Low temperature process for the synthesis of rutile phase titania through vapor phase hydrolysis

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The synthesis of titania nanoparticles through vapor phase reactions in an aerosol reactor is a classical example of the use of aerosol processes in material synthesis applications. Recently [1, 3], there has been a growing interest in hydrolysis based aerosol synthesis routes due to the much lower temperature requirements and the absence of a need for high purity oxygen. The precursor needed for the hydrolysis reaction could either be alkoxides [4] or chlorides [1]. The chlorides however have an advantage due to their much lower cost and ready availability.

As an independent preparation route, Bin Xia *et al.*, [1, 2] conducted experiments based on vapor phase hydrolysis of $TiCl_4$ in a vertical furnace to synthesize anatase phase titanium dioxide below 873 K and calcined above 1073 K to obtain rutile phase titania particles.

The major finding reported in this paper is the use of amorphous titanium oxide precursors generated during vapor phase hydrolysis with ethanol as a dopant for conversion to rutile phase titanium dioxide at the lowest transformation temperature reported so far. The addition of organic dopant reduces the amorphous to rutile phase conversion temperatures to as low as 423 K (150 °C). This finding has been patented recently [5].

The hydrolysis reaction takes place in an aerosol reactor of ID 2.5 cm and 1.5 m in length, heated externally in a horizontal electric furnace (Fig. 1). The reactor inlet is composed of three concentric metallic tubes made of inconel through which the reactants ($TiCl_4$, H_2O, and the dopant) are introduced as vapor.

The hot wall temperature of the reactor is maintained such that the reactant gas stream is heated from a temperature in the range 343–353 K at the inlet of the reactor to a temperature not exceeding 373 K at the exit of the reactor for obtaining amorphous titanium dioxide particles. The amorphous phase titanium dioxide particles are then converted to titanium dioxide particles having the rutile phase through calcination at temperatures as low as 423 K.

A possible mechanism based on hydrolysis reaction and the formation of oxo bridges is proposed for the production of titanium dioxide by vapor phase hydrolysis of titanium tetra chloride as follows:

Nucleation reaction

$$\mathrm{TiCl_4(g) + 4H_2O(g) \rightarrow Ti(OH)_4(s) + 4HCl(g)}$$

Growth reaction without dopant

$$\underset{\text{(Amorphous)}}{\mathrm{Ti(OH)_4 \xrightarrow[-H_2O]{} TiO_2{\cdot}H_2O}} \underset{\text{(Anatase)}}{\mathrm{\xrightarrow[-H_2O]{} TiO_2}}$$

Growth reaction with organic dopant (ethanol)

$$\underset{\text{(Amorphous)}}{\mathrm{Ti(OH)_4 \xrightarrow[-H_2O]{} TiO_2{\cdot}H_2O}} \underset{\text{(Rutile)}}{\mathrm{\xrightarrow[-H_2O]{} TiO_2}}$$

Fig. 2 shows the XRD pattern of amorphous titania synthesized through vapor phase hydrolysis of titanium tetrachloride 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. 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. 2).

The basis on which ethanol could influence the solid structure during nucleation could be due to the following phenomena:

1. It has been established [6–8] 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 vapor 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 [9] and

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TABLE I Comparison of rutile transition temperature observed with and without the dopant

Reaction temperature (K)	$H_2O/TiCl_4$ molar ratio	C_2H_5-$OH/TiCl_4$ molar ratio	Phase	Commencement of phase transformation to rutile temperature (K)	Completion of phase transformation to rutile, temperature (K)
353	14:1	–	Amorphous	673	973
353	14:1	2:1	Amorphous	423	673
387	15:1	–	Anatase	1073	1373
387	15:1	2:1	Anatase	773	1073

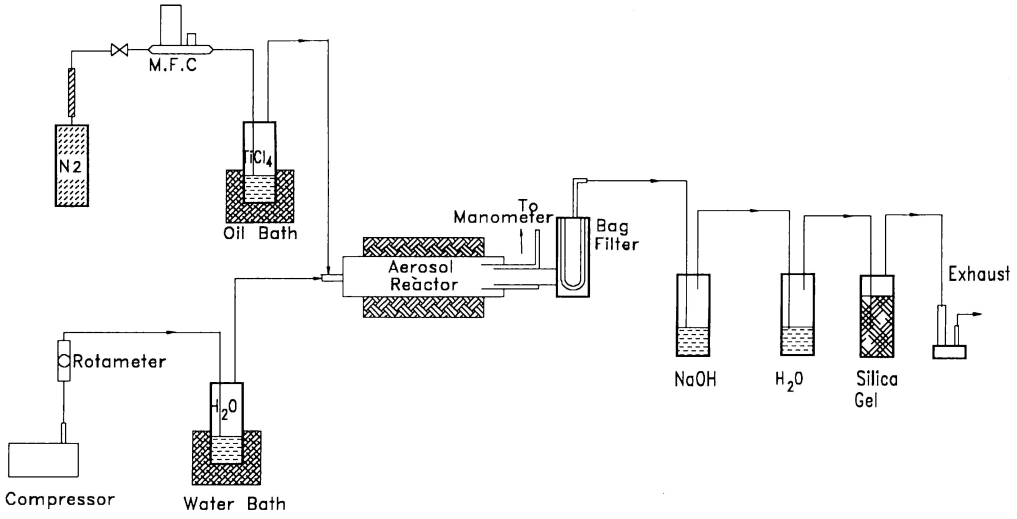

Figure 1 Experimental set-up for the synthesis of titania powders in aerosol reactor.

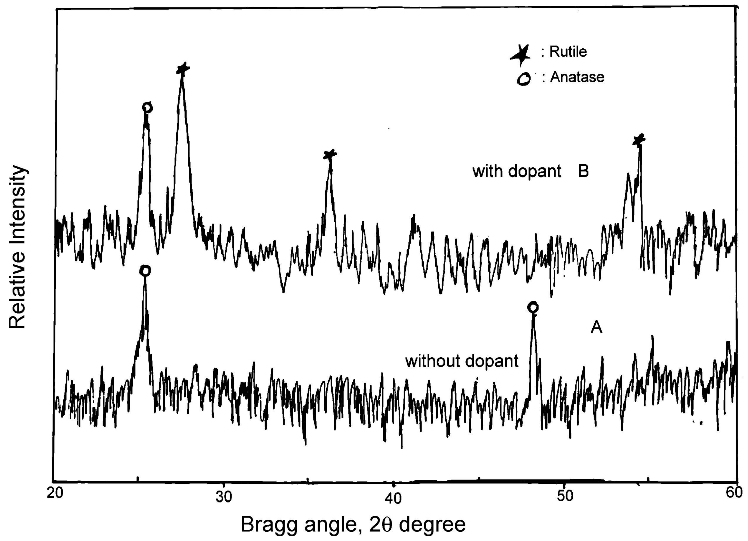

Figure 2 X-ray Diffraction pattern of amorphous phase titania particles synthesized through vapor phase hydrolysis of $TiCl_4$ in aerosol reactor. Conditions: Reaction temperature: 353 K, $H_2O/TiCl_4$ molar ratio: 14, $TiCl_4$ concentration: 1.5% (v/v). (A) Ethanol/$TiCl_4$ molar ratio = 0, (B) Ethanol/$TiCl_4$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

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.

Table I gives a comparison of transition temperatures observed for conversion to the rutile phase. The important role played by the dopant in terms of lowering the transition temperatures is evident.

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