CHAPTER VII
SYNTHESIS OF HIGH SURFACE AREA AND THERMALLY STABLE TiO$_2$ DIRECTLY FROM
TITANIUM TRIISOPROPANOLAMINE PRECURSOR

Abstract

High surface area mesoporous titania was prepared by titanium triisopropanolamine precursor directly synthesized from inexpensive starting materials and a much simpler and milder reaction condition using the oxide one pot synthesis process (OOPS). The effects of calcination rate, holding time and calcinations temperature were studied to obtain the suitable condition for the highest specific surface area. The TGA result of the calcined product shows no organic residue while XRD and SEM provide phase transformation and morphology, respectively. The highest specific surface area titania in anatase phase, 163 m^2/g, was indicated at calcination rate of 0.25°C/min, 2h holding time and 600°C calcination temperature. The resulting anatase TiO$_2$ is thermally stable up to 900°C before transformed to rutile phase.

Introduction

Titanium dioxide, TiO_2, is widely used as humidity and gas sensors, dielectric ceramics, catalyst supporter, solar cell and catalyst, especially, photocatalyst [1-6]. Generally, most catalysts are used at high temperature, thus must be highly thermal stability. Therefore, preparation of anatase nanoparticles with high surface area, uniform particle size, uniform pore structure and high anatase-rutile transformation temperature is truly desirable.

High surface area TiO_2 can be prepared by several methods, such as pyrolysis of titanium tetrabutoxide in oxygen containing atmosphere via the MOCVD method, giving a surface area of 180 m^2/g at 700°C[7], hydrothermal treatment [8,9], or the most famous method, so called sol-gel process [10-11]. Bickmore *et al.* prepared ultrafine titania using flame spray pyrolysis of a titanatrane complex, resulting in a mixture of anatase and rutile with a surface area of 45 m^2/g [12]. Although these processes are widely used, they are still holding two major drawbacks, viz. expensive and sensitive starting materials. In 2004, Calleja *et al.* [13] prepared the microstructure titanium dioxide from commercial titanium alkoxide precursors using a nonionic copolymer surfactant (Pluronic) as the structure-directing agent and the sol-gel process. The interfacial synthesis of hollow TiO_2 microsphere in ionic liquid was studied by Nagashima *et al.* [14], using $Ti(OBu)_4$ precursor for selective hydrolysis at the interface of oil droplet/C4mim. The titania gel microspheres were then calcined at 500°C for 5h to obtain the anatase TiO_2.

The important factor to produce titania with good properties is the purity of titanium alkoxide precursor. The titanium dioxide has most often been carried out using the titanium alkoxide, however, the synthesis of metal alkoxides is greatly challenging to scientists due to their extreme moisture sensitivity because they contain an unsaturated Ti^{IV} center which is highly reactive to air and moisture, therefore, the reaction must be carried out under inert gas. Another reason is that those titanium alkoxides are synthesized from very expensive starting materials, such as the synthesis of the titanium complexes that contain $(Et_3SiNCH_2CH_2)_3N$, $(C_6F_5NCH_2CH_2)_3N$, or $(Me_3SiNCH_2CH_2CH_2)_3N$ ligand [15], hydrothermal synthesis of titanium glycolate complex from tetraethylorthotitanate with ethylene glycol in an

autoclave for 5 days [16-17], the synthesis of (dimethylamino)triisopropyl azatitanatrane from $Ti(NMe_2)_4$ in $N(CH_2CH_2NHR)_3$ (where R = i-Pr[13]) and toluene under an atmosphere of pre-purified argon or nitrogen [18].

From our previous work, moisture stable titanium glycolate precursor was successfully synthesized from low cost starting material, TiO_2, using the Oxide One Pot Synthesis method (OOPS) [19] and used as precursor to produce nanocrystalline mesoporous high surface area titanium dioxide by the sol-gel process [20]. In this work, we demonstrate that moderately high surface area and thermally stable anatase TiO_2 can be obtained directly from the crude product, titanium triisopropanolamine precursor, synthesized by the reaction of TiO_2 and triisopropanolamine.

Experimental
Materials

UHP grade nitrogen; 99.99% purity was obtained from Thai Industrial Gases Public Company Limited (TIG). Titanium dioxide and triisopropanolamine (TIS) were purchased from Sigma-Aldrich Chemical, Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker, Inc. (USA), and purified by fractional distillation under nitrogen atmosphere at 200°C before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co., Ltd. (Bangkok, Thailand) and distilled under vacuum (0.1 mm/Hg) at 130°C prior to use.

Titanium triisopropanolamine precursor preparation

A mixture of TiO_2 (2g, 0.025 mol), triisopropanolamine (9.55g, 0.05 mol) and triethylenetetramine (3.65g, 0.0074 mol) was stirred vigorously in excess ethylene glycol (25 mL) and heated to the boiling point of EG for 24 h. The resulting solution was centrifuged to separate the unreacted TiO_2. The excess EG and TETA were removed by vacuum distillation (0.1 mm/Hg) at 150°C to obtain crude precipitate product which was characterized using FTIR, FAB^+-MS and TGA.

High surface area TiO_2 preparation

The crude titanium triisopropanolamine was directly calcined to obtain high surface area TiO_2. The calcination rate and temperature were studied. In addition,

holding time at certain temperature was also investigated. The obtaining white powder was ground and kept in a desiccator before characterization.
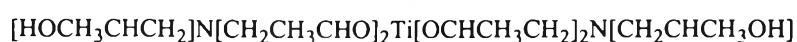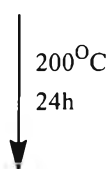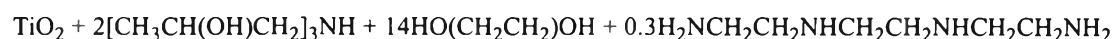
Titanium triisopropanolamine and TiO$_2$ characterization

High surface area TiO$_2$ was identified its structure using XRD technique on a D/MAX-2200H Rigaku diffractometer with CuKα radiation on specimens prepared by packing sample powder onto a glass holder. The diffracted intensity was measured by step scanning in the 2θ range of 5° to 90°. A fourier transform infrared spectra (FT-IR) was recorded on a VECOR3.0 BRUKER spectrometer with a spectral resolution of 4 cm^{-1} to determine the functional groups. Thermal stability was characterized on a Perkin Elmer thermal analysis system with a heating rate of 10°C/min over 30°-800°C temperature range. Samples pyrolyzed at various conditions were analyzed using SEM for morphology determination by attachment onto aluminum stubs and coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at x3,500 magnification. Specific surface area and nitrogen adsorption-desorption were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 cc/min. Nitrogen was used to calibrate the analyzer, and also as the adsorbate at liquid nitrogen temperature. The samples were throughly outgassed for 2h at 150°C, prior to exposure to the adsorbent gas.

Results and discussion

Titanium triisopropanolamine precursor characterization

Titanium triisopropanolamine was synthesized by a direct reaction of titanium dioxide and triisopropanolamine in the presence of ethylene glycol and triethylenetetramine, as solvent and catalyst, respectively (reaction 1).

$$TiO_2 + 2[CH_3CH(OH)CH_2]_3NH + 14HO(CH_2CH_2)OH + 0.3H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$$

$$\downarrow \begin{array}{l} 200^O C \\ 24h \end{array}$$

$$[HOCH_3CHCH_2]N[CH_2CH_3CHO]_2Ti[OCHCH_3CH_2]_2N[CH_2CHCH_3OH]$$

Reaction 1.

The crude titanium triisopropanolamine was characterized using FT-IR, TGA and FAB$^+$-MS. The IR spectrum (figure1) shows the expecting bands at 3400 cm^{-1} (OH group), 2927-2855 cm^{-1} (C-H stretching), 1460 cm^{-1} (C-H bending of CH$_2$ group), 1379 cm^{-1} (C-H bending of CH$_3$ group), 1085 cm^{-1} (C-O-Ti stretching), 1020 cm^{-1} (C-N bending) and 554 cm^{-1} (Ti-O stretching). The result from TGA analysis, as can be seen in figure 2a, shows two transitions at 280° and 365°C corresponding to the decomposition of the unreacted triisopropanolamine and the triisopropanolamine ligand, respectively. The final ash yield, 16.6%, calculated from the starting point of the second decomposition transition is close to the theoretical ceramic yield of [HOCH$_3$CHCH$_2$]N[CH$_2$CH$_3$CHO]$_2$Ti[OCHCH$_3$CH$_2$]$_2$N[CH$_2$CHCH$_3$OH], 18.7%. The mass spectrum result in table1 confirms the desired structure of the as-synthesized product.

TiO$_2$ characterization

Effect of calcination rate

The effect of calcination rate on the surface area is studied at 0.25, 0.5 and 1.0°C/min at calcination temperature of 600°C for 2h. The results of specific surface area summarized in table 2 show that at the lowest calcination rate (0.25°C/min) the highest surface area is observed. This is probably due to having more time for TiO$_2$ molecules to orderly arrange themselves.

Effect of holding time

Holding time at 600°C calcination temperature also affects to the surface area. In this study, 1, 2 and 4h holding times show that using calcination rate of 0.25°C/min, the highest specific surface area, 163.64 m^2/g (table 3), was found at 2h holding time while at 1h holding time the final powder was gray in color, meaning that some organic residues still remained in the sample. The TGA thermograph in figure 2b confirms that indeed there was still some organic residue, as indicated at the decomposition transition at 365°C. The TGA thermograph in figure 2c presents pure TiO$_2$ without any organic residue. As the holding time increased to 4h, the specific surface area came down to 74.04 m^2/g.

From the variations of calcination rate and holding temperature, the sample with calcination rate of 0.25°C/min and holding time of 2h was selected to study the effect of calcination temperature to determine the phase transformation of TiO_2. The calcined product is characterized using XRD, BET and SEM to confirm the active and thermally stable anatase phase of TiO_2. The XRD patterns in figure 3 and the particle morphology in figure 4 clearly illustrate the anatase phase of TiO_2, as previously studied [2]. Coincidentally, the nitrogen adsorption-desorption isotherm (figure 5) of the material calcined at 600°C for 2h indicates a mesoporous structure, having the isotherm of type IV.

Effect of calcination temperature

The phase transformation of TiO_2 is studied at different calcination temperature, viz. 300°, 500°, 600°, 700°, 800° and 900°C using 0.25°C/min calcination rate and 2h holding time. The sample at 300°C calcination temperature has black color, indicating incomplete removal of organic compounds. The XRD pattern (figure 6a.) and SEM micrograph (figure7a.) show the amorphous phase of sample. As increasing the temperature to 500°C, most of the sample has white color and little in gray. This is in agreement with the result of TGA (figure 2d.) showing moisture and organic residue decomposition transitions. The XRD pattern (figure 6b.) and SEM (figure 7b.) present the anatase phase of TiO_2 [2,10]. At the higher calcination temperatures (600°-800°C), the anatase phase is continuously formed, see the XRD patterns in figure 6c-e, and the intensity of the peaks increases with the calcination temperature, meaning that the higher cystallinity occurs as the temperature. The SEM micrographs of the anatase phase showed in figure 7c-e can confirm the crystallinity morphology. As the temperature was increased to 900°C the XRD pattern (figure 6f) and SEM micrograph (figure 7f) indicated the rutile phase of TiO_2 [21,22]. The specific surface area of TiO_2 at different calcinations temperatures are shown in table 4 which the highest specific surface area (163.64 m^2/g) is at calcinations temperature 600°C.

Conclusions

Moderately high surface area TiO_2 is successfully synthesized using as-synthesized titanium triisopropanolamine precursor directly produced from a much

simpler and milder reaction of inexpensive starting materials via the oxide one pot synthesis (OOPS) process. FT-IR, TGA and MS results show the expected structure. The effects of calcination rate, holding time and temperature indicate that the suitable condition to receive the highest surface area, 163.64 m^2/g, of the thermally stable phase anatase TiO_2 is to use 0.25 °C/min calcinations rate, 2h holding time and 600°C temperature. The anatase phase of TiO_2 is started to form at 500°C whereas the rutile phase is formed at 900°C.

Acknowledgement

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Table 7.1 The proposed structure of the synthesized titanium triisopropanolamine

m/e	%intensity	Proposed structure
428	10	$H^+[HOCH_3CHCH_2]N[CH_2CH_3CHO]_2Ti[OCHCH_3CH_2]_2N[CH_2CHCH_3OH]H^+$
410	5	$[CH_3CH_2CH_2]N[CH_2CHCH_3O]_2Ti[OCHCH_3CH_2]_2N$ $[CH_2CHCH_3OH]$
214	58	$[H_2NCHCH_3CH_2O]_2Ti[OH]$
192	100	$H+N[CH_2CHCH_3OH]_3$

Table 7.2 The specific surface area of calcined TiO_2 at various calcinations temperature rates

Calcination rate (°C/min)	Specific surface area (m^2/g)
0.25	163.64
0.5	86.65
1.0	67.00

Table 7.3 The specific surface area of calcined TiO_2 at various holding times

Holding time (h)	Specific surface area (m^2/g)
1	65.08
2	163.64
4	74.04

Table 7.4 The specific surface area of calcined TiO_2 at various calcination
temperatures

Calcination temperature (°C)	Specific surface area (m^2/g)
500	122.69
600	163.64
700	54.94
800	24.30
900	3.86
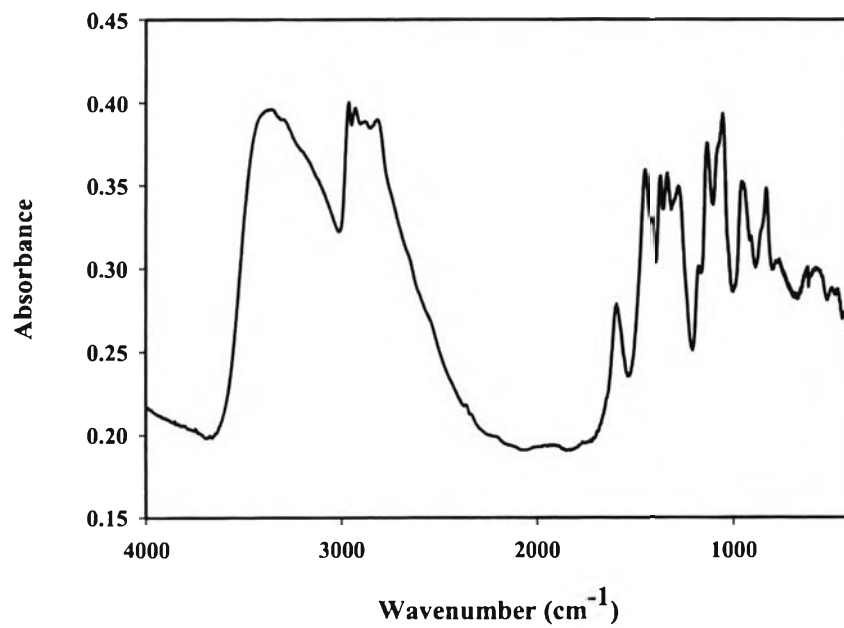
Figure 7.1   The FT-IR spectrum of titanium triisopropanolamine.
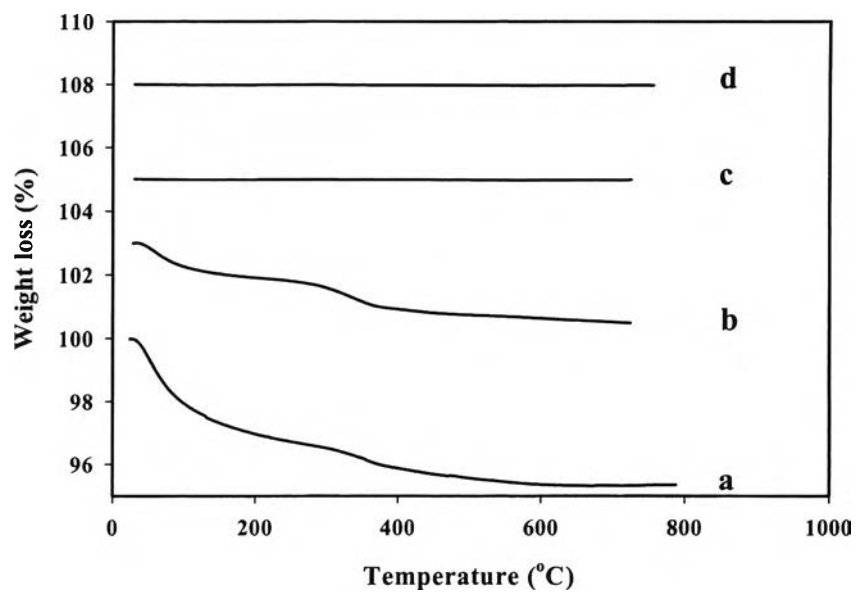
Figure 7.2   The TGA thermograms of a). titanium triisopropanolamine, b). TiO$_2$
calcined at holding time 1h, c). TiO$_2$ calcined at holding time 2h and d.)
TiO$_2$ calcined at 500°C.
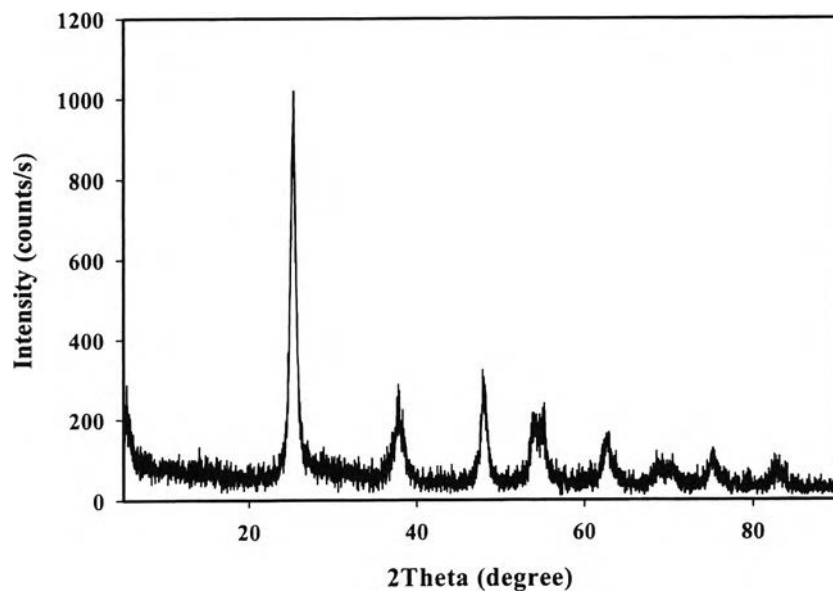
Figure 7.3   XRD pattern of TiO$_2$ at 0.25°C /min calcinations rate, 2h holding time
and 600°C calcination temperature.

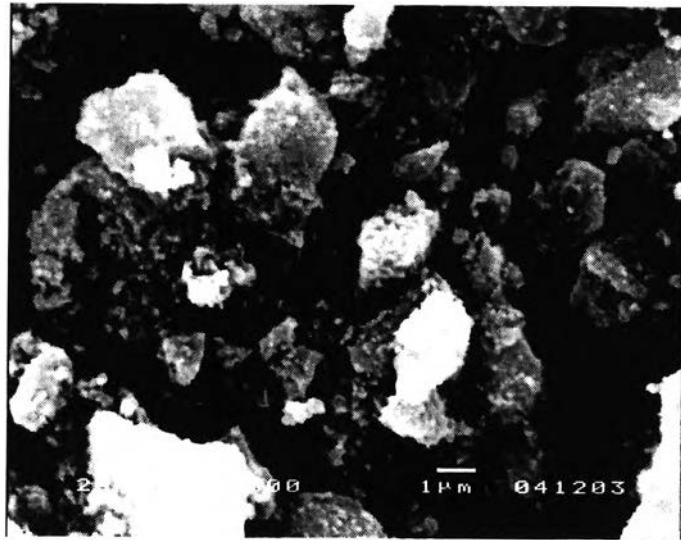Figure 7.4   The SEM micrograph of TiO_2 at 0.25°C /min calcinations rate, 2h holding time and 600°C calcination temperature.
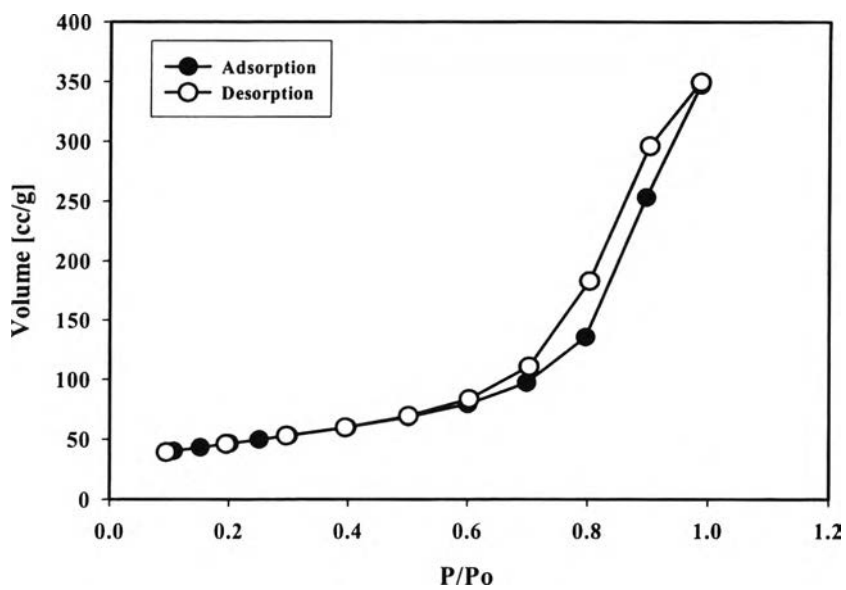
Figure 7.5   The nitrogen adsorption-desorption isoterm of the obtained

mesoporous TiO_2 at 0.25°C /min calcinations rate, 2h holding time and
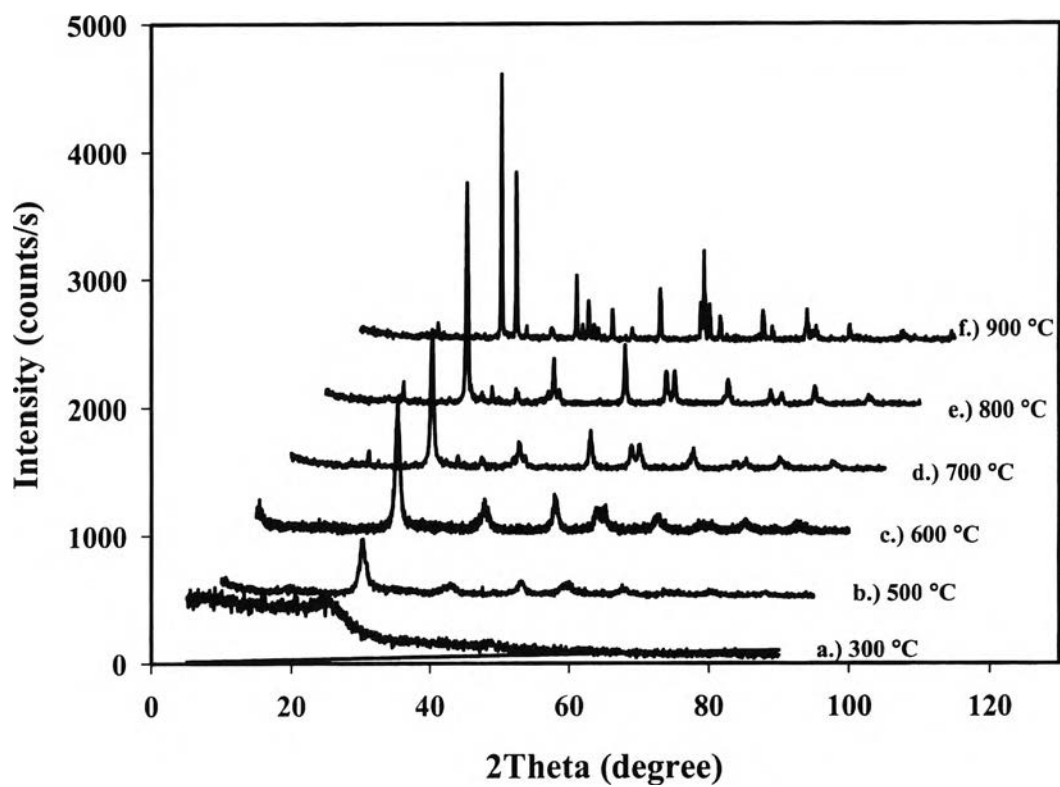
600°C calcination temperature.

Figure 7.6   XRD patterns of TiO_2 at the temperature of; a.) 300°, b.) 500°, c.) 600°,
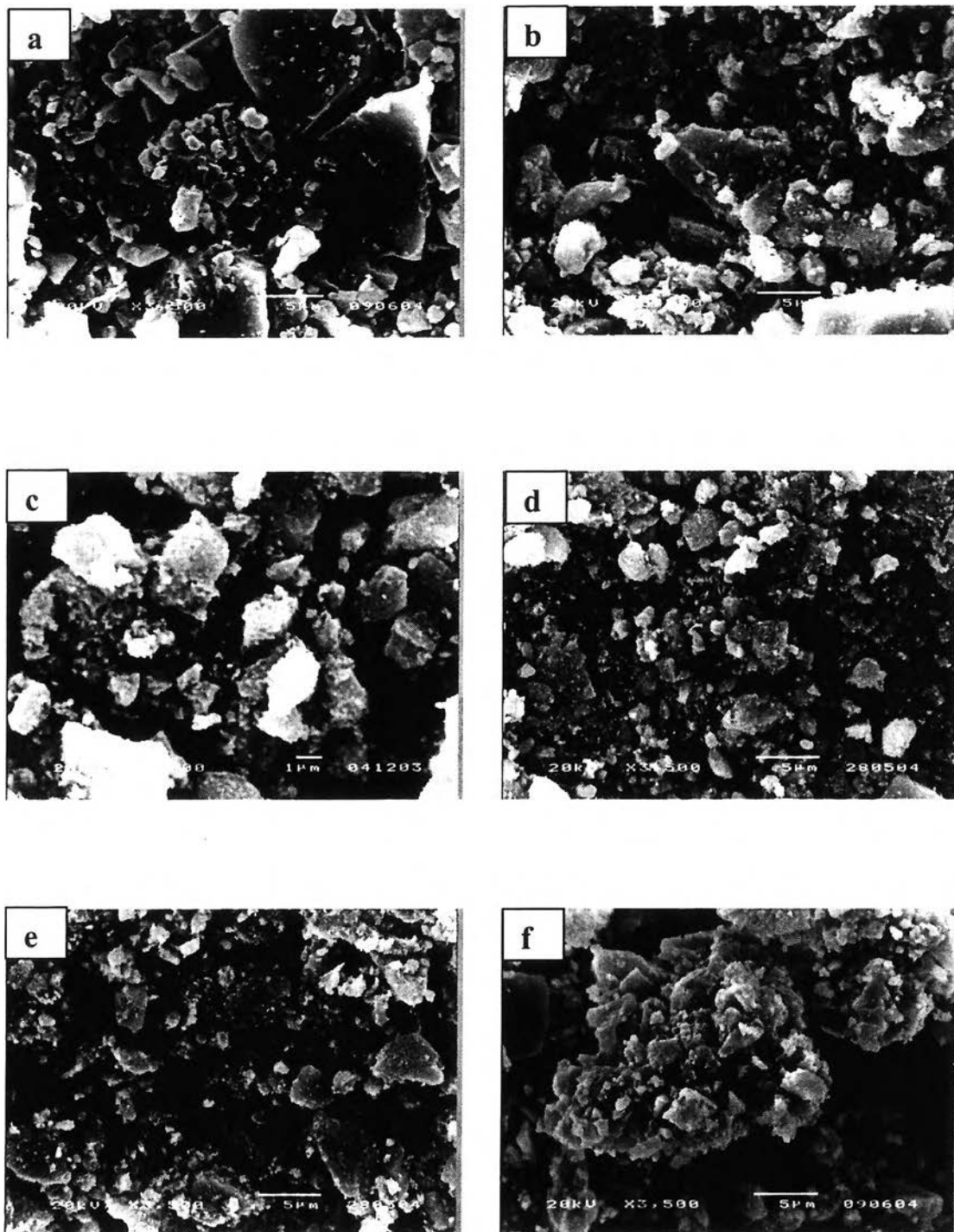
d.) 700°, e.) 800° and f.) 900°C.

Figure 7.7   The SEM micrographs of TiO_2 at the temperature of; a.) 300°, b.) 500°, c.) 600°, d.) 700°, e.) 800° and f.) 900°C.