CHAPTER III
EXPERIMENTAL

This chapter describes the experiments and methodology carried out in this project. The materials, analytical methods related to the synthesis and the characterization of TUD-1, Pd-TUD-1, and its subsequent products, and their applications are also given.

3.1 Materials

All the materials used for synthesizing TUD-1, Pd-TUD-1, and diphenyl product are following. To synthesize silatrane, fumed silica (99.8% SiO_2, Sigma-Aldrich), ethylene glycol (EG, QREC), and triethanolamine (TEA, J.T.Baker) were purchased. To synthesize TUD-1 and Pd-TUD-1, palladium (II) nitrate (99.999%) and tetraethylammonium hydroxide (TEAOH 35%wt) were purchased from Sigma-Aldrich. Distilled water was used throughout the experiments. For catalytic activity study, potassium carbonate anhydrous powder (99.99%), 1-bromo-4-fluorobenzene (99%), and phenylboronic acid (95%) as substrates were purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF, AR grade) as a solvent was purchased from LAB SCAN Analytical Sciences.

3.2 Equipments

The analytical equipments and techniques that are used to characterize and analyze the products synthesized in this project are listed below.

3.2.1 Hitachi FE-SEM S4800 /Scanning Electron Microscope (SEM)

The morphology of the synthesized mesoporous materials, i.e., TUD-1 and Pd-TUD-1, was characterized using SEM.

3.2.2 JEOLJEM-2100/Transmission Electron Microscope (TEM)

TEM images were utilized to provide further exploration in morphology and structure of TUD-1 and Pd-TUD-1, including dimension of samples.

3.2.3 Rigaku DMAX 2200 HV/X-Ray Diffractrometer (XRD)

The crystallinity and phase formation of TUD-1and Pd-TUD-1 were characterized by XRD with CuK_{α} emission line (λ=0.154 nm) over a 2θ range of 0.2–60° at a voltage of 40 kV and a current of 40 mA.

3.2.4 Quantachrome Autosorb-1/Surface Area Analyzer (SAA)

Specific surface area, pore volume and pore diameter of the samples (TUD-1 and Pd-TUD-1) were determined with nitrogen adsorption-desorption by the Brunauer-Emmett-Teller (BET) method on SAA.

3.2.5 AXIOS PW 4400/X-Ray Fluorescence Spectrophotometer (XRF)

To observe the Pd element contents in Pd-TUD-1 sample, XRF was employed.

3.2.6 Shimadzu UV 2500/Diffuse reflectance Ultraviolet-Visible Spectrometer (DRUV)

DRUV spectra in the 200–900 nm range were measured, using $BaSO_4$ as reference. This method was used to characterize the available of Pd contents in the framework of TUD-1.

3.2.7 Milestone ETHOS SEL Microwave Laboratory Systems

The Suzuki coupling reaction (for catalytic activity) was conducted using microwave irradiation. All substrates were heated in a Teflon-vessel sealed with a Teflon cap, using time-to-temperature program. The power of microwave irradiation during heating period was utilized at 800 W maximum and maintaining the target temperature at 300 W maximum.

3.2.8 Gas Chromatography-Mass Spectrometry (GC-MS)

The products from the Suzuki coupling reaction (for catalytic activity) were analyzed by GC-MS on Agilent gas chromatography, using RTX-5sil-MS (30m×0.25mm×0.25mm) as a capillary column equipped with Time of flight mass spectrometry (TOF-MS) as a detector and helium as a carrier gas with a flow rate of

1mL/min. Programmable temperature range of 80 (held for 2 min) to 270 °C (held for 5 min) with a lamp rate at 4 °C was set.

3.2.9 Temperature-programmed Reduction (TPR)

Reducibility of palladium species in Pd-TUD-1 was determined by temperature- programmed reduction method (TPR) using TPD/R/O 1100. The 0.1 g catalyst was placed in a quartz reactor and pretreated in the flow of N_2 (20 cm^3/min). Reduction was performed in the mixture of 5.04% H_2/N_2 at the flow rate of 20 cm^3/min and the linear temperature increase was 10 °C/min. All samples were heated up to 400 °C and held for 240 min.

3.3 Methodology

All main methods and techniques used to accomplish this study are herein described. The synthesis methods of silatrane used as the precursor of TUD-1, TUD-1 and Pd-TUD-1 via sol-gel and impregnation techniques, respectively, are illustrated. The catalytic activity of Pd-TUD-1 via Suzuki reaction is also described as a study of its application.

3.3.1 Synthesis of Silatrane

Wongkasemjit's synthetic method was followed to synthesize silatrane (Wongkasemjit *et al.*, 1999). This method is summarized in Fig. 3.1, using 0.1 mol fumed silica to mix with 100 ml EG and 0.125 mol TEA. The mixture was then refluxed at 200 °C under nitrogen atmosphere for 10 h in an oil bath before removing excess EG and water are removed in a vacuum at 100 °C. The product was washed with acetronitrile to remove the TEA and EG residue. The silatrane product was finally vacuum-dried overnight before characterization using TGA.

3.3.2 Synthesis of TUD-1 via sol-gel technique

To synthesize TUD-1, silatrane from Section 3.3.1 was dissolved in water. The mixture was stirred for 1 h, followed by adding TEAOH dropwise and stirring for 2 h. The molar composition ratio of the gel was fixed at silatrane:14H_2O:0.7TEAOH. The mixture was aged at room temperature for 2 h, followed by drying at 100 °C for 24 h. The resulting product was calcined at 600 °C

for 10 h with a heating rate of 1 °C /min. The synthesis procedure is summarized in Fig. 3.2.

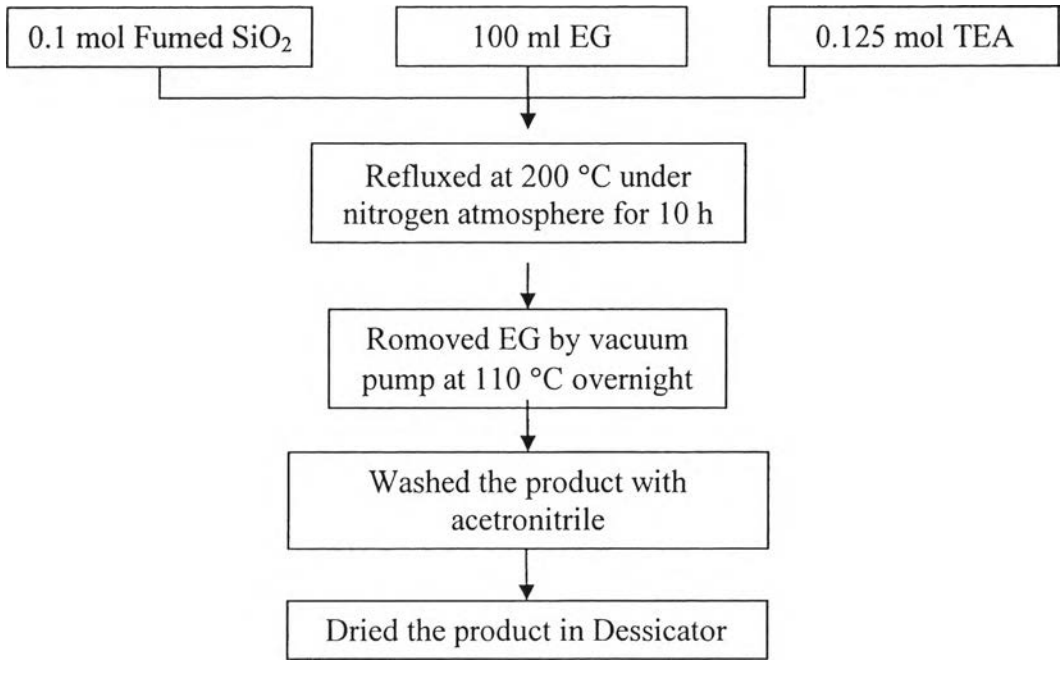

Figure 3.1 Flow diagram of Silatranes' synthesis.

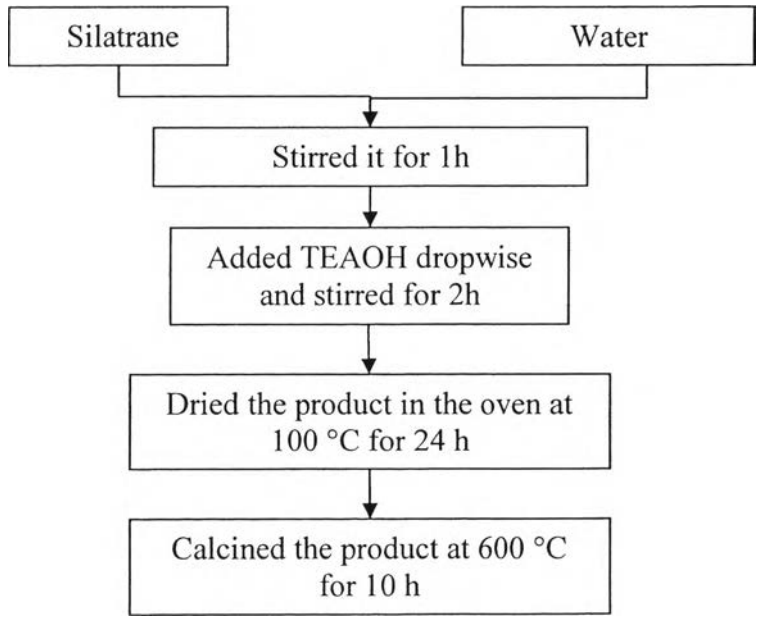

Figure 3.2 Flow diagram showing the synthesis of TUD-1 via sol-gel technique.

3.3.3 Synthesis of Pd-TUD-1 via impregnation technique

Pd-TUD-1 was prepared using various amount of Pd (1–5%wt). $PdNO_3$ solution and TUD-1 were firstly mixed in methanol solvent before aging at room temperature for 1 h. The product was dried at 110 °C for 20 h. The resulting Pd-TUD-1 product was finally calcined at 600 °C for 10 h using a heating rate of 1 °C /min. Figure 3.3 describes the impregnation technique for Pd-TUD-1 used in this project.

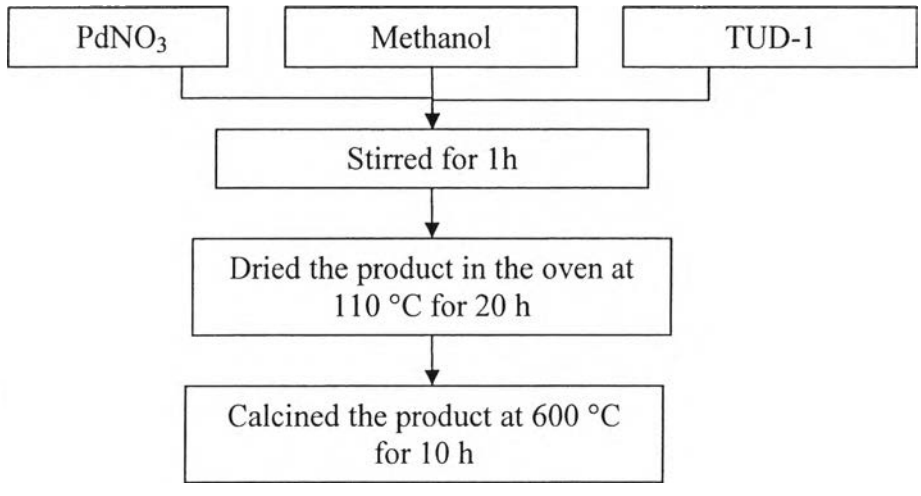

Figure 3.3 Flow diagram showing the synthesis of Pd-TUD-1 via impregnation technique.

3.3.4 Catalytic Activity of Pd-TUD-1 Using Microwave-assisted Suzuki Reaction

The study of Suzuki reaction using Pd-TUD-1 as a catalyst follows Chang's method (Chang *et al.*, 2012). This reaction was carried out by adding 1.5 mmol of phenyl boronic acid, 1.0 mmol of phenyl bromide, 1.0 mmol of K_2CO_3, 50 mg of Pd-TUD-1 as a catalyst, and 2 mL of DMF into a 5-mL microwave reaction vessel. The vessel was heated to 120 °C in a microwave reactor for various times (10, 20, and 30 min). After cooling the vessel to the room temperature, the aqueous product was characterized by GC-MS.