Speciation in diethanolamine-moderated TiO₂ precursor sols and their use in film formation

Wafa S. Al-Arjan^{1,2} · Andrew L. Hector¹ · William Levason¹

¹ Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ. UK. Email: A.L.Hector@soton.ac.uk

² King Faisal University, PO Box 380, Al Hofuf, Saudi Arabia

Abstract

The phase behaviour of TiO₂ films and powders produced from Ti(OⁱPr)₄-based sols in ethanol modified with diethanolamine is investigated. The anatase/rutile phase concentrations vary with conditions and are correlated with samples from an acid-catalysed sol used in the same way to make films and powders. Diethanolamine is effective in increasing smoothness of films and reducing cracking, but also results in rutile formation when samples are heated at 600 °C. Mass spectrometry and nuclear magnetic spectroscopy were used to interrogate the species present in solution, where specific cluster types were found to be prominent and the diethanolamine was shown to coordinate to titanium to via all three donor atoms.

Keywords: sol-gel, TiO₂, diethanolamine, moderator, speciation, NMR

1. Introduction

TiO₂ is a popular material in applications in photocatalysis [1] including self-cleaning surfaces [2], ceramic membranes [3], solar energy conversion [4, 5] and charge storage [6-8]. TiO₂ naturally forms three crystallographic phases: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). Rutile is the thermodynamically stable phase and is usually formed

in high temperature operations, but anatase has better properties for many applications. The thermal transformation of anatase to the rutile phase depends on starting materials, deposition method and calcination temperature. A variety of physical and chemical approaches have been used for preparing TiO₂ thin films including physical or chemical vapour deposition [9], pulsed laser deposition [10], hydrothermal growth [11] and colloidal sol-gel routes [12,13]. Hydrolytic sol-gel processing of TiO₂ films [14-17] as utilised herein is a low cost, simple process that can combine purity and homogeneity with coverage of large areas and control of the film thickness via the concentration of the sol and the withdrawal speed (dip coating) or spin rate (spin coating).

Metal alkoxides are the commonest precursors in sol-gel processing but are highly reactive towards water. In general the production of useful materials including crack-free transparent films requires well-controlled hydrolysis and condensation reactions in the sol. The sol-gel process can be controlled by many factors, including pH, catalyst, alkoxide/water ratio and temperature [18]. TiO₂ thin films and powders can often be prepared from acidic solutions which control reactivity through electrostatic repulsion between protonated species in the sol. For example, Kim *et al* [19] prepared TiO₂ from HCl-catalysed sols and on firing observed an anatase to rutile phase transformation at ~1000 °C, remarking that the phase transition temperature depends on the reagents used and the catalyst concentration. Nishide *et al* [20] investigated the effect of HNO₃ as the catalyst and reported the appearance of rutile between 550 and 600 °C, with the rutile phase fraction increasing with temperature. In colloidal sol-gel processes rutile can first be observed at temperatures between ~300 and 700 °C, depending on the colloid concentration, and lanthanide doping at low levels can increase this transition temperature above 950 °C [12,13].

Typically in metal oxide sol-gel processes it is necessary to include a reaction moderator to block coordination sites and hence control reactivity of the alkoxides [21]. Acetylacetone (acacH) has been used in the preparation of TiO₂ films on silicon substrates by dip coating, with smooth anatase films formed after heating at 400 °C and a mixture of the anatase and rutile phases at 800 °C. The rutile phase was formed at 700 °C in powder samples and the authors attributed the higher rutile phase crystallisation temperature to stabilisation of the anatase phase in the films by the silicon substrate [22]. Diethanolamine (DEA, HOC₂H₄NHC₂H₄OH) moderated sols have been used to prepare TiO₂ powders from ethanol solutions of Ti(OⁱPr)₄, with a transition between the anatase and rutile TiO₂ phases found at 561 [23] or 600 [21] °C. In the latter case the percentage of the rutile phase was increased by increasing the amount of DEA. A similar study in isopropanol as solvent reported the transformation from anatase to rutile to start between 550 and 600 °C [24]. Using Ti(OⁿBu)₄ to prepare TiO₂ thin films, no rutile was observed up to 500 °C [25,26] and it was suggested that DEA had the effect of increasing the rutile transformation temperature. The use of Ti(OⁱPr)₄ with DEA in ethanol solutions to prepare TiO₂ films was reported by Verma *et al* [23], who produced TiO₂ films by spin coating and observed anatase with no rutile content in films annealed up to 560 °C.

Limited studies into the mechanism of hydrolysis and polycondensation in titania sol-gel processes exist. Knowledge of the speciation in the TiO₂ sols is critical to understanding why the differences in the film morphology and phase behaviour observed in TiO₂ occur. Mass spectrometry (MS) and nuclear magnetic resonance (NMR) are obvious options to interrogate the species present in these solutions. Electrospray ionisation mass spectrometry (ESI-MS) allows the determination of accurate molecular masses of organic and inorganic species, including large molecular species [27] and allows mass spectral analysis of the species in the gas phase with minimum fragmentation. Simonsen *et al* [28] used ESI-MS to identify the

titanium clusters in solution from different titanium alkoxides and found the pH did not significantly affect the nature of the titanium clusters. The same group [29] concluded that the number of titanium atoms in the cluster was mainly determined by the alkoxide used. With titanium isopropoxide 11-12 Ti atoms were observed whereas with titanium butoxide this fell to 10-11 Ti atoms and with $\text{Ti}(\text{OEt})_4$ to 5-7 Ti atoms.

NMR spectroscopy can improve the understanding of polymeric systems, such as sols, by following the species present via their ^1H and ^{13}C NMR chemical shifts [30]. Jung *et al* [31,32] followed the preparation of modified $\text{Ti}(\text{O}^i\text{Pr})_4$ with different modifiers such as acac, ethylacetoacetate (Etac) and methylacetoacetate (Mtac). They found there was coordination of the modifier to titanium and that the degree of coordination decreased in the sequence $\text{Ti-Mtac} > \text{Ti-Etac} > \text{Ti-acac}$. Benfer *et al* [33] used ^{13}C NMR spectroscopy, to show that the isopropoxide groups of $\text{Ti}(\text{O}^i\text{Pr})_4$ were substituted by DEA.

Herein we describe the effect of the DEA moderator on the anatase/rutile phase behaviour of films and powders produced from TiO_2 precursor sols, and examine the speciation in those sols in an attempt to link speciation to phase behaviour.

2. Experimental procedure

Reagents were purchased from Sigma-Aldrich and solvents from Fisher, all were used without further purification. Sols for the production of titanium dioxide thin films and bulk powders were prepared with reagents/solvents as listed in Table 1, by dissolving the moderator or catalyst in the solvent followed by the titanium alkoxide, stirring for 2 h. and aging in a sealed bottle at room temperature for 24 h. The DEA-3 mL (0.85 eq) and DEA-7 mL (2 eq) sol compositions are adapted from the procedure for powders reported by Murugan *et al* [21].

Table 1 Components of TiO_2 sols mixed with 10 mL $\text{Ti}(\text{O}^i\text{Pr})_4$

Sol type	Solvent	Moderator or catalyst
Acid	ⁱ PrOH, 50 mL	HCl, 0.4 mL of 2 M solution
DEA-3 mL	EtOH, 30 mL	DEA, 3 mL = 0.85 eq
DEA-7 mL	EtOH, 30 mL	DEA, 7 mL = 2 eq

For MS experiments, sols were prepared as described above, and then diluted to 50 ppm concentration in dry acetonitrile using standard Schlenk and vacuum line techniques. The vials were sealed in the glove-box under a dry nitrogen atmosphere.

To record the NMR spectrum of the species in a sol, Ti(OⁱPr)₄ (5 mL) was mixed with 2 equivalents of DEA (3.5 mL) in EtOH (15 mL). The mixture was stirred for 2 h under nitrogen atmosphere, and aged for 24 h at room temperature. The solvent was removed completely under vacuum. In the glove box, 2 drops of the product was mixed with chloroform (CDCl₃, 1 mL) for NMR study. In some experiments Ti(OⁱPr)₄ was replaced with Ti(OEt)₄ (3.54 mL).

The reactions of DEA with Ti(OⁱPr)₄ were also studied without the alcohol, by replacing it with a deuterated NMR solvent (CDCl₃ or CD₂Cl₂). Under an inert atmosphere in a Schlenk tube, commercial Ti(OEt)₄ (0.6 mL) was dissolved in CDCl₃ or CD₂Cl₂ (9.4 mL), then mixed with DEA in sequentially increasing molar equivalent quantities (Table 2). Each spectrum was sampled by taking 1 mL of the solution, then an amount of DEA equivalent to 0.25 mol per mol of Ti was added (these amounts gradually decreased as Ti-containing samples were taken). The solution was then allowed to equilibrate for 1 h. before the next NMR sample was taken. Measurements were taken either at ambient temperature (22 °C with CDCl₃ solvent) or at low temperature (with CD₂Cl₂ solvent).

Table 2 Molar equivalent additions of DEA vs time at which samples were taken.

Sampling time (h)	Molar ratio of DEA:Ti(OEt) ₄	DEA volume (mL) added before equilibration
0	-	-
1	0.25	0.06
2	0.5	0.054
3	0.75	0.048
4	1	0.042
5	1.25	0.036
6	1.5	0.03
7	1.75	0.024
8	2	0.018

Glass microscope slides ($50 \times 15 \times 1$ mm) were used as substrates to produce TiO₂ films. Before use the slides were soaked in 1 mol dm⁻³ nitric acid for one hour to remove organic contamination, then ultrasonically cleaned with deionised water and dried in air at 130 °C for 24 h. Coating was achieved by immersing the slide into the sol and then withdrawing it at a constant speed of 60 mm min⁻¹. One side of the glass was immediately wiped with an ethanol moistened tissue, and then the film on the other side was left in air at ambient temperature for 1 h to allow aging and solvent evaporation. The resultant TiO₂ films were calcined at 600 °C in static air for various time periods (5, 10, 20 or 40 min).

TiO₂ powders were prepared by evaporating the remaining sol in a Petri dish at room temperature, grinding once dry and calcining under the same conditions as the films.

The crystallisation behaviours of the calcined films and powders were examined by X-ray diffraction using a Rigaku Smart Lab (films, parallel beam Cu-K_α X-rays at 1° incidence angle

and DTex250 1D detector) or Siemens D5000 (powders, Bragg-Brentano configuration with Cu-K α_1 X-rays). Rietveld fitting used the GSAS package [34] and structural models from ICSD [35]. Crystallite sizes were extracted from the GSAS particle size broadening term as described in the GSAS manual [36]. Film thickness and surface morphology were studied using a Philips XL30-ESEM microscope. Mass spectra were collected from diluted acetonitrile solutions with a Bruker maXis ESI-TOF spectrometer operating in ES⁺ mode. ¹H and ¹³C{¹H}NMR spectra were collected using a Bruker AV-300 (ambient temperature) or an AV-400 (low temperature) in CDCl₃ or CD₂Cl₂ and are referenced to the solvent residual proton or ¹³C resonance.

3. Results and discussion

TiO₂ films and powders were synthesised from sol recipes based on titanium isopropoxide with an acid catalyst or a DEA modifier. Films were produced by dip coating from aged sols, and then the remainder of the sol was evaporated to produce a xerogel. The effect of DEA on the phase behaviour of TiO₂ films and powders after firing at 600 °C was examined, with this temperature chosen in reference to previous studies where the anatase-rutile phase transition typically occurred just below 600 °C (introduction). The sol species formed when DEA is incorporated into a Ti(OⁱPr)₄-based TiO₂ precursor sol were then investigated, and we attempt to link the phase behaviour to sol speciation.

3.1. Phase behaviour of TiO₂ films and powders

XRD patterns (Fig. 1) for TiO₂ films and powders obtained from DEA-3 mL (0.85 eq) show mixtures of the anatase and rutile phases after heating at 600 °C for various time periods. The anatase peaks decreased in relative intensity with increasing firing time. The rutile peak intensities were of higher relative intensity in the powder samples and hence these contained more rutile. Such behaviour has previously been attributed to an interaction with a silicon

substrate [20], although it is difficult to see how a glass substrate as used herein would stabilise a specific phase. The addition of 7 mL of DEA (2 eq) to the sol led to an increase of the rutile phase fraction in the films after heating, again with this fraction increasing with time (Fig. 2).

Fig. 1 XRD patterns of TiO₂ films (left) and powders (right) prepared by sol DEA-3 mL and fired at 600°C for periods shown, compared with standard pattern for anatase [37] and rutile [38] from ICSD.

Fig. 2 XRD patterns of TiO₂ films (left) and powders (right) prepared by sol DEA-7 mL and fired at 600°C for periods shown, compared with standard pattern for anatase [37] and rutile [38] from ICSD.

The XRD patterns of TiO₂ films and powders prepared from an HCl catalysed sol are shown in Fig. 3. The TiO₂ films and powders are single phase anatase. As the heating period increased

from 5 to 40 min, the intensities of the anatase peaks for TiO₂ films and powders were increased slightly but no conversion to rutile was observed. Existing sol-gel routes to TiO₂ films and powders prepared under acidic condition typically employ Ti(OⁱPr)₄, isopropanol as a solvent and hydrochloric acid (HCl) as a catalyst [19,39,40], whereas some substitute ethanol [41] or n-propanol [42] as the solvent. Kim [19] and Ahn [39] prepared the TiO₂ sol under a dinitrogen atmosphere. Alzamani [40] deposited on windshields pre-coated with a SiO₂ layer. The anatase phase was obtained in all cases at low temperature and the ease of the transformation from anatase into rutile relied on the amount of acid catalyst.

Fig. 3 XRD patterns of TiO₂ films (left) and powders (right) prepared from an acidic sol and fired at 600 °C for periods shown, compared with standard pattern for anatase [37] from ICSD.

The characterisation parameters of each crystalline phase and their average crystallite size were obtained from the corresponding Rietveld refinement. The TiO₂-DEA-3 mL films varied from 97% anatase when fired for 5 min to 96% anatase when fired for 40 min, so little change. However in the powder samples the anatase fraction varied from 89% (5 min) to 63% (40 min). Using a sol made from DEA-7 mL, the fraction of anatase decreased significantly with firing time, falling to 70% in films and 37% in powders when fired for 40 min. (Fig. 4).

Fig. 4 Anatase content (left), average rutile crystallite size (middle) and average anatase crystallite size (right) of TiO_2 films and powders prepared from various sols and fired at 600 °C for times as shown.

The anatase-rutile transition was followed as a function of the heating time at 600 °C (Fig. 4). The rutile percentage depended on the quantity of DEA modifier: it is noteworthy that no rutile is found in the acid catalysed sol derived films or powders, with a larger rutile fraction when 3 mL DEA was used and a further increase at 7 mL. Verma *et al* [23] obtained anatase from a 1:0.3 molar ratio Ti:DEA sol and no rutile was observed after annealing the film at 560 °C, but anatase and rutile phases were found in powders heated at 561 °C. Takahashi *et al* [24] increased the molar ratio of DEA to 1:2 and the transition temperature was 550 °C for a TiO_2 film or 400 °C for a powder. Murugan *et al* [21] also suggested that the transformation from anatase-to-rutile phase in TiO_2 powders increases with DEA content. They explained this in terms of denser and thicker powders and films leading the small particles to be in more intimate contact and thus to interface to boundary defects forming at the interfaces between neighbouring anatase nanocrystallites, providing nucleation sites for rutile crystallite growth [21,43].

3.2. Effect of sol preparation on the TiO_2 film and powder microstructures

TiO_2 films were prepared from $\text{Ti}(\text{O}^i\text{Pr})_4$ in ethanol solution with DEA modifier or under acidic conditions (Table 1) and annealed at 600 °C, a temperature chosen to be just above the anatase

to rutile phase temperature range most often reported for TiO_2 and hence to allow the degree of transformation at a fixed temperature to be interrogated. Fig. 5 shows the surface morphology of different TiO_2 films made using DEA-3 mL (0.85 eq), DEA-7 mL (2 eq) and acidic sols, and annealed for 5 min. It was evident from the micrographs that the films produced from 7 mL DEA were flat and crack free with a thickness of ~ 960 nm. Cracks were more significant when reducing the DEA amount to 3 mL and thinner films were obtained (~ 540 nm). The differences in film thickness could be related to the lower viscosity of the film containing less of the viscous DEA component. Cracking in the films can be caused by shrinkage during drying or the difference in the thermal expansion coefficients between glass and the TiO_2 films. Both could be significant in the acid catalysed films (thickness ~ 1600 nm), but the retardation of the condensation reactions by the DEA moderator could increase cross-linking during evaporation and hence reduce cracking in those films.

The anatase and rutile crystallite sizes increased smoothly for films and powders as a function of temperature in agreement with Takahashi *et al* [24]. Both films and powders showed the anatase crystallite size to be smaller than the rutile crystallite size (Fig. 4). The larger rutile crystallite size compared with anatase could be due to the formation of the rutile phase from the anatase phase. On other hand, the anatase crystallite size under acidic conditions increased with the firing period in films and powders, showing these crystallites are also being annealed where rutile does not nucleate.

It is noteworthy that the rutile crystallite size of powders prepared with a DEA modifier was significantly larger than that in films produced under the same conditions (Fig. 5). The transition temperature from anatase to rutile in the films may have been increased by the presence of SiO_2 in the substrate. Nechache *et al* [44], Yu *et al* [45] and Alzamani *et al* [40]

have all reported that anatase is stabilised by contact with SiO₂ due to the Ti-O-Si interface preventing the formation of rutile nuclei.

Fig. 5 SEM images of the TiO₂ films prepared from (a) DEA-3 mL (0.85 eq) (b) DEA-7 mL (2 eq) and (c) Acidic catalyst (2 eq) and their thicknesses (inset).

The anatase crystallite sizes of the films and powders produced with acid catalyst were larger than those modified with DEA. The presence of chloride ions [24] and of high proton concentrations [42] have both previously been linked to the stabilisation of the anatase phase relative to rutile. The larger anatase crystallite sizes may also stabilise these particles and prevent transformation to rutile phase due to their lower surface energies relative to smaller particles [24,46]. The current work is in good agreement with Sayilkan *et al* [42] and So *et al* [47], who obtained single phase anatase from acid catalysed sols.

3.3. Speciation in TiO₂ precursor sols

The study of the speciation in the TiO₂ sols could provide us with a better understanding of why the differences in the film morphology and phase behaviour observed in TiO₂ occur. The morphology, particle size and phase behaviour of TiO₂ films were found to depend on the sol synthesis conditions. The higher stability of the titanium precursors in the presence of a modifier has been suggested to be due to differences in the cluster size of the primary building blocks created during the synthesis [48], so ESI-MS was used in an attempt to observe what

species are present in the sol prior to production of films. Distinct cluster sizes were observed reproducibly in the mass range 50-1500 m/z in sols produced from $\text{Ti}(\text{O}^i\text{Pr})_4$, DEA and ethanol and the increasing presence of high mass peaks with increasing sol aging time was noted. The highest mass cluster with significant intensity was observed at m/z 1359.03, with an isotopic splitting pattern corresponding to 8 or 9 Ti atoms. However, it was not possible to link the distinctive cluster sizes directly to plausible compositions so only general trends were taken from this data.

The changes induced by DEA, the moderator in the TiO_2 sols, were studied by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The investigation has tried to establish whether alcohol exchange occurred and whether the N-atom in the DEA was bonded to the Ti centre. Both NMR spectra were recorded, and peak assignments were accomplished by comparison with the spectra of the precursors used. In order to study the species present in a complete sol, a DEA (7 mL) sol with in 1: 2 molar ratio of $\text{Ti}(\text{O}^i\text{Pr})_4$:DEA in ethanol was produced as described in Table 2. The solvent was removed *in vacuo* at ambient temperature and the yellowish waxy solid was dissolved in CDCl_3 for NMR measurements at room temperature. The ^1H NMR spectra are shown in Fig. 6f. The 1.0 to 1.5 ppm region contains overlapping alkoxide and alcohol CH_3 signals. The CH_2 protons of DEA are shifted from 2.5 ppm (NCH_2) and 3.4 ppm (OCH_2), to 2.7 and 3.7 ppm, with loss of the splitting patterns. The 3.7 ppm signal is overlapped with the CH_2 of some residual ethanol, and the CH septet from isopropanol is also observed at 3.95 ppm. No sharp features due to sol oligomers are seen, although broad features are observed in the 4.0-4.7 ppm region that may be due to the DEA NH protons (c.f. Fig. 6a), the CH protons from isopropoxide groups (c.f. Fig. 6b) and the CH_2 protons from ethoxide groups (c.f. Fig. 6c and 6d). The most significant observation in this sol is the large change in the chemical shift of the DEA protons in the methylene group adjacent to the nitrogen, that suggests this nitrogen interacts strongly with the titanium and hence that the ligand bonds in a tridentate fashion.

Fig. 6 ^1H NMR spectra measured at 22 $^\circ\text{C}$ for $\text{Ti}(\text{O}^i\text{Pr})_4$ in EtOH and DEA sols: (a) DEA, (b) $\text{Ti}(\text{O}^i\text{Pr})_4$, (c) $\text{Ti}(\text{O}^i\text{Pr})_4 + \text{EtOH}$, (d) Commercial “ $\text{Ti}(\text{OEt})_4$ ”, (e) $\text{Ti}(\text{OEt})_4 + \text{EtOH} + 2 \text{ eq DEA}$ (aged sol and solvent pumped off) and (f) $\text{Ti}(\text{O}^i\text{Pr})_4 + \text{EtOH} + 2 \text{ eq DEA}$ (aged sol and solvent pumped off).

Following the previous results of Murugan [21] the DEA moderated sols were produced in ethanol. On mixing $\text{Ti}(\text{O}^i\text{Pr})_4$ with ethanol it was observed (Fig. 6c) that most of the isopropoxide was converted to ethoxide. Integration of this spectrum and that of commercial “ $\text{Ti}(\text{OEt})_4$ ” (Fig. 6d) showed both to have an approximate composition of $[\text{Ti}(\text{OEt})_{3.7}(\text{O}^i\text{Pr})_{0.3}]$. This suggested that ethoxide groups are more likely to still be present in the sol species than isopropoxide, and production of a sol from the same commercial $\text{Ti}(\text{OEt})_4$ resulted in a spectrum (Fig. 6e) that was very similar to that produced from $\text{Ti}(\text{O}^i\text{Pr})_4$ apart from the lack of a signal from residual isopropanol.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the Ti-containing products of the sol prepared with 2 equivalents DEA and aged for 24 h shows the presence of DEA, ethanol and isopropanol only. We did not observe resonances assignable to the sol oligomers that were observed in the proton spectra, presumably due to the lower sensitivity of the ^{13}C experiment.

Since the key interactions had already been shown in the ambient temperature proton spectra to involve mainly $\text{Ti}(\text{OEt})_4$ and DEA these were investigated in more detail in a series of low temperature experiments, where it was expected that the exchange would be less significant. A series of samples were prepared with sequential DEA additions, such that the DEA content increased in steps of 0.25 molar equivalents, and 1 h aging periods after each addition. At $-90\text{ }^\circ\text{C}$ the $\text{Ti}(\text{OEt})_4$ peaks split in the $^{13}\text{C}\{^1\text{H}\}$ NMR into 6 resonances each between 18.6 and 20.2 ppm (CH_3 , Fig. 7a) and between 68.5 and 72.6 ppm (CH_2), presumably due to the presence of a series of oligomers formed from bridging alkoxide groups. As the molar equivalent quantity of DEA was increased the peaks due to the ethoxide oligomers diminished. Those due to ethanol were visible from 0.5 eq onwards, with the CH_3 peak shifting from 18.1 to 18.0 ppm as more DEA was added and the $\text{O}-\text{CH}_2$ peak appearing broad at 0.5 equivalents then shifting from 57.2 to 56.9 ppm with further DEA additions. These shifts in ethanol peaks may be due to coordination to the Ti centre or to hydrogen bonding. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were also recorded at intermediate temperatures between 22 and $-90\text{ }^\circ\text{C}$ but although they show some (reversible) evolution of the spectra with changing temperatures, they add little to the discussion and are not presented.

Fig. 7 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra measured at $-90\text{ }^\circ\text{C}$ for $\text{Ti}(\text{OEt})_4$ with various molar equivalent quantities of DEA: (a) none; (b) 0.25 eq; (c) 0.5 eq; (d) 0.75 eq; (e) 1 eq; (f) 1.25 eq; and (g) 1.5 eq.

The ^1H NMR spectra of $\text{Ti}(\text{OEt})_4$ showed splitting due to oligomerisation only in the $\text{O}-\text{CH}_2$ proton signal at ~ 4.25 ppm (Fig. 8a), with the CH_3 protons observed at 1.16 ppm. On addition of 0.25 to 1.5 equivalents DEA, the ethoxide $-\text{CH}_3$ signal was smoothly replaced by that of ethanol at 1.11 – 1.05 ppm. As above, the shift in the position of this signal could imply some H-bonding or neutral ethanol binding to Ti. The ethanol $\text{O}-\text{CH}_2$ signal shifts from 3.76 ppm at 0.25 equivalents to 3.57 ppm at 0.5 equivalents then smoothly to 3.50 ppm at 1.25 equivalents (Fig. 8, inset). The ethoxide $\text{O}-\text{CH}_2$ signal ~ 4.3 ppm broadens as DEA is added but remains present, suggesting that it is overlapping with the $\text{O}-\text{CH}_2$ signal of the alkoxide groups of deprotonated DEA. The $\text{N}-\text{H}$ shift at ~ 5.7 ppm did change, but this was small suggesting it might also be due to variations in H-bonding. The DEA ($\text{N}-\text{CH}_2$) signal ~ 3 ppm changes with DEA addition and especially in the most DEA-rich samples, suggesting some unbound DEA, but the spectra are very broad.

Fig. 8 ^1H NMR spectra measured at -90°C for $\text{Ti}(\text{OEt})_4$ with various molar equivalent quantities of DEA: (a) none; (b) 0.25 eq; (c) 0.5 eq; (d) 0.75 eq; (e) 1 eq; (f) 1.25 eq; and (g) 1.5 eq.

The titanium complexes are clearly highly labile in solution and even at -90°C the low temperature limit situations have not been reached, clearly demonstrated by the presence of

broad resonances in the ^1H NMR spectra shown in Fig 8. Hence although the NMR spectra demonstrate the coordination of DEA (including that of the amine function) and replacement of the propoxide or ethoxide ligands, the spectra are unable to clearly identify the entire titanium coordination sphere or the number of species present.

4. Conclusions

Addition of DEA as a reaction moderator to $\text{Ti}(\text{O}^i\text{Pr})_4/\text{ethanol}$ sols was shown to improve the quality of films produced from the sols by reducing cracking and producing smoother films. In both films and powders it also increased the phase fraction of rutile after firing at $600\text{ }^\circ\text{C}$. Both of these effects may be linked to blocking of titanium coordination sites by the DEA. The anatase crystallite size is seen to be reduced and this may make rutile nucleation easier, but smaller species at the gel stage may also provide better opportunities for cross-linking. More rutile was also observed in the powders than in the films, this is consistent with others results and has been linked to interactions with the substrates in the case of films.

Mass spectrometry showed that some specific clusters are common in the sols. There was a gradual increase in the presence of heavier clusters as sols were aged, and a particularly prominent cluster with around 8 or 9 Ti atoms was frequently observed. NMR spectroscopic measurements showed most isopropoxide groups are substituted by ethoxide when ethanol is used as the solvent, and it is clear that DEA then substitutes ethoxide very effectively. The nitrogen atom of the DEA ligand also binds to titanium and it is the tridentate coordination of DEA that is probably responsible for the limitation of the network formation that results in the phase behaviour and film quality improvements observed in the sol-gel film preparations.

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