การสลายของไอโซโพรพานอลโดยแสงด้วยตัวเร่งปฏิกิริยาไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอล

นางสาวสุดารัตน์ มาตวัน

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PHOTOCATALYTIC DECOMPOSITION OF ISOPROPANOL OVER TiO_2 SYNTHESIZED BY THE GLYCOTHERMAL METHOD

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Thesis	Photocatalytic decomposition of isopropanol over titanium dioxide synthesized by the glycothermal method
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สุดารัตน์ มาตวัน: การสลายของไอโซโพรพานอลโดยแสงด้วยตัวเร่งปฏิกิริยาไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอล (PHOTOCATALYTIC DECOMPOSITION OF ISOPROPANOL OVER TiO_2 SYNTHESIZED BY THE GLYCOTHERMAL METHOD) อ. ที่ปรึกษา : ผศ.ดร.ธราธร มงคลศรี, อ. ที่ปรึกษาร่วม : ศร.ดร.ปิยะสาร ประเสริฐธรรม, 73 หน้า. ISBN 974-346-067-5

งานวิจัยนี้ทำการศึกษาถึงการสลายของไอโซโพรพานอลโดยแสงด้วยตัวเร่งปฏิกิริยาไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอล และเปรียบเทียบความว่องไวทางปฏิกิริยากับไทเทเนียมไดออกไซด์ที่ใช้เป็นมาตรฐานของประเทศญี่ปุ่น (JRC-TIO1 และ JRC-TIO4) จากการทดลองพบว่าไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอลมีพื้นที่ผิวมากกว่าไทเทเนียมไดออกไซด์ที่ใช้เป็นมาตรฐานทั้งสองตัว และมีโครงสร้างผลึกเป็นแบบอนาเทสเพียงอย่างเดียว เมื่อนำมาทดสอบในปฏิกิริยาการสลายของไอโซโพรพานอลโดยแสงแล้ว พบว่ามีการเลือกเกิดของคาร์บอนไดออกไซด์มากกว่าไทเทเนียมไดออกไซด์ที่ใช้เป็นมาตรฐานของประเทศญี่ปุ่นทั้งสองตัว แม้ค่าการเปลี่ยนของไอโซโพรพานอลมีค่าน้อยกว่า JRC-TIO1 แต่ผลิตภัณฑ์หลักที่ได้เป็นคาร์บอนไดออกไซด์และอะซิโตนในปริมาณเล็กน้อย ซึ่งถือว่าเป็นผลิตภัณฑ์ที่เป็นอันตรายน้อยกว่าเมื่อเปรียบเทียบกับผลิตภัณฑ์ที่ได้จากการใช้ JRC-TIO1 ซึ่งผลิตภัณฑ์หลักเป็นอะซิโตนและสารโมเลกุลเล็กอีกจำนวนหนึ่ง นอกจากนั้นยังพบว่าไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอลมีความคงทนต่อปฏิกิริยานี้ได้ดี ปฏิกิริยาการสลายของไอโซโพรพานอลโดยแสงด้วยไทเทเนียมไดออกไซด์ที่เตรียมโดยวิธีไกลโคเทอร์มอลเหมาะกับระบบที่มีความเข้มของสารตั้งต้นค่อนข้างต่ำ ผลของความเร็วเชิงสเปซที่ลดลงโดยการลดอัตราการไหลของอากาศมีผลให้เพิ่มค่าการเปลี่ยนแปลง ส่วนการเพิ่มปริมาณของตัวเร่งปฏิกิริยาจาก 0.2 เป็น 0.4 กรัมซึ่งความเร็วเชิงสเปซลดลงทำให้ค่าการเปลี่ยนแปลงเพิ่มขึ้นแต่เมื่อเพิ่มปริมาณมากถึง 1.0 กรัมเป็นผลให้ค่าการเปลี่ยนแปลงตกลง ส่วนผลของอุณหภูมิของปฏิกิริยาค่าการเปลี่ยนแปลงลดลงตามอุณหภูมิของปฏิกิริยาที่สูงขึ้น

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This research investigated the photocatalytic decomposition of isopropanol over TiO_2 synthesized by glycothermal method and compared the activity with Japan reference catalysts (JRC-TIO1 and JRC-TIO4). From the results, TiO_2 synthesized by glycothermal method has higher surface area than the both of Japan reference titanium dioxide and only anatase phase TiO_2 is found. For the photocatalytic decomposition of isopropanol test, it was found that TiO_2 synthesized by glycothermal method has higher CO_2 selectivity than the both of Japan reference catalysts. Although the conversion of isopropanol is lower, the main product is only CO_2 which is less harmful. The main products from this reaction using JRC-TIO1 are acetone and small intermediate compounds which are not the desired product and more harmful than CO_2. Moreover, TiO_2 synthesized by glycothermal method has good stability for this reaction. Photocatalytic decomposition of isopropanol is most appropriate for low concentration system. An increase in the space velocity by increasing the flow rate of air results in decreasing the conversion of isopropanol. Changing the space velocity by changing catalyst weight from 0.2 g to 0.4 g results in increasing conversion of isopropanol. When catalyst weight is increased to 1.0 g, the conversion of isopropanol is drop. The reaction temperature has an effect on the photocatalytic decomposition of isopropanol. The conversion of isopropanol decreases with increasing the reaction temperature.

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CHAPTER I

INTRODUCTION

Photocatalysis is a new field of science, scientific studies on photocatalysis started about two and a half decades ago. Photocatalysis consists of the combination of photo-chemistry and catalysis, implied that light and a catalyst are necessary to bring about or accelerate a chemically transformation through reduction and oxidation reaction simultaneously.

Initial studies are utilizing solar energy to produce hydrogen that is a promising fuel. In addition, following the production organic compounds through the reduction of carbondioxide. In recent times, applications to environmental clean up have been one of the most active areas in heterogeneous photocatalysis. This is inspired by the potential application of titanium dioxide (TiO_2) based photocatalyst for the total destruction of organic compounds in polluted air and wasted water.

Nowaday, many photocatalytic researches have been added and well known in many countries, especially Japan. Photocatalytic technology has been taken in many environmental applications in presence of titanium dioxide and ultraviolet irradiation to obtain the decomposition of organic contaminants [Alberici and Jardim (1997), Kozlov *et al.* (2000), Muggli *et al.* (1998a), Obuchi *et al.* (1999), Sopyan *et al.* (1996), Vorontsov *et al.* (1997)].

Volatile organic compounds (VOC) are an important class of air pollutants usually found in the atmosphere of all urban and industrial areas. Also, the emission of VOCs is found in the domestic areas. The common VOCs include alcohols, ketones, ethers and halogenated hydrocarbon are widely used in houses as the solvents. This extensive use results in their occurrence in aquatic, soil and atmosphere environments. Many VOCs are toxic and some are considered to be carcinogenic, isopropanol is one of these compounds. Several strategies have been identified in order to reduce their presence in indoor and industrial emission. From the above photocatalytic process is a good alternative way to handle it.

There are two main factors for photocatalytic process. One is catalyst, one of the most basic material is titanium dioxide (TiO_2) and the other one is light. Titanium dioxide has been most widely used for the study of photocatalytic decomposition because of its high stability against photocorrosion and its favorable band gap energy [Tabata *et al.* (1995)]. TiO_2 when used as photocatalyst, photoactivity of it depend on the synthesis. For the realization of their practical application, development of highly active TiO_2 photocatalyst is keenly desired. Based on the kinetic investigation of photocatalytic reactions, TiO_2 particles having both large surface area and high crystallinity must exhibit higher photocatalytic activity [Kominami *et al.* (1997)].

There are many methods for titanium dioxide synthesis and glycothermal method is a new method of titanium dioxide synthesis, which developed to obtain a highly active TiO_2. Therefore, TiO_2 synthesized by glycothermal method has been expected to use as photocatalyst in isopropanol decomposition.

Thus, this research is set up to demonstrate the effect of different catalyst, reaction temperature, concentration of isopropanol, and space velocity of air on the activity of TiO_2 synthesized by glycothermal method for photocatalytic decomposition of isopropanol.

This thesis is divided into the following chapter:

Chapter II presents a literature review of investigation over TiO_2 catalyst for the photocatalytic decomposition of isopropanol and some comment on the previous paper. The theory of this work, studies about the photocatalytic process, the main factors involved in photocatalytic process, inhibition of electron-hole recombination by oxygen. These topics are presented in chapter III.

In chapter IV, the experimental systems and the operational procedure are described. The experimental results obtained from a laboratory scale reactor is reported and discussed in chapter V. Chapter VI gives over all conclusions emerged from this work and presents some recommendations for any future works.

Finally, the operating condition of gas chromatograph, the condition of calcination the catalyst, the data of the reaction testing are included in appendices at the end of this thesis.

CHAPTER II
LITERATURE REVIEWS

The photocatalytic processes have been becoming increasingly attractive to environmental protection in both of liquid and gaseous phase systems. It is one of promising approach for remediating these systems by using semiconductor as photocatalyst. The most active semiconductor used catalyst is titanium dioxide. The reviews in this chapter will concentrate on using titanium dioxide in photocatalytic oxidation to obtain the mineralization of several substances or contaminants.

2.1 Reviewed papers

In this section, the relevant photocatalytic oxidation of several substances by titanium dioxide as photocatalyst papers are summarized to raise the problem issue. They are as follows:

Tabata *et al.* (1995) examined the influence of the direction of ultraviolet irradiation upon the yields of the photocatalytic decomposition of pure water in Pt/ TiO_2 aqueous suspension system. They reported that the yields of the photocatalytic decomposition irradiated from the top of the reaction cell are about 10^3 times higher than those irradiated from the bottom. The difference of photocatalytic activity between the two directions of light irradiation was based on the reverse reaction of H_2 and O_2. When the suspension is irradiated from the bottom of the reaction cell, H_2 and O_2 form far from the surface of suspension. Therefore, most of the H_2 and O_2 recombined before evolving from the surface of the suspension to the gas phase.

Fu *et al.* (1996) demonstrated the effect of reaction temperature and vapor content on the heterogeneous photocatalytic oxidation of ethylene. They studied over the temperature range 30-110^{o}C using a packed bed reactor containing sol-gel-derived TiO_2 or platinized TiO_2 particulates. The results of this study indicated that the reactivity of ethylene is enhanced at increased temperatures. Moreover, platinizing the TiO_2 photocatalyst and increasing the content of water vapor in the gaseous feed streams both decrease the rate of photocatalytic oxidation of ethylene.

Sopyan *et al.* (1996) investigated photocatalytic properties of the TiO_2 thin-film by measuring the photodegradative oxidation of gaseous acetaldehyde at various concentrations under strong and weak UV light irradiation conditions. A TiO_2 thin-film was prepared on a glass substrate by sintering a TiO_2 sol. The crystallographic characteristics were examined using x-ray diffraction and raman spectroscopy showed that the film was purely anatase. The TiO_2 film showed much higher photactivity than TiO_2 power, which is the most active commercial powders, Deggussa P-25. The kinetics of acetaldehyde degradation as catalyzed by the TiO_2 film as well as by P-25 powder was analyzed in terms of the Langmair-Hinshelwood model. It was shown that the number of adsorption sites per unit true surface area is larger with the TiO_2 film than with P-25 powder. Meanwhile the first order reaction rate constant was also much larger with the film than with P-25 powder. The quantum yield, calculated on the basis of the number of absorbed photons and under the assumption that only photogenerated holes took part in the oxidative decomposition of acetaldehyde, exceeded unity, thus it was concluded that the acetaldehyde oxidation is not mediated solely by photogenerated holes but also by adsorbed oxygen, superoxide radicals and/or hydrogen peroxide. In addition, the oxidation process may involve a carbonyl-radical-mediated chain reaction mechanism.

Vorontsov *et al.* (1997) presented a collection of the results concerning the photocatalytic oxidation of gaseous organic and CO over TiO_2 in different kinds of reactors. A static reactor, an annular flow reactor and a flow-circulating reactor were used. Oxidation of acetone, ethanol and diethyl ether in the static reactor with a short residence time, their conversion per pass is low and intermediate gaseous products are formed: none in the acetone oxidation, acetaldehyde in the ethanol oxidation, acetaldehyde and ethyl acetate in the diethyl ether oxidation: CO_2 is the final carbon-containing product for all the mentioned substrates. Complete photocatalytic oxidation of acetone was demonstrated during a single pass through the annular photocatalytic oxidation flow reactor having a high residence time for the acetone. Temperature dependence of the acetone photooxidation rate in the flow-circulating reactor has a maximum at 80^{o}C. Specimens of prepared by different methods were tested in the oxidation of acetone and CO in the flow-circulating reactor. It has been found that photoplatinization retards the acetone oxidation and prohibits considerably the CO oxidation. These results indicate that the process of heterogeneous photocatalytic oxidation can be substantially improved by optimization of both the catalyst and the conditions of the photocatalytic process.

Alberici and Jardin (1997) investigated the gas-phase photocatalytic destruction of 17 VOCs (alkanes, aromatic compounds, chlorinated compounds, alcohols, ketones and ethers) over illuminated TiO_2 using a plug flow reactor with the following experimental conditions 200 ml/min flow rate, 23% humidity, 21% oxygen and an organic compound concentration range of 400-600 ppmv. With these conditions, high conversion rates of VOCs were obtained and no reaction intermediates were detected only for toluene experiment. In addition, carbon tetrachloride photoreduction was investigated in the presence of methanol as an electron donor. It was observed that the presence of methanol results in higher degradation rates.

Augugliaro *et al.* (1997) studied photocatalytic oxidation of toluene in gas-solid regime by using polycrystalline anatase TiO_2. A fixed bed continuous photoreactor of cylindrical shape was used for performing the photoreactivity runs. And photoreactor was irradiated by a medium pressure Hg lamp. Air containing toluene and water vapors in various molar ratios was fed to the photoreactor. They found that toluene was mainly photooxidised to benzaldehyde although benzene, benzyl alcohol and traces of benzoic acid and phenol were also detected. The presence of oxygen was essential for the occurrence of the photoreaction while water was beneficial in order to achieve the almost complete photooxidation of toluene to CO_2 and H_2O particles. Water also played an important role in the maintenance of the catalytic activity. In addition, the results obtained in a preliminary Fourier transform infrared (FT-IR) investigation indicated that toluene is weakly stabilized on the particles by hydrogen bonding between the aromatic ring and surface hydroxyl groups.

Anpo *et al.* (1998) investigated the chemical doping of metal ions into the TiO_2 catalyst to explore the possibility of visible light absorption. The subsequent calcination of the implanted TiO_2 in oxygen at around 450^{o}C resulted in a large shift in the absorption spectra of the TiO_2 toward visible light regions, its extent being dependent on the amount and the kind of metal ions implanted. Specifically Cr ion-implanted TiO_2 allow the efficient absorption of visible light and they were active in carrying out various photocatalytic reactions such as the decomposition of NO into N_2, O_2 and N_2O under irradiation with visible light.

Muggli *et al.* (1998a) focussed on the photocatalytic decomposition of acetic acid on TiO_2. It was exhibited that acetic acid decomposes photocatalytically to CO_2, C_2H_4 and C_2H_6 on TiO_2 by two pathways. The first pathway does not require lattice oxygen ($CH_3COOH \rightarrow CH_4 + CO_2$) but the second pathway does ($2CH_3COOH + O_{(l)} \rightarrow C_2H_6 + CO_2 + H_2O$). No long-lived intermediates were produced during photocatalytic decomposition.

Muggli *et al.* (1998b) identified adsorbed species during steady state photoctalytic oxidation (PCO) of ethanol on TiO_2 by temperature programmed desorption (TPD) and oxidation (TPO). Ethanol and its partial oxidation intermediates (acetaldehyde, acetic acid, formaldehyde and formic acid) are on the catalyst surface and their concentrations depend on the ethanol, O_2 and water feed concentrations. The rate of POC was greater initially than at steady state for all experimental conditions and this initial deactivation may be due in part to the accumulation of acetaldehyde on the catalyst surface. Higher ethanol concentration increases the amount of weakly adsorbed ethanol, which preferentially form acetaldehyde during PCO. More strongly bound ethanol preferentially produces CO_2. Although water competes with ethanol for sites, increasing the gas phase concentration only marginally increases the amount of adsorbed water.

Ohno *et al.* (1998) studied epoxidation of olefins on photoirradiated titanium dioxide powder using molecular oxygen as an oxidant in the system which irradiated with a 500 W high pressure Hg lamp. It was found that the reaction rate was significantly dependent on the kind of TiO_2 powders used as the photocatalyst. Among the TiO_2 powders having the anatase crystalline form showed as the substrate and the active TiO_2 as the photocatalytic, the amounts of 1-decene decreased and the 1,2-epoxydecane and nonanol produced. Production of a very small amount of 2-decanone was found. In addition, the effect of solvents on the reaction rate was shown.

Wang *et al.* (1998) investigated the kinetics of photocatalytic degradation of trichloroethylene in gas phase over TiO_2 supported on glass bead under irradiation UV light. A packed bed filled with coated titanium dioxide glass beads. The reaction rate for photocatalysis of TCE decreased with increasing moisture content but increased with higher flow rate, initial concentration of TCE and light intensity. For flow rate above 300 ml/min the reaction remained with little change. Moreover, the reaction rate could be successfully predicted from the L-H kinetic form under different experimental conditions of this research.

Cao *et al.* (1999) studied the effects of preparation methods, humidity and calcination temperatures on the behavior of nanoscale TiO_2 photocatalysts. Application of these photocatalysts in the gas-phase decomposition of 1-butene demonstrated that the nanoscale catalysts prepared by the acid-assisted sol-gel technique showed higher photocatalytic reactivity than commercially available Degussa P-25 TiO_2, while lower photoactivity was obtained on TiO_2 catalysts prepared without adding acid to titanium isopropoxide. The experimental results revealed that the oxidation rates of 1-butene decreased exponentially with increasing water concentrations in the flowing stream. However, a trace amount of water vapor was indispensable in maintaining the stability of the catalysts. A calcination temperature of 300°C can help improve the resistance of TiO_2 against the effects of humidity. Higher calcination temperature unfavorably results in phase transformation from anatase to rutile. Amorphous and rutile typed TiO_2 showed less photocatalytic reactivity. In situ FTIR data show the presence of hydroxyl groups and large amounts of adsorbed water on TiO_2. The deactivation of TiO_2 photocatalyst under dry conditions results from the accumulation of carbonate species on active sites.

Marta *et al.* (1999) discussed the role of H_2O in the photocatalytic oxidation of toluene in vapor phase on anatase TiO_2 catalyst. This reaction has been carried out in fixed-bed continuous reactor. Air containing toluene and water vapor in various water ratios was fed to the photoreactor irradiated by a medium pressure Hg lamp. Toluene was mainly photo-oxidized to benzaldehyde, and small amount of benzene, benzyl alcohol and traces of benzoic acid and phenol were detected. In the presence of water, no decrease of photoreactivity was observed at steady state conditions. By removing water vapor from the feed, the conversion of toluene to benzaldehyde was almost completely inhibited, and an irreversible deactivation of catalyst occurred. FT-IR experiments carried out in model conditions indicated that the layer of surface OH groups is kept essentially uncharged under UV irradiation in the presence of H_2O vapor, whereas it is irreversibly depleted by exposure to the UV light in dry conditions. As surface hydroxyls are needed to photo-oxidized toluene to benzaldehyde, this may be the origin of the almost complete and irreversible depletion of the toluene conversion by using a dry reaction mixture.

Muggli and Falconer (1999) studied UV-Enhanced exchange of O_2 with H_2O adsorbed on TiO_2. They reported that Ultraviolet light dramatically increases the rate of isotope exchange between gas-phase O_2 and water adsorbed on TiO_2 at room temperature, but it does not affect the rate of CO_2-water exchange. Both ethanol and acetaldehyde, when coadsorbed with $H_2{}^{18}O$, dramatically decrease the rate of O_2 exchange, with adsorbed $H_2{}^{18}O$. This decrease is attributed to a combination of combination of competition for adsorbed oxygen between exchange and photoctalytic oxidation of adsorbed organic and blocking of the oxygen adsorption sites by the organic. The same oxygen species participate in O_2-$H_2{}^{18}O$ exchange and photocatalytic oxidation.

Obuchi *et al.* (1999) reported a promising method for the purification of air containing volatile organic compounds, photocatalytic decompositions of gaseous acetaldehyde over TiO_2/SiO_2 catalyst and over Pt-TiO_2/SiO_2 catalyst. Including the capture of intermediates on the catalyst surface and regeneration of the deactivated catalyst by heating have been investigated. From the observation of the photocatalyst surface before and after the reaction by FT-IR spectroscopy, they found that this was due to the adsorption of intermediates such as formic acid and acetic acid on the porous catalyst. When the Pt-TiO_2/SiO_2 catalyst was heated to temperature above 200°C, these substances can be removed and discharged as CO_2. The work suggests that the use of a Pt-TiO_2/SiO_2 catalyst will enable to construct a multifunctional reaction process for air purification. The harmful intermediates formed during the reaction were partly adsorbed on the porous catalyst and converted into CO_2 by heat treatment of the catalyst.

Sirisak *et al.* (1999) focussed on photocatalytic degradation of ethylene over thin films of titania supported on glass rings. Borosilicate glass rings were coated with a titania-sol generated by controlled hydrolysis of titanium isopropoxide. A reactant stream containing either 48.99 or 1055 ppm of ethylene was fed continuously to a tubular reactor packed with the coated glass rings and surrounded by blacklight blue fluorescent bulbs. At both high and low temperatures, titania supported on borosilicate glass rings exhibits higher photocatalytic activity for the oxidation of ethylene than unsupported titania pellets. Glass rings on which two layers of titania had been deposited have a higher activity than those on which only one layer of titania had been deposited. Preliminary kinetic studies of photocatalytic oxidation of ethylene suggest that the reaction rate can best be described using a Langmuir-Hinshelwood-Hougen-Watson rate expression.

Dumitriu *et al.* (2000) investigated photocatalytic degradation of phenol by TiO_2 thin films were prepared by directed current (dc) reactive sputtering, using various kinds of supports such as glass, silicon, alumina and glass coated with indium-tin oxide. Samples were characterized by x-ray diffraction (XRD), and automic force microscopy (AFM). Different TiO_{2-x} stoichiometries, crystal structures and morphologies were obtained by changing the best efficiency in respect with phenol mineralization was obtained for samples prepared using an Ar-H_2O mixture as the reactive gas. Indium-tin oxide supports provide the most efficient thin films. The adsorption of O could compete with adsorption of phenol or organic intermediates diminishing the degradation rate. Nearly stoichiometric, conducting TiO_2 thin films prepared with H_2O are better catalysts than semi-insulating films. The catalytic performances show some dependence on the nature of the supports used for TiO_2 immobilization.

Kozlov *et al.* (2000) demonstrated gas-phase ethanol photocatalytic oxidation on the series of TiO_2 samples by the FT-IR in situ method. TiO_2 samples were prepared by the hydrolysis of $TiCl_4$ under different pH, followed by annealing at 400^oC for 1 h. They found that the TiO_2 samples possessed similar physicochemical properties (porosity, specific area), but were found to have different photocatalytic activities because of the stability of the carboxylate species increase as the surface acidity decrease. The lower the acidity of TiO_2 surface, stronger is the interaction of carbon acids with it to form the carboxylate structures which form during the VOCs photooxidation. These carboxylate structures occupy the surface sites preventing further interaction of the gaseous reagents with the catalyst surface.

2.2 Comments

From the above reviewed literature, it can be seen that titanium dioxide shows high activity in photocatalytic decomposition of different classes of substances such as aldehyde, ketone, aromatic compounds, chlorinated compounds and alcohols. Most work, the concentration of reactant is used in the lower range (ppm). Moreover, titanium dioxide are used in many form as photocatalyst such as TiO_2 powder packed in the reactor, TiO_2 coated on substrate and platinized TiO_2.

There are many methods of titanium dioxide synthesis used for the photocatalytic reaction but a few works, TiO_2 synthesized by glycothermal method are not used in photocatalytic reaction. We think that this is the interesting point for using this titanium dioxide for isopropanol decomposition.

CHAPTER III

THEORY

The heterogeneous photocatalysis has been studies extensively for decontamination of air and water polluted by VOCs. Using TiO_2 as a catalyst appears to be a promising process. In this chapter an attempt is made to describe the photocatalytic process, the main factors involved in photocatalytic process, inhibition of electron-hole recombination by oxygen.

3.1 Photocatalytic process [Fujishima *et al.* (1999)]

The primary photocatalytic process occurring upon irradiation of a semiconductor catalyst. A semiconductor (SC) is characterized by an electronic band structure in which the highest occupied energy band, called valence band (VB), and the lower empty band called conduction band (CB), are separated by a band gap. The magnitude of the fixed energy gap between the electronically populated valence band and the largely vacant conduction band governs the extent of thermal population of the conduction band in its intrinsic state. The band gap also defines the wavelength sensitivity of the semiconductor to irradiation [Fox and Dulay (1993)]. When a photon of energy higher or equal to the band gap energy is absorbed by a semiconductor particle, an electron from the valence band is promoted to the conduction band with simultaneous generation of an electronic vacancy or "hole" (h^+) in the valence band. Figure 3.1 shows the photocatalytic process occurring on an illuminated semiconductor particle.

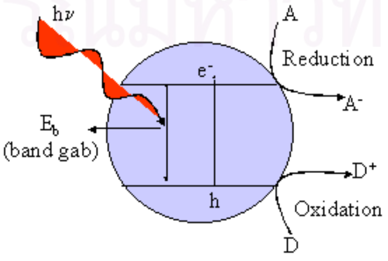


Figure 3.1 The photocatalytic process occurring on an illuminated semiconductor particle [Litter (1999)].

In most materials that are electrically conductive, i.e metals, two types of carriers – electrons (e^-) and holes (h^+) – immediately recombine on the surface or the bulk of particle in a few nanoseconds and the energy dissipated as heat (equation (3.1)). On semiconductor such as titanium dioxide, however, they survive for longer periods of time to allow these carriers can be trapped in surface states where they can react with donor (D) or acceptor (A) species adsorbed or close to the surface of the particle (equations (3.2), (3.3), (3.4)) [Litter (1999)].

Recombination $$h^+ + e^- \rightarrow \text{heat} \tag{3.1}$$

Photoexcitation $$\text{Semiconductor} + hv \rightarrow e^- + h^+ \tag{3.2}$$

$$h^+ + D \rightarrow D^+ \tag{3.3}$$

$$e^- + A \rightarrow A^- \tag{3.4}$$

Thereby, subsequent oxidation and reduction can be initiated.

In aqueous solution, hydroxyl radicals ($^{\cdot}OH$) production is favored because of the abundance of hydroxyl groups and water molecules on the surface of catalyst. However, in the gas phase, organic substrates can themselves act as adsorbed traps for the photogenerated hole since in the gas phase, water molecules are not the predominant species in contact with the catalyst. Although in the presence of water vapor, OH groups are presented on the catalyst surface and their contribution to photooxidation can not be discarded [Alberici *et al.* (1997)].

When adsorbed water molecules are oxidized by holes, hydroxyl radicals, which have strong oxidizing power are formed (equations (3.5), (3.6)).

$$h^+ + H_2O \rightarrow {}^{\cdot}OH + H^+ \tag{3.5}$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH \tag{3.6}$$

The hydroxyl radicals can then react with organic components, initially producing free radicals (unstable molecules that have one unpaired electron). When molecular oxygen is present (reactions always occur in the presence of oxygen from the air in the use of the photocatalyst for environment), because it also has unpaired electrons, it likes to react with these free radicals producing organic peroxyl radicals, which, in addition to containing an unpaired electron, also now contain two oxygens. These radicals can then take part in chain reactions. In a short time, organic compounds are completely degraded, i.e. converted into carbon dioxide and water.

Meanwhile, the electrons that are produced in the electron-hole pairs are also put to work. These electrons are used to reduce (i.e., add electrons) to oxygen in air. Because oxygen is easier to reduce than water, it will tend to be reduced, producing the superoxide radical anion ($O_2^{\cdot -}$) (equation 3.7).

$$e^- + O_2 \rightarrow O_2^{\cdot -} \qquad (3.7)$$

The superoxide anion attaches itself to the peroxyl radicals mentioned in the previous paragraph. The resulting unstable product now contains at least four oxygens and can decompose to produce a carbondioxide molecule. On the molecular scale, superoxide acts like a “ supercharge ”, greatly increasing the oxidation process, which is in fact a form of combustion. In addition to this mechanism, another interpretation proposed recently is that the formation in air of so-called atomic oxygen ($^{\cdot}O$), which is extremely reactive, directly acts on the carbon bonds in organic material

3.2 The main factors involved in photocatalytic process

There are two main factors involved in photocatalytic process. Photocatalysis is the combination of photochemistry and catalysis, it implies that light and catalyst are the main factors, which initiate the chemical transformation, oxidation and reduction reaction. Light is not only one, which can work effectively, but it, can work effectively when teamed up with catalyst especially titanium dioxide catalyst.

3.2.1 Photocatalyst [Fujishima *et al.* (1999)]

Catalyst that used in photocatalytic process usually called “photocatalyst”. In the previous section, photochemical process involves in electronic structure of photocatalyst.

Atoms have discrete energy levels for their electrons. Molecules often contain like atoms but the Pauli exclusion principle forbids identical quantum numbers in all respects, resulting in the “splitting” of a given atomic energy level into a set of closely spaced levels typically of order of the numbers of atoms involves energy levels split so finely that a so-called “band” structure of allowed energies (quantum states) emerges, with infinitesimal or virtually continual distribution of energy levels within a given “orbital”. For a semiconductor such as titanium dioxide (TiO_2), the highest filled band is termed the valence band, and the lowest unoccupied level is the conduction band. The separation of the valence band top from the conduction band bottom is termed the band gap [Ollis (1998)].

As already mentioned, the reaction starts with the exposure of photocatalyst to light. After light is absorbed by photocatalyst, two types of carriers - electron (e^-) and holes (h^+) - are generated. Unlike metals oxide, a semiconductor oxide is good photocatalyst because of the long live both of these carriers. For this reason semiconductor oxides are used in photocatalytic process such as TiO_2, ZnO, $SrTiO_3$, K_4NbO_2, Fe_2O_3 and SnO_2.

Especially titanium dioxide (TiO_2), titanium dioxide is one of the most basic materials in our daily life. It also has been used widely in photocatalytic process because of its radiation stability, non-toxicity and good reactivity [Alberici (1997)]. Naturally, the type of titanium dioxide that used as a pigment is different from that used as a photocatalyst. Might say that titanium dioxide has two aspects but one set of properties. Titanium dioxide is a semiconductor and is chemically activated by light energy. Its photoactivity tends to decompose organic materials that come in contact with it.

Titanium dioxide had take on any of the following three crystal structures.

1. Rutile, which tends to be more stable at high temperatures. Almost always a rutile type is used in industrial products such as paints, cosmetics foodstuffs and sometimes found in igneous rocks.

2. Anatase, which tends to be more stable at lower temperatures. This type generally shows a higher photoactivity than other types of titanium dioxide.

3. Brookite, which is usually found only in minerals and has a structure belonging to the orthorhombic crystal system.

Both of rutile and anatase type have a structure belonging to the tetragonal crystal system and they are showed in figure 3.2. The two tetragonal crystal types are more common because they are easy make. Comparisons of the principle physical properties of the rutile and anatase types of titanium dioxide are tabulated in the table 3.1.

One of the reasons for the anatase type titanium dioxide is more photoactive than the rutile type may lie in the differences in their so-called energy band structures.

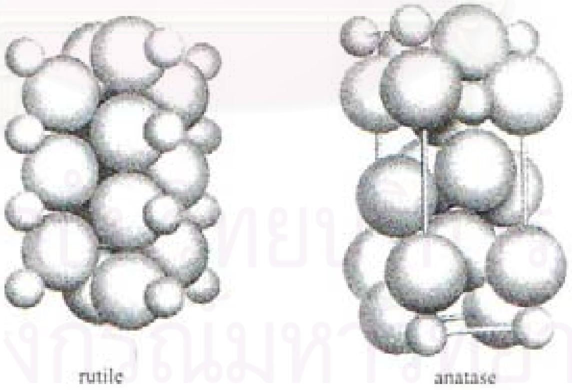


Figure 3.2 Crystal structure of TiO_2 [Fujishima *et al.* (1999)].

Table 3.1 Comparison of rutile and anatase [Fujishima *et al.* (1999)]

Properties	**Rutile**	**Anatase**
Crystalline form	tetragonal system	tetragonal system
Lattice constant a	4.58 Å	3.78 Å
Lattice constant c	2.95 Å	9.49 Å
Specific gravity	4.2	3.9
Refractive index	2.71	2.52
Hardness	6.0-7.0	5.5-6.0
Permittivity	114	31
Melting point	1858^{o}C	Changes to rutile at high temperature

The band gap energy of a semiconductor is the minimum energy of light required to make the material electrically conductive or in the other words, to get the electrons excited enough to get moving. For anatase –type titanium dioxide this energy is 3.2 electron volts (eV), which corresponds to UV light (388 nanometers), while the band gap energy for the rutile type is 3.0 eV, corresponding to violet light (413 nanometers). In more technical terminology, the band gap energy for a semiconductor indicates the minimum energy of light necessary to produce conduction band (CB) electrons, which, for example, can give rise to electrical conductivity (photoconductivity) and valence band (VB) “holes,” which are actually the absence of electron. These holes can react with water to produce the highly reactivitv hydroxyl radical ($^{\cdot}$OH). Both the holes and the hydroxyl radicals are very powerful oxidants, which can be used to oxidize most organic materials. The level of the CB for anatase turns out to be 0.2 eV higher than that for rutile (figure 3.3).

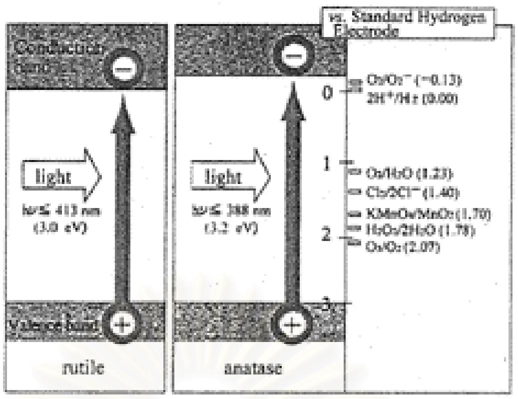


Figure 3.3 Energy diagram for TiO_2 and relevant redox potentials [Fujishima *et al.* (1999)].

The VB energies for anatase and rutile are both similar, which is very low in the energy diagram, meaning that, for both materials, the VB holes (and the hydroxyl radicals) have great oxidizing power. The CB energy for rutile is close to the potential required to electrolytically reduce water to hydrogen gas, but that for anatase is higher in the energy diagram, meaning that it has higher reducing power. This means that it can drive the very important reaction involving the electrolytic reduction of molecular oxygen (O_2) to superoxide ($O_2^{\cdot -}$). Superoxide is found that it's almost as important as the holes and hydroxyl radicals in breaking down organic compounds.

3.2.2 Light [Fujishima *et al.* (1999)]

Light is a form of energy characterized by waves, can be classified by wavelength, which is the distance between wave crests as indicated in figure 3.4. The light visible to eyes is only small part of total light spectrum, these range from about 400-700 nanometers (Note: one nanometer is one per million of a centimeter). But the visible light is not usually used for the photocatalytic process because the most active and usually used catalyst for this process is titanium dioxide which has band gap energy is about 3.0 eV or 400 nanometer, which falls in the near ultraviolet (figure 3.5). Photoexcitation of photocatalyst molecule involving absorption of energy equal to the energy difference between electron states using, so near UV or UV light (300-400 nanometer) is used for photocatalytic process.

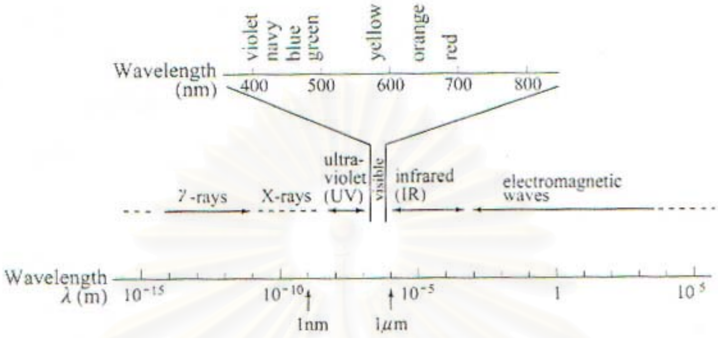


Figure 3.4 The spectrum of light [Fujishima *et al.* (1999)].

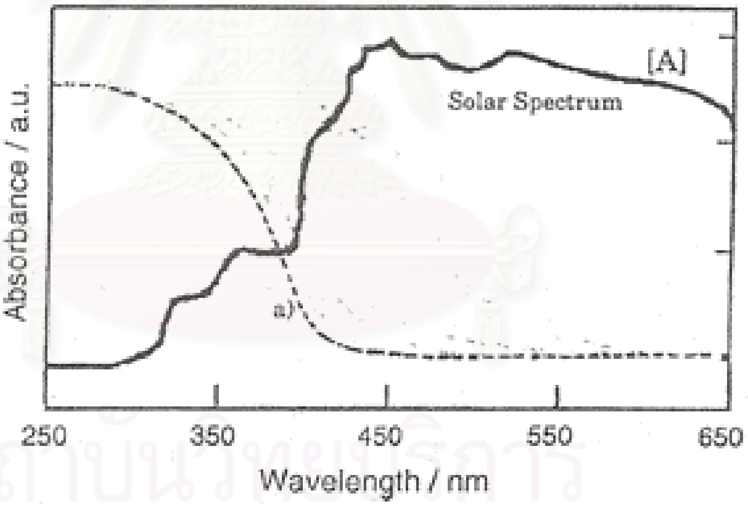


Figure 3.5 The absorption band of the TiO_2 photocatalyst to solar spectrum [Anpo *et al.* (1997)].

Ultraviolet light (UV), which includes wavelengths shorter than 400 nanometers. Although UV light is a part of solar light and even interior lighting, it is only limited part. Even in the outdoors, during daytime, UV light constitutes only about 1 mW cm^{-2} at the most. UV light, however, can work effectively when teamed up with titanuim dioxide.

3.3 Inhibition of electron-hole recombination by oxygen [Fox and Dulay (1993)]

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of oxygen or by the addition of several inorganic oxidizing species, such as peroxydisulfate, periodate, and peroxides. The effect of molecular oxygen is primarily as an efficient conduction band electron trap, suppressing electron-hole recombination.

Electron trapping similarly suppresses electron-hole recombination. Because the conduction band of TiO_2 is nearly isoenergetic with the reduction band potential of oxygen inert solvents, adsorbed oxygen serves as a trap for the photogenerated conduction band electron in many heterogeneous photocatalytic reactions. It is often found that photocatalytic activity is nearly completely suppressed in the absence of oxygen, possibly because of back interfacial electron transfer from active species present on the photocatalyst surface, and the steady-state concentration of oxygen has a profound effect on the relative rate of photocatalyzed decontamination occurring under ambient conditions. The resulting species, superoxide $O_2^{\cdot -}$, is highly active and can attack either organic molecules or adsorbed intermediates or, after protonation, can provides another source for surface-bound hydroxy radicals. Its precise role has yet to be established unambiguously.

Oxygen concentration dependence has been explained as involving O_2 adsorption and depletion, both in the dark and during illumination, at the photocatalyst surface. That rutile possesses much lower photoactivity than anatase (despite the fact that both forms of TiO_2 are thermodynamically capable of reducing

O_2) has been explained by the higher rate of electron-hole recombination on rutile because of its lower capacity to adsorb O_2.

The superoxide ($O_2^{\cdot -}$) thus formed is an effective oxygenation agent, attacking both neutral substrates and surface-adsorbed radicals and/or radical ions. This attack occurs before desorption from the surface since the presence of dissolved superoxide traps in solution does not inhibit photocatalytic reduction-protonation sequence generates hydrogen peroxide, which can be decomposed on the photocatalyst surface to form hydroxy radical, which can also initiate oxidative functional group interconversions.

CHAPTER IV

EXPERIMENT

This chapter contains details about: the catalyst preparation method, the photocatalytic activity measurements and the characteristic of catalyst. In each section, detail of experimental procedures, including the materials and apparatus are described.

The scope of this study:

Photocatalyst: TiO_2 synthesized by glycothermal method, JRC-TIO1 (photosensitive TiO_2) and JRC-TIO4 (normal anatase type) were Japan reference catalyst that obtained from Department of Material Science, Shimane University.

Reactant gas : Air (used as O_2 source)
Reactant liquid : Isopropanol ($(CH_3)_2CHOH$)
Source of light : 500 W Mercury lamp
Concentration of isopropanol : 4000-17000 ppm
Pressure operation : 1 bar
Reaction temperature : 40-80^{o}C
Space velocity of air : 1500-9000 ml.hr^{-1}.g^{-1}

4.1 Catalyst preparation method

TiO_2 photocatalyst was prepared by glycothermal method. Titanium (IV) alkoxides was dissolved in a portion of 1,4 butanediol in a test tube, then autoclaved at high temperature (300^{o}C) and high pressure for 2 hours. After the autoclave treatment, the resulting powders were washed repeatedly with methanol and dried in air overnight. The autoclaved TiO_2 were calcined in air 30 ml/min at 500^{o}C for 1 hour and the heating rate was 10^{o}C/min before being used as photocatalyst in reaction.

4.2 Catalyst characterization

4.2.1 Specific surface area Measurement

The BET surface area was determined by nitrogen absorption in an automatic apparatus ASAP-2000 constructed by Micromeritics U.S.A. The data obtained were recorded by a microcomputer.

4.2.2 Fourier Transform Infrared Spectrometer (FT-IR)

The functional group on the catalyst surface was determined by FT-IR using Nicolet model Impact 400. Each sample was mixed with KBr with ratio of sample: KBr equal to 1:100 before being formed into a thin wafer. Infrared spectra were recorded between 2000 to 400 cm^{-1} on a microcomputer. FT-IR spectra were measured at room temperature.

4.2.3 X-ray Diffraction Pattern (XRD)

The phase structure were determined by X-ray diffraction, Siemens D-5000 X-ray diffractometer using CuKα filtered radiation in the 2θ range of $20\text{-}60^{o}$. The sample is placed into XRD plate before placing on the measured position of XRD diffractometer.

4.3 The experimental operation and apparatus

The basic experimental set up used in the present work is shown in figure 4.1. The catalyst particles were spread along horizontal quartz tube with an internal diameter of 1.0 cm (the length of the catalyst spread; 9 cm) between quartz glass wool layer.

A cylinder of air, equipped with a pressure regulator (1 bar), an on-off valve and fine-metering valve used for adjusting the required values before bubbling through a glass saturator containing liquid isopropanol. The air containing isopropanol in a concentration range of 4000-17000 ppm was continuously supplied to the horizontal quartz at a constant flow rate. The isopropanol concentration was set up by changing the temperature of the water bath and then controlling the evaporation rate of isopropanol.

In a typical test, an air stream contaminating isopropanol under study was passed through the photoreactor in the absence of UV illumination until the gas-solid adsorption equilibrium under the flow was established. After the adsorption process reached equilibrium (typically 3-180 min, depending upon the nature and the concentration of the VOC), as indicated by identical inlet/outlet VOC concentrations. Then the 500 W mercury lamp (source of UV light), located outside the horizontal quartz (distance between the lamp and catalyst; 25 cm), were switched on to illuminate UV light onto surface of the catalyst particles and the outlet gas was sampled at regular intervals.

The feed and product stream was analyzed by flame ionization detector gas chromatograph Shmadzu 14A. The amount of CO_2 formed in the reaction was measured using a gas chromatograph Shimadzu GC-8A equipped with thermal conductivity detector. The operating conditions of GC are described in appendix B.

The temperature of reactor was controlled by an automatic temperature controller. An automatic controller consists of a magnetic contactor, a variable voltage transformer, temperature controller and Eurotherm digital temperature indicator. Temperature was measured at the initial of the catalyst spread along the quartz in the reactor. In operation at high temperature (above the room temperature), the reactor was heat to the required temperature before the feed reactant was fed into the reactor.

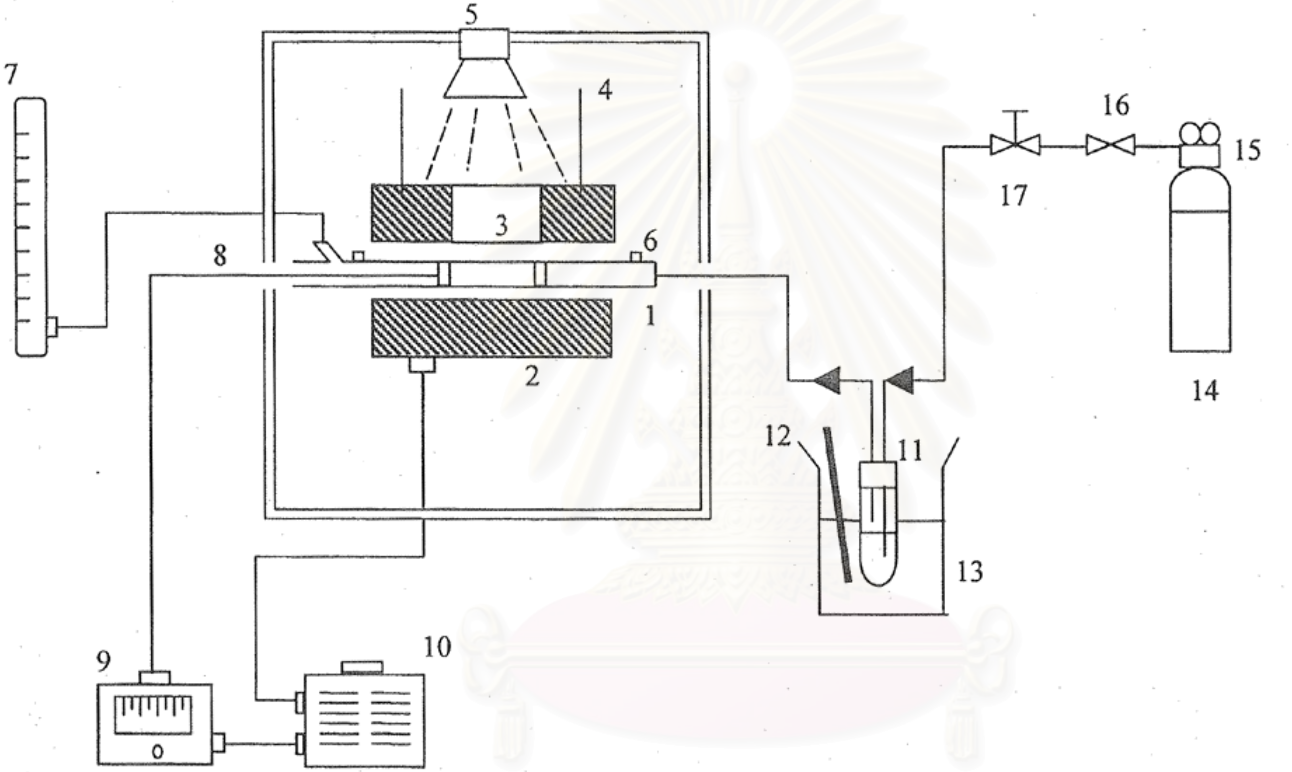
The result of photocatalytic test was calculated in the term of:

$$\%\ \text{A converted} = \frac{\text{mole of A reacted}}{\text{mole of A in feed}} \times 100\ \%$$

$$\%\ \text{selectivity to B} = \frac{\text{mole of A converted to B}}{\text{mole of A reacted}} \times 100\%$$

(A is reactant)

(B is product reaction)



1. Reactor
2. Furnace
3 Window for irradiation
4. Aluminium plate
5. Source of light
6. Sampling port
7. Bubble flow meter
8. Thermocouple
9. Temperature controller
10. Variable voltage transformer
11. Saturator
12. Thermometer
13. Solvent bath
14. Air tank
15. Pressure regulator
16. On-off valve
17. Metering valve

Fugure 4.1 Flow diagram of the photocatalytic reaction system

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are depicted into two major parts including the catalyst characterization and the photocatalytic test by decomposition of isopropanol.

5.1 Catalyst analysis

5.1.1 BET surface areas of the catalysts

BET surface areas of the catalysts which are determined by BET surface area measurement are listed in table 5.1 below.

Table 5.1 The BET surface areas of the catalysts

Catalysts	**BET surface area (m^2/g)**	**Synthesis of catalyst**
As-synthesized TiO_2	92.58	Glycothermal method
JRC-TIO1	79.12	Source, dissolved in H_2SO_4 and heated. Filtered washed, and calcined
JRC-TIO4	49.40	$TiCl_4 + O_2 + H_2 \rightarrow TiO_4 + HCl$ in gas phase

The data in table 5.1 shows that the surface area of TiO_2 synthesized by glycothermal method is higher than the both of Japan reference catalysts (JRC-TIO1 and JRC-TIO4). It can be seen that the TiO_2 synthesized in the different method having different surface area and glycothermal is a good method for obtaining high surface area TiO_2. Therefore, it is expected to be used for photocatalyst in many reactions.

5.1.2 X-ray Diffraction

The phase structure of catalysts is characterized by XRD. The X-ray diffraction patterns of all catalysts are depicted in figures 5.1-5.3. In the 2θ range from 20^o to 60^o, XRD spectrum of TiO_2 synthesized by glycothermal method and JRC-TIO1 shows evident five peaks, all of those peaks can be attributed to anatase. No peaks other than those attributable to anatase were observed. XRD spectrum of JRC-TIO4 shows peaks that can be attributed to anatase like TiO_2 synthesized by glycothermal method and JRC-TIO1 too and the rutile phase can be observed in the 2θ range, four peaks: 27.7, 36.4, 41.6 and 57.3.

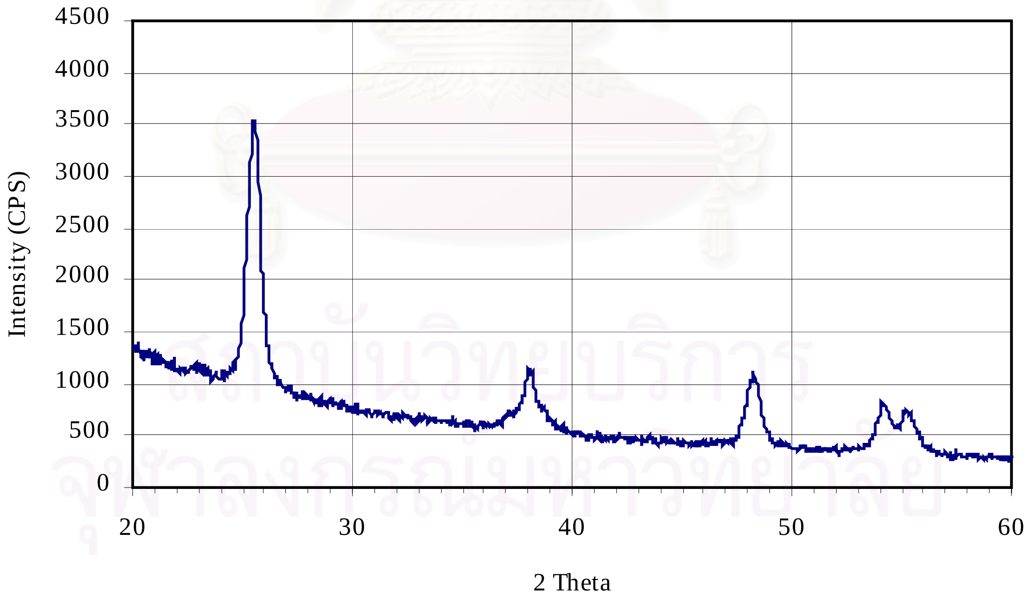


Figure 5.1 X-ray diffraction pattern of TiO_2 catalyst synthesized by glycothermal method

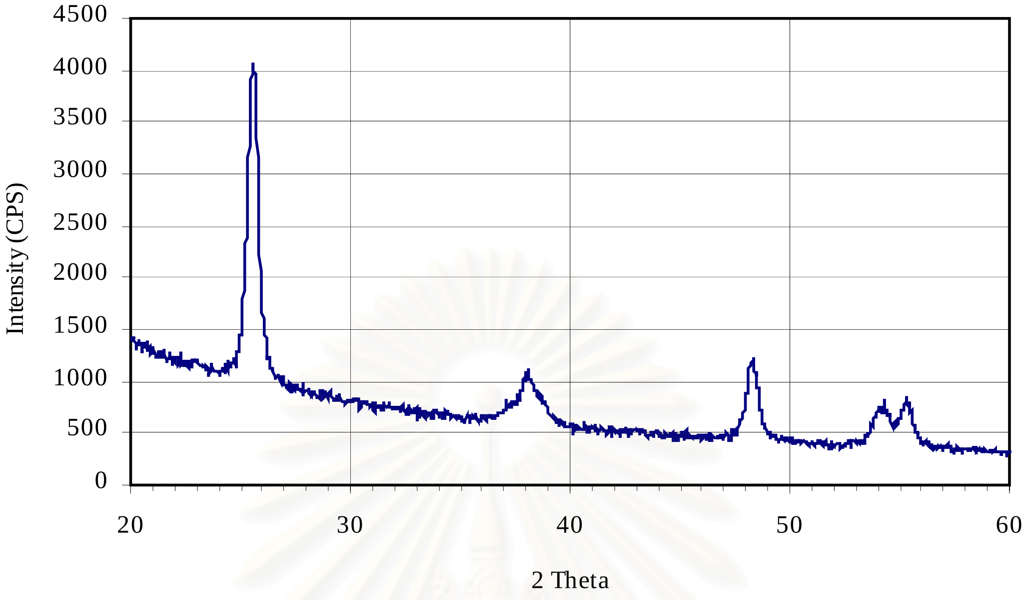


Figure 5.2 X-ray diffraction pattern of JRC-TIO1 catalyst

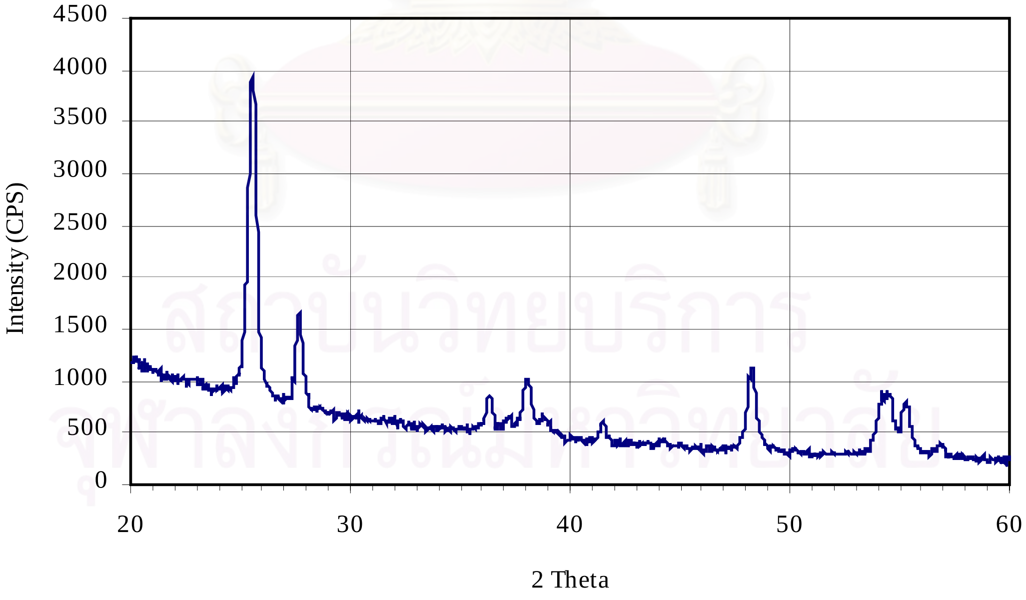


Figure 5.3 X-ray diffraction pattern of JRC-TIO4 catalyst

5.1.3 Fourier Transform Infrared Spectrometer (FT-IR)

Results of FT-IR spectrum of all catalysts are exhibited in figures 5.4-5.6. The infrared radiation in the proper wavelength of 400-2000 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 400-800 cm^{-1}for all catalysts.

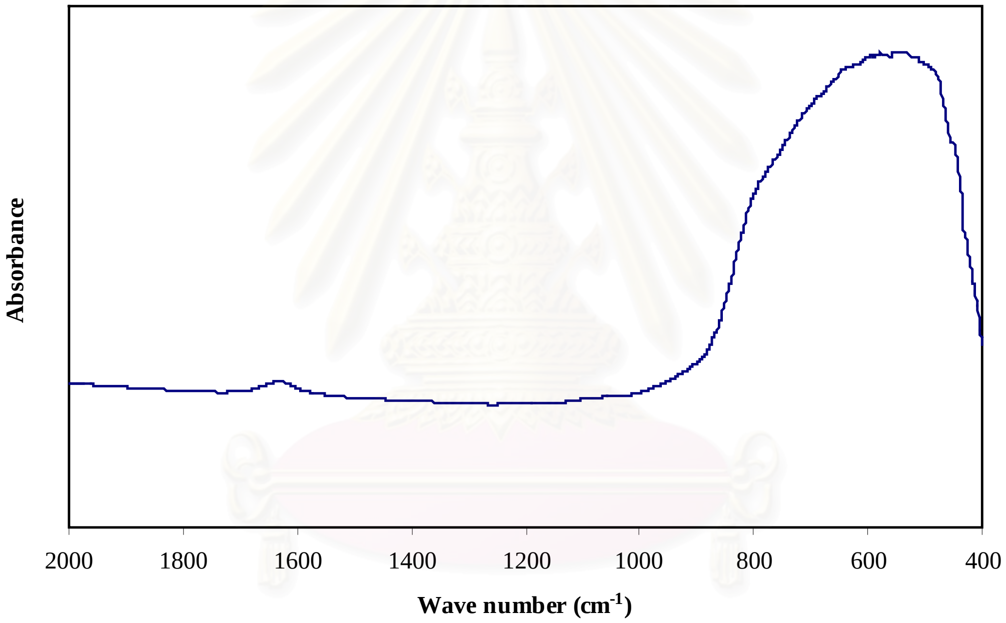


Figure 5.4 IR spectrum of TiO_2 synthesized by glycothermal method

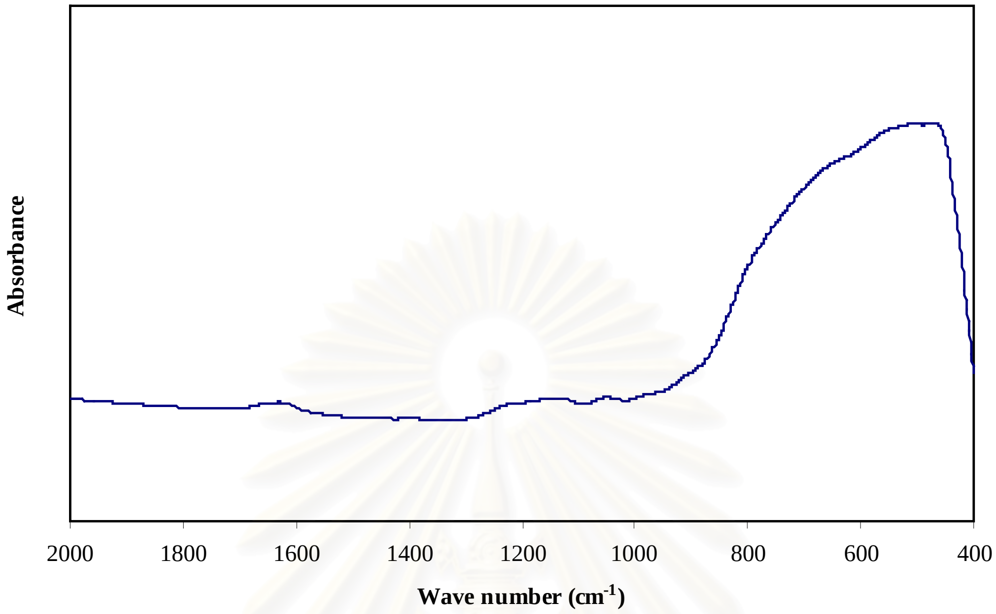


Figure 5.5 IR spectrum of JRC-TIO1 catalyst

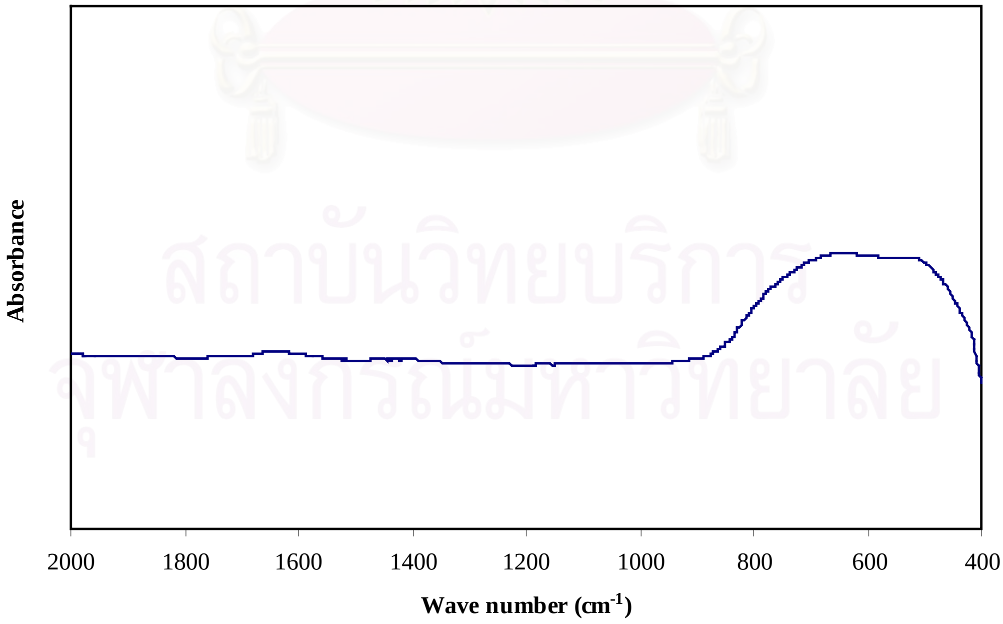


Figure 5.6 IR spectrum of JRC-TIO4 catalyst

5.2 Photocatalytic reaction test

5.2.1 Photocatalytic decomposition of isopropanol by using different catalyst

In this study, the catalysts used are TiO_2 synthesized by glycothermal method and two Japan reference TiO_2 (JRC-TIO1 and JRC-TIO4). All three catalysts were from different synthesis methods. Figure 5.7 shows the profiles of conversion of isopropanol using three different catalysts during photocatalytic decomposition of 4872 ppm gaseous isopropanol. The flow rate of air was set at 20 ml/min. The photocatalytic reaction operated at room temperature. After switching on the UV lamp of the reactor, the photocatalytic reaction started. A typical increase of temperature inside the furnace due to the heat released from the UV lamp is about $15^{o}C$ and final temperature inside reactor at equilibrium is about $40^{o}C$ for all runs at ambient temperature operation.

The first 150 minutes of running is the waiting time for system to reach an equilibrium between the gaseous and adsorbed isopropanol on the catalyst surface and the irradiation were not conducted. For all three catalysts, figure 5.7 shows the same behavior. After the beginning of UV irradiation, the conversion of isopropanol increases up to the highest conversion and decreases to the conversion at the steady state for 600 minutes operation time. The increase of conversion to the highest value in the initial period operation time due to the amount of species adsorbed on catalyst surface was at the saturated value. After that, a decrease conversion is observed due to the amount of species adsorbed on catalyst surface was decreased. Then, the conversion at the final time of operation was nearly constant due to the equilibrium between the adsorption of gaseous on the catalyst surface and the consumption of surface species.

The highest conversion is observed for the run using JRC-TIO1 catalyst. It takes about 180 minutes after UV irradiation began to reach the highest conversion (51%). The conversion is slightly constant at the final time of irradiation (33%).

Although the conversion of isopropanol for JRC-TIO1 catalyst is higher than that of TiO_2 synthesized by glycothermal method and JRC-TIO4, the main product detected is not CO_2. Acetone and traces of other small intermediate organic compound are detected. CO_2 production is almost not detected. The result of products selectivity is shown in figure 5.8.

For TiO_2 synthesized by glycothermal method used in this reaction, the isopropanol conversion of it is higher than JRC-TIO4 but lower than JRC-TIO1. Even if the conversion of it is lower than that of JRC-TIO1, the main product detected is CO_2. Small amount of acetone is observed (figure 5.8). The highest conversion of this TiO_2 is 42% in 120 min after starting photocatalytic reaction and decreases to the steady state (~27%). This conversion is 10% more than the conversion of JRC-TIO4.

In the reaction using JRC-TIO4 as the photocatalyst, the conversion observed is lowest in all three catalysts in this experiment. At steady state, the conversion is about 18% and the main product detected is CO_2. Small amount of acetone is observed (figure 5.8).

It can be seen that TiO_2 synthesized by glycothermal method has higher CO_2 selectivity than Japan reference TiO_2. Even if the conversion of isopropanol in this photocatalytic reaction is not much, the main product is only CO_2, which is the least harmful product. The product from this reaction using JRC-TIO1 is acetone which are not the desired product and more harmful than the CO_2. From XRD results, it can be seen that the structure phases of JRC-TIO4 are both of anatase and rutile. For TiO_2 synthesized by glycothermal method and JRC-TIO1, the structure phase observed is only anatase. This means that the activity in this reaction depends on the structure phase of catalyst. Moreover, the TiO_2 catalyst which has only anatase phase is not always necessary to be photoactive for photocatalytic reaction. It also depends on the synthesized method for obtaining the high activity TiO_2.

When TiO_2 is illuminated by the light of an energy greater than the band gap, e^- and h^+ are generated. The e^- and h^+ need to diffuse to catalyst surface where they are captured by electron and hole acceptors. Water and O_2 molecules adsorbed on surface catalyst are captured with h^+ and e^- and then produced $^{\cdot}OH$ and $O_2^{\cdot -}$, respectively. Both $^{\cdot}OH$ and $O_2^{\cdot -}$ are the active radicals to take a part in the chain reaction with organic compounds and then the organic compounds are degraded.

As mentioned, water is not the predominant species adsorbed on surface catalyst but isopropanol is the predominant species adsorbed in the photocatalytic decomposition of isopropanol. Apart from the reaction of water molecules, isopropanol can be trapped with h^+ and produced acetone, CO_2 and H_2O which are the most products found in this reaction and the trapping of e^-- h^+ are competitive with the recombination of e^- and h^+. It can be expected that reaction site of acetone oxidation (second step of isopropanol) are site on titanium dioxide, not site of oxygen. Hence, the acetone is not oxidized continuously to the small product in this reaction when all site of oxygen are used in the first step oxidation (isopropanol oxidation).

5.2.2 Effect of light to photocatalytic reaction

Blank test is performed at the same experimental conditions used for 5.2.1 section but in the absence of light. The titanium dioxide synthesized by glycothermal method is chosen for using as the photocatalyst in this case. The reactor is heated to 40°C instead of heating due to the UV lamp. No reactivity is observed in this case as shown in figure 5.9. The little conversion is observed in blank test. This may be caused by raised temperature when UV lamp is switched on and thus the density of gas is lower. Therefore, the amount of isopropanol per unit gas volume in gaseous phase is decreased (because gas samples were withdrawn at constant volume, not constant pressure). It shows that catalyst alone can not bring about the occurrence of the photocatalytic process. It can be seen that both light and photocatalyst are the main factor for photocatalytic reaction.

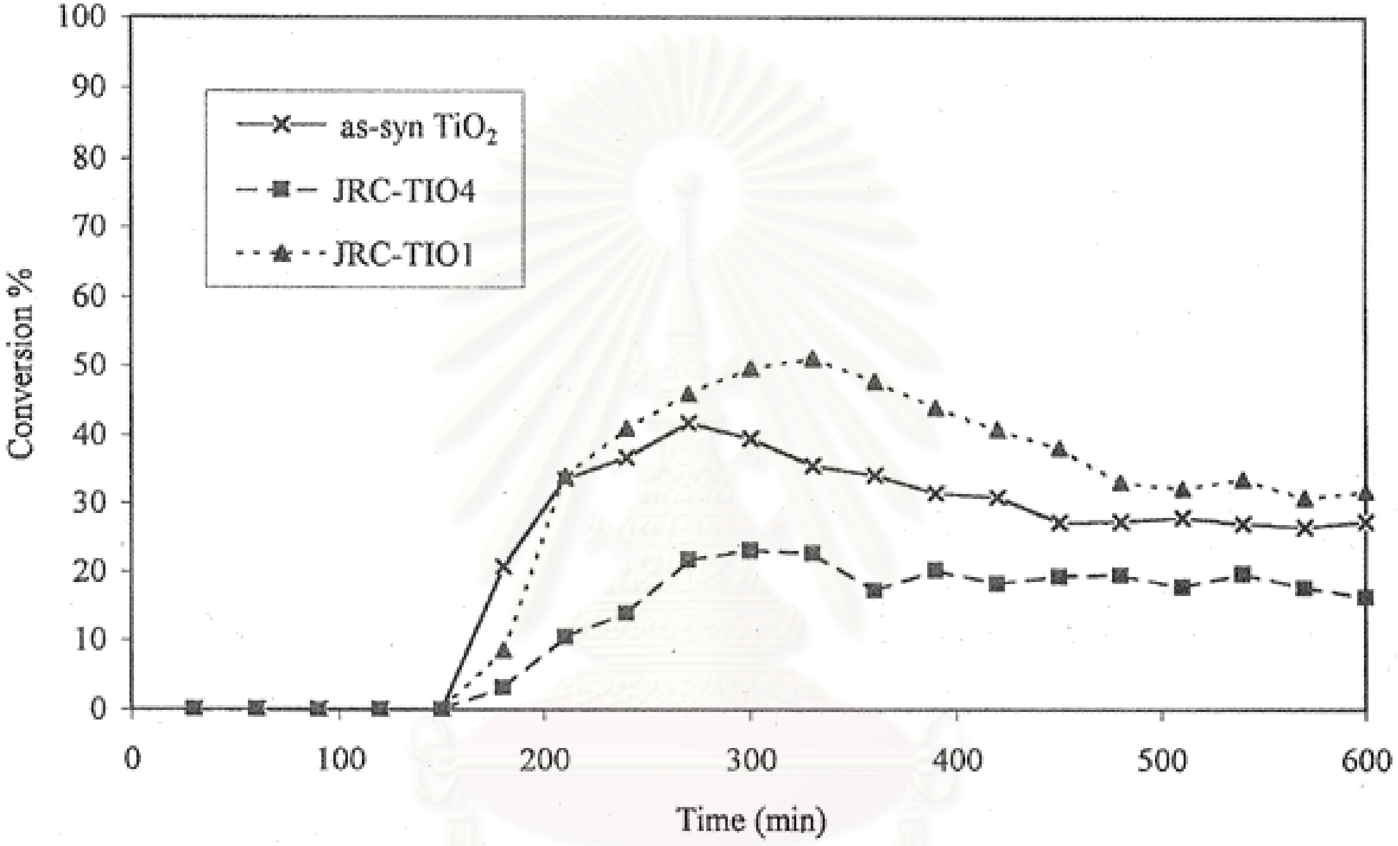


Figure 5.7 Time course of conversion in the photocatalytic decomposition of isopropanol over different catalysts. Experimental conditions: 20 ml/min flow rate of air, room reaction temperature and 4872 ppm isopropanol.

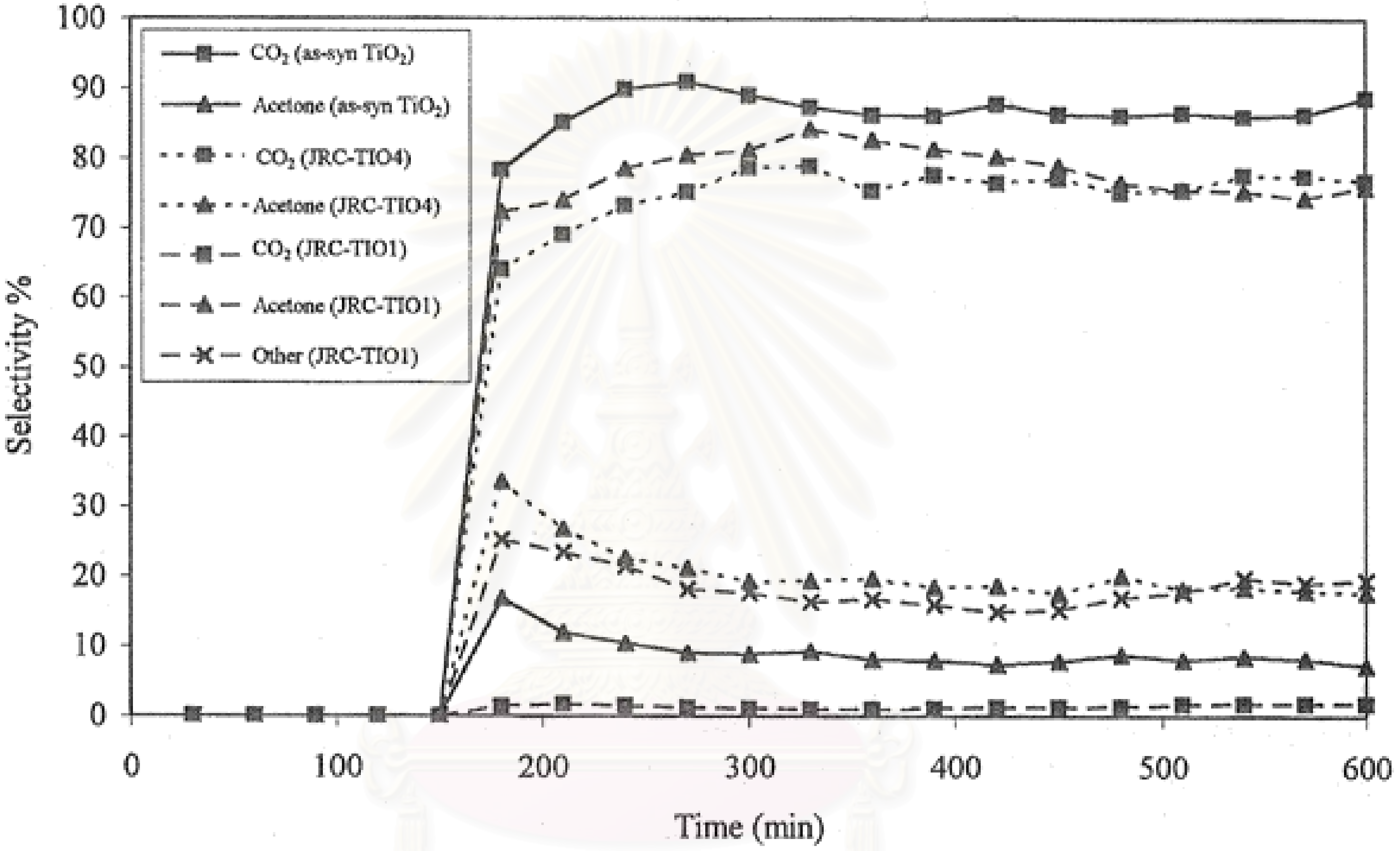


Figure 5.8 Time course of selectivity in the photocatalytic decomposition of isopropanol over different catalysts. Experimental conditions: 20 ml/min flow rate of air and 4872 ppm isopropanol.

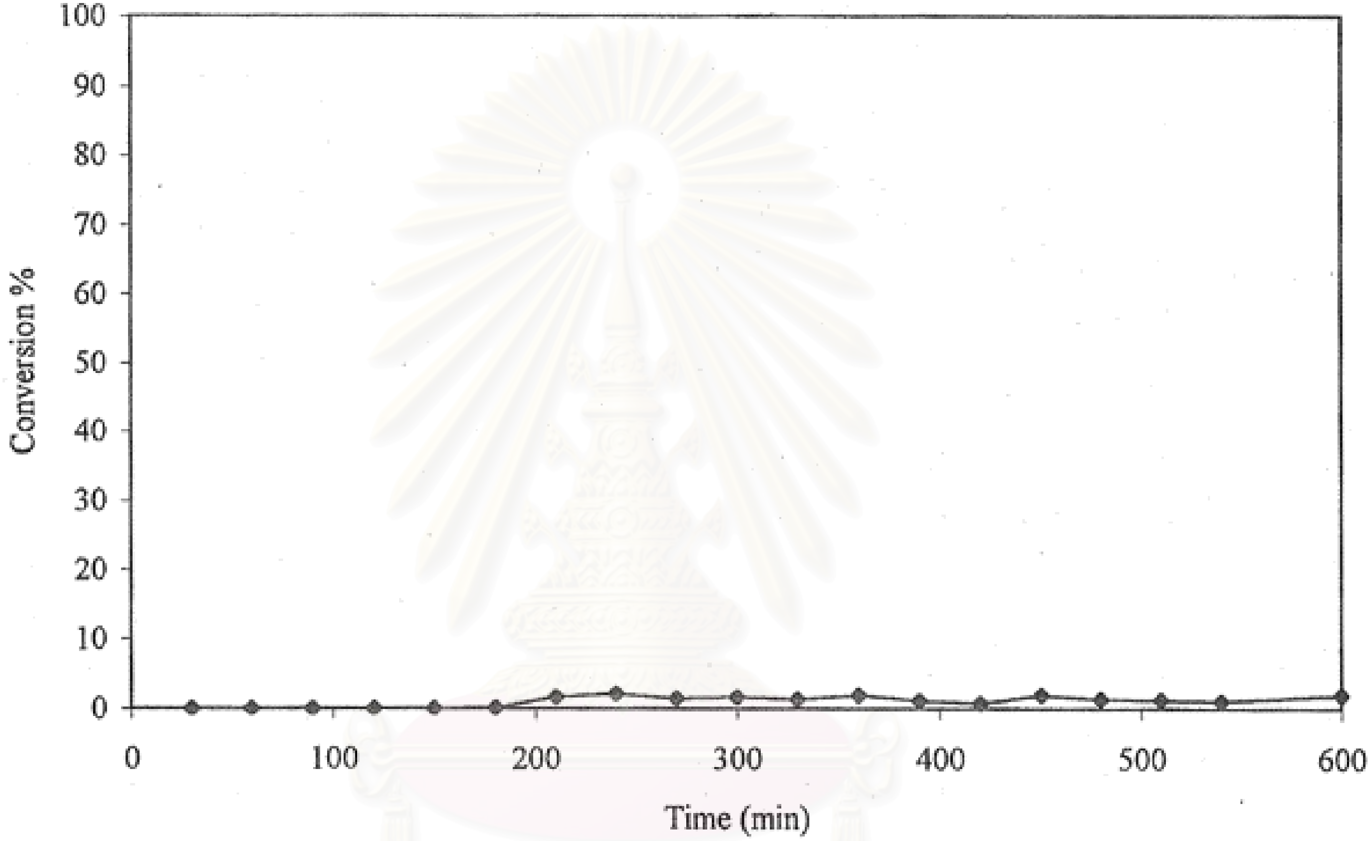


Figure 5.9 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO2 synthesized by glycothermal method for blank test. Experimental conditions: 20 ml/min flow rate of air and 4872 ppm isopropanol.

5.2.3 Effect of operational parameters on the decomposition of gaseous isopropanol

In this study, titanium dioxide synthesized by glycothermal method is chosen for all runs.

5.2.3.1 Effect of initial concentration of isopropanol

The initial concentration of gaseous isopropanol used for this experiment is in the range of 4000-17000 ppm. The conditions used were: flow rate of air 20 ml/min and ambient reaction temperature. The profiles of isopropanol decomposition over TiO_2 synthesized by glycothermal method are shown in figure 5.10. It shows that the photocatalytic decomposition of isopropanol depends on the initial concentration of isopropanol. The conversion of isopropanol increases with decreasing initial isopropanol concentration. But it is not clear at 7881 ppm isopropanol. For 4872, 12399 and 16527 ppm isopropanol, the conversion of isopropanol for each run reaches to the highest value 120 minutes after UV irradiation. The lowest conversion at steady state observed is 17% at 16527 ppm isopropanol and the highest one observed is 27% at 4872 ppm isopropanol. Further decrease of initial isopropanol concentration result in a progressive increasing conversion.

Figure 5.11 shows plot for the amount of isopropanol converted against different initial concentration of isopropanol in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by method. It can be seen that the decomposition rate (amount of isopropanol converted) of isopropanol increases rapidly with increasing initial concentration of isopropanol in a region of low concentration and tends to slow down in a region of high concentration. The conversion curve of isopropanol oxidation is the same as Langmuir adsorption isotherm curve. From this result, it can be concluded that this reaction depends on the adsorption on catalyst surface.

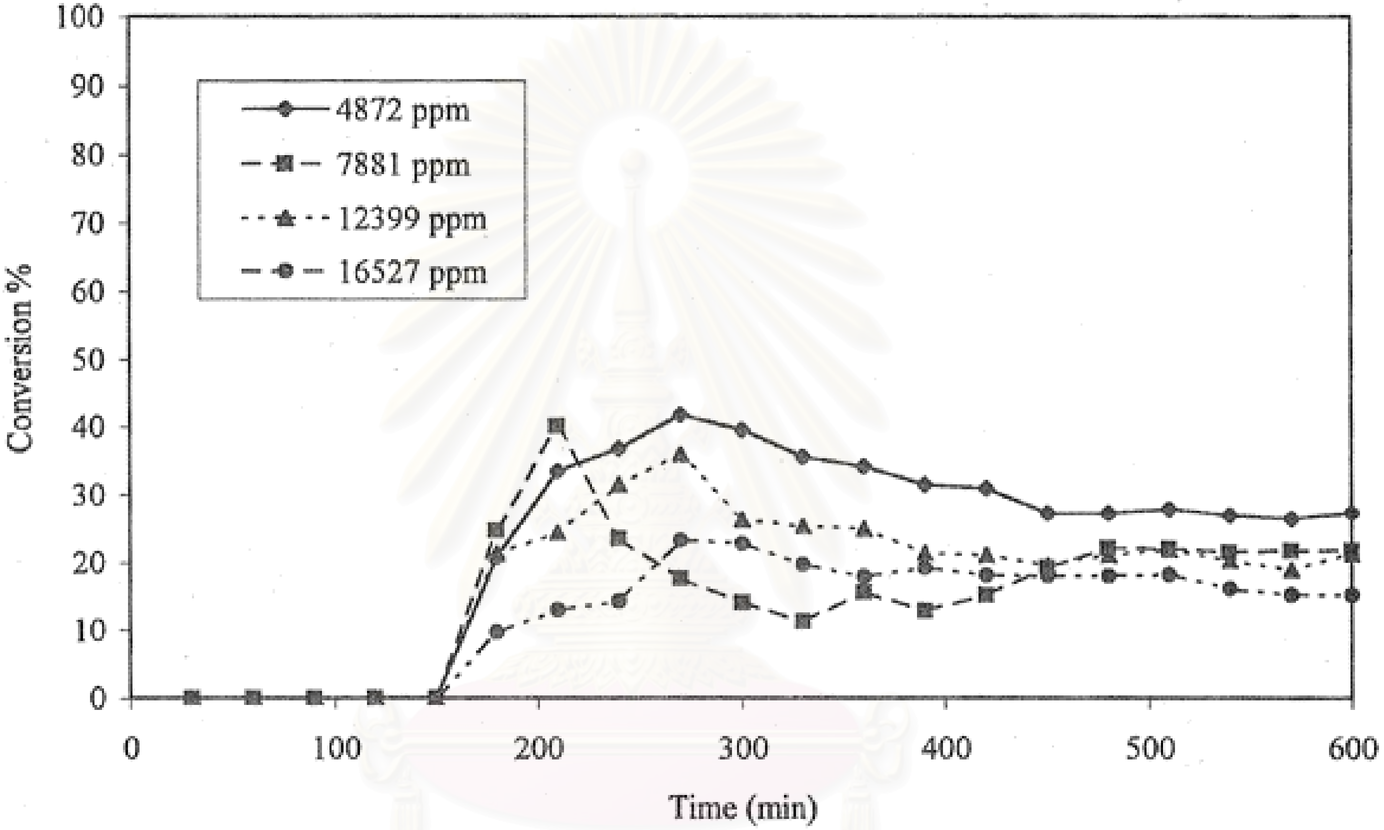


Figure 5.10 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by Glycothermal method. Experimental conditions: 20 ml/min flow rate of air and room reaction temperature.

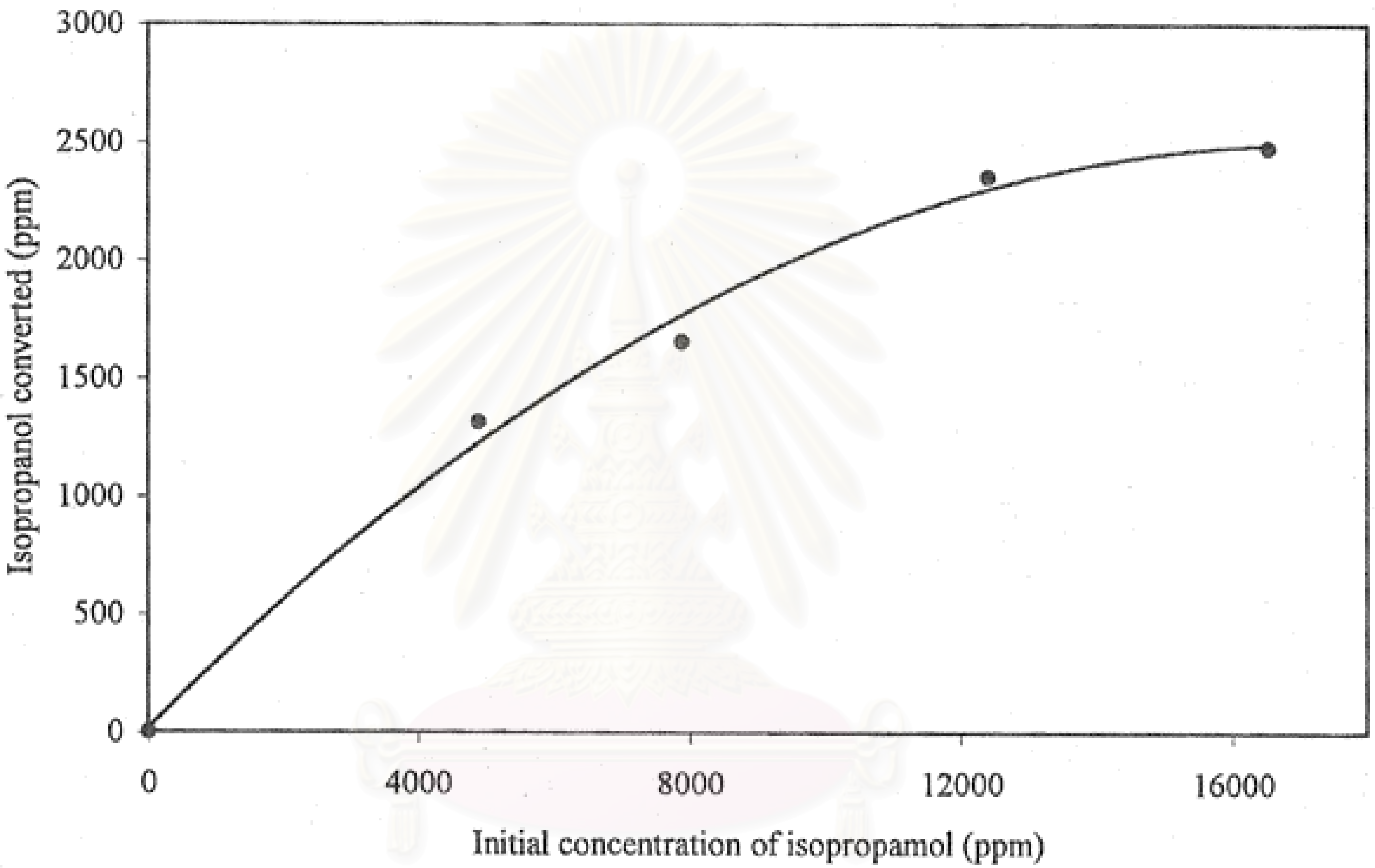


Figure 5.11 Langmuir plot of initial concentration of isopropanol vs isopropanol converted for photocatalytic reaction of Isopropanol over TiO_2 synthesized by glycothermal method

5.2.3.2 Effect of space velocity

This experiment is separated in two parts. In the first part, the space velocity is varied by changing flow rate of air. In the second part, the space velocity is varied by changing catalyst weight.

In first part, the isopropanol concentration is fixed at 4872 ppm. The amount of TiO_2 used is 0.4 g and the reaction operated at room temperature. The space velocity is varied by changing flow rate of air in the range 10-60 ml/min. The decomposition curves presented in figure 5.13. It shows that the conversion of isopropanol decreases with increasing space velocity of air (flow rate of air). The highest conversion at steady state observed is at 10 ml/min space velocity of air (30%).

The space velocity of air has an effect on the decomposition of isopropanol, since gaseous isopropanol is carried pass semiconductor surface by air. Therefore increasing flow of air results in decreasing time for generated active species ($^{\cdot}OH$ and $O_2^{\cdot -}$) to react with isopropanol molecules on the surface of photocatalyst. Moreover, the time for trapping of adsorbed molecules with e^- and h^+ photogenerated on the photocatalyst surface is short too. The opportunity of e^- and h^+ recombination is increase, consequently the active species is less generate and then react with the organic molecules.

In second part, the space velocity is varied by changing the weight of TiO_2 catalyst spread along quartz tube (the length of quartz spread with catalyst is 9 cm). Isopropanol concentration is fixed at 4872 ppm and flow rate of air is fixed at 20 ml/min. The weight of catalyst is varied in range 0.2-1.0 g. As shown in figure 5.14, when the catalyst is increased 0.2 g to 0.4 g, the conversion of isopropanol at steady state is up to 27% because of decreasing space velocity and increasing surface exposed UV light. Figure 5.12 shows the cross section of the reactor which was spread with the catalyst. When the catalyst weight was increased to 1.0 g, the amount of catalyst is so much more. Although the space velocity is slow, the catalyst surface exposed UV light is less than of using less catalyst weight. Therefore, a drop in conversion is observed when the catalyst weight was increased to 1.0 g. It can be seen that the surface exposed UV light in the reactor is important to the photocatalytic reaction.

Figure 5.12 The cross section of the reactor which spread with the catalyst

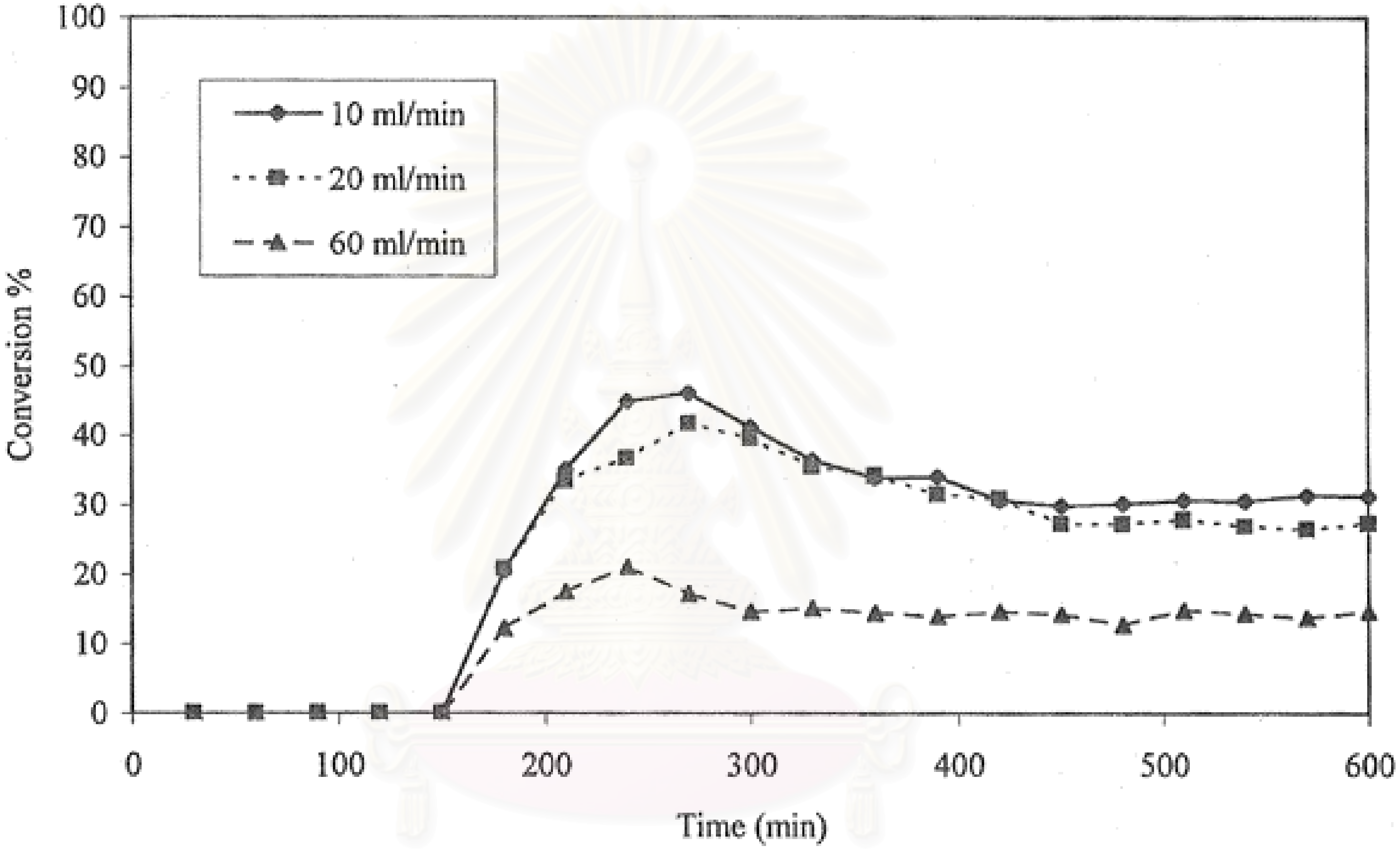


Figure 5.13 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by glycothermal method. Experimental conditions: room reaction temperature and 4872 ppm isopropanol.

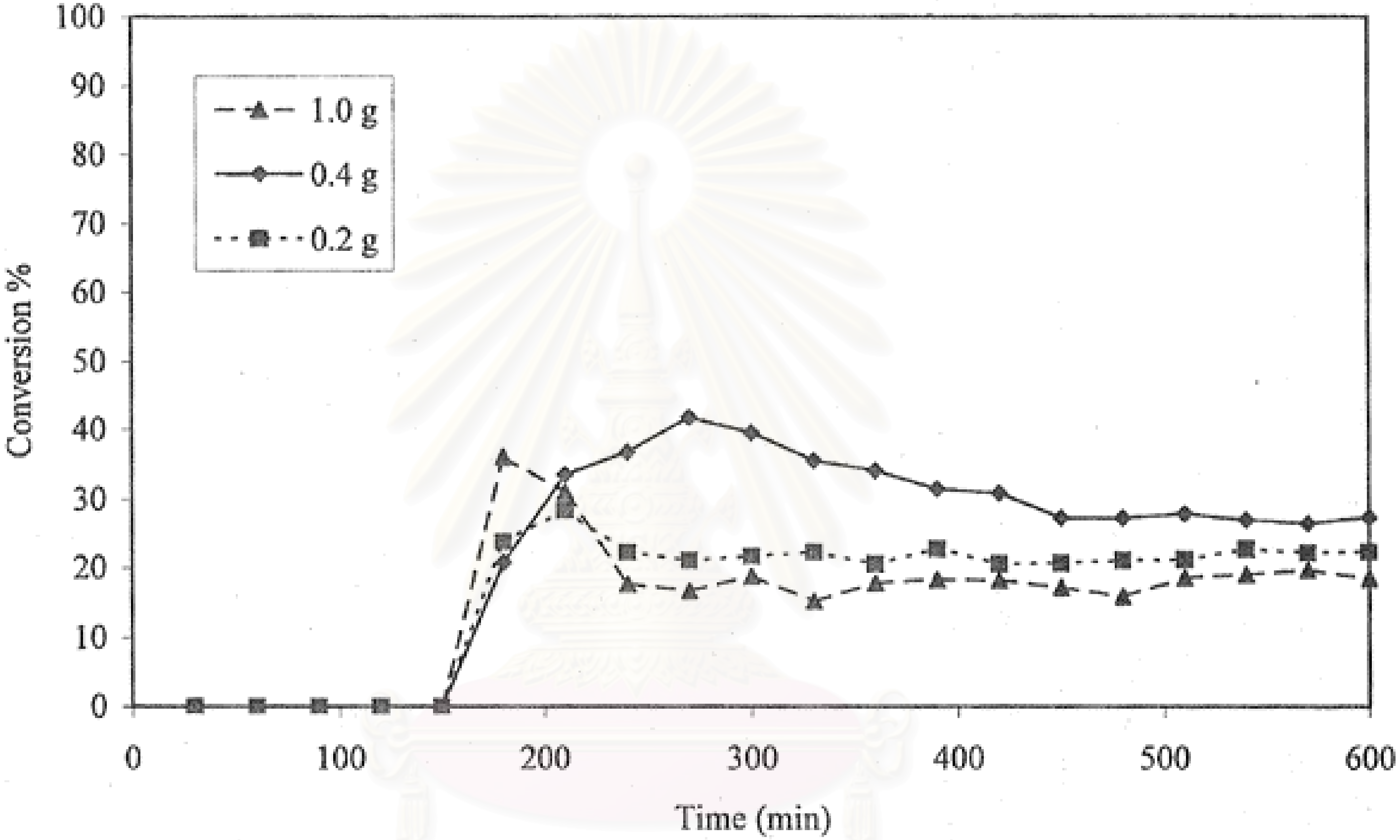


Figure 5.14 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by glycothermal method. Experimental conditions: 20 ml/min flow rate of air, room reaction temperature and 4872 ppm isopropanol.

5.2.3.3 Effect of reaction temperature

The initial concentration of gaseous isopropanol used for this study is 4872 ppm and the flow rate of air is 20 ml/min. The reaction temperatures were 40^{o}C (due to increasing heat from UV lamp), 60^{o}C and 80^{o}C. The results presented in figure 5.15 show that the conversion of isopropanol decreases with increasing reaction temperature. At the high reaction temperature (60^{o}C and 80^{o}C), conversion of isopropanol at steady state drop from the conversion of isopropanol at 40^{o}C. It is expected that for the high reaction temperature, molecules of gaseous isopropanol can be well desorbed from TiO_2 surface. Therefore, the molecules of gaseous isopropanol remaining to react with the active species on the catalyst surface are less than that at room temperature.

To test the hypothesis explained above, methanol is the other reactant that is chosen for this experiment apart from isopropanol due to its lower boiling point. Figure 5.16 shows the same profiles as figure 5.15 for photocatalytic decomposition of methanol. At temperature near and beyond boiling point, the conversion decreases due to lower amount of alcohol adsorb on catalyst surface. In addition, the effect of temperature on conversion appears to depend on the organic molecule being oxidized and the experimental conditions [Falconer and Magrini-Bair (1998)]. In some literatures, the reaction is enhanced at increased temperatures in photocatalytic oxidation of ethylene [Fu *et al.* (1996)]. Above that, the conversion during photocatalytic oxidation of propene decreased as temperature increased [Pichat *et al.* (1979)].

5.3 Long-term photocatalytic activity test

Figure 5.17 shows the long-term conversion obtained in this work for a feed stream containing 4872 ppm of isopropanol over TiO_2 synthesized by glycothermal method. This experiment was carried out using a flow rate of air 20 ml/min at room temperature. It shows that, upon irradiation, the initial low photocatalytic activity gradually increases with irradiation time and decreases until it reaches a steady value. An isopropanol conversion near 27 % is achieved during 30 hours of continuous operation.

It can be seen that catalytic activity of TiO_2 could be maintained. It is well-established that UV irradiation of hydroxylated titania in the presence of gaseous O_2 produces adsorbed $O_2^{\cdot -}$ and surface hydroxyl species prevents electron-hole recombination at the surface, thus allowing oxygen photoadsorption and electron transfer [Alberici and Jardim (1997)].

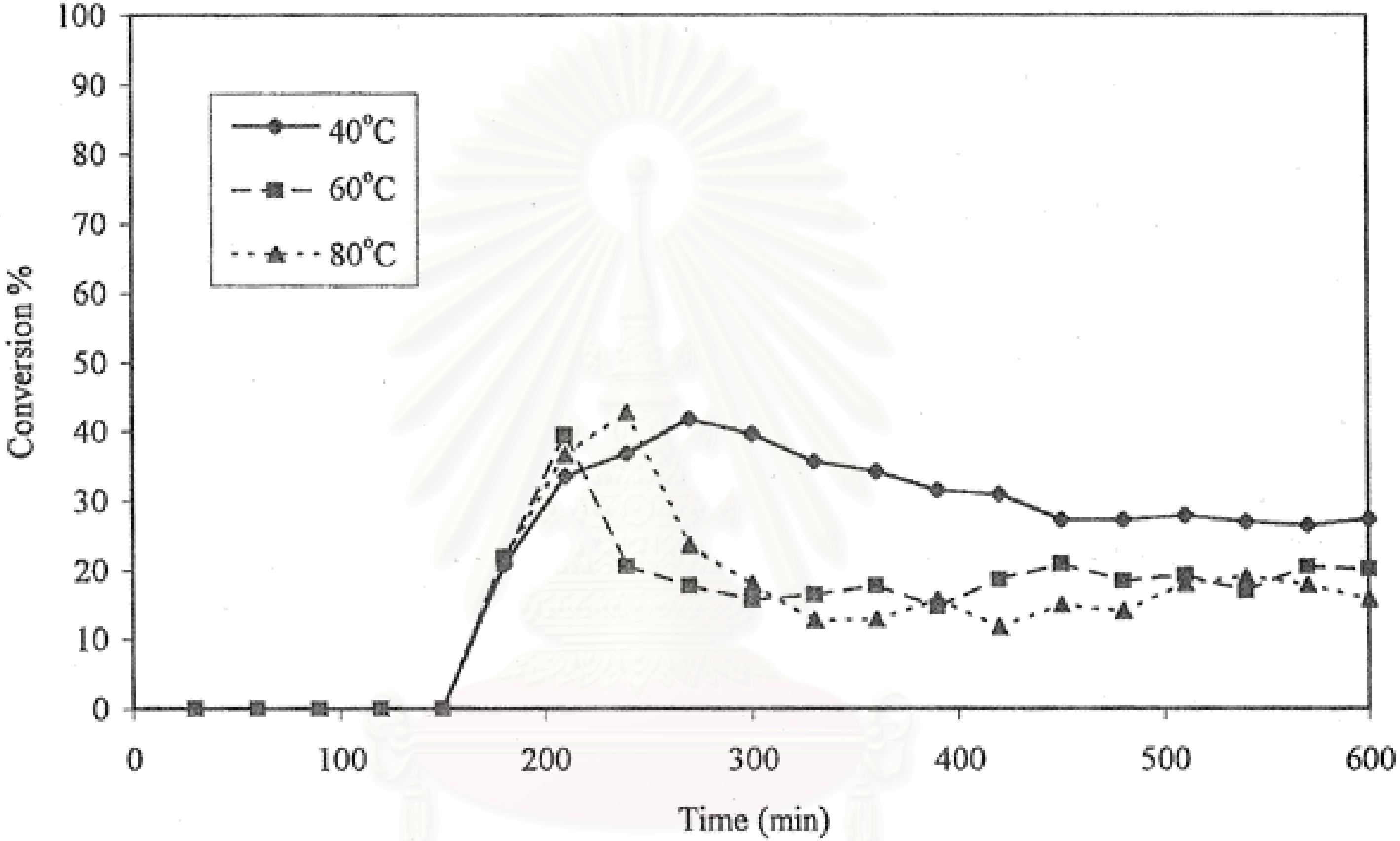


Figure 5.15 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by glycothermal method. Experimental conditions: 20 ml/min flow rate of air and 4872 ppm isopropanol.

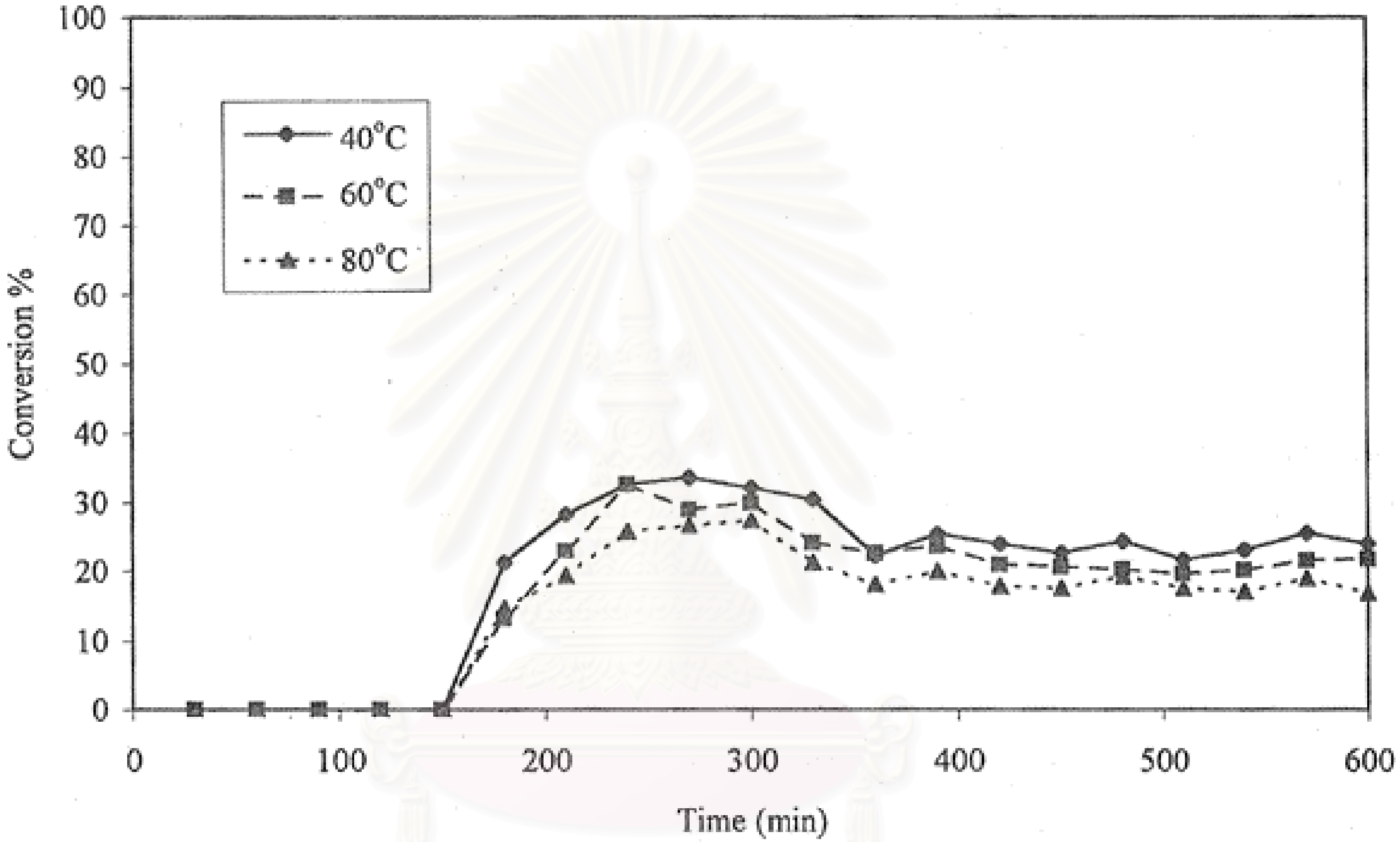


Figure 5.16 Time course of conversion in the photocatalytic decomposition of methanol over TiO_2 synthesized by glycothermal method. Experimental conditions: 20 ml/min flow rate of air and 15227 ppm methanol.

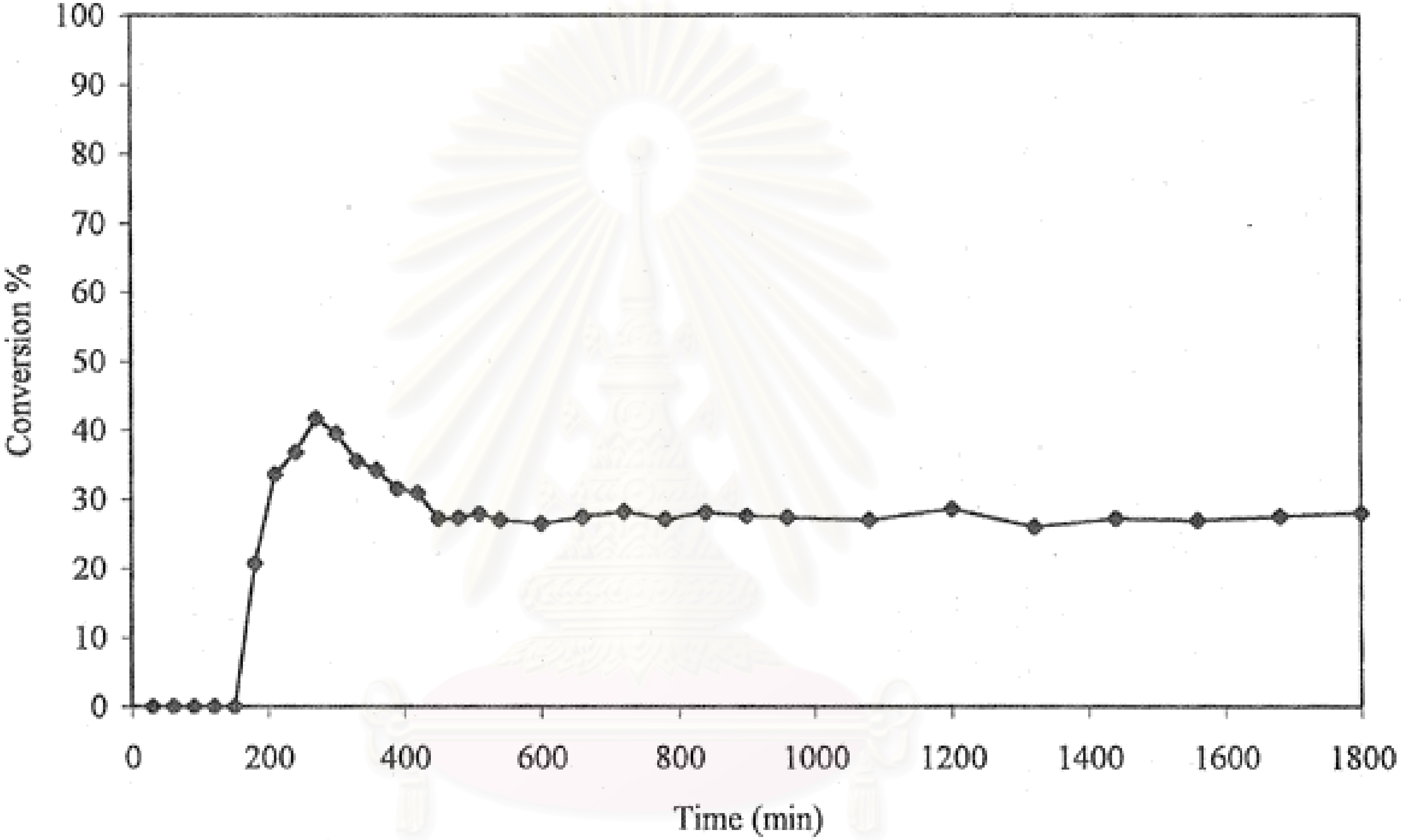


Figure 5.17 Time course of conversion in the photocatalytic decomposition of isopropanol over TiO_2 synthesized by glycothermal method for long term activity test. Experimental conditions: 20 ml/min flow rate of air and 4872 ppm isopropanol.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The conclusions emerged from this research are the following:

1. Glycothermal method is a promising method for obtaining high surface area TiO_2 and anatase TiO_2 that is expected to use for photocatalytic reaction.

2. TiO_2 synthesized by glycothermal method has higher CO_2 selectivity than both of Japan reference TiO_2 (JRC-TIO1 and JRC-TIO4) for photocatalytic decomposition of isopropanol. Although the conversion is lower, the main product is CO_2 which is less harmful than the initial substance. Moreover, it has good stability for this reaction.

3. Photocatalytic decomposition of isopropanol by TiO_2 synthesized by the glycothermal method is most appropriate for low concentration system.

4. An increase in the space velocity by increasing the flow rate of air results in decreasing the conversion of isopropanol. Changing the space velocity by changing catalyst weight from 0.2 g to 0.4 g results in increasing conversion of isopropanol. When catalyst weight is increased to 1.0 g, the conversion of that is drop.

5. The reaction temperature have an effect on the photocatalytic decomposition of isopropanol. The conversion of isopropanol decreases with increasing the reaction temperature.

Recommendation for the future works

In this research, we know that catalyst and light are important factors for the photocatalytic reaction. Type of catalyst should be adjusted for the most irradiated by UV lamp and exposed with the reactant. For example, immobilized TiO_2 on the support such as glass, it can be used the both of liquid and gas phase system. For the source of light, it should be more practical in real life such as fluorescent lamp.

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APPENDICES

APPENDIX A

THE CONDITIONS OF CALCINATION THE CATALYSTS

Temperature controller parameter:

Alarm 1, (A1) = 0

Alarm 2, (A2) = 0

Xp %, (Pb) = 2

T integral [sec], (τ_I) = Off

T derivative [sec], (τ_D) = Off

Approach, (Ap) = 1.0

Cycle time [sec], (Hc) = 10

Maximum power [heat], (H_L) = 100

Set point [celcius] = 500

Conditions of calcination:

Air flow rate = 30 ml/min

Rate of temperature program = 10°C/min

APPENDIX B
GAS CHROMATOGRAPH

B1 Operating condition

Flame ionization detector gas chromatographs, model 14A were used to analyze the concentrations of oxygenated compounds, acetone and isopropanol were analyzed by GC model 14A.

Gas chromatograph with the thermal conductivity detector, model 8A was used to analyze the concentrations of CO_2 by using Porapak QS.

The operating conditions for gas chromatograph are described below:

GC model	**Shimadzu GC-14A**	**Shimadzu GC-8A**
Detector	FID	TCD
Column	Capillary	Porapak QS
Nitrogen flow rate	25 ml/min	-
Helium flow rate	-	25 ml/min
Column temperature		
- initial	40°C	80°C
- final	140°C	80°C
Injector temperature	150°C	130°C
Detector temperature	150°C	130°C

B2 Calibration curve

The calibration curves of isopropanol, acetone, methanol and carbondioxide are illustrated in the following figures.

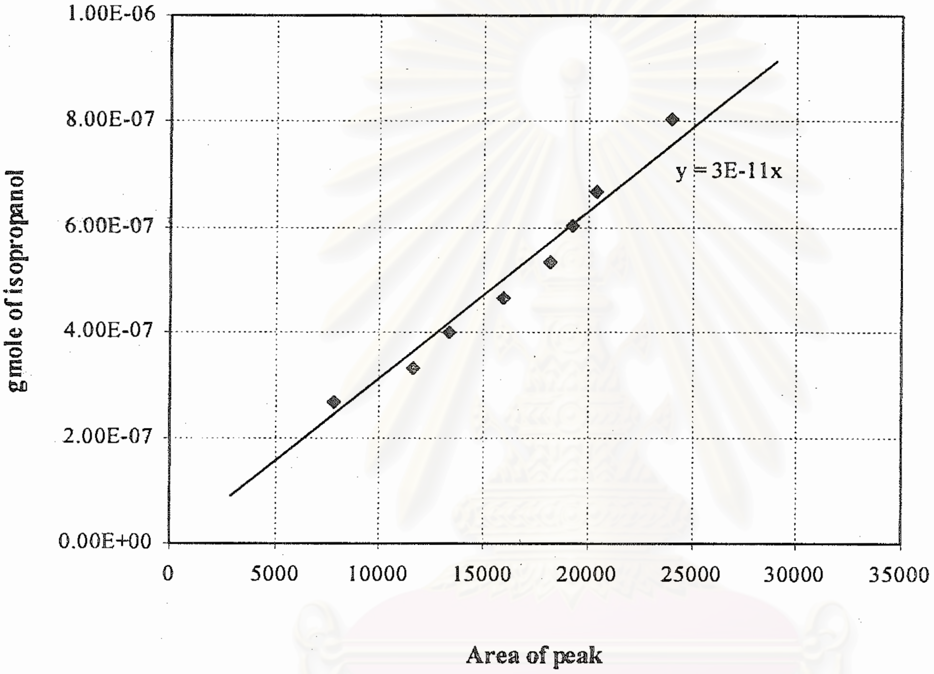

Figure B1 The calibration curve of isopropanol

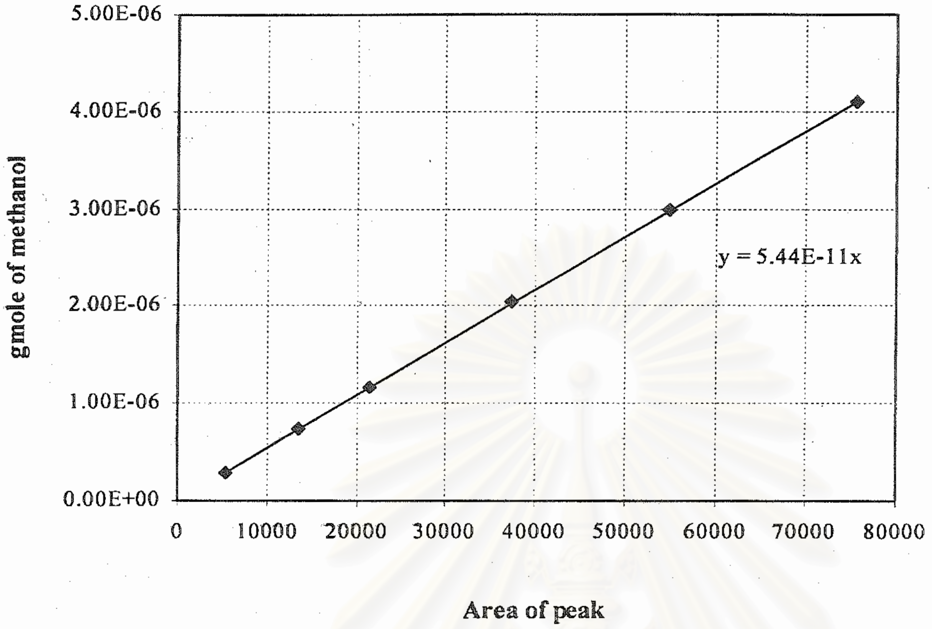

Figure B2 The calibration curve of methanol

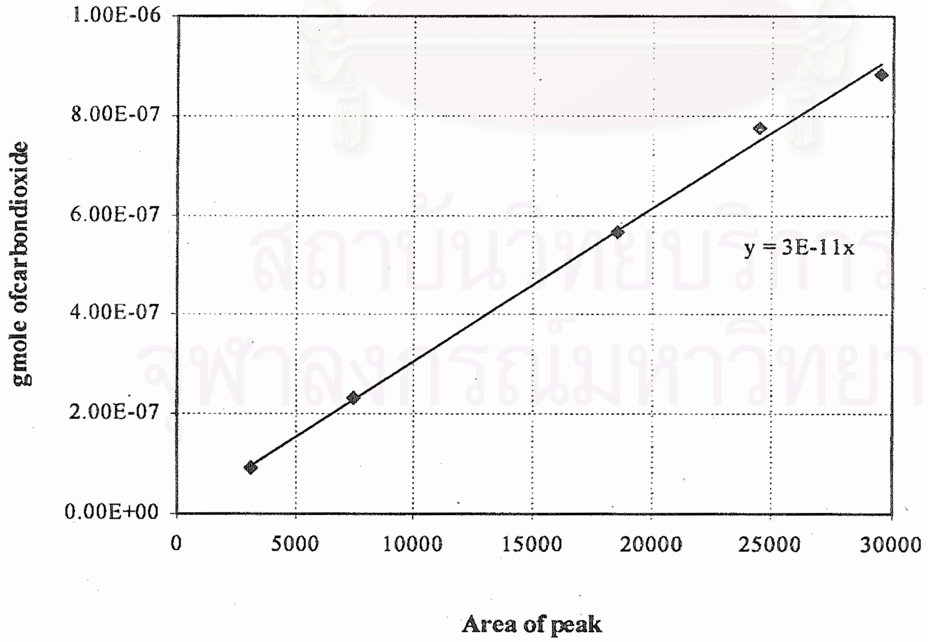

Figure B3 The calibration curve of acetone

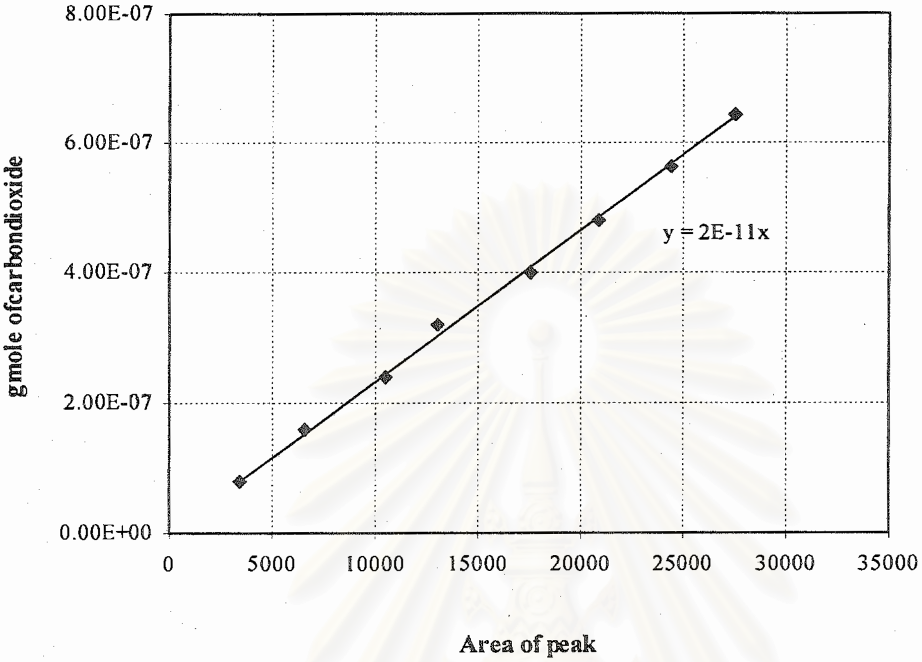

Figure B4 The calibration curve of carbondioxide

APPENDIX C

DATA OF EXPERIMENTS

Table C1 Data of figure 5.7

Time (min)	% isopropanol conversion of		
	as-syn TiO_2	JRC-TIO4	JRC-TIO1
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	20.74	3.13	8.54
210	33.51	10.53	33.92
240	36.70	13.96	40.97
270	41.73	21.77	45.91
300	39.50	23.14	49.62
330	35.53	22.70	51.12
360	34.13	17.34	47.70
390	31.47	20.24	43.96
420	30.89	18.31	40.77
450	27.21	19.33	38.09
480	27.25	19.57	33.08
510	27.85	17.83	32.13
540	26.95	19.77	33.57
570	26.45	17.72	30.73
600	27.32	16.38	31.61

Table C2 Data of the photocatalytic test of as-syn TiO_2 for figure 5.8

Time (min)	**% isopropanol conversion**	**% Selectivity**	
		CO_2	**Acetone**
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	20.74	78.33	16.77
210	33.51	85.22	11.94
240	36.70	89.87	10.46
270	41.73	91.00	9.02
300	39.50	89.07	8.89
330	35.53	87.34	9.29
360	34.13	86.28	8.06
390	31.47	86.14	7.97
420	30.89	87.91	7.35
450	27.21	86.39	7.83
480	27.25	86.19	8.73
510	27.85	86.56	8.09
540	26.95	86.06	8.50
570	26.45	86.34	8.11
600	27.32	88.81	7.24

Table C3 Data of the photocatalytic test of JRC-TIO4 for figure 5.8

Time (min)	% isopropanol conversion	% selectivity	
		CO_2	Acetone
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	3.13	63.98	33.59
210	10.53	69.08	26.73
240	13.96	73.31	22.54
270	21.77	75.12	21.11
300	23.14	78.77	19.14
330	22.70	78.89	19.26
360	17.34	75.32	19.57
390	20.24	77.59	18.43
420	18.31	76.51	18.59
450	19.33	77.24	17.48
480	19.57	75.15	19.94
510	17.83	75.45	18.10
540	19.77	77.62	18.36
570	17.72	77.53	17.91
600	16.38	76.80	17.67

Table C4 Data of the photocatalytic test of JRC-TIO1 for figure 5.8

Time (min)	% isopropanol conversion	% Selectivity		
		CO_2	Acetone	other
30	0	0	0	0
60	0	0	0	0
90	0	0	0	0
120	0	0	0	0
150	0	0	0	0
180	8.54	1.36	72.30	25.17
210	33.92	1.68	74.00	23.38
240	40.97	1.46	78.55	21.36
270	45.91	1.19	80.53	18.07
300	49.62	1.07	81.25	17.56
330	51.12	1.03	84.31	16.31
360	47.70	0.94	82.75	16.74
390	43.96	1.11	81.44	15.93
420	40.77	1.29	80.29	14.91
450	38.09	1.34	79.02	15.24
480	33.08	1.41	76.55	16.95
510	32.13	1.70	75.56	17.73
540	33.57	1.74	75.38	19.68
570	30.73	1.75	74.36	18.99
600	31.61	1.80	75.91	19.41

Table C5 Data of figure 5.9

Time (min)	% isopropanol conversion
30	0
60	0
90	0
120	0
150	0
180	0.09
210	1.61
240	2.15
270	1.43
300	1.67
330	1.38
360	1.89
390	1.20
420	0.73
450	1.93
480	1.32
510	1.26
540	1.04
570	1.97
600	1.91

Table C6 Data of figure 5.10

Time (min)	% isopropanol conversion at diferent initial concentration of isopropanol			
	4872 ppm	7881 ppm	12399 ppm	16527 ppm
30	0	0	0	0
60	0	0	0	0
90	0	0	0	0
120	0	0	0	0
150	0	0	0	0
180	20.74	24.76	21.27	9.72
210	33.51	40.10	24.35	13.03
240	36.70	23.44	31.51	14.27
270	41.73	17.62	35.97	23.21
300	39.50	14.07	26.32	22.71
330	35.53	11.28	25.33	19.70
360	34.13	15.62	24.96	17.89
390	31.47	12.90	21.39	19.21
420	30.89	15.18	21.01	18.10
450	27.21	19.16	19.58	18.02
480	27.25	22.05	21.04	17.94
510	27.85	21.94	21.87	18.13
540	26.95	21.45	20.24	16.12
570	26.45	21.60	18.91	15.18
600	27.32	21.75	21.29	15.18

Table C7 Data of figure 5.11

Time (min)	% isopropanol conversion at different flow rate of air		
	60 ml/min	20 ml/min	10 ml/min
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	12.19	20.74	20.48
210	17.47	33.51	35.04
240	20.95	36.70	44.88
270	17.19	41.73	46.12
300	14.58	39.50	41.15
330	15.11	35.53	36.37
360	14.41	34.13	33.83
390	13.86	31.47	33.92
420	14.58	30.89	30.55
450	14.21	27.21	29.78
480	12.73	27.25	30.12
510	14.79	27.85	30.58
540	14.33	26.95	30.49
570	13.75	26.45	31.25
600	14.59	27.32	31.23

Table C8 Data of figure 5.12

Time (min)	% isopropanol conversion at different weight of catalyst		
	1.0 g	**0.4 g**	**0.2 g**
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	36.04	20.74	23.77
210	31.02	33.51	28.37
240	17.65	36.70	22.27
270	16.68	41.73	21.04
300	18.77	39.50	21.66
330	15.15	35.53	22.27
360	17.81	34.13	20.52
390	18.32	31.47	22.72
420	18.19	30.89	20.52
450	17.14	27.21	20.63
480	15.84	27.25	21.04
510	18.54	27.85	21.15
540	19.01	26.95	22.68
570	19.63	26.45	22.17
600	18.47	27.32	22.29

Table C9 Data of figure 5.13

Time (min)	% isopropanol conversion at different reaction temperature		
	40°C	60°C	80°C
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	20.74	21.72	21.95
210	33.51	39.37	36.58
240	36.70	20.53	42.73
270	41.73	17.72	23.57
300	39.50	15.69	17.86
330	35.53	16.38	12.76
360	34.13	17.68	12.83
390	31.47	14.62	15.68
420	30.89	18.53	11.70
450	27.21	20.83	14.94
480	27.25	18.41	14.03
510	27.85	19.21	17.93
540	26.95	16.90	19.00
570	26.45	20.43	17.79
600	27.32	20.07	15.72

Table C10 Data of figure 5.14

Time (min)	**% methanol conversion at different reaction temperature**		
	40°C	60°C	80°C
30	0	0	0
60	0	0	0
90	0	0	0
120	0	0	0
150	0	0	0
180	21.16	13.24	14.67
210	28.21	22.83	19.33
240	32.53	32.58	25.71
270	33.52	28.90	26.50
300	32.00	29.91	27.30
330	30.40	23.99	21.21
360	22.12	22.59	17.97
390	25.30	23.53	19.88
420	23.83	20.88	17.79
450	22.51	20.57	17.52
480	24.23	20.16	19.20
510	21.61	19.56	17.53
540	22.94	20.05	17.03
570	25.42	21.47	18.88
600	23.85	21.67	16.84

Table C11 Data of figure 5.15

Time (min)	% isopropanol conversion	Time (min)	% isopropanol conversion
30	0	510	27.85
60	0	540	26.95
90	0	600	26.45
120	0	660	27.32
150	0	720	28.12
180	20.74	780	27.10
210	33.51	840	28.03
240	36.70	900	27.52
270	41.73	960	27.40
300	39.50	1080	26.94
330	35.53	1200	28.56
360	34.13	1320	25.98
390	31.47	1440	27.13
420	30.89	1560	26.87
450	27.21	1680	27.51
480	27.25	1800	27.92

VITA

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