

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are depicted into two major parts: characterization of different crystal size catalyst and photocatalytic testing using 2-propanol degradation.

5.1 Catalyst characterization

Reaction of titanium (IV) tetra-tert butoxide (TTB) in different volume ratio between 1,4 butanediol and 2-propanol at 300°C under autogeneous 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 BET surface area depend on the volume ratio between organic solvents used, i.e., 1,4 butanediol and 2-propanol.

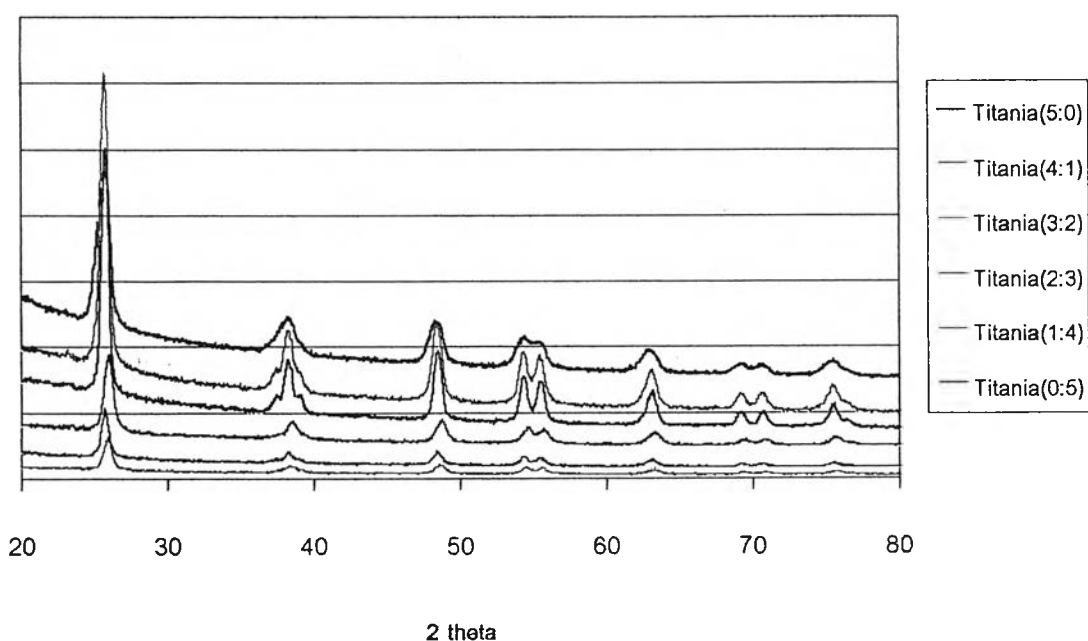
The emblems $TiO_2(x:y)$ in the subsequent paragraph represent titanium (IV) oxide synthesized by using $x:y$ volume ratio of 1,4 butanediol to 2-propanol where table 5.1 represents the meaning of these emblems.

5.1.1 X-Ray Diffraction (XRD) Pattern

The phase structure of the prepared catalysts is characterized by XRD technique. The XRD patterns of all catalysts are depicted in figures 5.1. In the 2θ range from 20° to 80°, XRD spectra of TiO_2 synthesized by glycothermal method show evident nine peaks (the values of 2θ were 25.3°, 37.8°, 48.1°, 54.0°, 55.2°, 62.8°, 68.0°, 71.9°, and 76.2°), all of those peaks can be attributed to anatase phase. No peaks other than those attributes to anatase are observed. Additionally, the crystal size of synthesized titania can be determined from the half-height width of the 101 diffraction peak of anatase using Scherrer equation. The example of crystal size determination by using the Scherrer equation is given in appendix B and crystal size of catalysts calculated by Scherrer equation are shown in table 5.2

Table 5.1 The meaning of $\text{TiO}_2(x:y)$ emblems

Emblem	Meaning
$\text{TiO}_2(5:0)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 5:0
$\text{TiO}_2(4:1)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 4:1
$\text{TiO}_2(3:2)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 3:2
$\text{TiO}_2(2:3)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 2:3
$\text{TiO}_2(1:4)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 1:4
$\text{TiO}_2(0:5)$	Titanium (IV) oxide synthesized by using volume ratio of 1,4 butanediol to 2-propanol as 0:5

**Figure 5.1** XRD pattern of all synthesized titanium (IV) oxide catalysts

5.1.2 Morphology

The average particle sizes determined from the transmission electron micrograph (TEM) of $\text{TiO}_2(5:0)$, $\text{TiO}_2(4:1)$, $\text{TiO}_2(3:2)$, $\text{TiO}_2(2:3)$, $\text{TiO}_2(1:4)$, and $\text{TiO}_2(0:5)$ shown in figures 5.2-5.7 are 16.7, 20.0, 20.0, 13.0, 14.7, and 40.0 nm, respectively. The average particle size measurement is given in an appendix C and the shape of as-prepared titanium (IV) oxide catalysts is rather spherical shape. The results are in good agreement with the crystallite size calculated by Sherrer equation. These results indicate that each primary particle observed by TEM is a single crystal of anatase.

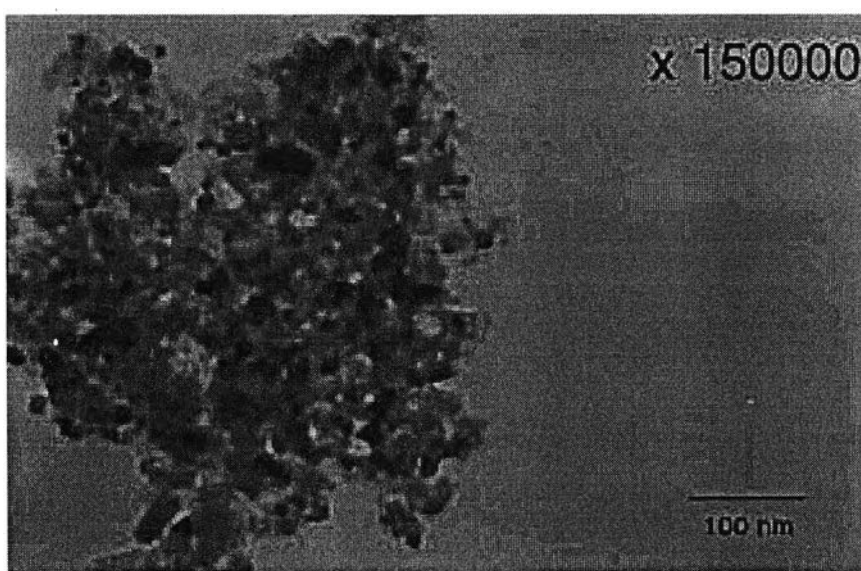


Figure 5.2 TEM photograph of titanium (IV) oxide (5:0)

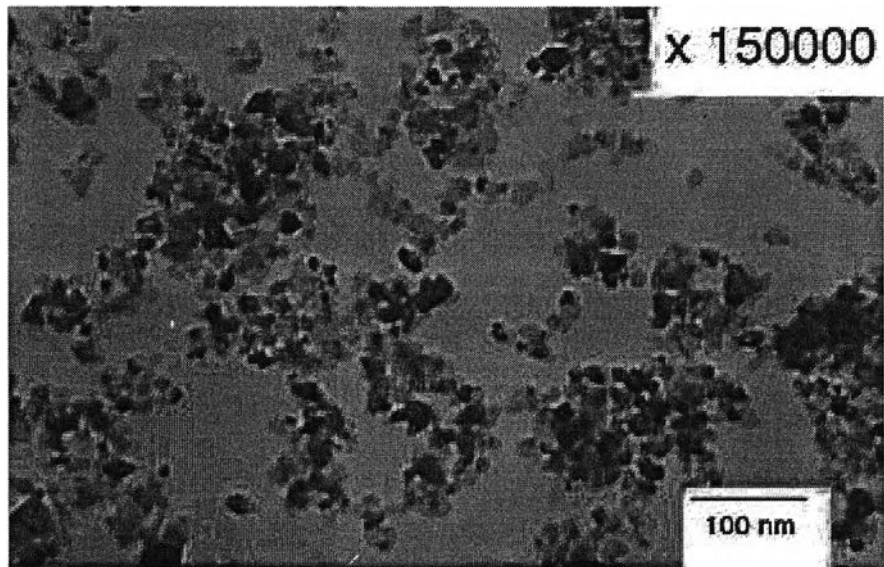


Figure 5.3 TEM photograph of titanium (IV) oxide (4:1)

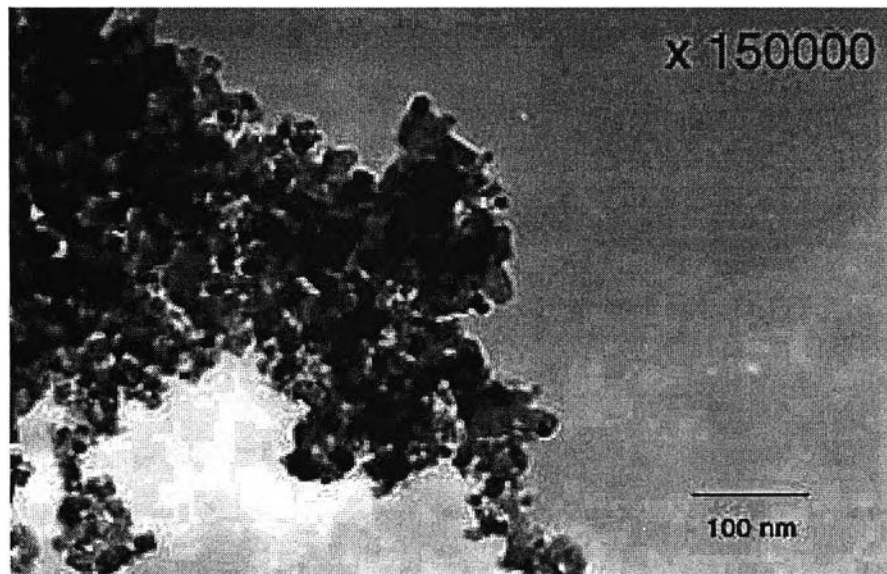


Figure 5.4 TEM photograph of titanium (IV) oxide (3:2)

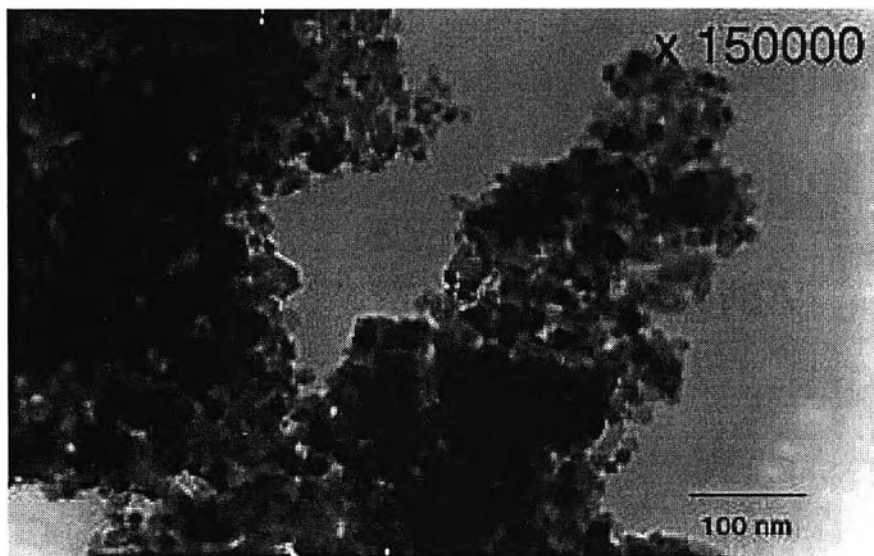


Figure 5.5 TEM photograph of titanium (IV) oxide (2:3)

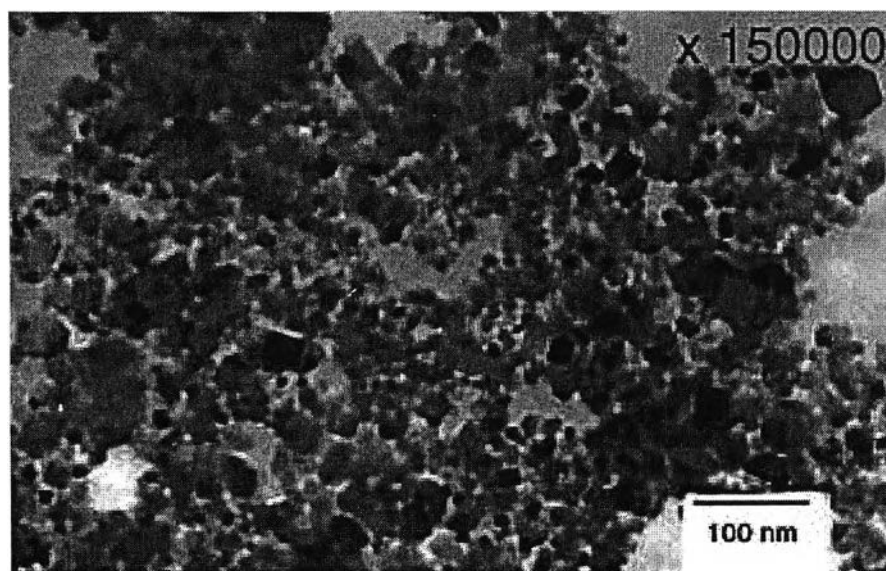


Figure 5.6 TEM photograph of titanium (IV) oxide (1:4)

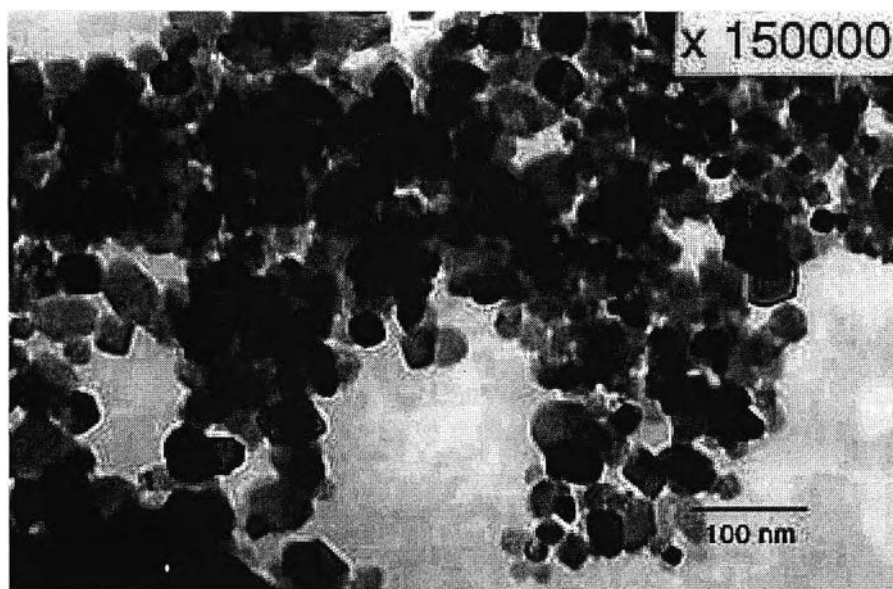


Figure 5.7 TEM photograph of titanium (IV) oxide (0:5)

5.1.3 Specific surface area measurement

BET surface areas of the catalysts determined by BET surface area measurement are tabulated in table 5.2.

The data in table 5.2 indicate that the TiO₂(4:1) possess the highest surface area. On the other hand, the surface area of TiO₂(0:5) is the lowest. In addition, TiO₂ synthesized in high volume ratio of 2-propanol has tendency to have low surface area.

All of the characteristic properties of the catalysts such as crystal size and surface area are summarized in table 5.2.

Table 5.2 Characteristic properties of the prepared TiO₂ catalysts

Catalysts	Crystal size by XRD (nm)	Crystal size by TEM (nm)	BET surface area (m ² g ⁻¹)
TiO ₂ (5:0)	17.1	16.7	71.4
TiO ₂ (4:1)	23.0	20.0	81.4
TiO ₂ (3:2)	23.2	20.0	72.1
TiO ₂ (2:3)	10.3	13.0	72.0
TiO ₂ (1:4)	14.7	14.7	68.9
TiO ₂ (0:5)	42.0	40.0	47.4

5.1.4 Fourier Transform Infrared (FTIR) spectroscopy

Results of FTIR spectra of all catalysts are exhibited in figure 5.8. The infrared radiation in the proper wavelength of $400\text{--}4000\text{ cm}^{-1}$ for determining the solid surface is used to identify the functional group on the catalyst surface. The major IR bands of TiO_2 exhibit in the range of $400\text{--}800\text{ cm}^{-1}$ for all catalysts. The signal occurred in other ranges, i.e., ca. 1600 cm^{-1} , might cause incomplete background subtraction.

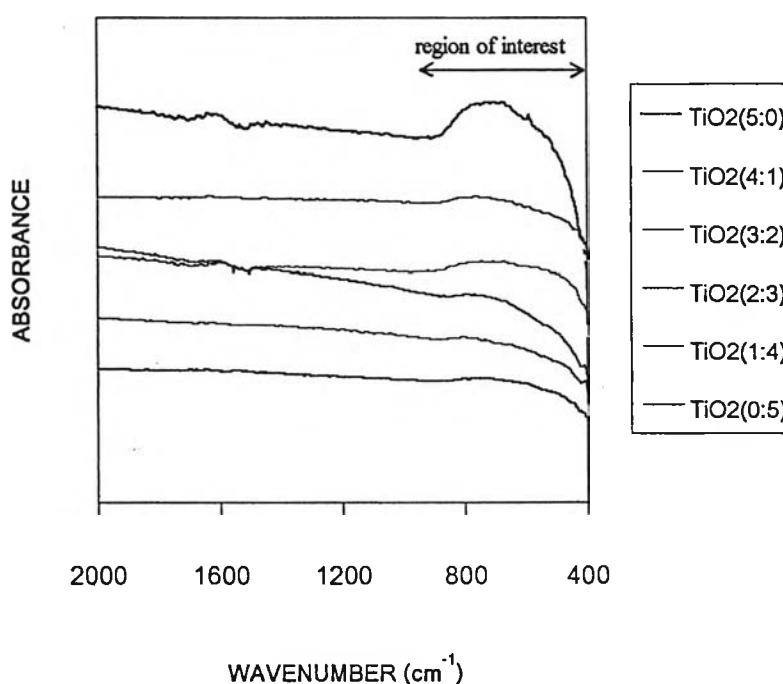


Figure 5.8 FTIR spectra of all titanium (IV) oxide catalysts synthesized by glycothermal method

5.2 photocatalytic reaction testing

In this work, the TiO₂ catalysts synthesized by glycothermal method from different volume ratio of 1,4 butanediol to 2-propanol are used in photocatalytic testing.

5.2.1 Crystal size effect on photo-oxidation of 2-propanol

Six different crystal sizes of TiO₂ are used to determine the effects of crystal size on the photo-oxidation of 2-propanol. Figures 5.9-5.14 show the profiles of conversion of 2-propanol for each TiO₂ crystal size during the photocatalytic degradation of 12400 ppm gaseous 2-propanol. The photocatalytic reaction was operated at room temperature and air flow rate was set at 20 ml min⁻¹. After switching on the UV lamp, the photocatalytic reaction started. A typical increasing temperature inside the reactor due to the heat released from the UV lamp is about 20°C and final temperature inside reactor in equilibrium is ca. 50°C for all experiments at outside ambient temperature. The main products occurred in this reaction for all catalysts are CO₂ and water. Trace of acetone is also detected.

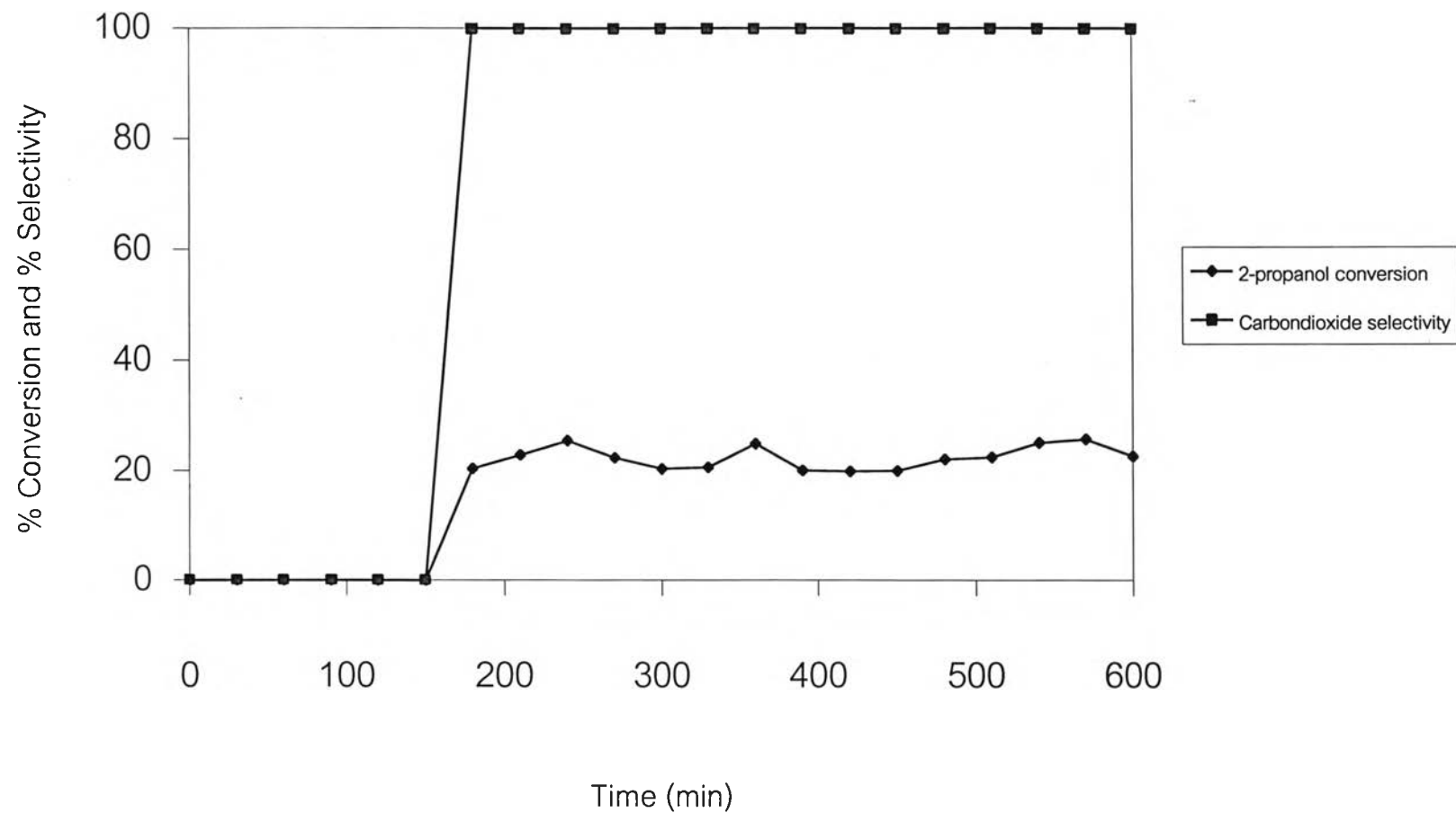


Figure 5.9 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (5:0) catalyst (17.1 nm). Experimental conditions: 20 ml min⁻¹ air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

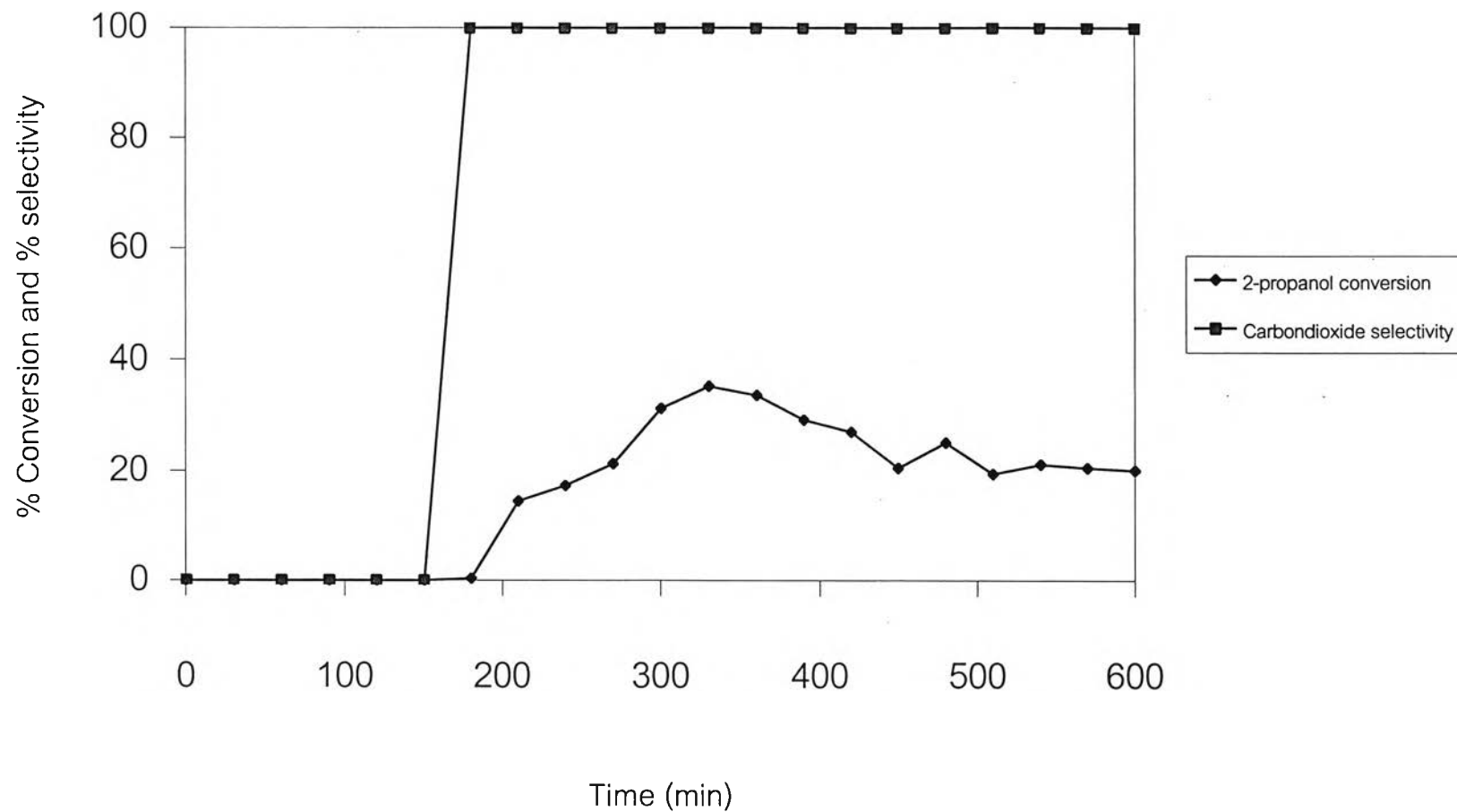


Figure 5.10 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (4:1) catalyst (23.0 nm). Experimental conditions: 20 ml min⁻¹ air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

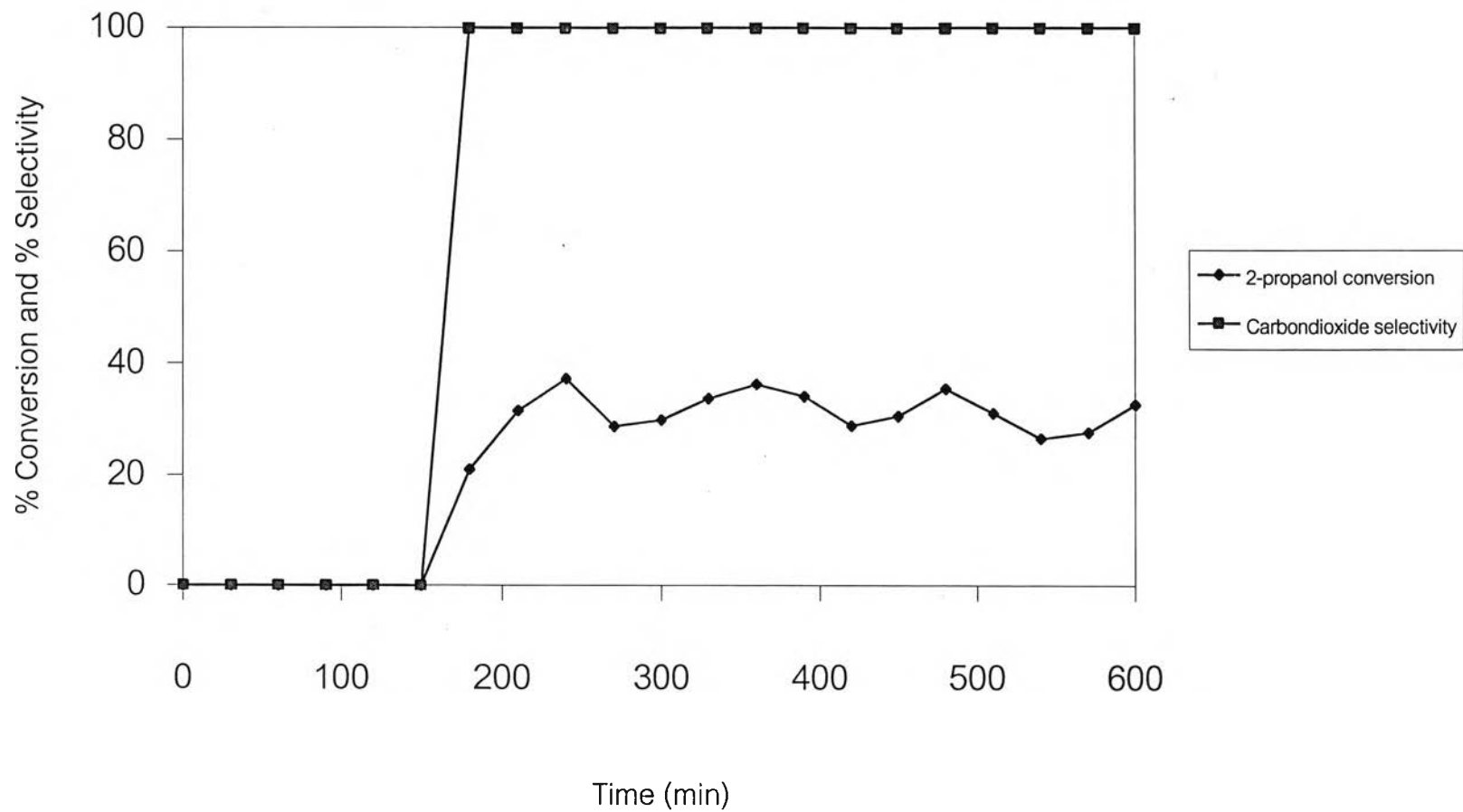


Figure 5.11 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (3:2) catalyst (23.2 nm). Experimental conditions: 20 ml min^{-1} air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

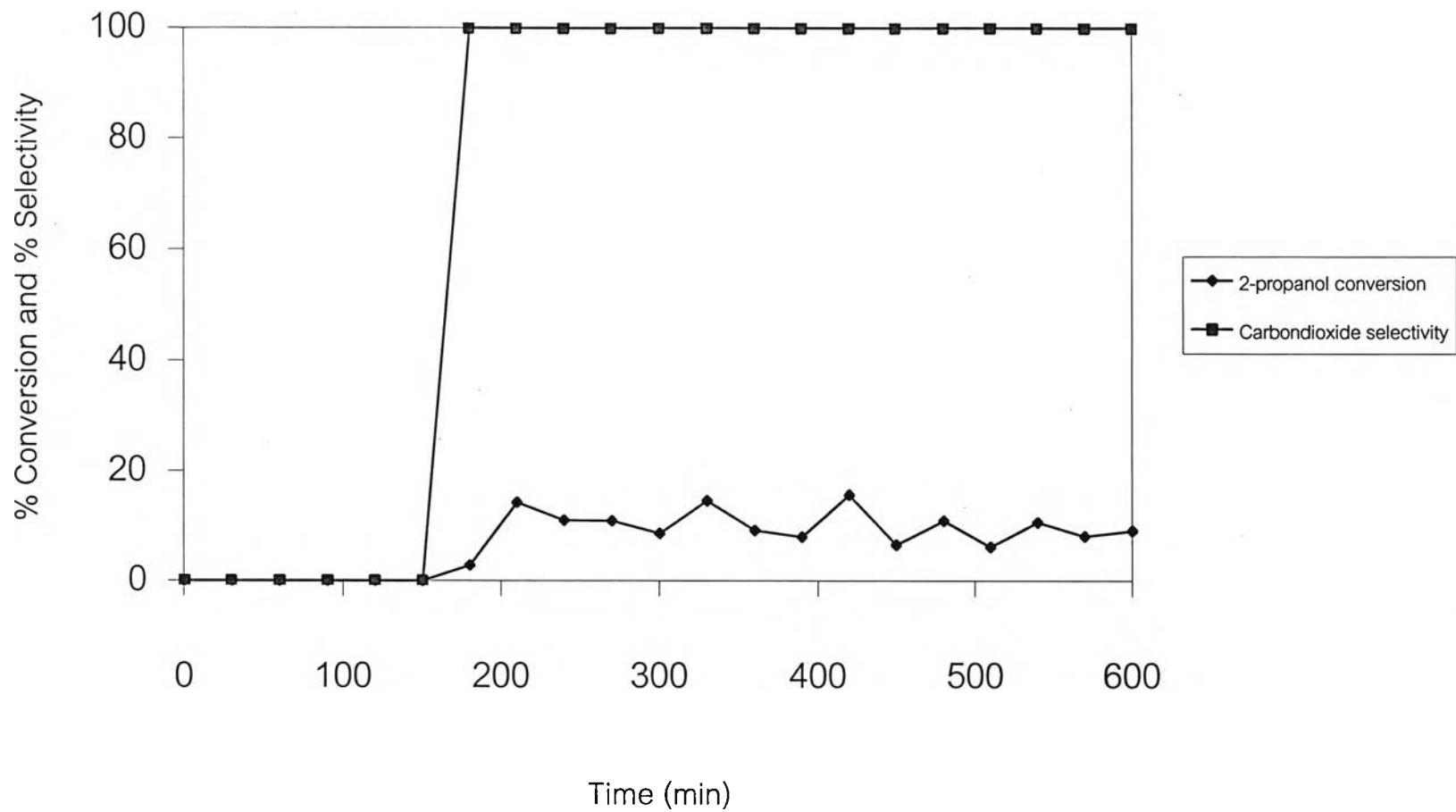


Figure 5.12 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (2:3) catalyst (10.3 nm). Experimental conditions: 20 ml min^{-1} air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

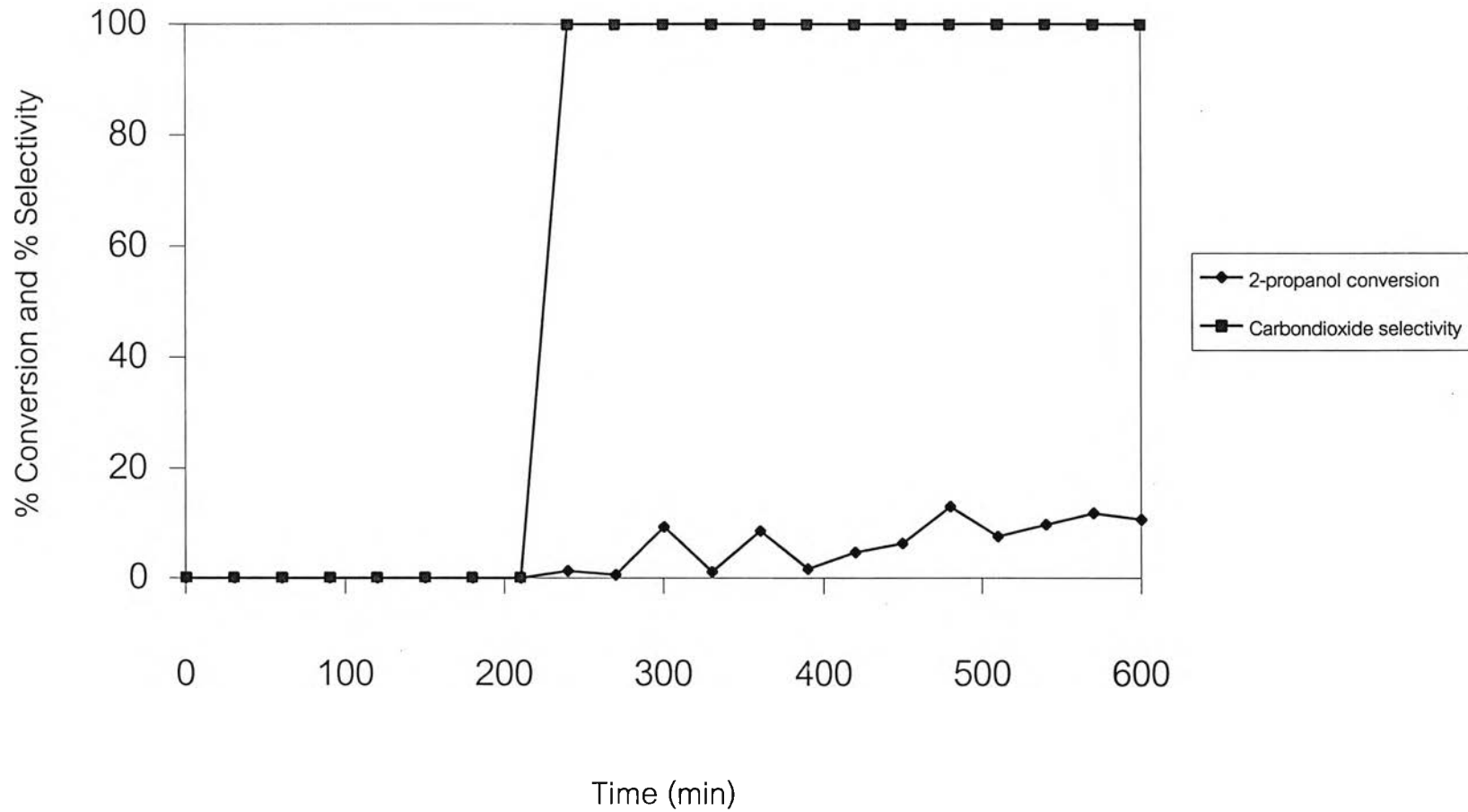


Figure 5.13 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (1:4) catalyst (14.7 nm). Experimental conditions: 20 ml min⁻¹ air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

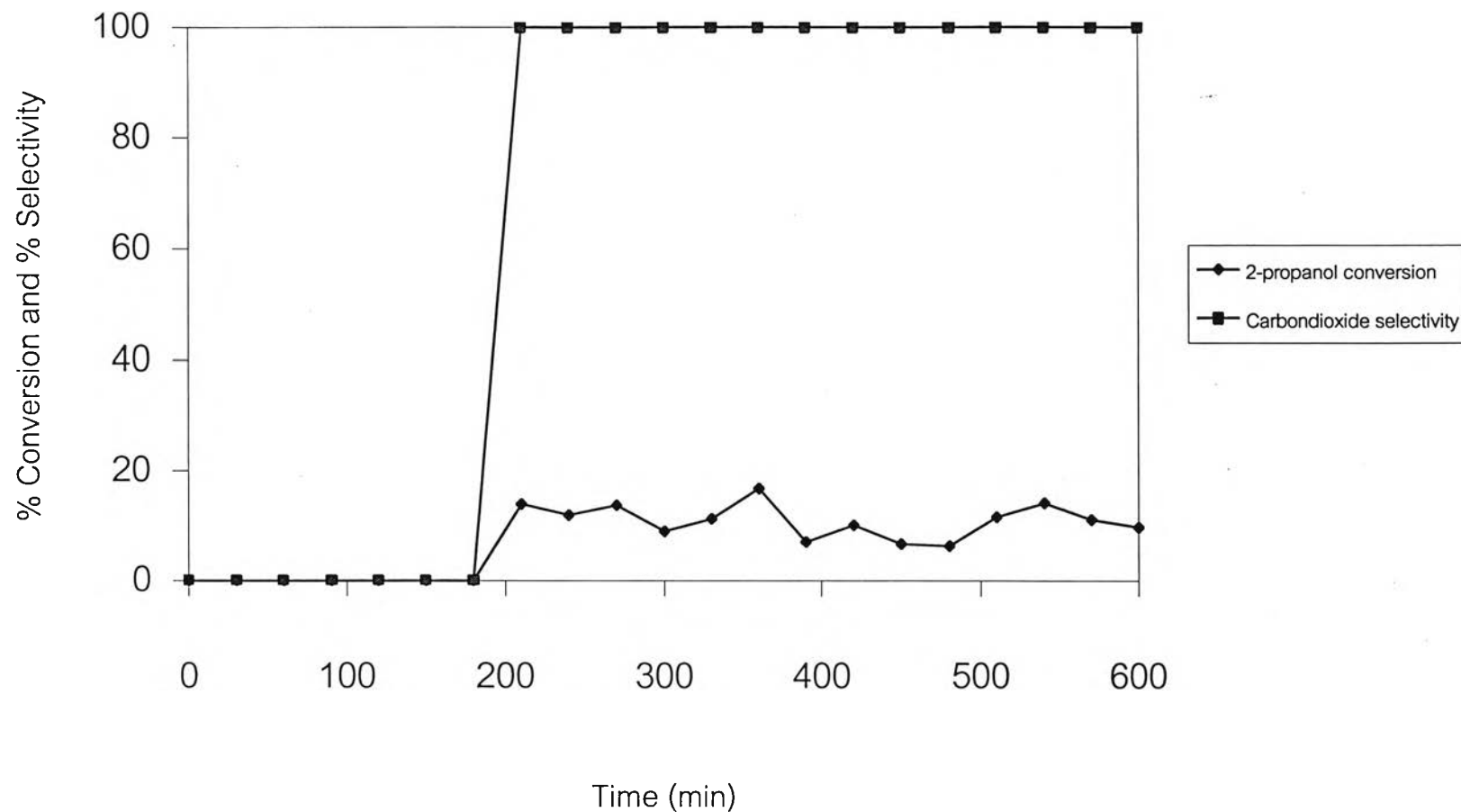


Figure 5.14 Time course of conversion in the photocatalytic decomposition of 2-propanol over titanium (IV) oxide (0:5) catalyst (42.0 nm). Experimental conditions: 20 ml min⁻¹ air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

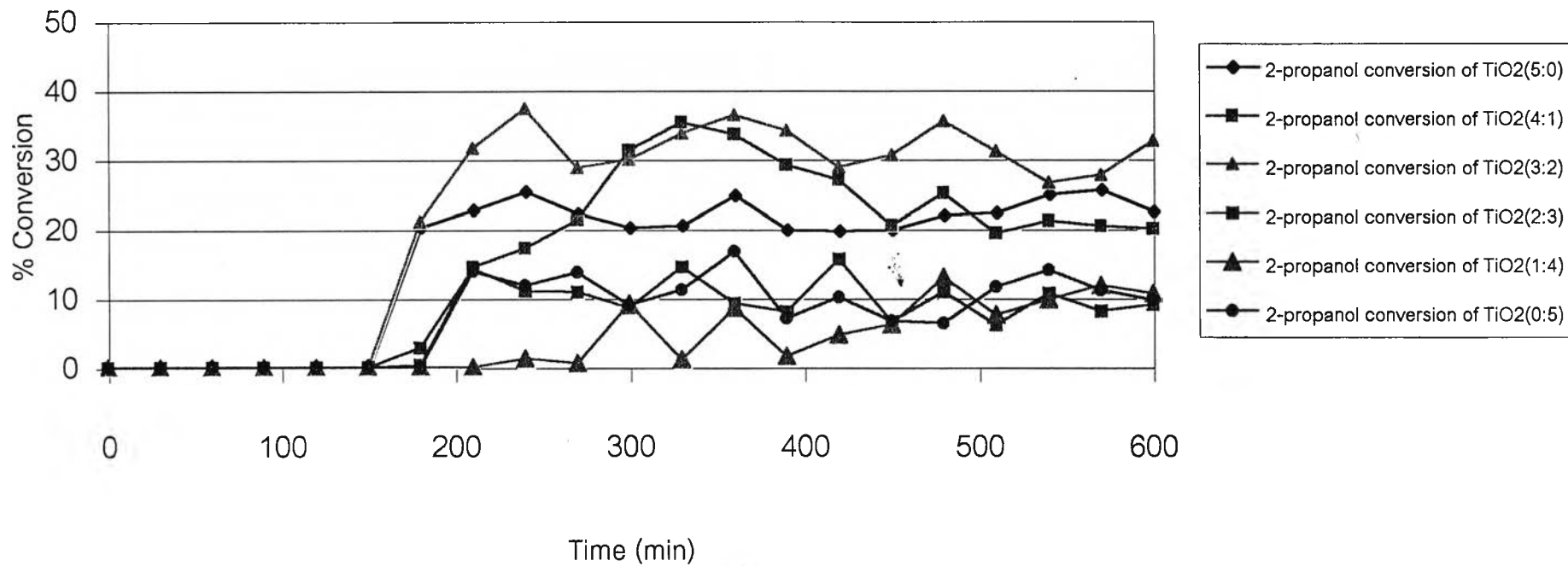


Figure 5.15 Time course of conversion in the photocatalytic decomposition of 2-propanol over all titanium (IV) oxide catalysts. Experimental conditions: 20 ml min⁻¹ air flow rate, ambient temperature, and 12400 ppm of 2-propanol.

The first 150 min of operation is the waiting time for the system to reach the equilibrium between gaseous and adsorbed 2-propanol on the catalyst surface in the conducted irradiation. After UV irradiation, the reaction reaches a steady state condition. The highest conversions are almost constant over the entire operation periods. From the figure 5.15, the crystal size of synthesized TiO₂ can be divided into 3 parts. The first part is a small scale of crystal size i.e., 10.3 and 14.7 nm. The second part is average scale of crystal size e.g., 17.1, 23.0, and 23.2 nm. The last part is large scale of crystal size for example 42 nm. The group of middle crystal sizes shows higher 2-propanol conversion than other groups, especially, crystal size 23.2 nm obtains 2-propanol conversion at equilibrium of 32%. For the TiO₂ crystal size of 17.1 and 23.0, the photoactivity in 2-propanol degradation is 22% and 20% respectively.

For small and large crystal size titanium (IV) oxide, i.e., 10.3, 14.7, and 42 nm, the equilibrium photoactivity for 2-propanol decomposition is rather low, 9%, 10% and 9%, respectively. Therefore, the optimum crystal size of TiO₂ in photo-oxidation of 2-propanol is ca. 23 nm.

In order to explain the effect of crystal size on the photocatalytic activity, the electron-hole recombination may be grouped into two categories: volume recombination and surface recombination. Volume recombination is a dominant process in well-crystallized large TiO₂ particles, which can be reduced by decreasing particle size. Reduction in particle size also leads to larger surface area, which increases the available surface active sites. In nanocrystalline semiconductor particles, when the crystal size becomes extremely small, surface recombination becomes the important process. In the regime of ultrafine particle size, most of the electron-hole pairs are generated sufficiently close to the surface. They may quickly reach the surface, and undergo rapid surface recombination mainly due to abundant surface trapping sites and the lack of driving force for electron-hole pair separation. Since the characteristic time for surface electron-hole recombination is much faster than that of the interfacial charge carrier transfer processes, the decrease in the interfacial transfer rate will be outweighed by the increased surface recombination

rate in ultrafine particles beyond a certain size reduction. Therefore, an optimal crystal size exists in the TiO_2 system for the maximum photoactivity. This argument is supported by the experimental results: the photoactivity of TiO_2 for gas phase photo-oxidation of 2-propanol increase when crystal size is increased from ca. 10 to 23 nm, but decrease when it is ca. 42 nm.

An interesting point is the catalyst prepared from 2-propanol only ($\text{TiO}_2(0:5)$). This catalyst has average crystal diameter much different from the others i.e., 10-23 and 42 nm. In addition, the $\text{TiO}_2(0:5)$ shows lower photoactivity than $\text{TiO}_2(3:2)$ average crystal diameter of 23.2 nm. Since there is only one data point, it is too early to conclude that if the average crystal diameter is larger than ca. 23 nm the photoactivity has chance to drop. The difficult is the only available information in the catalyst prepared from using 1,4 butanediol only that has crystal size smaller than the catalyst prepared from using 2-propanol only. The experiment reported in section 5.1 shows that there is no correlation between crystal diameter and ratio of 1,4 butanediol to 2-propanol. Therefore, a further experiment has been performed by preparing 2 catalysts using ratio 1,4 butanediol to 2-propanol of 0.5:4.5 and 0.2:4.8 $\text{TiO}_2(0.5:4.5)$ and $\text{TiO}_2(0.2:4.8)$, respectively. These ratios have been chosen with the hope that a small amount of 1,4 butanediol can slightly decrease the crystal size when the compare with the catalyst prepared from using 2-propanol only. Unfortunately, the catalysts obtained have average crystal diameters approximately 16 and 17 nm respectively. Because of this reason, no experiment with crystal size between 23-42 nm can be carried out. A new method for preparing catalyst with crystal size in the above range, 23-42 nm, should be available first.

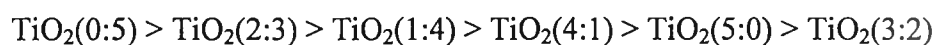
The contrast results reported by several research groups can be explained using the above explanation. The conclusion of each research group depended on the crystal size employed. For examples, Kominami et al. (1999b) found that the photoactivity increase with crystal size increasing from <5 to 9 nm. Because the crystal size of titanium (IV) oxide catalysts studied is extremely small (They are smaller than the optimum crystal size). In case of photo-oxidation of chloroform in the liquid phase [Zhang and co-workers (1998)] and gas phase photo-oxidation of

trichloroethylene [Maira et al. (2000)], the optimum particle size exists. And in case of photocatalytic degradation of methylene blue in a suspended aqueous solution [Xu et al. (1999b)], the result showed that the photoactivity monotonically increased as the crystal size of titanium (IV) oxide catalysts decreased from 49 to 0.03 micrometer. It can be explained that crystal sizes of titanium (IV) oxide catalysts applied to photocatalytic degradation of methylene blue are larger than the optimum crystal size. In this case, the volume recombination process is the main reaction for decreasing the photocatalytic degradation.

5.2.2 Effect of 2-propanol adsorption on the photocatalytic degradation of 2-propanol

Since the photocatalytic degradation of 2-propanol involve at least 2 species, 2-propanol and O_2/H_2O , the adsorption of each reactant can affect the catalytic activity of the catalyst. According to the Langmuir-Hinshelwood model, each species must exist on the surface in an appropriate amount. If any species excessively presents on the surface, the reaction rate will drop. In this work, the adsorption of 2-propanol was measured since it is easier to determine than O_2 or water.

The 2-propanol adsorbability (the amount of adsorbed 2-propanol on the surface of a catalyst per unit surface area of that catalyst) of prepared TiO_2 catalysts was determined by temperature programmed desorption, TPD technique. The result exhibited in table 5.3 shows that 2-propanol adsorbability is in the following order.

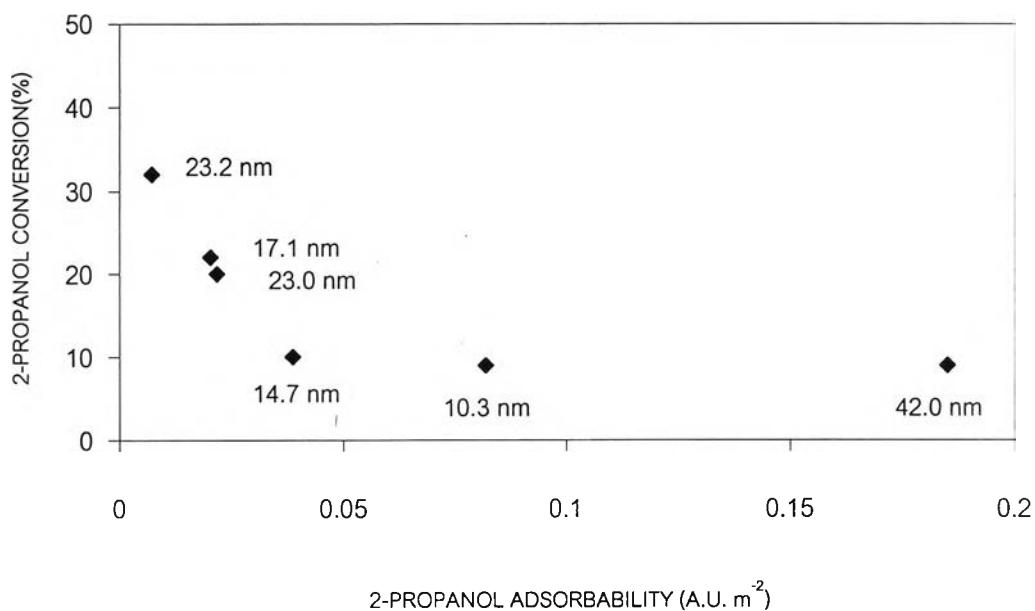


The 2-propanol adsorption on the surface of TiO_2 catalyst has directly impact to the photoactivity of gas phase photo-oxidation of 2-propanol. Figure 5.16 demonstrate the relationship between the photoactivity (2-propanol conversion) and 2-propanol adsorbability in arbitrary unit. From the experiment, when the 2-propanol adsorbability increases, the photoactivity seems to decrease to the constant value. This is because large amount of 2-propanol adsorbed on the surface of TiO_2 catalyst

Table 5.3 2-propanol adsorbability of synthesized titanium (IV) oxide catalysts

Catalysts	2-propanol adsorbability (a.u. m ⁻²)
TiO ₂ (5:0)	0.0203
TiO ₂ (4:1)	0.0218
TiO ₂ (3:2)	0.0072
TiO ₂ (2:3)	0.0820
TiO ₂ (1:4)	0.0387
TiO ₂ (0:5)	0.1850

can suppress the other species (Langmuir-Hinshelwood model), i.e., hydroxyl groups and oxygen molecules, important substances for the photo-oxidation reaction. Whereas low 2-propanol adsorbability TiO₂ hydroxyl groups and/or oxygen molecules can more adsorb than high 2-propanol adsorbability TiO₂. Therefore, when the TiO₂ is excited the 'OH' and 'O₂' can be formed. These two substances are very active in the photo-oxidation for organic degradation.

**Figure 5.16** Relationship between the photoactivity (2-propanol conversion) and 2-propanol adsorbability