SYNTHESIS AND CHARACTERISATION OF TITANOSILICATES USED AS CATALYSTS FOR THE EPOXIDATION OF CYCLOHEXENE

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Summary

In this work the synthesis of TS-1 from a titanosilicate cogel precursor is reported. The synthesis parameters were altered to optimise both the cogel and resultant framework material. The titanosilicate materials were characterised using a range of techniques including EDX analysis, XRD, ^{29}Si NMR, IR, UV-vis and SEM. Those materials which demonstrated the most catalytic potential were used as catalysts for the epoxidation of cyclohexene reaction, in which the use of aqueous H_2O_2 and a urea-H_2O_2 adduct were compared. It was shown that the cogel precursors themselves exhibited some catalytic reactivity and selectivity for all of the catalysis reactions exploited. However the TS-1 materials were more catalytically active, which highlighted the need of the ordered framework for the most effective catalysis. The TS-1 materials prepared from the cogel precursors exhibited similar catalytic ability to those analogous standard materials prepared via conventional processes. Thus TS-1 preparation by the cogel route was shown to be a viable alternative preparation method to the conventional process.

1. Introduction

In 1983, Taramasso and co-workers reported the formation of a new material, via the isomorphous substitution of Si (IV) by Ti (IV), with the crystalline structure of silicalite-1 (MFI) [1]. The catalytic properties of titanium silicalite-1 (TS-1) appeared to be unique and were attributed to the location of the titanium atoms on isolated lattice sites within a hydrophobic framework. It was reported that in oxidation reactions, with aqueous H_2O_2 as the oxidant, many organic compounds could be oxidised with high selectivity and reactivity. Additionally partial oxidation products could be obtained in high yields and almost all the oxygen available from H_2O_2 was used to produce the desired products [2]. Since industrialisation of the TS-1 catalyst, carried out successfully by EniChem in the mid-eighties, many efforts have been made towards the study of reactions involving this class of catalyst (Fig.1) [3 - 5]. TS-1 is currently used for two processes on an industrial scale (phenol hydroxylation and cyclohexanone ammoximation) and several companies are developing a third process, propylene epoxidation.

Several different TS-1 materials were synthesised from the cogel precursors, variations included: titanium

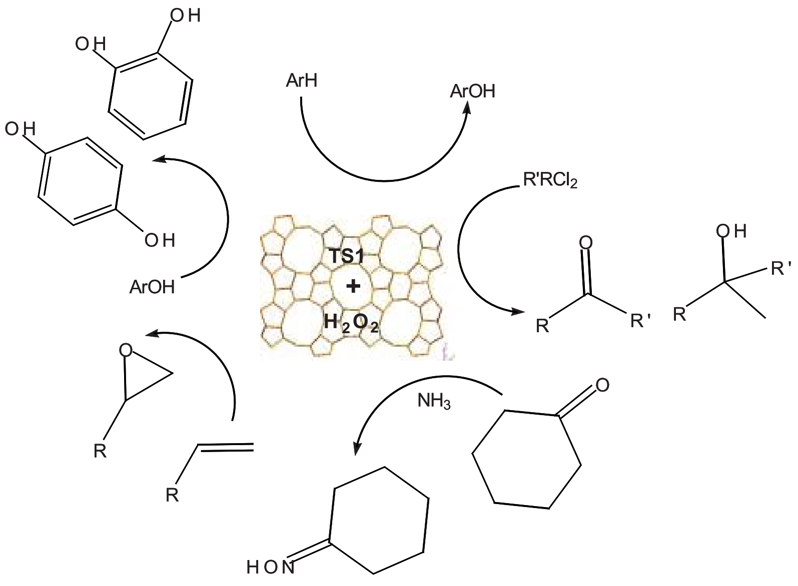


***Fig.1.** Common catalytic applications of TS-1*

Table 1. *Specific synthesis details of titanium cogels synthesised*

Cogel Code	Heteroatom Source	Si:Ti	Ti	Condensation Method	Condensation Reagent
1	Titanium butoxide	10	8.14g (23.00mmol)	Stirring	TPAOH
2	Titanium butoxide	80	1.02g (2.88mmol)	Stirring	TPAOH
3	Titanium butoxide	10	8.14g (23.00mmol)	Sonocation	TPAOH
4	Titanium butoxide	80	1.02g (2.88mmol)	Sonocation	TPAOH
5	Titanium butoxide	10	8.14g (23.00mmol)	Stirring	TEAOH
6	Titanium butoxide	80	1.02g (2.88mmol)	Stirring	TEAOH
7	Titanium butoxide	10	8.14g (23.00mmol)	Sonocation	TEAOH
8	Titanium butoxide	80	1.02g (2.88mmol)	Sonocation	TEAOH
9	Titanium isopropoxide	10	6.54g (23.00mmol)	Stirring	TEAOH
10	Titanium isopropoxide	80	0.82g (2.88mmol)	Stirring	TEAOH
11	Titanium isopropoxide	10	6.54g (23.00mmol)	Sonocation	TEAOH
12	Titanium isopropoxide	80	0.82g (2.88mmol)	Sonocation	TEAOH
13	Titanium ethoxide	10	5.25g (23.00mmol)	Stirring	TEAOH
14	Titanium ethoxide	80	0.66g (2.88mmol)	Stirring	TEAOH

concentration and silylation. The physical and catalytic properties of TS-1 materials formed from the cogel precursors were compared to those of TS-1 materials formed from conventional means.

This work focused on the:

- Synthesis of TS-1 materials from cogel precursors and comparison of their physical and catalytic properties to those of TS-1 materials produced by a conventional process.
- Characterisation of the physical and catalytic properties of the cogel precursors and comparison with resultant TS-1 materials.
- Application of TS-1 in the epoxidation of cyclohexene.

2. Experimental

2.1. Cogel Synthesis

The table below (Table 1) gives specific details of the titanium cogels formed (TPAOH: tetra-*n*-propylammonium hydroxide, TEAOH: tetra-*n*-ethylammonium hydroxide).

2.2. TS-1 Synthesis

TS-1 materials were synthesised from the cogel precursors, these framework materials being prepared from both the calcined and as-prepared cogel precursors (Table 2). Standard TS-1 was synthesised by co-workers at Pune University, India according to procedures given in the patent literature and was treated as a standard for comparison [1].

Table 2. *Details of TS-1 materials produced*

Cogel Source	TS-1 Code	Calcined/As Prepared Cogel
1	1 - 1	As Prepared
	1 - 2	Calcined
2	2 - 1	As Prepared
	2 - 2	Calcined
3	3 - 1	As Prepared
	3 - 2	Calcined
4	4 - 1	As Prepared
	4 - 2	Calcined
5	5 - 1	As Prepared
	5 - 2	Calcined
6	6 - 1	As Prepared
	6 - 2	Calcined
7	7 - 1	As Prepared
	7 - 2	Calcined
8	8 - 1	As Prepared
	8 - 2	Calcined
9	9 - 1	As Prepared
	9 - 2	Calcined
10	10 - 1	As Prepared
	10 - 2	Calcined
11	11 - 1	As Prepared
	11 - 2	Calcined
12	12 - 1	As Prepared
	12 - 2	Calcined
13	13 - 1	As Prepared
	13 - 2	Calcined
14	14 - 1	As Prepared
	14 - 2	Calcined

2.3. Blank material synthesis

Blank framework materials were synthesised from cogel precursors containing no titanium.

2.4. Epoxidation of Cyclohexene

The formation of the epoxide product from cyclohexene in this research was undertaken by employing titanium inserted catalysts. The catalyst (100mg), solvent (anhydrous acetonitrile, 99.8%, 6.0g, 0.1mol) internal standard (mesitylene, 99.8%, 500mg, 4.2mmol) and cyclohexene (500mg, 99.5%, 6.1mmol) were stirred to allow the temperature to equilibrate (60°C, 30 minutes). The oxidising reagent (hydrogen peroxide, 30% (aq), 0.6g, 6.1mmol) was then injected into the mix. Aliquots (~0.5mL) were periodically removed from the mix and quenched, over 6 hours.

3. Results and Discussion

3.1. Titanosilicate Materials

All of the cogel and TS-1 materials formed were fine white powders, however upon addition of aqueous H_2O_2 their colour changed to yellow.

EDX analysis was performed to evaluate the elemental composition of all TS-1 and cogel materials (Fig.2). All of the materials were pre-calcined to remove any organic residues. The percentage atomic composition of all of the materials was within 3.0% of the expected values (EDX accuracy ~ 1.0%).

XRD patterns of the cogels showed them to be amorphous with no long range order, regardless of the differences in synthesis procedure or titanium ratio (Fig.2). Conversely all of the TS-1 materials produced were crystalline and of framework type MFI. XRD patterns obtained were compared to those reported in the literature [10].

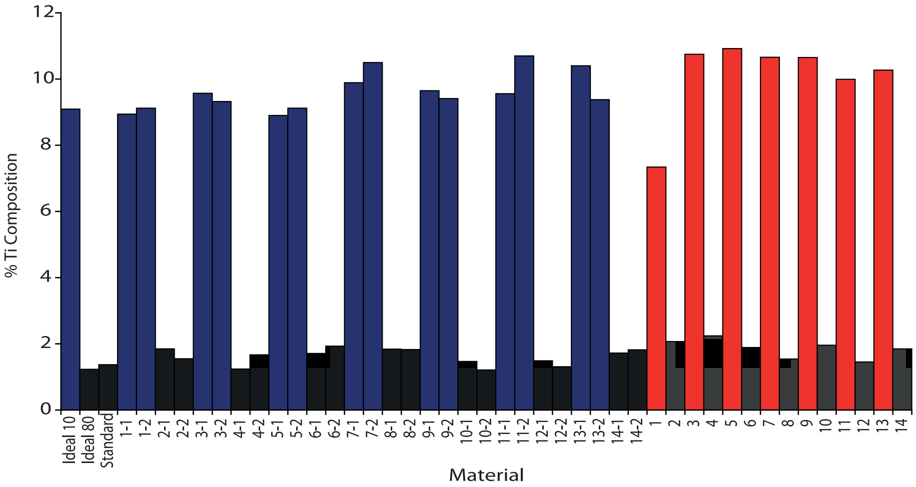


Fig.2. *Titanium composition (%) of TS-1 (blue) and cogel (red) materials of both Si:Ti 10 (solid colour) and Si:Ti 80 (striped)*

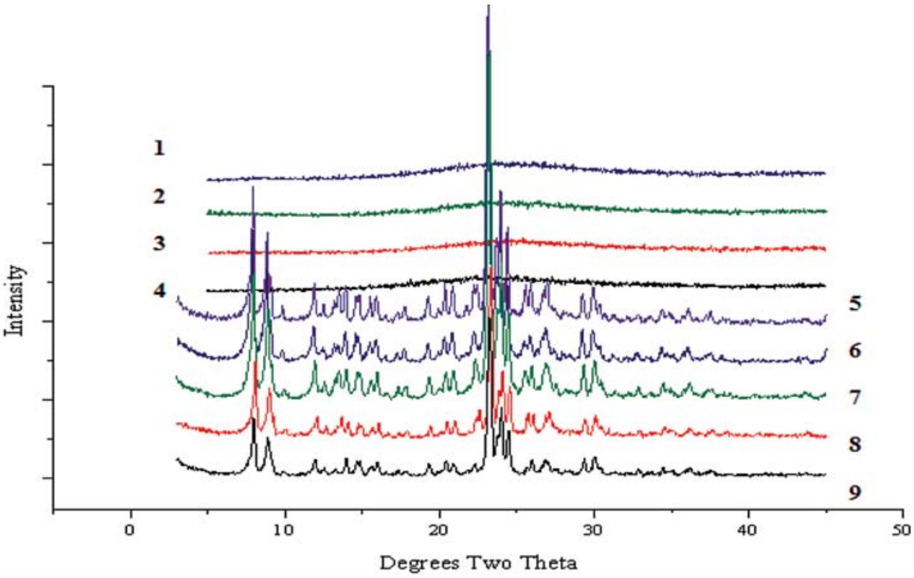
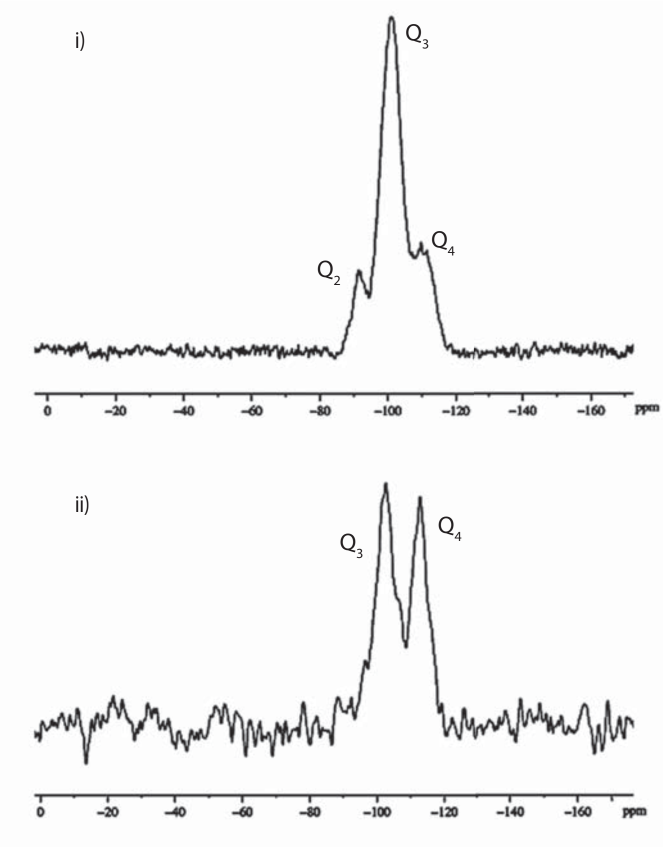


Fig.3. *XRD patterns of calcined cogel (1-4) and TS-1(5-9) materials. (1: Cogel 6, 2: Cogel 1, 3: Cogel 10, 4: Cogel 14)(5: TS-1 standard, 6: TS-1 6-2, 7: TS-1 1-2, 8: TS-1 10-1, 9: TS-1 14-2)*

^{29}Si NMR data was used to evaluate the different types of silicon environment within the titanosilicate materials (Fig.3). The spectrum of the cogel material exhibited three peaks, relating to three different Q_n environments within the material, whilst the TS-1 material only revealed two. Thus the less ordered cogel material exhibited a wider range of silicon environments than the corresponding framework material.

The concentration of silanol groups in a material was calculated as a ratio of Q_4/Q_n, where Q_4 was the number of silicon atoms present in silicalite $Si(SiO)_4$ environments and Q_n was silicon atoms in any silanol form ($Q_1 + Q_2 + Q_3$). The value of this ratio for the cogel examined was 0.28 and for the TS-1 was 0.75. Therefore the cogel had a much higher concentration of terminal hydroxyl groups than the TS-1 and was hence comparatively a more hydrophilic material [11]. The terminal silanol groups are sometimes referred to as Brønsted acid sites, thus the Brønsted acidity of any silicate material can be discussed regardless of the nature of the inserted heteroatom.

IR data was collected for pre-calcined, dehydrated cogel and TS-1 materials (Fig.5). Further evidence of titanium insertion in the zeolite framework was the presence of a band at 960cm^{-1} relating to the stretching vibration of [SiO_4] units bound to tetrahedrally coordinated titanium atoms. The appearance of this band in the cogel spectrum confirmed that the cogel contained titanium centres of the desired tetrahedral coordination geometry prior to crystallisation. It was notable that upon addition of aqueous H_2O_2 to the observed materials the intensity of the band at 960cm^{-1} decreased, this was attributed to coordination of H_2O_2 at the titanium sites. However the 960cm^{-1} band could be recovered by calcination of the samples, which removed the coordinated H_2O_2, thus providing more evidence that the incorporated titanium heteroatoms were capable of forming the peroxy species necessary for effective catalysis. The signal at 550cm^{-1} was characteristic for orthorhombic MFI frameworks and was visible in all TS-1 materials.



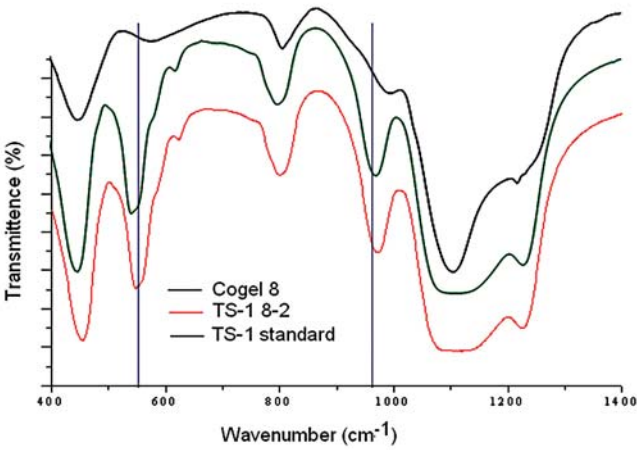


Fig.5. *IR spectra of titanosilicate materials (Dashed line: 550cm^{-1}and 960cm^{-1})*

Fig.6 depicts the UV-vis spectra of standard TS-1, TS-1 8-2 and the corresponding precursor cogel 8. In all cases there was no appreciable adsorption band (~ 330nm) thus portraying an absence of bulk TiO_2 phases, although the presence of small TiO_2 clusters cannot be completely discarded. The narrow bands of the TS-1 materials, centred ~ 220 nm, confirmed that the titanium atoms occupied mostly tetrahedral positions within the zeolite framework.

The cogel spectrum however depicted a broader band shifted to a higher wavelength, which suggested that titanium atoms were present in configurations other than tetrahedral. As predicted, UV-vis spectra of the cogel materials with different titanium concentrations exhibited broad bands in the range 200 to 300nm, which demonstrated that different titanium environments coexisted in these materials (Fig.7). This band was broader in the spectrum of cogel 7, which had a higher titanium concentration than cogel 8, additionally there was another peak at ~ 310nm which was attributed to either extra framework titanosilicate species or bulk TiO_2 phases.

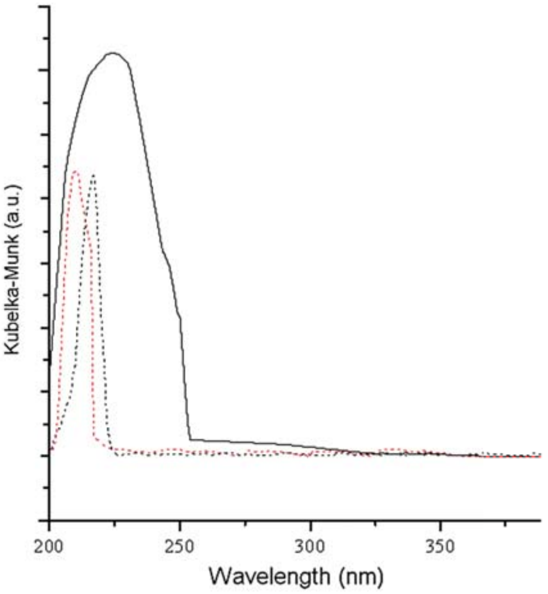


Fig.6. *UV-vis spectra of cogel 8 (black), TS-1 8-2 (green) and standard TS-1 (red) (Navy line = 220nm)*

The spectra obtained from TS-1 materials prepared from these cogels exhibited similar properties to each other. TS-1 7-2 (higher titanium concentration) produced a broader peak at ~ 220nm, and an additional peak at ~ 310nm. The UV-vis results obtained thus echoed the IR results wherein the materials with Si:Ti 80 appeared to contain titanium centres with predominately tetrahedral geometry, whilst the materials with Si:Ti 10 had titanium centres with a range of coordination geometries.

SEM images of the cogel materials showed no ordered morphology regardless of the synthesis parameters employed (Fig.8). SEM images of the TS-1 materials showed them to be of roughly spherical morphology with an average diameter of 0.5μm, compared with cubic crystals of the standard TS-1 with 0.15μm diameter [13]. The size and morphology of the TS-1 materials prepared from cogel precursors appeared comparable regardless of the synthesis parameters altered to produce them (titanium concentration, titanium source, condensation reagent, condensation method, use of calcined cogel precursor). It was reported that particle size influenced the catalytic activity of all molecular sieves, but it was especially influential in the case of TS-1. Reportedly the average particle size of an active TS-1 catalyst should be < 0.5μm, thus these TS-1 materials appeared to be at the limit of the ideal [5, 14].

BET surface area measurements were undertaken by co-workers at Pune University, India. The results found the cogel (10) material to have a surface area of $694m^2g^{-1}$ and the corresponding TS-1 (10-2) to have a surface area of $416m^2g^{-1}$. The surface area of TS-1 was close to the values reported in the literature of ~ $400m^2g^{-1}$ for TS-1 materials prepared by standard means.[7] The surface area of the cogel was higher than that of the TS-1 materials and was close to the value of ~ $700m^2g^{-1}$ reported for xerogels in the literature [16]. The high surface area of these titanosilicates was encouragingly similar to catalytically active materials, wherein the higher the surface area the more easily assessable the active sites are for the reagent materials.

3.2. Silicalite Materials

Silicalite materials (containing no titanium heteroatoms) were synthesised for use as standard materials, they were characterised employing some of the techniques utilised for the titanosilicate materials. Addition of aqueous H_2O_2 to any of the samples did not result in an observable colour change. XRD results confirmed the cogel to be amorphous and the silicalite-1 material to have the desired MFI framework. IR results for both the cogel and framework materials showed no noticeable peak at $960cm^{-1}$ and no peak at $550cm^{-1}$ for the silicalite-1 materials (Fig.5). UV-vis results showed no peaks for any of the standard materials tested.

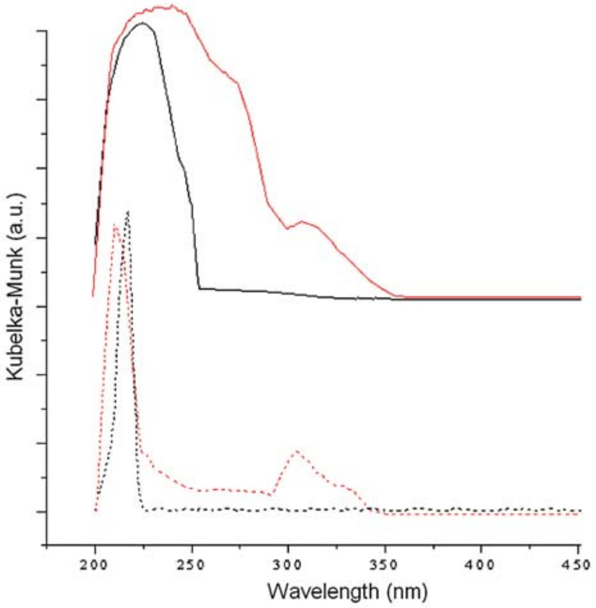


Fig.7. *UV-vis spectra of cogel and TS-1 materials with varying titanium concentrations: Cogel 7 (Si:Ti 10, solid red line), Cogel 8 (Si:Ti 80, solid black line),TS-1 7-2 (Si:Ti 10, dashed red line), TS-1 8-2 (Si:Ti 80, dashed black line)*

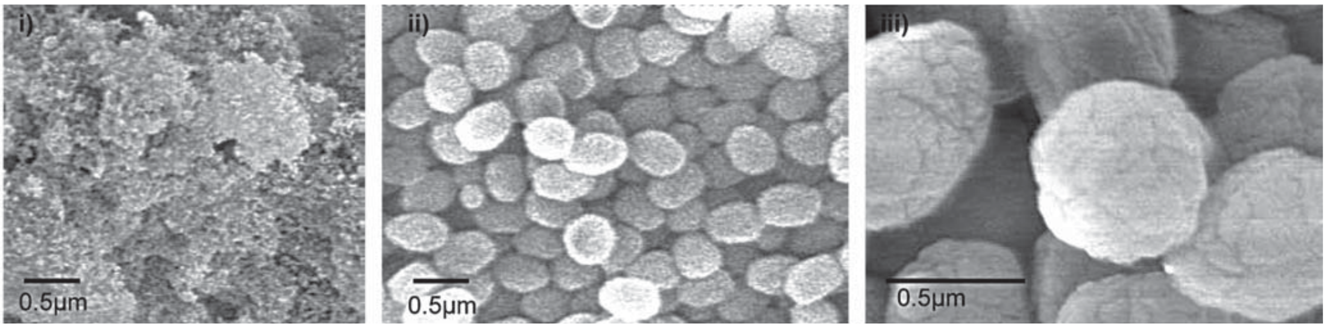


Fig.8. *SEM images of i) Cogel 8, ii) and iii) TS-1 8-2*

3.3. Epoxidation of Cyclohexene

The catalytic activity of titanosilicate materials for many different reactions has been well recognised and reported [17]. The surface structure of TS-1 has been described in terms of i) the state and framework coordination of titanium ii) surface hydroxyl groups present in the form of silanols and titanols. These structural characteristics influence the materials' catalytic reactivity and selectivity. However an amorphous TiO_2 - SiO_2 catalyst consisting of 2% TiO_2 dispersed on high-surface area silica has been reported to be an active and selective catalyst for the epoxidation of alkenes, thus demonstrating that a three-dimensional framework is not essential for active catalysis [18, 19].

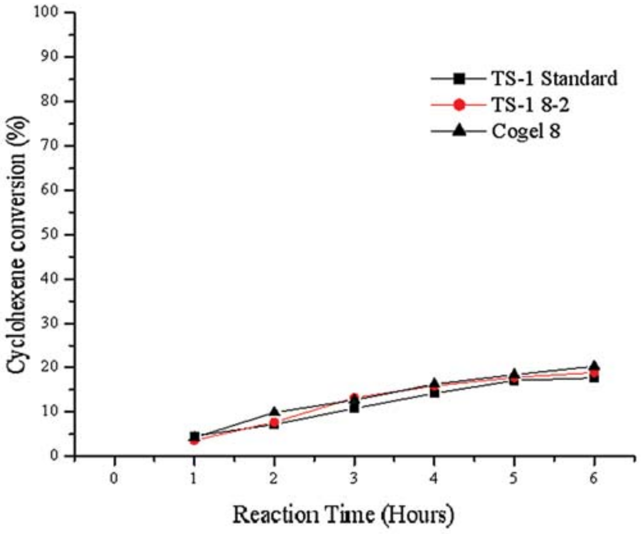


Fig.9. *Cyclohexene conversion (%) of titanosilicate materials over 6 hours*

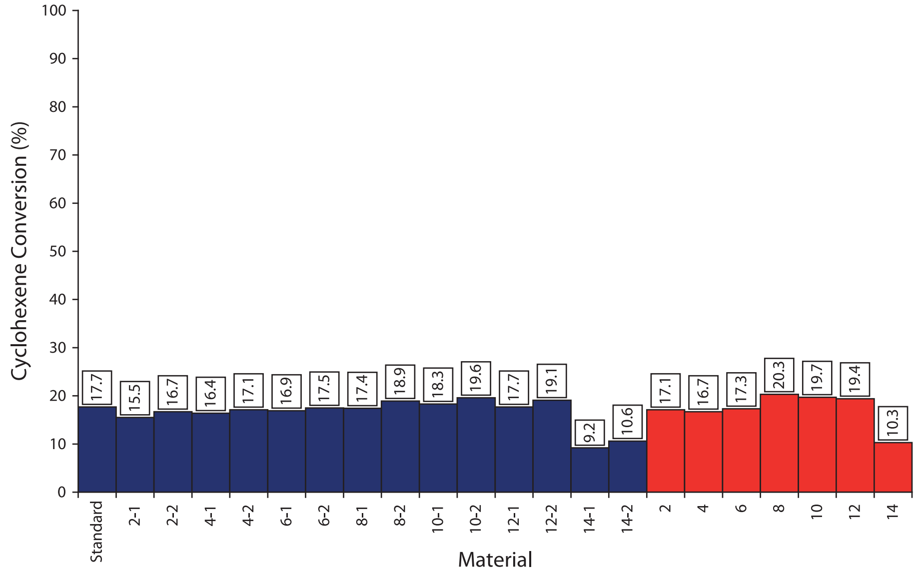


Fig.10. *Cyclohexene conversion (%) for TS-1 (blue) and cogel (red) materials after 6 hours of reaction*

The catalytic reactivity of both the TS-1 and cogel materials were tested for the epoxidation of cyclohexene. Only those titanosilicate materials with Si:Ti 80, which exhibited titanium centres in the desired optimal environment for catalysis, were used as catalysts. After 6 hours of reaction the cogel and TS-1 materials showed similar catalytic reactivity, with a cyclohexene conversion of ~ 20% (Fig.9).

All of the titanosilicate materials showed some reactivity for the epoxidation of cyclohexene (Fig.9). The percentage conversion of cyclohexene by the standard TS-1 (17.7%) and the cogel prepared TS-1 materials (16.8%) were comparable.

Cogel materials condensed under sonocation were overall slightly more catalytically reactive compared to materials condensed whilst stirred. The predictably lower reactivity of the stirred materials was due to the nature of the catalytically active titanium centres which (as discussed) were less tetrahedral than those atoms in materials condensed under sonocation. Cogel materials condensed using either TPAOH or TEAOH demonstrated similar catalytic reactivities to the TS-1 materials synthesised from them. Both UV-vis and IR data demonstrated the similarities of the titanium centres within these materials, thus it was predicted they should exhibit comparable catalytic reactivity.

TS-1 materials synthesised from as-prepared cogel precursors consistently had lower catalytic reactivity compared to similar materials prepared from calcined precursors. The titanium centres were on average more tetrahedral in TS-1 materials prepared from calcined cogel precursors. Both the cogels and corresponding TS-1 materials which contained titanium from a titanium ethoxide source (cogels 13 and 14, TS-1 13-1, 13-2, 14-1, 14-2) had lower catalytic reactivity (cyclohexene conversion) than those materials formed using other titanium sources. This was again expected from the IR and UV-vis results which showed the titanium centres in these materials on average to be less tetrahedral.

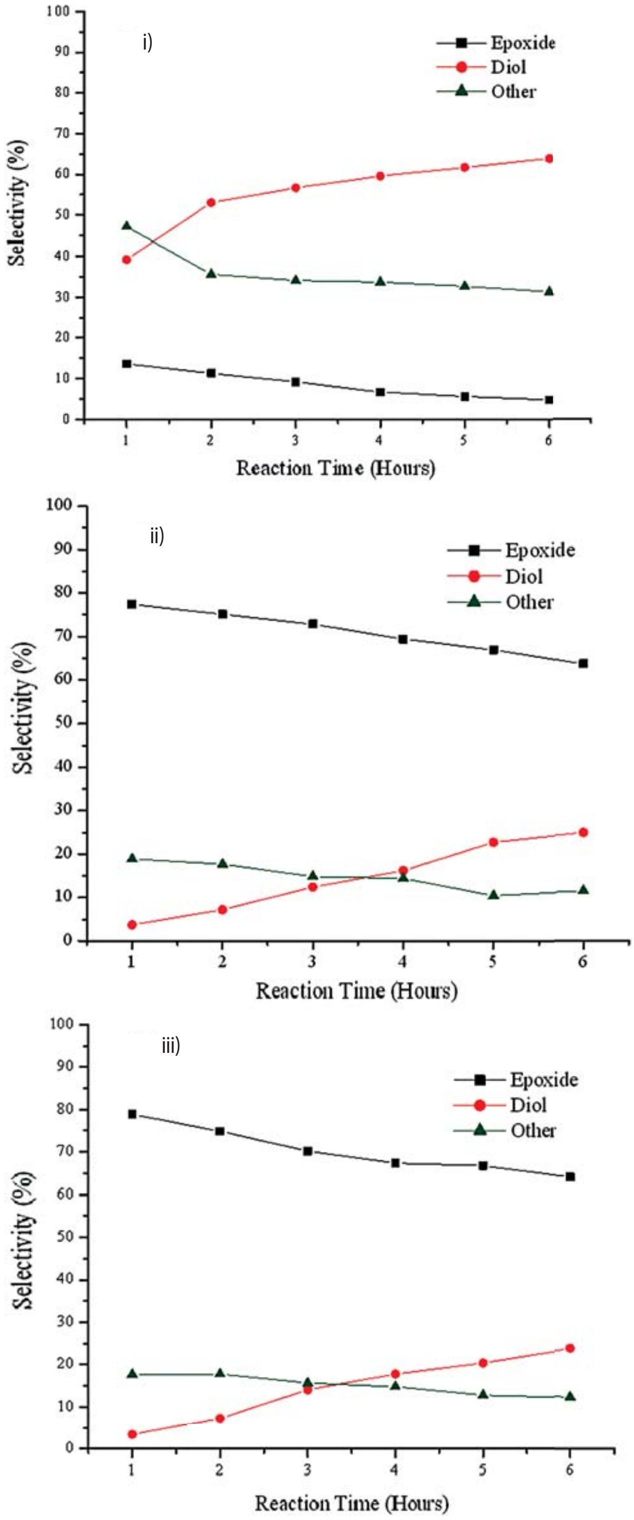


Fig.11. Catalytic selectivity of i) cogel 8, ii) TS-1 8-2, iii) standard TS-1, for the epoxidation of cyclohexene (Other denotes combined ketone and mono-alcohol selectivity)

The catalytic selectivity of cogel and TS-1 materials towards epoxide formation decreased as the reaction continued, the epoxide degraded to form the diol product (Fig.11). The cogel selectivity for epoxide formation was initially very low (~ 10%) and after 6 hours had decreased further still (< 5%). Conversely TS-1 materials exhibited a high initial selectivity towards epoxide formation (~ 75%), which again decreased (~ 60%) to produce the diol over 6 hours of reaction.

Thus the selectivity towards the formation of the epoxide was higher for TS-1 compared to cogel materials. The continued reaction to produce the diol product has been reported to occur via acid catalysed hydrolysis of the epoxide [20]. Thus it was hypothesised that the observed selectivities were due to the highly disordered structure of the cogel materials which contained a higher concentration of hydroxyl groups, in contrast to the crystalline TS-1 materials.

The TS-1 synthesised from the cogel precursor exhibited analogous catalytic selectivity to the TS-1 prepared by conventional means (~ 60%). No notable differences in the epoxide selectivity of all TS-1 or all cogel materials were observed, regardless of the alteration of the synthesis parameters (Fig.11).

All catalysts were collected and re-calcined after each experiment, for some catalysts their ability to regenerate was then tested (standard TS-1, TS-1 8-2, cogel 8). Results of all the catalysts retested were within 3% of those reported herein. Control catalytic experiments were also performed with either no catalyst present or using blank silicalite materials as the catalyst, these yielded no products.

3.4. Urea-H_2O_2 Adduct Alteration

When water is present in the epoxidation of cyclohexene reaction, the acid catalysed conversion of epoxide to diol can occur. Hence to enhance epoxide selectivity a non-aqueous source of H_2O_2 was used, a urea-H_2O_2 adduct, which slowly released H_2O_2 into solution [21]. Additionally the urea adduct can bind to terminal hydroxyl groups on the catalyst, thus preventing these sites being employed as acid centres for epoxide degradation. Whilst the catalytic reactivities of the TS-1 materials under the altered conditions were comparable with each other they were vastly different from the reactivity of the cogels (Fig.13). After 6 hours of reaction the TS-1 materials showed ~ 30% cyclohexene conversion whilst the cogel showed < 5% cyclohexene conversion.

This dramatic decrease in cogel selectivity was hypothesised to be due to the binding of the urea adduct

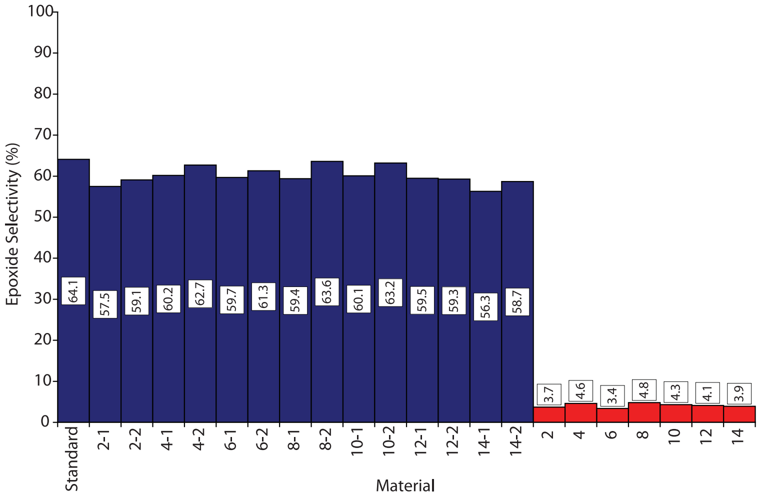


Fig.12. *Epoxide selectivity for TS-1 (blue) and cogel (red) materials after 6 hours for the epoxidation of cyclohexene reaction*

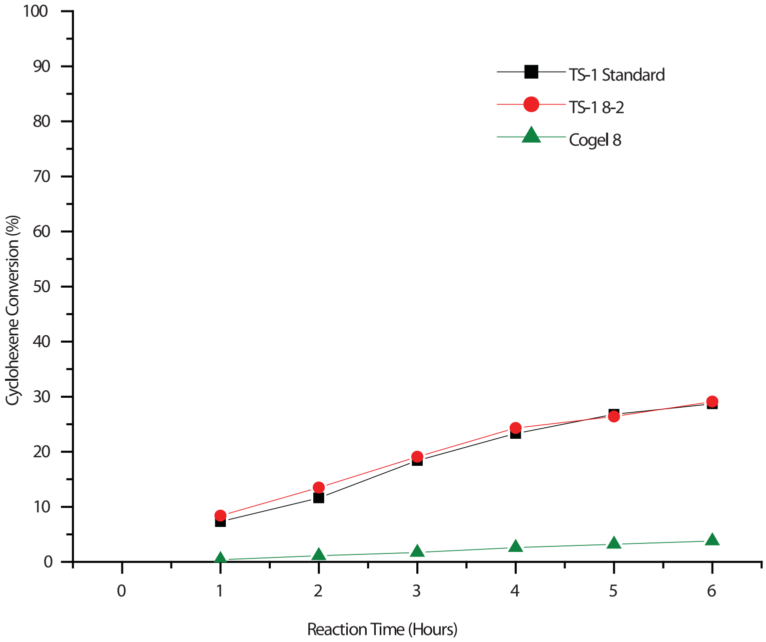


Fig.13. *Cyclohexene conversion (%) of titanosilicate materials over 6 hours, using urea-H_2O_2 oxidant*

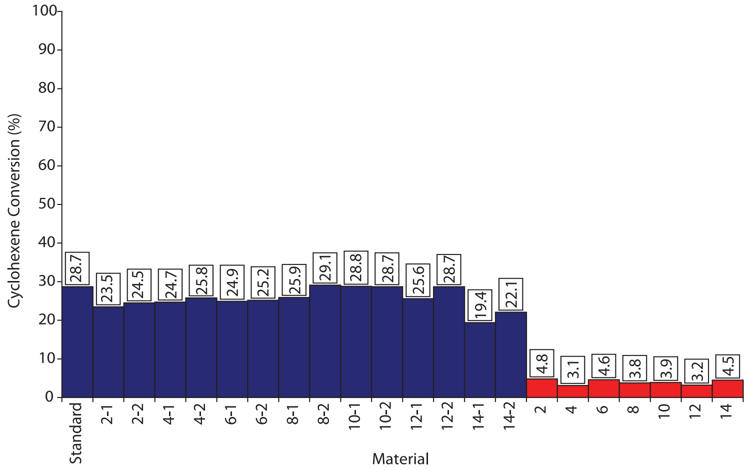


Fig.14. *Cyclohexene conversion (%) for TS-1 (blue) and cogel (red) materials after 6 hours, using urea-H_2O_2 oxidant*

to the surface hydroxyl groups. These hydroxyl groups could theoretically have been titanols or silanols, with either resulting in the lowering of the catalysts' reactivity. In the case of the titanol groups it has been reported that urea interacts very strongly with titanium centres, in some systems preventing any catalytic reaction occurring [5]. Whilst the binding of the adduct to the highly concentrated silanols on the cogel surface could have hindered access to the titanium active sites of the bulky cyclohexene reagent.

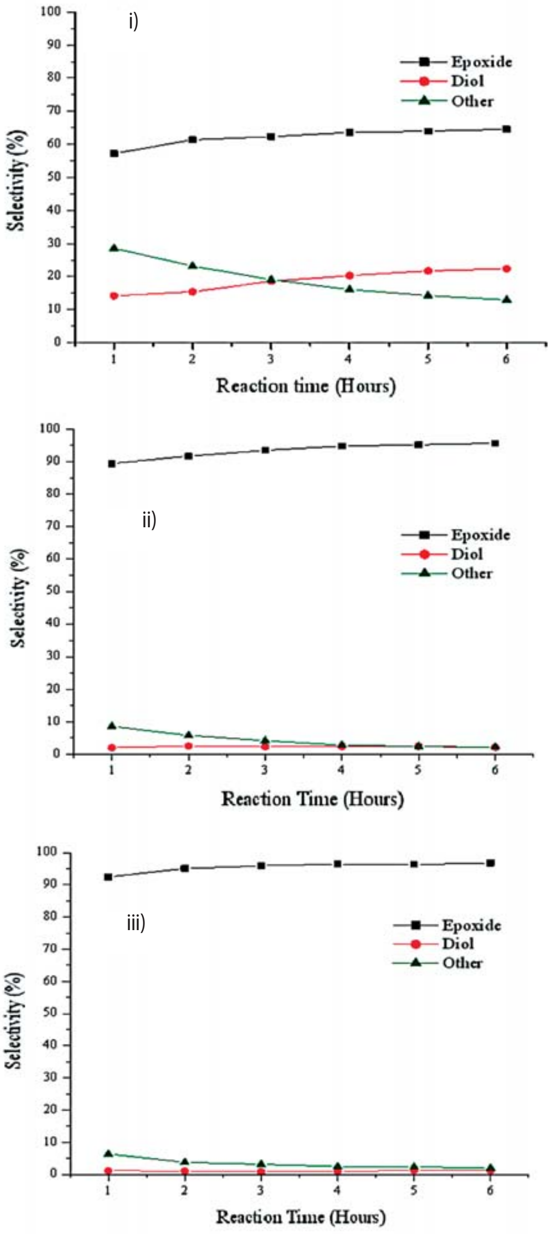


Fig.15. *Catalytic selectivity of i) cogel 8, ii) TS-1 8-2, iii) TS-1 standard, for the epoxidation of cyclohexene using urea-H_2O_2 oxidant. (Other denotes combined ketone and mono-alcohol formation (%))*

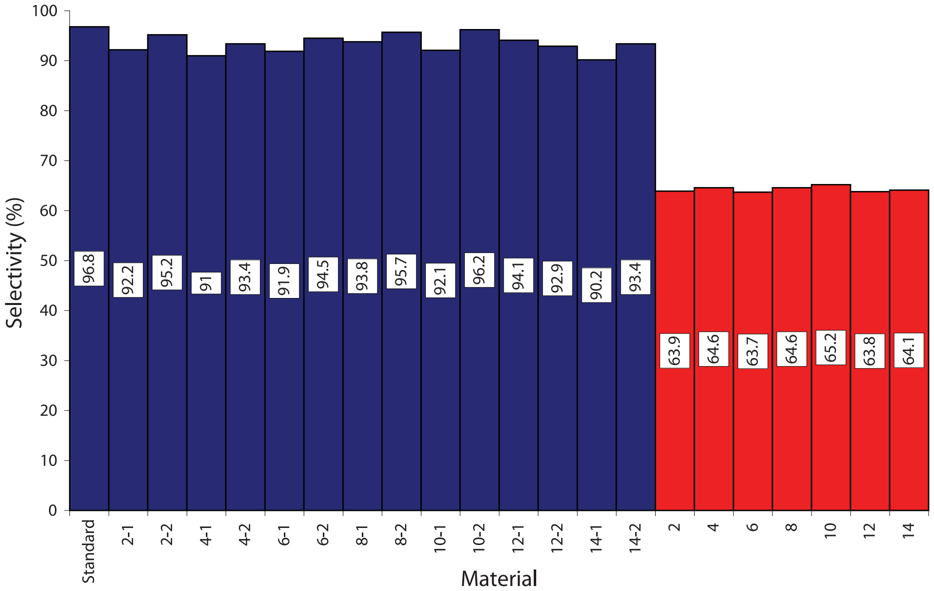


Fig.16. *Epoxide selectivity for TS-1 (blue) and cogel (red) materials for the epoxidation of cyclohexene using urea-H_2O_2 oxidant*

Alteration of the oxidant from aqueous H_2O_2 to the urea-H_2O_2 adduct greatly altered the reactivity of all of the titanosilicate materials (Fig.14). The reactivity of the TS-1 materials increased from ~ 20% cyclohexene conversion to ~ 30%. It was theorised that the comparative increase in hydrophilicity of the reaction medium enabled release of the organic products formed from the more hydrophobic TS-1 material. Conversely the reactivity of the cogel materials decreased (from ~ 20% cyclohexene conversion to ~ 5% conversion), and this could have been due to binding of the urea to either the titanol or silanol groups.

The catalytic selectivity of cogel and TS-1 materials towards epoxide formation remained approximately constant as the reaction continued, with no obvious epoxide degradation to the diol (Fig.15). Compared to results utilising aqueous H_2O_2, the epoxide selectivity of the TS-1 materials increased from ~ 60% to ~ 90%. The cogel materials also exhibited increased (to a larger extent) epoxide selectivity, rising from ~ 5% to ~ 60%.

The epoxide selectivity of the TS-1 materials remained higher than that for the cogel materials and appeared stable over the reaction time (Fig.16). It was therefore concluded that by altering the oxidant to the urea-H_2O_2 adduct, the acid sites of the titanosilicate materials were prevented from catalysing the degradation of the epoxide [22]. It was shown that the cogel materials contain a higher concentration of terminal hydroxyl groups which catalyse diol formation. Potentially not all of these groups were neutralised by the urea adduct, thus explaining the lower epoxide selectivity of these materials.

4. Conclusions

In summary, the cogel and TS-1 materials reported herein had good catalytic potential, containing titanium heteroatoms in the desired tetrahedral coordination geometry. Additionally all materials appeared capable of forming the necessary titanium peroxy species required for oxidation catalysis. However the catalytic ability may have been limited by the large size of the TS-1 crystals. Materials prepared with either the titanium isopropoxide or the butoxide showed comparable characteristics whilst materials prepared with titanium ethoxide were shown to have titanium heteroatoms in a wider range of coordination environments.

The epoxidation of cyclohexene reaction using these titanosilicate materials demonstrated that alteration of these synthesis parameters only had a minor effect upon the catalytic properties of the materials produced. For epoxidation of cyclohexene, the cogel and TS-1 materials exhibited similar catalytic reactivity but vastly different selectivity. The epoxide selectivity of the TS-1 materials was comparable to values reported in the literature (~ 60%), whilst the epoxide selectivity of the cogel was extremely poor (< 5%). The epoxide selectivity of all of the titanosilicate materials decreased over time due to the acid catalysed formation of the diol. The catalytic ability of the TS-1 materials prepared from the cogel precursors is comparable to those TS-1 materials prepared from conventional means.

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