

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

Fumed silica ( $\text{SiO}_2$ , 99.8%, Nippon Aerosil, Japan), HP grade nitrogen ( $\text{N}_2$ , 99.98% purity, Thai Industrial Gases Public Company Limited (TIG), Thailand), ethylene glycol (EG, 99%, J.T. Baker, USA), triethanolamine (TEA, QRęc chemical, Thailand), acetonitrile ( $\text{CH}_3\text{CN}$ , 99.9%, Labscan, Thailand), cerium(III)nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99%, Sigma-Aldrich, Germany), ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , 99.9%, Labscan, Thailand), sodium hydroxide ( $\text{NaOH}$ , 99%, Labscan, Thailand), cetyltrimethylammonium bromide (CTEB, 96.0%, Fluka, Germany), copper(II)nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99.5%, Merck, Germany), hydrogen tetrachloroaurate(III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 49.0% Au basis, Sigma-Aldrich, Germany), and sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.8%, Ajax, Thailand) were used without further purification.

#### 3.2 Precursor Synthesis

##### 3.2.1 Synthesis of Silatrane [Phiriyawirut *et al.*, 2003]

Silatrane is synthesized by following Wongkasemjit's method. A mixture was prepared by mixing 0.1 mol silica, 0.125 mol TEA, and 100 ml EG, and refluxed at 200 °C under  $\text{N}_2$  atmosphere for 10 h. Excess EG was removed at 110 °C under vacuum. A crude yellow solid was purified by washing with acetonitrile, followed by vacuum-drying overnight to obtain a fine white powder. The silatrane product was vacuum-dried overnight before characterization using TGA and FT-IR.

##### 3.2.2 Synthesis of MCM-48 [Longloilert *et al.*, 2011]

Synthesis of MCM-48 was followed Wongkasemjit's method by dissolving CTAB, used as surfactant, in a mixture of water and 2 M NaOH with heating at 50 °C until obtaining homogenous solution before adding silatrane. The solution was stirred for 1 h. The molar composition of the mixture is

1.0SiO<sub>2</sub>:0.3CTAB: 0.5NaOH:62H<sub>2</sub>O. The mixture was transferred to a Teflon-lined stainless steel autoclave and treated at 130°–150 °C for 16 h to obtain white solid. The product was collected by filtration and dried overnight at ambient conditions. The surfactant was removed by calcinations at 550 °C for 6 h to obtain light white powder. The product was characterized by XRD.

### 3.2.3 Synthesis of Ordered Mesoporous Cerium Oxide

[Deeprasertkul *et al.*, 2015]

The MCM-48 used as hard template and cerium(III)nitrate hexahydrate precursor with 50% weight of ceria were dissolved in 5 ml of ethanol and stirred for 30 min. The exceed ethanol was removed by evaporation in an oven at 100 °C. The obtained powder was heated in a ceramic crucible at 550 °C for 6 h to decompose the nitrate species. The silica hard template was removed by using 2 M NaOH at 50 °C for 3 times and the mixture was centrifuged to obtain the product. The product was washed by deionized water followed by centrifugation until neutral solution was obtained. The obtained powder was dried at 100 °C prior to characterization using XRD, TEM, XRF, and N<sub>2</sub> adsorption/desorption.

### 3.2.4 Synthesis of Copper Loaded Mesoporous Ceria

[Gamboa-Rosales *et al.*, 2012]

Cu loaded on MSP ceria catalyst was prepared by deposition-precipitation (DP) method, using aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O precursor with different copper loading (3, 5, 7 and 9 wt%). Catalyst prepared by DP was stirred at room temperature for 1 h. After that, heat to 80 °C and adjust pH = 7 with Na<sub>2</sub>CO<sub>3</sub> for 1 h, after reaching the time, the suspension was filtered and washed with warm deionized water to eliminate the residue ions. Then, Cu loaded ceria was dried at 110 °C in air and calcined in air at various temperatures 500 °C for 6 h. The synthesized products were characterized by XRD, TEM, AAS, XPS, DR UV-Vis, H<sub>2</sub>-TPR and N<sub>2</sub> adsorption/desorption, and evaluated the efficiency of the catalysts in the PROX reaction.

### 3.3 Materials Characterization

The phase of mesoporous products were characterized on a Rigaku TTRAX III Small Angle X-Ray Diffraction (SAXD) with a scanning speed of 1 °/min and CuK $\alpha$  source ( $\lambda = 0.154 \text{ \AA}$ ) in a range of  $2\theta = 2\text{--}6^\circ$ . Wide Angle X-Ray Diffraction (WAXD) was performed on a Rigaku Smartlab<sup>®</sup> with a scanning speed of 1 °/min and CuK $\alpha$  source ( $\lambda = 0.154 \text{ \AA}$ ) in a range of  $2\theta = 20\text{--}80^\circ$  to determine the metal nano crystals and dispersions. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) on a Quantasorb Jr. (Autosorb-1). Prior to each analysis, the product was degassed at 250 °C for 12 h. Identification of metal loaded Ceria support was analyzed in a range of 200-900 nm by ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy on a Shimadzu UV-2550 using BaSO<sub>4</sub> as the reference. The metal contents in samples were observed by X-ray fluorescence (XRF) on AXIOS PW 4400 and atomic adsorption spectroscopy (AAS). The surface composition and oxidation state of the surface elements were characterized by X-ray photoelectron spectroscopy (XPS). The temperature-programmed reduction under hydrogen (H<sub>2</sub>-TPR) was used to investigate the redox properties.

### 3.4 Activity Study

All catalytic activity measurements for PROX were evaluated in a fixed-bed U-tube micro-reactor at atmospheric pressure by packing with 100 mg of the catalyst of 80-120 mesh inside. The activity was investigated at various temperatures in the range of 50–250 °C. The composition of feed gas (in vol%) for PROX reaction was H<sub>2</sub>/O<sub>2</sub>/CO = 40/1/1, balanced in He with a total flow rate of 50 ml/min. The influent and effluent gases were analyzed by auto-sampling in an on-line gas chromatograph (Agilent Technologies 6890N) equipped with a packed carbosphere column (80/100 mesh and 10 ft x 1/8 inch) and a thermal conductivity detector (TCD). The CO conversion or catalytic activity calculations was based on the CO consumption. The CO selectivity was determined by the ratio of O<sub>2</sub> consumption for CO conversion

reaction to the total O<sub>2</sub> consumption. Moreover, The effect of feed component on catalyst for the PROX reaction was studied by adding 10 vol.% CO and 10 vol.% water into influent gases with maintaining a composition of prior feed gas (H<sub>2</sub>/O<sub>2</sub>/CO = 40/1/1) and a total flow rate of 50 ml/min.