

CHAPTER VI

PREPARATION OF AN ACTIVATED CARBON MONOLITH WITH HIERARCHICAL POROUS STRUCTURE BY INVERSE PHASE SUSPENSION

It has been well-known that sol-gel process plays an important role during gel complete formation of RF gel [58 - 67]. The process is started from an aqueous phase in which resorcinol and formaldehyde are contained, and reacted together with simultaneously hydrolysis and polycondensation reaction to form RF clusters. Then RF clusters react with each other and grow into colloidal particles, which subsequently joined to the other to form the network and followed by extending them throughout its structure [59-64]. During the network growth, in particularly near complete gel-formation [59, 63, 65, 66], it becomes to be separated from an aqueous phase because of highly increased density resulting from solid-network formation. It is particularly noticed that at nearly complete gel-formation the RF solution does not seem to favor the water phase. Therefore, it is possible that the RF solution at near complete gel formation can be induced with water to suspend the RF solution into particles in the micrometer range scale. Hence, the author would like to propose that the RF monolith gels fabricated via inverse-phase partial-suspension induced by adding water at nearly complete gel-formation and subsequently connecting the suspended gels to each other throughout a monolith shape are possible. The objective of this chapter is to propose a new and alternative method for preparation without using templates of RF monolith gels with interconnected macroporous structure.

6.1 Experimental

6.1.1 Formation of resorcinol-formaldehyde (RF) gels by inverse-phase suspension by water

6.1.1.1 Preparation of RF solution

At first, the resorcinol (R) was dissolved into the de-ionized water (W) and stirring it with magnetic stirrer until dissolution completely. Then, the resorcinol solution was added with sodium carbonate (C), for using as the basic catalyst, and followed continually by filling the formaldehyde solution (F). The reactant ratios of the resorcinol to formaldehyde, R/F, resorcinol to water, R/W, and sodium carbonate to water, C/W, were fixed at 0.5 mol/mol, 0.15 mol/mol and 10 mol/m³, respectively, throughout in this experimental. Next, the mixture was stirred with magnetic stirrer for 5 min at the room temperature, and followed by keeping at the constant temperature of 30 °C.

6.1.1.2 Inverse-phase suspension by water for formation of RF monolith

The complete RF gel formation synthesized as above mentioned condition was generally success for ~ 31 hr. This experimental, hence, need to conduct before gel formation to be complete. Then, the deionized water was filled into the RF mixture to induce phase suspension, synthesis condition such as gel keeping time before adding the water, t_{AD} , and volume ratios of the adding water to RF solution, W_{AD}/RF , are shown in the Table 6.1.

Under suitable t_{AD} and W_{AD}/RF , the phase separation phenomenon occurred, the color of the solution changed from transparence orange to clouded white. Then, the mixture was poured into the cylindrical glass tube in diameter of 0.5 mm and kept in the tube within a few minutes at temperature of 75 °C until complete gel formation. Finally, the obtained gel was aged in an oven at temperature of 75 °C for 3 day.

Table 6.1: Synthesis conditions for preparation of the interconnected macroporous RF monolith by inverse phase suspension.

Samples	t_{AD} [hr]	W_{AD}/RF [-]
C1	28	0.53
C2	26	0.53
C3	30	0.53
C4	30	0.33
C5	30	0.43
C6	30	0.67
C7	30	1.00

6.1.2 Preparation of carbon monoliths

The obtained wet-monolith gels were washed by distilled water 3 time /day for 3 day and dried at the temperature of 75 °C until constant their weight.

Subsequently, the direct thermal activation and the direct chemical activation processes as mentioned in the section 5.1.2 – 5.1.3 were conducted here for preparing the activated carbon monolith. The activating conditions of heating rate, activation temperature and time were fixed at 10 °C /min, 800 °C and 30 min, respectively, for both processes. Finally, the hierarchically micro-/ macroporous or micro-/ meso-/ macroporous carbon monoliths were obtained.

6.1.3 Characterizations

The texture of interconnected pore in monolithic forms of both RF gels and carbons were revealed by scanning electron microscope (JEOL, JSM-6700F). The macropore size distribution of the macroporous carbon monolith was obtained by mercury porosimeter (Micromeritics, Pore-Sizer-9320).

The micro/meso porosities were determined from the adsorption and desorption isotherms of N_2 at 77 K measured by adsorption apparatus (BEL, mini-

BEL Sorp.). According to IUPAC classification, pores could be divided into three categories depending on their sizes: micropores (≤ 2 nm), mesopores (2 – 50 nm) and macropores (≥ 50 nm). The definition of micropores and mesopores introduced by IUPAC was adopted. Then, the micropore volume, V_{micro} , was determined by t-plot while the mesopore volume and mesopore size distribution were derived from Dollimore-Heal method [43, 45]. For the specific surface area, S_{sp} , is obtained from an average values between the Brunauer-Emmett-Teller (BET) specific surface area, S_{BET} , and the t-plot specific surface area, $S_{\text{t-plot}}$, that they were usually applied to determine the specific surface area of the activated carbon [44], and were derived from BET model and t-plot model, respectively.

Fourier Transform Infrared (FTIR) spectra were recorded using spectrometer (Perkin Elmer, 1615), and the samples for analysis is formed as pellets made by crushing and mixing the samples with spectroscopy grade of KBr.

6.2 Results and discussion

6.2.1 Preparation of RF monolith gel with interconnected macroporous structure obtained by inverse-phase suspension

The inverse-phase suspension phenomenon of the RF solution at nearly complete gel-formation can obviously be observed by the sequent photographs as shown in Figure 6.1 (a) to (d). We can see that the transparent-orange color of the RF solution is instantly changed to the white suspensions. However, the phenomenon cannot be occurred if the water is added into the RF solution before 28 hrs-gel-formation time. The ratios of R/F, R/W and C/W of the demonstrated RF solution are fixed at 0.5mol/mol, 0.15mol/mol and 10mol/m³, respectively. Then, the RF solution is kept at 30 °C for 30 hr. It is noticed that the complete gel-formation time of the RF gel prepared under mentioned condition is about 31 hr.

According to the RF gel-formation behavior investigated by DLS and SAXs techniques and proposed by many authors [62, 63, 65], it is started from the resorcinol with formaldehyde reacted together with additional reaction and polycondensation in an aqueous phase. Then the RF clusters are formed and joined to each others to make colloidal network. Subsequently, they are continually extended themselves gradually time throughout an aqueous phase. Consequently, the viscosity of the RF solution is

continually higher resulting from the continuous growth of the colloidal network. Finally, the highly dense colloidal networks distributed throughout the viscose solution are initially separated from aqueous phase and fixed as the skeleton network to serve the solid gel structure. It is notice that at the nearly complete gel-formation the RF solution and water are separated away. Therefore, the inverse-phase suspension of the RF solution can be occurred when the water is added at nearly complete gel-formation as shown in Figure 6.1 (a) to (d).

The SEM images of cross-sectional area in the micrometer-range scale of the obtained RF monolith gels derived from different gel keeping time before adding the water, t_{AD} , at 26, 28 and 30 hr before complete gel-formation are shown in Figure 6.2. One can see that the interconnected macroporous structure formed by interconnecting of the micro-particles can obviously be observed for the RF monolith in conditions of t_{AD} at 28 and 30 hr. These results correspond with the observation that the suspension of RF solution can be appeared when adding the water at 28 hr of gel-formation time has passed. It is a confirmation that the added water can induce the RF solution to suspension at nearly gel-formation (complete gel-formation time ~ 31 hr in this case).

Figure 6.1 (e) shows the final form of the RF monolith gels fabricated by inverse-phase suspension by adding water at nearly complete gel-formation time (~ 30 hr) and at various W_{AD}/RF ratios of 1.00, 0.67, 0.53 and 0.33. One can see that the monolith shape can be obtained when the W_{AD}/RF ratio is less than 1.00.

Prior to further consideration, the possible mechanism for a formation of the RF gel in a monolithic shape that fabricated from interconnecting of the suspended RF particles is discussed. Figure 6.3 shows the schematic diagram of such mechanism. It has been known from previous section that the highly viscous RF solution can be inversed to suspensions with adding the water at nearly complete gel-formation time. Moreover, one of well-known properties of the RF gel is good adhesive glue [67]. Therefore, it is possible that the residue RF solution which does not suspended with adding water can play an important role as the glue in joining the suspensions together.

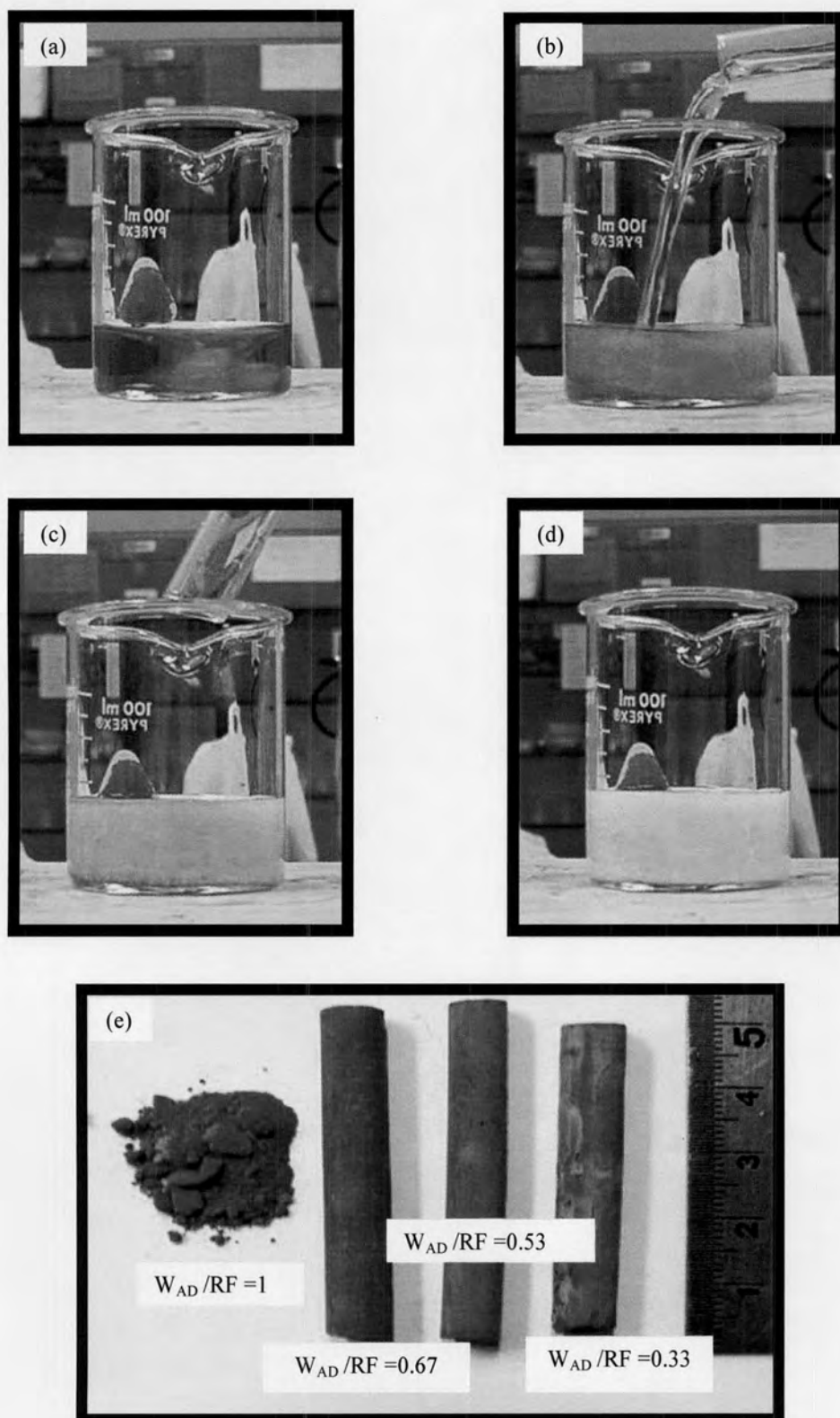


Figure 6.1: (a)-(d) Sequence photographs of the inverse-phase suspension phenomenon of resorcinol-formaldehyde (RF) solution by adding water at different gel keeping time and (e) final macroscopic shape of the gels in various W_{AD}/RF ratios.

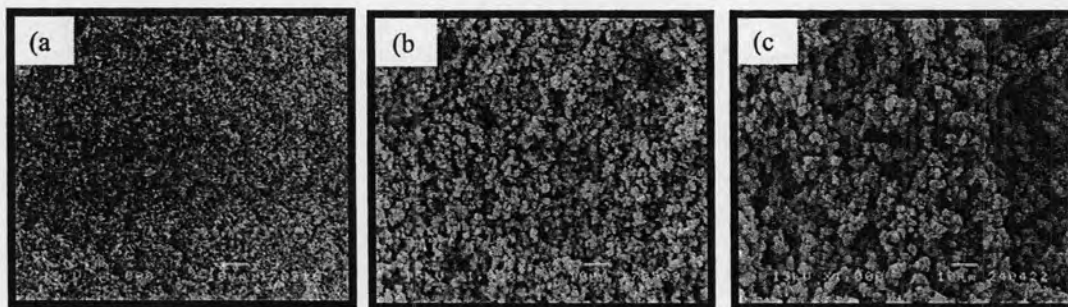


Figure 6.2: SEM images of macroporous structure within RF monolith synthesized via inverse phase separation of RF solution induced by adding water, $W_{AD}/RF = 0.53$, at t_{AD} ; (a) 26 hr, (b) 28 hr and (c) 30 hr gel keeping time.

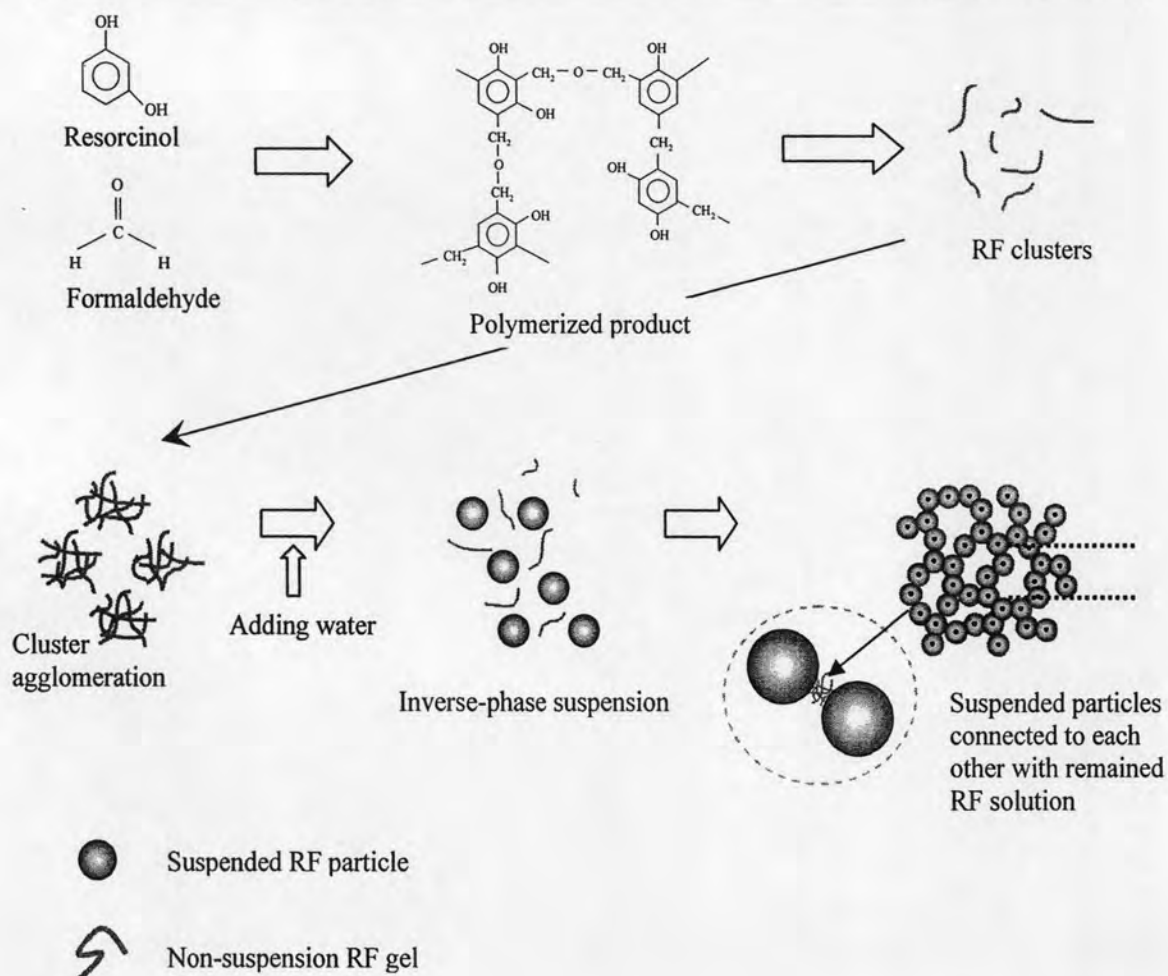


Figure 6.3: Schematic picture of the possible mechanism for a formation of RF monolith gel with the interconnected macroporous structure by inverse-phase suspension

Consequently, the monolith shape consisting of a connection of the suspended RF particles can be formed. However, the monolithic shape cannot be formed when W_{AD}/RF ratio is higher than 1.00. An explanation in this case may come from the large volume of the adding water that can result in separating each suspended RF particle far from the others. Hence, the chance of particles colliding with each other in joining together to form the interconnected particles is very slim. Consequently, the RF gel in a monolith shape cannot be obtained with excess volume of the adding water.

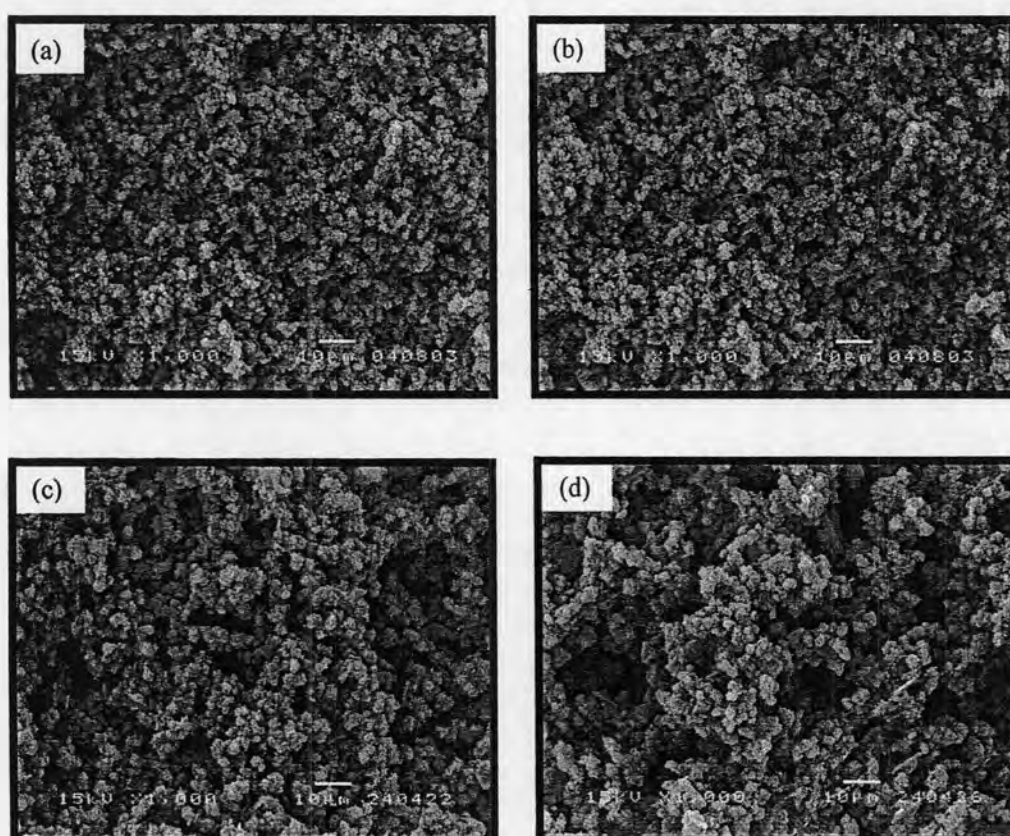


Figure 6.4: SEM images of macroporous structure of RF monoliths synthesized under various W_{AD}/RF ratios; (a) 0.33, (b) 0.43, (c) 0.53 and (d) 0.67.

The SEM images of cross-sectional area in the micrometer-range scale of the obtained RF monolith gels at volume ratios W_{AD}/RF of 0.33, 0.43, 0.53 and 0.67 are shown in Figure 6.4 (a), (b), (c) and (d), respectively. They clearly indicate that the

internal structure of the obtained RF monolith gels are formed by RF suspensions connected to each other together throughout a monolith. The SEM micrographs perfectly supported the proposed mechanism/concept.

Figure 6.5 shows the macropores size distributions measured by mercury intrusion of the RF monolith under various volume ratios W_{AD}/RF of 0.33, 0.43, 0.53 and 0.67. One can see that the macropore sizes increase with increasing volume ratio of W_{AD}/RF . As mentioned above, the macroporous structure corresponds to the interstitial particles which are connected to each other throughout the internal structure of the RF monolith gel. Hence, an increasing volume of water in the RF solution can result in excess amount of water remaining in the inverse phase suspension. The interstitial suspension particles, consequently, are more and more separated by water molecules. Therefore, distance between the interstitial particles increase outstandingly. As a result, the macropore size distributions are broader with the increase in the volume ratio.

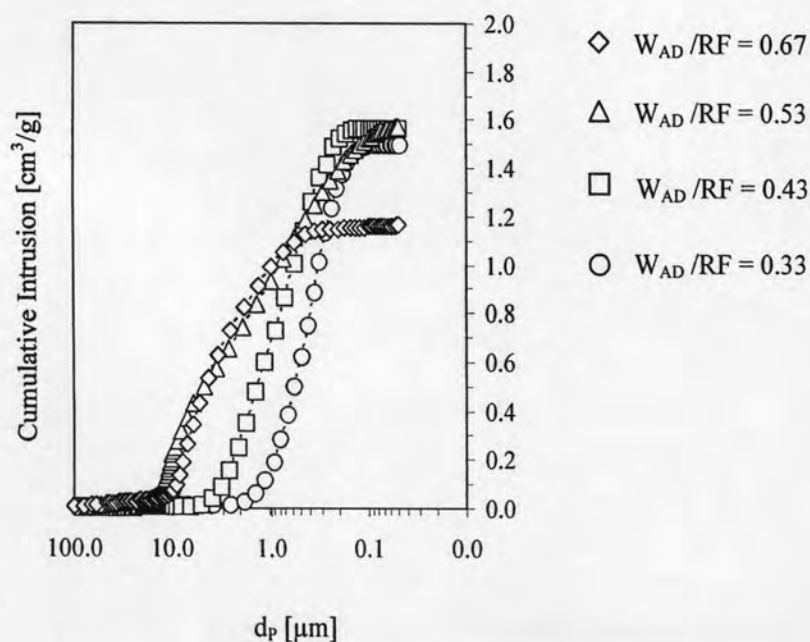


Figure 6.5: Macropore size distributions of carbon monolith synthesized from different W_{AD}/RF at 0.67, 0.53, 0.43 and 0.33.

Figure 6.6 shows the infrared spectrum of the RF monolith gel synthesized by inverse-phase suspension with adding water at nearly complete gel-formation. The observed peaks are in good agreement with the many RF gel related literatures [36-38]. The broad peak at 3409 cm^{-1} can be attributed to hydroxyl groups vibration involved hydrogen bonding. The peak bands at 1609 , 1471 and 1443 cm^{-1} correspond to C=C stretching vibration, C=C-H stretching, and bending vibration, respectively, within the aromatic rings.

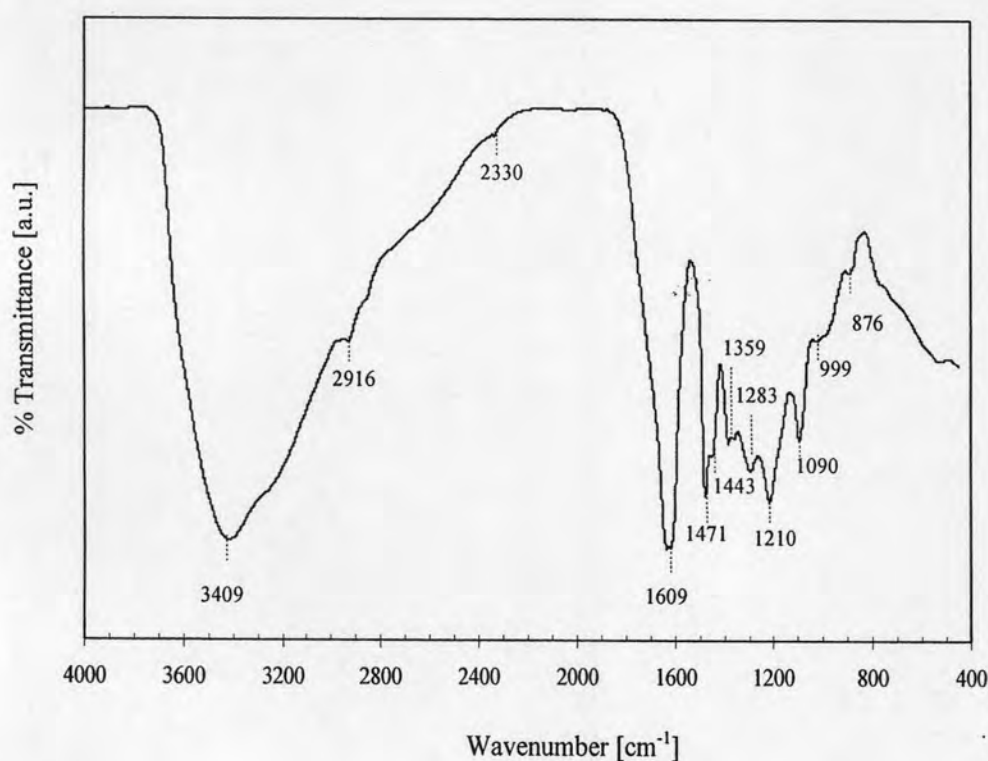


Figure 6.6: FTIR spectrum of RF monolith gel synthesized by inverse-phase suspension with adding water at nearly complete gel-formation at the condition of $t_{AD} = 30$ hr and $W_{AD}/RF = 0.53$.

The mainly functional groups corresponding to $-\text{CH}_2$ and C-O-C, which is the unique functionalities of the RF gel, are located at both 2916 and 1471 cm^{-1} , and at both 1210 and 1090 cm^{-1} for the first and second mentioned functionalities, respectively. The peaks at 1359 and 1280 cm^{-1} can be assigned to the presence of the phenol groups. It clearly indicates that the inverse-phase suspension of RF solution

can generate the macroporous structure whereas the chemical composition of the RF gel does not change.

6.2.2 Preparation of an activated carbon monolith with hierarchical porous structure prepared from RF monolith gel prepared by inverse-phase suspension

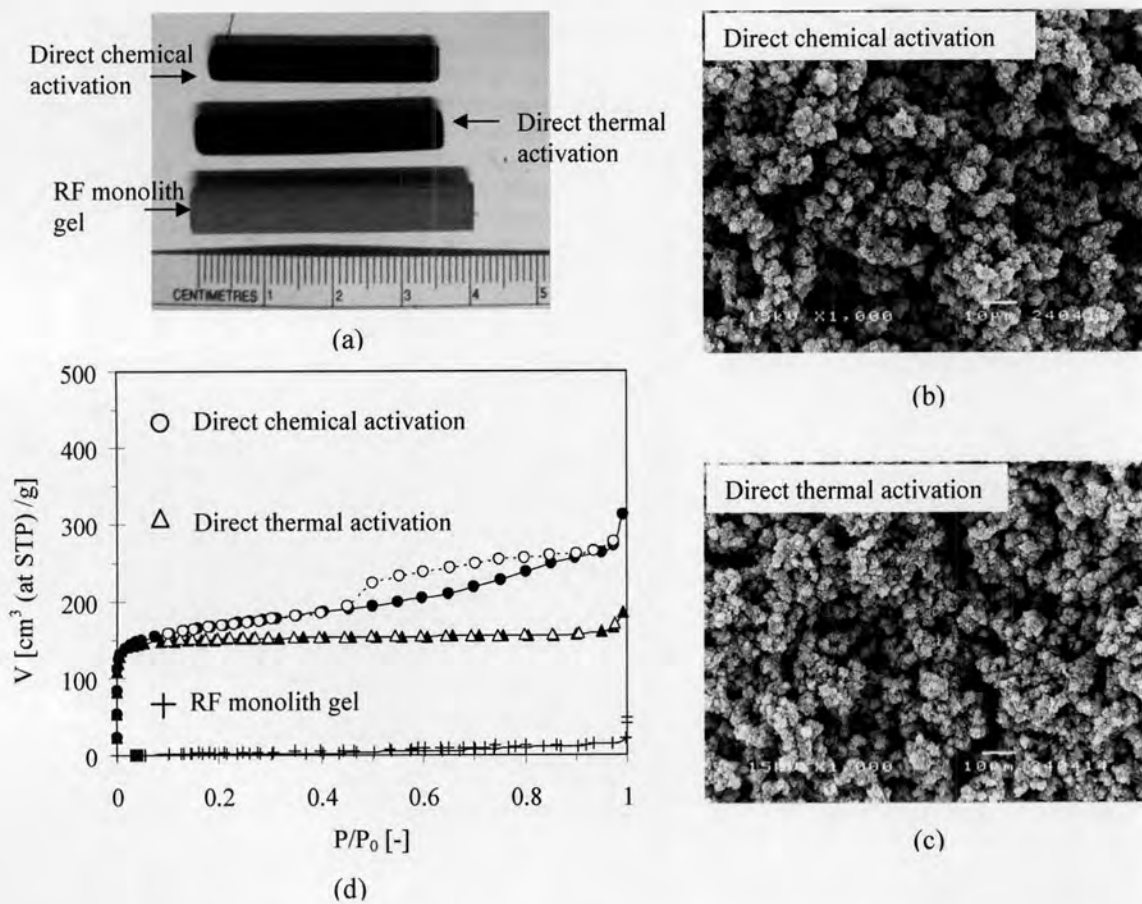


Figure 6.7: (a) Macroscopic shape of the carbon monoliths, prepared from RF monolithic gel under $W_{AD}/RF = 0.53$, after activation by direct thermal and chemical activation, (b) – (c) SEM images of macroporous structure after the different activations and (d) N_2 adsorption-desorption isotherms of RF monolithic gel in condition of $W_{AD}/RF = 0.53$ and the carbon monolith prepared from the

Hereto, it is well-known from previous chapter that both thermal activation process with CO_2 and $Ca(NO_3)_2$ -loaded followed by CO_2 thermal activation can

generate both micro-/ mesopores and oxygenate functionalities on the interconnected macroporous structure of the activated carbon. Likewise, both activation processes can be applied for the preparation of the activated carbon monolith with hierarchical porous structure derived from the RF monolith gel which synthesized by inverse-phase suspension under the same condition as C3 in Table 6.1.

Figure 6.7 (a) shows that the monolith shape of the activated carbon derived from both activations can be obtained. Moreover, the interconnected macropores within internal structure of the activated carbon monoliths, as shown in Figure 6.7 (b) and (c), can also be maintained after both activation processes.

Figure 6.7 (d) shows the N_2 adsorption-desorption isotherm at 77 K of the RF monolith gel and its two activated products. One can see that the N_2 can not be adsorbed on the RF monolith gel. It indicates that both microporosities and mesoporosities do not exist on the interconnected macroporous structure. However, the obtained N_2 adsorption-desorption isotherm Type I is given on the carbon monolith prepared by direct thermal activation with CO_2 , whereas the adsorption-desorption isotherm Type IV is given by direct chemical activation with $Ca(NO_3)_2/CO_2$.

Table 6.2: Porous characteristics of the RF monolith gel and carbon monoliths prepared from difference activation.

Samples	Type of Isotherm	Pore volumn [cm^3/g]		S_{sp} [m^2/g]
		V_{micro}	V_{meso}	
RF monolith gel*	Not adsorption	-	-	-
Carbon 1**	I	0.23	0.02	662 ± 70
Carbon 2***	I + IV	0.24	0.24	711 ± 87

Remarks; * It was prepared from inverse-phase suspension by adding water at conditions of $W_{AD}/RF = 0.53$ and $t_{AD} = 30$ hr.

** It was prepared from the direct thermal activation.

*** It was prepared from direct the chemical activation.

According to Table 6.2, it suggests that the RF monolith gel prepared by inverse-phase suspension with adding water does not contain both micro- and mesoporosities, while there are only microporous structure on the carbon monolith prepared by direct thermal activation ($V_{mic}=0.23 \text{ cm}^3/\text{g}$), and there are both micro- and mesoporous structure on the carbon monolith prepared by the direct chemical activation ($V_{mic}=0.24 \text{ cm}^3/\text{g}$ and $V_{mes}=0.24 \text{ cm}^3/\text{g}$). The specific surface area, S_s , of the carbon monolith prepared by the direct chemical activation ($S_{sp}= 771\pm 87 \text{ m}^2/\text{g}$) is much larger than the carbon monolith prepared by the direct thermal activation ($S_{sp}= 662\pm 70 \text{ m}^2/\text{g}$) as a result of additional mesopores. Furthermore, one can see that the results of both activation processes result in the formation of the microporosities and mesoporosities as well as using for activation of the RF monolith synthesized by ultrasonic irradiation during gel-formation as discussed in previous chapter. Therefore, the effect of activating temperature and activating time are not necessarily studied in this chapter.

6.3 Conclusions

In summary, the inverse-phase suspension at nearly complete gel-formation by adding water is an effective technique for preparation of the interconnected macroporous RF monolith that is suitable for the continuous preparation of carbon monolith with hierarchical porous structure, without using any templates, by either direct thermal activation or direct chemical activation process. The gel keeping time before adding water, t_{AD} , and the adding water volume are the important keys for the preparation. The inverse-phase suspension can be occurred when t_{AD} is near gelation time. The large volume of the adding water does not result in the formation of monolith shape, and a small volume adding cannot induce inverse-phase suspension of the RF solution therefore the interconnected macroporous structure cannot be obtained. However, the porous structure of the RF monolith gel prepared by this method is in the range of macropores only, the activation either by the direct thermal or the direct chemical process as applied in Chapter V is needed. The results of direct thermal activation process are the formation of microporosities only, whereas the direct chemical activation process results in the formation of both micro- and mesoporosities on the interconnected macroporous structure of the obtained activated carbon monolith.

It is worth to note that with simple preparation but without hi-tech equipments, the RF monolithic gel with hierarchical porous structure in a large monolith shape has successfully been prepared. There is possibility to extend this method for pilot-scale production of the hierarchical porous carbon monolith.