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EXPERIMENTAL AND MODELING STUDIES ON VAPOUR PHASE SYNTHESIS OF TITANIA NANO PARTICLES

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ABSTRACT

This paper highlights a novel process to achieve low cost production of both anatase and rutile phase TiO_2 in a single flexible process involving vapour phase hydrolysis of titanium tetrachloride. Rutile grade titanium dioxide is obtained through the use of an organic dopant at temperatures as low as 673K. Significant cost advantages is perceived due to the much lower temperatures of operation and the use of water vapour instead of pure oxygen as in the existing chloride process.With a view to interpret and understand the relationship between titanium dioxide particle characteristics and the process conditions, a mechanism of nucleation and particle growth has been proposed for the first time and the model validated with the experimental results. The comprehensive nature of the work involving an innovative process and a mechanistic interpretations of the results is expected to establish a firm foundation to demonstrate the process at larger scales, leading to significant impact on titanium dioxide industry.
Key words: *Titania, hydrolysis, aerosol reactor, Titanium chloride, modeling*

1. INTRODUCTION

Large-scale manufacture of titania powders worldwide is now based on the highly mature technologies of either the chloride process involving vapour phase generation of titania that was developed during the 1960's or the sulphate process involving liquid phase generation of titania, developed during the 1940's [1]. The chloride route has been the more preferred route due to its superior product performance characteristics and favourable environmental aspects. The chloride process involves high temperatures (1200-1400^{o}C) during the oxidation of titanium chloride. However, for commercial applications, vapour phase reactions with cheap precursors due to its amenability for continuous processing at a lower cost are likely to be preferred. Recently, there has been a growing interest [2,3] in hydrolysis based aerosol synthesis due to the much lower temperature requirements and the absence of a need for high purity oxygen.

In the 21st century, the emerging paradign is to develop technologies such as green technology, low temperature, low cost, flexible manufacturing processes. This paper highlights an alternate approach to the manufacture of anatase and rutile grade TiO_2 with 21st century requirements.

The novel process employs vapour phase hydrolysis of $TiCl_4$ to generate anatase phase or rutile phase TiO_2 particles of different average size and distribution for pigmentary and non-pigmentary applications. This paper has the following three sub themes:

1.1 Synthesis of anatase phase titanium dioxide particles through a low temperature (<387 K) vapour phase hydrolysis of titanium tetrachloride.

1.2 Synthesis of rutile phase titanium dioxide particles through a novel low temperature (<673 K) vapour phase hydrolysis of titanium tetrachloride.

1.3 Interpretation of the relationship between titanium dioxide particles and process conditions through mechanistic and computer aided process modeling.

1.1 SYNTHESIS OF ANATASE PHASE TITANIUM DIOXIDE PARTICLES THROUGH A LOW TEMPERATURE (<387 K) VAPOUR PHASE HYDROLYSIS OF TITANIUM TETRACHLORIDE

1.1.1. EXPERIMENTAL PROCEDURE

The experimental set-up (figure 2) consists of precursor vapour generation, aerosol reaction, powder collection and off-gas treatment. The reactor tube (2.5cm internal diameter and 150 cm long) 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 vapours were introduced into the reactor tube through two concentric tubes.

Titanium tetra chloride (Commercial grade, KMML, Kerala, India, 99.8%) and deionised water vapour were the main reactants used for the vapour phase hydrolysis reaction. $TiCl_4$ was evaporated at various temperatures to obtain different vapour pressures and its vapour was carried into the reactor by nitrogen carrier gas. Water vapour was introduced into the reactor by an air stream. The $TiCl_4$ vapour and water vapour react rapidly around the nozzle and form TiO_2 aerosol at atmospheric pressure. At the exit of the reactor, the product was collected on bag filters made of Teflon for characterization. The exhaust gas was completely absorbed by a set of bubblers. The filter bag was maintained at temperatures above the boiling point of water (378-383 K) to avoid condensation of moist HCl. The dry powder collected from the filter bag was anatase phase titanium dioxide.

1.1.2. CHARACTERIZATION OF TITANIA POWDERS

Particle size and morphology of the as synthesized powders were determined by Transmission Electron Microscopy (TEM Model H-600 Hitachi). The crystalline phase was investigated by X-ray diffractometry (Philips Analytical diffractometer). Thermal analysis of the titania powder was carried out with 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). Pigment characterization was carried out at Travancore Titanium Products, Trivandrum.

1.1.3. 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) vapour phase hydrolysis of titanium tetra chloride as follows:

Nucleation reaction

$$TiCl_4(g) + 4H_2O(g) \rightarrow Ti(OH)_4(s) + 4HCl(g) \quad (1)$$

Growth reaction without dopant

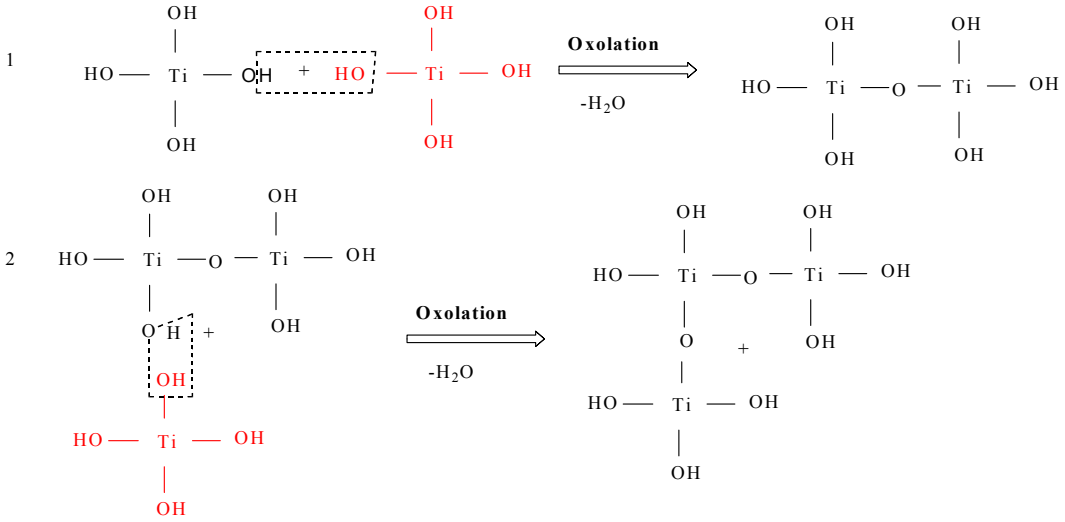
$$Ti(OH)_4 \xrightarrow[-H_2O]{} TiO_2.H_2O \xrightarrow[-H_2O]{} TiO_2 \quad (2)$$

(Amorphous) (Anatase/ Rutile)

when a reactive mixture of $TiCl_4$ and H_2O vapour 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 this 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 $Ti(OH)_4$



1.1.4. RESULTS AND DISCUSSION

1.1.4.1. EFFECT OF PROCESS CONDITIONS ON THE TIO_2 POWDER PRODUCED AT A REACTION TEMPERATURE OF 353K

The titania powder produced at 353K is amorphous as evidenced by the XRD analysis. Figure 2 depicts the effect of changes in $H_2O/TiCl_4$ molar ratio ($TiCl_4$ concentration = 1.1%) on crystalline phase when hydrolysis temperature was maintained at 353K. The $H_2O/ TiCl_4$ molar ratio employed in this study is far greater than the stochiometric ratio required for complete conversion of $TiCl_4$ (4:1). From the XRD patterns it is observed (Table 1) that up to a $H_2O/TiCl_4$ molar ratio of 15 titania with amorphous phase was synthesized, whereas at $H_2O/TiCl_4$ molar ratios greater than 15 a gradual increase in the fraction of anatase phase ultimately leading to pure anatase phase was obtained at a $H_2O/TiCl_4$ molar ratio of 27. Highly crystalline titanium dioxide nano-particles having anatase phase could be synthesized at much lower temperatures, (i.e., 357 K) in the presence of higher $H_2O/ TiCl_4$ molar ratio (15 to 27); thereby depicting the catalytic influence of water towards enhancing amorphous to anatase phase transition.

1.1.4.2. EFFECT OF PROCESS CONDITIONS ON THE TIO_2 POWDER PRODUCED AT A REACTION TEMPERATURE OF 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 $H_2O/TiCl_4$ molar ratio on the surface area of the titania powders synthesized at two different temperatures such as 353K and 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 3. The influence of $TiCl_4$ concentration (2.2 % to 0.5 %) as well as the molar ratio of $H_2O/TiCl_4$ on the decreasing trend in average particle diameter is evident in figure 3. The decreasing trend in particle size, as the mole ratio of $H_2O/TiCl_4$ increases is evident. At larger molar ratios of $H_2O/TiCl_4$ (>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 $Ti(OH)_4$ nuclei which are required to bridge primary particles.

Figure 4 depicts Transmission Electron Microscopy image of the powder prepared at reaction temperature of 387K, $H_2O/TiCl_4$ molar ratio of 15 and $TiCl_4$ concentration of 1.1%.

Figure 3 shows that particle size increases when the titanium tetrachloride concentration increases. Titanium dioxide particles obtained with a $TiCl_4$ concentration of 5.2% produces anatase particles with high tinting strength typical of anatase phase titanium dioxide pigment.

1.2 SYNTHESIS OF RUTILE PHASE TITANIUM DIOXIDE PARTICLES THROUGH A NOVEL LOW TEMPERATURE (<673 K) VAPOUR PHASE HYDROLYSIS OF TITANIUM TETRACHLORIDE.

1.2.1 EXPERIMENTAL PROCEDURE AND CHARACTERIZATION

The same experimental set-up (Figure 2) and characterization of powders described in section A is used for this process. The only difference in this process is in the addition of ethanol to the reaction mixture as the dopant. The dopant, ethanol, kept at room temperature was introduced into the reactor through the third concentric tube. The $TiCl_4$ vapour, water vapour and ethanol react rapidly around the nozzle and form TiO_2 aerosol at near atmospheric pressure. The molar concentration of ethanol molar concentration in the range of one to ten percent of the concentration of water vapour. Powders produced were heat treated in a conventional muffle furnace and calcined at various temperatures for 3 hrs.

1.2.2. RESULTS AND DISCUSSIONS

Titanium dioxide powders synthesized at different molar ratios of H_2O / ethanol in the reactor is given in Table 3, below and shows the specific surface areas of the powders produced as well as the rutile and anatase contents of these powders. Powders produced at the various molar ratios are designated as EH1, EH2, EH3 and EH4.
The main advantages of the present invention are:

1. Nano and sub micron size Titanium dioxide particles having the rutile phase, anatase phase and mixtures there of could be synthesized at temperatures less than 673K through vapour phase reaction with $TiCl_4$ as the precursor.
2. The other reactant involved in the process is water and ethanol, which are of low cost and are environmentally green chemicals.
3. *The process is less energy consuming than the other available processes and involves negligible maintenance*

Fig. 5 shows the XRD pattern of amorphous titania synthesized through vapour phase hydrolysis of titanium tetra chloride with and without the dopant. Specifically the XRD of the amorphous precursor synthesized with ethanol as dopant contains rutile fingerprints having shallow and broad peaks typical of non-crystalline structure. However, the above-mentioned features are absent in the XRD of amorphous precursors generated without ethanol. We can thus conclude that the use of organic dopant influences the nucleation process of titanium dioxide powder by generating unique solid structures capable of being converted to rutile phase at mild calcination temperatures.

The importance and significance of the role-played by ethanol to reduce the temperature of transformation of the amorphous phase to rutile is very clearly indicated in the XRD of the amorphous precursors (Fig. 5). The basis on which ethanol could influence the solid structure during nucleation could be due to the following phenomena:

1. It has been established [4,5,6] that the presence of alcohol could modify the size and morphology of titanium dioxide in aqueous phase due to changes in the dielectric constant. Although the above findings are strictly applicable to liquid phase titanium dioxide synthesis reactions, it could have a similar influence on the vapour phase reaction especially at low temperatures (close to the boiling point of water and ethanol) as reported in this work.

2. Ethanol molecules could be adsorbed onto the amorphous precursor and could be oxidized to CO_2 during calcination thereby creating oxygen vacancies in the lattice. The presence of oxygen defects enhances rutile transformation at lower temperatures.

3. It is well known that 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 edge sharing leads to the rutile phase.

Chelation of alcoholate groups (generated from the interaction of ethanol with the --OH group of the –Ti–OH- linkages) to the TiO_6 octahedra could be a decisive factor beneficial to edge sharing condensation leading to the rutile phase.

1.3. INTERPRETATION OF THE RELATIONSHIP BETWEEN TITANIUM DIOXIDE PARTICLES AND PROCESS CONDITIONS THROUGH MECHANISTIC AND COMPUTER AIDED PROCESS MODELING.

Process models based on physico-chemical principles and validated through comprehensive experimental data is crucial to accomplish design, scale-up and optimization of complex processes. In view of the absence of such a process model for vapour phase hydrolysis in an aerosol reactor, a model to predict the particle size characteristics as a function of the aerosol reactor parameters and process condition based on aerosol dynamics is proposed below. A mechanistic model based on lognormal distribution for particle size is presented here to predict the dynamic behaviour of titanium dioxide particle growth by nucleation through chemical reaction and particle growth through condensation and coagulation.

In this work, we use the lognormal approach of Pratsinis (1988) [7]. Particle size distributions are frequently observed to follow lognormal behaviour in experimental [8,9] as well as theoretical studies [10-14]. By assuming the log-normal form for the size distribution, the first three moments of the size distribution with respect to the particle volume is sufficient to characterize the aerosol particle growth completely. The change of the first three moments with time is given as follows: The zeroth moment M_0 (particle concentration) is only affected by nucleation and coagulation.

$$\frac{dM_0}{dt} = I - \xi M_0^2 \qquad (1)$$

The first moment M_1 (aerosol volume) is affected by nucleation condensation

$$\frac{dM_1}{dt} = Iv_1 \qquad (2)$$

The rate of change of the second moment M_2 (volume square of aerosol) is affected by nucleation, condensation, and coagulation,

$$\frac{dM_2}{dt} = Iv_1^2 + 2\zeta M_1^2 \qquad (3)$$

□and □ are the collision frequency functions that include both Brownian and shear induced coagulation terms [7].

Nucleation rate denotes the number of nuclei produced per unit volume per unit time. If the product particles have very low equilibrium vapour pressure (e.g. ceramic powders: TiO_2, Al_2O_3, SiO_2, etc), then even single molecules are thermodynamically stable particles [15]. Assuming, a first order reaction with respect to the precursor vapour, nucleation rate becomes:

$$I(1)\delta(0) = A\frac{dc}{dt} = kCA \qquad (4)$$

where A is the Avogadro number, C is the precursor vapour concentration (mole/ cm^3) and k is the rate constant for the reaction. A semi theoretical approach is proposed to compute the nucleation rate constant ki as a function of the thermodynamic characterization of the nucleation reaction.

It is proposed to use the concept of Linear Free Energy Relationships (LFER) was employed to identify a semi theoretical quantitative relationship between the nucleation rate constant ki and the equilibrium rate constant Kp [16]. By assuming a functional relationship of the form

$$k_i = f(Kp)$$
$$OR \qquad (5)$$
$$k_i = f(\Delta G)$$

Once the k value is known as a function of temperature T, the coupled ordinary differential equations (1,2,3 and 4) are solved with adaptive step size fifth order Runge Kutta method.

The validations of the process simulation model with the experimental results are shown in tables 4 and 5 to demonstrate the excellent prediction capabilities of the process model. A moment based aerosol dynamic equation incorporating the specific features of $TiCl_4$ hydrolysis has been developed desired with a view to establish a quantitative process model to predict the surface average particle size of titania as a function of precursor concentration, hydrolysis reaction temperature, molar ratio of $H_2O/TiCl_4$ for a any given reaction design parameter.

Figure 6 depicts overall comparison of experimental and model prediction with parity plots. The prediction of the model has been extensively validated using the experimental results reported in this work as well as those reported by Bin Xia et.al.,[2].

Apart from the establishment of a new process model for vapour phase hydrolysis of titanium tetrachloride the model includes two important concepts namely, *critical residence time* and the use of *Linear Free Energy Relationship* to predict the nucleation rate constant from equilibrium constant of $TiCl_4$ hydrolysis reaction. From the model, we observe that at a critical residence time, the concentration of the precursor becomes negligible coinciding with the completion of the nucleation and growth phase then by determining the average particle sizes. The critical residence time is thus defined as the residence time at which the rate of aerosol average particle volume tends to zero coinciding with the precursor $TiCl_4$ concentration-approaching zero.

It is expected that the modeling approach in this work would further contribute to the understanding of several other important vapour phase hydrolysis of volatile chlorides to synthesize particles.

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TABLES

Table 1: Effect of $H_2O/TiCl_4$ molar ratio on the phase and particle size of titania powders

Sample	Temperature, K	$TiCl_4$ concentration (v/v)	$H_2O/TiCl_4$ molar ratio	Phase	Specific surface area (m^2/gm)
1	387	1.1%	5	Anatase	20.6
2	387	1.1%	15	Anatase	39.0
3	387	1.1%	20	Anatase	43.4
4	387	1.1%	31	Anatase	52.0
5	353	1.1%	5	Amorphous	99.0
6	353	1.1%	12	Amorphous	144.0
7	353	1.1%	27	Anatase	55.8

Effect of Hydrolysis Temperature on average particle size:

Table 4: Comparison between experimental and simulated value of particle size with different Reaction temperature

$TiCl_4$ Concentration, vol.% (v/v)	H_2O /$TiCl_4$ molar ratio	Critical residence time, t_c (sec)	Reaction temperature, (K)	Particle size (experimental data), d_{BET} (nm)	Particle size (model prediction), d_p, (nm)
1.1	15:1	0.9	365 371 380 387	52 45 39 34	49 43 39 35

1.3.2. Effect of $TiCl_4$ concentration and H_2O/ $TiCl_4$ molar ratio on average particle size

Table 5: Comparison between experimental and simulated value of particle size with different H_2O/ $TiCl_4$ molar ratios

$TiCl_4$ Concentration, vol.% (v/v)	Reaction temperature, K	Critical residence time, t_c (sec)	H_2O /$TiCl_4$ molar ratio	Particle size (experimental data), d_{BET} (nm)	Particle size (simulated data), dp (nm)
1.5%	387	0.9	8	105	100
			12	69	72
			17	45	49
			24	40	39

FIGURES

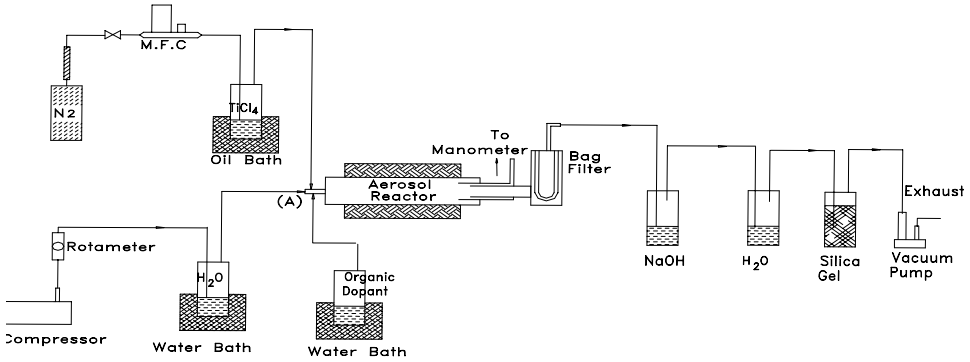

Figure 1: Experimental set up for the synthesis of Titania nano powders in Aerosol Reactor

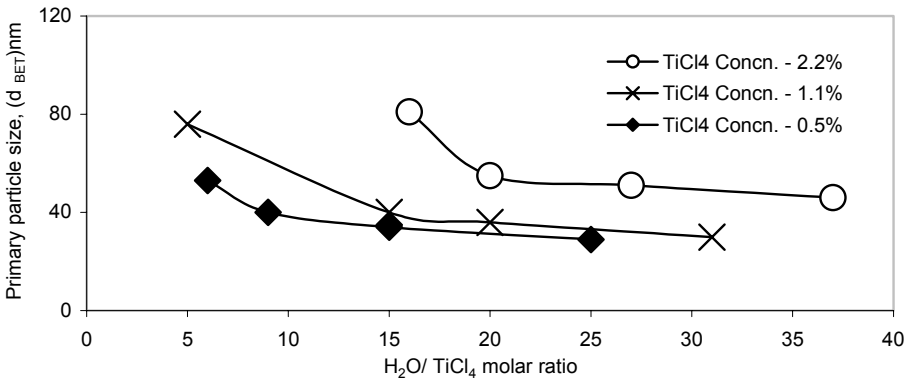

Figure 3:Variation of particle size with respect to H_2O/ $TiCl_4$ molar Ratio and $TiCl_4$ concentration at reaction temperature is 387K.

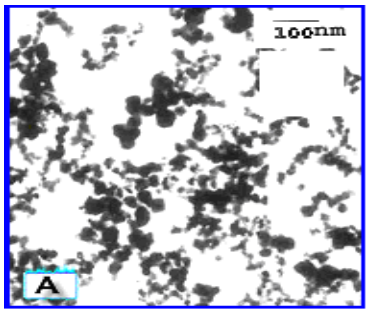

Figure 4: Transmission electron micrograph of Titania (100% Anatase) synthesized at Temperature = 387 K, $H_2O/TiCl_4$ molar ratio = 15, $TiCl_4$ concentration = 1.1%.

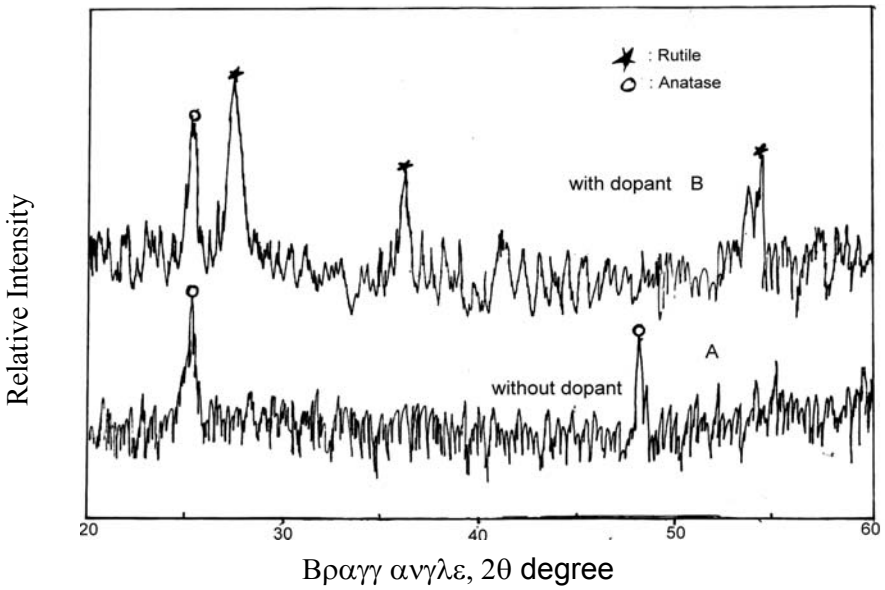

Figure 5: X-ray Diffraction pattern of amorphous phase titania particles synthesized through vapour phase hydrolysis of $TiCl_4$ in aerosol reactor. Conditions: Reaction temperature: 353K, $H_2O/TiCl_4$ molar ratio: 14, $TiCl_4$ concentration: 1.5%(v/v).
A) ethanol/$TiCl_4$ molar ratio = 0, B) ethanol/$TiCl_4$ molar ratio = 2.

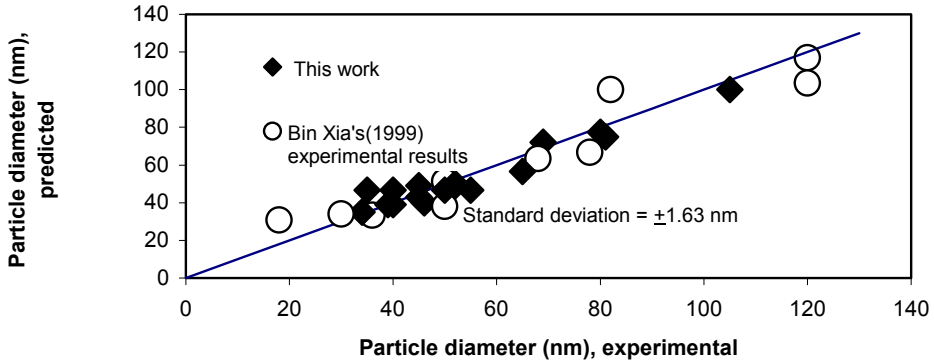

Figure 6: Overall comprison of experimental and model prediction with parity plots.