

## CHAPTER V

### RESULTS AND DISCUSSION

#### 5.1 Formation and transformation of pure anatase titanium (IV) oxide

Reaction of titanium (IV) tetra-*tert*-butoxide (TTB) alone in each kind of the organic solvent (1,4 butanediol, toluene and 2-propanol) at 300°C under autogenous pressure yielded nanocrystalline anatase titanium (IV) oxide. The XRD patterns of the products obtained by all the reactions show that anatase phase was directly crystallized. The crystallite size and the BET surface area depend on the type of organic solvents.

##### 5.1.1 Reaction in 1,4 Butanediol (Glycothermal reaction)

The XRD patterns of the as-synthesized product obtained from glycothermal reaction at 300°C for 2 h is given in Figure 5.1, which shows that anatase phase was formed without contamination with other phases of titanium (IV) oxide such as rutile and brookite. The crystallite size, which calculated by the XRD broadening was 17 nm. The average particle size determined from the transmission electron micrograph (TEM) of the product (Figure 5.4(a)) was 16.7 nm, which is in good agreement with the crystallite size, indicating that each primary particle observed by TEM is a single crystal of anatase. The BET surface area of this product was 89.3 m<sup>2</sup> g<sup>-1</sup>.

The product was calcined at temperature of 600 to 1000°C. The BET surface area and XRD patterns of the calcined products were investigated. BET surface area of the product after calcination at 600°C and 800°C were 38.4 and 16.1 m<sup>2</sup> g<sup>-1</sup>, respectively. Their XRD patterns were almost identical to that before calcination except the fact that the peaks were more sharp (Figure 5.1). As expected from this pattern, these products still preserved the anatase structure even after calcination. The anatase–rutile transformation occurred completely around 1000°C. This transformation temperature is much higher than that of the titanium (IV) oxide

prepared by the hydrazine method, and as high as that of titanium (IV) prepared by the non-hydrous sol-gel method. Figure 5.4(a) to 5.4(d) show TEM photographs of titanium (IV) oxide before and after calcination at various temperatures.

### **5.1.2 Reaction in Toluene (Thermal decomposition reaction)**

Thermal decomposition of titanium (IV) tetra-*tert*-butoxide in toluene at 300°C for 2 h yielded nanocrystalline titanium (IV) oxide powders. The XRD pattern of the as-synthesized product is given in Figure 5.2. It shows that anatase phase was formed without another phase of titanium (IV) oxide, which was similar to product prepared in 1,4 butanediol. A TEM photograph of as-synthesized product is shown in the Figure 5.5(a). The particle size of 16 nm observed by TEM photograph was in good agreement with the crystallite size determined by the XRD line broadening technique which is 15.7 nm. This suggests that each particle observed by TEM is a single crystal of anatase.

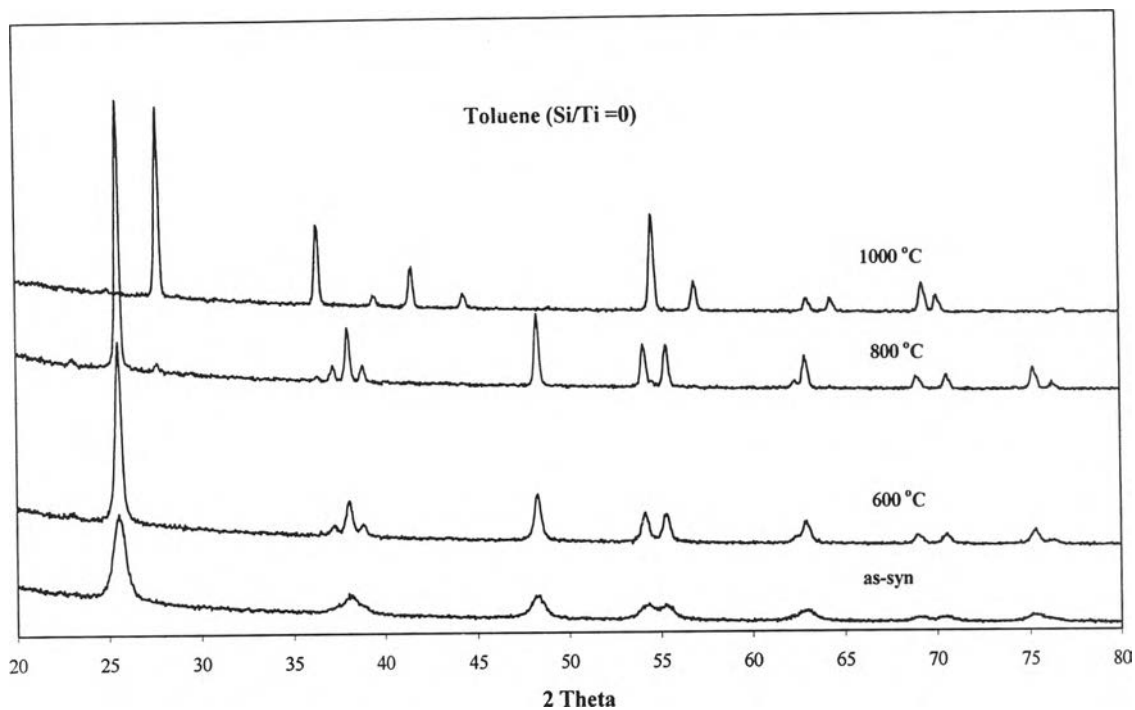
The as-synthesized product was produced by this method had a large surface area of 98.1 m<sup>2</sup> g<sup>-1</sup> and after calcination at 600°C and 800°C they decreased to 32 and 8.2 m<sup>2</sup> g<sup>-1</sup>, respectively. After calcination at 1000°C, the BET surface area drastically decreased because the product was completely transformed to the rutile phase (Figure 5.2).

### **5.1.3 Reaction in 2-Propanol (Transfer Hydrolytic Crystallization in Alcohols reaction, THyCA)**

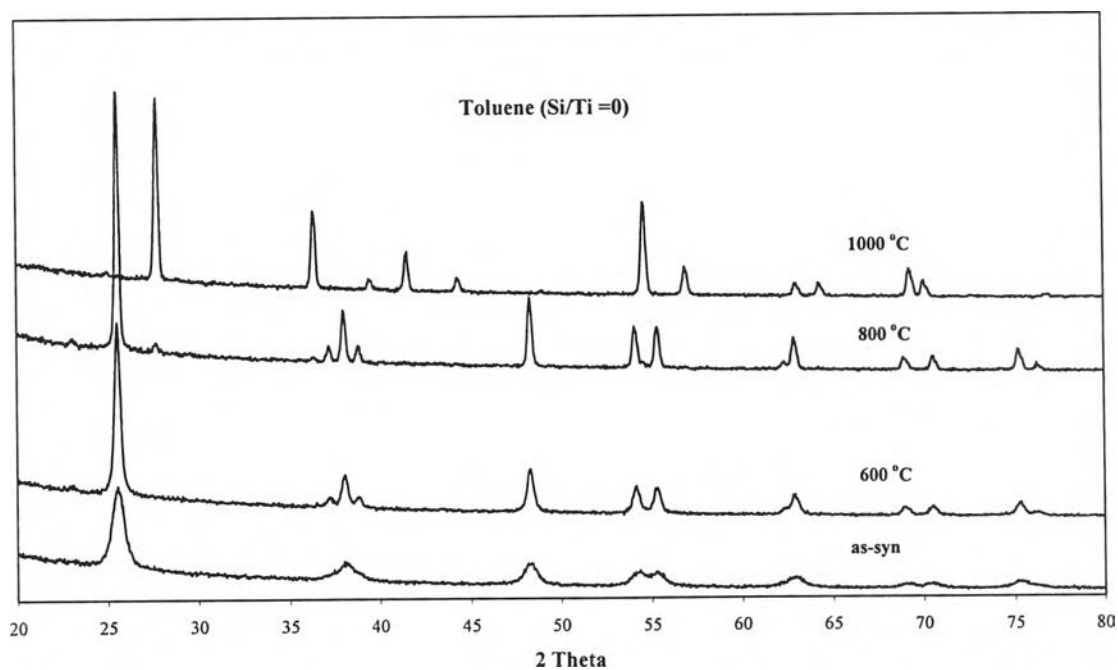
The as-synthesized product obtained by 2-propanol was large crystalline anatase titanium (IV) oxide with crystallite size of 42 nm, which is calculated by XRD broadening technique. The XRD pattern of the as-synthesized product is shown in Figure 5.3. The average particle size determined from TEM photograph of as-synthesized product as shown in Figure 5.5(b) was 40 nm. This result shows good agreement with the crystallite size that observed by XRD broadening technique. Then it can be indicated that the product is a single crystal of anatase.

The BET surface area of as-synthesized products prepared in 2-propanol was  $42 \text{ m}^2 \text{ g}^{-1}$ . After calcination at  $600^\circ\text{C}$ , the specific surface area and the crystallite size of the product obtained by this method was  $36 \text{ m}^2 \text{ g}^{-1}$  and  $47 \text{ nm}$ , respectively. The product prepared in 2-propanol with relatively large crystallite size ( $> 40 \text{ nm}$ ) before calcination showed negligible crystal growth and slightly decrease in the surface area by calcination at  $600^\circ\text{C}$ . This is presumably because the as-synthesized titanium (IV) oxide is well-crystallized having smaller tendency to sintering and contain less amount of amorphous -like phase to be crystallized in to anatase upon calcination. After calcination at  $1000^\circ\text{C}$ , the titanium (IV) oxide prepared in 2-propanol was predominantly composed of the rutile phase ( $92.6 \%$ ) and had small surface area, however the product still remained the anatase structure, indicating that titanium (IV) prepared in alcohol solvents is high thermal stability.

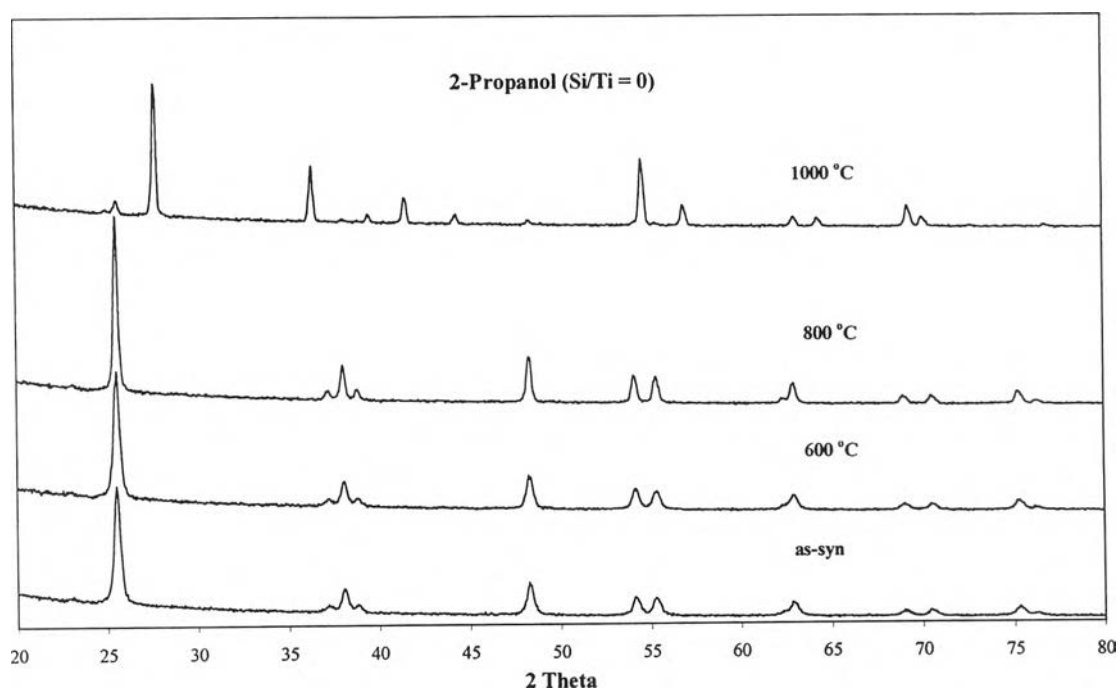
The fraction of rutile in the product was estimated using the following equation,  $X_R = [ 1+0.794 I_a / I_r ]^{-1}$ ,  $I_a$  and  $I_r$  are intensities of (101) and (110) reflection for anatase and rutile respectively [25].



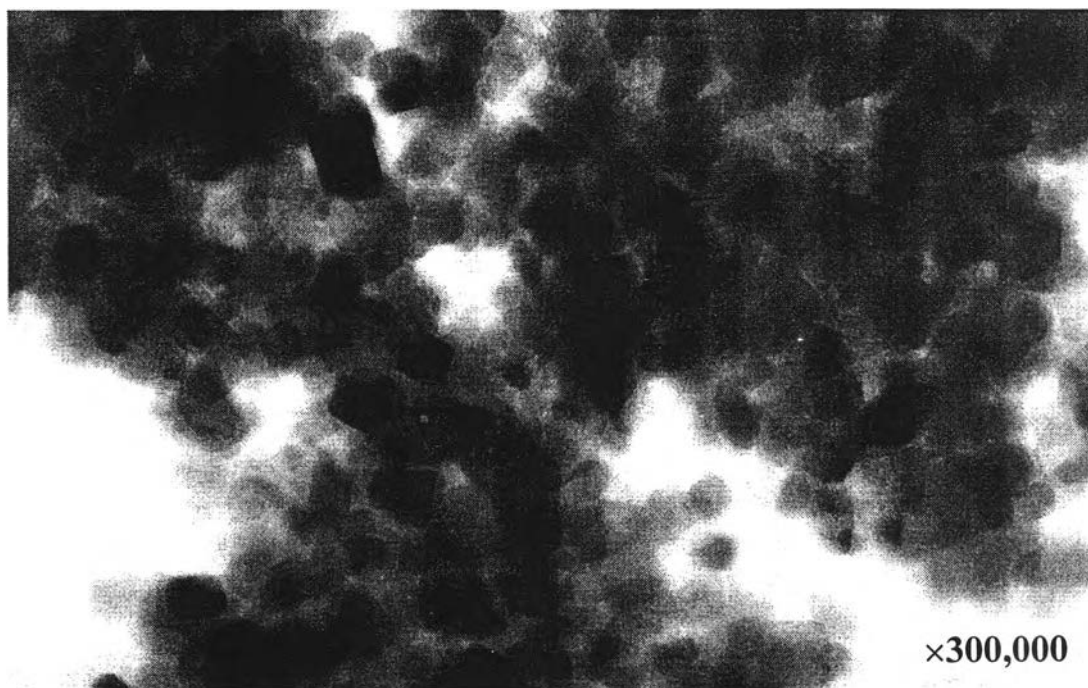
**Figure 5.1** XRD patterns of pure anatase titanium (IV) oxide synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.



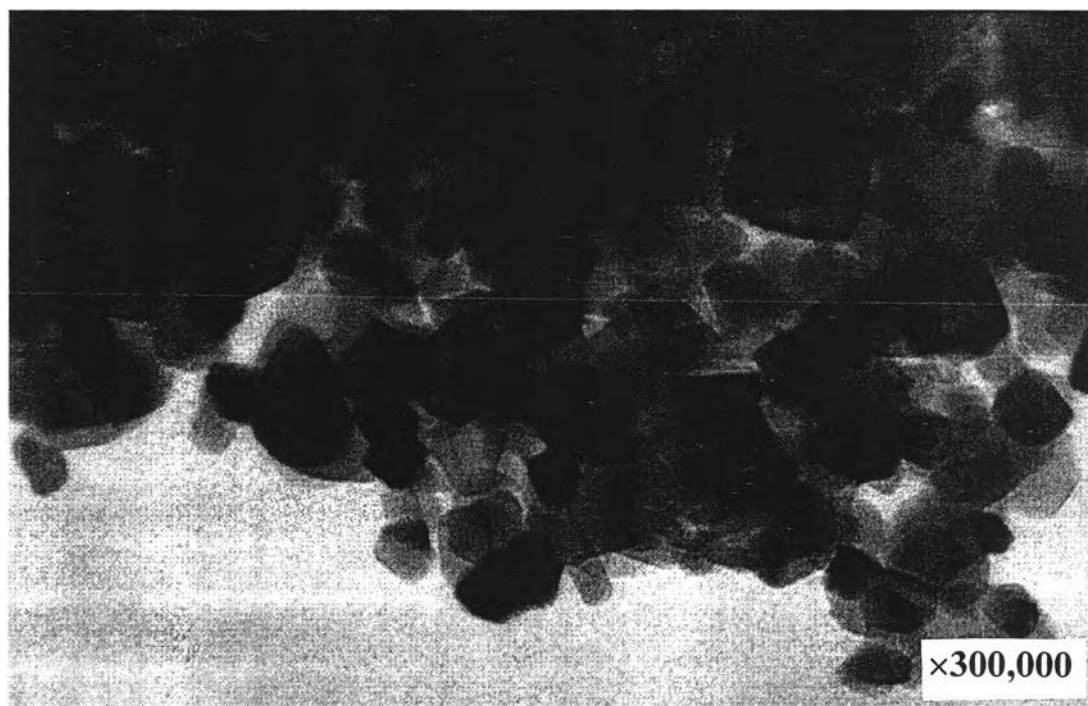
**Figure 5.2** XRD patterns of pure anatase titanium (IV) oxide synthesized by toluene before and after calcination at 600, 800 and 1000°C.



**Figure 5.3** XRD patterns of pure anatase titanium (IV) oxide synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.

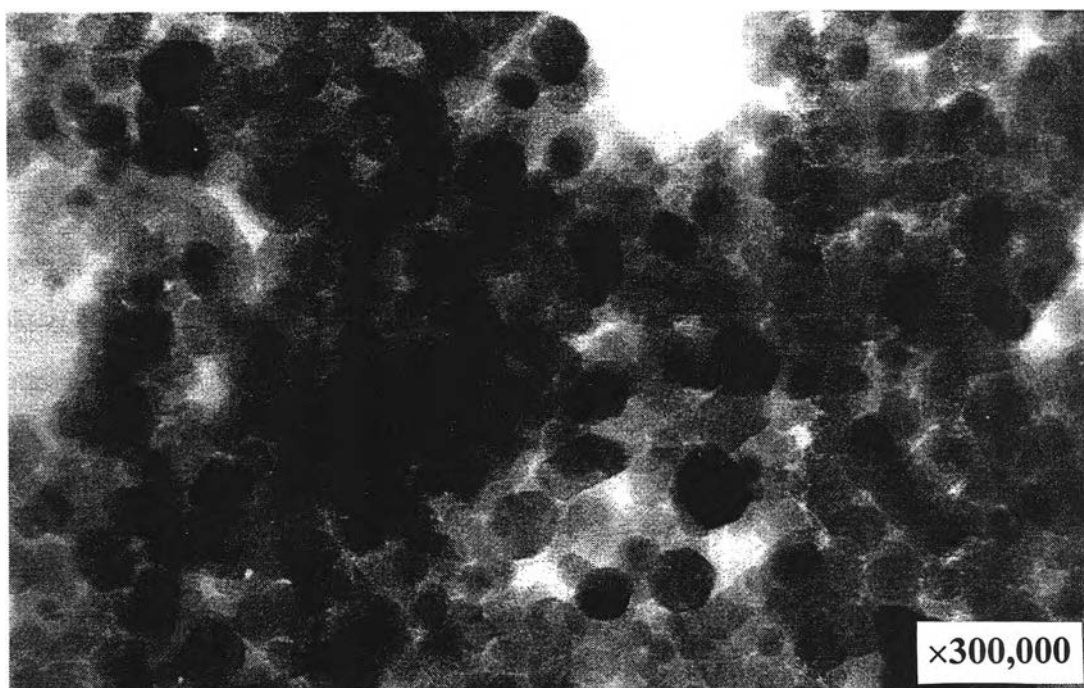


**Figure 5.4(a)** TEM photograph of as-synthesized titanium (IV) oxide synthesized by 1,4 butanediol.

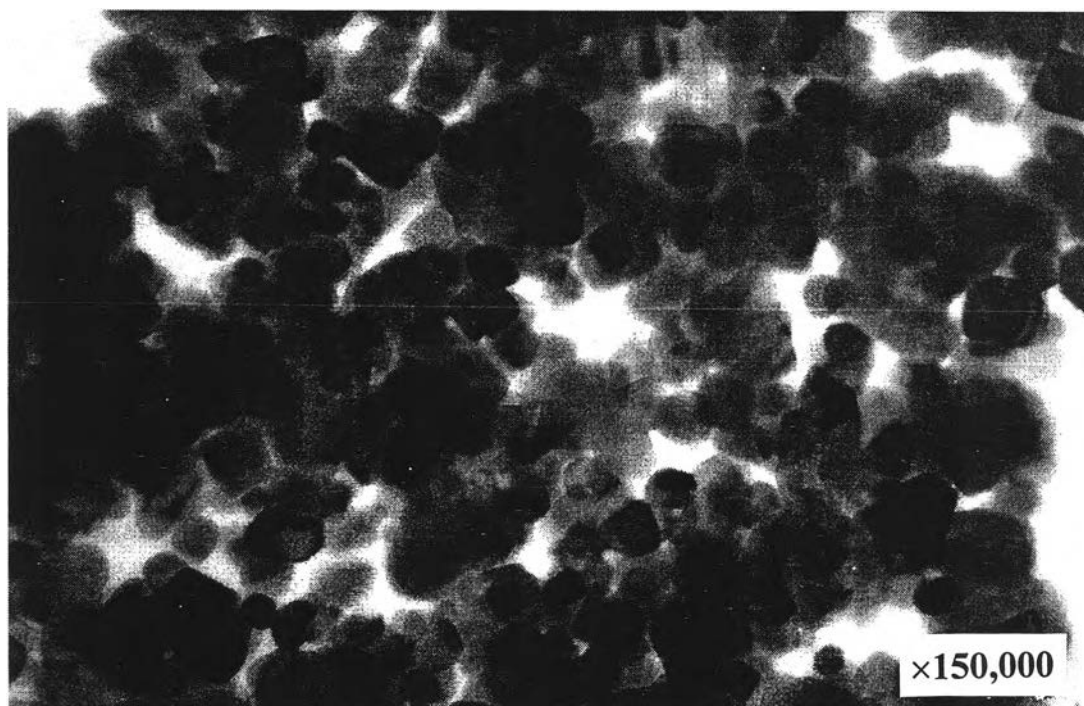


**Figure 5.4(b)** TEM photograph of pure anatase titanium (IV) oxide synthesized by 1,4 butanediol after calcination at  $600^{\circ}\text{C}$ .

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**Figure 5.5(a)** TEM photograph of as-synthesized titanium (IV) oxide synthesized by toluene.



**Figure 5.5(b)** TEM photograph of as-synthesized titanium (IV) oxide synthesized by 2-propanol.

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## 5.2 Formation and transformation of silica modified titanium (IV) oxide

Reaction of titanium (IV) tetra-*tert*-butoxide and tetraethyl orthosilicate with the atomic ratio of Si/Ti between 0.05 to 0.5 in each organic solvent was investigated. The XRD patterns of the products obtained with addition of TEOS revealed that all the products had the anatase structure and the peak intensities were not affected by the TEOS content in the reaction mixture. This result shows a sharp contrast against the titanium (IV) oxide synthesized by other methods, the peak intensities of anatase decreased with the increase in the silica content due to formation of amorphous phases as shown in Figure 5.6(a) to 5.6(c) [26]. The surface area and crystallite size of the products synthesized in each organic solvent were summarized in Table 5.1 to 5.3. With the increase of the amounts of TEOS added, the surface area increase and the crystallite size decreased.

### 5.2.1 Reaction in 1,4 Butanediol

The XRD patterns of the products after calcination are given in Figure 5.7, which shows that a small amounts of TEOS added to the reaction mixture caused the anatase-rutile phase transformation to shift markedly toward higher temperature. Change in the BET surface area and the crystallite size by the increasing the amount of TEOS and the calcination temperature are also shown in Table 5.1. Apparently, the grain growth of anatase was retarded with increasing the amount of TEOS added. After calcination at 1000°C for 1h, the products with Si/Ti > 0.2 maintained the BET surface area of more than 40 m<sup>2</sup> g<sup>-1</sup> and the crystallite size of smaller than 30 nm. The XRD pattern showed that silica modified titanium (IV) oxide preserved the anatase structure and had large surface area even after calcination at all temperatures. The TEM photograph of the silica modified titanium (IV) oxide samples as shown in Figure 5.8 as well did not show any the amorphous phase. The presence of Si in the titanium (IV) oxide lattice seems to contribute to the deceleration of the grain growth in anatase and the suppression of anatase-rutile transformation.

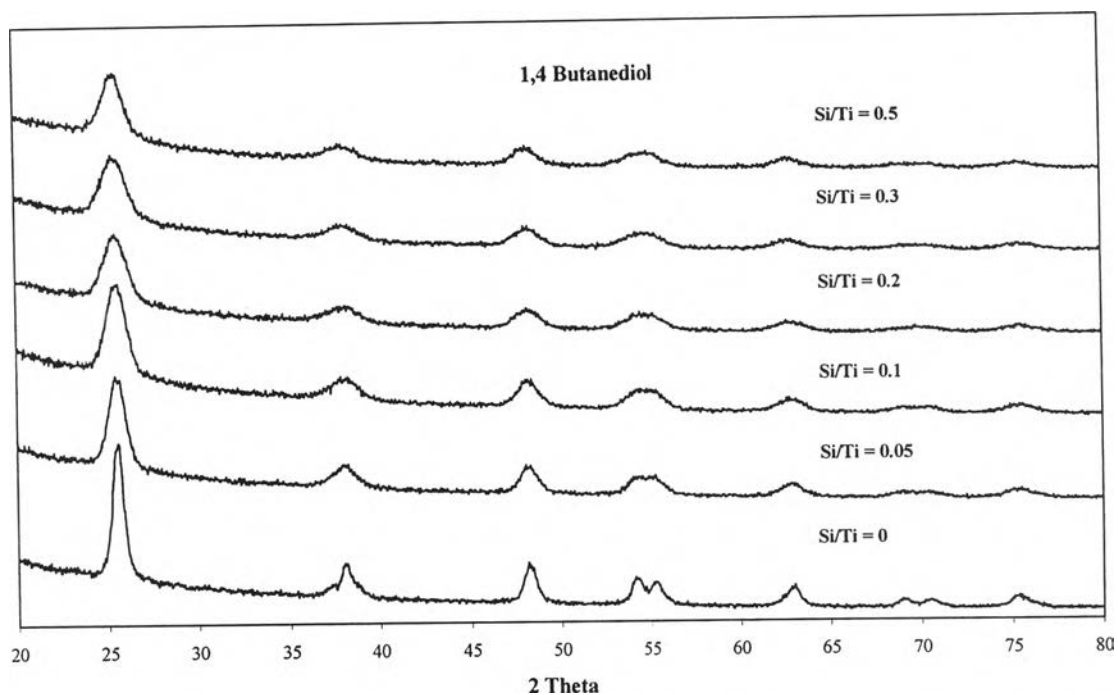
### 5.2.2 Reaction in Toluene

The XRD pattern of products after calcination at various temperatures are shown in Figure 5.9. Change in the BET surface area and the crystallite size of all Si/Ti atomic ratios of products by the increasing the amounts of TEOS and calcination temperature are shown in Table 5.2. Silica modified titanium (IV) oxides prepared in toluene were calcined at the temperature of 600 to 1000°C. The samples with addition silica content > 0.2 still preserved the large surface area of more than 88 m<sup>2</sup> g<sup>-1</sup> even after calcination at 600°C and 800°C, respectively. However, after the calcination at 1000 °C, the BET surface area decreased but these products still preserved the anatase structure, indicating that the anatase-rutile phase transformation to shift markedly toward higher temperature when the amounts of TEOS added to the reaction mixture. The TEM photographs of all Si/Ti ratios of products prepared in toluene are shown in Figure 5.10, indicating that crystallite size decreased with increase of the amount of TEOS added.

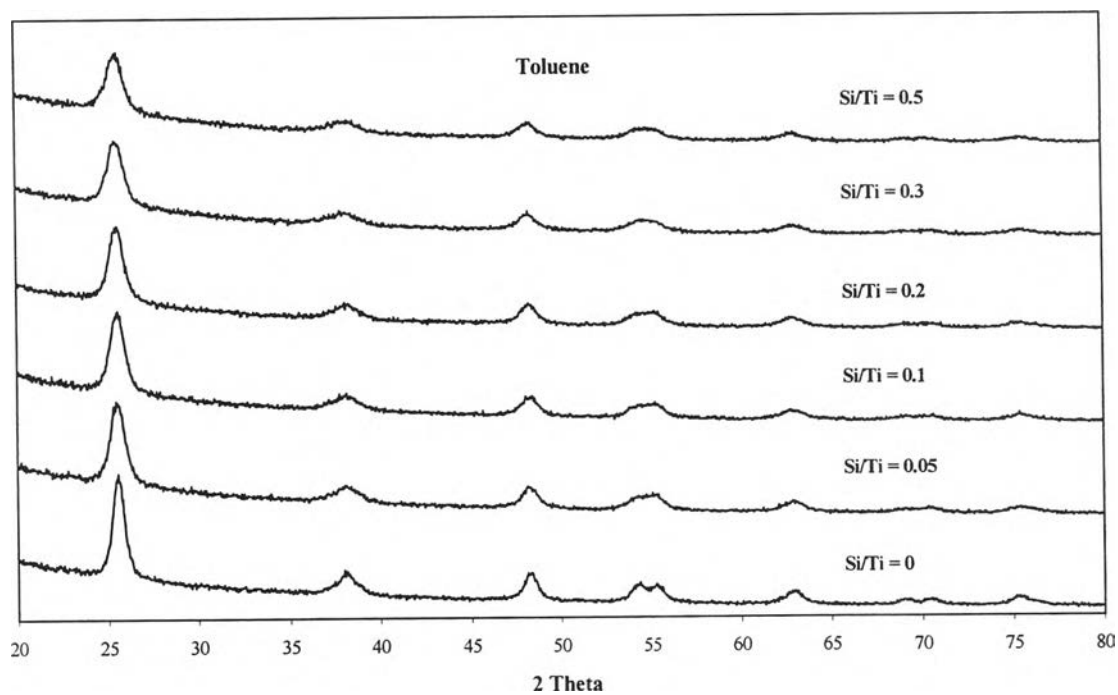
### 5.2.3 Reaction in 2-Propanol

Table 5.3 shows the BET surface area and the crystallite size of silica modified titanium (IV) oxide, which were synthesized in 2-propanol. The XRD patterns of the products are shown in Figure 5.11.

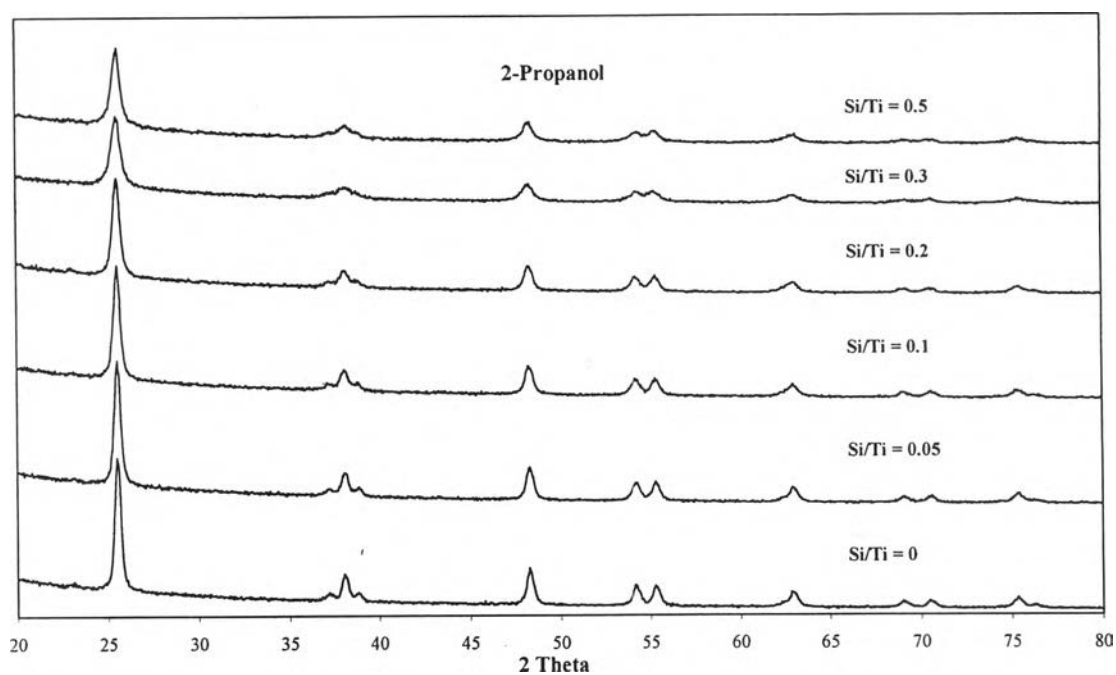
From Table 5.3, with an increase of the amounts of TEOS added, the surface area gradually increased and the crystallite size does not change when a small amount of TEOS added to the reaction mixture, indicating that a small amount of TEOS added to reaction mixture did not affect crystallization of anatase. The XRD patterns of product prepared in 2-propanol as shown in Figure 5.11 showed that the anatase-rutile transformation to shift toward higher temperature, which was similar to the product prepared in 1,4 butanediol and toluene. After the calcination at 1000 °C, the products with Si/Ti > 0.3 maintained BET surface area more than 40 m<sup>2</sup> g<sup>-1</sup> and the crystallite size about 42 nm. The TEM photographs of products synthesized by 2-propanol were shown in Figure 5.12.



**Figure 5.6(a)** XRD patterns of all Si/Ti ratios of silica modified titanium (IV) oxide synthesized by 1,4 butanediol.



**Figure 5.6(b)** XRD patterns of all Si/Ti ratios of silica modified titanium (IV) oxide synthesized by toluene.



**Figure 5.6(c)** XRD patterns of all Si/Ti ratios of silica modified titanium (IV) oxide synthesized by 2-propanol.

**Table 5.1** BET surface area and crystallite size of products synthesized by 1,4 butanediol and the samples calcined at various temperatures.

Charged Si/Ti ratio	Reaction Temperature ( $^{\circ}\text{C}$ )	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )				$d_{101}^{\text{b}}$ (nm)			
		$300^{\circ}\text{C}$	$600^{\circ}\text{C}$	$800^{\circ}\text{C}$	$1000^{\circ}\text{C}$	$300^{\circ}\text{C}$	$600^{\circ}\text{C}$	$800^{\circ}\text{C}$	$1000^{\circ}\text{C}$
0	300	89.3	38.4	16.1	2.8	17 (16.7) <sup>c</sup>	37	96	218
0.05	300	132	120	58.6	16.1	9.7 (10)	11	24	71
0.1	300	155	138	76.7	28.8	8.4 (8.3)	8.4	15	49
0.2	300	177	174	136	41.9	7.1 (6.7)	7.1	8.7	35
0.3	300	173	171	144	47	7 (6.7)	7	8.1	26
0.5	300	158	147	132	43.9	8.1 (8.3)	8.1	8.7	28

<sup>a</sup>BET surface area.

<sup>b</sup>Crystallite size of anatase from the 101 and 110 diffraction peak of anatase and rutile phases using Sherrer equation, respectively.

<sup>c</sup>Crystallite size of anatase from TEM photograph.

**Table 5.2** BET surface area and crystallite size of products synthesized by toluene and the samples calcined at various temperatures

Charged Si/Ti ratio	Reaction Temperature (°C)	$S_{\text{BET}}^{\text{a}}$ (m <sup>2</sup> /g)				$d_{101}^{\text{b}}$ (nm)			
		300°C	600°C	800°C	1000°C	300°C	600°C	800°C	1000°C
0	300	98.1	32.0	8.2	1.2	16 (15.7) <sup>c</sup>	53	152	307
0.05	300	114	107	66.4	10.2	12 (12)	15	30	110
0.1	300	135	121	81.6	17.6	12 (11.7)	13	22	71
0.2	300	164	151	88.3	22.4	12 (11)	12	16	56
0.3	300	168	142	115	26.6	11 (11)	11	13	47
0.5	300	185	176	142	31.2	10 (10)	10	11	40

<sup>a</sup>BET surface area.

<sup>b</sup>Crystallite size of anatase from the 101 and 110 diffraction peak of anatase and rutile phases using Sherrer equation, respectively.

<sup>c</sup>Crystallite size of anatase from TEM photograph.

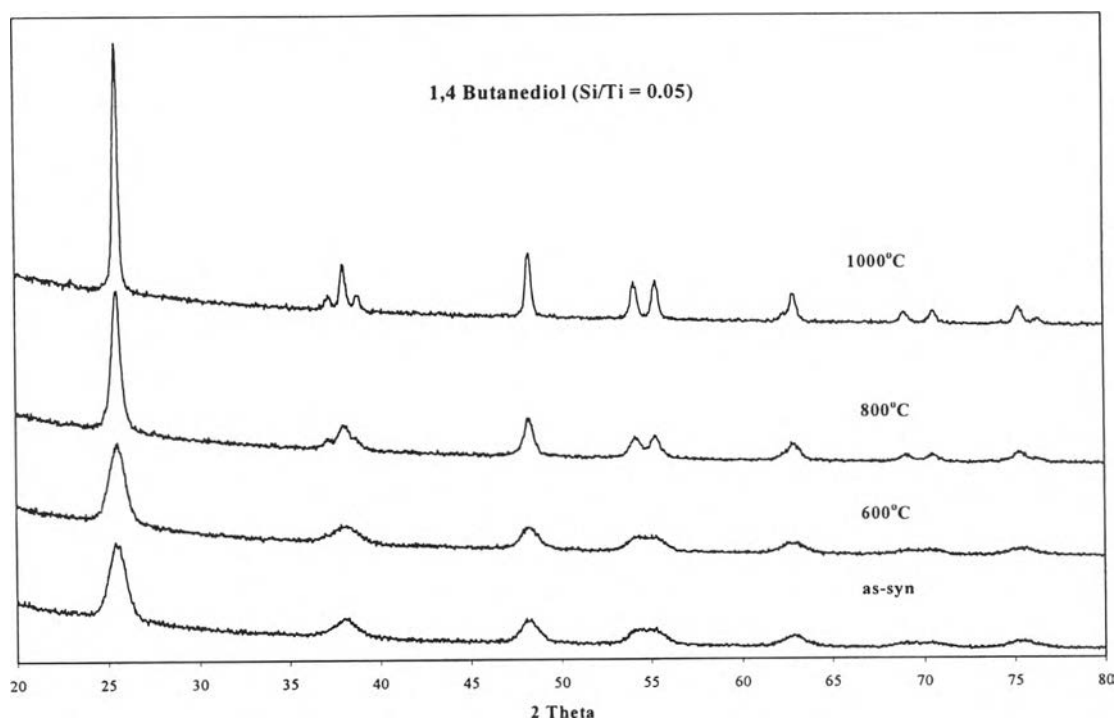
**Table 5.3** BET surface area and crystallite size of products synthesized by 2-propanol and the samples calcined at various temperatures

Charged Si/Ti ratio	Reaction Temperature ( °C)	$S_{\text{BET}}^{\text{a}}$ (m <sup>2</sup> /g)				$d_{101}^{\text{b}}$ (nm)			
		300 <sup>o</sup> C	600 <sup>o</sup> C	800 <sup>o</sup> C	1000 <sup>o</sup> C	300 <sup>o</sup> C	600 <sup>o</sup> C	800 <sup>o</sup> C	1000 <sup>o</sup> C
0	300	42.3	36.6	10.0	2.5	42 (40) <sup>c</sup>	47	110	245
0.05	300	43.2	35.1	26.6	15.8	42 (40)	42	47	72
0.1	300	45.7	41.9	31.2	18.0	38 (38)	38	40	61
0.2	300	53.9	48.8	36.0	29.5	32 (33)	32	35	53
0.3	300	78.1	71.0	67.9	40.0	22 (21)	22	23	42
0.5	300	72.0	66.1	61.5	41.2	24 (21)	26	28	42

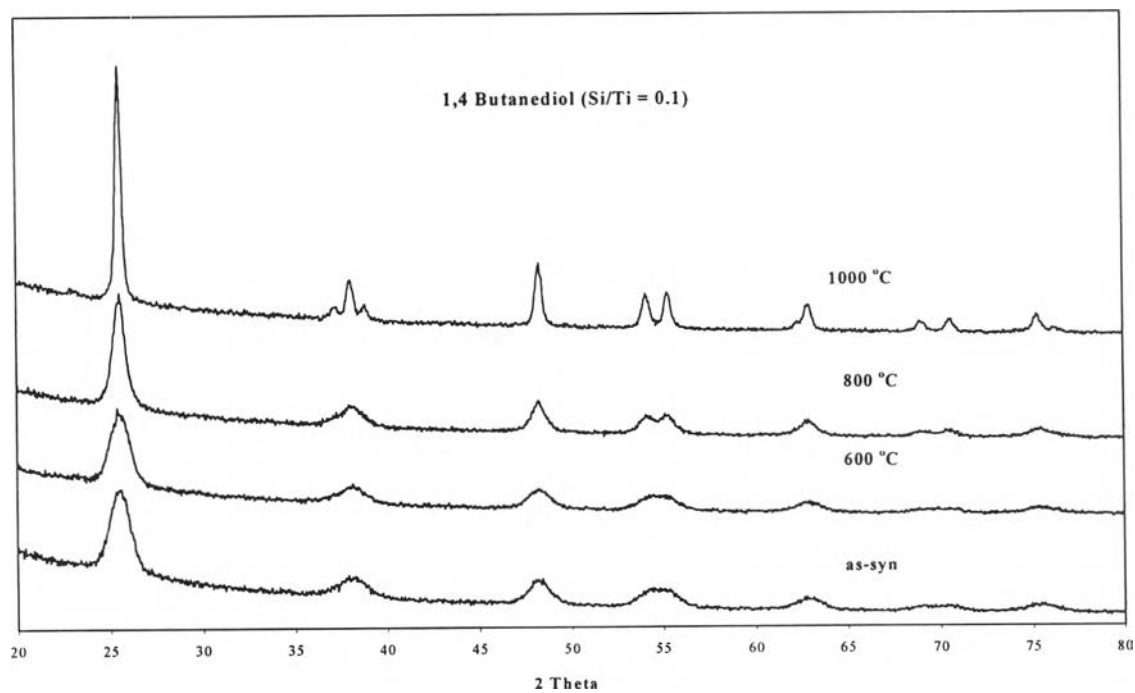
<sup>a</sup>BET surface area.

<sup>b</sup>Crystallite size of anatase from the 101 and 110 diffraction peak of anatase and rutile phases using Sherrer equation, respectively.

<sup>c</sup>Crystallite size of anatase from TEM photograph.

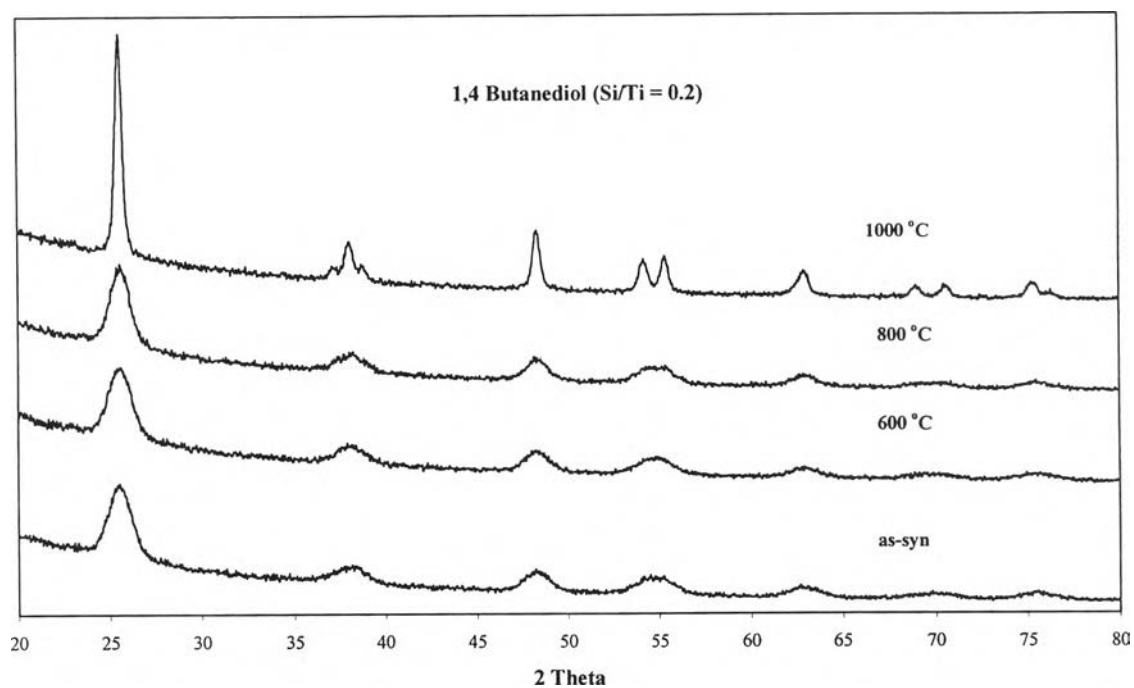


**Figure 5.7(a)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.05 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.

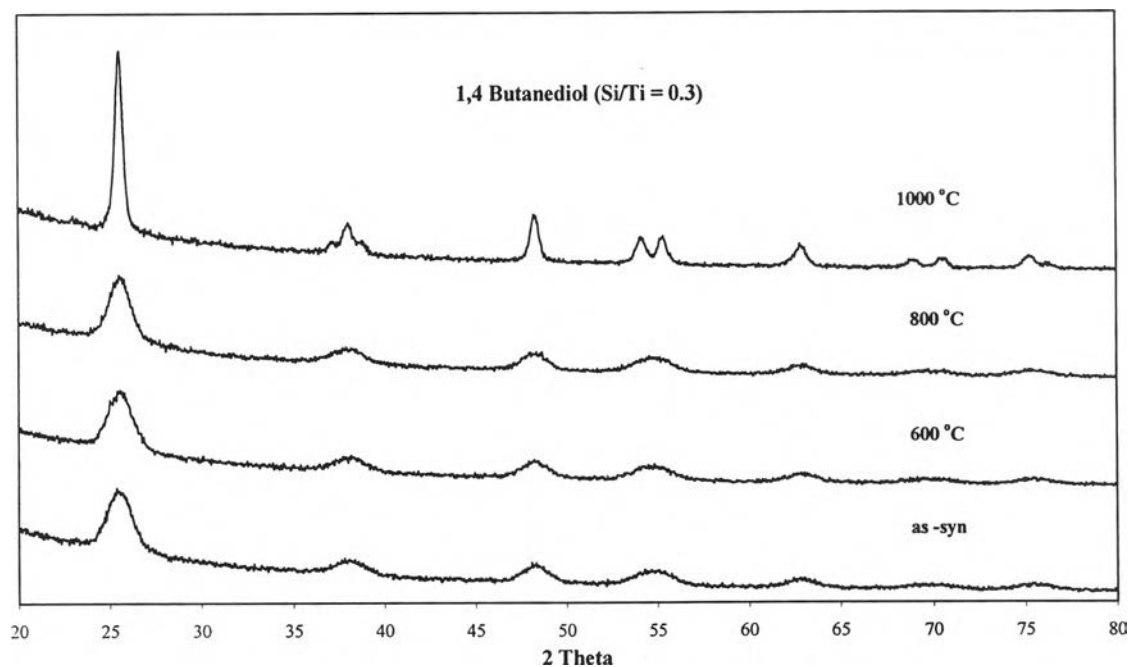


**Figure 5.7(b)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.1 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.

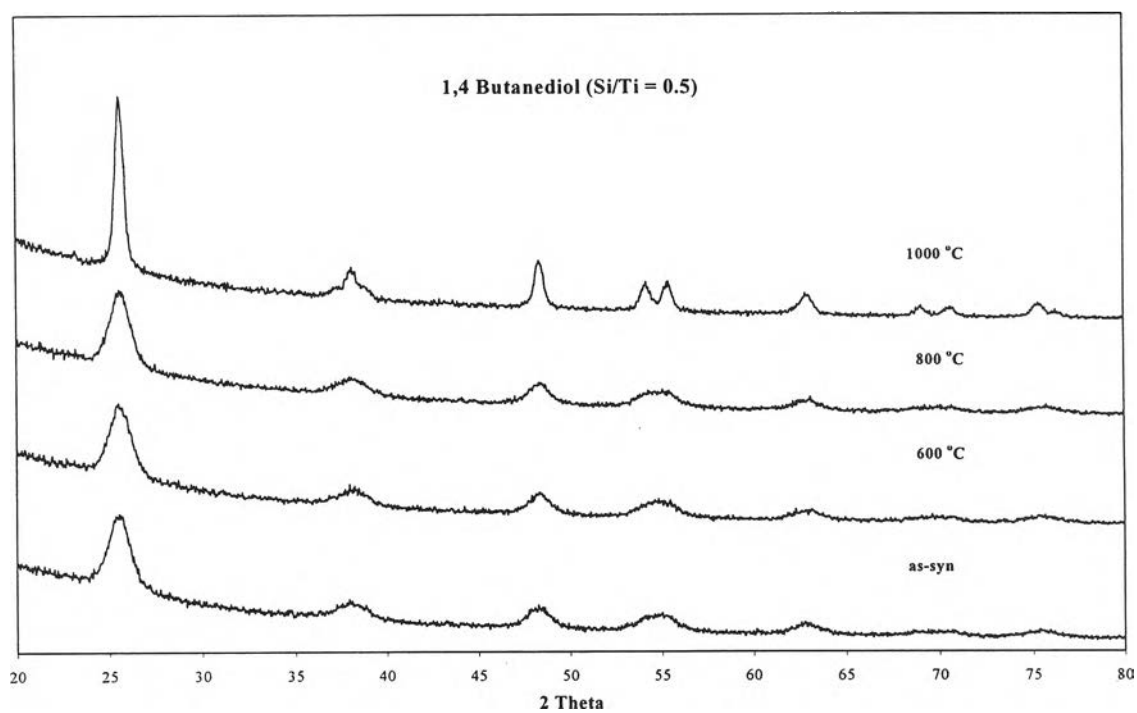




**Figure 5.7(c)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.2 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.

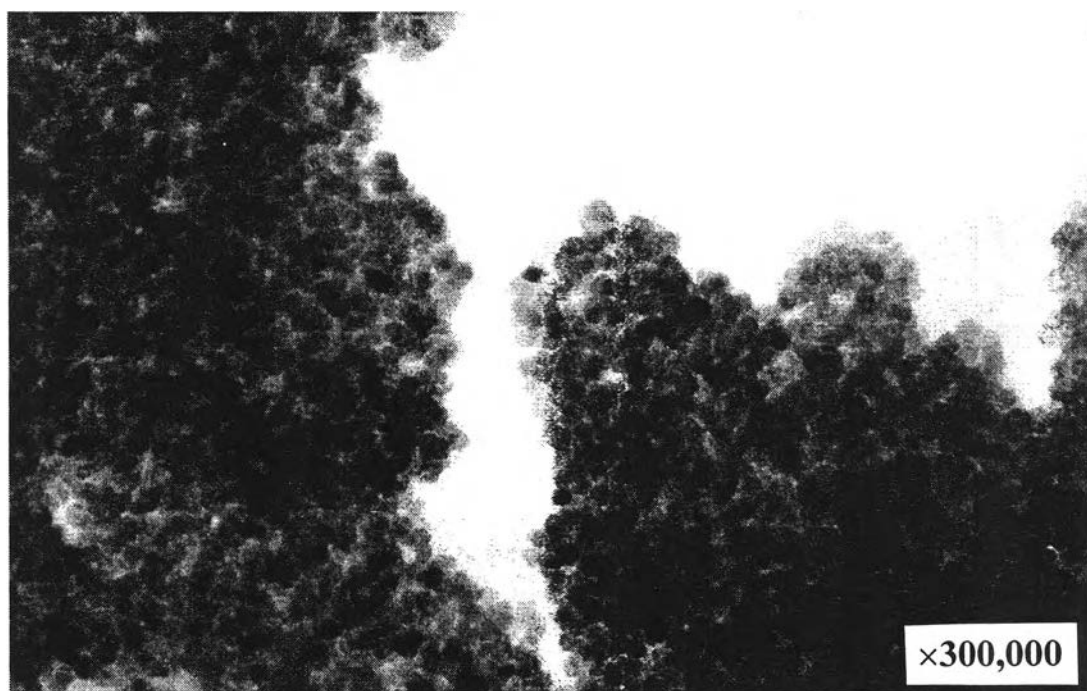


**Figure 5.7(d)** XRD pattern of silica modified titanium (IV) oxide with Si/Ti = 0.3 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.



**Figure 5.7(e)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.

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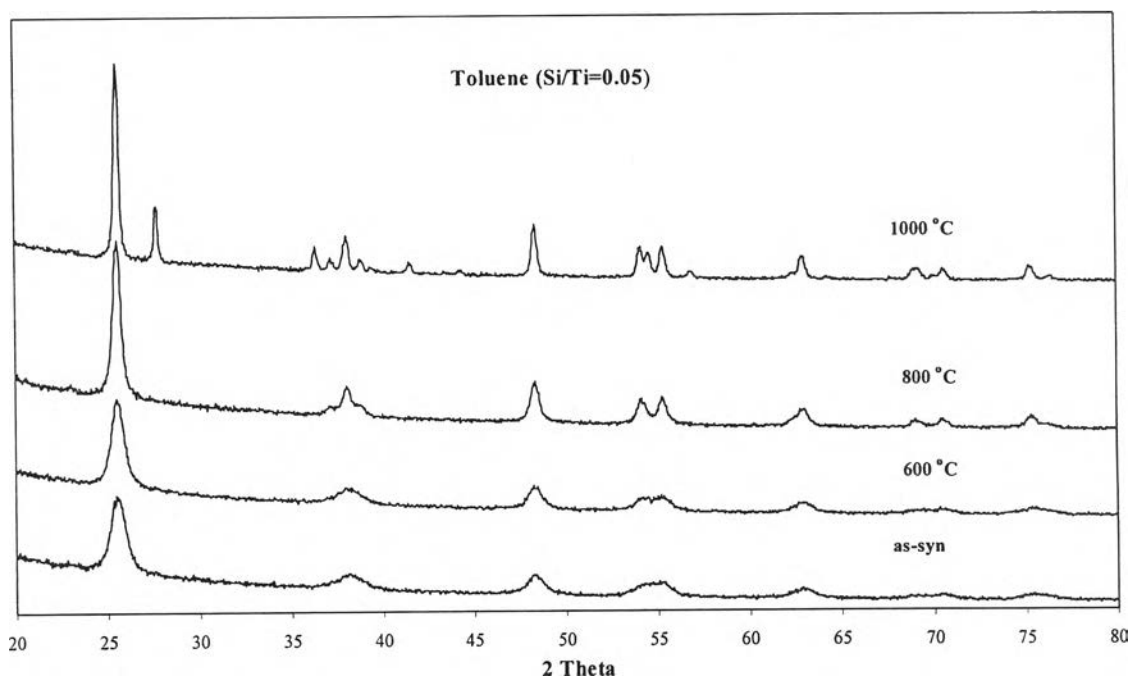
**Figure 5.8(c)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.2 synthesized by 1,4 butanediol.



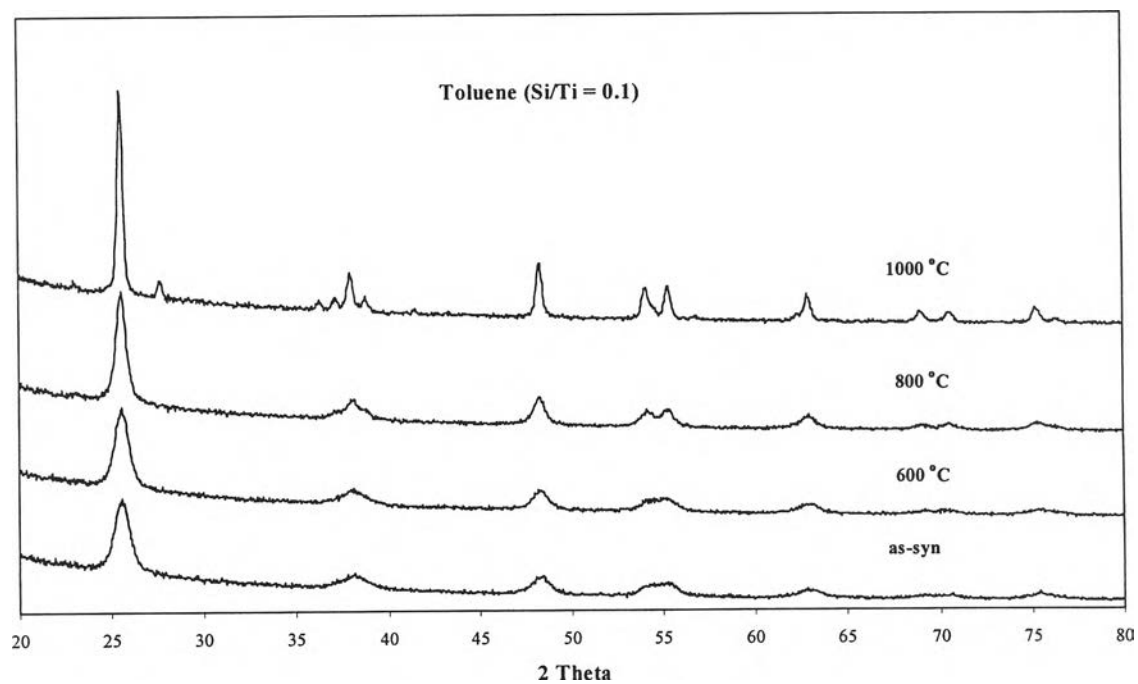
**Figure 5.8(d)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.3 synthesized by 1,4 butanediol.



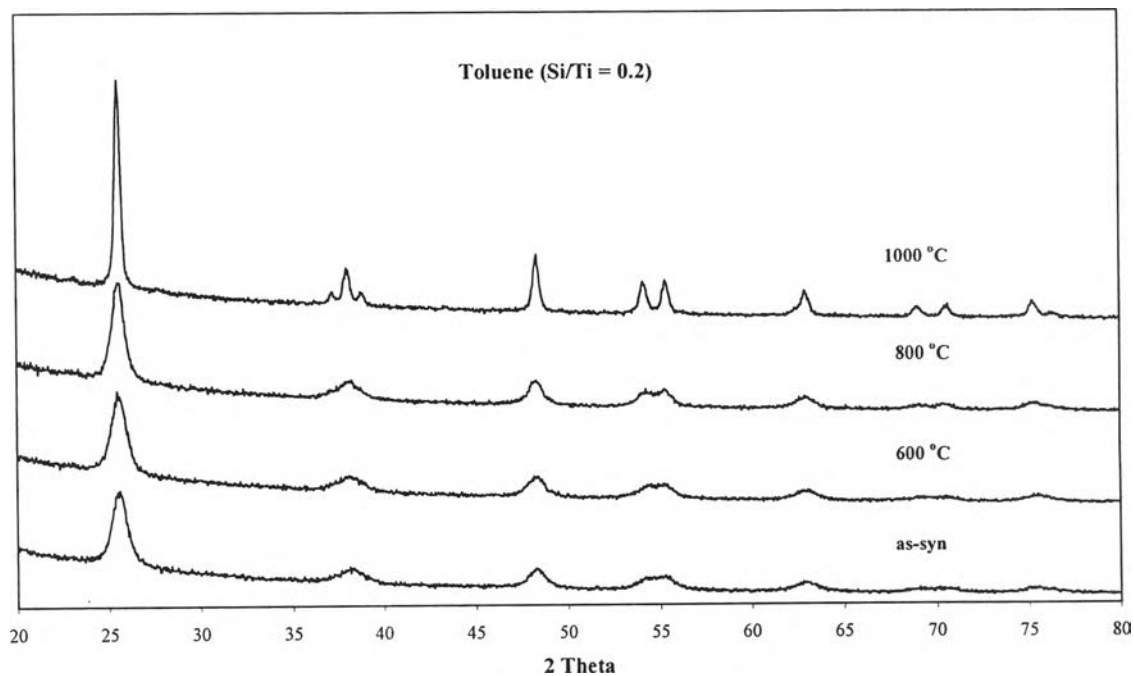
**Figure 5.8(e)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 1,4 butanediol.



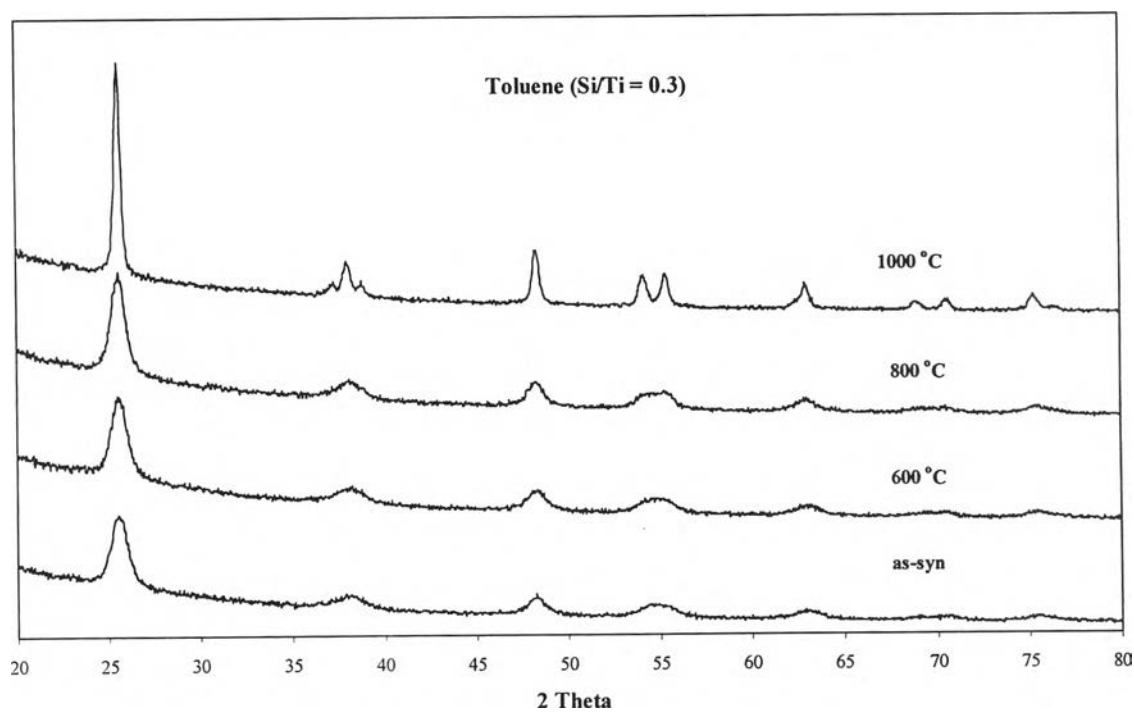
**Figure 5.9(a)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.05 synthesized by toluene before and after calcination at 600, 800 and 1000°C.



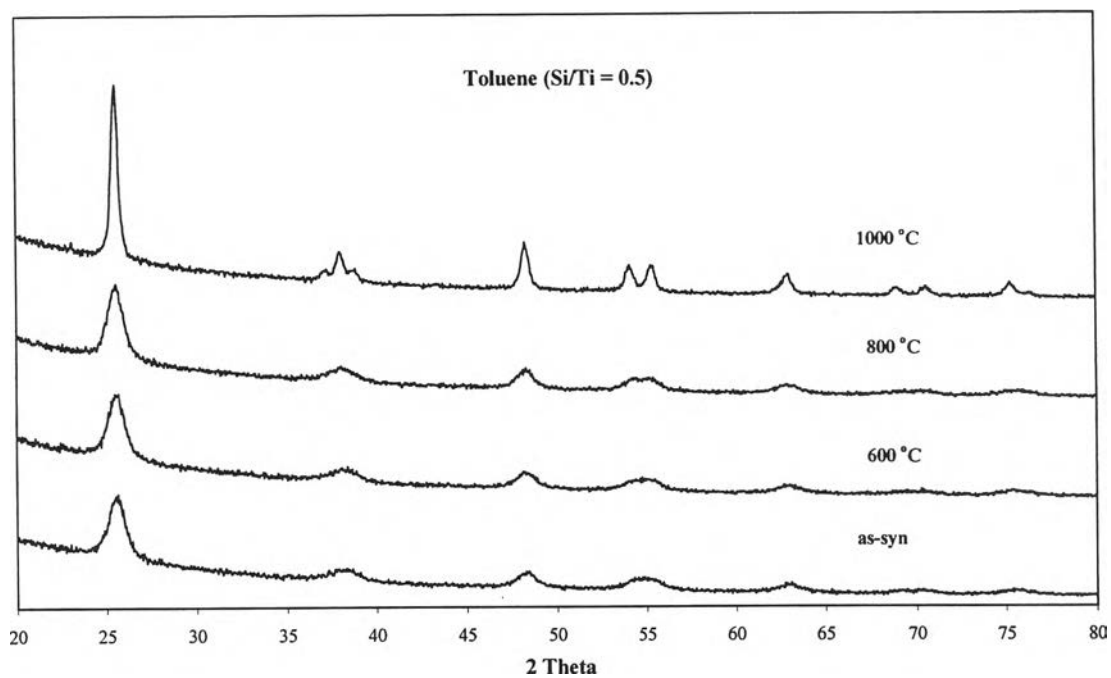
**Figure 5.9(b)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.1 synthesized by toluene before and after calcination at 600, 800 and 1000°C.



**Figure 5.9(c)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.2 synthesized by toluene before and after calcination at 600, 800 and 1000°C.

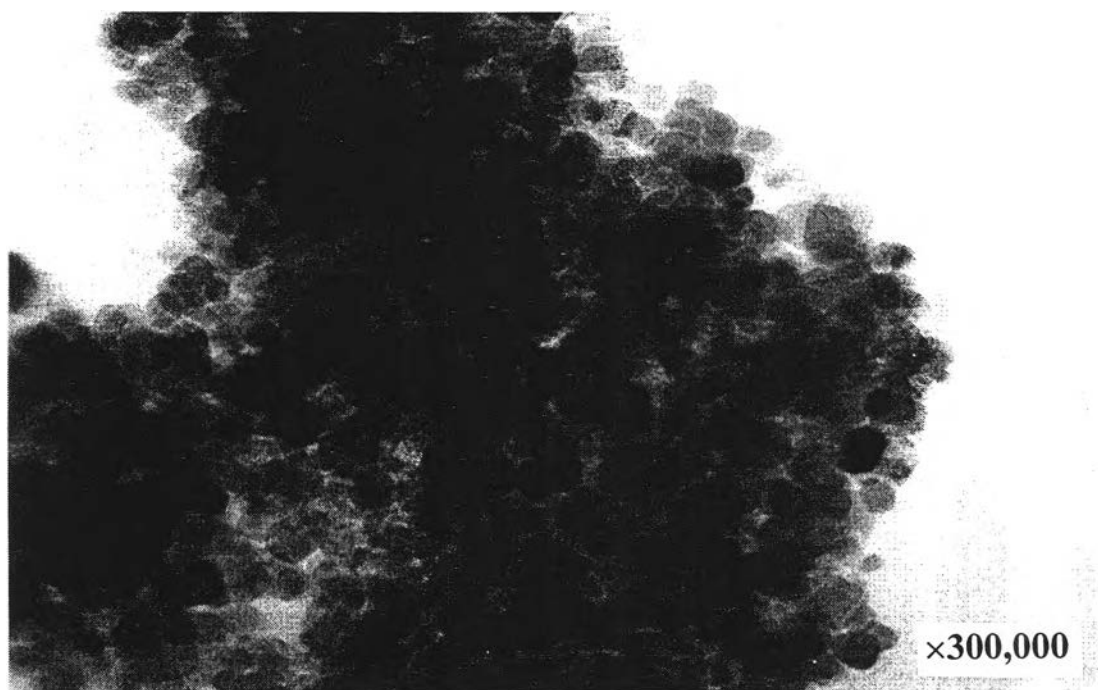


**Figure 5.9(d)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.3 synthesized by toluene before and after calcination at 600, 800 and 1000°C.

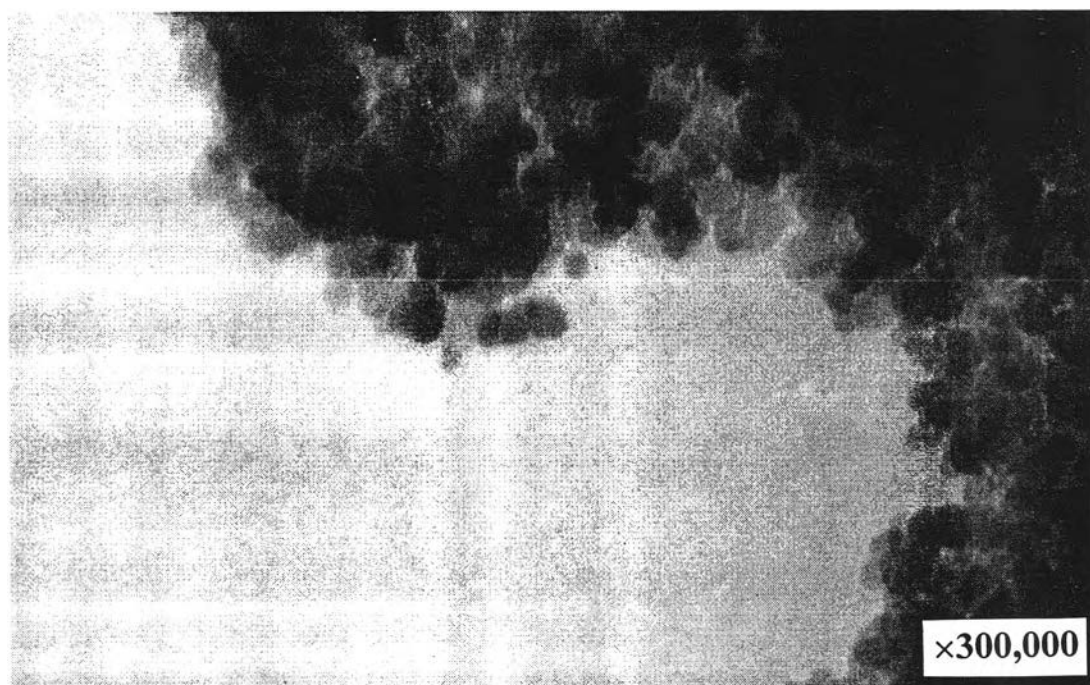


**Figure 5.9(e)** XRD pattern of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by toluene before and after calcination at 600, 800 and 1000°C.

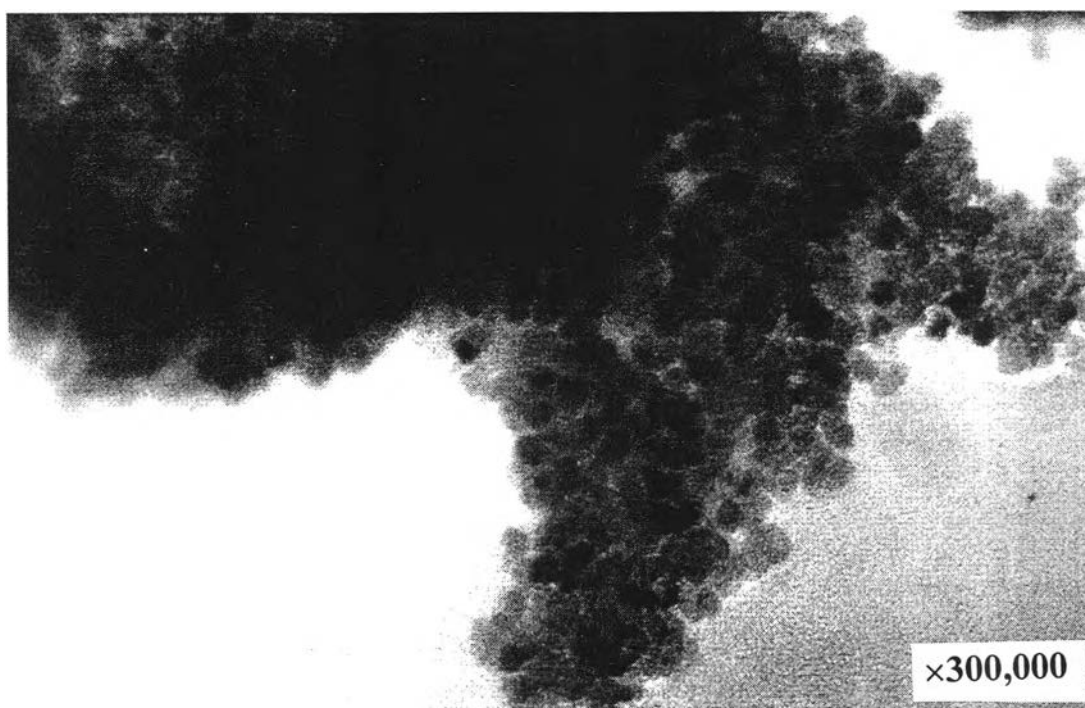




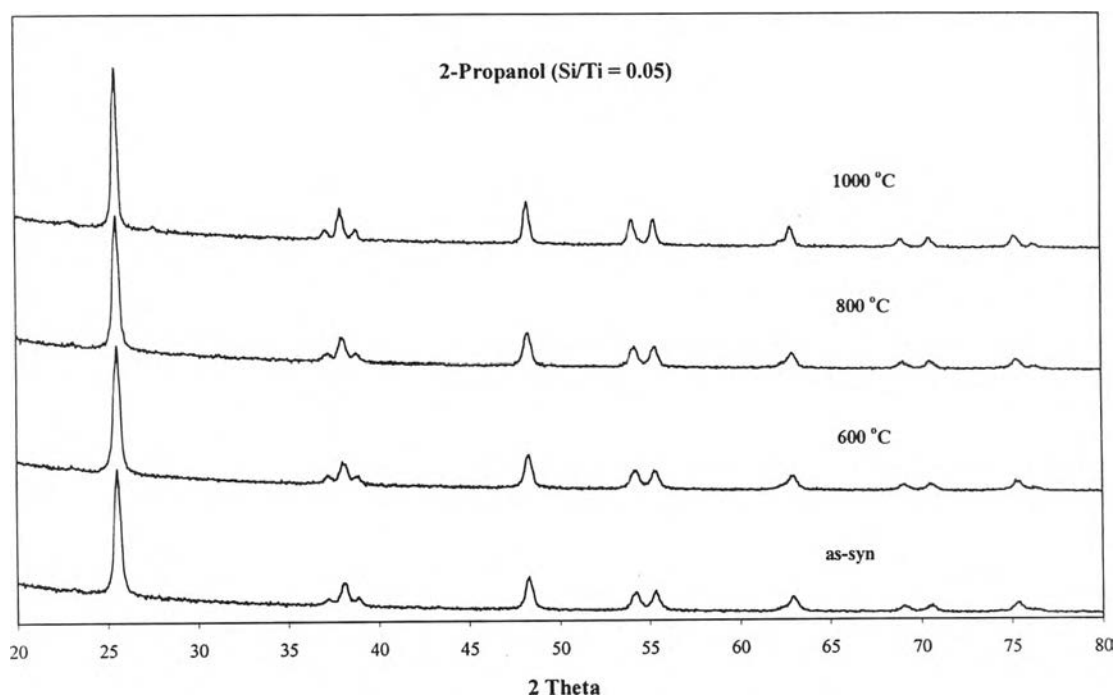
**Figure 5.10(a)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.05 synthesized by toluene.



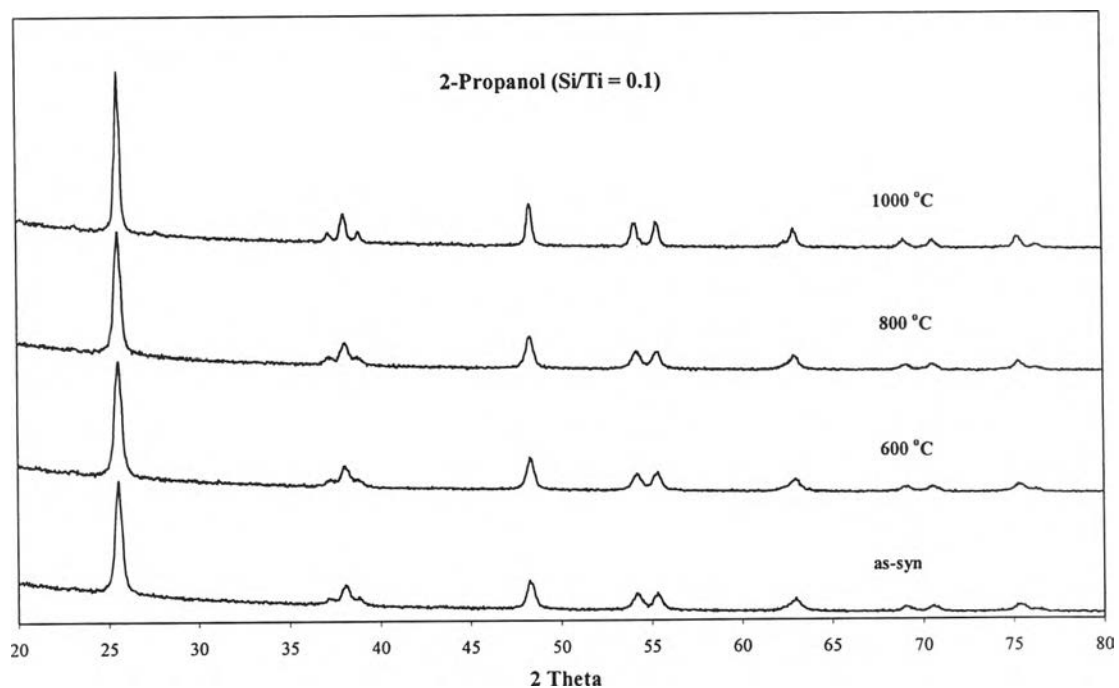
**Figure 5.10(b)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.1 synthesized by toluene.



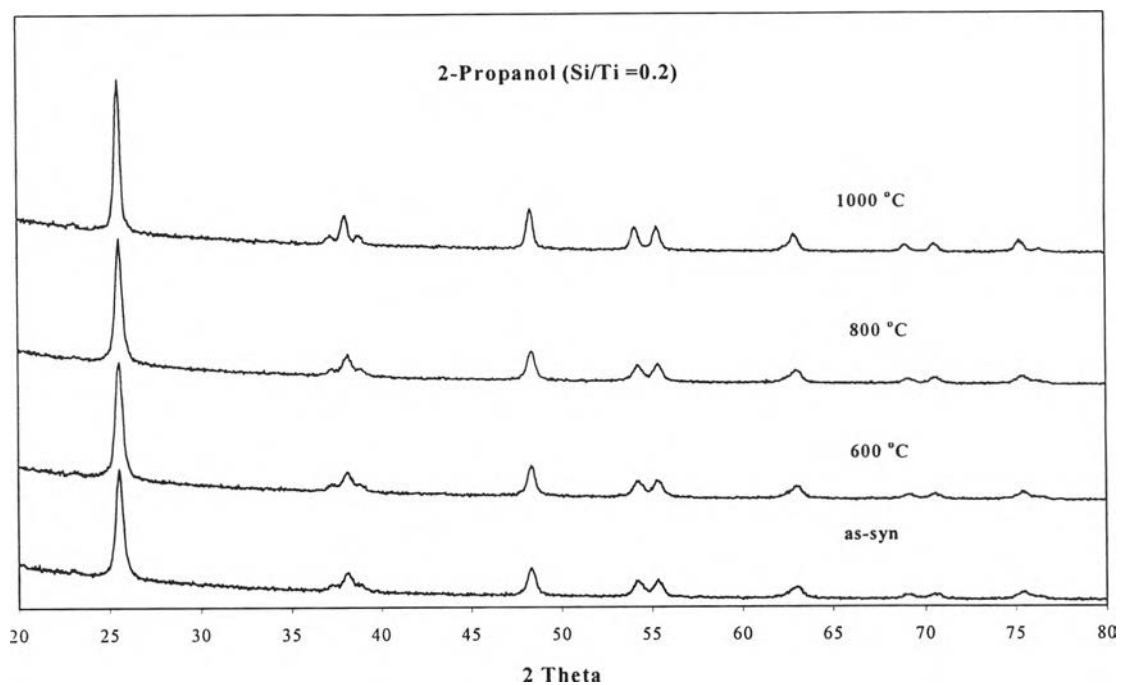
**Figure 5.10(e)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by toluene.



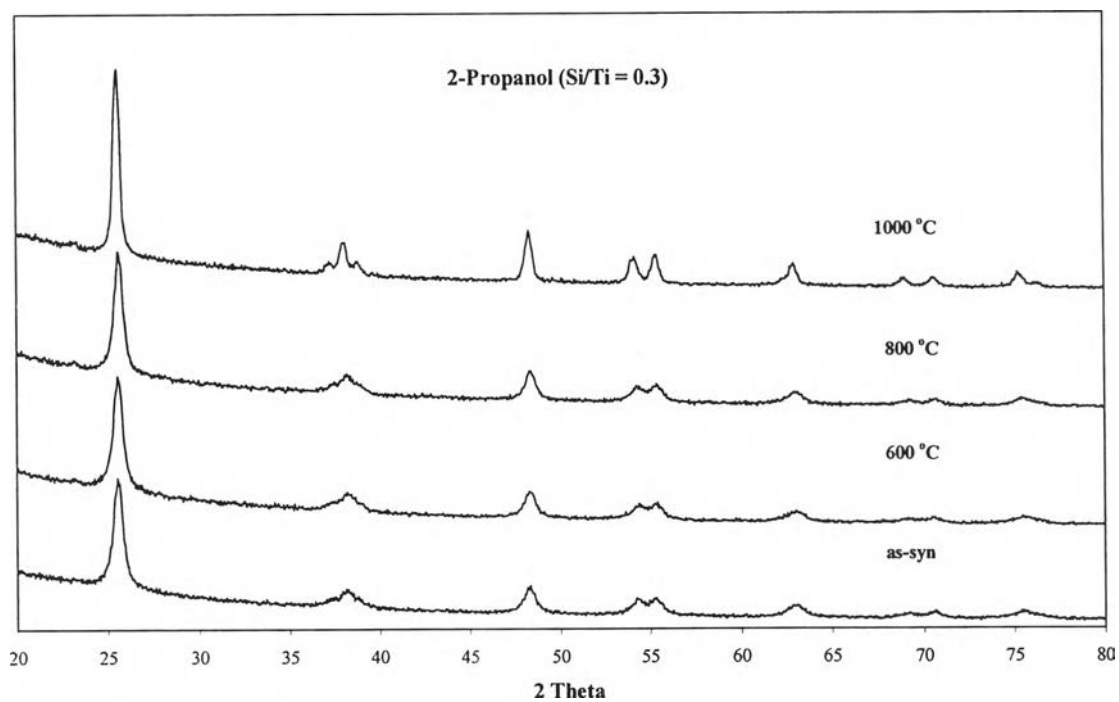
**Figure 5.11(a)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.05 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.



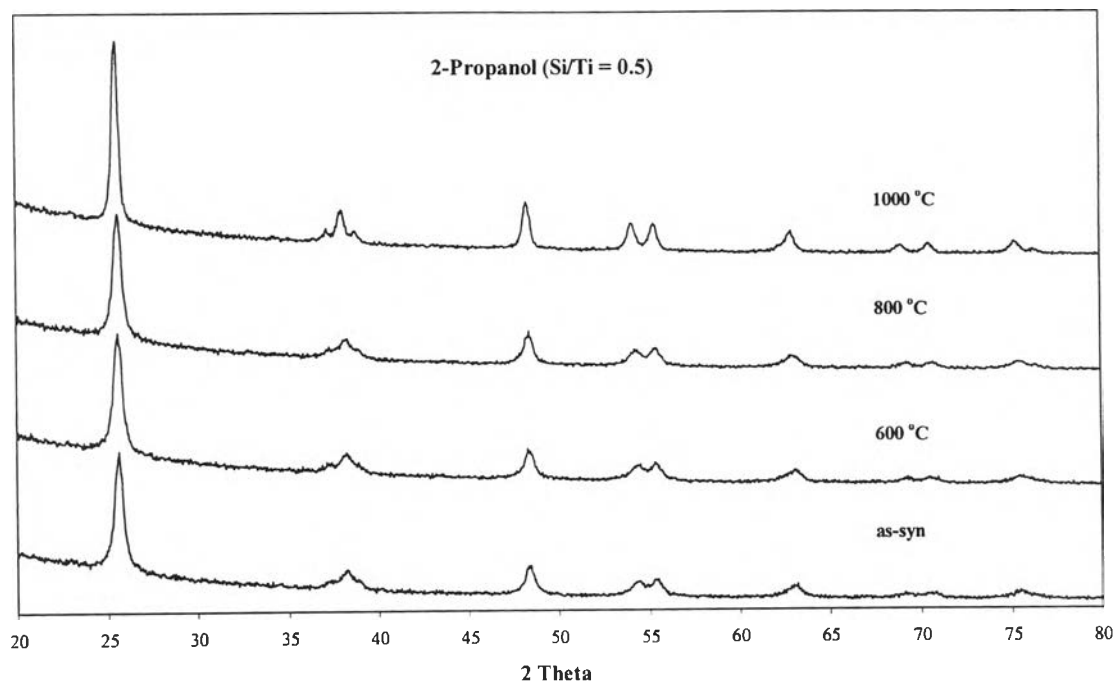
**Figure 5.11(b)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.1 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.



**Figure 5.11 (c)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.2 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.

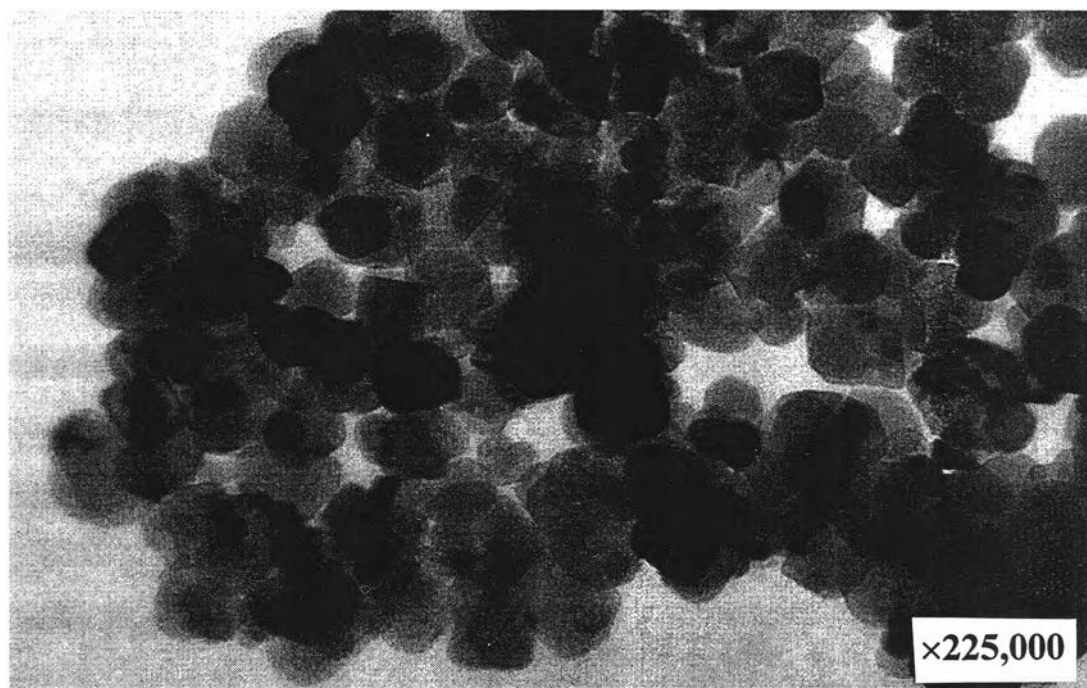


**Figure 5.11(d)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.3 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.

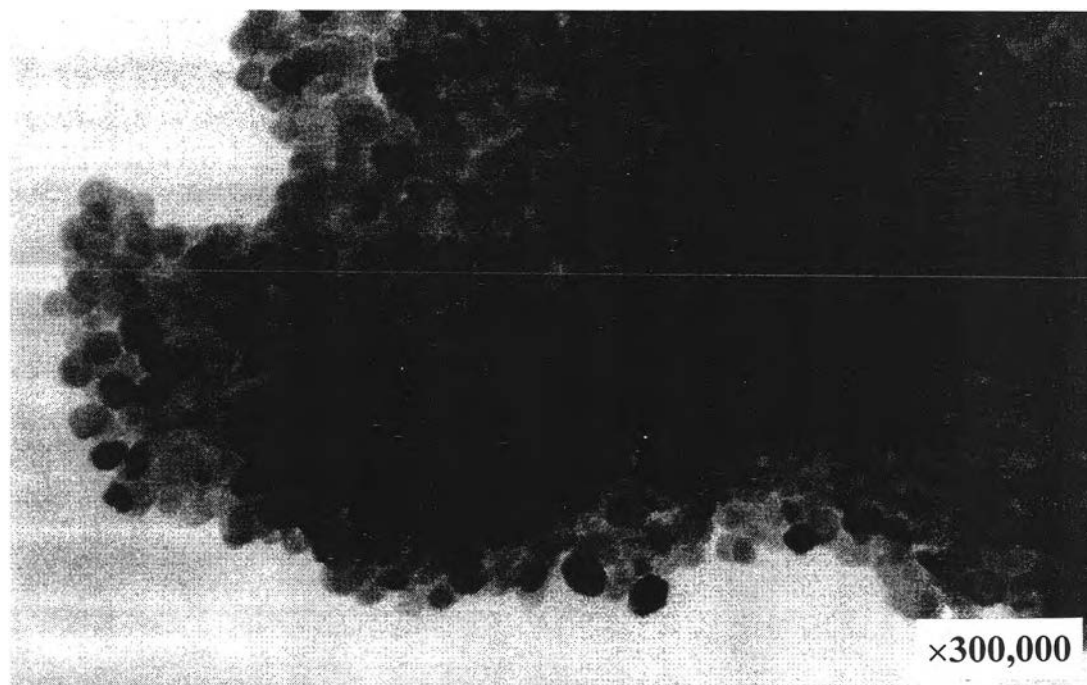


**Figure 5.11(e)** XRD patterns of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.

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**Figure 5.12(c)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.2 synthesized by 2-propanol.



**Figure 5.12(d)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.3 synthesized by 2-propanol.



**Figure 5.12(e)** TEM photograph of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 2-propanol.



### 5.3 Effect of an increase in silica content on the physical properties and the thermal stability of the products

As described in section 5.2, the XRD patterns of products obtained with addition of TEOS revealed that all the products had the anatase structure and that the peak intensities were not affected by the TEOS content in the reaction mixture. Their XRD patterns were almost identical to those of the product obtained without addition of the TEOS except for the fact that the peak intensities of anatase decreased due to formation of amorphous phase. This result shows that X-ray diffraction spectroscopy could not use to distinguish phase between silica and titanium (IV) oxide. Thus, in this study, the FT-IR spectroscopy was used to corroborate effect of the increase in silica content on properties and thermal stability of products.

The results of the FT-IR spectroscopic measurement are summarized in Figure 5.13 to 5.15. The spectra of pure anatase titanium (IV) oxides prepared in 1,4 butanediol, toluene and 2-propanol showed the same spectral feature (Figure 5.13 (a) to (c)). The spectrum of pure anatase titanium (IV) oxide synthesized in 1,4 butanediol is characterized by a very strong band with two adsorbance at 600 and 486  $\text{cm}^{-1}$ . Larbot et al. and Chhor et al. observed the same bands assigned to  $\nu_{\text{Ti-O}} = 653$  to 550  $\text{cm}^{-1}$  and  $\nu_{\text{Ti-O-Ti}} = 495$  to 436  $\text{cm}^{-1}$ . On the basis of the  $\nu_{\text{Ti-O-Ti}}$  frequency the formation of the Ti-O-Ti bonds by condensation reaction could be followed. Two OH stretching bands at 3352 to 3233  $\text{cm}^{-1}$  are also visible. The band at 1625  $\text{cm}^{-1}$  corresponds to the bending mode of adsorbed water [27].

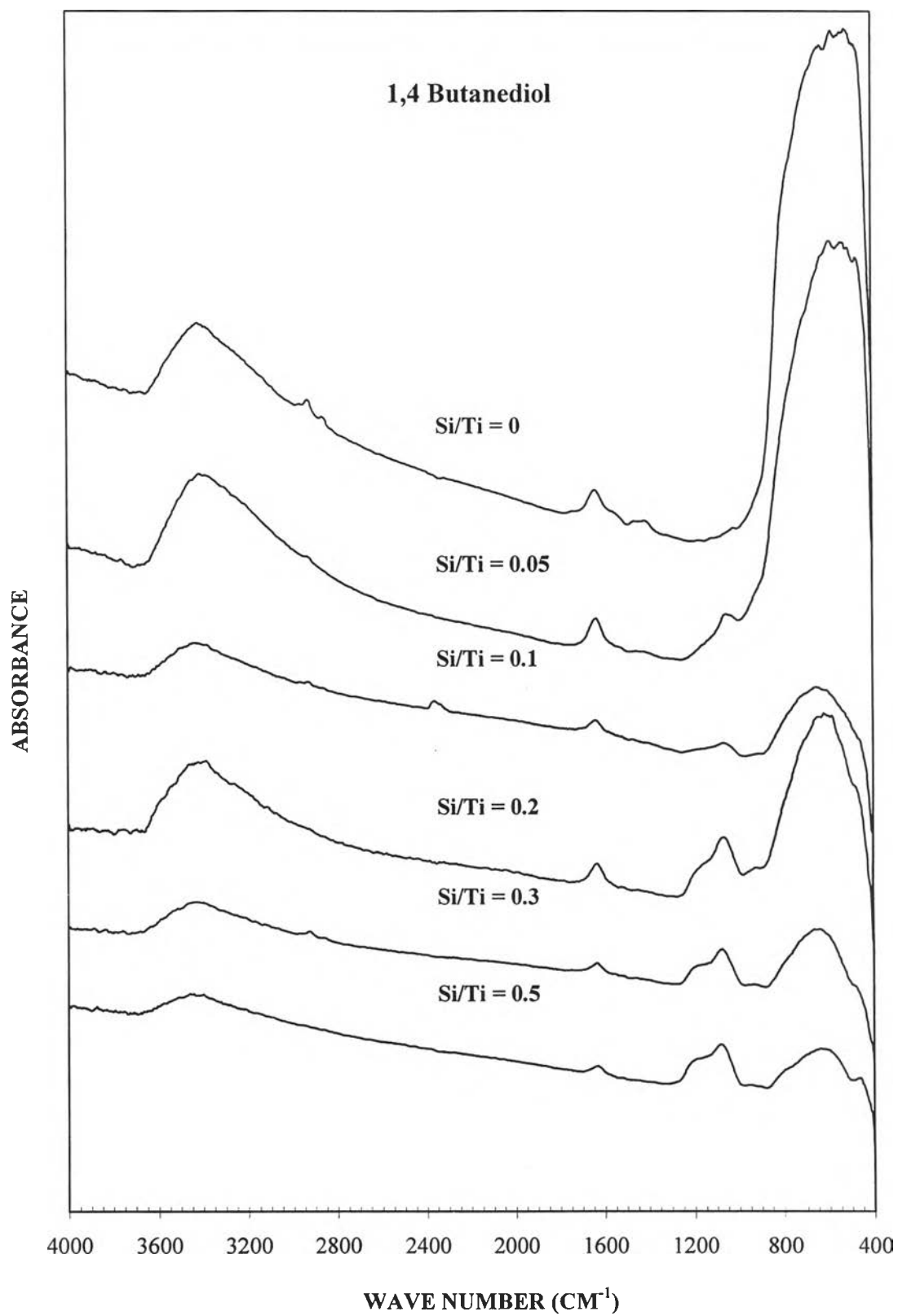
In the case of silica, with no titanium (IV) oxide, shows a strong absorption at 1100  $\text{cm}^{-1}$ , which is due to Si-O-Si bonds and another band at 974  $\text{cm}^{-1}$  due to the OH bending vibration of the silanol group. However, in the presence of titanium (IV) oxide the bending vibration band shifts to lower frequency and become broader with increasing titanium (IV) oxide content. This shift of the bending band of the silanol groups to a lower frequency is caused by the interaction between titanium (IV) oxide and silica [25,28,29].

For the silica modified titanium (IV) oxide shows all IR bands of pure anatase while IR bands of silica were shift to low frequency, peak at  $1086\text{ cm}^{-1}$  is due to Si-O-Si bonds and peak at  $940\text{ cm}^{-1}$  is due to Si-O-Ti bonds.

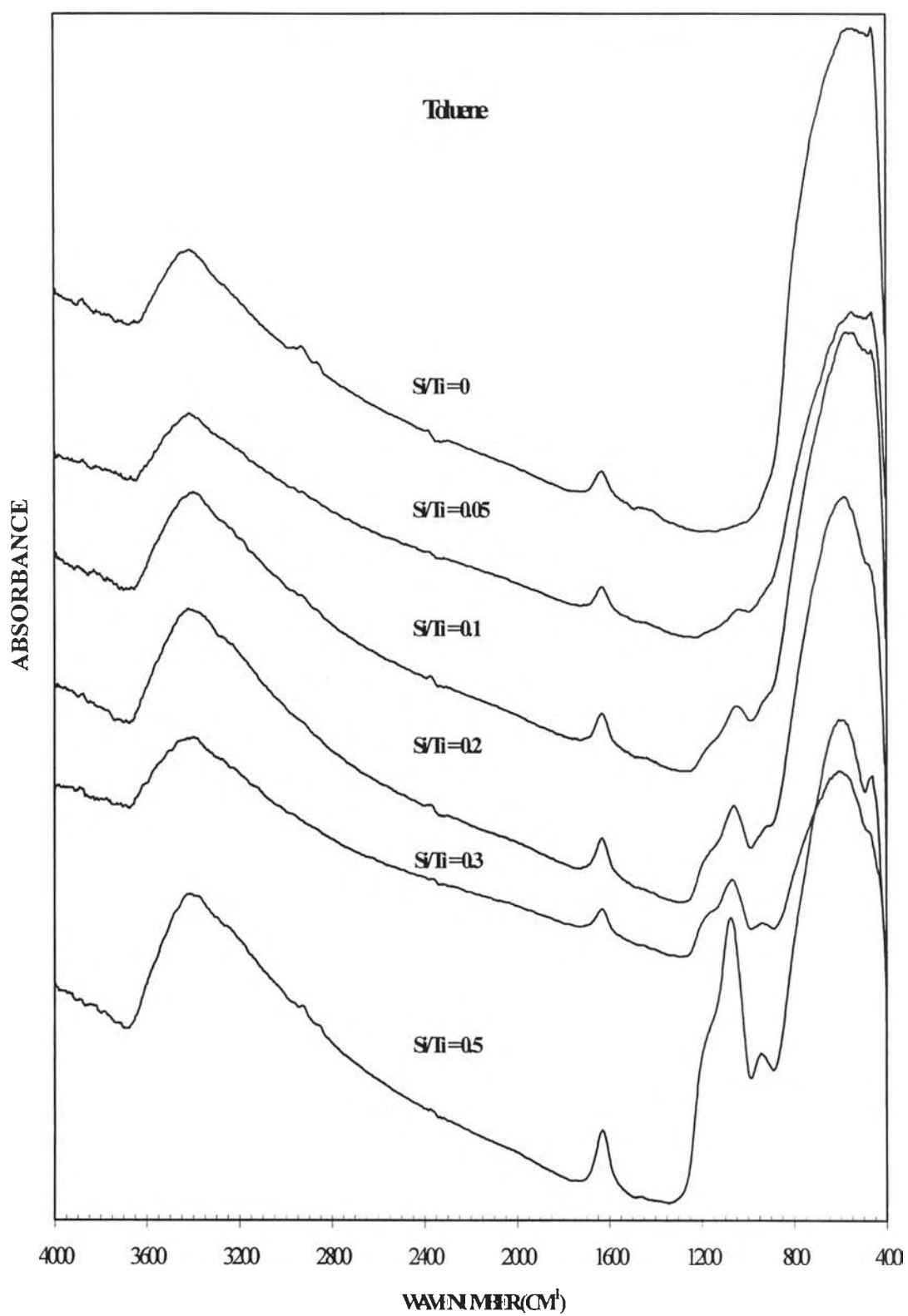
The FT-TR spectra of pure anatase titanium (IV) oxide prepare in 1,4 butanediol before and after calcination at various temperatures are given in Figure 5.13(a) to 5.13(c), which shown that the spectra of products before and after calcination at  $600\text{ }^{\circ}\text{C}$  and  $800\text{ }^{\circ}\text{C}$  had the same spectral features. However, after calcination at  $1000\text{ }^{\circ}\text{C}$ , the FT-TR spectra of product changed because this product was completely transformed to rutile phase. Thus, the FT-IR spectra of product calcined at  $1000\text{ }^{\circ}\text{C}$  was shown in Figure 5.14 can be ascribed to rutile. The results of FT-IR spectra of products obtained with silica content (prepared in 1,4 butanediol) were given in Figure 5.13(a), which showed that the peak at  $940\text{ cm}^{-1}$  (due to Si-O-Ti) and the peak at  $1086\text{ cm}^{-1}$  (due to Si-O-Si) increased when the amounts of TEOS in reaction mixture increased. This result indicated that amorphous silica was formed.

Table 5.1 and Figure 5.1 showed that the increase of silica content in the titanium (IV) oxide lattice seems to contribute to the deceleration of grain growth of anatase and the suppression of anatase-rutile transformation because the rearrangement of titanium (IV) oxide was prevented by the coexistence of silica. However, the grain growth and aggregation of anatase with calcination was not suppressed by the introduction of silica, because of the phase separation. The increase of silica content in product generated Si-O-Ti interaction (peak at  $940\text{ cm}^{-1}$ ), which these Si-O-Ti bonds are less stable than Ti-O-Ti and Si-O-Si bonds therefore, at high calcination temperature, the unstable Si-O-Ti bonds break and Ti-O-Ti and Si-O-Si bonds reform. Thus, the grain growth and aggregation of the anatase particles occurred [30].

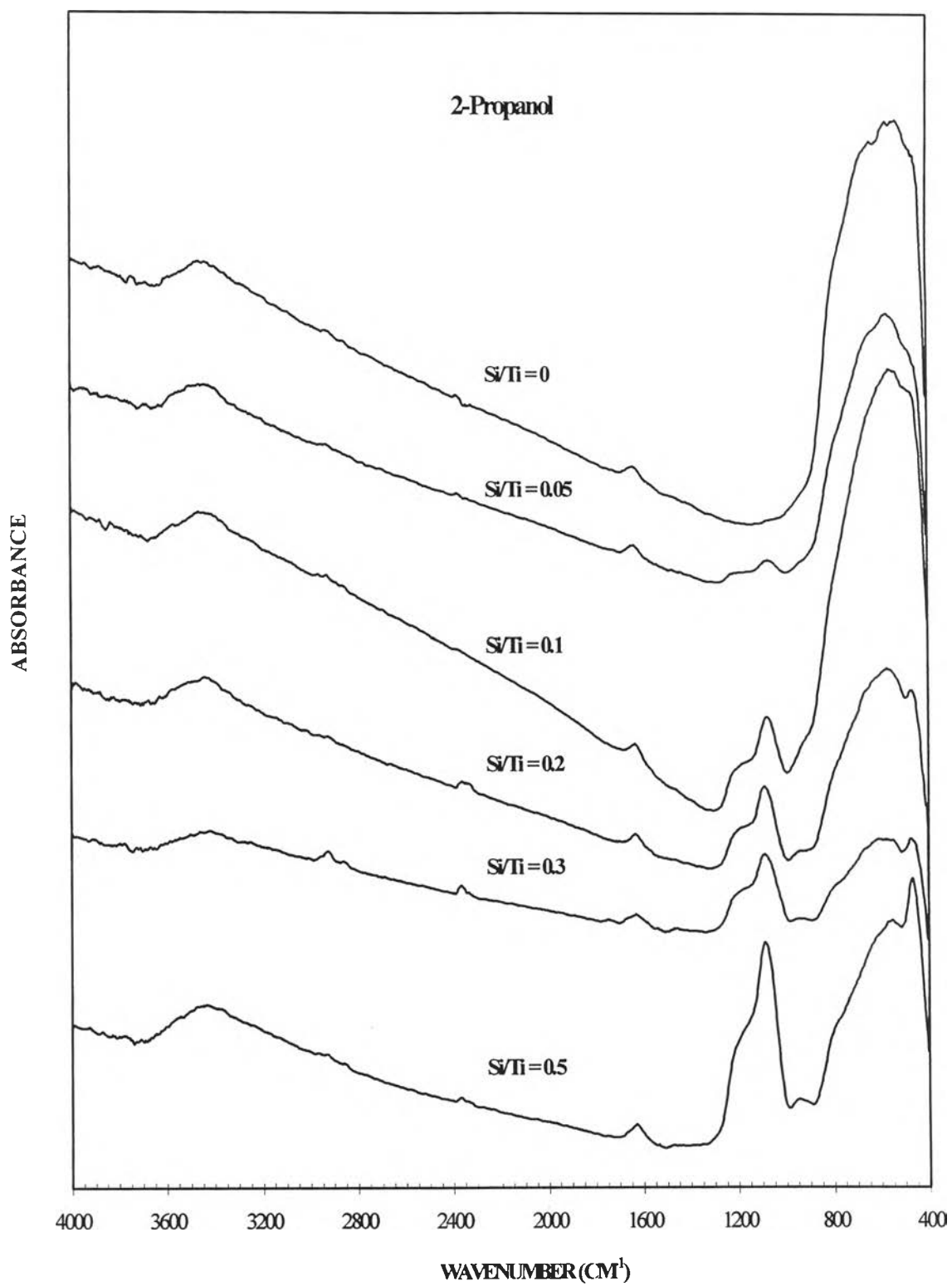
As described above, the increase of the amounts of TEOS added in reaction mixture over limit, tended to yield amorphous phase instead of anatase titanium (IV) oxide and the thermal stability of product drastically decreased.



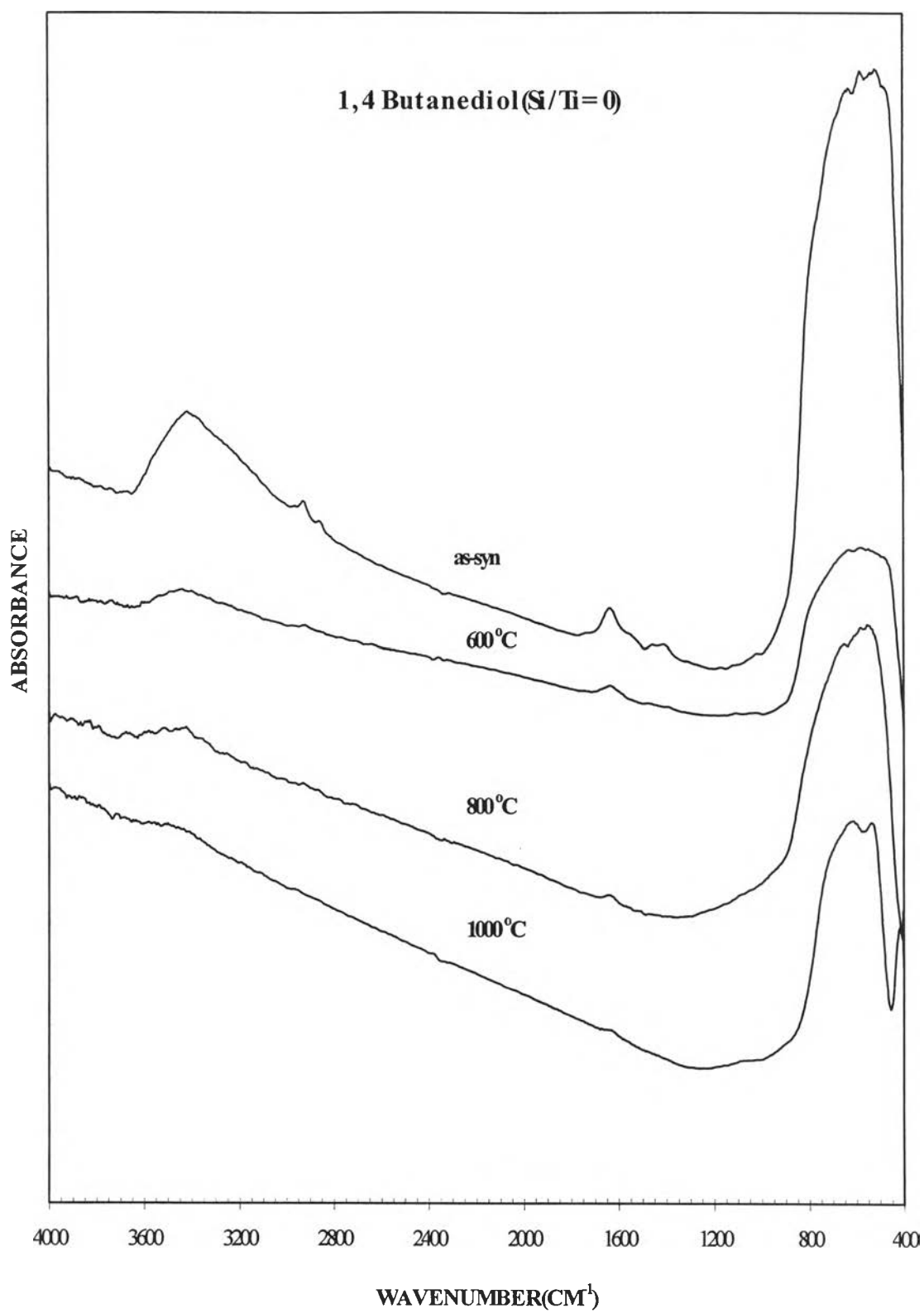
**Figure 5.13(a)** FT-IR spectra of titanium (IV) oxide and silica modified titanium (IV) oxide synthesized by 1,4 butanediol.



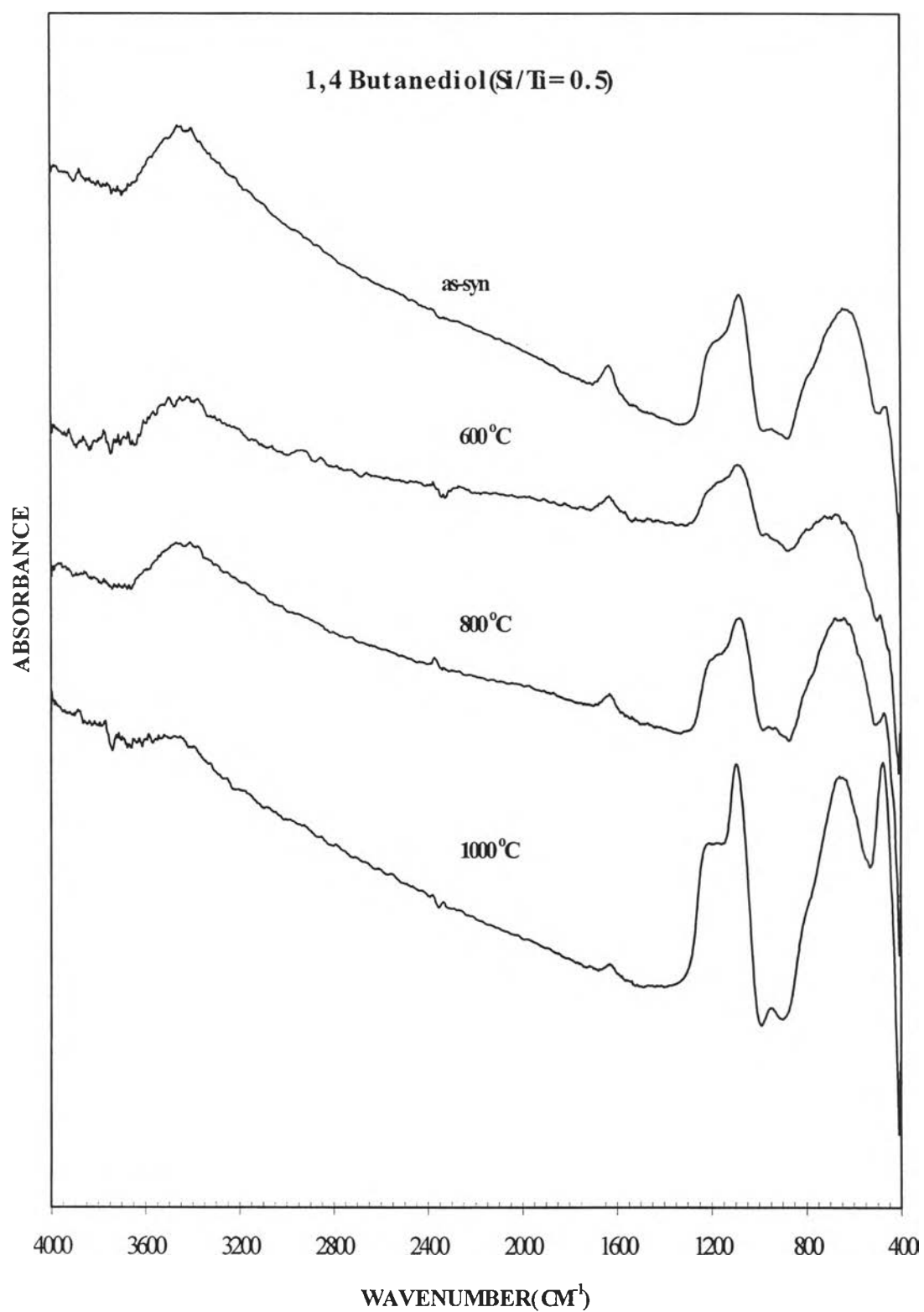
**Figure 5.13(b)** FT-IR spectra of titanium (IV) oxide and silica modified titanium (IV) oxide synthesized by toluene.



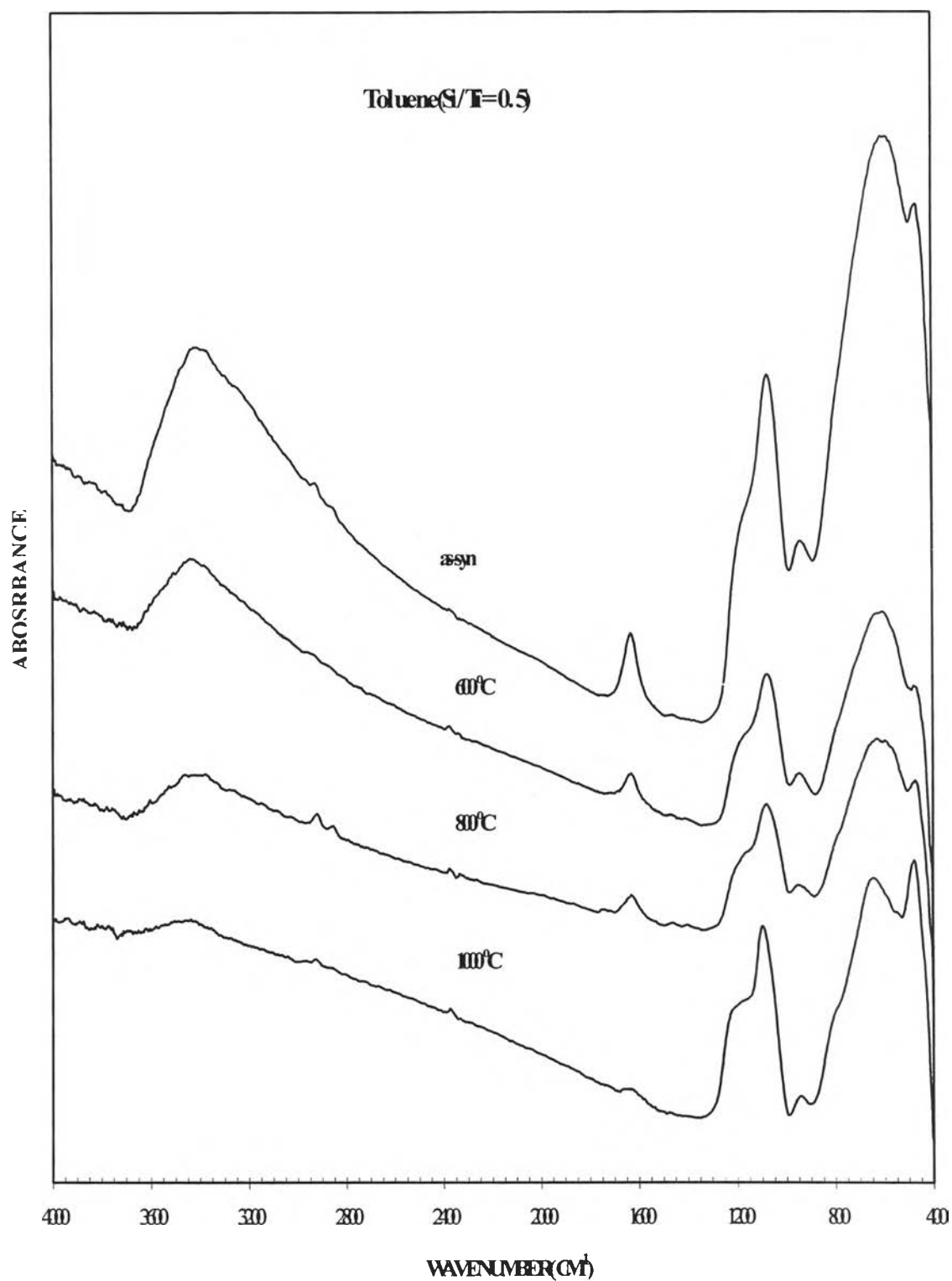
**Figure 5.13(c)** FT-IR spectra of titanium (IV) oxide and silica modified titanium (IV) oxide synthesized by 2-propanol.



**Figure 5.14** FT-IR spectra of pure anatase titanium (IV) oxide synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.

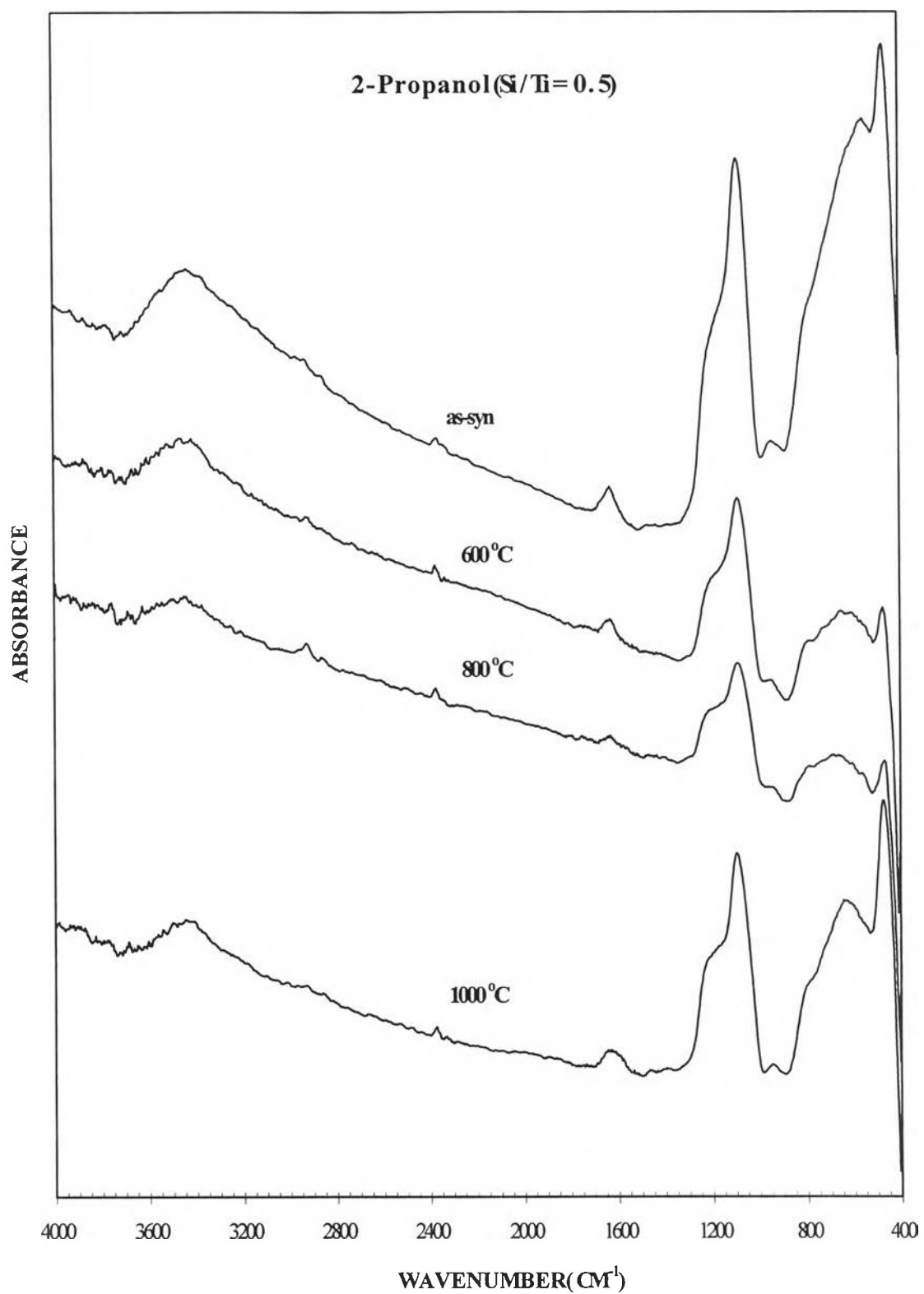


**Figure 5.15(a)** FT-IR spectra of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 1,4 butanediol before and after calcination at 600, 800 and 1000°C.



**Figure 5.15(b)** FT-IR spectra of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by toluene before and after calcination at 600, 800 and 1000°C.



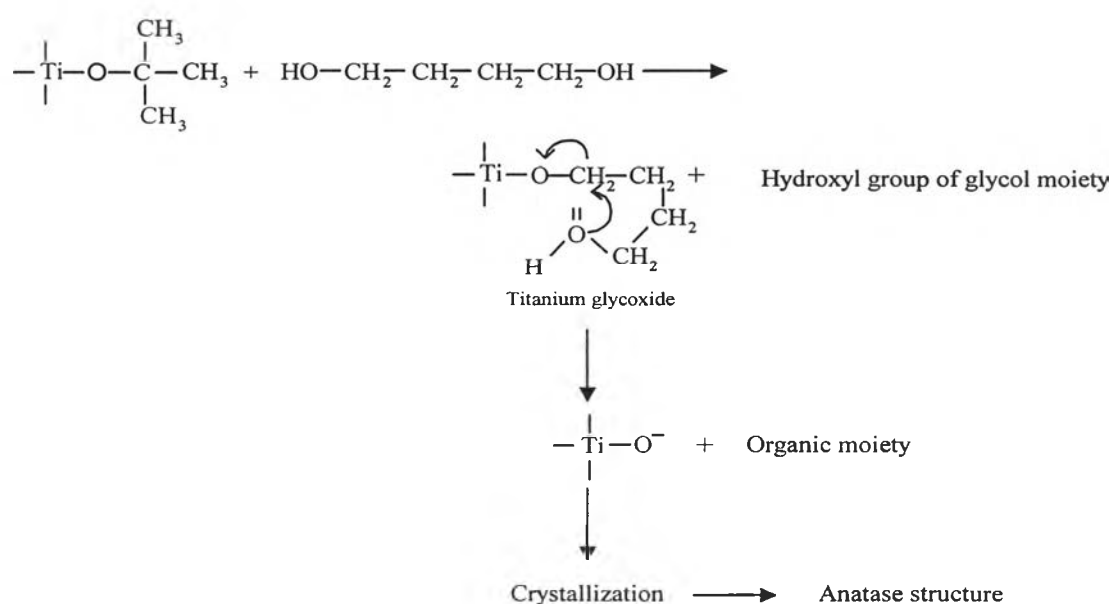


**Figure 5.15(c)** FT-IR spectra of silica modified titanium (IV) oxide with Si/Ti = 0.5 synthesized by 2-propanol before and after calcination at 600, 800 and 1000°C.

#### 5.4 Effect of the formation of anatase on the physical properties and the thermal stability of the products

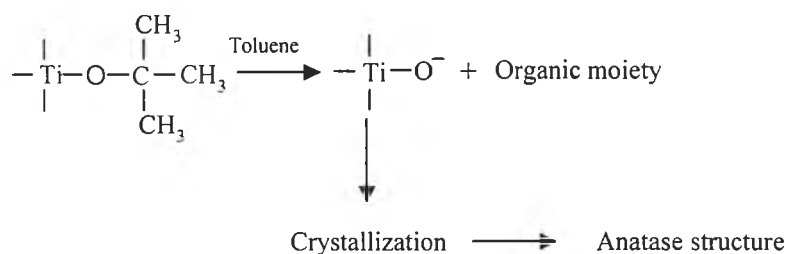
As described in section 5.1, the pure anatase titanium (IV) oxide prepared in each organic solvent have different physical properties and thermal stability. It shows that their properties and thermal stability can be controlled by the formation of anatase crystal (type of organic solvent) besides reaction condition and structure of starting material. Therefore, the explanation about the mechanism of the formation of anatase crystal was required to clarify the occurred phenomena.

The reaction of titanium (IV) tetra-tert-butoxide in 1,4 butanediol at 300 °C (Glycothermal reaction) yielded nanocrystalline titanium (IV) oxide having an approximate crystallite size of 17 nm. Under glycothermal conditions, titanium (IV) tetra-tert-butoxide was easily converted to glycooxide. Thermal decomposition of the glycooxide molecule proceeded by intra molecular participation of the remaining hydroxyl group of glycol moiety, yielding a  $\equiv\text{Ti-O}^-$  anion. The nucleophilic attack of this titanate ion on another ion and crystallization of titanium (IV) oxide took place, finally yielding the anatase titanium (IV) oxide. The mechanism of titanium (IV) tetra-tert-butoxide in 1,4 butanediol can be depicted as follow:



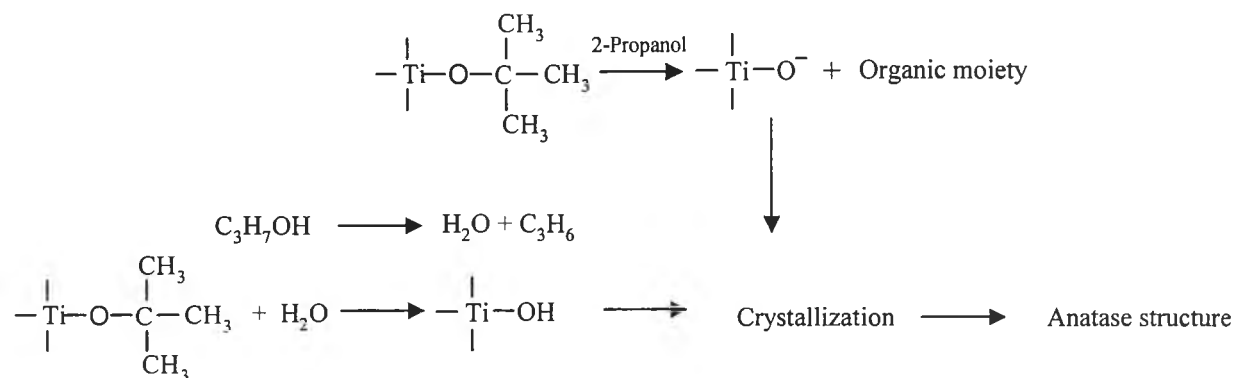
**Figure 5.16** Mechanism of glycothermal reaction for the anatase formation

Under inert organic solvent conditions, thermal decomposition of titanium (IV) tetra-tert-butoxide in toluene occurred, yielding a  $\equiv\text{Ti-O}^-$  anion. The nucleophilic attack of the titanate ion on another ion and crystallization took place, finally yielding the anatase titanium (IV) oxide. The mechanism of titanium (IV) tetra-tert-butoxide in toluene can be depicted as follow:



**Figure 5.17** Mechanism of reaction in toluene for the anatase formation

Under THyCA conditions, thermal decomposition of titanium (IV) tetra-tert-butoxide in 2-propanol occurred, yielding a  $\equiv\text{Ti-O}^-$  anion. Crystallization of anatase phase occurred, while 2-propanol was dehydrated to be water and titanium (IV) tetra-tert-butoxide was hydrolyzed, yielding a  $\equiv\text{Ti-OH}$  and crystallization of anatase phase took place, finally yielding the anatase titanium (IV) oxide. The mechanism of this reaction can be depicted as follow:



**Figure 5.18** Mechanism of THyCA reaction for the anatase formation

The reaction mechanism and experimental results as described above, indicating that hydrolysis of alkoxides with water liberated homogeneously from solvent alcohol and crystallization of anatase phase occurred simultaneously. In THyCA reaction, crystallization of products took place rapidly and yielded well – crystallized anatase, which had large crystallite size (40 nm) and high thermal stability. The XRD pattern of the product calcined at 1000°C showed that the anatase–rutile phase transformation completely occurred at over than 1000°C.

The reaction occurred in 1,4 butanediol and toluene, crystallization of products occurred slowly. The anatase crystals produced by these reactions were small crystallite size and consist of high amorphous –like phase, therefore thermal stability of these products were lower than products prepared in 2-propanol. However, products prepared in 1,4 butanediol were higher thermal stability than products prepared in toluene because under glycothermal condition, titanium glycooxides have been formed as an intermediate, which were easily converted to anatase crystal. These results indicated that thermal stability of anatase titanium (IV) oxide was affected by reaction of anatase formation and increased in the following order: toluene < 1,4 butanediol < 2-propanol.

As described in section 5.3, the increase of silica content in reaction mixture, products trended to form amorphous phase instead of anatase structure, therefore a small amount of silica added to reaction mixture ( $\text{Si/Ti} = 0.05$ ) in each organic solvent was investigated.

Even after calcination at 1000°C, products with  $\text{Si/Ti} = 0.05$  prepared in 2-propanol and 1,4 butanediol still preserved anatase structure without other phase of titanium (IV) oxide (Figure 5.7 and 5.11), on the other hand, the product prepared in toluene transformed to rutile phase. This result shown that the addition of silica in synthetic process improved thermal stability of products but physical properties and thermal stability of silica modified titanium (IV) oxide still depended on basic properties of titanium (IV) oxide prepared in each organic solvent.