CHAPTER III

EXPERIMENTAL

3.1 The chemical agents and equipments

The chemical agents

1. Resorcinol ($C_6H_4(OH)_2$) 99 % (Fluka)
2. Formaldehyde (HCHO) solution 38 %w/w (BDH)
3. Sodium carbonate (Na_2CO_3) analytical grade (Ajax)
4. t – Butanol (C_4H_9OH) analytical grade (Ajax)
5. Potassium carbonate (K_2CO_3) analytical grade (BDH)
6. Cesium carbonate (Cs_2CO_3) analytical grade (Fluka)
7. Calcium nitrate tetra hydrate ($Ca(NO_3)_2.4H_2O$ analytical grade (Ajax)
8. De-ionized water
9. Nitrogen gas 99.999 %
10. Carbon dioxide 99.8 %

The equipments

1. Ultrasonic generator 20 kHz (Sonic vibra cell, model VC 130)
2. Ultrasonic probe 6 mm diameter
3. Cooling bath
4. Freeze dryer
5. Tube furnace
6. Quartz tube
7. Oven
8. Water pump

3.2 Preparation of 3D interconnected macroporous carbon monoliths (3D – IMM)

1. Preparation of RF gel

The chemical agents are used to prepare RF gel compose of resorcinol (R), formaldehyde (F) ,sodium carbonate (C) and de-ionized Water (W).The ratio of chemical agents using are shown in Table 3.1.

Table 3.1 The chemical ratios to prepare RF gel

Chemical agent	Ratio
W	10 cc
R/F	0.5 mol/mol
C/W	8 mol/m^3
R/C	1000 mol/mol

The resorcinol is dissolved in water and sodium carbonate is added into this solution. After that formaldehyde is poured into solution and stir until well mixing. After that the resorcinol – formaldehyde solution 10 cm^3 is poured into reactor. The ultrasonic irradiation is applied into this solution. The power output of ultrasonic irradiation and the temperature of cooling water are controlled at 22 watt and 30 °C, respectively. After applying ultrasonic for about 7 hours, RF gel is formed in monolith shape by using a glass tube (8 mm inside diameter) as a mold.

RF gel is kept in mold for a day and then RF gel is aged at 75 °C for 3 days. After aging, solvent exchanging in RF gel is processed. The t –Butanol is used as solvent. The RF gel is immersed in solvent for 3 times. The RF gel is dried by freeze drying at – 40 °C for 2 days.

2. Preparation of RF carbon

The dried RF gel is carbonized in nitrogen atmosphere at 750 °C in horizontal tube furnace. RF gel which is contained in ceramic boat is inserted into quartz tube. Nitrogen flow rate is controlled at 200 cm^3/min. The pattern of carbonization is show in Figure 3.1.

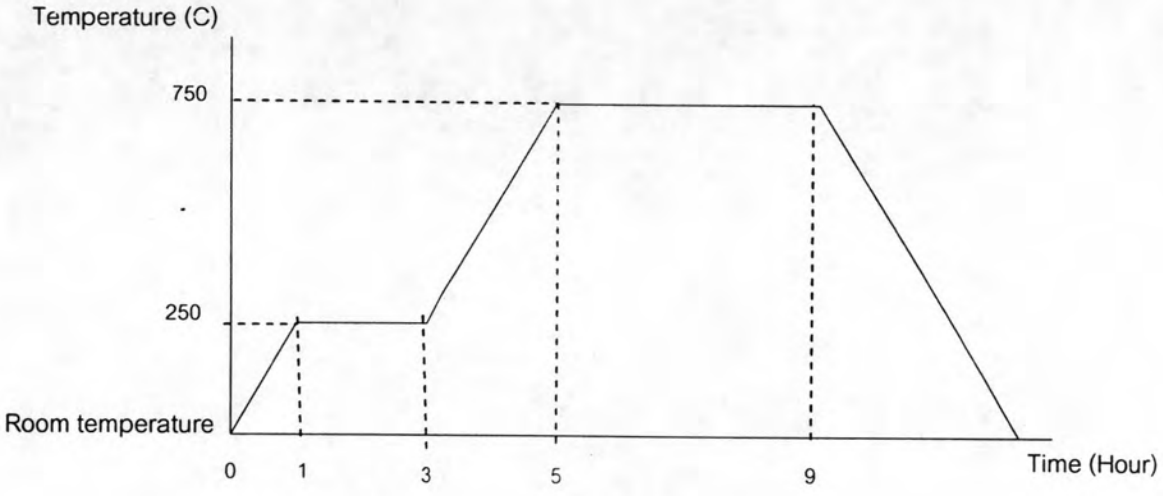

Figure 3.1 The diagram of carbonization pattern

3.3 Gas activation

In this section the effect of activation agents and the effect activation patterns are studied.

3.3.1 Effect of activation agents

The studied factor: activation agents

- Steam
- Carbon dioxide (CO_2)

The controlled factors

- Activation temperature: 800 °C
- Activation time: 1 hour
- Heating rate: 10 °C/min
- Water feed rate: 0.8 g/min
- CO_2 flow rate: 200 cm^3/min
- Nitrogen flow rate: 200 cm^3/min
- Sample length: 1.5 ± 0.1 cm

The dried RF gel is carbonized and then the obtain RF carbon is activated in quartz tube. During heating up and cooling down state, nitrogen is flowed (200 cm^3/min) in quartz tube. When temperature is risen up to desire level (800 °C), the activation agent is used instead of nitrogen gas. The diagram of activation process is shown in Figure 3.2.

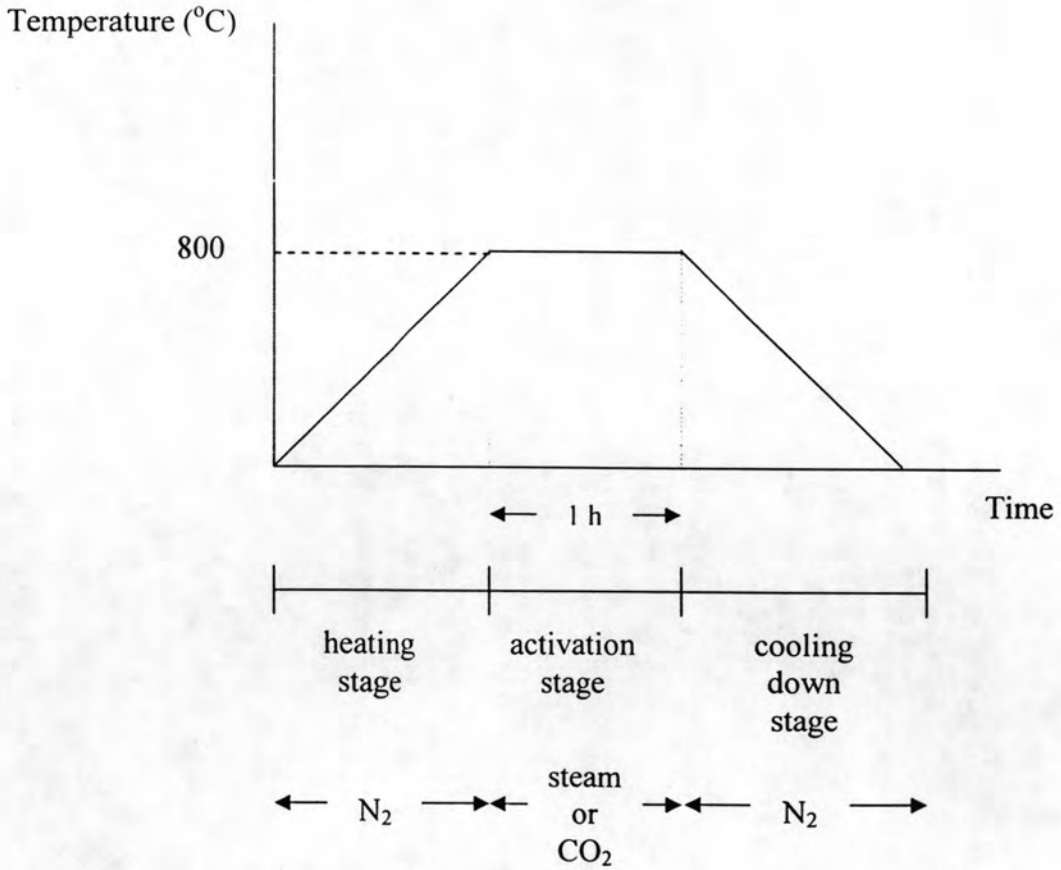

Figure 3.2 The diagram of activation process

In case of steam activation, water flow rate of 0.8 g/min is heated to produce steam. This steam is mixed with nitrogen (200 cm^3/min) before feed into quartz tube. The process of steam activation is shown below.

RF gel $\xrightarrow[\text{carbonization}]{}$ **RF carbon** $\xrightarrow[\text{steam activation}]{}$ **activated RF carbon**

For CO_2 activation, CO_2 is fed into quartz tube with CO_2 flow rate of 200 cm^3/min. The process of CO_2 activation is shown below.

RF gel $\xrightarrow[\text{carbonization}]{}$ **RF carbon** $\xrightarrow[\text{$CO_2$ activation}]{}$ **activated RF carbon**

The activation conditions are summarized in Table 3.2.

Table 3.2 The activation conditions for activation agents study

Samples	Starting Material	Activation agent	Activation agent flow rate	Activation temperature (°C)	Activation time (h)
TS	RF carbon	steam	steam (water flow rate 0.8 g/min) mix with nitrogen (200 cm^3/min)	800	1
TC	RF carbon	CO_2	200 cm^3/min	800	1

3.3.2 Effect of activation patterns

The study factor: activation patterns

- One step activation
- Two step activation

The controllable factors

- Activation temperature: 800 °C
- Activation time: 1 hour
- Heating rate: 10 °C/min
- Water feed rate: 0.8 g/min
- CO_2 flow rate: 200 cm^3/min
- Nitrogen flow rate: 200 cm^3/min
- Sample length: 1.5 ± 0.1 cm

The experimental procedure in one step and two step activation can be described as follow.

One step activation

RF gel is activated with activation agents (CO_2 and steam), at 800 °C for 1 hour. During heating up and cooling down state, nitrogen is flowed (200 cm^3/min) in quartz tube. When temperature is risen up to desire level (800 °C), the activation gas is used instead of nitrogen gas.

In case of steam activation, water flow rate 0.8 g/min is heated to produce steam. This steam is mixed with nitrogen (200 cm^3/min) before feed into quartz tube.

RF gel $\xrightarrow[\text{steam activation}]{}$ **activated RF carbon**

Another case in CO_2 activation, CO_2 is fed into quartz tube with CO_2 flow rate at 200 cm^3/min.

RF gel $\xrightarrow[CO_2 \text{ activation}]{}$ **activated RF carbon**

Two step activation

In the first step, RF gel is carbonized in inert atmosphere. After that, the obtained RF carbon is activated with activation agents (CO_2 and steam) at 800 °C for 1 hour. During heating up and cooling down state, nitrogen is flowed (200 cm^3/min) in quartz tube. When temperature is risen up to desire level (800 °C), the activation agent is used instead of nitrogen gas. The experimental procedure in this part is similar with the procedure in section 3.3.1.

The activation conditions are summarized in Table 3.3

Table 3.3 The activation conditions for activation patterns study

Samples	Starting Material	Activation agent	Activation agent flow rate (cm^3/min)	Activation temperature (°C)	Activation time (h)
one step activation					
OS	RF gel	steam	steam (water flow rate 0.8 g/min) mix with nitrogen (200 cm^3/min)	800	1
OC	RF gel	CO_2	200	800	1
two step activation					
TS	RF carbon	steam	steam (water flow rate 0.8 g/min) mix with nitrogen (200 cm^3/min)	800	1
TC	RF carbon	CO_2	200	800	1

3.4 Gas activation with metals loading

In this part the effect of alkali and alkaline earth compounds which are impregnated into RF gel will be studied. The procedures for experiment are described in details.

3.4.1 Preparation of impregnated RF gel

1. RF gel is prepared at controlled length of 1.5 ± 0.1 cm.

2. The Na_2CO_3, K_2CO_3, Cs_2CO_3 and $Ca(NO_3)_2.4H_2O$ solution with 0.4 M and 75 cm^3 are prepared.

3. RF gel is impregnated by immersion in the solution for 3 days with constant stirring.

4. After impregnation, the impregnated RF gel is dried at room temperature at least 12 h and then RF carbon is dried at 75 °C until constant weight.

3.4.2 Activation of impregnated RF carbon stage

The impregnated RF carbon is activated with CO_2 is fixed activation time and flow rate at 30 min and 50 cm^3/min, respectively. During heating up and cooling down state, nitrogen is flowed (200 cm^3/min) in quartz tube. The CO_2 is switched instead of nitrogen gas when temperature rises up to desire level. The activation conditions are summarized in table 3.4.

RF gel —impregnation→ **impregnated RF gel** —CO_2 activation→ **activated RF carbon**

Table 3.4 The activation conditions for gas activation with metals loading

Samples	Impregnation agents	Activation temperature (°C)	Activation gas
Effect of chemical agents in activation process (section 4.2.1)			
Ca800	$Ca(NO_3)_2.4H_2O$	800	CO_2
Na800	Na_2CO_3	800	CO_2
K800	K_2CO_3	800	CO_2
OC800	-	800	CO_2
Effect of carbon dioxide couple with calcium in activation process (section 4.2.2)			
Ca850	$Ca(NO_3)_2.4H_2O$	850	CO_2
Ca-heat	$Ca(NO_3)_2.4H_2O$	850	N_2
OC850	-	850	CO_2
Effect of activation temperature with calcium in activation process (section 4.2.3)			
Ca900	$Ca(NO_3)_2.4H_2O$	900	CO_2
Ca850	$Ca(NO_3)_2.4H_2O$	850	CO_2
Ca800	$Ca(NO_3)_2.4H_2O$	800	CO_2
Ca700	$Ca(NO_3)_2.4H_2O$	700	CO_2

Note; Starting material is RF gel and activation time for 30 min

N_2 flow rate is 200 cm^3/min

CO_2 flow rate is 50 cm^3/min

3.5 Characterization

1. Porosity is characterized by nitrogen adsorption – desorption at – 196 °C (BEL; BELSORP – mini)

1.1 BET surface (S_{BET}) is determined by BET equation

1.2 micropore volume (V_{mic}) is calculated by t – method

1.3 mesopore volume (V_{mes}) is estimated by DH – method

2. Microstructure is characterized by SEM (Scanning Electron Microscope) (JEOL; JSM – 5800LV)