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Synthesis of nanocrystalline TiO_2 by tartarate gel method

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Abstract. A gel was formed when a mixture of $TiOCl_2$ and tartaric acid was heated on a water bath. Ultrafine powders of TiO_2 in the anatase phase were formed, when the gel was decomposed at 623 K and the mole ratio of tartaric acid to titanium was 2. The anatase phase was converted into rutile phase on annealing at higher temperatures, > 773 K. When initial ratio of titanium to tartaric acid was < 2, the decomposition of gel leads to the formation of mixed phases of rutile and anatase. However, pure rutile phase was not formed by the decomposition of gel for any ratio of tartaric acid and titanium. These powders were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and surface area measurements. The average particle size obtained for anatase phase was 3 nm whereas it was 30 nm for rutile phase. Raman scattering experiments were also performed to confirm both anatase and rutile phases.

Keywords. Ceramics; oxides; chemical synthesis; X-ray diffraction; microscopy.

1. Introduction

Titanium dioxide (TiO_2) is an important industrial material as a main component of paint, pigment, cosmetics and as a support for vanadium $DeNO_x$ catalyst (Fox and Dulay 1993; Samuel *et al* 2004). It has also been used for optical coatings, beam splitters and anti reflection coatings because of its high dielectric constant and refractive index. There are reports on its use as a humidity sensor and high temperature oxygen sensor (Cheng *et al* 1995; Moritz *et al* 1997; Dhage *et al* 2003). The three crystalline polymorphs of TiO_2 are anatase, rutile and brookite. Rutile is a thermodynamically stable phase possessing a smaller band gap energy (3·0 eV) than the anatase phase (3·2 eV). A large number of preparation methods of TiO_2 have been investigated and reported in the literature (Moritz *et al* 1997; Nikumbh *et al* 2001). The starting materials have a profound influence on the formation of TiO_2 nanocrystallites with well-defined crystalline morphology. Nanocrystalline anatase is generally synthesized as hydrothermal methods and sol–gel methods using titanium alkoxides (Dhage *et al* 2003). Vapour phase decomposition of titanium alkoxide or $TiCl_4$ in an oxygen atmosphere at 1273 K is reported to yield TiO_2 particles. A mixture of anatase and rutile were produced by evaporation of Ti metal in a helium atmosphere, followed by the collection and subsequent oxidation of the Ti clusters thus formed (Dhage *et al* 2003). Recently, we have reported the preparation of ultrafine powders of TiO_2 by the citrate gel method (Dhage *et al* 2003) and digestion method (Dhage *et al* 2004). In the present work, ultrafine particles of anatase and rutile are produced by a simple tartarate gel method (Nikumbh *et al* 2001; Panda *et al* 2003; Ray *et al* 2003). The tartarate method is not commonly reported as the citrate gel method. To the best of our knowledge, this method has not been reported in the literature for the preparation of TiO_2 powders.

2. Experimental

$TiCl_4$ and tartaric acid ($C_4H_6O_6$) used for the preparation of TiO_2 are of AR grade. $TiCl_4$ was diluted with ice-cold distilled water and mixed with tartaric acid in a 1 : 2 molar ratio and heated on a water bath. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating on a water bath at 373 K, a brownish gel was formed after evaporation of water. Subsequently, the gel was decomposed at various temperatures ranging from 423 to 973 K. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consisted of very light and homogeneous flakes of very small particle size. Various techniques such as XRD (Philips PW1710 Diffractometer) and BET surface area measurements (Nova 1200 instrument) were employed to characterize these powders. For lattice parameter and interplanar distance (*d*) calculation, the samples were scanned in the 2*q* range of 10^o–80^o for the period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM

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copper grid. The samples were analysed for the presence of carbon by microanalysis technique on a CARLO ELBA EA-1108 analyser. The Raman scattering experiments were performed in the region 100–700 cm^{-1} in the back scattering mode using SPEX 1403 reflection grating type double spectrometer to confirm rutile and anatase phases of TiO_2.

3. Results and discussion

The tartaric acid added acts as a complexing agent. The mixture of tartaric acid and $TiOCl_2$ solution forms a gel on heating on a water bath which decomposes at higher temperatures, > 423 K. During calcination process, a black fluffy mass (foam-like) is formed which occupies large volumes of the furnace. As the temperature increases, the black mass turns to white in colour with the removal of carbon. Samples calcined at 773 K for 20 min shows < 1% of carbon. At higher temperatures of calcinations no carbon was found to be present. Figure 1 shows the XRD for the samples (ratio of titanium to tartaric acid is 2) heated at two different temperatures. The sample is X-ray amorphous until 473 K and no distinct peaks are observed. However, on increasing temperature to 623 K, anatase phase is found to be formed. The observed *d*-lines match the reported values for the anatase phase. The calculated lattice parameters for anatase are $a = 3{\cdot}772$ Å and $c = 9{\cdot}505$ Å. Further rise in temperature to 773 K leads to beginning of the conversion of anatase phase into rutile phase. The XRD shows the presence of both anatase and rutile phases. At 1073 K the conversion is complete and single phase rutile is produced. The calculated lattice parameters for rutile are $a = 4{\cdot}566$ Å and $c = 2{\cdot}950$ Å. When the ratio of titanium to tartaric acid is < 2, mixed phases of anatase and rutile are formed. However, our attempts to prepare pure rutile phase was not successful since the product always contained little anatase. In the case of TiO_2 prepared by citrate method, the product was always anatase irrespective of the ratio of citric acid and titanium. This is the main difference between citrate and tartarate precursors. The surface area of the anatase powders calcined at 623 K was found to be 80 m^2/g. The average particle size of anatase phase is found to be 3 nm and the particles of rutile phase are observed to be agglomerated (figure 2) and their average particle size is 30 nm. The crystallite size measurements were also carried out using the Scherrer equation,

$$D = k\,\lambda/b \cos q,$$

where *D* is the crystallite size, *k*, a constant (= 0·9 assuming that the particles are spherical), *l*, the wavelength of the X-ray radiation, *b*, the line width (obtained after correction for the instrumental broadening) and *q* the angle of diffraction. The average particle size obtained for ana-

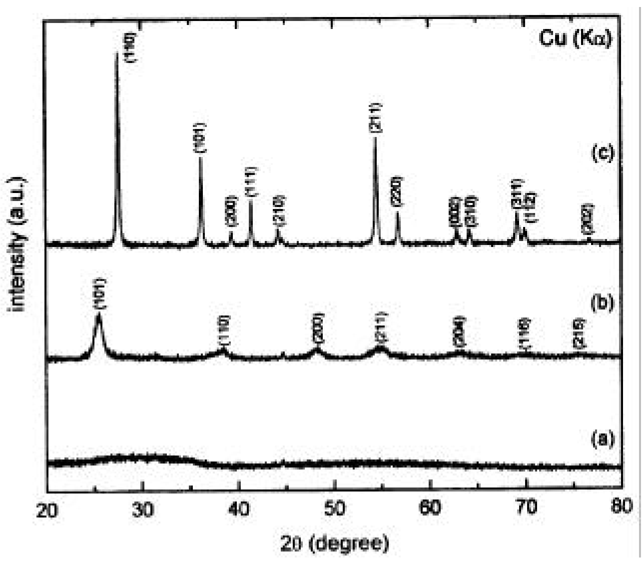

Figure 1. XRD of sample calcined at (a) 473 K, amorphous, (b) 623 K, anatase phase and (c) 1073 K, rutile phase.

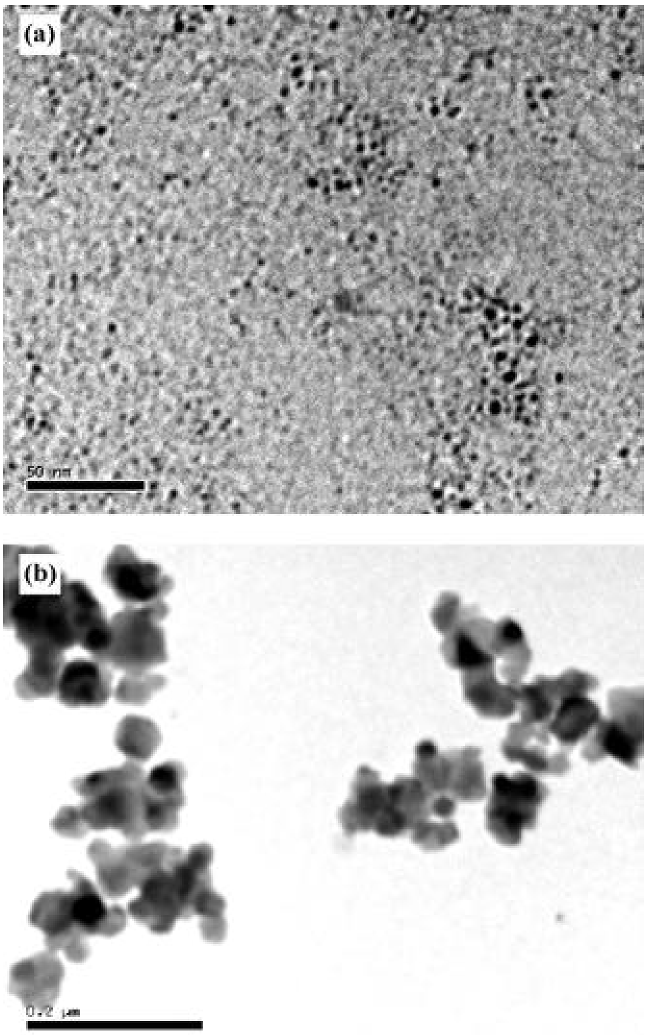

Figure 2. TEM pictures of (**a**) anatase, and (**b**) rutile powders.

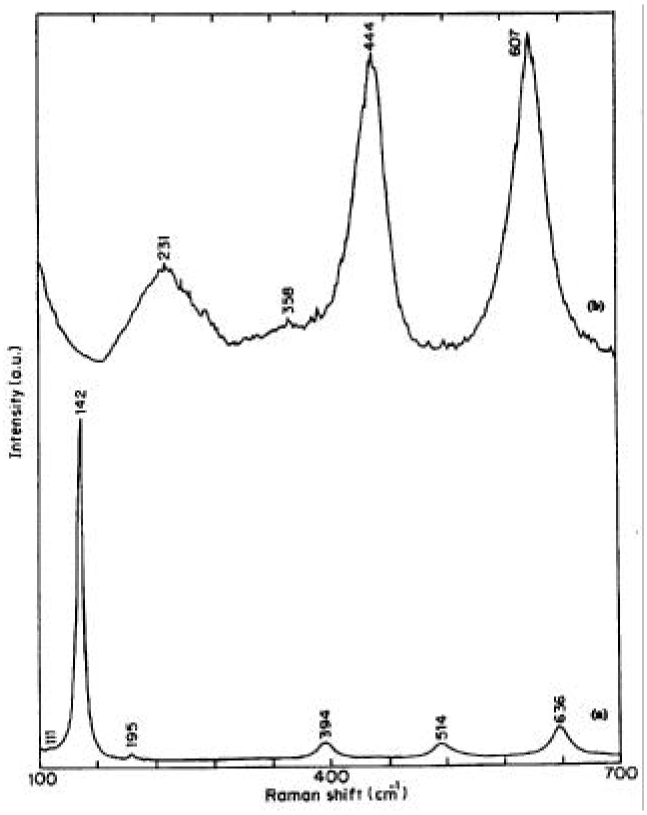

Figure 3. Raman shift in (a) anatase and (b) rutile powders.

tase and rutile phases from XRD data are 10 and 40 nm, respectively. The Raman spectrum of TiO_2 has been studied extensively but the investigation of the Raman spectrum of nanocrystalline TiO_2 is limited. Figure 3 shows the Raman spectrum of TiO_2 powders in both phases viz. anatase and rutile. The band near 608 cm^{-1} was identified as A_{1g} mode and the band near 446 cm^{-1} as the E_g mode for the rutile phase. The small differences in assigning peak wave numbers from the literature are considered to be arising out of intragrain defects present in the sample. The Raman bands for anatase phase are also similar to that reported in the literature (Cheng *et al* 1995).

It is well known that both anatase and rutile TiO_2 can grow from TiO_6 octahedra and that the phase transition proceeds by the rearrangement of the octahedra. Arrangement of octahedral through face sharing initiates the anatase phase while the edge sharing leads to the rutile phase. For pH < 3·5, the protonated surfaces of TiO_6 octahedra easily combine with –OH groups of other TiO_6 octahedra to form Ti–O–Ti oxygen bridge bonds by elimination of water molecule. In the presence of tartaric acid, the protonation followed by the possible face-sharing TiO_6 octahedra will result in formation of anatase phase. When the ratio of tartaric acid to TiO_2 was < 2, both edge sharing and face sharing was equally favoured resulting in the formation of mixed phases. In the hydrothermal conditions (Cheng *et al* 1995), the obtained average particle size of rutile is 20 nm whereas for anatase, it is 10 nm. It is also reported (Dhage *et al* 2003) that the presence of NaCl and $SnCl_2$ as mineralizers are essential for the formation of rutile phase. These fine powders of anatase phase obtained by tartarate method are potential candidates for photocatalyst for air and water purification. The properties that influence the photo catalytic activity of anatase phase are surface area, crystallinity, and crystalline size and crystal structure. Since this technique was not yet reported for the preparation of TiO_2 powders, experimental data for the applications is not available.

4. Conclusions

A simple tartarate gel method was used to prepare ultrafine particles of both anatase and rutile TiO_2. The average particle size obtained varies from 3·0–30 nm depending on annealing temperature and duration.

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