

## REFERENCES

- Alberici, R., and Jardim, W., "Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide", *Applied Catalysis B: Environmental*, 14 (1997), 55-68.
- Cao, L., Huang, A., Spiess, F., and Suib, S., "Gas-phase oxidation of 1-butene using nanoscale TiO<sub>2</sub> photocatalysts", *Journal of Catalysis*, 48 (1999), 48-57.
- Cao, L., Gao, Z., Suib, S., Obee, T., Hay, S., and Freihaut, J., "Photocatalytic oxidation of toluene on nanoscale TiO<sub>2</sub> catalysts: studies of deactivation and regeneration", *Journal of Catalysis*, 196 (2000), 253-261.
- Fujishima, A., Hashimoto, K., and Watanabe, T., "TiO<sub>2</sub> Photocatalysis Fundamentals and Applications", (1999), BKC, Inc.
- Kominami, H., Takada, Y., Yamagiwa, H., and Kera, Y., "Synthesis of thermally stable nanocrystalline anatase by high temperature hydrolysis of titanium alkoxide with water dissolved in organic solvent from gas phase", *Journal of Materials Science Letters*, 15 (1996), 197-200.
- Kominami, H., Kato, J., Takada, Y., Doushi, Y., Ohtani, B., Nishimoto, S., Inoue, M., Inui, T., and Kera, Y., "Novel synthesis of microcrystalline titanium (IV) oxide having high thermal stability and ultra-high photocatalytic activity: thermal decomposition of titanium (IV) oxide in organic solvents", *Catalysis Letter*, 46 (1997), 235-240.
- Kominami, H., Murakami, S., Kera, Y., and Ohtani, B., "Titanium (IV) oxide photocatalyst of ultra-high activity: a new preparation process allowing compatibility of high adsorptivity and low electron-hole recombination probability", *Catalysis Letter*, 56 (1998), 125-129.
- Kominami, H., Kohno M., Takada, Y., Inoue, M., Inui, T., and Kera, Y., "Hydrolysis of titanium alkoxide in organic solvent at high temperatures: A new synthetic method for nanosized, thermally stable titanium (IV) oxide", *Industrial Engineering Chemical Research*, 38 (1999a), 3925-3931.
- Kominami, H., Kato, J., Mutakami, S., Kera, Y., Inoue, M., Inui, T., and Ohtani, B., "Synthesis of titanium (IV) oxide of ultra-high photocatalytic activity: high-temperature hydrolysis of titanium alkoxides with water liberated

- homogeneously from solvent alcohols”, *Journal of Molecular Catalysis A: Chemical*, 144 (1999b), 165-171.
- Kozlov, D., Paukshtis, E., Savinov, E., “The comparative studies of titanium dioxide in gas-phase ethanol photocatalytic oxidation by the FTIR in situ method”, *Applied Catalysis B: Environmental*, 24 (2000), L7-L12.
- Linsebigler, A., Lu, G., and Yates, J., “Photocatalysis on TiO<sub>2</sub> surfaces: principles, mechanisms, and selected results”, *Chemical Reviews*, 95 (1995), 735-758.
- Litter, M., “Heterogeneous photocatalysis Transition metal ions in photocatalytic systems”, *Applied catalysis B: Environmental*, 23 (1999), 89-114.
- Maira, A., Yeung, K., Lee, C., Yue, P., and Chan, C., “Size Effects on gas-phase photo-oxidation of trichloroethylene using nanometer-sized TiO<sub>2</sub> catalysts”, *Journal of Catalysis*, 192 (2000), 185-196.
- Marta, G., Clouccia, S., Marchese, L., Augugliaro, V., Loddo, V., Palmisano, L., and Schiavello, M., “The role of H<sub>2</sub>O in the photocatalytic oxidation of toluene in vapour phase on anatase TiO<sub>2</sub> catalyst a FTIR study”, *Catalysis Today*, 53 (1999), 695-702.
- Matawan, S., “Photocatalytic decomposition of isopropanol over TiO<sub>2</sub> synthesized by the glycothermal method”, *Master of Engineering thesis Chulalongkorn University*, 2000.
- Mendez-Roman, R. and Cardona-Martinez, N., “Relationship between the formation of surface species and catalyst deactivation during the gas-phase photocatalytic oxidation of toluene”, *Catalysis Today*, 40 (1998), 353-365.
- Muggli, D., Keyser, S., and Falconer, J., “Photocatalytic decomposition of acetic acid on TiO<sub>2</sub>”, *Catalysis Letters*, 55 (1998), 129-132.
- Park, D., Zhang, J., Ikeue, K., Yamashita, H., and Anpo, M., “Photocatalytic oxidation of ethylene to CO<sub>2</sub> and H<sub>2</sub>O on ultrafine powdered TiO<sub>2</sub> photocatalysis in the presence of O<sub>2</sub> and H<sub>2</sub>O”, *Journal of Catalysis*, 185 (1999), 114-119.
- Satterfield, C., “Heterogeneous catalysis in industrial practice”, (1991), McGraw-Hill Book Company.

- Theinkaew, S., "Synthesis of large surface area silica modified titanium (IV) oxide ultrafine particles", *Master of Engineering thesis Chulalongkorn University*, 2000.
- Xu, Z., Shang, J., Liu, C., Kang, C., Guo, H., and Du, Y., "The preparation and characterization of TiO<sub>2</sub> ultrafine particles", *Materials Science and Engineering B*, 56 (1999a), 211-214.
- Xu, N., Shi, Z., Fan, Y., Dong, J., Shi, J., and Hu, M., "Effects of particle size of TiO<sub>2</sub> on photocatalytic degradation of methylene blue in aqueous suspensions", *Industrial Engineering Chemical Research*, 38 (1999b), 373-379.
- Zhang, Z., Wang, C., Zakaria, R., and Ying, J., "Role of particle size in nanocrystalline TiO<sub>2</sub>-based photocatalysts", *Journal of Physical Chemistry B*, 102 (1998), 10871-10878.
- Zhang, Q., Gao, L., and Guo, J., "Effects of calcination on the photocatalytic properties of nanosized TiO<sub>2</sub> powders prepared by the TiCl<sub>4</sub> hydrolysis", *Applied Catalysis B: Environmental*, 26 (2000), 207-215.

## **APPENDICES**

**APPENDIX A**  
**THE CALCINATION CONDITIONS OF THE PREPARED**  
**CATALYSTS AND CONTROLLER SETPOINTS**

*Temperature controller parameter:*

Alarm 1, (A1)	=	0
Alarm 2, (A2)	=	0
Xp %, (Pb)	=	2
T integral [sec], ( $\tau_I$ )	=	Off
T derivative [sec], ( $\tau_D$ )	=	Off
Approach, (Ap)	=	1.0
Cycle time [sec], (Hc)	=	10
Maximum power [heat], ( $H_L$ )	=	100
Set point [celcius]	=	550

*Conditions of calcination:*

Air flow rate = 30 ml min<sup>-1</sup>

Rate of temperature program = 10°C min<sup>-1</sup>

## APPEENDIX B

### CALCULATION OF CRYSTALLITE SIZE

#### Calculation of crystallite size by Sherrer equation

Crystallite size was calculated from the half-height width of the 101 diffraction peak of anatase using the Sherrer equation. The value of the shape factor, K was taken to be 0.9 and KCl was used to be internal standard.

From Sherrer equation:

$$t = \frac{0.9\lambda}{B \cos \theta_B} \quad (\text{B.1})$$

Where: t = crystallite size

K = shape factor = 0.9

$\lambda$  = X-ray wavelength, Cu K $\alpha$ :  $\lambda = 1.5418 \text{ \AA}$

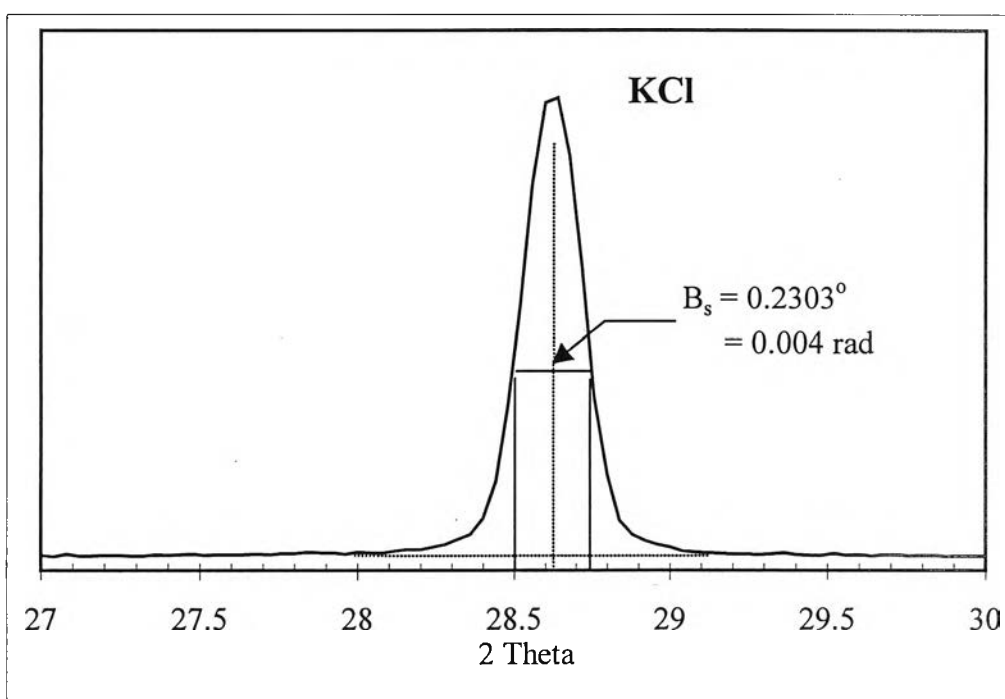
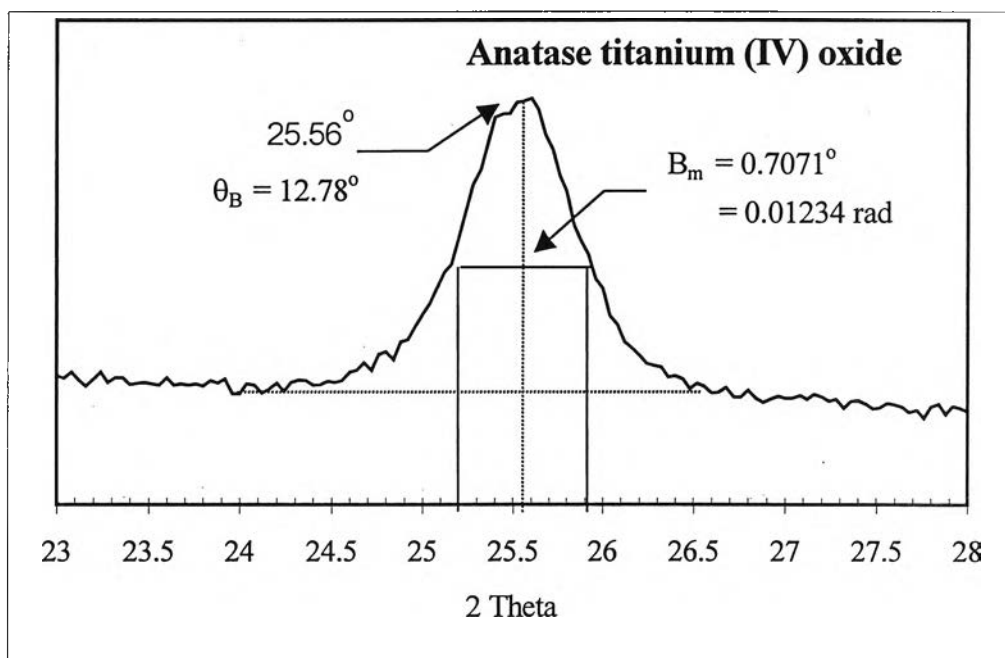
$\theta_B$  = the Bragg angle

$B^2 = B_M^2 - B_S^2$

$B_M$  = the measured peak width in radians at half peak height.

$B_S$  = the corresponding width of a standard material

**Example:** The crystallite size of pure anatase titanium (IV) oxide prepared in 1,4 butanediol is calculated as follow:



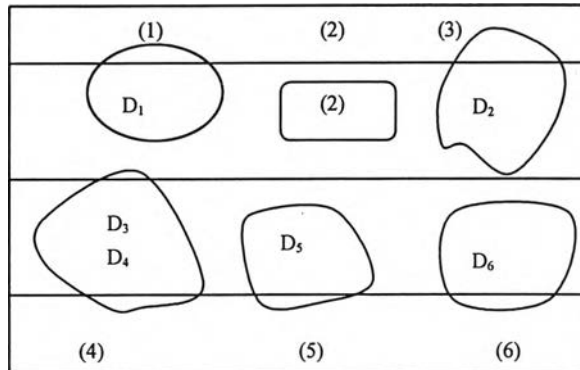
$$\begin{aligned}\text{From } B^2 &= B_M^2 - B_S^2 \\ &= 0.01234^2 - 0.00402^2 = 0.00013 \\ B &= 0.0117 \\ \theta_B &= 12.78^\circ \\ \lambda &= 1.5418 \text{ \AA}\end{aligned}$$

$$\begin{aligned}\text{So, } t &= (0.9 \times 1.5418) / (0.0117 \times \cos 12.78) \\ &= 121.6 \text{ \AA} = 12.2 \text{ nm}\end{aligned}$$



## APPENDIX C

### CRYATAL SIZE MEASUREMENT FORM TEM PHOTOGRAPH



**Figure C1** demonstrates how crystal diameter is determined

1. First grid lines at a determined interval were drawn on the photo.
2. Measure crystal diameter along the grid line that pass through the crystal.
3. Calculate the average diameter from the equation

$$D_{ave} = \frac{1}{N} \sum_{i=1}^N D_i$$

Where  $D_{ave}$  = Average diameter  
 $N$  = number of intersection between grid line and particles  
 $D_i$  = length of particle along the grid line intersection

For example, from the figure C1

$$D_{ave} = \frac{1}{6} (D_1 + D_2 + D_3 + D_4 + D_5 + D_6)$$

Note for particle number (4), 2 intersection exist hence there are 2 data used to calculate in this formula. For particle number (2), there is no intersection hence there is no data used to calculate.

In practices, each TEM photo is enlarged before measurement due to easy to measure.

## APPENDIX D

### GAS CHROMATOGRAPH

#### D1 Operating condition

Flame ionization detector gas chromatograph, model 14A was used to analyze the concentrations of oxygenated compounds, acetone and 2-propanol

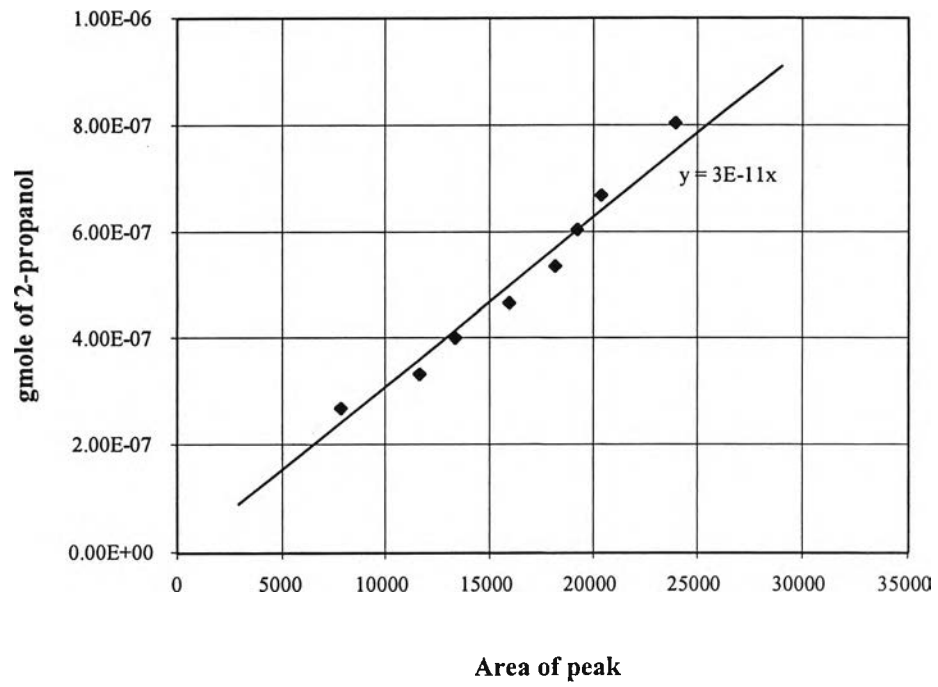
Gas chromatograph with the thermal conductivity detector, model 8A was used to analyze the concentrations of CO<sub>2</sub> by using Porapak QS.

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

## D2 Calibration curve

The calibration curves of 2-propanol, acetone, methanol and carbondioxide are illustrated in the following figures.



**Figure D1** The calibration curve of 2-propanol

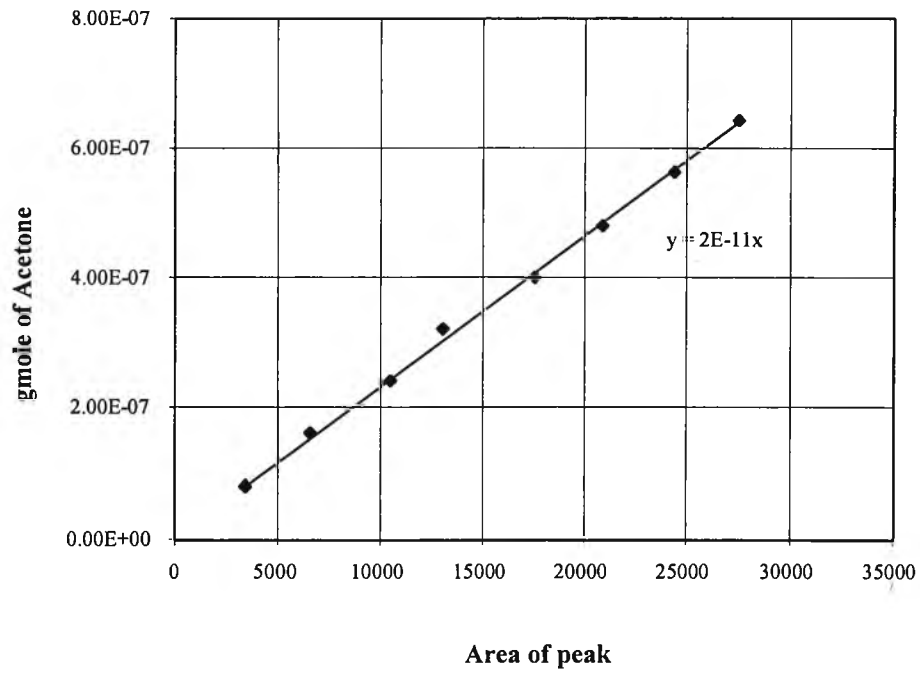


Figure D2 The calibration curve of acetone

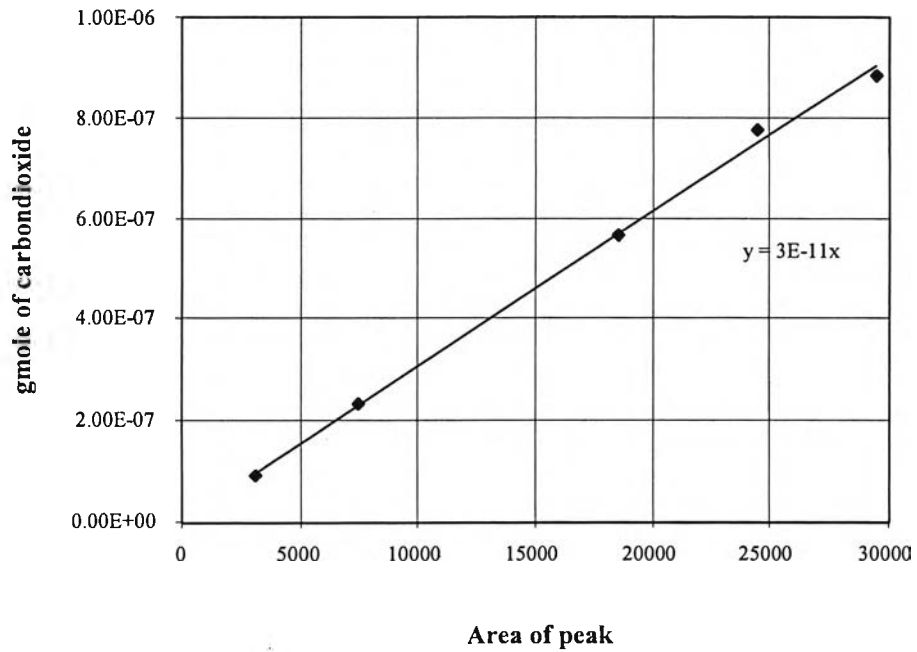


Figure D3 The calibration curve of carbondioxide

## APPENDIX E

### DATA OF EXPERIMENTS

**Table E1** Data of figures 5.9-5.14

Time (min)	% 2-propanol conversion of					
	TiO <sub>2</sub> (5:0)	TiO <sub>2</sub> (4:1)	TiO <sub>2</sub> (3:2)	TiO <sub>2</sub> (2:3)	TiO <sub>2</sub> (1:4)	TiO <sub>2</sub> (0:5)
0	0	0	0	0	0	0
30	0	0	0	0	0	0
60	0	0	0	0	0	0
90	0	0	0	0	0	0
120	0	0	0	0	0	0
150	0	0	0	0	0	0
180	20.41	0.35	21.03	2.84	0	0
210	22.83	14.49	31.56	14.27	0	13.91
240	25.47	17.24	37.33	11.03	1.3	11.86
270	22.33	21.29	28.76	10.89	0.56	13.76
300	20.28	31.27	29.92	8.61	9.23	8.94
330	20.63	35.31	33.75	14.56	1.1	11.23
360	24.91	33.61	36.33	9.19	8.56	16.74
390	20.03	29.16	34.12	7.99	1.62	7.07
420	19.85	26.96	28.81	15.66	4.65	10.09
450	19.98	20.47	30.56	6.57	6.23	6.66
480	22.08	25.07	35.46	10.89	12.98	6.32
510	22.45	19.38	31.15	6.14	7.54	11.56
540	25.1	21.09	26.59	10.64	9.73	14.06
570	25.7	20.43	27.7	8.12	11.83	11.09
600	22.6	20.03	32.64	9.05	10.62	9.69

**APPENDIX F****NOTATION**

A	= Electron acceptor
BET	= Brunauer-Emmett-Teller
D	= Electron donor
e <sup>-</sup>	= Electron
FTIR	= Fourier Transform Infrared Spectroscopy
GC	= Gas Chromatograph
h <sup>+</sup>	= Proton
MB	= Methylene Blue
STREC	= Scientific and Technological Research Equipment Center
TCE	= Trichloroethylene
TEM	= Transmission Electron Microscope
THyCA	= Transfer Hydrolytic Crystallization in Alcohols
TiO <sub>2</sub>	= Titanium (IV) oxide
TNB	= Titanium normal butoxide
TPD	= Temperature Programmed Desorption
TTB	= Titanium (IV) tetra-tert butoxide
UV	= Ultraviolet light
UV-Vis	= Ultraviolet- Visible light
VOC	= Volatile Organic Compound
XRD	= X-Ray Diffraction
XPS	= X-Ray Photoelectron Microscopy

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