

## REFERENCE

- Alherici, R. M. and Jardim, W. F. (1997). "Photocatalytic destruction of VOCs in the gas phase using titanium dioxide" *Applied Catalysis B: Environmental*, 14, 55-68.
- Burgos, M. and Langlet, M. (1999). "The sol-gel transformation of TIPT coatings: a FTIR study." *Thin Solid Films*, 349(1-2), 19-23.
- Campbell, L. K., Na, B. K., and Ko, E. I. (1992). "Synthesis and characterization of titania aerogels." *Chemistry of Materials*, 4(6), 1329-1333.
- Dagan, G. and Tomkiewicz, M. (1994). "Preparation and characterization of TiO<sub>2</sub> aerogels for use as photocatalysts." *Journal of Non-Crystalline Solids*, 175(2-3), 294-302.
- Fox, M. A. and Dulay, M. T. (1993). "Heterogeneous photocatalysis" *Chemical Reviews*, 93, 341-357.
- Fujishima, A., Hashimoto, K., and Watanabe, T. (1999). *TiO<sub>2</sub> photocatalysis: fundamental and applications.*, Tokyo: BKC.
- He, D. and Lin, F. (2007). "Preparation and photocatalytic activity of anatase TiO<sub>2</sub> nanocrystallites with high thermal stability." *Materials Letters*, 61(16), 3385-3387.
- Ivanova, T. and Harizanova, A. (2001). "Characterization of TiO<sub>2</sub> and TiO<sub>2</sub>-MnO oxides prepared by sol-gel method." *Solid State Ionics*, 138(3-4), 227-232.
- Kim, D. S. and Kwak, S.-Y. (2007). "The hydrothermal synthesis of mesoporous TiO<sub>2</sub> with high crystallinity, thermal stability, large surface area, and enhanced photocatalytic activity." *Applied Catalysis A: General*, 323, 110-118.
- Kistler, S. S. (1931). "Coherent Expanded Aerogels and Jellies." *Nature*, 127, 741.
- Kolen'ko, Y. V., Garshev, A. V., Churagulov, B. R., Boujday, S., Portes, P., and Colbeau-Justin, C. (2005). "Photocatalytic activity of sol-gel derived titania converted into nanocrystalline powders by supercritical drying." *Journal of Photochemistry and Photobiology A: Chemistry*, 172(1), 19-26.
- Li, Y.-Q., Fu, S.-Y., Yang, G., and Li, M. (2006). "Preparation and characterization of a novel solid titania precursor." *Journal of Non-Crystalline Solids*, 352(30-31), 3339-3342.
- Litter, M. L. (1999). "Heterogeneous photocatalysis transition metal ions in photocatalytic systems." *Applied Catalysis B: Environmental*, 23, 89-114.

- Liu, A. R., Wang, S. M., Zhao, Y. R., and Zheng, Z. (2006). "Low-temperature preparation of nanocrystalline TiO<sub>2</sub> photocatalyst with a very large specific surface area." *Materials Chemistry and Physics*, 99(1), 131-134.
- Music, S., Gotic, M., Ivanda, M., Popovic, S., Turkovic, A., Trojko, R., Sekulic, A., and Furic, K. (1997). "Chemical and micro structural properties of TiO<sub>2</sub> synthesized by sol-gel procedure." *Materials Science and Engineering B*, 47(1), 33-40.
- Othani, B., Ogawa, Y., and Nishimoto, S.-i. (1997). "Photocatalytic activity of amorphous-anatase mixture of titanium (IV) oxide particles suspended in aqueous solution." *Journal of Physical Chemistry B*, 101, 3746-3752.
- Othmer, K. (1991). *Encyclopedia of chemical technology.*, Jhon Wiley Son, New York: .
- Pajonk, G. M. (1997). "Catalytic aerogels." *Catalysis Today*, 35(3), 319-337.
- Porkodi, K. and Arokiamary, S. D. (2007). "Synthesis and spectroscopic characterization of nanostructured anatase titania: A photocatalyst." *Materials Characterization*, 58(6), 495-503.
- Schneider, M. and Baiker, A. (1997). "Titania-based aerogels." *Catalysis Today*, 35(3), 339-365.
- Song, K. C. and Pratsinis, S. E. (2000). "The Effect of Alcohol Solvents on the Porosity and Phase Composition of Titania." *Journal of Colloid and Interface Science*, 231(2), 289-298.
- Suriye, K., Praserthdam, P., and Jongsomjit, B. (2007). "Control of Ti<sup>3+</sup> surface defect on TiO<sub>2</sub> nanocrystal using various calcination atmospheres as the first step for surface defect creation and its application in photocatalysis." *Applied Surface Science*, 253(8), 3849-3855.
- Tursiloadi, S., Yamanaka, Y., and Hirashima, H. (2006). "Thermal evolution of mesoporous titania prepared by CO<sub>2</sub> supercritical extraction." *Journal of Sol-Gel Science and Technology*, 38, 5-12.
- Venkatachalam, N., Palanichamy, M., and Murugesan, V. (2007). "Sol-gel preparation and characterization of alkaline earth metal doped nano TiO<sub>2</sub>: Efficient photocatalytic degradation of 4-chlorophenol." *Journal of Molecular Catalysis A: Chemical*, 273(1-2), 177-185.

- Wang, C., Li, Q. and Wang, R.-D. (2004). "Synthesis and characterization of mesoporous TiO<sub>2</sub> with anatase wall." *Materials Letters*, 58(9), 1424-1426.
- Wetchakun, N. and Phanichphant, S. (2008). "Effect of temperature on the degree of anatase-rutile transformation in titanium dioxide nanoparticles synthesized by the modified sol-gel method." *Current Applied Physics*, 8(3-4), 343-346.
- Yu, J., Yu, H., Cheng, B., Zhou, M., and Zhao, X. (2006). "Enhanced photocatalytic activity of TiO<sub>2</sub> powder (P25) by hydrothermal treatment." *Journal of Molecular Catalysis A: Chemical*, 253, 112-118.
- Yu, J., Yu, J. C., Ho, W., Leung, M. K. P., Cheng, B., Zhang, G., and Zhao, X. (2003). "Effects of alcohol content and calcination temperature on the textural properties of bimodally mesoporous titania." *Applied Catalysis A: General*, 255(2), 309-320.

## **APPENDICES**

## APPENDIX A

### CALCULATION OF THE CRYSTALLITE SIZE

#### Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size can be calculated from the width at half-height of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{A.1})$$

- where
- D = Crystallite size, Å
  - K = Crystallite-shape factor = 0.9
  - $\lambda$  = X-ray wavelength, 1.5418 Å for CuK $\alpha$
  - $\theta$  = Observed peak angle, degree
  - $\beta$  = X-ray diffraction broadening, radian

The X-ray diffraction broadening ( $\beta$ ) is the pure width of a powder diffraction, free of all broadening due to the experimental equipment. Standard  $\alpha$ -alumina is used to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening ( $\beta$ ) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta^2 = B_M^2 - B_S^2 \quad (\text{A.2})$$

$$\beta = \sqrt{B_M^2 - B_S^2}$$

- Where
- $B_M$  = Measured peak width in radians at half peak height.
  - $B_S$  = Corresponding width of a standard material.

**Example:** Calculation of the crystallite size of titania

$$\begin{aligned} \text{The half-height width of (101) diffraction peak} &= 1.15464^\circ \\ &= 0.02015 \text{ radian} \end{aligned}$$

$$\text{The corresponding half-height width of peak of titania} = 0.003825 \text{ radian}$$

$$\begin{aligned} \text{The pure width} &= \sqrt{B_M^2 - B_S^2} \\ &= \sqrt{0.02015^2 - 0.003825^2} \\ &= 0.019786 \text{ radian} \end{aligned}$$

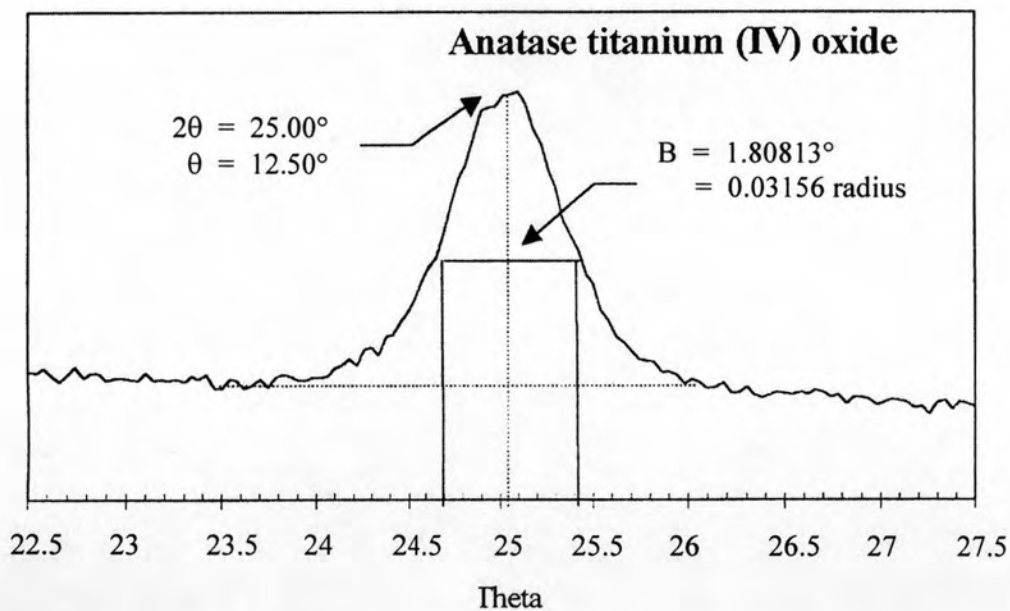
$$\beta = 0.019786 \text{ radian}$$

$$2\theta = 25.00^\circ$$

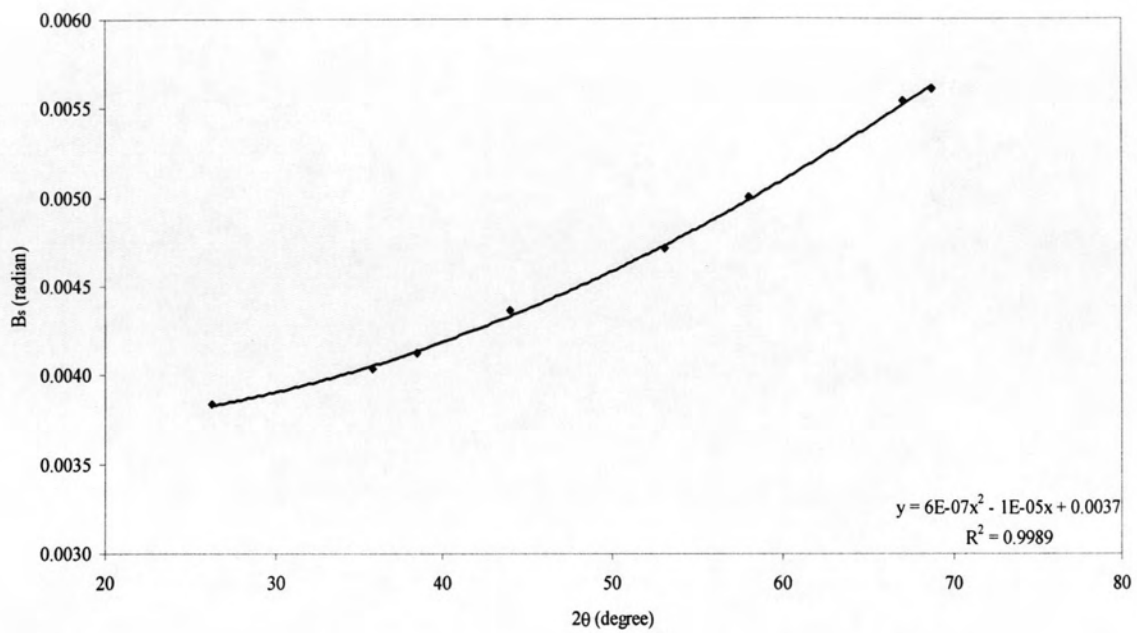
$$\theta = 12.50^\circ$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\begin{aligned} \text{The crystallite size} &= \frac{0.9 \times 1.5418}{0.019786 \cos 12.50} = 71.83 \text{ \AA} \\ &= 7.1 \text{ nm} \end{aligned}$$



**Figure A.1** The (101) diffraction peak of titania for calculation of the crystallite size



**Figure A.2** The plot indicating the value of line broadening due to the equipment. The data were obtained by using  $\alpha$ -alumina as standard.

## APPENDIX B

**THE OPERATING CONDITIONS OF  
GAS CHROMATOGRAPHY**

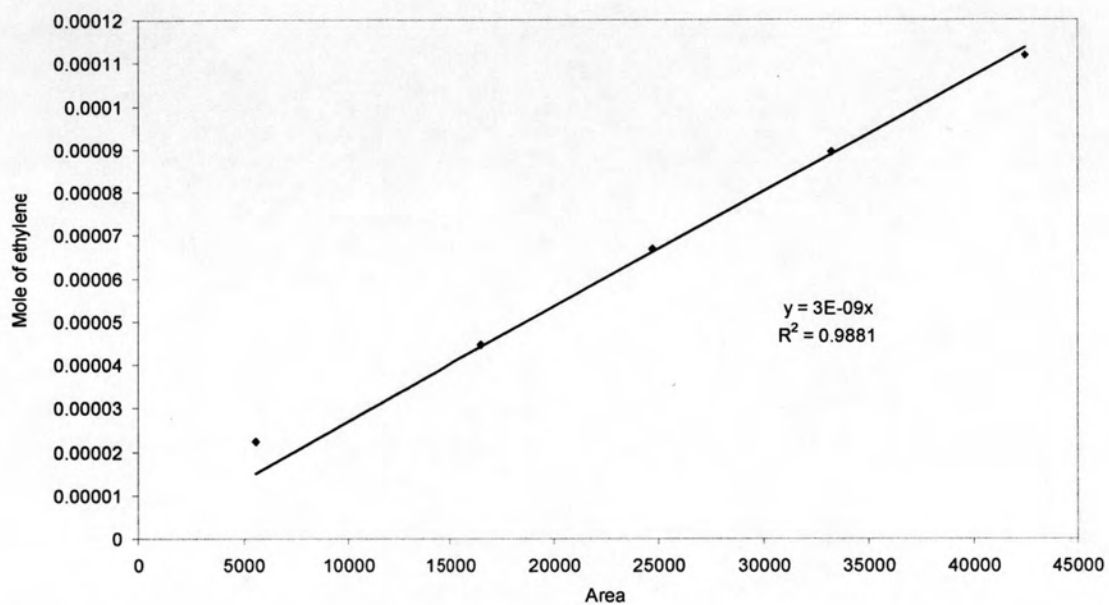
The composition of hydrocarbons in the product stream is analyzed by a Shimadzu GC14B gas chromatograph equipped with a flame ionization detector. The operating conditions for each instrument are shown in table B.1.

Gas Chromatograph	SHIMADZU GC-14B
Detector	FID
Column	VZ10
Carrier gas	H <sub>2</sub> (99.999%)
Carrier gas flow (ml/min)	30 cc/min
-initial Column temperature (°C)	70
-final Column temperature (°C)	70
Injector temperature (°C)	100
Detector temperature (°C)	150
Current (mA)	-
Analyzed gas	Hydrocarbon C <sub>1</sub> -C <sub>4</sub>

The calibration curve for calcination of composition of ethylene in reactor effluent was obtained and shown in Figure B.1.



Mole of ethylene as y-axis and area determined from gas chromatography as x-axis were plotted. The calibration curve of ethylene was illustrated in the following figure.



**Figure B.1** The calibration curve of ethylene

## APPENDIX C

**DETERMINATION OF Ti<sup>3+</sup> SURFACE DEFECT  
FROM ESR MEASUREMENT**

The amount of Ti<sup>3+</sup> surface defect from ESR measurement can be relatively determined from:

$$\text{Ti}^{3+} \text{ surface defects} = \frac{\text{Intensity of ESR peak height}}{\text{catalyst weight}}$$

**Example:** The Ti<sup>3+</sup> surface defect of pure titania are determined as follow;

$$\text{Ti}^{3+} \text{ surface defect} = \frac{2431}{0.1598 \text{ g}}$$

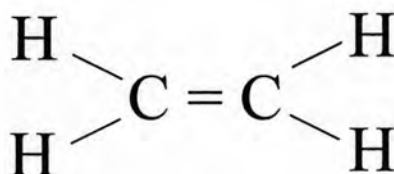
$$= 1901.6$$

Sample	Surface area (m <sup>2</sup> /g)	Weight (g)	Intensity of ESR peak height	Amount Ti <sup>3+</sup> surface defect
EXA350	153.0	0.1598	2431	1901.6
EXA400	144.7	0.1579	869	687.9
EXA500	95.3	0.1598	228	178.3
EXA600	32.0	0.1595	356	279.0

## APPENDIX D

THE CHARACTERISTIC OF REACTANT TESTED IN THE  
PHOTOCATALYTIC OXIDATION

Ethylene (or IUPAC name ethene) is the simplest alkene hydrocarbon, consisting of four hydrogen atoms and two carbon atoms connected by a double bond. Because it contains a double bond, ethylene is called an *unsaturated hydrocarbon* or an olefin.



**Figure C.1** The structural formula of ethylene

The molecule cannot twist around the double bond, and all six atoms lie in the same plane. The angle made by two carbon-hydrogen bonds in the molecule is  $117^\circ$ , very close to the  $120^\circ$  that would be predicted from ideal  $sp^2$  hybridization.

The double bond is a region of slightly higher electron density, and most of ethylene's chemistry involves other molecules reacting with and adding across its double bond. Ethylene can react with bromine, chlorine, and other halogens, to produce halogenated hydrocarbons. It can also react with water to produce ethanol, but the rate at which this happens is very slow unless a suitable catalyst, such as phosphoric or sulfuric acid, is used. Under high pressure, and, in the presence of a catalytic metal (platinum, rhodium, nickel), hydrogen will react with ethylene, saturating it.

**Table C.1** The specific and thermodynamic properties of ethylene

Properties		Properties	
Systemic name	Ethylene	Boiling point	-103.7 °C
Molecular formula	C <sub>2</sub> H <sub>4</sub>	Molecular shape	Planar
SMILES	C = C	Dipole moment	Zero
Molar mass	28.05 g/mol	<i>Thermodynamic :</i>	
Appearance	Colourless gas	Std enthalpy of	
Phase	Gas	formation ; $\Delta_f H^\circ$ gas	+52.47 kJ/mol
Solubility in water	Insoluble	Standard molar	
Flash point	Flammable gas	entropy ; $S^\circ$ gas	219.32 J·K <sup>-1</sup> ·mol <sup>-1</sup>
Melting point	-169.1 °C	Bond energy	~ 537 kcal/mol

Except where noted otherwise, data are given for materials in their standard state (at 25°C, 100 kPa)

#### Application of ethylene

Ethylene is used primarily as an intermediate in the manufacture of other chemicals, especially plastics. Ethylene may be polymerized directly to produce polyethylene (also called *polyethelene* or *polythelene*), the world's most widely-used plastic. Ethylene can be chlorinated to produce ethylene dichloride (1,2-Dichloroethane), a precursor to the plastic polyvinyl chloride, or combined with benzene to produce ethylbenzene, which is used in the manufacture of polystyrene, another important plastic. Smaller amounts of ethylene are oxidized to produce chemicals including ethylene oxide, ethanol, and polyvinyl acetate. Ethylene is also a widely-use refrigerant in commercial low temperature systems due to the low boiling point. Ethylene was once used as an inhaled anesthetic, but it has long since been replaced in this role by nonflammable gases. It has also been hypothesized that ethylene was the catalyst for utterances of the oracle at Delphi in ancient Greece.

## LIST OF PUBLICATIONS

Panomchai Sawangjai and Akawat Sirisuk. "Effects of preparation conditions on properties of titanium dioxide aerogel", Pure and Applied Chemistry International Conference 2008, Bangkok, Thailand, January 30- February 1, 2008.

## VITA

Mr. Panomchai Sawangjai was born on May, 1984 in Samutsakorn province, Thailand. He received the Bachelor Degree of Chemical Engineering from Faculty of Engineering, Srinakharinwirot University, in 2006. He continued his Master's study at Chulalongkorn University in June, 2006.