

Thermal transformations of titania hydrolysates prepared from tetraisopropoxytitanium(iv)

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Abstract

Titania hydrolysates prepared from the hydrolysis of both unmodified and modified tetraisopropoxytitanium(iv) are shown by both FT-Raman spectroscopy and X-ray diffraction to be amorphous with no long range ordering. The Raman hydrolysate spectra show three broad bands, consisting of multiple components, at Raman shifts of ~ 210 , 440 and 570 cm^{-1} . These bands do not correspond with any known phase of titania. Thermal analysis shows broad endothermic peaks centred at $106\text{--}136^\circ\text{C}$ and extending to $\geq 200^\circ\text{C}$ for each of the hydrolysates and is attributed to dehydration and loss of water. Strong, broad exothermic peaks are observed in the modified hydrolysate curves, in the $310\text{--}340^\circ\text{C}$ temperature range and are attributed to the combustion of the residual surface adsorbed organics. Weight loss occurred during these exotherms. Crystallisation of the disordered hydrolysates into anatase occurs in the $500\text{--}600^\circ\text{C}$ temperature range. The anatase \rightarrow rutile phase transition was found between 665°C and 691°C . © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrous titania powders, whether they are ultimately used as ceramic powders, or are dispersed to form colloidal dispersions, are normally produced by hydrolysis of either Ti(IV) salts [1–3] or alkoxides [2–19]. In general, the reactants in alkoxide-derived systems are diluted with alcohols to control the rates of hydrolysis and condensation, and produce fine,

monodisperse powders [4–7,20,21]. Some solids have been prepared from undiluted reactants [22,23], but these are relatively rare. The particle size, size distribution, degree of hydrolysis and condensation, morphology, and crystallisation and phase transformation properties of oxide powders are critical to the performance of the ceramic products [19,24]. These properties are mainly determined by the rate and degree of hydrolysis and condensation reactions when alkoxide and water are mixed. Those reactions are in turn controlled by manipulating factors such as the alkoxy group of the alkoxide, the diluting alcohol, the hydrolysis ratio, and the catalysing agent [4–7,16,20,21,25–27].

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Crystallinity of the oxides, which is critical to properties such as isoelectric point [28] and proton affinity of surface sites [29], is also determined by reaction conditions and choice of alkoxide [2,9,10,13,16,17].

While chemical modification of alkoxides is extensively used to control hydrolysis and condensation in polymeric sol–gel systems, this technique has found little application in particulate sol–gel processes. Some titania materials have been produced with catalysts such as ammonium hydroxide, acetic, nitric or hydrochloric acids which have been added to the water prior to hydrolysis [16,20]. Dilution of the alkoxide in non-parent alcohols, with the possibility of alcoholysis reactions has also been employed [13,30]. However, few other modification processes have been reported for particulate sol–gel systems. Modification of alkoxides with agents such as carboxylic acids and anhydrides and β -diketones and β -ketoesters prior to hydrolysis is virtually unknown in particulate sol–gel processing. Complete reaction of all carboxylate-modifying ligands from alkoxide-derived sol–gel materials is difficult to achieve [31]. It is likely that some proportion of the acetate, propanoate and butanoate groups will remain in the hydrolysates. Likewise, 100% condensation of the alkoxide to TiO_2 is unlikely when alkoxides are simply added to water [4,5,20], and some proportion of the hydroxyl groups formed during hydrolysis are likely to remain in the hydrolysates. Of principal interest are the quantities of TiO_2 and unreacted carboxylate ligands, if any are present, in the hydrous oxides. The objective of this research is to determine the phase transformations of the titania hydrolysates and how much of the alkoxy-groups remain in the hydrolysates.

2. Materials and methods

2.1. Synthesis of titania hydrolysates

All hydrolysates were prepared from the alkoxide known as tetraisopropyltitanate or tetraisopropoxytitanium(IV) (also known by the abbreviations TPT or TiPT). Acetic, propanoic and butanoic acids were used as modifying agents (analytical grade, BDH Chemicals), in a ratio of 1 mol acid per mole of TPT. The acids (21.1 g of acetic acid, 26.1 g of propanoic acid,

31.0 g of butanoic acid) were added to TPT (100 g) at a rate of $30 \text{ cm}^3/\text{min}$, with constant agitation by a magnetic stirrer and teflon-coated stirring bar over a period of 1 h. Exposure of the alkoxide to atmospheric water was minimised by sealing the reaction vessel immediately after addition of the carboxylic acid. Reactions between TPT and the carboxylic acids are highly exothermic. Modified alkoxides were allowed to cool to 25°C . Hydrolysis was performed by adding the modified alkoxides to $\sim 320 \text{ cm}^3$ of pure, deionised water (ionic conductivity $< 1 \mu\text{S cm}^{-1}$), at a rate of $100 \text{ cm}^3/\text{min}$, with constant, vigorous stirring. A hydrolysis ratio of 50 mol of water per mole of TPT was obtained when using the quantities of TPT and water detailed above. Stirring during the alkoxide addition produced a hydrolysate slurry and was left to stand for 30 min, to allow settling of the solid particulates. The liquid phase was decanted from the solid, and the hydrolysates were agitated and washed with fresh deionised water ($1000 \text{ cm}^3/\text{mol}$ of TPT). The hydrolysates were washed in this manner for a total of five times, in order to remove organic compounds such as iso-propanol or carboxylic acids during hydrolysis and condensation.

2.2. Thermal analysis

Simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) data were recorded with a Setaram TAG-24 instrument. Hydrolysate samples were first dried under a stream of dry nitrogen for 24 h at room temperature (25°C). The solids were then heated to 450°C to ensure complete combustion of hydroxyl and organic residues, during which time TGA/DTA data were collected. The hydrolysates were allowed to cool to room temperature, then heated to a temperature of 800°C , in order to obtain crystallisation and phase-transformation data. All analyses were performed in a flowing air atmosphere, and the samples heated at a rate of $5^\circ\text{C}/\text{min}$.

2.3. X-ray diffraction

XRD analyses were performed on a Philips wide angle PW 1050/25 vertical goniometer equipped with a graphite-diffracted beam monochromator. Intensity and d -spacing measurements were improved by application of a self-developed, computer-aided divergence

slit system enabling constant sampling area irradiation (20 mm long) at any angle of incidence. The goniometer radius was enlarged from 173 to 204 mm. The radiation applied was Co K α from a long fine focus Co tube, operating at 40 kV and 40 mA. The samples were measured at 50% relative humidity in stepscan mode with steps of 0.02° 2 θ and a counting time of 2 s. Measured data were corrected with the Lorentz polarisation factor (for oriented specimens) and for their irradiated volume. Hydrolysate samples were dried prior to analysis, by blowing a stream of dry nitrogen gas over the solids for several hours.

2.4. FT-Raman spectroscopy

FT-Raman spectra were collected with a Perkin-Elmer model 2000 Near Infrared/FT-Raman spectrometer, fitted with a quartz beam splitter and an Indium–Gallium–Arsenide (InGaAs) detector. Rayleigh line rejection was performed with a notch filter set which, when combined with the detector response, allowed collection of Stokes-scattered radiation over an effective Raman shift range of 3400–100 cm⁻¹. The excitation source was a water-cooled Spectron Laser Systems SL301 Nd-doped YAG laser, emitting at a wavelength of 1064 nm. Alkoxide spectra were accumulated by co-addition of 250 scans. To prevent

heat-induced hydrolysate sample damage during extended exposure to the excitation laser, it was important that hydrolysate spectra be accumulated as rapidly as possible. Depending upon the scattering properties of the solid samples, spectra of the moist hydrolysates were obtained over 600–800 co-added scans. The instrument parameters used for collecting FT-Raman spectra of the alkoxides and hydrolysates were as follows: instrument resolution of 4 cm⁻¹, optical path difference (OPD) velocity of 0.2 cm s⁻¹, and laser power of 500 mW. The lack of a thermoluminescent background in the hydrolysate spectra indicates that sample heating by the laser was not an important factor under the conditions used for these studies.

3. Results and discussion

3.1. Raman spectroscopy

FT-Raman spectra of the washed hydrolysates are shown in Fig. 1. The principle features of the hydrolysate spectra are three broad bands, appearing to consist of multiple components, at Raman shifts of ~210, 440 and 570 cm⁻¹. No significant similarities exist between the modified hydrolysate spectra and the

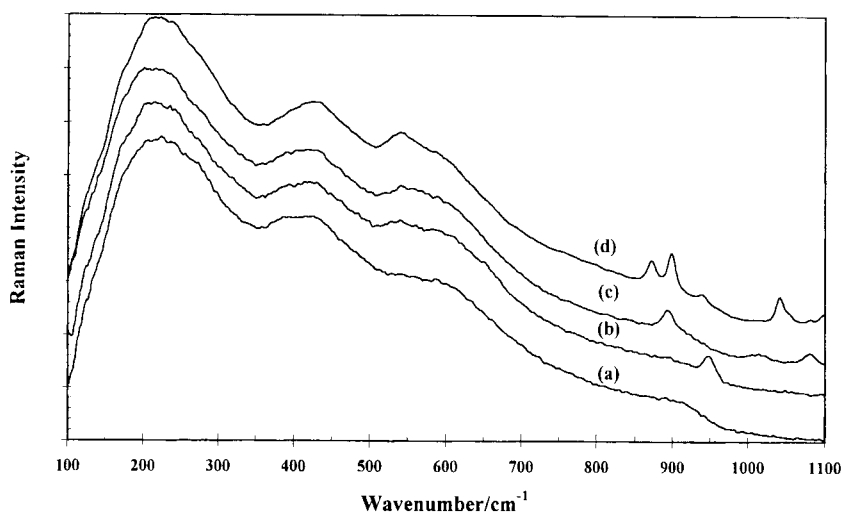


Fig. 1. FT-Raman spectra of the washed titania hydrolysates: (a) unmodified; (b) modified with acetic acid; (c) modified with propanoic acid; (d) modified with butanoic acid.

anatase spectrum [2,14,32–33,35–37]. The closest correlation between the hydrolysate spectra and the Raman spectra of titania phases is with rutile. Allowing for the uncertainty in locating the exact band centres in the hydrolysate spectra, the 440 and 570 cm^{-1} bands correspond roughly with the normal positions of 447 and 612 cm^{-1} for the rutile E_g and A_{1g} [14,33–36] modes respectively. Similarly, the band at $\sim 210 \text{ cm}^{-1}$ corresponds roughly with a band normally located at $\sim 235 \text{ cm}^{-1}$, which has been variously attributed to a disorder effect, second-order scattering or latent anharmonicity effects in rutile [14,35,36,38]. Melendres et al. [39] have suggested that the 235 cm^{-1} band does not originate from disordering in the material, but from stoichiometric deficiencies in the oxide. Hydrolysate FT-Raman spectra differ from the spectrum of crystalline rutile in at least two aspects aside from band position. Firstly, full width at half maximum (FWHM) values of the hydrolysate spectral bands are in the order of 100–200 cm^{-1} , while those for the E_g and A_{1g} modes of crystalline rutile are 30–50 cm^{-1} . Substantial band broadening is usually interpreted as indicative of a high degree of disordering in the materials [17,34]. Relative peak intensities in the hydrolysate spectra are also significantly different from those of rutile, suggesting that the constituent structural units are distorted in comparison with those

in crystalline rutile. This phase may be termed rutile-like.

3.2. X-ray diffraction

Characterisation of oxide powders is rarely performed by only one technique. While Raman spectroscopy is widely used, X-ray diffraction is extensively employed for the characterisation of oxide powders. XRD patterns of the acetate-modified hydrolysate, anatase and rutile are shown in Fig. 2. The XRD pattern for the hydrolysate is noisy and the features in the hydrolysate pattern are extremely weak and broad, and bear little resemblance to the XRD patterns of either anatase or rutile. This suggests that there is no long-range ordering in the modified hydrolysate structures, and that the solids are essentially X-ray amorphous. Other authors [8,14,17,39] have reported similar XRD and Raman spectroscopic results for titania powder precipitates. For this reason the three bands observed in the hydrolysate FT-Raman spectra at ~ 210 , 440 and 570 cm^{-1} are frequently associated with “amorphous” titania solids. However, a number of titania materials have been reported which exhibit no characteristics corresponding to those of a crystalline titania phase, in either the Raman spectra or the XRD patterns [39,40]. Thus, the hydrolysates, while

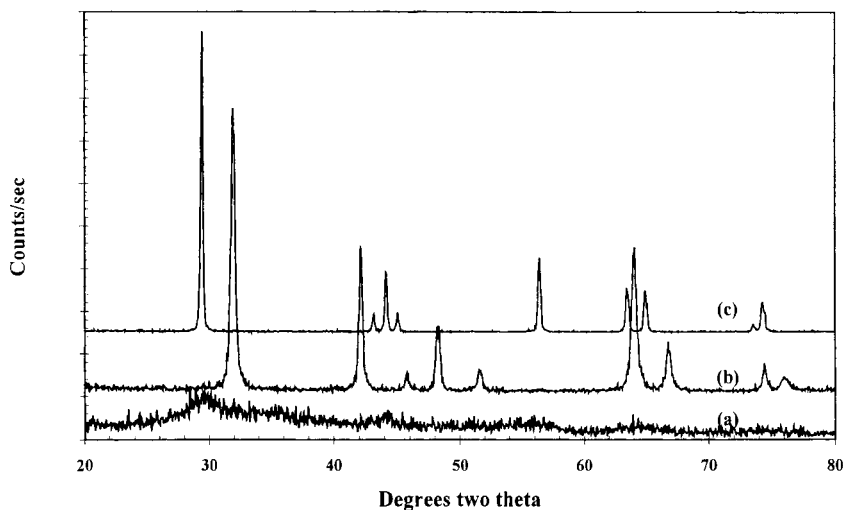


Fig. 2. X-ray powder diffraction patterns of: (a) titania hydrolysates modified with acetic acid; (b) modified with rutile; (c) modified with anatase.

sharing some Raman spectral characteristics with rutile, are clearly not highly-ordered, crystalline rutile. The term “rutile-like” is probably the most appropriate description for the hydrolysate structure.

3.3. Thermal analysis

DTA/TGA curves of several hydrolysates in the ambient 450°C temperature range are shown in Fig. 3.

A broad endothermic peak centred at 106–136°C and extending to $\geq 200^\circ\text{C}$ is attributed to dehydration and loss of water. The centres and temperature ranges of the endothermic peaks are summarised in Table 1. A strong, broad exothermic peak is observed in the modified hydrolysate curves, in the 310–340°C temperature range. This exothermic peak consists of at least two overlapping peaks. The larger peak, found at lower temperature than the second, is attributed to

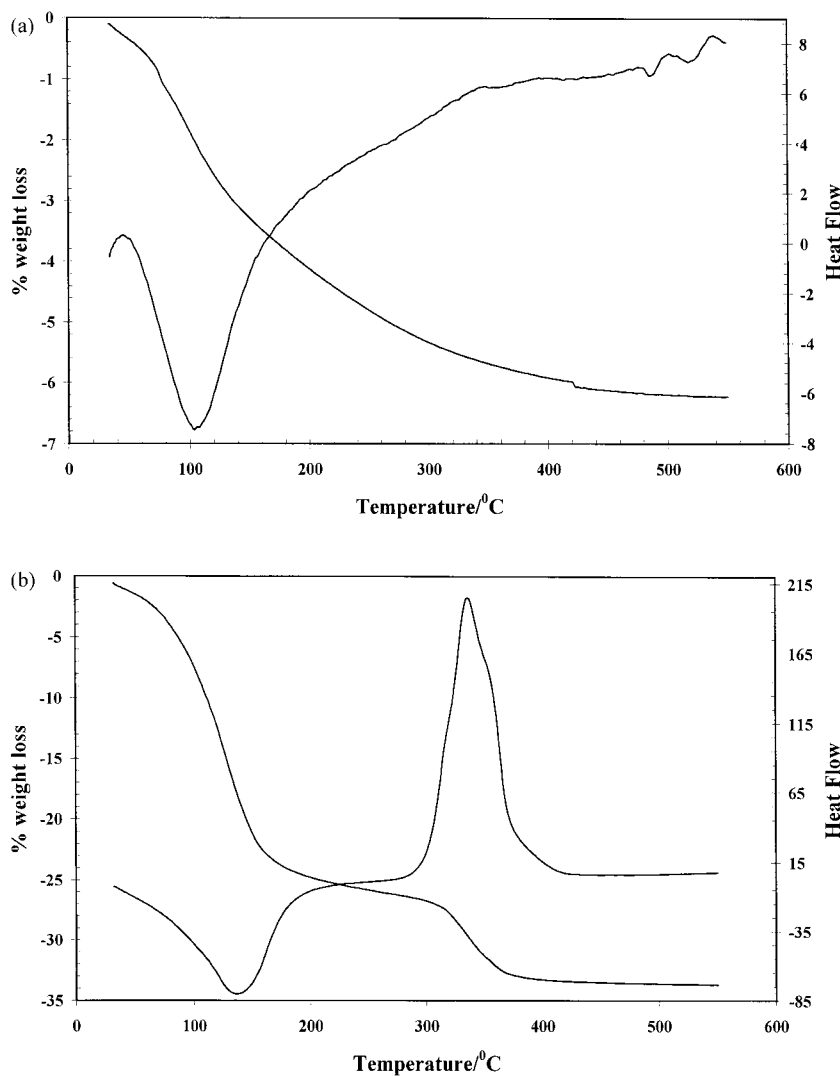


Fig. 3. (a) Thermal analysis curves for unmodified titania hydrolysates. (b) Thermal analysis curves for titania hydrolysates prepared from acetic acid modified tetraisopropoxytitanium(iv). (c) Thermal analysis curves for titania hydrolysates prepared from propanoic acid modified tetraisopropoxytitanium(iv). (d) Thermal analysis curves for titania hydrolysates prepared from butanoic acid modified tetraisopropoxytitanium(iv).

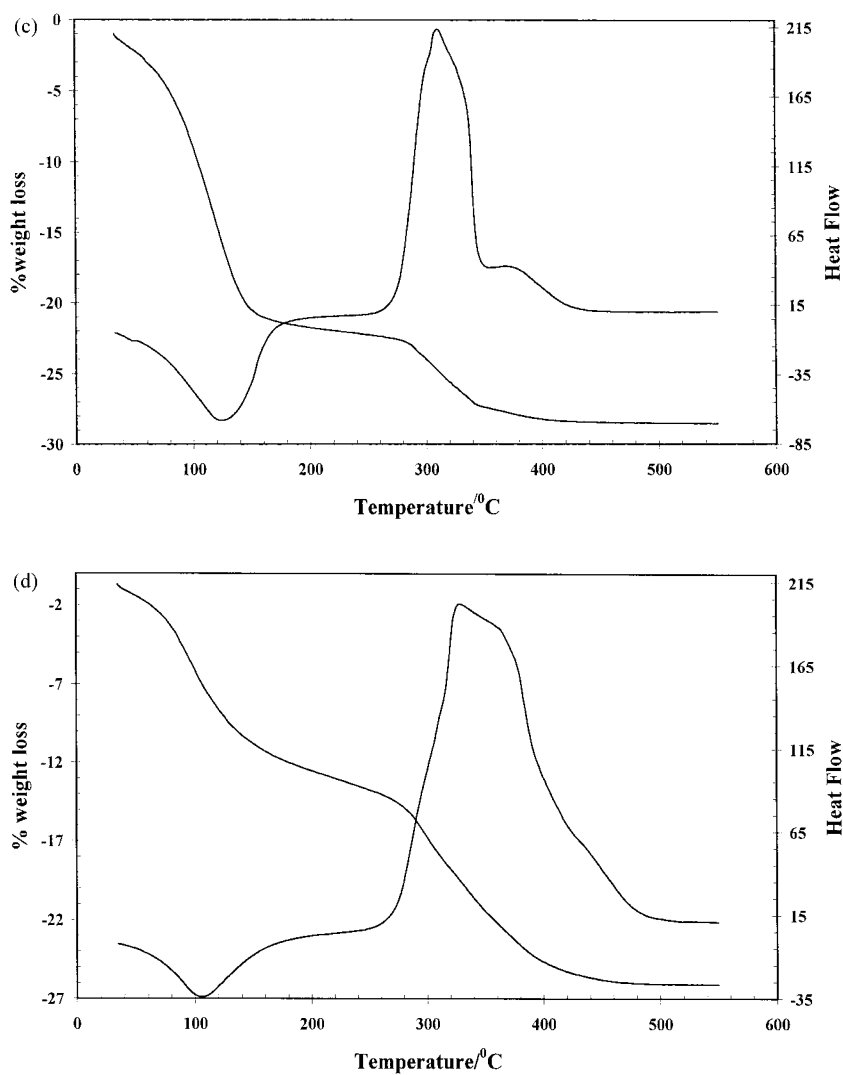


Fig. 3 (Continued).

Table 1

Centres of endothermic and exothermic peaks in DTA curves of the titania hydrolysates

| Modifying acid | Centre of endothermic water-loss peak (°C) | Centre of exothermic organic combustion peak (°C) | Temperature range of endothermic water-loss peak (°C) | Temperature range of exothermic organic combustion peak (°C) |
|----------------|--|---|---|--|
| None | 106 | – | <220 | – |
| Acetic | 136 | 336 | <215 | 215–420 |
| Propanoic | 124 | 310 | <215 | 215–440 |
| Butanoic | 106 | 330 | <200 | 200–490 |

combustion of residual organic species, consisting principally of carboxylate groups, with possibly a minor contribution from condensation of hydroxyl groups. Raman spectroscopy shows the presence of some residual carboxylic acid groups, which are retained on the surfaces of the hydrolysates. The second exothermic component peak is attributed to combustion of elemental carbon produced by thermal degradation of organic molecules in the hydrolysates.

Little or no weight loss occurs in the 310–340°C temperature range in the unmodified hydrolysate, and no exothermic peak is observed in the DTA plot. These results indicate that little organic material remains after hydrolysis and washing. This result is consistent with the FT-Raman spectra, which indicate that virtually no organic material remains in the unmodified hydrolysates, while significant quantities of carboxylate groups remain in the modified hydrolysates after hydrolysis and washing. The quantities of residual carboxylate, expressed as a percentage of dried hydrolysate weight and the molar ratios of carboxylate molecules per Ti atom, are listed in Table 2. Oxide contents of the hydrolysates are also listed in Table 2. The percentages of TiO₂ in the hydrolysates are average values calculated from a combination of several DTA/TGA and furnace calcination experiments. Hence the percentages of oxide and carboxylate in Table 2 do not necessarily total 100% for all materials. Error in these data is taken to be the standard deviation of the average oxide and carboxylate contents.

From TGA and oxide content data, it is concluded that hydrolysis and condensation proceed to the greatest degree in unmodified systems, yielding products with little or no organic residues and a high proportion of TiO₂. Among the modified hydrolysates, the quantities of organic material retained in the hydrolysates

increase with the length of the carboxylic acid alkyl chains, while the proportion of material completely condensed to TiO₂ decreases in the same order. The yield of oxide is a useful measure of the degree of hydrolysis and polycondensation in the system [20], with high yields indicating a high degree of reaction. It is concluded that unmodified TPT is more susceptible than modified TPT to hydrolysis and polycondensation reactions under the conditions employed in these investigations. This result is consistent with the stated objectives of chemical modification, to reduce the reactivity of the alkoxide [31]. Among the modified systems, those modified with acetic acid are most susceptible to hydrolysis and polycondensation reactions under the conditions employed for these studies, and those modified with butyric acid are least prone to hydrolysis and condensation. With increasing quantities of organic material, the time required for combustion of the organics will also increase, given an identical constant heating rate for all samples. Thus, the width of the exothermic DTA peak associated with carboxylate combustion increases with carboxylate chain length.

Oxide materials discussed in the literature have generally been prepared by hydrolysis reactions between alcoholic solutions of water and alkoxide [4,5,8–10,15,20], where the quantity of water may be barely sufficient for complete theoretical hydrolysis of the alkoxide, and alcohol is in large excess. Oxide yields of $\geq 90\%$ are possible for alcoholic systems, depending upon the hydrolysis ratio, the degree of reactant dilution, and the reaction temperature [4,5,20]. The predominant condensation reactions in such systems are likely to be substantially different from those in the systems studied here, where water is present in large excess, in a water:alkoxide molar ratio of 50:1, and reactants are not diluted in alcoholic

Table 2
Carboxylate content of dried titania hydrolysates produced at 25°C, as % w/w^a

| Modifying acid | % w/w TiO ₂ in hydrolysates ^a | % w/w carboxylate in hydrolysates | Molar ratio of carboxylate/Ti |
|----------------|---|-----------------------------------|-------------------------------|
| None | 96 | – | – |
| Acetic | 90 | 10 | 0.15 ± 0.01 |
| Propanoic | 88 | 13 | 0.17 ± 0.01 |
| Butyric | 77 | 23 | 0.27 ± 0.02 |

^a Error of ±4%.

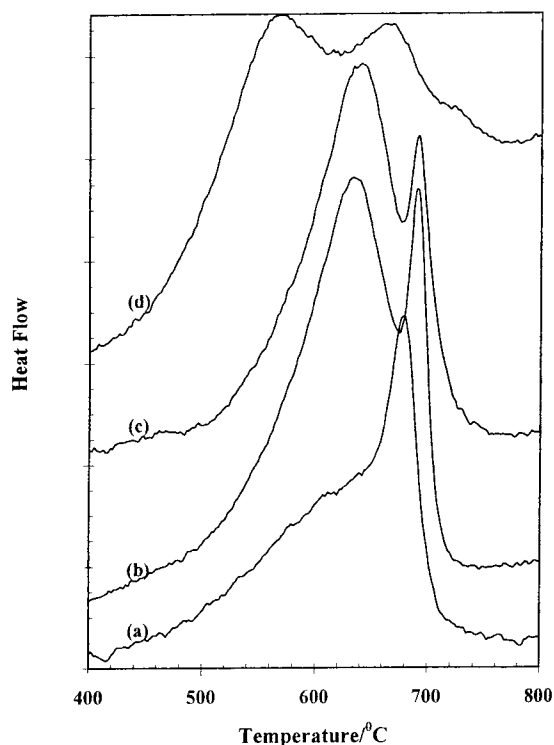


Fig. 4. DTA curves for the thermally treated hydrolysates: (a) unmodified; (b) modified with acetic acid; (c) modified with propanoic acid; (d) modified with butanoic acid.

solution. Despite the differences between the carboxylic acid systems and alcoholic systems, relatively high oxide contents are obtained in the systems studied. Thus it is possible to prepare high-oxide titania solids from carboxylic acid/alkoxide mixtures without alcoholic dilution.

Fig. 4 illustrates the DTA curves of the hydrolysates, re-heated after initially heating to a temperature of 450°C and subsequently cooled. As all water, hydroxyl species and residual organic material have

been removed by the first heat treatment, as shown by FT-Raman spectroscopy. The exothermic peaks observed in the DTA curves are attributed to *crystallisation and phase transformation processes*. The temperatures at which these processes occur are summarised in Table 3. X-ray diffraction shows that crystallisation of the disordered hydrolysates into anatase occurs in the 500–650°C temperature range. These temperatures are rather high in comparison with many amorphous or disordered titania materials, where crystallisation to anatase is frequently reported to occur in the 300–450°C temperature range [7,8,13–17,30,41,42]. The temperatures for the anatase → rutile transition, between 665°C and 691°C, are more consistent with literature values, which typically occur in the 550–1050°C range. It should be noted that the literature temperatures quoted here for crystallisation and phase transformation are only the more common values, and do not represent the entire range of temperatures, which have been reported. Due to the unusual TiO₂ preparation method employed in this work, the crystallisation and phase transformation characteristics of the hydrolysates will not necessarily be directly comparable with materials reported in the literature. In this work, material preparation differs from the usual alkoxide- or salt-based procedures in two significant respects: the alkoxide is modified with a carboxylic acid prior to hydrolysis, and in the hydrolysis step, water and alkoxide are reacted without dilution in alcohol.

Several factors are known to influence the crystallisation and phase transformation properties of oxide materials. Foremost among these are the presence of organic groups remaining after reaction of an alkoxide precursor [8,13,14], stoichiometric defects and the extent of hydrolysis and condensation in the materials [13,15–17], variations in the structure and packing of the materials [13], and in the case of anatase → rutile

Table 3

Crystallisation and anatase-rutile transition temperatures of modified titania hydrolysates

| Modifying acid | Disordered/amorphous → anatase crystallisation temperature (°C) | Anatase → rutile transformation temperature (°C) |
|----------------|---|--|
| None | 500–650 | 680 |
| Acetic | 636 | 691 |
| Propanoic | 640 | 691 |
| Butyric | 567 | 665 |

phase transformation, the size of the crystallites [15,35]. It is proposed that the main factor influencing the crystallisation and phase transformation characteristics of the modified hydrolysates is the presence of unreacted carboxylate material. In the acetic and propanoic hydrolysates, steric hindrance by the residual modifying ligands prevents long-range ordering, and inhibits both the crystallisation of the disordered/amorphous material into anatase, and the anatase \rightarrow rutile phase change [8,13]. As the quantities of carboxylate in these two systems are similar, their crystallisation and phase transformation temperatures are essentially identical. In the butyric hydrolysate, crystallisation and phase transformation are accelerated, occurring at temperatures lower even than those in the carboxylate-free unmodified material. Carboxylate groups, in disrupting the ordering of the materials, produce defects in the hydrolysate structure. During the organic combustion process, destruction of these defects release stored energy, which assists in overcoming the activation energy barrier to nucleation of a crystalline phase. These defects would also exist in the other modified hydrolysates. As the quantities of residual butanoate groups are $\sim 50\%$ greater than the remaining acetate and propanoate groups, the net effect in butyric hydrolysates is to decrease the energy required to induce crystallisation and phase transformation. In acetate- and propanoate-modified hydrolysates, the energy released by defect destruction is more than offset by the disordering effects of the organic molecules. The rate and temperature at which organic pyrolysis occurs will also change the anatase \rightarrow rutile transformation temperature of titania [15,16]. Stoichiometric defects produced by localised titanium or oxygen deficiencies may also reduce the energy required to induce crystallisation and phase transformation [16]. The modified hydrolysates do not consist of stoichiometric TiO_2 . The effect would again be most pronounced in butanoate-modified hydrolysates, as those materials are the least reactive of the systems studied.

The differences between crystallisation and anatase \rightarrow rutile transformation temperatures range from $\leq 180^\circ\text{C}$ for unmodified hydrolysate to 51°C for acetate- and propanoate-modified hydrolysates. Of the materials reported in the literature, the majority exhibit differences in the order of $300\text{--}400^\circ\text{C}$. The smaller differences observed in the modified hydrolysates are

attributed to retardation of the initial disordered/amorphous \rightarrow anatase crystallisation step by the residual carboxylate groups. In comparison with other titania materials reported in the literature, the crystallisation and phase transition properties of the modified hydrolysates studied are unremarkable. The chief point of interest is that crystallisation and the modifying carboxylate group influence phase transformation temperatures. Of the four hydrolysates, the butanoate-modified species offers the lowest processing temperature for production of the rutile phase, while the acetate- and propanoate-modified hydrolysates require the highest processing temperatures.

4. Conclusions

Physical and structural characteristics of hydrous titania precipitates prepared from tetraisopropoxytitanate chemically modified with short-chain carboxylic acids are reported for the first time. Hydrolysis of undiluted alkoxide with water, in a ratio of 50:1 water:Ti, produces solids which exhibit no evidence of crystallinity or long-range ordering, possessing only short-range, rutile-like ordering. With the experimental techniques employed (XRD and FT-Raman spectroscopy), no substantial differences are apparent between the structures of hydrolysates prepared from modified alkoxides, and the structure of the hydrolysate prepared from unmodified alkoxide.

The effects of carboxylic acid modification of the alkoxide are more pronounced for other hydrolysate properties studied. In all of the systems, nucleophilic substitution and elimination of alkoxy groups is virtually complete. Charge separation induced by the modifying ligands ensures that the removal of carboxylates is not complete, and does not occur to the same degree in the three systems. Elimination of carboxylic acid as the nucleophilic leaving groups is increasingly favourable with longer chain length, but the modifying groups also become more difficult to protonate. Despite the retention of carboxylate material, the yields of oxide in all systems are high, and comparable to or higher than those obtained for many alkoxide-derived oxide powders reported in the literature. The rate and extent of polycondensation decreases with carboxylic acid modification, and the acid chain length of the acid. Consequently, unmodified hydro-

lysates have a larger aggregate size than the modified hydrolysates. Unreacted carboxylate groups have a significant influence upon the crystallisation and phase transformation properties of the hydrolysates. In the acetate- and propanoate-modified hydrolysates, unreacted carboxylate inhibits crystallisation and phase transformation of the solids, elevating the temperatures at which these processes occur. In the butanoate-modified hydrolysates, carboxylate ligands are found in larger quantities, enhancing these processes and decreasing the crystallisation and phase transformation temperatures, to the extent that the anatase \rightarrow rutile phase transformation occurs at lower temperatures in butyric hydrolysates than in unmodified materials.

Acknowledgements

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