

## **CHAPTER IV**

# POLYBENZOXAZINE-BASED CARBON AEROGEL AS A CATALYST SUPPORT: INFLUENCE OF SUPPORT TYPES ON CATALYST ACTIVITY FOR THE ADSORPTION OF 4-CHLOROPHENOL

### 4.1 Abstract

Carbon aerogel is a mesoporous carbon material, presenting several advantages, including higher stability in both acidic and basic media, an easily tunable surface chemistry, and a well-developed porosity. Polybenzoxazine (PBZ) is a great candidate as an organic precursor to produce carbon aerogel. In this study, polybenzoxazine aerogels were cost-effectively prepared via ambient drying method, and characterized using <sup>1</sup>H-NMR, FT-IR, and SEM. The surface area of the obtained carbon aerogels is in the range of 350–450 m<sup>2</sup>/g. The performance of the carbon aerogel as a catalyst support, compared with other types of supports, was investigated its adsorption activity of 4-chlorophenol (4-CP) using Pt as a catalyst. It was found that the synthesized carbon aerogel was proved to be an impressive catalyst support to adsorp 4-CP.

Keywords: Carbon Aerogel; Polybenzoxazine; Catalyst support; 4-Chlorophenol

#### 4.2 Introduction

Carbon-supported catalysts are generally used in chemical industry. The most widely used support is activated carbon, although carbon black or graphite is sometimes considered. Comparing with other types of supports, such as alumina and silica, zeolites, carbon materials have many advantages: (i) they are stable in acid or basic media; (ii) they are resistant to high temperature; and (iii) the metal when used as a catalyst can be recovered easily after burning the support. For some types of carbons, their porous texture can easily be tailored, yielding high surface-area supports where the active phase can be well dispersed with the required pore-size distribution to facilitate the diffusion of reactants and products to, and from, the active phase [1]. Since they are also relative chemically inert, thus, prevent harmful metal-support interactions. Carbons have been utilized as a support for a number of active phases, including noble metals [2], base metal [3], and also metal compounds, such as sulfides and oxides [4].

Carbon aerogels are a novel porous carbon material that has received considerable attention over the past decade [5–9]. These materials can be obtained from the carbonization of organic aerogels prepared from the sol–gel polycondensation of certain organic monomers, such as resorcinol and formaldehyde, following Pekala's method [5, 6]. These carbon aerogels can be obtained in the forms of beads, powders or thin films. Their unique properties, viz. well controlled micro-and mesoporosity, and a large surface area, make them promising materials for application in adsorption and catalysis. Basically, carbon aerogels are a network structure of interconnected nanosized primary particles. In regard of their porous structure, micropores are related to the intra- particle structure whereas mesopores and macropores are produced by the inter-particle structure [10].

Polybenzoxazine (PBZ) provides high thermal stability, low shrinkage upon polymerization, no by-products or volatile generation, excellent dimensional stability, and rich molecular design flexibility [11-13]. It is, thus, a great candidate as a polymer precursor to produce carbon aerogel to be used as a catalyst support. In this study, the carbon aerogels derived from polybenzoxazines were developed as the catalyst support. Their performance as a catalyst support, comparing with other types of supports, was determined by following the adsorption reaction of 4-chlorophenol (4-CP) using Pt as a catalyst.

#### 4.3 Experimental

## 4.3.1 Materials

All chemicals were used without further purification. Triethylenetetramine (TETA) was purchased from FACAI Group Limited, Thailand. Aniline (99%) and phenol (analytical grade) were purchased from Panreac Quimica SA Company. Formaldehyde solution (37% by weight) was purchased from Merck, Germany. Paraformaldehyde (95%) was purchased from BDH Laboratory Supplies. Bisphenol-A (commercial grade) was kindly supported by Bayer Thai Co., Ltd. Xylene (98%) was obtained from Carlo Erba Reagenti. 1,4 – Dioxane (reagent grade) was purchased from Labscan asia Co., Ltd., Thailand. Ethylene diamine (EDA, commercial grade) was kindly supported by Thai epoxy's Company. Azodicarbonamide (AZD) used as a blowing agent was bought from A.F Supercell Co, Ltd. Titanium dioxide (TiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), hexachloroplatinate (IV) hydrate, and 4-chlorophenol were purchased from Aldrich, Germany. ZSM-5 was purchased from Zeolyst International.

#### 4.3.2 Measurements

The FT-IR spectra of polybenzoxazine precursor and carbon aerogel were obtained on a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrumentat a temperature range of 30° to 900°C, and a heating rate of 20°C/min under N<sub>2</sub> flow of 50 ml/min. Scanning electron microscope (SEM, JEOL/JSM model 5200) was used to observe the surface morphology of polybenzoxazine aerogel and carbon aerogel. Transmission electron microscope (TEM, JEOL model JEM-2100) was used to observe the porous structure of carbon aerogel. Nuclear magnetic resonance (<sup>1</sup>H-NMR) was used to characterize

the chemical structure of polybenzoxazine, using a Varian Mercury 300 (300 MHz) instrument. Deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) was used as a solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a heating rate of 10°C/min under a N<sub>2</sub> atmosphere with a flow rate of 10 ml/min. N<sub>2</sub> adsorption-desorption isotherms were obtained at 250°C on a Quantachrome Autosorb<sup>-1</sup>. Samples were degassed at 250°C for 12 hr in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the desorption branch of the nitrogen isotherm. UV–VIS spectrophotometer (Shimadzu UV-2550) was used to follow the adsorption of 4-chlorophenol.

### 4.3.3 Methodology

Two types of benzoxazine oligomer were prepared to be used as the organic precursors for carbon aerogel synthesis. Phenol-ethylenediamine base benzoxazine monomer (P-eda) was used as an organic precusor for carbon foam synthesis.

## 4.3.3.1. Carbon Aerogel/Foam Synthesis

# 4.3.3.1.1 Preparation of BA-teta Derived Carbon Aerogel

Synthesis of benzoxazine precursor using bisphenol A, formaldehyde and TETA with a mole ratio 1:4:1, as shown in Figure 4.1. Firstly, bisphenol A (4.52 g) was dissolved in dioxane (20 ml) in glass bottle and stirred until the clear solution was obtained. Formaldehyde solution (6.48 g) was then added into the bisphenol A solution. The temperature was kept under 10°C using an ice bath. Diamine (TETA) was then added drop wise into the mixture being continuously stirred for approximately 1 hr until transparent yellow viscous liquid was obtained. The benzoxazine precursor was heated in the oven at 80°C for 72 hr in a closed system. The partially cured benzoxazine hydrogels were then obtained. The organic aerogels were attained by evaporating solvent in hydrogels at ambient condition for 1 day. The obtained organic aerogel were then fully cured by step curing in an oven at 140°, 160°, and 180°C for 2 hr at each temperature and 200°C for 3 hr, respectively. Pyrolysis was performed at 800°C under nitrogen flow at 500 cm<sup>3</sup>/min, using the

following temperature program: (i) ramp at 3.7°Cmin<sup>-1</sup> to 250°C; (ii) ramp at 1.17°Cmin<sup>-1</sup> to 600°C; (iii) ramp at 3.3°Cmin<sup>-1</sup> to 800°C and hold for 120 min before slowly cooling to room temperature.



Figure 4.1 Preparation of benzoxazine precursor.

# 4.3.3.1.2 Preparation of BA-a Derived Carbon Aerogel

A benzoxazine monomer was synthesized by solventless process proposed by Ishida *et al* [11]. Bisphenol-A, aniline, and paraformaldehyde at a 1:2:4 molar ratio were mixed and heated at 110°C for 60 min until the mixture became transparent pale yellow color. The monomer was used without purification. The synthesis reaction of benzoxazine monomer is shown in Figure 4.2.

Benzoxazine monomer was prepared using 40 wt% monomer concentration in xylene solvent. The mixtures were moved into vials and sealed. The temperature was gradually raised up to 130°C for 96 hr in an oven. The products obtained at this stage were partially cured benzoxazine hydrogels. The hydrogels were dried at ambient temperature for 2 days to remove the xylene from their matrixes, yielding organic aerogels which were then subjected to step-curing in

an oven at 160°, 180°C for one hr at each temperature and 200°C for 2 hr, respectively, to give organic aerogels. Carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at 500 cm<sup>3</sup>/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min [14].



Benzoxazine monomer (P-eda)

Figure 4.2 The benzoxazine monomer synthesis.

# 4.3.3.1.3 Preparation of Phenol-ethylenediamine (P-eda) Derived Carbon Foam

P-eda based polybenzoxazine was synthesized from phenol, EDA, and paraformaldehyde with a mole ratio of 2:1:4 by solventless process proposed by Ishida *et al* [11]. The mixture was stirred continuously at 110°C for approximately one hr until clear yellowish monomer was obtained. The synthesis of benzoxazine monomer is shown in Figure 4.3. Orgaic foams was made from polybenzoxazine based Phenol-ethylenediamine (Poly(P-eda)) using AZD as a blowing agent. P-eda monomer was ground and mixed with 20%w/w of AZD until homogeneous. The mixtures were filled in vial and heated in an oven with a heating rate of 1°C/min from 30° to 200°C. Carbon foams were prepared by pyrolysis of the organic foam in a quartz reactor. The pyrolysis took place under nitrogen flow at 500 cm<sup>3</sup>/min using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min, and held at 800°C for 60 min. Then the furnace was cooled down to room temperature under nitrogen atmosphere prior to sample removal.



Figure 4.3 The synthesis reaction of P-eda derived benzoxazine monomer.

### 4.3.3.2 Catalyst Preparation

Pt (0.1 and 0.5 wt%) was loaded on the supports by incipient wetness impregnation, wherein a calculated amount of hydrogen hexachloroplatinate (IV) hydrate dissolved in a minimum amount of water was added dropwise before mixing with the supports. The Pt-loaded supports were then dried overnight before calcining at 450°C for 3 hr to remove the organic moieties.

## 4.3.3.3 Activity Measurements

To test performance of the prepared carbon aerogel as a catalyst support, the adsorption activity of 4-chlorophenol (4-CP) using Pt as a catalyst was investigated. The initial concentration of 4-chlorophenol (4-CP) was fixed at 40 ppm. The experiments were carried out at 298 K. The concentration of 4-CP was analyzed as a function of time using UV-VIS spectrophotometer.

### 4.4 Results and Discussion

#### 4.4.1 Preparation BA-teta Derived Polybenzoxazine Aerogel

Benzoxazine precursor was derived from the reaction of diamine, bisphenol-A and formaldehyde at the molar ratio of 1:1:4, using so called "quasi-solventless" method which is our first discovery. This method uses dioxane to only help mixing process and needs only 1 hr at low temperature for the reaction to occur, unlike the traditional method reported by Takeichi *et al.* [13] which required dioxane solvent and 5 hr reaction time at the boiling point of dioxane.

# 4.4.2 Characterization of BA-teta Derived Polybenzoxazine Aerogel and Carbon Aerogel

The chemical structure identification of benzoxazine precursor was carried out using <sup>1</sup>H-NMR, as shown in Figure 4.4. The characteristic peaks assigned to the methylene protons of O–CH<sub>2</sub>–N and Ar–CH<sub>2</sub>–N in the ring-closed benzoxazine structure were observed at 4.76 and 3.89 ppm, respectively. The methylene protons of the ring-opened benzoxazine Ar–CH<sub>2</sub>–N were also observed at 3.68 ppm. The aromatic protons appeared at 6.60–7.00 ppm. The methyl protons of bisphenol-A were observed at 1.55 ppm. These are strongly agreed with Garea and coworkers [15] who also found the characteristic signals corresponding to the methylene groups from the benzoxazine rings at 3.9–4.85 ppm, and aromatic protons at 6.5–7.5 ppm. The signal at 3.6 ppm from all <sup>1</sup>H-NMR spectra is assigned to the methylene groups in the oligomers produced by opening some benzoxazine rings during the monomer synthesis.



Figure 4.4 <sup>1</sup>H NMR spectrum of benzoxazine precursor.

The FT-IR spectrum in Figure 4.5a shows the characteristic absorption bands of partially-cured benzoxazine at 1260–1262 cm<sup>-1</sup> (asymmetric stretching of C-O-C of oxazine), 1180–1187 cm<sup>-1</sup> (asymmetric stretching of C-N-C), 920–950 cm<sup>-1</sup> and 1491–1500 cm<sup>-1</sup> (tri-substituted benzene ring). The absorption band of N-H stretching from TETA was observed around 3420–3429 cm<sup>-1</sup>. Comparing with FT-IR spectrum of polybenzoxazine (Figure 4.5b), the characteristic absorption bands of fully-cured polybenzoxazine at 920–950 cm<sup>-1</sup> disappeared. The structure of the fullycured polybenzoxazine is depicted in Figure 4.6. The FT-IR results are in agreement with the study of Takeichi *et al* [11], who suggested that the characteristic absorption was transformed when ring-opening polymerization of the benzoxazine took place. After pyrolysis, the FT-IR spectrum (Figure 4.5c) is rather flat due to the loss of all organic moieties.



**Figure 4.5** FT-IR spectra of benzoxazine precursor at 80°C (partially-cured) (a), polybenzoxazine at 200°C (fully-cured) (b), carbon aerogel at 800°C (c).



**Figure 4.6** The structures of benzoxazine precursor (a), and fully-cured polybenzoxazine (b).

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The progress of the ring-opening polymerization from the benzoxazine precusors was monitored by DSC, as shown in Figure 4.7. The DSC thermogram of partially-cured benzoxazine showed the exotherm peak, starting at 180°C with a maximum at 245°C, attributed to the polybenzoxazine ring-opening polymerization. After the polybenzoxazine was fully cured, the exothermal peak disappeared. The same result was also observed by Takeichi *et al.* [13], suggesting that the exotherm peak decreased with the increase of temperature. The exotherm completely disappeared after the end of curing temperature, implying that the ring-opening of oxazine was completed. This evidence can be concluded that the curing reaction of the benzoxazine precursor was practically completed. This DSC result is consistent with the FTIR results.



**Figure 4.7** DSC thermograms of partially-cured benzoxazine (a) and fully-cured polybenzoxazine (b).

The TGA thermogram of polybenzoxazine is presented in Figure 4.8. Polybenzoxazine (PB-teta) started to degrade after 250°C. The significant weight loss was observed between 250° and 600°C. The rate of the weight loss became slower after 600°C. The char residue of 37% was found at 800°C. Kasinee *et al* [16] identified the decomposition products of aromatic amine-based polybenzoxazine polymers investigated using TGA and GC–MS, and found that the degradation products were either from a direct result of polymer degradation or from the recombination or degradation of compounds formed during the thermal decomposition.



Figure 4.8 TGA thermogram during the pyrolysis of the polybenzoxazine (PB-teta).

The thermal stability of polybenzoxazine (PB-teta), as shown in Figure 4.8, resulted the  $T_d$  at 5 % weight loss and the char yield summarized in Table 4.1.  $T_{d5\%}$  of PB-teta is higher than 290°C and higher than that of PB-eda due to the presence of nitrogen atoms in the diamine chain enable more H-bonding when comparing with PB-eda. However, PB-a [14] has the highest thermal stability, as expected, because of the aromatic content.

Material	Amine group (R)	T <sub>d5%</sub> (°C)	Char yield(%) <sup>a</sup>
PB-a	NH <sub>2</sub>	330*	25*
PB-eda	H <sub>2</sub> N NH <sub>2</sub>	282	44
PB-teta	H <sub>2</sub> N NH <sub>2</sub> H	293	37

 Table 4.1 Thermal properties of polybenzoxazines

<sup>a</sup> At 800°C.

\* Lorjai et al, submitted [14]

For polybenzoxazine aerogel, the solid phase presented smooth, continuous polymer network incorporated with open macropores, as can be clearly seen in Figures 4.9 (a). The carbon aerogel microspheres (Figures 4.9 (b)) were smaller than those of organic aerogel, as a result of shrinkage during pyrolysis, as explained by Wen-Cui *et al.* [17]. In our case, the pyrolyzed carbon aerogel revealed a dense porous structure with the surface area of 368 m<sup>2</sup>/g. The average pore diameter was 3.64 nm (Figure 4.10) which can be classified as mesopore. The pore volume of carbon aerogel was approximately 0.33 cc/g. Shen *et al* [19] found that the porous structure of organic and carbon aerogel depends on several parameters such as the concentrations. From Figure 4.10 shown, the pore size distribution of carbon aerogel presents wide distribution that has mesoporous structure. When increasing relative pressure, the adsorption volume increase ripidly due to the capillary condensation (Figure 4.11).



**Figure 4.9** SEM micrographs of polybenzoxazine aerogels (a), BA-teta derived carbon aerogel (b).



Figure 4.10 The pore size distribution of BA-teta derived carbon aerogel.



Figure 4.11 The adsorption and desorption isotherms of BA-teta derived carbon aerogel.

Basically, carbon aerogels have a network structure with nano-sized carbon primary particles connected to each other. Concerning their pore structure, micropores are often related to the intra-particle structure, while mesopores and macropores are due to their interparticle structure [10]. Microstructure and morphology of carbon aerogel were investigated using TEM, as shown in Figure 4.12.



Figure 4.12 TEM morphology of BA-teta derived carbon aerogel.

### 4.4.3 Adsorption Activity of 4-Chlorophenol (4-CP)

The performance of the synthesized BA-teta derived carbon aerogel used as a catalyst support was carried out by studying the adsorption of 4-chlorophenol (4-CP) whose conentration was fixed at 40 ppm, using Pt as a catalyst at 298 K. As shown in Figure 4.13, the concentration of 4-CP decreased with the adsorption time. During the first 15 min, the concentration of 4-CP rapidly decreased and then slowly dropped down after 1 hr. The final concentration was only 2.7 ppm after 5 hr indicating that the adsorption was approximately 93%. Moreover, it was found that the amount of Pt used showed insignificant effect on the reduced concentration of 4-CP. The UV absorption spectra of effluent solutions were analyzed and are shown in Figures 4.14 and 4.15. Typically, 4-CP exhibits two absorption peaks at 225 and 280 nm, relating to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively [20]. As the reaction time increased, the absorption peaks of 4-CP decreased. After 15 min treatment time, the peak ratios of the treated and the original 4-CP were 0.13 and 0.11 at 225 and 280 nm, respectively. The adsorption rate seemed to slow down when the treatment went on to 5 hr since the peak ratios decreased to 0.07 and 0.08 at 225 and 280 nm, respectively. Furthermore, it was found that the synthesized BA-a derived carbon aerogel and P-eda derived carbon foam used as a catalyst support showed the same results as BA-teta derived carbon aerogel. Guifen et al [20] investigated the performance of carbon aerogel for aqueous phase electro-catalytic oxidation of phenol waste waters, and found that the intensity of the UV absorption spectra at 210 and 269 nm, relating to phenol decreased. The concentration removal got to 95% in 30 min



**Figure 4.13** The adsorption of 4-CP vs. the reaction time of 0 (---), 0.1 (-+-), and 0.5 wt% Pt loaded (---) on BA-teta derived carbon aerogel:



**Figure 4.14** UV spectrum profiles during adsorption of 4-CP of initial concentration (a), and after treatment with 0.1wt% Pt loaded on BA-teta derived carbon aerogel (b).



Figure 4.15 UV spectrum profiles during adsorption of 4-CP on 0.1wt% Pt loadedon Ba-TETA derived carbon aerogel for 15 min (\_\_\_\_\_), 30 min (\_ \_ \_ ), 45 min(\_\_\_\_\_), 1 hr (\_\_\_\_\_), 2 hr (\_\_\_\_\_), 3 hr (\_\_\_\_), 4 hr (\_\_\_\_\_), and 5 hr (\_\_\_\_\_).

#### 4.4.4 Effects of Support Type on 4-Chorophenol Adsorption

As can be seen in Figure 4.16, the different types of polybenzoxazine used as organic precusors for carbon aerogel and carbon foam applications had no effect on the adsorption of 4-CP. Because the physical characteristics of BA-teta derived carbon aerogel, BA-a derived carbon aerogel, and P-eda derived carbon foam as summarized in Table 4.2 were not much different. Compared with other types of supports, viz. TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, and ZSM-5, the results provided profound effect on the catalytic efficiency of Pt. When TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> were used as supports, only about 5% of 4-CP concentration decreased. This might be because TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> show the tendency to agglomerate. As a result, Pt had less potential to adsorb 4-CP. However, in the case of the ZSM-5 support, the adsorption activity was better—about 45% of 4-CP concentration decreased. The reason might be because oxygen atoms in ZSM-5 can form bonds with Pt; hence, the potential of Pt to form bonds with oxygen atoms of 4-chlorophenol was reduced. However, ZSM-5 is a high surface area material, that has the inter- and the intra-porous structure. As a result,

ZSM-5 gave larger active site for Pt loading (figure 4.17), as compared with TiO<sub>2</sub>,  $Al_2O_3$ , and SiO<sub>2</sub>

Material	Surface area (m²/g)	Average pore diameter (nm)	Total pore volume (cm <sup>3</sup> /g)
BA-teta derived carbon aerogel	368	3.6	0.34
BA-a derived carbon aerogel	391*	2.2*	0.21*
P-eda derived carbon foam	410	2.3	0.23

 Table 4.2 The physical characteristics of carbon supports

\*Lorjai et al ,submitted [14]



**Figure 4.16** Adsorption of 4-CP vs. reaction time of 0.1 wt% Pt loaded on BA-teta derived carbon aerogel (----), BA-a derived carbon aerogel (----), P-eda derived carbon foam (----), ZSM-5 (----), SiO<sub>2</sub> (----), Al<sub>2</sub>O<sub>3</sub> (-+-), and TiO<sub>2</sub> (----).



**Figure 4.17** Ring structure of ZSM-5. High level: ball and stick. Low level: wireframe. Dark spheres: O atoms. Light grey spheres: Si atoms.

# 4.4.5 Desorption of 4-Chlorophenol

The desorption was confirm by using methanol as solvent to extract 4-CP. (figure 4.18) When methanol was used as solvent, about 91% of 4-CP concentration was extracted from carbon support. Therefore, it was confirmed that the reduction of 4-CP concentration as mentioned in the previous session was due to the adsorption process.



**Figure 4.18** UV spectrum profiles during desorption of 4-CP on 0.1wt% Pt loaded on BA-teta derived carbon aerogel in methanol.

## 4.5 Conclusions

Polybenzoxazine was successfully used as organic precursors to prepare carbon aerogels with a well-developed and controlled micro- and mesoporosity, a narrow mesopore size distribution and a large surface area. The performance of carbon aerogel as a catalyst support on the adsorption of 4-CP, using Pt as a catalyst, was remarkably decrease of 4-CP within 15 min with the final concentration of 7%. The efficiency of 4-CP adsorption of BA-teta derived carbon aerogel, BA-a derived carbon aerogel, and P-eda derived carbon foam synthesized from different types of polybenzoxazine used as organic precusors was not different.

# 4.6 Acknowledgements

The authors wish to thank the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University and Ratchadapisake Sompote Research Funds, Chulalongkorn University for financial support of this research.

## 4.7 References

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