

Characteristics of Titania Nanoparticles Synthesized Through Low Temperature Aerosol Process

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Abstract

As one of the important process alternatives for the synthesis of nano materials with lower costs, flexibility and versatility, vapor phase synthesis of titania nano particles continue to attract attention. A low temperature aerosol process for the synthesis of titania nano particles is demonstrated by elucidating the influence of temperature, molar ratio of $H_2O/TiCl_4$ and concentration of precursors on particle size and phase composition. This paper highlights the advantages of employing amorphous phase titania powder as solid precursor for its transformation to the rutile phase at temperatures less than 973K through vapor phase hydrolysis of $TiCl_4$. A mechanistic hypothesis is proposed to explain the catalytic role of water vapor in the enhancement of amorphous to anatase phase transformation at high (15 to 27) molar ratio of $H_2O/TiCl_4$.

Keywords: vapor phase, hydrolysis, calcination, $TiCl_4$, amorphous.

1. Introduction

The various synthesis routes to titania has been studied extensively because of its wide applications as pigments, photo catalyst, catalyst supports, fillers, coatings, dielectric materials, UV-blocker and in electro-ceramics (Jang, 1997). Titania particles have also been employed to remove organic pollutants and heavy metals in waste water (Wu et al., 1998). Several investigations have been reported on the size and crystalline phase of titanium dioxide particles obtained either by high temperature gas phase process or by aqueous phase process. Two different chemical precursors have been typically used in these investigations namely, titanium tetra chloride ($TiCl_4$) and titanium tetra isopropoxide (TTIP). In high temperature processes, particles can be synthesized either by the oxidation of $TiCl_4$ (Suyama and Kato 1976; Morooka et al., 1989; Akhtar and Xiong, 1991; Akhtar and Vemury, 1994; Jang and Jeong, 1995; Yang et al., 1996; Yang et al., 1997; Windeler and Friedlander, 1997), or by the hydrolysis of $TiCl_4$ (Akhtar and Vemury, 1994; Xia et al., 1999a,b) or

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by the thermal decomposition of TTIP (Komiyama and Kanai, 1984; Okuyama et al., 1986; Okuyama et al., 1990) or by the hydrolysis of TTIP (Wu et al, 1998; Kirkbir and Komiyama 1988; Chan et al., 1999). Recently, considerable interest has been directed towards the synthesis of titania at low temperatures based on aqueous phase processing (Kim and Park, 1999; Park et al., 1999; Li and Fan, 2002; Yin et al., 2002; Tang and Zhang, 2002; Yang, 2003). TiO₂ powders produced by high temperature methods have encountered several problems such as control of product characteristics, corrosion of reactor, suitability of material of construction and operational problems due to the high temperatures and corrosive gases involved. However, compared with aqueous phase processes, the vapor phase process carried out in an aerosol reactor offers several advantages such as product purity, ease of collection, energy efficiency and absence of unit operations of filtration, washing and drying involving large liquid volumes. The high price of alkoxide limits the commercialization potential of aqueous phase processes. Therefore for commercial applications, aerosol processes with low cost precursors and continuous processing at lower temperature are likely to be preferred. Xia et al. (1999b) prepared anatase phase titania powder by vapor phase hydrolysis of titanium tetrachloride at temperature in the range less than 873K, the samples being obtained through electrophoretic deposition.

In this study the advantages of employing the amorphous phase titania synthesized through low temperature vapor phase hydrolysis of titanium tetrachloride as the precursor to obtain titania nano particles with either the anatase or rutile phase through calcination at low temperatures is experimentally demonstrated. Further, the catalytic role of water in the preferential enhancement the anatase phase compared to the amorphous phase during hydrolysis at high molar ratios of H₂O/TiCl₄ explained based on a mechanistic hypothesis (Ani et al, 2003).

2. Experimental Procedure

The experimental set-up (Figure 1) consists of precursor vapor generation and metering, aerosol reaction, powder collection and off-gas treatment. The reactor tube (2.5cm internal diameter and 150 cm length) is made of inconel. The tube is heated externally in an electrical furnace (Pyro Devices, Trivandrum), the length of the heating zone being 73 cm. The precursor vapors were introduced into reactor tube through two concentric tubes. Titanium tetra chloride (Commercial grade, KMML, Kerala, India, 99.8%) and deionised water vapor were the main reactants used for the vapor phase hydrolysis reaction. Mass flow controllers (MKS) were used to meter the flow rates while temperatures were measured using thermocouples. Nitrogen was used as the carrier gas. TiCl₄ vapor generated in the bubbler was carried into the central tube of the reactor by passing nitrogen at a flow rate of 200 cm³/min. through a gas-washing bottle (bubbler) containing liquid TiCl₄. The temperature of the TiCl₄ bubbler was maintained constant with the aid of a thermostat and thereby controlling the vapor concentration of TiCl₄ in the inlet stream.

Water vapor was generated by bubbling air at a flow rate of 1000 cm³/min. through bubbler containing water and by directing the humidified air (air with water vapor) into the reactor through the concentric outer tube. This procedure allowed for precise control of water vapor flow rate and concentration in the reactor. The TiCl₄ vapor and water vapor react rapidly around the nozzle inside the reactor and form TiO₂ aerosol at atmospheric pressure. At the exit of the reactor, the product was collected on a Teflon bag filter (Thermosystems, Trivandrum). The HCl gas in the exhaust gas was completely absorbed by a set of bubblers containing an alkali solution. The filter bag was maintained at temperatures above the boiling point of water (378-383 K) to avoid condensation of moist HCl. A vacuum pump was operated downstream to assist in particle collection on the filter while always maintaining atmospheric pressure in the aerosol reactor, which was monitored through a manometer. The vacuum created by the pump was adjusted so as to compensate for the increasing pressure drop across the filter during particle collection.

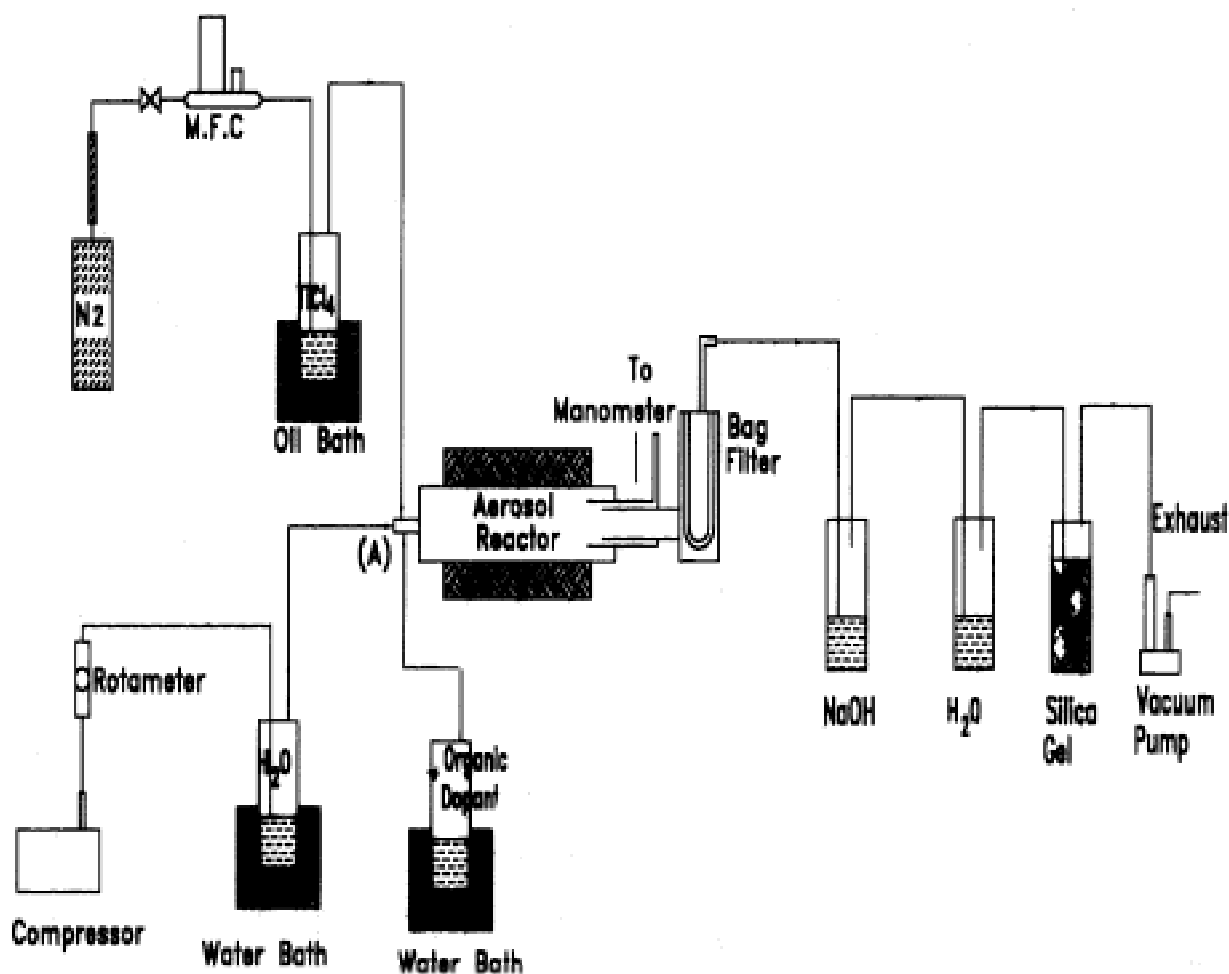


Figure 1. Experimental set up for the synthesis of Titania nano powders in Aerosol Reactor.

3. Characterization of Titania nano powders

Particle size and morphology of the as synthesized powders were examined by Transmission Electron Microscopy (TEM Model H-600 Hitachi). A small quantity of the particles was dispersed ultrasonically in acetone and allowed to settle on carbon coated copper grids for TEM specimen preparation. The average particle diameter was determined by counting more than 200 particles from the TEM pictures. The crystalline phase was investigated by X-ray diffractometry (Philips Analytical diffractometer). The fractions of anatase and rutile phases in the samples were calculated from the relative intensities of the primary peaks corresponding to anatase and rutile as described by (Spurr and Myers, 1957). The fraction of rutile in the sample was estimated using the equation:

$$x_R = \frac{1}{(1 + 0.8I_A/I_R)}$$

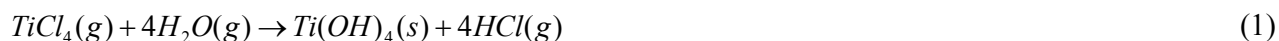
Where x_R is the weight fraction of rutile, I_A and I_R are relative intensities of the primary peaks corresponding to anatase (101) peak at $2\theta=25.4^\circ$ and rutile (110) peak at $2\theta=27.5^\circ$ respectively.

Thermal analysis of the titania powder was carried out with a Shimadzu DT/TG 50H thermal analyzer. The Specific surface area of powder was measured using the BET nitrogen adsorption apparatus (Gemini 2375 Version 4.02).

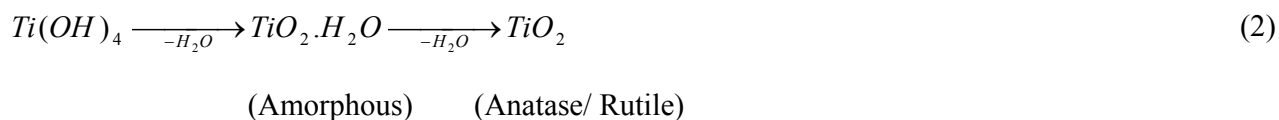
4. Reaction Mechanism

A mechanism based on hydrolysis reaction and the formation of oxo bridges is proposed for the production of titanium dioxide by low temperature (close to the boiling point of precursor) vapor phase hydrolysis of titanium tetra chloride as follows:

Nucleation reaction



Growth reaction without dopant



When a reactive mixture of $TiCl_4$ and H_2O vapor flows through a tubular reactor of length L and diameter D at steady state, chemical reaction occurs between $TiCl_4$ and H_2O forming HCl gas and

Ti(OH)₄ nuclei, which grow by the formation of oxo and hydroxyl bridges. These particles grow further by coagulation or condensation. The mechanism proposed in the paper accounts for the formation of amorphous phase titanium dioxide through oxolation; which involves the formation of titanium-oxo bridges. It is obvious that an oxo bridge results from two hydroxide ligands through dehydration viz.

Example of Growth Mechanism using the Bridging molecule Ti(OH)₄

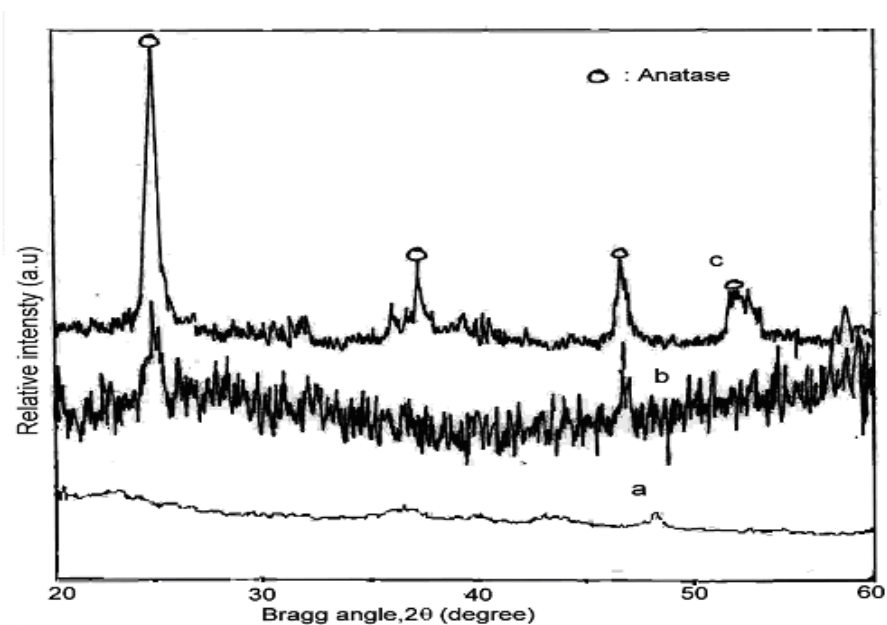
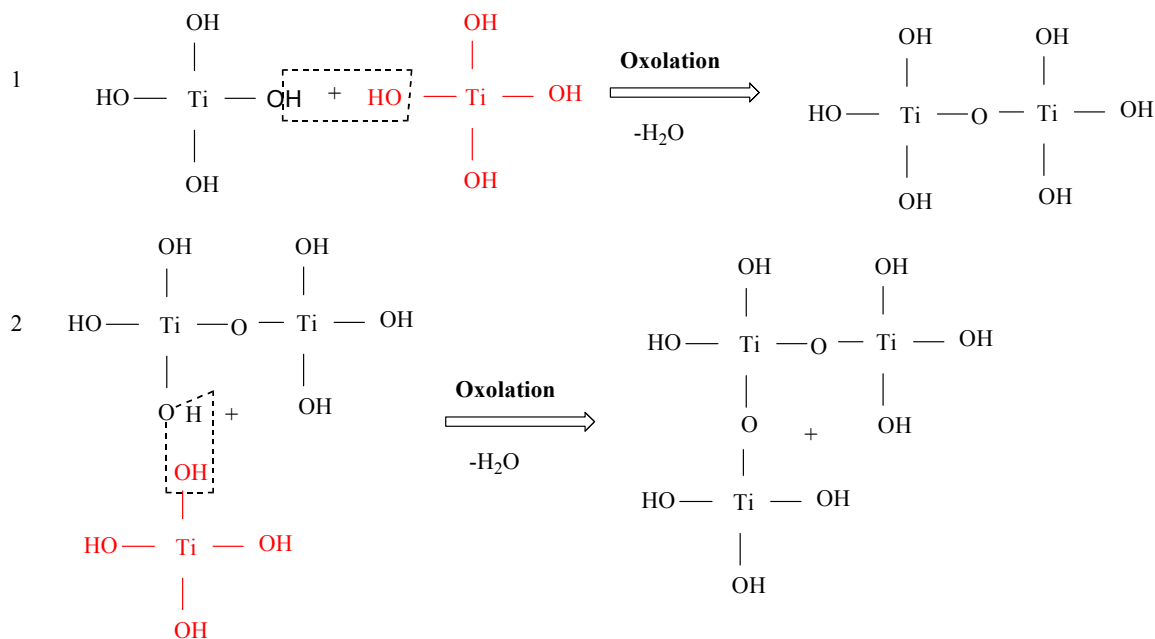


Figure 2. XRD pattern of effect of H₂O/TiCl₄ molar ratio on the crystalline phase of as prepared amorphous powder.

5. Results and Discussions

5.1. Effect of Process conditions on the TiO₂ powder produced at 353K

The titania powder produced at 353K is amorphous as evidenced by the XRD analysis. Figure 2 depicts the effect of changes in H₂O/TiCl₄ molar ratio (TiCl₄ concentration = 1.1%) on crystalline phase when hydrolysis temperature at 353K. The H₂O/ TiCl₄ molar ratio employed in this study is far greater than the stoichiometric ratio required for complete conversion of TiCl₄ (4:1). From the XRD patterns it is observed that up to a H₂O/TiCl₄ molar ratios of 15 titania with the amorphous phase was synthesized, whereas the H₂O/TiCl₄ molar ratio greater than 15 gradual increase in the fraction of anatase phase ultimately leading to a pure anatase phase at a H₂O/TiCl₄ molar ratio of 27. High crystalline titanium dioxide nano-particles having the anatase phase could be synthesized at much lower temperatures, (i.e., 357 K) in the presence of higher H₂O/ TiCl₄ molar ratio (15 to 27). Thereby exhibiting the catalytic influence of water towards enhancing amorphous to anatase phase crystalline transition. A similar effect highlighting the catalytic effect of water to promote anatase phase in hydrothermal synthesis has been reported by (Yanagisawa and Ovenstone, 1999).

5.2. Effect of Process conditions on the TiO₂ powder produced at 387K

The titania powders produced at 387K were found to have exclusively the anatase phase (Table 1) based on XRD analysis. Table 1 highlights the effect of H₂O/TiCl₄ molar ratio on the surface area of the titania powders synthesized at two different temperatures such as 353K and 387K. A similar catalytic effect of water vapor depicts in XRD (Figure 3) of which gradual progression to crystalline structures of anatase phase titania when the H₂O/TiCl₄ molar ratio increases.

Table 1. Effect of H₂O/TiCl₄ molar ratio on the phase and particle size of titania powders.

Sample	Temperature, K	TiCl ₄ concentration (v/v)	H ₂ O/TiCl ₄ molar ratio	Phase	Specific surface area (m ² /gm)	Percentage of Rutile content %, calcined at 1173K	Percentage of Rutile content %, calcined at 973K
1	387	1.1%	5	Anatase	20.6	26.0	-
2	387	1.1%	15	Anatase	39.0	68.0	-
3	387	1.1%	20	Anatase	43.4	82.0	-
4	387	1.1%	31	Anatase	52.0	>99.9	-
5	353	1.1%	5	Amorphous	99.0		>99.9
6	353	1.1%	12	Amorphous	144.0		>99.9
7	353	1.1%	27	Anatase	55.8		>90.0

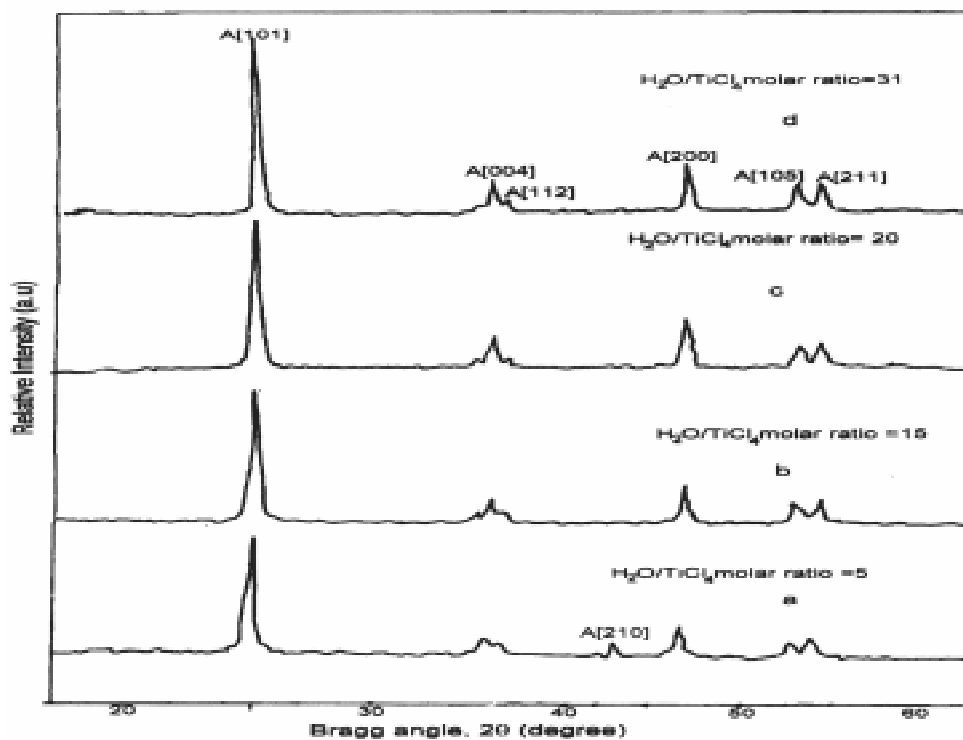


Figure 3. XRD pattern of effect of $H_2O/TiCl_4$ molar ratio on the crystalline phase of as prepared anatase powder at $TiCl_4$ concentration = 1.1 % and Temperature = 387K kept as constant.

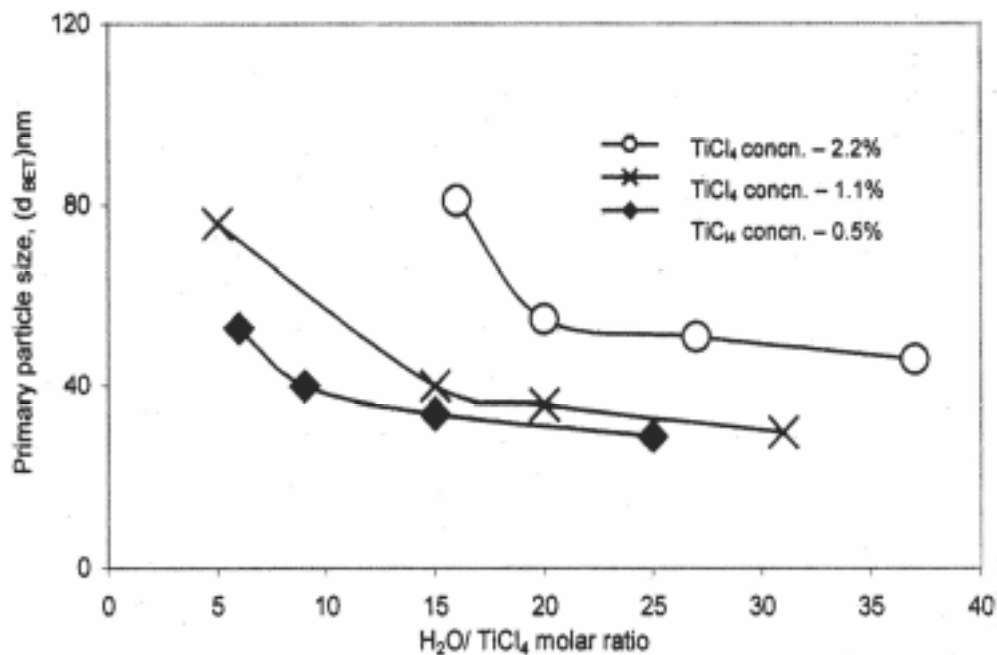


Figure 4. Variation of particle size with respect to $H_2O/TiCl_4$ molar ratio and $TiCl_4$ concentration at reaction temperature is 387K.

The average size of particles computed from the BET surface area synthesized at a reaction temperature of 387K and at different TiCl_4 concentrations are shown in Figure 4. The influence of TiCl_4 concentration (2.2 % to 0.5 %) as well as the molar ratio of $\text{H}_2\text{O}/\text{TiCl}_4$ on the decreasing trend in average particle diameter is evident in Figure 4. The decreasing trend in particle size as the mole ratio of $\text{H}_2\text{O}/\text{TiCl}_4$ increases is evident. At larger molar ratios of $\text{H}_2\text{O}/\text{TiCl}_4$ (>20) the average particle size becomes insensitive. This phenomenon could be attributed to the reduced probability for the growth of primary particles to larger particles due to the absence of $\text{Ti}(\text{OH})_4$ nuclei which are required to bridge primary particles.

Table 2. Properties of titania particles synthesized at different hydrolysis temperatures.

Sample	Temperature K	$\text{H}_2\text{O}/\text{TiCl}_4$ molar ratio	Vol. % of TiCl_4	Phase	Sp.Surface area, m^2/gm	d_{BET} , nm	Avg. pore diameter, Å
1	365	15	1.1	Anatase	28.5	54	24.9
2	371	15	1.1	Anatase	32.1	48	25.6
3	380	17	1.1	Anatase	36.6	42	24.3
4	387	15	1.1	Anatase	39.0	40	25.2
5	422	15	1.1	Anatase	51.3	30	24.8

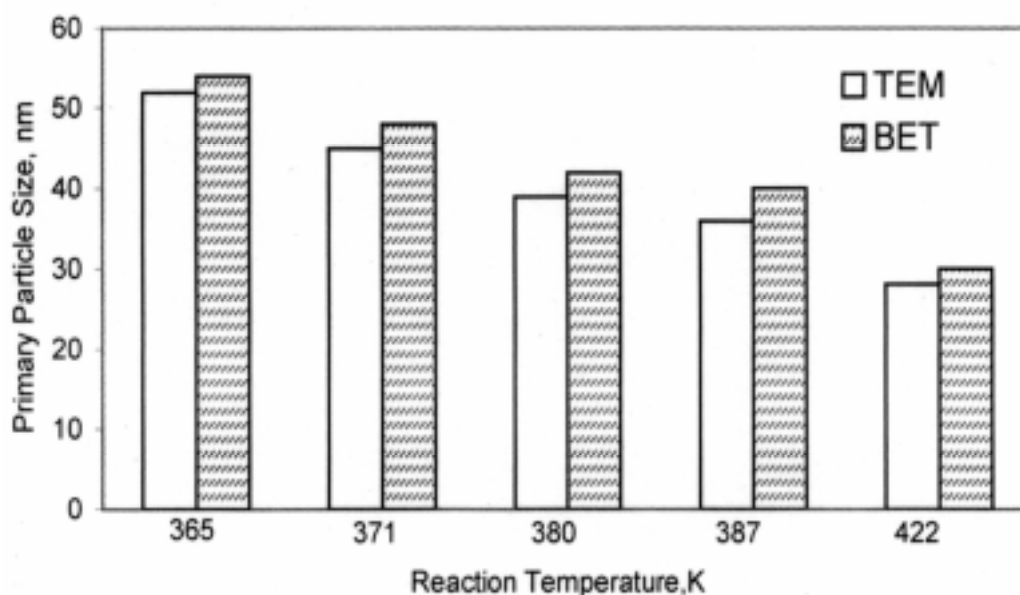


Figure 5. Average primary particle diameter as obtained by Transmission Electron Microscopy (TEM) and specific surface area (BET) measurements of the titania powders as given in Table 2.

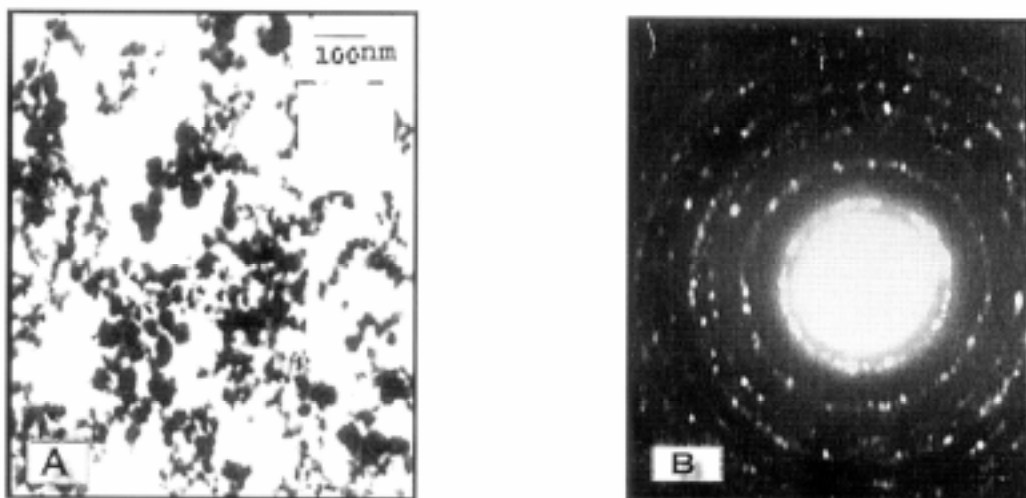


Figure 6. A) Transmission Electron Micrograph of Titania (100% Anatase) synthesized at temperature = 387K, $H_2O/TiCl_4$ molar ratio =15, $TiCl_4$ concentration = 1.1%.
B) Electron diffraction pattern for particles in (A).

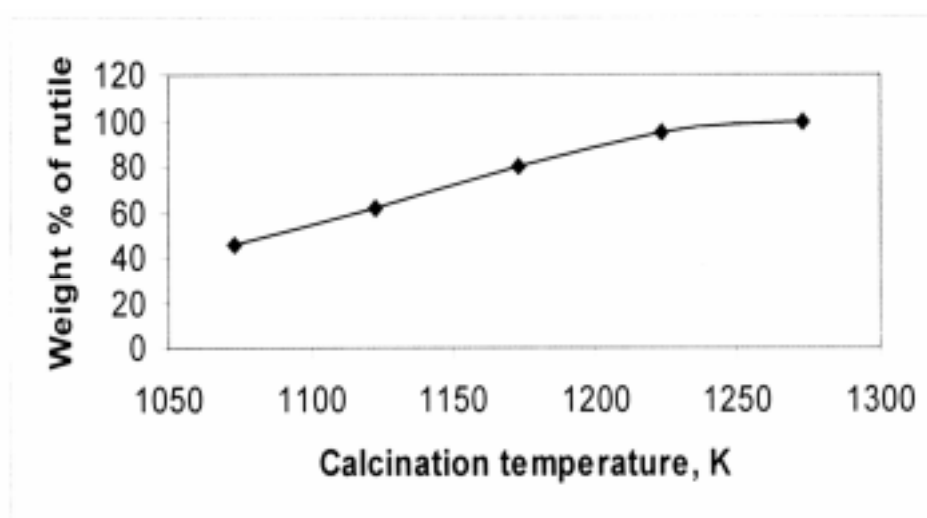


Figure 7. Effect of calcination temperature on fraction of rutile phase titania of as prepared anatase phase sample at reaction temperature= 387K, $H_2O/TiCl_4$ molar ratio = 12, $TiCl_4$ concentration=1.1%.

Figure 5 and Table 2 depict the effect of reaction temperature on average particle size when $H_2O/TiCl_4$ molar ratio =15 and Vol% of $TiCl_4$ = 1.1. The average particle diameters obtained from Transmission Electron Micrograph images was consistent with the average particle diameter computed from the BET surface area as shown in Figure 5. Particle size is primarily determined by the relative rate of nucleation and the rate of growth. Nucleation rate decreases with temperature due

to the increase of free energy of hydrolysis reaction with temperature as reported (Xia et al., 1999a; Ani et al., 2003).

However, the reversed trend of increasing particles with increasing reactor temperature are encountered for the high temperature oxidation of TiCl_4 and pyrolysis of $\text{Ti}(\text{OC}_4\text{H}_9)_4$. In the above cases the sintering/ coalescence of primary particles becomes the controlling factor.

Figure 6(A) depicts Transmission Electron Microscopy image of the powder prepared at reaction temperature of 387K, $\text{H}_2\text{O}/\text{TiCl}_4$ molar ratio of 15 and TiCl_4 concentration of 1.1%. Figure 6(B) shows the diffraction pattern of the titania sample.

5.3. Effect of Thermal Treatment (Calcination)

Precursor (as prepared through vapor phase hydrolysis) powders were calcined in a conventional muffle furnace. Powders produced at a hydrolysis temperature of 387K were calcined at 673, 973, 1073 and 1173K for 3 hrs. Figure 7 depicts the fraction of rutile phase in the calcined powders at various calcination temperatures. It is evident that the anatase to rutile transformation commences only at 1073K when the anatase samples were prepared at 387K.

Powders which were synthesized at hydrolysis temperature of 353K and calcined at 673K, 773K and 973K for 3hrs, exhibited progressive increase in the fraction of rutile peaks with increase in calcinations temperature leading to complete transformation at 973K. The percentage of rutile phase with the effect of particle size is listed in Table 1. The X-ray diffraction patterns (Figure 7) clearly establish this finding namely, that the as prepared amorphous powders could be converted to rutile at temperatures as low as 973K. This finding may be contrasted with the transformation of as prepared anatase powder to rutile at a temperature of only 1173K. Xia et al. (1999a) studied exclusively the calcination of as prepared anatase sample towards anatase to rutile transformation. However in this work, both the amorphous to rutile transformation and anatase to rutile transformation have been investigated.

Further, the new findings reported in this work may be summarized as follows. The transformation temperature to rutile is given by the sequence:

amorphous to rutile < anatase to rutile.

The range of temperature for obtaining the rutile phase titania from amorphous powder and from anatase phase powder are 673 - 973 K and 1073 - 1273 K respectively. In conclusion the experimental work clearly bring out the advantages of employing amorphous titania powder as a solid precursor for rutile phase transformation using the low temperature vapor phase hydrolysis of TiCl_4 .

5.4. Discussion on the mechanistic interpretation of the decrease of rutile transformation temperature when amorphous titania is used as the solid precursor

It is well known that (Yanagisawa and Owenstone, 1999) both anatase and rutile titanium dioxide can grow from TiO_6 octahedra and that phase transition proceeds by the rearrangement of the octahedra. Arrangement of the octahedra through face sharing initiates the anatase phase while the edge sharing leads to the rutile phase. Based on the nucleation and the growth mechanism proposed in this paper involving $\text{Ti}(\text{OH})_4$ nuclei, and oxolation / ololation leading to Ti-O-Ti linkages, it is suggested that the formation of TiO_6 octahedra could be a decisive factor beneficial to edge sharing condensation leading to the rutile phase.

The important role played by lower particle size to the phase transformation to rutile has been reported (Jang, 1997; Xia et al., 1999b). High rutile content (>90%) when the amorphous to rutile transformation takes place even at a temperature of 673K could be explained by the involvement of particles having the higher specific surface area ($144\text{m}^2/\text{gm}$, smaller average particle size) at high molar ratios of $\text{H}_2\text{O}/\text{TiCl}_4$.

6. Conclusions

A low temperature (353 – 387K, between the boiling point of liquid precursors ie, H_2O and TiCl_4) through vapor phase hydrolysis of TiCl_4 to synthesize TiO_2 nanoparticles has been demonstrated with the following new findings.

a) The surface average particle diameter decreases with an increase in hydrolysis temperature and decreases with an increase in $\text{H}_2\text{O}/\text{TiCl}_4$ molar ratio up to a ratio of 20 after which the average particle diameter becomes insensitive to changes in molar ratios of $\text{H}_2\text{O}/\text{TiCl}_4$. The catalytic role of water towards enhancement of anatase phase transformation has been experimentally demonstrated and mechanistically explained.

b) The calcination temperature for transformation from amorphous to the rutile phase is less than the temperature for the anatase to rutile phase transformation highlighting the advantages of employing amorphous powder as the solid precursor for obtaining the transformation to rutile phase through low temperature vapor phase hydrolysis of titanium tetra chloride.

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