High-temperature stabilized anatase TiO_2 from an aluminum-doped $TiCl_3$ precursor†

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The solid-state hydrolysis and air calcination of aluminum-doped $TiCl_3$ leads to crystalline anatase TiO_2 that is stable on heating to 1000 °C, in contrast to control studies with related $AlCl_3$ and $TiCl_3$ physical mixtures that produce rutile TiO_2 under the same conditions.

Group 4 (Ti, Zr, Hf) oxides each have a thermodynamically stable MO_2 phase, and at least one phase that is kinetically stable at low temperatures (<500 °C) and converts to thermodynamic or higher temperature kinetic phases upon heating. In the zirconium system, a tetragonal ZrO_2 phase crystallizes from amorphous precipitates and converts to monoclinic and cubic phases upon heating above ~800–1200 °C.[1] The monoclinic is the thermodynamically stable phase at room temperature. Many studies have shown that small amounts of secondary metals (<10%) such as Ca, Y and Ce will allow cubic or tetragonal ZrO_2 phases to be formed at relatively low temperatures and retained during high temperature heating (known as stabilized zirconias).[2] Similar phase stabilization processes occur in the HfO_2 system.

The smallest Group 4 element, titanium, also forms several TiO_2 structures. There are numerous solution routes which produce nanocrystalline or amorphous precipitates that crystallize upon heating to low-temperature anatase TiO_2 phase (body-centered tetragonal) and transform to the thermodynamically stable rutile TiO_2 form (primitive tetragonal) upon extended heating above 500 °C.[3] There is an example of direct anatase formation by ultrasound assisted hydrolysis.[4] Since anatase TiO_2 is generally more photocatalytically active than the rutile form,[5] it is desirable to produce crystallographically-ordered anatase structures and retard phase conversion. There are examples of anatase stabilization up to 800 °C using sulfate ions,[6] Al or Ga,[7] and Ce or Cu.[8] This report describes an observation that $TiCl_3$ containing trace aluminum, synthesized by an organometallic exchange reaction, can be air-hydrolyzed and calcined at 1000 °C to produce crystalline stabilized anatase TiO_2. This is in clear contrast to several control reactions with different types of $TiCl_3$ that only produce the rutile TiO_2.

The organometallic synthetic reduction of $TiCl_4$ by Me_3Al in heptane at elevated temperatures is reported to produce β-$TiCl_3$ (hexagonal, JCPDS #29–1358).[9] In the current study, this reaction produced crystalline brown β-$TiCl_3$ after drying and heating under vacuum, as determined by powder X-ray diffraction (XRD). The balanced chemical reaction in heptane is shown in eqn. 1 (see ESI for experimental details†). All components are dissolved unless noted.

$$TiCl_4 + Me_3Al \rightarrow TiCl_3(s) + Me_2AlCl + \tfrac{1}{2}C_2H_6 \quad (1)$$

ICP-AE analysis showed that the as-synthesized $TiCl_3$ contained a few percent of aluminum (~97 : 3, Ti : Al molar ratio). A portion of this material was heated in an evacuated glass ampoule at 350 °C for 16 h to produce dark purple α-$TiCl_3$ by XRD (hexagonal, JCPDS #29–1357), with a slightly lower residual aluminum content due to the transport of volatile aluminum species (Table 1). The $TiCl_3$ materials from the organometallic synthesis as-synthesized and after sublimation are denoted $TiCl_3$(om) and $TiCl_3$(om, sub), respectively. High purity α-$TiCl_3$ is most commonly synthesized *via* hydrogen reduction of $TiCl_4$ on a heated tungsten filament.[10] A commercial high purity α-$TiCl_3$ (99.9%) sample, $TiCl_3$(com), was used as a control and has essentially no detectable aluminum content by ICP-AE analysis (<0.05 wt% at baseline detection limits). Since $TiCl_3$ is one component of widely used Ziegler–Natta polymerization catalysis, another common and inexpensive form is a $3TiCl_3/AlCl_3$ mixture that is usually formed by the reaction of $TiCl_4$ and Al powder.[9a] A commercial sample of this physical mixture of the individual metal trichlorides, $TiCl_3$(com-25% Al), was heated under vacuum at 350 °C to sublime the $AlCl_3$ away from the $TiCl_3$ phase ($TiCl_3$(com-25% Al, sub)), thus completing a set of five different $TiCl_3$ samples for oxidation to TiO_2. Each of their Ti and Al contents and crystalline phases are listed in Table 1, and the data shows that the sublimed materials still contain measurable amounts of aluminum. Table S1 (ESI material†) lists ICP-AE weight percent data.

In each experiment, approximately 100 mg of the $TiCl_3$ precursor was loaded into a glass vial in an inert atmosphere glovebox and then placed in air overnight (~15 h) to allow room temperature hydrolysis and oxidation to slowly occur. The $TiCl_3$ precursors were well-behaved upon air exposure, and gained weight and lost most of their color. Room temperature and relative humidity were not regulated but were typically around 27 °C and 60% RH in the laboratory. Though the air reaction was a fairly uncontrolled process, it was likely to include some HCl formation and Ti(III) to Ti(IV) oxidation. It is reasonable that Ti and Al local mixing in the chloride precursor is retained after hydrolysis. The hydrolyzed materials were further oxidized and calcined in air in an open horizontal tube furnace using a rapid 30 min ramp to 1000 °C and holding it at this temperature for 2 h.

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, ICP and weight change data, and SEM images for calcined TiO_2 from $TiCl_3$(com-25% Al) and $TiCl_3$(com-25% Al, sub). See DOI: 10.1039/b512148e

Table 1 Precursor and product data for $TiCl_3$ hydrolysis and oxidation experiments

Sample[a]	$TiCl_3$ precursor Ti : Al molar ratio[b]	TiO_2 product Ti : Al molar ratio[b]	TiO_2 phases a : r (wt%)[e]	TiO_2 crystallite size/nm
β-$TiCl_3$(om)	96.8 : 3.2	98.5 : 1.5	83 : 17	a = 100, r > 300
α-$TiCl_3$(om, sub)	97.3 : 2.7	98.8 : 1.2	55 : 45	a, r = 130
α-$TiCl_3$(com)	99.7 : <0.3[c]	100 : 0[c]	0 : 100	100
α-$TiCl_3$(com-25% Al)[d]	74.4 : 25.6	78.3 : 21.7	0 : 100	130
α-$TiCl_3$(com-25% Al, sub)	97.4 : 2.6	98.6 : 1.4	0 : 100	230

[a] $TiCl_3$ phase (α or β) determined by XRD; om = organometallic synthesis, com = commercial, sub = sublimed. [b] From ICP-AE; molar ratio normalized to 100%. [c] Al at baseline detection limits. [d] No crystalline $AlCl_3$ was observed. [e] Wt% based on XRD peak ratio relationship using ref. 11 for anatase (a) and rutile (r) peaks near 25.5° and 27.5°, respectively.

A general overall reaction process for these two conversion steps is shown in eqn. 2.

$$Ti(Al)Cl_3 + H_2O/O_2 \rightarrow Ti(Al)O_x(OH)_yCl_z \rightarrow Ti(Al)O_2 \quad (2)$$

The annealed TiO_2 products were examined by XRD, and phosphoric/sulfuric acid-dissolved samples were quantitatively analyzed by ICP-AE. Table 1 lists data on the titanium and aluminum molar ratios for each TiO_2 sample after calcination. Table S1 (ESI material†) also lists weight changes before and after room temperature hydrolysis and calcination.

The XRD results show that $TiCl_3$ synthesized *via* organometallic reduction oxidizes to predominantly *anatase* TiO_2 and retains most of this structure at 1000 °C (Fig. 1a). The weight percent anatase *vs.* rutile was calculated using published XRD peak intensity relationships (Table 1).[11] This degree of anatase phase stabilization is also retained during longer calcination periods at 1000 °C for 24 h. This result was reproduced by several samples, and the anatase phase was greater than 80 wt% in every case. When this $TiCl_3$(om) precursor was heated under vacuum before hydrolysis ($TiCl_3$(om, sub)), it produced less high temperature stabilized anatase than the $TiCl_3$(om) sample (Fig. 1b). In sharp contrast, all other samples, even the ones with similar or greater bulk aluminum contents, only produced crystalline rutile after 1000 °C heating (Fig. 1c–e). In addition, Al_2O_3 (corundum) was observed in the calcined $TiCl_3$(com-25% Al) product. The metal halide hydrolysis appears to be a necessary step because direct heating of $TiCl_3$(om) sample in air to 1000 °C produced visible white smoke when the temperature reached 200 °C and the product was predominantly rutile with only 21 wt% of the anatase phase.

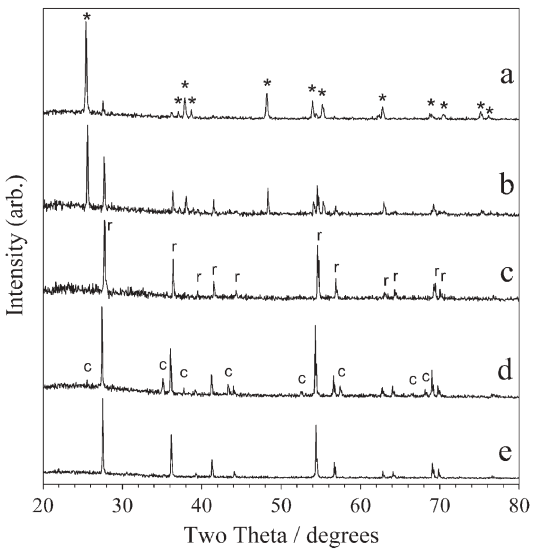

Fig. 1 X-Ray diffraction data for hydrolyzed and annealed $TiCl_3$ precursors after solid air hydrolysis and 1000 °C calcination. (a) $TiCl_3$(om), (b) $TiCl_3$(om, sub), (c) $TiCl_3$(com), (d) $TiCl_3$(com-25% Al) and (e) $TiCl_3$(com-25% Al, sub). * indicates anatase peaks, r indicates rutile peaks and c indicates corundum (Al_2O_3) peaks.

The annealed TiO_2 products are white aggregated solids that were easily ground into fine powders with a mortar and pestle. Estimates of crystallite sizes by XRD line broadening analyses are at or above 100 nm for all TiO_2 products (Table 1). Previous studies on unstabilized anatase report that crystallite grain growth above 15 nm leads to an irreversible conversion to rutile,[12] and similar observations have been made in ZrO_2 phase transformations.[13] Thus, another outcome of this work is that the anatase phase is stabilized at larger crystallite sizes than are usually observed in unstabilized systems.

The morphology of the stabilized anatase product is distinct from the rutile oxides. Scanning electron microscopy (SEM) images of anatase TiO_2 from $TiCl_3$(om) show larger, roughly spherical particles (~2 μm) decorated with smaller ~50 nm faceted particles (Fig. 2a and 2b). The larger particles are observed to be hollow with wall thicknesses close to 100 nm. The rutile TiO_2 products from low aluminum content precursors have micron thick, plate-like morphologies that seem to be built-up of fused particles (Fig. 2c and 2d). In contrast, the high Al content

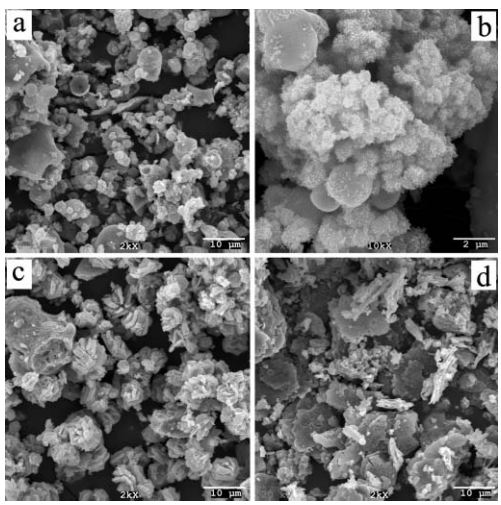

Fig. 2 SEM images of TiO_2 from air hydrolyzed and calcined (a, b) $TiCl_3$(om), (c) $TiCl_3$(om, sub) and (d) $TiCl_3$(com).

$TiCl_3$(com-25% Al) precursor produced much larger grained 5–10 μm expansive continuous regions, possibly because of its high Al_2O_3 content, along with clusters of smaller ~50 nm particles. When the $AlCl_3$ is sublimed away from this precursor, its calcined morphology reverts back to the plate-like shapes seen for similar low Al content products in Fig. 2 (ESI, Figure S1†).

Our working hypothesis as to why anatase phase stabilization only occurs for the $TiCl_3$ precursor from organometallic synthesis is that the small residual aluminum content in $TiCl_3$(om) is probably more homogeneously-mixed at an atomic level in the bulk structure than it is in the macroscopically-separate phases found in commercial Ti/Al samples, *e.g.* $TiCl_3$(com-25% Al, sub). The local bonding in $TiCl_3$ consists of distorted octahedra with all Cls shared between two Ti centers.[14] This is essentially the same as the $AlCl_3$ structure, and thus it is reasonable to presume that if Al is present during the $TiCl_4$ to $TiCl_3$ reduction and precipitation processes, small amounts of Al may be incorporated into Ti sites within the $TiCl_3$ structure. During hydrolysis, these would be intimately situated near other the titanium metals and form more homogeneously-mixed Al-containing TiO_2, after calcination. This is consistent with other studies that show evidence of enhanced anatase stability up to 800 °C,[6–8] though the current work shows added stability to 1000 °C for extended periods of time. Semi-quantitative energy dispersive spectroscopy of this stabilized anatase product shows that residual chlorine is below baseline detection (<0.1 wt%).

Since there is less anatase formed from the sublimed $TiCl_3$(om, sub) material, the phase of the starting $TiCl_3$ (α *vs.* β) along with the intimate mixing of aluminum might also play a role in the phase stabilization. Future work will spectroscopically compare the local aluminum and titanium bonding in the organometallic and commercial precursors and hydrolyzed samples to determine if there are clear structural distinctions that could explain why only the $TiCl_3$(om) sample, with its trace aluminum, leads to high temperature stabilized anatase TiO_2. The reasons are complex, since no anatase stabilization was observed when the system was overloaded with aluminum using $TiCl_3$(com-25% Al).

The UV photodegradation of methylene blue (MB) by TiO_2 was investigated so as to test the relative photocatalytic abilities of the synthesized TiO_2 powders *vs.* a commercial TiO_2 standard (Degussa P25, ~20 nm particle size, 75% anatase, 25% rutile; see ESI information for details†). A MB solution without any oxide catalyst was degraded by only 6% after 20 min of UV exposure, while the anatase TiO_2 from $TiCl_3$(om) and rutile TiO_2 from $TiCl_3$(com) degraded the MB solution by 48% and 16%, respectively. The smaller particle size P25 standard showed nearly complete MB degradation in 15 min, but based on particle size differences, its relative surface area is likely to be several orders of magnitude higher than the anatase from $TiCl_3$(om), which has an average particle size roughly five times larger than the P25 titania. Previous studies have also indicated that the presence of aluminum dopants (<1 wt%) can decrease TiO_2 photocatalytic ability,[7b,15] while at high aluminum concentrations (~10 wt% Al) others have reported an increase in photocatalytic ability.[7c] It has also been concluded that surface adsorbed Al^{3+} ions have improved organic surface cleaning during TiO_2 photocatalytic processes.[16]

In addition, recent reports have shown that lower valent Ti(III) residues in TiO_2 may also enhance visible absorption and photoactivity, something that may be accessible using a $TiCl_3$ precursor-based synthetic strategy.[17] Future studies will use the $TiCl_3$(om) precursor in conjunction with other transition metals to generate stabilized anatase structures with lower energy light absorptions to increase their potential for visible light photocatalysis. In summary, an organometallic synthesis of β-$TiCl_3$ containing ~0.5 wt% aluminum yields predominantly stabilized anatase TiO_2 after air oxidation and calcination at 1000 °C. Particle and crystallite sizes are at or above 100 nm, which is much larger than sizes observed for unstabilized anatase TiO_2 systems.

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