The Effects of Leaching Process to the TiO₂ Synthesis from Bangka Ilmenite

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Abstract. Ilmenite mineral is a naturally occurring iron titane (FeTiO₃) and is abundant in nature. The separation of components into TiO₂ and Fe₂O₃ must be expand. The purpose of this research is to synthesis TiO₂ nanoparticles from the filtrate of Bangka ilmenite leaching process. Leaching of ilmenite was done with H₂SO₄ and HCl at various concentrations. The formation of TiO₂ crystal determined by hydrolysis conditions and condensation reaction. TiO₂ synthesized from the filtrate of sulfuric acid leaching that produced from TiO₂ anatase phase when hydrolyzed in an aquaregia solvent and low concentrations of HCl (0.1M). Hydrolysis conditions at higher concentrations of HCl (1M) was produced TiO₂ anatase-rutile phase. The synthesis of TiO₂ from the filtrate of hydrochloric acid leaching was produced anatase phase. While the condition under the alcoholic solvent (2-propanol: H₂O (v/v) = 9: 1) anatase phase crystallites grow in the temperature range up to 550 °C, above this temperature, TiO₂ transform into rutile phase.

1. Introduction
Titanium dioxide (TiO₂) is a semiconductor that has been widely used as raw materials of paint, paper and plastic industry [1]. TiO₂ has also a potential for applications of a gas sensor, environmental cleanup and photovoltaic cells [2]. TiO₂ is widely studied as the base material of DSSC (Dye-sensitized solar cell). Two important phases of TiO₂ are anatase and rutile. TiO₂ P25 commercial from Degussa is produced from these two phases with an exact precise ratio of 70% anatase phase and 30% rutile phase. The optical properties and electrical properties of anatase and rutile are different. Studies have shown that the preparation methods [4], dopant concentrations [5], atmospheres [6] and particle size [7] can affect the anatase-rutile phase transformation, although each influence is unclear explained. Crystal size (grain size) is also very important to notice. Anatase synthesis would obtained less than 15 nm crystal size, whereas 100% rutile is not possible with small crystals size [8].

Anatase-rutile phase content, as well as crystal size are important characters of TiO₂ crystals. The two variables are connected to each other. The transformation of anatase phase into rutile phase is believed to be spontaneous, but not suitable for very low temperatures [9]. Anatase is a tetragonal system that strongly influenced by the size of the crystals. At high temperatures, a tetragonal system is more easily formed, whereas at lower temperatures monoclinic more easily formed. This is influenced by the TiO₂ rutile phase that more thermodynamically stable [9].
TiO$_2$ anatase is widely produced through sulfate process. Hydrolysis of Titanium (IV) Sulfate, purification of titanium dioxide hydrate and calcination, are factors that affect TiO$_2$ formation. Polymeric transformation is common in wide area temperatures between 400-1100 °C. Solid phase reactions have been observed to occur at 700-900 °C temperature region [10]. Anatase-rutile transformation influenced by the synthesis procedure of TiO$_2$, crystal size, temperature and time of calcination [8]. These factors can be used as a control of rutile-anatase transformation and plotting the composition of TiO$_2$ products and their properties.

2. Experimental
2.1 Pre-oxidation and Characterization of Bangka Ilmenite
Ilmenite was crushed and sieved using 180 mesh sieve. Then ilmenite was dried at 120 °C for 2 hours. Pre-oxidation is done by taking 5 grams of each ilmenite in 20 mL porcelain crust and roasting at 900 °C. The preparation process for more details has been published [10].

2.2 Leaching process
5 grams ilmenite from the roasting result in each experiment then added by iron powder (Fe$^0$) with the ratio of ilmenite:Fe$^0$ = 5:1 (w/w). The concentration of HCl used for leaching process is 4M, 6M, and 8M. While for the sulfate process, is using H$_2$SO$_4$ in several concentration (2, 3, 4, 5, 6, 7, 8 and 9 M). The acid solution was heated at ±105 °C until a boiled. 5 gram of ilmenite was inserted and heated for 20 minutes. 1 gram of Fe$^0$ is added and the leaching process is continued for 2 hours. Procedures without the addition of Fe$^0$ were also observed.

2.3 Synthesis of TiO$_2$ from filtrate ilmenite leaching
The synthesis of TiO$_2$ was carried out by hydrolysis and condensation process using aquades and 2-propanol. The filtrates are hydrolyzed and condensed by:

a) 200 mL aquades was heated at 60 °C, then the filtrate is added into warm aquades to obtain a white precipitate. TiO$_2$ xerogel washing was done with HCl 1M and aquaregia.

b) The filtrate is added to the 2-propanol and H$_2$O mixture with the ratio of 2-propanol:H$_2$O (v/v) 9:1, 8:2, 7:3, 6:4 and 5:5. Therefore, it’s allowed to precipitate and decanted. TiO$_2$ xerogel then washed with HCl 0.1 M.

3. Result and Discussion
3.1 Synthesis of TiO$_2$ Anatase-Rutile with Sulfate Process
The synthesis of TiO$_2$ from the filtrate of sulfate leaching at high concentration (H$_2$SO$_4$ 9M) was showed not rutile phase (Fig. 1). This is due to the using of high concentrations H$_2$SO$_4$ that able to dissolve ilmenite and natural rutile. Fig. 1 shows the diffractogram of TiO$_2$ microcrystalline and TiOSO$_4$ hydrolysis results before calcination. By calculation with Scherrer formulation, relatively small crystallite size (<10 nm) was obtained.

![Figure 1. Diffractogram of TiO$_2$ anatase (H$_2$SO$_4$ 9M) after washing HCl:HNO$_3$ (v/v) = 3:1](image)
TiO$_2$ washing is also affect the determination of a crystal phase. TiO$_2$ xerogel washing with aquaregia shows no formation of rutile phase (Fig. 1). The rutile phase can be produced from the preparation of TiO$_2$ xerogel by HCl 1M washing (Fig. 2). Peaks at 27.43°(d$_{110}$); 36.08°(d$_{101}$) was the characteristic peaks of rutile in accordance with the standard JCPDS No. 89-0920. This is influenced by a faster hydrolysis process at higher concentrations. Although, it appears that the TiO$_2$ microcrystalline is still amorphous with crystal size 8 nm, TiO$_2$ xerogel washing with HCl 1M able to form rutile phase. The highly acidic conditions in the TiO$_2$ show as a rutile phase with crystalline size above 15 nm, as has been done by previous researchers [9].

**Figure 2. Diffractogram of TiO$_2$ anatase-rutile after washing HCl 1M**

The hydrolysis and condensation reactions of TiO$_2$ formation shown in the reaction equation (1) and reaction equation (2):

$$\text{TiOSO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{TiO}(_2)\text{H}_2\text{O}_2(aq) + \text{H}_2\text{SO}_4(aq) + 2 \text{Cl}^-$$  
$$\text{TiO}(_2)\text{H}_2\text{O}_2(aq) \rightarrow \text{TiO}_2(s) + \text{H}_2\text{O}(l) + 2 \text{Cl}^- \quad (2)$$

The other experimental conditions, washing treatment with HCl solution (HCl 0.1 M) indicates a greater ability to suppress rutile phase Fig. 3. Condensation in this process runs better. HCl 0.1 M solution has also acted as a catalyst for acid hydrolysis process. This annealing process is performed at relatively low temperatures (450°C). Anatase-rutile phase has obtained with anatase phase more dominant. Peaks at 25.31°(d$_{101}$); 48.04°(d$_{200}$); and 37.79°(d$_{004}$) was the characteristic peaks of anatase in accordance with the standard JCPDS No. 78-2486.

**Figure 3. Diffractogram of TiO$_2$ from leaching residue (H$_2$SO$_4$ 2 M) after washing HCl 0.1 M.**

before and after annealing at 450 °C for 2 h.
3.2 Synthesis of TiO$_2$ Anatase Phase with Chloride Process

The condensation process at very acidic conditions was running slowly. The addition of 2-propanol may substitute the titanyl (TiOH) group to produce titanium isopropoxide. The synthesis of TiO$_2$ from this process was carried out using filtrate from leaching process with HCl 6M. The condensation process begins by changing the solvent conditions by addition of 2-propanol alcoholic solvents to various comparisons. The ratio of 2-propanol: H$_2$O(v/v) = 9:1 showed the condensation of titania sol gel. The hydrolysis and filtrate condensation reaction of the hydride solvent that dissolved in 2-propanol: H$_2$O (v/v) = 9:1 solvent possibly passes the reaction equation (3) and (4):

$$\text{TiOCl}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O} \text{Pr}} \text{TiO(OiPr)}_2 + 2\text{HCl} \quad (3)$$

$$\text{TiO(OiPr)}_2 \xrightarrow{\text{H}_2\text{O}} \text{TiO}_2 + \text{H}_2\text{O} \quad (4)$$

The titania sol-gel then separated, dried, washed with HCl 0.1 M, and calcinated at 450 °C. Fig. 4 showed TiO$_2$ that hydrolyzed by filtrate condensation of hydrated solution from the chloride process that using H$_2$O:2-propanol(v/v) = 9:1 as solvent. This process followed by HCl 0.1 M washing. The chloride process can not produce rutile until the annealing temperature reach 450 °C. The crystal size then calculated by the Sherrer formula, and obtain 60nm as the result. But that was not indicated a change to the rutile phase.

![Figure 4](image-url)

**Figure 4.** Diffractogram of TiO$_2$ from leaching HCl 6M washing HCl 0,1 M. Annealing at 450 °C 2h.

TEM analysis is used to determine the crystal size (grain size), crystallinity, and sample morphology. TEM results from TiO$_2$ nanopowder with high anatase abundance is shown in Figure 5 (a), while the lower anatase phases shown in Figure 5 (b). The bright field of TEM result in TiO$_2$ nanopowder exhibited a dominant anatase phase (Fig. 5 (a)), in line with the XRD results in Fig. 3. The morphological appearance of the anatase nanopowder was spherical (<10nm). Fig. 5b. is a synthesized TiO$_2$ nanopowder from TiOSO$_4$ ilmenite that dissolved in H$_2$SO$_4$ 3M after annealing at 600 °C. The rutile phase is more abundant (darker areas) compared to TiO$_2$ nanopowder synthesized from TiOSO$_4$ using lower H$_2$SO$_4$ concentrations (Fig. 5b.), with a spherical morphology of 10-15 nm. The crystal size results from the TEM analysis shows an equivalent value after calculated by Scherrer formula.

![Figure 5](image-url)

**Figure 5.** TEM of titanium dioxide from leaching filtrate with H$_2$SO$_4$ 2M, annealing at (a) 450 °C (b) 600 °C
3.3 Thermal Process of Formation of Rutile Anatase Phase
The crystallization of TiO$_2$ anatase phase occurs over a relatively wide temperature range up to 550 °C. TGA Thermogram (Fig. 6.) shows a very significant mass decrease that up to 400 °C heating temperature. The mass degradation in the early process is related to the dehydration and the polymerization condensation process. While the crystallization process that occurs in the next stage does not cause a significant mass loss that indicated by the endothermic process on a very clear DTA thermogram (Fig. 6.).

![Graph showing TGA/DTA thermogram](image)

**Figure 6.** Thermogram of the TGA/DTA sample of the condensed TiO$_2$ xerogel from leaching filtrates with H$_2$SO$_4$ measured up to a temperature of 700 °C. Line - is TGA curve profile and line - is DTA curve profile.

![Graph showing XRD patterns](image)

**Figure 7.** XRD TiO$_2$ as measured from the variation of annealing TiO$_2$ at (a) 150 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C. TiO$_2$ is synthesized from the starting material of titanium tetraisopropoxide [10].

The data of TGA/DTA and XRD to the temperature variation (Fig. 7) of TiO$_2$ synthesized using the starting material of titanium isopropoxide as pure TiO$_2$, it appears that anatase phase crystallites exist in the temperature range, up to 500 °C. In XRD TiO$_2$ annealing temperature of 600 °C and 700 °C, there has been anatase phase change into rutile. In the TGA/DTA thermogram of this temperature range, appears to be a slight decrease in mass. The density of the crystal occurs when anatase phase transform into rutile phase.

The formation of anatase and rutile phase comes through different approaches. This difference in approach and orientation has been shown to be influenced by the environmental state of the solvent and the pH system associated with the energy that accompanies the process. The very high acid
concentration is believed to cause the formation of anatase nuclei impaired and leads to the formation of a thermodynamically more easily formed rutile nucleus. Post and Burnham in 1986 [12] have demonstrated thermodynamic calculations that rutile is more stable than anatase with a Gibbs-free energy difference of $\sim 4$ kJ/mol and more stable than brookite with a Gibbs-free energy difference of $\sim 20$ kJ/mol.

4. Conclusion
Synthesis of TiO$_2$ can be worked out from filtrate of leaching ilmenite after roasting process. The formation of the TiO$_2$ crystalline phase is strongly determined by the current conditions of hydrolysis and condensation reactions which include acidity (pH), solvents, and environmental conditions for crystalline growth. The synthesis of TiO$_2$ from filtrate of diluted H$_2$SO$_4$ pathway resulted in anatase phase TiO$_2$ when hydrolyzed at aqua regia solvent condition and relatively low concentration HCl (0.1M), while hydrolysis at higher HCl concentration conditions (1M) yielded anatase-rutile TiO$_2$ phase. While the synthesis of TiO$_2$ from filtrate of diluted HCl solution yields TiO$_2$ anatase phase when hydrolyzed at 2-propanol:H$_2$O(v/v) = 9:1. Anatase phase crystallites grow in the temperature range up to 550 °C, at the above temperature undergoing phase transformation into rutile phase.

References
[1] Nayl A A, Awward N S, dan Aly H F 2009 J. Hazard. Mat. 168 793–799
[2] Zhang Y, Tao Q, dan Zhang Y 2009 Hydrometall. 96 52–56
[3] O’Regan B and Grätzel M. 1991 Nature 353 737-739
[4] Wilska, Seppo 1954 Acta Chemica Scandinavica 8
[5] MacKensize K J D 1975 Trans. J. Brit. Ceram. Soc. 74 29-34
[6] Banfield, Jillian F, Bishoff, Brian L, Marc A, Anderson 1993 Chem. Geol. 110
[7] Wahyuningsih S, Rahardjo S B, Pramono E, Hidayatullah H, Anatolia F, Sulistiyono E, Firdiyono F 2013 Asian J. Chem. 25(12) 6791-6794
[8] Wahyuningsih S, Kartini I, Narsito 2010 Eksakta 11(1) 1-8
[9] Post J E, Burnham C W 1986 American Mineralogist 71 142-150
[10] Wahyuningsih S, Pramono E, Firdiyono F, Sulistiyono E 2013 Asian J. Chem. 25(12) 6791-6794