Synthesis of ultra-fine TiO₂ powders by controlled hydrolysis of titanium tetrabutoxide

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Ultrafine titania (TiO₂) spherical powders have been prepared by controlled hydrolysis of titanium tetrabutoxide in presence of acetic acid/acetone solution. The powder X-ray diffraction shows that the as-dried precursor is crystalline in nature and shows broad peaks corresponding to hydrous titania (anatase) phase. The calcination of the hydrous titania precursor at 350°C/2hr under controlled conditions produces agglomerated spherical anatase titania powders (size 200nm) with improved crystallinity. These microporous agglomerates are found to be constituted of 14 nm primary anatase particles. These powders show high surface area (105 m²/g) as measured by BET technique.

Ultrafine titania (TiO₂) possesses important chemical and electrical properties which make it an attractive material for applications such as gas-sensing¹, dielectric², catalyst³, photovoltaic solar cells⁴, and ceramic membranes⁵. To prepare titania powders many synthesis routes, viz., sol-gel⁶, hydrolysis in vapor phase⁷, peptization in acidic medium⁸, pyrolysis of titanium alkoxide⁹ and hydrothermal¹⁰,¹¹ have been attempted. It was observed during these studies, that the formation of various phases of titania (anatase / rutile / brookite), their stability, crystallite sizes and morphology largely depend on the processing conditions. The starting precursor¹², method of preparation¹³ and heat-treatments¹⁴, also have profound effects on the characteristics of final titania particles. In this paper, a comparatively simpler and easier method of preparation based on hydrolysis of an alkoxide in presence of acetic acid and acetone is described. Unlike some studies¹⁶,¹⁷ involving the hydrolysis of titanium alkoxides in alcohol, the present study precipitated the powders under atmospheric conditions rather than in dry nitrogen. The results related to synthesis of ultrafine anatase TiO₂ particles and their characterization are reported.

Materials and Methods
Commercially available titanium tetrabutoxide (BTM) (Sythochem, Indore), anhydrous acetone (SD's) and glacial acetic acid (SD's) were used as starting chemicals. Anhydrous acetone was used as solvent and acetic acid as catalyst during hydrolysis reaction. The hydrolysis of BTM was carried out at room temperature using molar ratios of H₂O/BTM=10 and acetic acid / BTM = 0.285 (v/v). The volume ratio of acetone / BTM = 20 was maintained during the experiment. The titania precursor was synthesized by rapidly adding BTM to a solution containing (acetone + acetic acid + H₂O) with pH = 4.0 in proportions mentioned above with continuous stirring. The condition leading to instantaneous precipitation of precursor was optimized by systematically varying H₂O / BTM ratio and the sequence of mixing the solutions thereafter while stirring. Finally, very fine hydrous titania precipitate (precursor) thus obtained was aged overnight. Then it was filtered through Whatman filter paper No 42 using a Buckner funnel assembly, washed repeatedly with acetone and air-dried. The changes in the structure of as-dried titania precursor with temperature were monitored by thermogravimetry (DTA / TGA / DTG) and X-ray diffraction technique. The morphology and degree of agglomeration were determined by TEM technique. The standard BET method was applied for measurement of surface area of anatase TiO₂ powders obtained by calcination of the as-dried precursor at various temperatures.

Results and Discussion
It has been established¹⁸ that if the ratio of H₂O/BTM is > 4, titanium tetrabutoxide hydrolyses completely in presence of mineral acids like HCl / HNO₃. In order to
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Fig. 1 - DTA / TGA / DTG of as dried precursor.

Fig. 2 - XRD patterns of (a) as dried precursor and after its calcination at (b) 350°C / 2hr and (c) 700°C / 2hr.
Table 1- Average crystallite sizes of titania precursor / powders after heat-treatment for 2hr in air

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Crystallite size, nm</th>
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<tbody>
<tr>
<td>30</td>
<td>7-8</td>
</tr>
<tr>
<td>350</td>
<td>13-14</td>
</tr>
<tr>
<td>700</td>
<td>20-22</td>
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To confirm the composition of precursor formed by reaction (1), the as-dried precursor was subjected to DTA / TGA / DTG in air at the heating rate of 10°C / min. Fig. 1 shows DTA / TGA / DTG curves of the precursor in the temperature up to 900°C. The TGA curve shows that the total weight loss of 31.30% in the precursor occurred below 450°C. The major weight loss of 27.20% up to 200°C in TGA curve coincides with two endothermic peaks in DTA appearing at 60 and 115°C respectively. It is due to the removal of adsorbed / hydrated water from the precursor particles. The minor weight loss (4.10%) shown in TG corresponding to an exotherm at 340°C in DTA curve is related to the decomposition of residual organic species such as butoxy groups (-OC₂H₅) and occluded butanol / acetone and their further oxidation in air. At 600°C, a small broad exothermic hump is shown in DTA which may be assigned to phase transformation from anatase to rutile, as no weight loss is shown in TGA curves. After that, there is no weight loss is shown in DTA / TGA / DTG curves up to 900°C in air. If the complete hydrolysis of titanium tetrabutoxide is assumed, then the experimentally observed total weight loss (31.3%) is in agreement with that calculated from the formula for the hydrous titania (TiO₂·2H₂O) formed by reaction (1). In that case, no exotherm at 340°C would have appeared in DTA. However in our thermal results a minor weight loss of 4.1% is observed with an exotherm at 340°C in DTA. If it is considered to be due to oxidation of occluded / adsorbed butanol / acetone, etc., then the observed total loss in TG curve would be definitely higher than 31.3%. Therefore, to account for the observed wt. loss of 31.3% (including minor exothermic wt. loss of 4.10%), it is reasonable to expect that the precursor formed by reaction

\[ \text{Ti(OC}_2\text{H}_5)_4 + 4 \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 \text{ or TiO}_2 \cdot 2\text{H}_2\text{O} \]
(1) is not the hydrous titania (TiO$_2$·2H$_2$O) but may have the composition Ti(OH)$_x$(OR), where x ≤ 0.10. This conclusion is further supported by IR studies on vacuum dried precursor which showed clearly the presence of peaks corresponding to OH stretching and bending vibrations around 3400 and 1610 cm$^{-1}$ respectively. The peaks corresponding to stretching as well as bending vibrations of -CH groups are also shown around 2920 cm$^{-1}$ indicating thereby the presence of some unhydrolyzed groups associated with the precursor. Rubio et al. and Hague et al. have reported that the precursor formed during hydrolysis in acidic medium is a complex compound formed between titanium and organic constituents like ethoxy/butoxy group which further decompose on heating to form TiO$_2$ at 350°C. The associated OR groups provide steric hindrance and help to control the growth of the precursor particles in solution. To further substantiate our results, XRD studies on the as-dried precursor and powders obtained by its calcination at two different temperatures (350 & 700°C) were carried out. The XRD patterns for the same are shown in Fig.2 (a,b,c). It is interesting to note that the as-dried precursor showed broad peaks indicating the ultrafine nature of primary particles. All the reflections shown in Fig.2a match with anatase phase of TiO$_2$. Further calcination at 350 and 700°C for 2 hr, showed better crystallinity in anatase phase. No reflections corresponding to rutile phase were observed even in TiO$_2$ powders, obtained by calcination of precursor at 700°C/2 hr. This indicates that although a small broad exotherm near 600°C in DTA is shown, the transformation of anatase to rutile could be too sluggish. From the analysis of the X-ray line broadening using Scherrer formula, the calculated primary particle sizes of three powders are listed in Table1. The estimated crystallite sizes in our TiO$_2$ particles are comparable with those obtained by Ding et al. using sol-gel method utilizing titanium tetrabutoxide, hydrochloric/nitric acid and butanol as starting chemicals. The surface areas of our anatase TiO$_2$ powders were found to be 105 and 28 m$^2$/g respectively when calcination temperature of precursor was kept 350 and 700°C. To get information regarding particle size, morphology and degree of agglomeration in these reactive TiO$_2$ powders formed at 350°C (as indicated by DTA / TGA / DTG, XRD and surface area measurements), TEM studies were undertaken. The TEM photograph is shown in Fig.3 which indicates that most of the individual particles are spherical in shape with size 15-20 nm forming agglomerates because of their high reactivity. Therefore, the crystallites are generally grouped together to form larger spherical agglomerates with size ≥ 200 nm. The particle size estimated by using an equation $D = 6 / (\rho S_{BET})$ is 14.6 nm where $\rho$ is the theoretical density (3.9 g/cm$^3$) in anatase phase and $S_{BET}$ is the measured surface area in m$^2$/g. Thus, the measured particle size by TEM in 350°C calcined powder is comparable with that calculated from BET technique.

Though the powder XRD pattern of the sample calcined at 350°C C corresponds to the anatase phase, electron diffraction pattern from a few small crystallites (Fig. 3b) could be indexed as the brookite phase of TiO$_2$ having orthorhombic structure. The well defined spot pattern indicates the single crystal nature of the brookite particles. Since the most intense reflection in XRD pattern of both anatase and brookite is at the same diffraction angle, it is not possible to identify the presence of small amounts of brookite (metastable) particles from the XRD pattern. Bokhimi et al. have recently shown that the sol-gel derived TiO$_2$ sample calcined at 300°C contains some metastable brookite crystals apart from the major anatase phase and the brookite particles are shown to have size ≤ 10 nm. As the size of the TiO$_2$ particles obtained in present study is ≤ 15 nm, it is possible that some of the small single crystallites of brookite are formed during calcination of as-dried precursor formed by reaction (1). Further work to obtain unagglomerated ultrafine TiO$_2$ particles and study of their phase transition behaviour as a function of a temperature, is in progress.

Thus, the present study shows that the controlled hydrolysis of titanium tetrabutoxide in presence of acetic acid and acetone produces crystalline precursor. The precursor gave agglomerated anatase TiO$_2$ powders with size 200 nm by its calcination at 350°C / 2h in air as a major phase with some random metastable brookite crystallites. The anatase phase is stable upto 700°C / 2h without much increase in crystallite size.

References

6. Cot L, Larbot A & Guizard C, Ultrastructure processing of