

CHAPTER V

RESULTS AND DISCUSSION

This chapter presents results and discussion which were obtained from TGA/DSC, XRD, BET, FTIR, ESR and the photocatalytic activity measurements of photocatalytic oxidation of ethylene (section 5.1). In order to investigate effect of type solvent on properties of TiO₂, which used methanol as solvent were compared (section 5.2).

5.1 Characterization of TiO₂

TiO₂ samples were prepared by a sol-gel method with ethanol as solvent, followed by drying by supercritical CO₂ to form aerogel or drying under ambient atmosphere to form xerogel. After drying, heat treatment of gel was performed under a flow of either air or nitrogen at a temperature in the range of 350 °C - 600 °C. EAN and EAA denote TiO₂ aerogels that were calcined under nitrogen flow and air flow, respectively, while EXN and EXA denote TiO₂ xerogels that were calcined under nitrogen flow and air flow, respectively. The heat treatment temperature was indicated at the end of the type of sample.

5.1.1 *Crystal structure*

The XRD patterns of various titanium dioxide samples in the 2θ range between 20° and 80° are shown in Figures 5.1 and 5.2. The XRD peaks at 2θ values of 25.25°, 37.82°, 47.98°, 53.59° and 62.36° corresponded to the anatase phase, whereas the XRD peak at 2θ values of 27.42° and 30.8° belonged to rutile and brookite forms, respectively [Porkodi and Arokiamary 2007]. The average crystallite size of anatase was estimated from the half-height width of (101) diffraction peaks of anatase at 2θ values of 25.25° using the Scherrer's equation. The crystallite size of either brookite or rutile could not be determined because their XRD peaks were too small or were not detected.

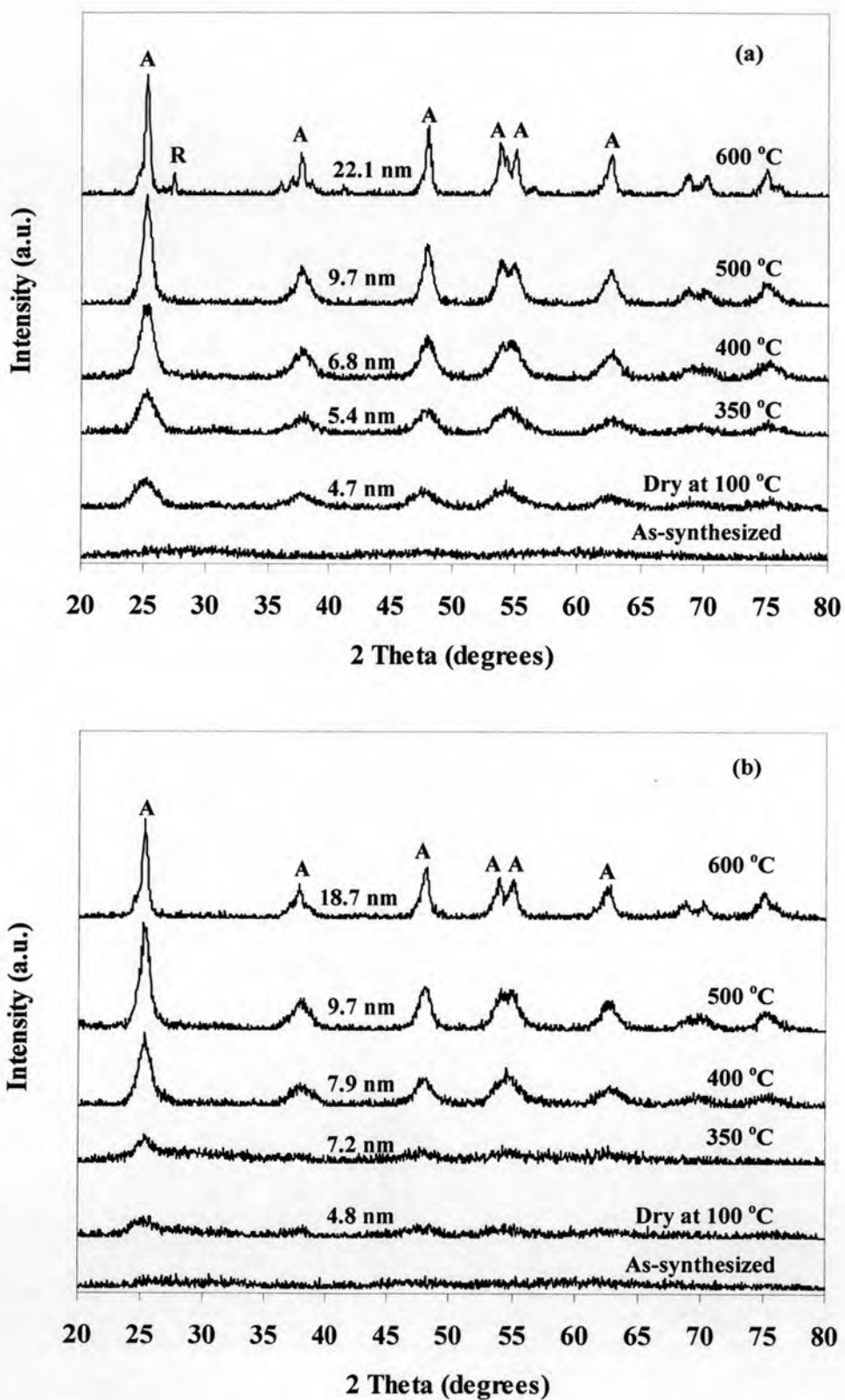


Figure 5.1 XRD patterns of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

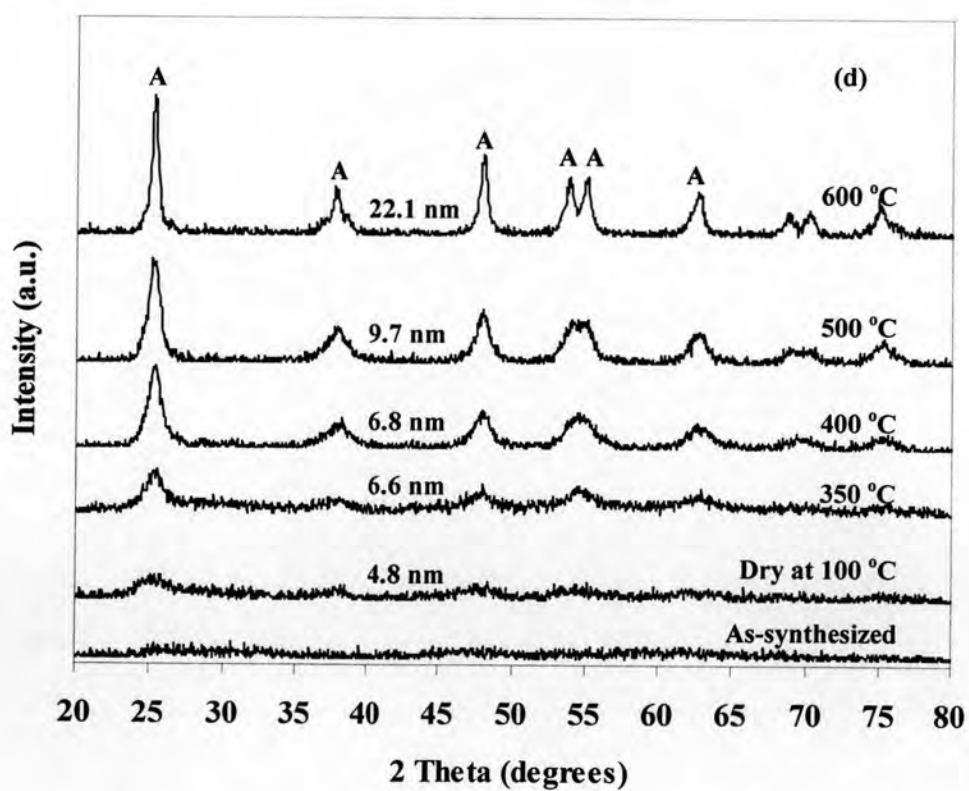
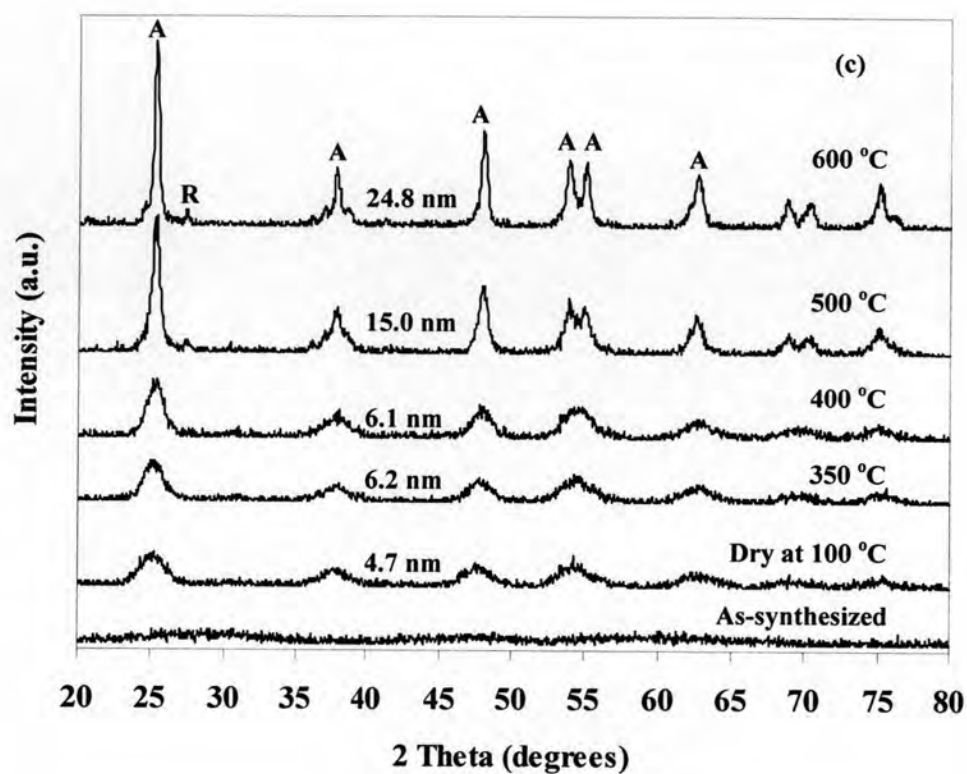


Figure 5.2 XRD patterns of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which were calcined under a flow of nitrogen for two hours at a temperature ranging from 350 °C to 600 °C.

According to Figures 5.1 and 5.2, as-synthesized aerogel and xerogel were amorphous. After drying at 100 °C overnight, some crystalline anatase was detected in the xerogel sample. The peaks corresponding to anatase were observed in the aerogel sample only when the samples were calcined at 350°C. This was probably due to a large amount of organic residues remained in aerogel preventing crystallization to form anatase in TiO₂. [Song and Pratsinis 2000; Yu et al 2003] reported that in the TiO₂ system, alkyl groups always remained in TiO₂ structure when the amount of water added during hydrolysis of titanium isopropoxide was small. The relative intensity of the main anatase peak at 2θ value of 25.25° became sharper and more pronounced with the increase in calcination temperature due to growth of crystallinity in the samples. The crystallite size increased with as the calcination temperature was raised. After calcination at 600 °C, a small rutile peak was detected in the xerogel but not in the aerogel. This result suggested that the phase transformation from anatase to rutile occurred at a lower temperature in xerogel than aerogel.

5.1.2 Thermal gravimetric analyzer

Thermal gravimetric analysis was performed to determine change in the catalysts weight with respect to temperature. The TGA-DSC curves were obtained under either air or nitrogen flow of 10 ml/min in a temperature up to 1000 °C with a heating rate of 10 °C/min. The TGA-DSC curves for various TiO₂ samples are displayed in Figures 5.3 and 5.4.

The weight loss of TiO₂ samples was divided into two segments. The first segment (50 °C-250 °C) was the removal of adsorbed water and alcohol, while the second segment (250 °C and beyond) was the oxidation of organic residue. Weight loss of TiO₂ xerogel (ca. 10%), as compared to that of TiO₂ aerogel (ca. 30%), suggested that more organic compounds remained in the aerogel samples. After calcination at 350 °C, xerogel powder was white, while aerogel powder was black, which was a result of carbonaceous residues derived from the decomposition of organics compounds. Organic compounds could remain completely encapsulated by the titania matrix [Wang et al 2004].

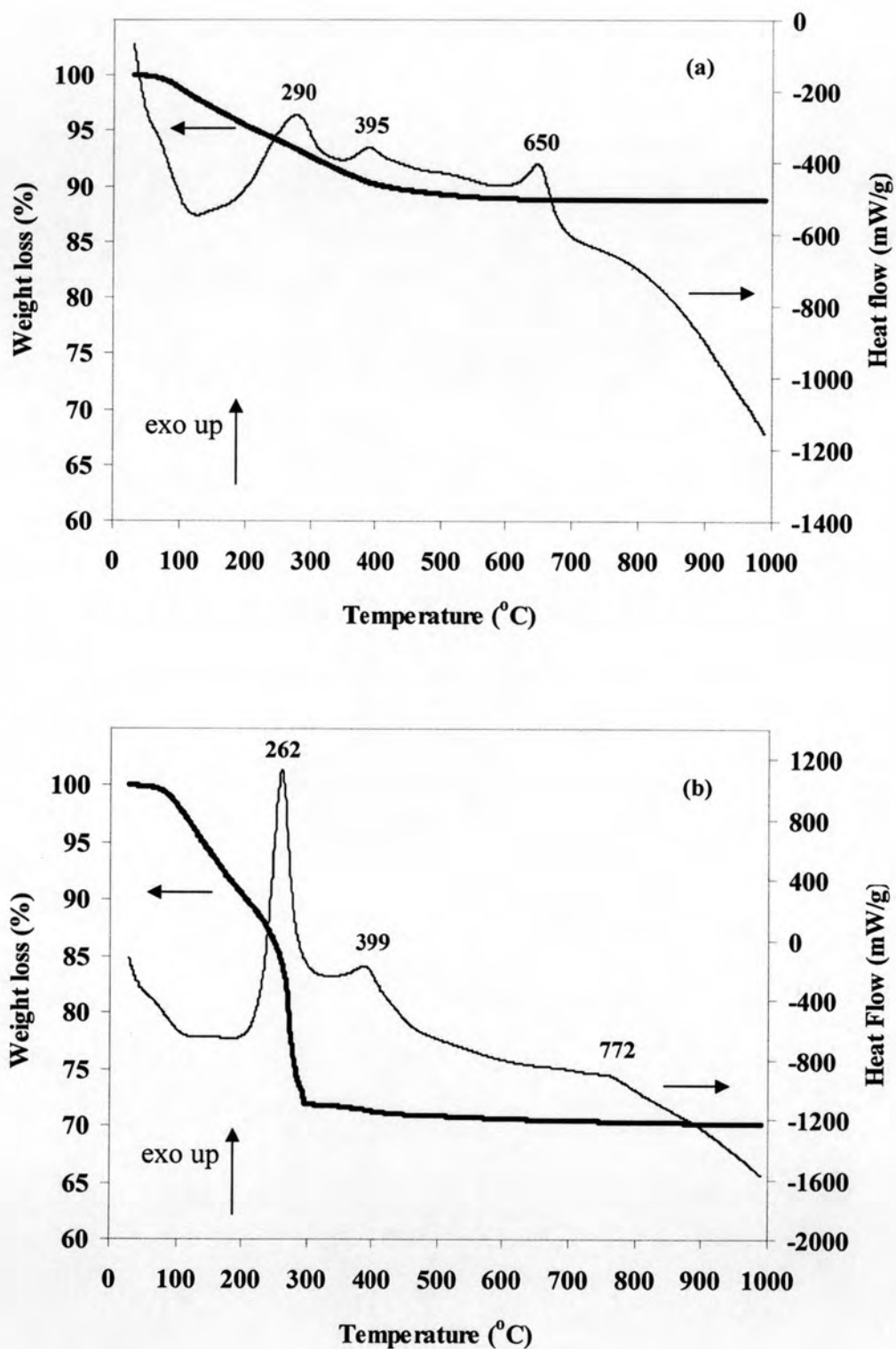


Figure 5.3 TGA/DSC curves under air flow of (a) TiO_2 xerogel and (b) TiO_2 aerogel

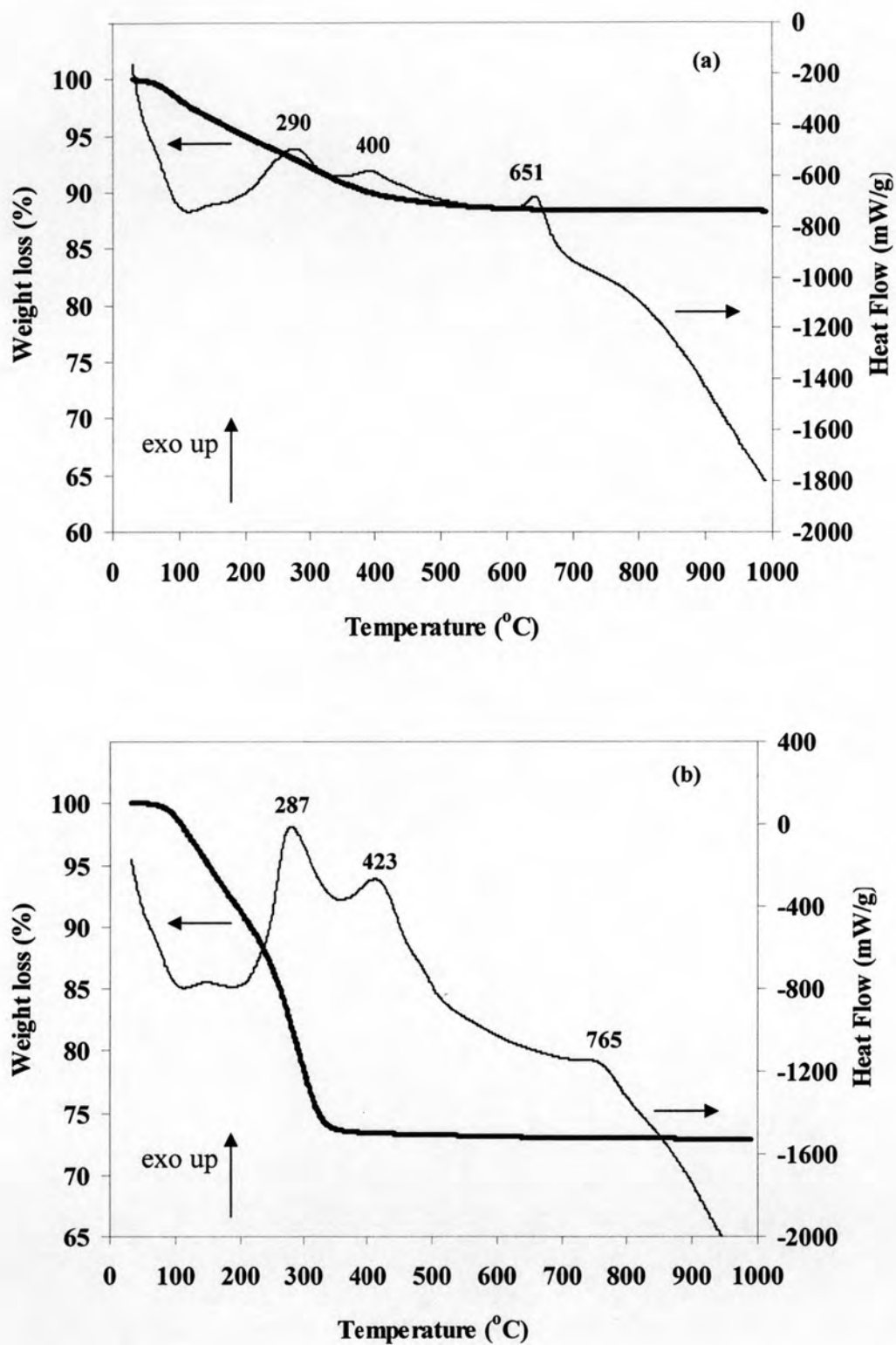


Figure 5.4 TGA/DSC curves under nitrogen flow of (a) TiO₂ xerogel and (b) TiO₂ aerogel

However, aerogel became white after it was calcined at 500 °C, which was a result of a complete removal of organic residue.

In Figures 5.3 and 5.4, the broad endothermic peak under 200 °C was assigned to losses of water and alcohol on the surface of catalyst. The exothermic peak at around 290 °C was attributed to combustion of organic residue. This peak was larger for the aerogel than the xerogel because of more organic residues present in the aerogel. The xerogel samples possessed an exothermic peak at around 400 °C, which was attributed to a transformation from amorphous to anatase, and another peak around 650 °C resulting from a transformation from anatase to rutile. The exothermic peak of the aerogel sample that was assigned to a transformation from anatase to rutile occurred at around 760 °C. The positions of the peaks for xerogel and aerogel were obviously different. This indicated that a transformation from anatase to rutile of as-synthesized aerogel sample occurred later than that of as-synthesized xerogel sample, which was consistent with XRD result.

5.1.3 *Specific surface area*

Specific surface area of various TiO₂ samples that were calcined at a temperature between 350 °C and 600 °C for two hours were determined by nitrogen physisorption and were displayed in Table 5.1. As-synthesized aerogel possessed almost three times as much surface area as as-synthesized xerogel. However, specific surface area of the gels decreased very quickly as a calcination temperature was increased from 350 °C to 600 °C due to pore collapse and growth of anatase crystal. The decline in surface area for xerogel was not as drastic as that for aerogel. The rapid decrease in surface area of aerogel between 350 °C and 400 °C was attributed to the phase transformation from amorphous to anatase phase, which agree with XRD results. Pore size distributions of TiO₂ samples were display in Figures 5.6 and 5.7. As calcination temperature was increased, average pore size increased but pore volume decreased.

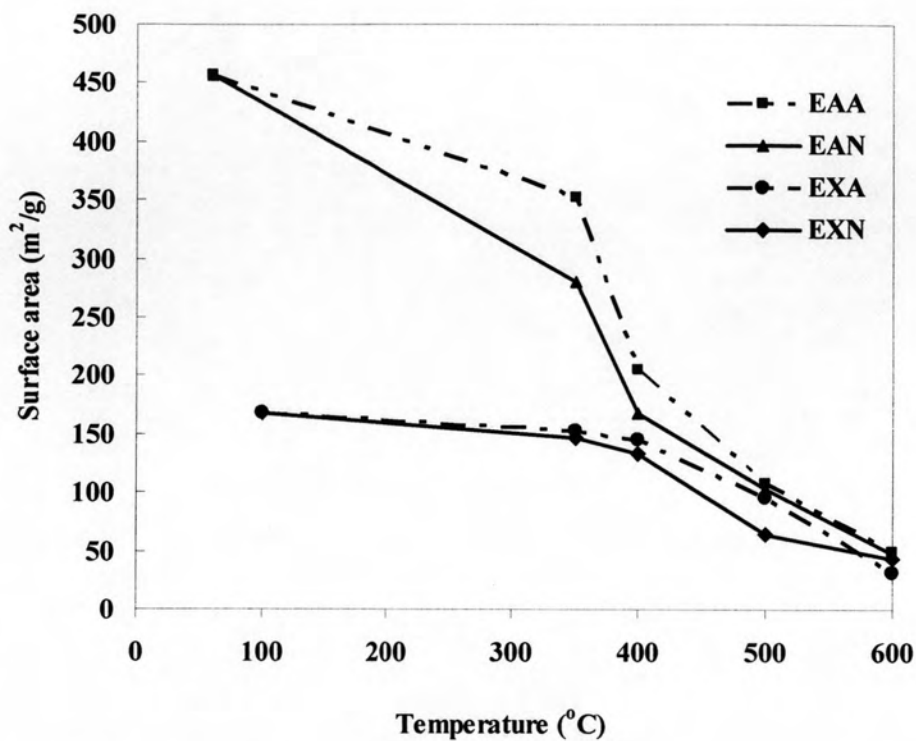


Figure 5.5 Specific surface area of TiO₂ samples were calcined under a flow of air or nitrogen for two hours at a temperature between 350 °C and 600 °C

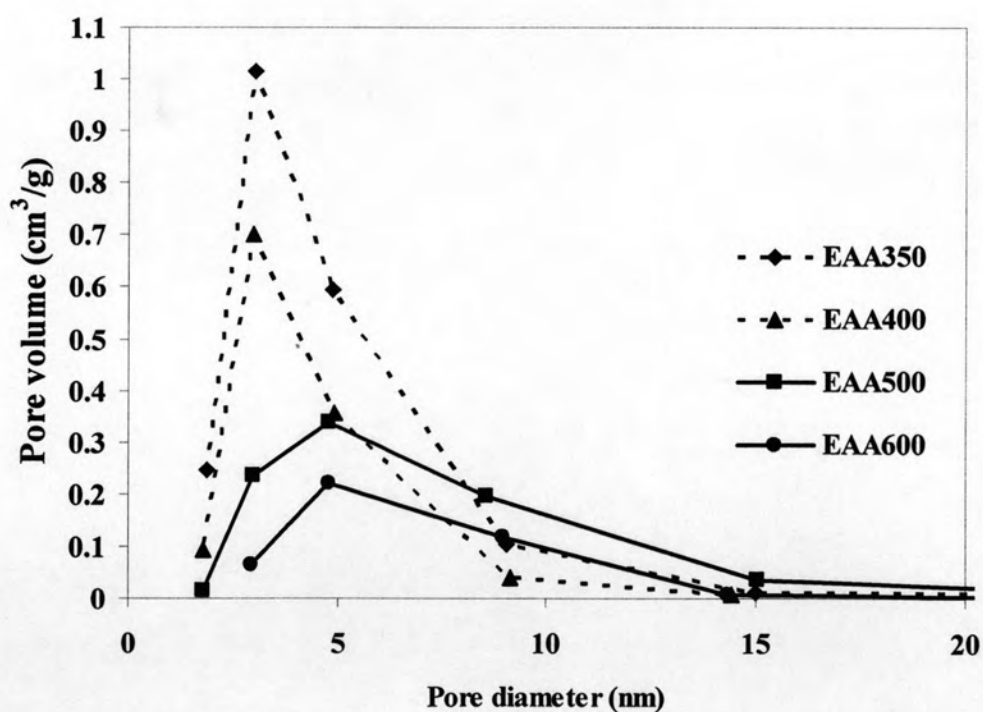
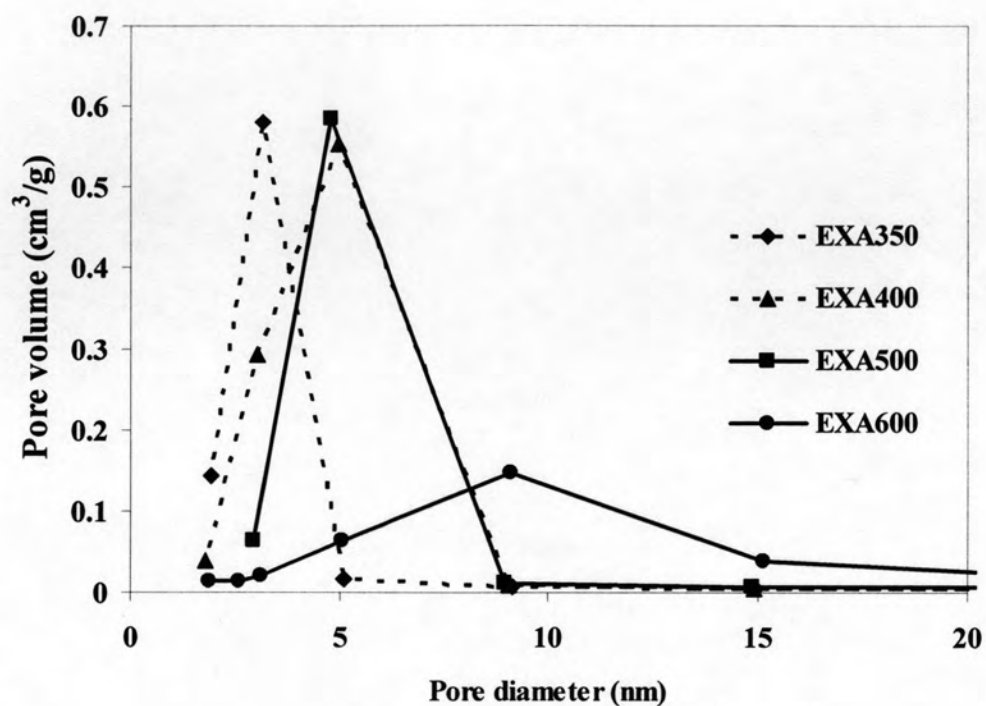


Figure 5.6 Pore size distribution of (a) TiO₂ xerogel and (b) TiO₂ aerogel were calcined under a flow of air for two hours at a temperature between 350 °C and 600 °C

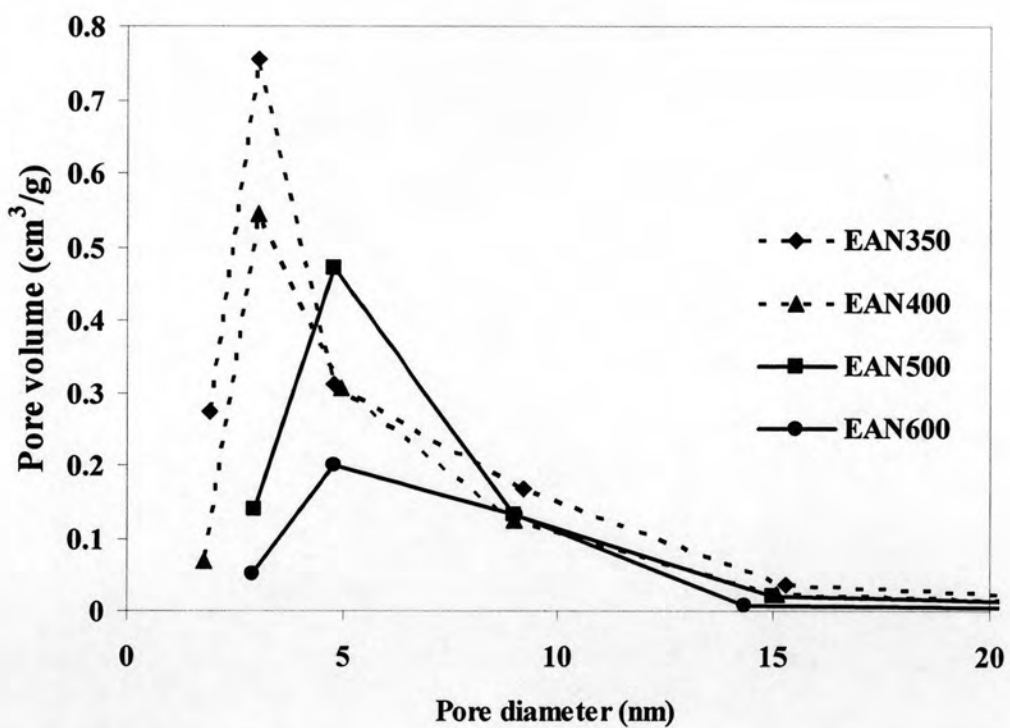
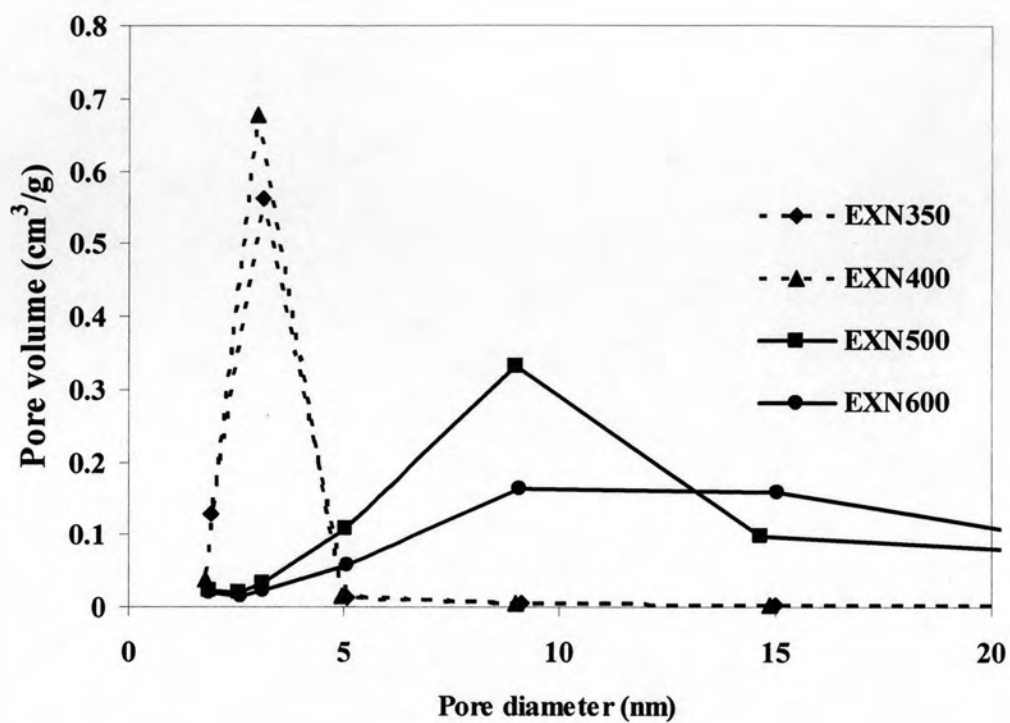


Figure 5.7 Pore size distribution of (a) TiO₂ xerogel and (b) TiO₂ aerogel were calcined under a flow of nitrogen for two hours at a temperature between 350 °C and 600 °C

Table 5.1 Pore structure information of TiO₂ aerogels and xerogel

Sample	Specific Surface area (m²/g)	Average Pore size (nm)	Pore volume (cm³/g)
aerogel	456.9	5.6	0.8918
xerogel	167.4	2.7	0.1319
EXA350	153.0	2.9	0.1586
EXA400	144.8	4.0	0.2260
EXA500	95.3	4.8	0.1864
EXA600	32.0	4.7	0.0682
EAA350	352.2	3.4	0.4463
EAA400	205.1	3.4	0.2788
EAA500	107.9	4.8	0.2014
EAA600	49.4	5.3	0.1086
EXN350	147.0	2.9	0.1537
EXN400	133.5	2.9	0.1642
EXN500	91.0	6.2	0.1892
EXN600	42.9	6.8	0.1107
EAN350	279.9	3.4	0.3428
EAN400	167.8	3.7	0.2479
EAN500	102.9	4.9	0.1980
EAN600	48.3	5.4	0.1020

5.1.4 Fourier Transform Infrared Spectroscopy measurement

To investigate the existence of organic compound in various TiO₂ samples, FTIR measurement was performed. Infrared spectra of various TiO₂ samples are displayed in Figures 5.8 and 5.9. The peaks at the 1620 cm⁻¹ and around 3200-3600 cm⁻¹ corresponded to a stretching vibration of adsorbed water molecules and surface hydroxyl groups, respectively [Kolen'ko et al 2005]. The broad band below 1200 cm⁻¹ was assigned to Ti-O-Ti vibration [Venkatachalam et al 2007].

From Figures 5.8 b and 5.9 b, the as-synthesized aerogel possessed a set of peaks at 2970, 2935, and 2860 cm⁻¹, which corresponded to symmetric and antisymmetric vibration modes of -CH₂- and -CH₃ groups in the alkoxide [Burgos and Langlet 1999]. The broad bands between 1000 and 1100 cm⁻¹ were attributed to the OR groups linked to Ti [Ivanova and Harizanova 2001]. The peak at 1385 cm⁻¹ belonged to the presence of nitrates, which was a result of nitric acid added during hydrolysis [Music et al 1997]. These groups of peaks, which disappeared after calcination corresponded to organic remaining on the surface even after the drying process. These results suggested that drying TiO₂ by supercritical CO₂ was less efficient in removing the solvent than drying under ambient condition. The peak at 3675 cm⁻¹, corresponding to Ti-OH bonds appeared after TiO₂ were fired at 400 °C. After calcination at temperature higher than 400 °C, the vibration bands of water and surface hydroxyl groups became much weaker. Therefore, surface hydroxyl group and water in TiO₂ were removed during calcination. The peak at around 2350 cm⁻¹ was believed to be CO₂ that was formed during the combustion of organic impurity and was partly adsorbed onto TiO₂ [Li et al 2006]. The peak corresponding to, CO₂ was more pronounced in the aerogel with an increase in calcination temperature because more organic residues remained in the aerogel than the xerogel.

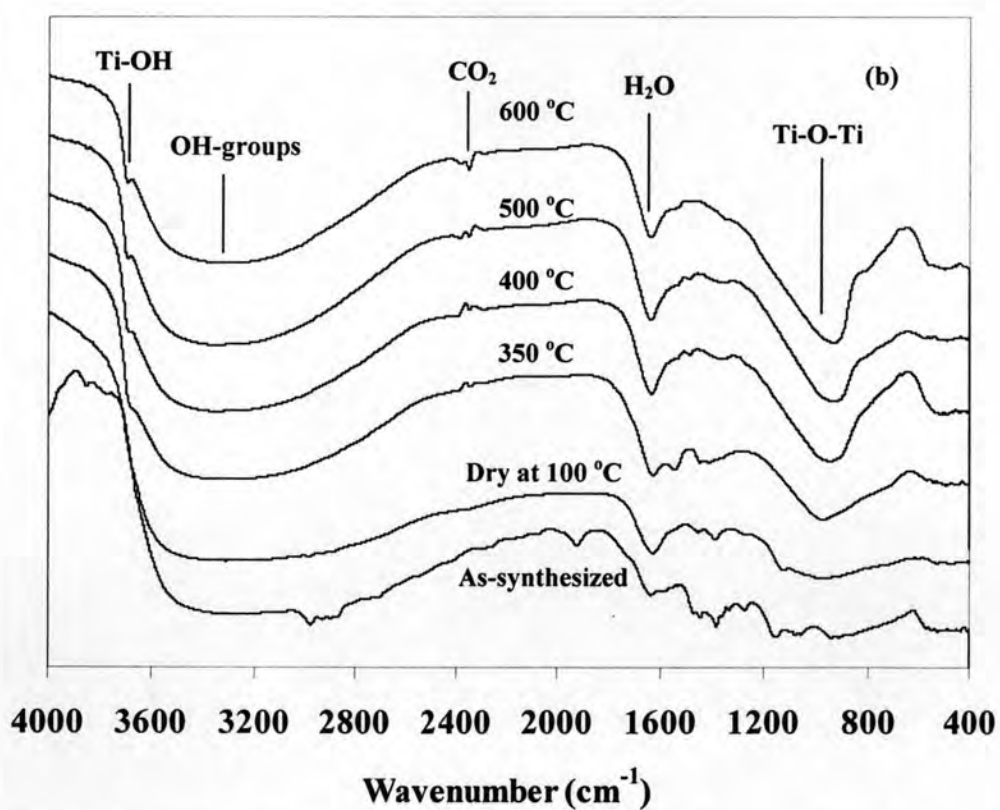
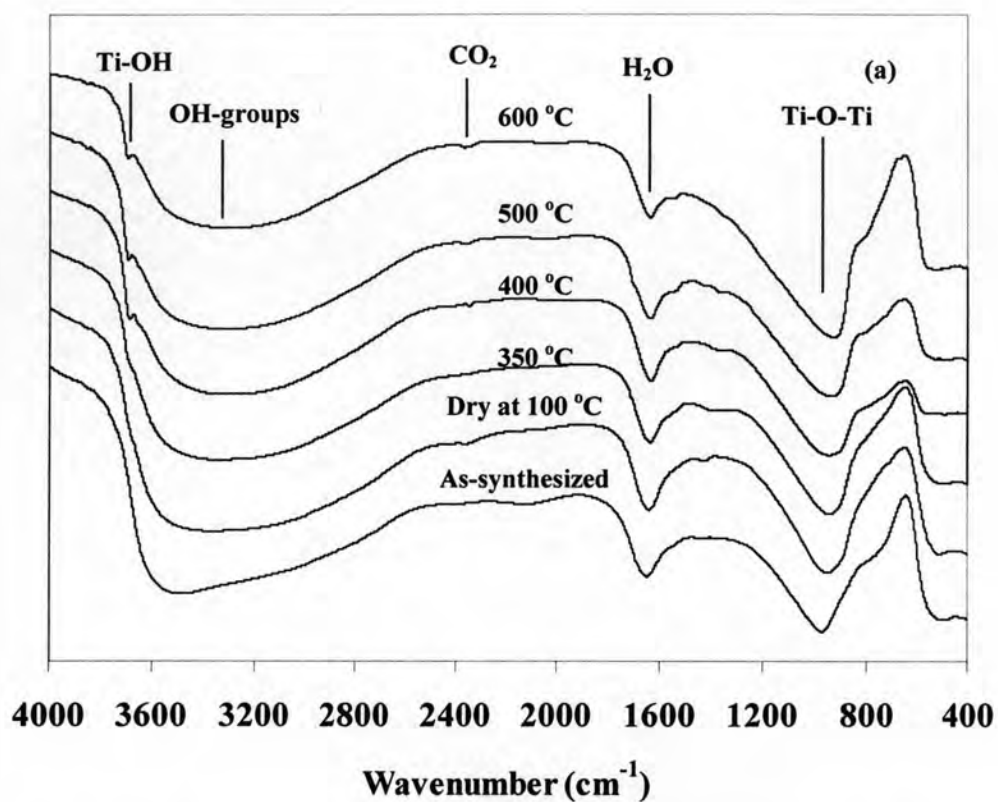


Figure 5.8 Infrared spectra of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

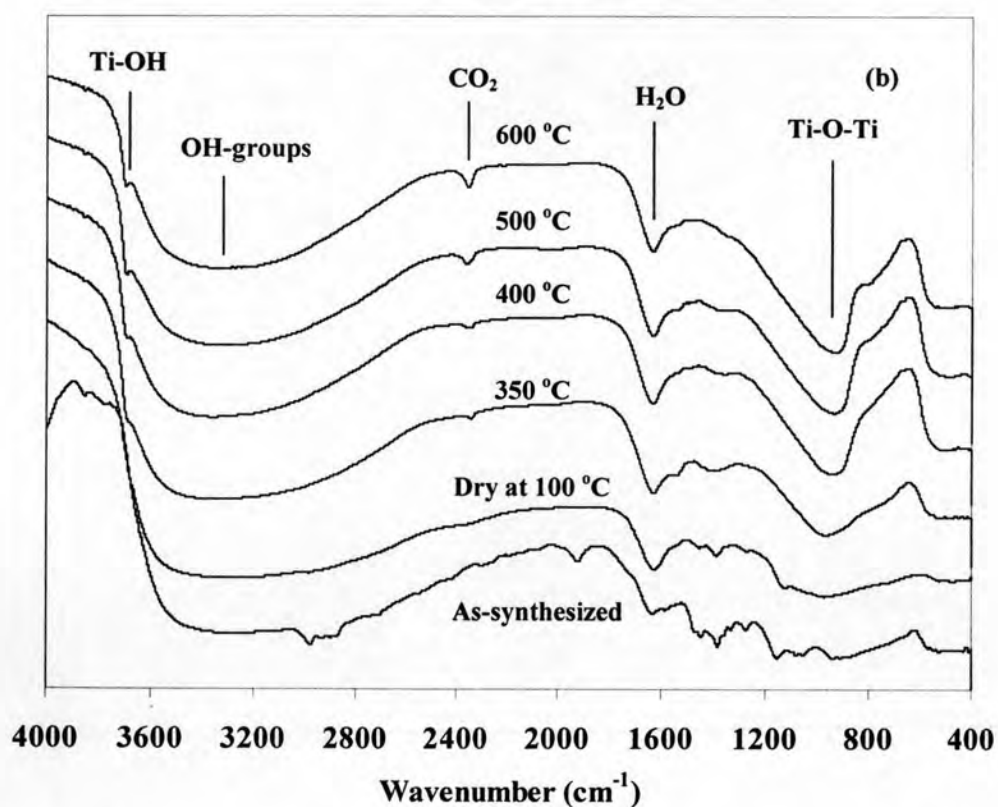
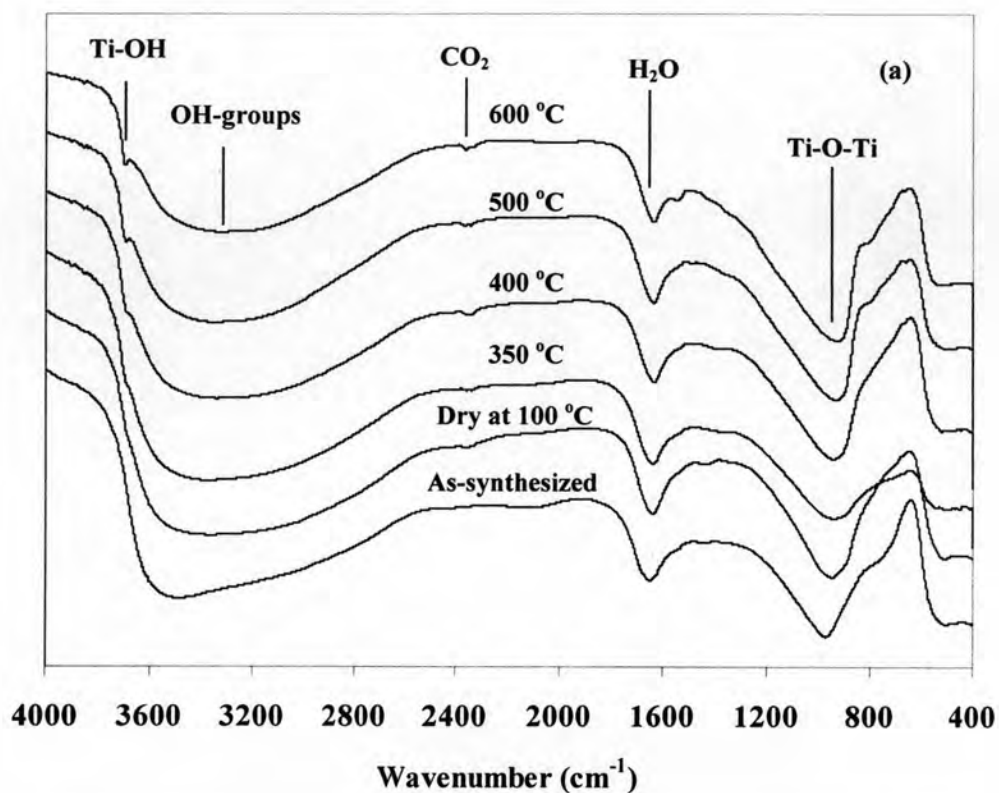


Figure 5.9 Infrared spectra of TiO₂ (a) TiO₂ xerogel and (b) TiO₂ aerogel, which were calcined under a flow of nitrogen for two hours at a temperature ranging from 350 °C to 600 °C.

5.1.5 Electron spin resonance spectroscopy measurement

ESR measurement was performed at 77 K with liquid nitrogen in vacuum for various TiO₂ xerogels and aerogels. The results are listed in Tables 5.2 and 5.3. As the calcination temperature increased, the intensity of a peak corresponding to Ti³⁺ surface defect became lower and thus the amount of Ti³⁺ surface defect decreased as a result of an increase in crystallinity [Othani et al.]. However, the amount of Ti³⁺ surface defect in aerogel was higher than that in xerogel because a larger amount of organic residues remained in aerogel. The surface defect site (Ti³⁺) was created by the removal of organic residues [Suriye et al 2007].

Table 5.2 Amount of Ti³⁺ surface defect of TiO₂ xerogel and aerogel, which were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

Sample	Surface area (m ² /g)	Weight (g)	Amount of Ti ³⁺ surface defect
xerogel	167.4	-	-
aerogel	456.4	-	-
EXA350	153.0	0.1598	1901.6
EXA400	144.7	0.1579	687.9
EXA500	95.3	0.1598	178.3
EXA600	32.0	0.1595	279.0
EAA350	352.2	0.0622	50836.0
EAA400	205.1	0.0629	24483.3
EAA500	107.9	0.0618	11828.5
EAA600	49.4	0.0638	3087.8

Table 5.3 Amount of Ti^{3+} surface defect of TiO_2 xerogel and aerogel, which were calcined under a flow of nitrogen for two hours at a temperature ranging from 350 °C to 600 °C.

Sample	Surface area (m^2/g)	Weight (g)	Amount of Ti^{3+} surface defect
xerogel	167.4	-	-
aerogel	456.4	-	-
EXN350	147.0	0.1581	2800.4
EXN400	133.5	0.1560	2705.1
EXN500	64.8	0.1566	1017.7
EXN600	42.8	0.1583	171.4
EAN350	279.9	0.0630	67857.1
EAN400	167.8	0.0644	33183.2
EAN500	102.9	0.0643	11353.0
EAN600	45.3	0.0618	3155.3

5.1.6 Photocatalytic activity

In this work, TiO_2 aerogel and xerogel which were calcined at a temperature in the range between 350 °C and 600 °C were used as photocatalysts in the photocatalytic oxidation of ethylene. Approximately 0.02 g of catalyst was used. The main products in this reaction were carbon dioxide and water.

The conversion of ethylene as a function of a calcination temperature for various TiO_2 samples was shown in Figure 5.10. When the calcination temperature increased, the photocatalytic activities of all TiO_2 increased and then decreased. TiO_2 that was calcined at 400 °C exhibited highest the photocatalytic activities. These results may be explained by two factors, i.e. crystallinity of TiO_2 and Ti^{3+} surface defect.

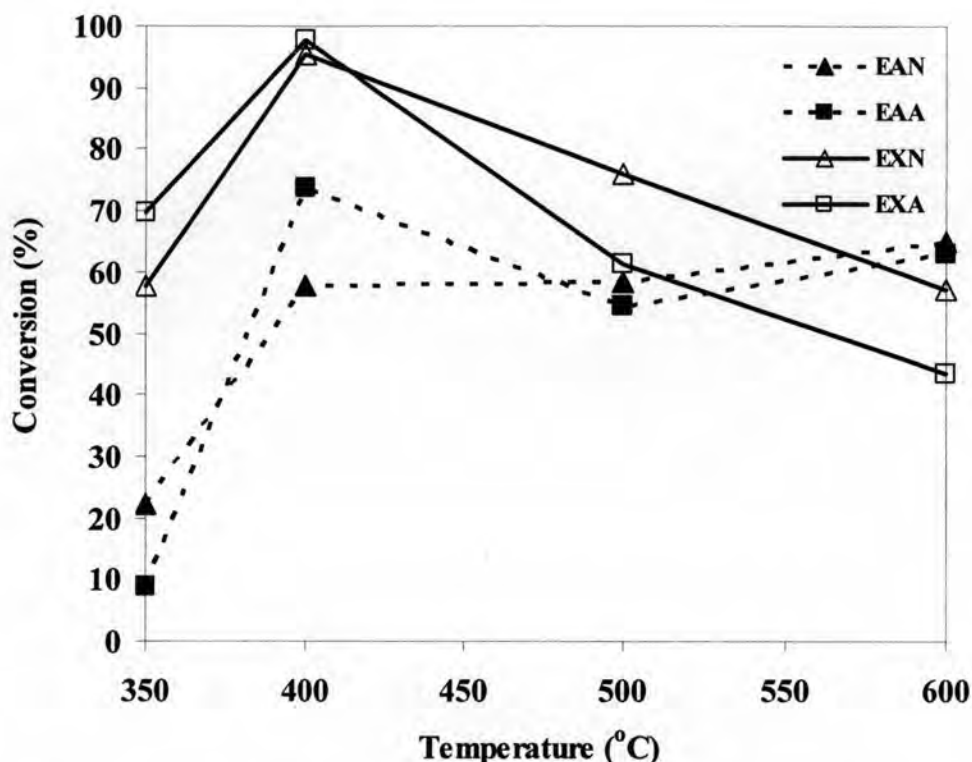


Figure 5.10 Photocatalytic activities of various TiO₂ aerogels and xerogels

When the calcination temperature was increased from 350 to 400 °C, the crystallinity of anatase in the samples became greater. This was demonstrated by the growth in the intensity of the (101) XRD diffraction peak of anatase (see Table 5.6). The higher amount of anatase crystal led to greater amounts of holes and electrons generated upon exposure to ultraviolet irradiation, thereby enhancing the photocatalytic activity of the sample. After 400 °C, the photocatalytic activity of TiO₂ samples decreased despite higher crystallinity of anatase in samples. This could be attributed to a smaller amount of Ti³⁺ found in sample (see Table 5.2 and 5.3). Ti³⁺ surface defect acted as a trap for photogenerated electrons and prevented recombination of electrons and holes [Suriye et al 2007]. Therefore, the smaller amount of Ti³⁺ led to lower activity of TiO₂ samples that were calcined at a temperature higher than 400 °C. Between 350 °C and 400 °C, the photocatalytic activities of aerogel were lower than those of xerogel in spite of the fact that aerogel possessed greater amount of Ti³⁺ than xerogel did. These results could be explained by the smaller amount of anatase crystal present in the aerogel samples (as suggested

by Table 5.4), which limited the photogeneration of electron-hole pairs. As a result, the photocatalytic activities of aerogel were lower than those of xerogel.

Table 5.4 Intensity of (101) XRD diffraction peak of various TiO₂ samples

Sample	Intensity of (101) diffraction peak *	Sample	Intensity of (101) diffraction peak *
EXA350	241	EXN350	192
EXA400	401	EXN400	275
EXA500	600	EXN500	648
EXA600	663	EXN600	880
EAA350	151	EAN350	200
EAA400	388	EAN400	386
EAA500	566	EAN500	482
EAA600	522	EAN600	642

* In order to estimate crystallinity in TiO₂ samples, equal amount of samples (0.100g) was used.

5.2 Characterization of TiO₂ used methanol as solvent

TiO₂ samples were prepared by a sol-gel method with methanol as solvent, followed by drying by supercritical CO₂ to form aerogel or drying under ambient atmosphere to form xerogel. After drying, heat treatment of gel was performed under a flow of either air or nitrogen at a temperature in the range of 350 °C- 600 °C. MAN and MAA denote TiO₂ aerogels that were calcined under nitrogen flow and air flow, respectively, while MXN and MXA denote TiO₂ xerogels that were calcined under nitrogen flow and air flow, respectively. The heat treatment temperature was indicated at the end of the type of sample.

5.2.1 *Crystal structure*

The XRD patterns of various titanium dioxide samples in the 2θ range between 20° and 80° are shown in Figures 5.11 and 5.12. The XRD peaks at 2θ values of 25.25° , 37.82° , 47.98° , 53.59° and 62.36° were attributed to the anatase phase, whereas the XRD peak at 2θ values of 27.42° and 30.8° belonged to rutile and brookite forms, respectively [Porkodi and Arokiamary 2007]. The average crystallite size of anatase was estimated from the half-height width of (101) diffraction peaks of anatase at 2θ values of 25.25° using the Scherrer's equation. The crystallite size of either brookite or rutile could not be determined because their XRD peaks were too small or were not detected.

According to Figures 5.11 and 5.12, as-synthesized aerogel and xerogel were amorphous. After drying at 100°C overnight, some crystalline anatase was detected in the xerogel sample. The peaks corresponding to anatase were observed in the aerogel sample only when the samples were calcined at 350°C . This was probably due to a large amount of organic residues remained in aerogel preventing crystallization to form anatase in TiO_2 . [Song and Pratsinis 2000; Yu et al 2003] reported that in the TiO_2 system, alkyl groups always remained in TiO_2 structure when the amount of water added during hydrolysis of titanium isopropoxide was small. The relative intensity of the main anatase peak at 2θ value of 25.25° became sharper and more pronounced with the increase in calcination temperature due to growth of crystallinity in the samples. The crystallite size increased with as the calcination temperature was raised. After calcination at 600°C , a small rutile peak was detected in the xerogel but not in the aerogel. This result suggested that the phase transformation from anatase to rutile occurred at a lower temperature in xerogel than aerogel.

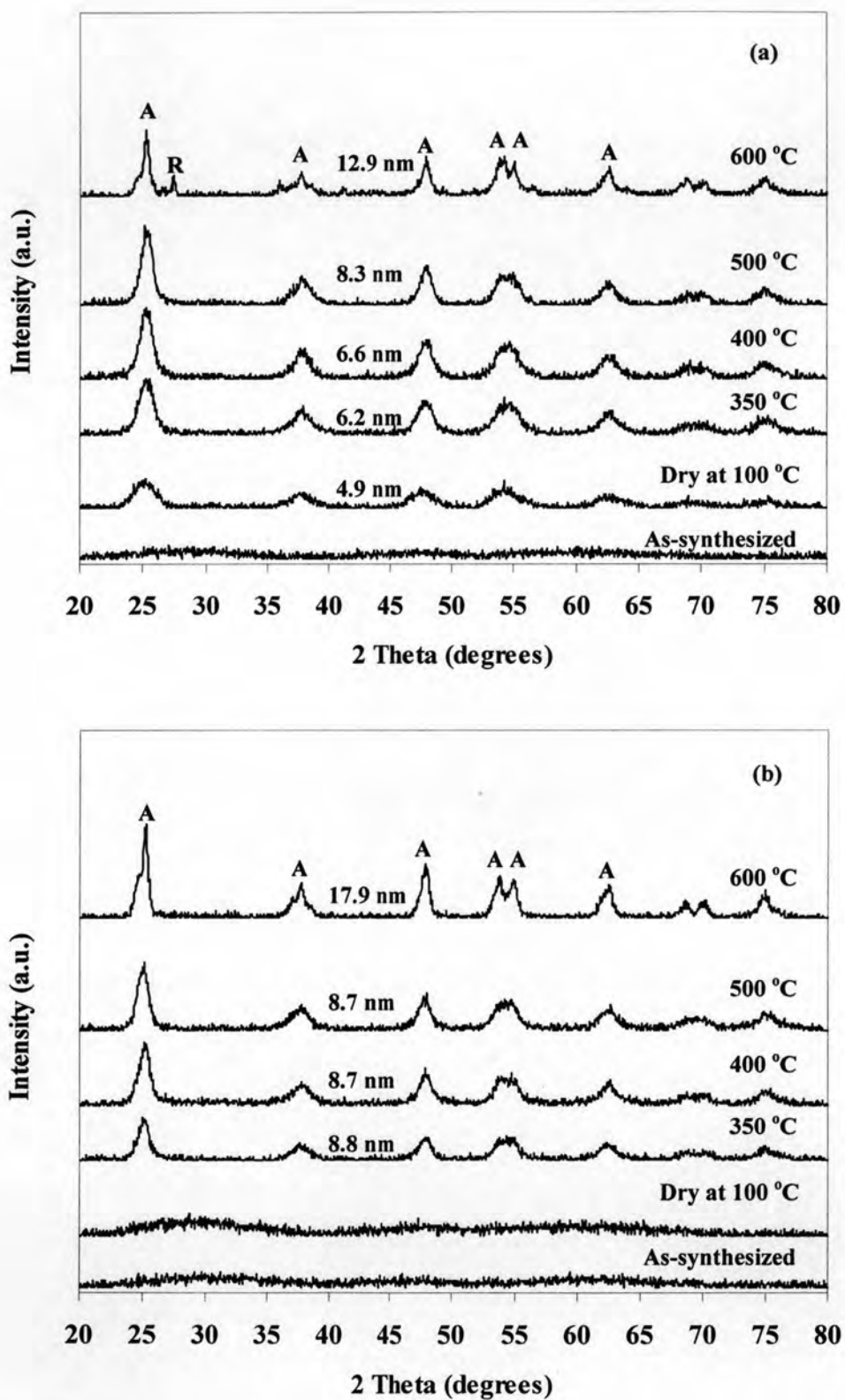


Figure 5.11 XRD patterns of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

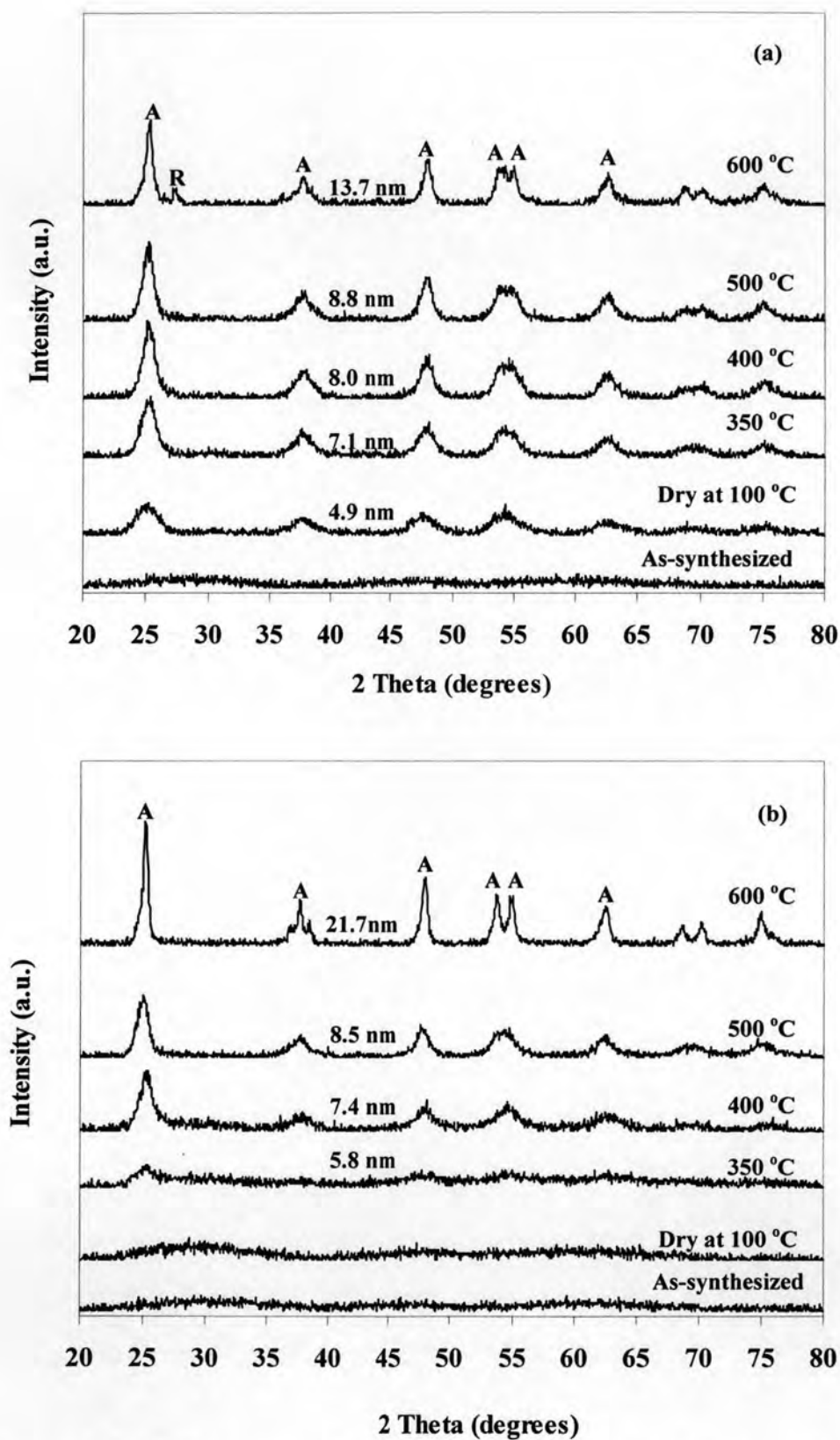


Figure 5.12 XRD patterns of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of nitrogen for two hours at a temperature ranging from 350 °C to 600 °C.

5.2.2 Thermal gravimetric analyzer

Thermal gravimetric analysis was performed to determine change in the catalysts weight with respect to temperature. The TGA-DSC curves were obtained under either air or nitrogen flow of 10 ml/min in a temperature up to 1000 °C with a heating rate of 10 °C/min. The TGA-DSC curves for various TiO₂ samples are displayed in Figures 5.13 and 5.14.

The weight loss of TiO₂ samples was divided into two segments. The first segment (50 °C - 250 °C) was the removal of adsorbed water and alcohol, while the second segment (250 °C and beyond) was the oxidation of organic residue. Weight loss of TiO₂ xerogel (ca. 15%), as compared to that of TiO₂ aerogel (ca. 35%), suggested that more organic compounds remained in the aerogel samples. After calcination at 350 °C, xerogel powder was white, while aerogel powder was black, which was a result of carbonaceous residues derived from the decomposition of organics compounds. Organic compounds could remain completely encapsulated by the titania matrix [Wang et al 2004]. However, aerogel became white after it was calcined at 500 °C, which was a result of a complete removal of organic residue.

In Figures 5.13 and 5.14, the broad endothermic peak under 200 °C was assigned to losses of water and alcohol on the surface of catalyst. The exothermic peak at around 300 °C was attributed to combustion of organic residue. This peak was larger for the aerogel than the xerogel because of more organic residues present in the aerogel. The exothermic peak of aerogel sample at around 210 °C was attributed to combustion of unreacted alkoxide [Yu et al. 2003]. The xerogel samples possessed an exothermic peak at around 400 °C, which was attributed to a transformation from amorphous to anatase, and another peak around 600 °C resulting from a transformation from anatase to rutile. The exothermic peak of the aerogel samples that was assigned to a transformation from anatase to rutile disappeared at around 600 °C. The positions of the peaks for xerogel and aerogel were obviously different. This indicated that a transformation from anatase to rutile of as-synthesized aerogel sample

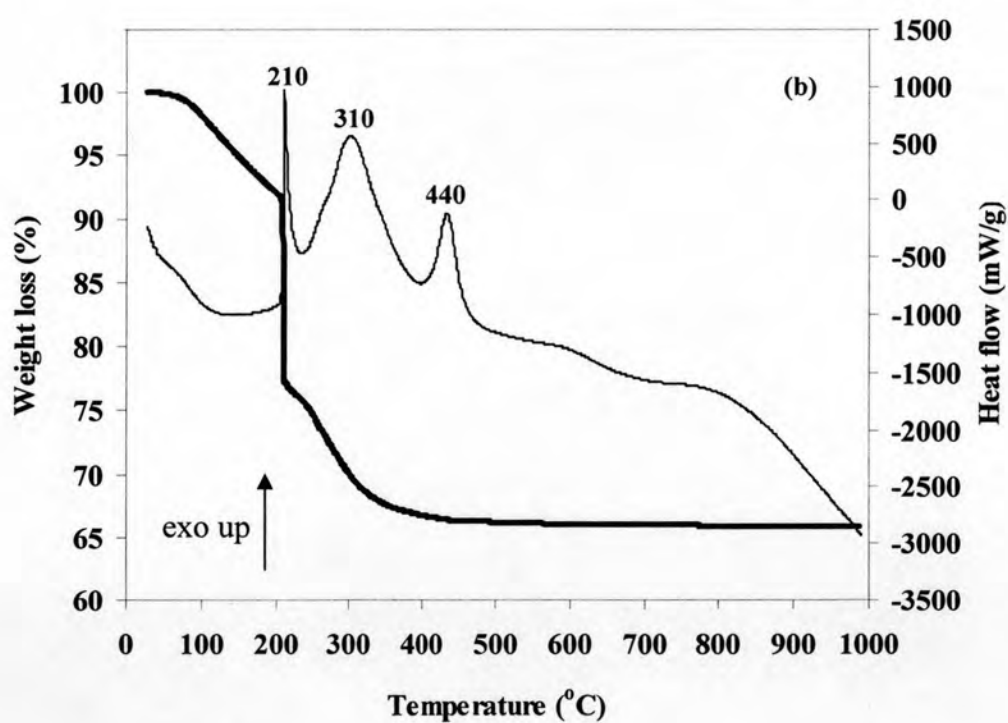
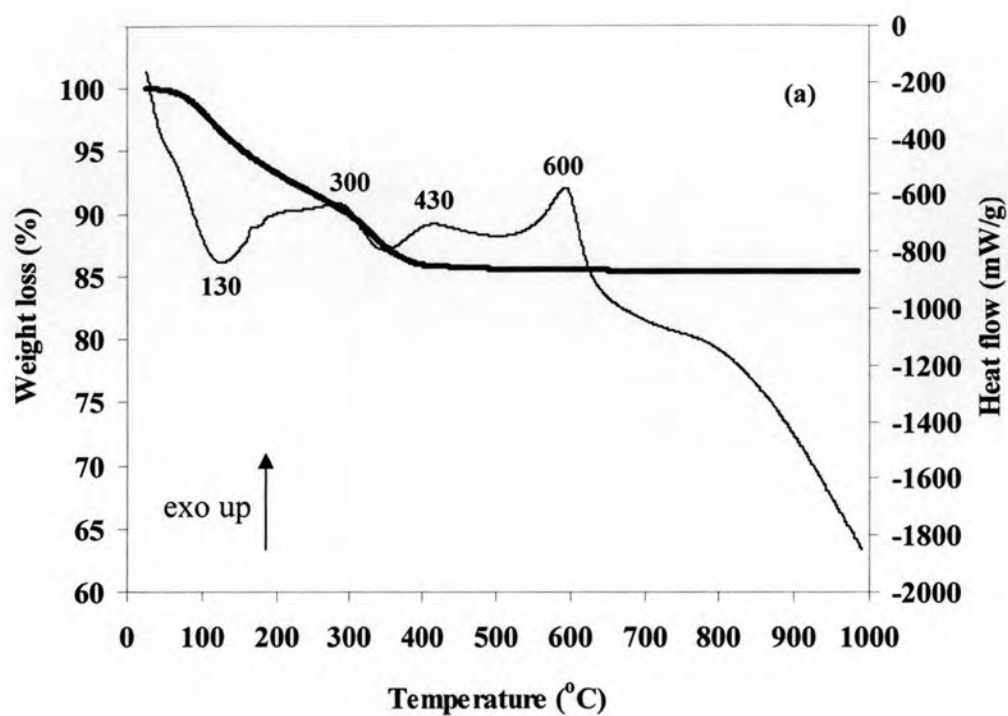


Figure 5.13 TGA/DSC curves under air flow of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent.

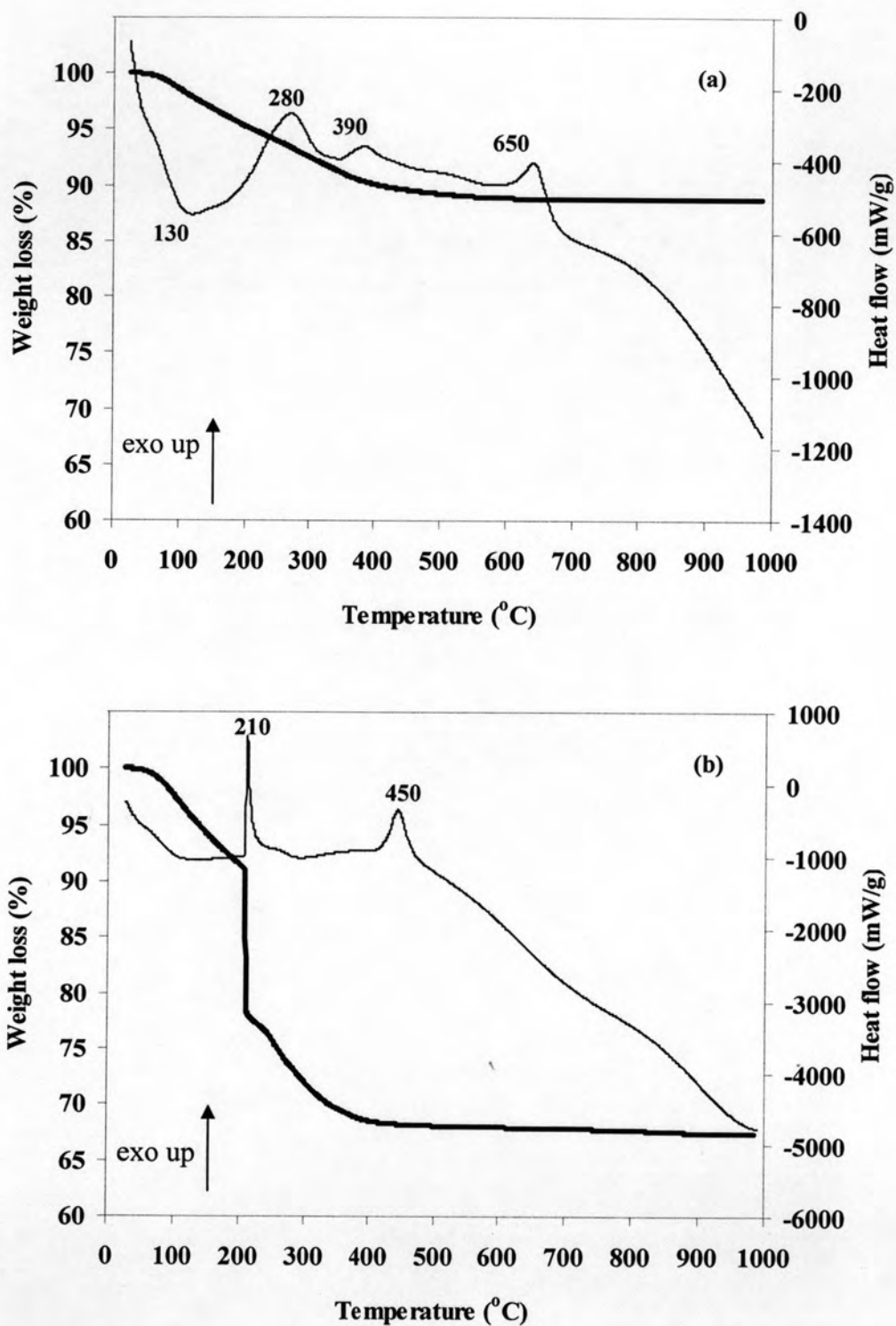


Figure 5.14 TGA/DSC curves under air flow of (a) TiO_2 xerogel and (b) TiO_2 aerogel, which used methanol as solvent.

occurred later than that of as-synthesized xerogel sample, which was consistent with XRD result.

5.1.3 Specific surface area

Specific surface area of various TiO_2 samples that were calcined at a temperature between $350\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$ for two hours were determined by nitrogen physisorption and were displayed in Table 5.5. As-synthesized aerogel possessed almost three times as much surface area as as-synthesized xerogel. However, specific surface area of the gels decreased very quickly as a calcination temperature was increased from $350\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ due to pore collapse and growth of anatase crystal. The decline in surface area for xerogel was not as drastic as that for aerogel. The rapid decrease in surface area of aerogel was attributed to the phase transformation from amorphous to anatase phase, which agree with XRD results. Pore size distributions of TiO_2 sample were display in Figure 5.16 and 5.17. As calcination temperature was increased, average pore size increased but pore volume decreased.

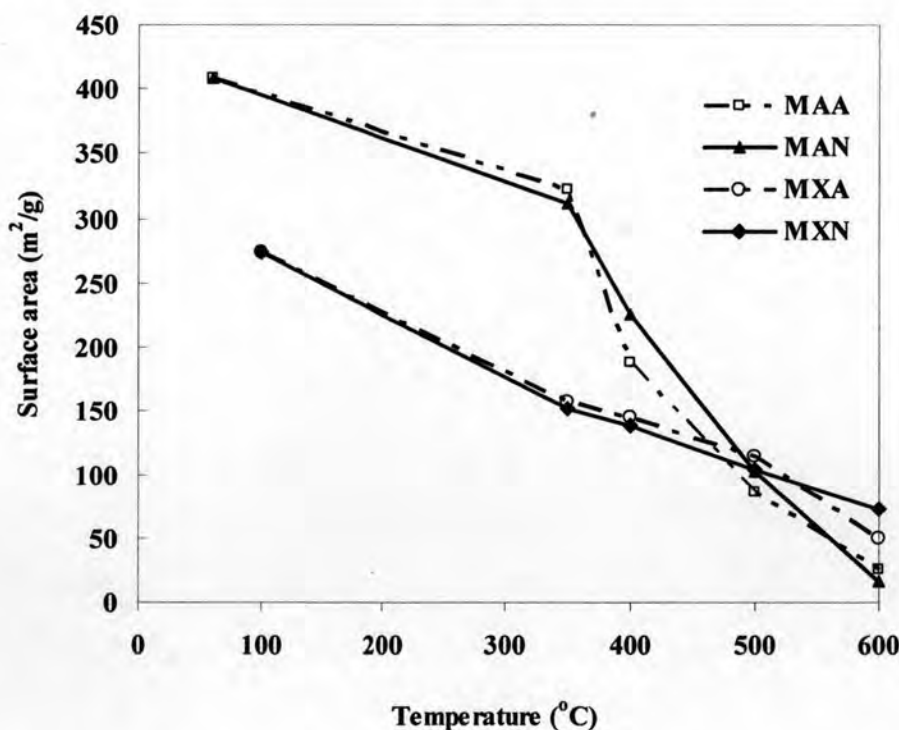


Figure 5.15 Specific surface area of TiO_2 sample, which used methanol as solvent and were calcined under a flow of air or nitrogen for two hours at temperature between $350\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$

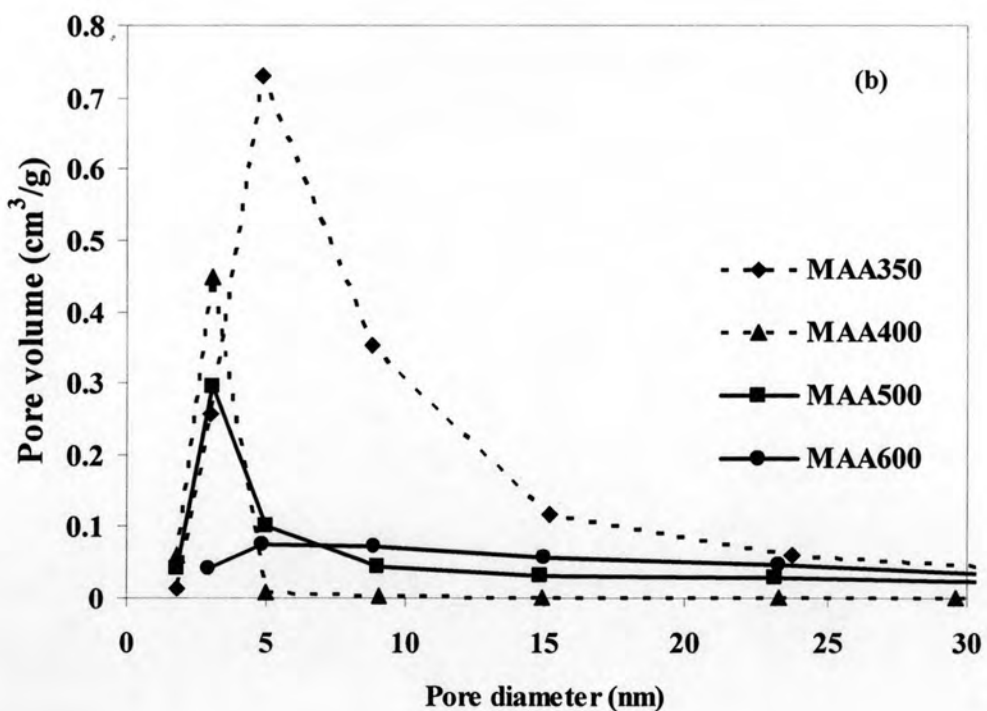
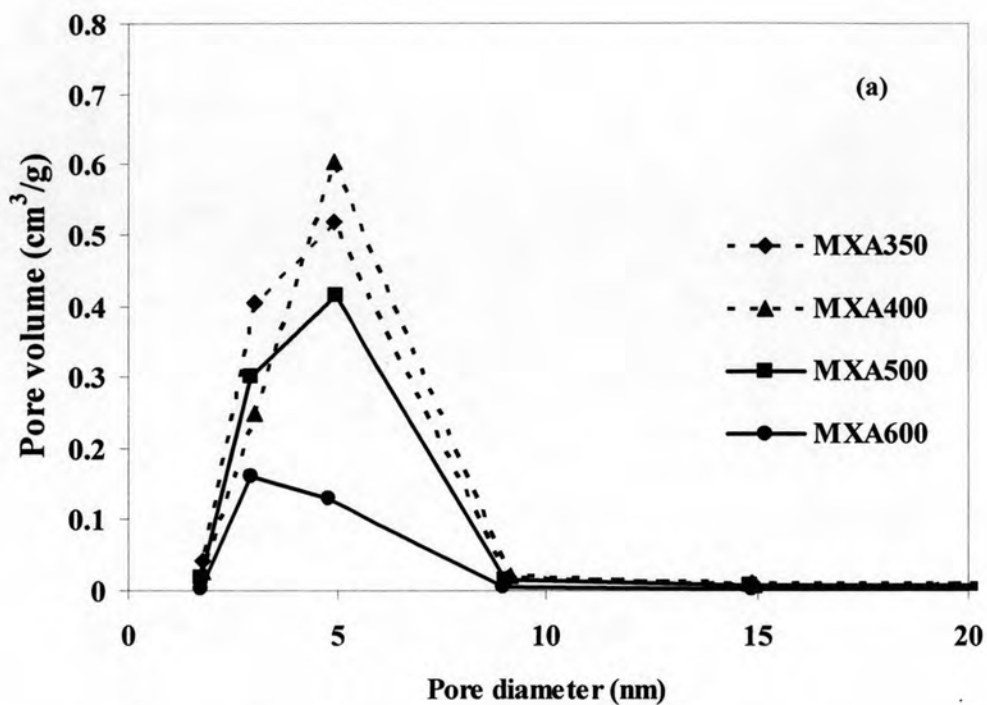


Figure 5.16 Pore size distribution of TiO₂ (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of air for two hours at temperature between 350 °C and 600 °C

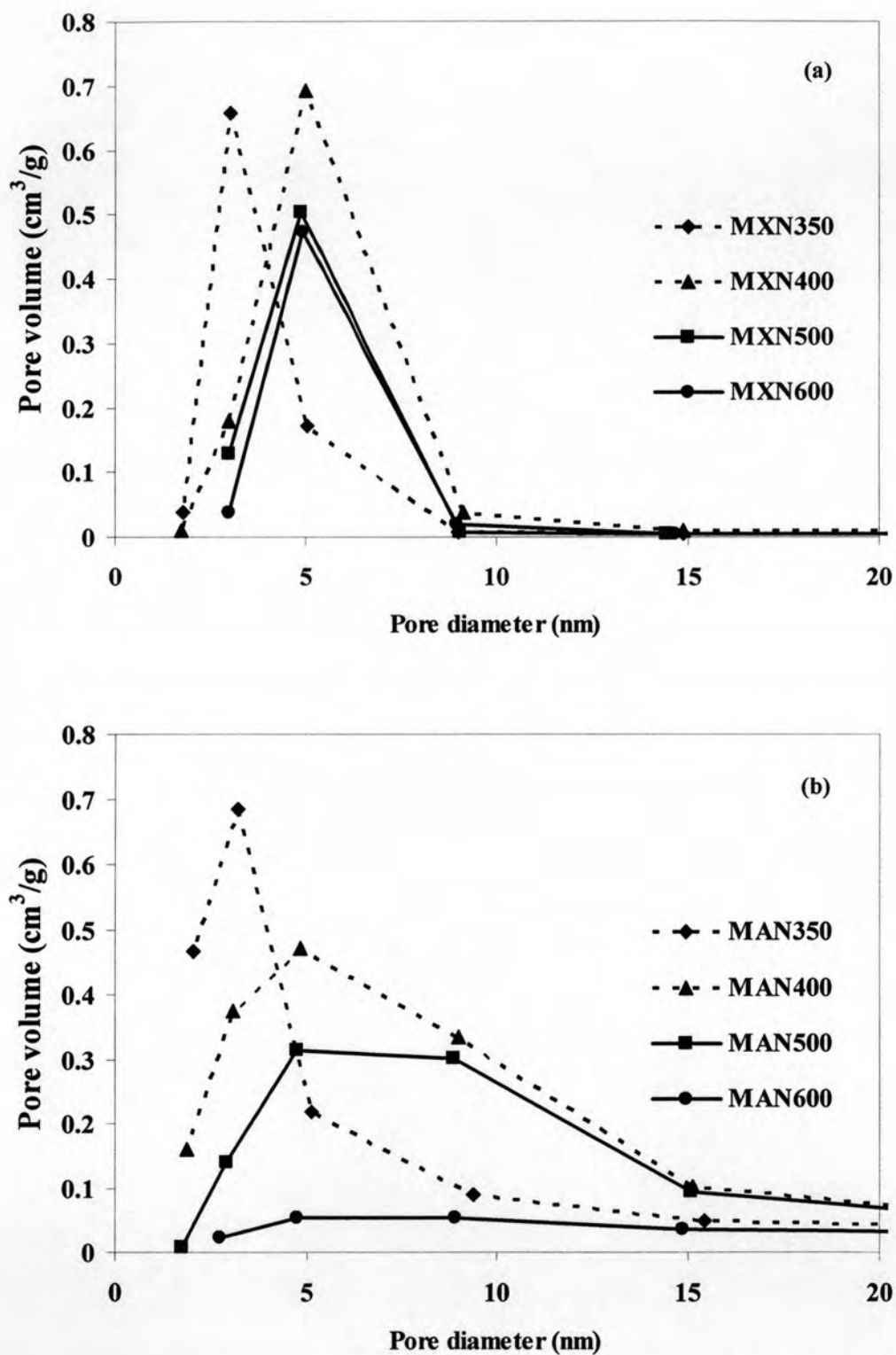


Figure 5.17 Pore size distribution of TiO₂ (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of nitrogen for two hours at temperature between 350 °C and 600 °C

Table 5.5 Pore structure information of TiO₂ aerogels and xerogels, which used methanol as solvent.

Sample	Specific surface area (m ² /g)	Average Pore size (nm)	Pore volume (cm ³ /g)
aerogel	408.6	4.4	0.4786
xerogel	274.7	2.5	0.1032
MXA350	156.6	3.9	0.2483
MXA400	145.6	4.3	0.2375
MXA500	113.8	4.0	0.1923
MXA600	49.7	3.8	0.0737
MAA350	322.9	3.8	0.0790
MAA400	187.4	4.6	0.1043
MAA500	85.9	3.8	0.1241
MAA600	25.0	6.9	0.0715
MXN350	151.3	3.3	0.2016
MXN400	138.2	4.6	0.2419
MXN500	103.3	4.4	0.1753
MXN600	72.1	4.9	0.1430
MAN350	312.1	3.2	0.3234
MAN400	226.2	4.4	0.3471
MAN500	102.1	5.8	0.2214
MAN600	16.3	7.0	0.0506

5.2.4 Fourier Transform Infrared Spectroscopy measurement

To investigate the existence of organic compound in various TiO₂ samples, FTIR measurement was performed. Infrared spectra of various TiO₂ samples are displayed in Figures 5.18 and 5.19. The peaks at the 1620 cm⁻¹ and around 3200-3600 cm⁻¹ corresponded to a stretching vibration of adsorbed water molecules and surface hydroxyl groups, respectively [Kolen'ko et al 2005]. The broad band below 1200 cm⁻¹ was assigned to Ti-O-Ti vibration [Venkatachalam et al 2007].

From Figures 5.18 b and 5.19 b, the as-synthesized aerogel possessed a set of peaks at 2947 and 2837 cm⁻¹, which corresponded to symmetric and antisymmetric vibration modes of -CH₂- and -CH₃ groups in the alkoxide [Burgos and Langlet 1999]. The broad band around 1065 cm⁻¹ was attributed to the OR groups linked to Ti [Ivanova and Harizanova 2001]. The peak at 1385 cm⁻¹ belonged to the presence of nitrates, which was a result of nitric acid added during hydrolysis [Music et al 1997]. These groups of peaks, which disappeared after calcination, corresponded to organic residue remaining on the surface even after the drying process. These results suggested that drying TiO₂ by supercritical CO₂ was less efficient in removing the solvent than drying under ambient condition. The peak at 3675 cm⁻¹, corresponding to Ti-OH bonds, appeared after TiO₂ were fired at 400 °C. After calcination at a temperature higher than 400 °C, the vibration bands of water and surface hydroxyl groups became much weaker. Therefore, surface hydroxyl group and water in TiO₂ were removed during calcination. The peak at around 2350 cm⁻¹ was believed to be CO₂ that was formed during the combustion of organic impurity and was partly adsorbed onto TiO₂ [Li et al 2006]. The peak corresponding to CO₂ was more pronounced in the aerogel with an increase in calcination temperature because more organic residues remained in the aerogel than the xerogel.

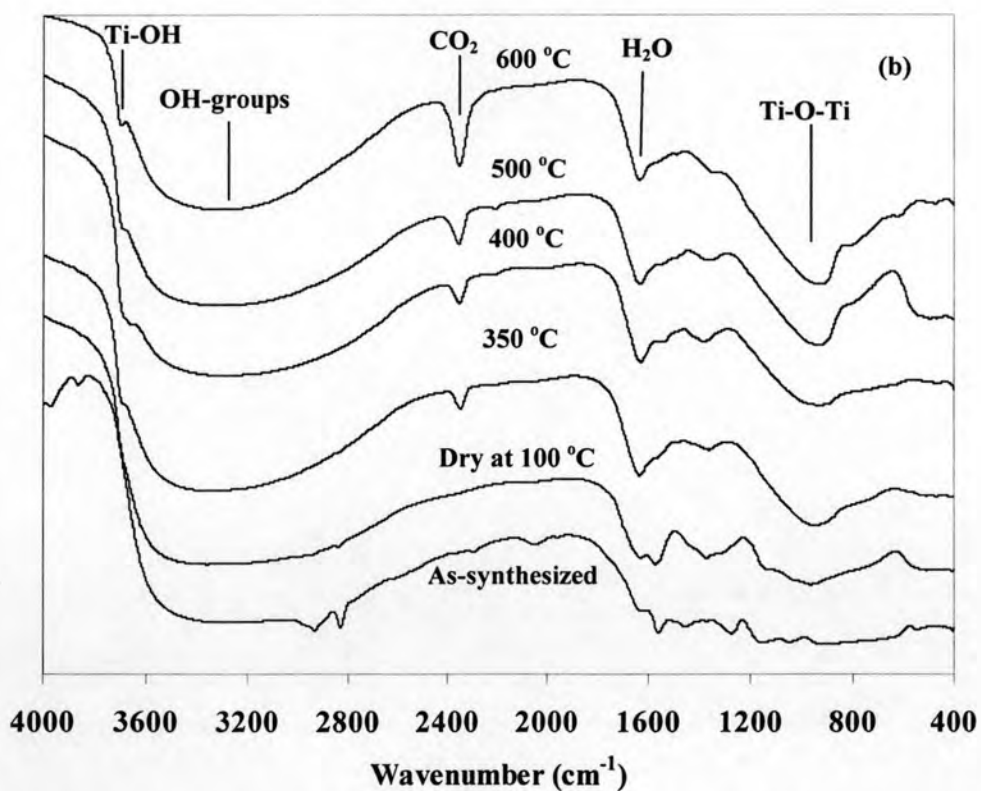
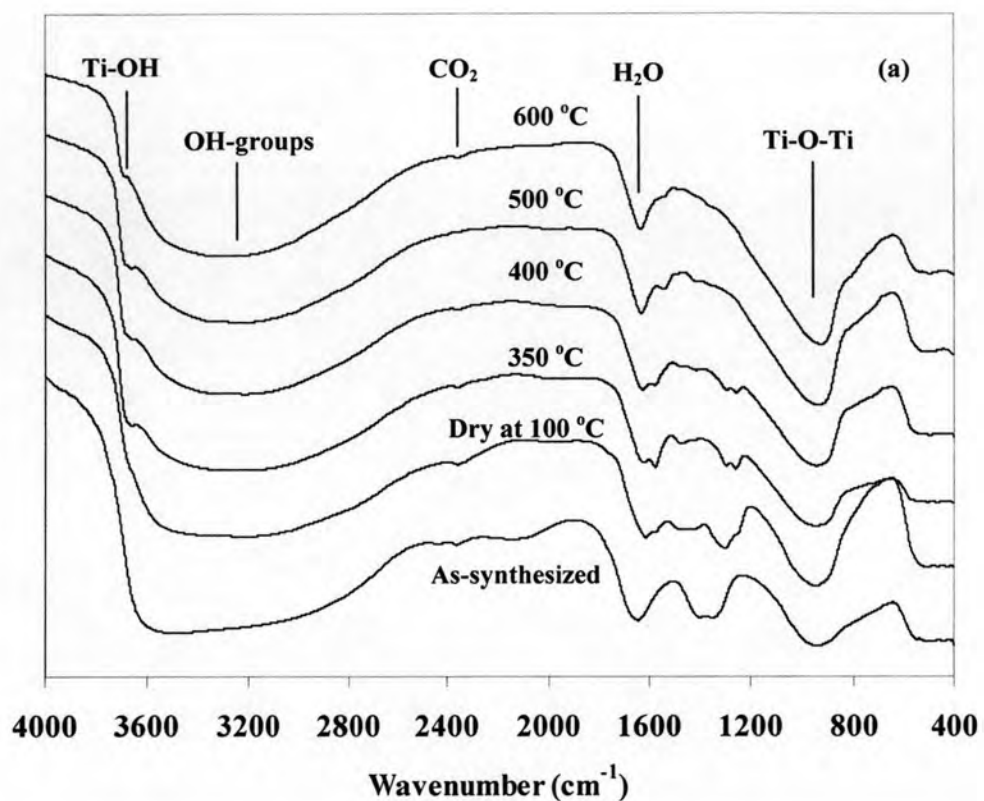


Figure 5.18 Infrared spectra TiO₂ (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

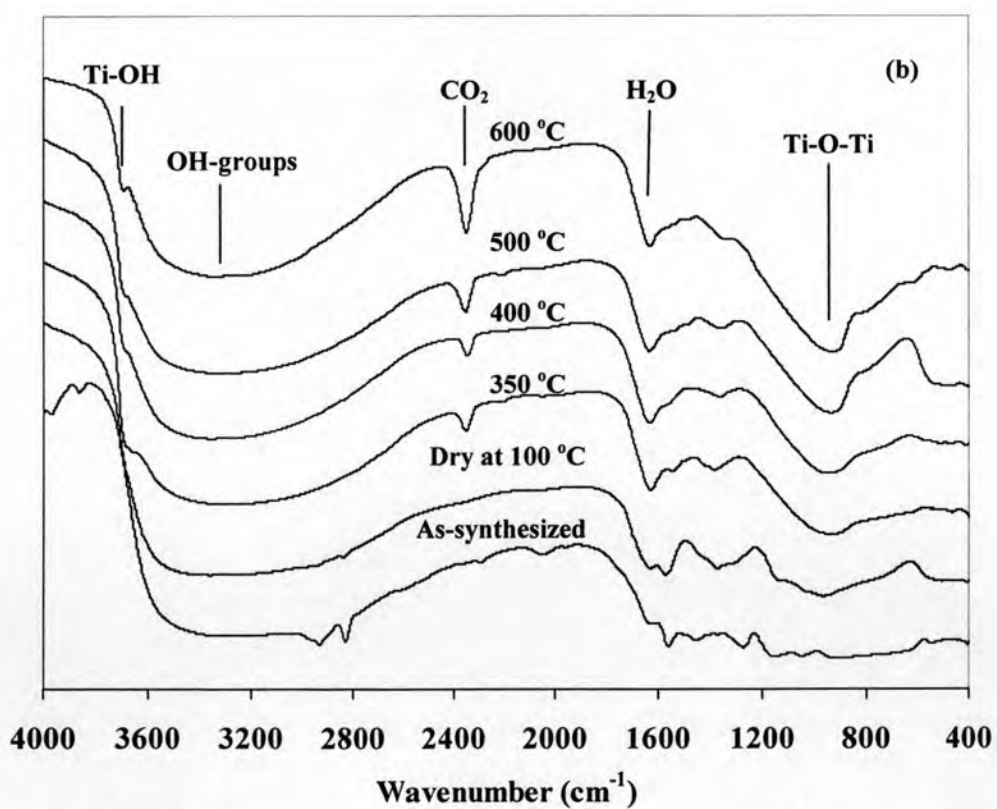
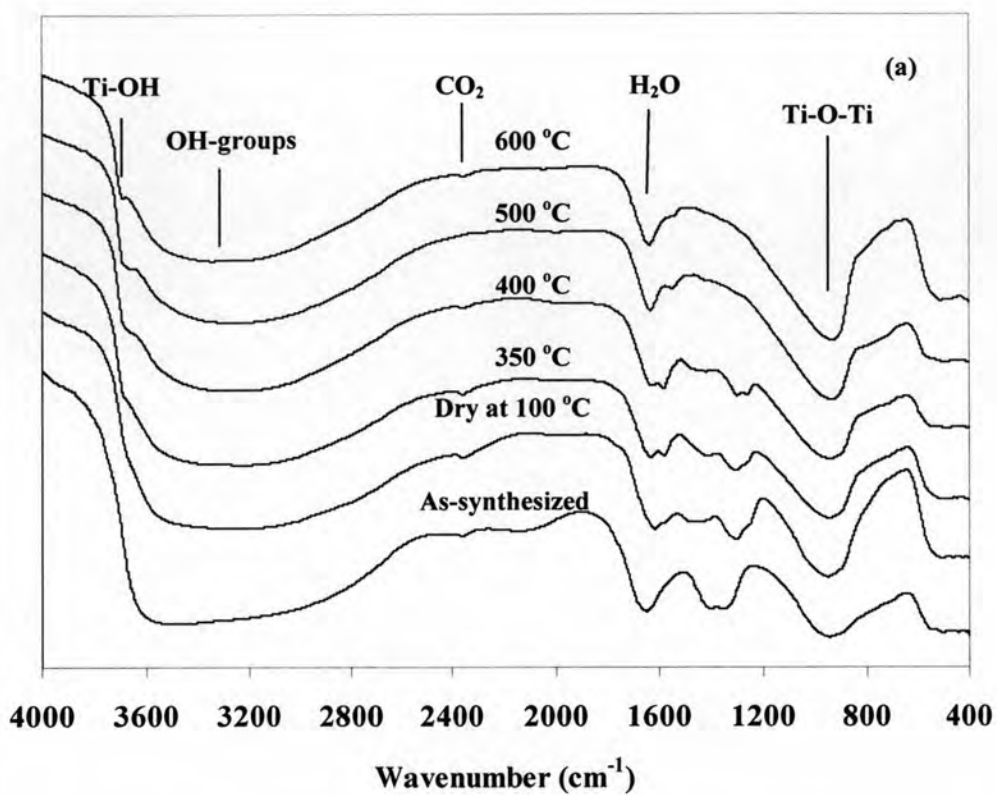


Figure 5.19 Infrared spectra of (a) TiO₂ xerogel and (b) TiO₂ aerogel, which used methanol as solvent and were calcined under a flow of nitrogen for two hours at a temperature ranging from 350 °C to 600 °C.

5.2.5 Electron spin resonance spectroscopy measurement

ESR measurement was performed at 77 K with liquid nitrogen in vacuum for various TiO₂ xerogels and aerogels. The results are listed in Tables 5.6 and 5.7. As the calcination temperature increased, the intensity of a peak corresponding to Ti³⁺ surface defect became lower and thus the amount of Ti³⁺ surface defect decreased as a result of an increase in crystallinity [Ohtani et al. 1997]. However, the amount of Ti³⁺ surface defect in aerogel was higher than that in xerogel because a larger amount of organic residues remained in aerogel. The surface defect site (Ti³⁺) was created by the removal of organic residues [Suriye et al 2007].

Table 5.6 Amount of Ti³⁺ surface defect of TiO₂ xerogel and aerogel, which were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

Sample	Surface area (m ² /g)	Weight (g)	Amount of Ti ³⁺ surface defect
aerogel	408.6	-	-
xerogel	274.7	-	-
MXA350	156.6	0.2979	7680.4
MXA400	145.6	0.2979	6173.2
MXA500	113.8	0.2970	2646.5
MXA600	46.1	0.3002	3244.5
MAA350	64.7	0.0416	147980.8
MAA400	68.3	0.0430	119069.8
MAA500	85.9	0.0431	20543.9
MAA600	25.0	0.0448	23472.8

Table 5.7 Amount of Ti^{3+} surface defect of TiO_2 xerogel and aerogel, which were calcined under a flow of air for two hours at a temperature ranging from 350 °C to 600 °C.

Sample	Surface area (m^2/g)	Weight (g)	Amount of Ti^{3+} surface defect
aerogel	408.6	-	-
xerogel	274.7	-	-
MXN350	151.3	0.2912	5618.1
MXN400	139.0	0.2960	5932.4
MXN500	103.3	0.2960	2172.3
MXN600	72.1	0.1413	1946.2
MAN350	312.2	0.0422	150473.9
MAN400	226.2	0.0431	99907.2
MAN500	102.1	0.0448	24158.0
MAN600	16.3	0.0433	20902.2

5.2.6 Photocatalytic activity

In this work, TiO_2 aerogel and xerogel which were calcined at a temperature in the range between 350 °C and 600 °C were used as photocatalysts in the photocatalytic oxidation of ethylene. Approximately 0.02 g of catalyst was used. The main products in this reaction were carbon dioxide and water.

The conversion of ethylene as a function of a calcination temperature for various TiO_2 samples was shown in Figure 5.20. When the calcination temperature increased, the photocatalytic activities of all TiO_2 increased and then decreased. TiO_2 that was calcined at 500 °C exhibited highest the photocatalytic activities. These results may be explained by two factors, i.e. crystallinity of TiO_2 and Ti^{3+} surface defect.

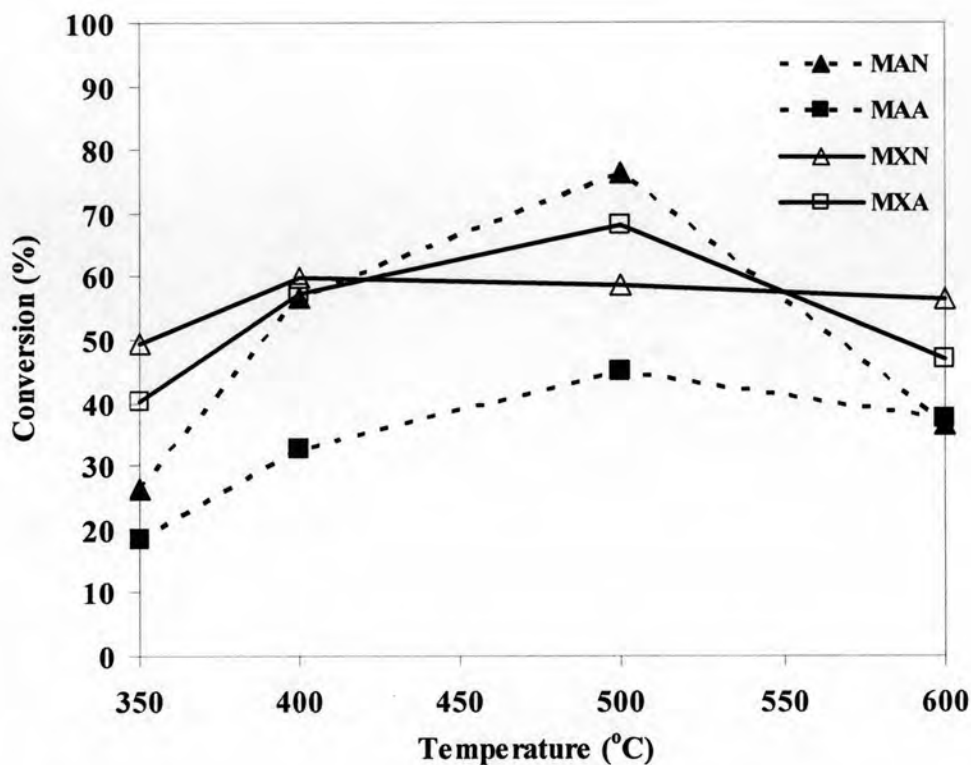


Figure 5.20 Photocatalytic activities of various TiO₂ aerogels and xerogels, which used methanol as solvent.

When the calcination temperature was increased from 350 to 500 °C, the crystallinity of anatase in the samples became greater. This was demonstrated by the growth in the intensity of the (101) XRD diffraction peak of anatase (see Table 5.8). The higher amount of anatase crystal led to greater amounts of holes and electrons generated upon exposure to ultraviolet irradiation, thereby enhancing the photocatalytic activity of the sample. After 500 °C, the photocatalytic activity of TiO₂ samples decreased despite higher crystallinity of anatase in samples. This could be attributed to a smaller amount of Ti³⁺ found in sample (see Table 5.6 and 5.7). Ti³⁺ surface defect acted as a trap for photogenerated electrons and prevented recombination of electrons and holes [Suriye et al 2007]. Therefore, the smaller amount of Ti³⁺ led to lower activity of TiO₂ samples that were calcined at a temperature higher than 500 °C.

Table 5.8 Intensity of (101) XRD diffraction peak of various TiO₂ samples, which used methanol as solvent.

Sample	Intensity of (101) diffraction peak *	Sample	Intensity of (101) diffraction peak *
MXA350	303	MXN350	308
MXA400	387	MXN400	396
MXA500	407	MXN500	412
MXA600	307	MXN600	399
MAA350	225	MAN350	148
MAA400	333	MAN400	329
MAA500	367	MAN500	330
MAA600	507	MAN600	667

* In order to estimate crystallinity in TiO₂ samples, equal amount of samples (0.100g) was used.