CHAPTER III
EXPERIMENTAL

3.1 Materials

Aluminium hydroxide ($Al(OH)_3$) and fumed silica (SiO_2) were purchased from Sigma Chemical Co. Triisopropanolamine (TIS, $N[CH_2CH(CH_3)OH]_3$) and triethanolamine ($N[CH_2CH_2OH]_3$) were supplied from Aldrich Chemical Co. Inc., USA. Ethylene Glycol (EG, $HOCH_2CH_2OH$) was received from J.T. Baker, Inc., Phillipsburg, USA. Acetonitrile (CH_3CN) was obtained from Lab-Scan Company Co., Ltd. Triethylamine (TEA, $N[C_2H_5]_3$) was purchased from Fisher Scientific. Phosphoric acid solution (H_3PO_4) and hydrofluoric acid (HF) were supplied from Merck. Tetraamine Platinum (II) Chloride ($[NH_3]_4PtCl_2$) was received from Alfar Aesar. All chemicals were used without pretreatment.

3.2 Materials Characterization

Powder X-ray diffraction (XRD) patterns were carried out using a Rigaku X-ray diffractometer with CuKα as a source in a range from 5 ° to 50 ° with a step of 5 °/min. Functional groups of materials were followed using an FTIR spectrophotometer (Nicolet, NEXUS 670) with a resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) was carried out using TG-DTA (Pyris Diamond Perkin Elmer) with a heating rate of 10 °C/min in a range of room temperature to 750 °C under nitrogen atmosphere to determine the thermal stability. The BET surface area measurement, pore volume, and pore size distribution were measured using nitrogen at 77 K in an Autosorb-1 gas sorption system (Quantasorb JR). Morphology was studied on a JEOL 5200-2AE scanning electron microscope. TEM (JEOL JEM 2100) was conducted to determine particle size and distribution of Pt metal. Chemical composition of the samples was clarified by X-ray fluorescence (XRF Philips PW 2400). Calcination was conducted using a Carbolite furnace (CFS 1200) with a heating rate of 1 °C/min. Hydrothermal crystallization was carried out using Milestone's

Ethos Microwave Solvent Extraction Lab-station. The frequency of the microwave radiation was 2.45 GHz. The crystallinity of the samples was determined from the XRD pattern diffraction data using the following equation;

$$\% \text{ crystallinity} = (\Sigma I/\Sigma I_s)*100$$

where I is the line intensity of the sample and I_s is the line intensity of the standard sample. The standard sample is the sample with the highest crystallinity and no amorphous as identified by XRD and supported by SEM. The line intensities of the XRD pattern at 2θ = 7.5, 14.9, 19.8, 21.1, 22.5, and 26.0 (Wan *et al.*, 2000) were employed for these calculations.

3.3 Precursor Preparation

In this study metal alkoxide precursors were prepared by the Oxide One Pot Synthesis (OOPS) Process.

3.3.1 Alumatrane Synthesis

The preparation of alumatrane or tris(alumatranyloxy-*i*-propyl)amine, followed the work of Wongkasemjit *et al.* (Opornsawad *et al.*, 2001). Aluminium hydroxide (0.1 mole), TIS (0.125 mole), and EG (100 mL) were added to a 250 mL two-necked round bottom flask. The mixture was homogeneously stirred at room temperature before being heated to 200 °C under nitrogen in an oil bath for 10 h. Excess EG was removed under vacuum (10^{-2} Torr) at 110 °C to obtain crude product. The crude solid was washed with acetonitrile and dried under vacuum at room temperature. Dried products were characterized using TGA and FTIR.

3.3.2 Silatrane synthesis

The method of Wongkasemjit and coworkers (Piboonchaisit *et al.*, 1999) was followed by mixing fume silica (0.1 mole), triethanolamine (0.125 mole), and EG (100 mL) in a 250 mL two-necked round bottom flask. The mixture was heated to the boiling point of EG under nitrogen for 10 h in oil bath. The rest of EG was removed under vacuum at 110 °C. The brownish white solid was washed with acetronitrile to obtain white powder and dried under vacuum at room temperature before characterization using TGA and FTIR.

3.4 Catalyst Preparation

3.4.1 Synthesis of Mesoporous $AlPO_4$-5 (AFI)-type via Microwave Technique Using Alumatrane Precursor

The $AlPO_4$-5 was prepared using TEA as a structure-directing agent. Alumatrane was mixed with 1M phosphoric acid solution and homogeneously stirred at room temperature, followed by adding TEA and various specified amounts of water. HF was added successively to the gel. The mixture was stirred until becoming homogeneous before transferring to a Teflon-lined vessel sealed with a Teflon cap contained in a microwave for further heating at a reaction temperature range of 180 °–200 °C for 0.5–2 h. The product was washed and dried, followed by calcining at 600 °C for 7 h. Amounts of structure-directing agent and of water, microwave time, and temperature were varied.

3.4.2 Synthesis of Mesoporous SAPO-5 (AFI)-type via Microwave Technique Using Atrane Precursors

Alumatrane was mixed with diluted phosphoric acid solution at room temperature. Silatrane was added to the mixture with various mole ratios of SiO_2/Al_2O_3, followed by adding TEA as a structure-directing agent. The mixture was aged under homogeneously stirring at various aging times before being loaded into a Teflon line vessel sealed with a Teflon cap and placed in a microwave oven. The reaction mixture was heated for hydrothermal crystallization. The products were filtered, washed, and dried. The as-synthesized products were calcined at 600 °C for 7 h. The reaction temperature (180 °–200 °C) and time (0.5–2 h) of the microwave heating, the amount of SiO_2 content, and the aging time were varied.

3.4.3 Synthesis of Flower-like SAPO via Microwave Technique Using Atrane Precursors

Flower-like SAPO was synthesized by mixing alumatrane with 1M phosphoric acid solution and homogeneously stirred at room temperature. Silatrane was added into the synthesis mixture. The mixture was stirred until homogenous before loading into a Teflon-lined vessel sealed with a Teflon cap, followed by hydrothermal heating with microwave radiation at a reaction temperature range of 180 °–200 °C for

0.5–2 h. The product was washed and dried, followed by calcining at 600 °C for 7 h. The microwave heating time and temperature, pH, and the aging time were varied.

3.4.5 Synthesis of Pt/$AlPO_4$-5, Pt/SAPO-5 and Pt/Flower-like SAPO

All supports, mesoporous $AlPO_4$-5, mesoporous SAPO-5 and flower-like SAPO, were impregnated with an aqueous solution of $(NH_3)_4PtCl_2$. The impregnation of Pt content of 1, 3, and 5 % w/w were loaded, followed by drying at 110 °C and calcining at 500 °C for 4 h before catalyst testing.

3.5 Catalytic Activity Testing over PROX of CO

3.5.1 Catalytic Testing of Pt/$AlPO_4$-5, Pt/SAPO-5 and Pt/Flower-like SAPO

All catalysts were tested over PROX of CO. The catalytic activity was measured in a fixed-bed, U-tube, reactor loading with 100 mG of catalyst. The reaction was carried out in a temperature range of 80 °–300 °C with a total flow rate of 50 mL min^{-1}. A gas reactant consists of 1 % CO, 1 % O_2 and 40 % H_2 balanced in He. The gas compositions were measured by gas chromatography equipped with thermal conductivity detector (TCD). The conversions of CO and O_2 were calculated from the ratio of the amounts of CO and O_2 used during the reaction to the amounts of CO and O_2 initially present (in volume %). The selectivity of CO_2 was determined by the oxygen consumed for CO oxidation toward CO_2 divided by the total oxygen reacted (in volume %).