

CHAPTER III EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2), molybdenum oxide (MoO_3) and 4-nitrophenol (4-NP) were purchased from Aldrich Chemical Co. Titanium dioxide (TiO_2), potassium bromide (KBr), ammonium hydroxide and hydrogen peroxide (H_2O_2) were purchased from Carlo Erba. 2-[(4-hydroxyphenyl)(4-oxo-2,5-cyclohexadien-1-ylidene)methyl] benzene sulfonic acid (phenol red), ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$), nitric acid and triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$) were supplied by Labscan Asia Co., and used as received. Acetonitrile (CH_3CN) was also obtained from Labscan Asia Co. and distilled before use. Cetyltrimethylammonium bromide (CTAB) and sodium hydroxide were purchased from Sigma Chemical Co. HEPES buffer solution (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) and bismuth (III) nitrate pentahydrate were obtained from Fluka.

3.2 Materials Characterization

FTIR spectroscopic analysis was conducted using a Bruker Instrument (EQUINOX55) with a resolution of 4 cm^{-1} . The solid sample was prepared by mixing 1% of sample with anhydrous KBr. Laser Raman was conducted using Horiba HR800. Thermal properties were analyzed using Du Pont Instrument TGA 2950 thermogravimetric analysis (TGA). The mesoporous product was characterized using a Rigaku X-ray diffractometer (XRD) with $\text{CuK}\alpha$ source at a scanning speed of 0.75 degree/sec . The working range was $2\theta = 1.5\text{-}10$. Electron microscope study (TEM micrographs and electron diffraction patterns) were carried out using JEOL 2010F. Surface area and average pore size were determined by BET method using a Quantasorb JR. (Autosorb-1). The product was degassed at 250°C for 12 hr prior to analysis. Diffuse reflectance ultraviolet spectroscopy was used to identify the location and the coordination of transition metal in hexagonal structure. The

reflectance output from the instrument was converted using Kubelka-Munk algorithm. The metal content was characterized using SEM/EDS and XRF. Particle size analyzer was conducted using Malvern Instrument. The calcination was conducted using a Carbolite Furnace (CFS 1200) with the heating rate of 1°C/min.

3.3 Precursor Synthesis

3.3.1 Silatrane Synthesis

Wongkasemjit's synthetic method was followed by mixing silicon dioxide, and triethanolamine in a simple distillation set using ethylene glycol solvent. The reaction was done at the boiling point of ethylene glycol under nitrogen atmosphere to remove water as a by-product along with ethylene glycol from the system. The reaction was run for 10 hr and the rest of ethylene glycol was removed under vacuum (1.6 Pa) at 110°C. The brownish white solid was washed with acetonitrile for three times to obtain the final white powder product having theoretical ceramic yield of around 19%.

3.3.2 Titanium Glycolate Synthesis

A mixture of titanium dioxide (0.025 mol, 2 g), triethylenetetramine (0.007 mol, 3.7 g), used as a catalyst, and 25 mL of ethylene glycol, used as a solvent were heated to the boiling point of EG for 24 hr, followed by separating the unreacted TiO₂ from the solution part. The excess EG and TETA were removed by vacuum distillation to obtain the crude white solid product. The crude product was then washed with acetonitrile and dried in a vacuum desiccator before characterization using FTIR, FAB⁺-MS and TGA.

3.3.3 Molybdenum Glycolate Synthesis

The method of Wongkasemjit was followed. Molybdenum oxide and ethylene glycol were mixing in a simple distillation set. The reaction was done at 150°C for 15 min under nitrogen atmosphere followed by separating of unreacted MoO₃ from the solution part. The obtained solution was left to crystalline. Then, the crystalline solid was washed with dried acetonitrile for three times to obtain white crystal product.

3.4 Catalyst Synthesis

3.4.1 Synthesis of MCM-41

4×10^{-3} mol silatrane precursor was added to a solution containing x mol of CTAB, y mol of NaOH and 14×10^{-3} mol of TEA. 36×10^{-2} mol of water was then added with vigorous stirring. The mixture was stirred for various times to follow the reaction using XRD, BET and TEM. The obtained crude product was filtered and washed with water to obtain a white solid. The white solid was dried at room temperature and calcined at 550°C for 3 hrs to obtain mesoporous MCM-41. In this study, surfactant concentration, ion concentration, mixing temperature and aging time were varied to find an optimum condition.

3.4.2 Synthesis of Ti-MCM-41

Various ratios of silatrane and titanium glycolate precursors in the range of 1-35 % Ti were studied by adding into a solution containing 112×10^{-5} mol CTAB, 1×10^{-3} mol NaOH and 14×10^{-3} mol TEA. 36×10^{-2} mol of water was then added with vigorous stirring at 60° and 80°C . The mixture was stirred for various times to follow the reaction using DRUV. The obtained crude product was filtered and washed with water to obtain a white solid. The white solid was dried at room temperature and calcined at 550°C for 3 hr to obtain mesoporous Ti-MCM-41 characterized using XRD, XRF, EDS, BET and TEM.

3.4.3 Synthesis of Mo-MCM-41

In this work incipient wetness impregnation was used to incorporate Mo onto the supports using 3, 5, 7, 10 mol% molybdenum glycolate precursor. The precursor was dissolved in the water and dropped into catalyst supports, MCM-41(c)/(u) (synthesized as explain previously). The water was evaporated out at 100°C in the oven for 12 hrs, followed by calcination at 550°C . The product obtained was characterized using DRUV, XRD, EDS, FTiR, Laser Raman and BET.

3.4.4 Synthesis of $\text{Bi}_{12}\text{TiO}_{20}$

Bismuth (III) nitrate pentahydrate was dissolved in nitric acid, and the stoichiometric amount of titanium glycolate was added to the solution with vigorously stirring until the mixture turned clear. The pH of the mixture was adjusted

in the range of 3 to 10 using ammonium hydroxide and nitric acid. After stirring for 1 hr, the mixture was centrifuged to separate the precipitate out and washed with water until the filtrate became neutral. The white solid obtained was dried at 60°C and calcined at 300°-600°C.

3.5 Catalytic Activity Testing

3.5.1 Catalytic Testing of Ti-MCM-41 and Mo-MCM-41

The peroxidative bromination test was used to qualitatively study catalyst activity. Ti-MCM-41 and Mo-MCM-41 were added into a mixture of 0.2 mM phenol red, 0.1 M KBr, 10 mM H₂O₂ in 0.1M HEPES buffer having pH 6.5. Then, the mixture was stirred for various times. The total volume of the mixture was 3.5 mL. The formation of 2-[(3,5-dibromo-4-hydroxyphenyl)(3,5-dibromo-4-oxo-2,5-cyclohexadien-ylidene)methyl]benzenesulfonic acid (bromophenol blue) from phenol red was monitored by UV-vis spectrophotometer after removing the solid catalyst.

3.5.2 Catalytic Testing of Bi₁₂TiO₂₀

Photocatalytic activity test was carried out in the UV box containing magnetic stirrer. Each reaction suspension was prepared by adding the prepared sample into a 100 ml solution mixture of 44 ppm 4-nitrophenol in water. Prior to irradiation, the suspension was magnetically stirred in the dark for 1 hr to establish adsorption equilibrium. Simultaneously, UV tests without catalysts were investigated to exclude direct photolysis. The suspensions of catalysts in 4-NP were then illuminated using a 100 Watt Hg Philip UV lamp without bubbling oxygen into the solution. The distance between the liquid surface and light source was about 4-5 cm. During photocatalytic testing, the samples were continuously stirred using magnetic stirrer. Sampling was done at the same time intervals for all the samples. The samples were filtered using 0.45 µm Nylon filters before analysis for 4-nitrophenol concentration by UV-Vis spectrometer and TOC analyzer.