Effect of Halide Contaminant Ions in the Hydrothermal Treatment of Amorphous Titania on the Phase Change from Anatase to Rutile During Calcination

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Hydrothermal treatment in salt solutions has been used to crystallise and stabilise the anatase phase of titania. Halide contaminants have been shown to accelerate crystallisation of anatase when compared to reactions in pure water, but as anion size increases, the crystallisation improvement is less. The crystallised anatase has then been calcined to form rutile. The impurity ions appear to adsorb to the titania surface and have been shown to have a strong influence on the anatase/rutile transition, reducing the rutile formation during calcination due to the steric hindrance of the rutile nucleation sites on the titania surface. The adsorption sites for the anions affecting anatase crystallisation and rutile formation are different.

1. Introduction

Many factors which influence the phase change from anatase to rutile in titania have been investigated,[1,2,3] and in particular, the influence of doping ions. It has been proposed that the presence of Co^{2+}, Cu^{2+}, K^+, Na^+, Fe^{3+}, Li^+, and Mn^{4+}, all accelerate the transformation of anatase to rutile by increasing the oxygen ion vacancy concentration, while the presence of W^{6+}, NO_3^-, Cl^-, F^-, SO_4^{2-}, PO_4^{2-}, and Nb^{5+} all hinder the transformation by reducing the oxygen ion vacancy concentration.[4,5,6,7] Most of these studies have only been concerned with the final phase change during calcination, however, and very little work has considered the effects of the synthesis method of the anatase itself.

Previous results have shown that the control over the hydrothermal conditions, as well as over the contaminant ions present after the amorphous titania production are vital to controlling the crystallisation properties of the anatase powder.[8,9] In addition, the preparation route for the amorphous precursor has been shown to be vital for controlling the properties of the hydrothermally crystallised anatase. In recent work we have shown that the presence of a small amount of brookite contaminant in the anatase phase can strongly enhance the phase change to rutile. The preparation route for the amorphous titania, as well as the hydrothermal conditions can be used to control how much brookite is present in the anatase powder.[10]

Criado and Real showed how the presence of the phosphate ion inhibited the formation of rutile during calcination, by adsorption to the titania surface, rather than by lattice ion substitution.[11] In the current work, particular attention has been paid to the hydrothermal systems including the halide ions, since these are common contaminants in titania powders, but also to the influence of the preparation route of the amorphous precursor, as this can also be an important factor.

2. Results and Discussion

2.1 Crystallisation of the Ethoxide Derived Powder

Hydrothermal reactions in 0.5 M sodium halide salt solutions were studied to see their effect on the phase change to rutile. The hydrothermal products were all anatase, except for the reaction in NaF, which formed a different phase, which has been noted before.[9] This phase could not be identified from the JCPDS database files and will be the subject of further work at a later date. Figure 1 shows the X-ray powder diffraction (XRD) traces for the products after hydrothermal treatment. Anatase has formed in all cases (except for the fluoride reaction).

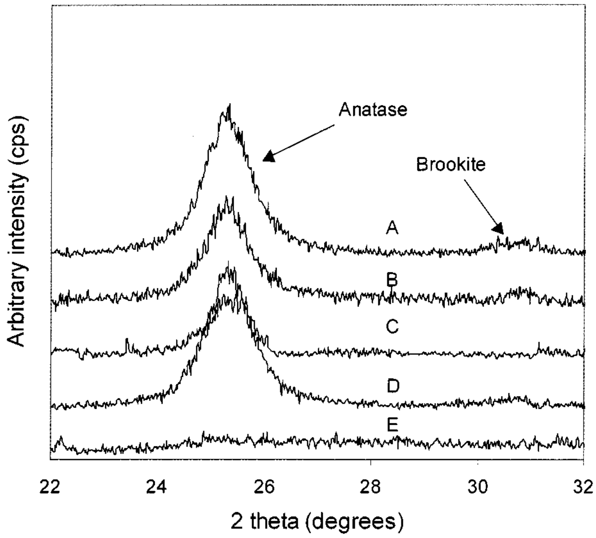

Figure 1. XRD traces of products from hydrothermal treatments in 0.5 M sodium halide salt solutions. A) H_2O, B) NaI, C) NaBr, D) NaCl, E) NaF

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The extent of crystallisation was estimated from the loss in specific surface area from the original high surface area amorphous material (Figure 2).[8] Ion coupled plasma mass spectrometry (ICPMS) results showed that the concentration of adsorbed contaminant ions after hydrothermal treatment remained constant at around 15 wt% ±5%. Therefore, the number of mol of contaminate ions per mol of titania fell as the molecular weight of the contaminate ion increased. This would suggest that the adsorption of the salts to the surface of the titania powder is controlled by the anion rather than the cation. Clearly, the presence of the halide salts increased the rate of crystallisation (since in all cases the surface area was lower, indicating less amorphous material present). It can also be seen that the rate of crystallisation was enhanced most by the presence of the chloride ion and least by the iodide ion, indicating that the larger ions have the least effect. Furthermore, as the halide ion size increases, so the crystallite size of the anatase formed, decreases. The mechanism by which the ions accelerate the crystallisation is considered to be a surface reaction, where the halide ion can adsorb to the surface, distorting the lattice due to its large size, and thus enabling the rearrangement of the titanium and oxygen ions. Due to the large size difference between the halide contaminant ions and the oxide ions (compare 1.4 Å for O^{2-} with 1.81 Å for Cl^{-}) it would be extremely unlikely that the halides could enter the lattice under the relatively mild conditions of the crystallisation (120 °C). As the anion size increases, its growth accelerating effect decreases, since the ions fluctuate too rapidly between the solvated and surface bound states in the autoclave. This limits the time for anatase crystallite growth, and gives smaller anatase crystallite sizes (Figure 2). As a result, after hydrothermal treatment, the powders treated in salt solutions with larger anions, still have a considerable amount of high surface area amorphous material remaining (measured using the Brunauer, Emmett, and Teller isotherm (BET), Figure 2).[9]

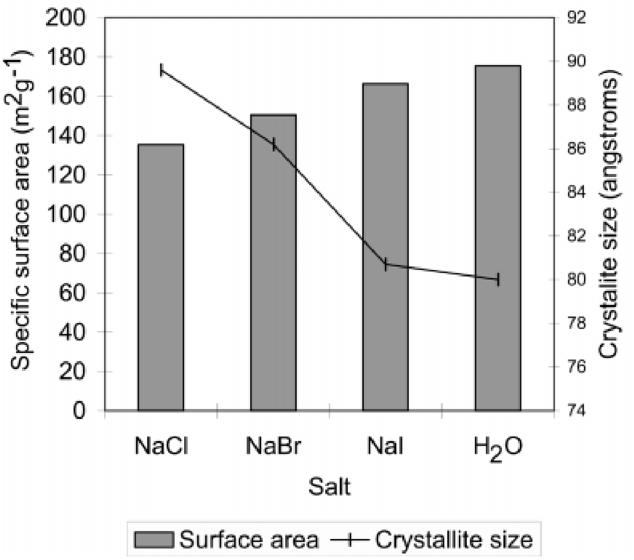

Figure 2. Chart showing the variation in specific surface area (SSA) and crystallite size with salt for hydrothermal reactions carried out at 120 °C for 90 minutes

2.2 Calcination to Form Rutile

The powders treated hydrothermally, produced mostly rutile after calcination, as can be seen from Figure 3, although when sodium fluoride was used, again other phases were formed. Although absolute intensities of peaks in XRD spectra are not quantitatively comparable there is still a very obvious difference in the amount of rutile formed between the samples with different contaminants, with the largest contaminant ions producing the least amount of rutile. Crystallite size data (calculated from the XRD data) showed that the rutile produced from each reaction had a very similar particle size (around 65 nm). This is surprising, since usually, the larger the crystallite size in the anatase product after hydrothermal treatment, then the lower the crystallinity of the rutile after calcination (i.e. the anatase is stabilised). Therefore, the remaining adsorbed salts must have a strong influence over the phase change during calcination.

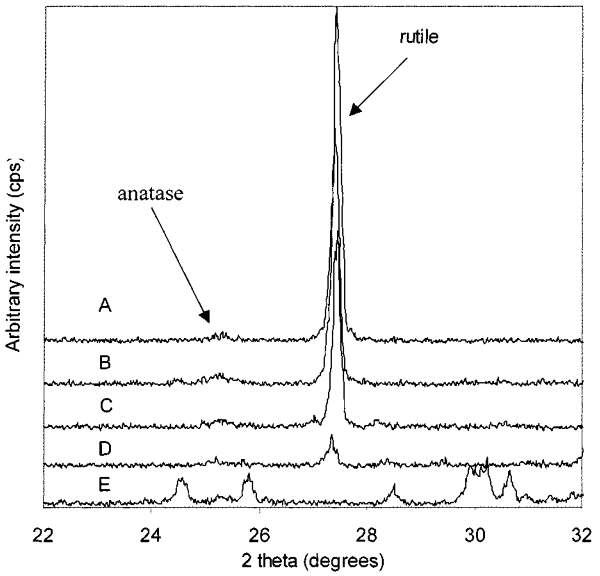

Figure 3. XRD traces for C3 powders hydrothermally treated in 0.5 M sodium halide salt solutions then heated in a DTA apparatus at 20 °C per min to 1000 °C and cooled. A) H_2O, B) NaCl, C) NaBr, D) NaI, E) NaF

This can be explained in terms of the initial reaction in the autoclave, where the anions bind to the surface of the amorphous titania, accelerating the growth of anatase as described previously.[9] The crystallised material has a considerably smaller surface area, and therefore less halide material bound to the surface. The remaining amorphous titania, however, still has a considerable amount of contaminating ions adsorbed to its high surface area material after hydrothermal treatment and these ions (the halide contaminants), reduce the rate of crystallisation by a different mechanism under the dry, ion immobilising, calcination conditions. The literature explanation for the slowing of the phase change of rutile by monovalent anions is the replacement of O^{2-} ions by the cations which would result in the reduction of O^{2-} ion vacancies in the lattice to compensate for the change in charge.[4−7] However, this seems unlikely due to the difference in size between the monovalent anions used and the oxide ions (ionic radius = 1.4 Å), and particularly doubtful in the case of the large iodide ion (ionic radius = 2.20 Å). In addition, replacement of the small O^{2-} ions in the lattice by the larger halide ions, would doubtless cause a detectable shift in the lattice parameters of the titania, and a noticable shift in the XRD peaks. This is not the case. Therefore, a surface chemistry solution is more likely. Since the halide ions clearly exert a larger stabilising effect than the difference in crystallite size of the hydrothermal anatase product, it would then seem logical that the halide ions in some way block the rutile nucleation site on the titania surface. Since the binding site for the iodide and other halide ions should be the same, and the other halide ions have a far smaller inhibiting effect on the phase change, the binding site may not be the actual rutile nucleation site (which is also on the surface).[1] Instead, a site, which is close to the rutile nucleation site, may be the adsorption point for the halide ions, so that only an ion as large as the iodide ion could sterically inhibit its rearrangement to the rutile phase.

Further evidence for the phase stabilisation as a surface effect rather than an ion exchange is in the products for the reactions carried out in sodium fluoride solutions. Only the hydrothermal treatment in sodium fluoride resulted in phases other than anatase during the hydrothermal stage, and these phases changed to completely new phases during calcination. This implies that only the fluoride ion (1.33 Å) is small enough to either replace the oxide ions in the titania lattice, or enter other sites within the lattice, and that such an incorporation results in the formation of various new phases depending on the reaction conditions. In addition, the incorporation of the cation (sodium) also seems to be controlled by the size of the anion, as only the sodium fluoride formed new phases. If the cation was the controlling agent, the sodium would be expected to enter the lattice in all cases, forming new phases.

2.3 Effect of Changing Amorphous Precursors

As the preparation route to the amorphous titania precursor has been shown to have a strong influence on the anatase product after hydrothermal treatment,[8] and upon the subsequent phase change to rutile,[10] the effect on the phase change of the use of different precursors has been investigated after treatment in different salt solutions. Comparative studies of the effects of the halide ion solutions have been made on two other anatase powders precipitated by different methods. Powder A3 was precipitated from $TiCl_4$ under predominantly acidic conditions, resulting in a powder which retained some adsorbed chloride contamination. This powder was also shown by Raman spectroscopy to have some anatase like short range order, despite being X-ray amorphous. Powder B3 was also precipitated from $TiCl_4$, but under strongly basic conditions, thus eliminating any chloride contamination, but leaving the powder with some ammonium ions adsorbed to the surface. Raman spectroscopy showed this powder to be truly amorphous, as was the C3 powder.[8]

The A3 powder gave products similar to those for the C3 powder after hydrothermal treatment, both in the extent of the reaction when compared to pure water, and in the order of crystallinity of product between the salts. The B3 powder produced much less crystalline powders after hydrothermal treatment, and the relative effects of the different salts on the crystallisation of the anatase was much less clear. After calcination, however, both the A3 and the B3 powders showed a similar trend in rutile formation to the original experiments with the C3 powder.

These results indicate that there may be two types of surface adsorption site on the titania. The first is an acidic site on the amorphous powder and, in the presence of a halide contaminant, allows the rapid growth of the anatase phase after its nucleation by the water. Hence the B3 powder exhibited almost no anatase crystallite growth due to its high surface basicity. The second is probably a less acidic site, on the anatase itself, and so the surface basicity of the B3 powder did not hinder the adsorption of the halide, nor the subsequent effect on the phase change to rutile of the halide ion. The A3 and C3 powders are both effectively neutral, and so would also be expected to exhibit this behaviour during calcination.

To summarise, in terms of contaminant ions, it can be seen that the ion size is crucial in determining its influence on the phase change. Anions can strongly influence the anatase crystallisation, increasing the rate of crystallisation. It has been shown that as their size increases, the strength of surface adsorption decreases in hydrothermal solution, producing less crystalline anatase. The expected surface adsorption site for the halide ions causing this effect is basic in nature. The halide ions also hinder the nucleation of the rutile phase during calcination, however, by means of a steric hindrance effect. The larger halide ions have a larger stabilising effect on the anatase, as they can block the rutile nucleation site more effectively. The ions causing this effect are expected to adsorb to neutral or basic surface sites. The effects of surface adsorbed salts are controlled predominantly by the cations, since the anion (sodium) is capable of entering the lattice (as demonstrated by the NaF reactions), but did not unless the anion was sufficiently small.

Experimental Section

$TiCl_4$ (30 mL, 0.273 mol) was diluted with ice cold water (300 mL). A 1.5 M NH_3 solution was added dropwise to the clear $TiCl_4$ solution until the pH was raised from 0.5 to 3.0 (appox.740 mL). The white precipitate formed was aged for 24 hours before washing with water until the pH reached 7. The amorphous powder (A3) was then dried for 24 hours at room temperature.

$TiCl_4$ (20 mL, 0.182 mol) was diluted with ice cold water (200 mL), and added dropwise to a 7.5 M ammonia solution (1000 mL). The pH fell from 12.5 to 10.9 as the white precipitate formed. Again the amorphous precipitate was aged for 24 hours before washing until the pH reached 9.2. The amorphous powder (B3) was then dried for 24 hours at room temperature.

$Ti(OC_2H_5)_4$ (25 g, 0.108 mol) was added to 550 mL of dry ethanol, and mixed thoroughly before being added to a 0.6 M solution of water in ethanol [5.94 mL (0.330 mol) of water in 550 mL of ethanol]. After ageing for 25 minutes, the reaction mixture was centrifuged and washed twice with ethanol before drying in a vacuum dessicator.[12]

Hydrothermal crystallisation was carried out by dispersing 60 mg of amorphous titania powder in 10 mL of distilled water in an autoclave (internal volume 20 mL), and then heating the autoclave to 120 °C for 90 minutes. 1 M salt solutions (sodium fluoride, sodium chloride, sodium bromide, and sodium iodide) were sometimes used in place of water.

After treatment in the autoclaves, the powders were washed with water and dried at room temperature under vacuum. Samples of the powders were dissolved, and their halide ion contents and titanium contents measured by ICPMS. The phase was determined by XRD (Rigaku Rotaflex), using a 2θ range of 10−70°, a step size of 0.02°, and a scan speed of 4°/min. A Cu-K_α source with a wavelength of 1.5406 Å, and equipped with a nickel filter to remove the K_β lines. The crystallite size was estimated by Scherrer's method. The formula used for calculation of the particle size was $p_m = k\lambda/\beta_{1/2}\cos\theta°$. In this case, p_m is the mean particle diameter (in nanometres), k is a constant (0.89), λ is the wavelength of the X-ray radiation, and θ is the diffraction angle of the peak. $\beta_{1/2}$ is the pure diffraction breadth at half the maximum value of the peak. This is calculated as $\beta = B - b$, where B is the experimentally observed width, and b is the breadth of a highly crystalline material (particle size >> 1000 Å). In this case silicon powder was used. The XRD step size was reduced to 0.006° at a rate of 0.5°/min. For anatase, the peak with the Miller indices 101 (100%) was used, while for rutile the 110 (100%) peak was used. Although it is not possible to accurately estimate the particle sizes using this method, it is extremely sensitive to the trends in particle size for the same material. In addition, TEM was used to confirm that the particle sizes were in a suitable region. The specific surface area was measured using the 3 point BET method using a Yuasa Ionics NOVA 1000 instrument. Differential thermogravimetric analysis (TG/DTA) was carried out on a Seiko SSC5200H system. The TG/DTA apparatus was used to calcine samples by heating at a ramp of 20 °Cmin^{-1} to 1000 °C before allowing to cool. The phase of these samples was then checked again by XRD, and the anatase/rutile composition estimated by the method outlined by Spurr and Myers.[13] The anatase/rutile proportions using the equation $f = 1/[1+1.26(I_R/I_A)]$. Here f is the weight fraction of anatase, I_R is the intensity of the main rutile XRD peak (Miller indices = 110), and I_A is the intensity of the main anatase XRD peak (Miller indices = 101). They estimated the error in this measurement to be within 1%. Raman spectroscopy was carried out using a Kaiser Optical Systems Holoprobe rpt. System. Salt concentrations in hydrothermal products were obtained using atomic absorption spectroscopy.

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[1] A.W. Czanderna, C.N.R. Rao, J.M. Honig, *Trans. Farad. Soc.* **1957**, *54*, 1069−1073.
[2] J.C. Jamieson, B. Olinger, *Am. Mineral.* **1969**, *54*, 1477−1481.
[3] F. Dachille, P.Y. Simons, R. Roy, *Am. Mineralol.* **1968**, *53*, 1929−1939.
[4] Y. Ohtsuka, Y. Fujiki, Y. Suzuki, *J. Jap. Assoc. Min.* **1982**, *77*, 117−124.
[5] E.F. Heald, C.W. Weiss, *Am. Mineralol.* **1972**, *57*, 10−23.
[6] F.C. Genari, D.M. Pasquevich, *J. Mater. Sci.* **1998**, *33*, 1571−1578.
[7] S. Hishita, M. Takata, H. Yanagida, *Yogyo-Kyokai-shi* **1978**, *86(12)*, 631−632.
[8] K. Yanagisawa, J. Ovenstone, *J. Phys. Chem. B* **1999**, *103(37)*, 7781−7787.
[9] J. Ovenstone, K. Yanagisawa, submitted to: *J. Am. Ceram. Soc.*, July **1999**.
[10] J. Ovenstone, K. Yanagisawa, *Chem. Mater.* **1999**, *11(10)*, 2770−2774.
[11] J. Criado, C. Real, *J. Chem. Soc., Faraday Trans.* **1983**, *79*, 2765−2771.
[12] E.A. Barringer, H.K. Bowen, *J. Am. Ceram. Soc.* **1981**, *65*, C199−C201.
[13] R.A. Spurr, H. Myers, *Anal. Chem.* **1957**, *29(5)*, 760−762.

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