

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Characterization of Studied Photocatalysts

##### 4.1.1 Crystal Structures of Studied Photocatalysts

The crystal structures of the photocatalysts prepared by the sol-gel method were identified by the X-ray diffractometer using Cu ( $\lambda = 0.154$  nm) radiation. For the XRD patterns of TiO<sub>2</sub>, the anatase peak is observed at  $2\theta = 25.3^\circ$ , whereas the rutile one is observed at  $2\theta = 27.5^\circ$ . The crystallite sizes of the catalysts can be calculated from the Scherrer equation as shown in Equation 4.1.

$$d = k\lambda/b\cos\theta \quad (4.1)$$

where  $d$  = crystallite size (nm),

$b$  = the angular width of the X-ray line at the mid height,

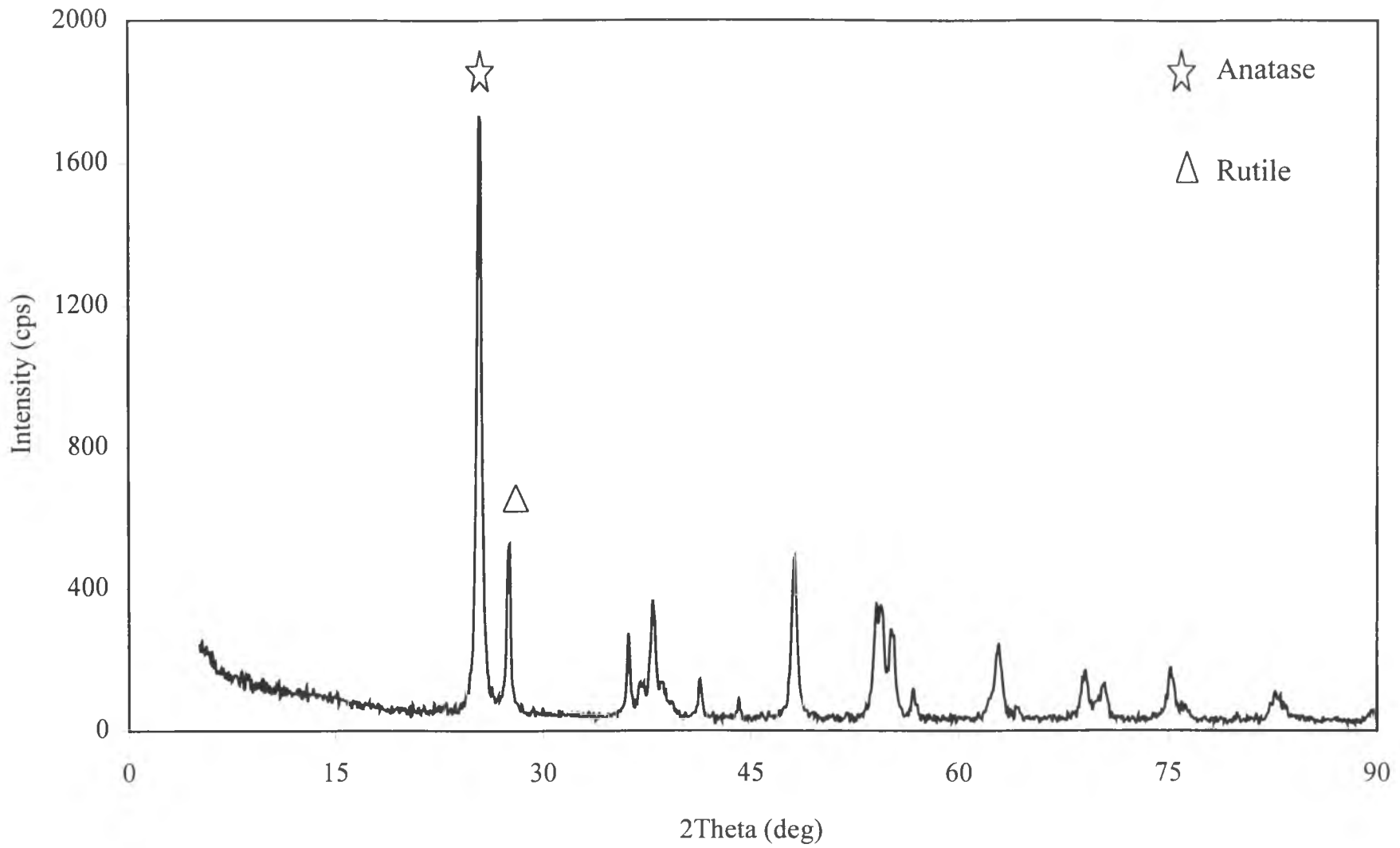
$\theta$  = the corresponding peak (for anatase  $\theta = 25.3/2^\circ$ ),

$k$  = the constant that is close to one, and

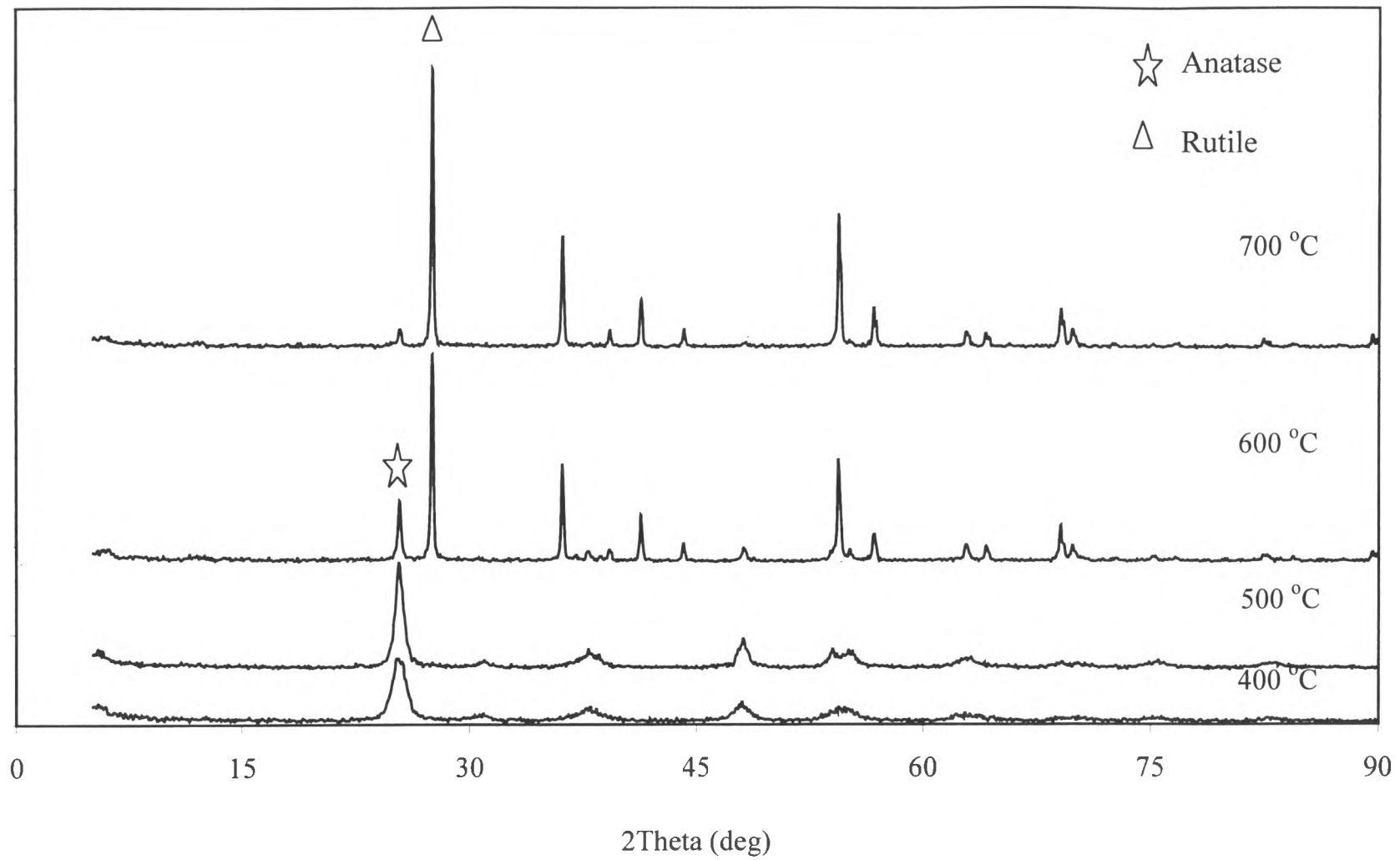
$\lambda$  = the wavelength (0.154 nm for Cu radiation source).

##### *4.1.1.1 Crystal Structure of TiO<sub>2</sub> Photocatalysts*

Figures 4.1 and 4.2 show the XRD patterns of commercial TiO<sub>2</sub> (Degussa P25) and TiO<sub>2</sub> prepared by the sol-gel method, respectively. For the commercial TiO<sub>2</sub>, the two phases of anatase and rutile were observed. The highest peak at  $2\theta = 25.3^\circ$  shows that the major phase is anatase and rutile one exists as the minor phase. For TiO<sub>2</sub> prepared by the sol-gel method, the anatase peaks were observed as the single major phase for the calcination temperatures of 400 and 500 °C. For the calcination temperature over 500 °C, it results in the phase transformation from anatase to rutile. The crystallite sizes of Degussa P25 and the sol-gel TiO<sub>2</sub> are shown in Table 4.1.



**Figure 4.1** X-ray diffraction pattern of Degussa P25



**Figure 4.2** X-ray diffraction patterns of TiO<sub>2</sub> prepared at different calcination temperatures

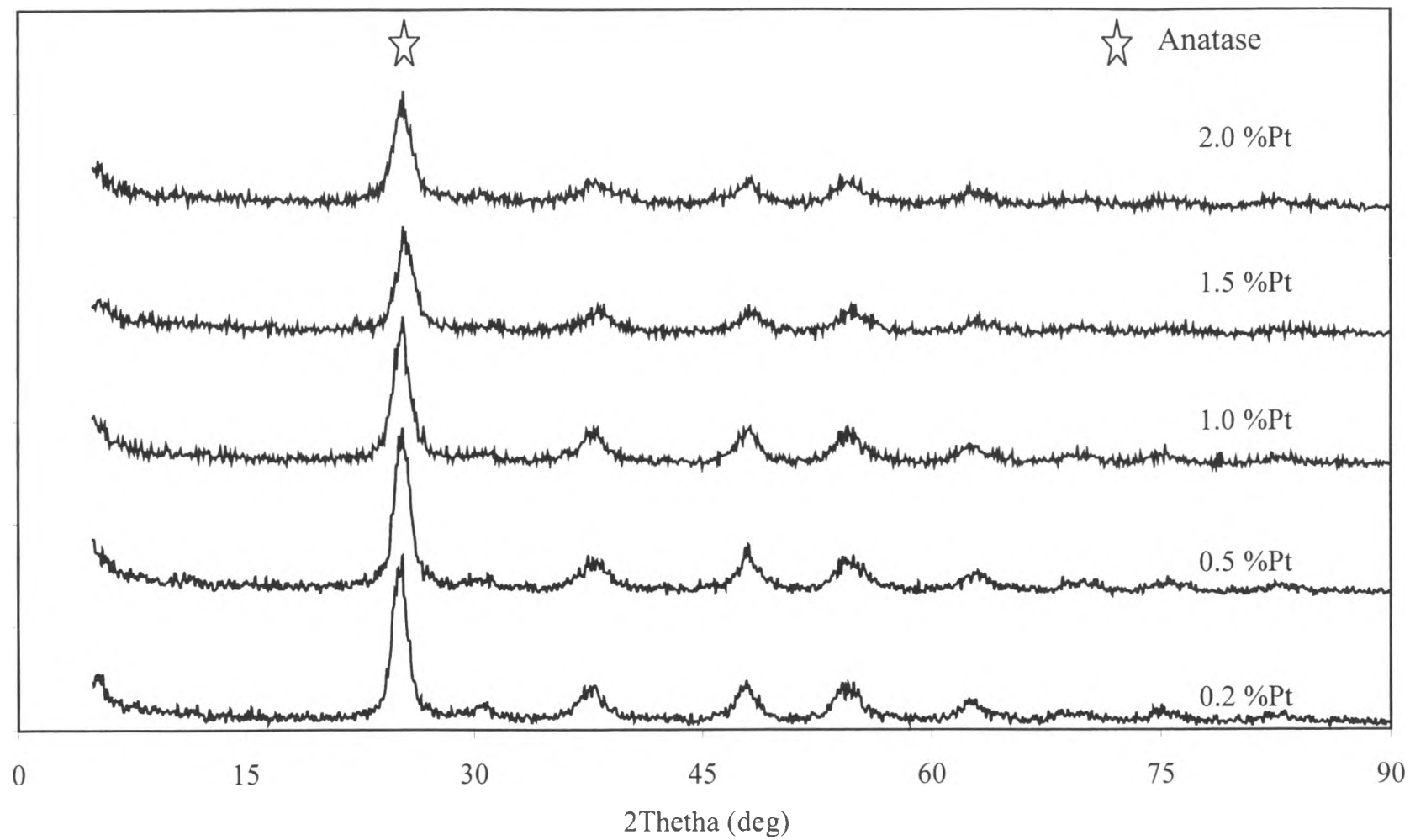
For the prepared TiO<sub>2</sub>, the crystallite sizes increased with increasing the calcination temperature since the crystal structure of TiO<sub>2</sub> transform from anatase to rutile.

**Table 4.1** The crystallite sizes of Degussa P25 and sol-gel TiO<sub>2</sub> calcined at different temperatures

Catalyst	Crystallite Size (nm)
Degussa P25	27.48
TiO <sub>2</sub> (400 °C)	10.38
TiO <sub>2</sub> (500 °C)	16.00
TiO <sub>2</sub> (600 °C)	38.48
TiO <sub>2</sub> (700 °C)	127.37

#### 4.1.1.2 Crystal Structure of Pt/TiO<sub>2</sub> Photocatalysts

The XRD patterns of Pt/TiO<sub>2</sub> catalysts at different % Pt loadings are shown in Figure 4.3. For Pt/TiO<sub>2</sub> catalysts calcined at 400 ° C and having 0.2-2.0 mol% Pt, it can be observed that TiO<sub>2</sub> was only in the anatase form and no peaks of platinum at  $2\theta = 40^\circ$  and  $48^\circ$  were observed. It is suggested that Pt can be dispersed well on TiO<sub>2</sub> in case of Pt/TiO<sub>2</sub>. Table 4.2 shows that the amount of Pt does not significantly affect the crystallite size of the photocatalysts but the presence of Pt decreases remarkably the crystallite size of Pt/TiO<sub>2</sub> in comparison with TiO<sub>2</sub>.



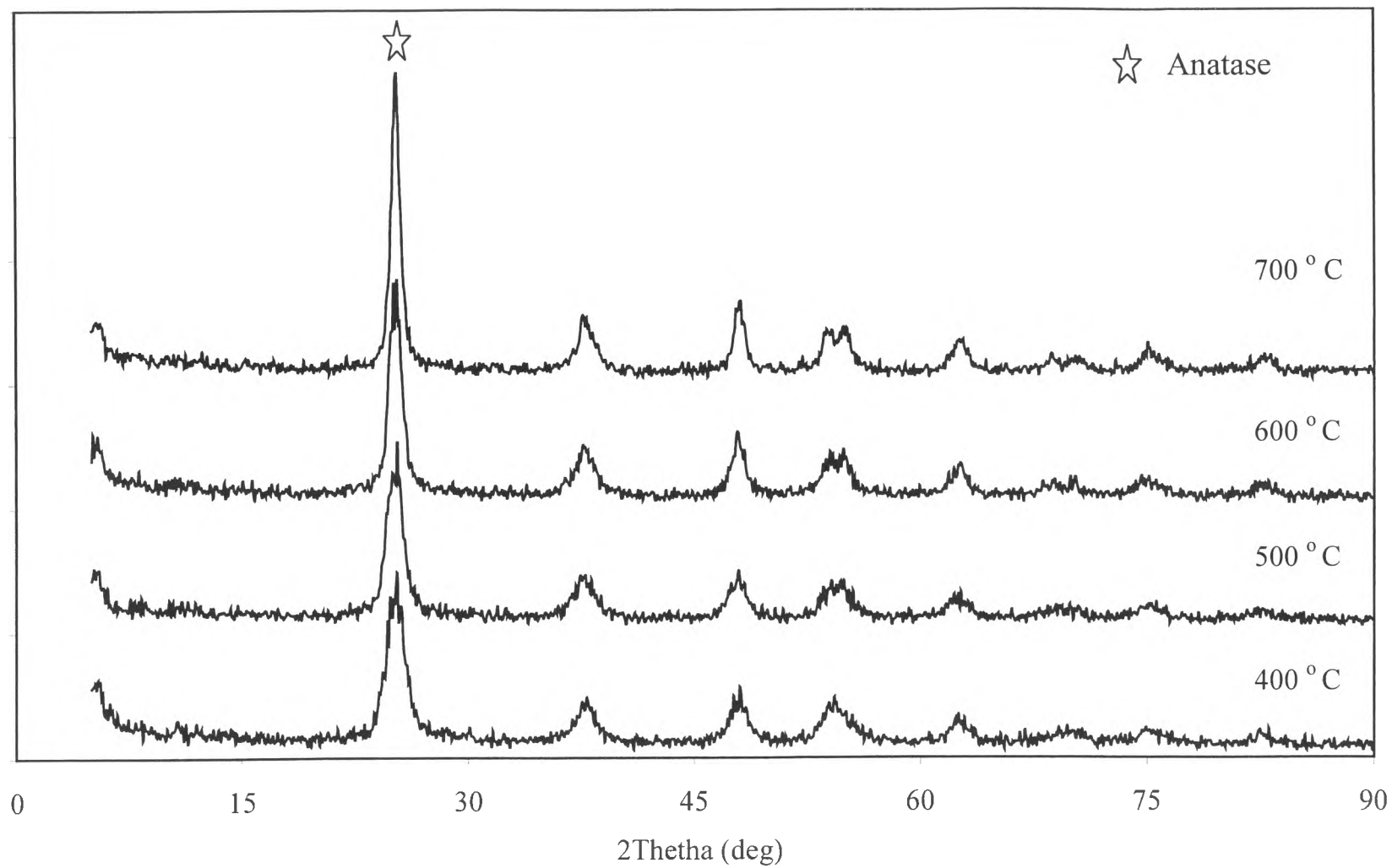
**Figure 4.3** X-ray diffraction patterns for Pt/TiO<sub>2</sub> catalysts at different Pt loadings prepared at calcination temperature of 400 °C

**Table 4.2** The crystallite size of Pt/TiO<sub>2</sub> at the calcination temperature 400 ° C

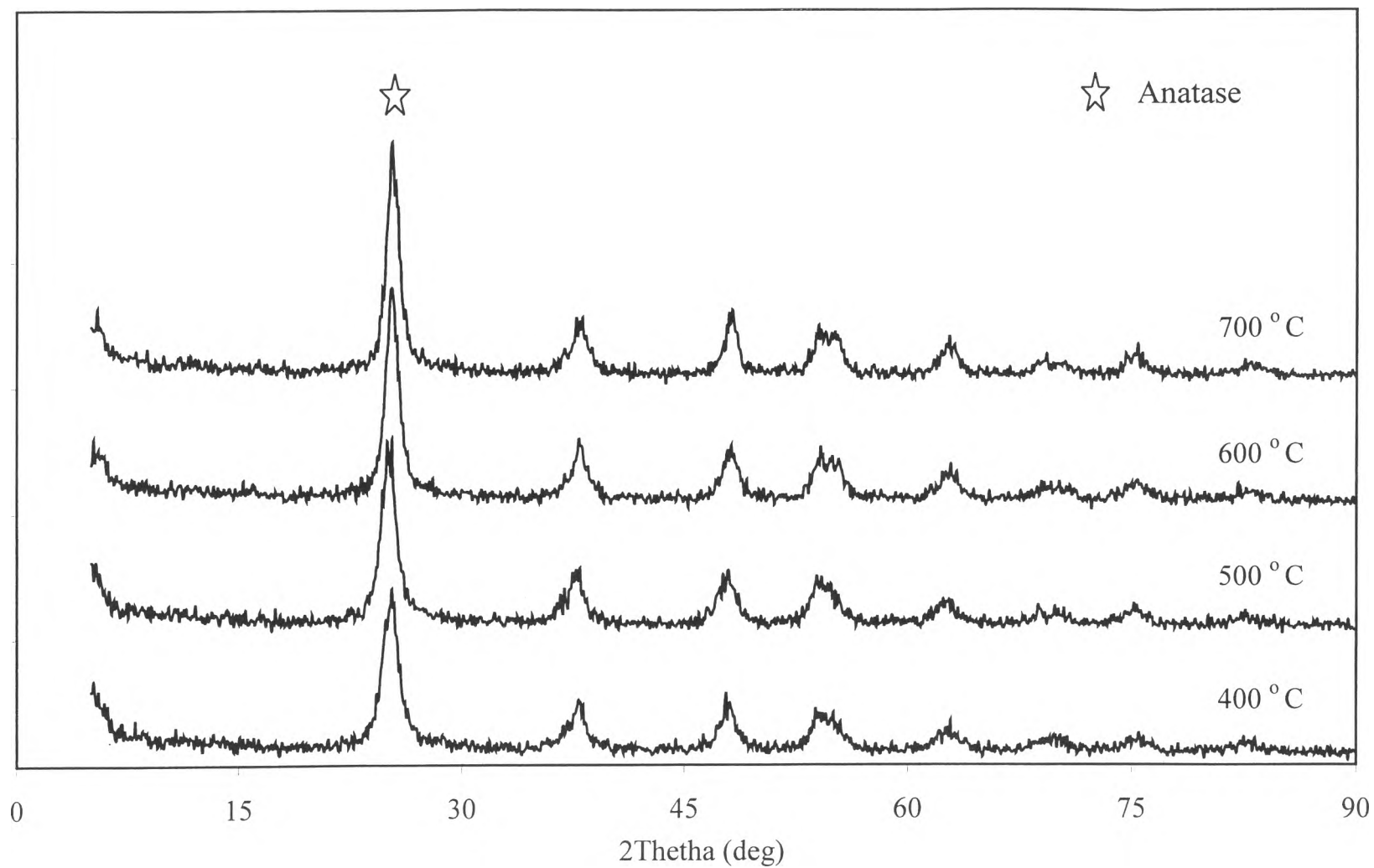
Catalyst	Crystallite Size (nm)
TiO <sub>2</sub>	10.38
0.2 %Pt/TiO <sub>2</sub>	8.01
0.5 %Pt/TiO <sub>2</sub>	8.90
1.0 %Pt/TiO <sub>2</sub>	7.54
1.5 %Pt/TiO <sub>2</sub>	7.25
2.0 %Pt/TiO <sub>2</sub>	6.20

#### 4.1.1.3 Crystal Structure of TiO<sub>2</sub>-SiO<sub>2</sub> Photocatalysts

Figures 4.4-4.7 show the XRD patterns of TiO<sub>2</sub>-SiO<sub>2</sub> at different %SiO<sub>2</sub> and calcination temperatures. It was clearly seen that adding silica up to 30 % did not change the crystal form of TiO<sub>2</sub>. Moreover, addition of silica increased the thermal stability of TiO<sub>2</sub> resulting in the suppression of the phase transformation from anatase to rutile at higher calcination temperatures. From the XRD patterns, TiO<sub>2</sub>-SiO<sub>2</sub> could be calcined up to 700 ° C without the phase transformation as opposed to TiO<sub>2</sub> alone. The crystallite sizes of TiO<sub>2</sub>-SiO<sub>2</sub> prepared at different calcination temperatures and having different %SiO<sub>2</sub> are shown in Table 4.3. At the calcination temperature of 400 °C, the crystallite sizes of 5%SiO<sub>2</sub>-TiO<sub>2</sub> and 10%SiO<sub>2</sub>-TiO<sub>2</sub> were smaller than that of TiO<sub>2</sub> while the crystallite sizes of 20%SiO<sub>2</sub>-TiO<sub>2</sub> and 30%SiO<sub>2</sub>-TiO<sub>2</sub> were larger. For 5%SiO<sub>2</sub>-TiO<sub>2</sub>, the crystallite size increased with increasing the calcination temperature. However, the trend of the crystallite size was uncertain at the high amount of silica and high calcination temperature. Based on the results shown in Table 4.3, 20%SiO<sub>2</sub>-TiO<sub>2</sub> calcined at 600 °C gives the highest crystallite size of 19.20 nm among TiO<sub>2</sub>-SiO<sub>2</sub> catalysts prepared.

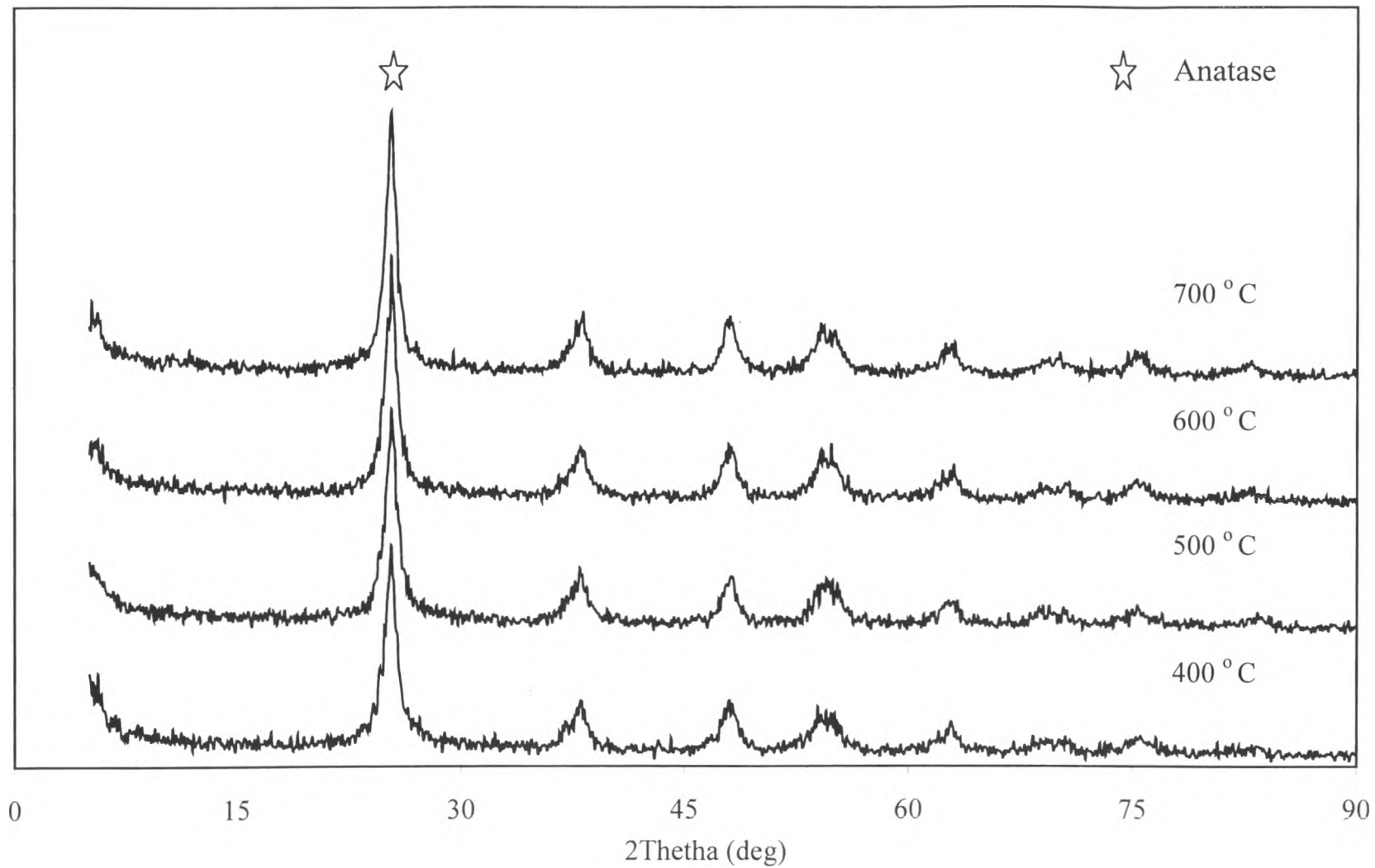


**Figure 4.4** X-ray diffraction patterns of 5%SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures

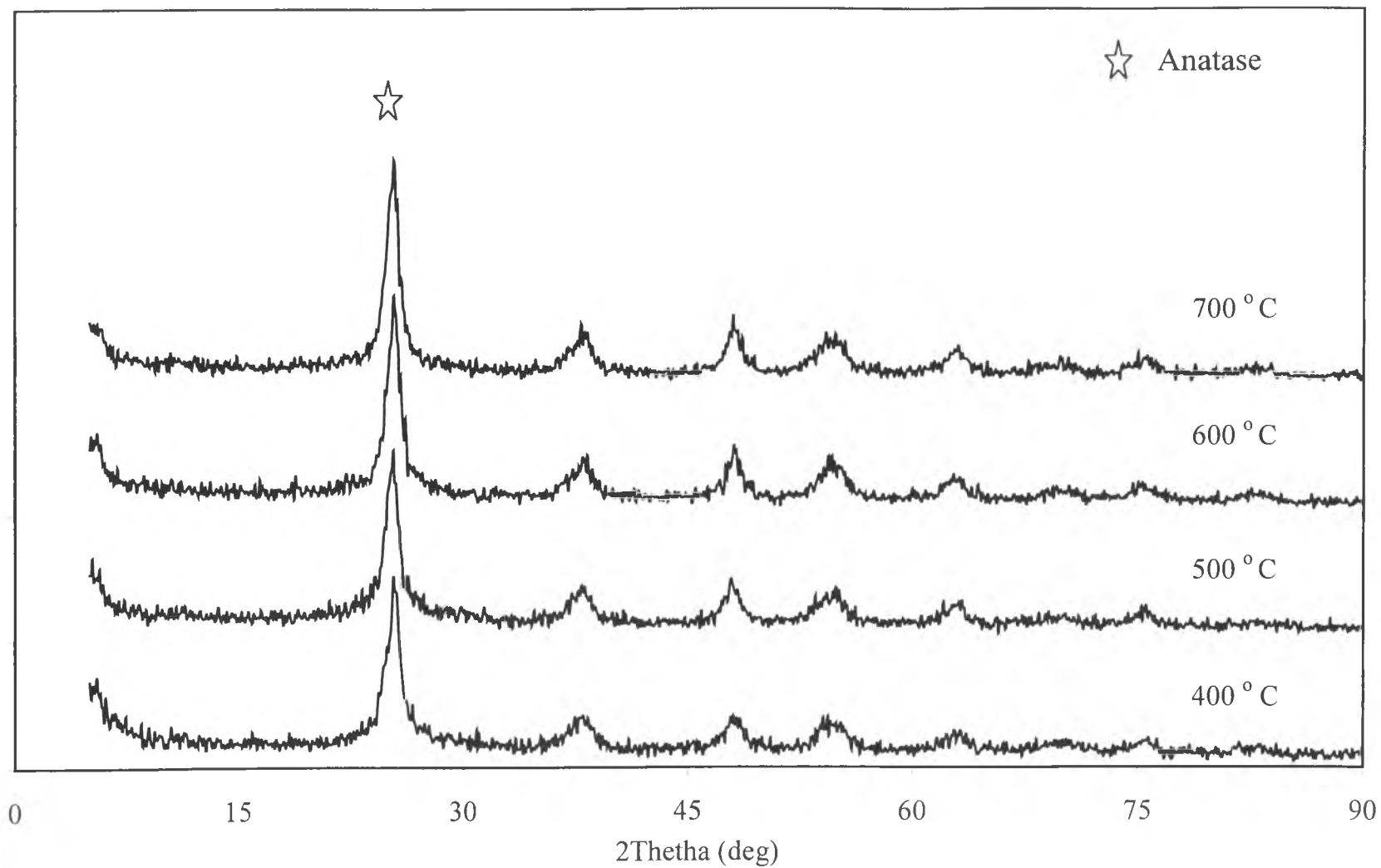


**Figure 4.5** X-ray diffraction patterns of 10%SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures





**Figure 4.6** X-ray diffraction patterns for 20%SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures



**Figure 4.7** X-ray diffraction patterns for 30% SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures

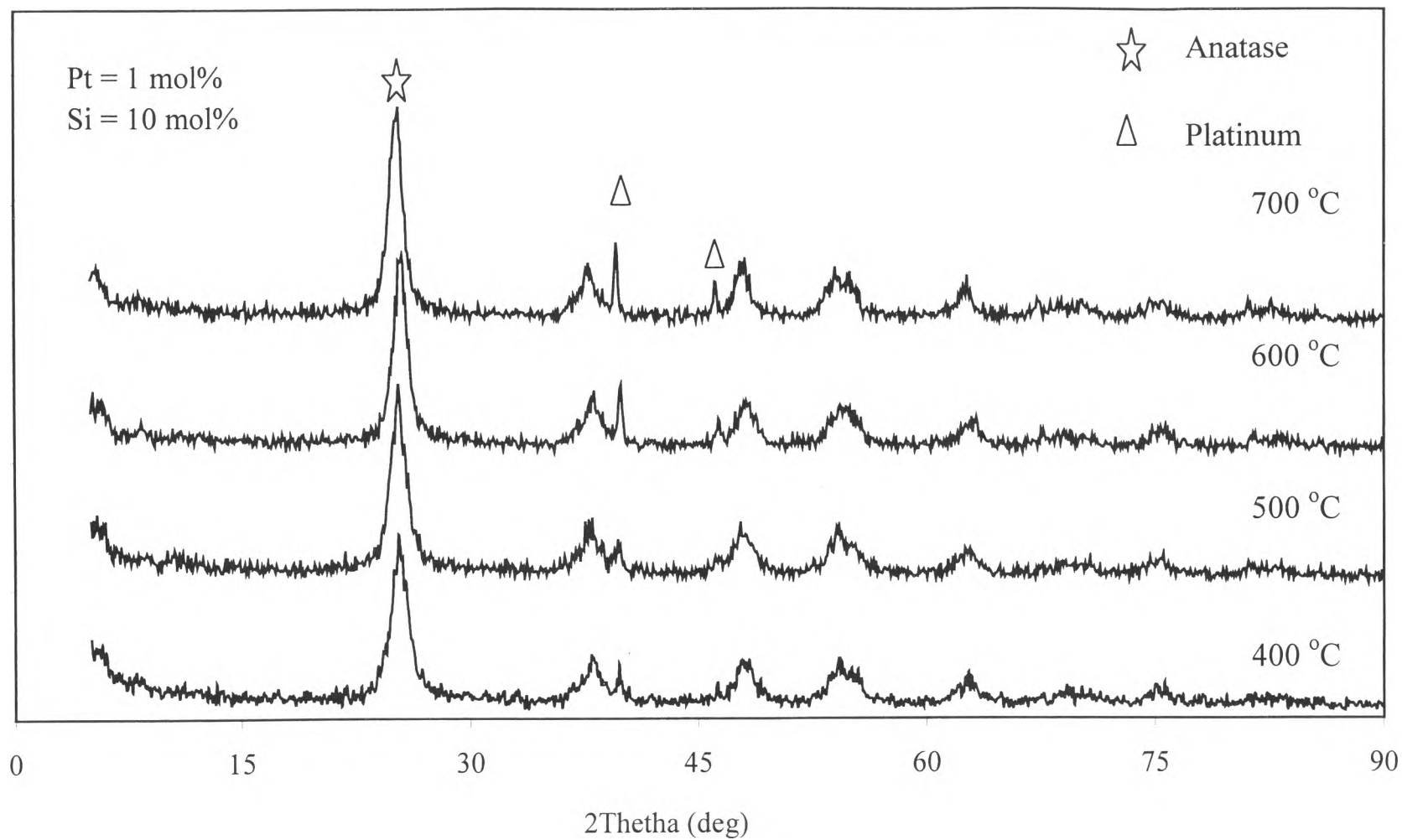
**Table 4.3** The crystallite sizes of TiO<sub>2</sub>-SiO<sub>2</sub> at different %SiO<sub>2</sub> and calcination temperatures

Catalyst	Crystallite Size (nm)			
	400 °C	500 °C	600 °C	700 °C
TiO <sub>2</sub>	10.38	16.00	38.48	127.37
5% SiO <sub>2</sub> -TiO <sub>2</sub>	7.25	7.69	9.85	14.24
10% SiO <sub>2</sub> -TiO <sub>2</sub>	7.69	8.54	9.85	9.37
20% SiO <sub>2</sub> -TiO <sub>2</sub>	12.01	16.00	19.20	15.38
30% SiO <sub>2</sub> -TiO <sub>2</sub>	13.26	10.38	12.01	13.26

#### 4.1.1.4 Crystal Structure of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> Photocatalysts

The XRD patterns of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> (1 mol% Pt and 10 mol% SiO<sub>2</sub>) at different calcination temperatures ranging 400-700 °C are shown in Figure 4.8. Unlike the results of TiO<sub>2</sub>-SiO<sub>2</sub>, the peaks of Pt could be observed at  $2\theta = 40^\circ$  and  $48^\circ$ . The crystallite sizes of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> at different calcination temperatures are shown in Table 4.4. The crystallite sizes of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> were not much different from the crystallite sizes of 10%SiO<sub>2</sub>-TiO<sub>2</sub> for any given calcination temperature. As can be seen in Table 4.4, the crystallite size of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> increases with increasing the calcination temperature. The maximum size of the catalysts was found at 600 °C.





**Figure 4.8** X-ray diffraction patterns for Pt/TiO<sub>2</sub>-SiO<sub>2</sub> at different calcination temperatures

**Table 4.4** The crystallite sizes of 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> at the calcination temperature of 400-700 ° C

Calcination temperature	Crystallite Size (nm)
400 °C	7.68
500 °C	8.73
600 °C	11.65
700 °C	10.12

#### 4.1.2 Surface Structures of Studied Photocatalysts

##### 4.1.2.1 *Surface Structure of TiO<sub>2</sub>*

The surface area, pore volume and pore size of Degussa P25 and sol-gel TiO<sub>2</sub> at different calcination temperatures are shown in Table 4.5. The BET surface area of Degussa P25 was much lower than that of sol-gel TiO<sub>2</sub> calcined at 400 °C. On the contrary, the pore size and pore volume of Degussa P25 were higher than those of TiO<sub>2</sub> calcined at 400 °C. The surface area and the pore size of sol-gel TiO<sub>2</sub> decreased drastically with increasing the calcination temperature from 400 to 600 °C. In contrast, an increase in the calcination temperature increased the pore size of the sol-gel TiO<sub>2</sub> catalysts. The transformation of TiO<sub>2</sub> crystal structure from anatase to rutile resulting in the change in its surface structure as confirmed by the XRD results mentioned before.

**Table 4.5** The surface areas, pore sizes and pore volumes of Degussa P25 and sol-gel TiO<sub>2</sub> at different calcination temperatures

Catalyst	BET Surface Area (m <sup>2</sup> /g)	Pore Size (nm)	Pore Volume (cm <sup>3</sup> /g)
Degussa P25	78.4	173	0.340
TiO <sub>2</sub> (400 °C)	119.6	64	0.191
TiO <sub>2</sub> (500 °C)	70.1	81	0.143
TiO <sub>2</sub> (600 °C)	3.8	135	0.013
TiO <sub>2</sub> (700 °C)	4.0	187	0.019

#### 4.1.2.2 Structure Surface of Pt/TiO<sub>2</sub>

Table 4.6 shows the surface areas, pore sizes and pore volumes of Pt/TiO<sub>2</sub> catalysts calcined at 400 °C and having different % Pt loadings. An increase in platinum loading resulted in decreasing both the pore size and the pore volume of the catalyst but the BET surface area increased significantly with increasing Pt loading. The reduction of the pore size might result from the deposition of platinum particles.

#### 4.1.2.3 Surface Structure of TiO<sub>2</sub>-SiO<sub>2</sub>

Tables 4.7-4.9 show the surface areas, pore volumes and pore sizes of TiO<sub>2</sub>-SiO<sub>2</sub> catalysts having different %SiO<sub>2</sub> and calcined at different temperatures. For any given calcination temperature, the surface area increased with increasing %SiO<sub>2</sub> but it decreased with increasing the calcination temperature for any given SiO<sub>2</sub> content. The pore volume and pore size increased with increasing %SiO<sub>2</sub> and reached a maximum value at 20%SiO<sub>2</sub> over the range of the calcination temperatures. The pore volume decreased with increasing the calcination temperature while the pore size increased.

**Table 4.6** The surface areas, pore sizes and pore volumes of Pt/TiO<sub>2</sub> catalyst having different Pt loadings

Catalyst	BET Surface Area (m <sup>2</sup> /g)	Pore Size (nm)	Pore Volume (cm <sup>3</sup> /g)
TiO <sub>2</sub>	119.6	64	0.191
0.2 % Pt/TiO <sub>2</sub>	119.0	56	0.168
0.5 % Pt/TiO <sub>2</sub>	119.0	49	0.144
1.0 % Pt/TiO <sub>2</sub>	136.6	44	0.150
1.5 % Pt/TiO <sub>2</sub>	138.5	35	0.121
2.0 % Pt/TiO <sub>2</sub>	141.7	32	0.112

**Table 4.7** The surface areas of TiO<sub>2</sub>-SiO<sub>2</sub> catalyst having different mol% of SiO<sub>2</sub> calcined at different temperatures

Catalyst	BET Surface Area (m <sup>2</sup> /g)			
	400 ° C	500 ° C	600 ° C	700 ° C
TiO <sub>2</sub>	119.6	70.1	3.8	4.0
5 %SiO <sub>2</sub> -TiO <sub>2</sub>	197.5	170.6	119.1	96.3
10 %SiO <sub>2</sub> -TiO <sub>2</sub>	216.8	201.8	168.5	156.0
20 %SiO <sub>2</sub> -TiO <sub>2</sub>	294.4	245.3	227.6	196.8
30 %SiO <sub>2</sub> -TiO <sub>2</sub>	309.4	283.7	231.2	203.3

**Table 4.8** The pore volumes of TiO<sub>2</sub>-SiO<sub>2</sub> catalyst having different mol% of SiO<sub>2</sub> and calcined at different temperatures

Catalyst	Pore Volume (cm <sup>3</sup> /g)			
	400 ° C	500 ° C	600 ° C	700 ° C
TiO <sub>2</sub>	0.191	0.143	0.013	0.019
5 %SiO <sub>2</sub> -TiO <sub>2</sub>	0.222	0.219	0.194	0.160
10 %SiO <sub>2</sub> -TiO <sub>2</sub>	0.337	0.337	0.326	0.313
20 %SiO <sub>2</sub> -TiO <sub>2</sub>	0.492	0.455	0.452	0.441
30 %SiO <sub>2</sub> -TiO <sub>2</sub>	0.398	0.356	0.337	0.337

**Table 4.9** The pore sizes of TiO<sub>2</sub>-SiO<sub>2</sub> catalyst having different mol% of SiO<sub>2</sub> and at different calcination temperatures

Catalyst	PoreSize (nm)			
	400 ° C	500 ° C	600 ° C	700 ° C
TiO <sub>2</sub>	64	81	135	187
5 %SiO <sub>2</sub> -TiO <sub>2</sub>	45	51	65	67
10 %SiO <sub>2</sub> -TiO <sub>2</sub>	62	67	77	80
20 %SiO <sub>2</sub> -TiO <sub>2</sub>	67	74	79	90
30 %SiO <sub>2</sub> -TiO <sub>2</sub>	51	50	58	66

#### 4.1.2.4 Surface Structure of Pt/TiO<sub>2</sub>-SiO<sub>2</sub>

Table 4.10 shows the BET surface areas, the pore sizes and the pore volumes of 1 mol% Pt and 10 mol% SiO<sub>2</sub> on TiO<sub>2</sub> at the calcination temperatures of 400-700 °C. It was found that both surface area and pore size decreased substantially when the calcination temperature increased. In contrast, the pore sizes of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> decreased with



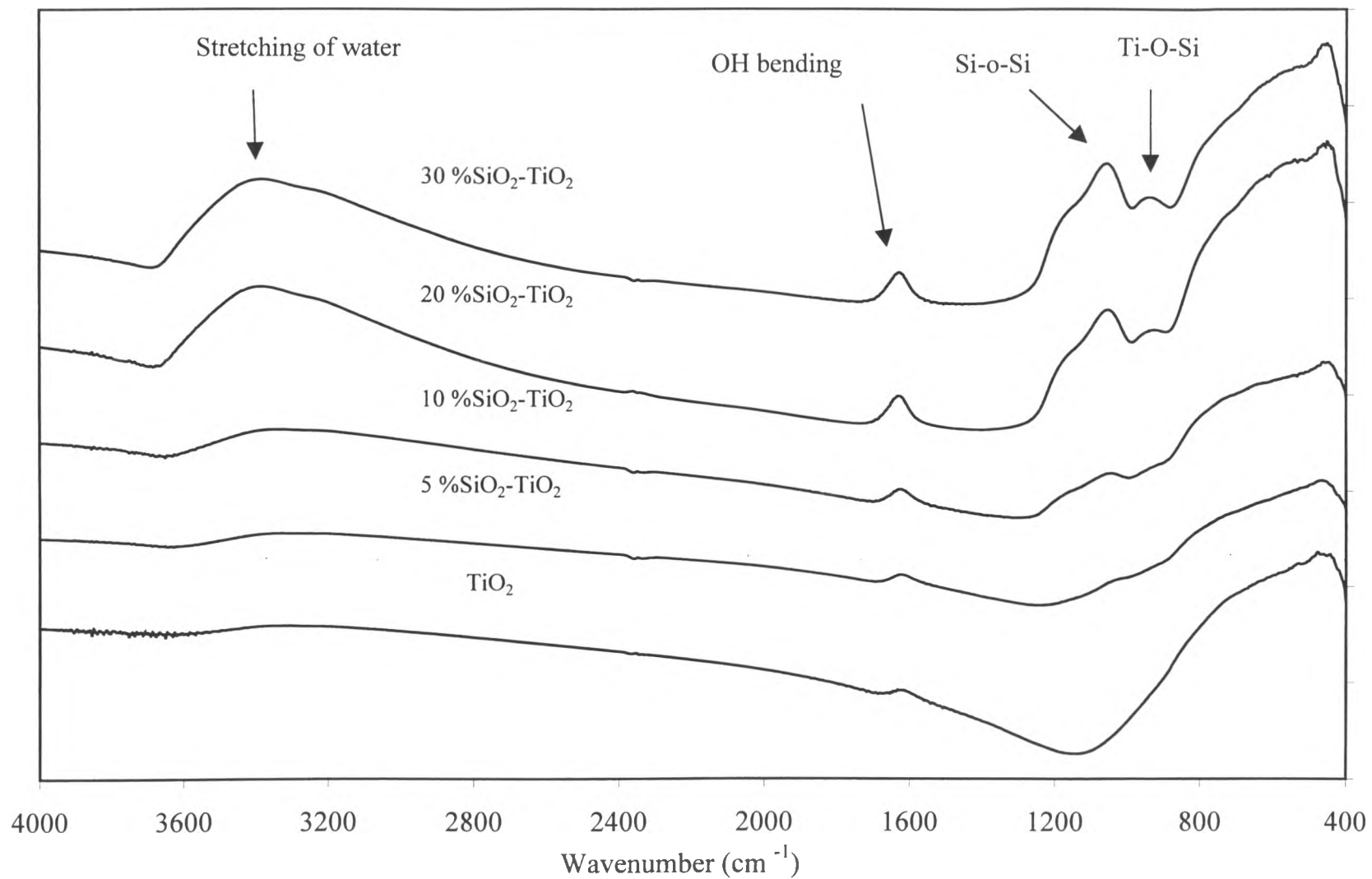
increasing the calcination temperature due to the deposition of Pt on TiO<sub>2</sub>-SiO<sub>2</sub>.

**Table 4.10** The surface areas, pore sizes and pore volumes of Pt/TiO<sub>2</sub>-SiO<sub>2</sub> at different calcination temperatures (1 mol% Pt and 10 mol% SiO<sub>2</sub>)

Calcination Temperature	BET Surface Area (m <sup>2</sup> /g)	Pore Size (nm)	Pore Volume (cm <sup>3</sup> /g)
400 ° C	233.3	53	0.311
500 ° C	209.8	58	0.305
600 ° C	180.3	65	0.293
700 ° C	161.2	69	0.277

#### 4.1.3 Chemical Bond of TiO<sub>2</sub>-SiO<sub>2</sub>

The chemical bonds of Ti and Si of the TiO<sub>2</sub>-SiO<sub>2</sub> catalysts calcined at different temperatures can be characterized from FT-IR spectra. It has been reported that the peak at wavenumber of 800 or 810 cm<sup>-1</sup> corresponds to the symmetric vibration of Si-O-Si, 1080-1105 cm<sup>-1</sup> for asymmetric Si-O-Si vibration and 940-960 cm<sup>-1</sup> for Ti-O-Si vibration (Jung and Park, 2000). The FT-IR spectra of TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub> calcined at 400 ° C are shown in Figure 4.9. When the silica content was over 20 %, the formation of Ti-O-Si was observed. It has been reported that the atomically mixed TiO<sub>2</sub>-SiO<sub>2</sub> oxides can only be obtained at low TiO<sub>2</sub> content, with the maximum TiO<sub>2</sub> less than 15 wt% or a Si/Ti atomic ratio higher than 7.5. At higher Ti content, TiO<sub>2</sub> crystallite tends to form a separate phase (Gao and Wachs, 1999). Therefore, Ti-O-Si bond of TiO<sub>2</sub>-SiO<sub>2</sub> may not always be observed in the FT-IR spectra, especially for a very low amount of silica. From the XRD and FT-IR results, the amorphous silica does not mix atomically with TiO<sub>2</sub> but some fractions of Ti-O-Si were observed over the 20 mol% SiO<sub>2</sub> (Jung and Park, 2000).



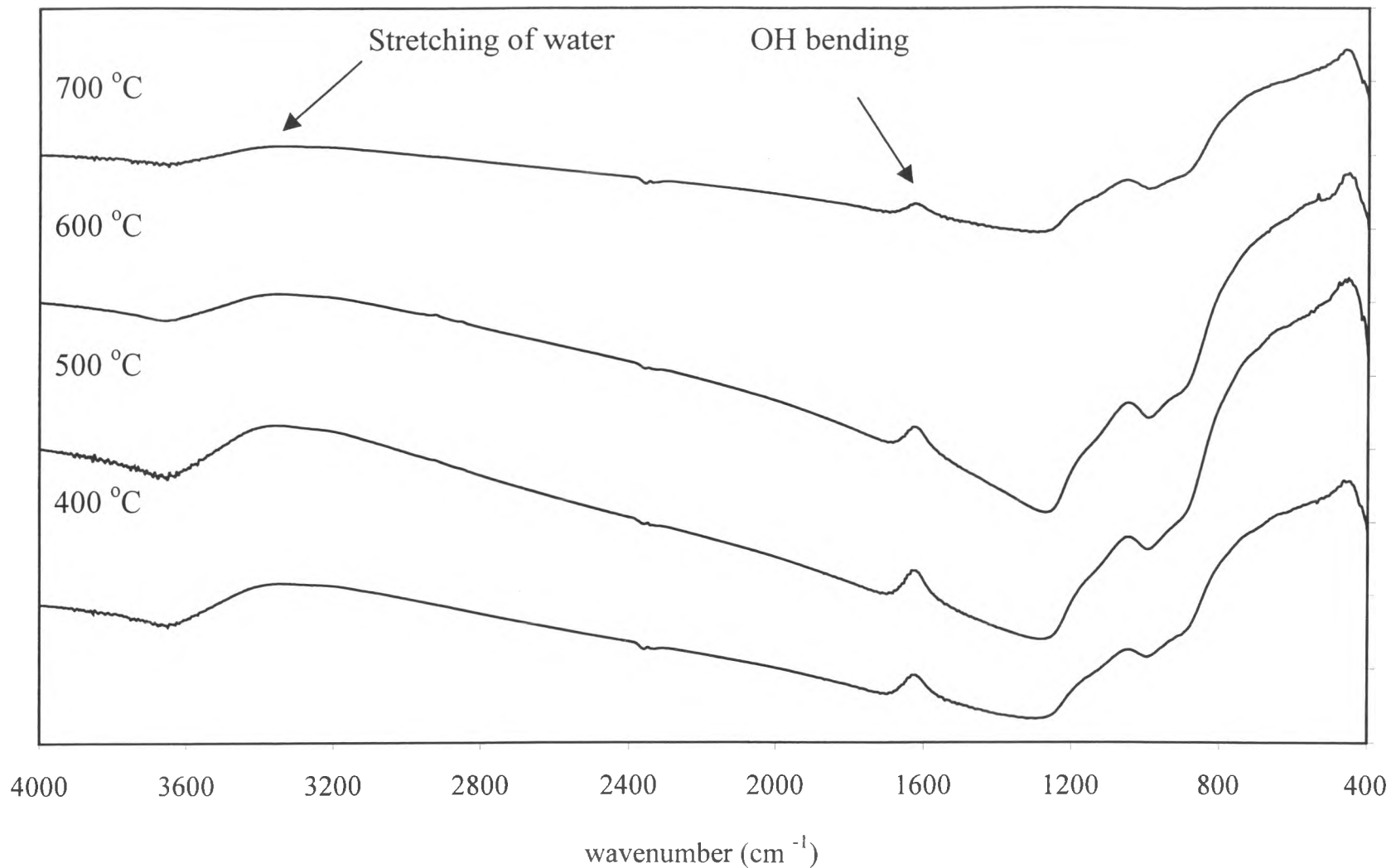
**Figure 4.9** FT-IR spectra of TiO<sub>2</sub> and TiO<sub>2</sub>-SiO<sub>2</sub> having different SiO<sub>2</sub> content at the calcination temperature of 400 °C

Figure 4.10 shows the FT-IR spectra of 10% SiO<sub>2</sub>-TiO<sub>2</sub> at the calcination temperatures of 400-700 ° C. The peaks at the wavenumbers of 1628 and 3431 cm<sup>-1</sup> are the OH bending and stretching of water, respectively. It was found that both the OH bending and stretching of water decreased with increasing the calcination temperature. The OH group and adsorbed water on the catalyst surface involve the formation of the reactive hydroxyl radical, OH<sup>•</sup>, that is important in the photocatalytic oxidation process. The less OH group and adsorbed water on the catalyst surface decrease the OH<sup>•</sup> formation and may result in a decrease in the activity of catalyst.

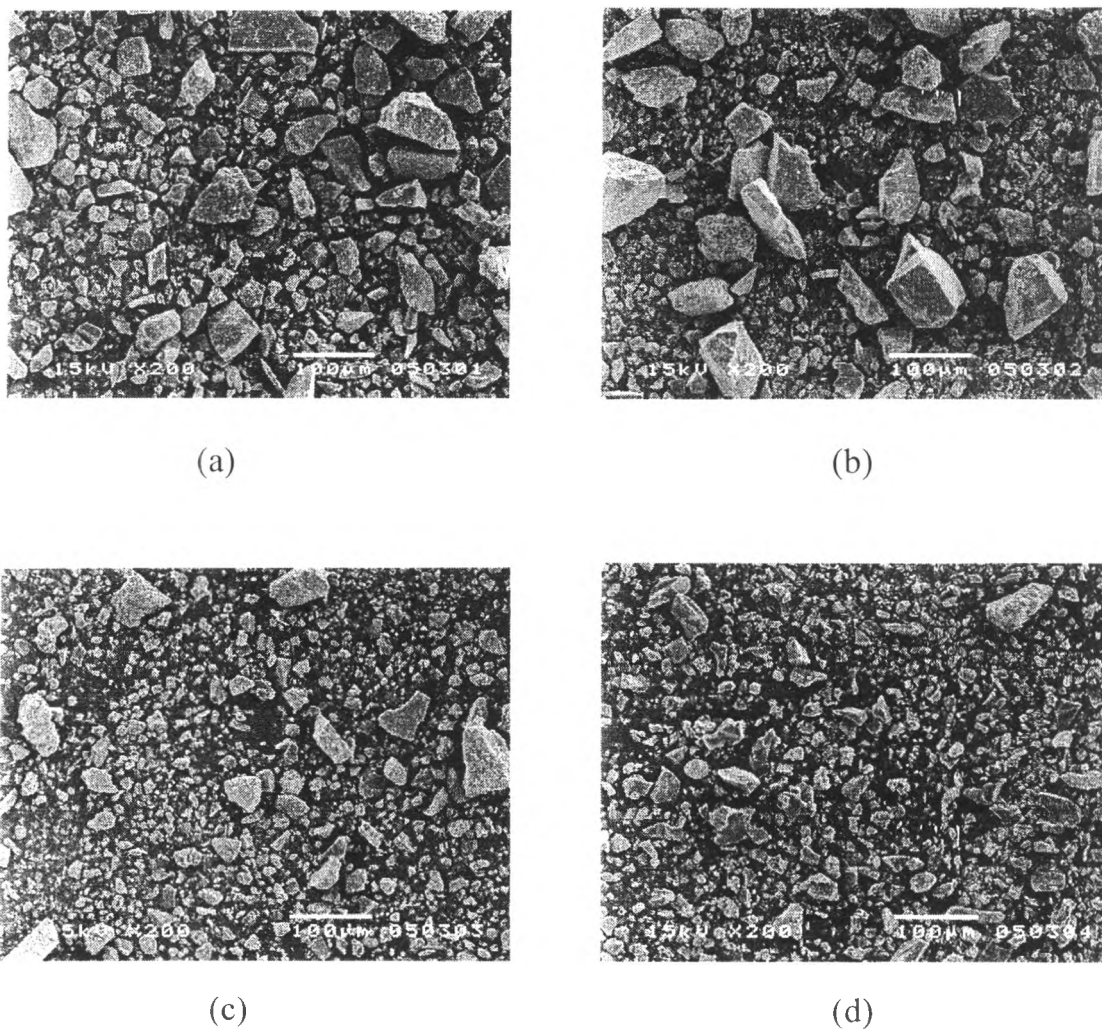
#### 4.1.4 Morphology of Studied Photocatalysts

The particle sizes and the surface characteristics of the catalysts prepared were studied by using a scanning electron microscope or SEM. Figures 4.11 shows the SEM photographs of TiO<sub>2</sub>, 1%Pt/TiO<sub>2</sub>, 10%SiO<sub>2</sub>-TiO<sub>2</sub> and 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub>. As seen from the figure, the particle sizes of 10%SiO<sub>2</sub>-TiO<sub>2</sub> and 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> were relatively smaller than those of TiO<sub>2</sub> and 1%Pt/TiO<sub>2</sub>. It was shown that the presence of Pt did not significantly change the particle sizes of both TiO<sub>2</sub> and 10%SiO<sub>2</sub>-TiO<sub>2</sub>. Interestingly, an addition of SiO<sub>2</sub> to TiO<sub>2</sub> resulted in a significantly reduction in the size of the clusters.

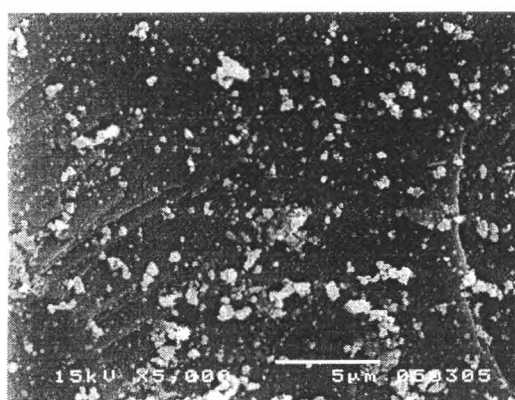
Figure 4.12 shows more closely the surfaces of TiO<sub>2</sub>, 1%Pt/TiO<sub>2</sub>, 10%SiO<sub>2</sub>-TiO<sub>2</sub> and Pt/TiO<sub>2</sub>-SiO<sub>2</sub>, respectively. Compared to TiO<sub>2</sub> surface, the deposition of Pt on TiO<sub>2</sub> is clearly seen from Figure 4.12 (b). It can also be observed from Figures 4.12 (a) and 4.12 (c) that the presence of silica makes the catalyst surface become more porous, consequently increases the surface area. The observation is consistent with the results shown in Table 4.7 that there is an increase of the surface area when silica was added. Figure 4.12 (d) indicates that the agglomeration of catalyst is observed when 1 %Pt was loaded on 10%SiO<sub>2</sub>-TiO<sub>2</sub>.



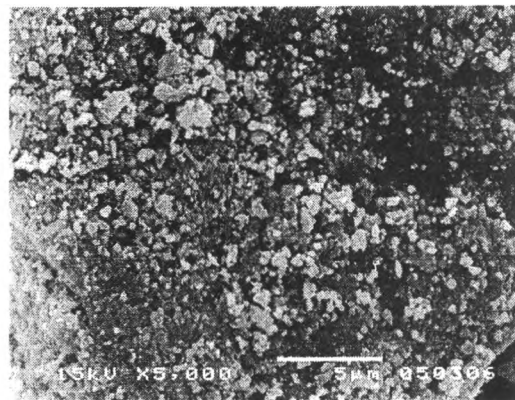
**Figure 4.10** FT-IR spectra of 10 %SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures



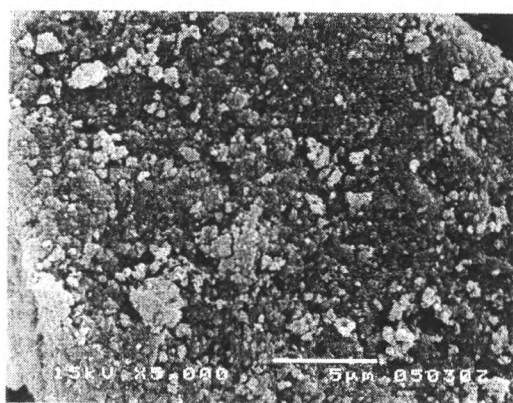
**Figure 4.11** SEM photographs of studied catalyst (a)  $\text{TiO}_2$ , (b) 1%Pt/ $\text{TiO}_2$ , (c) 10% $\text{SiO}_2$ - $\text{TiO}_2$  and (d) 1%Pt/10% $\text{SiO}_2$ - $\text{TiO}_2$



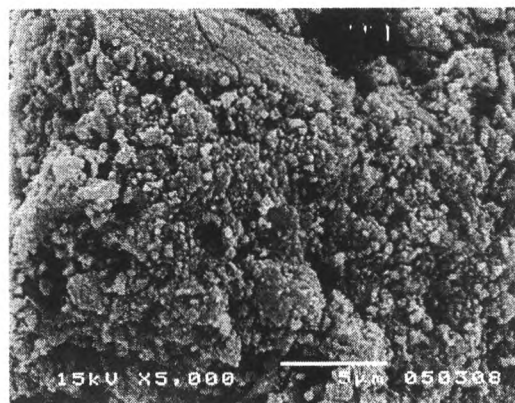
(a)



(b)



(c)



(d)

**Figure 4.12** SEM photographs of the catalysts surfaces (a)  $\text{TiO}_2$ , (b)  $1\% \text{Pt}/\text{TiO}_2$ , (c)  $10\% \text{SiO}_2\text{-TiO}_2$  and (d)  $1\% \text{Pt}/10\% \text{SiO}_2\text{-TiO}_2$

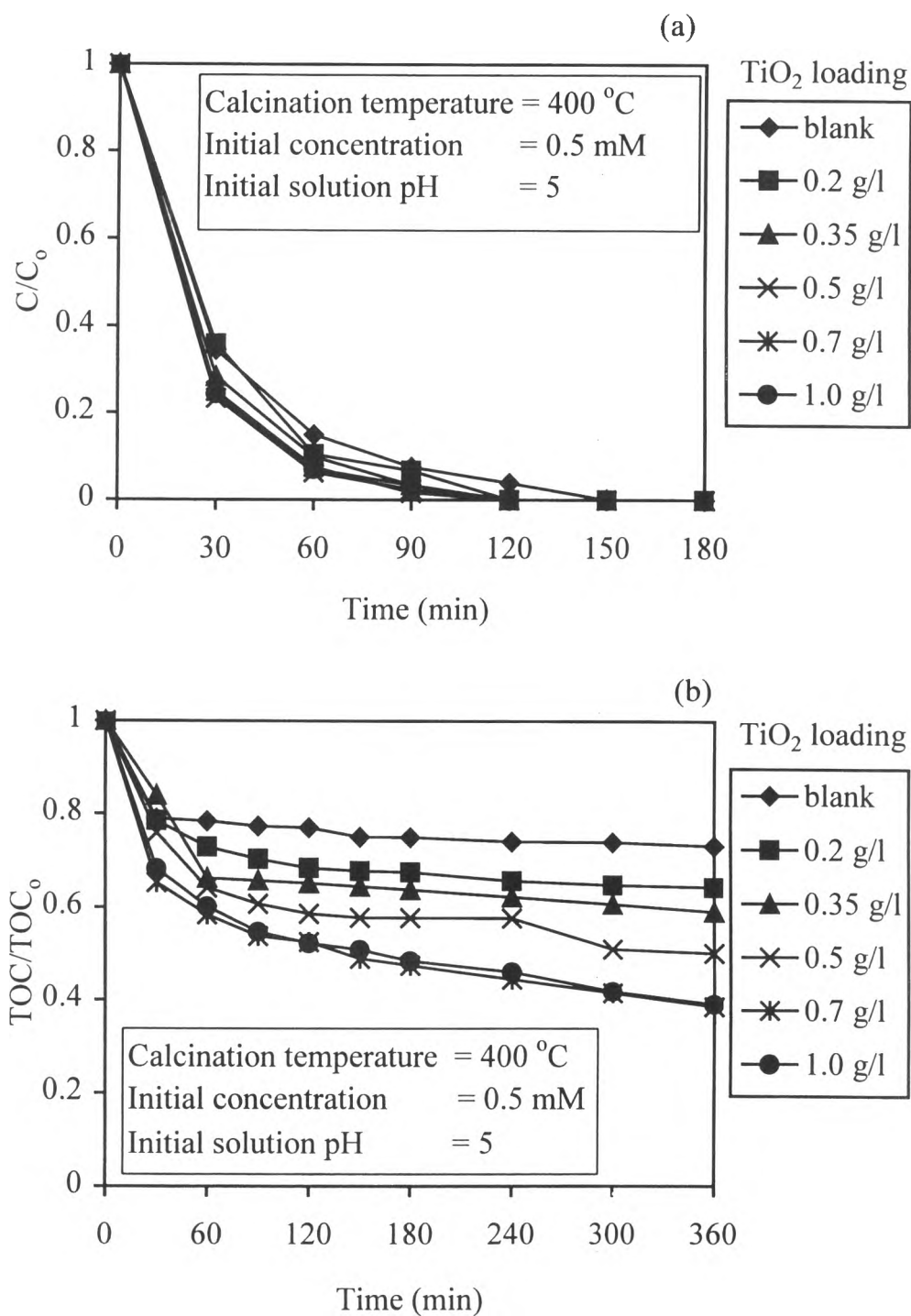
## 4.2 Photocatalytic Degradation of 4-chlorophenol with TiO<sub>2</sub>

In this experimental part, TOC was also used to represent the 4-chlorophenol concentration.  $C/C_0$  is represented the remaining fraction of 4-chlorophenol concentration at any time with respect to its initial concentration.  $TOC/TOC_0$  is the remaining fraction of TOC in the solution at any time with respect to its initial TOC in the solution.

In this study, the effect of catalyst amount, calcination temperature and initial pH of 4-chlorophenol solution were investigated by using pure TiO<sub>2</sub> as a catalyst. The comparison of the photocatalytic activity between commercial TiO<sub>2</sub> (Degussa P25) and sol-gel TiO<sub>2</sub> prepared at calcination temperature of 400 °C was also studied. The reaction temperature was controlled constant at 25 °C for all experiments. The solution with an initial 4-chlorophenol concentration of 0.5 mM was firstly irradiated without TiO<sub>2</sub>. As shown in Figure 4.13 (a), 4-chlorophenol concentration decreases and disappears within 150 minutes but the TOC decreases only 26.8 % after the irradiation for 360 minutes as shown in Figure 4.13 (b). It could be explained that the UV lamp with the short wavelength destroys the chemical bond of the 4-chlorophenol molecule and transforms into other intermediates products rather than CO<sub>2</sub>. However, an addition of small amount of TiO<sub>2</sub> (0.2 g/l) resulted in decreasing of TOC to 35.6 % from the initial TOC after the irradiation for 360 minutes. Therefore, the presence of TiO<sub>2</sub> photocatalyst is necessary for both 4-chlorophenol and TOC decreases.

### 4.2.1 Effect of TiO<sub>2</sub> Loading on 4-chlorophenol Degradation

In this experiment, the amount of TiO<sub>2</sub> catalyst was varied from 0.2-1.0 g/l with a constant initial 4-chlorophenol concentration of 0.5 mM. The degradation of 4-chlorophenol and TOC for different amounts of the catalyst are shown in Figure 4.13 (a) and Figure 4.13 (b), respectively.



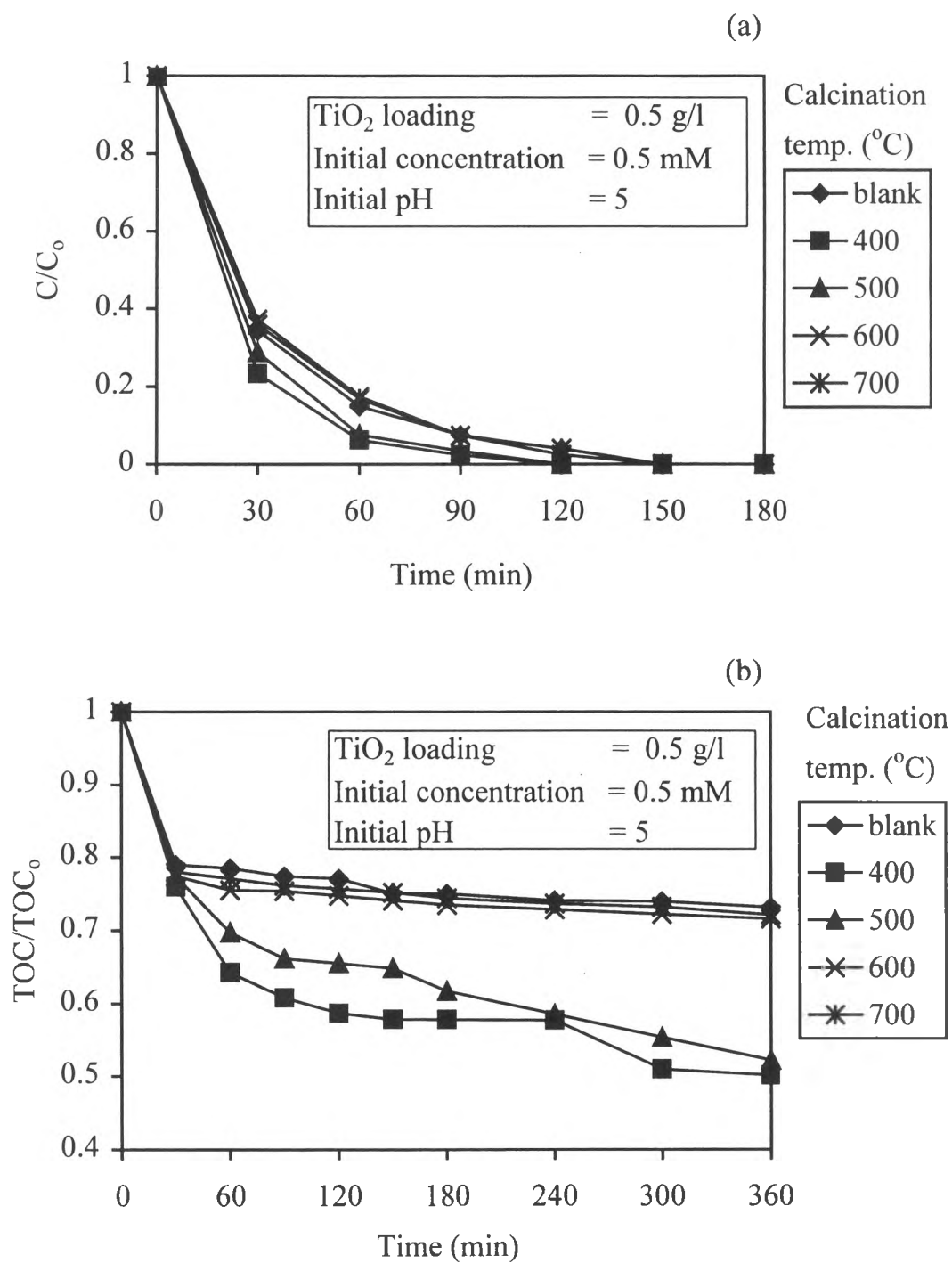
**Figure 4.13** Photocatalytic degradation of 4-chlorophenol as a function of reaction time at different TiO<sub>2</sub> loadings (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction



Compared to the blank experiment result, the amounts of the catalyst had little effect on the 4-chlorophenol degradation rate especially at the first 30 minutes. On the contrary, it can be seen that the amount of the catalyst plays a significant role in the TOC reduction and the optimum amount of  $\text{TiO}_2$  for the maximum TOC reduction was 0.7 g/l. The increases in both rates at the higher catalyst loadings can be explained in terms of light transmission. At the lower catalyst loadings, much of the light is transmitted and the transmitted light is not utilized in the photocatalytic reaction (Stafford *et al.*, 1997). When the catalyst loading increases, more photons are adsorbed by the catalyst and involved in the reaction. The other reason is that 4-chlorophenol and other intermediates could be adsorbed in a larger amount at the higher catalyst loadings.

#### 4.2.2 Effect of Calcination Temperature on 4-chlorophenol Degradation

In this study, the calcination temperature was varied from 400-700 °C. The 4-chlorophenol concentration of 0.5 mM and a catalyst loading of 0.5 g/l were used. Figure 4.14 shows the effect of the calcination temperature of  $\text{TiO}_2$  catalyst on the degradation of 4-chlorophenol. Both rates decreased with an increase in the calcination temperature. This may be described by the phase transformation of  $\text{TiO}_2$  from anatase to rutile and the lower surface area and pore volume at the higher calcination temperatures as shown in Figure 4.2 and Table 4.5, respectively. The lower surface area and pore volume of  $\text{TiO}_2$  calcined at higher temperature leads to a lower amount of 4-chlorophenol molecules adsorbed on the catalyst surface. Hence, low reaction rates were observed.



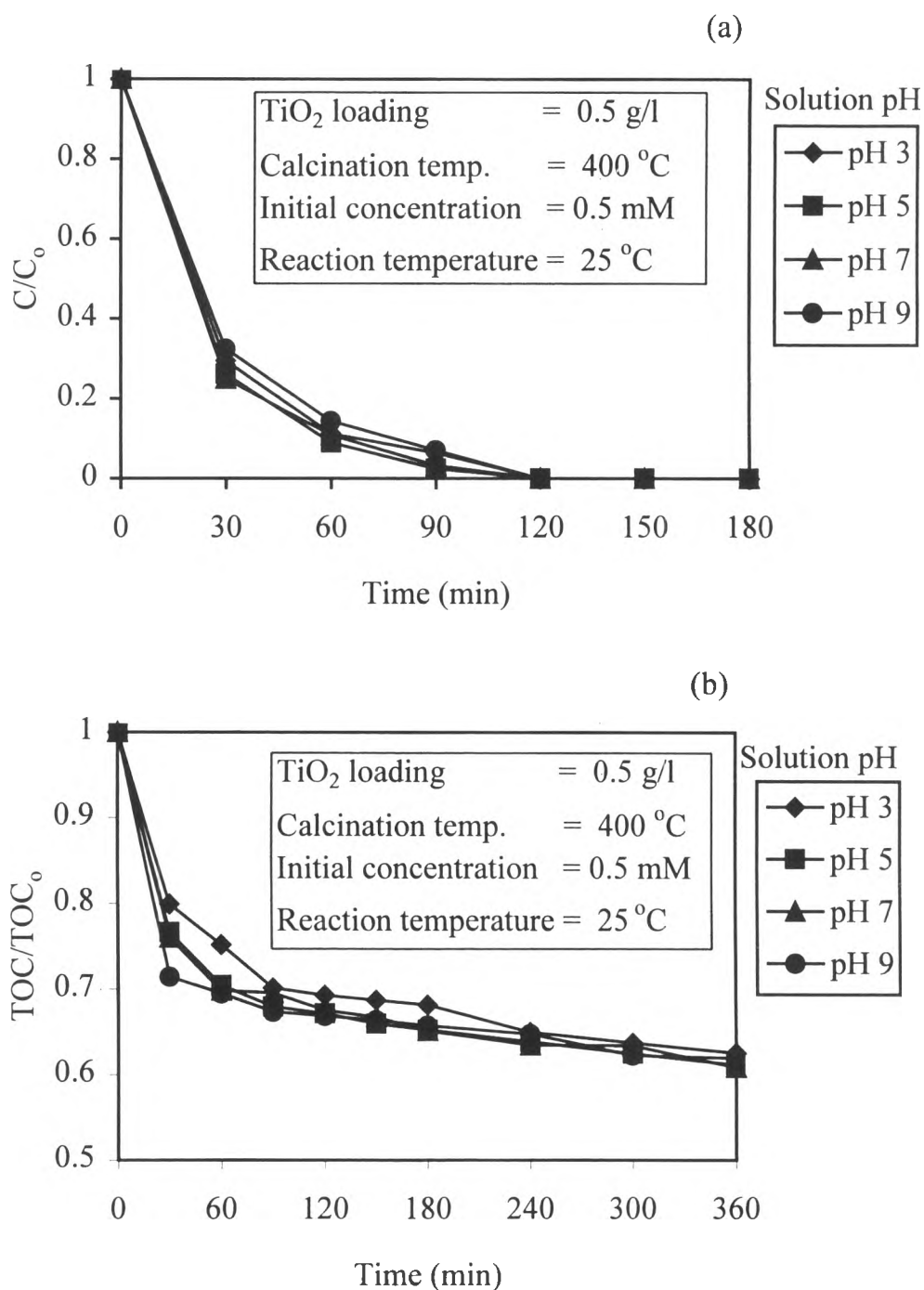
**Figure 4.14** Photocatalytic degradation of 4-chlorophenol as a function of reaction time at different calcination temperature of TiO<sub>2</sub> catalyst (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction

#### 4.2.3 Effect of Initial Solution pH on 4-chlorophenol Degradation

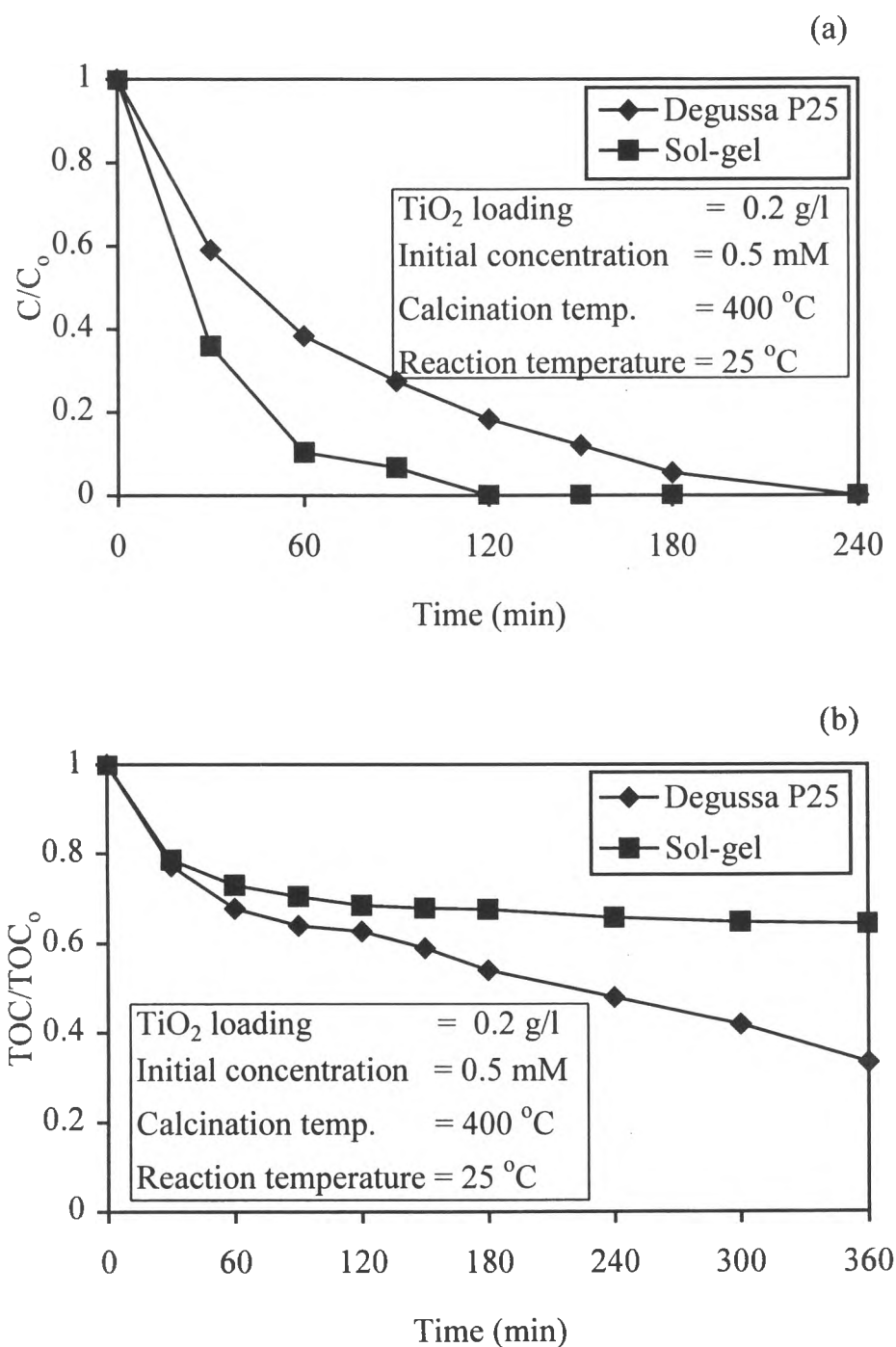
To determine the effect of the initial solution pH, the initial pH of 4-chlorophenol solution was varied from 3-9. The catalyst amount of 0.5 g/l and 4-chlorophenol concentration of 0.5 mM were used. The degradation rates of 4-chlorophenol are shown in Figure 4.15. It was found that the initial pH of 4-chlorophenol solution did not have a significantly effect on both the degradation and TOC decreasing rates.

#### 4.2.4 Comparision between Degussa P25 and Sol-Gel TiO<sub>2</sub> for 4-chlorophenol Degradation

To compare the activities of the two catalysts, 0.2 g/l of either catalyst and 0.5 mM 4-chlorophenol were used. Figure 4.16 (a) shows comparatively the degradation rates of 4-chlorophenol using Degussa P25 and sol-gel TiO<sub>2</sub> calcined at 400 °C. With the sol-gel TiO<sub>2</sub>, the degradation rate was much faster than that with Degussa P25. On the contrary, the TOC degradation rate with Degussa P25 is much higher than that with the sol-gel TiO<sub>2</sub> as shown in Figure 4.16 (b). That may be attributed to the differences in physical properties of the two catalysts as described in Tables 4.1 and 4.5. A higher surface area of the sol-gel TiO<sub>2</sub> results in the larger amount of 4-chlorophenol adsorbed on the catalyst surface. Therefore, the degradation rate is faster with the sol-gel TiO<sub>2</sub>. Degussa P25 gave a higher degradation rate of TOC than sol-gel TiO<sub>2</sub> because the pore size and crystallite size of Degussa P25 were larger than those of the sol-gel TiO<sub>2</sub>. The larger pore size facilitates the mass transfer of the intermediates formed from the initial reactions and the higher crystallite size reduces the e<sup>-</sup>/h<sup>+</sup> recombination. When the recombination decreases, there are more electrons and holes diffuse to the catalyst surface and react with the substrate molecules adsorbed on the surface at the faster rate.



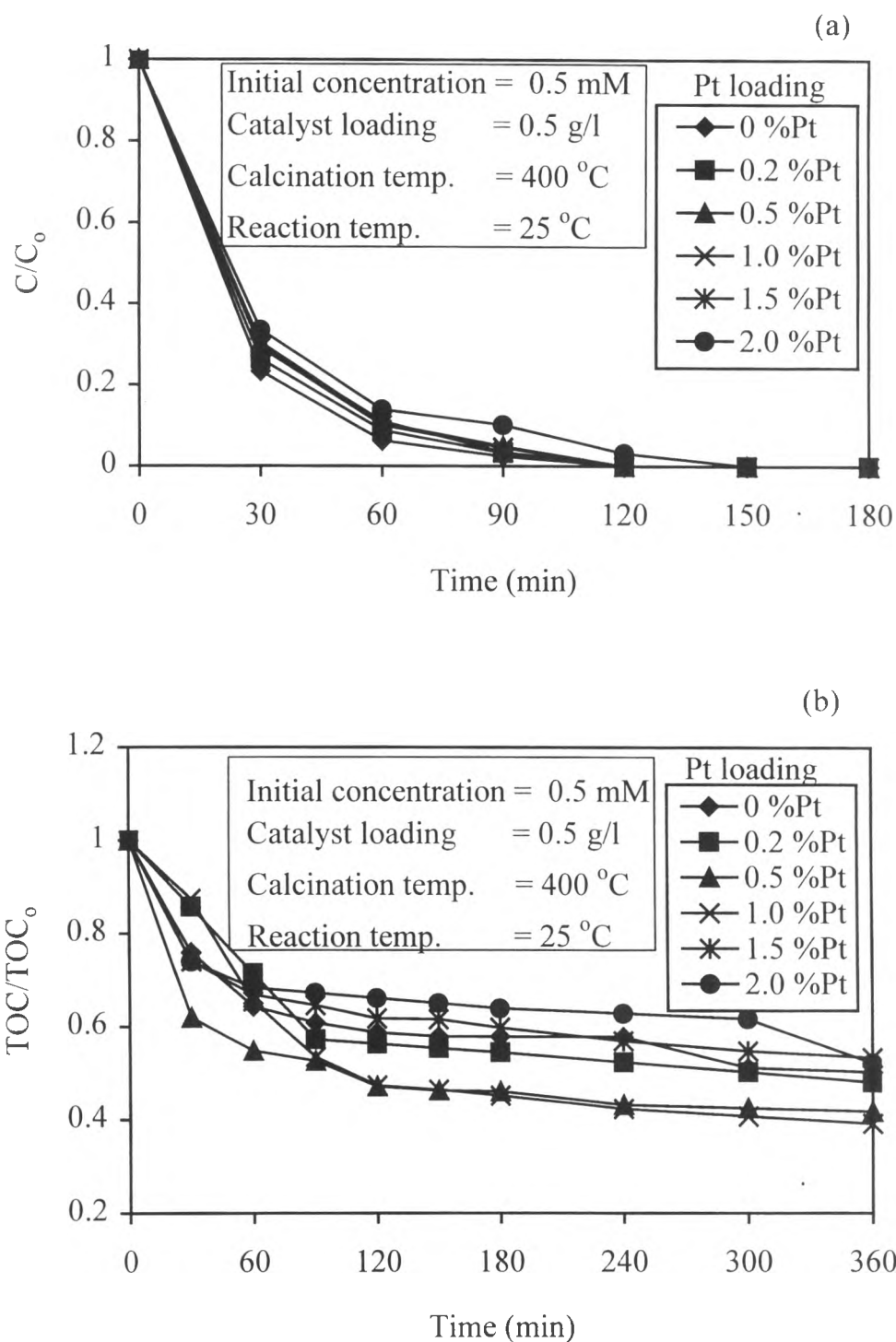
**Figure 4.15** Photocatalytic degradation of 4-chlorophenol as a function of reaction time at different solution pH (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction



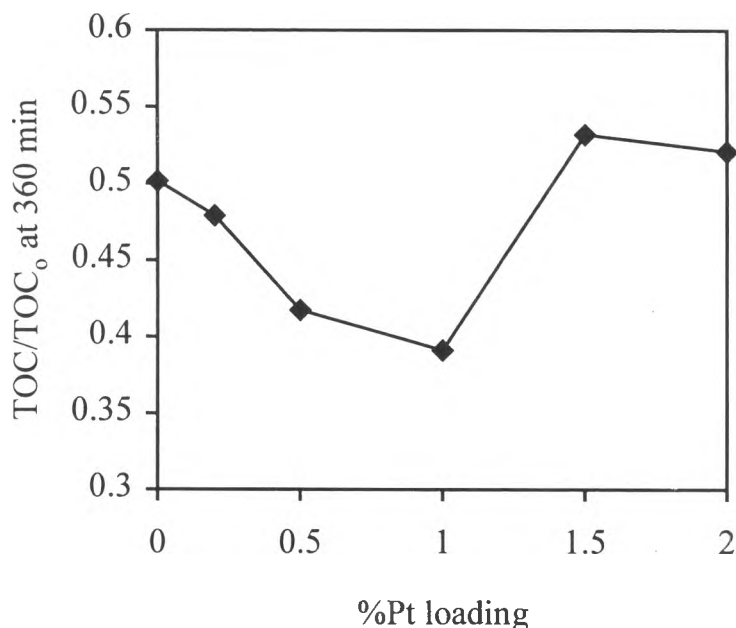
**Figure 4.16** Comparison of commercial  $\text{TiO}_2$  and sol-gel  $\text{TiO}_2$  prepared for photocatalytic degradation of 4-chlorophenol (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction

### 4.3 Photocatalytic Degradation of 4-chlorophenol with Pt/TiO<sub>2</sub>

Since TiO<sub>2</sub> calcined at 400 °C had highest activity of photocatalytic degradation of 4-chlorophenol, the TiO<sub>2</sub> catalyst prepared at 400 °C was selected for the study to determine the effect of Pt loading on TiO<sub>2</sub> by preparing Pt loadings from 0.2-2.0 mol%. 0.5 mM 4-chlorophenol and 0.5 g/l catalyst were used. The degradation rates of 4-chlorophenol at different Pt loadings are shown in Figure 4.17. The amount of Pt did not significantly affect the degradation of 4-chlorophenol but had the effect on the remaining TOC fraction. The value of TOC/TOC<sub>0</sub> at 360 minutes and the loadings are plotted to compare the effect of Pt loadings on the TOC reduction rates as shown in Figure 4.18. It was found that an increase in the Pt loading decreased the value of TOC/TOC<sub>0</sub> at 360 minutes and reached a minimum value of TOC/TOC<sub>0</sub> for 1.0 % Pt/TiO<sub>2</sub>. For the amount of Pt greater than 1 mol %, the value of TOC/TOC<sub>0</sub> increased with increasing Pt loading. The less TOC/TOC<sub>0</sub> indicates that more organic compounds react and convert into CO<sub>2</sub>. Therefore, in this study, a small amount of Pt added could improve the photocatalytic activity of TiO<sub>2</sub> and the optimum amount of Pt loading was 1 mol %. It was explained that a small amount of Pt on TiO<sub>2</sub> is attributed to the acceleration of superoxide radical anion, O<sub>2</sub><sup>•-</sup>, formation and consequently decreasing the recombination process and enhance the photocatalytic activity. But when the amount of Pt increases to a certain level, the photoelectron will transfer from the semiconductor to metal particles as well as the decrease of O<sub>2</sub><sup>•-</sup> resulting in the increase of recombination and lower the photocatalytic activity (Blazkova *et. al.*, 1998).



**Figure 4.17** Photocatalytic degradation of 4-chlorophenol by Pt/TiO<sub>2</sub> having different Pt loadings (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction

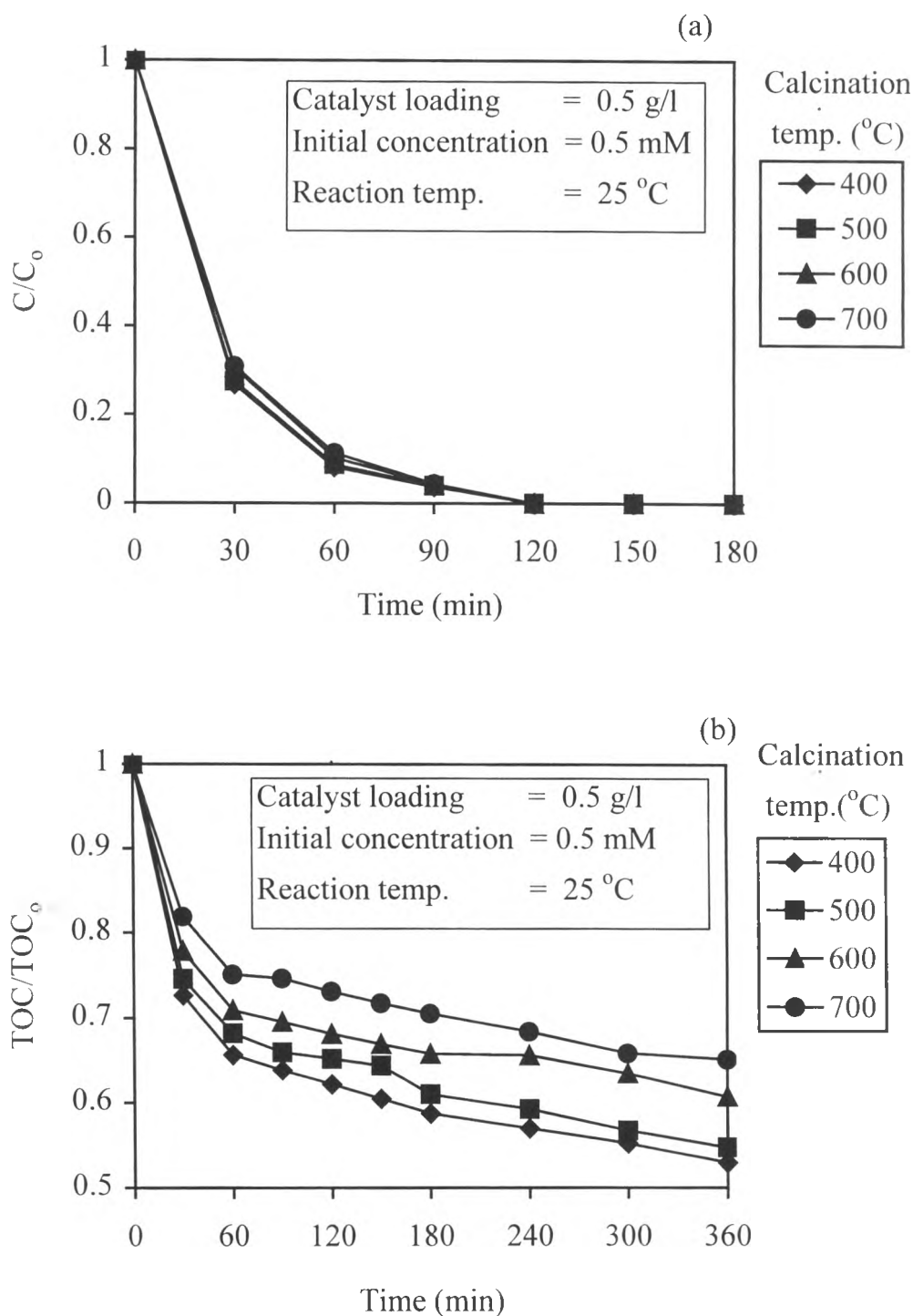


**Figure 4.18** TOC/TOC<sub>0</sub> at 360 min for different %Pt loadings on TiO<sub>2</sub>

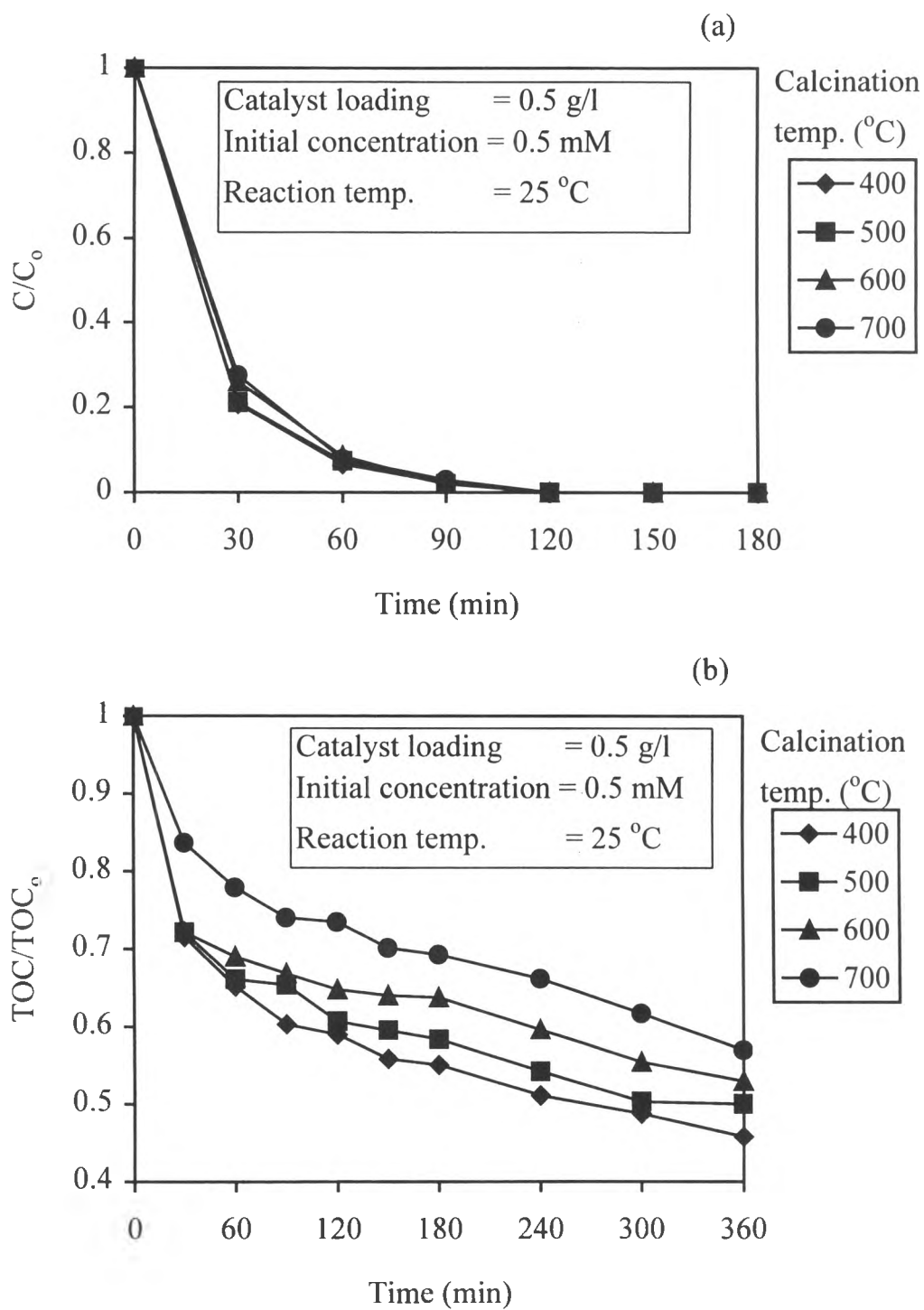
#### 4.4 Photocatalytic Degradation of 4-chlorophenol with TiO<sub>2</sub>-SiO<sub>2</sub>

In this experiment, TiO<sub>2</sub>-SiO<sub>2</sub> with 5, 10, 20 and 30 mol% SiO<sub>2</sub> were prepared and calcined between 400-700 °C. The activities of TiO<sub>2</sub>-SiO<sub>2</sub> catalysts with different %SiO<sub>2</sub> and different calcination temperature were compared with pure TiO<sub>2</sub> for 4-chlorophenol degradation. The 0.5 mM of 4-chlorophenol and 0.5 g/l of catalyst were used. Figures 4.19-4.22 show the degradation of 4-chlorophenol using TiO<sub>2</sub>-SiO<sub>2</sub> catalysts having different SiO<sub>2</sub> contents. From Figures 4.19 (a)-4.22 (a), the degradation rates of 4-chlorophenol do not depend on both the amount of SiO<sub>2</sub> and the calcination temperature. On the other hand, the remaining TOC fraction was significantly affected by both parameters as shown in Figures 4.19 (b)-4.22 (b). The values of TOC/TOC<sub>0</sub> at 360 minutes are plotted with the % Si and the calcination temperatures as shown in Figure 4.23. As can be seen from Figure 4.23, the maximum TOC reduction is achieved at 10%SiO<sub>2</sub>-TiO<sub>2</sub> catalyst calcined at 400 °C.

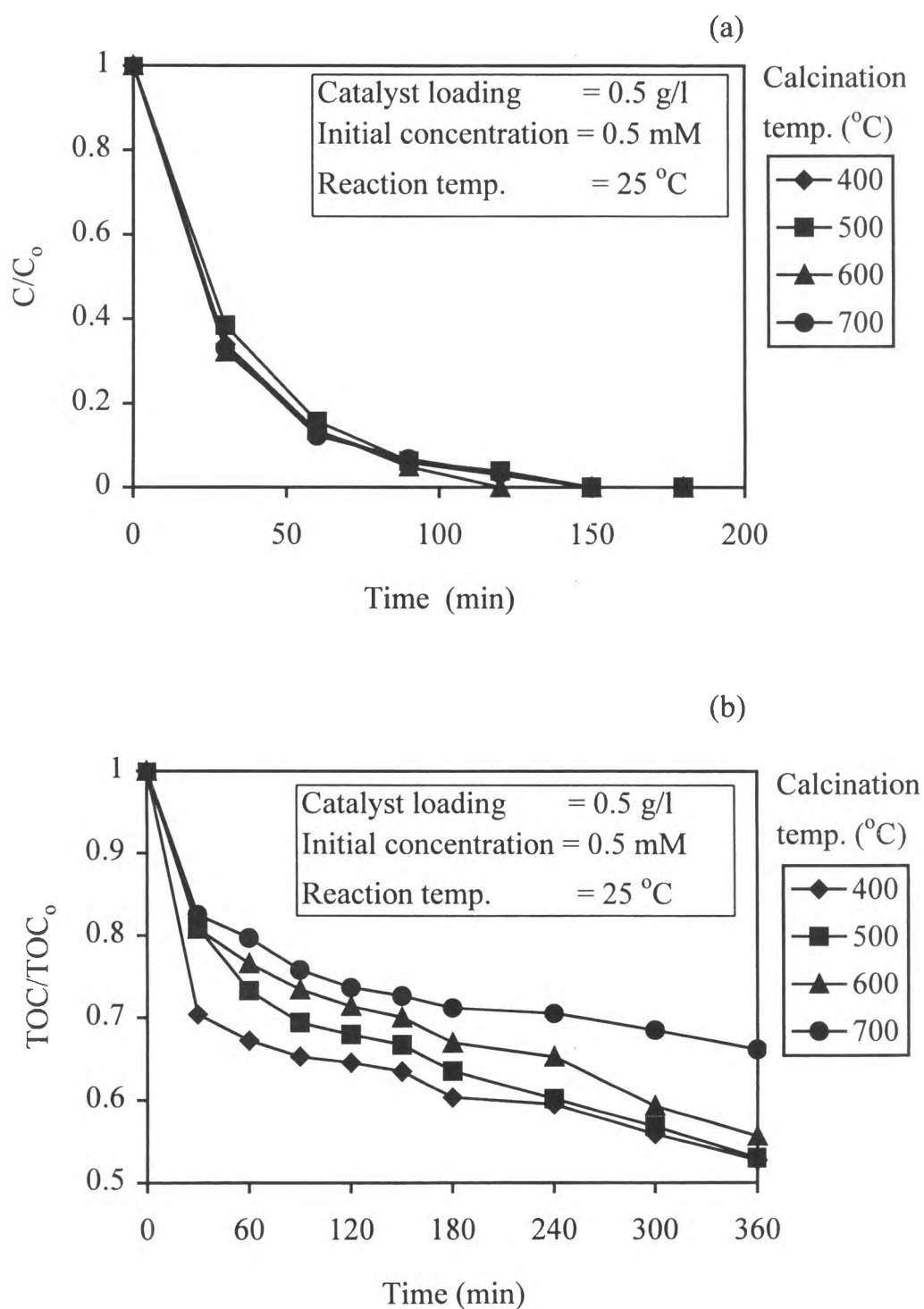




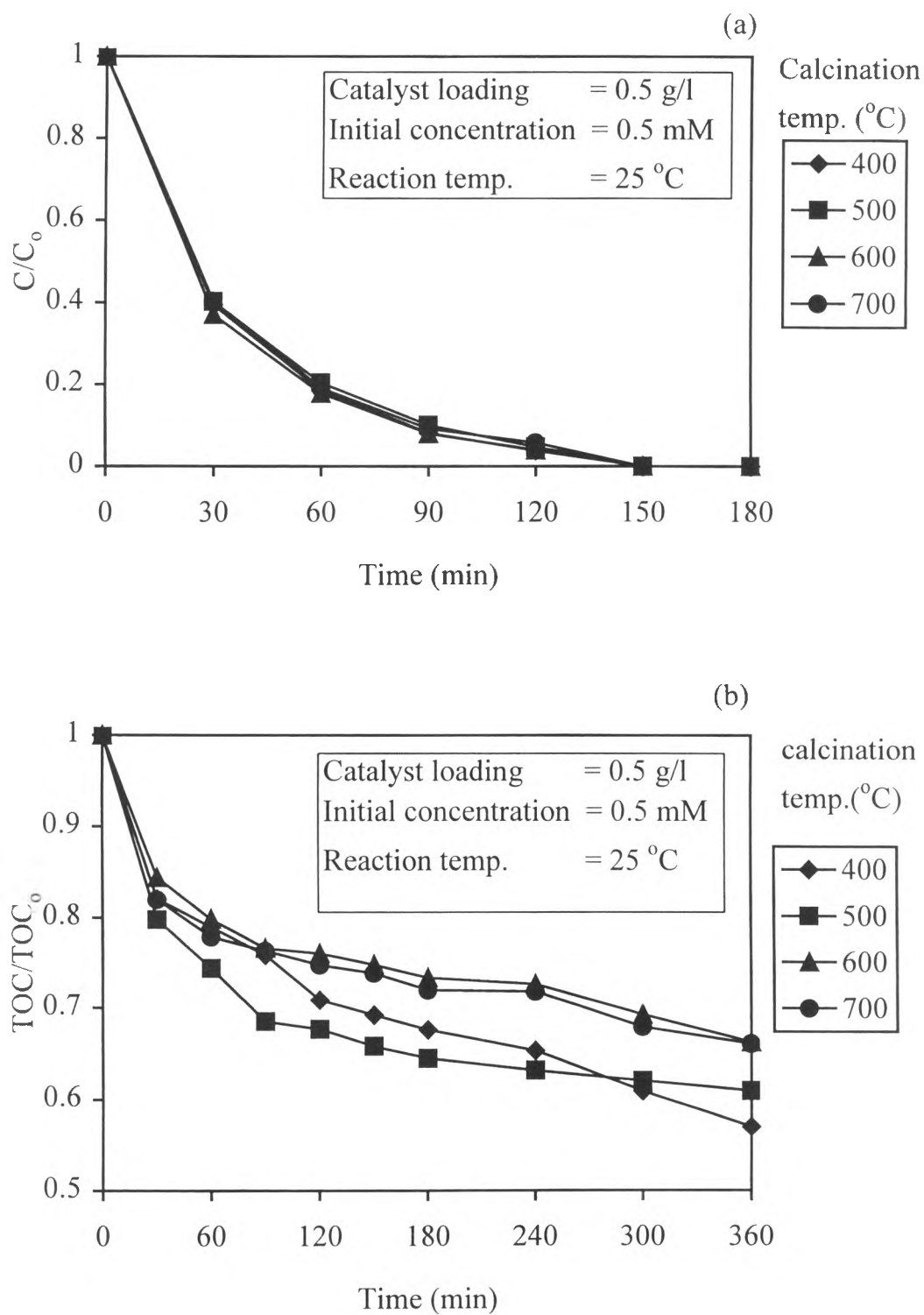
**Figure 4.19** Photocatalytic degradation of 4-chlorophenol by 5%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction



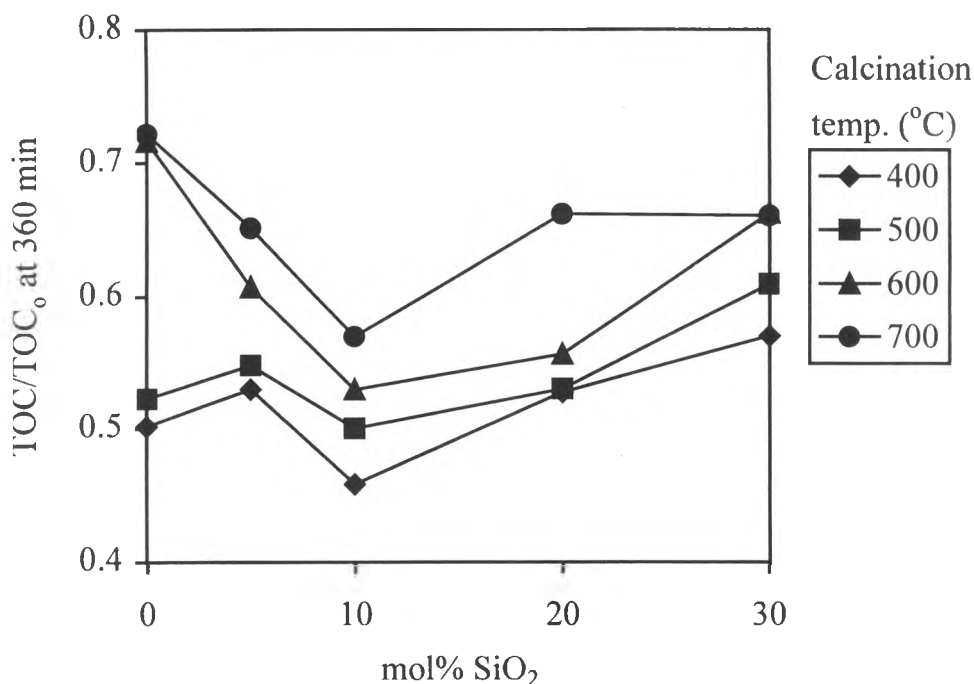
**Figure 4.20** Photocatalytic degradation of 4-chlorophenol by 10%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction



**Figure 4.21** Photocatalytic degradation of 4-chlorophenol by 20%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction



**Figure 4.22** Photocatalytic degradation of 4-chlorophenol by 30%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction

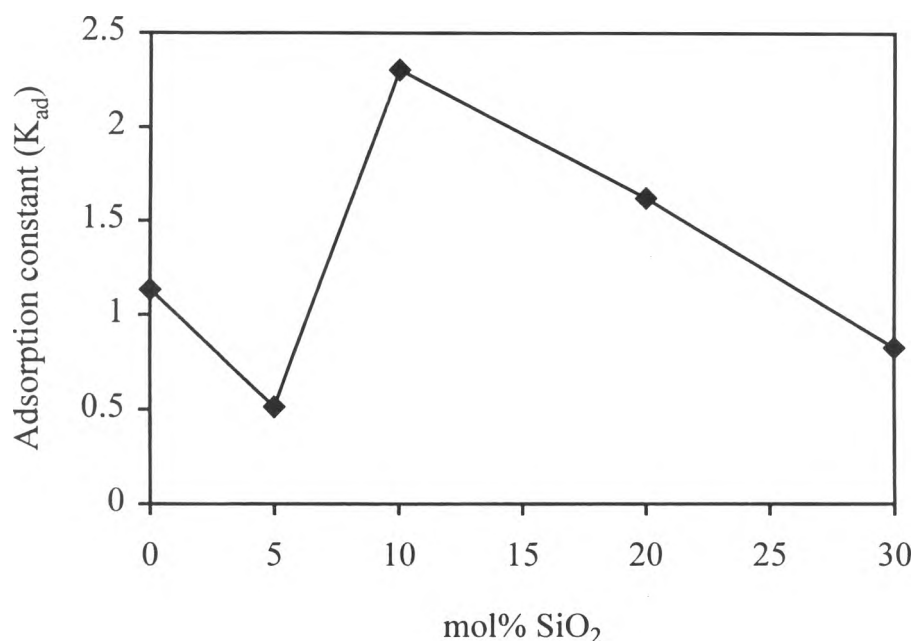


**Figure 4.23** TOC/TOC<sub>0</sub> at 360 minutes by TiO<sub>2</sub>-SiO<sub>2</sub> catalysts having different mol% SiO<sub>2</sub> and calcined at different temperatures

Jung and Park (2000) reported that the photocatalytic activity of TiO<sub>2</sub>-SiO<sub>2</sub> increased with increasing the silica content and reached the highest activity at 30 mol% Si. It was suggested the highest pore size and pore volume at 30 mol% Si facilitated the mass transfer of the reactants. The photocatalytic activity of 30 %SiO<sub>2</sub>-TiO<sub>2</sub> increased with increasing the calcination temperature because of the increase in crystallinity of the catalyst. The result obtained from this study was not consistent with Jung and Park's results. Although the surface area increases with increasing the amount of Si and the highest pore volume and pore size were obtained at 20%SiO<sub>2</sub>-TiO<sub>2</sub> as shown in Tables 4.7-4.9, but 10%SiO<sub>2</sub>-TiO<sub>2</sub> had the highest activity and higher than pure TiO<sub>2</sub>. The activity of TiO<sub>2</sub>-SiO<sub>2</sub> decreased with increasing the calcination temperature.

Gao and Wachs (1999) reported that the adsorption of ammonia appeared to have a decreasing trend with increasing the Si content. Since the adsorption is the first step before the reaction, the higher adsorption capacity

can lead to a higher rate of reaction. Therefore, the adsorption of 4-chlorophenol on  $\text{TiO}_2$  and  $\text{TiO}_2\text{-SiO}_2$  calcined at temperature of  $400\text{ }^\circ\text{C}$  were performed to determine the adsorption behavior of each catalysts. The relationship between the adsorption constant ( $K_{\text{ad}}$ ) and mol% Si is shown in Figure 4.24. The calculation of the adsorption constants is presented in the Appendix B. From Figure 4.24, it is found that 10% $\text{SiO}_2\text{-TiO}_2$  has the highest adsorption constant. The higher adsorption constant means that more organic molecules are adsorbed and reacted on the catalyst surface. Hence, the highest activity of 10% $\text{SiO}_2\text{-TiO}_2$  can be explained by its highest adsorption capacity. This explanation is consistent with Torimoto *et al.* (1996) who observed that the highest rate of  $\text{CO}_2$  production resulted from the catalyst with the highest adsorption constant.

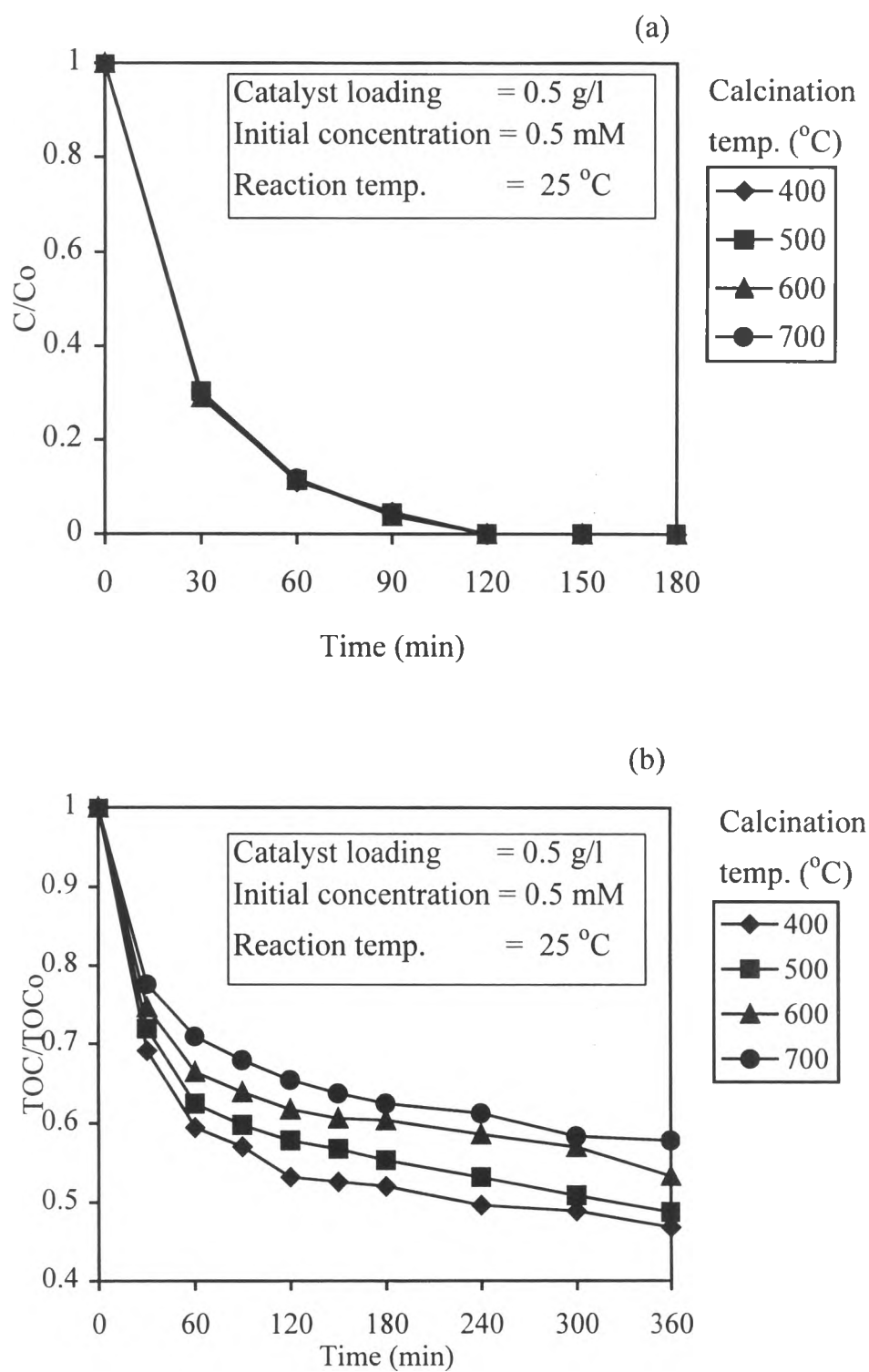


**Figure 4.24** The relationship between mol%  $\text{SiO}_2$  and adsorption constant

A decrease in the activity of 10%SiO<sub>2</sub>-TiO<sub>2</sub> with increasing the calcination temperature can be described by the FT-IR spectra as shown in Figure 4.10. The OH bending and the stretching of water decreases with increasing the calcination temperature. The adsorbed water and OH groups on the catalyst surface are important for the formation of reactive hydroxyl radical (OH<sup>•</sup>) as shown in Equations (2.5) and (2.6). The hydroxyl radical plays a significant role of the photocatalytic oxidation reaction. Therefore, a decrease in adsorbed water and OH group at a higher calcination temperature leads to the decrease in the activity of the catalyst. The other reason is that the lower surface area and pore volume at the higher calcination temperature causes the lower amount of 4-chlorophenol adsorbed on the catalyst surface resulting in decreasing the reaction rate.

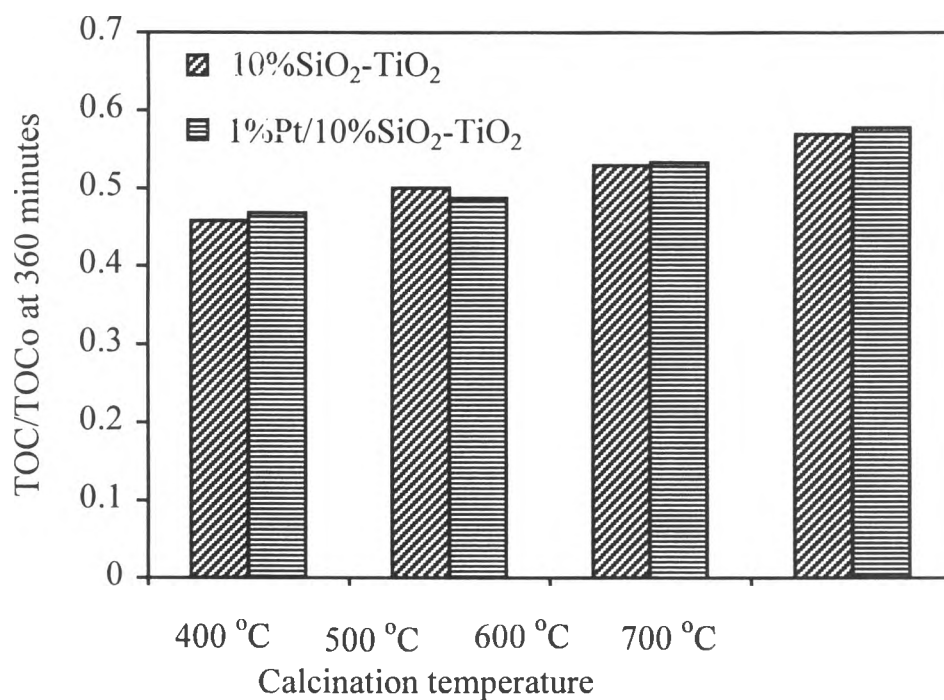
#### 4.5 Photocatalytic Degradation of 4-chlorophenol with Pt/TiO<sub>2</sub>-SiO<sub>2</sub>

In this study, Pt/TiO<sub>2</sub>-SiO<sub>2</sub> with 1 mol%Pt and 10 mol%SiO<sub>2</sub> was prepared and calcined at 400-700 °C in order to investigate the synergistic effect of Pt and SiO<sub>2</sub> on the degradation rate of 4-chlorophenol. The degradation of 4-chlorophenol and the reduction of TOC at different calcination temperatures are shown in Figure 4.25. The degradation rate of 4-chlorophenol did not depend on the calcination temperature but the remaining TOC fraction decreased with increasing the calcination temperature. The activities of 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> and 10%SiO<sub>2</sub>-TiO<sub>2</sub> at different calcination temperatures are compared using the values of TOC/TOC<sub>0</sub> at 360 minutes as shown in Figure 4.26. It was found that the TOC/TOC<sub>0</sub> values at 360 minutes of 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> were not much different from 10%SiO<sub>2</sub>-TiO<sub>2</sub> over the studied range of the calcination temperatures. In addition, the values of TOC/TOC<sub>0</sub> at 360 minutes of TiO<sub>2</sub>, 1%Pt/TiO<sub>2</sub>, 10%SiO<sub>2</sub>-TiO<sub>2</sub> and 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> calcined at 400 °C are also compared as shown in Figure

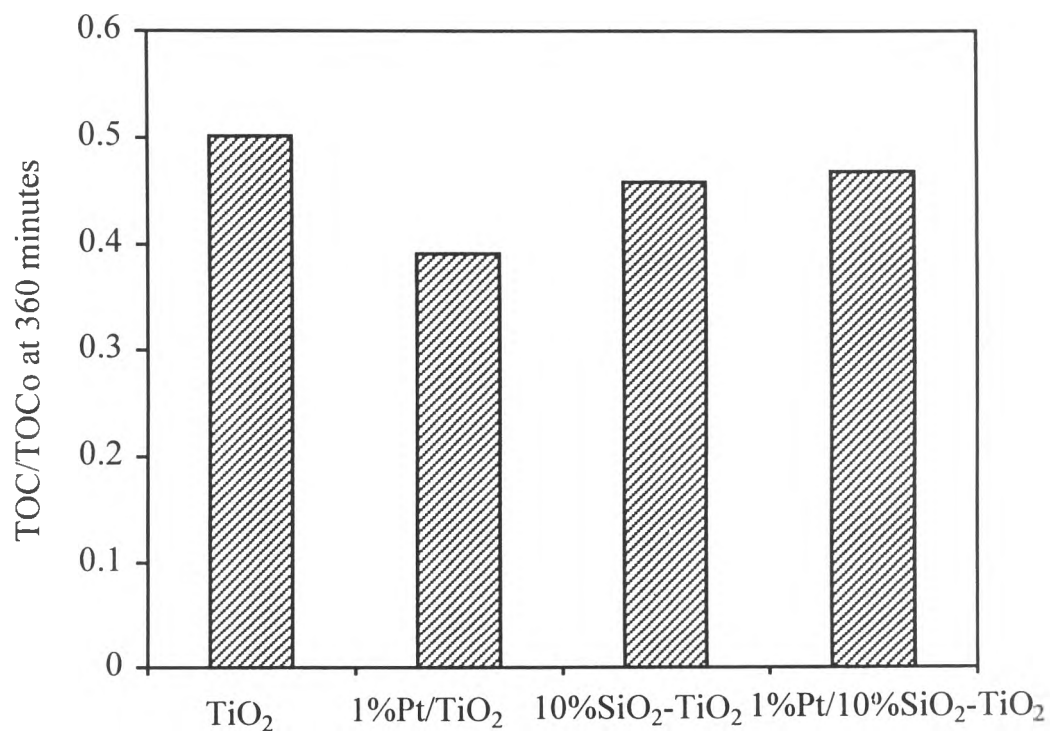


**Figure 4.25** Photocatalytic degradation of 4-chlorophenol as a function of reaction time by 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures (a) remaining 4-chlorophenol fraction (b) remaining TOC fraction





**Figure 4.26** TOC/TOC<sub>0</sub> at 360 minutes for 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> and 10%SiO<sub>2</sub>-TiO<sub>2</sub> catalysts calcined at different temperatures



**Figure 4.27** TOC/TOC<sub>0</sub> at 360 minutes for different catalysts

4.27. Although the activity of  $\text{TiO}_2$  could be improved by adding 1 %Pt or 10 %Si on  $\text{TiO}_2$ , but the synergistic effect of adding both 1 %Pt and 10 %Si on  $\text{TiO}_2$  was not observed in this experimental study.

From the XRD patterns of 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> as shown in Figure 4.8, the Pt peaks are observed while the Pt peaks are not observed from the XRD patterns of Pt/TiO<sub>2</sub>. It can be explained that the appearance of Pt peaks in 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> is due to the large particle size of Pt agglomerated on the catalyst surface. This assumption is confirmed by comparing the SEM photographs of 10 %SiO<sub>2</sub>-TiO<sub>2</sub> and 1%Pt/10%SiO<sub>2</sub>-TiO<sub>2</sub> as shown in Figures 4.12 (c) and 4.12 (d). The agglomeration of catalyst was observed when 1 %Pt was added to 10%SiO<sub>2</sub>-TiO<sub>2</sub>. Again, the synergistic effect of adding both 1 %Pt and 10 %SiO<sub>2</sub> was not observed because of two reasons described as the followings. The agglomeration of the catalyst decreases the catalyst active area and consequently lowers the catalyst activity (Pozzo *et al.*, 1997). The other reason is that the large particle of Pt on the surface can act as the recombination centers resulting in the decrease of the catalytic activity.