CHAPTER IV

RESULTS AND DISCUSSIONS

In this chapter, the experimental results are discussed. Gas activation and gas activation with metals loading on the starting materials are considered.

4.1 Gas activation

In this section RF carbon without any metals loading is activated. The effect of activation agents (steam and CO_2) and the effect of activation patterns (one step and two step activation) are discussed.

4.1.1 Effect of activation agents

Steam and CO_2 are the activation agents which are used in this study. Before activation, RF carbon is produced from the carbonization of RF gel. RF carbon is activated to increase porosity by activation process. The summary in samples preparation is shown in Table 4.1. The physical properties of activated RF carbon are shown in Table 4.2.

Table 4.1 The summary of samples preparation (TS and TC)

Samples	Starting material	Activation agent
TS	RF carbon	steam
TC	RF carbon	CO_2

Note; Activation temperature and time is 800 °C and 1 hour, respectively

4.1.1.1 Physical properties and morphology

Table 4.2 The physical properties of RF carbon and activated RF carbon (RF carbon, TS and TC)

Samples	Total burn off (%)	Total volume shrinkage (%)	Length shrinkage (%)	Diameter shrinkage (%)	Apparent density (g/cm^3)	Cracking on monolith surface
RF carbon	52	54	23	23	0.56	no
TS	62	56	24	24	0.48	no
TC	55	54	23	23	0.55	no

After activation, the total samples burn off are 62 % and 55 % for steam and CO_2 activation, respectively. An increase in total burn off indicates some mass loss in activation process. Furthermore, volume shrinkage in activated RF carbon is similar to RF carbon. In brief, there is more change in mass loss compared to volume shrinkage in activation process.

In the part of apparent density, TC (0.55 g/cm^3) and RF carbon (0.56 g/cm^3) show similar result because there is a little mass loss in TC sample. While high mass loss in TS sample, its apparent density is 0.48 g/cm^3. The external appearance of activated RF carbon is retained in monolith form and the SEM images of activated RF carbon are indicated in Figure 4.1. There is no difference in interconnected macroporous structure before and after activation in the steam and CO_2. The interconnected macroporous structure is preserved after activation.

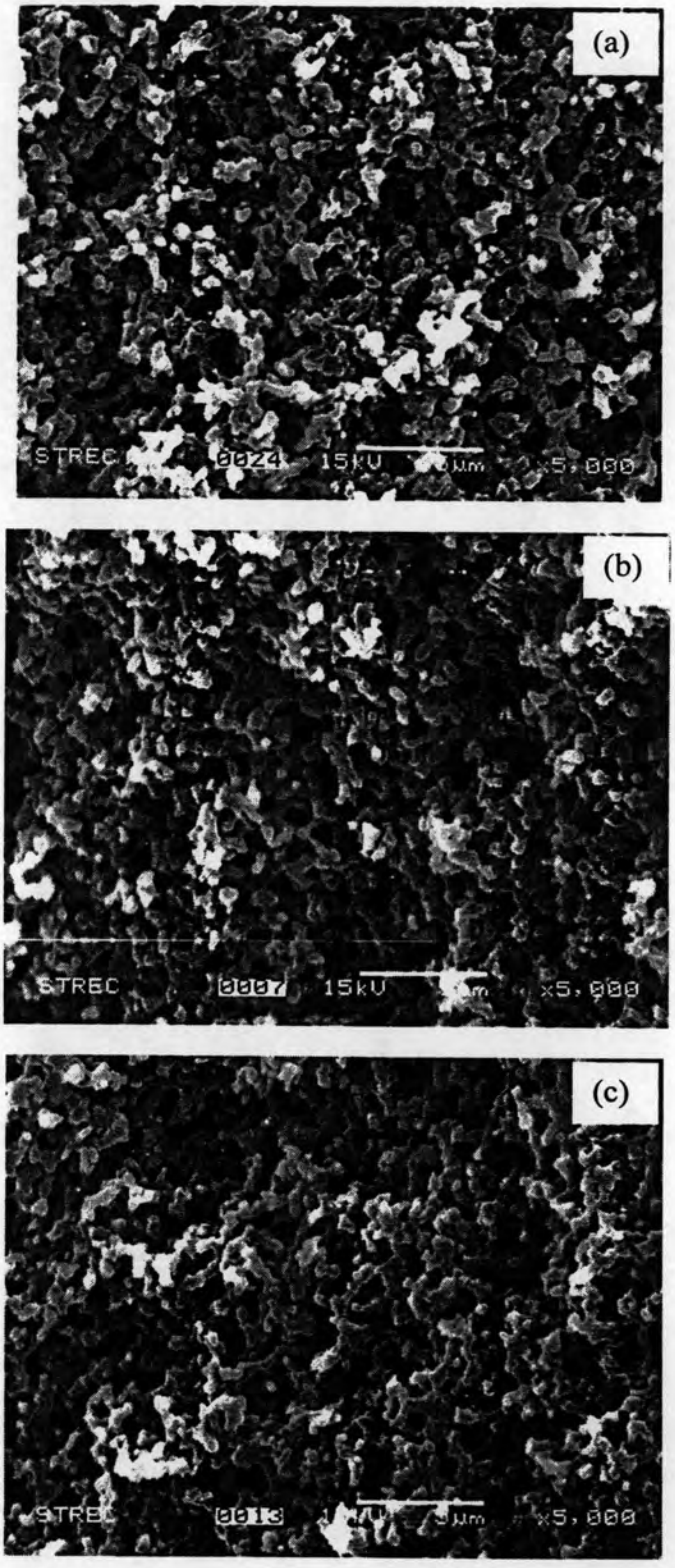


Figure 4.1 SEM images (cross section 5000x) of (a) RF carbon, (b) TS and (c) TC

4.1.1.2 Porous properties

Table 4.3 The porous properties of RF carbon and activated RF carbon (RF carbon, TS and TC)

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)
RF carbon	465	0.23	n/d
TS	774	0.38	n/d
TC	515	0.26	n/d

n/d mean not detectable

The nitrogen adsorption – desorption isotherms of activated RF carbon (Figure 4.2) are type I which is classified by IUPAC. The micropore structure is obtained after activation. There is an increase in V_{mic} of TS and TC (0.38 and 0.26 cm^3/g, respectively) compared to RF carbon (0.23 cm^3/g) in Table 4.3. Moreover, TS and TC have higher BET surface area (774 and 515 m^2/g, respectively) compared with RF carbon (465 m^2/g). The increase in surface area can be explained by micropore contribution [13].

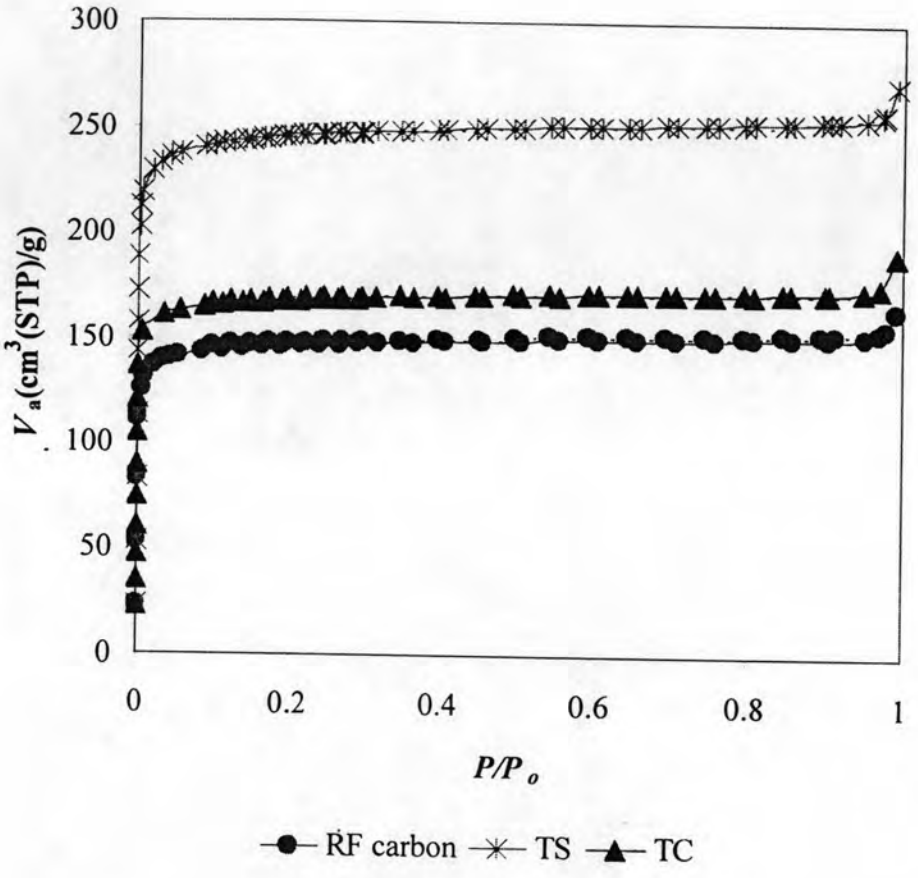


Figure 4.2 Nitrogen adsorption – desorption isotherms of RF carbon and activated RF carbon (RF carbon, TS and TC)

Although the exact mechanism of the activation process is not completely understood, it can be visualized as an interaction between the activation agents and the carbon atom [14]. The activation process is a complex heterogeneous process compose of the transport of reagents to the surface of particles, their diffusion into the pore, chemisorption on pore surface, reaction with carbon atom, desorption of the reaction product and diffusion of these products to the particle surface [15]. In the chemisorption on pore surface, the oxygen atoms from activation agents (gas phase) is transferred to carbon on solid surface to form some types of surface – oxygen

complex. The reactions of activations gas with carbon atom occur to remove carbon from solid material [16].

The reasonable reactions of carbon with steam and CO_2 are as follow [15, 17]

Steam activation

Overall reaction; $C + H_2O \longrightarrow CO + H_2$ $\Delta H = 117$ kJ/mol

$$C + H_2O \longleftrightarrow C(H_2O)$$

$$C(H_2O) \longrightarrow C(O) + H_2$$

$$C(O) \longrightarrow CO$$

CO_2 activation

Overall reaction; $C + CO_2 \longrightarrow 2CO$ $\Delta H = 159$ kJ/mol

$$C + CO_2 \longleftrightarrow C(O) + CO$$

$$C(O) \longrightarrow CO$$

From reaction above, carbon atoms in solid particles can be removed in CO form and resulted in micropore development [18, 19].

4.1.2 Effect of activation patterns

There are two patterns of activation in this part one step and two step activation.

4.1.2.1 Physical properties and morphology

In one step activation, RF gel is transformed into activated RF carbon by using activation agents.

Table 4.4 The summary of samples preparation (OS, OC, TS and TC)

Samples	Starting material	Activation agent
one step activation		
OS	RF gel	steam
OC	RF gel	CO_2
two step activation		
TS	RF carbon	steam
TC	RF carbon	CO_2

Note; Activation temperature and time is 800 °C and 1 hour, respectively

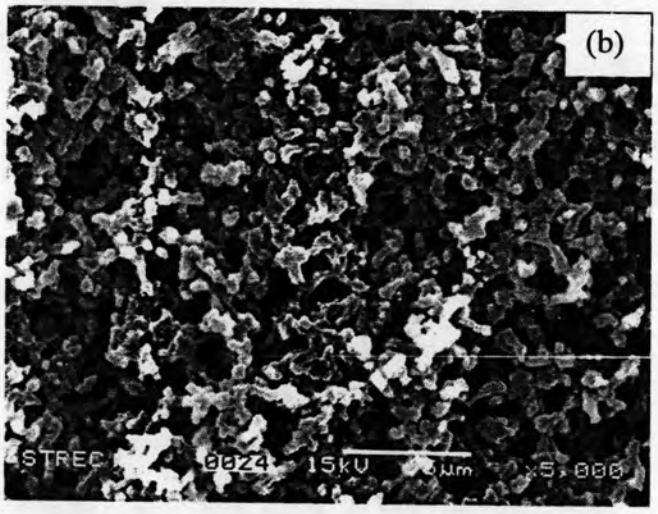
While in two step activation, RF gel is transformed into RF carbon by carbonization in the first and then the obtained RF carbon is activated with activation agents to transform into activated RF carbon. The summary samples preparation is shown in Table 4.4.

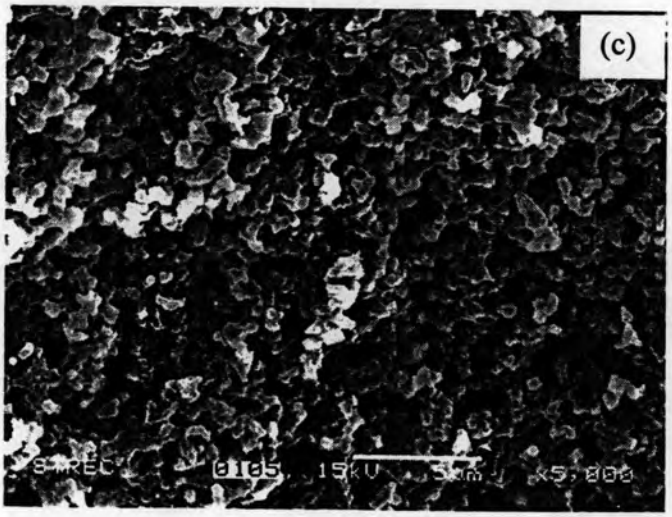
Table 4.5 The physical properties of RF carbon and activated RF carbon (OS, TS, OC and TC)

Sample	Total burn off (%)	Total volume shrinkage (%)	Length shrinkage (%)	Diameter shrinkage (%)	Apparent density (g/cm^3)	Cracking on monolith surface
RF carbon	52	54	23	23	0.56	no
OS	65	58	25	25	0.44	no
TS	62	56	24	24	0.48	no
OC	56	52	23	21	0.53	no
TC	55	54	23	23	0.55	no

The physical properties of activated RF carbon are shown in Table 4.5. All samples which are activated by difference activation agents (steam and CO_2) in the difference activation patterns (one step and two step activation) do not show any significant difference. The SEM images of activated RF carbon in the cross section plan are shown in Figure 4.3. There is no difference in the interconnected macroporous structure before and after activation. The interconnected macroporous structure is preserved after activation which can be concluded.


(a)
STREC
0200
15kV
5μm
x5,000


(b)
STREC
0024
15kV
x5,000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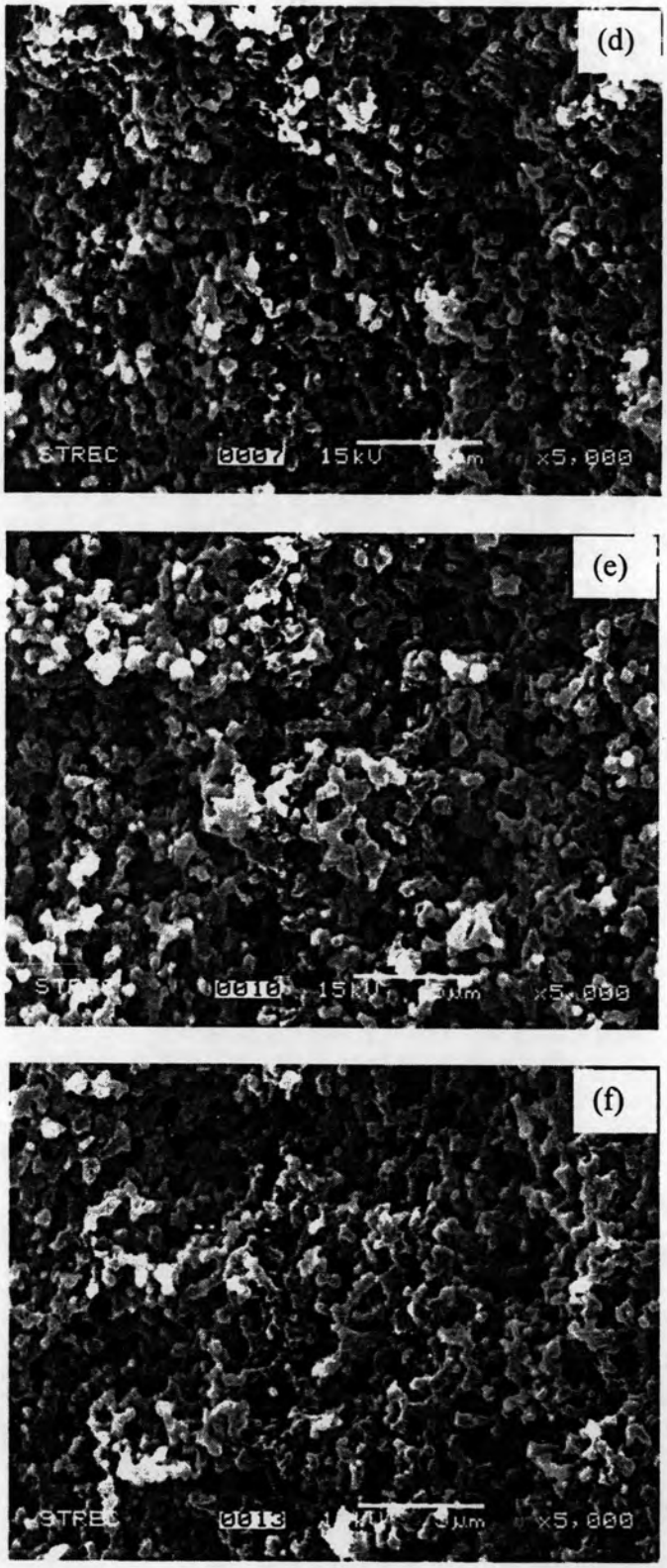


Figure 4.3 SEM images (cross section 5000x) of (a) RF gel, (b) RF carbon, (c) OS, (d) TS, (e) OC and (f) TC

4.1.2.2 Porous properties

Table 4.6 The porous properties of RF gel, RF carbon and activated RF carbon (OS, TS, OC and TC)

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)
RF carbon	465	0.23	n/d
RF gel	5	n/d	n/d
OS	923	0.45	n/d
TS	774	0.38	n/d
OC	572	0.28	n/d
TC	515	0.26	n/d

n/d mean not detectable

In activation with steam and CO_2, both one step and two step activation influence on microporosity development obviously are seen in type I nitrogen adsorption – desorption isotherms (Figure 4.4). In one step activation both steam and CO_2, higher in V_{mic} is observed compared with two step activation due the simultaneous process effect of the volatile releasing from the RF gel and the reaction of carbon and activation agents. The effect of volatile releasing on micropore development can be detected from the obtained RF carbon. RF gel is transform into RF carbon by carbonization process. After carbonization, the obtained RF carbon can be detected as V_{mic} is 0.23 cm^3/g (Table 4.6) whereas V_{mic} is not observed in RF gel. The cause of development in micropore may come from releasing of volatile matter from RF gel during carbonization step [20]. While the effect of carbon and activation agents reaction on micropore development has already shown in section 4.1.1.

The simultaneous process between volatile releasing and carbon – activation agents (steam and CO_2) reaction is expected in one step activation, as a consequence, the higher microporosity can be developed in one step activation compared with two step activation.

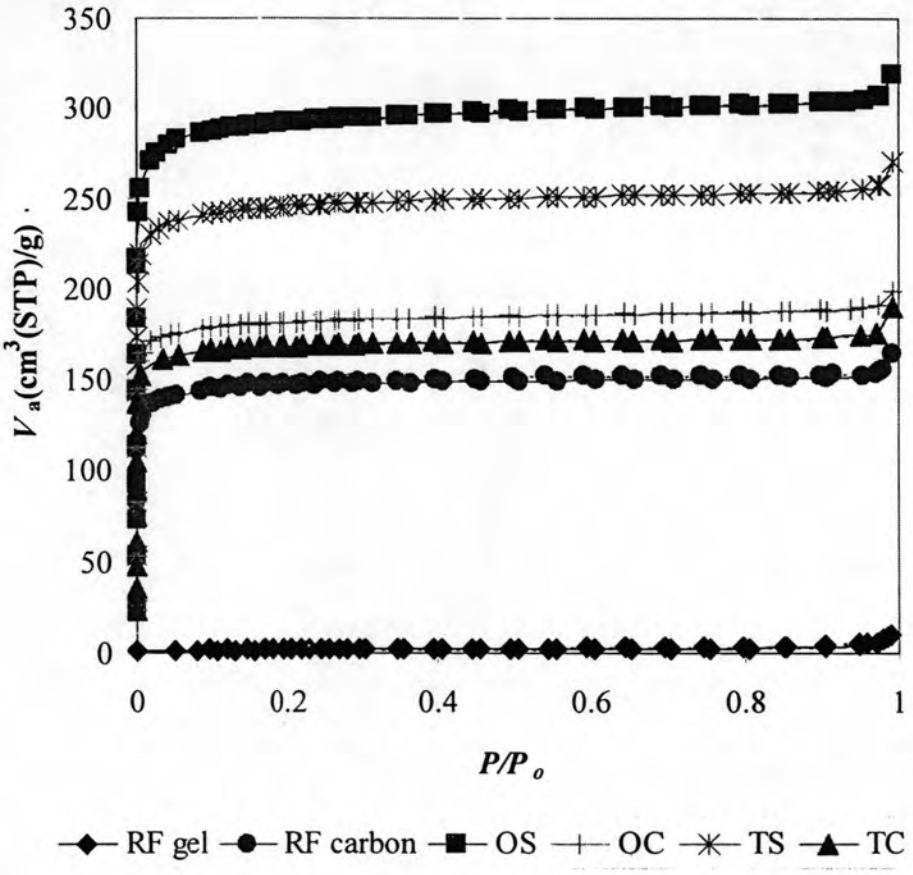


Figure 4.4 Nitrogen adsorption – desorption isotherms of RF gel, RF carbon and activated RF carbon (OS, OC, TS and TC)

Whereas in two step activation, RF carbon has already released volatile matter in carbonization step and then RF carbon is activated. In activation step, the dominant phenomenon in microporosity development is the reaction between carbon and activation agents.

In brief, the carbonization step is not necessary used for the preparation of activated RF carbon.

4.2 Gas activation with metals loading

In this part, the RF gel which is impregnated with alkali and alkaline earth metals and activation in CO_2 atmosphere is discussed.

4.2.1 Effect of chemical agents in activation process

The alkali and alkaline earth compounds are used for impregnation onto RF gel and the impregnated RF gel is activated in CO_2 atmosphere. The samples preparation is summarized in Table 4.7 and the physical properties are shown in Table 4.8.

Table 4.7 The summary of samples preparation (Ca800, Na800, K800 and OC800)

Samples	Impregnation agents
Ca800	$Ca(NO_3)_2.4H_2O$
Na800	Na_2CO_3
K800	K_2CO_3
OC800	-

Note; All samples are activated with CO_2 at 800 °C for 30 min

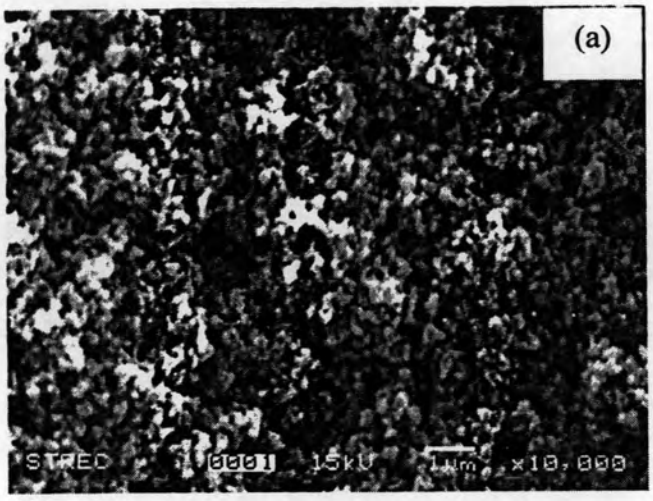
CO_2 flow rate is 50 cm^3/min

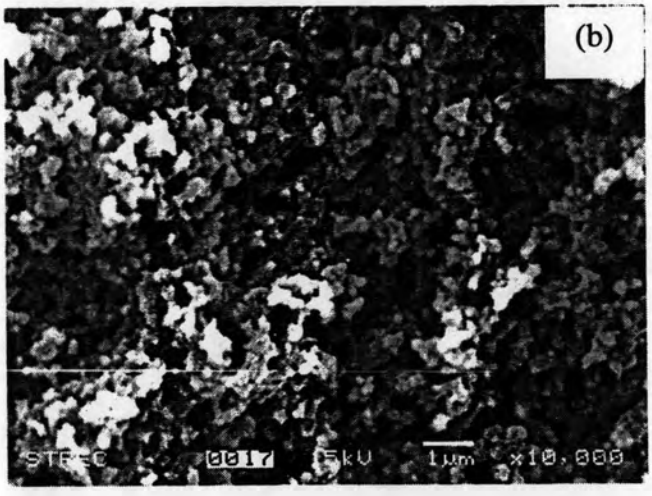
Table 4.8 The physical properties of RF carbon and activated RF carbon (OC800, Ca800, Na800 and K800)

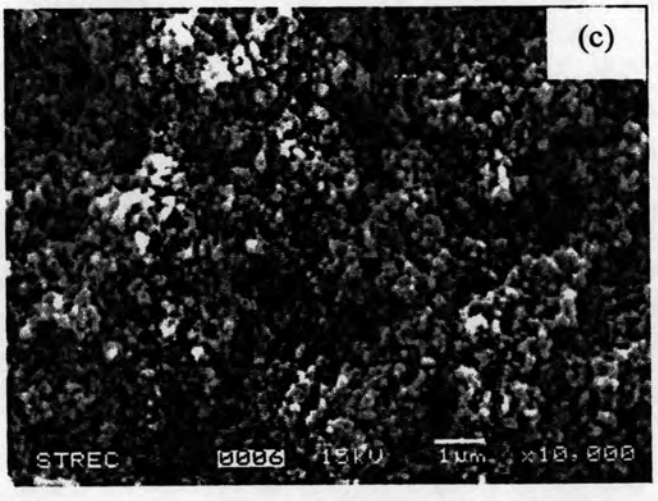
Samples	Total burn off (%)	Total volume shrinkage (%)	Length shrinkage (%)	Diameter shrinkage (%)	Apparent density (g/cm^3)	Cracking on monolith surface
RF carbon	52	54	23	23	0.56	no
OC800	54	47	23	23	0.48	no
Ca800	65	51	21	21	0.47	no
Na800	72	70	43	27	0.62	no
K800	69	70	35	32	0.78	yes

The effect of alkali metals is considered. The sodium, potassium and cesium carbonate is used for impregnation onto RF gel and the impregnated RF gel is activated in CO_2 atmosphere.

Normally, the alkali metals are used as catalyst in carbon – CO_2 reaction [12]. But from porous properties results (Table 4.9) of the sample Na800 and K800 which are impregnated with sodium and potassium, respectively, is not observed in porosity development. The nitrogen adsorption – desorption isotherms (Figure 4.6) of both samples show in type I. The V_{mic} of Na800 and K800 is 0.13 and 0.15 cm^3/g, respectively which is lower than V_{mic} of OC800 (0.23 cm^3/g) which has no metal loading.


(a)
STREC 0001 15kV 1μm x10,000


(b)
STREC 0017 15kV 1μm x10,000


(c)
STREC 0006 15kV 1μm x10,000

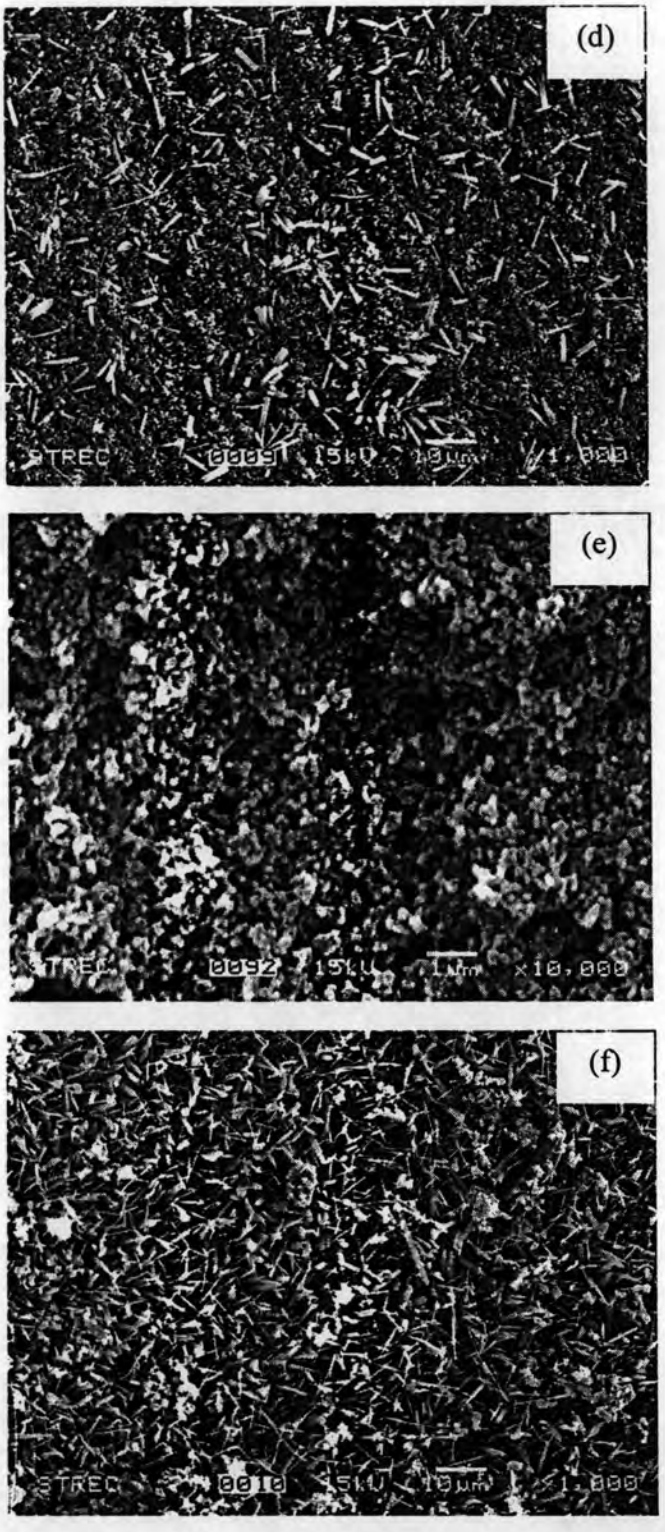


Figure 4.5 SEM images of cross section plane interconnected macroporous structure (a) Ca800 before activation, (b) Ca800 after activation, (c) K800 before activation, (d) K800 after activation, (e) Na800 before activation, (f) Na800 after activation (the magnification of (a), (b), (c), (e) at 10000x and (d), (f) at 1000x)

From Figure 4.5 show the cross section images of interconnected macroporous structure before and after activation. For the cross section images of interconnected macroporous structure before activation (Figure 4.5 (c), (e)), crystals are not detected on the interconnected macroporous structure. Whereas the crystals can be observed on the interconnected macroporous structure in the activated samples Na800 and K800 (Figure 4.5 (d), (f) respectively). The formation of crystals may be the cause for low porosity due to the blockage of pores by the crystals after activation. Furthermore, sample K800 cracks after activation.

Table 4.9 The porous properties of RF carbon and activated RF carbon (OC800, Ca800, Na800 and K800)

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	$r_{peak,mes}$
RF carbon	465	0.23	n/d	n/d
OC800	424	0.25	n/d	n/d
Ca800	475	0.16	0.31	1.88
Na800	217	0.13	n/d	n/d
K800	269	0.15	n/d	n/d

n/d mean not detectable

In case of cesium impregnation, when this sample is kept at room temperature (approximate 30 ± 2 °C) after the RF gel has already impregnated with cesium. This sample does not remain in monolith form thus the impregnation with cesium is not suitable for preparation of activated RF carbon.

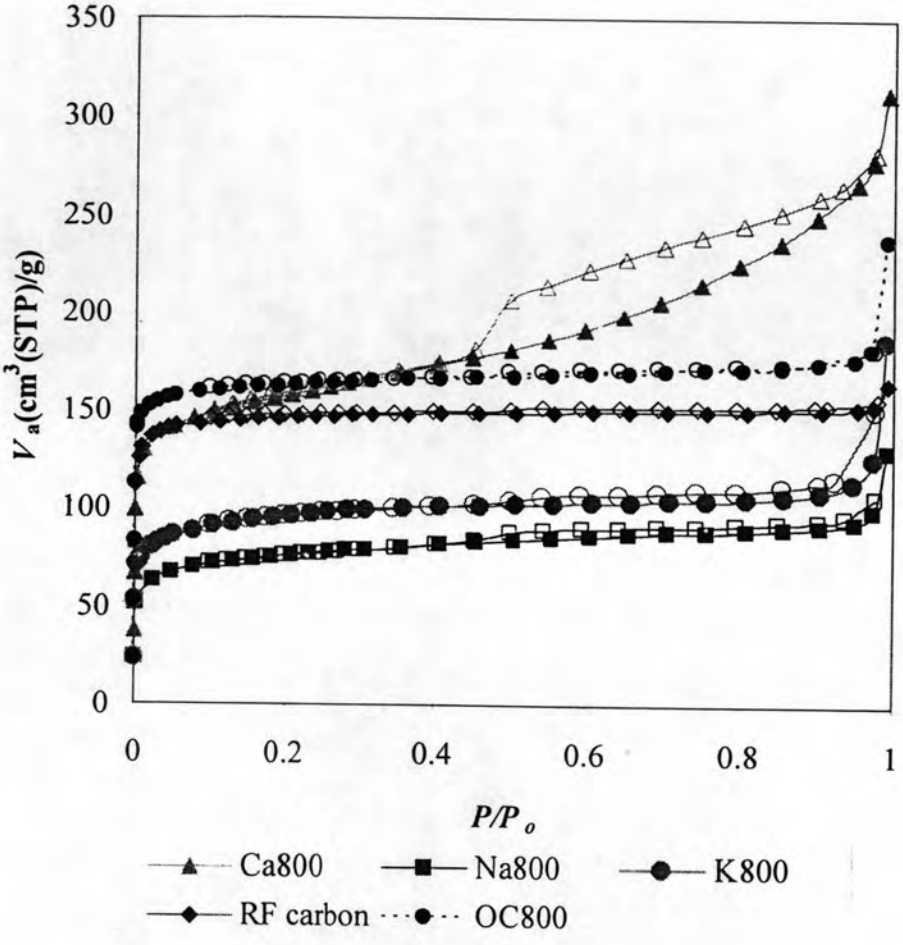


Figure 4.6 Nitrogen adsorption – desorption isotherms of RF carbon and activated RF carbon (Ca800, Na800, K800 and OC800)

Whereas the effect of alkaline earth on activation process can be observed in sample Ca800 which is impregnated by calcium nitrate and activation in CO_2 atmosphere. Mesoporosity can be confirmed by type IV nitrogen adsorption – desorption isotherms (Figure 4.6). The V_{mes} is 0.31 cm^3/g (Table 4.9). This sample can be detected mesoporosity development in its structure while in Na800 and K800 the mesoporosity cannot be detected. So that calcium is chosen for study in more details in mesoporosity development which will be discussed in the details in section 4.2.2 and 4.2.3.

4.2.2 Effect of carbon dioxide couple with calcium in activation process

The effect of calcium which is impregnated into RF carbon in the appearance and absence of CO_2 in activation process will be discussed in this section. The samples preparation and the physical properties of activated RF carbon are shown in the table 4.10 and 4.11, respectively.

Table 4.10 The summary of samples preparation (Ca850, Ca-heat, and OC850)

Samples	Impregnation agents	Activation gas
Ca850	$Ca(NO_3)_2.4H_2O$	CO_2
Ca-heat	$Ca(NO_3)_2.4H_2O$	N_2
OC850	-	CO_2

Note; All samples are activated at 850 °C for 30 min, CO_2 and N_2 flow rate are 50 and 200 cm^3/min, respectively

Table 4.11 The physical properties of RF carbon and activated RF carbon (Ca850, Ca-heat and OC850)

Samples	Total burn off (%)	Total volume shrinkage (%)	Length shrinkage (%)	Diameter shrinkage (%)	Apparent density (g/cm^3)	Cracking on monolith surface
RF carbon	52	54	23	23	0.56	no
Ca850	71	52	24	20	0.39	no
Ca-heat	55	50	20	21	0.65	no
OC850	56	55	24	23	0.55	no

Sample OC 850 is the activated RF carbon with no calcium impregnation and activation under CO_2 atmosphere at 850 °C. Microporosity development can be detected in OC850 from type I the nitrogen adsorption – desorption isotherm (Figure 4.7) and the increasing of V_{mic} compared with RF carbon (from 0.23 to 0.28 cm^3/g). Mesoporosity development is not detected when no calcium impregnation is applied which can be concluded.

In Ca-heat is the sample which is impregnated with calcium. This sample is activated in the absence of CO_2 at 850 °C. The 850 °C is chosen for this experiment because the effect of molten calcium form (melting point of calcium is 839 °C) on the porous development is needed to be observed. The nitrogen adsorption – desorption isotherm of Ca-heat show in type I which present micropore. The present in calcium on structure of RF gel without activation agent (CO_2) in activation step, mesoporosity development is not detected in this activated RF carbon (Ca-heat).

Table 4.12 The porous properties of RF carbon and activated RF carbon (Ca850, Ca-heat and OC850)

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	$r_{peak,mes}$
RF carbon	465	0.23	n/d	n/d
Ca850	624	0.22	0.54	1.88
Ca-heat	395	0.19	n/d	n/d
OC850	474	0.28	n/d	n/d

n/d mean not detectable

For the sample Ca850 is prepared by the calcium impregnation and activation with CO_2. Mesopore can be detected on this sample which can be indicated by type IV nitrogen adsorption – desorption isotherm (Figure 4.7) and the V_{mes} (0.54 cm^3/g) shown in Table 4.12. For the conclusion, calcium may act as catalyst in reaction between carbon and CO_2 and lead to development in mesopore [21, 22].

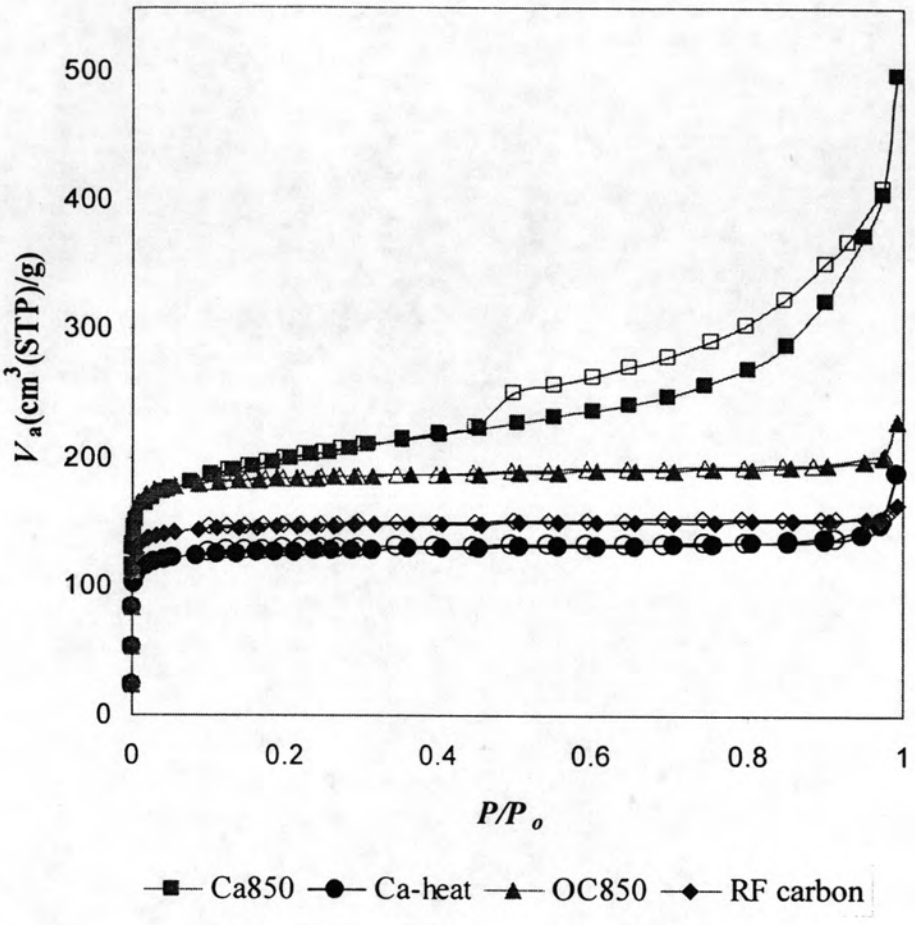


Figure 4.7 Nitrogen adsorption – desorption isotherms of RF carbon and activated RF carbon (Ca850, Ca-heat and OC850)

4.2.3 Effect of activation temperature with calcium in activation process

The effect of activation temperature is discussed in this section. The samples preparation is summarized in Table 4.13. The total burn off, length shrinkage, diameter shrinkage increase (Table 4.14) when the activation temperature is increased.

Table 4.13 The summary of samples preparation (Ca900, Ca850, Ca800 and Ca700)

Samples	Activation temperature (°C)
Ca900	900
Ca850	850
Ca800	800
Ca700	700

Note; All samples are impregnated with $Ca(NO_3)_2.4H_2O$ and activation with CO_2 for 30 min, CO_2 flow rate at 50 cm^3/min

Table 4.14 The physical properties of RF carbon and activated RF carbon (Ca900, Ca850, Ca800 and Ca700)

Sample	Total burn off (%)	Total volume shrinkage (%)	Length shrinkage (%)	Diameter shrinkage (%)	Apparent density (g/cm^3)	Cracking on monolith surface
RF carbon	52	54	23	23	0.56	no
Ca900	76	59	28	24	0.37	yes
Ca850	71	52	24	20	0.39	no
Ca800	65	51	21	21	0.47	no
Ca700	52	47	20	19	0.62	no

The V_{mic} shown in Table 4.15 increases upon the increasing of activation temperature. The increase of activation temperature influences on the rate of carbon – CO_2 reaction which has a strong effect on carbon removal [4, 23]. As a result an increase in carbon removal leads to an increase in microporosity development.

Table 4.15 The porous properties of RF carbon and activated RF carbon (Ca900, Ca850, Ca800 and Ca700)

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	$r_{peak,mes}$
RF carbon	465	0.23	n/d	n/d
Ca900	739	0.34	0.45	1.88
Ca850	624	0.22	0.54	1.88
Ca800	475	0.20	0.31	1.88
Ca700	352	0.19	n/d	n/d

n/d mean not detectable

The effect of an increase in activation temperature on the mesoporosity development is discussed as follow.

When activation temperature is higher than 700 °C as a consequence the calcium may play an efficient role in catalyst leads to development in mesopore. During the reaction, calcium has high possibility dispersion in CaO form [12, 22]. When the temperature is 600 – 700 °C, the CaO dispersion undergoes thin film formation on the carbon surface and plays a role in catalytic mode [22] therefore mesoporosity development occurs. Furthermore, activation temperature at 900 °C, the external appearance of Ca900 shows in monolith cracking. So that activation temperature 900 °C is not appropriate for activation of this system.

In summary, calcium may play an efficient role as catalyst in carbon – CO_2 reaction in the temperature range 700 – 900 °C which has great effect on mesoporosity development.

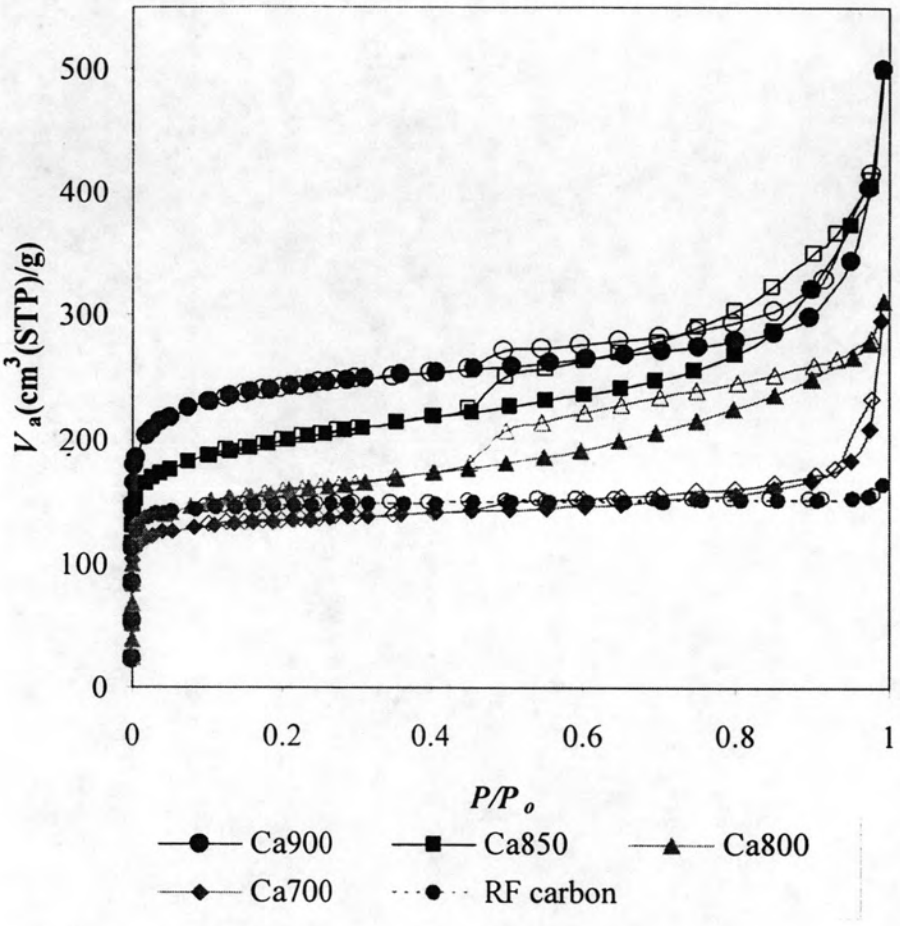


Figure 4.8 Nitrogen adsorption – desorption isotherms of RF carbon and activated RF carbon (Ca900, Ca850, Ca800 and Ca700)