Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.
PREPARATION OF NANOCRYSTALLINE TITANIUM DIOXIDE PARTICLES FROM NEW-ZEALAND ILMENITE

by

RANJEETH KUMAR RAJASHEKAR R

A Thesis Submitted in
Fulfillment of the
Requirements for the Degree of
Master of Engineering
In Chemical Engineering and Nanotechnology
At
Massey University, New Zealand
May 2011
Acknowledgements

I would like to take this opportunity to express my special gratitude to my supervisor, Prof. Richard Haverkamp, not only for giving me once in a lifetime opportunity to go further distance, but also for his invaluable guidance, encouragement and inspiration in my academic life. His willingness to provide me with technical training on some instruments is deeply appreciated, not to mention his advice and unsurpassed knowledge in the field of Chemical Engineering and Nanotechnology. I had almost lost track in thesis work but he got me back to my groove and gave me a chance even though he was tied up with his busy schedule, for which I am extremely grateful. Thank you very much for believing in me sir.

I would like to acknowledge my appreciation to technical staff of School of Engineering and Advanced Technology, in particular Mrs. Ann-Marie Jackson and Mr. John Sykes for their endless assistance with all technical issues I faced during the course of the project. I would like to say special thanks to Mr. Doug Hopcroft from MMIC Electron Microscopy for getting my samples analyzed within the specified time frame. Further I would like to extend my thankfulness to administration staffs, Mrs. Linda Lowe and Mrs. Michele Wagner for their commendable support and assistance.

I am thankful to my family for being very supportive and understanding throughout the research period. They have always inspired me to show positive attitude at rough times. Last but not least I thank Massey University for giving me this wonderful opportunity. I am greatly indebted to all people who are directly and indirectly involved in my research work.
Abstract

Titanium dioxide being one of the most important composite precursors has wide range of application due to the unique properties that it exhibits. TiO₂ with varying amount of anatase and rutile phases were prepared by controlled hydrolysis of dissolved liquor (Ti—Fe—Cl solution) from dissolution of New Zealand ilmenite followed by calcination of the hydrate sample at different temperatures. The kinetics of ilmenite digestion is examined based on the factors affecting the ilmenite dissolution rate such as acid/ilmenite ratio, additive (iron powder) and optimum dissolution temperature. In hydrolysis, the use of structure determining agents (SDA) that alters the morphology of TiO₂ fine particles is analyzed. Samples without SDA have resulted in rutile phase formation at 110°C, while samples with SDA (phosphoric acid/tri-sodium citrate/citric acid) resulted in either anatase phase or mixed phase (both anatase and rutile) at 110°C. The phosphate and citrate ions (0.35% P₂O₅ and 0.4% citrate) helps in promoting an anatase phase of TiO₂ particles. Along with SDA, parameter such as hydrolysis temperature and percentage seed also affects the intermediate product.

The influence of calcination temperature ranging from 925°C—1000°C on anatase-rutile phase transformation and variation in crystallite size was studied. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to characterize the resultant TiO₂ phase, crystallite size and particle size and shape. The degree of conversion to rutile was higher at higher calcination temperature. Introducing potassium additive (0—2 mass% K₂O) in the hydrate sample enhanced the anatase-rutile phase transformation at higher calcination temperature. However, the potassium content in the hydrate sample has a negligible effect on the crystallite
size of anatase and rutile after calcination. The XRD pattern shows an increase in the rutile peak intensity and a decrease in the anatase peak intensity with higher calcination temperature. SEM images show that the particle size of the calcined product at 975°C with 1% K₂O ranges from 230nm—300nm.
Table of Contents

Acknowledgements ........................................................................................................................................... i

Abstract ......................................................................................................................................................... ii

Table of Contents .......................................................................................................................................... iii

List of Figures ................................................................................................................................................... vii

List of Tables .................................................................................................................................................. x

List of Graphs .................................................................................................................................................. xi

List of Abbreviations ...................................................................................................................................... xiii

1 Outline of Research.................................................................................................................................... 1

1.1 Research Aim ........................................................................................................................................ 1

1.2 Key Questions Guiding Research ........................................................................................................ 1

1.3 Research Objectives .......................................................................................................................... 2

1.4 Scope of the Project .......................................................................................................................... 2

2 Literature Review..................................................................................................................................... 4

2.1 Introduction .......................................................................................................................................... 4

2.1.1 Submicron structured Titanium Dioxide .................................................................................. 5

2.2 Properties of Titanium Dioxide ........................................................................................................ 6
2.2.1 Photocatalytic Property .............................................................................................. 6
2.2.2 Super-Hydrophilic Property .................................................................................... 10
2.2.3 Electrocataytic Property .......................................................................................... 11
2.2.4 Structural Property .................................................................................................... 13
2.2.5 Thermodynamic Property ........................................................................................ 14
2.2.6 Electronic Property .................................................................................................... 16
2.2.7 Optical Property ......................................................................................................... 18

2.3 Preparation methods ....................................................................................................... 21
2.3.1 The sulphate process ................................................................................................. 21
2.3.2 Sol-Gel Method .......................................................................................................... 23
2.3.3 Micelle and Inverse Micelle Method ....................................................................... 25
2.3.4 Sol Method .................................................................................................................. 27
2.3.5 Hydrothermal Method .............................................................................................. 31
2.3.6 Solvothermal method .............................................................................................. 35
2.3.7 Direct Oxidation Process .......................................................................................... 38
2.3.8 Chemical Vapor Deposition (CVD) ........................................................................ 39
2.3.9 Physical Vapor Deposition ....................................................................................... 40
2.3.10 Microbial Method .................................................................................................... Error! Bookmark not defined.
2.4 Applications of Titanium dioxide

2.4.1 Photocatalytic application

2.4.2 White Pigment

2.4.3 Catalyst Support/Promoter

2.4.4 Gas Sensors

2.4.5 Photoinduced Hydrophilicity

2.4.6 Other applications

3 Experimental Design

4 Ilmenite Dissolution

4.1 Introduction

Source

4.2 Mechanism of Ilmenite dissolution

4.2.1 Factors affecting dissolution rate of Ilmenite

4.3 Experimental

4.3.1 Materials

4.3.2 Equipments

4.3.3 Procedure

4.4 Analysis of Ti, Fe and Ti³⁺
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 Results and Discussion</td>
<td>63</td>
</tr>
<tr>
<td>5 Hydrolysis</td>
<td>69</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>69</td>
</tr>
<tr>
<td>5.1.1 Hydrothermal Hydrolysis</td>
<td>69</td>
</tr>
<tr>
<td>5.1.2 Hydrolysis in Micro emulsion</td>
<td>70</td>
</tr>
<tr>
<td>5.1.3 THyCA method</td>
<td>70</td>
</tr>
<tr>
<td>5.2 Structure Determining Agents</td>
<td>73</td>
</tr>
<tr>
<td>5.2.1 Phosphoric acid</td>
<td>75</td>
</tr>
<tr>
<td>5.2.2 Citric acid</td>
<td>77</td>
</tr>
<tr>
<td>5.3 Experimental Procedure</td>
<td>78</td>
</tr>
<tr>
<td>5.3.1 Materials</td>
<td>79</td>
</tr>
<tr>
<td>5.3.2 Equipments</td>
<td>79</td>
</tr>
<tr>
<td>5.3.3 Procedure (Rutile formation without SDA)</td>
<td>79</td>
</tr>
<tr>
<td>5.3.4 Procedure (Anatase formation using SDA)</td>
<td>80</td>
</tr>
<tr>
<td>5.4 Sample Characterization by X-Ray Diffraction (XRD) and Scanning</td>
<td>82</td>
</tr>
<tr>
<td>Electron Microscopy (SEM)</td>
<td>82</td>
</tr>
<tr>
<td>5.5 Results and Discussion</td>
<td>83</td>
</tr>
<tr>
<td>6 Calcination</td>
<td>90</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td>90</td>
</tr>
</tbody>
</table>
6.1.1 Heating medium........................................................................................................ 90
6.2 Effect of Calcination......................................................................................................... 90
6.3 Additives used during calcination ................................................................................ 94
   6.3.1 Phosphate content ..................................................................................................... 96
   6.3.2 Potassium/Lithium content...................................................................................... 96
6.4 Experimental procedure.................................................................................................. 97
6.5 Results and Discussion.................................................................................................... 98

7 Environmental Consideration of TiO2 Plant on Industrial Scale ................................. 113
   7.1 Environmental impact ................................................................................................. 113
   7.2 Recycling...................................................................................................................... 114
   7.3 Operating cost.............................................................................................................. 115

8 Conclusion ............................................................................................................................. 117

Appendices ............................................................................................................................... 119

References ................................................................................................................................. 133

List of Figures

Figure 1: Rutile (left), Anatase (Center), Brookite (right)......................................................4
Figure 2: TiO2 Photo-catalyst (H. A. Lim, 2003) and Chlorophyll ........................................7
Figure 3: Band energy level diagram of TiO2 photocatalyst (Bahnemann, D et.al 2004) ... 8
Figure 4: The schematic representation of the mechanism of photocatalysis (Kathirvelu, S., D’Souza, L., & Dhurai, B. 2008) ..............................................................9

Figure 5: Hydrophilic mechanism (T. Hashimoto, Yoko, & Sakka, 1994) ............10

Figure 6: Molecular-orbital bonding structure for anatase TiO$_2$: (a) atomic levels, (b) crystal-field split levels, and (c) final interaction states. The thin-solid and dashed lines represent large and small contributions, respectively (Asahi, R et.al 2000) ....17

Figure 7: Schematic energy level diagram of the lowest unoccupied MOs of a [TiO$_6$]$^{8-}$ cluster with O$_h$, D$_{2h}$ (rutile), and D$_{2d}$ (anatase) symmetry (Wu, Z.Y et.al 1997) ......18

Figure 8: Energy diagram of optical brighteners and transitions (Siegrist, A.E et.al 2003) A = absorption; F = fluorescence; IC = internal conversion; ISC = intersystem crossing; S = singlet state; T = triplet state ......................................................................................20

Figure 9: Schematic diagram of the sulphate process (Reck and Richard 1999)........23

Figure 10: TEM images of TiO$_2$ nanoparticles prepared by hydrolysis of Ti(OR)$_4$ in the presence of tetramethylammonium hydroxide (Chemseddine, A et.al 1999) Error! Bookmark not defined.

Figure 11: TEM images of TiO$_2$ nanoparticles (Sugimoto, T et.al 2003) .......... Error! Bookmark not defined.

Figure 12: TEM image of TiO$_2$ anatase by sol-gel (Miao et.al 2004) Error! Bookmark not defined.

Figure 13: SEM images of the TiO$_2$ tubules (Lee et.al 2004)....... Error! Bookmark not defined.

Figure 14: TEM and HRTEM images of TiO$_2$ particles shuttle-like and round-shaped after annealing by micelle and inverse micelle method (Zhang, D et.al 2002; Lin, J et.al 2002) .....................................................................................................................................26

Figure 15: TEM image of TiO$_2$ particles derived from reaction of TiCl$_4$ and TTIP in TOPO/heptadecane at 300 °C (Trentler, T.J et al 1999) .........................................................28

Figure 16: TEM of TiO$_2$ particles (Cozzoli, P. D et.al 2003)........................................29
Figure 17: TEM images of TiO₂ rods with lengths of (A) 12 nm, (B) 30 nm, and (C) 16 nm. (D) 2.3 nm TiO₂ particles (Zhang, Z et.al 2005) .................................................................30

Figure 18: TEM images of 7-nm-sized TiO₂ particles prepared from 0.10 M titanium isopropoxide in 4:1 ethanol/water (a), 15-nm particles prepared from 0.04 M titanium isopropoxide in 1:2 ethanol/water (b), 25-nm particles prepared from 0.02 M titanium isopropoxide in 1:8 ethanol/water (c), and a high-resolution TEM image for a 7-nm particle (d) (Chae S, Y et.al 2003) ...........................................................................33

Figure 19: TEM image of TiO₂ material prepared with the hydrothermal method (Zhang, Q et.al 2003) ...........................................................................................................34

Figure 20: TEM image of TiO₂ submicron tubes (Kasuga, T. 1998) ............................ 35

Figure 21: TEM micrographs of TiO₂ particles prepared with the solvothermal method (Li, X.L et.al 2006) .........................................................................................37

Figure 22: TEM micrographs and electron diffraction patterns of products prepared from solutions at the weight ratio of precursor/solvent/surfactant) 1:5:3 (Kim, C.S et.al 2003) ...........................................................................................................37

Figure 23: SEM images of large-scale sub-micron rod arrays prepared by oxidizing titanium with acetone at 850 °C for 90 min by direct oxidation method (Peng, X & Chen, A. 2004) ...........................................................................................................38

Figure 24: SEM images of TiO₂ sub-micron rods grown at 560 °C by CVD method (Wu, J.J et.al 2004) .............................................................................................................40

Figure 25: SEM images of the TiO₂ sub-micron wires arrays prepared by the PVD method (Wu, J.M 2005) .................................................................................................41

Figure 26: Process flow diagram for preparation of titanium dioxide by using New Zealand Ilmenite (Barrytown, West Coast of South Island) ...........................................51

Figure 27: Ti (IV) – chloride speciation diagram for 0.1 Ti (IV) activities at 298 K as calculated by Cservenya’k et al. (1996) .............................................................................55
Figure 28: ESEM micrograph of TiO₂ fine particles showing the size and shape of different samples [(A), (B), (C) and (D)] with 1.5% K2O calcined at 975°C. (A) – Rutile3 (no SDA); (B) - Anatase phosphate1 (phosphoric acid); (C) - anatase citrate1 (tri sodium citrate); (D) - anatase citrate3 (citric acid). .............................................................. 110

List of Tables

Table 1 : Major constituents of New Zealand ilmenite (Barrytown)(Christie, Douch, Winfield, & Thompson, 2000; Judd, 1986).......................................................................................................................................................... 52

Table 2 : TiO₂ and FeO concentration at different optimum dissolution temperature..... 67

Table 4 : Crystallite size of rutile and anatase obtained using different SDA in hydrolysis.................................................................................................................................................. 88

Table 5 : Rutile3 (no SDA) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0%K₂O and 1.5%K₂O).......................... 102

Table 6 : Anatase phosphate1 (phosphoric acid) after calcination showing percentage and crystallite size of rutile and anatase at different potassium content (0%K₂O and 1.5%K₂O).......................................................................................................................................... 103

Table 7 : Anatase citrate1 (tri sodium citrate) after calcination showing percentage and crystallite size of rutile and anatase at different potassium content (0%K₂O and 1.5%K₂O).......................................................................................................................................... 104

Table 8 : Anatase citrate3 (Citric acid) after calcination showing percentage and crystallite size of rutile and anatase at different potassium content (0%K₂O and 1.5%K₂O).......................................................................................................................................... 105

Table 9 : shows the behavior of temperature with time during the 1st hour of digestion process for different sample liquor............................................................................. 119

Table 10 : shows the amount of K₂O to be added in the form of KCl ........................................... 119
Table 11: Rutile1 (no SDA) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0-2%K2O) and at different calcination temperature ................................................................. 119

Table 12: Rutile2 (no SDA) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0-2%K2O) and at different calcination temperature ........................................................................................................ 121

Table 13: Rutile1 (no SDA) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0.5%K2O, 1%K2O and 2%K2O) and at different calcination temperature ........................................................................................................ 122

Table 14: Anatase phosphate1 (phosphoric acid) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0.5%K2O, 1%K2O and 2%K2O) and at different calcination temperature ........................................................................................................ 123

Table 15: Anatase phosphate2 (phosphoric acid) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0—2%K2O) and at different calcination temperature ........................................................................................................ 124

Table 16: Anatase citrate1 (tri sodium citrate) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0.5%K2O, 1%K2O and 2%K2O) and at different calcination temperature ........................................................................................................ 125

Table 17: Anatase citrate2 (tri sodium citrate) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0—2%K2O) and at different calcination temperature ........................................................................................................ 126

Table 18: Anatase citrate3 (citric acid) after calcination showing Rutile percentage (%) and crystallite size at different potassium content (0.5%K2O, 1%K2O and 2%K2O) and at different calcination temperature ........................................................................................................ 128

**List of Graphs**

Graph 1: Behavior of temperature with time during the 1st hour of the digestion process by plotting temperature versus time. R1, R2, R3, A1, A2, A3, A4, A5 are different sample names. The condition of these samples are shown in table 2........ 65
Graph 2: Relation between TiO₂ and FeO concentration with optimum dissolution temperature.........................................................................................................................67

Graph 3: Illustration of peak intensity of anatase and rutile by plotting 2θ versus intensity for hydrate samples produced using different SDA additives.....................85

Graph 4: Illustration of different sample [(a), (b), (c) and (d)] showing peak intensity after calcination of hydrate samples with 1.5% K₂O calcined at 975°C by plotting intensity versus 2θ. (a) – Rutile3 (no SDA); (b) - Anatase phosphate1 (phosphoric acid); (c) - anatase citrate1 (tri sodium citrate); d - anatase citrate3 (citric acid)......99

Graph 5: Different samples [(a), (b), (c) and (d)] illustrating the degree of rutilization at different calcination temperature and potassium content (a) – Rutile3 (no SDA); (b) - Anatase phosphate1 (phosphoric acid); (c) - anatase citrate1 (tri sodium citrate); (d) - anatase citrate3 (citric acid). Note: different scale is chosen for TiO₂ without SDA (a). ............................................................................................................................................101

Graph 6: Illustrates the relation between FWHM and calcination temperature of different samples [(1), (2), (3) and (4)]. (1) – Rutile3 (no SDA); (2) - Anatase phosphate1 (phosphoric acid); (3) - anatase citrate1 (tri sodium citrate); (4) - anatase citrate3 (citric acid), βᴿ – FWHM of rutile peak .........................................................................................................................108

Graph 7: Illustrates the influence of calcination temperature on crystallite size of TiO₂ particles on different samples [(i), (ii), (iii) and (iv)]. (i) – Rutile3 (no SDA); (ii) - Anatase phosphate1 (phosphoric acid); (iii) - anatase citrate1 (tri sodium citrate); (iv) - anatase citrate3 (citric acid), dᴿ – crystallite size of rutile phase.........................................................109

Graph 8: Illustration of peak intensity of anatase and rutile of different samples [(a), (b), (c) and (d)] by plotting 2θ versus intensity for hydrate samples produced using different SDA additives. (a) – Rutile1 (no SDA); (b) – Rutile2 (no SDA); (c) - Anatase phosphate2 (phosphoric acid)); (d) - anatase citrate2 (tri sodium citrate)129

Graph 9: Different samples [(1), (2), (3) and (4)] illustrating the degree of rutilization at different calcination temperature and potassium content. (1) – Rutile1 (no SDA); (2) – Rutile2 (no SDA); (3) - Anatase phosphate (phosphoric acid)); (4) - anatase citrate (tri sodium citrate).........................................................................................................................130
Graph 10: Influence of calcination temperature on crystallite size of TiO₂ fine particles on different samples [(i), (ii), (iii) and (iv)] (i) – Rutile1 (no SDA); (ii) – Rutile2 (no SDA); (iii) - Anatase phosphate2 (phosphoric acid)); (iv) - anatase citrate2 (tri sodium citrate), dᵣ – crystallite size of rutile .................................................................................. 131

Graph 11: Relation between FWHM and calcination temperature of different samples [(A), (B), (C) and (D)] (A) – Rutile1 (no SDA); (B) – Rutile2 (no SDA); (C) - Anatase phosphate2 (phosphoric acid)); (D) - anatase citrate2 (tri sodium citrate, βᵣ–FWHM of rutile peak .......................................................................................................................... 132

**List of Abbreviations**

1D- one dimensional  
2D- two dimensional  
2θₐ – Braggs angle of anatase peak  
2θᵣ – Braggs angle of rutile peak  
3D- three dimensional  
AAM - anodic alumina membrane  
ALD - atomic-layer deposition  
CF-CVC – combustion flame-chemical vapor condensation  
CMC – critical micelle concentration  
CVD – Chemical vapor deposition  
dₐ – crystallite size of anatase sample  
dᵣ – crystallite size of rutile sample  
DSSC – dye-sensitized solar cell
EPA – Environmental protection agency

ESEM – Environmental scanning electron microscopy

Et-OH – Ethanol

FWHM – Full width at half maximum

GENS – Green earth nano science

HF – Hydrogen fluoride

IA – Intensity of anatase peak

Ir - Intensity of rutile peak

MOCVD – metal organic chemical vapor deposition

OA - oleic acid

PDMAEMA-b-PFOMA - dimethyl amino ethyl methacrylate-block-1H,1H,2H,2H-perflourooctyl methacrylate

PTCB – peroxo-titanium solution chemical bath

PVC – Poly vinyl chloride

PVD – physical vapor deposition

RBF – Round bottom flask

SDA – Structure determining agent

SEM - scanning electron microscopy

TEOA – triethanolamine
THyCA – transfer hydrolytic crystallization in alcohols

TOPO – trioctylphosphine oxide

TTIP - titanium tetraisopropoxide

UV – Ultra violet

XRD – X-Ray powder diffraction

$\beta_A$ – FWHM of anatase peak

$\beta_R$ – FWHM of rutile peak