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Effect of Calcination Temperature on Titanium Dioxide Synthesized by Sol-Gel Method

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ABSTRACT. In this paper, the effects of calcination temperatures on the sol-gel synthesized TiO_2 powder were studied. TiO_2 powder was prepared through sol-gel method and further heat treated by different calcination temperature of 400 °C, 500 °C, 600 °C and 700 °C. Thermal analysis of the dried TiO_2 powder catalysts was carried out using DTA-DTG. While all treated powder were characterized by using XRD and SEM. Meanwhile the crystallite size of TiO_2 samples increased as calcination temperature increased. The morphology of synthesized TiO_2 also revealed the increment in particle size with increasing the calcinations temperature.

Keywords: *Titanium dioxide, Photocatalyst, Sol-gel method, DTA-DTG, Phase transformation;*

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1. INTRODUCTION

Since the discovery of photocatalytic properties of titanium dioxide (TiO_2) by Fujishima and Honda, TiO_2 had become one of the most popular and promising photocatalyst due to its strong oxidizing power of its holes, high photostability, redox selectivity and easy to prepare in the laboratory [1, 2]. This photocatalyst usually used in discovering application of materials, for example, shades, sunscreen salves, electrochemical terminals, capacitors, solar cells and even act as food colouring agent in toothpastes. There are various methods are available for the preparation of TiO_2 powder. Among all methods, sol-gel are the most convenient due to the ability to control reaction at low temperature and able to design nanomaterial with demanded surface properties [3].

There are many studies have been carried out in the phase transition of TiO_2 [4-6]. The phase transition of TiO_2 from anatase phase to rutile phase, a symmetry change from $I4_1/amd$ to $P4_2/mnm$ due to low stability of low density solid phase of anatase. Kais and Misra studied that the conversion from anatase structure to rutile structure can be done by annealing at temperature 600 °C and completed at 1000 °C [7,8]. However, Su et al. [1], Papoulis et al. [9] and Wang et al. [10] found that small fraction of rutile mixed with anatase had shown excellent photocatalytic activities. The aim of this work was to investigate on the thermal composition and effect of calcination temperature on phase transformation of synthesized TiO_2. Morphology of synthesized TiO_2 powder were also revealed.

2. MATERIALS AND METHODS

In this study, TiO_2 was synthesized by using sol-gel method with volume ratio $Ti(OC_3H_7)_4$:H_2O:C_2H_5OH:CH_3COOH is 1:2:1:0.53. First, 50 mL of deionized water was pre-heated up to 80 °C. Meanwhile,

13.25 ml of acetic acid was added into 25 ml of ethanol to formed solution 1. After that, 25 ml of $Ti(OC_3H_7)_4$ was slowly added into solution 1 to form solution 2 andaged for 5 min at room temperature. Next, solution 2 was added slowly into the heated deionized water at 80 °C under magnetic stirring. The TiO_2 sol was stirred vigorously for 30 min and then aged for 3 hours. It was then dried in hot oven at temperature of 110 °C for 24 hours to remove excess water content in the gel and form precursor powder. The synthesized TiO_2 powders was calcined at different temperature. Powder 1(P-0) was the TiO_2 precursor powders while powder 2 (P-400), powder 3 (P-500), powder 4 (P-600) and powder 5 (P-700) were prepared at calcination temperature of 400 °C, 500 °C, 600 °C and 700 °C, respectively. The calcination process was carried by using muffle furnace.

Thermal analysis of 10 g to 15 g TiO_2 precursor powders were carried out using differential thermal analysis and thermogravimetric analysis (DTA/TGA) (Rigaku TG 8120) started at room temperature until 1400 °C with heating rate of 10 °C/min in air atmosphere. The crystal structure of calcined TiO_2 powders were analyzed with X-ray diffractometer (XRD) (D/max-III, Rigaku using Cu-Kα radiation). All XRD patterns were collected at room temperature in range of 2θ = 5-80° at a scan speed of 2 °/min while the diffraction signals were collected with step size of 0.02°. Rietveld refinement was performed by using XpertHighScore Plus software to quantify phase and refine the crystal structure. The crystallite size was measured using Williamson-Hall plot. The morphology of the samples were observed by using a scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA).

3. RESULTS AND DISCUSSION

3.1 Thermal analysis of TiO_2 precursor powder.

Differential thermal analysis and thermogravimetric analysis (DTA/TGA) curves recorded on the thermal behaviour of the TiO_2 precursor powders from room temperature to 1400 °C as shown in Fig. 1. As can been see in Fig. 1(a), the DTA curve has been segregated into four region with corresponding temperature interval, which was zone A (29-292 °C), B (292-385 °C), C (385-697 °C) and D (697-1400 °C) respectively. The initial state of precursor powder of TiO_2 was a non-heat treated and stable xerogel formed. From zone A which shows the thermal data, there is a broad endothermic peak with minimum peak at temperature of 64.98 °C as shown in Fig. 1. Although the TiO_2 precursor powder had been gone through drying process, there was still some content of solvent and water left which represented by the endothermic peak. After this peak onwards including in zone B, it had been transformed into amorphous TiO_2 which exist in a range around 300 °C [11]. Next, the exothermic peak with maximum of 346.213 °C in zone B indicates to the crystallization of anatase. Meanwhile, the TiO_2 would transform from amorphous into active anatase phase as the temperature keep increasing in zone C [12]. According to Pagacova and Huang [13,14], the crystallization of anatase to rutile phase was occur at a maxima exothermic peak. However, there was an almost non-detectable exothermic peak at temperature of 697.852 °C in this study and it was same as the observation of DTA results by Huang [14]. Moreover, in zone D, increased in temperature would lead to rutile phase crystallized and presented as the main phase of TiO_2. The overall transformation shown as below:

Xerogel ⟶ Amorphous ⟶ Anatase ⟶ Rutile

In Fig. 1(b), the TGA plot was labelled by stages which included stage I, II, III and IV which is located at temperature range of 29-87 °C, 87-292 °C, 292-383 °C and 383-697 °C, respectively. In TGA results, there are drastic drop of 6% in weight percentage in stage I. In this stage, weight loss indicate present of desorption of physisorbed water [6]. Next, there was a mass loss of 4% in stage II which indicated the degradation of the solvent including the isopropoxy group which still bonded with Ti after aging process [14]. While in stage III, there are a mass loss of 5% in weight percentage of organic compound such as carbonic species or carbon dioxide which may oxidized from the ethanol. Finally, there are slightly loss of 0.8% in weight percentage in

stage IV because it takes time for total removing the excess organic compound. After all the organic compound burnt of, TiO_2 rutile left in the alumina crucible was 84%.

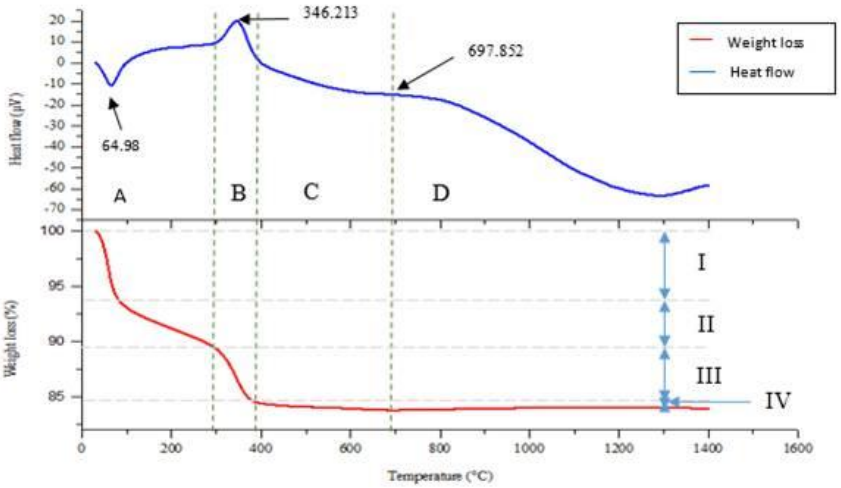

Fig. 1(a) DTA and (b) TGA data of TiO_2 precursor powder, P-0

3.2 Crystallography of calcined TiO_2.

As demonstrated in the Fig. 2, all samples contain TiO_2 anatase phase. However, only sample P-700 contain a small fraction of rutile phase. High intensity of rutile phase was diffracted at 27° corresponded to reflection from (110) crystal plane. In this study, there was no brookite phase present. According to Table 1, anatase phase and rutile phase have the same crystal system which was tetragonal but different in space group. During the conversion from space group I41/amd to P42/mnm, it can be said to be a phenomena of reconstructive polymorphism which caused by reassembly of atoms and extensive rearrangement of atomic bonds [7]. According to kais and Misra [7,8], anatase structure can be converted into rutile structure by annealing from 600 °C and completed at 1000 °C. Besides, this also can be proven by the DTA plot as discussed in section 3.1. The quantification of phases were tabulated in Table 4.1.

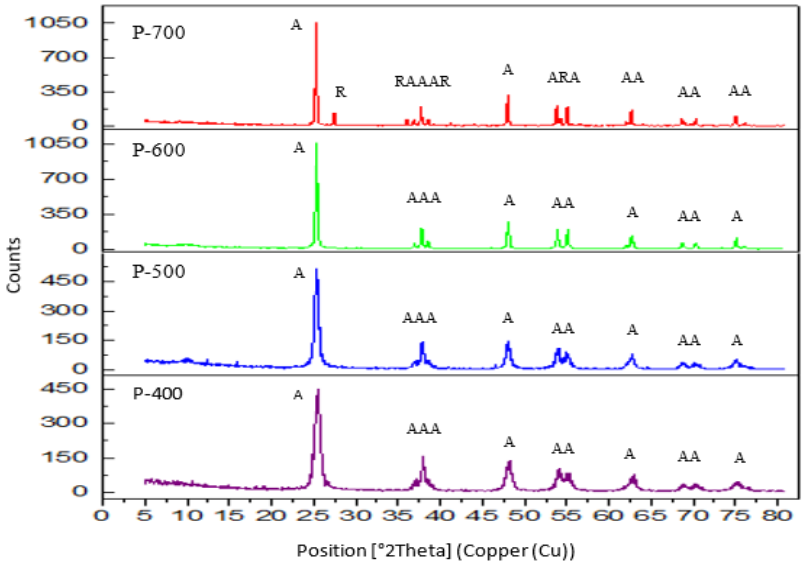

Fig. 2 XRD pattern of TiO_2 under different calcination temperature

Table 1 Crystal structure and space group of TiO_2 under different calcination temperature

Sample	Symbol	Phase	wt.%	Crystal system	Space group
P-400	A	Anatase	100	Tetragonal	I41/amd
P-500	A	Anatase	100	Tetragonal	I41/amd
P-600	A	Anatase	100	Tetragonal	I41/amd
P-700	A	Anatase	88.1	Tetragonal	I41/amd
	R	Rutile	11.9	Tetragonal	P42/mnm

Fig. 3 shows the XRD pattern for the main peak of TiO_2 anatase under different calcination temperature. The highest intensity peaks of anatase at (011) crystal plane were overlaid to be compared. The peak shifted to the low angles as the calcination temperature increased. At higher temperature, the lattice site was substituted by ion and thus increase in d spacing and shifted happen [15]. This also can be explained by lattice parameter as shown in Table 2. There was no significant change in lattice 'a' and 'b' unit cell but in 'c' unit cell. As the temperature increased, lattice 'c' unit cell was increased which indicated the elongation happen in the unit cell and thus leading to increase in d-spacing. Meanwhile, samples P-600 and P-700 have higher peaks as compare to sample P-400 and P-500 with 1055 and 1054 counts respectively. This indicates that they both have higher concentration of anatase phase or higher degree of crystallinity compound and larger grain size as compare to samples P-400 and P-500 [12,16].

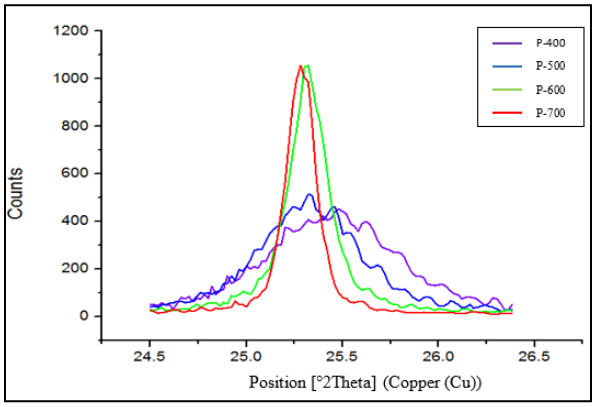

Fig. 3 XRD pattern of TiO_2 (011) crystal plane under different calcination temperature.

In addition, the crystallite size, lattice strain and crystal density of TiO_2 under different calcination temperature was shown in Table 3. By using Williamson-Hall plot, all the phase was in nano range crystallite size. The crystallite size increased as the calcination temperature increased while the lattice strain tends to decrease. This indicate that heat treatment would enhanced the growth of anatase while rutile formed larger [12]. In addition, based on He's study [17], the stronger and sharpen diffraction peaks as increased the calcination temperature indicate the formation of larger crystal size and higher crystal degree. While undergoing phase transition of sample P-700 resulted in increased densification and coarsening of TiO_2 particles as shown in SEM image Fig. 4 [7].

Table 2 Lattice parameter of TiO_2 under different calcination temperature

Sample	Symbol	Lattice parameter			Crystal volume
		a	b	c	
P-400	A	3.78665	3.78665	9.50570	136.2995
P-500	A	3.78672	3.78672	9.50913	136.3535
P-600	A	3.78444	3.78444	9.51696	136.3015
P-700	A	3.78455	3.78455	9.52639	136.4445

	R	4.59551	4.59551	2.96066	62.52526

Table 3 Structural parameter of TiO_2 under different calcination temperature

Sample	Symbol	wt.%	Crystallite size (nm)	Lattice strain (%)	Crystal density (g/cm^3)
P-400	A	100	11.66	0.000	3.89
P-500	A	100	15.40	0.150	3.89
P-600	A	100	46.70	0.109	3.89
P-700	A	88.1	70.05	0.093	3.89
	R	11.9	114.5	0.087	4.24

3.3 Morphology of synthesized TiO_2 powders.

In this study, all powder samples are agglomerated and distributed randomly. The TiO_2 precursor powder, P-0 showed that the particles is in irregular shape, uneven surface and cubic like structure as shown in Fig. 4(a).While sample P-400 and P-500 were observed with an uneven surface and spherical in shaped but the particle size was increased as the temperature increased. For morphology of P-600, the shapes were elongated into irregular, sharpen in particle edges and changed into larger in particle size. At last, P-700 grew into larger particle size, possessed irregular and uneven surface with some sharp faced structure. From the morphologies observations, it shows that the higher the calcination temperature, the larger the particles size which has similar trend with what has been found by Wetchakun et al. [4]. This is due to the particles tend to stick together and agglomerated while crystal growth happen in higher calcination temperature.

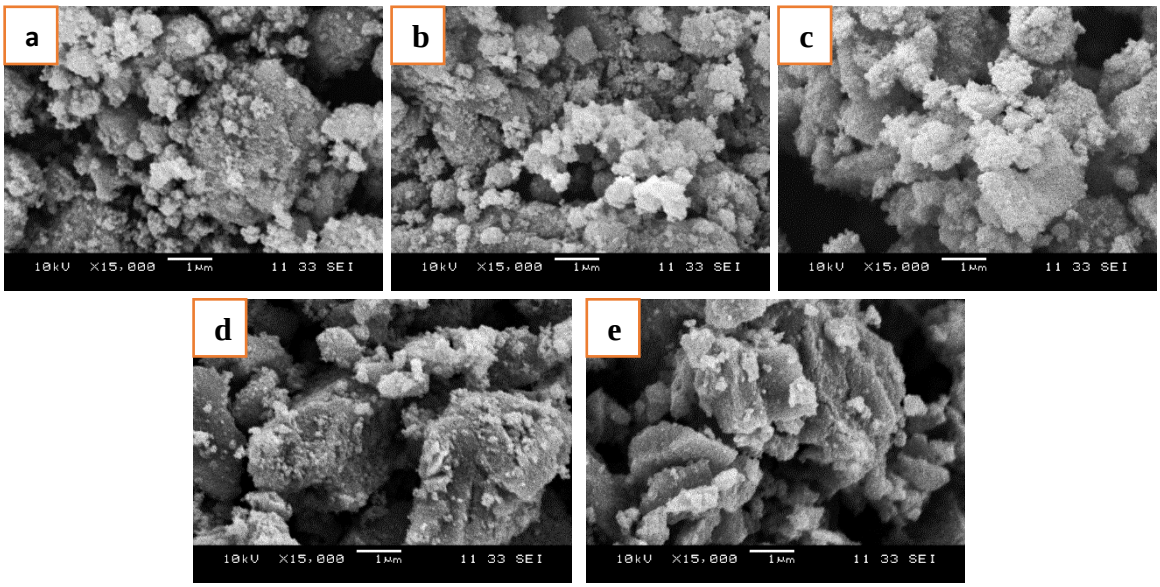

Fig. 4 SEM morphology of TiO_2 powders with different calcination temperature (a) P-0 (b) P-400 (c) P-500 (d) P-600 and (e) P-700 under magnification of 15 KX

4. SUMMARY

In this study, TiO_2 has been synthesized by using the sol-gel method. From the DTG thermal analysis, TiO_2 was degraded in four stage. There was mass loss of 6%, 4%, 5% and 0.8% in temperature range of 29-87 °C, 87-292 °C, 292-383 °C and 383-697 °C respectively. The very first and major weight loss in stage I was due to desorption of physisorbed water. The degradation of solvent, organic compound and excess organic compound were happen in stage II, III and IV respectively. Besides, phase transformed from xerogel,

amorphous, anatase to rutile phase ascendingly with transformation of temperature of 65 °C, 346 °C and 697 °C are revealed in DTA and XRD analysis. From XRD analysis, it was found that single phase of anatase phase was obtained when calcined up to 600 °C and at 700 °C small amount of rutile started to crystallize. The crystallite size of the anatase phase also increased as a function of calcination temperature. The morphology of TiO_2 powder shows the higher the calcination temperature, the larger and sharpened the particles.

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