

CHAPTER I

INTRODUCTION

Nowadays, development of carbon materials is becoming the great topic of research due to the growth of carbon materials consumption in many applications such as bio- and chemical adsorption (Hartmann, 2005), catalyst supporting material (Su *et al.*, 2005; Moreno-Castilla and Maldonado-Hodar, 2005), energy storage (Pekala *et al.*, 1998; Fuertes *et al.*, 2005), molecular sieve membrane for gas separation (Jones and Koros, 1994; Ismail and David, 2001), etc. The popular carbon materials are carbon gels, which possess various outstanding properties. Some of these properties are: light weight, high surface area, high porosity, high thermal stability, and low density, etc. Carbon gels could be mainly classified into three type viz. carbon aerogel (obtained through super critical CO₂ drying), carbon cryogel (obtained through cryogenic drying), and carbon xerogel (obtained through evaporation drying), depending on drying method during solvent removal process of organic gels (Job *et al.*, 2005). Carbon gels are mainly synthesized by using Resorcinol (R) and Formaldehyde (F) as carbon precursor. Resorcinol(R)-Formaldehyde(F)-based organic gel and its carbon gel after pyrolysis were first introduced by Pekala and Schaefer (1989, 1993). However, there are some drawbacks that limit the utilization of RF as a carbon precursor, for example, the synthesis process took around two weeks to complete the process. In addition, volatile by-product was released during polymerization process (Pekala, 1989; Pekala and Schaefer, 1993; Tamon *et al.*, 1997). Moreover, harsh catalyst and supercritical drying were required to promote polymerization and remove solvent to preserve the porous structure. Even if the pore structure of gels could be maintained, supercritical drying is still not a cost-effective drying method. Not only it requires multi-step procedures, but also yields low production rate, resulting in considerable amount of time and energy consumption. In comparison to the supercritical drying, the ambient drying (evaporation) method is much more economical, although the morphology and physical properties of the ambient-dried products are typically different from those obtained by supercritical drying (Job, *et al.*, 2005; Tamon *et al.*, 1999; Shen *et al.*, 2005; Liu *et al.*, 2006; Arbizzani *et al.*, 2007).

Polybenzoxazine (PBZ), a new type of cationic ring-opening polymerized phenolic system, is the new class of phenolic type resin which possesses many exceptional properties that overcome several shortcomings of traditional phenolic resin. For example, benzoxazine resins do not require harsh catalyst or initiator, do not release toxic by-products during polymerization, show near-zero shrinkage upon polymerization, show high molecular design flexibility by changing amine and phenol derivatives leading to different properties, and possess easy processibility. Cross-linked polybenzoxazines exhibit excellent mechanical integrity, high thermal and chemical stability, high char yield, and low water absorption (Ning and Ishida, 1994; Ishida and Allen, 1996; Ghosh *et al.*, 2007; Agag and Takeichi, 2007; Ishida, 2011). The shorter preparation time with fewer steps is required when PBZ-based carbon is prepared (Lorjai *et al.*, 2009; Katanyoota *et al.*, 2010; Chaisuwan *et al.*, 2010; Chaisuwan, 2011; Thubsuang *et al.*, 2012). Moreover, PBZ is a cross-linked polymer with additional extensive hydrogen bonded networks which can withstand pore collapse without the need of supercritical CO₂ drying process. Therefore, in this work, author proposed a new type of additional-cure phenolic system, called polybenzoxazine (PBZ), as a candidate starting material for producing carbon xerogels.

It is known many parameters can affect the properties of organic and carbon aerogels such as concentration of polymer, type of starting materials, amount of catalyst, concentrations and types of surfactants, hard template loading, types of solvents, etc. Especially, types of solvents, different solvents can change the conformations of polymers during sol-gel process, yielding different morphologies and properties (Holmqvist *et al.*, 1997; Zipfel *et al.*, 1999; Alexandridis and Yang, 2000; Antoniou and Alexandridis, 2010). In this study, the effects of solvents, such as DMF, dioxane, and isopropanol, on cluster growth behavior during the sol-gel process, the pore characteristics of polybenzoxazine-derived xerogels, and their corresponding carbon xerogels, were mainly studied in order to obtain knowledge on the control parameters for the pore structure of PBZ-based carbon xerogels for targeted applications. The effects of resin concentrations and drying methods were also investigated. After the proper solvent was founded, the as-synthesized carbon

xerogels are going to be used as hard template confinement for controlling micron-sized catalyst, named ZSM-5, into nanosized catalyst.

Zeolite Sieve of Molecular porosity – 5, (structure type MFI – mordenite framework inverted), ZSM-5, has been used in various applications especially as a catalyst in organic syntheses, oil refining, environmental management, and petrochemical industry (Yogo *et al.*, 1993; Hollander *et al.*, 2002; Perez-Ramirez *et al.*, 2003; Borges *et al.*, 2007; Feng *et al.*, 2009; Serrano *et al.*, 2010), because of its outstanding properties. Some of these properties are: shape-selectivity, surface acidity, well-ordered pore network, high thermal stability, and cation-exchange capability. Generally, ZSM-5 is a microporous, aluminosilicate material, having crystal size in a micrometer range. These properties could influence the catalytic performance for synthesis of large molecules due to a limitation of mass transfer (Perez-Ramirez *et al.*, 2003; Donk *et al.*, 2001). The way to improve the catalytic performance of ZSM-5 is decreasing the crystal size to nanoscale to enable more active sites, resulting in the increased catalytic efficiency (Serrano *et al.*, 2010; Viswanadham *et al.*, 2009). Using this ZSM-5 nanocatalyst, Serrano *et al.* (2010) studied the epoxidation rearrangement reactions and found that nanocrystalline ZSM-5 with the crystal size in the range of 20-50 nm showed higher epoxide conversion than microcrystalline ZSM-5 with the crystal size of 5 μm . Generally, ZSM-5 nanoparticles were synthesized by using resorcinol-formaldehyde (RF)-based carbon aerogel (or carbon xerogel) as a templating confinement to control the size and the pores of the ZSM-5 crystals (Tao *et al.*, 2003, 2004, 2005, 2006; Ozaki *et al.*, 2006). As mentioned earlier about the drawbacks of resorcinol-formaldehyde (RF)-based carbon aerogel/xerogel, PBZ-based carbon xerogel will be used, instead of RF-based carbon aerogel/xerogel, as novel hard template confinement for controlling the size of ZSM-5 into nano scale. The effects of PBZ-based carbon xerogel on properties of ZSM-5 catalyst were also investigated.

In 2009, PBZ-based carbon aerogel derived from bisphenol-A – aniline (hereinafter abbreviated as BA-a) was first introduced by Lorjai *et al.* who found that their carbon showed the microporous property with pore diameter of less than 2 nm. Furthermore, the surface area and total pore volume of their carbon aerogel was around 384-391 m^2/g and 0.21 cc/g , respectively.

PBZ-based carbon aerogel was further reported by Katamyoota *et al.* (2010). They found that surface area of $368 \text{ m}^2/\text{g}$ and total pore volume of 0.34 cc/g with 3.67 nm in average pore diameter, were obtained from PBZ-based carbon aerogel derived from bisphenol-A – tetra (hereinafter abbreviated as BA-tetra). PBZ-based carbon aerogel derived from BA-tetra also showed good performance as electrode for supercapacitor comparing to those of PBZ-based carbon aerogel derived from BA-a.

However, as mentioned above, according to the phase separation phenomena during the sol-gel process, it was found that PBZ-based carbon aerogel/xerogel shows smaller pore diameter in a range of small micro-mesopore, lower specific surface area, and lower amount of pore volume comparing to those of carbon aerogel/xerogel derived from resorcinol-formaldehyde (Lorjai *et al.*, 2009; Katamyoota *et al.*, 2010; Chaisuwan *et al.*, 2010; Chaisuwan, 2011; Thubsuang *et al.*, 2012; Han and Hyeon, 1999a, b; Gorka and Jaroniec, 2011). These properties could affect the utilization of polybenzoxazine-based carbon for various applications. For application as the catalyst supporting material, those small pore sizes of PBZ-based carbon aerogels might limit the catalytic efficiency for reactions that are involved with large molecules due to the limitation of mass transfer of large molecules (Perez-Ramirez *et al.*, 2003; Donk *et al.* 2001).

Han and Hyeon (1999a, b) founded that the ordered-narrow uniform of mesopore in carbons structure was obtained by using colloidal silica nanoparticles as hard template. The specific surface area and pore volume of the obtained carbons were increased up to $1089\text{-}1512 \text{ m}^2/\text{g}$ and $1.69\text{-}4.70 \text{ cc/g}$, respectively. Moreover, in 2002, Lee and Oh founded that nanosphere carbons derived from resorcinol-formaldehyde were obtained by using cethyletrimethylammonium bromide (cationic surfactant, CTAB) as soft template. The pore diameter of the obtained carbon was varied from 7.4 nm to $>60 \text{ nm}$. Therefore, in this work, cationic/non-ionic surfactant and colloidal silica nanoparticles, are used as soft and hard template for improving porous properties of PBZ-based carbon xerogels, respectively. The effects of soft and hard template on the textural characteristic of the obtained carbon xerogels will also be investigated.