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Effect of calcination temperature on the characteristics of TiO_2 synthesized from ilmenite and its applications for photocatalysis

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Abstract. Titanium dioxide (TiO_2) contained in the Ilmenite Bangka mineral was synthesized by varying the calcination temperature to obtain characteristics that can improve the photocatalytic ability. It can be a solution to handling of waste in the textile industry. Synthesis starts from a caustic fusion process using NaOH to decompose of ilmenite into the titanate compound were more soluble in acid, so that can reduce acid consumption in the leaching process. The leaching process uses 8 M H_2SO_4 in 5% solid to produce TiOSO_4 as a filtrate. Then the filtrate was hydrolyzed to obtain the precipitate $\text{TiO}_2\text{-Fe}_2\text{O}_3$. Calcination with variation of temperature was came after leached the precipitate with the water until neutral pH is obtained. The temperature used is: 350 °C (TiO_2 T₁), 450 °C (TiO_2 T₂), 550 °C (TiO_2 T₃), 650 °C (TiO_2 T₄), and 750 °C (TiO_2 T₅). The results of photocatalytic activity test using a solution of Rhodamin B (RhB) and Methylene Blue (MB) revealing that the highest photocatalyst efficiency was achieved by TiO_2 which calcined at a temperature of 650 °C, with 69.33% (RhB) and 83.41% (MB). Where in this temperature, rutile phase began to form about 15.38%, the band gap energy on 2.4 eV, and the growth of crystalite size become 53.41 nm which affected the increase in photocatalytic activity.

1. Introduction

Titanium dioxide (TiO_2) is one of semi-conductor material which is one of the products from ilmenite oxide minerals (FeTiO_3) [11]. In Indonesia Ilmenite reserves are very abundant as a result of tin ore processing by-products on the island of Bangka [1]. This material has been widely used in applications in various fields such as paint pigments, cosmetics, solar cells, sensors, photocatalysts and others [4].

The synthesis process of TiO_2 uses large amounts of acid reagent with relatively high production prices. As Aristanti (2016) stated, that to make 1 ton of TiO_2 will produce 8 tons of dilute sulfate waste, so to reduce the negative impact, a new alternative method used namely caustic fusion [18]. The caustic fusion aims to decompose a mineral or sample using reactive alkali compounds such as NaOH and KOH [4]. This will make it easier for the TiO_2 compound to dissolve in acidic solutions [2, 3, 5].



In this research, we want to know about the photocatalytic ability of TiO_2 for being catalyst to decompose the waste of textile industry. Photocatalysis itself is a chemical reaction that utilizes the absorption of ultraviolet (UV) light energy which is accelerated by the presence of a catalyst [2, 3, 4]. Photon energy absorption will activate the catalysis process and produce hydroxyl radicals which will degrade an organic pollutant and produce an environmentally friendly end product [16]. Photocatalytic reactions begin with the formation of electron-hole pairs in semiconductor particles. If a semiconductor absorbs energy equal to or greater than the energy of the band gap, then electrons (e^-) in the valence band (valence band, VB) will be excitation to the conduction band (CB), leaving a positive hole (hole, h^+) Thermodynamically, the energy level of a conduction band (E_{CB}) is a measure of electrons' reduction strength in semiconductors, whereas the energy level of a valence band is a measure of hole oxidation power [16].

Many factors will affect to the photocatalytic activity of TiO_2 in the synthesis process. One of them is the calcination temperature. Calcination aims to eliminate the water content which trapped in TiO_2 [2, 3]. Besides that calcination will change the structure of TiO_2 which is still amorphous to crystalline. The change of crystalite structure is accompanied by a phase transformation from anatase to rutile phase. This transformation in crystalite structure is closely related to energy balance as a function of crystallite size [2]. The anatase phase tends to be unstable at high temperatures, so that the higher calcination temperature of the anatase particles stick together to form the larger particles and the interface of the anatase particles then becomes the rutile phase spinning point [6]. During the transformation process an electron-hole pair will be formed on the crystal structure that will activate the photocatalyst process [7].

In addition to TiO_2 , Fe_2O_3 also dissolves and is extracted into impurities. However, according to Rias and Das (2004), this will have a good effect on photocatalyst applications because it can slow down phase transformations from anatase to rutile and also reduce the band gap energy of the TiO_2 itself. In addition, Fe_2O_3 can also prevent recombination of electrons from the conduction band to the valence band so that photocatalyst activity increases [8].

2. Experimental Procedures

2.1 Synthesis of TiO_2

200 mesh of high grade ilmenite concentrate was mixed with Merck 99% NaOH with a mol ratio of 1: 4 [5], then done the caustic fusion at a temperature of 650 °C for 2 hours until got the frit as the product. To remove the salt compounds from the caustic fusion product, frit was leached by water with a ratio of 1: 5 (w / v) [18]. After that, leached the frit used the sulfate method to dissolve TiO_2 compound and produce TiOSO_4 as a precursor. Then the precursors was hydrolyzed with the sol-gel method [15] by adding NH_4OH 10% to get a pH of 1.00 with a temperature of 90 °C for 2 hours to form $\text{TiO}(\text{OH})_2$ precipitates. Finally calcination process was conducted with temperature variations 350 °C (TiO_2 T₁), 450 °C (TiO_2 T₂), 550 °C (TiO_2 T₃), 650 °C (TiO_2 T₄), and 750 °C (TiO_2 T₅) with 1 hour holding time.

2.2 Photocatalytic Activity TiO_2

To find out the efficiency of photocatalyst activity, TiO_2 was applied to Rhodamin B and Metilen Blue solutions. The concentration used in the solution is 50 ppm with 0.1 gram of TiO_2 . The solution that has been mixed with TiO_2 then left under solar radiation for 1.5 hours.

2.3 Instrumentations

In this research, we use 4 instruments to characterize the samples. To find out the compounds contained in ilmenite concentrate XRF was carried out. To determine the Ti and Fe concentrations found in TiOSO_4 precursors, AAS analysis was carried out. From the concentration of Ti and Fe, recovery can be obtained from the extraction results. Then on synthetic TiO_2 samples XRD tests were performed in order to identify phases and calculate the size of crystallites formed at each temperature change using the Scherrer equation, $L = k\lambda/\beta \cos \theta$ [14]. And the last to find out the efficiency of photocatalysis, UV-Vis analysis was performed on RhB and MB solution resulting from photocatalysis test. In addition to UV-Vis on RhB and MB solutions, UV-Vis was also carried out for TiO_2 synthesis powder to determine band gap energy using the Kubelka Munk method.

3. Results and Discussion

3.1 Analysis of TiO_2 Synthesis Results

XRF results conducted by Mulyono (2017) stated that the TiO_2 content of high grade Bangka ilmenite had the highest percentage compared to other compounds that are 45.13% while Fe_2O_3 content is 32.15% [3]. Based on the visuals of titanium dioxide from calcination temperature variations, it can be seen that the higher of temperature, then more brown the color produced as shown in Figure 1. This is due to the thermal expansion of the lattice which occurs reversible. Besides that brownish color was obtained because of the many compounds of Fe_2O_3 which are oxidized at high temperatures.

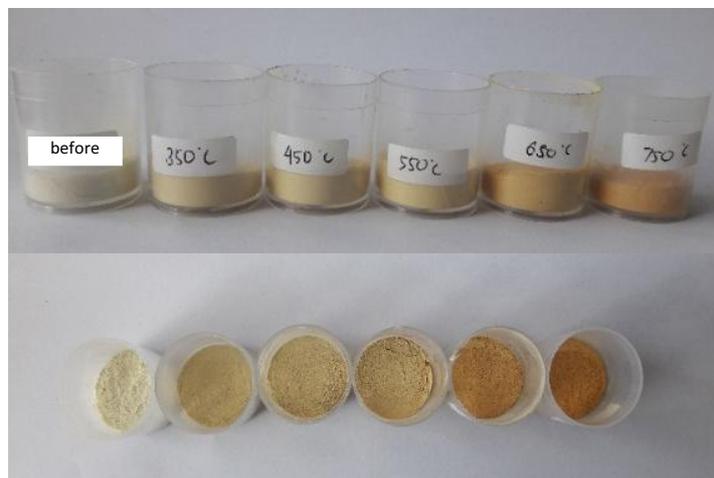


Figure 1. Visualization of TiO_2 synthesized

3.2 Effect of Calcination Temperature on TiO_2 Characteristics

The effect of calcination temperature on phase formation can be seen from the XRD test results which shown in Figure 2. In the literature, it was explained that TiO_2 compound with the crystal structure of anatase marked by the maximum intensity appears at an angle of 2θ about 25° [19]. If the maximum intensity changes it is an indication that the rutile phase appears.

Figure 2 explained that the transformation from anatase to rutile was slow, because rutile appeared in T4 (Temperature of calcination at 650 °C) with a percentage of 15.38%. But, in T5 (Temperature of calcination at 750 °C) percentage of rutile rises significantly up to 89.57%. It caused the maximum intensity has changed to an angle of 2θ about 27°. The slowness of phase transformation occurs due to the presence of Fe_2O_3 impurities in the synthesis product [2, 8]. Furthermore, Fe_2O_3 can reducing the band gap energy [8] and prevent recombination of electrons from conduction band to valance band [10].

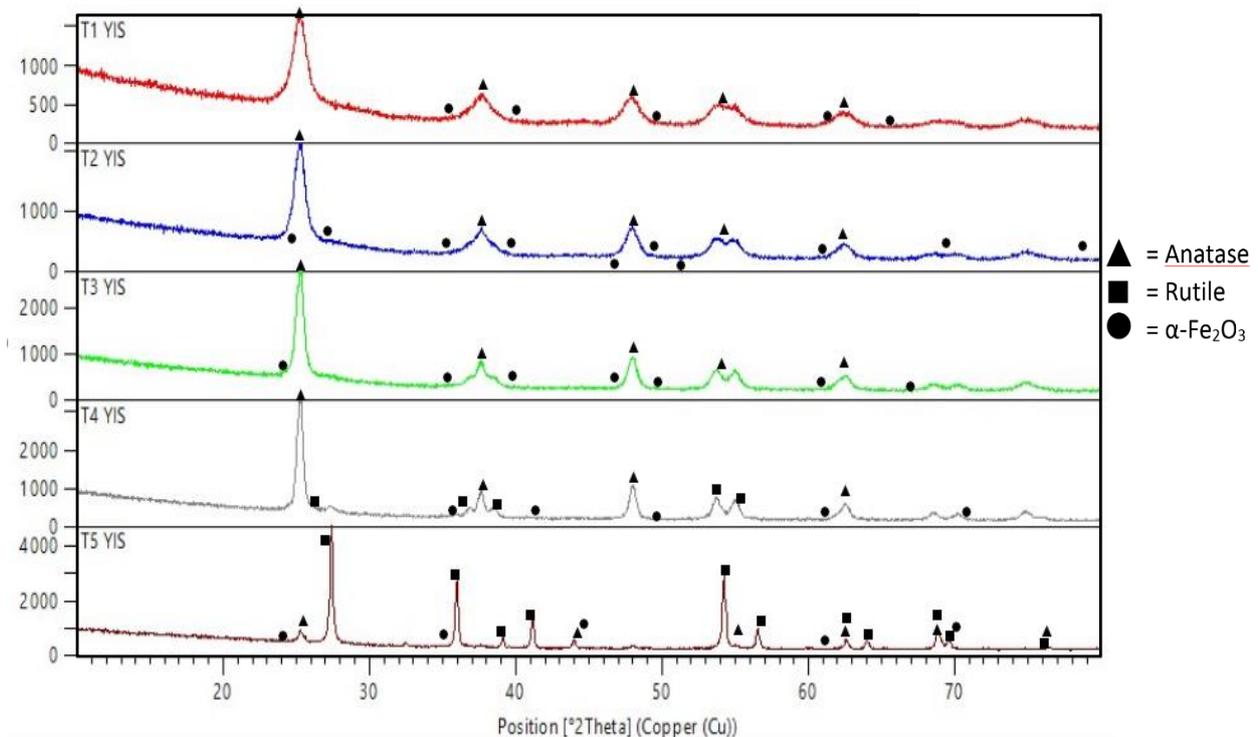


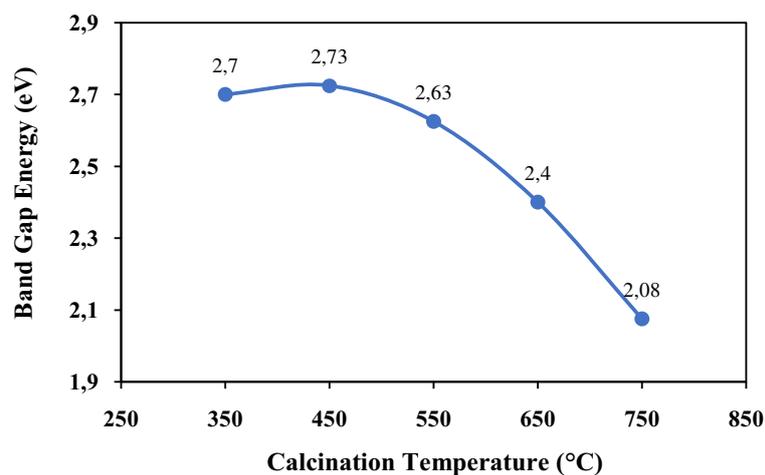
Figure 2. XRD pattern of TiO_2 synthesized

Besides the phase transformations, from the diffraction pattern can determine the size of crystallites using the Scherrer equation. The results of Scherrer's calculations can be seen in table 1. The higher calcination temperature will produce larger crystallite sizes. As Zang (2006) stated, the instability of the anatase phase at high temperatures causes anatase particles stick together to form larger particles and the interface of the anatase particles will become the rutile phase nucleation [6].

Table 1. The size of crystallite TiO₂ at each increase in calcination temperature

Sampel	Size(nm)
T1	5,66
T2	8,8
T3	11,31
T4	53,41
T5	104,89

The temperature of calcination indirectly affected to the band gap energy value. The curve in Figure 3 obtained from UV-Vis powder testing using the Kubelka Munk method. More higher of calcination temperature make the band gap energy will decrease. It caused by presence of Fe₂O₃ as impurity which have a theoritical band gab energy around 2.2 - 2.3 eV [9]. Furthermore, appearance of Fe as impurities also changes the electron configuration of the TiO₂ system, so the band gap energy to decrease [17].

**Figure 3.** Effect of calcination temperature on TiO₂ band gap energy

The decreasing of band gap energy value affected to the photocatalytic ability for TiO₂. Photocatalysis mechanism start from the excitation of electrons (e⁻) from valence band to conduction band and leaves a positive hole (h⁺) in the valence band. The positive hole (h⁺) will react with H₂O to form OH[·] free radicals as oxidizing agents. On the other hand, the electrons (e⁻) in conduction band will react with O₂ to form O²⁻ free radicals as reducing agents. That pairs agent can reduce the amount of metal ion and organic compound in solution and produce the friendly environment solution.

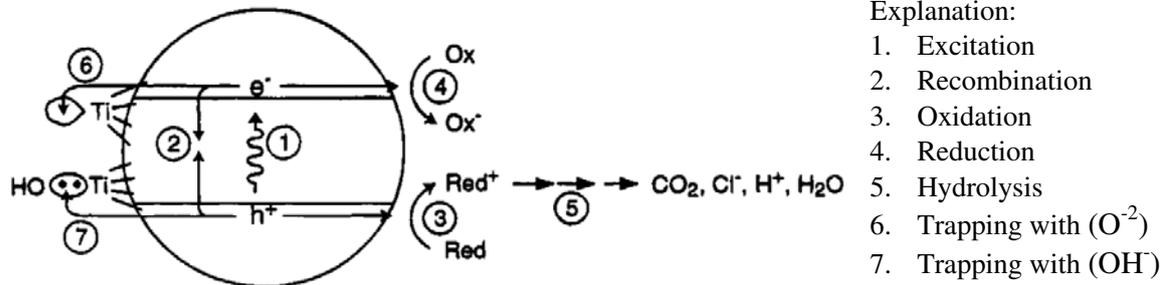


Figure 4. Photocatalysis Mecanism [16]

Low band gap energy causing the process runs faster and make the forming of reducing and oxidizing agent runs fast too. Because we just need a smaller energy to make the electrons (e⁻) excited from valence band to conduction band rather than the larger band gap energy. Consequently, the degradation process will reaching the maximum level and photocatalytic activity of TiO₂ increases

3.3 Photocatalytic Activity of TiO₂

The discussion above is very affected for photocatalyst activities. The phase, the crystal size, and the band gap energy of TiO₂ will affect the decomposition level of RhB and MB solutions. In a previous study conducted by Fujisima and Honda (1972) explained that the anatase phase produces optimal photocatalysts. However, after further investigation and research, TiO₂ with the anatase phase system and rutile mixture showed higher photocatalyst activity than each phase individually [13]. This provides a synergistic effect that can improve photocatalyst efficiency more significantly.

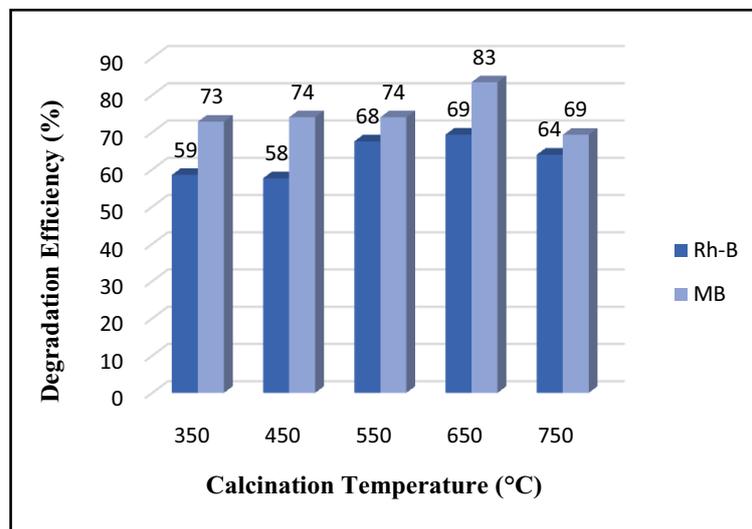


Figure 5. The degradation efficiency of TiO₂ with the calcination temperature variable

Evidently, the results of photocatalyst testing using the Rh-B and MB solution reached the maximum level at 650 °C of calcination temperature. When the rutile phase begin to form about 15.38%, the crystal size growth to 53.41 nm and the band gap energy decreases to 2.4 eV. As shown in Figure 5 the degradations efficiency a chief. However, at 750 °C temperature degradation efficiency dropping off. It caused by the size of the crystallite is too large so that the specific surface area decreases. Then, at this temperature the percentage of rutile rises significantly up to 89.57% makes the band gap energy too small and causing the recombination of electrons from the conduction band to the valence band. Recombination makes the formation of electron pairs and holes to bind pollutants unstable.

4. Conclusion

The synthesis of TiO₂ was not pure, there is Fe₂O₃ compound as impurities. Because of Fe₂O₃, rutile phase growth occurs at a temperature of 650 °C. Calcination temperature variations affect the TiO₂ crystal structure. The more higher temperature of calcination, the rutile phase will increase than make the crystallite size will increase too. Because in high temperature will trigger crystallite growth and encourage the occurrence of rutile phase nucleation. The presence Fe₂O₃ as impurity in semiconductor TiO₂ will decrease the amount of band gap energy from 3,2 eV to 2,7 eV. In addition, presence of rutile is causing the band gap energy become more lower. When the percentage of rutile is 89.57%, the band gap energy will decrease until 2.08 eV. It causes poor photocatalytic properties for TiO₂ because of the recombination. So, the maximum photocatalytic activity of TiO₂ was obtained at 650 °C of calcination temperature, when the rutile phase begins to form about 15.38%, the band gap energy is 2,4 eV and the crystallite size was 53.41 nm, causing the highest degradation efficiency reach 69% in Rh-b solution and 83% in MB solution.

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