CHAPTER III
EXPERIMENTAL

3.1 Materials

Fumed silica (SiO_2, 99.8%, Nippon Aerosil, Japan), UHP grade nitrogen (N_2, 99.99% purity, Thai Industrial Gases Public Company Limited (TIG), Thailand), ethylene glycol (EG, 99%, J.T. Baker, USA), TEA (QRëc chemical, Thailand), acetonitrile (CH_3CN, 99.9%, Labscan, Thailand), ethanol (CH_3CH_2OH, 99.9%, Labscan, Thailand), cetryltrimethylammonium bromide ($C_{19}H_{42}BrN$, 99.9%, Fluka Analytical), sodium hydroxide (NaOH, 99%, Labscan, Thailand), cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, 99%, Aldrich), zirconium oxide chloride octahydrate ($ZrOCl_2.8H_2O$, 99.9%, Merck) were directly employed with no further purification.

3.2 Synthesis

3.2.1 Synthesis of Silatrane

The synthetic method was followed Wongkasemjit's method (Charoenpinijkarn *et al.*, 2001) by mixing 0.1 mol fumed silica, 100 ml EG, and 0.125 mol TEA. The mixture was refluxed at 200°C under nitrogen atmosphere for 10 h in an oil bath. The excess EG was removed under vacuum at 110°C. The white silatrane product was washed with acetronitrile to remove excess TEA and EG. The white silatrane product was vacuum-dried overnight before characterization using TGA and FT-IR.

3.2.2 Synthesis of Mesoporous MCM-48

The synthesis of mesoporous MCM-48 was followed Wongkasemjit's synthetic method (Longloilert *et al.*, 2011) by using 2M NaOH to dissolve and CTAB, as surfactant, at 50°C. Silatrane was then added to the mixture solution and stirred for 1 h. The molar composition ratio of the mixture was $0.3CTAB:0.5NaOH:62H_2O:1.0SiO_2$. The mixture was treated at 140°C for 16 h in a Teflon-lined stainless steel autoclave to obtain solid product. The white solid product

was collected by filtration and dried at ambient conditions. The surfactant was removed by calcinations at 550 °C for 6 h with a heating rate of 0.5 °C/min to obtain MCM-48. The obtained white product, MCM-48, was characterized by FE-SEM and XRD.

3.2.3 Synthesis of Mesoporous Ceria-Zirconia

The synthesis of mesoporous ceria-zirconia was followed Wongkasemjit's synthetic method (Deeprasertkul *et al.*, 2011) by mixing cerium nitrate and zirconium oxide chloride with various ratios (100:0, 75:25, and 60:40 mol%) and MCM-48 as silica hard template in ethanol. After stirring for various times (30 min, 1, 2, and 4 h), ethanol in the mixture was removed by evaporation in an oven set at different temperatures (ambient temperature, 50 °C, 100 °C). The obtained powder was heated in a ceramic crucible at 550 °C for 6 h to decompose the nitrate and chloride species. Removal of the hard template was carried out using 2M NaOH at 50 °C for 3 times and the mixture was centrifuged to obtain the product. The product was washed by deionized water and centrifuged until it was neutral and dried at 100 °C. The obtained products were characterized by FE-SEM, TEM, XRD, XRF, and N_2 adsorption/desorption.

3.3 Materials Characterization

X-ray diffractrometer (XRD) was used to identify the crystalline phases present in the structure. The diffraction pattern was the fingerprint of any crystalline phase. The phase of mesoporous products was characterized on a Rigaku DMAX 2200HV XRD with a scanning speed of 1 °C/min and CuKα source (λ= 0.154 Å) in a range of 2θ = 2–6°. Transmission electron microscope (TEM, JEOL JEM-2010) was used to provide further exploration in morphology and structure, including dimension of samples. Temperature programmed reduction (TPR, Thermofinnigan) with hydrogen was performed in a flow reaction system using 9.6 % hydrogen in argon used as a carrier gas (flow rate: 18.3 ml/min). The ordered mesoporous ceria, mesoporous bimetallic ceria-zirconia (0.10 g) were heated from room temperature to 900 °C with a linear ramp rate of 5 °C/min. Field emission scanning electron

microscope (FE-SEM, Hitachi FE-SEM TM-3000) was used to determine the size, morphology, and the pore system of particles. Thermogravimetric analyzer (TGA, Perkin-Elmer) was used to analysis thermal properties by measuring the change in mass of solid material as a function of temperature or time. N_2 adsorption/desorption measurement was used to determine into the pore structure of porous material, such as the inner pore surface area, the pore volume and the pore diameter distribution. Fourier transforms infrared spectrophotometer (FT-IR, Nicolet) was used to investigate the functional groups of chemical composition. X-ray fluorescence spectrophotometer (XRF, AXIOS PW 4400) was used to analyze the metal contents in samples.