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Synthetic routes to microfine biphasic titania–alumina powders

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Abstract

Microfine composite titania–alumina powders were prepared using mixed alkoxide or mixed chloride starting materials. Amorphous coprecipitated precursors formed on hydrolysis were subjected to various heat treatments: calcination, hydrothermal processing or heating as an aqueous slurry under reflux conditions. The effects of preparation conditions on the polymorphous form and microstructure of these biphasic powders were studied. Samples were characterised by X-ray powder diffraction and electron microscopy, and preliminary ^{27}Al solid state magic angle spinning (MAS) NMR data is also reported. The hydrolysis of $TiCl_4$ and mixed $TiCl_4/AlCl_3$ was shown to yield crystalline rutile at unexpectedly low temperatures.

Keywords: Titania; Alumina; Composites; Calcination; Hydrothermal

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1. Introduction

The commercial applications of titanium dioxide are widespread. TiO_2, having a high refractive index and low visible absorption, renders it the most important white pigment in the paint, plastic and paper industries [1]. Practical pigments for specialist applications are frequently coated with inorganic oxides to enhance durability, gloss and dispersibility in a polymeric system. The inert surface oxide provides a physical barrier to surface photoredox processes, which initiate the detrimental "chalking" effect—the photooxidation of polymeric binders [2]. We have also demonstrated an increased concentration of long-lived luminescence centres in coated pigments relative to the parent oxide [3]. Industrially, coating of titania pigment particles is usually carried out in batch mode by precipitation of oxyhydrates of aluminium or silicon, although oxide coatings of zirconia, tin, cerium and boron have also been reported [1]. Furthermore, composite mixtures of titania with a second oxide have long been of interest as catalysts, photocatalysts and advanced ceramics. In this work the titania–alumina system will be considered.

Anpo et al. demonstrated an enhancement of TiO_2 photocatalytic activity in mixed oxide catalysts [4]. Anderson and Bard reported increased photocatalytic activity from mixed oxides of titania

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and alumina, whereby the adsorptive properties of alumina are exploited, to concentrate a substrate in close proximity to photoactive sites [5].

The only compound in the TiO_2–Al_2O_3 binary phase diagram is β-Al_2TiO_5 (a structural ceramic commonly known as tialite), which undergoes a eutectoid like decomposition to TiO_2 and α-Al_2O_3 [6]. However, on the atomic scale, Gesenhues and Rentschler have reported low level incorporation of alumina into the titania lattice. Initially Ti^{4+} ions are substituted by Al^{3+} with associated charge compensation by oxygen vacancy formation, although as the dopant level is increased, Al^{3+} enters interstitial sites [7]. Similar defect chemistry is exploited in a commercial context when Al^{3+} is added to titania pigments during manufacture, to compensate for discolouration due to the presence of Nb^{5+} ions incorporated from ore feedstocks [1].

Effective compositional control, of the binary titania–alumina system is inextricably linked to the preparative route employed, and, in this regard, solution based routes offer the potential for compositional, microstructural and textural manipulation of oxides to tight tolerences [8]. In this work, we describe the synthesis of a series of microfine titania–alumina powders by the hydrolysis of mixed alkoxide and chloride starting materials. Although the former has been widely applied to these systems [9–12], chlorides are a more economical alternative. Indeed, $TiCl_4$ has been examined as a precursor of nanocrystalline TiO_2, but not to date a mixed oxide system. Matijevic and co-workers reported the preparation of TiO_2 hydrosols by ageing highly acidic solutions of $TiCl_4$ in the presence of sulfate ions [13]. Indeed several workers have exploited the fact that an aqueous titanium oxychloride solution may be produced by the reaction of $TiCl_4$ with ice cold water. Kutty and Vivekanadan heated such a solution under hydrothermal conditions [14], and formed highly crystalline rutile between 160 and 230 °C. The anatase polymorph preferentially formed if sulfate ions were added. This was further developed by Zhang et al. who prepared nanocrystalline TiO_2 by hydrolysis of $TiCl_4$, and reported that added sulfate inhibits the anatase-rutile transformation [15]. A recent paper by Yin and coworkers described the selective formation of either anatase or rutile by the hydrothermal treatment of $TiCl_4$ aqueous solutions, which was controlled by additives [16].

In this work, three methods of heat treating precipitates produced by hydrolysis of alkoxide or chloride mixtures are examined, and differences in the phase evolution and microstructure reported. The alkoxide-derived precipitates were calcined at various temperatures in air, in a muffle furnace. Alternatively powders formed by the hydrolysis of both alkoxides and chlorides were heat treated as a slurry in water, under hydrothermal conditions in an autoclave, or using standard reflux apparatus. The latter is simply a variant on the hydrothermal method, and was initially utilised by Oguri et al. who refluxed alkoxide derived amorphous powders to produce crystalline anatase [17].

2. Experimental

All starting materials were obtained from the Aldrich Chemical Company and used without further purification. Samples with the following nominal compositions (mol%) were prepared: Al_2O_3/TiO_2 90/10, 75/25, 50/50. These fractional labels are used in the text for the sake of brevity, 100Ti, and 100Al represent pure titania and alumina, respectively. To a solution of aluminium isopropoxide in propan-2-ol at 0 °C, the required amount of titanium isopropoxide was added with constant stirring. Distilled-deionised water was added drop wise to give a molar ratio (alkoxide: H_2O) of 1:4. The precipitates were allowed to age for 1 week.

For chloride-derived powders, all manipulations were carried out under a nitrogen atomosphere. $AlCl_3$ was added to a stirred white precipitate formed from the addition of $TiCl_4$ to water (this process is considered in more detail in Section 3.2) at room temperature.

The precipitates were subjected to various heat treatments. Alkoxide-derived powders were calcined at 120, 300, 500, 600, 700, 800, 1000, 1100 and 1200 °C for 12 h in air in a muffle furnace, respectively. Alkoxide- and chloride-derived powders were suspended in water and hydrothermally treated in a PTFE-lined autoclave for 4 h at 200 °C and under autogenous pressure (approximately 15 Bar). Alternatively, precipitates were heated as a slurry in deionised water with constant stirring, using a heating mantle and standard "Quickfit" reflux apparatus.

X-ray diffraction (XRD) measurements were carried out using a Siemens D5000 diffractometer employing Cu-K_α radiation. Structural assignments were made with reference to the JCPDS powder diffraction file. Tables 1–3 quote the phase composition of the as-produced powders, which was determined from X-ray diffraction patterns using MAUD (material analysis using diffraction), a Java programme developed by Lutterotti and coworkers [18]. This also facilitates analysis of amorphous materials including determination of crystalline fractions without the need for internal or external standards. Average particle sizes were also obtained using the MAUD programme, from the Scherrer equation:

$$D = 0.9\lambda/(\beta \cos \theta)$$

where β is the full width of the diffraction line at half the maximum intensity, λ is the X-ray wavelength and θ is the Bragg angle. In this work the term "particle" refers to a small single crystal, the size of which was determined by XRD. The morphology of "grains", which are predominantly polycrystals, and aggregated or agglomerated particles were measured from electronmicrographs.

Scanning electron microscopy (SEM) was carried out using a JEOL 820 microscope with an EDX attachment. Transmission electron microscopy (TEM) was carried out using a JEOL 2000fx microscope, operating at 200 kV. A JEOL EX400 spectrometer, equipped with a JEOL EX

Table 1
Structural and compositional data for titania–alumina powders prepared by calcination of alkoxide derived precipitates

Nominal composition	Temperature calcined	Crystalline phase	Average particle size (nm)	% by volume of crystalline fraction
90/10 Al/Ti	Unheated	Amorphous	–	–
	120 °C	Amorphous	–	–
	300 °C	Amorphous	–	–
	500 °C	Amorphous	–	–
	700 °C	Amorphous	–	–
	800 °C	γ Alumina	1.3	–
	1000 °C	α Alumina	62.7	91.0
		Rutile	60.9	9.0
75/25 Al/Ti	Unheated	Amorphous	–	–
	120 °C	Amorphous	–	–
	300 °C	Amorphous	–	–
	500 °C	Amorphous	–	–
	700 °C	Amorphous	–	–
	800 °C	Rutile	6.6	17.6
		Anatase	27.7	10.5
		γ Alumina	2.5	71.9
	1000 °C	Rutile	93.6	22.4
		α Alumina	111.0	77.6
50/50 Al/Ti	Unheated	Amorphous	–	–
	120 °C	Amorphous	–	–
	300 °C	Amorphous	–	–
	500 °C	Anatase	1.8	–
	700 °C	Anatase	37.3	–
	800 °C	Anatase	18.2	31.9
		Rutile	25.4	47.3
		α Alumina	45.5	20.8
	1000 °C	Rutile	127.2	50.5
		α Alumina	64.0	49.5

Table 2
Structural and compositional data for titania, alumina and titania–alumina powders prepared by treating alkoxide derived precipitates hydrothermally in an autoclave, or under reflux conditions

Nominal composition	Crystalline phase	Average particle size (nm)	% by volume of crystalline fraction
Hydrothermal			
100 Al	Boehmite	25.5	–
90/10 Al/Ti	Boehmite	7.9	95.3
	Anatase	3.5	4.7
75/25 Al/Ti	Boehmite	10.3	84.1
	Anatase	4.2	15.9
50/50 Al/Ti	Boehmite	7.4	49.0
	Anatase	9.3	51.0
Reflux			
100 Ti	Anatase	15.6	–
100 Al	Boehmite	5.9	–
90/10 Al/Ti	Boehmite	3.5	97.1
75/25 Al/Ti	Boehmite	7.1	97.8
	Brookite	1.4	2.2
50/50 Al/Ti	Boehmite	4.4	80.7
	Anatase	2.8	10.5
	Brookite	<2.0	8.8
100 Ti	Anatase	10.8	80.7
	Brookite	7.5	19.3

Table 3
Structural and compositional data for titania, alumina and titania–alumina powders prepared by treating chloride derived precipitates hydrothermally in an autoclave, or under reflux conditions

Nominal composition	Crystalline phase	Average particle size (nm)	% by volume of crystalline fraction
Hydrothermal			
100 Al	Boehmite	11.1	–
90/10 Al/Ti	Boehmite	8.5	92.3
	Anatase	3.6	7.7
75/25 Al/Ti	Boehmite	9.8	22.0
	Anatase	5.5	78.0
50/50 Al/Ti	Boehmite	2.3	48.8
	Anatase	14.2	49.7
100 Ti	Anatase	11.7	–
Reflux			
100 Al	$AlCl_3$ hydrate	–	–
90/10 Al/Ti	$AlCl_3$ hydrate	–	–
75/25 Al/Ti	Anatase	5.2	51.0
	Rutile	1.1	8.5
	Brookite	2.3	40.5
	$AlCl_3$ hydrate	–	–
50/50 Al/Ti	Anatase	5.1	83.6
	Rutile	0.7	11.0
	Brookite	1.9	5.4
	$AlCl_3$ hydrate	–	–
100 Ti	Anatase	6.6	38.4
	Rutile	15.2	61.6

Solid State NMR facility was used to obtain the ^{27}Al MAS (magic angle spinning) NMR spectra a 104.169 MHz. ^{27}Al chemical shifts were quoted relative to an external $Al(H_2O)_6^{3+}$ reference standard. Spectra were recorded at room temperature.

3. Results and discussion

Throughout this study, there was no evidence for the formation of β-Al_2TiO_5, composite oxide mixtures being formed in all cases.

3.1. Alkoxide derived powders

The structural and compositional data for all the alkoxide derived mixed oxides is summarised in Table 1. For all compositions, hydrolysis of titanium, and mixed titanium and aluminium alkoxides produced an amorphous precipitate as gauged by XRD. In contrast XRD revealed the formation of boehmite (γ-AlOOH) having an average particle size of 2.2 nm, from the dried precipitate formed from hydrolysis of aluminium isopropoxide. This transformed to γ-alumina having a particle size of 1.6 nm, following heating at 800 °C (Fig. 1). Clearly incorporation of the second component inhibited the formation of crystalline oxyhydrate under these conditions.

On heating the mixed precipitates in air, crystallisation occurred with variations in phase evolution and crystallinity, depending on composition and firing temperature (Table 1). This is illustrated in Fig. 1, which shows XRD patterns of powders fired at 800 °C. The pure titania powder comprised highly crystalline rutile, which was in line with earlier investigations [19]. However on introducing 50% alumina, highly crystalline anatase also formed. Mixed anatase and rutile were also detected in the 75/25 material, but there was no evidence for crystalline titania in the 90/10 powder.

As a general trend, the temperature necessary to drive crystallisation of titania increased as the concentration of the second component increased. This was accompanied by a broadening of the XRD lines indicative of lower crystallinity and greater amorphous content. This behaviour is in accord with expectation, as the proximity of amorphous titania regions would be reduced at higher TiO_2 levels, which in itself, implies a homogeneous distribution of both components in the initial precipitate. This was supported by EDX measurements on the amorphous powders, which revealed no evidence for segregation into aluminium, or titanium rich regions. A decrease in the anatase to rutile transition temperature was also observed as the titania content increased. As the polymorphs of titania are not in equilibrium, the anatase to rutile transition does not occur at a specific temperature, and has been shown to depend on a host of variables [20,21]. Ding et al. [22], observed a similar response in sol-gel synthesised titania–alumina powders. This was attributed to a reduction in the number of rutile nucleation centres, due to the presence of aluminium oxide clusters on grain surfaces acting as a physical barrier. However, their proposal does

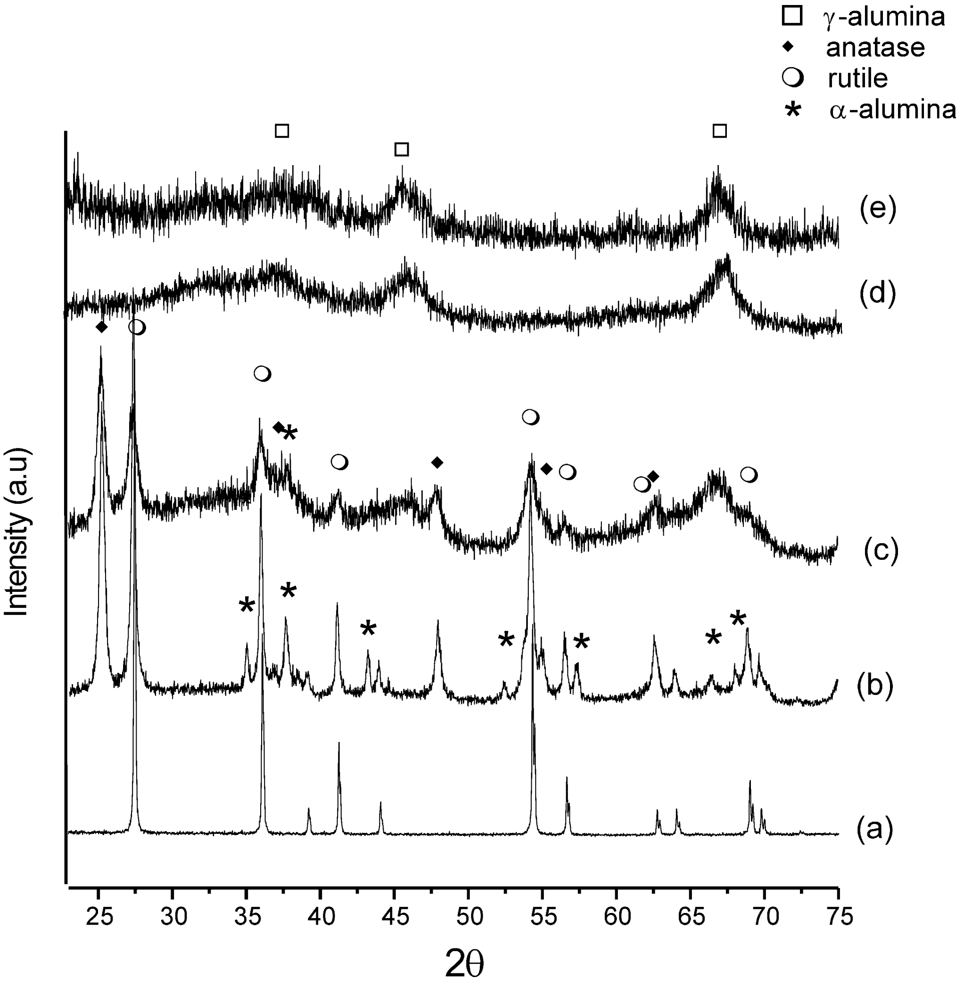

Fig. 1. XRD patterns of (a) 100Ti, (b) 50/50, (c) 75/25, (d) 90/10 and (e) 100 Al, all calcined at 800 °C.

assume a degree of phase separation, and certainly EDX measurements on our samples over the whole compositional and calcination range, revealed no evidence for this, with compositions being in reasonable agreement with the nominal value throughout.

Furthermore, consideration of our data reveals a subtle, but important difference from the work of Montoya et al. [11] who suggested that in alkoxide-derived titania–alumina powders, rutile forms directly with no anatase intermediate. Under our conditions anatase was clearly formed, albeit either yielding broad reflections in the XRD pattern characteristic of small particle size (Fig. 2), or in a more crystalline state in combination with rutile (Fig. 1b). We suggest this inconsistency may be traced to the differences in preparative methodology. Montoya and coworkers used alkoxide starting materials, but formed gels by acid catalysed hydrolysis and polycondensation, in contrast to the coprecipitation of a mixed hydroxide precursor reported here. In general, it has been shown that the crystalline form of titania is particularly sensitive to the chemistry of hydrolysis of the parent titanium alkoxide [20,23].

Calculated particle sizes (Table 1) were in the nanosize regime, increasing with firing temperature. Considering for example the 50/50 system: anatase formed at 500 °C, increasing in size from 1.8 to 37.3 nm at 700 °C, following firing at 800 °C

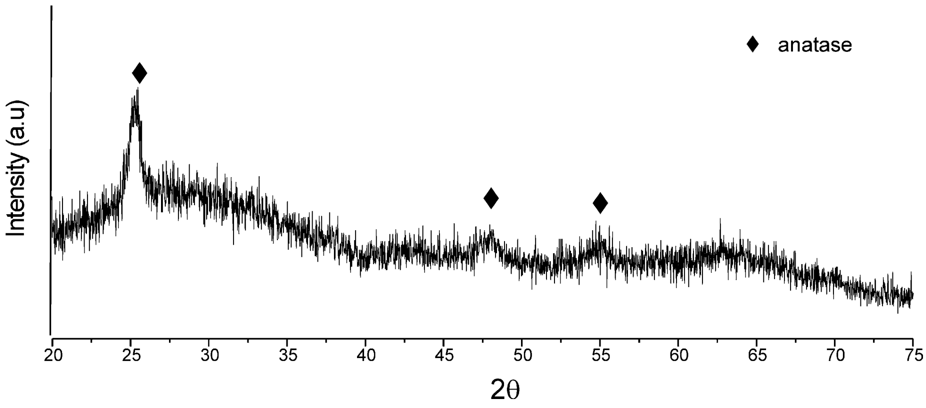

Fig. 2. XRD pattern of 50/50, calcined to 500 °C.

the overall particle size continued to grow, but this was partially rutile as a consequence of the nucleation and growth of the thermodynamically stable polymorph.

After calcining at 1000 °C, α-Al_2O_3 and rutile mixtures formed for all mixed oxides (a representative XRD pattern is shown in Fig. 3a). This is in contrast to pure alkoxide derived alumina, where γ-Al_2O_3 was the only phase detected after firing at this temperature (Fig. 3b), with α-Al_2O_3 only forming after heating at 1100 °C. Brugger and Mocellin have suggested the formation

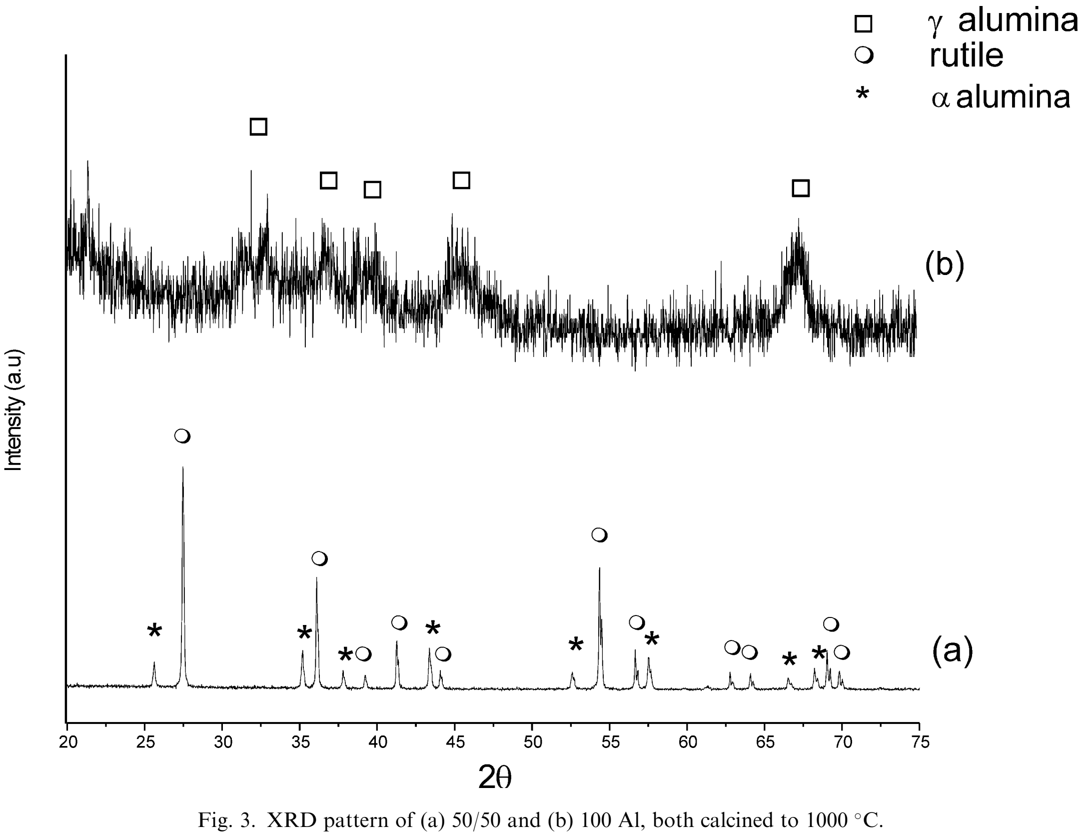

Fig. 3. XRD pattern of (a) 50/50 and (b) 100 Al, both calcined to 1000 °C.

temperature is reduced due to the seeding effect of rutile [9]. Indeed, α-Al_2O_3 is formed at 800 °C in the 50/50 sample, with some evidence for this polymorph in the 75/25 sample. Notably crystalline rutile was also present in these materials.

The calculated composition of the crystalline fraction for samples fired at 1000 °C correspond closely to the nominal value. This indicates the product is completely crystalline. In contrast there are significant anomalies in the two values following calcination at lower temperatures. In principle this can be attributed to a contribution from amorphous material. For example, considering the 50/50 system following firing at 800 °C: the total titania fraction, i.e. the sum of the anatase and rutile contributions is 79.2%, whereas the alumina fraction is 20.8%. The latter was present as the thermodynamically stable corundum phase, and the discrepancy might suggest a contribution from the γ-Al_2O_3 polymorph, which given the broad peaks in its XRD pattern was not detectable under the experimental conditions used here.

The microstructure of powders prepared by this route as gauged by SEM, were reasonably regular up to firing temperatures of 800 °C. Fig. 4 shows a micrograph of the 50/50 powder after heating at 800 °C, revealing uniform grains of 1–2 μm. When heated to 1000 °C extensive agglomeration occurred, together with the expected grain growth and coarsening of a polycrystalline ceramic.

In addition to annealing over a range of temperatures, alkoxide derived powders were also heated as a slurry in water under hydrothermal conditions using an autoclave, or standard reflux apparatus (Table 2). To the best of our knowledge these treatments have not yet been reported in the context of biphasic titania–alumina powders, which is particularly surprising as hydrothermal processing has long been used to produce highly crystalline ceramics at relatively low temperatures [8]. Following treatment in the autoclave, the pure alumina system yielded crystalline boehmite, the particle size of which fell dramatically on introduction of titania. Powders consisting of microfine boehmite in combination with anatase were formed over the whole series (Fig. 5). The amorphous titania content (as gauged by the relative contribution of alumina and titania to the crystalline fraction) decreased as the titania content increased over the series.

Boehmite was also formed following reflux treatment (Fig. 6a), however the phase formation

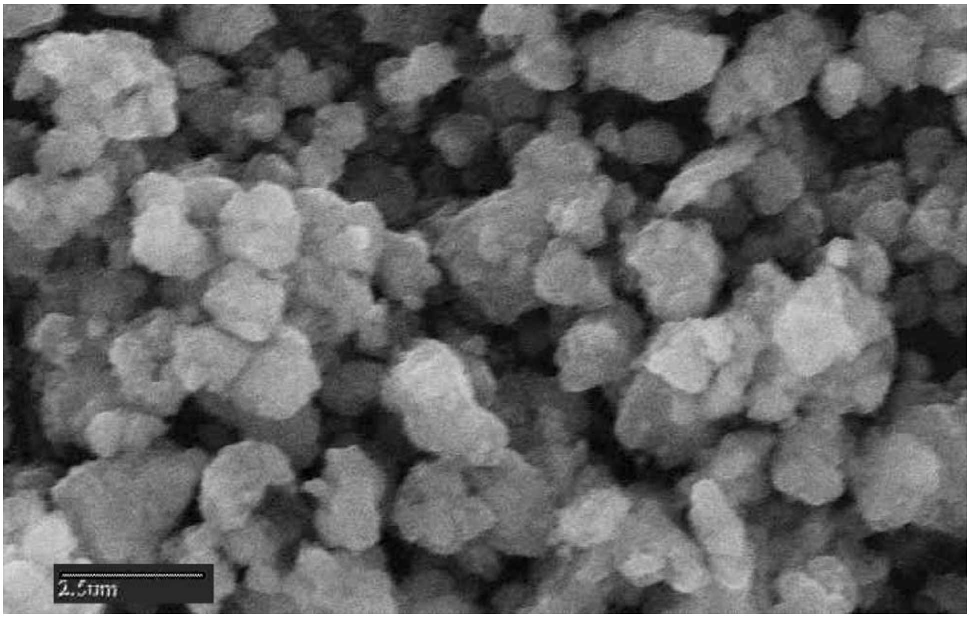

Fig. 4. SEM micrograph for the alkoxide derived 50/50 powder, calcined to 800 °C.

of the TiO_2 component differed markedly from the samples treated in the autoclave, and it was clear crystallisation was greatly impeded. In the 90/10 system, titania was amorphous following reflux treatment, unlike the autoclaved sample where a significant contribution of anatase to the crystalline fraction was apparent. This was also predominantly the case in the 75/25 material, although there was some evidence for crystalline brookite. Anatase was only formed, (in combination with brookite) in the 50/50 system, although here again, the total contribution of titania to the crystalline fraction is significantly lower than was apparent in the sample treated in the autoclave. The 100Ti sample contained a significant contribution from the brookite polymorph following reflux treatment, in contrast to the autoclaved sample where anatase only was formed. The formation of brookite under these conditions is worthy of comment, as this polymorph tends to crystallise at elevated pressure and in acidic conditions, or where high chloride concentrations persist in the reaction medium [24]. In addition a highly basic environment ($pH > 8$) has also been shown to promote brookite formation under hydrothermal conditions [25].

The microstructure of the powders produced by both the autoclave and reflux methods were rather irregular, with a wide grain size distribution (an example is shown in Fig. 7), in contrast to the alkoxide derived calcined powders. This was somewhat surprising as hydrothermal treatment generally facilitiates the formation of uniform grains with regular microstructure [8]. However,

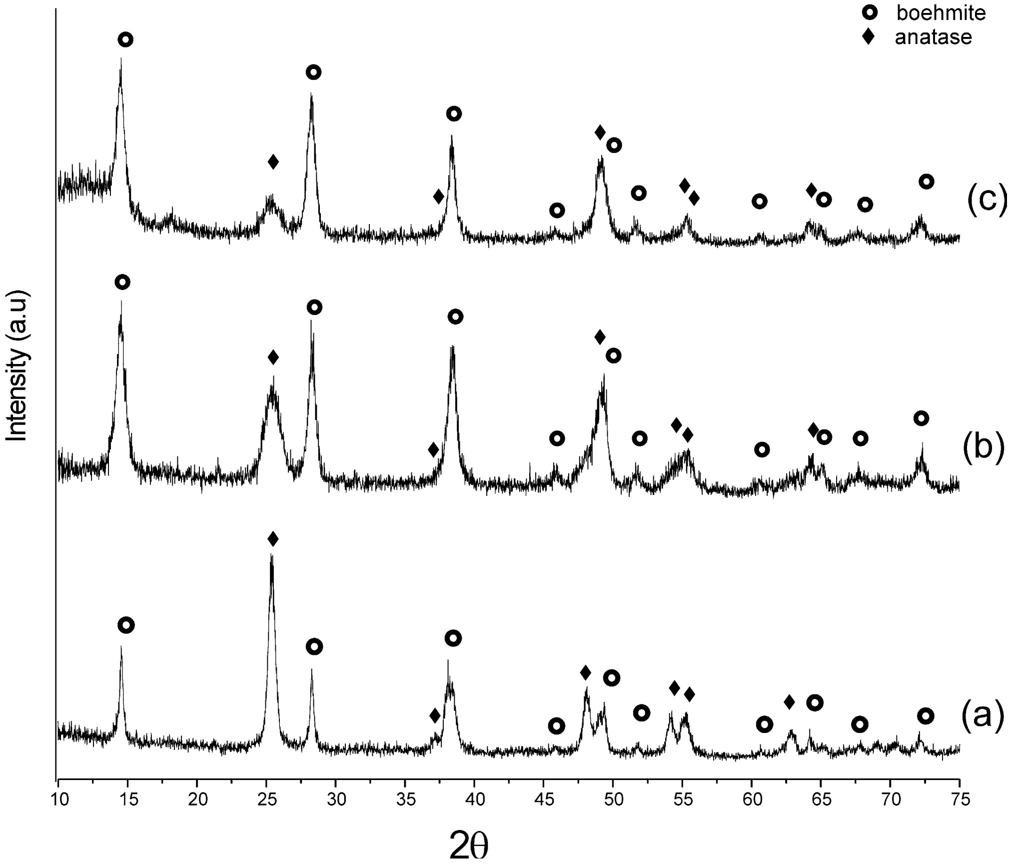

Fig. 5. XRD patterns for powders produced by treatment of alkoxide-derived precipitates in an autoclave: (a) 50/50, (b) 75/25, (c) 90/10.

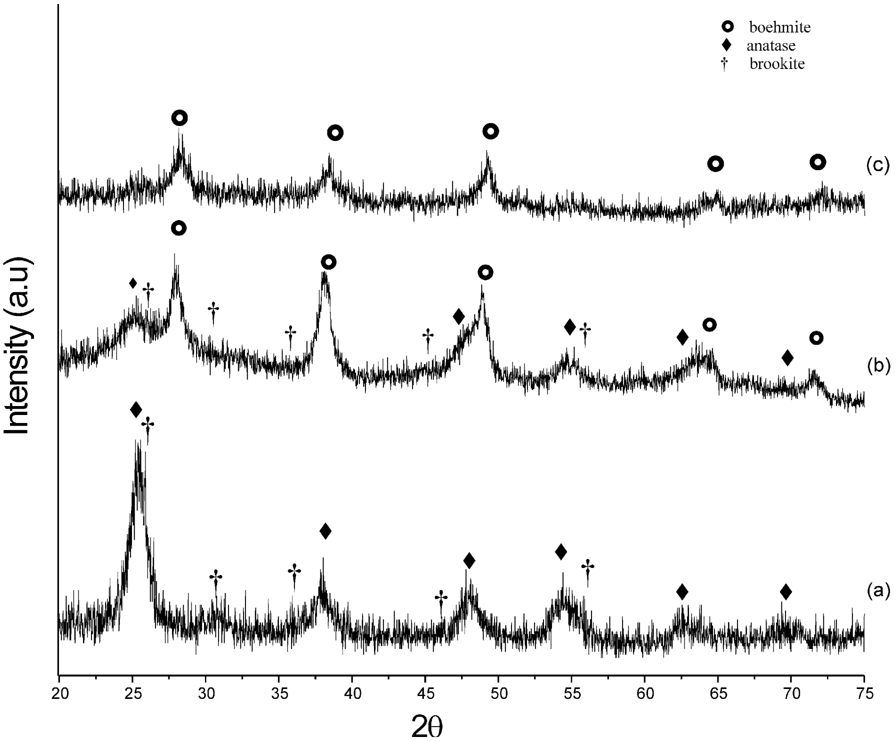

Fig. 6. XRD patterns for powders produced by alkoxide hydrolysis and heating as a slurry in water under reflux conditions: (a) 100 Ti, (b) 50/50, (c) 100 Al.

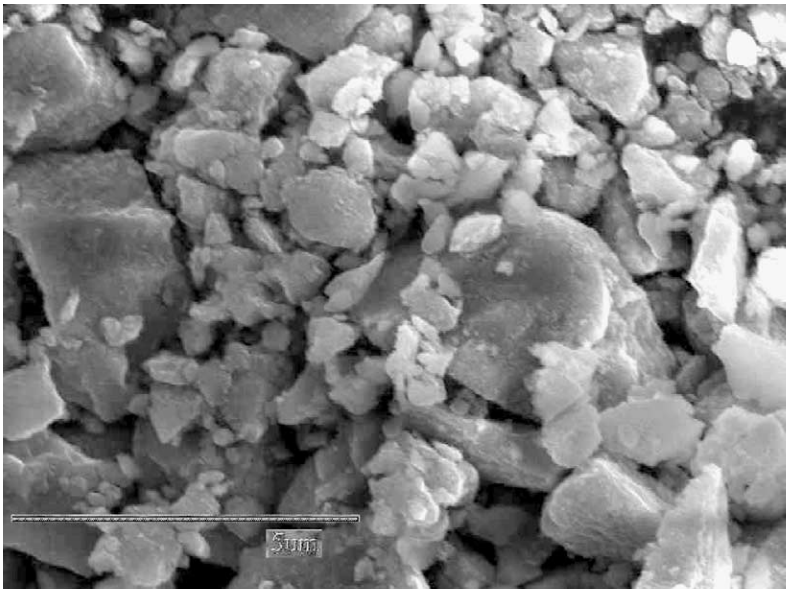

Fig. 7. SEM micrograph for the alkoxide-derived 50/50 powder, following hydrothermal treatment.

this generally involves judicious manipulation of reaction conditions such as pH, temperature and pressure.

We also include here a initial study of some of the reflux-derived materials using ^{27}Al solid-state NMR. This technique has been widely applied to aluminium containing solids, providing a valuable probe of the immediate environment of aluminium nuclei, and coordination geometry [26,27]. The spectra shown in Fig. 8, consist of a major resonance in the range 6–9 ppm, the low intensity bands on either side of the main resonance are spinning sidebands. This is characteristic of aluminium in an octahedral (AlO_6) environment and is in accord with the XRD data which revealed the formation of boehmite, which contains Al^{3+} in a distorted, edge-sharing octahedral array of oxide ions. There is also some evidence for an additional weak resonance in the 60–70 ppm region (indicated by the arrow). This chemical shift range is a feature of 4-coordinate aluminium [26]. In this regard, Fitzgerald and coworkers have carried out a detailed NMR study of the dehydration of pseudo-boehmite, and observed the growth of similar low intensity four coordinate peaks as γ-alumina crystalises [28]. The latter is a cation deficient spinel structure with Al^{3+} occupying octahedral and tetrahedral sites. Our preliminary data tentatively suggests that the presence of titanium atoms may be affecting the phase changes in this system, or generating lower symmetry aluminium species. However, the nature and extent of titanium incorporation into the boehmite structure in the mixed systems is currently unclear and in the subject of ongoing investigation in our laboratory using this technique.

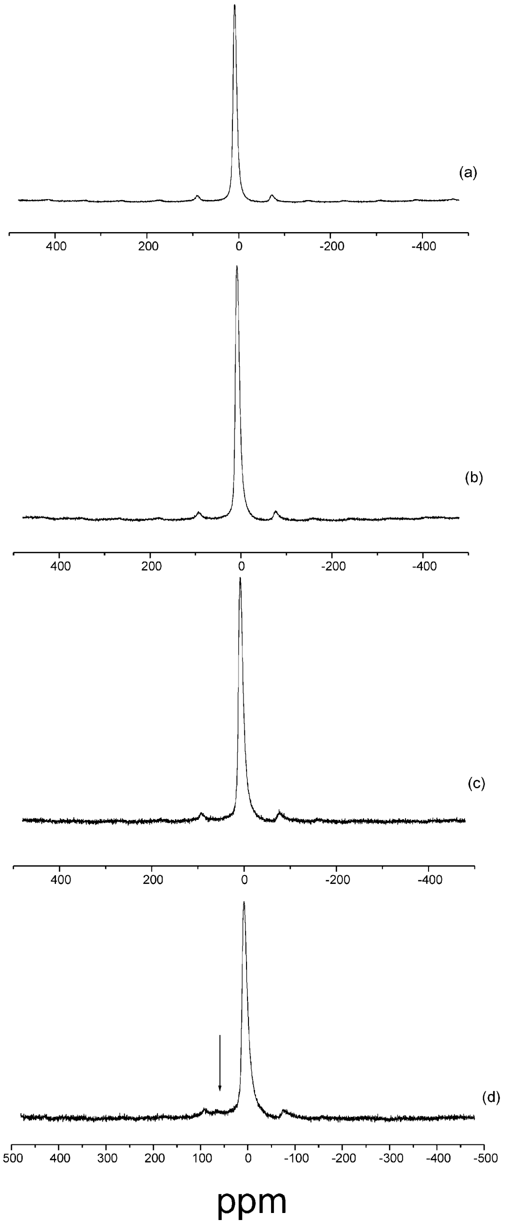

Fig. 8. ^{27}Al MAS–NMR spectra powders produced by alkoxide hydrolysis and heating as a slurry in water under reflux conditions: (a) 50/50, (b) 75/25, (c) 90/10, (d) 100 Al.

3.2. Chloride-derived powders

Given the well-documented interest in aspects of the aqueous chemistry of $TiCl_4$ in the context of the synthesis of nanocrystalline titania [13–15], it was felt a closer examination of the 100Ti system prepared under our synthetic conditions, was warranted here prior to a consideration of the biphasic system.

In contrast to previous reports, hydrolysis was carried out by drop wise addition of $TiCl_4$ to water at room temperature, rather than at 0 °C. Initially a small amount of fine white precipitate was formed and the temperature of the solution increased to ca. 46 °C. This was essentially amorphous, although weak reflections which could be tentatively indexed to titanium oxychloride hydrate, were detected by XRD. As the system was allowed to cool to room temperature, the solid dissolved, but on re-heating to ca. 46 °C, a voluminous white precipitate formed. To the best of our knowledge, this aspect of the solution chemistry of $TiCl_4$ has not been discussed in the context of titania synthesis. The XRD pattern of this precipitate revealed the formation of crystalline rutile (Fig. 9a), the mean particle size being

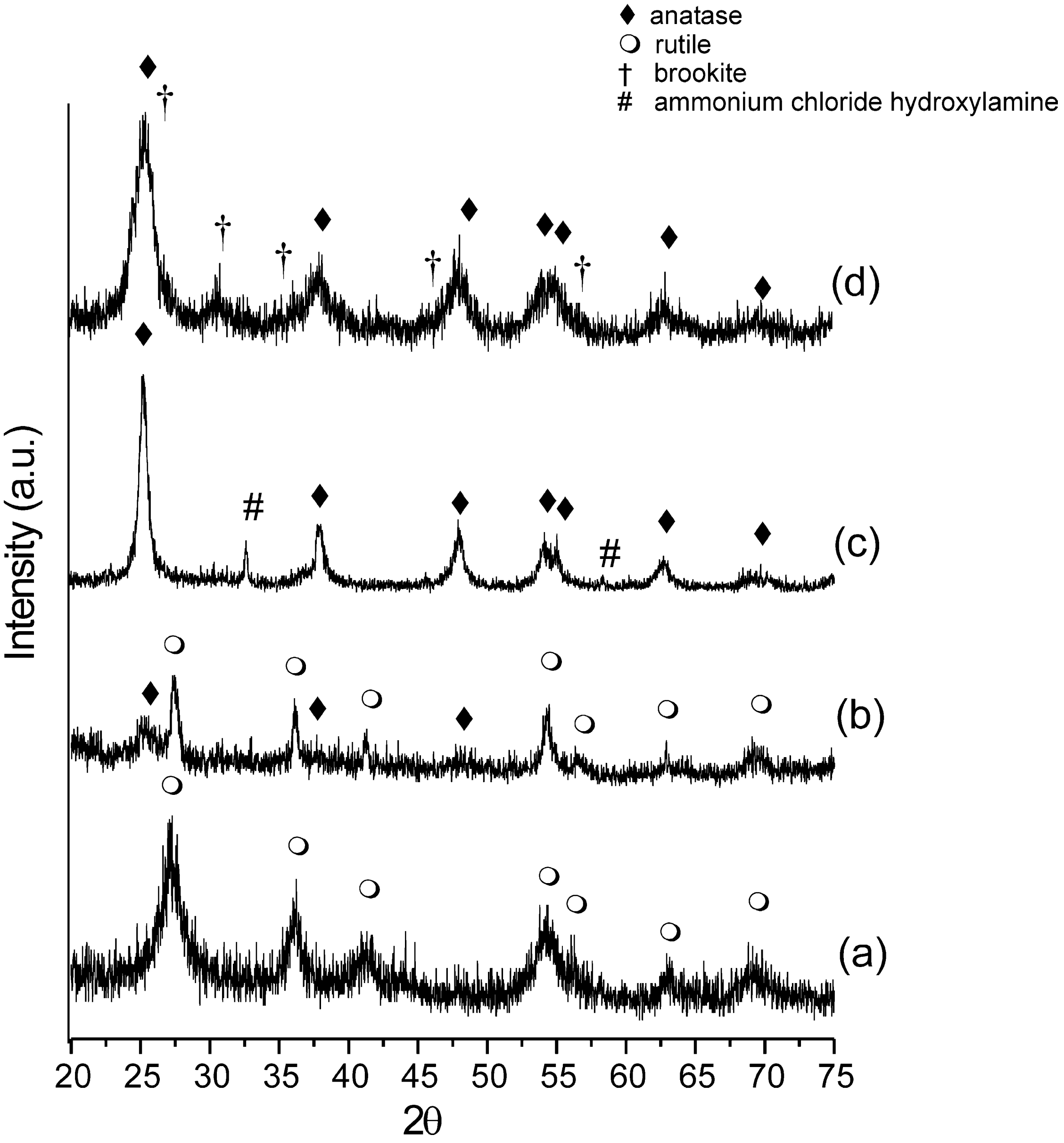

Fig. 9. XRD patterns for: (a) precipitate produced by hydrolysis of $TiCl_4$ and heating to ca. 46 °C, (b) powder produced by hydrolysis of $TiCl_4$ and heating to ca. 46 °C followed by heating as a slurry in water under reflux conditions, (c) precipitate produced by addition of 35% aqueous ammonia to $TiCl_4$ and heating as a slurry under reflux conditions, weak peaks assigned to ammonium chloride hydroxylamine are noted, and (d) powder produced by hydrolysis of titanium isopropoxide, refluxed in the presence of excess Cl^- ions.

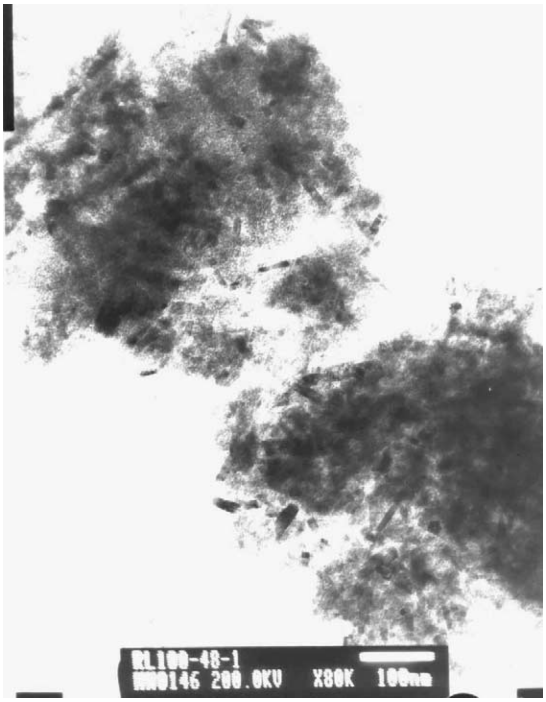

Fig. 10. TEM micrograph of powder powder produced by hydrolysis of $TiCl_4$ and heating to ca. 46 °C followed by heating as a slurry in water under reflux conditions.

8.5 nm. The observation of rutile formation at such a low temperature was somewhat surprising, but not unprecedented. Park and co-workers reported the formation of rutile below 65 °C on warming a $TiOCl_2$ solution, thought to be due to direct crystallisation of an intermediate $TiO(OH)_2$ phase, avoiding complete hydrolysis to the hydroxide [29]. The $TiCl_4$ derived precipitate was refluxed, as described above, the reaction medium being highly acidic ($pH < 1$) during this process. The XRD of the resulting powder revealed a mixed phase material containing both anatase and rutile (Fig. 9b). We suggest that at the higher temperature, the kinetic product forms preferentially. The mean particle size of anatase, and the rutile had increased to 15.2 nm. In contrast, if an identical reflux treatment was carried out on an amorphous $Ti(OH)_4$ powder, precipitated by addition of 35% aqueous ammonia to $TiCl_4$, a highly crystalline anatase powder formed (Fig. 9c) with no evidence for rutile. A TEM of the mixed phase material is shown in Fig. 10. This shows clear evidence for crystallites having a needle-like habit which are characteristic of the rutile polymorph, and also anatase, with its flatter, platelet-like morphology [1].

For comparative purposes, conjoint experiments were carried out using an alkoxide precursor, as described in Section 3.1. However, concentrated hydrochloric acid was added prior to the reflux treatment to produce a strongly acidic medium ($pH < 1$) with excess chloride ions. In this case, XRD revealed evidence for the brookite polymorph in addition to anatase (Fig. 9d). This may be reconciled by consideration of the work of Pottier et al. [30] who reported that high chloride concentrations promotes brookite formation, and stabilises this polymorph with respect to crystallisation to rutile. These workers considered formation of complexes of the type $[Ti(OH)_2Cl_3(H_2O)]^-$ and $[Ti(OH)_2Cl_4]^{2-}$ which account for the solubility of hydrolysed $TiCl_4$, also seen in our work. They suggested that depending on the solution acidity and chloride ion concentration, either elimination of chloride ions occurs which leads to brookite formation, or a hydroxo-ligand is lost which yields rutile.

In order to investigate the application of a mixed chloride precursor to prepare biphasic TiO_2/Al_2O_3, $AlCl_3$ was added to a stirred white precipitate formed by the addition of $TiCl_4$ to water, as described above followed by heat treatment either in an autoclave or under reflux conditions. Powders produced by the former treatment were compositionally very similar (Table 3) to those resulting from identically treated alkoxide derived precipitates (Table 2). A combination of fine particle anatase and boehmite formed throughout (Fig. 11a–c). However, significant differences were observed on treating the mixed chloride derived precipitate under reflux conditions. Over the whole series, the aluminium component was crystalline aluminium chloride hydrate (chloroaluminite). We suggest that this formed from the reaction of hydrated alumina with chloride ions, a process which has formed the basis of the industrial preparation of this material [31]. The formation of brookite was observed here, which could be attributed to the high chloride content of the reaction medium [24].

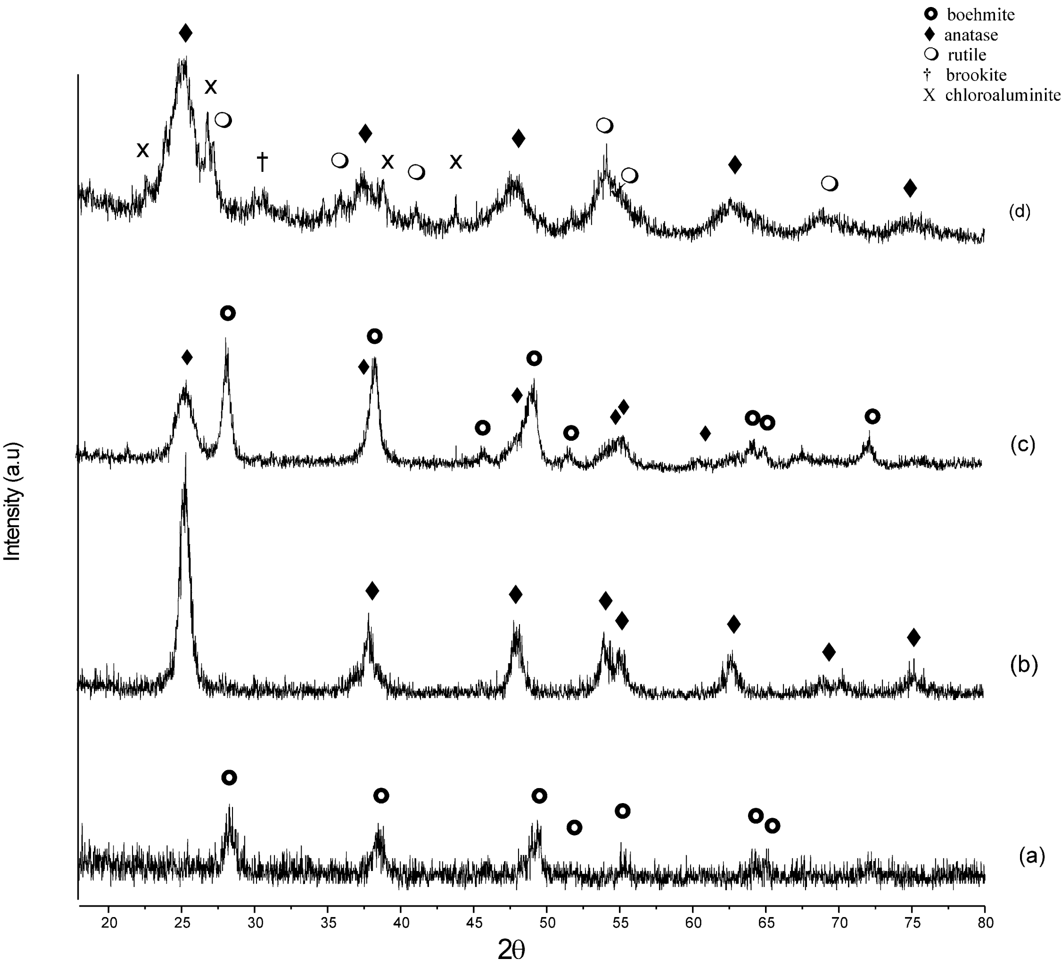

Fig. 11. XRD patterns for: (a) 100 Al from hydrolysed $AlCl_3$ following hydrothermal treatment, (b) 100 Ti from hydrolysed $TiCl_4$ following hydrothermal treatment, (c) 75/25 powder from hydrolysis of a mixed chloride precursor and hydrothermally treated, and (d) 75/25 powder produced by hydrolysis of a mixed chloride precursor and heated as a slurry in water under reflux conditions.

4. Conclusions

Titania–alumina powders having microfine dimensions have been prepared by heat treatment of precipitates resulting from the hydrolysis of alkoxide or chloride precursors. The preparative route employed had significant effects on the composition, crystallite size and microstructure of the product. The synthesis of biphasic powders by hydrothermal methods (either in an autoclave or under reflux conditions), and using mixed chloride precursors was reported for the first time in this work. The phase growth and composition of the powders, as a function of starting composition and heat treatment method, reflected the complex synergism, which exists between the components of this biphasic system, and will provide a focus for future investigation.

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