



CHAPTER I

INTRODUCTION

1. Background and motivation

A hierarchical porous material has an interesting structure which contains the combination pores of micropore or mesopore throughout a macroporous monolith. The macropore structure allows fluid flow under low back pressure and high convective mass transfer, which is an explanation for high column efficiency and high speed separation under continuous flow conditions. [1-5] Therefore, the hierarchical porous monolith has a great potential for many applications such as enzyme immobilization for high-throughput bioreactor [6], HPLC monolithic column for high speed separation [7,8], membrane emulsification [9], electro catalyst support [10] etc. Furthermore, one good example in the application of the hierarchical porous monolith is to use this material for a capillary column which is suitable for sample analysis in a very small amount [11].

Most hierarchical porous monoliths are generally produced from two main materials; one is an organic polymer [1, 12-14] and the other is an inorganic polymer [15-17]. However, there are some limitations of the both materials. An organic polymer exhibits insufficient mechanical strength, especially for swollen polymer gels, while an inorganic polymer cannot resist strong acidic and alkaline conditions [18, 20]. Regarding these drawbacks, the hierarchical porous carbon monolith is considered as a promising alternative. The hierarchical porous carbon monolith has an interesting structure which can be fitted in any applications of activated carbon [19] such as air and water purification, adsorption, separation and catalyst support. The hierarchical porous carbon monolith can usually be produced through polymerization or sol-gel processes of various polymeric materials, such as resorcinol-formaldehyde gel [20, 21], polymer of sucrose [22], furfuryl alcohol [23, 24] etc., with hard-template replication of, for instance, hierarchical porous silica monolith [20, 22, 23], suspension of silica beads [21], powdery silica [24] and so on [25], and followed by

carbonization under inert gas. Hence, the porous structure and external shape of the carbon monoliths are determined by the morphology of these templates. In addition, this preparation method is quite complicate because removing the templates from carbon skeleton is needed. Therefore, the synthesis without using any hard-templates for preparation of the carbon monolith containing both macroporous and nanoporous structure is the new and challenged preparation technique in the field of porous material design.

One possible strategy to reach the goal is based on two individual steps. The first step is to prepare a carbon precursor in a monolithic shape that contains the interconnected macropores throughout its internal structure, and the second step is to generate the microporous or mesoporous structure on the surface of the macroporous structure by either carbonization or activation processes. In particular, both macroporous structure and monolithic shape of the carbonaceous product can also be maintained after processing.

This dissertation proposes an achievement for preparation of the hierarchical porous carbon monolith according to above strategy. At the first step, resorcinol-formaldehyde (RF) gels synthesized by two novel techniques for preparation of monolith shape with interconnected macroporous structure are established. The first technique is to irradiate with high intensity ultrasonic wave into the RF solution during gel-formation. The second technique is to induce the inverse-phase suspension of the RF solution at nearly complete gel-formation by adding water. The first and the second technique are introduced in Chapter IV and Chapter VI, respectively. The next important step is to produce the carbon monolith from the macroporous RF-monolithic gel that the nanoporous structure must be generated in the carbon monolith as well as to maintain both monolith shape and macroporous structure after processing. The carbonization with N_2 , direct thermal activation with CO_2 and direct chemical activation with $Ca(NO_3)_2/CO_2$ are studied as the carbon monolith preparation processes. The macroporous RF-monolithic gel synthesized by ultrasonic irradiation during gel-formation as mentioned in Chapter IV is used as the carbon precursor for study. The study of carbon monolith preparation from the macroporous RF-monolithic gel is introduced in Chapter V.

1.2 Objective

The new method without using any hard-templates for preparation of a carbon monolith with hierarchical porous structure of either bi-modal pores (micropores on interconnected macropores) or tri-modal (micro- / and mesopores on interconnected macropores) are mainly focused.

The objectives in this work can be separated into three parts as followed;

1. A study on the preparing and controlling of the interconnected macropores within the internal structure of a carbon monolith derived from N_2 -carbonization of a RF monolith, which is synthesized by ultrasonic irradiation during gel-formation.
2. A study on the preparation of the activated carbon monolith with hierarchical porous structure by two different activations. The first preparation is direct thermal activation with CO_2 . The second preparation is direct chemical activation performed by impregnation of $Ca(NO_3)_2$ into the RF monolith gel, and followed by CO_2 -thermal activation. The RF monolith gel used as carbon precursor is synthesized by ultrasonic irradiation during gel-formation.
3. A study on the preparation of the interconnected macroporous RF monolith gel synthesized by inverse-phase suspension at nearly complete gel-formation, as a carbon precursor for preparation of the hierarchical porous carbon monolith.

1.3 Scope of work

All experiments in this work are performed in laboratory scale. The scopes for study in this work are classified into two main sections as shown in Figure 1.1. The first section corresponds to the preparation of the macroporous RF-monolithic gel by two novel techniques without using any hard-templates; that composes with the technique of ultrasonic irradiation during gel-formation (Chapter IV) and the technique of inverse-phase suspension with adding water (Chapter VI). The second section (Chapter V) concerns with the method to produce the carbon monolith with macroporous and nanoporous structure from the macroporous RF-monolithic gel synthesized via the technique in Chapter IV. The carbon production methods to study

compose with carbonization with N_2 , direct thermal activation with CO_2 and direct thermal activation with $Ca(NO_3)_2/CO_2$. The scopes for experimental in each chapter are described as below.

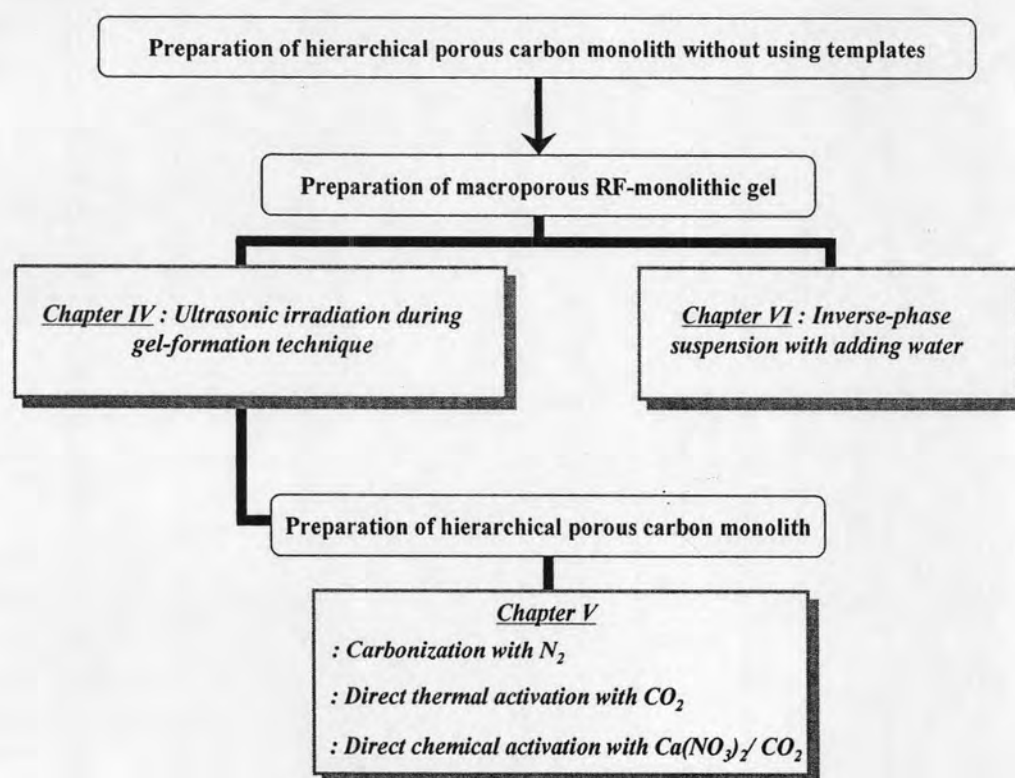


Figure 1.1: Schematic diagrams to express the scopes in this work.

1.3.1 Section I: the preparation of macroporous RF-monolithic gel

Chapter IV: ultrasonic irradiation during gel-formation technique

This chapter, the high intensity ultrasound is irradiated into the RF solution during gel-formation for synthesis of RF monolith gel, and subsequently dried via hot air drying. The synthesis variables are focused on initial pH value of RF solution, pH_{Int} , gel-formation temperature during ultrasonic irradiation, T_{US} , power of ultrasonic irradiation, P_{US} , and ultrasonic irradiation time, t_{US} , are studied. The range of these variables are confined to the range of 4.8 to 6.9, 20 to 50 °C, 12 to 30 W and

0 hr to 8 hr for the pH_{Int} , T_{US} , P_{US} and t_{US} , respectively. The other synthesis conditions are fixed as below.

- Resorcinol (R), formaldehyde (F), sodium carbonate (C) and deionized water (W) are used as reactants.
- The reactant ratios of R/F and R/W are fixed at 0.5 and 0.15 mol/mol, respectively.
- The ultrasonic probe is made from titanium alloy with diameter of 0.6 mm connecting to the ultrasonic generator (Sonic&Material; VibraCell Model 120). Its frequency produced from the generator is fixed at 20 kHz, and the ultrasonic power can be tuned up to 30 W.
- The cylindrical glass tube in diameter of 2.5 cm is used as the reactor, and its maximum volume containing RF solution is 10 cm^3 .

Chapter VI: inverse-phase suspension with adding water

In this chapter, the alternative technique is to induce phase suspension of the RF solution by adding water at nearly complete gel-formation in order to generate the interconnected macropores throughout the internal gel structure by connecting each suspended gel particles altogether. The synthesis variables are focused on gel keeping time before adding water, t_{AD} , and volume ratios of the adding water to RF solution, W_{AD}/RF . The range for study of t_{AD} is varied from initial stage to nearly complete gel-formation whereas W_{AD}/RF is varied from 0.10 – 1.00. The other synthesis conditions are fixed as below.

- Resorcinol (R), formaldehyde (F), sodium carbonate (C) and deionized water (W) are used as reactants.
- The reactant ratios of R/F and R/W are fixed at 0.5 and 0.15 mol/mol, respectively.

All of the RF monolith gels which obtained from the both parts will be aged with the oven at the temperature of $75 \text{ }^\circ\text{C}$ for 3 days prior to the production of the carbon monolith.

1.3.2 Section II (Chapter V): preparation of hierarchical porous carbon monolith

In this chapter the simple procedure to improve both mesoporous structure and oxygenated functional groups in the activated carbon monolith consisting of the interconnected macroporous structure is the aim of this study. The RF monolith gel synthesized by ultrasonic irradiation during gel-formation technique is used as the carbon precursor for this study. The study is focused on the direct thermal activation with CO_2 and the direct chemical activation of the RF monolith gel. The direct thermal activation is carried out by activating the RF monolith gel with CO_2 . While the direct chemical activation is performed by impregnation of $\text{Ca}(\text{NO}_3)_2$ into the RF monolith gel and followed by directly activating with CO_2 .

The influence of the main parameters, activation temperature (T_D) and time (t_D), on the obtained porous structure and oxygenated functional groups of both direct thermal activation and direct chemical activation are mainly emphasized here. This parameters is limited in the range of 500 °C to 1000 °C and 15 min to 120 min for T_D and t_D , respectively. Moreover, the comparison of the hierarchical porous structure and the oxygenated functional groups of the hierarchical porous carbon monoliths prepared from carbonization with N_2 , direct thermal activation and direct chemical activation are discussed also.

The other synthesis conditions are fixed as below.

- A horizontal furnace with a quartz tube (60 cm in length and 10 cm in diameter) is used for both carbonization and activation throughout the research. Its maximum temperature is 1200 °C.