



CHAPTER III

MATERIALS AND METHODS

3.1 Catalyst preparation

3.1.1 Materials

- Nitric acid (65%wt HNO₃; CARLO-ERBA)
- Iron (III) nitrate nanohydrate (99% Fe(NO₃)₃.9H₂O; MERCK)
- Titanium (IV) n-butoxide (99%wt Ti(OC₄H₉)₄; ACROS)
- Deionized (DI) water
- Dodecylamine (98%wt C₁₂H₂₇N; ACROS)
- Triethylamine (98%wt C₆H₁₅N; Fluka)
- Octadecylamine (90%wt C₁₈H₃₉N; MERCK)

3.1.2 Catalyst Preparation

Based on the method conducted by Hao and Zhang (2009), the co-doped samples were synthesized via sol-gel method by using nitric acid and iron (III) nitrate nanohydrate as a nitrogen and iron (III) source.

Firstly, 10 ml of Ti(OC₄H₉)₄ was added dropwise slowly into the solution between 45 ml HNO₃ of 1.8 M and 0.1176 g of Fe(NO₃)₃.9H₂O with vigorous stirring at 40°C to get two layers solution, the upper layer was an organic and the lower layer was a transparent sol. The transparent sol was separated from the organic and refluxed at 80°C for 2 h. The white precipitate was obtained. After that, 0.0147 mol of template was added dropwise to the white precipitate with vigorous stirring for 30 min. The mixture was aged at 80°C for 48 h in a closed flask until white gel was appeared, then transferred to a Petri dish and dried at 80°C for 24 h to give a yellow xerogel. Finally, the as-synthesized samples were calcined at 400°C for 2 h with heating rate of 1°C/min (Figure 3.1). The co-doped sample were marked Fe-N-TiO₂-xC, where x is the number of carbon in the chemical formula of each template as 6C (triethylamine), 12C (dodecylamine) and 18C (octadecylamine).

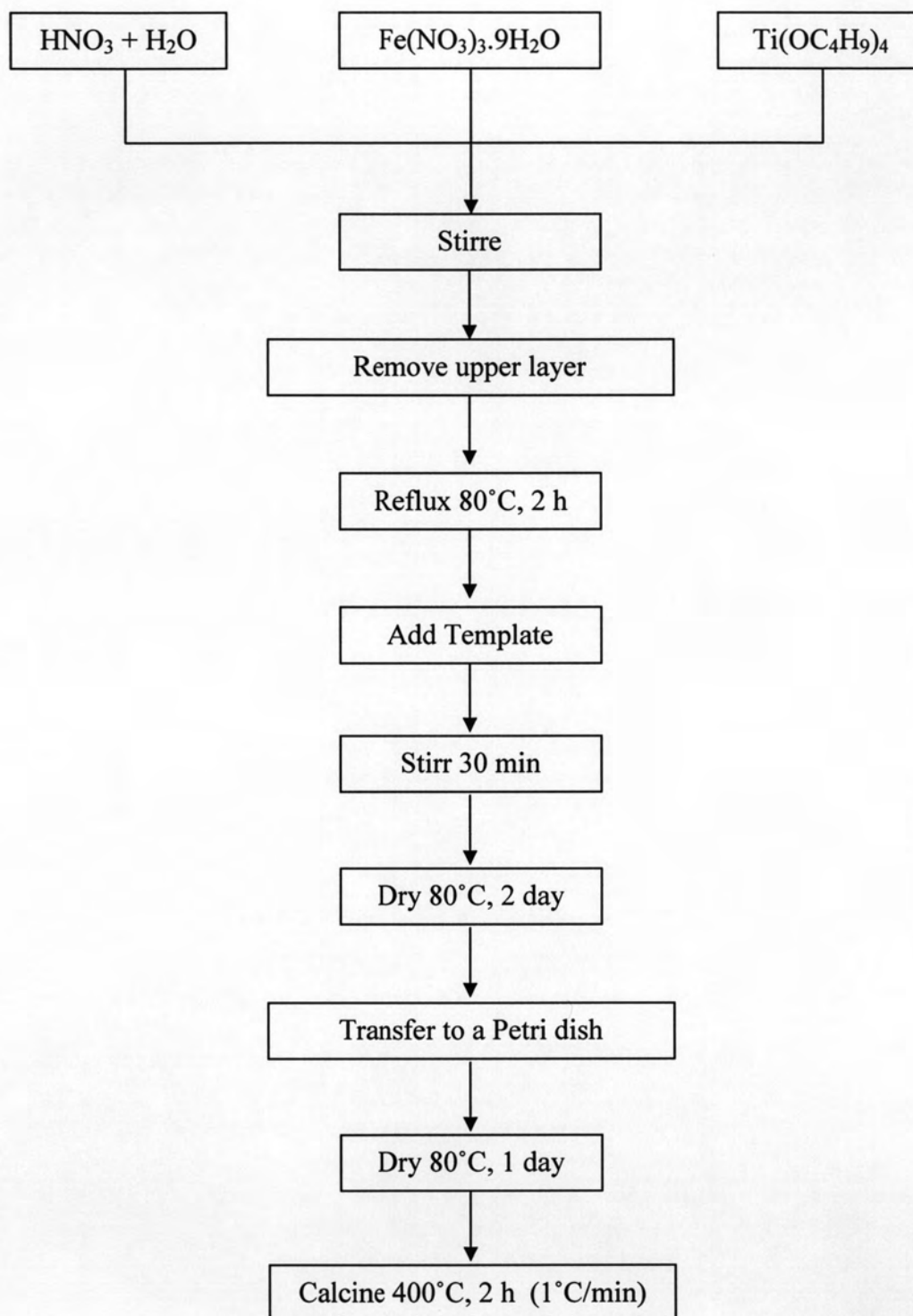


Figure 3.1 Diagram for preparation of photocatalyst

3.2 Characterization

3.2.1 Thermogravimetric-differential thermal analysis (TG-DTA)

Thermogravimetric-differential thermal analysis (TG-DTA) (STA 449C NETZSCH) with a heating rate of 10°C/min in static air up to 800°C was employed to determine the temperature for decomposition and crystallization of the as-synthesis powders. The complete burning of sol gel precursor and template could be discussed from the temperature profile.

3.2.2 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) was used to identify the crystalline structure and composition of the photocatalysts. A Bruker D8 powder X-ray diffractometer was carried out at room temperature with an apparatus using Cu K α radiation with continuous scanning mode. Diffraction patterns were recorded in the angular range of 20°-80° with a stepwidth of 0.02°/sec. The strongest peak of TiO₂ corresponding to anatase (101) was selected to evaluate the crystallite size according to Equation (3.1), commonly known as the Scherrer's equation:

$$D = K\lambda / \beta \cos\theta \quad (3.1)$$

Where:

D	=	the crystallite size (nm)
K	=	the Scherrer constant (0.89)
λ	=	the X-ray wavelength (1.5496 Å)
β	=	the half-height width of the diffraction peak of anatase (degree)
θ	=	the diffraction angle (degree)

3.2.3 Brunauer-Emmett-Teller (BET) method

Specific surface area of all photocatalysts was obtained by using BET-surface area analyzer (Autosorb 1, QuantaChrom) with common adsorbate N₂, at -196°C. The photocatalyst was first outgased to remove the humidity and volatile adsorbents

adsorbed on its surface under vacuum at 250°C for 2 h before starting the analysis to determine the surface area.

3.2.4 UV-visible diffuse reflectance spectrophotometer (UV-DRS).

UV-DRS (HITACHI U-3501) was used to record the of the photocatalyst samples at room temperature and the scanning range was between 250 to 800 nm with BaSO₄ as the reference. The direct band gap energy (E_b) of photocatalyst can be calculated by fitting the absorption data to the direct transition equation (Santi, Paveena, and Promarak., 2006) presenting in Equation 3.2:

$$\alpha h\nu = E_D (h\nu - E_g)^{1/2} \quad (3.2)$$

Where:

- α = the optical absorption coefficient
- $h\nu$ = the photon energy
- E_g = the direct band gap
- E_D = the constant

3.2.5 X-ray Absorption Near Edge Structure (XANES)

XANES was used as a probe of the unoccupied band structure of a material. Due to, the near-edge structure is characteristic of an environment and valence state hence one of its more common uses is in fingerprinting. The XANES spectra were normalized with the Athena program, the edge shifts were corrected with standard reference compounds to determine characteristics of the photocatalyst.

This experiment was performed at Beamline-8 of Synchrotron Light Research Institute (SLRI), Thailand.

3.2.6 Zeta Potential (ZP)

A Zeta-meter model 3.0+ was used to measure the electrokinetic potential (zeta-potential) of photocatalyst powder surfaces. The photocatalyst 0.5 mg were suspended in 20 ml of a solution which was adjusted pH by HNO₃ or NaOH. Each photocatalyst was repeated at least 8 times to get the average values.

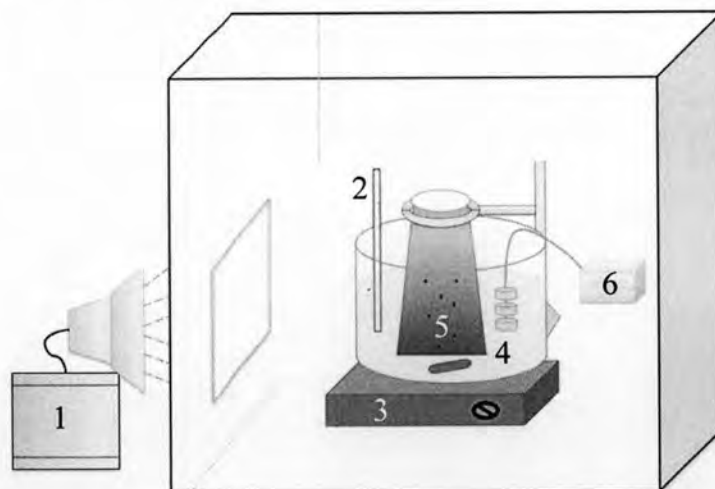
3.3 Testing for photocatalytic performance

3.3.1 Materials

- 2,4-dichlorophenol, (99% C₆H₄Cl₂O; ACROS)
- Nitric acid, (69-70% HNO₃; JT Baker)
- Sodium hydroxide (99% NaOH; Merck)
- Deionized (DI) water
- Methanol (99.9% CH₃OH (for HPLC); RCI Labscan)
- Acetonitrile (99.9% CH₃CN (for HPLC); RCI Labscan)
- Water (H₂O (for HPLC); RCI Labscan)

3.3.2 Photoreactor setup

The photodegradation of 2,4-DCP with Fe-N-TiO₂-xC photocatalyst powder was carried out in glass batch reactor (Figure 3.2). The light source was a 500W Xenon lamp. The cut-off wavelength solution (1M NaNO₂) was used to control the wavelength in visible light range only. The cooling water system provided a constant temperature of 25±2°C in the reactor.



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|---------------------|--|
| 1. Xenon lamp | 4. Cut-off solution |
| 2. Thermometer | 5. Photocatalyst dispersed in 2,4-DCP solution |
| 3. Magnetic stirrer | 6. Cooling water |

Figure 3.2 Diagram of experiment setup for photocatalytic reaction.

3.3.3 Photocatalytic procedures

The initial pH of the 2,4-DCP solution was adjusted to 5.5 with HNO₃ and NaOH, measured with pH meter (Ultrabasic pH meter, Denver instrument). The Fe-N-TiO₂-xC powder was suspended and completely dispersed in an aqueous of 2,4-DCP solution by stirrer in the dark for 1 h. After that, the xenon lamp was turn on. Samples were filtered with syringe filter (0.45 μm, PTFE) to remove photocatalyst powder. Sample were collected at different times until the almost of the initial 2,4-DCP were degraded. Blank experiments were also carried out without photocatalyst powder for checking the photo-induced self-sensitized photodegradation.

3.3.4 Analytical method

The concentration of 2,4-DCP were analyzed by using high performance liquid chromatography with diode-array detector (HPLC-DAD 1200 series detector, 1100 series pump and controller, Agilent technologies) and maximum absorption wavelength at 280 nm. The analysis column was Hypersil C18 ODS (125x4 nm I.D, 5 μm column). The mobile phase was a mixture of 60%CH₃OH and 40%H₂O with flow rate of 1.0 mL/min. The mobile phase was filtered and degassed for 30 minutes prior to use. The retention time was kept at 6.5 minutes.

The concentrations were calculated using the standard calibration curves of 2,4-DCP. The photodegradation efficiency (X) is given by the Equation 3.3.

$$X = [(C_0 - C_t) / C_0] \times 100\% \quad (3.3)$$

Where:

- C₀ = Initial concentration of 2,4-DCP
 C_t = 2,4-DCP concentration at time t.

3.3.5 Experimental design and statistical analysis

The classical method of studying one variable at a time can be effective in some cases, but it is useful to consider the combined effects of all the factors involved. Response surface methodology (RSM) is a powerful mathematical model

with a collection of statistical techniques by which interactions between multiple process variables can be identified with fewer experimental trials. It is widely used to examine and optimize the operational variables for experimental design, model developing, and factors and conditions optimization. There are various advantages in using statistical methodologies in terms of rapid and reliable short listing of process conditions, understanding interactions among them, and a tremendous reduction in total number of experiments, resulting in saving time (Karuppaiya et al., 2009)

By using RSM analysis, it is able to determine whether factor is significant by referring to 'p' value based on the analysis result. To determine whether the factor is affecting the degradation percentage of 2,4-DCP, the 'p' value should be less than 0.5

In this study, we adopted RSM experiments based on a Box-Behnken design (BBD) with a quadratic model in order to find out the optimal operating conditions for the next laboratory work. The experiment data were analyzed statistically using Minitab® 15.1 software. Three parameters (mol% Fe: 0, 0.5, 1.0, photocatalyst loading: 0.5, 1.0, 1.5 g/L, type of template: 6C, 12C, 18C) were chosen for studying the effect of individual factors and the effects of interactions of studied factors. The chosen levels for each parameter were mol% Fe: The number of experiments required (N) is given by (Equation 3.4):

$$N = 2k(k-1) + C_0 \quad (3.4)$$

Where:

- k = the number of parameters
 C₀ = the number of center points

For three parameters (n=3) with three central points and two replicates, the total number of experiments in this study were 30. The experiments were performed in a random manner in order to avoid any systematic bias in the outcomes.