

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fume silica (99.8% SiO₂ purity), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH) was purchased from Sigma-Aldrich. Ethylene glycol (EG) was purchased from J.T. Baker. Triethanolamine (TEA) was purchased from QREC chemical. Acetonitrile (ACN) was purchased from LAB SCAN Analytical Sciences. Methanol of HPLC grade, palladium (II) nitrate (99.999% purity), phenylboronic acid, 1-bromo-4-fluorobenzene, dimethylformamide (DMF) and potassium carbonate were purchased from S.M. chemical. All chemicals were used without further purification.

3.2 Experimental

3.2.1 Synthesis of Silatrane

According to Longoilert *et al.*, silatrane precursor was synthesized by mixing fumed silica (0.1 mol), TEA (0.125 mol) and EG (100 ml). The mixture was refluxed at 200 °C in oil bath under nitrogen flow for 10 h. The excess EG was eliminated under vacuum at 110 °C. The solid product was washed by acetonitrile to remove TEA and EG residues. The silatrane product was vacuum dried overnight.

3.2.2 Synthesis of MCM-48

Following the Longoilert's method using hydrothermal approach, 0.656g of CTAB was dissolved in 2 M NaOH solution, followed by adding silatrane and slightly heating for 1 h. The molar composition of the gel was 1.0SiO₂:0.3CTAP:0.5NaOH:62H₂O. The mixture was transferred to a Teflon-lined stainless steel autoclave and treated at 140 °C for 16 h. The solid product was recovered by filtration and dried overnight at ambient conditions. The resulting mixture is calcined at 550 °C for 6 h with a heating rate of 0.5°C/min.

3.2.3 Synthesis of Pd-MCM-48 via Impregnation Method

Pd-MCM-48 was synthesized by mixing MCM-48, palladium (II) nitrate, and methanol solvent. The mixture was stirred for 1 h and heated in the oven at 110 °C. Then the powder mixture was calcined at 550°C for 6 h.

3.2.4 Catalytic Activity Study

Phenylboronic acid (183 mg), 1-bromo-4-fluorobenzene (157 mg), potassium carbonate (138 mg), DMF (2 ml), and Pd-MCM-48 catalyst (50 mg of 1, 3, and 5% Pd contents loaded on MCM-48) were placed in microwave reaction Teflon vessel. The reaction was carried out at 120 °C with 300 W for 10, 20, and 30 min. The product was filtered and analyzed by GC-MS.

3.3 Characterization Techniques

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) was used for identifying the mesoporous product, using a scanning speed of 1°C/min, a CuK α source ($\lambda = 0.154 \text{ \AA}$), a scanning range of $2\theta - 2-8^\circ$ for MCM-48/Pd-MCM-48 products.

3.3.2 N₂-Adsorption and Desorption

The surface properties (area and pore volume distribution) were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods on Quantasorb Jr. (Autosorb-1). Before analysis, the MCM-48 products were degassed at 200 °C for 26 h.

3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used for observing the morphology of mesoporous product microstructure. SEM was obtained on JOEL Model 5200

3.3.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was utilized to provide further exploration in morphology and structure, including metal distribution. The

measurement was on JEOL JEM-2010 model using thermionic emission, LaB6 type, with 200 KeV

3.3.5 X-Ray Fluorescence Spectrophotometer (XRF)

X-Ray fluorescence spectrophotometer (XRF) was employed to observe the metal element contents in samples.

3.3.6 UV-2550 Spectrophotometer

UV-visible spectra were recorded on a Shimadzu UV-2550 using BaSO₄ as the reference.

3.3.7 Gas Chromatography-Mass Spectrometry (GC-MS)

The gas products were analyzed by Agilent gas chromatography (GC), using RTX-5sil-MS (30m×0.25mm×0.25mm) as a capillary column equipped with mass spectrometry (TOF) as a detector and helium as a carrier gas with a flow rate of 1mL/min. Programmable temperature range of 80 °C (hold for 2 min) to 270 °C (hold for 5 min) with a ramp rate of 4°C was set.

3.3.8 Temperature Programmed Reduction (TPR)

Reducibility of palladium species was determined by temperature-programmed reduction method (TPR) using TPD/R/O 1100. The catalyst of about 0.1 g was placed in a quartz reactor. Reduction was performed in the gas mixture of 5.04% H₂/N₂ at a flow rate of 20 cm³/min with the linear temperature increase of 10°C/min. The samples were pretreated under N₂ flow (20 cm³/min), followed by heating up to 400°C, hold for 240 min.