

HYDROLYSIS OF TITANIC ACID IN HYDROCHLORIC ACID SOLUTION FOR
SYNTHESIS OF TIO₂ POWDER WITH CONTROLLED PARTICLE SIZE:
PROCESSES, MORPHOLOGY, AND KINETICS STUDY

by

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ABSTRACT

A method for producing pure titanium dioxide with controlled particle size and morphology has been developed. The TiO_2 powder produced by this method can be used as the starting material to produce pure Ti metal powder.

In this method, the upgraded Ti-slag (UGS) is used as the starting material. Upgraded Ti-slag is first roasted with NaOH to produce sodium titanate. The roasted product is washed by water to remove alkaline soluble impurities like Si and Al. The titanate is then dissolved into HCl solution and filtered to prepare the solution for hydrolysis of titanic acid.

Hydrolysis of titanic acid is performed at different temperatures with varied free acid concentration and equivalent TiO_2 concentration. The titanic acid is then calcined to remove combined water to produce TiO_2 powder. The particle size and morphology of the titanic acid particles produced by this method depend strongly on factors including temperature, free acid concentration, equivalent TiO_2 concentration, and agitation. To optimize the parameters of the hydrolysis process, a systematic parametric study was conducted.

TiO_2 powders with different morphology and particle size were obtained. The desired morphology of TiO_2 powder is determined to be around $30\mu\text{m}$, with a round shape and smooth surface. Porosity was found on the surface of TiO_2 particles after calcination. The dependence of particle size and morphology of solid titanic acid particles on those process parameters was studied.

The effect of the process parameters on the kinetics of the hydrolysis process were also studied. The mechanisms of nucleation and growth of titanic acid particles during hydrolysis was discussed.

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CHAPTER 1

INTRODUCTION

1.1 Ti and TiO₂

Titanium is known for its wonderful properties such as high strength, light weight, corrosion resistance, and bio-compatibility[1]. Titanium has been applied in aerospace, army, mobile cars, biomedical engineering, sports, and many other fields[2]. However, the market for titanium is limited due to the high cost of titanium manufacture[3].

Titanium is the 9th most abundant metal on the earth. The reason for the high price of titanium is mainly due to its difficulty of extraction which is because of its high affinity to oxygen. In industry, titanium is produced by the Kroll process commercially. It usually starts with Ti-slag or synthetic rutile. The feed material goes through reduction of ilmenite, the chlorination of Ti slag, the purification of TiCl₄, the Mg reduction of TiCl₄, the distillation separation of MgCl₂ and Mg, and the final stage of collection of sponge Ti[4]. Many steps such as Mg reduction of TiCl₄ and distillation of MgCl₂ are energy intensive which require high temperature and long amounts of time. The Kroll process is also a batch process which makes the extraction of titanium an expensive process.

Titanium dioxide is the oxide form of Ti metal. TiO₂ occurs in nature in three major forms: anatase, rutile, and brooktite. The typical minerals for TiO₂ is ilmenite which contains around 40-50 wt% of TiO₂. TiO₂ also occurs in nature as rutile, which contains more than 90% TiO₂. The occurrence of nature rutile is very rare now. Titanium dioxide is

known for its high refractive index, negligible color, photoactivity and inertness. It has been widely used in paints, paper plastics, ceramics, cosmetics, surface coating, photocatalyst and dye-sensitized solar cells[5].

Industrially, there are two major methods for producing TiO_2 : the sulfate process and chloride process. For the sulfate process, ilmenite is used as the starting material. The production of pigment grade TiO_2 involves sulfuric acid dissolving, precipitation of ferrous sulfate, filtering, hydrolysis of titanic acid, washing, calcination, and post treatment[6]. As for the chloride process, ilmenite ore is first reduced by coke to obtain Ti-slag with 60-70% TiO_2 . Ti-slag will go through some further purification to obtain upgraded Ti-slag or synthetic rutile which contains around 90% TiO_2 . Then upgraded Ti-slag goes through chlorination, purification, oxidization, calcination, and surface treatment to produce pigment grade TiO_2 [7].

Many attempts have been made to reduce the cost of Ti making which can be divided into two major categories: electrochemical reduction methods and thermal reduction methods. FFC is an electrochemical reduction process of Ti in CaCl_2 electrolyte[8] and TiO_2 cathode and carbon anode. Armstrong process is a thermal reduction method which uses Na for the reduction of TiCl_4 process. In addition, there are many other reports on using Mg or Ca vapor to reduce TiO_2 pellets directly[9].

The HAMR (hydrogen assisted magnesium reduction) process is a new method of producing Ti metal proposed by Dr. Fang[1]. It uses Mg powder to reduce TiO_2 powder in a H_2 atmosphere at an elevated temperature. The reduced TiO_2 powder will go through a second reduction step using Mg powder for deoxygenation to make Ti powder. The starting TiO_2 powder for Mg reduction is 25-40 μm , monodispersed, round particles made from

hydrolysis. This thesis will focus on the process of making TiO_2 powder by hydrolysis in terms of its process parameters, products characterizations, and kinetics study.

1.2 HAMR process

HAMR stands for hydrogen assisted magnesium reduction. The HAMR process is a new method for synthesizing Ti metal powder proposed by Dr Fang. The whole process consists of two major steps: Mg reduction of TiO_2 powder in H_2 atmosphere and Mg deoxygenation of TiH_2 powder. The strong ability to remove oxygen in TiO_2 using the HAMR process has been demonstrated experimentally.

In the HAMR process, TiO_2 powder is reduced by Mg powder at 750°C for 6 hr in H_2 atmosphere. TiO_2 will be converted to TiH_2 with less than 1% oxygen. Mg will be converted to MgO. The excess Mg and MgO formed during the reduction can be removed by leaching using hydrochloric acid.

The oxygen content in the TiH_2 is around 0.5-1 wt% after Mg reduction. To meet the ASTM specification for sponge Ti which is 0.15%, the oxygen in TiH_2 can be further removed by a deoxygenation step using either Mg or Ca powder. The procedures of the HAMR process are shown in Figure 1.1.

1.3 Hydrolysis of titanic acid

In this work, the production of TiO_2 powder starts with upgraded Ti-slag (UGS) provided by RTIT in Quebec. UGS is extracted from ilmenite which is the titanium-iron oxide mineral. Ilmenite is reduced by coke to separate the iron with TiO_2 and will go through a series of purification processes to obtain upgraded-Ti slag. UGS contains around 94.5% of TiO_2 . The main impurities in UGS are Fe_2O_3 , SiO_2 , MgO, and Al_2O_3 [10]. UGS

is purified using the alkaline roasting and hydrolysis (ARH) process to produce pure TiO_2 powder. The general procedures of ARH are introduced below.

UGS is mixed with NaOH pellets and roasted at $500\text{ }^\circ\text{C}$ for 2.5 hr. The roasted UGS is then washed by water to remove the extra sodium hydroxide. During roasting, TiO_2 is converted into Na_2TiO_3 , and SiO_2 is converted to Na_2SiO_3 . The roasted UGS is then washed with water to remove the alkaline soluble impurities like Na_2SiO_3 and NaAlO_2 . The washed product is filtered and dried in air.

Roasting UGS powder with sodium hydroxide pellets at an elevated temperature will transform TiO_2 into sodium titanate, the ideal formula of which is Na_2TiO_3 . Compared with UGS, sodium titanate can be dissolved in HCl solution almost completely at $50\text{ }^\circ\text{C}$. Alkaline roasting serves as a very important step in the preparation of the hydrolysis solution. Besides, impurities like Si and Al can be removed in this step.

Water washed product is dissolved in hydrochloric acid to prepare a solution with a certain concentration of equivalent TiO_2 and free acid. The solution is filtered to removed undissolved solids. The solution is then heated up to $100\text{ }^\circ\text{C}$ and stirred at 250rpm for 16 hr to synthesize titanic acid. Titanic acid is filtered and then washed by 6M HCl, water, and ethanol. The dried titanic acid is calcined to remove the combined water to make TiO_2 powders.

Hydrolysis is a selective precipitation process of titanic acid as solid particles out of the solution. Titanic acid is titanium oxide with hydrated water which is often expressed as $\text{TiO}_2 \cdot x\text{H}_2\text{O}$. Many impurities like Fe, Mg, and Al ions will remain in the solution during hydrolysis. Besides purification, the most important purpose of hydrolysis is to obtain titanic acid particles with controlled morphology in terms of particle size, shape, surface

area, etc.

For a typical batch of hydrolysis of titanate acid conducted in this work, the process of the reaction usually involved 3 stages: nucleation, crystal growth, and equilibrium. The initial nucleation stage happens in the first 2 hr. The nuclei of titanate acid start to form in this stage. The solution will turn from clear into cloudy. The nuclei of titanate acid in this stage are very small and with irregular shape. The concentration of equivalent TiO_2 starts to decrease slowly.

From the second hour to the 12th is usually considered as the growth stage. During this stage, most of the titanate acid will precipitate out from the solution and grow to its final size. The way the titanate acid grows is believed to be a process of agglomeration. In other words, the newly precipitated titanate acid nuclei will attach on the existed titanate acid particles, thus growing the existing particle to a larger size and more uniform shape. The equilibrium concentration of TiO_2 will decrease rapidly to its equilibrium level. The free acid concentration will increase significantly based on the chemical equation listed above.

In the third stage, the equilibrium stage happens from the 12th hour to the 16th hour. There will be no obvious change of the particle size and morphology of the titanate acid. The concentration of TiO_2 will stay constant or have a very minor decrease. Since the free acid concentration is very high at this stage, there will be some dissolution of titanate acid. Once the dissolved titanate acid has raised the equivalent TiO_2 concentration to a certain level, it will precipitate out again. This dissolution and precipitation process will keep the concentration of equivalent TiO_2 and free acid at a dynamic equilibrium.

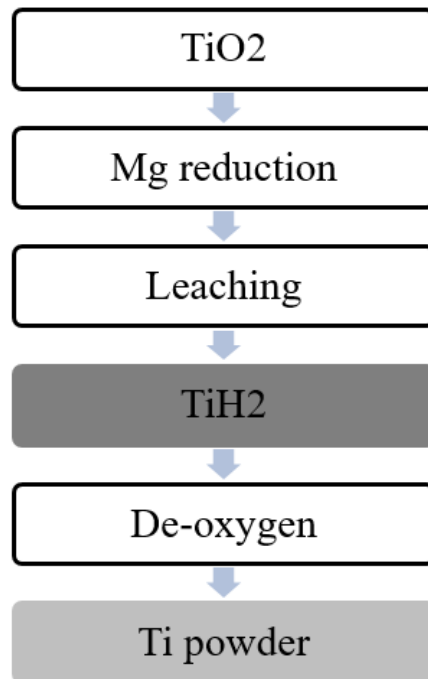


Figure 1.1 Flow chart of HAMR proces

CHAPTER 2

RESEARCH SCOPE AND OBJECTIVES

2.1 Research scope

As discussed in the previous section, to meet the specification of ASTM standard for Ti sponge, the oxygen content of final Ti product has to be as low as 0.15 wt%. In the HAMR process, to reduce the oxygen in TiO₂ powder, the step of Mg reduction itself plays a vital role in terms of many factors including reduction time, temperature, excess ratio, etc. Besides, it has been found that using feeding TiO₂ powder with well-controlled size and morphology can significantly help facilitating the effect of Mg reduction. Therefore, the goal of this work is to prepare pure TiO₂ powder with suitable size and morphology that can be used as the feed material for Ti production.

Because of titanium's high affinity to oxygen, titanium powder with small particle size (several microns) can easily pick up the oxygen in the air due to its large surface area which will increase the final oxygen content[11]. On the other hand, oversized TiO₂ powder can hinder the Mg reduction by slowing down the reaction. However, on the current market, the commercial TiO₂ powder produced by either the chloride process or sulfate process has very small particle size which is around several hundred nanometers. Meanwhile, although there have been a great amount of investigations about the synthesis of TiO₂ powder, almost all of the products reported have nanosized particles which are usually applied in the field such as solar cells, photo catalysts, and pigments[12, 13]. The morphology of

TiO₂ powder also needs to be controlled. In general, irregular and complex morphology can cause a higher surface area which increases the risk of oxygen pick-up for Ti powder after reduction. Besides, compared with agglomerated particles, monodispersed powder is preferred since it ensures a more complete leaching of excess Mg and by-product MgO. As for the TiO₂ powder on the market, the particles are agglomerated together and in irregular shape.

Therefore, it is very important to find a way to prepare TiO₂ powder with size and morphology that is most efficient for Ti production. In this study, a new method for producing TiO₂ powder with controlled size and morphology through hydrolysis in HCl solution was proposed. As mentioned earlier, most investigations in this field have been focusing on producing nanosized TiO₂ powder for traditional applications. Only a few studies have been found that can produce TiO₂ with around 15μm particle size[14].

In this work, the alkaline roasted upgraded Ti-slag is first dissolved into HCl solution to prepare hydrolysis solution. Hydrolysis of titanic acid is then performed at various temperatures and free acid concentration. Among all the steps, hydrolysis of titanic acid is the key step for controlling the particle size and morphology of TiO₂ powder. A possible hydrolysis reaction is expressed as:



The particle size and morphology of the titanic acid particles produced by this method depend strongly on factors including temperature, free acid concentration, equivalent TiO₂ concentration, etc.

According to the preliminary results, many different morphologies of TiO₂ powder such as needles, porosities, bumps, agglomerations, broken pieces, etc. were observed. At

the same time, particle size for a single particle can be varied from nanosize to nearly 60 μm . To optimize the parameters of the hydrolysis process and get consistent products, a systematic parametric study is conducted to evaluate the dependence of particle size and morphology of solid titanic acid particles on those process parameters. The effects of the process parameter on the kinetics and the hypothetical mechanisms of the hydrolysis process are also studied. See Figure 2.1 for the comparison of commercial TiO_2 and TiO_2 produced by in this work.

2.2 Research objectives

Therefore, the research objectives in this works are:

1. To optimize the parameters for each unit process of TiO_2 production including milling, roasting, dissolving, hydrolysis, and calcination.
2. To prepare high purity TiO_2 powder with controlled size and morphology using upgraded Ti slag as raw material.
3. To investigate the effect of free acid concentration and initial equivalent TiO_2 concentration on particle size, morphology, and hydrolysis rate of titanic acid particles.
4. To determine optimized parameters for producing TiO_2 powder with desired particle size and morphology for the HAMR process.
5. To try to understand the mechanisms of hydrolysis of titanic acid.

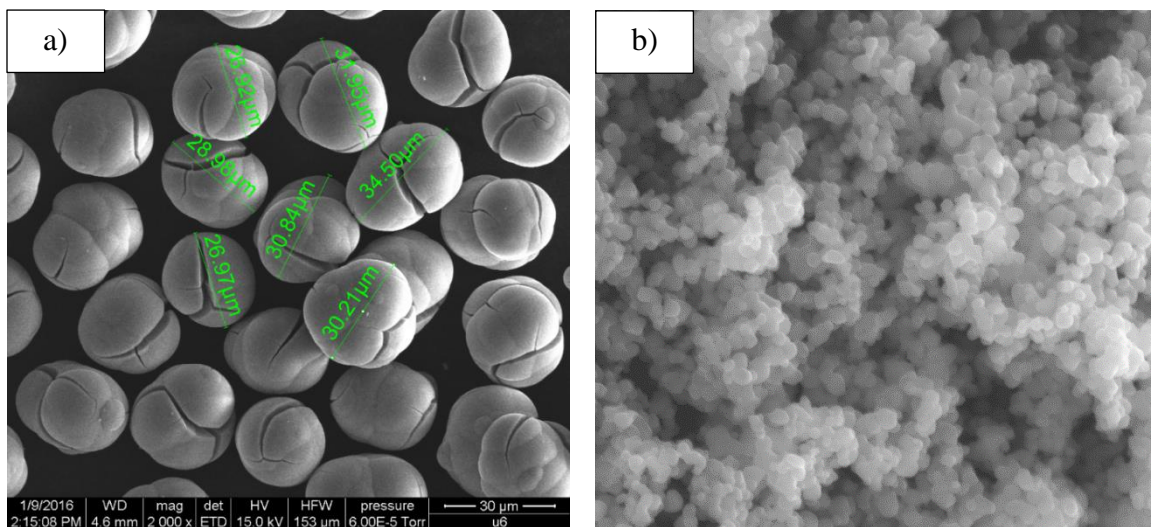


Figure 2.1 A comparison of TiO_2 powder produced in this work and commercial TiO_2 produced by sulfate process. a) TiO_2 produced in this work, b) commercial TiO_2 .

CHAPTER 3

LITERATURE REVIEW

3.1 The synthesis of TiO₂

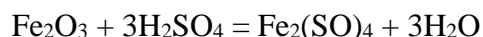
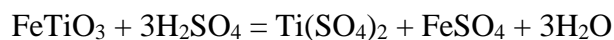
3.1.1 Sulfate process

The sulfate process is the traditional process for making TiO₂ powder which uses concentrated sulfuric acid to dissolve titanium ore to convert the Ti compound in the ore to a Ti-bearing solution[15]. After the Ti-bearing solution is purified, it goes through hydrolysis to produce hydrated TiO₂ which is then washed, calcined, and posttreated to make final TiO₂[16]. The process can vary depending on the grade of final product and the starting material.

The sulfate process typically contains five major steps: the preparation of Ti-bearing solutions, the hydrolysis of Ti-bearing solutions, the washing of titanic acid, the calcination of titanic acid, and posttreatment of TiO₂. The production of pigment grade TiO₂ usually has the most complicated processes.

The preparation of Ti-bearing solution includes acid dissolution, reduction of Fe³⁺, settling, low temperature crystallization, filtration of ferrous sulfate, and concentration of Ti-bearing solution. The starting material for the sulfate process can be ilmenite or Ti slag. When ilmenite is chosen as the starting material, it is mixed with 92 to 98 wt% sulfuric acid and a certain amount of water. The water added to the mixture will generate some heat that can help the dissolution process. Water vapor is then applied to the mixture to trigger

the main reaction of dissolving. It usually takes about 5 to 10 minutes of heating before the reaction can start. The reactions during acid dissolution are shown below,



Other impurities like MgO, CaO, and Al₂O₃ also react with sulfuric acid to form their sulfate salts.

Fe is a major impurity in ilmenite which has to be removed before hydrolysis. The solubility of FeSO₄ in Ti bearing solution decreases with the decrease of temperature. After the temperature of the solution is cooled down to under 0 °C, Fe will crystallize in the form FeSO₄ • 7H₂O and precipitate out of the solution[17].

After the removal of Fe, the solution is further purified by filtering to remove the undissolved small solid particles. These small particles have to be removed before hydrolysis, otherwise they could become nucleation centers for titanium acid nuclei[18]. Titanic acid nuclei forming on these small particles will have poor morphology.

The composition of Ti bearing solution has to be adjusted to a certain level before hydrolysis. Usually, the concentration of equivalent TiO₂ concentration is adjusted to 200~240g/L. The Ti bearing solution is concentrated by evaporating the water under a pressure lower than one atmosphere. It keeps the boiling point of the solution lower than 80°C to prevent hydrolysis[19].

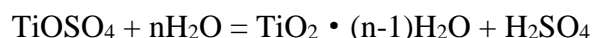
Hydrolysis is the key step to control the quality of the final TiO₂ powder. Factors including equivalent TiO₂ concentration, F value, Ti/Fe ratio, and stability of the solution can all influence the quality of titanic acid in terms of morphology, purity, and particle size.

The equivalent TiO_2 concentration and F value are the two key factors for hydrolysis in sulfate process which are introduced in detail below.

For pigment grade TiO_2 , the concentration of TiO_2 is usually controlled at 200~240g/L. For non-pigment grade TiO_2 , the concentration of TiO_2 is around 160g/L. It is reported that high concentration of TiO_2 can increase the whiteness of TiO_2 and low concentration of TiO_2 can increase the yield of hydrolysis.

F value is another important factor during the hydrolysis of sulfate process. The sulfuric acid used for dissolving titanium ores can be divided into three parts. The first part of sulfuric acid reacts with the Ti in titanium ores during acid dissolution. The second part of sulfuric acid reacts with other compounds in titanium ores. The third part is excess sulfuric acid which is referred to free acid. The sum of the first and the third parts of sulfuric acid is called effective acid. The concentration ratio of the effective acid to TiO_2 in Ti bearing solution is the F value[20]. Different F values will result in different TiOSO_4 to $\text{Ti}(\text{SO}_4)_2$ ratio in the solution which will affect the nucleation and growth of titanic acid during hydrolysis. Besides, the F value will have a great effect on the yield of titanic acid as well as the initial particle size of titanic acid.

The purified Ti bearing solution with proper equivalent TiO_2 concentration and F value is ready for hydrolysis. The solution is kept boiling during hydrolysis in the sulfate process. The chemical reaction of hydrolysis of titanic acid is shown below.



Hydrolysis is performed at a very high acid concentration. As the hydrolysis reaction goes on, the SO_4^{2-} combined with TiO^{2+} will be released and react with H^+ in the water to form H_2SO_4 , thus increasing the free acid concentration in the solution. TiO^{2+} will react

with OH^- in water to form titanitic acid. Most impurity cations will remain in the solution during hydrolysis at such a high acid concentration.

In the sulfate process, seeds are added into the Ti bearing solution before hydrolysis. The presence of seeds can accelerate the hydrolysis reaction and increase the yield of titanitic acid as well as improving the quality of final TiO_2 powder[21]. There are two types of seeds which are self-generated seeds and external seeds. Self-generated seeds are produced by adding hydrolysis solution into boiling water. The rest of hydrolysis solution is then added gradually. External seeds are added after the hydrolysis solution is heated up to 80°C . The hydrolysis solution is then boiled for 3 to 4 hr before the end of hydrolysis[22].

The titanitic acid after hydrolysis is washed by water to remove the attached hydrolysis solution. The titanitic acid is first separated from the hydrolysis solution by a vacuum filter. A filter cake will form on the filter cloth during filtering. Washing solution is then added to the top of the filter cake to flush the attached hydrolysis solution away. The temperature of washing solution is usually kept at 40°C to increase the solubility of FeSO_4 . Titanitic acid is then calcined to remove hydrated water to make TiO_2 powder. TiO_2 powder will go through a series of posttreatment to improve its quality.

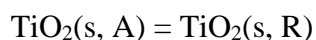
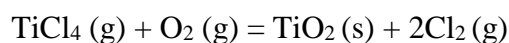
3.1.2 Chloride process

Upgraded Ti slag is usually used as the starting material in the chloride process. Upgraded Ti slag is first reacted with chlorine gas to transfer the TiO_2 and other oxides into their chlorides.

The other impurities like SiCl_4 , AlCl_3 , FeCl_3 , FeCl_2 , VOCl_3 , TiOCl_2 , Cl_2 , and HCl are mixed with TiCl_4 after chlorination[23]. The mixture is a cloudy solution that is red brown in color. TiCl_4 has to be separated from those impurities before the oxidization step. The

impurities can be divided into 3 categories according to their boiling point. High boiling point impurities like FeCl_3 have very low solubility in TiCl_4 solution and stay in the solution as suspensions. Low boiling point impurities include soluble gas and most liquid chlorides. These impurities are removed from TiCl_4 by distillation. The temperature of distillation is controlled at around 140 to 145 °C which is a little higher than the boiling point of TiCl_4 . Impurities with low boiling points will leave the distillation tower before TiCl_4 . TiCl_4 will evaporate next when the temperature is increased to 140 to 145 °C. Impurities with high boiling point will stay in the bottom of distillation tower.

Purified TiCl_4 is then reacted with oxygen at a high temperature to produce TiO_2 and Cl_2 . Based on the thermodynamic calculation, from 1600 to 2400 K, the Gibbs free energy of this reaction is negative which means it can happen spontaneously. Meanwhile, the conversion of TiCl_4 to TiO_2 is most complete in this temperature range. The presence of suboxides like TiO , Ti_2O_3 , and Ti_3O_5 is very little and TiO_2 is almost the only oxide product. The phase of TiO_2 produced in chloride process is rutile since it is a more stable phase than the anatase phase. The chemical reactions are shown below.

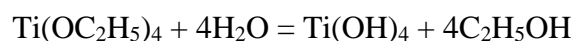


The reaction time is usually controlled between 0.05 to 0.08s. If the reaction time is too long, the size of the TiO_2 particles will increase and thus influence the property of TiO_2 product like pigment. To produce TiO_2 powder with a mean size of 0.2 μm and narrow particle size distribution in a short time, 1-2wt% of AlCl_3 is added to TiCl_4 to promote nucleation and phase transformation[24]. The chlorine gas produced in this step is collected and reused in the chlorination step. TiO_2 powder will go through a series posttreatment to

produce the final TiO₂ product.

3.1.3 Others

Many investigators have prepared TiO₂ powder using TiCl₄ liquid as starting material. The TiCl₄ liquid is mixed with ethanol and water, acid, or other additives. The solution is next hydrolyzed in organic media at a temperature varying from room temperature to the boiling point of the solution[12-14, 25]. The chemical reaction is shown below.



Ti(OC₂H₅)₄ can also be written as Ti(EtO)₄ which is the product of the mixture of TiCl₄ and ethanol. Normally, the equivalent concentration of TiO₂ is around 10 to 40g/L and the free acid concentration is 1 to 2 M. TiO₂ powder synthesized by this method usually is nanosized particles with certain morphology such as spheres, pores, rods, and hollow structure[14, 26-29]. The product is mostly used for photonic catalyst, pigments, and ceramic. A flow sheet of this process is shown in Figure 3.1.

Eric et al. synthesized monodispersed TiO₂ powder of 300 to 600nm with spherical shape and amorphous structure by hydrolysis of TiCl₄ in dilute ethanoic solution[30]. S. Eiden et al. synthesized TiO₂ from Ti(EtO)₄ with addition of salt and polymer solution[31]. The TiO₂ powder is around 800 to 1000nm with spherical shape, porous surface, and hollow structure. Wei et al. synthesized TiO₂ powder with TiCl₄ in hydrochloric acid and alcohol aqueous solutions at 40-90°C[13]. Rod shaped rutile TiO₂ with particle size from 100 to 800nm was produced.

Other investigators have used alkaline roasting to digest titanium feed stocks. The compounds in Ti feed stocks are converted into their sodium metallate salts during roasting[32, 33]. TiO₂ is converted into Na₂TiO₃ which is a titanate intermediate that can

be dissolved by low-concentration acid. The solution can be used for the hydrolysis of titanic acid. Compared to sulfate process, the use of concentrated sulfuric acid is avoided in alkaline roasting process. Liu et al. have roasted upgrade Ti slag (>90% TiO₂) using sodium hydroxide and washed the product with water to prepare Na₂TiO₃[34]. It is also reported that they can dissolve the product with sulfuric acid and making nanosized titanic acid by hydrolysis.

3.2 Hydrolysis

3.2.1 Nucleation and crystal growth theory

Hydrolysis is essentially a process of soluble substances that precipitate out from the pregnant solution. It usually experiences crystal nucleation, crystal growth, and secondary changes in the resulting crystal suspension such as agglomeration, dissolution, and precipitation. Depending on the reaction conditions, these processes can proceed either consecutively or simultaneously throughout the whole hydrolysis process.

The nucleation and crystal growth of solid particles can be described by the Lamer mechanism based on the nucleation rate and concentration of monomeric species[35-37]. It mainly goes through 3 steps: 1) prenucleation stage, 2) nucleation stage, and 3) growth stage. The essence of mechanism was illustrated in Figure 3.2. C_s corresponds to the solubility level of bulk solid. C_{min} corresponds to the critical level for nucleation. C_{max} corresponds to the maximum supersaturation.

In a typical hydrolysis system, the monomeric species are initially accumulated in the system through some reaction from a reservoir of the monomeric species involved in the system. In prenucleation stage, no appreciable nucleation occurs, even if the concentration of the monomeric species exceeds the solubility level of bulk solid. The concentration of

monomeric species keeps building up until it reaches the critical concentration (C_{\min}), then the nucleation can be observed. The nucleation rate is still slow during this stage, but it is the origin of the nucleation stage[38-40].

In the nucleation stage, the nucleation rate is low at first. However, as the concentration of monomeric species continues to increase, the nucleation is drastically accelerated. The concentration of monomeric species will reach the maximum supersaturation level(C_{\max}).

After the burst of monomeric species, its concentration in the hydrolysis solution starts to decrease. The nucleation rate keeps increasing which is called a rapid self-nucleation stage. As the concentration of monomeric species decreases, the nucleation rate will reach a balance with the consumption rate of monomeric species. This leads us to the crystal growth stage in which the nucleated crystals aggregate on the formerly nucleated crystals to grow the crystals into larger particles.

Finally, the concentration of monomeric species will reach its equilibrium in the hydrolysis solution and stop decreasing anymore. During this time, the crystals tends to aggregate with other crystals and grow large. Besides, the crystals could be dissolved again because of the decrease of monomeric species in the solution. The dissolved solution can also re-precipitate out and form new crystals. This dissolution and precipitation process is in a dynamic balance.

The behavior of nuclei during nucleation and crystal growth are also studied by many investigators. The hydrolysis reaction is usually triggered by the high supersaturation of the monomeric species in the solution. The reaction starts with the nucleation of small seeds formed at the very beginning of the entire hydrolysis process. Some seeds may simply be dissolved because they are still in unstable state. Other seeds will reach a balance

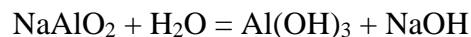
between generation and either dissolution or growth. The nuclei of radius less than the critical radius r^* will dissolve, while those of radius greater than r^* will grow. These grown seeds become stable nuclei and later turn into the final particles. As the nucleation proceeds, the supersaturation level will decrease and r^* will increase which will slow down the nucleation rate. The nucleation will come to the end when r^* reaches the size of a grown particle (r_p). This point is also the start of crystal growth stage.

3.2.1.1 Application of hydrolysis

Hydrolysis is a common method for synthesizing metal oxides in industry such as Al_2O_3 , TiO_2 , SiO_2 , etc.

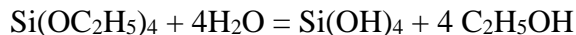
Al_2O_3 is produced by the Bayer process using bauxite (a mixture of Al_2O_3 , Fe_2O_3 , and SiO_2) as raw material. The ore is first digested in a solution of about 30% NaOH at a temperature between 150°C and 230°C in large pressure vessels at a pressure sufficient to suppress boiling[41, 42]. Silica dissolves in NaOH as sodium silicate which will combine with sodium aluminate to form an insoluble aluminosilicate. Fe_2O_3 will form the “red mud” which is an insoluble material. The solution of NaAlO_2 with excess NaOH is separated from the insoluble mud by settling and filtration.

The solution is then diluted and hydrolyzed in the presence of $\text{Al}(\text{OH})_3$ seed to promote the nucleation of $\text{Al}(\text{OH})_3$. The precipitate is next calcined to Al_2O_3 at $1200\text{-}1350^\circ\text{C}$. The hydrolysis reaction is shown as follows:



It is reported that silica (SiO_2) particles with uniform spherical shape were prepared by hydrolysis of tetra-alkyl silicates and subsequent condensation of silicic acid in alcoholic solutions containing water and ammonia at low temperatures around room temperature[43].

The reaction is as follows:



The mean size ranged from 0.05 to 2 μm and the mean size could be chosen from this size range by controlling the compositions of water and the alcohols[44]. Anionic surfactants, sodium dodecyl sulfate, can also be added in the hydrolysis solution to help control the size of silica particles[45-47].

This method of preparing SiO_2 is now widely applied to the synthesis of monodispersed particles of different metal oxides[48, 49]. Uniform acicular particles of β - FeOOH are prepared by hydrolysis of Fe^{3+} ions in dilute FeCl_3 solutions for several months at room temperature[50]. Highly uniform spherical particles of chromium hydroxide ($\text{Cr}(\text{OH})_3$) are formed by hydrolysis of chromium ions in acidic media at around 80°C [51]. Uniform particles of titania (TiO_2)[52], and zinc oxide(ZnO)[53] have been prepared by hydrolysis of corresponding metal alkoxides in alcohol solutions.

During these processes, most of the hydrous metal oxides particles were prepared by heating dilute solutions of metal salts ($10^{-4} - 10^{-2}$ mol/L) over 50 to 150°C at low pH (1.0-4.0) for several hours or days. The size of the metal oxide particles prepared can be varied from nano to submicrometer size, but mostly submicrometer size. The shape of the particles can also be different depending on the property of metal ions. Shapes such as spheres, cubes, ellipsoids, and rods have all been reported[54, 55].

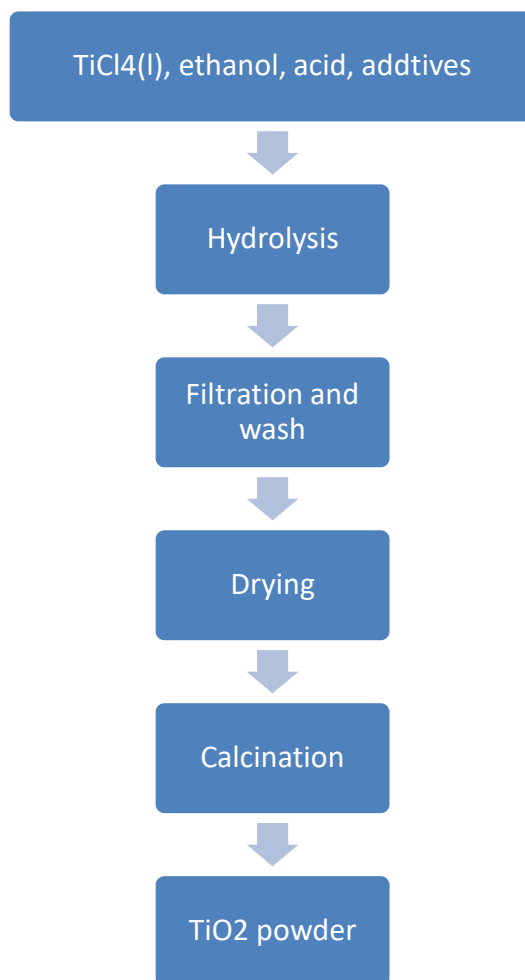


Figure 3.1 Flow sheet of the hydrolysis in organic media using TiCl₄ liquid

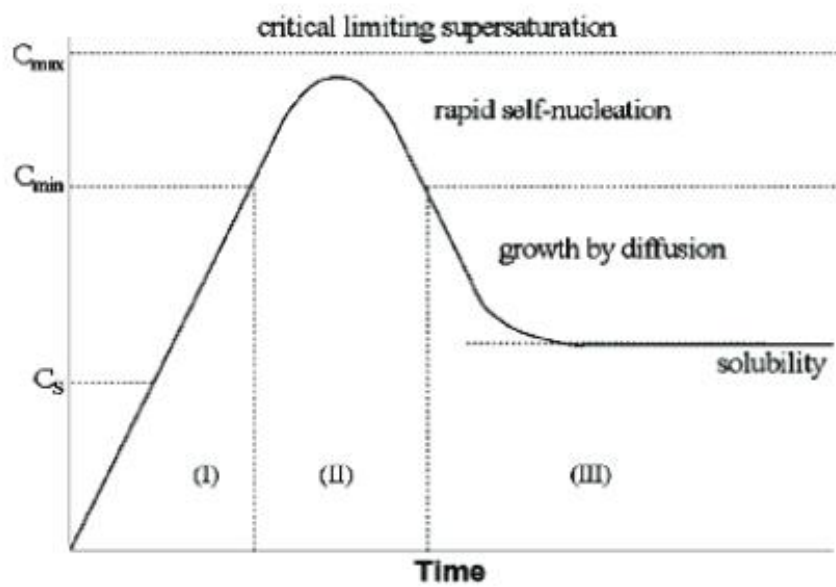


Figure 3.2 The Lamer mechanism of nucleation, the change of concentration of monomeric species with time[37].

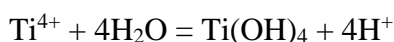
CHAPTER 4

PARAMETRIC STUDY OF HYDROLYSIS OF TITANIC ACID

4.1 Introduction

The hydrolysis of titanic acid in HCl solution is seen as a new approach for producing TiO₂ with relatively large particle size by selectively choosing the parameters. The coarse TiO₂ powder produced by this method can be used as the starting material for Mg reduction in the HAMR process to make Ti powder.

Hydrolysis is a method that has been used for recovering metal oxides from a pregnant solution in the form of precipitated metal compounds. In the case of recovering TiO₂, the titanium oxide with hydrated water is precipitated out of the titanium chloride solution in the form of solid particles. The titanium hydroxide precipitation is a combination of titanium oxide and hydrated water which is usually referred to as titanic acid in hydrometallurgy. Ti(OH)₄ can also be written as TiO₂ • 2H₂O.



The precipitated titanic acid solids were then separated from the solution by filtration. Impurities like Fe, Mg, and Ca stayed in the solution and were thus separated from TiO₂. However, impurity like silicon will precipitate out along with TiO₂ during hydrolysis. Thus, it is necessary to remove the silicon before hydrolysis. The impurity in the TiO₂ will directly go into the final Ti powder. The mechanical properties are highly dependent on the purity content of Ti powders. Impurity removal will be discussed in detail in this chapter.

Once the titanate acid was washed and dried, it was calcined at an elevated temperature to remove the hydrated water. The crystal structures of the titanate acid were rutile which is determined by XRD. The crystal structure stays the same through the calcination process. As for the sulfate process, both rutile and anatase particles can be produced.

Though a lot of investigations have been done on the hydrolysis of chloride solutions to produce TiO_2 nanoparticles, there is currently no commercial pigment production using the hydrolysis of chloride solutions. Moreover, only very limited work can be found on using chloride solutions to produce monodispersed TiO_2 with large particle size. It is attributed to the application of TiO_2 powder, such as paint, photo catalysis, and surface coating, which demands nano-sized TiO_2 powder from conventional production methods.

Our preliminary work has demonstrated that many factors including equivalent TiO_2 concentration, free acid concentration, temperature, and time have great effects on the particle size and morphology of the TiO_2 powder made by hydrolysis. A parametric study has been conducted to determine the effects of various hydrolysis parameters on the recovery and quality of TiO_2 from Ti bearing solution. The products were characterized with respect to their particle size, morphology, crystal structure, and surface area.

4.2 Experimental

4.2.1 Preparation of hydrolysis solution

The starting material for this study was upgraded Ti slag provided by RTIT in Quebec. It contains around 94.5wt% of TiO_2 . The main impurities were Fe_2O_3 , SiO_2 , MgO , and Al_2O_3 . The chemical composition of upgraded Ti slag is shown in Table 4.1.

The particle size of as-received upgraded Titanium slag was around 200 to 300 μm in irregular shape. The morphology of the as-received UGS is shown in Figure 4.1. To help

to achieve a complete conversion in the NaOH roasting step, the upgraded Ti-slag was milled to minus 20 μm by stainless steel balls in an attritor mill. The mass ratio of ball to UGS was 2 to 1. The milling was performed in water for 4 hr with a mass ratio of water to UGS of 1 to 1. The milled UGS was then separated from water by filtration and dried in air.

The milled UGS was then roasted with NaOH pellets in an Inconel crucible in a box furnace. The milled UGS was blended with NaOH pellets at a mass ratio of 1 to 1.5 in an agitator. The roasting was conducted at 500°C for 6 hr. Based on the current capacity of our lab, 1 kilogram of milled UGS can be roasted in each batch. During roasting, TiO_2 was reacted with NaOH and transformed into Na_2TiO_3 and H_2O . After the reaction is finished, the product was washed with water for several times to remove the excess NaOH. Concentrated HCl solution was added dropwise during washing until the pH of the washing solution was almost neutral. The washed product was filtrated and dried in air. The major composition of the product after washing was H_2TiO_3 along with some impurities like, Na, Fe, Mg, Ca, etc. The morphology of washed product is shown in Figure 4.2.

The washed product was then dissolved in HCl solution to prepare hydrolysis solution. The dissolution was performed at 50°C for 2 hr under continuous stirring. The weight of the washed product and the concentration and volume of HCl solution were controlled to achieve a certain composition of equivalent TiO_2 and free acid in hydrolysis solution. The solution was then filtered to remove the undissolved solids. The pregnant solution for hydrolysis is clear and in dark yellow.

4.2.2 Hydrolysis and calcination

Hydrolysis is normally conducted between 90°C to 100°C in an oil bath for 16 hr with continuous stirring. Five milliliter of hydrolysis solution was taken in every 2 hr for the analysis of the change of equivalent TiO₂ concentration with time.

The hydrolysis reactor is shown in Figure 4.3. The volume of the hydrolysis beaker is around 1.1L. The beaker is sealed by a plastic lid with a rubber O ring inside. The four openings on the lid were used for taking samples, stirring paddle, condensation, and thermometer, respectively. Normally, 0.9L of hydrolysis solution is used for each experiment.

The hydrolysis solution was heated from room temperature to the target temperature in an oil bath. The solution started to become cloudy when the temperature reached 80°C. The temperature will stay constant at 90°C for about 10 minutes. The solution then became a complete cloudy mixture when the temperature was 95°C. It took approximately 1 hr to heat the hydrolysis solution from room temperature to 98°C.

The temperature was kept at 98°C during the entire hydrolysis process. The solution was stirred continuously at 250rpm using a stirring paddle. A thermometers was used to keep track of the temperature. During the hydrolysis, a sample of 8 ml solution was taken in every 2 hr. The samples were analyzed by ICP to determine the change of the equivalent TiO₂ concentration with time. The change of yield with time was thus calculated and plotted in a curve.

After hydrolysis is completed, the post-hydrolysis solution is filtered to separate the titanic acid particles from the liquid. The titanic acid was washed by 6M HCl solution for the first several times to avoid peptization and then washed with DI water to remove the

hydrolysis solution attached on the surface of the titanitic acid particles. The titanitic acid particles were then dried in air. The particle size of titanitic acid particles was measured by particle size analyzer. The microstructure of titanitic acid particles is analyzed by scanning electron microscopy (SEM).

Titanic acid is normally expressed as $\text{TiO}_2 \cdot x\text{H}_2\text{O}$. In order to produce TiO_2 , titanitic acid was calcined to remove the hydrated water. Calcination of titanitic acid particles was performed in a ceramic crucible in a box furnace. The temperature profile of calcination is shown in Figure 4.4.

After calcination, the TiO_2 powder was sieved to collect the powder with the size favored by the Mg reduction step which is normally from 20 to 45 μm . The crystal structure of the product from hydrolysis before and after calcination is discussed in detail in this chapter, as well as the change of morphology of the particles during calcination.

The preliminary results showed that when the equivalent TiO_2 concentration was between 60 to 100g/L and free acid concentration was between 2 to 3M, the particle size of the titanitic acid from hydrolysis was likely to be around 20-45 μm . A series of experiments were designed to systematically study the effect of free acid concentration on hydrolysis rate, particle size, and morphology of titanitic acid particles at 4 different equivalent TiO_2 concentrations, and the results are shown in this chapter.

The experiment design was shown in Table 4.2. In the first two series of experiments, the equivalent TiO_2 concentration was fixed at 70g/L and 100g/L to evaluate the effect of free acid concentration on hydrolysis. Four different levels of the free acid concentrations were chosen at 2M, 2.5M, 3M, and 3.5M. At 40g/L of equivalent TiO_2 , the free acid concentrations used were 3.5M, 4M, and 4.5M due to the extremely fast reaction rate at

low free acid concentration.

4.2.3 The analysis of equivalent TiO₂ and free acid concentration

Equivalent TiO₂ concentration and free acid concentration are two essential parameters for hydrolysis. The composition of hydrolysis solution samples and solid TiO₂ powder was analyzed with ICP-OES. The free acid concentration was measured by titrating the hydrolysis solution with NaOH solution.

The compositions of solid TiO₂ samples were measured to ensure that the impurity content is low enough to meet the specification of Ti sponge after reduction. TiO₂ powder was roasted with Na₂CO₃ and H₃BO₄ (2:1 weight ratio) mixture at 950 °C for 10 minutes in a platinum crucible. The roasted powder was dissolved in 50mL of 18wt% HCl. The HCl solution was heated and kept boiling until the roasted product was dissolved completely. The solution was then transferred to a 100ml volume metric flask for ICP analysis.

A 5ml sample of hydrolysis solution was taken in every 2 hr for ICP analysis to measure the change of equivalent TiO₂ concentration with time. The initial concentration of equivalent TiO₂ is at around 40 to 115g/L according to the experiments' design. The content of Ti element that ICP can measure accurately is around 5 to 30ppm. The sample solution was diluted 2500 times in 5 Vol. % hydrochloric acid for measurement.

The free acid concentration in the experiments design was calculated in theory. The actual free acid concentration was measured by titration of pre-hydrolysis solution using NaOH solution. Pre-hydrolysis solution was measured by ICP to know equivalent TiO₂ concentration. Five milliliter of 150g/L NaOH solution was put into the flask with 45ml DI water. Phenolphthalein was used as PH indicator. The burette is filled with pre-

hydrolysis solution. The pre-hydrolysis solution was added to the NaOH solution drop by drop. The change of the volume of pre-hydrolysis solution was measured once the NaOH solution turned from purple into milky. The concentration of free acid in the pre-hydrolysis solution was calculated based on the following equation:

$$c(\text{NaOH})(\text{g/L}) * 5\text{ml} / 40(\text{g/mole}) = (c(\text{TiO}_2) (\text{g/L}) / 80(\text{g/mole}) * 4 + c (\text{Free acid})) * V(\text{measured})$$

4.3 Results and discussion

4.3.1 Purity

The starting material used for producing TiO₂ in this method was upgraded titanium slag. Upgraded titanium slag is usually called UGS for short. UGS contains 94.5 wt% TiO₂. The chemical composition of UGS in terms of elements is given in Table 3.1. Impurities like Fe, Si, Mg, and Al have relatively high content.

The impurity content in the TiO₂ powder will directly determine the impurity content in the final Ti powder since there will be no further purification steps in the following process for Ti production. It is necessary to remove the impurities before Mg reduction of TiO₂. For the HAMR process, to produce Ti powder that can meet the ASTM standard specification of Ti-sponge (B299-13), the starting TiO₂ powder has to be as pure as possible.

The impurities in the UGS can be classified into two categories: alkali-soluble impurities including Si, Al, V, Mn, and Cr, and acid-soluble impurities including Fe, Al, V, Ca, Mg, Si, Mn, and Cr. Most of the impurities do not exist as independent phases; they form solid solutions with TiO₂ in the form of rutile. In other words, most of the impurities are locked within the lattice of rutile. It will be extremely difficult to purify the UGS by picking up each impurity out of the lattice. Therefore, the structure of UGS has to be

destroyed before the impurities can be exposed.

For typical hydrometallurgical methods, such as the sulfate process, it uses concentrated sulfuric acid to dissolve ilmenite or Ti slag which forms titanium sulfate solution. This reaction has to be triggered by water steam. The actual temperature during the dissolution is around 180 to 190 °C. For the chloride process in the Kroll process, Ti-slag is reacted with chlorine gas and carbon at 1100 °C forming TiCl_4 and CO_2 . In these two commercial methods, the titanium bearing materials are transformed into different phases as well as the impurities. In other words, the original crystal structure of the titanium slag is destroyed, so the impurities in the lattice are exposed which makes it possible to remove them.

Similar to the two processes mentioned above, alkaline roasting of UGS and hydrolysis of TiO_2 use the same principle in terms of purification. During roasting, the TiO_2 and other impurity oxides are converted into sodium metal compound. The roasted product is readily dissolved in HCl solution. Compared with the two methods above, this work eliminated the use of concentrated sulfuric acid and high temperature process.

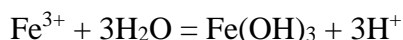
During NaOH roasting, the two categories of impurities go through different changes. On the one hand, titanium dioxide and alkali-soluble impurities can be transformed during roasting into their sodium metallate salts, mainly Na_2TiO_3 accompanied by Na_2SiO_3 , Na_2AlO_2 , Na_3VO_4 , Na_2CrO_4 , and Na_3MnO_4 . On the other hand, alkali-insoluble impurities can also be hosted by their sodium metallate salts or metal hydroxide compounds, such as Na_2FeO_2 , Na_2MgO_2 , and $\text{Ca}(\text{OH})_2$. After roasting, the reaction product can be washed by water to dissolve the excess NaOH. Most of the sodium combined with Na_2TiO_3 will be released to form water-soluble NaOH and alkaline-insoluble metatitanic acid (H_2TiO_3). A

great amount of alkali-soluble impurities will be dissolved during the water washing step, for example, Na_2SiO_3 , Na_2AlO_2 , and Na_3VO_4 . Additionally, the alkali-insoluble metals will be retained with metatitanic acid in their metal hydroxide compounds of $\text{Fe}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, and $\text{Ca}(\text{OH})_2$.

Among all these impurities, Fe and Si are the two major impurities. A high content of Fe will make the TiO_2 powder look yellow. Si is also known for being very difficult to remove for Ti extraction. Si has very high affinity to Ti due to their similar properties. The removal of Fe and Si are discussed in detail below.

4.3.1.1 The removal of Fe and Si

Due to the high free acid concentration, the ferrous ion will remain in the leaching solution during the hydrolysis of titanate acid. The hydrolysis reaction of Fe^{3+} and H_2O forming $\text{Fe}(\text{OH})_3$ will not happen. The reaction of the hydrolysis of Fe^{3+} is shown below.



The content of Fe before and after hydrolysis was measured by ICP which is shown in Table 4.3. It is shown that Fe content almost stays constant with a slight increase which is because of the consumption of water during hydrolysis.

The change of Si content with time during hydrolysis is shown in the Figure 4.3. Si content will decrease with time. The behavior of Si during hydrolysis is similar to Ti. The silicon in the solution will react with H_2O forming $\text{Si}(\text{OH})_4$ and releasing H^+ . The reaction is shown below. With the increase of free acid concentration, the precipitation of silicic acid becomes slower. Unlike Fe, Si has to be removed before hydrolysis, otherwise it will co-precipitate out with Ti.

As shown in Figure 4.5, the removal rate of Si is calculated as 97.5%. Si exists in

UGS in the form of SiO_2 . It is transformed during roasting into its sodium metallate salts, Na_2SiO_3 , which is dissolved into the washing solution.

4.3.1.2 Summary

Generally speaking, the impurities were removed in two major steps: roasting and hydrolysis. Roasting is a process in which impurities are transformed into their sodium metallate salts or metal hydroxide compounds, most of which are soluble in alkaline solution, thus being removed during the following water washing step. In addition to roasting, many impurities can be removed during hydrolysis. Hydrolysis is essentially a selective precipitation process. Impurities such as Fe, Mg, Al, Ca, and Mn will stay in the solution during hydrolysis, thus separated from Ti. Other impurities like Si and V will precipitate together with Ti which have to be removed prior to hydrolysis.

The chemical composition of the residue after roasting and washing was analyzed using ICP and the results are shown in Table 4.4. Based on the composition, it is deduced that the residue is primarily composed of H_2TiO_3 . The effectiveness of the alkaline roasting process in terms of the removal rates of the impurities was calculated and they are as high as 97.5%, 94.5%, 88.8%, 83.0%, and 78.8%, for Si, Al, V, Mn, and Cr, respectively. Even alkali-insoluble impurities like Mg and Fe were partially dissolved by the alkaline solution, which may be attributed to their limited but detectable solubility in the alkaline solution.

As mentioned already, hydrolysis is another major step for purification. Fe content as well as other compositions before and after the hydrolysis are compared in Table 4.5. It is clearly shown that the Fe content is significantly and sufficiently minimized in TiO_2 .

The impurity contents in the final TiO_2 powder produced in this work were analyzed by ICP and the results are shown in Table 4.6 which is also compared to commercial rutile.

It is apparent that the impurity of TiO_2 produced by this process is comparable to that of commercial rutile.

4.3.2 Calcination

As mentioned already, titanitic acid is essentially hydrated TiO_2 , the composition of which is $\text{TiO}_2 \cdot x\text{H}_2\text{O}$. To make pure TiO_2 powder, the hydrated water has to be removed by calcination. Calcination was performed in a box furnace at an elevated temperature. The titanitic acid samples were put in ceramic crucibles after drying in air. The samples were then calcined for 2 hr at 300, 600, and 900°C.

According to the weight loss during calcination, it was confirmed that the water content in the precipitate was approximately 10%, suggesting that the precipitate was pyrotitanic acid. The morphology of the rutile particles inherits that of the titanitic acid in shape. The microstructure on the surface of titanitic acid at each holding temperature was analyzed by scanning electron microscopy. The change of microstructure of the particles during calcination is discussed in this chapter.

4.3.2.1 The effect of calcination on phase compositions

The XRD patterns of calcined samples at each holding temperature are shown in Figure 4.6. Before calcination, weak peaks of rutile phase were observed. As the calcination temperature increases, the peaks sharpen, indicating an increase in the size of the crystallites. After 300 °C, the intensity and sharpness of the rutile peaks increased dramatically with each raise in temperature. The phase of titanitic acid before and after calcination is pure rutile. No anatase phase was found. The change of crystal size with calcination temperature is shown in Table 4.7. The crystal size was calculated by the

Scherrer equation:

$$D_p = \frac{0.94\lambda}{\beta_{1/2} \cos \theta}$$

Where D_p = Average Crystallite size,

β = Line broadening in radians.

θ = Bragg angle.

λ = X-ray wavelength.

4.3.2.2 The effect of calcination on morphology

The microstructure of titanic acid samples after calcination were analyzed by scanning electron microscopy (SEM). The sample used for this study is conducted at 100g/L of equivalent TiO_2 and 2M free acid. It can be seen in Figure 4.7 that the surface of the particles was not completely smooth. Cracks and small bumps were found on the surface of each particle. Inside the cracks, the needle-shaped structure was observed. It might imply that the particle consists of small needles which growing from the center to the edge of the particles. More detailed discussion is shown later for the mechanisms of hydrolysis. It is shown that the shape and size of the particles are identical before and after calcination. There is no agglomeration between particles under this conditions.

Pores were found on the surface and internal sections of the particles after calcination. The size of the pore is between 18 to 50nm. It is believed that these pores were formed during calcination while the hydrated water was vaporizing from the particle to air. Before calcination, the surface of the particle is smooth and no pores can be found. After being calcined at 300°C for 2 hr, in Figure 4.8, the morphology has no difference from the before-calcined particles. At 600°C , in Figure 4.9, pores start to form but are still small and only

have a small amount. After calcining at 900°C for 2 hr, in Figure 4.10, the porosities can be seen clearly on the surface as well as in the cracks.

4.3.3 Effect of temperature

The temperature of hydrolysis can have significant effects on the hydrolysis rate of titanic acid. The rate of the hydrolysis reaction increases with the rise of temperature since hydrolysis is an endothermic reaction. In this section, a set of experiments were designed to investigate the effect of temperature on hydrolysis of titanic acid. The experimental design is shown in Table 4.8.

It can be seen from Figure 4.11 that the hydrolysis rate of titanic acid increases with the rise of temperature. The yield of titanic acid at 90°C is very low between 4 to 10 hr which is due to the high free acid concentration in the initial stage of hydrolysis and low hydrolysis rate, thus the hydrolyzed titanic acid will be re-dissolved and since the driving force for hydrolysis at 90°C is lower than dissolution, the solution will stay in a balance of precipitation and dissolution. When temperature is at 100, the hydrolysis rate increases since the driving force for hydrolysis is larger than dissolution, thus the reaction moves forward easier. When temperature is at 105°C and the solution is boiling, the hydrolysis rate is too fast which will result in small particle size, agglomeration, as well as other unpredictable morphology of titanic acids. Therefore, the optimized temperature for hydrolysis of titanic acid is determined to be 100°C.

4.3.4 Effect of free acid concentration

Hydrolysis is basically a reaction of splitting H₂O into H⁺ and OH⁻. In this case, Ti⁴⁺ combined with OH⁻ to form Ti(OH)₄ which precipitated out during the hydrolysis. The

remaining H^+ become into free acid.

As we can see from the reaction formula, the concentration of free acid will increase during hydrolysis reaction. The free acid in the hydrolysis solution comes from two parts: one is from the excess concentrated HCl solution added during the dissolution of titanate solids, and the other part is from H^+ released during hydrolysis.

As a product of hydrolysis reaction, the free H^+ in the solution will hinder the hydrolysis reaction from moving forward which is the direction of forming $Ti(OH)_4$ precipitation. Generally, it is believed that the higher the free acid concentration is, the slower the rate of hydrolysis is.

The concentration of free acid will also have an effect on the particle size and morphology of the titanic acid by affecting the nucleation and crystal growth. As mentioned before, when the concentration of free acid is high, the hydrolysis reaction tends to be slow. In other words, it takes more time for the titanic acid nuclei to form. The first few nucleated titanic acids will act as crystal grow sites. The lately nucleated titanic acids tend to agglomerate on those initially formed nuclei and thus leads to larger particle size of the final titanic acid powders.

4.3.4.1 Morphology

The microstructure of the titanic acid obtained from varied free acid concentration at 70g/L of equivalent TiO_2 was examined by scanning electron microscopy (SEM). The results are shown in the following figures.

For 2M free acid, the titanic acid particles have irregular shape and are agglomerated together. The mean particle size is around 18 μm . One titanic acid particle consists of several smaller particles (Figure 4.12 a). For 2.5M free acid, the particle is much larger and

less agglomerated. The mean particle size is around 26 μm . The particles are more round but with many bumps on the surface (Figure 4.12 b). For 3M free acid, the particles are monodispersed with a larger mean size of 32 μm . The particles become a regular round shape and have a smoother surface (Figure 4.12 c). For 3.5M free acid, the particle size is slightly larger. Other than that, other features are similar to 3M free acid (Figure 4.12 d). The results show that with the increase of free acid concentration, the particle size of titanic acid will increase. The particles become more and more regular in a round shape with a smoother surface.

For 100g/L of equivalent TiO_2 , at 2M free acid, the mean particle size is around 26 μm . The particles are not very uniform. One particle is an agglomeration of several smaller particles (Figure 4.13 a). For 2.5M free acid, the titanic acid particles are larger which has a mean particle size of 35 μm . The particles are more uniformly dispersed in a round shape (Figure 4.13 b). For 3M free acid, many small particles around 10 μm or less were found. The rest are round particles with a mean size of 30 μm (Figure 4.13 c). For 3.5M free acid, the particle size distribution is very broad. Many large particles as well as many small particles were found. The small particles are agglomerated with each other or attached on larger particles. From 2M to 2.5M, the particle size increased with the free acid concentration and the morphology became more uniform. From 3M to 3.5M, the particle size distribution became broader. Many smaller particles were obtained and agglomerations were found as well.

At 115g/L of equivalent TiO_2 , the free acid concentrations were selected at 3.5M, 4M, and 4.5M. Though the target concentration is 130g/L, the actual concentration of equivalent TiO_2 is 115g/L since there are some undissolved solids during HCl leaching of roasted

product. There will always be some deviation between the target concentration and the actual concentration which is more obvious when the targeted TiO₂ concentration is high. As shown in Figure 4.14, for 1.5 M free acid, the particles were around 20 µm in a round shape. It can be seen that the titanic acid particles were agglomerated by smaller particles. For 2M free acid, the particle size was larger which is around 25 µm and less agglomerated as well. For 2.5M free acid, the particle size distribution of titanic acid is broad. The large particles are around 35 µm and the small particles are around 15 µm. Agglomeration of small particles was found.

At 40g/L of equivalent TiO₂, the free acid concentrations were selected at 3.5M, 4M, and 4.5M. For 3.5M free acid, the titanic acid particles have obvious agglomeration, as shown in Figure 4.15. The size of each separate particle is around 5 µm. For 4M free acid, the particles are still agglomerated but with a slightly larger particle size which is approximately 9 µm. For 4.5M free acid, the agglomeration between particles is less obvious. The size of one agglomeration is around 20 µm. It can be seen that at a lower equivalent TiO₂ concentration like 40g/L, the particles of titanic acid have a strong tendency to be small and agglomerated together.

4.3.4.2 Particle size

It is shown in Figure 4.16 and Table 4.9 that when the equivalent TiO₂ concentration is 40g/L, the D50% of the particle size is 14.465 µm, 16.721 µm, and 18.529 µm for 3.5M, 4M, and 4.5M, respectively. D50% for these three samples is less than 20 µm. The particle size of titanic acid particles ranges from approximately 10 to 25 µm using the above parameters. The particle size distribution is narrow. Sample 1 has the largest standard deviation of 0.138. The standard deviation of sample 2 and sample 3 is smaller, which is

0.115 and 0.117, respectively.

When the equivalent TiO_2 concentration is 100g/L, as shown in Figure 4.17 and Table 4.10, the D50% of the particle size is 26.273 μm , 29.852 μm , 29.560 μm , and 34.972 for 2M, 2.5M, 3M, and 3.5M free acid, respectively. The particle size of titanic acid particles ranges from approximately 18 to 40 μm for samples 1, 2, and 3. The particle size distribution is narrow for sample 1, 2, and 3, which are all around 0.1. Sample 4 has the broadest particle size distribution, with D10% of 13.548 μm and D90% of 90.368 μm .

When the equivalent TiO_2 concentration is 115g/L, as shown in Figure 4.18 and Table 4.11, the D50% of the particle size is 0.046 μm , 20.052 μm , and 32.847 μm for 1.5M, 2M, and 2.5M, respectively. Sample 3 has the largest standard deviation of 0.348, the particle size of which ranges from 11 μm to 93 μm . The particle size distribution of sample 2 and sample 3 is narrow with standard deviation of 0.107 and 0.104, respectively.

4.3.5 Effect of initial equivalent TiO_2 concentration

The effect of initial equivalent TiO_2 concentration on the morphology and particle size of titanic acid during hydrolysis with same free acid concentration was investigated. Similar to free acid concentration, the equivalent TiO_2 concentration can also affect the rate of hydrolysis. Five different levels of initial TiO_2 concentration, 50g/L, 70g/L, 100g/L, and 115g/L, are used, free acid concentration is fixed at 2.5M, temperature is controlled at 100°C, and stirring speed is 250 r/min.

When the initial TiO_2 concentration is low, the hydrolysis rate is fast and the yield of titanic acid is high. When the initial TiO_2 concentration is high (100-115g/L), the hydrolysis rate is slow and the yield of hydrolysis is low.

4.3.5.1 Morphology

When the initial TiO₂ concentration is 50g/L, the particle size of titanic acid is very small, mostly around 5 to 6µm. The particle is in a round shape but not entirely monodispersed. Many agglomerations of tiny particles of several hundred nanometers can be found on the surface of a big particle (Figure 4.19).

When the initial TiO₂ concentration is 70g/L, the particle size of titanic acid increased dramatically to a mean size of around 25µm. The particles are monodispersed but a little amount of agglomerations made of small particles can be seen on the surface of some monodispersed single particles. The particles are in a round shape (Figure 4.20).

When the initial TiO₂ concentration is 100g/L, the mean particle size increased to around 33µm. The particle size distribution also becomes broader. Many small particles with size of around 10 microns can be found as well as some extent of agglomerations between them (Figure 4.21).

When the initial TiO₂ concentration is 115g/L, the particle size distribution becomes even broader compared with lower TiO₂ concentration. Particles with size smaller than 10µm have obvious agglomerations. Particles larger than 10µm are mostly monodispersed. Some very big agglomerated particles can be found. Besides, needle-like morphology on the surface is observed (Figure 4.22).

4.3.5.2 Particle size

The particle size distribution of titanic acid from different initial TiO₂ concentrations are shown in Table 4.12 and Figure 4.23. At 50g/L of TiO₂, the particle size distribution is broad with a standard deviation of 0.327. The particle size is small with a mean size of 5.49µm. At 70g/L of TiO₂, the particles have larger mean particle size of 30.21µm and are

also narrowly distributed. At 100g/L, the particles grow slightly larger and with narrower distribution. The mean particle size is 30.57 μ m and the standard deviation is 0.119. At 115g/L of TiO₂, the particle size distribution becomes broad again with a standard deviation of 0.367. The mean particle size is 35 μ m which is slightly larger than 70g/L and 100g/L.

It is shown that, when the free acid concentration is the same, the mean particle size of titanic acid will become larger with the increase of equivalent TiO₂ concentration. The particle size increased dramatically from 5.49 μ m to 30.25 μ m as the concentration of TiO₂ changed from 50g/L to 70g/L. However, no significant differences of particle size were found as the TiO₂ concentration increased from 70g/L to 115g/L. Standard deviation of titanic acid is very broad when the equivalent TiO₂ concentration is either very low or very high. The distribution becomes narrow when the TiO₂ concentrations are 70g/L and 100g/L.

4.4 Summary

The effect of free acid concentration, initial equivalent TiO₂ concentration, and temperature on hydrolysis of titanic acid was studied in this chapter.

It is shown that at a constant equivalent TiO₂ concentration, with the increase of free acid concentration, the mean size of titanic acid particles becomes larger and the particle size distribution becomes broader. The titanic acid particles have a round shape and smooth surface with a particle size of around 30 μ m which is the desired morphology for this work when the free acid concentration is chosen appropriately. The free acid concentration required to obtain these morphologies is between 2.5M to 3.5M which depends on the equivalent TiO₂ concentration.

When the free acid concentration is fixed at 2.5M, with the increase of TiO₂

concentration, the mean size of titanic acid particles becomes larger in general. The particle size will increase dramatically as the TiO_2 concentration increases from 50g/L to 70g/L. The particle size distribution is broad when TiO_2 concentration is either too low (50g/L) or too high (115g/L). The desired morphology can be obtained when the equivalent TiO_2 concentrations are 70g/L and 100g/L.

The optimized parameters for the hydrolysis of titanic particles were determined to be: 70g/L of equivalent TiO_2 with 3 to 3.5M free acid; 100g/L of equivalent TiO_2 with 2.5 to 3M free acid. The typical morphology of titanic acid particles obtained using the optimized parameters is shown in Figure 4.24. The titanic acid particles are monodispersed with a mean size of around 30 μm and narrow distribution. The particles are in round shape with smooth surface.

Table 4.1 Chemical composition of upgraded Ti slag

Compound	TiO ₂	Fe ₂ O ₃	SiO ₂	MgO	Al ₂ O ₃	V ₂ O ₅	CaO	Cr ₂ O ₃	MnO	Total
wt%	94.5	1.4	1.8	0.7	0.5	0.4	0.12	0.07	0.04	99.53
Element	Ti	O	Fe	Mg	Al	Ca	Si	Cr	Mn	V
wt%	56.7	40.4	1.0	0.42	0.26	0.09	0.84	0.05	0.03	0.22

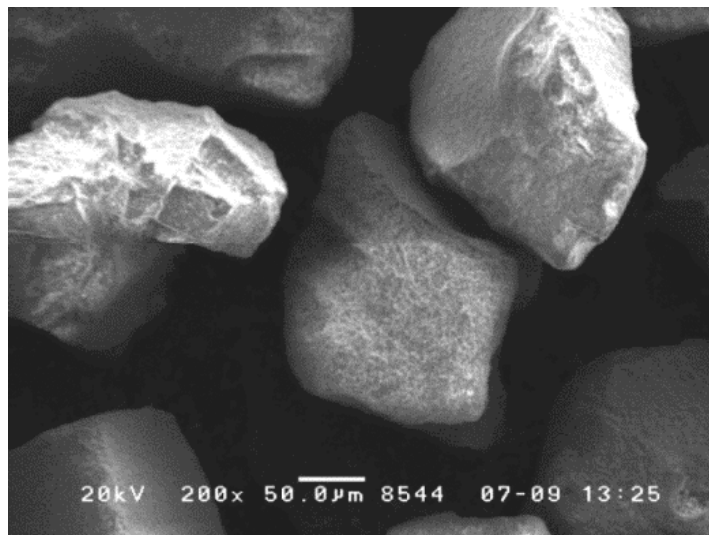


Figure 4.1 Microstructure of as-received upgraded-Ti slag

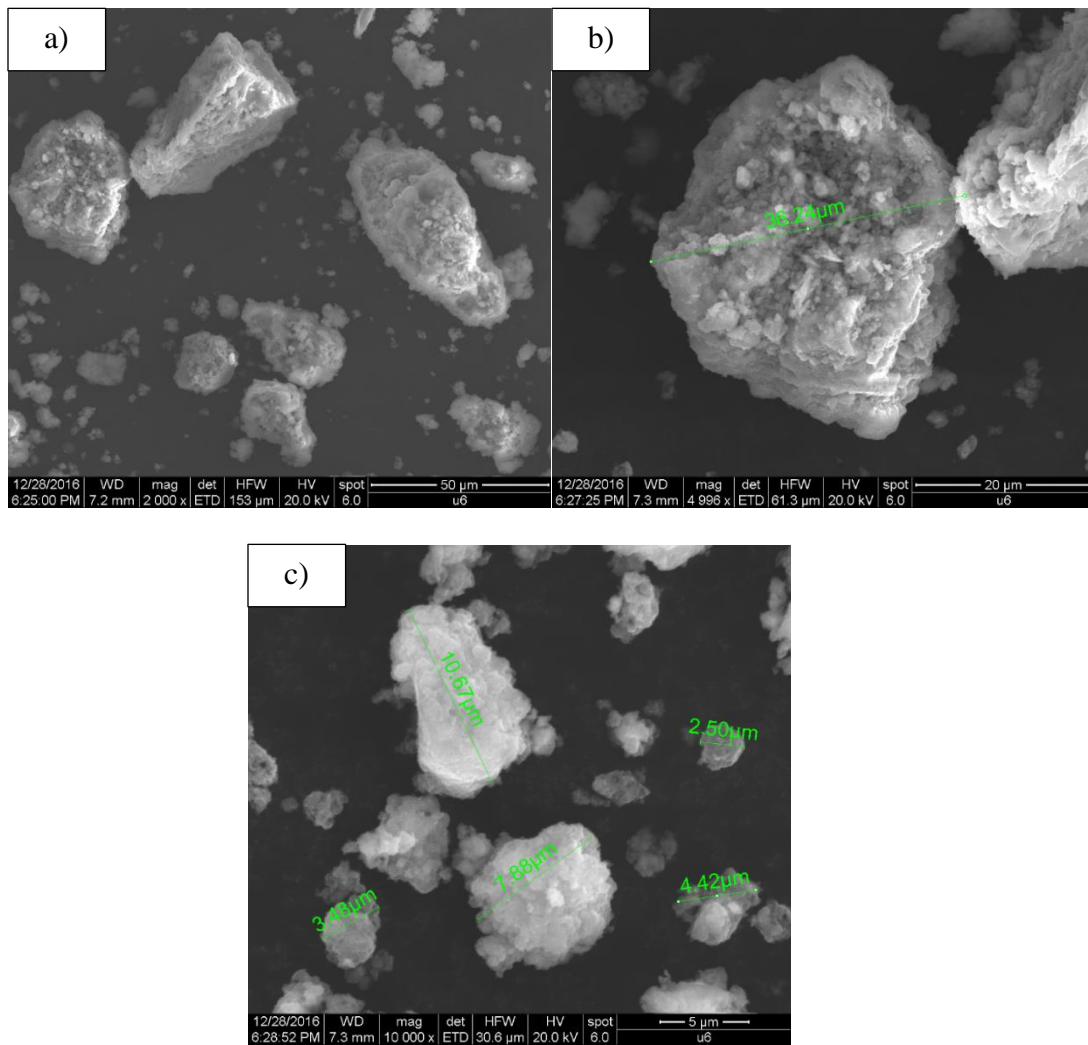


Figure 4.2 Morphology of roasted product a) 2k Mag, b) 5k Mag, c) 10k Mag.

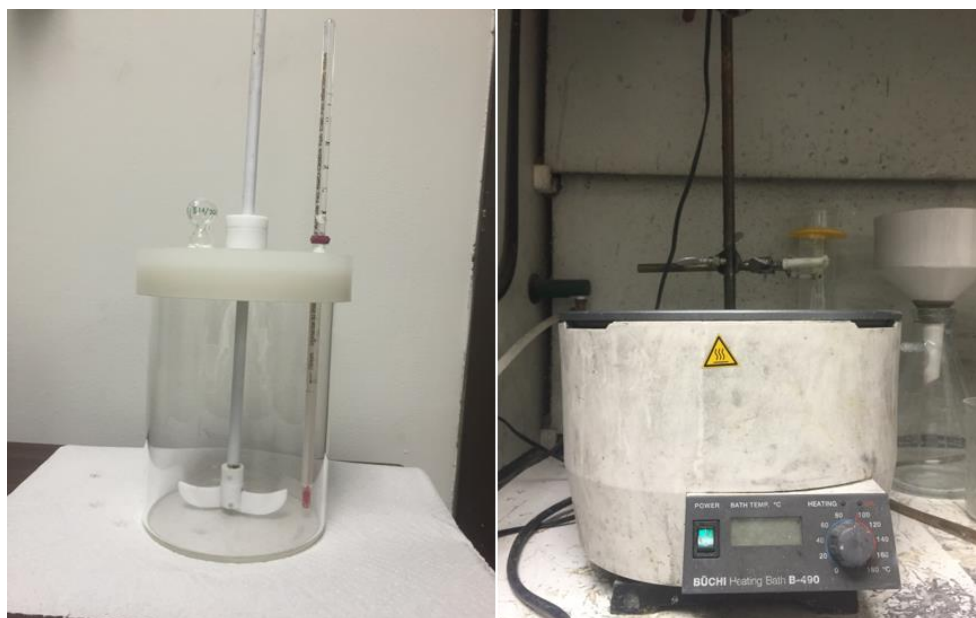


Figure 4.3 Hydrolysis reactor and heating bath

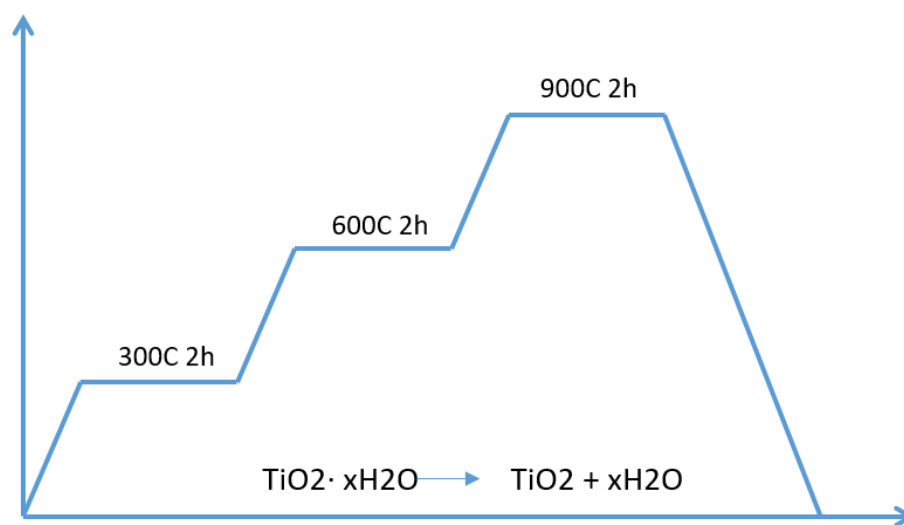


Figure 4.4 Temperature profile of calcination of titanic acid particles

Table 4.2 Singe effect study on free acid conc. on hydrolysis at varied TiO₂

TiO ₂ (g/L)	Free acid conc.(M)	HCl(L)	H ₂ O(L)	Titanate(g)
40	4	0.45	0.45	56
	4.5	0.49	0.41	
70	2	0.42	0.48	100
	2.5	0.45	0.45	
	3	0.48	0.42	
	3.5	0.51	0.39	
100	2.0	0.39	0.51	145
	2.5	0.54	0.36	
	3	0.61	0.29	
	3.5	0.69	0.21	
115	1.5	0.6	0.3	180
	2	0.64	0.26	
	2.5	0.675	0.225	

Table 4.3 Fe content before and after hydrolysis of titanic acid

Element	Fe
Pre-hydrolysis	664
Post-hydrolysis	690

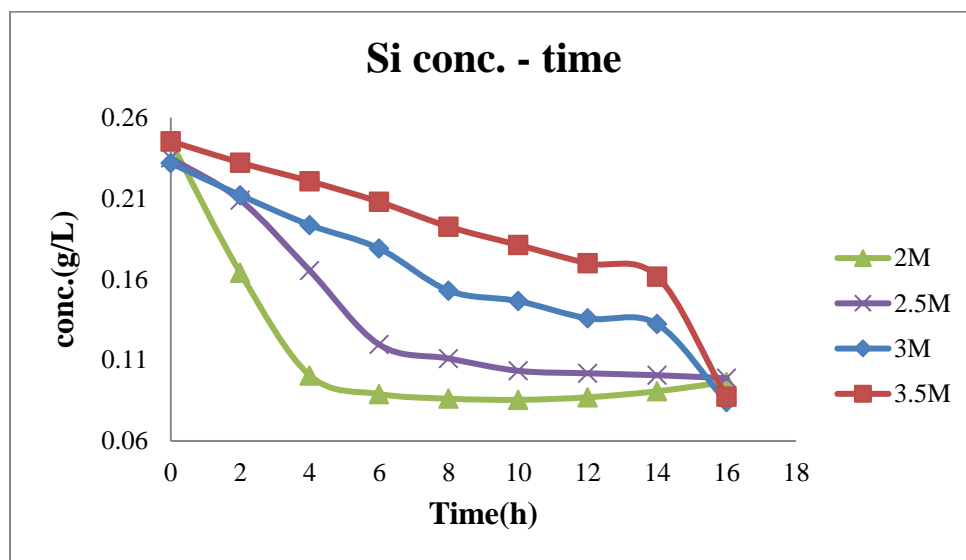


Figure 4.5 The change of Si content with time during hydrolysis

Table 4.4 Chemical composition of the dried residue and the impurity removal rates

Element	Ti	Fe	Mg	Al	Ca	Si	Cr	Mn	V
wt%	40	0.483	0.156	0.010	0.072	0.038	0.008	0.004	0.017
Removal rate %	0	31.5	47.3	94.5	0	97.5	78.8	83.0	88.8

Table 4.5 Chemical composition of the solution before and after hydrolysis (mg/L)

Element	Ti	Mg	Fe	Al	Ca	Si	Cr	Mn	V
Pre-hydrolysis	49,000	222	664	7	45	18	7	4	19
Post-hydrolysis	880	231	690	8	52	4	5	5	4

Table 4.6 Comparison of the impurity contents in rutile prepared by this work and in commercial pigment grade rutile(cite), wt%

Element	Mg	Al	Fe	Si	Ca	Cr	V	Mn	C
This work	0.048	0.006	0.043	0.030	0.029	0.018	0.037	0.005	0.0035
Commercial	0.030	NA	0.0012	0.0386	0.0112	<0.0013	NA	<0.0007	NA

Table 4.7 The change of crystal size of titanic acid particles before and after calcination

Temperature(°C)	Crystal size(nm)
W/O calcination	4.2
300	5.8
600	16.8
900	39.5

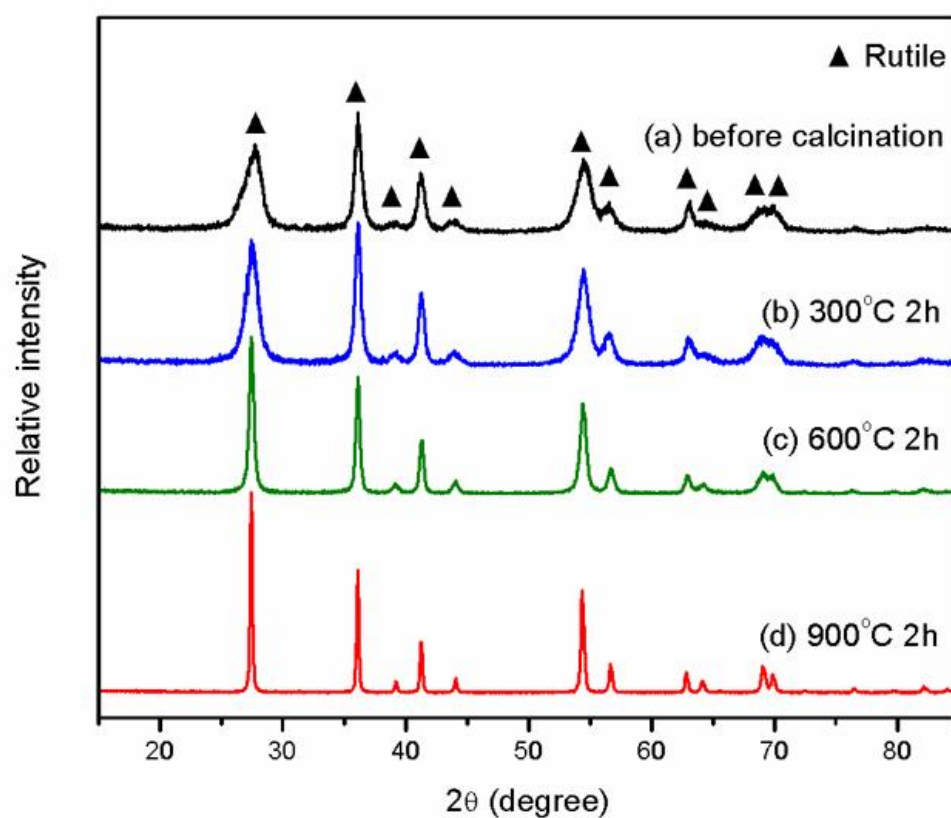


Figure 4.6 X-ray diffraction patterns of titanic acid powders from hydrolysis a) before calcination b) 300°C for 2 hr c) 600°C for 2 hr d) 900°C for 2 hr

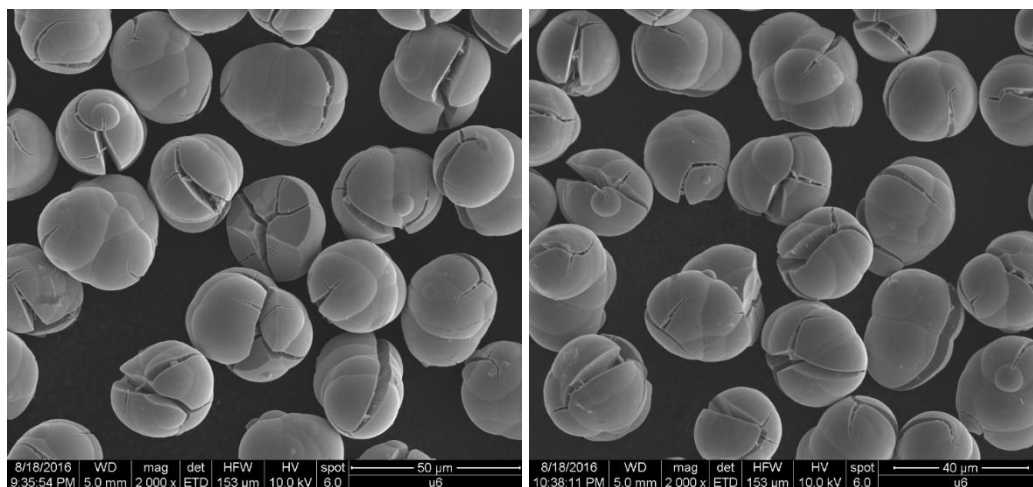


Figure 4.7 Microstructure of titanic acid samples before and after calcination from 100g/L equi. TiO_2 and 2M free acid. left) before calcination 2000x mag, right) after calcination 2000x mag.

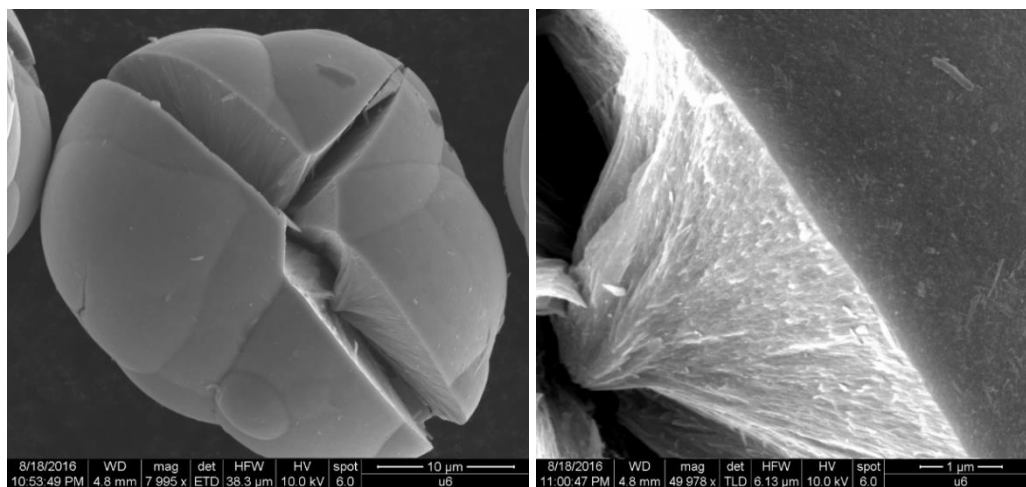


Figure 4.8 Microstructure of titanic acid samples calcined at 300°C from 100g/L equi. TiO_2 and 2M free acid. left) 8kx mag, right) 50kx mag.

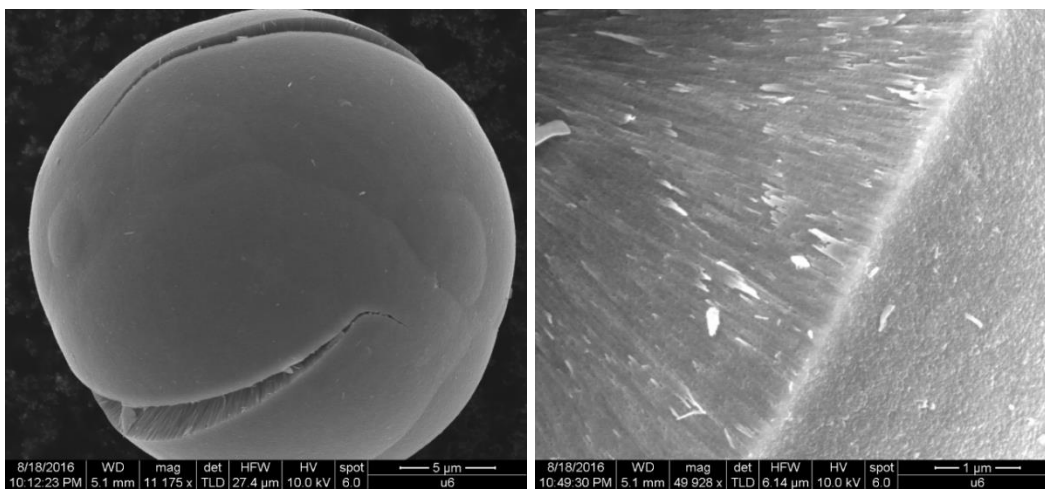
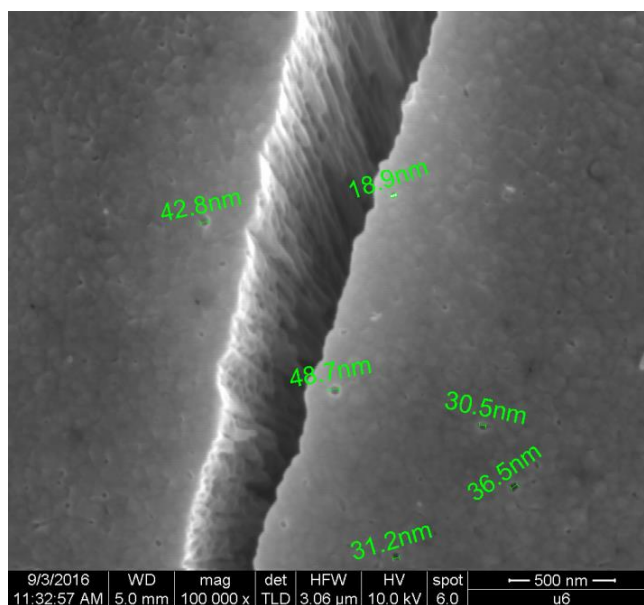
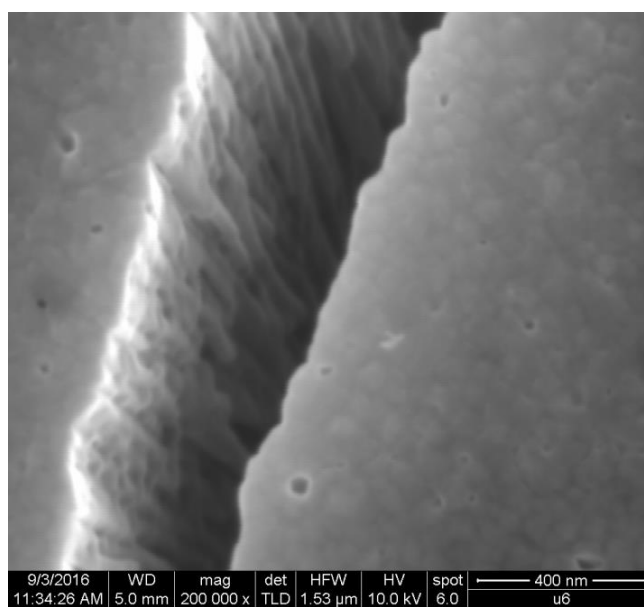


Figure 4.9 Microstructure of titanic acid samples calcined at 600°C from 100g/L equi. TiO₂ and 2M free acid. left) 11kx mag, right) 50kx mag.



a)



b)

Figure 4.10 Microstructure of titanic acid samples after calcination from 100g/L equi. TiO_2 and 2M free acid. left) 100kx mag, right) 200kx mag.

Table 4.8 Experimental design of the effect of temperature on hydrolysis rate

Temp (°C)	TiO ₂ conc.(g/L)	Free acid conc.(M)	HCl(mL)	H ₂ O(mL)	White mud(g)
105	70	2.9	480	420	100
98	70	2.9	480	420	100
90	70	2.9	480	420	100

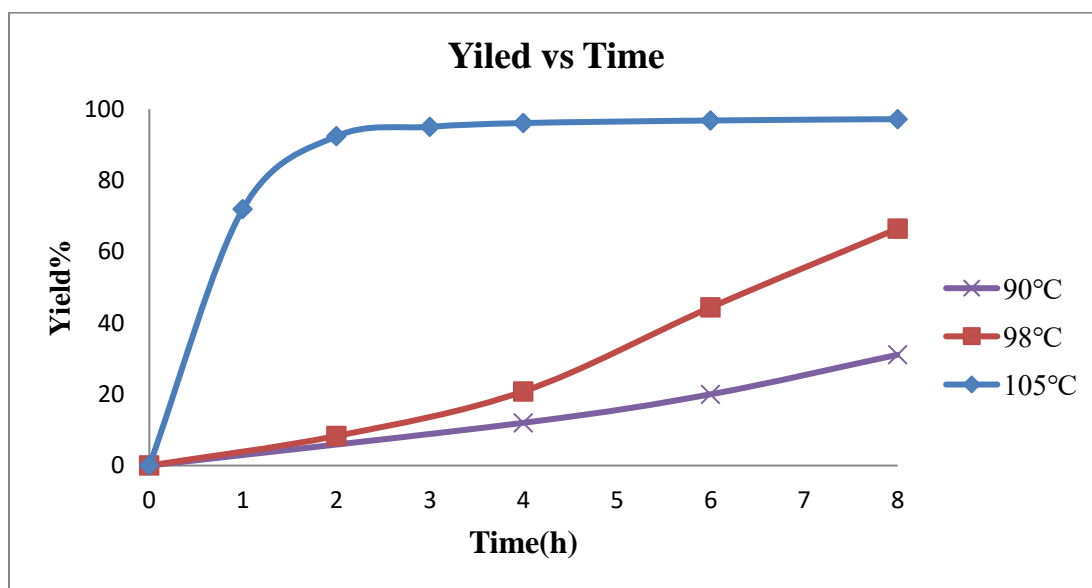


Figure 4.11 Hydrolysis rate of titanate acid at 90°C, 98°C, and 105°C

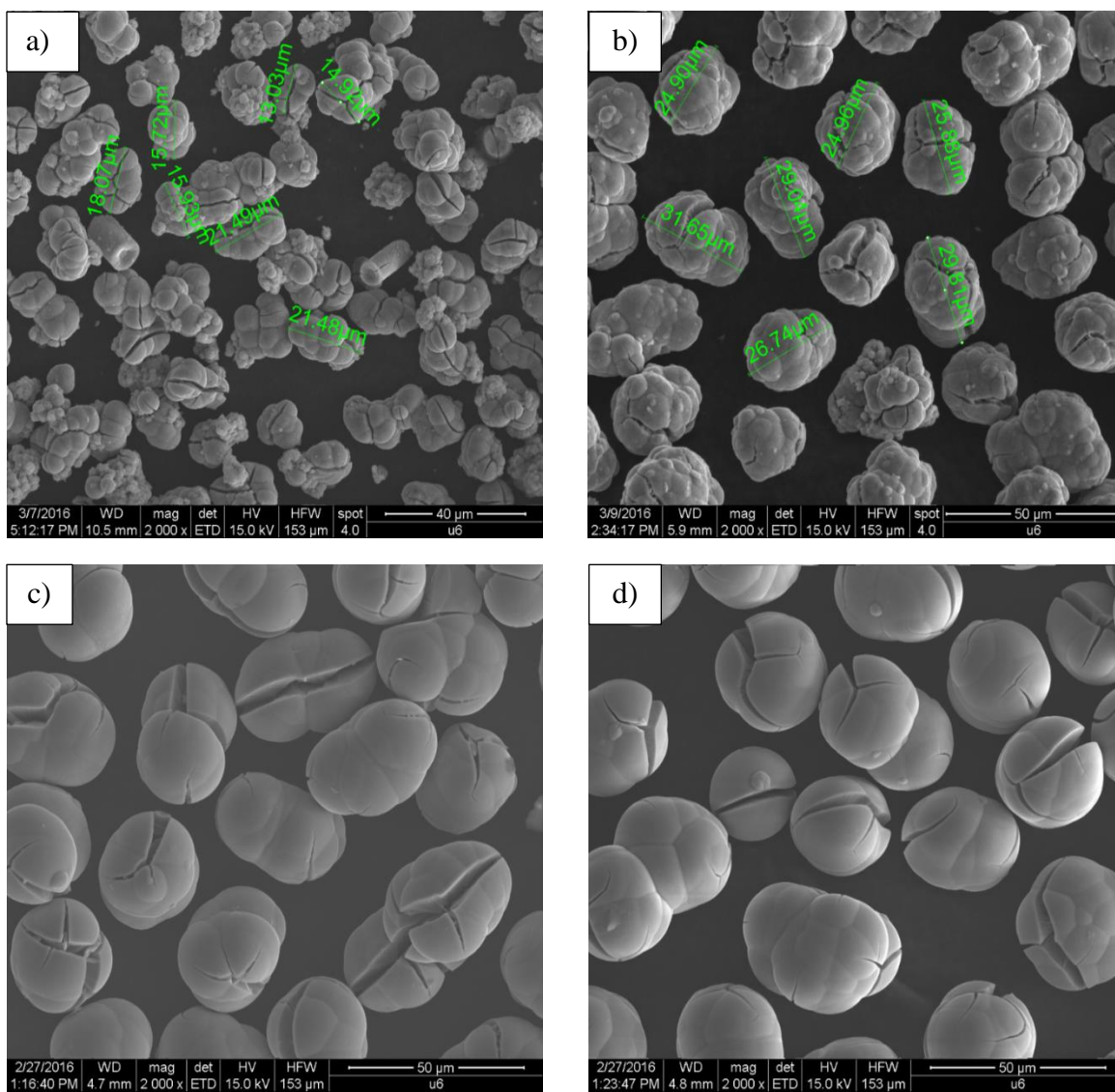


Figure 4.12 SEM images of titanic acid from 4 different free acid conc. at 70g/L of equi. TiO₂, a) 2M; b) 2.5M; c) 3M; d) 3.5M.

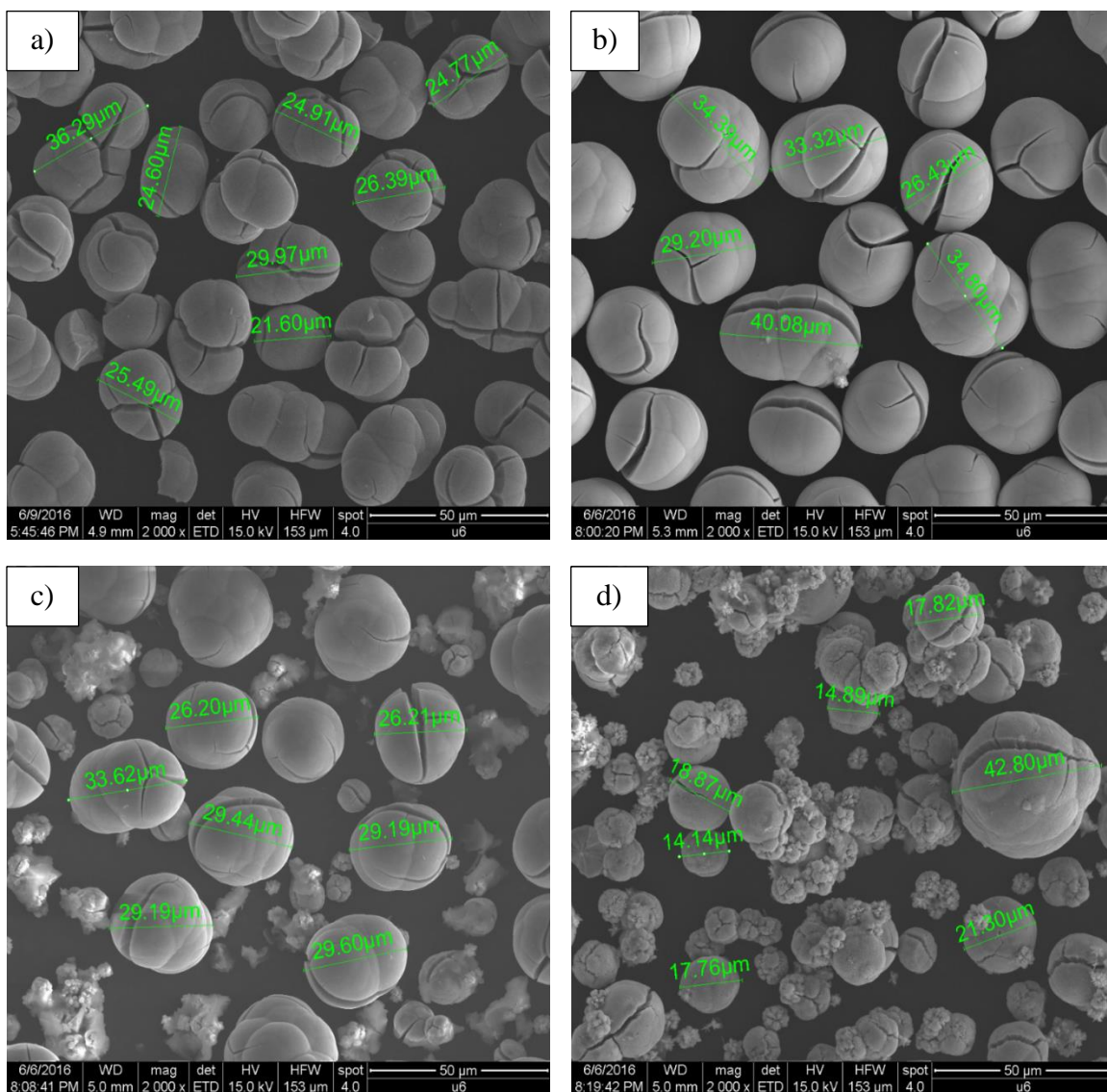


Figure 4.13 SEM images of titanic acid from 4 different free acid conc. at 100g/L of equi. TiO₂, a) 2M; b) 2.5M; c) 3M; d) 3.5M.

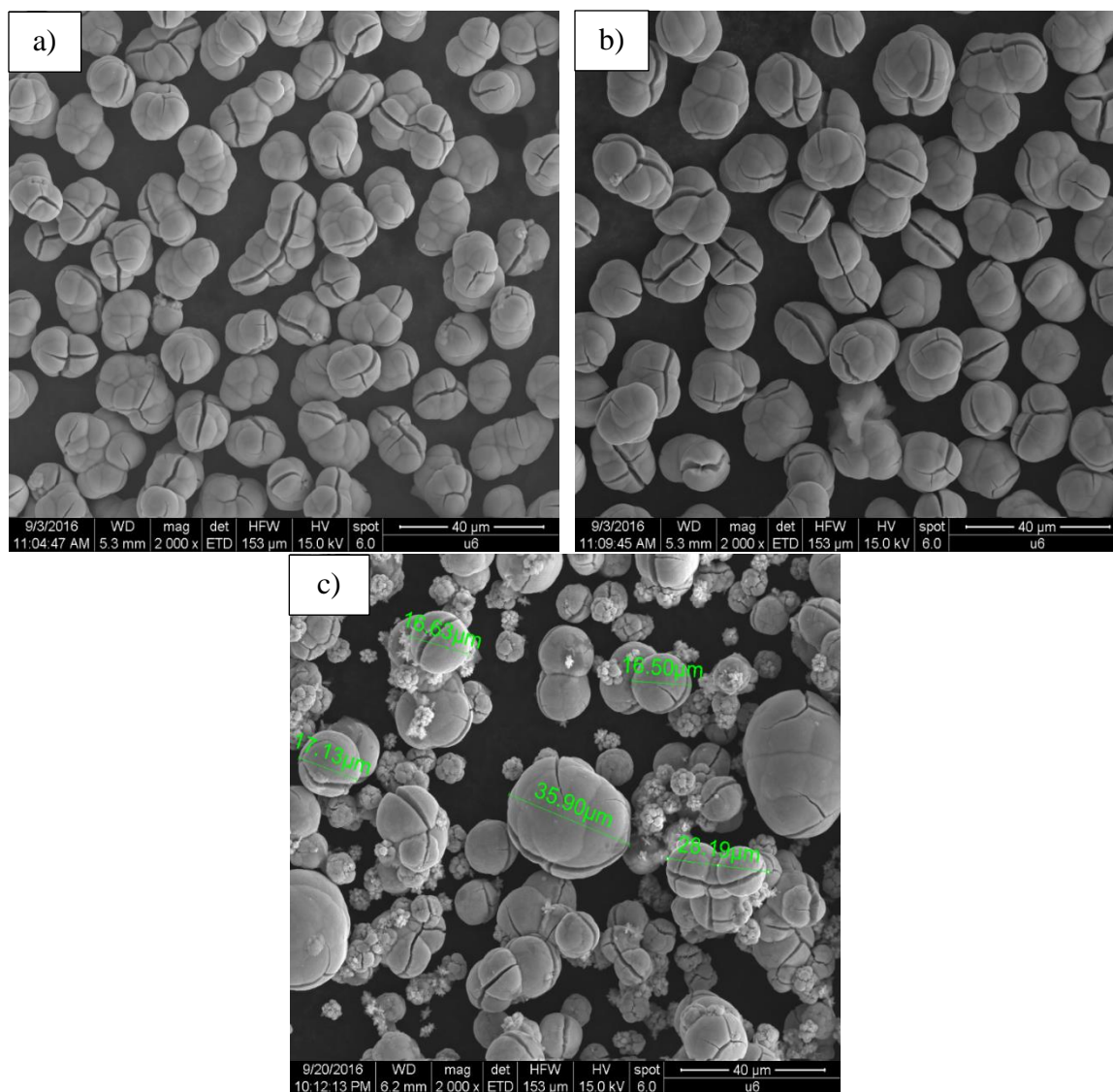


Figure 4.14 SEM images of titanic acid from 3 different free acid conc. at 115g/L of equi. TiO₂, a) 1.5M; b) 2M; c) 2.5M.

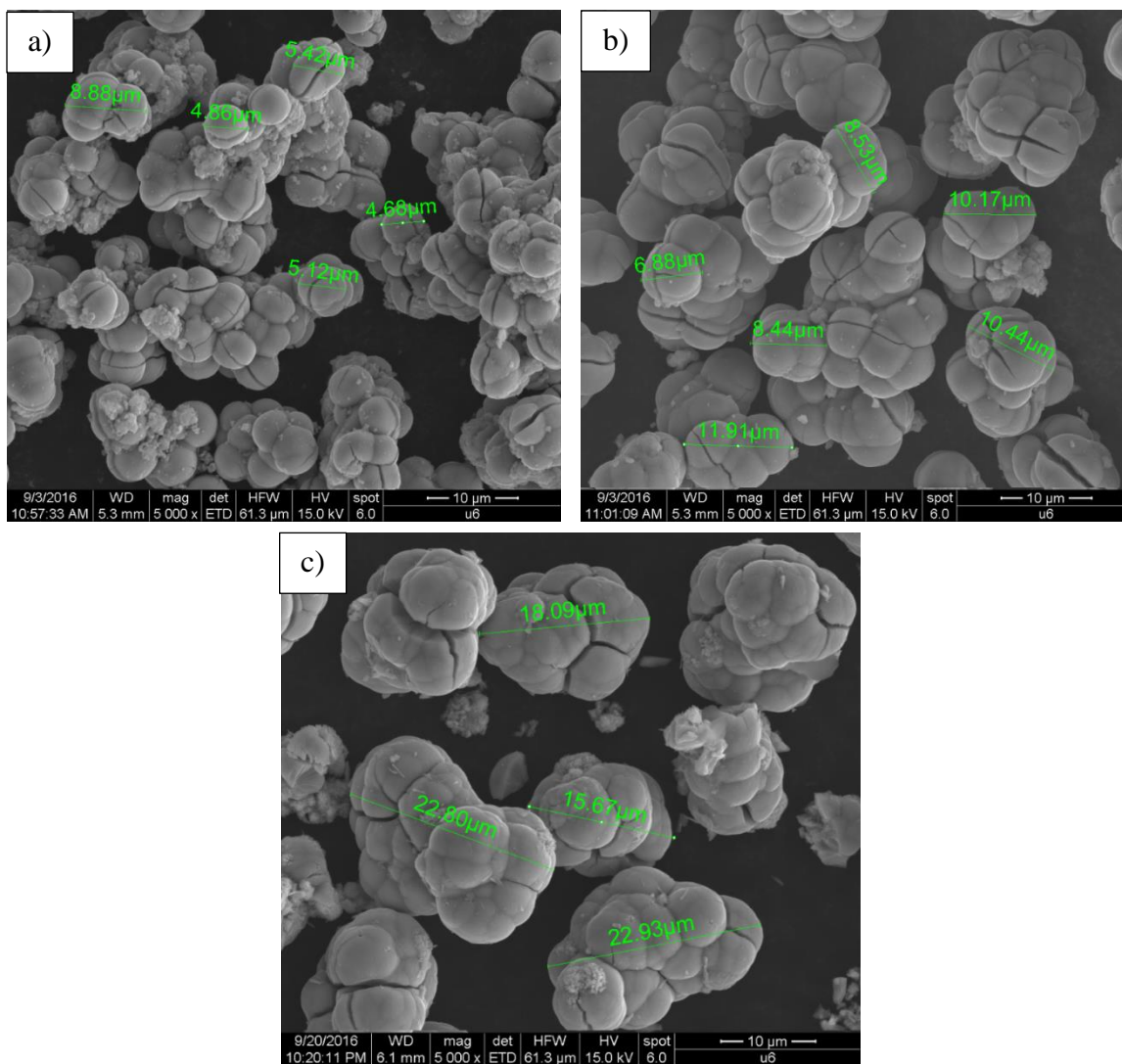


Figure 4.15 SEM images of titanic acid from 3 different free acid conc. at 40g/L of equi. TiO₂, a) 3.5M; b) 4M; c) 4.5M.

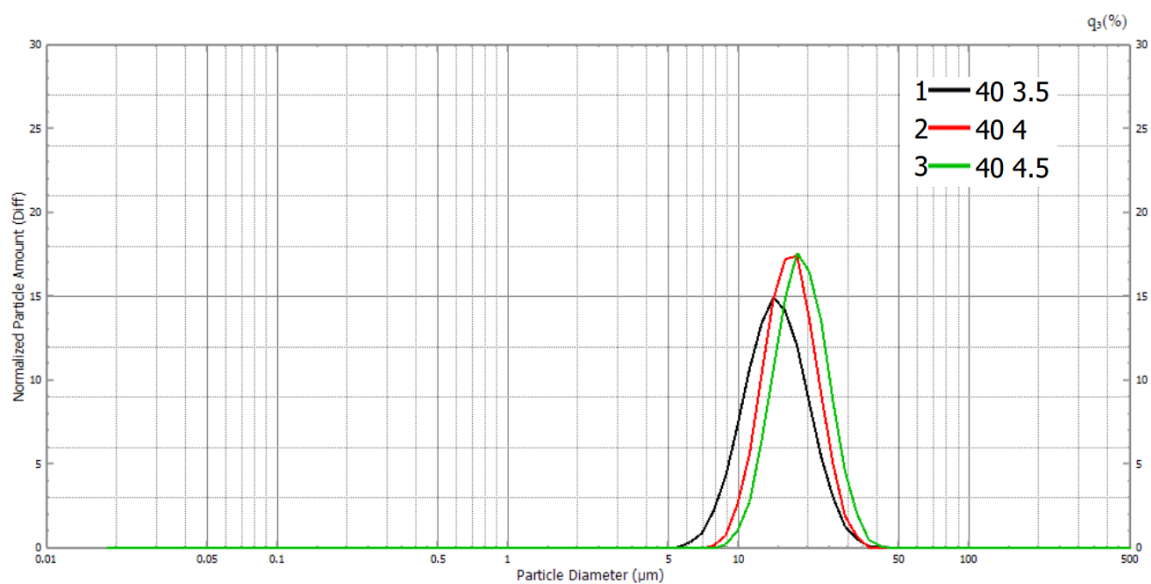


Figure 4.16 Particle size distribution of titanic acid particles hydrolyzed from 40g/L of equi. TiO_2 at varied free acid concentration.

Table 4.9 Particle size and standard deviation of titanic acid particles from 40g/L of equi. TiO_2 at varied free acid concentration.

Sample#	Description	D10% (μm)	D50% (μm)	D90% (μm)	Std Dev
1	40g/L 3.5M	9.553	14.465	22.189	0.138
2	40g/L 4M	11.667	16.721	23.785	0.115
3	40g/L 4.5M	13.052	18.529	24.486	0.117

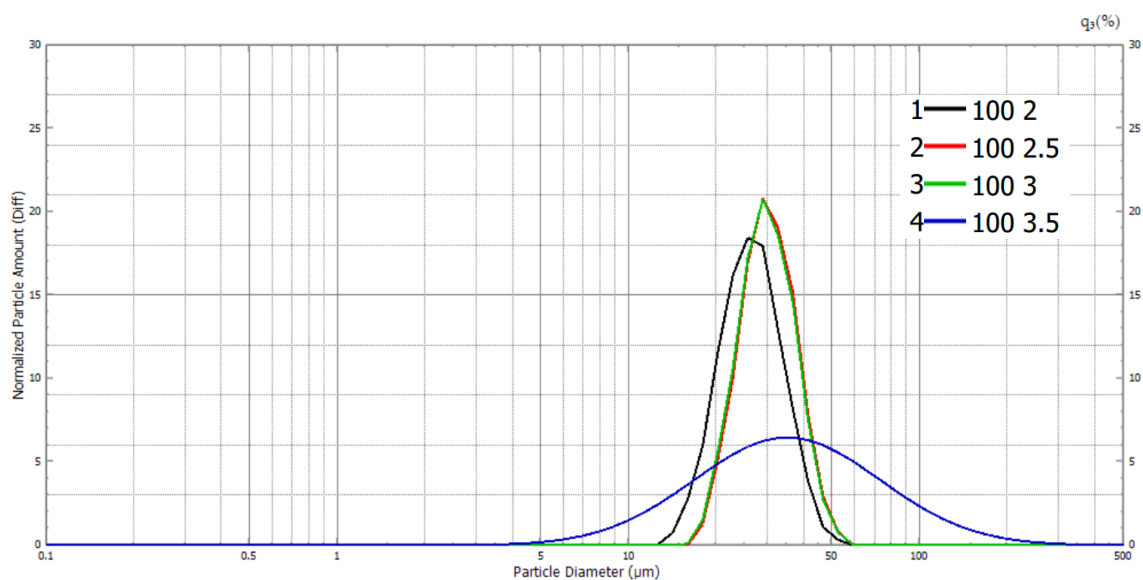


Figure 4.17 Particle size distribution of titanic acid particles hydrolyzed from 40g/L of equi. TiO₂ at varied free acid concentration.

Table 4.10 Particle size and standard deviation of titanic acid particles from 40g/L of equi. TiO₂ at varied free acid concentration.

Sample #	Description	D10%	D50%	D90%	Std Dev
1	100g/L 2M	18.737	26.273	36.886	0.108
2	100g/L 2.5M	21.904	29.852	39.563	0.097
3	100g/L 3M	21.656	29.560	39.391	0.098
4	100g/L 3.5M	13.548	34.972	90.368	0.319

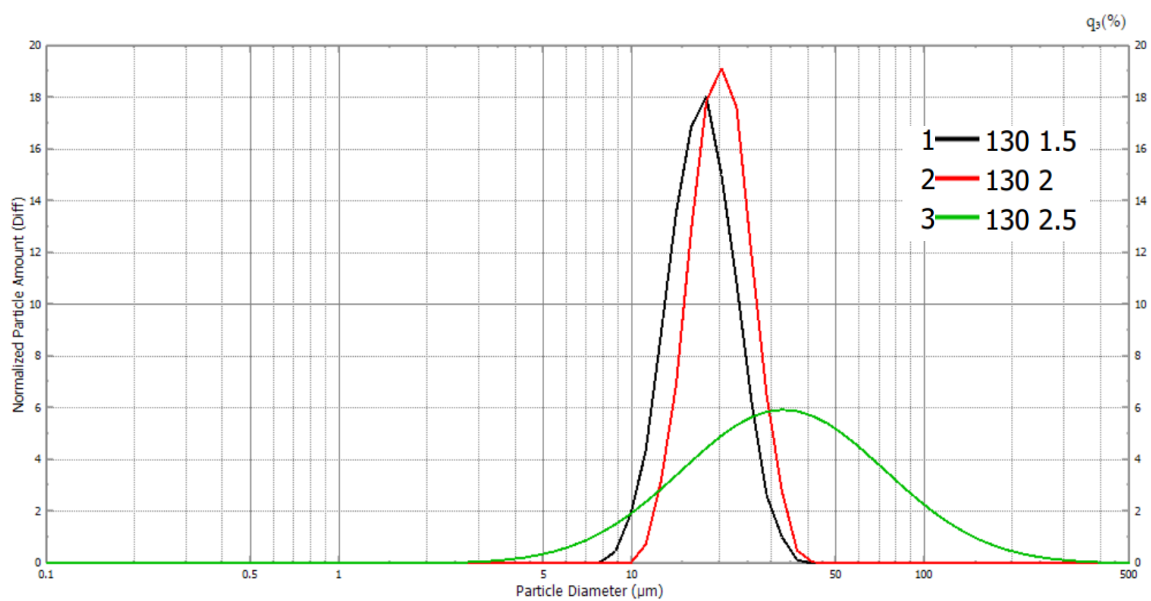


Figure 4.18 Particle size distribution of titanic acid particles hydrolyzed from 40g/L of equi. TiO₂ at varied free acid concentration.

Table 4.11 Particle size and standard deviation of titanic acid particles from 40g/L of equi. TiO₂ at varied free acid concentration

Sample name	D10%	D50%	D90%	Std Dev
115g/L 1.5M	12.402	17.342	24.388	0.114
115g/L 2M	14.410	20.052	27.910	0.104
115g/L 2.5M	11.710	32.847	92.162	0.348

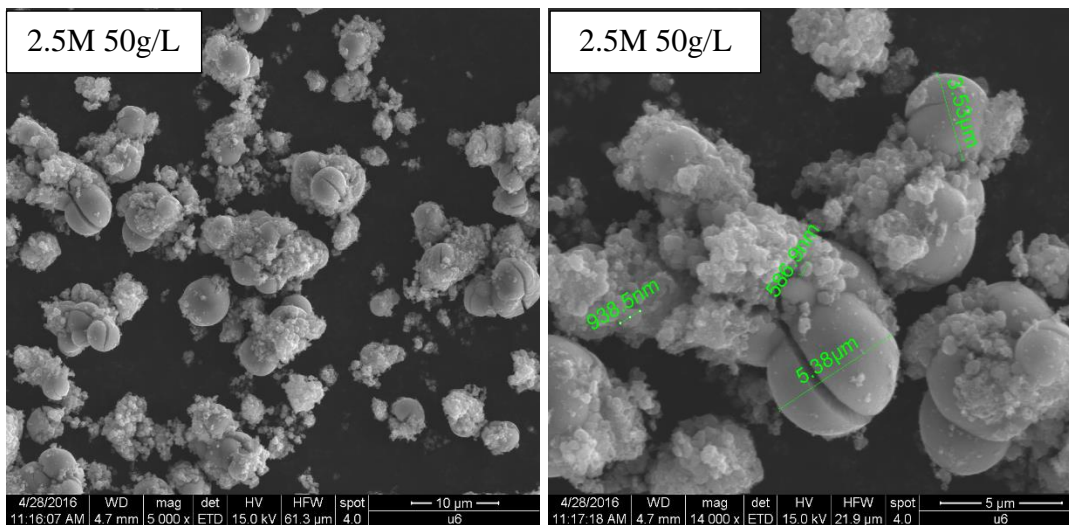


Figure 4.19 SEM images of titanic acid from 50g/L at 2.5M of free acid

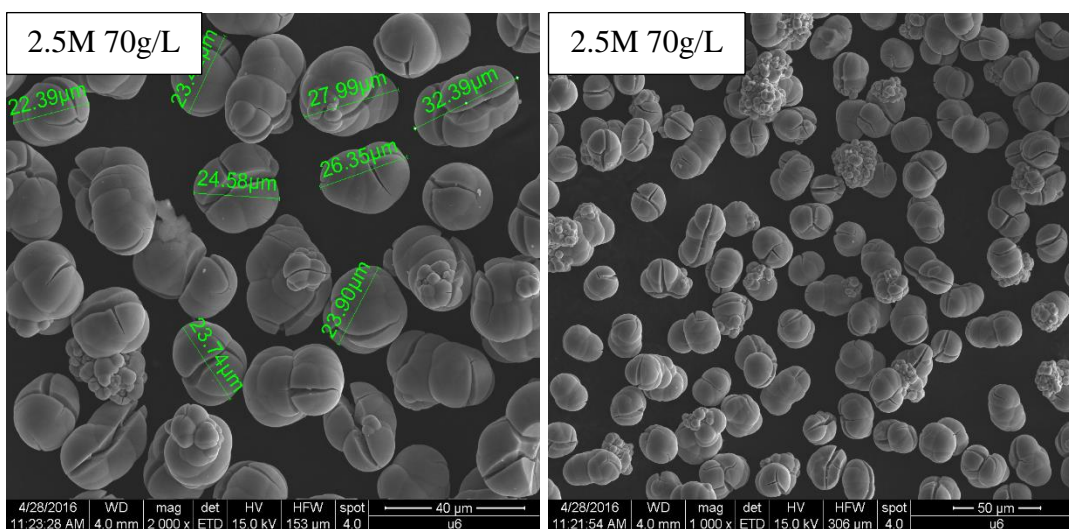


Figure 4.20 SEM images of titanic acid from 70g/L at 2.5M of free acid

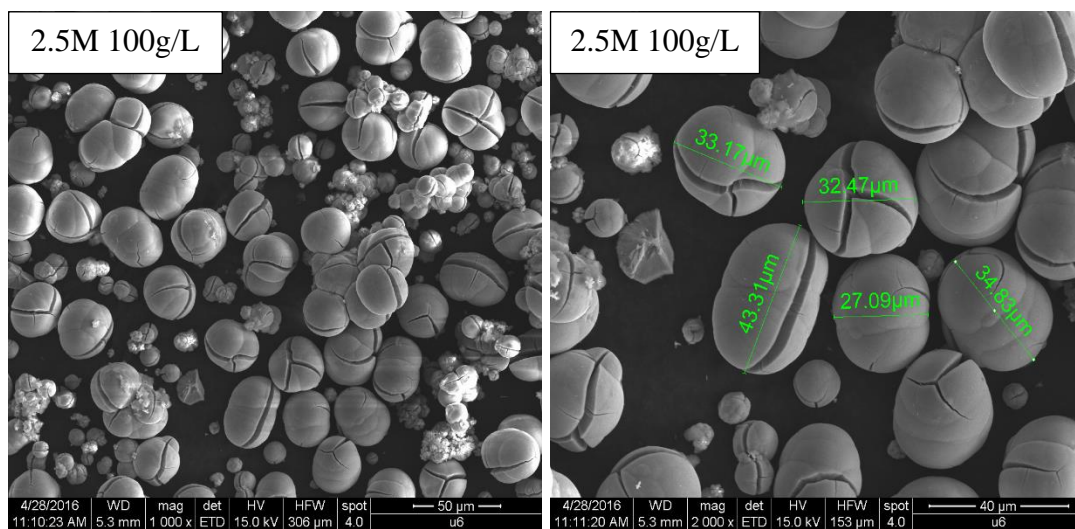


Figure 4.21 SEM images of titanic acid from 100g/L at 2.5M of free acid

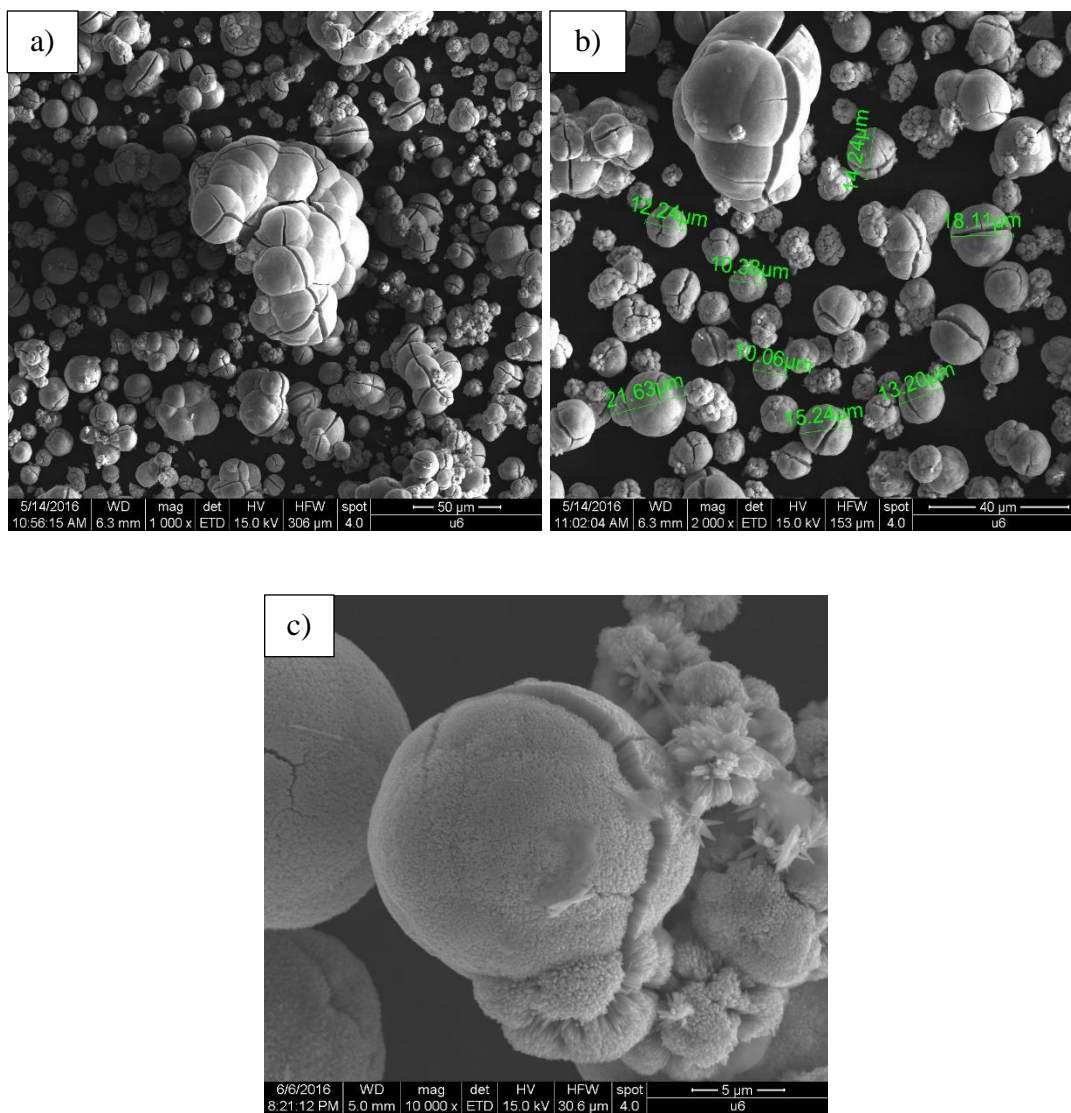


Figure 4.22 SEM images of titanic acid from 3 different free acid conc. at 2M of free acid, a) 70g/L; b) 100g/L; c) 115g/L.

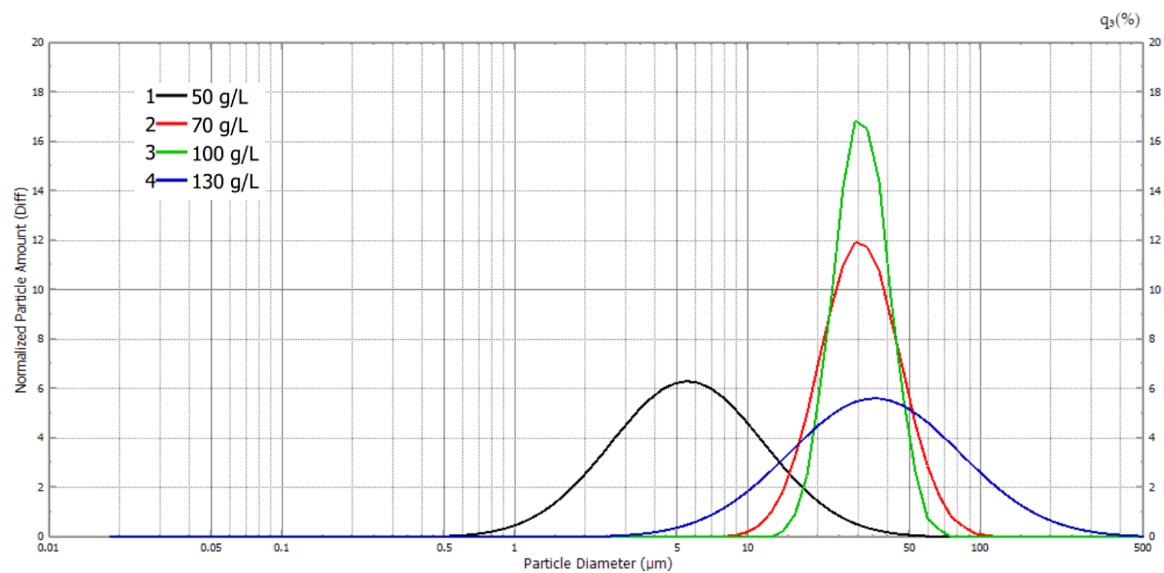


Figure 4.23 Particle size distribution of different TiO_2 concentration at 2.5M free acid, 1) 50g/L; 2) 70/L; 3) 100g/L; 4) 115g/L.

Table 4.12 The particle size distribution data of titanamic acid from different TiO_2 concentration at same free acid concentration

TiO_2 conc. (g/L)	Mean (μm)	10% D(μm)	50% D(μm)	90% D(μm)	Std Dev
50	5.49	2.08	5.49	14.52	0.327
70	30.248	17.93	30.21	50	0.172
100	30.638	21.19	30.57	44.56	0.119
115	35	11.79	35	103.6	0.367

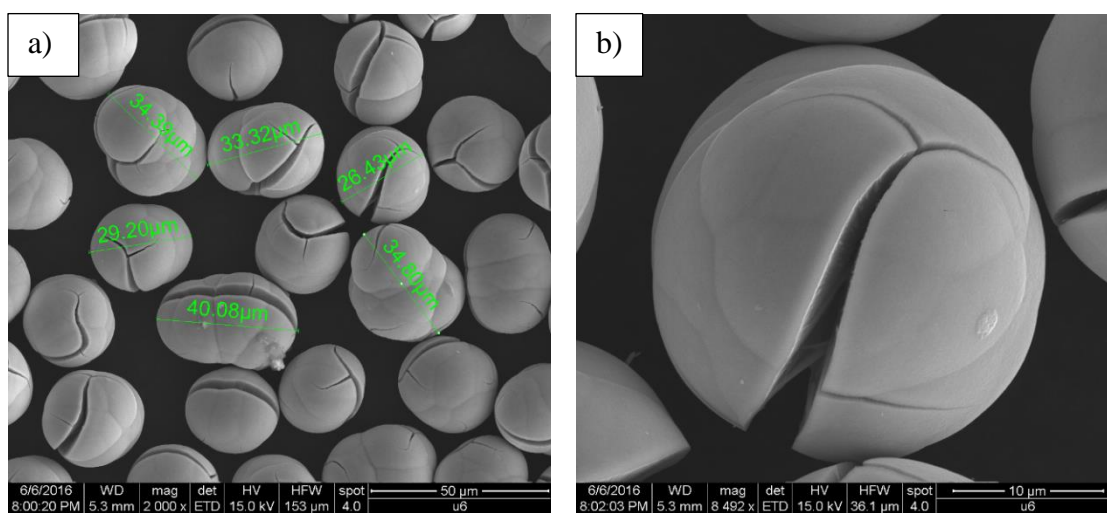


Figure 4.24 SEM images of titanic acid with desired morphology, a) 70g/L TiO_2 conc., 3M free acid, 2000x mag; b) 70g/L TiO_2 conc., 2.5M free acid, 8500x mag.

CHAPTER 5

KINETICS AND MECHANISM

5.1 Hydrolysis kinetics

In the chloride process, the dwell time of TiCl_4 during oxidization at 1300°C is only 0.05-0.08s to achieve TiO_2 powders with a mean size of $0.2\mu\text{m}$ and narrow distribution. For the sulfate process, it usually takes 2-4 hr to complete the hydrolysis of titanic acid at a boiling point of the hydrolysis solution.

In this work, the hydrolysis of titanic acid is performed in hydrochloric acid which usually takes 10 to 20 hr to complete one batch of hydrolysis. The time it takes to complete a batch of hydrolysis can vary a lot depending on the parameters used for the reaction. With the goal to obtain monodispersed TiO_2 particles with relatively large particle size and regular shape, the hydrolysis rate has to be controlled properly. The effect of free acid concentration, and initial equivalent TiO_2 concentration on the hydrolysis rate was studied in this chapter.

The hydrolysis rate is illustrated in this work by plotting a curve of yield versus time. The Y axis was the yield of titanic acid which was determined by the change of equivalent TiO_2 content in the solution divided by the initial equivalent TiO_2 content in the solution. The X axis is time. The equation for the calculation of yield is shown below,

$$\text{Yield}\% = \frac{\text{the change of equi.TiO}_2 \text{ concentration(g/L)}}{\text{the initial equi.TiO}_2 \text{ concentration(g/L)}}$$

5.1.1 Effect of free acid concentration on kinetics

As shown in Figure 5.1, when the equivalent TiO_2 concentration was 40g/L, the free acid concentrations used were 3.5M and 4M. The trend of hydrolysis rate was the same as previous results. The hydrolysis rate at 3.5M is faster than 4M. In general, the hydrolysis rate of 40g/L equivalent TiO_2 is faster than other equivalent TiO_2 concentrations. The yield of both 3.5M and 4M free acid is over 95% in 12 hr.

As shown in Figure 5.2, the hydrolysis has the fastest reaction rate at 2.0M free acid. The yield reached around 90% within 4 hr of reaction. The reaction almost completed in 6 hr. The hydrolysis rate is the slowest when the free acid concentration is 3.5M. It takes 16 hr for the yield of titanate to reach 85%. The yield is just 9% in 4 hr. The trend of the hydrolysis rate at these four free acid levels implied that with the increase of the free acid concentration, the hydrolysis rate of titanate became slower.

As discussed before, in Figure 5.3, the free acid concentration was designed to be 2M, 2.5M, 3M, and 3.5M when the equivalent TiO_2 concentration is 100g/L. 3.5M free acid was the slowest in hydrolysis of titanate. The yield of TiO_2 at 3.5M in 18 hr is around 30% which is much lower than the rest of the samples. 2M free acid has the fastest hydrolysis rate and highest yield which is around 97.4%. The hydrolysis rate follows the sequence of $2\text{M} > 2.5\text{M} > 3\text{M} > 3.5\text{M}$. The yield of TiO_2 also followed the same sequence. To conclude, solution with lower free acid concentration will have faster hydrolysis rate and higher yield.

In Figure 5.4, when the equivalent TiO_2 concentration is 115g/L, the free acid concentration was designed to be 1.5M, 2M, and 2.5M. The hydrolysis rate followed the sequence of $1.5\text{M} > 2\text{M} > 2.5\text{M}$. 2.5M free acid had the slowest hydrolysis rate. The yield of

titanic acid at 1.5M and 2M was much higher than 2.5M which was over 91% in 13 hr.

5.1.2 Effect of equivalent TiO₂ concentration on kinetics

See Figure 5.5 for the comparison of hydrolysis rate of titanic acid at different equivalent TiO₂ concentration. The hydrolysis rate follows the sequence 70g/L>100g/L>115g/L. When the equivalent TiO₂ concentration was 70g/L with 2M free acid, the hydrolysis reaction has the fastest rate. It took 4 hr for the yield of titanic acid to reach 90%. The hydrolysis is almost completed in just 6 hr. At higher equivalent TiO₂ concentration, like 100g/L and 115g/L, the hydrolysis rate is slower. It took nearly 16 hr for the yield of hydrolysis to reach over 90%.

In Figure 5.6, when the free acid concentration is 2.5M, the hydrolysis rate follows the same sequence: 70g/L>100g/L>115g/L. The hydrolysis rate of titanic acid at 115g/L is much slower than the other two samples. The yield of titanic acid is only 6% in the first 8 hr. For 70g/L and 100g/L of equivalent TiO₂, the yield in the first 6 hr is 73% and 27%, respectively.

5.2 Hypothetical mechanisms of hydrolysis of titanic acid

The mechanism of hydrolysis of titanic acid was studied by evaluating the change of particle size and morphology of titanic acid particles with time. The titanic acid sample used in this work is obtained at 70g/L of equivalent TiO₂, 3M of free acid, and hydrolyzed at 100°C. 8 ml of hydrolysis solution was taken in every 2 hr. The liquid part of the sample was analyzed by ICP to determine the Ti content change with time. The solid part of the sample was dried and analyzed by SEM to examine the microstructure of the change of titanic acid particles with time.

For the reaction of hydrolysis of titanic acid, the forward and backward reaction rates have to be taken into considered. The net rate of a reaction is the difference between forward and backward rates which can be expressed as

$$R_{\text{net}} = R_{\text{forward}} - R_{\text{backward}}$$

More specifically, it be can expressed as

$$R_{\text{total}} = k_f \cdot C_{(\text{equiTiO}_2)} \cdot C_{(\text{H}_2\text{O})}^4 - k_b (\text{free acid}) \cdot C_{(\text{Free acid})}$$

k_f is the forward reaction rate constant. k_b is the backward reaction rate constant. Based on the equation above, the concentration of each species is associated with the reaction rate. It can be seen from the equation that the increase of equivalent TiO_2 concentration can facilitate the total reaction rate of hydrolysis, which is contrary to the experimental results shown in the previous section. This is because when the equivalent TiO_2 concentration increases, the amount of water in the solution will reduce, thus decreasing the total reaction rate. Based on the equation, water has a 4th power which shows that it has greater effect on the hydrolysis rate than the equivalent TiO_2 concentration. The result of the effect of free acid concentration on the reaction rate is consistent with the equation.

For hydrolysis performed under 70g/L of equivalent TiO_2 , 3M of free acid at 100°C, It usually takes 40 minutes for the temperature of the hydrolysis solution to reach 80°C which is when the precipitated titanic acid particles can be observed. At this point, the titanic acid particles are tiny and suspended in the solution. In another 20 minutes, the solution turns from transparent to cloudy which implies that the amount of titanic acid particles has increased. It can be said that the size of the particles is still small since they are very hard to settle based on the observation from the sample of 1 hr hydrolysis. After the first hour,

the temperature will stay at 100°C for the rest of the time of hydrolysis. The change of microstructure of the titanic acid particles and hydrolysis rate during these times are shown in Figure 5.7, Figure 5.8, and Figure 5.9.

After 2 hr of hydrolysis, the particles already have a mean size of around 16µm. It can be seen that each particle is made of many smaller particles since the boundary can be clearly observed. The shape of particles is irregular due to the random agglomeration between particles.

From 2 to 8 hr, the morphology changed from irregular shape into a relatively round shape. The hydrolysis rate has a dramatic increase in this stage. The newly generated titanic acid will aggregate on the existing particles. Since heterogeneous nucleation requires lower energy than homogeneous nucleation, the nucleation tends to first take place on those irregular surfaces where heterogeneous nucleation happens. After the irregular sites for nucleation are filled by the newly generated titanic acid, the particles grow larger and more round.

From 8 to 16 hr, the particles will keep growing but at a slower rate. The hydrolysis rate also becomes slower as the concentration of TiO₂ in the solution decreases. The Ti⁴⁺ remaining in the solution will keep reacting with water until the equilibrium is reached. After that, the particles will reach their final size and morphology. During this stage, the particle size distribution becomes more obvious. Many small particles with round shapes can be found.

The mean size of titanic acid particles in 2 hr is 16.32µm which is already very large compared with the titanic acid particles obtained from the sulfate process. The mean size of particles went through a dramatic increase from 2 to 6 hr from 16.32µm to 27.31µm.

After that, the mean size keeps a steady increase from 6 to 16 hr from 27.31 μm to 35.85 μm .

In stage A, the hydrolysis rate is very slow. The yield of titanic acid is 4% in 2 hr of hydrolysis. This stage is corresponding to the nucleation of titanic acid particles. The hydrolysis rate in this stage will affect the particle size and morphology of the initial titanic acid particles and thus affect the property of the final TiO_2 particles. In this stage, hydrolysis should be controlled at a relatively low rate to allow the nucleation to proceed slowly. In this way, the initial nuclei of titanic acid will become larger and uniformly distributed.

In stage B, the hydrolysis rate increased dramatically. The yield of titanic acid increased from 4% to 85% from 2 to 12 hr. This stage is usually corresponding to the growth of titanic acid particles which is accompanied by the decrease of equivalent TiO_2 concentration and increase of free acid concentration in the hydrolysis solution. The hydrolysis rate with a steady increase in this stage is very important to prepare titanic acid particles with narrow size distribution, coarse size, and controlled morphology. Either too fast or too slow hydrolysis can lead to unexpected morphology of titanic acid particles such as agglomerations, broad size distribution, and irregular shape. A moderate rate of hydrolysis which takes 8-12 hr for the growth of particles is usually used for production of titanic acid powder in this work.

In stage C, almost all the equivalent TiO_2 in the solution precipitated out as titanic acid particles and the concentration of free acid raises to the initial concentration HCl solution used for digesting the roasted product. The reaction reaches its equilibrium and the yield of titanic acid reaches 92% after 16 hr of hydrolysis. This stage is corresponding to the balance stage.

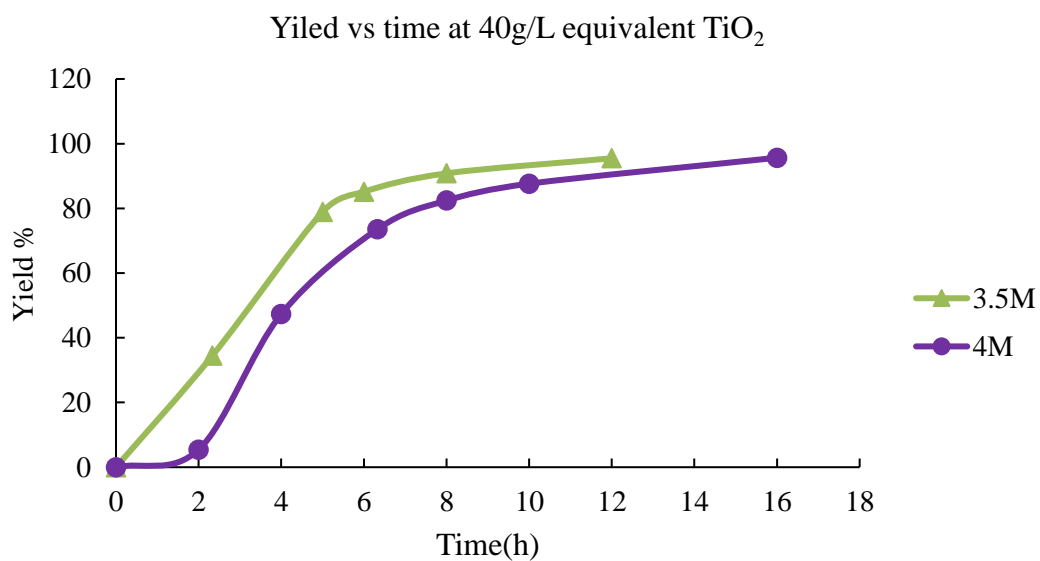


Figure 5.1 Hydrolysis rate of titanitic acid at 40g/L equi. TiO_2 with varied free acid conc.

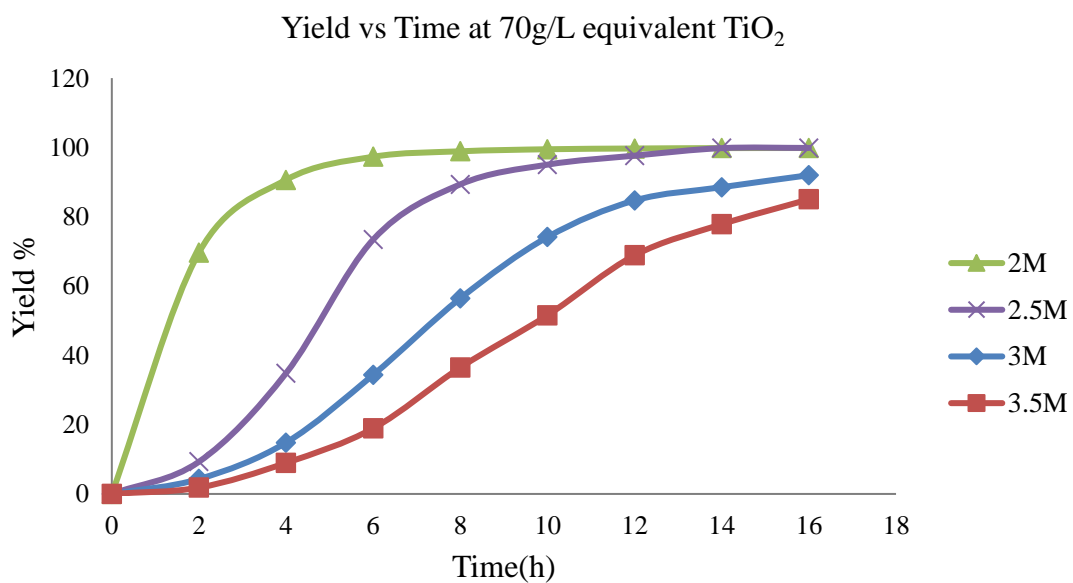


Figure 5.2 Hydrolysis rate of titanitic acid at 70g/L equi. TiO_2 with varied free acid conc.

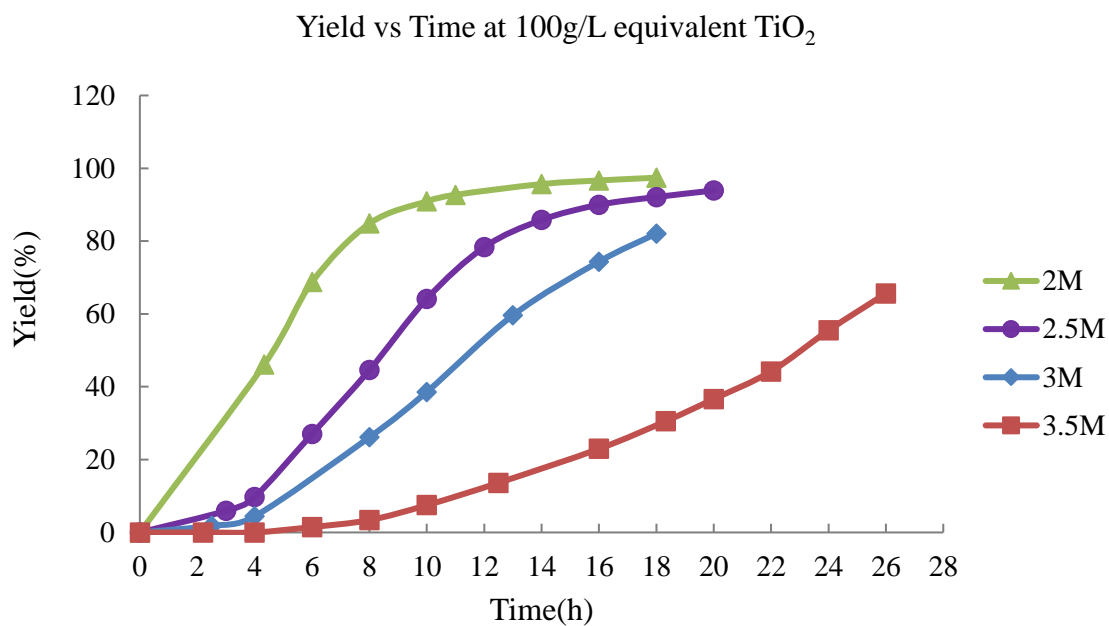


Figure 5.3 Hydrolysis rate of titanitic acid at 100g/L equi. TiO_2 with varied free acid conc.

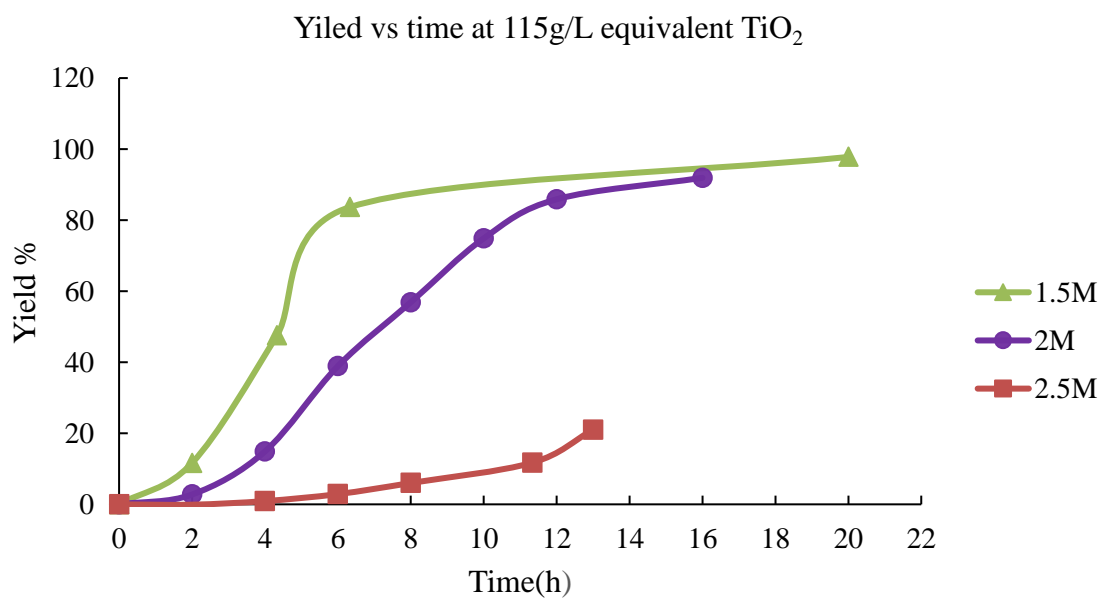


Figure 5.4 Hydrolysis rate of titanitic acid at 115g/L equi. TiO_2 with varied free acid conc.

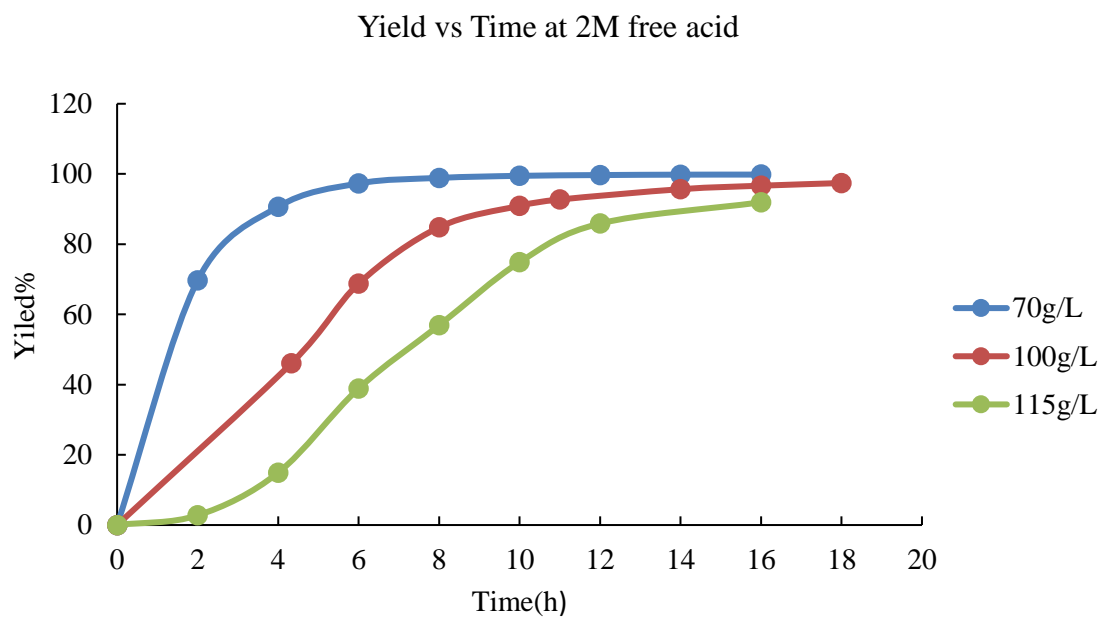


Figure 5.5 Hydrolysis rate of titanitic acid at 2M free acid with varied equi. TiO_2 conc.

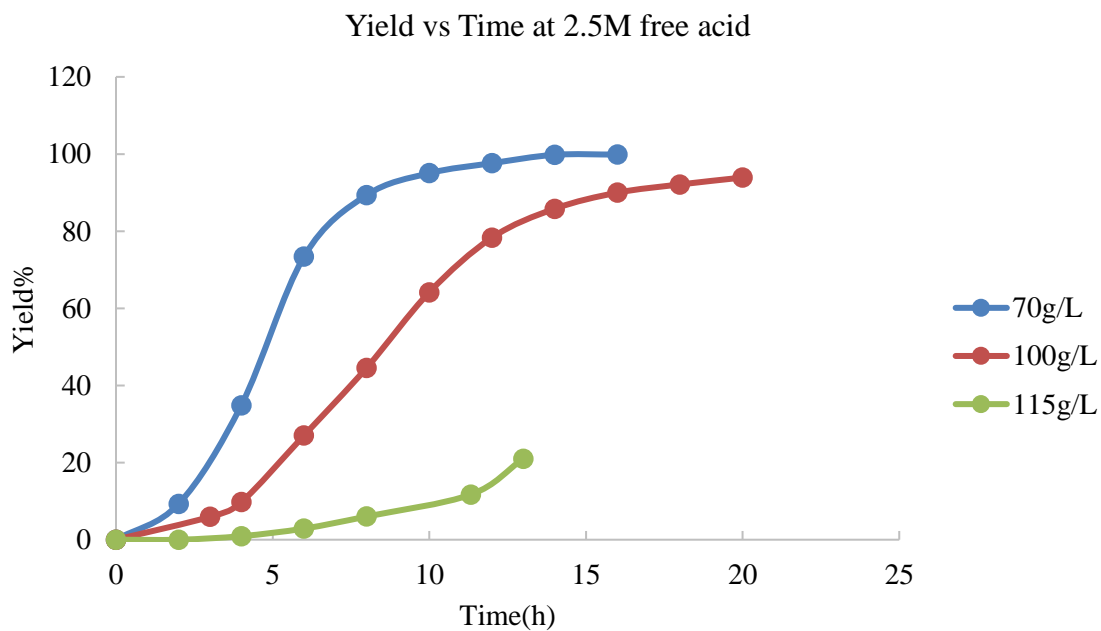


Figure 5.6 Hydrolysis rate of titanitic acid at 2.5M free acid with varied equi. TiO_2 conc.

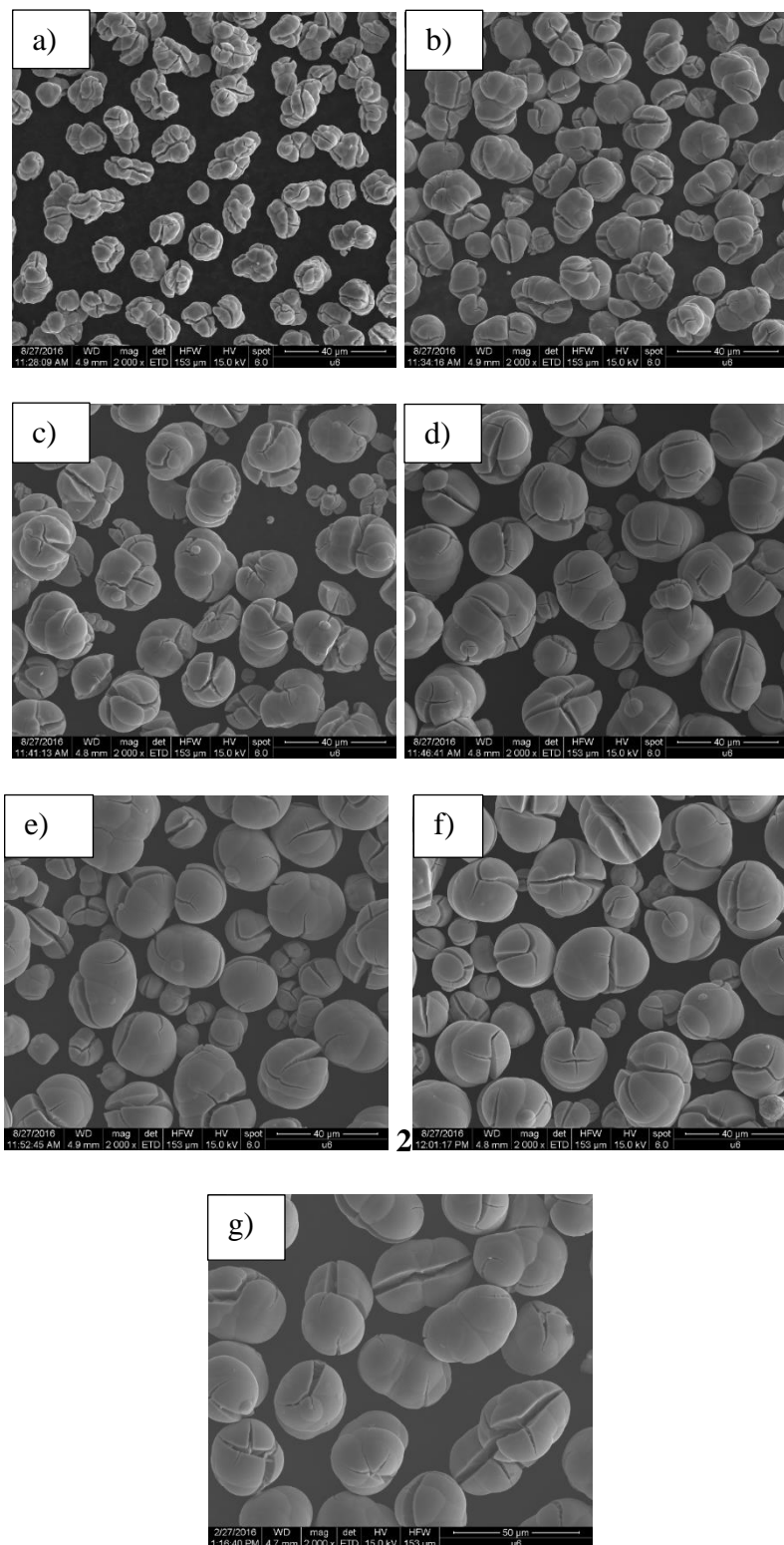


Figure 5.7 The microstructure of titanic acid particles from a) 2 h, b) 4 h, c) 6 h, d) 8 h, e) 10 h, f) 12 h, g) 16 h hydrolysis.

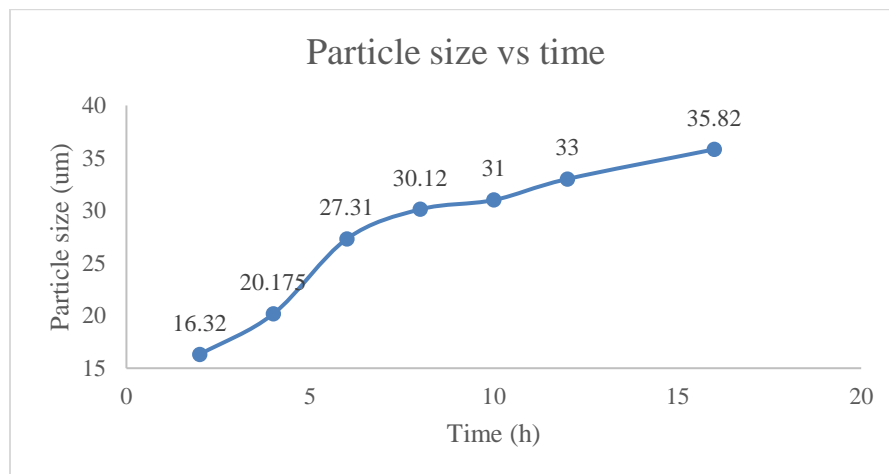


Figure 5.8 The change of particle size with hydrolysis time

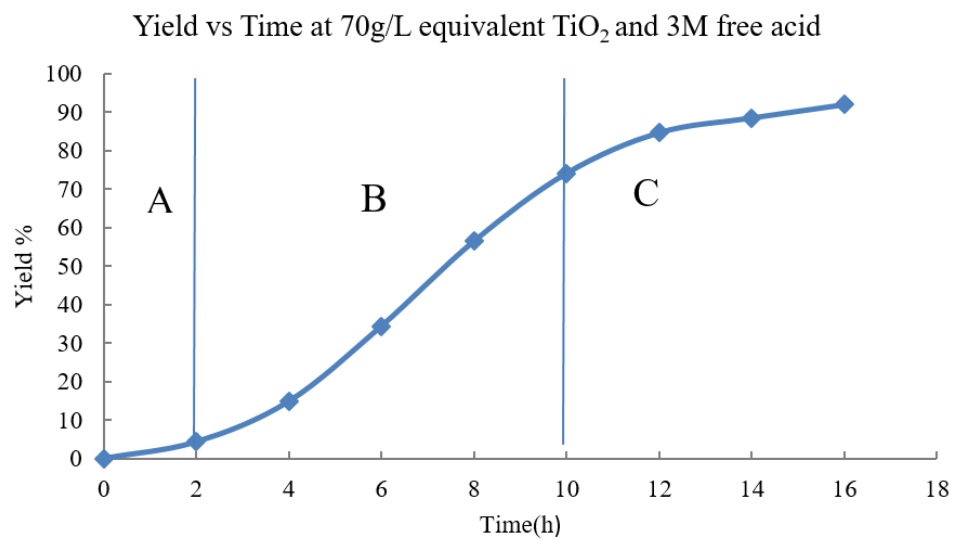


Figure 5.9 Yield%-time curve at 70g/L equivalent TiO_2 with 3M free acid.

CHAPTER 6

CONCLUSIONS

The effect of free acid concentration, and initial equivalent TiO_2 concentration on the particle size, morphology, and hydrolysis rate of titanic acid were investigated. The primary results are concluded as follows:

1. The particle size of titanic acid will increase as the concentration of free acid increases at a constant initial TiO_2 concentration. The particle size distribution of titanic acid powder becomes broader at the same time. Meanwhile, the titanic acid particles become more spherical with a smoother surface as the concentration of free acid increases.

2. At fixed free acid concentration, the particle size of titanic acid will increase as the initial TiO_2 concentration increases. The particle size distribution is broad when the initial TiO_2 concentration is either too low or too high. The titanic acid turns from irregular shaped small particles to round particles with smooth surface as the initial TiO_2 concentration increases. However, particles with unpredictable morphology such as bumps, pores, and needles on the surface were found when initial TiO_2 concentration is too high, such as 115g/L.

3. At fixed initial TiO_2 concentration is a constant, and the hydrolysis rate will become slower as the concentration of free acid increases. The time it takes to reach the equilibrium of the hydrolysis reaction under varied free acid concentration has great difference. For example, at 70g/L of equivalent TiO_2 , it only takes 4 hr to complete the hydrolysis reaction

when free acid concentration is 2M. However, it will take more than 20 hr for the reaction to reach the equilibrium when the concentration of free acid is 3.5M.

4. The hydrolysis rate of titanate acid will decrease as the concentration of equivalent TiO_2 increases under a constant free acid concentration. When free acid concentration is 2.5M, the hydrolysis rate is very fast when TiO_2 concentration is low, such as 40g/L, which takes less than 4 hr to reach the equilibrium of hydrolysis reaction. On the contrary, when initial TiO_2 concentration is 115g/L, the hydrolysis rate becomes extremely slow, the yield of which is around 21% after 13 hr of hydrolysis.

5. To produce relatively coarse TiO_2 powder with round shape and smooth surface, a proper hydrolysis rate has to be used since either a too fast or a too slow hydrolysis rate will lead to irregular particle size and morphology of the final titanate acid particles.

6. The optimized parameters for hydrolysis to produce monodispersed and round titanate acid particles with around 30 μm mean size is concluded as: free acid concentration from 3 to 3.5M with 70g/L of equivalent TiO_2 . Free acid concentration from 2.5 to 3M with 100g/L of equivalent TiO_2 . The hydrolysis is performed at 100°C for 16 hr with continuous agitation of 250 rpm. In fact, the initial equivalent TiO_2 concentration used for the hydrolysis can be from 70 to 100g/L and a free acid concentration corresponding to that TiO_2 concentration can be used to obtain the products with desired size and morphology by following the processes for TiO_2 production in this work; monodispersed pure TiO_2 powder with particle size from 20 to 45 μm and round shape can be prepared.

REFERENCES

- [1] Z. Z. Fang, S. Middlemas, J. Guo, and P. Fan, "A New, Energy-Efficient Chemical Pathway for Extracting Ti Metal from Ti Minerals," *Journal of the American Chemical Society*, vol. 135, no. 49, pp. 18248-18251, 2013/12/11 2013.
- [2] G. Lutjering, *Titanium*. 2007.
- [3] F. H. S. Froes, M. N. Gungor, and M. Ashraf Imam, "Cost-Affordable Titanium: The Component Fabrication Perspective," *Journal of Minerals, Metals and Materials Society*, vol. 59, no. 6, pp. 28-31, 2007.
- [4] W. Kroll, "The Production of Ductile Titanium," *Transactions of the Electrochemical Society*, vol. 78, no. 1, pp. 35-47, 1940.
- [5] J. H. Braun, A. Baidins, and R. E. Marganski, "TiO₂ Pigment Technology: A Review," *Progress in Organic Coatings*, vol. 20, no. 2, pp. 105-138, 1992.
- [6] K. K. Sahu, T. C. Alex, D. Mishra, and A. Agrawal, "An Overview on the Production of Pigment Grade Titania from Titania-Rich Slag," *Waste Management & Research*, vol. 24, no. 1, pp. 74-79, 2006.
- [7] G. McNulty, "Production of Titanium Dioxide," in *Proceedings of NORM V International Conference, Seville, Spain, 2007*, pp. 169-189: Citeseer.
- [8] K. Mohandas and D. Fray, "FFC Cambridge Process and Removal of Oxygen from Metal-Oxygen Systems by Molten Salt Electrolysis: An Overview," *Transaction of Indian Institute of Metals*, vol. 57, no. 6, pp. 579-592, 2004.
- [9] C. G. McCracken, C. Motchenbacher, and D. P. Barbis, "Review of Titanium-Powder-Production Methods," *International Journal of Powder Metallurgy*, vol. 46, no. 5, 2010.
- [10] M. Gueguin and F. Cardarelli, "Chemistry and Mineralogy of Titania-Rich Slags Part 1—Hemo-Ilmenite, Sulphate, and Upgraded Titania Slags," *Mineral Processing and Extractive Metallurgy Review*, vol. 28, no. 1, pp. 1-58, 2007.
- [11] Y. Zhang *et al.*, "A Novel Chemical Pathway for Energy Efficient Production of Ti Metal from Upgraded Titanium Slag," *Chemical Engineering Journal*, vol. 286, pp. 517-527, 2016.

- [12] D. Reyes-Coronado, G. Rodríguez-Gattorno, M. Espinosa-Pesqueira, C. Cab, R. d. de Coss, and G. Oskam, "Phase-Pure TiO₂ Nanoparticles: Anatase, Brookite and Rutile," *Nanotechnology*, vol. 19, no. 14, p. 145605, 2008.
- [13] W. Wang, B. Gu, L. Liang, W. A. Hamilton, and D. J. Wesolowski, "Synthesis of Rutile (A-TiO₂) Nanocrystals With Controlled Size and Shape by Low-Temperature Hydrolysis: Effects of Solvent Composition," *The Journal of Physical Chemistry B*, vol. 108, no. 39, pp. 14789-14792, 2004.
- [14] Y. Liu *et al.*, "Preparation of Rutile TiO₂ by Hydrolysis of TiOCl₂ Solution: Experiment and Theory," *RSC Advances*, vol. 6, no. 64, pp. 59541-59549, 2016.
- [15] L. Piccolo, A. Paolinelli, and T. Pellizzon, "Process for the Hydrolysis of Titanium Sulphate Solutions," Google Patents, 1977.
- [16] M. J. Gázquez, J. P. Bolívar, R. Garcia-Tenorio, and F. Vaca, "A Review of the Production Cycle of Titanium Dioxide Pigment," *Materials Sciences and Applications*, vol. 2014, 2014.
- [17] W. Mo, G. Deng, and F. Luo, *Titanium Metallurgy*. Beijing, 1998.
- [18] J. W. Mullin, *Crystallization*. Butterworth-Heinemann, 2001.
- [19] H. S. Holger, "Titanium Dioxide Pigment Production," Google Patents, 1949.
- [20] C.-X. Tian *et al.*, "Influence of Hydrolysis in Sulfate Process on Titania Pigment Producing," *Transactions of Nonferrous Metals Society of China*, vol. 19, pp. s829-s833, 2009.
- [21] E. R. Lawhorne, "Titanium Dioxide With High Purity and Uniform Particle Size and Method Therefore," Google Patents, 1990.
- [22] P. Run, "Sulfate Process TiO₂ Pigment Production," Beijing: Chemical Industry Press, 1991.
- [23] S. J. Gerdemann, "Titanium Process Technologies," *Advanced Materials & Processes*, vol. 159, no. DOE/ARC-2002-007, 2001.
- [24] J. Winkler, *Titanium dioxide: production, properties and effective usage*. Vincentz Network, 2013.
- [25] G. Li, L. Li, J. Boerio-Goates, and B. F. Woodfield, "High Purity Anatase TiO₂ Nanocrystals: Near Room-Temperature Synthesis, Grain Growth Kinetics, and Surface Hydration Chemistry," *Journal of the American Chemical Society*, vol. 127, no. 24, pp. 8659-8666, 2005.
- [26] I.-S. Park, S.-R. Jang, J. S. Hong, R. Vittal, and K.-J. Kim, "Preparation of Composite Anatase TiO₂ Nanostructure by Precipitation from Hydrolyzed TiCl₄

- Solution Using Anodic Alumina Membrane," *Chemistry of Materials*, vol. 15, no. 24, pp. 4633-4636, 2003.
- [27] J. Jean and T. Ring, "Nucleation and Growth of Monosized Titania Powders from Alcohol Solution," *Langmuir*, vol. 2, no. 2, pp. 251-255, 1986.
- [28] S. J. Kim, S. D. Park, Y. H. Jeong, and S. Park, "Homogeneous Precipitation of TiO₂ Ultrafine Powders from Aqueous TiOCl₂ Solution," *Journal of the American Ceramic Society*, vol. 82, no. 4, pp. 927-932, 1999.
- [29] Y. Zhu, L. Zhang, C. Gao, and L. Cao, "The Synthesis of Nanosized TiO₂ Powder Using A Sol-Gel Method With TiCl₄ as a Precursor," *Journal of Materials Science*, vol. 35, no. 16, pp. 4049-4054, 2000.
- [30] E. A. Barringer and H. K. Bowen, "High-Purity, Monodisperse TiO₂ Powders by Hydrolysis of Titanium Tetraethoxide. 1. Synthesis and Physical Properties," *Langmuir*, vol. 1, no. 4, pp. 414-420, 1985.
- [31] S. Eiden-Assmann, J. Widoniak, and G. Maret, "Synthesis and Characterization of Porous and Nonporous Monodisperse Colloidal TiO₂ Particles," *Chemistry of Materials*, vol. 16, no. 1, pp. 6-11, 2004.
- [32] S. Middlemas, Z. Z. Fang, and P. Fan, "A New Method for Production of Titanium Dioxide Pigment," *Hydrometallurgy*, vol. 131, pp. 107-113, 2013.
- [33] Y. Zhang, T. Qi, and Y. Zhang, "A Novel Preparation of Titanium Dioxide from Titanium Slag," *Hydrometallurgy*, vol. 96, no. 1, pp. 52-56, 2009.
- [34] L. Yahui, M. Fancheng, F. Fuqiang, W. Weijing, C. Jinglong, and Q. Tao, "Preparation of Rutile Titanium Dioxide Pigment from Low-Grade Titanium Slag Pretreated by the Naoh Molten Salt Method," *Dyes and Pigments*, vol. 125, pp. 384-391, 2016.
- [35] V. K. LaMer and R. H. Dinegar, "Theory, Production and Mechanism of Formation of Monodispersed Hydrosols," *Journal of the American Chemical Society*, vol. 72, no. 11, pp. 4847-4854, 1950.
- [36] N. T. Thanh, N. Maclean, and S. Mahiddine, "Mechanisms of Nucleation and Growth of Nanoparticles in Solution," *Chemical Reviews*, vol. 114, no. 15, pp. 7610-7630, 2014.
- [37] T. Sugimoto, *Monodispersed particles*. Elsevier, 2001.
- [38] T. Sugimoto, "Preparation of Monodispersed Colloidal Particles," *Advances in Colloid and Interface Science*, vol. 28, pp. 65-108, 1987.
- [39] T. Sugimoto, F. Shiba, T. Sekiguchi, and H. Itoh, "Spontaneous Nucleation of Monodisperse Silver Halide Particles from Homogeneous Gelatin Solution I: Silver

- Chloride," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 164, no. 2, pp. 183-203, 2000.
- [40] T. Sugimoto, X. Zhou, and A. Muramatsu, "Synthesis of Uniform Anatase TiO₂ Nanoparticles by Gel–Sol Method: 1. Solution Chemistry of Ti(OH)_n(4–n)⁺ Complexes," *Journal of Colloid and Interface Science*, vol. 252, no. 2, pp. 339-346, 2002.
- [41] J. D. Gilchrist, "Extraction Metallurgy," *Pergamon Press plc*, 1989, p. 431, 1989.
- [42] J. Kong, B. Chao, T. Wang, and Y. Yan, "Preparation of Ultrafine Spherical AlOOH and Al₂O₃ Powders by Aqueous Precipitation Method With Mixed Surfactants," *Powder Technology*, vol. 229, pp. 7-16, 2012.
- [43] W. Stöber, A. Fink, and E. Bohn, "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," *Journal of Colloid and Interface Science*, vol. 26, no. 1, pp. 62-69, 1968.
- [44] S. Doeuff, M. Henry, C. Sanchez, and J. Livage, "Hydrolysis of Titanium Alkoxides: Modification of the Molecular Precursor by Acetic Acid," *Journal of Non-crystalline Solids*, vol. 89, no. 1-2, pp. 206-216, 1987.
- [45] Y.-S. Her, S.-H. Lee, and E. Matijević, "Continuous Precipitation of Monodispersed Colloidal Particles. II. SiO₂, Al(OH)₃, and BaTiO₃," *Journal of materials research*, vol. 11, no. 01, pp. 156-161, 1996.
- [46] G. Bogush and C. Zukoski, "Studies of The Kinetics of the Precipitation of Uniform Silica Particles Through the Hydrolysis and Condensation of Silicon Alkoxides," *Journal of Colloid and Interface Science*, vol. 142, no. 1, pp. 1-18, 1991.
- [47] G. Bogush and C. Zukoski, "Uniform Silica Particle Precipitation: An Aggregative Growth Model," *Journal of Colloid and Interface Science*, vol. 142, no. 1, pp. 19-34, 1991.
- [48] J. Livage, M. Henry, and C. Sanchez, "Sol-Gel Chemistry of Transition Metal Oxides," *Progress in Solid State Chemistry*, vol. 18, no. 4, pp. 259-341, 1988.
- [49] J. Livage, C. Sanchez, M. Henry, and S. Doeuff, "The Chemistry of the Sol-Gel Process," *Solid State Ionics*, vol. 32, pp. 633-638, 1989.
- [50] R. S. Sapiieszko and E. Matijević, "Preparation of Well-Defined Colloidal Particles by Thermal Decomposition of Metal Chelates. I. Iron Oxides," *Journal of Colloid and Interface Science*, vol. 74, no. 2, pp. 405-422, 1980.
- [51] R. Demchak and E. Matijević, "Preparation and Particle Size Analysis of Chromium Hydroxide Hydrosols of Narrow Size Distributions," *Journal of Colloid and Interface Science*, vol. 31, no. 2, pp. 257-262, 1969.

- [52] D. Hague and M. Mayo, "The Effect of Crystallization and a Phase Transformation on the Grain Growth of Nanocrystalline Titania," *Nanostructured Materials*, vol. 3, no. 1-6, pp. 61-67, 1993.
- [53] A. Chittofrati and E. Matijević, "Uniform Particles of Zinc Oxide of Different Morphologies," *Colloids and Surfaces*, vol. 48, pp. 65-78, 1990.
- [54] C. J. Brinker and G. W. Scherer, *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press, 2013.
- [55] L. L. Hench and J. K. West, "The Sol-Gel Process," *Chemical Reviews*, vol. 90, no. 1, pp. 33-72, 1990.