



CHAPTER II

LITERATURE SURVEY

2.1 Preparation of a carbon monolith with hierarchical porous structure

The template replication is a popular synthesizing method for preparation of a carbon monolith with hierarchical porous structure. Briefly, the template material, which generally is either a silica monolith with hierarchical porous structure or a silica micro-bead, is synthesized. Then, the carbon sources that generally obtained from organic materials are introduced into the internal structure of the template and followed by carbonization of the composite materials. Finally, the template is removed by strongly acidic or basic solution, and the replica carbon monolith with hierarchical porous structure can be obtained. Some works that based on such synthesizing method are summarized in this section.

Zhi-Guo Shi et.al [21]: In this paper the synthesis of hierarchical porous carbon monolith in various shapes, i.e. cylindrical, triangular, square, loop and pentagonal shapes, and wide macropore range via using template replication method was reported. The template being used in this work was silica monolith synthesized by the combination of sol-gel polycondensation and phase separation. In this synthesis, the shapes of the obtained carbons were predetermined by the forms of the silica templates, while the skeleton size and the pore size were predicted by the skeletons thickness and the total skeleton size of the silica templates. By delicate template selection, carbon monolith in cylindrical, triangular, square, loop and pentagonal shapes can be synthesized, with their skeleton pore size varying from 6.5 to 7.6 nm and textural pores ranging from one micrometer to several micrometers. The advantage of this method is the shape and the textural pores of the silica monolith templates were easily controlled by changing the preparation condition.

Xiqing Wang et.al [23]: In this paper the template replication procedure, using powdery mesoporous silicas as the template, for preparation of carbon monoliths with hierarchical porous structure integrating macroporosity, ordered mesoporosity and controlled microporosity, was reported. The templates were made from powdery mesoporous silicas, with either hexagonal (SBA-15) or cubic (KIT-6) mesostructure, by gel-casting method. The hierarchical porous carbon monoliths were prepared via immersion of the silica templates into a trimethylbenzene (TMB) solution of furfuryl alcohol (FA) containing oxalic acid overnight for complete wet impregnation. The polymerization was performed in the integrating macropore of the template at about 80 °C for 24 hours. Subsequently, the composite materials were carbonized under N₂ at 850 °C for 4 hours. In addition, the chemical vapor decomposition (CVD) method was brought to apply in this work for controlling the well-ordered mesostructure with either hexagonal or bicontinuous cubic symmetry of the carbon monolith. In the case of CVD method, N₂-saturated acetonitrile was passed through the composite materials at temperature of about 800 °C for 3 hours. Finally, the silica templates were removed by hydrofluoric (HF) acid, the hierarchically porous monolith carbons were obtained.

An-Hui Lu et.al [22]: In this paper a simple process to fabricate carbon monoliths with meso- and macropores was established. Furfuryl alcohol, mesoporous silica SBA-15 and sodium chloride were employed as carbon precursors, mesoporous template and agent for building up the monolith form, respectively. In addition, the resulting carbon monolith was also used as template to further replicate other nano-structural monolith materials, CoAl₂O₄ spinel was selected as an example. In synthetic procedure, the silica SBA-15 was impregnated with furfuryl alcohol containing oxalic acid following polymerization at 80 °C for 24 hr. Subsequently, the obtained composite powders were mixed with the fine powder of NaCl with a size of 0.2 μm and built up into cylindrical monolith form by pressing via hydraulic pressure of 1000 kg/m². The composite monoliths were further cured and carbonized,

respectively, under argon. The carbon monoliths were obtained by resolving the NaCl and removal of the silica by HF and NaOH, respectively.

Akira Taguchi et.al [24]: In this paper the preparation of monolithic carbon processing a hierarchical bimodal meso- and macroporosity via template replication method was proposed. Briefly, they used the hierarchical bimodal pore of silica monolith, which prepared via combination techniques of phase separation and sol-gel synthesis route, as the template. Furfuryl alcohol (FA) was introduced into both the meso- and macropore of the template by wet impregnation. The impregnated sample was then put into the cylindrical glass tube and kept at room temperature for 3 h. After, the sample was kept at 90 °C for 15 h to polymerize FA inside the silica template and followed by carbonizing under nitrogen gas flow. Finally, the replica carbon monolith was obtained via removal of the silica template by hydrofluoric (HF) acid and followed by washing it with deionized water.

Zhi-Guo Shi et.al [13]: In this paper the synthesis of a carbon monolith with co-continuous structure and tri-modal pores by a template replication method using a hierarchical porous silica monolith as the template was reported. The template was synthesized by the combination routes of phase separation and sol-gel process. In brief, the tetramethoxysilane (TMOS), poly(ethyl glycol) (PEG) and acetic acid were mixed and stirred until a homogenous solution was obtained. Then it was poured in cylindrical mold and followed by polymerizing in an oven at 40 °C for 48 hr. The silica monolith obtained was washed with large amounts of water, carefully dried and calcined at 400 °C for 3 hr. After that the silica monolith was impregnated with aqueous solution of sucrose and sulfuric acid. After being dried, it was thermally treated at 160 °C for 5 hr. Then the same procedures were repeated until no infiltration not observed. Subsequently, the composite material was carbonized at 950 °C for 5 hr. Finally the carbon monolith was liberated by dissolving the silica template in a NaOH solution.

2.2 Activation process for a development of micro-/ and mesoporosity

Activation process, either thermal activation with oxidative gas or chemical activation by impregnation of some metal catalysts following by thermal activation with oxidative gas, is the popular method for preparation of the activated carbon with large specific surface area, high porosity and more oxygenated surface functional group. Therefore, there are many works to report the preparation of the activated carbon by both thermal and chemical activation in order to develop either physical structure or chemical property. However, some works on thermal and chemical activation for preparation of the activated carbon are summarized in this section.

T. Yang et.al [26]: The activation process for preparation of the activated carbon from pistachionut shells by activation with CO₂ in two-steps activation was proposed. The effects of different parameters such as the activation temperature, the dwell time and the CO₂ flow rate on the pore evolution of the activated carbons was studied. With an increase in dwell time or temperature, increased carbon-CO₂ reaction occurred, resulting in the enhancement of existing pores and the formation of new pores. However, too long a dwell time or too high a temperature would cause the widening of pores and the collapse of some pore walls.

M. J. Halat et.al [27]: The synthesis of the activated carbon from Polish high volatile bituminous coal with steam and carbon dioxide activation was studied. Before activation, coal was oxidized in air at 400 °C for 40 h. The oxidation coals resulted in an increased in micropore volume. Both steam and CO₂ activation developed micropore by opening (removing constrictions) and also widening the very narrow micropore. Steam activation led to greater micropore volume than CO₂ activation.

J. Hayashi et.al [28]: The preparation of the activated carbon from impregnated lignin with chemical activated (K₂CO₃, Na₂CO₃, KOH, NaOH, ZnCl₂ and H₃PO₄) and carbonized in nitrogen atmosphere by various temperature in 500 – 900 °C ranges was presented. The activated carbon

prepared by impregnation of ZnCl_2 and H_3PO_4 shown the maximum BET surface area as large as commercial activation carbon (coconut shell AC and coal AC) at 600 °C. The BET surface area and micropore volume of the activated carbons prepared by impregnation of ZnCl_2 and H_3PO_4 are increased with the activating temperature over the range 500 – 600 °C, and are decreased with the activation temperature in 600 – 900 °C. They indicated that, ZnCl_2 and H_3PO_4 worked effective as activating reagents as the activating temperature is below 500 °C. Moreover, they also proposed that ZnCl_2 worked as dehydration reagent, restricted the formation of tar, and promoted the charring of the carbon at the activating temperature below 600 °C. Consequently, the porous structure of the activated carbon was modified. In the part of K_2CO_3 , Na_2CO_3 , KOH and NaOH activation, the maximum BET surface area were larger than commercial activation carbon (except for Na_2CO_3) at 800 °C. The BET surface area and micropore volume increased with increasing of the activating temperature up to 800 °C. The pores enlarged up to this temperature. When the activating temperature was above 800 °C, it could result in an increasing of mesopore and reducing of micropore volume. Finally, they propose that, K_2CO_3 could modify the carbonization behavior of the lignin in two temperature ranges, below 500 °C and above 600 °C. K_2CO_3 worked as the dehydrogenation reagent when the activating temperature was below than 500 °C. When the activating temperature was higher than 600 °C, the carbon was removed as CO_2 and the surface area and the pore volume were increased.

K. Okada et.al [29]: The preparation of the activated carbon from old newspaper and paper by using the chemical and physical (steam) activation was proposed. The alkali carbonates (K_2CO_3 , Rb_2CO_3 , Cs_2CO_3 , Li_2CO_3 and Na_2CO_3) and hydroxide (KOH and NaOH) were used as activation agents. In chemical activation, the impregnated starting materials with various chemical agents were activated in 700 – 950 °C ranges and activated in nitrogen atmosphere. The porous properties of activation carbon which impregnated with larger alkali cations sizes (K, Rb and Cs) show higher BET – surface area

than impregnated with smaller sizes (Li and Na). The little effect of different anions was shown. Moreover, they proposed that the alkali cations had stronger effect on pore formation and pore size of activation carbon by alkali cations intercalated into the interlayers of carbon network structure. They suggested that the smaller cations had little effect on the expansion of interlayers. Whereas the larger cations could expand the interlayers, therefore, they resulted in the formation of larger pores. In the case of Rb and Cs, their excessively large size may hinder their intercalation into the carbon layers, making them less effective than K. Furthermore, the melting point of K_2CO_3 (891 °C) was close to the activating temperature of 900 °C, possibly making in accelerating its intercalation and the formation of larger pores. Moreover, activation carbon with HCl washing shows larger BET – surface area and pore volume than the sample with no washing. This represented that the HCl washing was effective in reduction ash content.

J. Miyamoto et.al [30]: The production of mesoporosities in the activated carbon fiber (ACF), which had uniform micropore and high surface area using chemical and physical activation, was studied. In chemical activation, ACF was immersed in 0.3 M solution of Na_2HPO_4 , $Ca(NO_3)_2$, and K_2CO_3 at room temperature after pre-evacuation at 373 K. The dried impregnate ACF was activated with steam at 1073 K under Ar flow (100 cc/min). The activation with Na_2HPO_4 , $Ca(NO_3)_2$ produced mesopores without destroying of the original microporosity. On the other hand, K_2CO_3 activation didn't show the mesoporosity production and reduced the microporosity. They suggested that there was no mesoporosity in K_2CO_3 due to the melting point of K_2CO_3 (1164 K) is higher than the activation temperature. K_2CO_3 cannot efficiently play a role of catalyst for gasification. Furthermore, the remaining K_2CO_3 blocked the pore thus decreasing microporosity.

S. Lei et.al [31]: The preparation of the activated carbon fibers (ACF) by impregnation with $Ca(NO_3)_2$ solution and activated by steam was proposed. The ACF was immersed in 50 ml $Ca(NO_3)_2$ solutions with concentration

between 0.05 – 1 mol/l in vacuum for one day after evacuation at 10 mPa and 383 K for 2 hr. The increase of $\text{Ca}(\text{NO}_3)_2$ concentration of more than 0.2 mol/l provides an explicit hysteresis loop, indicating a predominant development of mesopores and resulting in the decreased micropore volume, whereas mesopore volume increased remarkably. The burn-off percent value gradually increased with the increasing concentration. Consequently, the $\text{Ca}(\text{NO}_3)_2$ impregnation partially transformed micropores to mesopores. The pore size distribution of mesopores was very broad considerably (20 ± 10 nm). Accordingly, the longer activation time (2 hr) and temperature (800 – 900 °C) resulted in an increasing mesopore volume.