CHAPTER III
METHODOLOGY

3.1 Materials and Chemicals

1. Coconut shell activated carbon (supported by Carbonkarn Co., Ltd.)

2. Benzene-derived carbon nano spheres (supported by Green Mobility Collaborative Research Center, Nagoya University)

3. Pyridine-derived carbon nano spheres (supported by Green Mobility Collaborative Research Center, Nagoya University)

3. Nitric acid 70 % (AR grade purchased from RCI Labscan)

4. Nitrogen gas (purity 99.99 % purchased from Praxair)

5. Ammonia gas (purity 99.5 % supported by Poontaveeporn Part., Ltd.)

6. Carbon dioxide gas (purity 99.99 % purchased from Praxair)

3.2 Equipment

1. Surface Area Analyzer (Sorptomatic) (Thermo Finnigan, Sorptomatic 1990)

2. CHN analyzer (Leco TruSpec Micro CHN)

3. X-ray photoelectron spectroscope (XPS) (Kratos Axis Ultra DLD)

4. Simultaneous Thermal Analyzer (STA) (Netzsch STA 449 F3 Jupiter).

5. Valves and fittings (purchased from Swagelok)

3.3 Experimental Procedures

3.3.1 Preparation of Activated Carbon Nano Spheres

3.3.1.1 Synthesis of Carbon Nano Spheres

The two CNSs synthesized by solution plasma process were supported by the Green Mobility Collaborative Research Center, Nagoya University. The details of SPP for preparing CNSs were described elsewhere (Kang et al., 2014). In brief, a 100 mL glass vessel was used as a reactor. Tungsten electrodes insulated by ceramic tube were placed with a distance of 1 mm in the reactor and connected

with a bipolar-DC pulse power supply. After applying a 20 min of plasma discharge within the aromatic solvent (benzene or pyridine), approximately 0.5 g of CNSs were obtained. The samples of obtained CNSs were denoted as CB and CP, corresponding to the starting solvents of benzene and pyridine, respectively.

3.3.1.2 Carbonization and Activation Processes

a. The CNS was dried overnight in the oven at 110 °C to remove moisture.

b. 1 g of CNS was weighed and then put into a quartz reactor which was then placed in the furnace.

c. The furnace was heat up from room temperature to 200 °C under a nitrogen flow (100 mL/min) using the heating rate of 3 °C/min.

d. After the temperature reached 200 °C, the furnace was heat up to 700 °C using the rate of 1 °C/min and continually heated up to 900 °C using the rate of 3 °C/min.

e. After that, the sample was held at 900 °C for 1 hour and then carbonized CNS was obtained.

f. Finally, the carbonized CNS was activated with CO_2 (100 mL/min) at 900 °C for 2 hours. The resulting samples were denoted as ACB and ACP.

3.3.2 Surface Modification

3.3.2.1 Oxidative Treatment

a. Activated carbon was first dried overnight at 110 °C to remove moisture.

b. Activated carbon was loaded into a round bottom flask with a solution of 10M HNO_3 (Carbon: HNO_3 = 1 g:10 mL).

c. The content was heated to 60 °C with stirring for 6, 8 and 12 hours under reflux.

d. The resulting sample was filtered with the subsequent of washing in a soxhlet extractor with boiling distilled water for removing the excess acid.

e. The oxidized sample was then dried overnight at 110 °C and kept in desiccator.

3.3.2.2 Ammonia Heat Treatment

a. Activated carbon was dried overnight at 110 °C to remove moisture.

b. 1 g of activated carbon was added in a quartz reactor that was placed in a vertical furnace.

c. The furnace was then heated up to the desired temperature (400, 600 and 800 °C) using the rate of 10 °C/min under N_2 flow (75 mL/ min).

d. When the temperature reached the desired value, the gas flow was switched from N_2 to NH_3 (75 mL/ min) and then held for 1 hour.

e. The quartz was taken out of the furnace prior to cooling down to 100 °C under NH_3 flow.

f. After the temperature reached 100 °C, the gas flow was switched back to N_2 for cooling down to room temperature.

g. Finally, the aminated sample was dried under vacuum at 105 °C for 2 hours and then stored in desiccator.

3.3.3 Characterization of Adsorbents

3.3.3.1 Textural Characterisation

Surface Area Analyzer (Thermo Finnigan, Sorptomatic 1990) was used to investigate surface area, micro pore volume, total pore volume, and average pore diameter of the samples. Before analysis, the sample was outgassed to remove the adsorbed gases on the surface and the humidity at 150 °C under vacuum for approximately 15 hours. After that, the sample was analyzed from N_2 adsorption isotherms at -196 °C. Brunauer-Emmett-Teller (BET) method was applied to determined apparent surface area and total pore volume. The average micropore width and micropore volume were calculated by Horvath Kawazoe (HK) method.

3.3.3.2 Ultimate Analysis

The amount of carbon, hydrogen, nitrogen, and oxygen elemental was assessed by CHN elemental analyzer (Leco TruSpec Micro CHN). Assuming that only carbon, hydrogen, and nitrogen would be gasified from carbon samples; hence, the content of oxygen could be calculated by difference.

3.3.3.3 Surface Chemical Analysis

X-ray Photoelectron Spectroscope (XPS) (Kratos Axis Ultra DLD) was employed to investigate the presence of surface functionalities on carbon surface. The sample was first out gas under an ultrahigh vacuum condition. After that, wide and narrow scans were performed at resolution pass energy of 160 and 40 eV, respectively. The narrow scans were corrected for the charging effect with reference to the main C1s peak at 284.6 eV.

3.3.4 CO_2 Adsorption Measurement

Simultaneous Thermal Analyzer (STA) (Netzsch STA 449 F3 Jupiter) was used to studied the CO_2 adsorption/desorption performance of the samples. The CO_2 capture capacity was evaluated from the mass uptake when the sample was purged with CO_2 gas at 40 °C and 1 atm.

a. 10 mg of sample was loaded in a crucible and then introduced into the STA analyzer.

b. Prior to measurement, the humidity was first removed by heating the sample to 100 °C under 50 mL/min of N_2 flow and holding at this temperature for 30 min.

c. The sample was cooled down with a rate of 5 °C/min to 40 °C and held at this temperature for 30 min in order to stabilize the temperature.

d. To determine the CO_2 capture, the flow gas was changed from N_2 to CO_2 (50 mL/ min) and held for 2 hours

e. Finally, the gas flow was changed back to N_2 at the same flowrate and temperature and then held for 1 hours for the CO_2 desorption.