

# Synthesis and characterisation of Ti(IV) and Zr(IV)-containing elastomeric polysiloxane networks: a possible route to interesting heterogeneous catalysts

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Polysiloxane gels have been prepared in bulk and in non-aqueous suspension using an oligomeric dimethyl silanol, S5 or S10, and tetraethoxysilane (TEOS) as the main reactants, with a tin-based catalyst. Controlled levels of Ti and Zr have been introduced into the polysiloxane networks by replacing part of the TEOS by either Ti tetraisopropoxide (TIPO) or Ti tetrakis(2-ethylhexyl oxide) (TEHO) in the case of Ti, and Zr tetraisopropoxide (ZPO) in the case of Zr. Providing TEOS is maintained as the major crosslinking component, toluene insoluble gels are formed with Ti and Zr covalently incorporated into the network.

The Ti- and Zr-containing elastomeric polysiloxane gels have been used as heterogeneous catalysts in the epoxidation of cyclohexene using *t*BHP or 30% aqueous H<sub>2</sub>O<sub>2</sub>. With the former oxidant the gels are indeed active and selective catalysts; however, essentially no activity was observed when aqueous H<sub>2</sub>O<sub>2</sub> was employed.

The structure of the gels and their role in catalysis is discussed in the context of Ti and Zr-containing zeolite and other mixed oxide catalysts.

## Introduction

There has been much attention given recently to the class of heterogeneous catalysts consisting of mixed Si and Ti oxides. Those based on zeolite crystal structures such as TS-1<sup>1</sup> are interesting as they catalyse the oxidation of small molecules<sup>2</sup> using aqueous hydrogen peroxide which has environmental benefits over organic alkyl peroxides. Ti silicates with larger pore sizes have also been made to deal with the reaction of larger substrates. These include TS- $\beta$ ,<sup>3</sup> Ti-MCM-41<sup>4</sup> and Ti-MCM-48,<sup>5</sup> which have pores in the range 16–100 Å. The scope of Ti-substituted zeolites is limited however as there is a maximum amount of Ti that can be incorporated and only a certain range of crystal structures and topologies are accessible. The sol–gel strategy used in forming mixed oxides is another route to Ti-containing silica materials that possess Ti(IV) sites well-dispersed in the matrix. Advantages are intimate mixing of components, control over the composition of the matrix, control over the level of Ti incorporated, and the ability to vary the porosity. The pore size of such sol–gel products is generally 10–100 Å<sup>6</sup> which is larger than the pores of TS-1, and therefore there is the possibility of the materials being active catalysts in the oxidation of large and bulky substrates. Studies have been carried out by Neumann *et al.*,<sup>7</sup> Klein *et al.*<sup>8</sup> and others<sup>9</sup> and some extremely active mixed oxide catalysts have been reported by these groups.

Elegant work involving the grafting or attachment of Ti sites to the surface of Si oxides,<sup>10</sup> for example within the channels of Ti-zeolite MCM-41,<sup>11</sup> has produced species which prove to be active catalysts in alkene epoxidation. This suggests that the Ti(IV) centres do not need to be located within the zeolite framework itself in order to be catalytically active. This has been confirmed by the synthesis of structurally well-defined low molecular weight Ti-containing silsequioxanes<sup>12</sup> which are also active alkene epoxidation catalysts, with alkyl hydroperoxides as the oxidant. Very recently the preparation of a Pd-doped Ti silicate has been reported and used to catalyse the epoxidation of propene.<sup>13</sup>

Literature concerning Zr-containing molecular sieves, *cf.* TS-

1, is much more scarce, as incorporating the large Zr(IV) cation into a crystalline framework is rather difficult. The Zr equivalent of TS-1 has however been synthesised,<sup>14</sup> but it showed very poor catalytic activity in oxidation reactions using H<sub>2</sub>O<sub>2</sub>. Recently, Zr silicates with a silicalite-2 (ZSM-11 MEL) structure<sup>15</sup> have been made successfully and used as catalysts in the hydroxylation of phenol using H<sub>2</sub>O<sub>2</sub>. Mixed oxides of Zr and Si have very high acid strengths among oxide pairs (Tanabe model),<sup>16</sup> and therefore have been used to catalyse reactions such as alcohol dehydration<sup>17</sup> and alkene isomerisation.<sup>18</sup> Zr/Si mixed oxide catalysts are also active for the oxidation of molecules with peroxides.<sup>19</sup> With alkenes however these catalysts give very poor selectivity to epoxide, and this is thought to be due to the intrinsic acidity of these oxides, leading to the ring-opening of the epoxide product. This acidity arises from charge differences created by the mixing of silicon and zirconium oxides, and is predicted by the Tanabe model.

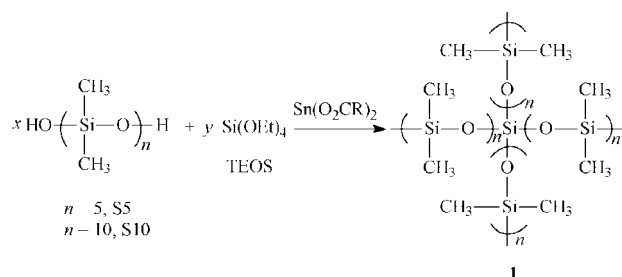
In the various catalyst developments described above the combination of Ti/Si and Zr/Si has always been such as to maintain essentially the oxide or inorganic nature of the products, where any organic (CH) component is present at a low or very low level. This is the case even in the recent work reported by Corma *et al.*<sup>20</sup> Within the material science area, however, parallel work has been in progress directed at the development of inorganic/organic hybrid materials, in some cases at the nanoscopic scale.<sup>21</sup> For example, sol–gel condensation of Ti(OR)<sub>4</sub> with a stoichiometric excess of Me<sub>2</sub>Si(OR)<sub>2</sub> has produced elastomeric poly(dimethylsiloxane) (PDMS) chains with rigid nanodomains of TiO<sub>2</sub>.<sup>22</sup> Similarly crosslinking of dimethylsiloxane oligomers with O=V(O–)<sub>3</sub> units has yielded poly(siloxane–vanadate) hybrid materials with interesting physical properties.<sup>23</sup> Since silanols (dihydroxy terminated poly- or oligosiloxanes) will react readily with tetraalkoxyoxysilanes in the presence of *e.g.* organotin dicarboxylate catalysts<sup>24</sup> to yield three dimensional elastomeric polysiloxane networks, we decided to synthesise such networks, which are substantially organic in nature with some of the crosslinking Si sites replaced by analogous Ti or Zr sites. Such species would represent interesting novel elastomeric materials

in their own right, *e.g.* possibly providing improved adhesion, but we were also conscious that they might function *e.g.* as alkene epoxidation catalysts, hence extending the range of Ti/Si and Zr/Si-based catalysts to include species with substantial organic character. We further thought that the known intensely hydrophobic nature of polysiloxanes might inhibit penetration of water to the active Ti or Zr site and hence allow catalysis of alkene epoxidation using aqueous H<sub>2</sub>O<sub>2</sub> as the oxidant, similar to TS-1. We have already made a preliminary disclosure of our methodology for producing spherical polysiloxane-based particulates<sup>25</sup> and this paper reports in more detail our findings in this area.

## Results and discussion

### Ti-containing polysiloxane networks

**Bulk gel synthesis.** Oligomeric silanols S5 and S10 containing average numbers of dimethylsiloxy units of 5 and 10 respectively were condensed with tetraethoxysilane (TEOS) in a molar ratio S5 or S10/TEOS of 2/1 in order to generate a uniformly crosslinked matrix (**1**) (Scheme 1). The catalyst employed was either stannous 2-ethylhexanoate (SO) or dibutyltin diacetate (DBTDA). The structure **1** is of course idealised and assumes no mutual condensation of silanol building blocks. To assess superficially the extent of cross-linking, reactions were carried out in glass vials to allow visual observation of any gel formation. A range of reactions was carried out with progressive levels of TEOS replaced either by Ti(IV) isopropoxide (TIPO) or by Ti(IV) 2-ethylhexoxide (TEHO). Table 1 shows details of the reactions in which the Ti(IV) alkoxide component was added neat to the pre-mixed silanol/TEOS. In some cases this led to immediate formation of a precipitate or a sticky gel. This either remained insoluble in the bulk reaction mixture or was gradually solubilised to yield a more homogeneous mixture. However, this did suggest that the



**Scheme 1** Polysiloxane network formation from silanols S5 and S10 and TEOS.

initial reaction of the Ti alkoxide with silanol groups was too fast to allow formation of a highly regular network. Nevertheless reactions were allowed to continue until whole reaction mixtures gelled.

The complexation of Ti alkoxides by *e.g.* acetylacetonate or dibutyl phosphate<sup>26</sup> is reported to reduce the reactivity of the Ti component and provide closer parity with analogous Si species, hence maximising the prospects of forming a uniform gel. Accordingly therefore a second range of gels were synthesised in which the TEHO or TIPO component was added as a 1:1 molar mixture with ethyl acetoacetate (EACAC). The initial tendency to form a microgel was reduced but not eliminated in all reactions, but re-sorption of any microgel took place quickly with macrogelation occurring uniformly beyond ~24 h. The results are shown in Table 2.

Reactions using silanol precursor S5 proved less prone to forming the initial microgel and so only preparation TS10 (Table 1) was repeated as TS10a (Table 2) with the EACAC complexand. It is possible that the lower viscosity of S5 relative to S10 allows faster dispersion of the Ti alkoxide and hence minimises microgelation. Most of the reactions formed a rigid gel over varying timescales, and high temperature provided faster gelation only in the case when a high level of Ti alkoxide was used (TS5, TS5a, TS10a, TS11). Reactions involving a level of TEOS ≥ 0.5 mole fraction tended to gel most quickly. Strangely, reactions using TEOS with TEHO at 0.5 mole fraction each, with both S5 and S10 (*i.e.* TS2 and TS7), failed to form a solid gel at all. Those gels prepared with a high level of TEOS (TS1, TS4, TS6 and TS9) proved to be insoluble in toluene and hence seem to be fully developed crosslinked elastomeric networks. On the other hand attempts to use high levels of TEHO and TIPO tended to produce gels which did solubilise in toluene. This suggests that network formation was not complete in this case and it seems that despite initially fast reactions of these Ti tetraalkoxides with S5 and S10 (*cf.* microgel formation) effective condensation involving all four alkoxide groups is inhibited. TEOS is therefore the main network former with TEHO and TIPO incorporated possibly *via* only 2 or 3 co-ordination sites. Other general observations are that the quantity and type of catalyst are not crucial in terms of macrogelation, and TIPO seems to be more reactive than TEHO as would be expected from the relative sizes of their alkoxy groups.

A third set of gels was therefore prepared using TEOS and TIPO with S5 and S10 in order to ascertain more precisely the maximum level of the Ti component that could be incorporated while still providing a toluene insoluble crosslinked gel. The compositions examined are shown in Table 3. All reactions gelled and each gel was extracted with hot toluene for 48 h to remove all unbound fragments. Those gels produced from compositions containing TEOS mole fraction 0.5 and below

**Table 1** Composition of Ti-containing bulk polysiloxane gels produced using non-complexed Ti alkoxides

Silanol	Gel	Reactants (mole ratio)				Ti content <sup>a</sup> (theor. mol%)	Catalyst (wt%)			Gel time/days	Soluble in toluene?
		S10/S5	TEOS	TEHO	TIPO		SO	DBTDA	T/°C		
S10	TS1	2	0.9	0.1	—	3.3	5	—	~20	1	no
	TS2	2	0.5	0.5	—	16.6	1	—	~20	no gel	yes
	TS3	2	0.1	0.9	—	30.0	—	1	80	13	yes
	TS4	2	0.9	—	0.1	3.3	—	1	~20	1	no
	TS5	2	0.1	—	0.9	30.0	—	5	80	3	no
S5	TS6	2	0.9	0.1	—	3.3	1	—	~20	4	no
	TS7	2	0.5	0.5	—	16.6	—	1	~20	no gel	yes
	TS8	2	0.1	0.9	—	30.0	1	—	80	7	yes
	TS9	2	0.9	—	0.1	3.3	1	—	~20	1	no
	TS10	2	0.1	—	0.9	30.0	—	1	~20	3	yes

<sup>a</sup>Calculated from reactant feed ratios.

**Table 2** Composition of Ti-containing bulk polysiloxane gels produced using Ti alkoxides complexed with EACAC

Silanol	Gel	Reactants (mole ratio)				Ti content <sup>b</sup> (theor. mol%)	Catalyst (wt%)		T/°C	Gel time/days	Soluble in toluene?
		S10/S5	TEOS	TEHO <sup>a</sup>	TIPO <sup>a</sup>		SO	DBTDA			
S10	TS1a	2	0.9	0.1	—	3.3	5	—	~20	4	no
	TS2a	2	0.5	0.5	—	16.6	1	—	80	4	yes
	TS3a	2	0.1	0.9	—	30.0	—	1	~20	no gel	yes
	TS4a	2	0.9	—	0.1	3.3	—	1	~20	1	no
	TS5a	2	0.1	—	0.9	30.0	—	5	80	3	yes
S5	TS10a	2	0.1	—	0.9	30.0	—	1	80	5	yes
	TS11	2	—	—	1.0	33.0	1	—	80	7	yes

<sup>a</sup>1/1 alkoxide/ethyl acetoacetate. <sup>b</sup>Calculated from reactant feed ratios.

dissolved completely in toluene. The weight loss from the other three gels decreased significantly with increase in the mole fraction of TEOS.

**Spherical particulate gels.** Suspension polymerisation is a well-developed technique for making spherical particulate resins or beads for use as supports,<sup>27</sup> and we have already made a preliminary disclosure of our non-aqueous suspension methodology for the preparation of spherical particulate polysiloxane resins.<sup>25</sup> Here the same methodology has been employed to prepare particulate analogues of the bulk Ti-containing polysiloxanes described above. S5 was chosen as the silanol component to be crosslinked with TEOS. Varying levels of Ti were introduced by progressive replacement of some of the TEOS with TEHO. The S5/TEOS/TEHO mixtures were prepared as homogeneous solutions prior to their introduction as the dispersed phase in liquid paraffin as the continuous phase. The TEHO mole ratio was kept low enough to avoid any initial microgelation as observed in the bulk condensation reactions. In all cases SO was used as the catalyst. Table 4 summarises the syntheses carried out. With a mole ratio S5/TEOS/TEHO of 1/0.5/0.021 and an adequate stirrer speed (700 rpm) good quality spherical particulate polysiloxane resins were obtained (STS2 and STS3, Table 4). Optical photomicrographs are shown in Fig. 1; typically average particle diameters were in the range 50–200 µm. Attempts to increase the level of TEHO resulted in a breakdown of the suspension and the formation of the product as irregular solid lumps. Use of TEHO only as the crosslinker (STS6) failed to produce any solid product. The results confirm the observation from the synthesis of bulk gels that TEHO is not sufficiently reactive to be an efficient crosslinker and that relatively high levels of TEOS are required to produce stable crosslinked polysiloxane networks.

**Ti-containing polysiloxane gels from CpTiCl<sub>3</sub>.** Thomas *et al.*<sup>11</sup> have shown that a Ti-siloxane site with one siloxane bond replaced with a cyclopentadienyl (Cp) moiety displays catalytic activity in alkene epoxidation. In an attempt to produce polysiloxane gels with related Ti sites silanol S10 was reacted with CpTiCl<sub>3</sub> under a variety of conditions. Though gels and

elastomeric solids could be obtained they all proved to be soluble in toluene and chloroform suggesting that crosslinking was incomplete. <sup>1</sup>H NMR spectra did indicate the presence of aromatic protons at ~6.5 ppm suggesting that the approach has merit. Krijnen *et al.*<sup>28</sup> has used this strategy to attach a Cp–Ti site to silsequioxanes and so with further effort related polysiloxane elastomers do seem accessible.

### Structural analysis

Adequate molecular structural characterisation of the Ti-containing polysiloxanes proved to be difficult. The elastomeric nature of the products made sample preparation for FTIR analysis problematical. Freezing of a sample in liquid N<sub>2</sub> followed by rapid KBr disc preparation allowed some spectra to be obtained. Gels that were soluble in *e.g.* toluene could also be cast as films onto NaCl plates. The literature indicates that vibrational bands at ~960–970 cm<sup>-1</sup> are characteristic of Ti-containing silica zeolites and various structural assignments have been proposed<sup>29</sup> involving Ti and Si associated with O. In the spectra of Ti/Si mixed oxides a similar band at somewhat lower frequency (940–950 cm<sup>-1</sup>)<sup>7,26</sup> has also been taken as evidence of Ti–O–Si linkages, with the degree of hydration seemingly being important in defining the band position more precisely. The present polysiloxane-based species are not, of course, pure inorganic oxides and therefore are unlikely to show exactly the same behaviour with respect to the IR spectra. All samples examined however did display a new band at ~920–935 cm<sup>-1</sup> (Table 5) which may indeed be diagnostic of the Ti–O–Si linkage.

Diffuse reflectance (DR) UV-visible absorption spectra were also used to try to confirm the presence of covalently bound Ti. This technique has been applied successfully in the case of Ti-silicalites. The wavelength range of interest is ~200–500 nm. Anatase, for example, absorbs at ~370 nm, octahedral TiO at ~250–300 nm and tetrahedral TiO at ~210 nm.<sup>30</sup> The spectra of some of the resins were recorded and all showed a broad absorption at ~225–350 nm with multiple maxima. For comparison the spectrum of a non-Ti-containing resin was also recorded and this displayed a much sharper absorption centred at ~230 nm. Since pure SiO<sub>2</sub> is transparent in this region the latter band must be associated with the –OSi(CH<sub>3</sub>)O– unit.

**Table 3** Composition of extended range of Ti-containing bulk polysiloxane gels

Gel	Reactants (mole ratio)				Gel time (days)	Soluble in toluene?	Weight loss on extraction (%) <sup>a</sup>
	S10	S5	TEOS	TPO			
TS9b	—	2	0.9	0.1	2	no	12
TS12	—	2	0.75	0.25 <sup>b</sup>	7	no	38
TS13	2	—	0.6	0.4 <sup>b</sup>	7	partially	73
TS14	—	2	0.5	0.5	7	yes	100
TS5b	2	—	0.1	0.9	7	yes	100
TS11	—	2	0	1.0 <sup>b</sup>	7	yes	100

<sup>a</sup>Using toluene. <sup>b</sup>1:1 complex with EACAC.

**Table 4** Preparation of Ti-containing spherical particulate polysiloxane resins *via* a non-aqueous suspension polymerisation methodology<sup>a</sup>

Resin	Reactants (mole ratio) <sup>a</sup>			Ti content <sup>b</sup> (theor. mol%)	Phase <sup>c</sup> ratio	T/°C	Stirrer speed/rpm	Appearance of product
	S5	TEOS	TEHO					
STS1	1	0.5	0.021	1.4	1:4	45	500	aggregated spherical particles
STS2	1	0.5	0.021	1.4	1:7	45	700	individual spherical particles
STS3	1	0.5	0.021	1.4	1:7	45	700	individual spherical particles
STS4	1	0.45	0.05	3.3	1:7	45	700	aggregated lumps
STS5	1	0.375	0.125	8.3	1:7	45	700	aggregated lumps
STS6	1	0	0.5	33.0	1:7	70	1500	no solid product

<sup>a</sup>Using paraffin oil as a continuous phase, SO (1 wt%) as catalyst. <sup>b</sup>Calculated from reactant feed composition. <sup>c</sup>Ratio of dispersed silane phase to paraffin continuous phase.

Thus the component of absorption from say  $\sim 270$ – $350$  nm in the Ti-containing species seems to be characteristic of the incorporation of Ti centres, and this is confirmed in the case of TS11 which utilised only TIPO as the crosslinker and displays a broad absorption band from 240 to 400 nm. Overall however, it is very difficult to assign the features seen in the various spectra to particular TiO structures, but since gels generally showed no sharp feature at  $\sim 370$  nm it at least seems clear that domains of TiO<sub>2</sub> are absent.

Those bulk gels and particulate resins insoluble in toluene were extensively extracted for 48 h to remove any reaction fragments not incorporated into the polysiloxane network and then dried. Attempts to digest these in preparation for Ti analysis also proved difficult. Treatment with aqueous base did eventually produce a white residue presumed to be largely

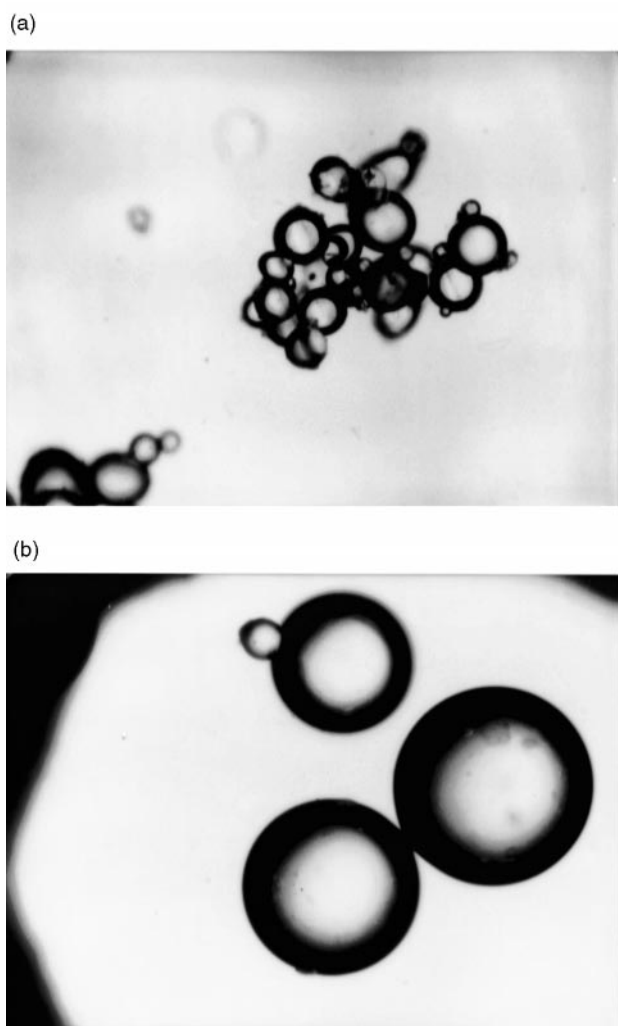
TiO<sub>2</sub>. Dissolution of this and analysis by ICP–AAS yielded a Ti content in STS2 and STS3 of 0.065 and 0.083 (mmol Ti) g<sup>-1</sup> resin. The theoretical values calculated from the component feed ratios are both 0.058 (mmol Ti) g<sup>-1</sup>. In the case of TS9b analysis of the toluene soluble component showed the leaching of Ti to be  $\sim 0.2\%$  of the original Ti feed. With STS3 the paraffin continuous phase was shaken with aqueous ethylamine solution to hydrolyse any TEHO leached into the paraffin. No precipitate was observed confirming a high incorporation of the Ti component into the polysiloxane particulate. Attempts to detect any Si–O–Ti linkages *via* <sup>29</sup>Si NMR unfortunately failed since the spectrum was dominated by the Si signals from the dimethylsiloxane chain.

Overall, however, this is good evidence that most of the Ti component in gel and resin preparations is covalently incorporated into the polysiloxane network, and hence it was felt worthwhile to examine if these species displayed any catalytic activity in alkene epoxidation.

The surface areas of two gels TS9b and STS2 were determined by application of the BET theory to N<sub>2</sub> sorption isotherms and very low values, 2.2 and 1.8 m<sup>2</sup> g<sup>-1</sup> respectively, were obtained. These data reflect the elastomeric gel nature of these species and suggest that chemical exploitation of the Ti sites would require use of a swelling solvent. Thermogravimetric analysis (TGA) of STS2 indicated that degradation commenced at 330 °C with 10% mass loss at 420 °C. Use of these Ti-containing polysiloxanes at temperatures up to  $\sim 250$  °C would therefore present no stability problems.

**Zr-containing polysiloxane networks.** Bulk Zr-containing gels were prepared similarly to the Ti-containing species using various levels of Zr(IV) isopropoxide (ZPO) partially replacing TEOS, again with silanols S5 and S10 and catalysts SO and DBTDA. Table 6 shows the compositions explored. Again there was a problem of microgel formation on addition of the ZPO and so some reactions were repeated with the ZPO complexed with EACAC (Table 7) which helped to reduce this effect. Overall the results are very similar to those with the Ti-containing gels in that fully crosslinked toluene-insoluble networks could be formed only when low levels of ZPO were used to replace some of the TEOS. Exhaustive extraction of gels ZS1 and ZS2 with toluene led to no degradation of the network, and analysis of the extraction solvent showed that only 0.02 and 0.01% respectively of the theoretical Zr feed content was leached out. Interestingly the Ti-containing gel TS14 with a composition analogous to ZS2 did slowly dissolve in toluene, suggesting that Zr incorporation may be more complete and the network formed more robust than analogous Ti species. In studies on ZrO<sub>2</sub>–SiO<sub>2</sub> and TiO<sub>2</sub>–SiO<sub>2</sub> glasses the Zr–O–Si linkage has also been shown to be more stable than the Ti–O–Si linkage.<sup>31</sup>

As with the Ti-containing gels, obtaining definitive molecular structural evidence for covalent incorporation of Zr residues proved difficult. FTIR spectra did show the emergence of a band at  $\sim 940$ – $950$  cm<sup>-1</sup> in the samples examined

**Fig. 1** Optical micrographs of a) resin STS2 ( $\times 50$ ); b) resin STS3 ( $\times 100$ ).

**Table 5** Characteristic bands observed in FTIR spectra of Ti-containing bulk polysiloxane gels

Gel	Original Ti source	Ti content (mole fraction crosslinker)	Sample form	Band/cm <sup>-1</sup>
TS1	TEHO	0.1	solid	934 (v. weak)
TS2a	TEHO	0.5	cast film from toluene	934 (weak)
TS5b	TIPO	0.9	cast film from toluene	927 (weak)
TS7	TEHO	0.5	neat liquid	923 (strong)
TS8	TEHO	0.9	cast film from toluene	923 (weak)
TS10a	TIPO	0.9	cast film from toluene	923 (strong)
TS11	TIPO	1.0	cast film from toluene frozen N <sub>2</sub> /KBr disc	928 (weak), 923 (strong)

(Table 8). In the literature<sup>32</sup> bands at 970, 960 and 945 cm<sup>-1</sup> have been assigned to Zr–O–Si vibrations.

### Epoxidation of cyclohexene catalysed by Ti-containing polysiloxanes

We have reported previously on a number of polymer-supported Mo(vi) species which are extremely active and selective heterogeneous catalysts in the liquid phase epoxidation of alkenes using *tert*-butyl hydroperoxide as the oxidant.<sup>33</sup> Indeed, recently we have shown that similarly supported Ti based complexes are also active catalysts.<sup>34</sup> One of our objectives in synthesising these polysiloxane networks containing Ti (and Zr) centres was to mimic to some extent the local Ti structure in Ti-silicalites. Accordingly therefore following exhaustive extraction with toluene and drying spherical particulate resin STS3 and bulk gel TS9b were employed as potential catalysts in the *t*BHP epoxidation of cyclohexene under both anaerobic and aerobic conditions. Fig. 2 and 3 show the conversion curves obtained. Reactions were performed under conditions of excess alkene to optimise selectivity, and conversion to cyclohexene oxide (%) is quoted relative to the initial level of *t*BHP used. Clearly both Ti-containing polysiloxanes are indeed active catalysts with high selectivity for epoxide production (essentially no co-products formed). Both catalysts examined behaved very similarly providing 70–85% epoxide in 1200 min under anaerobic conditions (Fig. 2). This activity is, of course, very much poorer than that of conventional TiO<sub>2</sub>/SiO<sub>2</sub> catalysts, and indeed our own polymer-supported Mo(vi) catalysts. However, the fact that Ti centres incorporated into the network of “organic” polysiloxanes represents a significant broadening of the catalytic versatility of Ti species. The similarity in the conversion curves for reactions with STS3 and TS9b (0.06 mmol Ti in each case) suggests that the nature and distribution of active Ti sites is similar in both catalysts. When the reactions were repeated without exclusion of air conversions to epoxide nominally in excess of 100% were observed (Fig. 3). We have reported this behaviour before with both Mo(vi)<sup>35</sup> and Ti(IV)<sup>34</sup> based polymer-supported catalysts. This arises from autoxidation of cyclohexene and the production of cyclohex-2-enyl hydroperoxide which functions as an additional hydroperoxide source to *t*BHP. Allylic oxidation products, cyclohex-2-en-1-ol and cyclohex-2-en-1-one are

also formed, and this was the case also in this work. The latter species however were not quantified.

Analysis of the supernatant reaction mixtures from the above four reactions showed the Ti leached to be ~0.09 and 0.12% for STS3 used with and without air respectively, and 1.13 and ~0% for TS9b used with and without air respectively. A more telling test of leaching however was performed by repeating the anaerobic reaction using a new sample of STS3 and then filtering off the catalyst after 23 h when the reaction was complete. More *t*BHP was then added and the reaction continued for a further 7 h. No increase in conversion of cyclohexene to epoxide was observed (Fig. 4) showing that the level of Ti leached was too low to be catalytically active, or that the leached Ti was present in a non-catalytic form.

Attempts have also been made to utilise aqueous H<sub>2</sub>O<sub>2</sub> (30%) as the oxidant in catalysing cyclohexene epoxidation using STS3 and TS9b. Our hope was that the very hydrophobic nature of the polysiloxane network might exclude water and provide activity related to zeolite TS-1 with propene. Reactions run with STS3 and TS9b using toluene as the solvent showed no conversion after 7 h at 60 °C. However, it was quite clear that both systems consisted of 3 phases, with toluene and the aqueous H<sub>2</sub>O<sub>2</sub> being immiscible, each in contact with the catalyst gel. The solvent was therefore changed to propan-2-ol which afforded a single liquid phase with the aqueous H<sub>2</sub>O<sub>2</sub>. Interestingly the STS3 particles turned yellow on addition of the oxidant. This colour has been noted before by other authors and it is suggested that this is an indication of the formation of a peroxy compound formed by interaction of H<sub>2</sub>O<sub>2</sub> with a Ti centre.<sup>36</sup> Despite this optimistic indication no epoxidation was observed when the reaction mixture was maintained at 60 °C for 24 h. Alcohols might, of course, coordinate to active Ti centres in competition with peroxide, and van der Waal *et al.*<sup>37</sup> have reported an optimum activity for their zeolite TS-β catalyst using 20% propan-2-ol in acetonitrile. Using this mixture as solvent ~2% cyclohexene oxide was detected after 24 h reaction. Switching to 100% acetonitrile and diglyme, both of which gave homogeneous solutions with aqueous H<sub>2</sub>O<sub>2</sub>, essentially gave no reaction. To ensure that all components were penetrating the catalyst gel the sorption of toluene, propan-2-ol and aqueous H<sub>2</sub>O<sub>2</sub> into STS3 and TS9b was measured. For STS3 the liquid up-take was 1.1; 0.8; and 0.3 g liquid per g resin respectively, and for TS9b the results were 0.2; 0.2; and 0.06 g liquid per g gel respectively. It is clear

**Table 6** Composition of Zr-containing bulk polysiloxane gels produced using non-complexed ZPO

Silanol	Gel	Reactants (mole ratio)			Zr content <sup>a</sup> (theor. mol%)	Catalyst (wt%)		<i>T</i> /°C	Gel time/days	Soluble in toluene?
		S10/S5	TEOS	ZPO		SO	DBTDA			
S10	ZS1	2	0.9	0.1	3.3	—	5	~20	1	no
	ZS2	2	0.5	0.5	16.6	1	—	80	2	no
	ZS3	2	0.1	0.9	30.0	—	1	~20	2	yes
S5	ZS4	2	0.9	0.1	3.3	5	—	~20	2	no
	ZS5	2	0.5	0.5	16.6	—	1	~20	3	yes
	ZS8	2	0.1	0.9	30.0	1	—	80	2	partially

<sup>a</sup>Calculated from reactant feed ratios.

**Table 7** Composition of Zr-containing bulk polysiloxane gels produced using ZPO complexed with EACAC

Silanol	Gel	Reactants (mole ratio)			Zr content <sup>b</sup> (theor. mol%)	Catalyst (wt%)			Gel time/days	Soluble in toluene?
		S10/S5	TEOS	ZPO <sup>a</sup>		SO	DBTDA	T/°C		
S10	ZS1a	2	0.9	0.1	3.3	—	5	80	1	no
	ZS2a	2	0.5	0.5	16.6	1	—	~20	7	yes
	ZS3a	2	0.1	0.9	30.0	—	1	~20	no gel	yes
S5	ZS4a	2	0.9	0.1	3.3	5	—	~20	4	no
	ZS5a	2	0.5	0.5	16.6	—	1	80	5	yes
	ZS8a	2	0.1	0.9	30.0	1	—	~20	no gel	yes

<sup>a</sup>1/1 ZPO/ethyl acetoacetate. <sup>b</sup>Calculated from reactant feed ratios.

**Table 8** Characteristic bands observed in FTIR spectra of Zr-containing polysiloxane gels

Gel	Original Zr source	Zr content (mole fraction crosslinker)	Sample form	Band/cm <sup>-1</sup>
ZS3	ZPO	0.3	cast film from toluene	948 (weak)
ZS3a	ZPO	0.3	cast film from toluene	944 (medium)
ZS5	ZPO	0.17	cast film from toluene	943 (weak)
ZS6	ZPO	0.3	cast film from toluene	949 (weak)

from these data that the polarity of the liquid component is more important than the size in controlling up-take by the polysiloxanes; and while the level of sorption of H<sub>2</sub>O<sub>2</sub> is rather low it does seem sufficiently high not to inhibit catalysis.

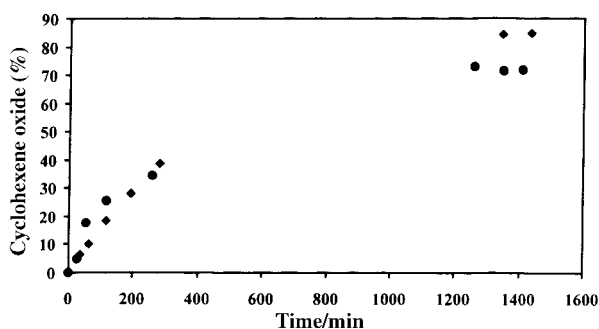
On balance therefore it seems that the water component of the 30% aqueous H<sub>2</sub>O<sub>2</sub> is the limiting factor, although more detailed studies are required to confirm this. A corollary of this observation is that the active Ti site, and/or the environment of the site, in our polysiloxane gels is sufficiently different to that in zeolite TS-1 for the special catalytic properties of the latter not to be replicated in our species. It has been suggested<sup>38</sup> that the most plausible intermediate in catalyses by zeolite TS-1 using H<sub>2</sub>O<sub>2</sub> as oxidant is a five-membered cyclic species formed by interaction of H<sub>2</sub>O<sub>2</sub> and an alcohol molecule with the resting or initial Ti centre (**2**, Scheme 2). A similar intermediate can be envisaged when *t*BHP replaces H<sub>2</sub>O<sub>2</sub> (**3**). Epoxidation occurs by approach of the alkene to the distal oxygen, the latter being very electrophilic.<sup>39</sup> Formation of **2** (and **3**) is seen as occurring by fission of a Ti–O bond in the zeolite framework. However, results from work using silsequioxane model compounds<sup>12</sup> with tripodal binding of Ti–OR (*etc.*) (**4**) and bipodal binding of Ti(OR)<sub>2</sub> (**5**) have shown that active intermediates for alkene epoxidation can be generated by reaction with *t*BHP. Likewise Thomas *et al.*<sup>11</sup> have designed specific tripodal binding sites for Ti in the channels of the Ti zeolite MCM-41, and shown this to be capable of generating the reactive intermediate for alkene epoxidation with *t*BHP. It seems extremely likely that with our Ti-containing polysiloxanes a distribution of Ti sites is created with Ti co-ordinated to one, two, three and four dimethylsilyloxy segments (**6**). In principle all of these species are capable

of interacting with peroxide oxidants to generate reactive intermediates for alkene epoxidation. This undoubtedly occurs when *t*BHP is the oxidant. It seems very likely that this does not occur when H<sub>2</sub>O<sub>2</sub> is the oxidant, at least with 30% aqueous H<sub>2</sub>O<sub>2</sub>, or if Ti co-ordinated reactive species are formed they undergo deactivation before productive alkene epoxidation can occur. A corollary of this is that the sites in zeolite TS-1 are indeed special and provide a sufficiently long-lived reactive intermediate to achieve epoxidation of propylene where superficially similar unimolecular sites fail.

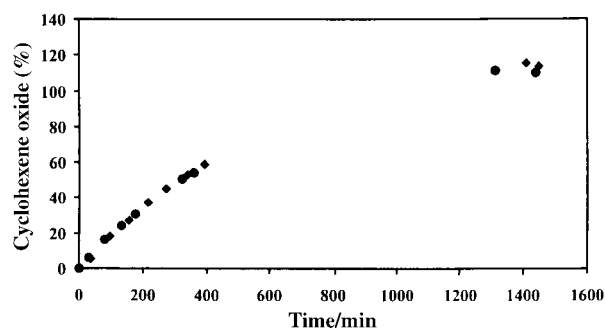
#### Epoxidation of cyclohexene catalysed by Zr-containing polysiloxanes

Use of Zr-containing polysiloxane ZS5 gel as a potential catalyst for epoxidation of cyclohexene by *t*BHP both in the presence and absence of air yielded the conversion curves shown in Fig. 5. While the activity is significantly lower than that displayed by the analogous Ti-containing gels, nevertheless these species also are catalysts. Attempts to use 30% aqueous H<sub>2</sub>O<sub>2</sub> as the oxidant met with no more success than with the Ti analogues. With 20% propan-2-ol-acetonitrile as the solvent a trace of cyclohexene oxide was produced, and in the case of the aerobic reaction allylic by-products were also seen again. No Zr was detected in the supernatant reaction mixtures from both *t*BHP and H<sub>2</sub>O<sub>2</sub> reactions.

Investigation of the mechanism of alkene epoxidation catalysed by Zr-centred catalysts has not been anywhere near as intense as with the Ti species. The Zr(IV) centre is a much larger one than the Ti(IV) and so major differences are possible. Use of Zr-containing polysiloxanes may minimise this factor.



**Fig. 2** Epoxidation of cyclohexene using *t*BHP catalysed by Ti-containing polysiloxane gels under N<sub>2</sub>; 72 mmol cyclohexene, 5 mmol *t*BHP, 60 °C, 0.06 mmol Ti in: ◆ TS11; ● TS9b.



**Fig. 3** Epoxidation of cyclohexene using *t*BHP catalysed by Ti-containing polysiloxane gels under aerobic conditions: ◆ TS11; ● TS9b (see Fig. 2 for conditions).

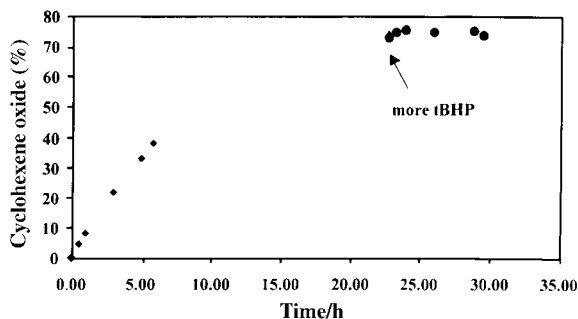


Fig. 4 Test for Ti leaching in epoxidation of cyclohexene using *t*BHP catalysed by Ti-containing polysiloxane gel TS11, the latter removed at 23 h (see Fig. 2 for conditions).

Interestingly it seems that appropriate Zr sites may be more tolerant to water than are Ti sites. In this context Quignard *et al.*<sup>40</sup> have reported active sites of the form  $\equiv\text{SiO}-\text{Zr}(\text{OH})_3$  and  $\equiv(\text{SiO})_3-\text{Zr}-\text{OH}$  by reaction of silica with  $\text{Zr}(\text{Np})_4$  and both of these appear to be active in the epoxidation of cyclohexene with 70% aqueous  $\text{H}_2\text{O}_2$ . It would be interesting to see the effect of using more dilute  $\text{H}_2\text{O}_2$ . Further studies of Zr-containing polysiloxane networks may therefore also be worthwhile in the context of exploiting dilute aqueous  $\text{H}_2\text{O}_2$  more widely.

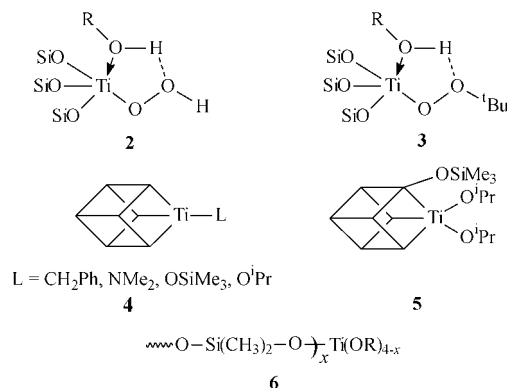
## Experimental

### Materials

Silanols S5 and S10 (molecular weight dispersity  $\sim 2$ ) (Scheme 1) were obtained as a gift from Dow Corning. *tert*-Butyl hydroperoxide (Aldrich) was dried, produced as a toluene solution ( $\sim 4$  M) and standardised as reported previously.<sup>41</sup> Tetraethoxysilane (TEOS), titanium tetraisopropoxide (TIPO), cyclopentadienyltitanium trichloride ( $\text{CpTiCl}_3$ ) and zirconium tetraisopropoxide (ZPO) were from Aldrich. Titanium tetrakis(2-ethylhexyl oxide) (TEHO) was from Strem. Stannous 2-ethylhexanoate (SO) was from Sigma, and dibutyltin diacetate (DBTA) was from Aldrich. Toluene, ethyl acetoacetate (EACAC), cyclohexene, cyclohexene oxide and 30% aq.  $\text{H}_2\text{O}_2$  were from Aldrich. *p*-Dichlorobenzene was from May and Baker, and paraffin oil was from Beveridge. Materials were used as supplied unless stated otherwise.

### Synthesis of bulk Ti- and Zr-containing polysiloxane gels

a) Using non-complexed Ti or Zr alkoxides (see Tables 1 and 6). Typically silanol S5 (4 g, 5.28 mmol), TEOS (0.05–1.03 g, 0.26–4.95 mmol), TEHO (0.16–0.97 g, 0.55–2.38 mmol) and SO (1–5 wt%) were weighed into a glass vial (10 ml) and mixed together thoroughly. The vial was closed with a cap and then left to stand at room temperature ( $\sim 20^\circ\text{C}$ ) or heated at  $80^\circ\text{C}$



Scheme 2 Reactive Ti–O–Si containing structures.

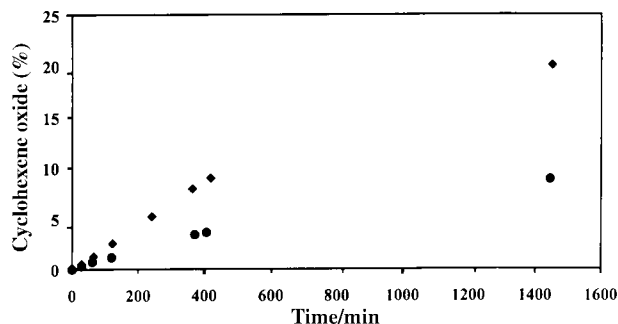


Fig. 5 Epoxidation of cyclohexene using *t*BHP catalysed by Zr-containing polysiloxane gel ZS1 under:  $\blacklozenge$ , aerobic and  $\bullet$ , anaerobic conditions (see Fig. 2 for conditions).

in an oil-bath. The onset of macrogelation was monitored visually. Before use in catalysis a sample of gel was weighed accurately into a paper thimble and extracted in a Soxhlet apparatus with toluene for 48 h. The recovered gel was dried under vacuum then reweighed. The toluene from extractions was evaporated on a rotary evaporator and any residue digested ready for metal analysis (see later).

b) Using Ti and Zr alkoxides complexed with ethyl acetoacetate (EACAC) (see Tables 2 and 7). Typically TEHO (2 g, 6.78 mmol) was weighed into a glass vial and EACAC (0.88 g, 6.78 mmol) was added to afford a 1 : 1 molar mixture. The vial was closed, the contents mixed thoroughly by shaking and left at room temperature for 2 h.

Silanol S5 (4 g, 5.28 mmol), TEOS (0.05–1.03 g, 0.26–4.95 mmol), TEHO/EACAC complex (0.23–1.06 g complex, 0.55–2.57 mmol TEHO) and SO (1–5 wt%) were weighed into a vial and thoroughly mixed. The procedure was then as before.

### Synthesis of spherical particulate Ti-containing polysiloxane resins via non-aqueous suspension polymerisation<sup>25</sup> (see Table 4)

Suspension polymerisations were carried out in a 250 ml parallel-sided jacketed baffled glass reactor fitted with a metal stirrer with a propeller-type impeller driven downwards by an overhead motor (IKA Eurostar Basic). The reactor was thermostatted using a water bath circulator (Grant W6-KD).

Typically silanol S5 (16.15 g, 0.046 mol), TEOS (4.9 g, 0.024 mol) and TEHO (0.56 g, 1 mmol) were combined with the SO catalyst (1 wt%), and the mixture suspended in the reactor in paraffin oil (138 ml) by stirring at 700 rpm. The suspension was heated at  $45^\circ\text{C}$  for 24 h. The resulting beads were filtered off and extracted with toluene in a Soxhlet extractor for 24 h.

### Ti and Zr analyses

Initially bulk polysiloxane gel samples were digested with  $\text{KNO}_3/\text{HNO}_3$  in a silica crucible using a protocol we have previously reported.<sup>35</sup> Where this method produced a water-soluble residue ICP–AAS was performed (Perkin Elmer Optima 3000, Centre for Particle Characterisation and Analysis, University of Paisley, UK).

Some samples, however, proved intractable to acid digestion and 1.5 M sodium hydroxide at  $\sim 100^\circ\text{C}$  was more successful. This tended to produce a white solid ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ) which was analysed by ICP–AAS at Ti oxide Ltd (Billingham, UK) following digestion in HF.

### Epoxidation of cyclohexene catalysed by Ti- and Zr-containing polysiloxanes

Typically polysiloxane gel (mass equivalent to 0.06 mmol Ti or Zr) was charged into a jacketed three-necked 20 ml glass reactor equipped with a condenser, overhead stirrer,  $\text{N}_2$  inlet

and septum; the jacket being connected to a thermoregulated water circulation bath. To the vessel was added cyclohexene (7.5 ml, 74 mmol) and *p*-dichlorobenzene (0.5 ml) as an internal GC standard. Toluene was added to bring the total volume to 10 ml. The reactor was brought to temperature as appropriate, and *t*BHP (~4 M in toluene, ~400 fold molar excess over catalyst) added by syringe to start the reaction (time=0). The reaction was allowed to proceed for 24 h with regular monitoring of conversion by GC analysis. For aerobic reactions the N<sub>2</sub> supply was not operated and reactions run in air. For anaerobic reactions mixtures were flushed with N<sub>2</sub>, and an atmosphere of N<sub>2</sub> maintained for the duration of reaction.

With 30% aqueous H<sub>2</sub>O<sub>2</sub> used as the oxidant, the procedure was similar with variation of the solvent and the oxidant introduced in the same way.

### Instrumentation

**GC analysis.** Samples were analysed on a Carlo Erba Mega Series 5300 gas chromatograph with cold on-column injection (0.1 µl) using a flame ionisation detector (230 °C)—column: SGE BPX5 (12 m × 0.32 mm, 0.5 µm film thickness); inlet pressure: 20 kPa; oven conditions: 70 °C (1 min), ramped (45 °C min<sup>-1</sup>) to 120 °C (1 min).

**<sup>1</sup>H and <sup>29</sup>Si NMR.** NMR spectra were generated using a Bruker AMX250 instrument.

**FTIR and DR UV-visible spectroscopic analysis.** FTIR spectra were obtained on a Nicolet 400D instrument; UV-visible spectra were recorded on a Philips PU8740 DR-UV/vis spectrophotometer.

**Surface area and thermogravimetric analysis.** N<sub>2</sub> sorption/desorption isotherms were recorded on a Micromeritics ASAP2010 and surface area computed using a BET treatment. Thermal stability data were generated on a Perkin Elmer TGA7 instrument over the temperature range 25–600 °C.

### Summary and future prospects

Ti- and Zr-containing polysiloxane gels have been prepared with the mutant metal centre covalently incorporated. The resultant elastomeric gels are effective heterogeneous catalysts in the epoxidation of cyclohexene using *t*BHP and the results shed further light on this field.<sup>42</sup> Although only very low activity was observed with 30% aq. H<sub>2</sub>O<sub>2</sub> as the oxidant, further work seems worthwhile exploring the reaction conditions employed, including use of a somewhat more concentrated aq. H<sub>2</sub>O<sub>2</sub>. These Ti- and Zr-containing polysiloxane gels may also provide improved materials properties such as adhesion and wettability, and this avenue of research also seems worthwhile pursuing.

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### References

- 1 M. Taramasso, G. Perego and B. Notari, *US Patent* 4410 501, 1983; *Chem. Abstr.*, 1981, **95**, 206272k.
- 2 B. Notari, *Catal. Today*, 1993, **18**, 163.
- 3 M. A. Cambor, A. Corma, A. Martinez and J. Perez-Pariante, *J. Chem. Soc., Chem. Commun.*, 1992, 589; A. Corma, P. Esteve, A. Martinez and S. Valencia, *J. Catal.*, 1995, **152**, 18.
- 4 D. T. Tanev, M. Chibwe and T. Pinnavaia, *Nature*, 1994, **368**, 321.
- 5 S. M. Kuznicki, *US Patent* 4938 939, 1990; *Chem. Abstr.*, 1990,

- 113, 175033s; D. P. Serrano, H. X. Li and M. E. Davis, *J. Chem. Soc., Chem. Commun.*, 1992, 745.
- 6 C. Brinker and G. W. Scherer, *Sol-gel Science*, Academic Press, San Diego, 1990.
- 7 R. Neumann and M. Levin-Elad, *J. Catal.*, 1997, **166**, 206; R. Neumann, M. Chava and M. Levin, *J. Chem. Soc., Chem. Commun.*, 1993, 1685.
- 8 S. Klein, S. Thorimbert and W. F. Maier, *J. Catal.*, 1996, **163**, 476; W. F. Maier, J. A. Martens, S. Klein, J. Heilmann, R. Parton, K. Verduyck and P. A. Jacobs, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 180.
- 9 M. A. Uguina, G. Ovejero, R. Van Grieken, D. P. Serrano and M. Camacho, *J. Chem. Soc., Chem. Commun.*, 1994, 27; G. M. Pajonk, *Catal. Today*, 1997, **35**, 319; S. Sai, C. Prakash, J. Brinker, A. J. Hurd Sudeep and M. Rao, *Nature*, 1995, **374**, 439; J. L. Sotelo, R. Van Grieken and C. Martos, *Chem. Commun.*, 1999, 549.
- 10 M. Fraile, J. I. Garcia, J. A. Mayoral, L. C. De Menorval and F. Rachdi, *J. Chem. Soc., Chem. Commun.*, 1995, 539.
- 11 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.
- 12 F. J. Feher, T. A. Budzichowski, R. L. Blanski, K. J. Weller and J. W. Ziller, *Organometallics*, 1991, **10**, 2526; M. Crocker, R. H. M. Herold and A. G. Orpen, *Chem. Commun.*, 1997, 2411; T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shephard, J. M. Thomas and B. F. G. Johnson, *Chem. Commun.*, 1997, 1847.
- 13 W. Laufer, R. Meiers and W. Hölderich, *J. Mol. Catal.*, 1999, **141**, 215.
- 14 M. K. Dongare, P. Singh, P. P. Moghe and P. Ratnasamy, *Zeolites*, 1991, **11**, 690.
- 15 B. Rakshe, V. Ramaswamy and A. V. Ramaswamy, *J. Catal.*, 1996, **163**, 501.
- 16 K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura and J. Kitagawa, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1064.
- 17 H. J. M. Bosman, E. C. Kruissink, J. van der Spoel and F. van den Brink, *J. Catal.*, 1994, **148**, 660; R. Gomez, T. Lopez, F. Tzompantzi, E. Garciafigueroa, D. W. Acosta and O. Novaro, *Langmuir*, 1997, **13**, 970.
- 18 J. B. Miller and E. I. Ko, *J. Catal.*, 1996, **159**, 58; S.-C. Moon, M. Fujino, H. Yamashita and M. Anpo, *J. Phys. Chem. B*, 1997, **101**, 369.
- 19 S. Gontier and A. Tuel, *Appl. Catal. A*, 1996, **143**, 125.
- 20 A. Corma, J. L. Jorda, M. T. Navaro and F. Rey, *Chem. Commun.*, 1998, 1899.
- 21 J. E. Mark, C. Y.-C. Lee and P. A. Bianconi (Eds.), *Hybrid Organic-Inorganic Composites*, ACS Symposium Series 585, American Chemical Society, Washington DC, 1995.
- 22 C. Sanchez and F. Ribot, *New J. Chem.*, 1994, **18**, 1007; F. Babonneau, *New J. Chem.*, 1994, **18**, 1065.
- 23 B. Alonso, J. Maquet, B. Viana and C. Sanchez, *New J. Chem.*, 1998, **22**, 935.
- 24 F. W. van der Weije, *Makromol. Chem.*, 1980, **181**, 2541; B. Jousseame, V. Gordon, M. Pereyre and J. M. Francis, *Appl. Organomet. Chem.*, 1991, **5**, 135.
- 25 K. I. Alder and D. C. Sherrington, *Chem. Commun.*, 1998, 131.
- 26 M. Aizawa, Y. Nosaka and N. Fujii, *J. Non-Cryst. Solids*, 1991, **128**, 77; B. Wang, B. Brennan, H. Huang and G. L. Wilkes, *J. Macromol. Sci. A: Chem.*, 1990, **27**, 1447; A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, 1957, **79**, 4344.
- 27 P. Hodge and D. C. Sherrington (Eds.), *Polymer-supported Reactions in Organic Synthesis*, J. Wiley and Sons, Chichester, UK, 1980, p. 469.
- 28 S. Krijnen, H. C. L. Abbenhuis, R. W. J. M. Hanssen, J. M. C. van Hooff and R. A. van Santen, *Angew. Chem., Int. Ed.*, 1998, **37**, 356.
- 29 M. R. Boccuti, K. M. Rao, A. Zecchina, G. Leofanti and G. Petrini, *Stud. Surf. Sci. Catal.*, 1989, **48**, 133; W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, Butterworths-Heinemann, London, UK, 3rd edn., 1991, pp. 138 and 192; D. Scarano, A. Zecchina, S. Bordiga, F. Geobaldo, G. Spoto, G. Petrini, G. Leofanti, M. Padovan and G. Tozzola, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 4123; D. R. C. Huybrechts, I. Vaesen, H. X. Li and P. A. Jacobs, *Catal. Lett.*, 1991, **8**, 237; G. Bellussi, A. Carati, M. G. Clerici, G. Maddinelli and R. Millini, *J. Catal.*, 1992, **133**, 220.
- 30 S. Klein, B. M. Weckhuysen, J. A. Martens, W. F. Maier and P. A. Jacobs, *J. Catal.*, 1996, **163**, 489.
- 31 L. Delattre and F. Babonneau, *Chem. Mater.*, 1997, **9**, 2385.
- 32 M. Andrianainarivelo, R. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1996, **6**, 1665; B. Rakshe,



- V. Ramaswamy and A. V. Ramaswamy, *J. Catal.*, 1996, **163**, 501;  
Z. Dang, B. G. Anderson, Y. Amenomiya and B. A. Morrow,  
*J. Phys. Chem.*, 1995, **99**, 14437.
- 33 D. C. Sherrington, *Polymer-supported Transition Metal Complex Alkene Epoxidation Catalysts*, in *Supported Reagents and Catalysts in Chemistry*, ed. B. K. Hodnett, Royal Society of Chemistry, Cambridge, UK, 1998, p. 220.
- 34 G. Olason and D. C. Sherrington, *React. Funct. Polym.*, 1999, **42**, 163.
- 35 G. Olason and D. C. Sherrington, *Macromol. Symp.*, 1998, **131**, 127.
- 36 D. C. M. Dutoit, M. Schneider and A. Baiker, *J. Catal.*, 1995, **153**, 165; R. Hutter, T. Mallat and A. Baiker, *J. Catal.*, 1995, **153**, 177.
- 37 J. C. van der Waal and H. van Bekkum, *J. Mol. Catal., A*, 1997, **24**, 137.
- 38 M. G. Clerici and P. Ingallina, *J. Catal.*, 1993, **140**, 71.
- 39 M. Neurock and L. E. Manzer, *Chem. Commun.*, 1996, 1133.
- 40 F. Quignard, A. Choplin and R. Teissier, *J. Mol. Catal., A*, 1997, **120**, L27.
- 41 M. Miller, D. C. Sherrington and S. Simpson, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2091.
- 42 E. C. Lipse, *J. Atmos. Chem.*, 1999, **8**, 11.