

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals:

- Bisphenol A
- Dimethylformamide (DMF)
- Formaldehyde
- Triethylenepentamine (TEPA)
- Silica suspension
- Hydrofluoric acid (HF)
- Surfactant cetyltrimethylammonium bromide (CTAB)
- Ethanol (EtOH)
- Acetone, 99.9%

3.1.2 Gases

- High purify (99.99%) carbondioxide, Thai Industrial Gases Public Co., Ltd.
- High purity (99.99%) nitrogen, Thai Industrial Gases Public Co., Ltd.

3.2 Equipment

3.2.1 Differential Scanning Calorimetry (DSC)

Cured polybenzoxazine were analyzed by using a Perkin-Elmer DSC 7 instrument. Approximately 5–10 mg samples were sealed in aluminum pans. The sample was heated from 30 to 300 °C with heating rate 10 °C/min under nitrogen gas with flow rate 20 ml/min. Finally, the heating profile, curing temperature and completely cured polybenzoxazine were obtained.

3.2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was analyzed by using Perkin Elmer Thermogravimetric/Differential Thermal Analyzer (TG-DTA). The sample was loaded in rang 4-8 mg on the alumina pan and heated from 30 to 800 °C under nitrogen gas with flow rate 50 ml/min. and heating rate 10 °C/min. The pyrolyzed temperature of polybenzoxazine was investigated from the onset temperature whereas char yield as the weight residue at 800 °C was reported. Moreover, nanoporous carbon without silica template could ensure by heating from 30 to 800°C under oxygen gas with flow rate 50 ml/min. and heating rate 10 °C/min.

3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of benzoxazine precursor and fully-cured polybenzoxazine were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 64 scans at a resolution of 2 cm^{-1} . KBr pellet technique was applied in the preparation of powder samples.

3.2.4 Scanning Electron Microscope (SEM)

Microstructure and surface morphology of nanoporous carbon materials were observed by a field emission scanning electron microscope (FE-SEM; JSM-7001F) at voltage of 15 kV. The specimens were coated with platinum under vacuum before observation to make them electrically conductive. Furthermore, the amount of silica template on the surface can be determined by Energy Dispersive X-Ray Spectrometer (EDX) mode.

3.2.5 Surface Area Analyzer (SAA)

BET surface area, total pore volume, and average pore diameter of polybenzoxazine-based nanoporous carbon were determined by the N_2 physisorption using a Quantachrome Autosorb-1 MP surface area analyzer on the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. Before analyzing, the samples were heated in vacuum atmosphere at 250°C

overnight to eliminate volatile species that had adsorbed on the surface and then calculated from nitrogen adsorption isotherms at 77 K

3.2.6 X-ray Diffraction (XRD)

The X-ray diffractometer (XRD) patterns of the nanoporous carbon were carried out on a Rigaku DMAX 2200HV using $\text{CuK}\alpha$ radiation ($\lambda=0.154 \text{ nm}$) at 40 kV and 30 mA, scan speed of 5 /sec, and 2θ of 10 to 80.

3.2.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy, XPS (Kratos Axis Ultra DLD) was used to determine the oxidation states of NIs. A monochromatic AlK α was used as an X-ray source (anode HT = 15 kV). The residual pressure in the ion-pumped analysis chamber was lower than 5×10^{-7} torr. The binding energies were referenced to the C1s peak (284.6 eV) to account for the effects of charging.

3.2.8 CO_2 Adsorption Process

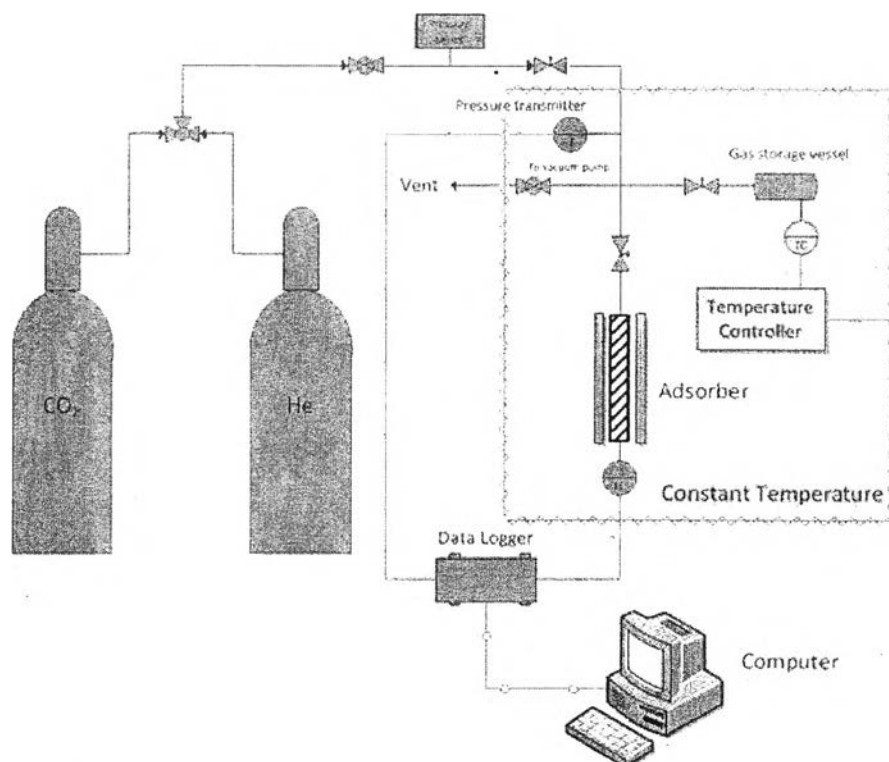
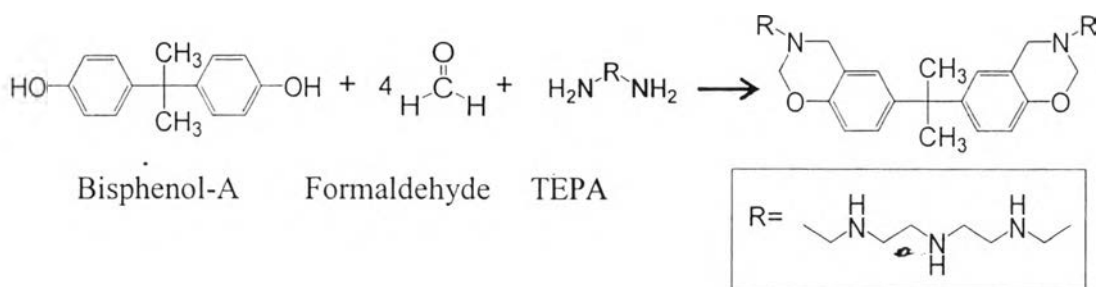


Figure 3.1 CO_2 adsorption process flowcharts.

3.3 Methodology

3.3.1 Synthesis of Benzoxazine Precursor

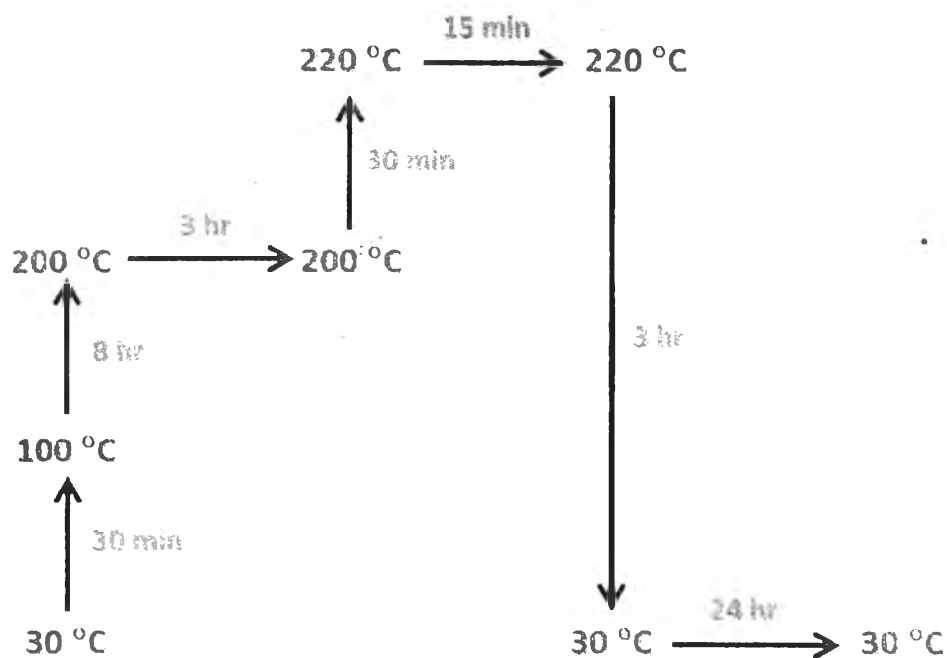
Benzoxazine precursors were synthesized by dissolving Bisphenol-A in N,N,-dimethylformamide (DMF) in the glass bottle and stirred continuously until the clear solution was obtained. Formaldehyde solution was then added into the bisphenol-A solution and mixed with various silica colloids and CTAB (cetyltrimethylammonium bromide) respectively. After that Tetraethylenepentamine (TEPA) in DMF was added dropwise into the mixture solution and stirred continuously for approximately 1 hour before putting in a closed system and heating at 80°C for 2 days in an oil bath to let the gel set. After that, CTAB and solvent were removed by ambient pressure drying (Soxhlet Extraction). The synthetic reaction is shown in Scheme 3.1 by the molar ratio of bisphenol-A : formaldehyde : TEPA was 1:4:1.



Scheme 3.1 Preparation of polybenzoxazine precursor.

3.3.2 Curing of Benzoxazine Xerogel

The obtained organic xerogel was then fully cured by step curing in an oven at room temperature to 100 °C in 30 min, 100 to 200 °C in 8 hr, holding at 200 °C for 3 hr, 200 to 220 °C in 30 min, holding at 220 °C for 15 min, and finally cooling down to room temperature.



Scheme 3.2 Schematic of a step of curing

3.3.3 Pyrolysis Process

Polybenzoxazines were pyrolyzed under nitrogen flow rate of 500 cm³/min. The pyrolysis temperatures varied in four conditions were 400, 500, 600 and 800 °C. The heating profile was as follows: heating from room temperature to 200 °C in 1 hr, 200 to vary pyrolysis temperatures and heating time followed in the table 1, and holding each pyrolysis temperatures for 2 hr and finally cooling down to room temperature.

Table 3.1 Pyrolysis temperatures and heating time of each sample

Pyrolysis temperatures	Heating time (hr)
400 °C	3
500 °C	4
600 °C	5
800 °C	7

3.3.4 Silica Removal

Silica colloids were removed from carbon xerogels (CX) by immersing in 15% wt hydrofluoric acid for 24 h.

Preparation of 15% wt of HF

Mixed solvents = EtOH 50:50 H₂O (mass ratio)

Total weight of mixed solvent = 200 g (From EtOH 100 g and H₂O 100 g)

Calculation

$$\frac{\text{HF}}{200 \text{ g of mixed solvents} + \text{HF}} \times 100 = 15\% \text{ wt of HF solution}$$

$$\text{HF} = 35.29 \text{ g}$$

However, the commercial HF solution bought is 48% wt in water. Therefore, 35.29 g HF can be calculated from the following equation:

$$\frac{35.29 \times 100}{48} = 73.52 \text{ g}$$

In addition, the amount of water in 73.52 g of 48% wt HF solution is $73.52 - 35.29 = 38.23 \text{ g}$.

Therefore, the amount of water added is $100.00 - 38.23 = 61.77 \text{ g}$

The preparation of 15 % wt of HF aqueous solution can be prepared as the following formula:

100 g EtOH : 61.77 g Water : 73.52 g of 48% wt HF solution

After that, the solution of 15% HF will be weighted for etching PBZ-Silica composite. The amount of 15% wt HF solution used, comparing to amount of PBZ-Silica, can be calculated by the following mass ratio:

$$\frac{\text{Weight of mixed solvent}}{\text{Weight of PBZ-Silica}} = 100$$

- The 48% of HF solution shows the density of 1.16 g/cc.
73.52 g of 48% wt HF solution can be calculated in term of volume

$$\frac{73.52 \text{ g}}{1.16 \text{ g/cc}} = 63.38 \text{ cc}$$