity of the sample as an oxidation catalyst, although a more recent study by Huybrechts et al. [20] has shown that this correlation is only valid for samples containing $<2\%$ Ti. On first inspection the potential correlation between the intensity of the 960 cm^{-1} band and reactivity of the TS-1 appears to be consistent with the data of the present study. The 960 cm^{-1} band of catalysts 5 and 10, which are both highly active catalysts, are more intense than

those of the inactive catalyst 4 and the low activity catalyst 9. However, the silica/titania co-gels also exhibit an intense 960 cm^{-1} band but these materials are found to be totally inactive for the epoxidation reaction. The samples of TS-1 prepared by the fluoride method exhibit different intensities of the 960 cm^{-1} band. Catalyst 8, which contains significant amounts of amorphous material, gives a more intense band than catalyst 9, which contains much lower levels of amorphous material. Sulikowski and Klinowski [21] have shown that the amorphous material present on the surface of TS-1 crystallites prepared by the fluoride method is mainly rutile. Hence TiO_2 supported in this way could be responsible for the increased intensity of the 960 cm^{-1} band for sample 8, since the silica/titania co-gel samples comprise TiO_2 supported on SiO_2 and these materials also give the 960 cm^{-1} band. It is therefore apparent that the observation of a particular band in the infrared spectrum of a titanium containing silicate lattice cannot in itself be used as an indication that the titanium is located in a specific site which is catalytically active for oxidations. It is the combination of the MFI crystal structure together with titanium incorporation and small crystallite size that is of crucial importance for the attainment of high catalytic activity.

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