

CHAPTER III EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2) and Reactive Black 5 dyes were purchased from Sigma Aldrich Chemical Co. Inc. (USA). Titanium dioxide was supplied by Carlo Erba. Ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) was obtained by J.T. Baker (White Group). Sodium hydroxide, acetonitrile (CH_3CN) and triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) were purchased by Labscan Asia Co., and used as received. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd. (Bankkok Thailand). Cetyltrimethylammonium bromide (CTAB) was obtained from Sigma Chemical Co. Hydrogen peroxide was supplied by Ajax Finechem (Aus.). Hydrochloric acid (HCl) was purchased from MERCK Co. (Germany).

3.2 Experimental Equipment

3.2.1 Fourier Transform Infrared Spectrophotometer (FT-IR)

Infrared spectroscopy provided functional groups information on the vibration of the precursors (silatrane, titanium glycolate and molybdenum glycolate) which the spectra were obtained using a Nicolet, NEXUS 670 with a resolution of 4 cm^{-1} . The solid samples were mixed and pelletized with dried KBr.

3.2.2 Thermal Gravimetric Analysis (TGA)

TGA thermograms were carried out using TG-DTA (Pyris Diamond Perkin Elmer) with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of room temperature to 750°C under nitrogen atmosphere to determine the thermal stability of silatrane, titanium glycolate and molybdenum glycolate.

3.2.3 X-Ray Diffraction (XRD)

X-ray patterns were carried out to characterize crystallinity on Rigaku X-ray diffractometer with $\text{CuK}\alpha$ as a X-ray source. Sample was ground using

alumina mortar and spread on a glass slide specimen holder. A range from 1.5° to 10° was investigated using a rate of 1°/min.

3.2.4 Diffuse Reflectance UV-VIS Spectroscopy (DRUV)

DRUV was extensively used to detect the framework and extra-framework titanium and molybdenum species using SHIMADZU UV 2550-VISIBLE spectrophotometer in the range of 200 to 500 nm. The spectra were used to probe the band structure, or molecular energy level, in the materials because UV excitation created photo-generated electron and hole. The band at 220 nm was originated from the charge transfer of the $p\pi-d\pi$ transition between titanium and oxygen of the framework titanium species, Ti-O-Si, in Ti-MCM-41. The tail of the band centered at 220 nm was actually extended to 330 nm due to the presence of extra-framework titanium species, TiO₂. Traditionally, the absorption band from 230-280 nm was assigned to Mo (T_d) and the band from 270-330 nm was assigned to Mo (O_h).

3.2.5 Surface Area and Average Pore Size

Surface area and average pore size were measured by BET method using a Quantasorb JR. (Autosorb 1). The catalyst was degassed at 250°C for 10 h before analysis.

3.2.6 Total Organic Carbon (TOC)

The concentration of organic carbons (all carbon atoms covalently bonded in organic molecules) in solution was determined by oxidation of the organic matter into carbon dioxide using a TOC-Vcsh.

3.3 Methodology

3.3.1 Synthesis of Silatrane [Si(TEA)₂]

Silatane (tris(silatanyloxy-ethyl)amine or SiTEA) was synthesized following Wongkasemjit's method by reacting 0.125 mol triethanolamine with 0.1

mol silicon dioxide using ethylene glycol as solvent at 200°C under nitrogen atmosphere. The reaction was complete within 10 h., and the reaction mixture was allowed to cool to room temperature before removing solvent by distilling under vacuum (10^{-2} torr) at 110°C overnight. The resulting brownish white solid was washed three times with dry acetonitrile to fine white powder. (Piboonchaisit *et al.*, 1999) The product obtained was characterized using TGA and FTIR.

3.3.2 Synthesis of Titanium Glycolate

The titanium glycolate was synthesized following Phonthammachai's method. A mixture of TiO₂ (2g, 0.025 mol) and TETA (3.65 g, 0.0074 mol) was stirred vigorously in excess EG (25 cm³) and heated at the boiling point of EG under N₂ atmosphere. After heating for 24 h, the solution was centrifuged to separate the unreacted TiO₂ from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain crude precipitate. The white crude solid product was washed with acetonitrile and dried in a vacuum desiccator. (Phonthammachai, N *et al.*, 2002). The product obtained was characterized using TGA and FTIR.

3.3.3 Synthesis of Molybdenum Glycolate

The molybdenum glycolate was synthesized following Wongkasemjit's method by mixing MoO₃ (4.2886 g) and EG (50 ml) with stirring vigorously and heating at the boiling point of EG under N₂ atmosphere for 15 min. The solution was centrifuged to separate the unreacted MoO₃ from the solution part which was left at room temperature for 3 days to obtain the molybdenum glycolate solid. The product was washed with acetonitrile and dried in a vacuum desiccator. The product obtained was characterized using TGA and FTIR.

3.3.4 Synthesis of Ti-MCM-41

Various ratios of silatrane and titanium glycolate precursors in the range of 1-5 % Ti were studied by adding into a solution containing 0.5 mol CTAB, 0.001 mol NaOH, 0.014 mol TEA and 0.36 mol of water. The mixture was stirred for 3 h to obtain crude product which was filtered and washed with water to result in white solid. The white solid was dried at room temperature and calcined at 550°C to

result in mesoporous Ti-MCM-41. The product obtained was characterized using DRUV, XRD and BET.

3.3.5 Synthesis of Mo-MCM-41

In this work incipient wetness impregnation was used to incorporate Mo onto the MCM-41 support using 1-5% molybdenum glycolate precursor. The precursor was dissolved in water and dropped into catalyst supports, MCM-41. Evaporation of water was carried out at 100°C in the oven for 12 h, followed by calcinations at 550°C. The product obtained was characterized using DRUV, XRD and BET.

3.3.6 Photocatalytic Oxidation Process

The influences of variables, namely, pH (3, 5, 7, and 9) while using 10 mmol of H₂O₂ condition, concentration of H₂O₂ (10, 20 and 30 mmol) while using the best pH condition, %Ti loading and %Mo dispersion using the best condition of both pH and H₂O₂ conditions were studied. The initial pH was adjusted using either hydrochloric acid or sodium hydroxide. Photocatalytic oxidation process using 40 mg/L of reactive black 5 dyes solution as a model for degrading dyes under condition of UVA (400 nm > λ > 300 nm) light source, air bubble, 6 h. reaction time and 0.3 g/L of catalyst was carried out. Before starting the photocatalytic oxidation process, the reaction mixture was stirred in a dark box for 1 h. to supposedly reach good mixing solution. Aqueous solution of degraded dye was characterized using TOC and UV-Vis spectroscopy at 580 nm which is the maximum absorbance of the reactive black 5 dyes solution. Moreover, the degradation and decolorization of the dye were confirmed by UV-Vis absorption spectra analysis from 190 to 900 nm.